AMORPHOUS SOLIDS: THEIR STRUCTURE, LATTICE DYNAMICS AND ELASTICITY

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Contents

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Abstract

Amorphous solids fall into any reasonable definition of a solid. This means that it should be possible to describe amorphous solids in terms of an expansion in deviations from a well defined rigid microscopic reference frame – as in the Cauchy–Born lattice-dynamics of periodic crystals. The continuum limit of this microscopic expansion is a field theory – continuum elasticity. It follows that different types of amorphous solids can differ from each other and from crystalline solids only because of differences in the nature of their microscopic reference states. A theory of amorphous solids which implements this general point of view must satisfy two very general restrictions: (1) translation–rotation invariance of the expansion and (2) the reference state must be a stable equilibrium state. We construct such a general theory and also describe some results of its application to specific types of amorphous solids. The monograph consists of three parts.

Part I. The Cauchy–Born Theory of Solids, describes a general and explicitly translation–rotation invariant formulation of the Cauchy–Born expansion. This is done by using the fact that the translation–rotation invariant energy of a many particle system can be regarded as a function of the interparticle distances. The resulting formalism leads to local expressions for the continuum limit which can be used to derive microscopic expressions for the local elastic constants and for the stresses from the coefficients in the microscopic expansion around a specific reference state. One finds that the initial stresses in the microscopic reference state lead to special stress induced terms in the harmonic expansion whose continuum limit is the second order strain. Their effect on the bulk stability of the reference states of tenuous solids is closely analogous to the role of stresses in continuum stability theory.

Part II. The Rigidity of Floppy Bonded Networks, studies the stability of tenuous reference states. The theory developed in this section extends the standard considerations of the effect of stresses on the elastic stability of thin rods and shells to the complex internal structures which describe the bulk of solids. There is a geometric aspect. The interaction scheme of a physical model, the bond structure, defines a graph – the bonded network. When this network can be deformed continuously in d-dimensions even when all its bonded distances are fixed is geometrically floppy. A model which is described by such a network has a manifold of free degrees of freedom which have no rigidity for unstressed reference states. Mostly the free modes describe collective deformations of the reference state. We show that their number can be very large and that they often constitute a significant fraction of all eigenmodes. Like the bending of a thin rod these free modes are sensitive to stresses in the reference state around which one is expanding. When there are stresses they can become unstable, leading to structural buckling instabilities, or stable – depending on the sign of the relevant stresses. The theory of floppy networks thus allows us to study structural buckling, the bulk analog of the Euler buckling of rods and shells, and the stabilization of bulk shears by stretching which is the origin of the shear rigidity of most soft solids.

Part III. The Role of Stresses in Amorphous Solids, applies these results. The emphasis is on the stability of the reference state. We require stability against structural buckling and on the role of stresses in stabilizing the soft modes of tenuous bonding structures. The shear rigidity of rubbers and wet gel-likes is that of floppy bonded networks which are stretched. Like the shear rigidity of stretched membranes it is that of a network of stretched springs. We show that this is possible only because such solids are not rigid down to the atomic level. We discuss the stability of stressed granular packings emphasizing the fact that the packing has to be stable against structural buckling. This gives considerable insight into the internal mechanics of granular packings because it not only considers the equilibrium conditions on the individual grains but also the collective linear stability of a stressed packing. We then describe a new model of quenched glasses which emphasizes the role of the internal stresses in the glass. The essence of this model is the distinction between the molecular configuration in the quenched liquid, the "snapshot state" and the stable equilibrium reference state of the glass which emerges from it even for the most rapid ideal quench. We argue that structural buckling dominates the restructuring in the ideal quench and show that this predicts strong correlations between the local structure of the reference state and the internal stresses. Some of the most striking properties of glasses appear naturally in this microscopic model.

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0. Preface

The development of the microscopic theory of amorphous solids which I describe in this monograph is the result of a prolonged effort which started about 15 years ago. The road by which I reached the conclusions I present was quite tortuous but I have made an effort to erase the traces of this in the final version of the manuscript. I can only hope that this effort, which involved continuous rewriting, was successful and that the manuscript is reasonably clear and comprehensible. I am particularly worried about getting the message I am trying to convey across in view of the fact that my earlier attempts to present my results on the role of stresses in rubbers and gels by publishing two papers (Alexander, 1984, 1985a) did not prove very successful.

The basic ideas on which the theory I present are fairly straightforward. First, I claim that amorphous solids are really solids and can be described by a *Cauchy–Born* expansion around a rigid microscopic reference states (see Section 2). This then means that any differences between amorphous and crystalline solids and between different types of amorphous solids must reflect differences in the nature of their microscopic reference states which are reflected in their properties. Finally, the main new physical ingredient I introduce is the emphasis on the role of initial stresses. I shall claim that the peculiarities of the different reference states of amorphous solids can all be traced to the role of stresses.

Born and Huang in their classical (1954) monograph "*The Dynamical Theory of Crystal Lattices*" "define" an "equilibrium solid" as a solid which has no stresses in its reference state. This approximation is incorporated into the formalism they develop. It is very often justified because the effect of initial stresses on the linear bulk properties of crystalline solids is usually negligible. I will claim that, in contrast, for amorphous solids the effect of the initial stresses is crucial. One cannot even begin to understand amorphous solids if one does not consider the effect of stresses on the linear stability of their reference states. The reference states of amorphous solid are stable equilibrium states but they are stressed and the role of stresses cannot be neglected. The Born–Huang approximation is not justified in discussing the lattice dynamics of amorphous solids. The reason for this is that the structures of amorphous solids are determined by dynamic processes and not by minimizing the global interaction energy of the system. The reference states of amorphous solids are therefore, almost always, rather tenuous and stresses are important both in the structural buckling processes which produce them and in the stability of the reference states themselves.

I believe that anyone who reaches Part III of this monograph where I discuss the properties of specific amorphous solids – soft solids, packings and glasses – will concede that, at the very least, I make a strong case. This in spite of the fact that these specific discussions are mostly rather preliminary efforts.

Most of the results and derivations which I present are new and have not been published. This is of course rather unusual considering the length of the manuscript and the time I have spent working on it. The reason for this is that the structure of the theory is intrinsically complex. It is not too difficult to explain and summarize what I claim I am doing but to show that I can really analyze the properties of the expansion around an amorphous reference state I need a suitable formalism and some general results on the role of stresses in bulk structures which I have to construct and derive first. To discuss specific types of amorphous solids in Part III I rely on the general rotation invariant formalism for the Cauchy–Born expansion which is constructed in Part I and the theory of the rigidity of floppy networks which is developed in Part II using this formalism.

I will try to explain the structure of the whole monograph and the contents of its various parts in the Introduction and also, in more detail, in the introductory paragraphs of each of the three parts.

1. Introduction

1.1. What this monograph tries to do

I have long felt that the fact that we have so little understanding of the microscopic mechanical properties of amorphous solids is surprising. For many reasons one expects solids to be much simpler than liquids and it is therefore strange that the theories of dense liquids provide much more information and insight than anything available for glasses.

My purpose in this monograph is to construct a proper microscopic theory of amorphous solids which can explain their observed properties. We mean by this a theory of amorphous solids as solids, in the Cauchy–Born tradition (Cauchy, 1827, 1828; Born and von Kármán, 1912, 1913) which derive their properties – their microscopic lattice dynamics and the continuum limit – from the expansion of their mechanical energy around a rigid microscopic reference state which describes a stable equilibrium state of the amorphous solid.

Doing this has a technical side.

One requires a formalism which makes it possible to construct, study and analyze the translation–rotation invariant Cauchy–Born expansion and its continuum limit when the reference state is random and not a periodic lattice. One also needs this formalism for a careful investigation of the character of an amorphous reference state in a form in which it can be incorporated into the theory in a reasonably translucent way. The first requirement of such a formalism is obviously that it assures both translation and rotation invariance for the energy in the most general way and, term-by-term for the expansion. As we will show the main technical advantage of the formalism we develop is that it allows one to separate out the effects of stresses and bond tensions on the lattice dynamics and on the linear stability of the reference state.

It emerges from this analysis that initial stresses, the stresses which are properties of the reference state, play a crucial role in amorphous solids. I will argue, I believe convincingly, that one cannot understand the bulk mechanical properties of amorphous solids without understanding the role of the initial stresses in their reference states in determining them. Thinking about the reference state of an amorphous solid simply as a "random medium" without worrying about the way it emerged and its internal structure is misleading. One has to incorporate the effects of stresses into the theory – both their effect in the dynamics which determined the structure of the reference state and their effect in determining the properties of the Cauchy–Born expansion around it. Both structural buckling – the structural analogs of Euler (1755) buckling – and the stabilization of bulk shears by stresses – as in the transverse rigidity of stretched strings and drumheads – are important.

We will argue that the essential and deep origin of the many differences between the well-understood properties of crystalline solids, and those observed in amorphous solids is that the initial stresses are important in the latter but not in the former. Specifically, this will be shown in the detailed discussion of three types of amorphous solids in Part III. We discuss *soft solids*, in particular rubbers and gels in Section 14, *random packings* of rigid particles in Section 15 and *glasses* produced by a rapid quench in Section 16. For physical reasons the initial stresses are different, are correlated to the structure in a different way and play a different role in each case.

1.2. Understanding the properties of amorphous solids

We want to put this in context.

Our theoretical understanding of solids is based on a microscopic description of their reference states. The theory assumes rigid reference positions at the microscopic level and expands the energy in the deviations from these positions. In essence this goes back to Cauchy (1828) who already used this expansion procedure for the derivation of the equations of continuum elasticity. The modern formulation, the theory of Lattice Dynamics, is due to Born and von Kármán (1912, 1913) and forms part of most undergraduate physics curricula.

There is no obvious reason why, in principle, a Cauchy–Born expansion should not be used to describe amorphous solids – in terms of an expansion around a suitable random reference state. In practice the procedure one actually uses and teaches in standard "lattice dynamics" relies very heavily on the periodicity of the lattice and also makes some other implicit and less obvious assumptions which will become clear later. For this reason one cannot construct a useful theory of amorphous solids by simply applying the Born–von Kármán algorithms to amorphous solids. This is not simply a question of expanding around a random reference state. It remains true even if one is willing to compute the eigenfunctions numerically or finds some way to handle the expansion around a realization of a random reference state. Attempts to do this explicitly – e.g., by applying replica techniques (John et al., 1983), or by simulations (Webman and Grest, 1985) – lead to definite results, but these results are very different from the properties observed in any real amorphous system.

Something is clearly missing.

The result of these theoretical difficulties is that very little is known about the microscopics of amorphous solids. Even dynamic modes which definitely exist and distinguish amorphous solids like two-level systems (Anderson et al., 1972; Phillips, 1972) and the soft "Bose peak" modes are to this day interpreted by phenomenological models which do not even attempt to relate them to the microscopic structure, e.g. the "soft potential theories of Karpov et al. (1983), Karpov and Parshin (1983), Il'in et al. (1987), Buchenau et al. (1991), Buchenau et al. (1992), Parshin et al. (1993), Gurevich et al. (1993).

This is the situation for almost all amorphous solids. The only exception we are aware of are the polymeric network theories of rubbers and gels originally proposed by Flory (Flory, 1953, 1976; Graessly, 1975; Deam and Edwards, 1976; Pearson 1977). These are detailed and very powerful microscopic theories which, undoubtedly, contain the essential physics of the systems they describe. They also predict the results of experiments very well. Polymeric network theories are however constructed along very different lines from the general *Cauchy–Born* (CB) theory of solids. They do not use an expansion around a reference state and do not determine macroscopic response from a formal continuum limit. This is very strange because the CB theory is the only systematic approach to the description of solids one has.

The discrepancy with the standard theories of solids becomes even more striking when one notes that the networks of springs used in the theories of rubbers and gels do not satisfy the standard criteria for the shear rigidity of such networks. Nevertheless they calculate the shear rigidity correctly. How can it be true, e.g., that shear rigidity appears at the gel-point – as soon as an infinitely connected network is formed? (Stockmayer, 1943, 1944; Zimm and Stockmayer, 1949).

Is this an accident? Is it an accident that the only systematic theory of an amorphous material one has, is not a *CB* theory and has these strange consistency problems?

1.3. The shear rigidity of stressed networks

My initial motivation in starting the work which I describe below was an attempt to understand these discrepancies. I tried to find a way to formulate the network theories of gellation and rubber elasticity in the framework of the general CB theory of the mechanical properties of solids. The hope was that this would then explain why the theories work and, in particular, how such very tenuous networks of springs can have shear rigidity.

As a motivation for a research program this is a somewhat unconventional point of view. The question one is asking is primarily a question of theoretical consistency between two theoretical approaches and not a question of agreement between theory and experiment. The theories of rubbers and gels are, of course, not perfect in all details but this is irrelevant. There is certainly no reason to doubt their essential correctness. The polymeric-network and percolation models which they use describe the essence of the underlying physical situations and they also "work" extremely well. To argue that the models miss essential physical ingredients, e.g., explicit angular bending forces, simply does not make sense.

In two papers (Alexander, 1984, 1985a) I showed that one can quite easily reformulate the network theories of rubbers and gels as a CB expansion. One then finds that polymeric networks have shear rigidity only because they are stressed. They have shear rigidity because the polymeric springs which constitute them are stretched by the osmotic pressure. One finds that the term in the elastic energy which is responsible for the shear rigidity of polymeric networks is

$$p \cdot \sum (\partial_\alpha u_\beta)^2 \,. \tag{1.1}$$

The shear rigidity is completely due to the fact that the network is stressed. The shear rigidity, Eq. (1.1), vanishes with the osmotic pressure, p. One also finds that when identical networks are constructed from springs which are not stretched they have no shear rigidity at all. The result for unstretched springs is thus in full agreement with the standard rigidity criteria (see, e.g., Dewdney, 1991).

One also notes that the expression (1.1) for the dependence of the elastic energy on the shears $\partial_\alpha u_\beta$ is anomalous. It does not vanish when

$$\partial_\alpha u_\beta = -\partial_\beta u_\alpha \tag{1.2}$$

as for a rotation even though the symmetric linear strain – $(\partial_\alpha u_\beta + \partial_\beta u_\alpha)$ – vanishes. This demonstrates that p in Eq. (1.1) does not play the role of a proper shear modulus and that the shear rigidity of rubbers and gels is qualitatively different from that of the "ordinary" solids discussed in texts on elasticity.

Thus the results I presented in 1984/1985 fully solved my initial problem.

They showed that when one uses a suitable formalism the Flory theory can be reformulated as a CB expansion – as expected. They also show that "rubber elasticity" is qualitatively different from the elasticity of crystals. The elasticity of rubbers and gels is the elasticity of stressed networks, its origin is in the "scalar elasticity" terms in the harmonic expansion of the energy of a stretched spring which are proportional to

$$u_{ij}^2 = (\boldsymbol{u}_i - \boldsymbol{u}_j)^2 \, . \tag{1.3}$$

Such terms do not show up when the spring is not stretched. This means that the bulk shear rigidity of rubbers and gels falls into the same category as the transverse rigidity of stretched strings and drumheads and is therefore qualitatively different from the bulk rigidity of most solids.

1.4. Why this monograph was written?

I returned to these problems a decade later for two reasons:

One concerned the theory of rubbers and gels. It became evident that the message I had tried to convey in 1984 did not get across – this in spite of considerable efforts I made. I thought, and still think that this is a pity. The implications of this difference are usually not dramatic but they are real and observable. It was also frustrating to realize that I was unable to explain something which seemed perfectly straightforward to me – so much so that I was even suspected of ignoring rotational invariance – presumably because the expressions in Eqs. (1.1) and (1.3) do not "look" right. Anyway I felt that I should try once more.

The second reason for trying to work out the theory fully and in detail was the hope that it would turn out that the theory of rubbers and gels provided a clue to the understanding of other amorphous solids – in particular glasses. I knew I could handle rubbers and gels so there was a chance that one would also be able to handle glasses in the same way. If initial stresses were so important in rubbers and gels they could also be important in understanding the properties of other types of amorphous solids like glasses. This was of course just a hope but it was also a challenge.

For these reasons I decided to go back and work out the implications of using a completely general translation–rotation invariant formalism in the CB expansion – in full detail.

1.5. The structure

This work consists of three parts.

Part I, the Cauchy–Born theory of solids, describes a general and explicitly translation–rotation invariant formulation of the Cauchy–Born theory. The configuration of a system of particles relative to each other can always be regarded as determined by the distances between them. Because of this the translation–rotation invariance, energy of a many particle system can be regarded as a general function of the interparticle distances. Using this we derive the most general CB expansion. The formalism allows a local derivation of the continuum limit which is convenient for calculating the elastic constants and the initial stresses from the microscopic expansion around a specific reference state. This brings out the specific role of the initial stresses in the reference state of the solid.

In Part II – the rigidity of floppy bonded networks – we study rigidity using the formalism developed in Part I. The theory developed in this section extends the standard considerations of the effect of stresses on the elastic stability of solids with anisotropic shapes (see, e.g., Landau and Lifshitz, 1970, ch. II) to the complex internal structures which describe the bulk of solids.

The interaction scheme of a physical model, the bond structure of its energy, defines a graph – the bonded network of the model. A network in d-dimensions which does not become rigid when all its bonded distances are fixed is geometrically floppy and can be deformed continuously. We show that a model which is described by a floppy bonded network has a manifold of free degrees of freedom which have no restoring force constants in the expansion around unstressed reference states. When the reference state around which one is expanding is stressed these modes become either unstable, leading to structural buckling instabilities, or stable – depending on the sign of the relevant stresses.[1] The theory of floppy networks allows us to study structural buckling, the bulk analogs of Euler (1755) buckling, and the stabilization of bulk shears by stretching which is particularly important in soft solids like rubbers and gels.

In Part III – the role of stresses in amorphous solids – we apply these results to specific physical situations. The emphasis is on the linear stability of the reference state – stability against structural buckling – and on the role of stresses in stabilizing the soft modes of tenuous bonding structures.

Rubbers and wet gels are described by floppy bonded networks and their shear rigidity is then that of stretched networks which, like stretched membranes, exert forces on their external boundaries. We show that this is consistent with mechanical equilibrium only because such solids are not rigid down to the atomic level. Their properties as solids are described by partially averaged thermodynamic potentials, parametrized free energies, and not by the atomic Born–Oppenheimer energies.

We discuss the stability of stressed granular packings emphasizing the fact that the packing has to be stable against structural buckling. This gives considerable insight into the internal mechanics of granular packings because it not only considers the equilibrium conditions on the individual grains but also the collective linear stability of a stressed packing.

We then describe a new model of quenched glasses which emphasizes the role of the internal stresses in the glass. The essence of this model is the distinction between the molecular configuration in the quenched liquid, the "snapshot state" and the stable equilibrium reference state of the glass which emerges from it even for the most rapid ideal quench. We argue that structural buckling dominates the restructuring in the ideal quench and show that this predicts strong correlations between the local structure of the reference state and the internal stresses. Some of the most striking properties of glasses appear naturally in this microscopic model.

2. The definition of a solid

2.1. The macroscopic definition

Our intuitive concept of a solid is macroscopic. A solid has shear rigidity. It retains its shape when external forces are applied to it or rather returns to it when the external forces are removed. This can be regarded as a macroscopic definition of a solid.

On a more sophisticated level the macroscopic behavior of a solid is described by a continuum field theory, *the theory of elasticity*, which describes the way a solid deforms when external forces are applied. The deformation of the solid is described by a vectorial field, $\boldsymbol{u}(\boldsymbol{r})$, which describes

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[1] This has a long history. The stabilization of shears by stresses is important in musical instruments and destabilization, buckling goes back at least to Euler (1755).

the distortion of a continuum space – the reference frame of the solid. The derivatives of this displacement field $\partial_\alpha u_\beta$, describe the infinitesimal local distortions of the solid – the volume changes and the shears – or, equivalently, the changes in the metric (Landau and Lifshitz, 1970, ch. 1). These dimensionless variables and their conjugate stresses are the basic variables in the continuum theory of the elasticity of solids.

The field theory constructed in this way is specific to solids. It is not just that fluids have no shear modulus. One cannot define a rigid reference space for a fluid and therefore also no deviation field, $\boldsymbol{u}(\boldsymbol{r})$.

This shows up clearly when one considers the description of relative density changes, $\delta\rho/\rho$, which appear in the description of the response of both fluids and solids. The density change of a solid can be computed from the deviation field, $\boldsymbol{u}(\boldsymbol{r})$

$$\delta\rho/\rho = \operatorname{div}\boldsymbol{u} + \text{h.o.t.}$$

The density change of a fluid cannot be described in this way because a fluid has no rigid reference frame.

One can therefore generalize the intuitive concept of a solid and regard the existence of a rigid reference frame as definition. A solid has a rigid reference frame and can therefore be described by the theory of elasticity. This is a *macroscopic* definition of a solid. But the rigid reference frame must have a microscopic meaning on the atomic level. There is therefore also a *microscopic* definition.

2.2. The microscopic definition

The rigid reference frame assumed in the theory of elasticity must have some physical meaning. In most cases this means a rigid underlying arrangement of microscopic particles. The microscopic description of the solid then starts with the definition of a *rigid reference configuration* of the constituent particles:

$$\{\boldsymbol{R}\} = \{\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_i, \ldots\}\,. \tag{2.1}$$

The requirement that one can define such a microscopic reference state consistently – as a rigid reference state for the deformations of the solid – amounts to a *microscopic* definition which is distinct from the macroscopic definition of a solid. The two intuitive definitions of a solid are connected by the CB theory of solids.

2.2.1. Non-atomic solids

One tends to think of the particles in this microscopic description as well defined particles – atoms, molecules, etc. We will assume this implicitly in most of our discussion below. It is however obvious that there are other possibilities.

Some solids – rubbers, gels, foams, etc. – are not rigid at the elementary molecular level. One can define a rigid framework – of the type (2.1) – but only at scales considerably larger than the elementary atomic scales. We shall discuss this in detail when we discuss soft solids in Section 14.

For completeness we also note that when one discusses solidification in a Landau symmetry breaking form – as the breaking of continuous translational–rotation symmetry (Landau, 1937b; Alexander and Mctague, 1978; Alexander, 1981, 1985b; Baym et al., 1971; Brazovskii et al., 1975, 1978; Lebedev et al., 1995) – one gets a continuum description of a solid phase with no explicit microscopic building blocks. The most obvious realizations of this are mesophases, and in particular the "blue phases" of Cholesteric liquid crystals (Brazovskii et al., 1975, 1978; Alexander, 1981).

2.3. Consistency of the Cauchy–Born theory

2.3.1. The CB expansion

The CB theory of solids is well known and is described in all standard texts on the physics of solids.[2]

Within the CB scheme the mechanical energy of a solid is regarded as a function of the positions of the particles which constitute the solid

$$\mathscr{E} = \mathscr{E}(\{\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_i, \ldots\}) . \tag{2.2}$$

One expands this energy around the many-particle reference state, $\{\boldsymbol{R}\}$, in the deviations of the positions of the particles from their equilibrium values:

$$\boldsymbol{u}_i = \boldsymbol{r}_i - \boldsymbol{R}_i . \tag{2.3}$$

This gives a microscopic description of the mechanical properties of the solid – its "Lattice Dynamics". One then derives the continuum field equations of elasticity from the continuum limit of the CB expansion.

This procedure is quite old.[3] Navier (1827) and Cauchy (1828b, c) have already used such microscopic models in their derivation of the concepts and of the general field equations of continuum elasticity. The more general modern version of the microscopic expansion procedure, the theory of Lattice Dynamics, was developed by Born (Born and von Kármán, 1912, 1913; Born, 1915, 1923, 1943).

2.3.2. Consistency – the Lindemann rigidity criteria

The *Cauchy–Born* expansion procedure assumes that the reference state $\{\boldsymbol{R}\}$, Eq. (2.1), is sufficiently rigid so that the expansion makes sense. The theory requires that one can define a rigid microscopic reference state $\{\boldsymbol{R}\}$ around which one can expand consistently. One can write down a many particle energy, Eq. (2.2), for any collection of N particles. The requirement that it has a rigid reference state $\{\boldsymbol{R}\}$, Eq. (2.1), is then a physical requirement which depends on the conditions imposed on the system.

It is natural to express this as a consistency condition on the CB expansion itself by calculating the fluctuations and comparing them to the equilibrium separations. Consistency requires

$$\frac{\langle \delta r_{ij}^2 \rangle_{\mathrm{CB}}}{R_{ij}^2} < 1 \tag{2.4}$$

for any pair of particles i, j, where $R_{ij} (= |\boldsymbol{R}_i - \boldsymbol{R}_j|)$ is the equilibrium distance and $\langle \delta r_{ij}^2 \rangle_{\mathrm{CB}}$ the mean square deviation calculated from the CB expansion.

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[2] We only mention some of the more classical texts and monographs – Peierls (1955) ch. I and II, Kittel (1963) ch. 2, Born and Huang (1954) and the discussion in Landau and Lifshitz (1980), ch. VI.

[3] A fascinating and very illuminating description of the history of the theory of elasticity is given by Love (1927b).

We will call this the *Lindemann rigidity criterion* (LRC).[4]

Within the CB scheme macroscopic shear rigidity, Section 2.1, is assured by the long range limit of the Lindemann rigidity criterion

$$\lim_{r\to\infty} \mathscr{L}(r) = 0\,, \tag{2.5}$$

where

$$\mathscr{L}(r) = \left\langle \frac{\langle \delta r_{ij}^2 \rangle_{\mathrm{CB}}}{R_{ij}^2} \right\rangle_{R_{ij}=r} . \tag{2.6}$$

Eq. (2.5) assures that one can calculate a finite shear modulus, μ, from the CB expansion because

$$\mathscr{L}(r) \propto (\mu r^d)^{-1}$$

for large r – a very general and familiar result.

But the consistency of the CB expansion also requires consistency at the local level down to the smallest separations 'a':

$$\mathscr{L}(a) < 1 \tag{2.7}$$

which is obviously a necessary condition for the rigidity of the reference state.

2.3.3. *Long range order*

In discussing crystals one usually requires "long range order" which can be expressed as

$$\lim_{R_{ij}\to\infty} \frac{\langle \delta r_{ij}^2 \rangle_{\mathrm{CB}}}{a^2} \approx \lim_{R\to\infty} \left(\frac{R^2}{a^2} \mathscr{L}(R) \right) < 1\,. \tag{2.8}$$

This is, obviously, a much stronger condition than the long range LRC (2.5) which we required for the definition of a macroscopic shear modulus. In particular, one and two dimensional solids are solids according to (2.5), and one can define a shear modulus, but have no long range order.

In three-dimensions long range order is usually assured automatically – throughout the solid range – by the empirical Lindemann melting criterion

$$\frac{\langle \boldsymbol{u}_i^2 \rangle}{a^2} < 0.1 \tag{2.9}$$

(Lindemann, 1910) which predicts melting quite accurately for periodic crystals and apparently also for amorphous glasses.

Because

$$2\frac{\langle \boldsymbol{u}_i^2 \rangle}{a^2} = \lim_{R_{ij}\to\infty} \frac{\langle \delta r_{ij}^2 \rangle_{\mathrm{CB}}}{a^2} \gg \mathscr{L}(a) \tag{2.10}$$

it follows that the microscopic Lindemann consistency criterion (2.7) is obeyed as a strong inequality throughout the solid range, at least in 3-D.

Evidently our simple consistency argument cannot tell how small the left-hand side of the inequality (2.7) has to be.

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[4] We will discuss this criterion and its implications in detail in Section 14.1.

2.4. Crystals versus amorphous solids – periodicity and solidification

According to any reasonable criterion for defining a solid an amorphous glass is just as solid as a crystal.

On the theoretical side this is shown by our discussion above. None of the consistency criteria for the CB theory seem to make any sharp distinction between crystalline solids – with periodic reference states – and amorphous solids with reference states which are random. Even long range order is defined in Eq. (2.8) in a most natural way which applies equally to amorphous and crystalline materials. There is simply no valid reason why the low temperature properties of an amorphous glass should not be described by a CB expansion just as well as the low temperature properties of a crystal are described by such an expansion around its periodic reference state.

This agrees with the empirical experimental situation. There are differences between crystalline and amorphous solids which are important and intriguing but they are much smaller than the differences between solids of either type and liquids. Amorphous solids do not "flow" more than crystals and both the real and the imaginary parts of the shear modulus are comparable. There is no way one could justify classifying SiO_2 window glass as a liquid.

When a liquid crystallizes continuous translation–rotation symmetry is broken and only the discrete space group symmetry of the periodic crystal remains. This is a dramatic symmetry change – certainly the most obvious example of symmetry breaking in our everyday experience. Nothing like this occurs at the glass transition. Translation–rotation (TR) symmetry is not broken. Thus if one wants to classify amorphous solids as solids one cannot associate solidification with the breaking of TR symmetry as is often done.

We will argue that there is nevertheless a *universal symmetry* which is broken by solidification and that this is *permutation* symmetry which is broken by quenching. Permutations of equivalent particles are a real active symmetry in the fluid and this symmetry is *always* broken on solidification. The solid is described by a unique state which realizes one special permutation of the constituent atoms on the lattice sites – out of $N!$ possible ones.[5]

2.5. In the CB theory the particles are labeled

The CB expansion labels the particles in a solid by their respective equilibrium positions. On a deeper and more formal level this means that they are treated by the theory as *distinguishable* even when they are equivalent. Their permutation symmetry is quenched. States related by the exchange of equivalent particles are treated by the CB theory as separate states.

The quenching of permutation symmetry is the reason why the theoretical description of solids is much simpler than that of the corresponding liquids. Even an amorphous solid can be described by expanding around a specific, rigid and well defined atomic arrangement – its specific random reference state. The CB theory does not allow the particles to interchange their equilibrium positions. This means that most of the complex averaging between different configurations which is essential in the theory of real fluids – and the corresponding complex entropy considerations – disappear when one is considering the solid.

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[5] Obviously this assumes that the solids can be described as consisting of some sort of identifiable "particles" whose positions can be permuted.

This simplification is illustrated by the dramatic difference in the description of the phase transition between the two phases. Melting, the *solid-to-liquid* transition is predicted quite accurately and almost quantitatively by the simple and very intuitive Lindemann melting criterion (Lindemann, 1910). On the other hand, even the best microscopic descriptions of freezing, the *liquid-to-solid* transition, are complicated, controversial and inaccurate.

2.5.1. The correlation functions of solids

The quenching of permutation symmetry in solids is clearly seen in the correlation functions one calculates and which dominate the theory.

The *Cauchy–Born* expansion is a many body expansion. One does not expand in the deviation of one specific particle, $\boldsymbol{u}_i$, but in the deviations of many essentially equivalent but distinct particles

$$\{\boldsymbol{u}\} = \{\boldsymbol{u}_1, \boldsymbol{u}_2, \ldots, \boldsymbol{u}_i, \boldsymbol{u}_{i+1}, \ldots, \boldsymbol{u}_j, \ldots, \boldsymbol{u}_N\}\,. \tag{2.11}$$

Expanding in the deviation $\boldsymbol{u}_i(t)$ follows the particle "i", the specific particle whose equilibrium position is $\boldsymbol{R}_i$, along its path. The calculation keeps track of particle "i" without confusing it with some other particle, "j". This labeling of the particles by their separate equilibrium positions is an essential ingredient of the *Cauchy–Born* theory of solids. The essence of the *microscopic* CB description of a solid is that it is possible to describe the properties of the solid in this way. The CB theory *assumes* that the particles in the solid can be treated as distinguishable and can be labeled by their equilibrium positions.

In the CB theory the solid is described by the labeled positional correlation functions:

$$S_{ij}(\tau) = \langle \boldsymbol{r}_i(t) * \boldsymbol{r}_j(t+\tau)\rangle = \boldsymbol{R}_i * \boldsymbol{R}_j + \langle \boldsymbol{u}_i(t) * \boldsymbol{u}_j(t+\tau)\rangle \tag{2.12}$$

where the asterisk implies the dyadic external product of two vectors. $S_{ij}(\tau)$ are correlation functions between particles labeled by their equilibrium positions.

The CB procedure treats the two particles "i" and "j" as separate even when they are indistinguishable particles. The calculation follows the particle i in time and, separately, the particle j and labels the particles by their respective equilibrium positions – 'i' means "the particle with equilibrium position $\boldsymbol{R}_i$". The possibility that at some time the particles may interchange their positions so that $\boldsymbol{R}_j$ will become the new equilibrium position of the particle *labeled i*, and $\boldsymbol{R}_i$ that of particle j is not taken into account by the CB theory which, nevertheless, describes the properties of the solid correctly. Thus the *Cauchy–Born* theory of solids treats the microscopic particles as *labeled* and *distinguishable* – and this was not changed by the discovery of quantum mechanics and quantum statistics. The CB theory of the solid disregards the "$N!$" permutation symmetry of classical statistics and deals only with one specific permutation of the constituent particles.

The long-time average of the correlation function of the average positions of two labeled particles is treated by the CB theory as a constant.

$$\overline{\langle \boldsymbol{r}_i(t) * \boldsymbol{r}_j(t+\tau)\rangle} = \boldsymbol{R}_i * \boldsymbol{R}_j + \langle \boldsymbol{u}_i(t) * \boldsymbol{u}_j(t+\tau)\rangle \approx \boldsymbol{R}_i * \boldsymbol{R}_j\,. \tag{2.13}$$

One can treat the solid in this way because the fluctuations in the relative positions of the constituent particles are small even when they are close neighbours, (2.7). The physical processes which exchange particle positions, single particle diffusion and tunneling, are slow and relatively unimportant in the solid and can therefore be neglected in the CB theory. The correlation in the average positions of labeled particles, the r.h.s of (2.13), decays by single particle diffusion and, in the solid, this happens very slowly – on time scales relevant to the rapidly fluctuating part, $\langle \boldsymbol{u}_i(t) * \boldsymbol{u}_j(t+\tau)\rangle$. For this reason the CB theory can neglect these processes and can treat the particles as labeled.

2.5.2. Labeled correlation functions in fluids

It is instructive to compare this to the situation in fluids – gases or liquids.

Formally one can of course also label the particles in a fluid and use this to define labeled correlation functions

$$S_{ij}(\tau) = \langle \boldsymbol{r}_i(t) * \boldsymbol{r}_j(t+\tau)\rangle \tag{2.14}$$

as in (2.12). Just as in the solid these are the correlation functions one obtains directly from the solution of Newton's equations of motion for the many particle system. But in a fluid such correlations decay very rapidly – in microscopic times. Two particles, i and j which were close to each other at time t_0 loose all memory of this fact after a short time – when they are separated by a few interatomic distances.

The correlation functions which are important and dominate the theory of both classical and quantum liquids are density–density correlation functions:

$$g(|\boldsymbol{r} - \boldsymbol{r}'|, \tau) = \langle \rho(\boldsymbol{r}(t))\rho(\boldsymbol{r}'(t+\tau))\rangle \tag{2.15}$$

whose definition already assumes averaging over the permutations of equivalent particles.

Since the density can be regarded as a sum over the positions of labeled particles

$$\rho(\boldsymbol{r}) = \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \tag{2.16}$$

the density correlation functions (2.15) can, in principle, be computed from labeled correlation functions (2.14). This would however be an extremely laborious and cumbersome procedure because it is very difficult to keep track of the complex movement of labeled particles in the time evolution of fluids. Even in a simulation it is prohibitively difficult to keep track of the distinction between the states related by permutations.

In a fluid the particle dynamics is such that the theory does not and *cannot* distinguish between identical particles and the physically important correlation functions have to be computed as averages over their permutations.

2.5.3. Quantum statistics in solids

The CB theory treats the particles as distinguishable and therefore as classical particles. In a quantum mechanical description one can say that exchange can be neglected. The labeled N-particle "wave function" which describes the solid

$$\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i, \ldots, \boldsymbol{r}_j, \ldots, \boldsymbol{r}_N)$$

is orthogonal to the wave function related to it by a permutation

$$\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_j, \ldots, \boldsymbol{r}_i, \ldots, \boldsymbol{r}_N)\,.$$

Because of this the particles can be treated as distinguishable and labeled even in a fully quantum mechanical description because permutations have (almost) no physical effect. Quantum fluids are very different from classical fluids but quantum solids are very rare and, moreover, not really very different from classical solids. This includes even the most extreme cases of quantum solids – the Wigner lattice and solid helium. Anderson (1984) discusses this in somewhat greater detail.

We note that a related physical *quenching* of permutation symmetry by physical barriers occurs in molecular physics. The quantum statistics of the nuclei is important in the classification of the states of polyatomic molecules (Breit and Wilson, 1935) but only permutations which can be realized without overcoming high potential barriers have to be considered. Thus, e.g., only the symmetric permutations of the protons appear in the classification of the rotation spectrum of methane (CH_4). These permutations can be realized by rotations. The antisymmetric permutations can only be realized by breaking the chemical C–H bonds and are therefore quenched.[6]

2.6. Permutation entropy

The role of the permutations of the atoms in a solid is in essence a classical problem. One should therefore understand and interpret it within the framework of classical Boltzmann statistics. The natural way for doing this is to consider the "permutation entropy" as a classical missing entropy – in the same category as the missing entropy one observes when the low temperature state is disordered.

We shall discuss this interpretation here briefly even though it is not relevant to our argument in the rest of this article.

Quenched disorder in the low temperature state shows up as a *missing entropy* in thermodynamic measurements.

When the low temperature phase is disordered only one out of a very large number of possible arrangements which are essentially equivalent is actually realized. Transitions between the different possible realizations are non-ergodic – they are very slow and do not occur on the time scales relevant to the measurements. Because of this the entropy associated with the multiplicity of possible realizations of the disorder is quenched and does not show up in specific heat measurements:

$$S_{T=\infty} - \int_0^\infty \frac{c(T)}{T}\,\mathrm{d}T = S_{\mathrm{miss}} \propto \log \mathscr{m} \neq 0\,, \tag{2.17}$$

where $\mathscr{m}$ is the number of possible states. Nernst's third law of thermodynamics is violated. This is observed in many situations – e.g., for ice,[7] for glasses and for spin glasses.

The quenched *missing entropy*, S_{miss}, has a purely classical origin. Quantum statistics and quantum mechanics play no role in the understanding of the disorder in the low temperature state. We believe that one should interpret the role of "permutation entropy" in the same way – as a purely classical missing entropy. A "real" entropy which is not observed because the $N!$ multiplicity is quenched.

2.6.1. Permutation entropy is a missing entropy

One relates Statistical Mechanics to Thermodynamics by Gibbs ensemble averages. This involves counting the states of the system. For an N particle state the only way one can do this counting in

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[6] A somewhat more detailed discussion can be found in Alexander and Lerner Naor (1972) and Wong et al. (1969).

[7] I believe the first observation of a missing entropy was by Giauque, in the 1930s, in experiments on ice. The missing entropy there is due to the many arrangements of the hydrogen bonds consistent with the ice rules.

practice is by treating identical particles as distinguishable. One labels the particles and counts what Gibbs calls "*specific phases*" (Gibbs, 1901, ch. XV). The number of states one gets in this way, $\varkappa_{\mathrm{spec}}$, contains a factor $N!$ – the number of permutations of N identical particles.

In classical statistical mechanics this $N!$ degeneracy cannot be removed by any physical mechanism. Gibbs therefore concludes that all the "*specific phases*" which only differ in such permutations should be counted as one state, a "*generic phase*" (Gibbs, loc. cit.)

$$\varkappa_{\mathrm{gen}} = \varkappa_{\mathrm{spec}}/N!\,. \tag{2.18}$$

Counting generic phases recovers Nernst's third law of thermodynamics from the statistical definition of the entropy

$$\lim_{T\to 0} S \propto \lim_{T\to 0} \ln \varkappa_{\mathrm{gen}} = 0 \tag{2.19a}$$

while

$$\lim_{T\to 0} \ln \varkappa_{\mathrm{spec}} = \ln N! \neq 0\,. \tag{2.19b}$$

Within classical mechanics this is purely formal. It obviously cannot make any difference to experimental predictions if one chooses to count "*specific phases*" or "*generic phases*". The only difference is in the interpretation.

If the "correct" states are the "*specific phases*" then there is a permutation entropy but it cannot be observed. The low temperature phase is then solid and, as we explained above, permutation symmetry is quenched. A solid realizes *one* specific permutation of the labeled particles – out of the $N!$ possibilities. From this point of view the "missing" permutation entropy is not different from any other missing entropy.

Alternatively one can count "*generic phases*". This is the procedure favored in most modern discussions. This means that there is no permutation entropy at all. It is not a missing entropy but simply does not exist. As a practical device for obtaining the correct answer this is of course an equivalent procedure. As Gibbs suggested[8] there are also practical considerations for describing a fluid in terms of "*generic phases*" as we indicated above in Section 2.5.2. But this is quite different from attributing some deep meaning to this procedure.

The obvious explanation as to why it is adequate to count "*generic phases*" in classical physics is that this symmetry cannot be broken and is therefore never observed. To argue that counting "*generic phases*" is correct because of some deep connection to quantum statistics is simply not correct. The classical states related by permutations are not one state. Counting "*generic phases*" means that states which are obviously distinct in the dynamic evolution of the system and are represented by $N!$ different points in phase space – are *counted* as one state. Claiming that they are "really" one seems highly mysterious to students, and not only to students.

To see how strange this interpretation is, consider the implications for solids. At $T=0$ there are obviously $N!$ different realizations of the classical solid. One can even transform them into each other

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[8] One notes that in contrast to most modern texts Gibbs (loc. cit.) was quite cautious in his discussion of the relative merits of using the two types of "phases". It is evident from Gibbs' discussion that he was aware of the fact that there are situations where the *specific phase* is more natural and that the choice of "*phase*" is really a matter of convenience. Even for classical Boltzman statistics it should, and does, depend on the actual physical situation which is a better choice.

by suitable experimental procedures. Saying that they are all "one state" has no physical meaning whatsoever. It is also, and quite obviously, quite different from the statement that the coherent quantum mechanical superposition of these states must be symmetric or antisymmetric because this coherent superposition has no relation whatsoever to the description of what one observes in the real world.

Quantum statistics does not make any difference. The CB theory treats the atoms as classical and this is correct in both classical and quantum physics. One can also say that in this sense solids are always classical. Permutations which are not realized physically do not distinguish between quantum and classical particles. Even mentioning the effects of quantum statistics on permutations in this context complicates the explanation of a fairly straightforward and *purely classical* problem – without any evident advantages.

A self-contained version of the discussion in this chapter is available in Alexander (1997).

PART I. THE CAUCHY–BORN THEORY OF SOLIDS

We want to apply the *Cauchy–Born* approach to amorphous solids. This means we want to study the CB expansion around reference states which are random. There is no fundamental reason why this should not be possible – as we argued in detail in Section 2. In practice it is however not at all obvious how one should go about this because many of the features of the standard textbook algorithms cannot be carried over to situations when the reference state is random. We therefore have to reformulate the derivation to put it into a form suitable for formulating the theory and its derivation in the most general way possible which is consistent with the general symmetry requirements.

In principle the *Cauchy–Born* expansion procedures are so general that they are almost synonymous to the definition of a solid. One describes the solid in terms of the positions of suitably defined particles and by an expansion around a microscopic reference configuration of the positions of the particles (Eq. (2.1))

$$\{\boldsymbol{R}\} = \{\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_i, \ldots\}\,.$$

As we explained in Section 2 one expects this to be adequate for the description of both crystalline and amorphous solids.

In practice one has a very good CB theory of periodic crystalline solids but nothing comparable for amorphous materials. In fact the only really successful microscopic theory of the mechanical properties of an amorphous material, the polymeric network theory of rubber elasticity, carefully avoids the CB framework and arrives at its results by a very different route. We believe that the reason for this is essentially technical.

The procedures one uses traditionally in carrying out the CB expansion were developed with periodic crystals in mind. One expands the many-particle energy $\mathscr{E}(\{\boldsymbol{r}\})$ directly in the components of the single particle deviations $\boldsymbol{u}_i$:

$$\mathscr{E}(\{\boldsymbol{r}\}) = \mathscr{E}(\{\boldsymbol{R}\}) + \sum (\boldsymbol{u}_j \cdot \boldsymbol{\nabla}_j)(\boldsymbol{u}_i \cdot \boldsymbol{\nabla}_i)\mathscr{E} + \cdots$$

and then proceeds to calculate the vibrational eigenstates and their long wavelength continuum limit. This is feasible only as long as one can use the lattice periodicity to carry out an explicit expansion in the vibrational eigenmodes. Attempts to apply this procedure to the description of amorphous solids in general have not proved very effective. We believe that this is largely responsible for the unsatisfactory state of the microscopic theory of such solids. There are a number of features one wants in the formalism:

(a) *Automatic rotational invariance.* One obviously requires that the energy $\mathscr{E}(\{\boldsymbol{r}\})$ is invariant under translations and rotations both globally, for the system as a whole, and also locally, for the part of $\mathscr{E}(\{\boldsymbol{r}\})$ which describes the internal interactions in any region. *Translation–rotation invariance* (TRI) must therefore be a property of the CB expansion around any reference state, and to any order in the components of $\boldsymbol{u}_i$.

If one chooses a specific TRI function $\mathscr{E}(\{\boldsymbol{r}\})$ and expands it around a specific reference state $\{\boldsymbol{R}\}$ this is of course automatic. In constructing a *general* theory one wants a formalism for which TRI symmetry is manifested in the form of the expansion itself – without reference to the functional form of the energy and to the atomic arrangement in the reference state.

The general relations between the expansion coefficients which assure *translational* invariance are familiar and easy to derive. Any expansion in the relative deviations, the components of

$$\boldsymbol{u}_{ij} = \boldsymbol{u}_i - \boldsymbol{u}_j$$

is automatically TI. This can also be expressed as a condition on the expansion coefficients – for example

$$\sum_j K_{i,j}^{\alpha,\beta} = 0\,.$$

It is however not possible to derive similar simple criteria for *rotational* invariance[9] (RI) which would assure that the coefficients of the expansion describe an RI series. In a general theory one wants a formalism in which full TR symmetry is assured automatically without first specifying $\{\boldsymbol{R}\}$ and $\mathscr{E}(\{\boldsymbol{r}\})$.

(b) *Stresses in the reference state.* The reference states of amorphous materials are often tenuous, at least locally. One therefore expects stresses in the reference state to be much more important in amorphous materials than in crystals. Internal stresses are dominant in the shear rigidity of rubbers and gels (Alexander, 1984, 1985) and this suggests that they could also be important in other amorphous solids. But stresses do not show up at all when one expands directly in the $\boldsymbol{u}_i$ because all linear terms must vanish in equilibrium.

One needs a formalism in which the role of stresses can be studied.

(c) *Many-body interactions.* It is well known that microscopic *many-body interactions* – in particular 3-body bending and 4-body twist interactions – have important effects on the shear rigidity of solids. Such interactions are expected to be particularly important for weakly bound tenuous structures (Bergman and Kantor, 1984; Kantor and Webman, 1984; Feng, 1985).

When one writes the harmonic expansion in terms of the components of the $\boldsymbol{u}_i$ the distinction between 2-body interactions and many-body interactions gets obscured. Each term in the expansion has – at most – *two* site-indices so that many-body interactions can leave no obvious signature.

(d) *Local continuum limit.* One is also interested in a formalism in which the relationship between the microscopic expansion and its continuum limit and the local meaning of this limit will be clear.

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[9] This can be seen in the detailed discussion of rotational invariance in Born and Huang (1954).

Important properties of the energy – rotational invariance and many-body interactions – and of the reference state – the "initial" stresses – are thus obscured when one expands directly in terms of the single particle deviations $\boldsymbol{u}_i$. This makes it difficult to study the *general* formal structure of the TRI microscopic expansion and the effect of stresses in the reference state on this expansion.

In constructing a formalism which avoids these problems we will use the fact that a TRI energy can always be considered as a function of the internal configuration of the interacting particles and therefore of the distances between them. Any function of the distances

$$r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$$

between the particles, $\mathscr{E}(\{r\})$ is TRI. This is often used in the theory of molecular vibrations (Herzberg, 1945). We will use this to construct a general TRI formalism for the CB expansion. This automatically guarantees TRI as a global symmetry of the system as a whole and also as a local symmetry.

As we will show it is also easy to define the local stress as a property of the reference state and to derive the stress induced terms in the CB expansion to distinguish the contributions of many-body terms and to obtain a local continuum limit for the expansion.

Historical comment. The classical – mostly 19th century – work on elasticity relied heavily on microscopic models in clarifying continuum field concepts such as *stress* and *strain.* It was generally assumed that the energy had to be a sum of two-body central force interactions (the Cauchy model). Thus the energy appeared as a function of the distances between interacting particles and microscopic expressions for the stress appeared naturally in the expansion.

These features disappeared in the later analysis of lattice dynamics which allowed more general forms for the energy. In theoretical discussions of lattice dynamics the microscopic stress induced terms are not mentioned explicitly even when local stresses and such stress induced terms clearly appear in the expansions, e.g. ionic crystals (Born and Huang, 1954). It is also customary to neglect stresses in the reference state. Born and Huang (1954) even *define* an equilibrium reference state as a state in which there are no stresses.

In the theory of vibrations of small molecules it is also common practice to assure TR invariance of the energy by writing the mechanical energy as a function of distances (e.g. Herzberg, 1945).

What we do here is a generalization (and revival) of the old formal procedure – to general translation–rotation invariant forms of the energy. We also introduce a more modern and compact formalism. In the continuum limit we essentially rederive the classical results. The main new result is in the expressions we get for the microscopic expansions which were of relatively little interest in the 19th century work. We distinguish clearly between the stress induced terms in these expansions and those which appear in expansions around unstressed reference states.

Presenting this form of the CB and working it out in detail is the contents of Part I of this article. We present a detailed derivation of the microscopic expansion of the mechanical energy around a general equilibrium reference state which can be stressed. We then derive the continuum limit of this expansion. We demonstrate that the general rotation invariant microscopic expansion contains special stress-induced terms which are qualitatively different from those one finds when there are no stresses in the reference state.[10] In the continuum limit these terms are responsible for the appearance of the second order strain, $\Sigma_\gamma \partial_\alpha u_\gamma \partial_\beta u_\gamma$, in the elastic energy.

We discuss the equilibrium conditions and the linear expansion in Section 3. We then discuss the continuum limit and the derivation of the stress–strain relations in Section 4. The standard expansion

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[10] We are not aware of any discussion of these microscopic stress induced terms except for Alexander (1984, 1985). Their continuum limit, the product of the stress and the second order strain is of course familiar in the discussion of elastic stability (Landau and Lifshitz, 1970). In Part II we show that they are extremely important in understanding the dynamics of floppy networks.

around an *unstressed* reference state which we call the *Born–Huang* (BH) expansion is derived in Section 5. We show there explicitly that the continuum limit of the BH harmonic expansion yields the usual form of the elastic energy as an expansion in the components of the symmetric linear strain $\frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha)$. In Section 6 we then discuss the effect of the local stresses on the microscopic expansion. We derive the microscopic stress induced terms (Alexander, 1984) and show that their continuum limit provides the terms in the elastic energy in which the second order strain appears.

3. The expansion in distances

3.1. Parametrization of the energy in terms of distances

The internal energy of a system consisting of N particles can be regarded as a function of their positions

$$\mathscr{E} = \mathscr{E}(\{\boldsymbol{r}\}), \tag{3.1}$$

where

$$\{\boldsymbol{r}\} = \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i, \ldots, \boldsymbol{r}_j, \ldots, \boldsymbol{r}_N\} \tag{3.2}$$

and the vector $\boldsymbol{r}_i$ describes the position of atom i in space.

3.1.1. The internal degrees of freedom

The energy, $\mathscr{E}(\{\boldsymbol{r}\})$ describes the interactions among the N particles. It therefore must be invariant under rigid translations and rotations (TRI). The energy $\mathscr{E}(\{\boldsymbol{r}\})$ does not depend on the

$$\varkappa_{\text{rig}} = \tfrac{1}{2}d(d+1) \tag{3.3}$$

rigid body degrees of freedom of the system as a whole. It depends only on the remaining

$$\varkappa_{\text{int}} = \mathrm{d}N - \varkappa_{\text{rig}} \tag{3.4}$$

internal degrees of freedom of the N-particle system. This is equivalent to saying that the energy depends only on the *internal* geometric configuration of the N atoms relative to each other in the state described by $\{\boldsymbol{r}\}$.

Elementary geometrical considerations show that one can always describe this internal configuration by specifying $\varkappa_{\text{int}}$ *independent* distances

$$r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j| \tag{3.5}$$

between the particles.

Altogether there are of course $\frac{1}{2}N(N-1)$ different pairs $[ij]$ and distances, r_{ij}, among N particles but these distances cannot all be chosen independently. In d-dimensions $\varkappa_{\text{int}}$ distances are sufficient to determine all the others if they are independent so that none of these $\varkappa_{\text{int}}$ distances can be determined as a function of the others

$$\{r\} \Rightarrow \{r\}_{\text{ind}} = \{r_{12}, r_{13}, \ldots, r_{ij}, \ldots\} = \{r^1, r^2, \ldots, r^\nu, \ldots, r^{\varkappa_{\text{int}}}\}\,. \tag{3.6}$$

Any set, $\{r\}_{\text{ind}}$, of $\varkappa_{\text{int}}$ *independent* distances determines the internal configuration of the N points completely. It determines all the other distances between the points.

The atomic configuration which determines the TRI energy in the state described by the set of N atomic positions $\{\boldsymbol{r}\}$, Eq. (3.2), can therefore also be described as a function of the set of $\varkappa_{\text{int}}$ *independent* distances $\{r\}_{\text{ind}}$. The atomic positions $\{\boldsymbol{r}\}$ determine $\{r\}_{\text{ind}}$ and also the $\varkappa_{\text{rig}}$ rigid-body translational and rotational degrees of freedom of the system as a whole which are not determined by the distances and do not affect the energy.

3.1.2. The general translation–rotation invariant energy

Since a translation–rotation invariant energy depends only on the *internal* configuration of the interacting atoms one can always write it as a *function* of the set of independent distances, $\{r\}_{\text{ind}}$ which parametrizes this internal configuration. This means that the dependence of a TRI energy on the positions $\{\boldsymbol{r}\}$ can always be expressed as a dependence of the energy on a set of distances $\{r\}_{\text{ind}}$:

$$\mathscr{E}(\{\boldsymbol{r}\}) \Leftrightarrow \mathscr{E}(\{r\}_{\text{ind}}) . \tag{3.7}$$

The two forms of writing a TR invariant energy are equivalent and are related by substituting

$$r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j| = \sqrt{\sum (x_i^\alpha - x_j^\alpha)^2} . \tag{3.8}$$

Writing the energy as a *function* of the distances $\{r\}$ has the advantage that it *automatically* assures TRI for any functional form of the dependence of $\mathscr{E}(\{r\})$ on its arguments. Substituting Eq. (3.8) into any function $\mathscr{E}(\{r\})$ gives the most general TRI function of the atomic positions

$$\mathscr{E}(\{\boldsymbol{r}\}) = \mathscr{E}(\{|\boldsymbol{r}_i - \boldsymbol{r}_j|\}) = \mathscr{E}(\{r\}) ; \qquad r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j| . \tag{3.9}$$

This is completely general. There is no restriction on the functional form of $\mathscr{E}(\{r\})$ or on the distances which appear in $\{r\}$. Any function of the $\frac{1}{2}N(N-1)$ distances between N particles generates a TRI function $\mathscr{E}(\{\boldsymbol{r}\})$ when one substitutes Eq. (3.8) for the r_{ij}.[11] The implied relations between the distances and the restrictions on their ranges are all purely geometrical and follow automatically from the substitution.

3.1.3. Choosing the pairing scheme

Any TRI function of N particles can be written as a function of $\varkappa_{\text{int}}$ independent distances, Eq. (3.7).

The choice of the set of distances $\{r\}_{\text{ind}}$ assumes a definite pairing scheme $\{[ij]\}_{\text{ind}}$ – the choice of a *specific* set of pairs $[ij]$ whose distances appear in $\{r\}_{\text{ind}}$. When N is larger than $d+1$ this pairing scheme is not unique and can be chosen in many different ways which are formally equivalent. The atomic configuration described by $\{\boldsymbol{r}\}$, can be parametrized by different sets of $\varkappa_{\text{int}}$ independent distances. In this sense $\{r\}_{\text{ind}}$ is not unique. One can regard the set of distances $\{r\}_{\text{ind}}$ as coordinates which span the $\varkappa_{\text{int}}$-dimensional space of all the possible configurations of N points in d-dimensional

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[11] An illustration of this parametrization is the possibility of writing the most general interaction between three particles as a function of the three distances between the particles and the most general four-body interaction as a function of six distances (see Appendix A).

space. Different pairing schemes are related by trigonometric relations

$$\{r'\}_{\mathrm{ind}} = \{r'\}_{\mathrm{ind}}(\{r\}_{\mathrm{ind}})\,; \qquad r_{i'j'} = r_{i'j'}(\{r\}_{\mathrm{ind}}) \tag{3.10}$$

which follow from (3.8) and relate the distances r_{ij}. As long as the n_{int} distances, r_{ij}, are geometrically independent they all describe the same configurations of the N points. The specific choice of a pairing scheme is a matter of convenience.

We note that the fact that r_{ij} represent distances between points in d-dimensional space, Eq. (3.8), also imposes restrictions on the range of the distances in $\{r\}_{\mathrm{ind}}$. The *independent* distances are related by inequalities. An example is the familiar "triangle" inequalities

$$(r_{ij} + r_{jk}) \geq r_{ik} \geq |r_{ij} - r_{jk}|\,. \tag{3.11}$$

For a given pairing scheme the set of n_{int} independent distances $\{r\}_{\mathrm{ind}}$ is restricted by such inequalities to some specific regions of the n_{int} dimensional space defined by $\{r\}_{\mathrm{ind}}$.

3.2. Expanding the energy

3.2.1. The reference state

To describe a solid one has to be able to define an *equilibrium* configuration

$$\{\boldsymbol{R}\} = \{\boldsymbol{R}_1, \ldots, \boldsymbol{R}_i, \ldots, \boldsymbol{R}_j, \ldots, \boldsymbol{R}_N\} \tag{3.12}$$

in which there are no forces on any of the particles in the configuration $\{\boldsymbol{R}\}$. Each atom, separately, is in equilibrium when the positions of all the other atoms with which it interacts are kept fixed:

$$\boldsymbol{f}_i = 0\,. \tag{3.13}$$

The existence of such an equilibrium reference state, $\{\boldsymbol{R}\}$, which can serve as a *reference state* around which one can expand $\mathscr{E}(\{\boldsymbol{r}\})$ is obviously a pre-requisite for the development of the theories describing the mechanical properties of solids.

In general the force on the atom i can be divided into the contribution of the interactions between the particles:

$$\boldsymbol{f}_i(\{\boldsymbol{R}\}) = [\boldsymbol{\nabla}_i \mathscr{E}(\{\boldsymbol{r}\})]_{\{R\}} \tag{3.14}$$

and external forces $\boldsymbol{f}_i^{\mathrm{ext}}$ which are not due to the interactions between the N particles:

$$\boldsymbol{f}_i = \boldsymbol{f}_i(\{\boldsymbol{R}\}) + \boldsymbol{f}_i^{\mathrm{ext}}\,. \tag{3.15}$$

3.2.2. Expansion procedure

We can now use the parametrization of the energy in terms of the distances r_{ij} to derive the most general form of the expansion of a translation–rotation invariant energy $\mathscr{E}(\{\boldsymbol{r}\})$ around the reference state $\{\boldsymbol{R}\}$.

The mechanical properties are described by the deviations of the particles from their reference positions in the embedding space – the expansion of $\mathscr{E}(\{\boldsymbol{r}\})$ in the single particle deviations

$$\boldsymbol{u}_i = \boldsymbol{r}_i - \boldsymbol{R}_i \tag{3.16}$$

around the reference configuration $\{\boldsymbol{R}\}$. The *internal* configuration in the reference state $\{\boldsymbol{R}\}$, can be described by a set of n_{int} equilibrium distances, R_{ij}

$$\{\boldsymbol{R}\} \Rightarrow \{R\}_{\mathrm{ind}} = \{R_{12}, R_{13}, \ldots, R_{ij}, \ldots\} . \tag{3.17}$$

Using the description of the energy in terms of distances it is natural to derive the expansion in three steps:

1. We first expand $\mathscr{E}(\{r\})$[12] directly around the internal reference configuration $\{R\}$

$$\mathscr{E}(\{r\}) = \mathscr{E}(\{R\}) + \sum \left[\frac{\partial \mathscr{E}}{\partial r_{ij}}\right]_{\{R\}} \delta r_{ij} + \frac{1}{2} \sum \left[\frac{\partial^2 \mathscr{E}}{\partial r_{ij} \cdot \partial r_{kl}}\right]_{\{R\}} \delta r_{ij}\, \delta r_{kl} + \text{h.o.t.} , \tag{3.18}$$

where

$$\delta r_{ij} = r_{ij} - R_{ij} \tag{3.19}$$

is the change in the distance r_{ij} from its reference value R_{ij}.

2. One can then use the expansion of δr_{ij} in the relative deviation of the pair $[ij]$

$$\boldsymbol{u}_{ij} = \boldsymbol{u}_i - \boldsymbol{u}_j , \tag{3.20}$$

i.e.,

$$\delta r_{ij} = u_{ij}^{//} + [(u_{ij}^{\perp})^2 / 2R_{ij}] + \text{h.o.t.} , \tag{3.21}$$

where

$$u_{ij}^{//} = \boldsymbol{u}_{ij} \cdot \hat{\boldsymbol{R}}_{ij} , \qquad u_{ij}^{\perp} = \sqrt{u_{ij}^2 - u_{ij}^{//2}} \tag{3.22}$$

are, respectively, the components of the relative deviation, $\boldsymbol{u}_{ij}$, parallel and perpendicular to the reference vector $\boldsymbol{R}_{ij}$ and, as usual, we have used the notation

$$\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j ; \qquad \hat{\boldsymbol{R}}_{ij} = \boldsymbol{R}_{ij} / R_{ij} . \tag{3.23}$$

Substituting the expansion of δr_{ij}, Eq. (3.21), in the expansion of the energy, Eq. (3.18), gives an expansion of the energy which is written explicitly in terms of $u_{ij}^{//}$ and $u_{ij}^{\perp}$, i.e., in the components of the relative deviation of two particles, $\boldsymbol{u}_{ij}$, with respect to the local coordinate frame defined by the vector $\boldsymbol{R}_{ij}$.

Our derivation demonstrates that this is always possible.

3. Finally, one can use the definitions in Eqs. (3.20) and (3.22) and the values of the vectors $\boldsymbol{R}_{ij}$ in the reference state $\{\boldsymbol{R}\}$ to obtain the explicit expansion of the energy in the components of the single particle deviations, $\boldsymbol{u}_i$.

Any expansion constructed in this way is evidently TRI.

The intermediate steps in this procedure, the expansions in δr_{ij} and in the components of $\boldsymbol{u}_{ij}$, depend on the specific pairing scheme. Only the final result – the expansion in the components of $\boldsymbol{u}_i$ – is general and does not depend on this choice.

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[12] In the following we will omit the subscript ind in the description of the set of distances on which the energy depends. This emphasizes that the derivation only uses the fact that the energy can be written as a function of a set of distances and this is not restricted to independent ones.

3.2.3. Singularities in the expansion procedure

For completeness we note here that the expansion procedure we have described – the substitution of Eq. (3.21) into Eq. (3.18) to derive an expansion in $u_{ij}^{\parallel}$ and $u_{ij}^{\perp}$ – can become singular when the reference configuration $\{R\}_{\mathrm{ind}}$ is on the boundary of a consistency region of its pairing scheme – e.g., when the triangle inequality, (3.11), becomes an equality.[13] When this occurs some care is required. We shall return to this when we discuss the description of microscopic angular and twist interactions in Section 5 and in Appendix A.

3.2.4. Binary forces, bond tensions and equilibrium conditions

It is convenient to introduce a more compact notation for this formal procedure. If the energy is written as a function of the distances $\{r\}$ – Eq. (3.7) – the derivatives of $\mathscr{E}(\{\boldsymbol{r}\})$ with respect to the components of the vectors $\boldsymbol{r}_i$ can be calculated from the derivatives of $\mathscr{E}(\{r\})$ with respect to the variables r_{ij} using

$$\partial/\partial \boldsymbol{r}_{ij} = (\partial r_{ij}/\partial \boldsymbol{r}_{ij})\,\partial/\partial r_{ij} \tag{3.24}$$

and

$$\partial r_{ij}/\partial \boldsymbol{r}_{ij} = \partial r_{ij}/\partial \boldsymbol{r}_i = -\partial r_{ij}/\partial \boldsymbol{r}_j = \boldsymbol{r}_{ij}/r_{ij}\,. \tag{3.25}$$

The force which the network exerts on atom i, $\boldsymbol{f}_i(\{\boldsymbol{r}\})$, appears as the sum of binary forces, $\boldsymbol{f}_{ij}(\{\boldsymbol{r}\})$

$$\boldsymbol{f}_i(\{\boldsymbol{r}\}) = \partial/\partial \boldsymbol{r}_i\, \mathscr{E}(\{\boldsymbol{r}\}) = \sum_j \boldsymbol{f}_{ij}(\{\boldsymbol{r}\})\,, \tag{3.26}$$

where the force of atom j on atom i in the configuration $\{\boldsymbol{r}\}$ is

$$\boldsymbol{f}_{ij}(\{\boldsymbol{r}\}) = [\partial/\partial \boldsymbol{r}_{ij}]_{\{r\}} \mathscr{E}(\{r\}) = \mathscr{T}_{ij}(\{r\}) \cdot \boldsymbol{r}_{ij}/r_{ij}\,, \tag{3.27}$$

and

$$\mathscr{T}_{ij}(\{r\}) = [\partial \mathscr{E}(\{r\})/\partial r_{ij}]_{\{r\}} \tag{3.28}$$

can be thought of as the *tension* of the "bond" $[ij]$ in the configuration $\{r\}$.

If there are no external forces on the atom i the condition for atomic equilibrium in the configuration $\{\boldsymbol{R}\}$, Eq. (3.13), can be written in the form

$$\boldsymbol{f}_i(\{\boldsymbol{R}\}) = \sum_j \boldsymbol{f}_{ij}(\{\boldsymbol{R}\}) = \sum_j \mathscr{T}_{ij} \cdot \boldsymbol{R}_{ij}/R_{ij} = 0\,, \tag{3.29}$$

where

$$\mathscr{T}_{ij} = \mathscr{T}_{ij}(\{R\}) \tag{3.30}$$

is the tension in the bond $\{ij\}$ in the reference configuration $\{R\}$.

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[13] That is when the three points $\boldsymbol{R}_i, \boldsymbol{R}_j, \boldsymbol{R}_k$ are collinear.

3.3. Bonded networks

The parametrization in terms of independent distances which we described is quite general and applies to any functional form of the energy $\mathscr{E}(\{r\})$. As we discussed above this description was a formal device for expressing translation–rotation invariance which did not depend on any specific physical assumptions. It was therefore natural to describe the energy as a function of the minimal number of distances – a set $\{r\}_{\mathrm{ind}}$ of $\mathscr{n}_{\mathrm{int}}$ geometrically independent distances. This is however not always the best way to describe a physical situation.

3.3.1. The Cauchy model

In many models the energy is a sum of interactions between small numbers of particles. Thus Navier (1827) and Cauchy (1827, 1828) assumed that the mechanical energy can be described as a sum of binary central-force interactions between pairs. For a *Cauchy model* the energy $\mathscr{E}(\{\boldsymbol{r}\})$ is of the form

$$\mathscr{E}_{\mathrm{Cau}}(\{\boldsymbol{r}\}) = \mathscr{E}_{\mathrm{Cau}}(\{r\}) = \sum_{\mathrm{bonds}} \mathscr{V}_{ij}(r_{ij})\,, \tag{3.31}$$

where the summation is over the $\mathscr{n}_{\mathrm{bond}}$ interacting pairs, $[ij]$, and $\mathscr{V}_{ij}(r)$ is a binary potential. The energy of a Cauchy model, $\mathscr{E}_{\mathrm{Cau}}(\{r\})$, Eq. (3.31), is explicitly a function of the "*bonded*" distances which appear in the interactions

$$\{r\}_{\mathrm{bond}} = \{r_{12}, r_{13}, \ldots, r_{ij}, \ldots\}_{\mathrm{bond}} = \{r^1, r^2, \ldots, r^\nu, \ldots, r^{\mathscr{n}_{\mathrm{bond}}}\}_{\mathrm{bond}}\,. \tag{3.32}$$

For all the pairs $[ij]$ which do not appear in the bonded set $\{r\}_{\mathrm{bond}}$ there is no interaction

$$\mathscr{V}_{ij}(r_{ij}) \equiv 0\,.$$

Thus one can write the energy of a Cauchy model as a function of the bonded distances

$$\mathscr{E}_{\mathrm{Cau}}(\{\boldsymbol{r}\}) = \mathscr{E}_{\mathrm{Cau}}(\{r\}_{\mathrm{bond}})\,. \tag{3.33}$$

The choice of the distances in the set $\{r\}_{\mathrm{bond}}$ is of course determined by the physical model. It is not arbitrary in the way the choice of the independent set $\{r\}_{\mathrm{ind}}$ – Eq. (3.6) – was arbitrary.

It is natural to consider the pairs which appear in $\{r\}_{\mathrm{bond}}$ as "bonds" and call a Cauchy model a *bonded network* model.

3.3.2. Generalization to sums of many-body interactions

The concept of a bonded network can be generalized to models for which the energy also includes sums of many-body interactions between small numbers of particles. One can always parametrize the interaction between a specific set of point particles in terms of the distances between these particles. Thus, e.g., the interactions between the three particles $[ijk]$ can quite generally be written as a function of the three distances (r_{ij}, r_{jk} and r_{ik}) which determine the triangle $[ijk]$

$$\mathscr{E}_{ijk}(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k) = \mathscr{E}_{ijk}(r_{ij}, r_{jk}, r_{ki}) \tag{3.34}$$

even when the interactions between the three particles are not a sum of two-body Cauchy interactions and include also a true irreducible three-body interaction

$$\mathscr{V}^3_{ijk} = \mathscr{V}^3(r_{ij}, r_{jk}, r_{ki})\,. \tag{3.35}$$

Similarly an irreducible four-body interaction can be described as a function of the six distances which determine the triangular pyramid $[ijkl]$. For all such models one can define a set of bonded distances, $\{r\}_{\text{bond}}$, for the full N particle system which contains all the distances which appear in the parametrization of the separate interactions. The energy can then be regarded as a function of this set of distances

$$\mathscr{E}(\{r\}) = \mathscr{E}(\{r\}_{\text{bond}}) . \tag{3.36}$$

3.4. Classifying bonded networks

The description of the energy of a bonded network model $\mathscr{E}(\{r\}_{\text{bond}})$, in terms of the bonded distances, $\{r\}_{\text{bond}}$ – Eq. (3.36) – is of course reminiscent of the general parametrization of the energy in terms of distances – Eq. (3.7). In particular one can use the parametrization in terms of distances in expanding $\mathscr{E}(\{r\}_{\text{bond}})$ in the $u_{ij}^{//}$ and $u_{ij}^{\perp}$ corresponding to the *bonded* distances, $\{r\}_{\text{bond}}$, exactly as we used the general parametrization in deriving the expansion of $\mathscr{E}(\{r\}_{\text{ind}})$ in the $u_{ij}^{//}$ and $u_{ij}^{\perp}$ corresponding to the independent distances which appear in $\{r\}_{\text{ind}}$. We even used this intuitive analogy in calling the first derivative of the energy, $\mathscr{T}_{ij}$ defined in Eq. (3.28) a “bond tension” in analogy to the usual definition of the tension in a spring.

The two descriptions are of course related but they are not equivalent.

The set of bonded distances, $\{r\}_{\text{bond}}$, on which a Cauchy energy – or a general bonded-network energy – depends is a property of the *physical model* which determines which interactions appear. This set defines a graph which consists of the vertices $\{i\}$ connected by the bonds $[ij]$. We shall call this graph a bonded network.

The bonded network describes a common property of a class of models. For example *all* the Cauchy models – Eq. (3.31) – with summations over the same bonds $[ij]$ but arbitrary forms of the binary interactions $\mathscr{V}_{ij}(r_{ij})$ are described by the same bonded network.

On the other hand the parametrization in Eq. (3.6) is general and fairly arbitrary. Since it depends on purely geometrical considerations it applies to all models.

The most important difference between parametrization by bonds and the parametrization by independent distances relates to the nature of the set of distances. The number of *geometrically independent* distances among N points is always exactly $\mathscr{n}_{\text{int}}$ – Eq. (3.4). On the other hand, the number of terms in the sum (3.31) or the number of bonds in its generalization, the number of “*bonded distances*”, $\mathscr{n}_{\text{b}}$, can be both larger and smaller than $\mathscr{n}_{\text{int}}$.[14] This is an important distinction.

3.4.1. Redundant surplus bonds

When the number of bonds is *larger* than $\mathscr{n}_{\text{int}}$:

$$\mathscr{n}_{\text{bond}} > \mathscr{n}_{\text{int}} , \tag{3.37}$$

the bonded distances cannot all be independent. One can express all the $\mathscr{n}_{\text{bond}}$ bonded distances in $\{r\}_{\text{bond}}$ as functions of a set of $\mathscr{n}_{\text{int}}$ independent distances – $\{r\}_{\text{ind}}$ – e.g., a subset of $\mathscr{n}_{\text{int}}$ independent distances in $\{r\}_{\text{bond}}$. This transforms the expression of the energy $\mathscr{E}(\{r\}_{\text{bond}})$ which is written as

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[14] There is also no reason why the bonded distances one obtains from a physical model must all be geometrically independent – whatever their number.

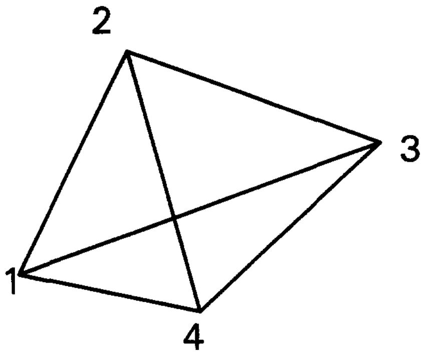

Fig. I.1. Parametrization of the configuration of four points in the plane. Only five of the six distances are required.

a function of *all* the $\mathscr{n}_{\text{bond}}$ separate bonded distances $\{r\}_{\text{bond}}$, Eq. (3.28) into a different formal expression for the same energy in which all the $\mathscr{n}_{\text{bond}}$ distances in $\{r\}_{\text{bond}}$ are expressed as functions of a smaller set of $\mathscr{n}_{\text{int}}$ geometrically independent distances $\{r\}_{\text{ind}}$:

$$\mathcal{E}(\{r\}_{\text{bond}}) = \mathcal{E}(\{r\}_{\text{bond}}(\{r\}_{\text{ind}})) = \mathcal{E}(\{r\}_{\text{ind}}) . \tag{3.38}$$

Formally this is always possible but it may not always be a very convenient procedure.

3.4.1.1. An example – the line tensions between four co-planar particles. The general expression for the "line tensions", Eq. (3.28), is of course reminiscent of the expression of the spring tensions of the Cauchy model

$$\mathcal{T}^{\text{c}}_{ij}(\{r\}) = \mathcal{T}^{\text{c}}_{ij}(r_{ij}) = [\partial \mathcal{V}_{ij}(r)/\partial r]_{r=r_{ij}} . \tag{3.39}$$

Nevertheless one cannot simply identify the two expressions for the "line tension" – even for Cauchy models. To show this clearly we consider the simple example illustrated in Fig. I.1.

There are six distances, r_{ij}, among the four points 1, 2, 3, 4 and a general Cauchy energy has the form

$$\mathcal{E} = \sum_{[i>j=1]}^{4} \mathcal{V}_{ij}(r_{ij}) . \tag{3.40}$$

There are therefore six bond tensions

$$\mathcal{T}^{\text{bond}}_{ij} = \frac{\mathrm{d}\mathcal{V}_{ij}}{\mathrm{d}r_{ij}} \tag{3.41}$$

for the six bonds $[ij]$.

In the plane *five* distances are however sufficient to determine the configuration of four points ($\mathscr{n}^{d=2}_{\text{int}} = 5$). The sixth distance is not independent in the plane and can be expressed as a function of the remaining five distances

$$r_{12} = r_{12}(r_{13}, r_{14}, r_{23}, r_{24}, r_{34}) . \tag{3.42}$$

This can be substituted into the interaction $\mathscr{V}_{12}(r_{12})$ in Eq. (3.40) to obtain a parametrization of the general four-particle Cauchy energy in terms of five “independent” distances. In this new form r_{12} no longer appears as a variable in the energy

$$\mathscr{E}_{\mathrm{C}} = \mathscr{V}_{12}(r_{12}(r_{13}, r_{14}, \ldots)) + \sum_{ij\neq 12} \mathscr{V}_{ij}(r_{ij})\,. \tag{3.43}$$

There are therefore also only five “line tensions” and they are different from the “bonded” tensions in Eq. (3.41)

$$\mathscr{T}_{ij}(\{r\}_{\mathrm{ind}}) = \mathscr{T}_{ij}^{\mathrm{bond}}(r_{ij}) + \mathscr{T}_{12}^{\mathrm{bond}}(r_{12}) \cdot \frac{\partial r_{12}(\{r_{ij}\})}{\partial r_{ij}}; \quad [ij] \neq [12]\,. \tag{3.44}$$

3.4.2. *Floppy networks*

The number of bonds, $\mathscr{n}_{\mathrm{b}}$, can also be *smaller* than $\mathscr{n}_{\mathrm{int}}$

$$\mathscr{n}_{\mathrm{b}} < \mathscr{n}_{\mathrm{int}}\,. \tag{3.45}$$

The $\mathscr{n}_{\mathrm{b}}$ bonded distances, $\{r\}_{\mathrm{bond}}$, then cannot determine $\mathscr{n}_{\mathrm{int}}$ independent distances. They therefore cannot determine the geometric configuration of N particles in d-dimensions completely. The values of the $\mathscr{n}_{\mathrm{b}}$ bonded distances only amount to constraints on the allowed configurations. If we fix the distances in $\{r\}_{\mathrm{bond}}$ this restricts the configurations of the N particles but does not determine it completely.

We shall call such bonded networks floppy. We shall develop the theory of *floppy bonded networks* (FBN) in Part II.

4. The microscopic definition of stress

4.1. *The first order expansion of energy*

We can use the first derivatives we calculated above to expand the energy $\mathscr{E}(\{\boldsymbol{r}\})$ around an atomic reference configuration $\{\boldsymbol{R}\}$. To first order the expansion is

$$\mathscr{E}^1 = \frac{1}{2}\sum_{ij} (\boldsymbol{f}_{ij}(\{\boldsymbol{R}\}) \cdot \boldsymbol{u}_{ij}) = \frac{1}{2}\sum_{ij} \mathscr{T}_{ij} \cdot u_{ij}^{\parallel}\,, \tag{4.1}$$

where the pair forces $\boldsymbol{f}_{ij}$ are defined in Eq. (3.28). As written this is an expansion in the parallel component of the relative deviations $u_{ij}^{\parallel}$ defined in (3.22).

We will show that the continuum limit of this microscopic first order energy is the linear elastic energy

$$\mathscr{E}^1 \underset{\text{continuum}}{\Longrightarrow} \mathscr{E}_{\mathrm{elastic}} = -\left(\frac{1}{2}\right) \int \mathrm{d}\boldsymbol{r} \cdot \sum_{\alpha,\beta} \sigma_{\mathrm{ini}}^{\alpha\beta}(\boldsymbol{r}; \{\boldsymbol{R}\}) \cdot e_{\alpha\beta}^{1}(\boldsymbol{r}) \tag{4.2}$$

where $\sigma_{\mathrm{ini}}(\boldsymbol{r}; \{\boldsymbol{R}\})$ is the stress at $\boldsymbol{r}$ in the reference state $\{\boldsymbol{R}\}$. Following Love (1927a, Section 75) we shall call the stresses in the reference state *initial stresses*. The strain, $e^1(\boldsymbol{r})$, is the symmetric linear strain with components

$$e^1_{\alpha\beta} = \tfrac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha) \tag{4.3}$$

and is defined with respect to the stressed reference state $\{\boldsymbol{R}\}$.

The continuum limit involves a *double* expansion. It is an expansion in powers of the components of the deviation field $\boldsymbol{u}(\boldsymbol{r})$ and is also a *gradient* expansion in the derivatives of this field.[15] The elastic energy – Eq. (4.2) – is the *linear* contribution of the *linear* strain – Eq. (4.3) – to the elastic energy. We will show that it is the leading term in the gradient expansion of the microscopic linear energy – Eq. (4.1). We will derive explicit expressions for the stresses in the reference state as the coefficients of the linear strains and compare them to the general mechanical definition.

4.2. The continuum limit

We replace the atomic deviations $\boldsymbol{u}_i$ by a continuous vector field, $\boldsymbol{u}(\boldsymbol{r})$ defined so that

$$\boldsymbol{u}(\boldsymbol{R}_i) = \boldsymbol{u}_i\,. \tag{4.4}$$

To lowest order in the gradient expansion one then has

$$\boldsymbol{u}_{ij} \cong -(\boldsymbol{R}_{ij}\cdot\boldsymbol{\nabla})\cdot\boldsymbol{u}(\boldsymbol{r}) = -\left(\sum X^\alpha_{ij}\cdot\partial_\alpha\right)\cdot\boldsymbol{u}(\boldsymbol{r})\,, \tag{4.5}$$

where X^α_{ij} is the α component of the vector $\boldsymbol{R}_{ij}$. The component of $\boldsymbol{u}_{ij}$ parallel to $\boldsymbol{R}_{ij}$ is therefore

$$u^{\parallel}_{ij} \cong -(\boldsymbol{R}_{ij}\cdot\boldsymbol{\nabla})\boldsymbol{u}\cdot\hat{\boldsymbol{R}}_{ij} = -\sum_{\alpha\beta}\frac{X^\alpha_{ij}\cdot X^\beta_{ij}}{R_{ij}}\cdot\partial_\alpha u_\beta\,. \tag{4.6}$$

We note the *transposition symmetry* between the derivative index, α, and the index β of the component of $\boldsymbol{u}$, in Eq. (4.6). In the continuum limit of $u^{\parallel}_{ij}$ the transposed derivatives $\partial_\alpha u_\beta$ and $\partial_\beta u_\alpha$ appear with the same coefficient

$$-\frac{X^\alpha_{ij}\cdot X^\beta_{ij}}{R_{ij}}\,.$$

Because of this symmetry one can write Eq. (4.6) in terms of the symmetric linear strain tensor, $\boldsymbol{e}^1(\boldsymbol{r})$, defined in Eq. (4.3)

$$u^{\parallel}_{ij} \cong -\sum_{\alpha\beta}\frac{X^\alpha_{ij}\cdot X^\beta_{ij}}{R_{ij}}\cdot e^1_{\alpha\beta} = -\,\mathrm{Tr}\left\|\frac{\boldsymbol{R}_{ij} * \boldsymbol{R}_{ij}}{R_{ij}}\right\| \circ \|\boldsymbol{e}^1\|\,. \tag{4.7}$$

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[15] Thus the continuum limit *assumes* that one can construct a *smooth* field $\boldsymbol{u}(\boldsymbol{r})$, which gives a reasonable description of all the $\boldsymbol{u}_{ij}$ so that a gradient expansion makes sense.

In the last expression the "$*$" represents the dyadic external product of two vectors and "$\circ$" stands for the matrix product and Tr for the trace.

4.3. The definition of stress in a solid

Substituting the continuum limit of u_{ij}'' from Eq. (4.7) into (4.1) the first order energy becomes

$$\mathscr{E}^1(\{\boldsymbol{R}\}) \cong -\mathrm{Tr}\sum_i \boldsymbol{s}_i \circ \boldsymbol{e}^1(\boldsymbol{R}_i) = -\sum_{i,\alpha\beta} s_i^{\alpha\beta} \circ e_{\alpha\beta}^1(\boldsymbol{R}_i) \tag{4.8}$$

to lowest order in the gradient expansion of the deviation field.

The substitution introduces a symmetric tensor

$$\boldsymbol{s}_i = -\sum_j \mathscr{T}_{ij} \cdot \frac{(\boldsymbol{R}_{ij} * \boldsymbol{R}_{ij})}{R_{ij}} \tag{4.9}$$

which one can call the *site-stress* for the lattice site i.

The properly normalized continuum limit of the site stresses, $\boldsymbol{s}_i$, is the stress field $\sigma(\boldsymbol{r})$. The site-stress, $\boldsymbol{s}_i$, has the dimensions of an energy while the continuum stress field, $\sigma(\boldsymbol{r})$, has the dimensions of an energy density. It is therefore natural to relate $\boldsymbol{s}_i$ to the average of the continuum stress field.

$$\boldsymbol{s}_i = \int_{\mathscr{V}_i} \mathrm{d}\boldsymbol{r} \cdot \sigma(\boldsymbol{r}) = \mathscr{V}_i \cdot \bar{\sigma}_i\,, \tag{4.10}$$

where $\mathscr{V}_i$ is the volume of the Voronoi cell of the site i.

$$\bar{\sigma}_i = -1/\mathscr{V}_i \cdot \sum_j \mathscr{T}_{ij} \cdot \frac{(\boldsymbol{R}_{ij} * \boldsymbol{R}_{ij})}{R_{ij}}\,. \tag{4.11}$$

The continuum stress field $\sigma(\boldsymbol{r})$ is defined by this equation just as $\boldsymbol{u}(\boldsymbol{r})$ is defined by Eq. (4.4).

We derived the microscopic expression (4.11) which defines the local stress in terms of the bond tensions from the continuum limit of the first order terms in the microscopic expansion of the mechanical energy – Eq. (4.1). This derivation and the definition of a stress in terms of the bond tensions, $\mathscr{T}_{ij}$, is specific to the description of solids. It assumes the existence of a rigid reference state, $\{\boldsymbol{R}\}$, and describes the stress as a property of the energy in this state.

The general definition of a stress is of course not restricted to solids. The average stress in a volume V is

$$\bar{\sigma}_V = \frac{1}{2V}\oint [\boldsymbol{f}(\boldsymbol{r}) * \boldsymbol{r} + \boldsymbol{r} * \boldsymbol{f}(\boldsymbol{r})] \cdot \mathrm{d}s\,, \tag{4.12}$$

where $\boldsymbol{f}(\boldsymbol{r})$ is the force per unit area acting on the boundary of the volume V at $\boldsymbol{r}$ and the integral is over the boundary surface of this volume (Landau and Lifshitz, 1970, Eq. (2.9)). This can be rewritten as a sum over forces

$$\bar{\sigma}_V = \frac{1}{2V}\sum_\alpha (\boldsymbol{f}_\alpha * \boldsymbol{r}_\alpha + \boldsymbol{r}_\alpha * \boldsymbol{f}_\alpha)\,, \tag{4.13}$$

where the point force $\boldsymbol{f}_\alpha$ crosses the boundary of V at the point $\boldsymbol{r}_\alpha$, and we have assumed that there is no net force on V

$$\sum_\alpha \boldsymbol{f}_\alpha = 0 . \tag{4.14}$$

For the cell of i and the pair forces acting on it this becomes

$$\bar{\sigma}_i = -\frac{1}{2\mathscr{V}_i} \cdot \sum_j (\boldsymbol{f}_{ij} * \boldsymbol{R}_{ij} + \boldsymbol{R}_{ij} * \boldsymbol{f}_{ij}) \tag{4.15}$$

which reproduces Eq. (4.11) when one substitutes

$$\boldsymbol{f}_{ij} = \mathscr{T}_{ij} \cdot \hat{\boldsymbol{R}}_{ij} .$$

4.3.1. The network stress and the total stress

The identification of the general definition of the average stress in a volume – Eq. (4.12) – with the definition which we derived from the continuum limit of the CB expansion of a bonded network model, Eq. (4.11), assumed that one can identify the forces acting on the volume V or on the Voronoi cell $\mathscr{V}_i$ with the forces exerted by the bonds of the bonded network model which describes the solid. This is correct in many cases. It is however important to emphasize that there are exceptions. The contribution of the bonded network to the stress – the *network stress* defined by (4.11) – is not necessarily the total stress in the material. There can be other contributions to the forces on the boundary of the volume element V beside those which can be attributed to the bond tensions. Since the network stress describes the stress exerted by a solid completely this always means that the material is in some sense composite and there are additional terms in the mechanical energy which cannot be described as originating in a solid. This means that there are contributions to the total stress which have to be added to the network stress of Eq. (4.11). When the distinction is important – in particular when we shall discuss the square foam in Section 8.1.3 and, more generally, soft matter in Section 14, we will therefore emphasize the distinction between a network stress and the total stress.

4.4. Mechanical equilibrium

Eq. (4.1) is written as an expansion in the relative deviations $\boldsymbol{u}_{ij}$. Using (3.20), this expansion can obviously be rewritten in terms of the single particle deviations:

$$\mathscr{E}^1 = \sum_i \boldsymbol{f}_i(\{\boldsymbol{R}\}) \cdot \boldsymbol{u}_i , \tag{4.16}$$

where $\boldsymbol{f}_i(\{\boldsymbol{R}\})$ is the force exerted by the network on i. It follows that $\mathscr{E}^1$ must vanish when there are no external forces because equilibrium, Eq. (3.13), then requires

$$\boldsymbol{f}_i(\{\boldsymbol{R}\}) = 0 .$$

In the general case there is an exact cancellation of the forces. The energy associated with the external forces across the boundary

$$\sum_i \boldsymbol{f}_i^{\text{ext}} \cdot \boldsymbol{u}_i$$

cancels the linear contribution of the internal stresses to the energy for the same deformation

$$\frac{1}{2}\sum_{ij}\mathcal{T}_{ij}\cdot u''_{ij}+\sum_{i}\boldsymbol{f}_i^{\mathrm{ext}}\cdot\boldsymbol{u}_i=0 \tag{4.17}$$

for any deviation from an equilibrium reference state $\{\boldsymbol{u}\}$.

In the continuum limit this amounts to the requirement that the *average* stress in any volume element must represent a mechanical equilibrium state with respect to the external forces acting on it.

5. The Born–Huang expansion around unstressed reference states

5.1. The Born–Huang approximation

We shall now use the parametrization of the energy in terms of the distances – Eq. (3.9) – to derive the second order terms in the expansion of the harmonic energy. One has to evaluate the second derivatives of the energy.

Starting from the expressions (3.27) for the first derivatives one gets

$$\frac{\partial}{\partial\boldsymbol{r}_{kl}}*\boldsymbol{f}_{ij}(\{\boldsymbol{r}\})=\frac{\boldsymbol{r}_{ij}}{r_{ij}}*\frac{\partial}{\partial\boldsymbol{r}_{kl}}\left[\frac{\partial\mathscr{E}(\{\boldsymbol{r}\})}{\partial r_{ij}}\right]_{\{\boldsymbol{R}\}}+\delta([ij][kl])\left[\frac{\partial\mathscr{E}(\{\boldsymbol{r}\})}{\partial r_{ij}}\right]_{\{\boldsymbol{R}\}}\cdot\frac{\partial}{\partial\boldsymbol{r}_{ij}}*\frac{\boldsymbol{r}_{ij}}{r_{ij}}, \tag{5.1}$$

where we have used the notation defined in Eq. (3.24).

There are thus two types of terms. The first term on the r.h.s of Eq. (5.1) involves a *second* derivative of the energy with respect to distances

$$\frac{\boldsymbol{r}_{ij}}{r_{ij}}*\frac{\partial}{\partial\boldsymbol{r}_{kl}}\left[\frac{\partial\mathscr{E}(\{\boldsymbol{r}\})}{\partial r_{ij}}\right]_{\{\boldsymbol{R}\}}=\left[\frac{\partial^2\mathscr{E}(\{r\})}{\partial r_{ij}\cdot\partial r_{kl}}\right]_{\{R\}}\cdot\frac{\boldsymbol{R}_{ij}*\boldsymbol{R}_{kl}}{r_{ij}\cdot r_{kl}}. \tag{5.2}$$

This represents the contributions of the second order terms in the expansion of the energy in distances, (3.18):

$$\left[\frac{\partial^2\mathscr{E}(\{r\})}{\partial r_{ij}\cdot\partial r_{kl}}\right]_{\{R\}}\delta r_{ij}\cdot\delta r_{kl}$$

to the harmonic energy.

The second term in (5.1)

$$\left[\frac{\partial\mathscr{E}(\{r\})}{\partial r_{ij}}\right]_{\{R\}}\cdot\frac{\partial}{\partial\boldsymbol{r}_{ij}}*\frac{\boldsymbol{r}_{ij}}{r_{ij}}$$

is proportional to a *first* derivative of the energy $\mathscr{E}(\{r\})$ with respect to a distance, a bond tension

$$\mathscr{T}_{ij}=\left[\frac{\partial\mathscr{E}(\{r\})}{\partial r_{ij}}\right]_{\{R\}}$$

– Eq. (3.28). Its origin is the first order term in the expansion in distances, (3.18),

$$\left[\frac{\partial\mathscr{E}(\{r\})}{\partial r_{ij}}\right]_{\{R\}}\cdot\delta r_{ij}$$

and they appear in the harmonic energy only because the expansion of δr_{ij} is not linear

$$\delta r_{ij}=u_{ij}^{\prime\prime}+(u_{ij}^{\perp})^{2}/2R_{ij}+\text{h.o.t}$$

– Eq. (3.21).

The two types of terms are qualitatively different. In the rest of this section we will only consider the expansion which originates from the second derivatives of the energy, Eq. (5.2). This means that in effect we set

$$\mathscr{T}_{ij}=\left[\frac{\partial\mathscr{E}(\{r\})}{\partial r_{ij}}\right]_{\{R\}}\equiv 0\,. \tag{5.3}$$

It is evident from (5.1) that in general the initial bond tensions appear explicitly in the harmonic energy. Because of this the stresses also appear in the harmonic energy. These terms disappear when one imposes (5.3).

Because the classical monograph of Born and Huang on lattice dynamics (Born and Huang, 1954) *defines* an "equilibrium solid" as a solid with no stresses in its reference state we will call (5.3) the *Born–Huang* (BH) approximation[16] and the harmonic expansion around an unstressed reference state a BH (harmonic) energy, $\mathscr{E}_{\mathrm{BH}}^{\mathrm{h}}$. For convenience we will sometimes assume that (5.3) holds strictly for the reference state. We shall call such a reference state a BH reference state, $\{\boldsymbol{R}\}_{\mathrm{BH}}$.

In principle the BHA is a real physical approximation whose validity in specific situations has to be justified. The BH condition – Eq. (5.3) – is an *additional* requirement on the reference state which has to be added to the atomic equilibrium condition (3.13).

Taken literally the BHA is clearly very restrictive. A microscopic state such that, separately and simultaneously, all binary potentials are at their minimum, as (5.3) would suggest, must be very exceptional. One can only formally construct and analyze models for which this is assumed. As an approximation the BHA is however applicable in a very wide range of situations. For most crystalline materials one does indeed find that the effects of deviations from the BHA, the effects of stresses on the bulk elastic properties are small and the BH terms are therefore dominant.[17] The initial stresses often also average out on fairly small scales, as in the cores of dislocations, so that they can only have fairly local effects. It is therefore often convenient and correct to disregard the initial stresses in the theory of the bulk properties.[18]

The continuum limit of the BH harmonic expansion is the standard elastic energy of a solid – a binary form in the symmetric linear strain tensors – $\frac{1}{2}(\partial_\alpha u_\beta+\partial_\beta u_\alpha)$.

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[16] Interpreting the BH definition of an equilibrium solid in this strict sense is not quite accurate. The text in Born and Huang (1954) is imprecise but the authors may not have had such a strict interpretation of the absence of stresses in mind.

[17] We shall discuss the reason for this in Section 14.

[18] In practice the formalism used in describing the lattice dynamics of crystals does not display the stresses so that the use of the BHA is only implicit.

We shall investigate the effect of the BH approximation, the terms proportional to the stress in the elastic energy and the less familiar microscopic terms whose coefficients are the bond tensions, in Section 6.

5.2. *General form of the harmonic expansion*

When one expands around a Born–Huang reference state, $\{\boldsymbol{R}\}_{\mathrm{BH}}$, the second term on the right-hand side of Eq. (5.1) vanishes because the initial bond tensions vanish – Eq. (5.3). Thus, for the Born–Huang reference state, $\{\boldsymbol{R}\}_{\mathrm{BH}}$, the second derivatives of $\mathscr{E}(\{\boldsymbol{r}\})$ with respect to the components of the $\boldsymbol{r}_i$ are always also *second* derivatives of $\mathscr{E}(\{r\})$ with respect to its arguments – the distances r_{ij}. Thus in the BH approximation one neglects the first term in Eq. (3.18) so that

$$\mathscr{E}(\{r\}) - \mathscr{E}(\{R\}) = \frac{1}{2}\sum \left[\frac{\partial^2 \mathscr{E}}{\partial r_{ij}\cdot \partial r_{kl}}\right]_{\{R\}_{\mathrm{BH}}} \delta r_{ij}\cdot \delta r_{kl} + \text{h.o.t.} \tag{5.4}$$

The linear term *in the expansion in distances* is neglected.

Substituting δr_{ij} from Eq. (3.21) into (5.4), or directly from (5.2) one obtains the general form of the BH harmonic expansion:

$$\mathscr{E}^{\mathrm{h}}_{\mathrm{BH}} = \sum \left[\frac{\partial^2 \mathscr{E}(\{r\})}{\partial r_{ij}\cdot \partial r_{kl}}\right]_{\{R\}} u''_{ij}\cdot u''_{kl} = \sum \left[\frac{\partial^2 \mathscr{E}(\{r\})}{\partial r_{ij}\cdot \partial r_{kl}}\right]_{\{R\}} \sum_{\alpha\beta} \frac{X^{\alpha}_{ij}\cdot X^{\beta}_{kl}}{R_{ij}\cdot R_{kl}} (u^{\alpha}_i - u^{\alpha}_j)(u^{\beta}_k - u^{\beta}_l)\,. \tag{5.5}$$

5.2.1. *Two, three and four body terms*

The coefficients in the BH harmonic expansion are the second derivatives of the energy with respect to distances. There are three types of terms which differ in the number of different site indices in the derivatives of the energy:

(a) *Two-body terms.* We can take two derivatives of $\mathscr{E}(\{r\})$ with respect to the same distance r_{ij} – $[ij] = [kl]$. These terms in the expansion have only *two* site indices, $[ij]$:

$$\mathscr{K}_{ij} = \frac{\partial^2 \mathscr{E}(\{R\})}{\partial r^2_{ij}}\,. \tag{5.6a}$$

The $\mathscr{K}_{ij}$ can be regarded as the spring constants of the bonds $[ij]$. Such contributions show up in the expansion of $\mathscr{E}_{\mathrm{Cau}}$, Eq. (3.27), and are the only terms in the harmonic expansion of the Cauchy model around an unstressed BH reference state. We call the sum of these contributions to the harmonic energy, $\mathscr{C}^{\mathrm{h}}$.

(b) One then has *three-site contributions* from derivatives with respect to two different distances with one common vertex – say r_{ij} and r_{ik}. Such a derivative has three site indices $[i, jk]$.

$$\mathscr{K}_{i,jk} = \frac{\partial^2 \mathscr{E}(\{R\})}{\partial r_{ij}\cdot \partial r_{ik}}; \quad i \neq j \neq k\,. \tag{5.6b}$$

Such terms appear in the expansion when the parametrization of the energy, $\mathscr{E}(\{r\})$, contains many-body interactions among at least three particles, e.g., in the description of microscopic angular bending interactions. We shall call the sum of the three-body terms in the harmonic expansion $\mathscr{A}$.

(c) Finally all four indices $[ijkl]$ can be different.

$$\mathscr{K}_{ij,kl} = \frac{\partial^2 \mathscr{E}(\{R\})}{\partial r_{ij} \cdot \partial r_{kl}}; \quad i \neq j \neq k \neq l \tag{5.6c}$$

describes *four-body* interactions. This describes twist and we call the harmonic contribution which contains these terms $\mathscr{W}$.

As long as one is only interested in the second derivatives there are no other possibilities even if $\mathscr{E}(\{r\})$ can have mixed derivatives with more than four site indices.

5.2.2. The two-body Cauchy contribution

From (5.4) for $[ij] = [kl]$ one finds

$$\frac{1}{4} \sum_{i,j} \mathscr{K}_{ij} \cdot (\delta r_{ij})^2 , \tag{5.7}$$

where $\mathscr{K}_{ij}$ is the 2-site spring constant defined in (5.6a). We substitute

$$\delta r_{ij} \approx u_{ij}^{\prime\prime}$$

to get a harmonic expansion in the atomic deviations

$$\mathscr{C}^{\mathrm{h}} = \frac{1}{4} \sum_{i,j} \mathscr{K}_{ij} \cdot (u_{ij}^{\prime\prime})^2 . \tag{5.8}$$

5.2.2.1. The expansion in parallel components and rotational invariance. We saw that $\mathscr{C}^{\mathrm{h}}$ depends only on the $u_{ij}^{\prime\prime}$, the components of $\boldsymbol{u}_{ij}$ *parallel* to $\boldsymbol{R}_{ij}$ like the first order expansion of the energy in Eq. (4.1). The component of $\boldsymbol{u}_{ij}$ normal to $\boldsymbol{R}_{ij}$, $u_{ij}^{\perp}$, appear only as higher order terms in the expansion of δr_{ij} and therefore only contribute to anharmonic terms in the BH expansion of the energy.

One can interpret this result as a direct consequence of rotational invariance. The argument goes as follows:

Only two site-indices, i and j, appear for each term in the summation, Eq. (5.7). The only vector relevant to these two-body terms in the expansion is therefore $\boldsymbol{R}_{ij}$. The transverse component of $\boldsymbol{u}_{ij}$, $u_{ij}^{\perp}$, describes a rotation of $\boldsymbol{R}_{ij}$

$$\delta\varphi \cong u_{ij}^{\perp} / R_{ij} \tag{5.9}$$

and therefore cannot appear in the expansion of a rotationally invariant energy. One concludes from this argument that only $u_{ij}^{\prime\prime}$ can appear in the expansion – as in Eq. (5.8) – and that this follows from rotational invariance.

This argument is obviously more or less correct. As a criterion for rotational invariance it is however incomplete because it is only valid to first order in the expansion of δr_{ij} and $\delta\varphi$ in the components of $\boldsymbol{u}_{ij}$. Because of this it does not apply to the harmonic expansion in stressed systems, around stressed reference states, where the linear terms in the expansion in δr_{ij}, Eq. (3.18), do not vanish and give rise to contributions to the two-particle Cauchy harmonic energy which cannot be expressed in terms of the $u_{ij}^{\prime\prime}$.

We shall discuss this in detail in Section 6.

5.2.3. *Many-body contributions*

As we have seen three-site terms, $\mathscr{A}$, and four-site terms, $\mathscr{W}$, can also appear in the harmonic expansion. Using the definition (5.6b) one obtains the three-body expansion

$$\frac{1}{2}\sum_{i\neq j\neq k} \mathscr{K}_{i,jk}\cdot\delta r_{ij}\cdot\delta r_{ik} \tag{5.10}$$

which gives the contribution to the harmonic expansion

$$\mathscr{A}=\frac{1}{2}\sum_{i\neq j\neq k} \mathscr{K}_{i,jk}\cdot u_{ij}^{\prime\prime}\cdot u_{ik}^{\prime\prime}\,. \tag{5.11}$$

Similarly, using (5.6c) when i, j, k, l are all different, one obtains

$$\frac{1}{8}\sum_{i\neq j\neq k\neq \ell} \mathscr{K}_{ij,kl}\cdot\delta r_{ij}\cdot\delta r_{k\ell}\,, \tag{5.12}$$

$$\mathscr{W}=\frac{1}{8}\sum_{i\neq j\neq k\neq \ell} \mathscr{K}_{ij,kl}\cdot u_{ij}^{\prime\prime}\cdot u_{k\ell}^{\prime\prime}\,. \tag{5.13}$$

These are the most general terms.

5.2.4. *Completeness of the expansion in parallel components*

The expression of the harmonic expansion of the three and four-site terms in Eqs. (5.11) and (5.13) in *parallel* deviations, $u_{ij}^{\prime\prime}, u_{ik}^{\prime\prime}, u_{lk}^{\prime\prime}, \ldots$, arose naturally when we used the parametrization of the energy in terms of distances – Eq. (3.9) – in deriving the expansion. It is also evident that such an expansion is automatically TRI – whatever the coefficients. It is however obvious that this is an unusual way for writing these terms in the expansion. If the derivation is indeed general then these terms must describe the familiar three-body bending and four-body twist interactions which are commonly expressed in terms of changes in angles and are therefore usually related to the *transverse* deviations of the relevant vectors. It is also evident that our simple rotational invariance argument in Section 5.2.2.1 does not apply to the many-body interactions. It does not *follow* from TRI that the internal deformations of the triangle $[ijk]$ and of the pyramid $[ijkl]$ must be expressed in terms of $u_{ij}^{\prime\prime}$.

This raises questions. Specifically the question is whether the formal procedure we have used which led to Eqs. (5.11) and (5.13) is completely general and, in particular, whether and how it incorporates bending and twist interactions – as we claim. The question is whether the most general three-point and four-point interactions can be expressed in the form of Eq. (5.4). The problem has actually been discussed extensively in the literature on molecular vibrations – often also using the same formal device we use – parametrizing the energy in terms of distances to assure rotational invariance.[19]

One finds that the expansion in $u_{ij}^{\prime\prime}$ is complete and therefore sufficient as long as all possible deviations $\boldsymbol{u}_i$, can be expanded in terms of $\boldsymbol{R}_{ij}$

$$\boldsymbol{u}_i=\sum_j \eta_i^{ij}\cdot\hat{\boldsymbol{R}}_{ij}\,. \tag{5.14}$$

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[19] We only mention Herzberg (1945) but there are obviously innumerable later references.

This is obviously possible as long as the vectors $\boldsymbol{R}_{ij}$ of the reference state which are relevant to the interaction span a d-dimensional space for every site i. An expansion of the form (5.14) cannot describe all the components of the vector $\boldsymbol{u}_i$ when the $\hat{\boldsymbol{R}}_{ij}$ are restricted to a subspace. For a three-point interaction the exception is the situation when the three points – $\boldsymbol{R}_i$, $\boldsymbol{R}_j$, $\boldsymbol{R}_k$, the vertices of the triangle $[ijk]$ – are colinear and for a four-point interaction when the four points – $\boldsymbol{R}_i$, $\boldsymbol{R}_j$, $\boldsymbol{R}_k$, $\boldsymbol{R}_l$, the vertices of the pyramid $[ijkl]$ – are coplanar. In these special cases the expansion in $u_{ij}^{/\!/}$ is incomplete and one has to invoke some transverse deviations $u_{ij}^{\perp}$ to expand the interaction energy. The expansion in $u_{ij}^{/\!/}$ describes all other situations.

For completeness we show explicitly in Appendix A how an angular interaction can be expressed in terms of distances and how the singularities in the expansion arise when the triangle inequality (3.9) becomes an equality

$$(r_{ij}+r_{jk})=r_{ik}\,.$$

The problems for such special reference states do not really limit the generality of our expansion procedure. As a formal procedure for describing the solid the expansion in $u_{ij}^{/\!/}$ is general. One can always consider the singular reference state as the limit of a nonsingular configuration or choose to re-express the singular interaction in a regular way by invoking additional distances.

5.2.5. *The full BH expansion*

We have demonstrated two results which are general and apply to the second order harmonic expansion around an unstressed reference state of any translation rotation invariant function.

1. We have shown that the harmonic expansion around an unstressed reference state can be written as an expansion in the parallel components $u_{ij}^{/\!/}$.

2. We have also shown that this expansion can always be regarded as a sum of two-body terms, $\mathscr{C}$ – Eq. (5.8), three-body terms, $\mathscr{A}$ – Eq. (5.11), and four-body terms, $\mathscr{W}$ – Eq. (5.13).

To show this we only used the existence of a parametrization of the energy in terms of distances, $\{r\}$, which is a direct consequence of TR invariance and therefore quite general. This does not assume that the energy $\mathscr{E}(\{r\})$ is really a sum of two, three and four particle interactions. The expressions we derived apply both to the case where the separation into 2, 3 and 4 body terms is a formal result of the parametrization of the energy, as in our derivation above, and to bonded network models where it reflects the specific physical interactions – as in Section 3.4. The most general form of a TR invariant harmonic expansion around an unstressed BH reference state can always be written

$$\mathscr{E}_{\mathrm{BH}}^{\mathrm{h}}=\mathscr{C}+\mathscr{A}+\mathscr{W}\,. \tag{5.15}$$

One can always write the harmonic energy in this form as long as one can neglect the direct effect of initial stresses in the reference state. As we shall see writing the expansion in this way is also very useful as a theoretical tool. Both TR invariance and the absence of initial stresses in the reference state are automatically assured when one writes the harmonic expansion explicitly in terms of $u_{ij}^{/\!/}$.

5.3. *Bonded network models*

As we noted in Section 3.4 one is often interested in physical models for which the energy is a sum of interactions between small numbers of particles – e.g., models with central, angular and twist interactions. Since each term in such a sum can be written as a function of a small number of specific bonded distances – the distances between the interacting particles – it is then natural to express the full N-particle energy as a function of these "bonded" distances rather than in terms of a minimal set of $\mathscr{n}_c$ independent distances which describe the system as a whole.

5.3.1. The Cauchy model

Consider first the Cauchy model of Eq. (3.31). The energy is a sum of binary interactions

$$\mathscr{E}(\{r\})=\mathscr{E}(\{r\}_{\mathrm{bond}})=\sum_{\mathrm{bonds}}\mathscr{V}_{ij}(r_{ij})$$

so that the many-body terms of Eqs. (5.8) and (5.9) cannot appear. Thus the harmonic energy has the form of Eq. (5.6) and the summation is over all the bonded distances for which there are interactions. The coefficients in this expansion are the force constants of the bonds at the minima of the respective potentials

$$\widehat{\mathscr{K}}_{ij}(\{r\}_{\mathrm{bond}})=\widehat{\mathscr{K}}_{ij}(r_{ij}^0)=\left[\frac{\partial^2\mathscr{V}_{ij}(r)}{\partial r^2}\right]_{r=r_{ij}^0},\qquad\left[\frac{\partial\mathscr{V}_{ij}(r)}{\partial r}\right]_{r=r_{ij}^0}=0\,. \tag{5.16}$$

Evidently no many-body terms appear in this expansion and there can be very many interactions.

Expressing such a model explicitly in terms of the set of bonded distances, $\{r\}_{\mathrm{bond}}$ is obviously much more convenient than to introduce complicated trigonometric, relations in order to re-express the same energy as a function of some smaller set of independent distances with the help of trigonometric identities.

5.3.2. Many-body interactions

Many-body interactions are usually discussed as bending and twist interactions. The standard way of writing these interactions is as functions of angles rather than of distances. Thus the leading term in the expansion of an angular interaction is usually written as

$$\left[\frac{\partial^2\mathscr{V}_{ijk}}{\partial\varphi_{i,jk}^2}\right]\cdot(\delta\varphi_{i,jk})^2=\mathscr{B}^{ijk}\cdot\delta\varphi_{i,jk}^2\,, \tag{5.17}$$

where $\delta\varphi_{ij}$ is the change in the angle $\{jik\}$. Similarly the twist interaction is written as a function of the twist angle. This has to be converted into an expansion in the $\boldsymbol{u}_i$.

For our purposes it is most convenient to start by rewriting the interactions as functions of the distances between the interacting particles and then write an expansion of the form (5.4) in terms of the changes in these distances δr_{ij}. This results in contributions to the harmonic energy which have explicit many-body features as in Eq. (5.11) for angular interactions and in Eq. (5.13) for four-body twist interactions.

In Appendix A we show in detail how the angular expansion, Eq. (5.17), can be rewritten as an expansion in the longitudinal deviations $u_{ij}^{/\!/}$ as in Eqs. (5.11) and (5.13).

For completeness we add a comment concerning the separation of the harmonic energy into two, three and four body terms. When we express the energy in terms of the bonded distances which appear in the interactions $\{r\}_{\mathrm{bond}}$ defined in Section 3.4 this separation is unique. Evidently, by construction

$$A_{\mathrm{C}} = W_{\mathrm{C}} \equiv 0 \tag{5.18}$$

but this assumes that we used the full set $\{r\}_{\mathrm{bond}}$ in deriving the expansion. If instead we choose a smaller set as parameters, say a set of $\varkappa_{\mathrm{int}}$ independent distances $\{r\}_{\mathrm{ind}}$, then some of the distances in $\{r\}_{\mathrm{bond}}$ can become complicated functions of the parameters

$$r_{ij} = r_{ij}(\{r\}_{\mathrm{ind}})$$

as in Eq. (3.42). Fortuitous many-body terms can then appear in the expansion.[20]

5.4. The continuum limit and the elastic constants

We have shown that the unstressed BH harmonic energy can be written as an expansion in the parallel components of the relative deviations u_{ij}'' – Eqs. (5.8), (5.11) and (5.13). To derive explicit expressions for the elastic constant tensors we need the continuum limit of u_{ij}''. We derived expressions for this in Eqs. (4.6) and (4.7).

$$u_{ij}'' \cong -(\boldsymbol{R}_{ij} \cdot \boldsymbol{\nabla})\boldsymbol{u} \cdot \hat{\boldsymbol{R}}_{ij} = -\sum_{\alpha\beta} \frac{X_{ij}^{\alpha} \cdot X_{ij}^{\beta}}{R_{ij}} \cdot \partial_{\alpha} u_{\beta} = -\sum_{\alpha\beta} \frac{X_{ij}^{\alpha} \cdot X_{ij}^{\beta}}{R_{ij}} \cdot \frac{1}{2}(\partial_{\alpha} u_{\beta} + \partial_{\beta} u_{\alpha}) .$$

Substituting these expressions into the BH harmonic energy transforms the microscopic expansion in u_{ij}'' into an expansion in the components of the symmetric linear strain.

The coefficients in this expansion which we shall derive are explicit microscopic expressions for the elastic constants.

5.4.1. The Cauchy model

First we substitute the continuum expression for u_{ij}'', Eq. (4.6), into Eq. (5.8) for $\mathscr{C}^{\mathrm{h}}$

$$\mathscr{C}^{\mathrm{el}} = \overline{\mathscr{C}^{\mathrm{h}}} = \frac{1}{2} \sum_{i,j} \mathscr{K}_{ij} \cdot \left(\frac{(\boldsymbol{R}_{ij} \cdot \boldsymbol{\nabla}) \cdot (\boldsymbol{u}(\boldsymbol{R}_j) \cdot \boldsymbol{R}_{ij})}{R_{ij}} \right)^2 . \tag{5.19}$$

Rearranging terms as in Eq. (4.7) this leads to an elastic energy of the form

$$\mathscr{C}^{\mathrm{el}} = \frac{1}{2} \sum_{i,j} \mathscr{K}_{ij} \cdot \left(\frac{\mathrm{Tr} \| \| \boldsymbol{R}_{ij} * \boldsymbol{R}_{ij} \| \circ \| \boldsymbol{e}^{1}(\boldsymbol{R}_j) \| \| \|}{R_{ij}} \right)^2 . \tag{5.20}$$

In the continuum form this becomes

$$\mathscr{C}^{\mathrm{el}}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r} \cdot \boldsymbol{g}(\boldsymbol{r}) , \tag{5.21}$$

where

$$\boldsymbol{g}(\boldsymbol{r}) = \sum_{\alpha\beta\gamma\delta} \boldsymbol{D}_{\mathrm{C}}^{\alpha\beta,\gamma\delta}(\boldsymbol{r}) \cdot \boldsymbol{e}_{\alpha\beta}^{1}(\boldsymbol{r}) \cdot \boldsymbol{e}_{\gamma\delta}^{1}(\boldsymbol{r}) = \boldsymbol{e}^{1}(\boldsymbol{r}) \circ \| \boldsymbol{D}_{\mathrm{C}}(\boldsymbol{r}) \| \circ \boldsymbol{e}^{1}(\boldsymbol{r}) \tag{5.22}$$

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[20] This is seen clearly in the example discussed in Section 3.3.2.

is the elastic energy density. In this equation the fourth rank elastic constant tensor $\|D_{\mathrm{C}}(\boldsymbol{r})\|$ is defined by the site tensors

$$\|\boldsymbol{D}_{\mathrm{C}}(\boldsymbol{r})\|_j = \frac{1}{2\mathcal{V}_j}\sum_i \mathcal{K}_{ij}\left\|\frac{\boldsymbol{R}_{ij} * \boldsymbol{R}_{ij} * \boldsymbol{R}_{ij} * \boldsymbol{R}_{ij}}{R_{ij}^2}\right\| \tag{5.23}$$

and $\mathcal{V}_j$ is the volume of the Voronoi cell j. We also write the components of this tensor explicitly

$$\boldsymbol{D}_{\mathrm{C}j}^{\alpha\beta,\gamma\delta} = \frac{1}{2\mathcal{V}_j}\sum_i \mathcal{K}_{ij}\cdot\frac{X_{ij}^{\alpha}\cdot X_{ij}^{\beta}\cdot X_{ij}^{\gamma}\cdot X_{ij}^{\delta}}{R_{ij}^2}\,. \tag{5.24}$$

One notes the high symmetry of the tensor $\|\boldsymbol{D}_{\mathrm{C}}\|$. The elements of this tensor, $\boldsymbol{D}^{\alpha\beta,\gamma\delta}$, are the same for all permutations of the four indices $[\alpha\beta\gamma\delta]$.

In three-dimensions the fourth rank tensor $\boldsymbol{D}$ has 81 ($=3^4$) elements but, because the indices α, β, γ, δ can only take three values (x, y, z), only 15 of them can be different. One can at most have 3 different elements of the type $D^{\alpha\alpha\alpha\alpha}$, 3 different elements of the type $D^{\alpha\beta\alpha\beta}$ ($=D^{\alpha\alpha\beta\beta}$, etc.), six of the type $D^{\alpha\alpha\alpha\beta}$ where $\alpha \neq \beta$ and 3 of the type $D^{\alpha\beta\gamma\gamma}$ ($=D^{\alpha\gamma\beta\gamma}$, etc.) where $\alpha \neq \beta \neq \gamma$. Thus

$$n_C(d=3) = 15 \tag{5.25a}$$

and, counting the elements in two dimensions

$$n_C(d=2) = 5\,. \tag{5.25b}$$

5.4.2. Many-body interactions

Using (4.6) in Eqs. (5.11) and (5.13) one gets

$$\mathcal{E}_{\mathcal{A}}^{\text{elastic}} = \overline{\mathcal{A}} = \frac{1}{2}\sum_{i\neq j\neq k}\mathcal{K}_{i,jk}\left(\frac{(\boldsymbol{R}_{ij}\cdot\boldsymbol{\nabla})\cdot(\boldsymbol{u}(\boldsymbol{R}_i)\cdot\boldsymbol{R}_{ij})}{R_{ij}}\right)\cdot\left(\frac{(\boldsymbol{R}_{ik}\cdot\boldsymbol{\nabla})\cdot(\boldsymbol{u}(\boldsymbol{R}_i)\cdot\boldsymbol{R}_{ik})}{R_{ik}}\right) \tag{5.26a}$$

and

$$\mathcal{E}_{\mathcal{W}}^{\text{elastic}} = \overline{\mathcal{W}} = \frac{1}{8}\sum_{i\neq j\neq k\neq l}\mathcal{K}_{ij,kl}\left(\frac{(\boldsymbol{R}_{ij}\cdot\boldsymbol{\nabla})\cdot(\boldsymbol{u}(\boldsymbol{R}_i)\cdot\boldsymbol{R}_{ij})}{R_{ij}}\right)\cdot\left(\frac{(\boldsymbol{R}_{kl}\cdot\boldsymbol{\nabla})\cdot(\boldsymbol{u}(\boldsymbol{R}_k)\cdot\boldsymbol{R}_{kl})}{R_{kl}}\right). \tag{5.26b}$$

Rearranging terms this leads to elastic energies

$$\mathcal{E}_{\mathcal{A}}^{\text{elastic}} = \overline{\mathcal{A}} = \frac{1}{2}\sum_{i\neq j\neq k}\mathcal{K}_{i,jk}\left(\frac{\|\boldsymbol{R}_{ij} * \boldsymbol{R}_{ij}\| \circ \|\boldsymbol{e}^1(\boldsymbol{r})\|}{R_{ij}}\right)\left(\frac{\|\boldsymbol{R}_{ik} * \boldsymbol{R}_{ik}\| \circ \|\boldsymbol{e}^1(\boldsymbol{r})\|}{R_{ik}}\right), \tag{5.27a}$$

$$\mathcal{E}_{\mathcal{W}}^{\text{elastic}} = \overline{\mathcal{W}} = \frac{1}{8}\sum_{i\neq j\neq k\neq l}\mathcal{K}_{ij,kl}\left(\frac{\|\boldsymbol{R}_{ij} * \boldsymbol{R}_{ij}\| \circ \|\boldsymbol{e}^1(\boldsymbol{r})\|}{R_{ij}}\right)\left(\frac{\|\boldsymbol{R}_{kl} * \boldsymbol{R}_{kl}\| \circ \|\boldsymbol{e}^1\|(\boldsymbol{r})}{R_{kl}}\right), \tag{5.27b}$$

or, in tensorial form

$$\mathcal{E}_{\mathcal{A},\mathcal{W}}^{\text{elastic}} = \int \mathrm{d}\boldsymbol{r}\cdot\sum_{\alpha\beta\gamma\delta}\boldsymbol{D}_{\mathcal{A},\mathcal{W}}^{\alpha\beta,\gamma\delta}(\boldsymbol{r})\cdot e_{\alpha\beta}^1(\boldsymbol{r})\cdot e_{\gamma\delta}^1(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}\cdot \boldsymbol{e}^1(\boldsymbol{r})\|\boldsymbol{D}_{\mathcal{A},\mathcal{W}}(\boldsymbol{r})\|\boldsymbol{e}^1(\boldsymbol{r})\,. \tag{5.28}$$

In this equation the fourth rank elastic constant tensor $\|\boldsymbol{D}_{\mathscr{A}}(\boldsymbol{r})\|$ is the continuum limit of

$$\|\boldsymbol{D}_{\mathscr{A}}\|_i = \frac{1}{2\mathscr{V}_i}\sum_{j\neq k}\mathscr{K}_{i,jk}\left\|\frac{\boldsymbol{R}_{ij}*\boldsymbol{R}_{ij}*\boldsymbol{R}_{ik}*\boldsymbol{R}_{ik}}{R_{ij}\cdot R_{ik}}\right\| \tag{5.29a}$$

and $\|\boldsymbol{D}_{\mathscr{W}}(\boldsymbol{r})\|$

$$\|\boldsymbol{D}_{\mathscr{W}}(\boldsymbol{r})\|_i = \frac{1}{8\mathscr{V}_i}\sum_{j\neq k\neq l}\mathscr{K}_{ij,kl}\left\|\frac{\boldsymbol{R}_{ij}*\boldsymbol{R}_{ij}*\boldsymbol{R}_{kl}*\boldsymbol{R}_{kl}}{R_{ij}\cdot R_{kl}}\right\| . \tag{5.29b}$$

Again we also write the components explicitly

$$D_{\mathscr{A}}^{\alpha\beta,\gamma\delta}|_i = \frac{1}{2\mathscr{V}_i}\sum_{j\neq k}\mathscr{K}_{i,jk}\left\|\frac{X_{ij}^{\alpha}*X_{ij}^{\beta}*X_{ik}^{\gamma}*X_{ik}^{\delta}}{R_{ij}\cdot R_{ik}}\right\| , \tag{5.30a}$$

$$D_{\mathscr{W}}^{\alpha\beta,\gamma\delta}|_i = \frac{1}{8\mathscr{V}_i}\sum_{j\neq k\neq l}\mathscr{K}_{ij,kl}\cdot\left\|\frac{X_{ij}^{\alpha}*X_{ij}^{\beta}*X_{kl}^{\gamma}*X_{kl}^{\delta}}{R_{ij}\cdot R_{kl}}\right\| . \tag{5.30b}$$

5.4.3. The Cauchy relations

Comparing the expression (5.24) for the elastic constants of the Cauchy model to the expressions (5.30) one immediately notes the lowering in the symmetry when many-body interactions are introduced.

The elements of the fourth-rank tensor in (5.30) exhibit transposition symmetry in the interchange of the "left-hand side" indices α and β and in the interchange of the right-hand side pair of indices γ and δ. They are also symmetric in the interchange of the pair $[\alpha\beta]$ with the pair $[\gamma\delta]$.

$$D_{\mathscr{A},\mathscr{W}}^{\alpha\beta\gamma\delta} = D_{\mathscr{A},\mathscr{W}}^{\beta\alpha\gamma\delta} = D_{\mathscr{A},\mathscr{W}}^{\alpha\beta\delta\gamma} = D_{\mathscr{A},\mathscr{W}}^{\gamma\delta\alpha\beta}\cdots \tag{5.31}$$

This is the symmetry of the elements of the *most general* elasticity tensor, $\|\boldsymbol{D}\|_{\text{gen}}$. It is the symmetry of the coefficients of a binary form in the components of a (six-component) symmetric tensor (Landau and Lifshitz, 1970, p. 10).

It can be seen that Eqs. (5.31) mean that the general tensor $\|\boldsymbol{D}_{\mathscr{A},\mathscr{W}}(\boldsymbol{r})\|$ can at most have 21 independent components in three-dimensional space and six in two dimensions:

$$n_{\text{gen}}(d=3)=21\,;\qquad n_{\text{gen}}(d=2)=6\,. \tag{5.32}$$

For central forces the elements of the tensor, Eq. (5.24), were symmetric under all permutations of the four indices. The additional symmetries which reduce the maximum number of independent elastic constants from 21 to 15 are known as the *Cauchy relations*. In the Cartesian notation they are (e.g. Love, 1927b)

$$D^{\alpha\alpha\beta\beta} = D^{\alpha\beta\alpha\beta}\,;\qquad D^{\alpha\beta\gamma\gamma} = D^{\alpha\gamma\beta\gamma}\,. \tag{5.33}$$

The general symmetries, Eq. (5.31), express the fact that the BH elastic energy is a binary form in the elements of the symmetric linear strain tensor $\boldsymbol{e}^1$. The Cauchy relations represent an additional symmetry. It does not follow from the symmetry of the strain tensor that terms in the elastic energy such as

$$e_{\alpha\alpha} \cdot e_{\beta\beta} \quad \text{and} \quad (e_{\alpha\beta})^2 \quad \text{or} \quad e_{\alpha\beta} \cdot e_{\gamma\gamma} \quad \text{and} \quad e_{\alpha\gamma} \cdot e_{\beta\gamma} \tag{5.34}$$

have identical coefficients in the expansion of elastic energy. This is an additional symmetry of the Cauchy model, a result of the restriction to central forces.

Note. The Cauchy relations played a relatively important role in the 19th century history of the theory of elasticity (see Love, 1927b, Note B) because they were believed to express an explicit macroscopic test of a microscopic model – the Cauchy assumption that the fundamental microscopic interactions were two-body interactions. When sufficiently accurate experiments became available it was found that the Cauchy relations are often violated.

Several authors (Poisson, 1842; Voigt, 1887; Thomson, 1890; Born, 1915) showed that this did not really test the central force assumption. They found that even for pure Cauchy interactions the macroscopic elastic constants need not satisfy the Cauchy relations when the unit cell is complex. Kelvin (Thomson, 1890) showed that this can be traced to non-affinity, i.e., to the fact that in a complex unit cell the *internal* deformation inside the cell need not be described by the macroscopic average strain.

From a modern point of view there is obviously no reason why the atomic interactions should be two body central force interactions. Interest in the Cauchy relations has therefore essentially disappeared. We mention them here because they seem to be the first context in which the importance of affinity was discussed.

5.4.4. *Affinity*

We have derived explicit microscopic expressions for the elastic constants – Eqs. (5.24) and (5.30). It is however important to add a reservation concerning the validity of these results.

The derivation we have constructed describes the change in the mechanical energy of the solid when all positions are changed in accordance with the affine transformation defined by the average strain $\langle \boldsymbol{e}^1 \rangle$.

$$\langle u''_{ij} \rangle_{\text{aff}} = \operatorname{Tr} \frac{\| \boldsymbol{R}_{ij} * \boldsymbol{R}_{ij} \| \circ \| \langle \boldsymbol{e}^1 \rangle \|}{R_{ij}} \tag{5.35}$$

say

$$\left(\frac{u''_{ij} - \langle u''_{ij} \rangle_{\text{aff}}}{\langle u''_{ij} \rangle_{\text{aff}}} \right)^2 \ll 1 \,, \tag{5.36}$$

where u''_{ij} is the actual relative change in the positions of i and j when the average strain is $\langle \boldsymbol{e}^1 \rangle$ and $\langle u''_{ij} \rangle$ is the affine deformation predicted by this strain. But this assumption is by no means always justified. In some situations, in particular for materials which are not very tightly interconnected, the deformations become affine only when averaged over sufficiently large regions – larger than a suitably chosen affinity length and the inequality (5.36) does not hold for smaller distances. Thus, e.g., the *internal* deformations of a complex unit cell can be very different from the uniform distortion described by the average macroscopic strain. Such non-affinity can have large effects on the values of the macroscopic elastic constants.

As we noted above Kelvin (Thomson, 1890) discovered that non-affinity can also lead to violations of the Cauchy relations for purely central force interactions. In general, the expressions we derived for the elastic constants assume affinity and can only be trusted when this assumption is justified.

We will discuss some dramatic effects of non-affinity on the shear rigidity of floppy networks in Part II.

5.5. Irreducible representation of the elastic constants

In Section 5.4 we discussed the elastic constant tensors using a Cartesian description. This is the form which arises directly from the expansion and is also the traditional approach. For some purposes this description is cumbersome and inconvenient. As in other problems symmetries are easier to handle if one decomposes the Cartesian tensors into their irreducible components (Lyubarski, 1960). This is particularly useful when one wants to analyze the effects of the symmetry of the solid phase in determining the number of independent elastic constants.

5.5.1. The general case

The symmetry relations of the elements of the general elastic constant tensor $\|\boldsymbol{D}\|_{\mathrm{gen}}$ which we derived, Eq. (5.31), are equivalent to saying that $\|\boldsymbol{D}\|_{\mathrm{gen}}$ is the symmetrized external product of two symmetric second rank tensors $\|\boldsymbol{Q}\|$ (Landau and Lifshitz, 1970)

$$\|\boldsymbol{D}\|_{\mathrm{gen}} = \| \, \|\boldsymbol{Q}\| * \|\boldsymbol{Q}'\| \, \|_{\mathrm{sym}} \,. \tag{5.37}$$

The symmetrized external product of two symmetric second rank tensors is also the most general form of the fourth-rank elastic constant tensor. Constructing $\|\boldsymbol{D}\|$ in this way is equivalent to the definition of its elements as the coefficients of a quadratic form in the components of the strain.

We first decompose the symmetric tensor $\|\boldsymbol{Q}\|$ into its irreducible components

$$\|\boldsymbol{Q}\| = \mathcal{Q}_2 + \mathcal{Q}_0 \,, \tag{5.38}$$

where $\mathcal{Q}_2$ is a (5-component) $L=2$ irreducible second rank tensor and

$$\mathcal{Q}_0 \propto \mathrm{Tr}\|\boldsymbol{Q}\|$$

is an $L=0$ scalar. Decomposing $\|\boldsymbol{D}\|_{\mathrm{gen}}$, the symmetrized square of $\|\boldsymbol{Q}\|$ one derives

$$\|\boldsymbol{D}\|_{\mathrm{gen}} = \mathcal{D}_4 + \mathcal{D}_2 + \mathcal{D}_0 + \overline{\mathcal{D}}_2 + \overline{\mathcal{D}}_0 \,, \tag{5.39}$$

where we have used

$$[\mathcal{Q}_2 * \mathcal{Q}_2] = \mathcal{D}_4 + \mathcal{D}_2 + \mathcal{D}_0 \,; \qquad [\mathcal{Q}_2 * \mathcal{Q}_0] = \overline{\mathcal{D}}_2 \,; \qquad [\mathcal{Q}_0 * \mathcal{Q}_0] = \overline{\mathcal{D}}_0 \tag{5.40}$$

and $\mathcal{D}_L$ is an irreducible tensor of rank L with $2L+1$ components. The maximum number of components is thus

$$n_{\mathrm{gen}}(d=3) = 9 + 5 + 1 + 5 + 1 = 21 \tag{5.41}$$

as also found by the explicit counting of independent Cartesian components using the symmetry relations (5.31).

The above is the result in three dimensions. In two dimensions the irreducible representations have a single index, M and are two dimensional for $M \neq 0$. One has

$$\|\boldsymbol{Q}\| = q_2 + q_0 , \tag{5.42}$$

$$\|\boldsymbol{D}\|_{\text{gen}} = d_4 + d_2 + d_0 + \overline{d}_0 , \tag{5.43}$$

so that

$$n_{\text{gen}}(d=2) = 2 + 2 + 1 + 1 = 6 . \tag{5.44}$$

5.5.2. The Cauchy model

We have to decompose the fourth-rank Cartesian tensor $\|\boldsymbol{D}\|_{\text{Cauchy}}$, Eq. (5.23), into its irreducible components. $\|\boldsymbol{D}\|_{\text{Cauchy}}$ is the sum of the totally symmetric external products of four vectors, $\boldsymbol{R}$ $(=\mathscr{R}_1)$, and therefore

$$\|\boldsymbol{D}\|_{\text{Cauchy}} \propto \|\boldsymbol{R} * \boldsymbol{R} * \boldsymbol{R} * \boldsymbol{R}\|_{\text{sym}} = \mathscr{D}_4^c + \mathscr{D}_2^c + \mathscr{D}_0^c \tag{5.45}$$

in three dimensions. Thus

$$n_{\text{Cauchy}}(d=3) = 9 + 5 + 1 = 15 \tag{5.46}$$

as we found earlier, in Eq. (5.25), by explicit counting of the independent Cartesian tensor elements.

In the irreducible description the Cauchy relations, Eq. (5.33), mean that there is only one scalar and one irreducible second rank tensor for Cauchy models while there are two of each in the general case.

$$\mathscr{D}_2, \overline{\mathscr{D}}_2 \rightarrow \mathscr{D}_2^c , \qquad \mathscr{D}_0, \overline{\mathscr{D}}_0 \rightarrow \mathscr{D}_0^c . \tag{5.47}$$

The two scalars also coalesce in two dimensions

$$\|\boldsymbol{D}\|_{\text{Cauchy}} = d^4 + d^2 + d^0 . \tag{5.48}$$

The Cauchy relations, Eq. (5.33), are symmetries of the elastic constant tensor which make different elements equal to each other – as described explicitly in Eq. (5.34). Writing the expansion in its irreducible form only amounts to a regrouping of the terms in the expansion. The meaning of (5.45) is therefore that the coefficients of the respective expressions in the expansion of the energy in the general case become proportional to each other for Cauchy models.

5.5.3. Effect of the symmetry of the solid

Writing the elastic tensors in irreducible form is particularly useful when one wants to investigate the effects of the symmetry of the solid on its elasticity. We consider two cases:

5.5.3.1. Isotropic materials with full rotational symmetry. Only scalars can appear as invariants. Full rotational symmetry therefore implies

$$\mathscr{D}_4 = \mathscr{D}_2 = \overline{\mathscr{D}}_2 \equiv 0 . \tag{5.49}$$

In the general case, Eq. (5.39), there are then *two* independent elastic moduli – $\mathscr{D}_0$ and $\overline{\mathscr{D}}_0$. We can relate this to the notation and terminology of Elasticity (e.g., Landau and Lifshitz, 1970). As can be seen in Eq. (5.40) $\bar{\mathscr{D}}_0$ is the coefficient of the product of two scalars $\mathscr{Q}_0$ and $\mathscr{Q}_0'$. It therefore multiplies the square of the scalar density change

$$e_0 = \mathrm{Tr}\|e\| . \tag{5.50}$$

$\bar{\mathscr{D}}_0$ is thus proportional to the bulk modulus K. $\mathscr{D}_0$ is the scalar square of an irreducible second rank tensor $\mathscr{Q}_2$. It describes the response to a strain without volume change and is proportional to the shear modulus μ.[21]

$$\mathscr{D}_0 \propto \mu ; \qquad \bar{\mathscr{D}}_0 \propto K . \tag{5.51}$$

For a Cauchy model there is only *one* scalar as is seen in Eqs. (5.45) and (5.47). For Cauchy models the shear modulus, μ, and the bulk modulus, K, are therefore not independent. The two moduli are proportional to each other

$$\mathscr{D}_0 \propto \mu \propto K . \tag{5.52}$$

Alternatively one could also use Eq. (5.31) directly to obtain two independent rotational invariants for an isotropic solid, e.g., the square of the trace of $\|\boldsymbol{Q}\|$

$$\mathscr{I}_1 = (\mathrm{Tr}\|\boldsymbol{Q}\|)^2 = \sum_{\alpha} D^{\alpha\alpha\alpha\alpha} + \sum_{\alpha\neq\beta} D^{\alpha\alpha\beta\beta} \tag{5.53}$$

and the trace of the square

$$\mathscr{I}_2 = (\mathrm{Tr}\|\boldsymbol{Q} * \boldsymbol{Q}\|) = \sum_{\alpha} D^{\alpha\alpha\alpha\alpha} + \sum_{\alpha\neq\beta} D^{\alpha\beta\beta\alpha} . \tag{5.54}$$

It can be seen by direct inspection that $\mathscr{I}_1$ and $\mathscr{I}_2$ become equal to each other when the Cauchy relations, Eq. (5.33), hold so that $D^{\alpha\beta\beta\alpha} = D^{\alpha\alpha\beta\beta}$.

This result is actually quite old. Navier's original paper (1827), used central forces and found one elastic constant for isotropic solids. Navier's explicit calculation showed that this predicts a ratio ($\sqrt{3}$) between the longitudinal and transverse velocities of sound which is a test of the Cauchy relations.

5.5.3.2. Cubic symmetry[22]. There are three elastic constants (Landau and Lifshitz, 1970, ch. 10). First the two scalars, $\mathscr{D}_0$ and $\bar{\mathscr{D}}_0$ which we also had for full rotational symmetry – Eq. (5.51). In addition, the fourth rank tensor $\mathscr{D}_4$ also has a cubic invariant which we denote $\mathscr{A}_4$. Thus there are three independent elastic constants in the general case which are reduced to two for Cauchy models.

This counting is correct but the description is not quite satisfactory.

$\bar{\mathscr{D}}_0$ is indeed the compressibility, K, as in the isotropic case. But the cubic symmetry implies that what one really wants are always linear combinations of the two shear moduli $\mathscr{D}_0$ and $\mathscr{A}_4$.

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[21] The proportionality constants here and in Eq. (4.46) are numerical coefficients which are determined by the normalization of $\mathscr{D}_L$.

[22] For simplicity we assume full cubic symmetry O or $\mathrm{O_h}$.

In cubic symmetry the five component irreducible part of the strain tensor, $\boldsymbol{e}_2$, is decomposed into a two dimensional part, $\boldsymbol{e}_{\mathrm{E}}$ $(=(3e_{zz}-e_{xx}-e_{yy}),(e_{xx}-e_{yy}))$, and a three dimensional part $\boldsymbol{e}_{\mathrm{T}}$, $(=e_{xy},e_{yz},e_{zx})$.

$$\|\boldsymbol{e}\| = e_0 + e_2\,; \qquad e_2 = e_{\mathrm{E}} + e_{\mathrm{T}}\,, \tag{5.55}$$

so that the elastic energy can be written

$$\mathscr{E}^{\text{elastic}} = K(e_0)^2 + \mu_{\mathrm{E}}|\boldsymbol{e}_{\mathrm{E}}|^2 + \mu_{\mathrm{T}}|\boldsymbol{e}_{\mathrm{T}}|^2\,. \tag{5.56}$$

Thus the proper elastic constants for cubic symmetry are the bulk modulus $K(\overline{\mathscr{D}}_0)$ and the two specifically cubic elastic constants μ_{E} and μ_{T}. Both μ_{E} and μ_{T} are linear combinations of $\mathscr{D}_0$ and $\mathscr{d}_4$. For Cauchy models the two scalars $\mathscr{D}_0$ and $\overline{\mathscr{D}}_0$ become equal but this only shows up indirectly in the constants μ_{E} and μ_{T}. The Cauchy relations thus imply a linear relationship between the three elastic constants of a cubic crystal

$$\alpha\cdot K + \beta\cdot\mu_{\mathrm{T}} + \gamma\cdot\mu_{\mathrm{E}} = 0\,. \tag{5.57}$$

6. Stressed reference states

6.1. The two effects of stresses

Our purpose in this chapter is to discuss the effect of the *initial stresses*[23] in the reference state on the microscopic harmonic expansion and on the elastic energy.

In the macroscopic theory of elasticity second order terms in which the stress appears as a *coefficient* are well known – namely the terms in the elastic energy in which the stress multiplies the second order strain (e.g. Landau and Lifshitz, 1970, ch. 1)

$$-\sum_{\alpha,\beta}\boldsymbol{\sigma}_{\text{ini}}^{\alpha\beta}\cdot\boldsymbol{e}_{\alpha\beta}^{2} = -\frac{1}{2}\sum_{\alpha\beta\gamma}\boldsymbol{\sigma}_{\text{ini}}^{\alpha\beta}\cdot\partial_\alpha u_\gamma\partial_\beta u_\gamma\,. \tag{6.1}$$

Using a different notation Love (1927a, b, p. 75 and Note B) discusses the expansion around a stressed reference state in detail. These contributions to the elastic energy have been known for a long time. They dominate the transverse vibrations of stretched strings and drumheads – as in musical instruments. They also play a central role in the analysis of elastic stability (Landau and Lifshitz, 1970, ch. 21) as in the Euler buckling of loaded columns (ibid. ch. II). All these are examples of situations in which the directly stress induced contributions to the elastic energy described by Eq. (6.1) are very important and often dominant. In the examples discussed there the reason they are important is that the geometry of the material is very anisotropic – thin rods and thin plates – so that the stress induced terms of Eq. (6.1) compete with relatively weak BH bending and curvature energies.

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[23] We follow Love (1927a) in calling the stresses in the reference state for the expansion initial stresses.

The *microscopic* counterpart of these terms is less familiar.[24] For a stressed reference state, $\{\boldsymbol{R}\}_{\text{str}}$, there are non-vanishing bond tensions

$$\mathcal{T}_{ij} = \mathcal{T}_{ij}(\{\boldsymbol{R}\}_{\text{str}}) \neq 0\,. \tag{6.2}$$

When one expands around such a reference state one finds scalar terms in the harmonic expansion which depend on the *magnitude* of the relative deviations

$$\propto \frac{\mathcal{T}_{ij}}{R_{ij}}\,|\boldsymbol{u}_{ij}|^2 = \frac{\mathcal{T}_{ij}}{R_{ij}}\,u_{ij}^2 \tag{6.3}$$

(Alexander 1984, 1985). These terms in the harmonic expansion are *qualitatively* different from those appearing in the expansion around an unstressed BH reference state – Eqs. (5.8), (5.11) and (5.13). The continuum limit of these terms is the contribution of the second order strain to the elastic energy – Eq. (6.1) – just as the product of the linear strain with the stress – Eq. (4.2) – was the continuum limit of the linear microscopic expansion around such a reference state – Eq. (4.1).

6.1.1. *Direct and induced effects of stresses*

There is an important formal point in the expansion procedure which we want to emphasize.

We expand around a *stressed* reference state, $\{\boldsymbol{R}\}_{\text{str}}$. There are then terms in the *microscopic* harmonic expansion in which the first derivatives of the energy with respect to the interparticle distances, the *initial bond tensions*

$$\mathcal{T}_{ij}^{\text{ini}} = \mathcal{T}_{ij}(\{R\}_{\text{str}}) = [\partial\mathcal{E}/\partial r_{ij}]_{\{R\}_{\text{str}}} \tag{6.4}$$

appear as coefficients. These terms, Eq. (6.3), result from the terms

$$\mathcal{T}_{ij}\cdot\frac{\partial}{\partial \boldsymbol{r}_{ij}} * \frac{\boldsymbol{r}_{ij}}{r_{ij}} = \mathcal{T}_{ij}\left\|\frac{1}{r_{ij}} - \frac{\boldsymbol{r}_{ij} * \boldsymbol{r}_{ij}}{r_{ij}^3}\right\| \tag{6.5}$$

in the general TRI harmonic expansion – Eq. (5.1). In the continuum limit they give rise to terms in the elastic energy which are quadratic in the first derivatives of the deviation field in which the components of the *initial stress*, $\sigma_{\text{ini}}^{\alpha\beta}$, appear as coefficients – Eq. (6.1). The bond tensions appear as coefficients in the *microscopic* expansion and the macroscopic stresses appear as coefficients in the elastic energy. We shall call this the *direct* effect of the stresses. This is the effect of stresses which we shall discuss in this chapter.

Stresses also have an *indirect* effect on the mechanical properties. The positions in a stressed reference state are different from those in the unstressed state of the same material.

$$\{R\}^{\text{str}} = \{R\}(\sigma^{\text{ini}}) \neq \{R\}(\sigma=0)\,, \qquad \{\delta R\} = \{R\}(\sigma^{\text{ini}}) - \{R\}(\sigma=0) \neq 0\,.$$

When the difference is small one can relate a stressed state to an unstressed state of the same material by induced stresses

$$\boldsymbol{e}^{\text{ind}} = \boldsymbol{e}^{\text{ind}}(\sigma^{\text{ini}}) \xrightarrow[\sigma^{\text{ini}}\to 0]{} 0$$

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[24] We are not aware of discussions of the effect of stresses on the microscopic expansions except for our own earlier ones (Alexander 1984, 1985).

which are induced by the initial stresses, $\boldsymbol{\sigma}^{\mathrm{ini}}$, and vanish with these stresses. Because of these induced strains the microscopic second derivatives in the stressed state

$$\mathscr{K}^{\mathrm{str}}_{ij,kl} = \left[\frac{\partial^2 \mathscr{E}}{\partial r_{ij}\, \partial r_{kl}} \right]_{\{R\}^{\mathrm{str}}} \tag{6.6}$$

are different from what they would have been in the unstressed state.

The induced effect of the strain reflects the modified geometry of the stressed reference configuration $\{R\}^{\mathrm{str}}$. The mechanical properties of the *strained* material are different from those of the unstrained one because its geometry is different. We shall call this the *induced* effect of the stresses. It represents the effect of the induced strains on the mechanical properties.

One might think that these are simply two equivalent descriptions of the same physical effect but this is not the case. They are quite different.

If the initial stresses are large, e.g., because of large external pressures, the induced effect can become quantitatively large so that the inter-particle interactions become quite different from those in the unstressed state, but the induced microscopic interactions are still of the BH type and can be expressed in terms of the $u^{\prime\prime}_{ij}$. The indirect effect of the stress does not create any terms which are qualitatively different from those one obtains from a BH expansion around an unstressed state. Only the magnitude of the second derivatives of the energy is changed. The expansion depends only on the reference state itself. One simply expands around a different reference state. As long as one does not include the bond tensions, the specific terms – Eq. (6.5) – which are responsible for the direct effect, everything we did in Section 5 also applies to the expansion around a stressed reference state.

The *definition* of *induced* strains in $\{\boldsymbol{R}\}^{\mathrm{str}}$ which are caused by the stresses also assumes that there exists a "*true*" reference state, $\{\boldsymbol{R}\}^{\mathrm{true}}$, which is not stressed and is different from $\{\boldsymbol{R}\}^{\mathrm{str}}$. The difference between $\{\boldsymbol{R}\}^{\mathrm{str}}$ and the true reference state defines the induced strain. Thus to lowest order the induced strain is given by

$$\boldsymbol{e}^{\mathrm{ind}} = \boldsymbol{D}^{-1} \cdot \boldsymbol{\sigma}_{\mathrm{ini}}\,, \tag{6.7}$$

where $\boldsymbol{D}$ is the elastic constant tensor in the unstressed reference state $\{\boldsymbol{R}\}^{\mathrm{true}}$. The expansion around $\{\boldsymbol{R}\}^{\mathrm{str}}$ can then be regarded as an expansion around the unstressed state $\{\boldsymbol{R}\}^{\mathrm{true}}$ in which the initial stresses also appear. When derived in this way the indirect effect depends on the third (and higher) order terms in the expansion around the "true" reference state. It has no meaning outside the comparison of the coefficients of the expansion around the stressed reference state $\{\boldsymbol{R}\}^{\mathrm{str}}$ to those of the expansion around the unstressed "true" reference state $\{\boldsymbol{R}\}^{\mathrm{true}}$. Thus, e.g.,

$$\delta \boldsymbol{D}(\boldsymbol{\sigma}_{\mathrm{ini}}) \approx \boldsymbol{D}_3 * \boldsymbol{e}_{\mathrm{ind}}(\boldsymbol{\sigma}_{\mathrm{ini}})\,, \qquad \delta D^{\alpha\beta,\gamma\delta} \approx \sum_{\mu\nu} D_3^{\alpha\beta,\gamma\delta,\mu\nu} \cdot e^{\mathrm{ind}}_{\mu\nu}(\boldsymbol{\sigma}_{\mathrm{ini}})\,, \tag{6.8}$$

where $\boldsymbol{D}_3$ is a higher order elastic constant tensor in the unstressed state $\{\boldsymbol{R}\}^{\mathrm{true}}$.

The magnitude of the higher order coefficients in the expansion around the true reference state determines how large the strains have to be to produce a significant change in the elastic constants.

The induced effect can be very important in its own right – when the stresses are large. It is however a completely different effect from the *direct effect* of the same stresses.

We shall illustrate the distinction between the direct effect of stresses and the effect of the strains induced by the same stresses in a simple and familiar example:

6.1.2. *Stresses and induced strains in the vibrations of strings and drumheads*

One analyzes the vibrations of stretched strings and the transverse fluctuations of drumheads using a *stressed* reference state. In both cases one expands around a stressed equilibrium state – a stretched string for which the *string tension* does not vanish and a stretched membrane, drumhead or surface for which the *surface tension* does not vanish. It is well known that in both cases this initial stress is directly responsible for the leading terms in the bending rigidity of the string or membrane. Specifically,

The leading terms in the elastic eigenmode energies and (squared) frequencies, ω_q^2, are proportional to q^2 and to the stress, σ – the line or surface tension

$$\begin{aligned} &\mathscr{E} \approx \int \mathrm{d}x \cdot [-\boldsymbol{\sigma} \cdot (\boldsymbol{\nabla} h)^2 + \Gamma \cdot (\boldsymbol{\nabla}^2 h)^2] \\ &\omega_q^2 \propto -\boldsymbol{\sigma} \cdot q^2 + \Gamma \cdot q^4 \,, \end{aligned} \tag{6.9}$$

where h $(=h(x))$ is the transverse deviation, σ is the stress – the surface tension – and Γ is a bending modulus which represents the BH contribution to the transverse rigidity. The result is well known in many versions.

We note that the stress, σ, appears *explicitly* as a coefficient in Eq. (6.9). When the string is long and thin enough σ completely dominates the transverse rigidity. The contributions of the regular, unstressed bending modulus, Γ, are proportional to q^4 and can therefore be neglected for long wavelengths. For negative σ this was already used by Euler (1755) in his explanation of buckling and it is the essence of the analysis of elastic stability (Landau and Lifshitz, 1970, ch. 21).

Obviously a stretched string will also be *elongated* by the stress when compared to its "true", unstressed, length L_0. The initial stress in the reference state, the line tension σ, induces an elongation, δL, or equivalently a strain, $\delta L/L_0$, in the string – as in Eq. (6.7). If this strain is large enough it can significantly change the mechanical properties of the material constituting the string. In general one therefore expects that the induced strain will also change the bending rigidity, Γ – Eq. (6.8). The stressed string can even break when the strain is large enough. This is the *induced* effect of the stress. In this example it affects the coefficient of the term proportional to q^4 in Eq. (6.9)

$$\Gamma(0) \neq \Gamma(\delta L/L_0) \,.$$

The induced strain, the elongation of the string induced by the initial stress, plays no role at all in the *direct* term in Eq. (6.9) which is proportional to q^2. Only the stress itself appears there. As long as the string remains intact, and does not break, this term in Eq. (6.9) is not changed.

The effect of the elongation of the string on its mechanical properties, the effect of the induced strain, and the transverse rigidity induced directly by the tension are two separate and qualitatively different effects.

The direct effect of stresses on the mechanical properties is familiar for these anisotropic geometries because even relatively small stresses become important for the transverse long wave modes of thin rods and plates when

$$\Gamma q^2 < \sigma \,. \tag{6.10}$$

The distinction between two different effects of stress on the mechanical properties is however a general phenomenon.

6.2. Bond-tensions in the harmonic expansion

6.2.1. The harmonic expansion

We want to discuss the effect of the term in Eq. (5.1) which is neglected in the BH approximation

$$\frac{\partial \mathscr{E}(\{r\})}{\partial r_{ij}} \frac{\partial}{\partial \boldsymbol{r}_{ij}} * \frac{\boldsymbol{r}_{ij}}{r_{ij}} = \frac{\mathscr{T}_{ij}}{r_{ij}} \left(1 - \frac{\boldsymbol{r}_{ij} * \boldsymbol{r}_{ij}}{r_{ij}^2} \right) \tag{6.11}$$

which appear when the reference state is stressed

$$\mathscr{T}_{ij} = [\partial \mathscr{E} / \partial r_{ij}]_{\{\mathrm{R}\}} \neq 0 .$$

This gives a contribution to the harmonic energy

$$\mathscr{P} = \frac{1}{4} \sum_{ij} \frac{\mathscr{T}_{ij}}{R_{ij}} (u_{ij}^2 - u_{ij}^{\prime\prime 2}) . \tag{6.12}$$

The terms in the sum on the right-hand side of Eq. (6.12) are second order in the components of the deviations, $\boldsymbol{u}_i$, and contain only two site indices – $[ij]$. Thus $\mathscr{P}$ is part of the two-body, Cauchy, harmonic energy. In the harmonic expansion $\mathscr{P}$ appears to the same order in the components of the $\boldsymbol{u}_i$ as the unstressed Cauchy energy, $\mathscr{C}^{\mathrm{h}}$ – Eq. (5.8), the angular three-body contributions, $\mathscr{A}$ – Eq. (5.11), and the four-body twist contributions, $\mathscr{W}$ – Eq. (5.13), which we discussed in Section 5. There is therefore no general reason why one should neglect the direct effect of the stresses – the tension induced terms $\mathscr{P}$ – compared to the terms in the BH harmonic expansion, Eq. (5.15).

We note that once $\mathscr{P}$ is expanded in the single particle deviations, the u_i^α, it is no longer possible to single out these stress-induced terms in the harmonic energy – in spite of the underlying differences between them and the BH contributions to the same expansion.

6.2.2. Rotational invariance

The intuitively most striking peculiarity of the terms in $\mathscr{P}$ is that they seem to violate the standard rotational invariance criteria for two-body interactions. The contribution of a pair $[ij]$ to $\mathscr{P}$ cannot be expressed in terms of the component of $\boldsymbol{u}_{ij}$ parallel to the reference vector, $\boldsymbol{R}_{ij}$, separating the pair – $u_{ij}^{\prime\prime}$. $\mathscr{P}$ can even be written explicitly in terms of the *transverse* deviations, $u_{ij}^{\perp}$, alone

$$\mathscr{P} = \frac{1}{4} \sum_{ij} \frac{\mathscr{T}_{ij}}{R_{ij}} (u_{ij}^{\perp})^2 \tag{6.13}$$

and it would seem that this is not consistent with rotational invariance because of the identification of $u_{ij}^{\perp}$ with a rotation – Eq. (5.9). We discussed this rotational invariance criterion in Section 5.2.2.1. Eq. (6.13) cannot be written in terms of $u_{ij}^{\prime\prime}$ but this cannot be a real violation of rotational invariance. The energy we expanded, $\mathscr{E}(\{\boldsymbol{r}\})$, is obviously rotationally invariant and the formal derivation of Eq. (6.13) is elementary. Terms which violate rotational invariance cannot appear in such an expansion.

The origin of this apparent contradiction is that the identification of $u_{ij}^{\perp}$ with a rotation in Eq. (5.9)

$$u_{ij}^{\perp} \approx R_{ij} \delta \varphi_{ij}$$

is valid only to first order in the components of $\boldsymbol{u}_{ij}$.

For a pure rotation, $\delta\varphi$, the distance r_{ij} cannot change. δr_{ij}, must vanish exactly and to all orders. This is rotational invariance. But for a purely transverse deviation

$$u_{ij}^{\perp} \neq 0\,, \qquad u_{ij}^{\prime\prime} = 0\,, \tag{6.14}$$

one has, to second order

$$\delta r_{ij} = \frac{(u_{ij}^{\perp})^2}{2R_{ij}} \tag{6.15}$$

so that δr_{ij} does not vanish. Evidently this means that $u_{ij}^{\perp}$ does not describe the rotation correctly to *second order*. To this order the rotation $\delta\varphi_{ij}$ is described by a vector with the components

$$u_{ij}^{\perp}\,; \qquad u_{ij}^{\prime\prime} = -\frac{(u_{ij}^{\perp})^2}{2R_{ij}} \tag{6.16}$$

which assures $\delta r = 0$ to second order. To second order the rotation cannot be described by the purely transverse deviation (6.14). When $\mathscr{T} \neq 0$ these second order corrections appear in the harmonic expansion of the energy.

Since the apparent violation of rotational invariance may seem surprising, and even counterintuitive, we discuss the transverse response of a stressed spring in detail in Appendix B. The purpose of this discussion is of course purely didactic.

6.3. *"Scalar elasticity"*

It is convenient to consider the *scalar* part of $\mathscr{P}$ in Eq. (6.8) separately.

$$\mathscr{P}_{\text{scalar}} = \frac{1}{4}\sum_{ij} \frac{\mathscr{T}_{ij}}{R_{ij}} \cdot u_{ij}^2\,. \tag{6.17}$$

We have called this "*scalar elasticity*" because of the appearance of the scalar *magnitude* of the deviation $\boldsymbol{u}_{ij}$ (Alexander, 1984).

6.3.1. *The Born model*

In studies of lattice dynamics expressions which look like $\mathscr{P}_{\text{scalar}}$

$$\mathscr{B} = \frac{1}{4}\sum_{ij} \mathscr{B}_{ij} \cdot u_{ij}^2 \tag{6.18}$$

are sometimes added to the harmonic expansion to increase the shear rigidity. This is known (to the experts) as the *Born model* (Born and Huang, 1954, ch. 5). The "Born" terms are introduced as a substitute for the many-body, angular and twist terms – because the expansion of these scalar two-body terms is much simpler and more convenient than that of the many-body terms they replace. When introduced in this way the coefficients of the scalar Born terms are essentially fitting parameters and it is evident that they violate rotational invariance. These "Born model" terms are of course always qualitatively different from the BH bending and twist interactions which they replace.

Our derivation of Eq. (6.17) shows that such scalar terms can also appear in the expansion of a *rotationally invariant* energy around a stressed reference state.

6.3.2. Correction of the spring constants

The rest of $\mathscr{P}$, the contributions of the u''_{ij} to $\mathscr{P}$,

$$\mathscr{P} - \mathscr{P}_{\text{scalar}} = -\frac{1}{4}\sum_{ij} \mathscr{T}_{ij}/R_{ij}\,(u''_{ij})^2 \tag{6.19}$$

can be incorporated into the Cauchy energy by redefining the coefficients in Eq. (5.8)

$$\mathscr{C}^{\text{h}} \Rightarrow \mathscr{C}'^{\text{h}}; \quad \mathscr{P} + \mathscr{C}^{\text{h}} = \mathscr{P}_{\text{scalar}} + \mathscr{C}'^{\text{h}} \tag{6.20}$$

where

$$\mathscr{C}'^{\text{h}} = \frac{1}{2}\sum_{ij} \mathscr{K}'_{ij}\,(u''_{ij})^2\,, \qquad \mathscr{K}'_{ij} = \mathscr{K}_{ij} - \mathscr{T}_{ij}/2R_{ij}\,. \tag{6.21}$$

The effect of the line tensions on the force constants is small when the bond tensions are not too large so that

$$\frac{\mathscr{T}_{ij}}{R_{ij}\,\mathscr{K}_{ij}} \ll 1\,. \tag{6.22}$$

One can then neglect the difference between the corrected Cauchy energy, $\mathscr{C}'^{\text{h}}$, Eq. (6.21), and $\mathscr{C}^{\text{h}}$, Eq. (5.8).

Thus the special effect of the stress which is qualitatively different from the BH harmonic energy is the effect of $\mathscr{P}_{\text{scalar}}$. Because of this the inequality (6.22) does not necessarily justify the neglect of $\mathscr{P}_{\text{scalar}}$. The inequality implies that the terms in $\mathscr{P}_{\text{scalar}}$ are small compared to the BH terms in the expansion. However, because $\mathscr{P}_{\text{scalar}}$ is qualitatively different in structure from the BH terms it can become important for modes for which the BH terms are for some reason ineffective even when the stresses are small. We will see in Part II that this happens in tenuous materials and is crucial to understanding their properties.

6.3.3. The sign of the bond tensions

It is evident that the bond tensions, the $\mathscr{T}_{ij}$, have a sign. They can be positive – as in a stretched spring – or negative – as for loaded columns. Since the $\mathscr{T}_{ij}$ are coefficients in the harmonic expansion terms in $\mathscr{P}$ – Eq. (6.13) – and in the scalar contributions, (6.17), these terms also can have different signs. Positive tensions have a stabilizing effect on the transverse bending rigidity while negative tensions destabilize it.

6.4. The continuum limit

6.4.1. The second order strain

We want to show that the terms in the elastic energy in which the second order strain appears, Eq. (6.1), are indeed the continuum limit of $\mathscr{P}_{\text{scalar}}$.

We first evaluate the continuum limit of u_{ij}^2. From Eq. (4.5) one finds

$$u_{ij}^{\gamma} \cong \sum_{\alpha} X_{ij}^{\alpha} \cdot \partial_{\alpha} u_{\gamma} \tag{6.23}$$

so that

$$u_{ij}^2=\sum_{\gamma}(u_{ij}^{\gamma})^2 \cong \sum_{\alpha,\beta}[X_{ij}^{\alpha}\cdot X_{ij}^{\beta}]\cdot\sum_{\gamma}\partial_{\alpha}u_{\gamma}\partial_{\beta}u_{\gamma}\,. \tag{6.24}$$

Substituting this into $\mathscr{P}_{\text{scalar}}$ we can write the continuum limit of Eq. (6.17) as

$$\mathscr{P}_{\text{scalar}} \Rightarrow \mathscr{P}^{\text{elastic}} = -\left(\frac{1}{2}\right)\int \mathrm{d}\boldsymbol{r}\cdot\sum_{\alpha\beta}\boldsymbol{\sigma}^{\alpha\beta}(\boldsymbol{r})\cdot \boldsymbol{e}^2_{\alpha\beta}(\boldsymbol{r})\,, \tag{6.25}$$

where the microscopic expression for the stress tensor $\boldsymbol{\sigma}(\boldsymbol{r})$ is

$$\sigma_i = -\mathscr{V}_i^{-1}\cdot\sum_j \mathscr{T}_{ij}\cdot\frac{(\boldsymbol{R}_{ij}*\boldsymbol{R}_{ij})}{R_{ij}} \tag{6.26}$$

exactly as in Eq. (4.10) and the components of the *second order strain* tensor, $\boldsymbol{e}^2$, are

$$\boldsymbol{e}^2_{\alpha\beta} = \left(\frac{1}{2}\right)\sum_{\gamma}\partial_{\alpha}u_{\gamma}\partial_{\beta}u_{\gamma}\,. \tag{6.27}$$

We have thus shown that the "scalar elasticity" terms in the harmonic expansion, Eq. (6.17), are the terms in the microscopic expansion which, in the continuum limit, are the origin of the second order strain in the stress–strain relations.

6.4.2. *Direct effect of the stress on the elastic constants*

Because of the redefinition of the force constants in Eq. (6.21) stresses also have a "direct" effect on the continuum limit. The change in the force constants

$$\delta\mathscr{K}_{ij} = -\mathscr{T}_{ij}/2R_{ij}$$

causes a correction in the elastic constants

$$\delta\|\boldsymbol{D}(\boldsymbol{r})\|_{\{\mathscr{T}_{ij}\}} = -\frac{1}{4}\sum_i\frac{\mathscr{T}_{ij}}{R_{ij}}\cdot\left\|\frac{\boldsymbol{R}_{ij}*\boldsymbol{R}_{ij}*\boldsymbol{R}_{ij}*\boldsymbol{R}_{ij}}{R_{ij}^2}\right\| \tag{6.28}$$

which has the Cauchy form – Eq. (5.23).

While this contribution to the elastic constants at $\boldsymbol{r}$ is also a *direct* effect of the stresses on the elastic energy it cannot be expressed as a simple function of the stress, Eq. (6.26). The contributions of the $\mathscr{T}_{ij}$ for different bonds are weighed differently in the definition of the stress, Eq. (6.26), and in Eq. (6.28).

We only mention this for completeness and shall not discuss these corrections further. When the line tensions and local stresses are small – Eq. (6.22) – the corrections to the elastic constants defined in Eq. (6.28) are not important.

6.5. *Network stresses are elastic constants*

Our purpose in Part I was to restructure the derivation in a form which would assure rotational invariance and make the effect of the stresses manifest. Rotational invariance and stresses are not evident when one writes the microscopic expansion in the standard text-book form – i.e., directly as an expansion in the components of the $\boldsymbol{u}_i$. One cannot really see in these expansions whether the expansion is rotationally invariant and if the reference state is stressed. In the continuum limit the situation is different. The rotationally invariant structure of the theory of elasticity is quite transparent and this is also apparent in the inclusion of initial stresses and of the second order strain in the discussion of many problems. One sees immediately that the presence of stresses introduces a qualitatively different type of term into the elastic energy and that it does not violate any symmetry.

In this sense the continuum limit demonstrates clearly that the scalar terms in the harmonic expansion, Eq. (6.17), are *qualitatively* different from the BH terms. Only these terms give rise to the terms in the elastic energy in which the second order strain appears. The continuum limit of all other terms in the expansion can be written as an expansion in the symmetric first order strain.

We saw this explicitly. Eqs. (5.22) and (5.28) contain products of the *fourth rank* elastic constant tensor $\|\boldsymbol{D}\|$ with a *second order* form in the components of the symmetric tensor $\boldsymbol{e}^1$ – Eq. (4.3) – which is *linear* in the first derivatives of the deviation field $\boldsymbol{u}(\boldsymbol{r})$. On the other hand, the coefficient in Eq. (6.25) is the *second rank* stress tensor $\|\boldsymbol{\sigma}^{\mathrm{ini}}\|$. The equation is *linear* in the symmetric second rank tensor $\boldsymbol{e}^2$, the second order strain, which is itself *of the second order* in the derivatives of the deviation field. The two expressions are *qualitatively* different and cannot be transformed into each other. Both types of terms are second order in the first derivatives of the deviation field but their tensorial structure is different.

When the reference state is stressed the initial stresses of the network appear in the elastic energy as *elastic constants*. Clausius (1849) was apparently the first who noted that the initial stresses appeared as elastic constants in the results of Cauchy (1828c)[25] (see Love, 1927[a,b]). At least formally the components of the *second rank* initial stress tensor in the reference state – $\|\boldsymbol{\sigma}_{\mathrm{ini}}\|$ – are *elastic constants* of the pre-stressed solid exactly like the components of the fourth-rank elastic constant tensor $\|\boldsymbol{D}\|$ and for the same reason. Both tensors are local properties of the energy $\mathscr{E}(\{\boldsymbol{r}\})$, and of the specific equilibrium reference state $\{\boldsymbol{R}\}$.

In general both types of "elastic constants" have to be included.

6.6. Breaking transposition symmetry

We have seen that in stressed materials new terms appear in the elastic energy which have a different structure and whose continuum limit is proportional to the second order strain. These contributions to the mechanical energy can dramatically enhance the shear rigidity of a mechanical network – at the macroscopic level and also at the local microscopic level. This will be important for our discussions in Parts II and III. There is however also a *qualitative* difference between $\mathscr{P}^{\mathrm{elastic}}$, Eq. (6.25), and the most general BH expansion in the components of the linear strain.

6.6.1. Breaking transposition symmetry

To second order the BH elastic energy can be written as an expansion in the components of the symmetric linear strain – $\frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha)$. Such an expansion is completely symmetric in the *transposition* of the derivative index and the index of the component of the deviation. The shears

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[25] Cauchy (1828c) found 21 elastic constants – the 15 BH constants of the Cauchy model and the 6 components of the initial stress.

$\partial_\alpha u_\beta$ and $\partial_\beta u_\alpha$ appear in the elastic energy in *exactly* the same way. We shall call this symmetry of the unstressed BH elastic energy *transposition symmetry* (TS).

As we saw in Section 4 the origin of transposition symmetry is in the continuum limit of u''_{ij}

$$u''_{ij} \cong -\frac{\sum_{\alpha,\beta} X^\alpha_{ij} \cdot X^\beta_{ij} \cdot \partial_\alpha u_\beta}{R_{ij}}$$

– Eq. (4.6). TS for the expansion as a whole follows from the fact that the microscopic harmonic expansion around an unstressed BH reference state can be expressed as an expansion in the u''_{ij}.

TS is a general symmetry of the BH elastic energy which cannot be broken by lowering the spatial symmetry of the solid. TS can be broken in the harmonic expansion only when the reference state is stressed.

It is convenient to write the elastic energy (6.25) in a coordinate system in which the stress tensor $\boldsymbol{\sigma}$ is diagonal

$$\mathscr{F}^{\text{elastic}} = -\sum_\alpha \boldsymbol{\sigma}^{\alpha\alpha}_{\text{ini}} \cdot e^2_{\alpha\alpha} = -\sum_\alpha \left[\boldsymbol{\sigma}^{\alpha\alpha}_{\text{ini}} \cdot \sum_\beta (\partial_\alpha u_\beta)^2\right] . \tag{6.29}$$

When the stress is an isotropic pressure

$$p_{\text{ini}} = \boldsymbol{\sigma}^{\alpha\alpha}_{\text{ini}}$$

the elastic energy (6.29) becomes

$$\mathscr{F}^{\text{elastic}} = -p_{\text{ini}} \cdot \sum_{\alpha,\beta} (\partial_\alpha u_\beta)^2 \tag{6.30}$$

and the coefficients of $(\partial_\alpha u_\beta)^2$ and of $(\partial_\beta u_\alpha)^2$ are identical. Thus the elastic energy has full TS symmetry. This symmetry is broken when the spatial symmetry is reduced so that

$$\boldsymbol{\sigma}^{\alpha\alpha}_{\text{ini}} \neq \boldsymbol{\sigma}^{\beta\beta}_{\text{ini}} . \tag{6.31}$$

The coefficient of $(\partial_\alpha u_\beta)^2$, $\sigma_{\alpha\alpha}$ is then different from $\sigma_{\beta\beta}$, the coefficient of the transposed shear $(\partial_\beta u_\alpha)^2$. Thus transposition symmetry is broken by applying anisotropic stresses. Since the two shears $\partial_\alpha u_\beta$ and $\partial_\beta u_\alpha$ differ only by the "rotation" $\partial_\alpha u_\beta - \partial_\beta u_\alpha$ this looks like a violation of rotational invariance.

One can therefore design experiments which can distinguish between the shear

$$\partial_\alpha u_\beta \neq 0 , \qquad \partial_\beta u_\alpha = 0 ,$$

and the transposed shear

$$\partial_\alpha u_\beta \neq 0 , \qquad \partial_\beta u_\alpha \neq 0 .$$

One could do this, e.g., by comparing the frequency of a phonon polarized along β and propagating in the α direction with wave vector q, to that of the transposed phonon polarized along α and propagating along β with the same wave vector.

If the elastic energy can be written in terms of the symmetric linear shears then one must have

$$\omega_{\alpha\beta}(q) = \omega_{\beta\alpha}(q) . \tag{6.32}$$

This must hold even when the solid is very anisotropic so that the α and β directions are not at all equivalent. This symmetry can be broken by the direct stress induced terms in the elastic energy, (6.29). If one finds

$$\omega_{\alpha\beta}(q) \neq \omega_{\beta\alpha}(q) \tag{6.33}$$

the difference must be due to the direct effect of anisotropic stresses.

An example would be a situation where the solid has uniaxial symmetry around z. One compares a transverse phonon propagating along z (α) with a transverse phonon propagating in a direction normal to z but polarized in the z direction. Any difference would demonstrate the violation of TS – i.e. the *direct* effect of anisotropic network stresses.

6.6.2. The second order strain and the symmetric linear strains

An expansion in the components of the symmetric linear strain is always symmetric under transposition but TS is not *sufficient* to assure that an expansion in the derivatives can be written in terms of the symmetric linear strains. One cannot express the second order strain as a binary form in the components of the symmetric *linear* strain tensor.

For example, the square of the antisymmetric component of the deformation

$$(\partial_\alpha u_\beta - \partial_\beta u_\alpha)^2 = \partial_\alpha u_\beta^2 + \partial_\beta u_\alpha^2 - 2\partial_\alpha u_\beta \cdot \partial_\beta u_\alpha$$

has full TS but, of course, cannot be written in terms of the symmetric linear strain.

The apparent violation of rotational invariance in stressed systems which we noted at the microscopic level in Eq. (6.13) appears again in the continuum field equations. The naive rotational invariance argument says that the expansion of the energy in the first derivatives of the deviation field $\boldsymbol{u}(\boldsymbol{r})$ can be expressed as an expansion in the components of the symmetric (linear) strain

$$e^1_{\alpha\beta} = \tfrac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha)$$

because the antisymmetric part of the derivative tensor

$$a_{\alpha\beta} = \tfrac{1}{2}(\partial_\alpha u_\beta - \partial_\beta u_\alpha) \quad (= \tfrac{1}{2}(\operatorname{rot} \boldsymbol{u})_\gamma) \tag{6.34}$$

is a rotation which cannot appear in the elastic energy. This argument is analogous to the argument in 5.2.2.1 that the perpendicular deviation $u_{ij}^{\perp}$ is a rotation – Eq. (5.9). It is the continuum equivalent of that argument and also breaks down to second order – i.e., when there are initial stresses and the second order strain appears.

Consider for example the *isotropic* component of the second order strain

$$e^2_{\text{iso}} = \frac{1}{2}\sum_{\alpha,\gamma}(\partial_\alpha u_\gamma)^2 \tag{6.35}$$

which multiplies the isotropic component of the network stress – the network pressure π – in the elastic energy:

$$\mathcal{P}^{\text{elastic}}_{\text{iso}} = -\pi \cdot e^2_{\text{iso}}\,, \tag{6.36}$$

e^2_{iso} is obviously rotationally invariant. Also, as we already noted, it has full transposition symmetry. However, since

$$(\partial_\alpha u_\gamma)^2 + (\partial_\gamma u_\alpha)^2 = \tfrac{1}{2}[(\partial_\alpha u_\gamma + \partial_\gamma u_\alpha)^2 + (\partial_\alpha u_\gamma - \partial_\gamma u_\alpha)^2]\,, \tag{6.37}$$

it cannot be expressed in terms of the symmetric *linear* strains alone. If one chooses to introduce the linear strain, $\boldsymbol{e}^1$, into Eq. (6.36) one finds that one also needs the components of the "rotation" – rot $\boldsymbol{u}$:

$$e^2_{\mathrm{iso}} = \mathrm{Tr}\|\boldsymbol{e}^1\|^2 + \tfrac{1}{4}(\mathrm{rot}\,\boldsymbol{u})^2 . \tag{6.38}$$

Thus the isotropic contribution to the energy, Eq. (6.36), cannot be written in terms of the symmetric linear strain even though it does not violate TS.

This can be generalized.

The geometric deformation of a solid is described by the derivatives of the field $\boldsymbol{u}(\boldsymbol{r})$ – the matrix

$$\|\boldsymbol{\nabla} * \boldsymbol{u}\| = \|\boldsymbol{d}\| ; \qquad d_{\alpha\beta} = \partial_\alpha u_\beta . \tag{6.39}$$

In terms of this derivative matrix the second order strain can be written as a matrix product

$$\|\boldsymbol{e}^2\| = \|\boldsymbol{d}\| \cdot \overline{\|\boldsymbol{d}\|} , \tag{6.40}$$

where $\overline{\|\boldsymbol{d}\|}$ is the transpose of the derivative matrix $\|\boldsymbol{d}\|$.

In general the matrix $\boldsymbol{d}$ is not symmetric since

$$\partial_\alpha u_\beta \neq \partial_\beta u_\alpha . \tag{6.41}$$

It can then be decomposed into a symmetric part, the linear strain, $\boldsymbol{e}^1$, and an antisymmetric part

$$\|\boldsymbol{d}\| = \|\boldsymbol{e}^1\| + \|\boldsymbol{a}\| ; \qquad \overline{\|\boldsymbol{d}\|} = \|\boldsymbol{e}^1\| - \|\boldsymbol{a}\| \tag{6.42}$$

and therefore quite generally

$$\|\boldsymbol{e}^2\| = (\|\boldsymbol{e}^1\| + \|\boldsymbol{a}\|) \circ (\|\boldsymbol{e}^1\| - \|\boldsymbol{a}\|) = (\|\boldsymbol{e}^1\|^2 - \|\boldsymbol{a}\|^2 - [\|\boldsymbol{e}^1\| \circ \|\boldsymbol{a}\| - \|\boldsymbol{a}\| \circ \|\boldsymbol{e}^1\|] . \tag{6.43}$$

Evidently the second order strain cannot be expressed in terms of the symmetric part of the derivative tensor alone. The antisymmetric part of this tensor also appears.

6.7. *What is the second order strain?*

The second order strain defined in Eq. (6.26) is a rather peculiar object. When it appears it plays a strange role in the elastic properties of a stressed material. We want to discuss this in some detail.

6.7.1. *Thermodynamic and physical definitions of the strain*

In texts on thermodynamics (e.g., Callen, 1960) one defines the isotropic stress, the pressure, through its relation to the volume:

$$p = -[\partial\mathcal{F}(N, V)/\partial V]_{N=\mathrm{constant}} , \tag{6.44}$$

where N is the number of particles in the volume V and $\mathcal{F} = \mathcal{F}(N, V)$ is a free energy. This leads to

$$\delta\mathcal{F} = -p \cdot \delta V . \tag{6.45}$$

This can also be written as a stress–strain relation. The change in the energy density, $\boldsymbol{f}$, caused by the isotropic stress p is

$$\delta f = -\boldsymbol{p} \cdot \boldsymbol{e}^{\mathrm{iso}} , \tag{6.46}$$

where

$$f=\mathscr{F}/V \tag{6.47}$$

is the free energy density and one defines the dimensionless isotropic strain as a relative volume or density change

$$e^{\mathrm{iso}}=[\delta V/V]_{N=\mathrm{const}}=\delta c/c\,, \tag{6.48}$$

where N is the number of particles in the volume element V and c $(=N/V)$ is the particle density.

In this standard thermodynamic derivation the isotropic strain which multiplies the pressure is *defined* as a relative volume change. It is somewhat surprising to note that this identification of the isotropic strain with a volume change is *strictly* valid only for fluids. For solids it is only valid to lowest order in the expansion of the strain in the derivatives of the deviation field.

In the theory of elasticity one generalizes Eq. (6.40) to the stress–strain expansion of the mechanical energy (Callen, 1970, ch. 13; Landau and Lifshitz, 1970, ch. 10)

$$\delta f=-\boldsymbol{\sigma}\circ\boldsymbol{e}=-\sum\sigma^{\alpha\beta}\cdot e_{\alpha\beta}\,, \tag{6.49}$$

where $\boldsymbol{\sigma}$ is the stress tensor and $\boldsymbol{e}$ the dimensionless strain tensor.

The definition of the stress in terms of the forces acting on the boundaries of a volume element is unique and general (see Landau and Lifshitz, 1970, Eq. (2.9) and Section 4.3 above). The definition of the strain, $\boldsymbol{e}$, conjugate to the stress is a much more delicate matter and depends on the physics.

The purely thermodynamic definition as a variable conjugate to the stress

$$e_{\alpha\beta}=-\partial f(\boldsymbol{\sigma})/\partial\sigma^{\alpha\beta} \tag{6.50}$$

is quite general but, in itself, not very instructive. One needs to supplement it by an explicit physical and geometrical definition of the strain – analogous to the definition of the isotropic strain in a fluid as a density change in Eq. (6.48). This *physical* definition of the strain depends on the model which is appropriate in describing the specific situation. In particular the physical definition of the isotropic strain for a solid is *different* from the definition of the isotropic strain for a fluid. The physical definition of the strains in a solid is also different from the definition of the strains conjugate to the same stresses in a mesophase.

For a solid one defines the strain in terms of the overall deformation of the solid material. The continuous field, $\boldsymbol{u}(\boldsymbol{r})$, describes this deformation as a geometric transformation of space. More formally one can say (Landau and Lifshitz, 1970, Eq. (1.3)) that the local strain is *defined* as the metric of the continuous transformation of space, $\boldsymbol{u}(\boldsymbol{r})$. This is the continuum limit of the description of the deformation of the reference configuration

$$\{\boldsymbol{R}\}\;\Rightarrow\;\{\boldsymbol{R}+\boldsymbol{u}\}$$

which we used. This procedure gives the thermodynamic strain as an expansion in the derivatives of $\boldsymbol{u}(\boldsymbol{r})$. As we saw this gives

$$e_{\alpha\beta}=\tfrac{1}{2}(\partial_\alpha u_\beta+\partial_\beta u_\alpha)+\tfrac{1}{2}\sum\partial_\alpha u_\gamma\partial_\beta u_\gamma+\mathrm{O}((\partial_\alpha u_\beta)^3) \tag{6.51}$$

which is the quantity one should substitute into Eq. (6.49) for a solid.

6.7.2. Second order volume changes are not second order strains

The second order strain, $e^2_{\alpha\beta}$, in (6.51) multiplies the stress, $\sigma^{\alpha\beta}$, just as the first order strain, $e^1_{\alpha\beta}$, does. Contrary to what one might guess this does not mean that the second order strain is the second order term in the description of the *geometric deformations* which we intuitively associate with the first order strain. We want to show this explicitly for the isotropic strain.

In the elastic energy the isotropic strain, $e_{\mathrm{iso}}(= e^1_{\mathrm{iso}} + e^2_{\mathrm{iso}})$ multiplies the *network pressure*, π.

$$\pi \cdot e_{\mathrm{iso}} = \pi \cdot e^1_{\mathrm{iso}} + \pi \cdot e^2_{\mathrm{iso}} .$$

The first order isotropic strain of the solid, $e^1_{\mathrm{iso}} = \operatorname{div} \boldsymbol{u}$, is a relative volume change. It describes the relative change in volume – to first order in the derivatives of the deviation field $\boldsymbol{u}$. We want to show that the isotropic second order strain does not describe a volume change at all. It can have identical values for deformations which change the volume and for deformations which do not change it at all. The contributions to the volume changes which are second-order in the derivatives of the field $\boldsymbol{u}(\boldsymbol{r})$ are not part of the second order strain.

The relative volume change of the volume element dx.dy.dz due to the field $\boldsymbol{u}(\boldsymbol{r})$ is given by the determinant

$$\frac{\delta V}{V} = \det \begin{Vmatrix} 1+\partial_x u_x & \partial_x u_y & \partial_x u_z \\ \partial_y u_x & 1+\partial_y u_y & \partial_y u_z \\ \partial_z u_x & \partial_z u_y & 1+\partial_z u_z \end{Vmatrix} - 1 . \tag{6.52}$$

The first order volume change is indeed the trace of the first order strain tensor

$$\delta^1 V/V = \sum \partial_\alpha u_\alpha = e^1_{\mathrm{iso}} . \tag{6.53}$$

This is familiar. The second order term in the volume change is

$$\delta^2 V/V = \frac{1}{2} \sum_{\alpha\beta} (\partial_\alpha u_\alpha \cdot \partial_\beta u_\beta - \partial_\alpha u_\beta \cdot \partial_\beta u_\alpha) . \tag{6.54}$$

This is the contribution to the relative volume change which is second order in the derivatives of $\boldsymbol{u}$. Evidently none of the terms in this sum appears in e^2_{iso} – Eq. (6.35).

The isotropic second order strain which multiplies the pressure, $e^2_{\mathrm{iso}} = \frac{1}{2}\sum_{\alpha,\beta}(\partial_\alpha u_\beta)^2$, is a sum of squares. It can only vanish when $\boldsymbol{u}(\boldsymbol{r})$ is constant and $\partial_\alpha u_\beta \equiv 0$. There is always an isotropic second order strain when $\boldsymbol{u}(\boldsymbol{r})$ is not constant. A second order volume change, $\delta^2 V$ – Eq. (6.54) – can also appear but this is not necessary. For some forms of $\boldsymbol{u}(\boldsymbol{r})$ there is a second order volume change while for others which lead to the same value of the isotropic strain there is no such change. It is quite possible to have deformation fields for which $\delta^2 V = 0$ while the isotropic second order strain does not vanish.

6.7.3. Some examples

We want to illustrate this by a few examples. Consider a pure shear

$$\partial_\alpha u_\beta \neq 0 , \quad \alpha \neq \beta \tag{6.55}$$

with all other derivatives vanishing. The second order strain tensor is diagonal and has one non-vanishing component

$$e^2_{\alpha\alpha} = \tfrac{1}{2}(\partial_\alpha u_\beta)^2 . \tag{6.56}$$

Thus $e^2_{\rm iso} \neq 0$ but there is obviously no second order volume change – Eq. (6.52) – because $\partial_\beta u_\alpha = 0$. For a pure shear the first order volume change vanishes because $\operatorname{div} \boldsymbol{u} = 0$.

A second example is a uniaxial strain. Only one component of the derivative tensor

$$\partial_\alpha u_\alpha \neq 0 \tag{6.57}$$

is non-vanishing. Again the second order strain has one component – $e^2_{\alpha\alpha}$. There is a first volume change, and a finite contribution to the isotropic second order strain: $e^2_{\rm iso} = \frac{1}{2}(\partial_\alpha u_\alpha)^2$, but no second order volume change, Eq. (6.53).

Even when there is a second order volume, or density change, Eq. (6.53), this volume change does not appear explicitly in the elastic energy of the solid. *Only* the isotropic second order strain $e^2_{\rm iso}$ multiplies the pressure for a solid. One cannot tell from the value of the isotropic second order strain tensor if there is a (first or second order) volume change or how large it is. Even though the volume change, $\delta^2 V$, and the isotropic second order strain, $e^2_{\rm iso}$ for a solid are both determined by the same field $\boldsymbol{u}(\boldsymbol{r})$ they are only indirectly related. This is qualitatively different from the situation for fluids where the relative volume change itself is the isotropic strain and explicitly multiplies the pressure. Because of this the isotropic second order strain can give rise to restoring forces *at constant volume* – as it does, e.g., for the surface vibrations of a balloon.

We discuss a simple illustrative example in Appendix C where we describe two deformations with identical contributions to the second order strain but different volume changes.

PART II. THE RIGIDITY OF FLOPPY BONDED NETWORKS

Our purpose in this section is to develop a theory of the mechanical properties of tenuous solids. By this we mean materials which are solid but are only tenuously bound – solids which are described by physical models which, *prima facie*, cannot define a rigid reference configuration. The motivation for studying tenuous solids is of course that many materials one encounters are described by such models as we noted in the Introduction. The discussion in this section is however still purely theoretical and we do not refer to any specific physical models.

To formulate the theory of tenuous solids in a systematic way we shall use the concept of *bonded networks* (BN) associated to physical models which we introduced in Section 3.3. We shall systematically analyze the mechanical rigidity of such networks. We shall discuss the rigidity of bonded networks as a property of the graph when it is embedded in space. This will lead us to the study of geometrically *floppy bonded networks* (FBN) which are connected but nevertheless not rigid because they are not sufficiently interconnected to fix all the $\mathscr{n}_{\rm int}$ internal degrees of freedom of the N particle network. This floppiness is a geometrical property of the graph of the FBN.

We shall then show that models which are described by FBN always have soft eigenmodes with no harmonic restoring forces when the reference state is a BH reference state. The analysis of the *bulk* mechanical properties of solids described by FBN is thus similar to that of objects with very anisotropic shapes "*…whose dimension in* [*some*] *direction*[*s*] *is small*" such as thin rods and plates (Landau and Lifshitz, 1970, p. 3). For thin rods and plates stresses are always important – even when they are relatively small – because their BH transverse bending rigidity is small. For FBN the soft modes result from the floppy *internal geometry* of the bonding and not from the external shape. The stress-induced terms of Section 6 become important for these modes and the initial stresses are therefore crucial in determining bulk properties. Like their macroscopic analogs stresses can either stabilize the soft modes, as in stretched strings and drumheads or cause their buckling.

7. Rigidity and dynamic stability

7.1. Bonded networks

We want to discuss the *rigidity* of the reference states for the description of the mechanical properties of solids. To analyze the rigidity it will be useful to relate the energy to a BN. We first recall the definition of the BN in Section 3.3 in detail.

We consider models for which the mechanical energy $\mathscr{E}(\{\boldsymbol{r}\})$ is the sum of short range interactions among small numbers of particles

$$\mathscr{E}(\{\boldsymbol{r}\})=\sum \mathscr{V}^n_{[ij...]}\,, \tag{7.1}$$

where

$$\mathscr{V}^n_{[ij...]}=\mathscr{V}^n(\boldsymbol{r}_i,\boldsymbol{r}_j,\ldots)=\mathscr{V}^n(\{r\}^n_{[ij...]}) \tag{7.2}$$

is an interaction among the n particles $[ij\ldots]$ and can be written as a function of the distances

$$\{r\}^n_{[ij...]}=\{r_{ij},\ldots\} \tag{7.3}$$

between the interacting particles.

We define the set of bonded distances, $\{r\}_{\text{bond}}$, as the set of all the distances which appear in the parametrizations of the separate interactions

$$\{r\}_{\text{bond}}=\{r_{12},r_{13},\ldots,r_{ij},\ldots\}_{\text{bond}}=\sum \{r\}^n_{[ij...]}\,. \tag{7.4}$$

The energy can then be written as a function of the bonded distances:

$$\mathscr{E}(\{\boldsymbol{r}\})=\mathscr{E}(\{r\}_{\text{bond}})\,. \tag{7.5}$$

The distance r_{ij}, which appears in $\{r\}_{\text{bond}}$ can be represented by a bond – $[ij]$, which connects the points i and j.

The BN relevant to such a physical model is the graph one obtains by drawing bonds between the vertices i and j whenever the distance r_{ij} appears in $\{r\}_{\text{bond}}$. The bonded network is completely determined by the pairing scheme in $\{r\}_{\text{bond}}$. It has N vertices and $\mathscr{n}_{\text{bond}}$ bonds which are arranged in a way prescribed by the pairing scheme $\{[ij]\}$.

The bonded network can be regarded as a property of the physical model one uses to describe a physical system. When the energy is given as a sum – Eq. (7.1) – one can always associate it with a specific bonded network. On the other hand, the same BN evidently can describe a family of physical models which differ in detail.

7.2. The geometric rigidity of bonded networks

Once one has determined the bond structure of the network one can discuss its rigidity in d-dimensions as a property of the graph defined by $\{r\}_{\text{bond}}$. This rigidity is a purely *geometric* property of the graph – the bonding structure of the network. A bonded network is *geometrically rigid* (GR) in d-dimensions if it cannot be deformed without changing the lengths of some of its bonds. A geometrically rigid bonded network becomes completely rigid when all its bonds $[ij]$ are replaced by rigid links of fixed length. The links are connected at the vertices but, since we have chosen to represent angles by distances, they are freely linked there.

Geometrical rigidity obviously requires that *all* the vertices of the network are connected by bonds. A sufficiently interconnected bonded network of N vertices is always geometrically rigid but, in general, connected bonded networks are not necessarily GR. Bonded networks which are not GR remain floppy even when all their bonds are made into completely rigid links. The rigid bonds *constrain* the possible configurations of the network but do not fix a unique configuration. We shall call such networks *geometrically floppy* (GF). The fact that a network is GF in d-dimensional space is a property of the graph – the internal bonding structure of the bonded network. A GF bonded network can be deformed continuously without changing any of the bonded distances which appear in $\{r\}_{\text{bond}}$. Any configuration of a GF network belongs to a *manifold* of equivalent configurations which can be deformed into each other without changing the bonded distances.

7.3. Three types of floppy networks

Bonded networks can be floppy in different ways. For our purposes it will be useful to distinguish three types of floppy networks with different degrees of floppiness. We first illustrate this with simple examples:

7.3.1. Examples

- The *square lattice* with nearest neighbor bonds, Fig. II.1, has no *shear rigidity* in the plane. It can be sheared without changing the lengths of any bonds and cannot maintain shear stresses. This is a *macroscopic* floppiness. But this is not a full description of the floppiness of the square lattice. One can rotate the horizontal edges of all the squares belonging to the same column, i, by an angle φ_i and the vertical edges in each row, j, by an angle ψ_j. This results in a configuration of the network which can be obtained from the square lattice by a continuous deformation of its boundaries which is not a simple shear.[26] Rubinstein et al. (1992) and Ajdari et al. (1992) have discussed this "infinite" and continuous floppiness in detail. The square lattice thus belongs to a continuous manifold of configurations all of which have the same bonds as the nearest neighbor square lattice. If one fixes the *external boundary* of such a network in any one of the continuum of allowed shapes – the whole network becomes completely rigid. The positions of *all* the interior vertices are determined by fixing the boundary. The square lattice is thus *macroscopically floppy* (MaF) because its boundary is floppy. Its macroscopic shape, can be changed continuously without changing the lengths of any bonds. This floppiness includes macroscopic shears of the lattice as a whole but also many more subtle deformations of the boundary. Because the positions of all *interior* points are fixed by the shape of the boundary this is the only floppiness of this network.

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[26] In general these configurations are not periodic.

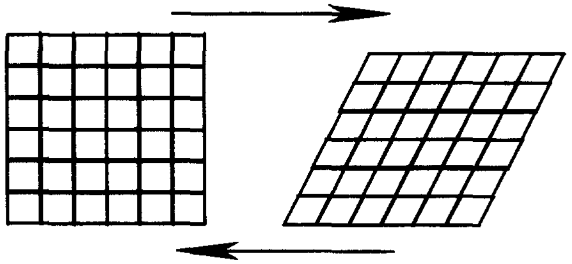

Fig. II.1. The freely-linked nearest-neighbor square lattice has macroscopic floppiness.

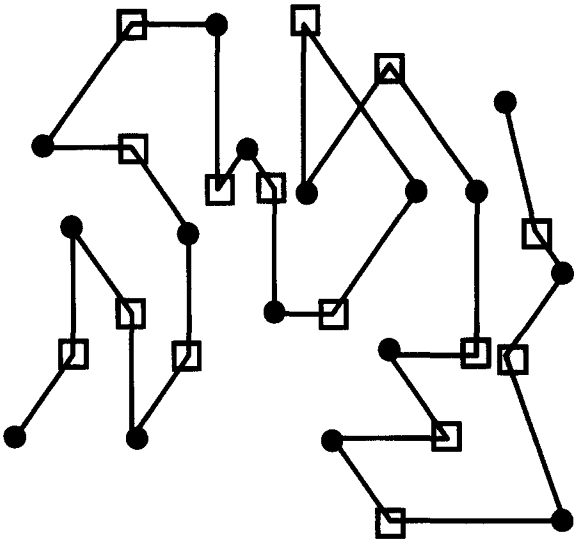

Fig. II.2. The freely linked linear chain. In 2-dimensions the chain is locally stable but still has both macroscopic and microscopic floppiness.

- Our second example is a *freely linked linear chain* in the plane – Fig. II.2. Such a network is much more floppy than the square lattice. It cannot be made rigid by a macroscopic boundary condition – or even by any condition which only determines the positions of a small fraction of the vertices – which becomes negligible when N is large – as was the case for the square net. One can only fix the positions of all the N vertices by a "boundary condition" which determines the positions of a finite fraction (one half) of these points – see Fig. II.2. This means that one cannot only deform the chain as a whole but there is also additional *microscopic* internal floppiness. Any segment of a linear chain with more than two links can be deformed continuously even when its ends are fixed (see Fig. II.9). This is a collective *microscopic floppiness* (MiF). In the plane the position of every vertex is completely determined by the links connecting it to the two neighbors to which it is directly bonded. There is no freedom for any single junction on its own.[27] Thus the fraction of points whose positions one has to fix is $\frac{1}{2}$ – the points marked by black disks in Fig. II.2. Sequences of three bonds are however floppy. This floppiness is collective and requires the correlated motion of two vertices.
- As a third example we consider a network with the geometry of a *branching tree* – Fig. II.3. Such a network obviously has the two types of flexibilities of the linear chain – macroscopic floppiness (MaF) and collective microscopic floppiness (MiF). Besides that it also has singly connected points at all the free ends of its branches whose positions are not determined by the bonds connecting them. They can be moved *even when all the other vertices are fixed.* There are many "dead-end" branches and the position of the atom connected by a single bond, at the

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[27] Such freedom does of course appear in three-dimensions where every junction can move freely perpendicular to the plane determined by the bonds connecting it to its immediate neighbors.

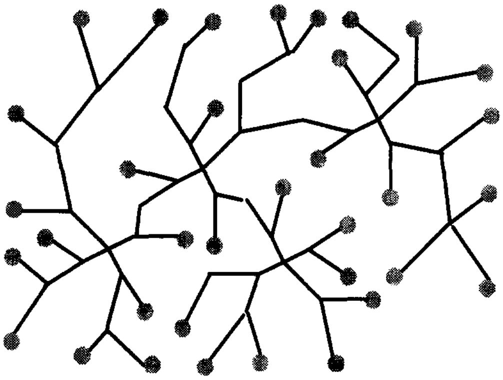

Fig. II.3. A tree. The gray circles mark the dead-end points which are not locally rigid.

head of such a dead-end, is evidently not fixed by the bonded network. We can say that the tree is not *Locally Rigid* (LR) while the square lattice and the linear chain are LR in the plane.

7.3.2. Macroscopic, microscopic and local rigidity

These illustrations suggest three different types of rigidity – as a property of floppy networks:

(a) *Macroscopic rigidity.* A network is macroscopically rigid if the shape of its boundary is determined by the bonded distances and cannot be changed without changing them. Otherwise it is macroscopically floppy (MaF). This obviously includes rigidity – or floppiness – with respect to uniform shears but as we saw is more general.

(b) *Microscopic rigidity.* The square lattice in Fig. II.1 becomes completely rigid when one fixes the macroscopic boundaries. For the networks depicted in Figs. II.2 and II.3 there is still a lot of local microscopic floppiness even when the external boundary is fixed. A network which is floppy in the macroscopic sense may or may not also be floppy in the microscopic sense. The question is whether all the microscopic geometrical *degrees of freedom* (DOF) are fixed by the bonding structure (Phillips, 1979, 1981, 1982). When a homogeneous material is *microscopically floppy* some of the microscopic DOF remains free and are not determined by the bonding structure – even when the external boundaries are fixed.

(c) *Local rigidity.* As we saw in Fig. II.3 microscopic floppiness can appear in a trivial way when the positions of some of the particles are not completely determined by the bonds. We shall call the requirement that the position of every particle is fixed completely by the positions of the particles to which it is directly bonded – *local rigidity.* Evidently the requirement that all particles are in locally rigid positions is a necessary condition for microscopic rigidity but, as we saw for the linear chain, it is by no means sufficient.

We emphasize that MaF, MiF, and LR are three essentially independent properties of networks. All combinations of the three types of floppiness are possible. In particular, a macroscopically rigid network can be MiF if it has a rigid scaffolding in which floppy regions are embedded.

7.3.3. Geometric rigidity criteria and geometrically floppy networks

We called a network *geometrically rigid* when the configuration of the vertices could not be deformed without changing the lengths of some of the bonds. This only depends on the bonding structure – the geometry of the network. The *geometrical* question is whether the bonded distances can determine the configuration of the N junctions – i.e., whether they can determine all the $\frac{1}{2}N(N-1)$ distances r_{ij} among the N vertices. In principle this is a straightforward criterion for the *geometrical rigidity* of a bonded network. Checking whether a specific network is macroscopically, or completely rigid, is nevertheless often a fairly complex and delicate geometrical problem. In particular this is true close to the macroscopic rigidity threshold – as discussed, e.g., by Deweney (1991) and Sen et al. (1985). For many networks, it is however obvious that they cannot possibly obey the geometrical rigidity requirements. Examples are the networks described in Figs. II.1–II.3 above.

We shall call networks which do not obey the geometrical rigidity requirements because the set $\{r\}_{\mathrm{bond}}$ is insufficient – *geometrically floppy* (GF). In a geometrically floppy network some distances, r_{ij}, between points are not defined by the bonding structure – some degrees of freedom (DOF) among its $\varkappa_{\mathrm{int}}$ DOF are free and are not determined by fixing the distances in $\{r_{\mathrm{bond}}\}$.

We shall discuss some examples of geometrically floppy networks in detail in Section 8 and sufficient formal criteria in Section 9.

7.4. Dynamically floppy bonded networks

In the discussion above we used a purely *geometric* definition of rigidity as a property of a bonded network embedded in space. The bonded network is however a theoretical construction and because of this geometrical rigidity is not directly accessible to experiments on real materials. The geometrical rigidity of a bonded network is however not the only approach to the question of rigidity. The alternative is to check for the *stability* of the expansion of the energy $\mathscr{E}(\{\boldsymbol{r}\})$ around the reference configuration $\{\boldsymbol{R}\}$. Since the theory of the mechanical properties starts with the energy, $\mathscr{E}(\{\boldsymbol{r}\})$, and not with the bonded network defined by $\{r\}_{\mathrm{bond}}$, this is probably the more obvious approach in the context of materials science. The experimentally verifiable questions related to rigidity which one asks – the vanishing of a shear modulus, the vanishing of the velocity of sound in some directions and the presence of local modes with no harmonic restoring forces – are all questions of dynamical stability.

What one needs eventually is to describe the mechanical properties in terms of the expansion of the energy of an N particle system, $\mathscr{E}(\{\boldsymbol{r}\})$, in the deviations of the particles from their respective reference positions $\boldsymbol{R}_i$. This is an expansion in the Nd dimensional space of positions

$$[\mathscr{R}]\,,\quad [\boldsymbol{r})=[\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_i,\ldots,\boldsymbol{r}_N) \tag{7.6}$$

around a specific reference configuration

$$[\boldsymbol{R})=[\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_i,\ldots,\boldsymbol{R}_N) \tag{7.7}$$

and the continuum limit of this expansion. The problem of the rigidity of the bonded network then becomes a question of the *stability* of this expansion. The usual way to check for stability is by analysis of the linear stability of the expansion around a reference state $\{\boldsymbol{R}\}$.

If we choose $[\boldsymbol{R})$ as the origin in $\{\mathscr{R}\}$ we define the Nd dimensional space of atomic deviations $[\mathscr{U}]$

$$[\mathscr{U}]\,,\quad [\boldsymbol{u})=[\boldsymbol{u}_1,\boldsymbol{u}_2,\ldots,\boldsymbol{u}_i,\ldots,\boldsymbol{u}_N)\,, \tag{7.8}$$

where $\boldsymbol{u}_i$ is the deviation of atom i from its equilibrium position $\boldsymbol{R}_i$. We want to expand around the origin of $[\mathscr{U}]$ – the reference state $[\boldsymbol{R})$.

The harmonic expansion of the energy can then be written as

$$\mathscr{E}_h = (\boldsymbol{u}]\|\boldsymbol{K}\|[\boldsymbol{u}) , \tag{7.9}$$

where $\|\boldsymbol{K}\|$ is the Nd dimensional dynamical matrix for this expansion.

The dynamical matrix $\|\boldsymbol{K}\|$ is defined by the N single-vertex matrices

$$\boldsymbol{K}_{ii} = \|[\boldsymbol{\nabla}_i * \boldsymbol{\nabla}_i]\mathscr{E}(\{\boldsymbol{r}\})\|_{\{\boldsymbol{R}\}} \tag{7.10}$$

and by the $\frac{1}{2}N(N-1)$ two vertex matrices $\boldsymbol{K}_{ij}$

$$\boldsymbol{K}_{ij} = \tilde{\boldsymbol{K}}_{ji} = \|[\boldsymbol{\nabla}_j * \boldsymbol{\nabla}_i]\mathscr{E}(\{\boldsymbol{r}\})\|_{\{\boldsymbol{R}\}} , \quad i \neq j \tag{7.11}$$

one for each pair $[ij]$. Both the symmetric matrices $\boldsymbol{K}_{ii}$ and the matrices $\boldsymbol{K}_{ij}$ are d-dimensional.

The matrix $\|\boldsymbol{K}\|$ has dN eigenvalues. Of these eigenvalues $\mathscr{n}_{\text{rig}}$ $(= \frac{1}{2}(d+1)d)$ correspond to the rigid-body DOF of the system as a whole and therefore vanish because of global translation–rotation invariance. The remaining $\mathscr{n}_{\text{int}}$ eigenvalues, κ^α, are the force constants for the internal harmonic eigenmodes $[\boldsymbol{u}^\alpha)$

$$\|\boldsymbol{K}\|[\boldsymbol{u}^\alpha) = \kappa^\alpha [\boldsymbol{u}^\alpha) , \tag{7.12}$$

where

$$[\boldsymbol{u}^\alpha) = [\boldsymbol{u}_1^\alpha, \boldsymbol{u}_2^\alpha, \ldots, \boldsymbol{u}_i^\alpha, \ldots, \boldsymbol{u}_N^\alpha) \tag{7.13}$$

is an eigenvector and $\boldsymbol{u}_i^\alpha$ is the d dimensional vector which describes the deviation of the junction i in the mode α. If the equilibrium state $\{\boldsymbol{R}\}$ is dynamically stable all these force constants have to be positive

$$\kappa^\alpha > 0 \quad \text{for all } \alpha . \tag{7.14}$$

For geometrically floppy networks there are restrictions on the dynamical matrix $\|\boldsymbol{K}\|$ which may reduce its rank and cause some eigenvalues to vanish. One actually expects this to happen.

In Section 7.2 we defined GF networks, as networks which can be deformed continuously without changing the length of any bonded distances. The energy of the model is obviously constant along the path of these deformations. We can therefore say that GF networks have free degrees of freedom (DOF) which have no effect on the energy. It is natural to assume that, in general, there are also free linear eigenmodes, $[\boldsymbol{u}^\beta)_{\text{free}}$ corresponding to these free DOF. This means that there are no restoring forces for these free modes

$$\kappa^\beta = 0 \quad \text{for all free modes } \beta . \tag{7.15}$$

This means that the equilibrium reference configuration of the floppy network, $\{\boldsymbol{R}\}$, is not properly *stable* with respect to these *free eigenmodes*, β, because they have no restoring force constants.[28] This always means that there are large fluctuations and that anharmonic effects become important.

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[28] Formally one should probably say that such modes are marginally stable rather than unstable.

One can also formulate this in a different way as a statement on the structure of the dynamical matrix $\|\boldsymbol{K}\|$ as a matrix in the space $[\mathscr{U}]$. Eq. (7.15) is equivalent to saying that the harmonic expansion of the energy around the reference state $\{\boldsymbol{R}\}$ is confined to a linear subspace of $[\mathscr{U}]$ which is determined by the n_{b} bonded distances – $[\mathscr{U}_{\mathrm{b}}]$. The complementary subspace of $[\mathscr{U}]$, $[\mathscr{U}_{\mathrm{free}}]$ is free. The dynamical matrix $\|\boldsymbol{K}\|$ has no elements connecting the space $[\mathscr{U}_{\mathrm{b}}]$ to $[\mathscr{U}_{\mathrm{free}}]$ or between vectors in $[\mathscr{U}_{\mathrm{free}}]$. The coefficients of the harmonic expansion of the energy in this subspace of $[\mathscr{U}]$ vanish.

The formal criteria for dynamical stability are different from the criteria for geometrical rigidity. They are properties of an expansion. In general one would therefore expect that the stability of the expansion in eigenmodes depends on the form of the energy and on the specific reference state around which one is expanding – and not just on the underlying BN. This is not just a formal distinction. Geometrical rigidity and dynamic stability are really distinct properties of the mechanical system. In particular the bonded network can be geometrically floppy and for suitable energies and reference states – the Cauchy–Born expansion can nevertheless be linearly stable. We will show this and also that it can only happen when the reference state is stressed.

We shall show below in Section 10 that the intuitive guess that the "free" DOF will appear as "free" linear eigenmodes, Eq. (7.13), is indeed justified in the Born–Huang (BH) approximation, i.e., when the direct effect of the initial stresses in the reference state $[\boldsymbol{R}]$ is neglected. In the BH approximation of Section 5 the harmonic terms in the expansion of the energy in the $\boldsymbol{u}_i$ at $\{\boldsymbol{R}\}$ are confined to a linear subspace $[\mathscr{U}_{\mathrm{b}}]$ of $[\mathscr{U}]$. When there are stresses the correspondence between free DOF and free eigenmodes no longer holds. We will show that one can have stable stressed reference states for bonded networks which are geometrically floppy and also truly unstable reference states which exhibit structural buckling.

7.5. Classifying dynamically floppy networks

In Section 7.3 we distinguished between macroscopic rigidity, microscopic rigidity and local rigidity using the geometrical rigidity criteria. One can classify dynamical stability in the same way.

The stability condition for all eigenmodes, Eq. (7.14), guarantees complete stability for all eigenmodes. When this criterion holds it assures *macroscopic stability*, *microscopic stability* and *local stability*. For floppy networks which have free modes, Eq. (7.15), one has to be more careful.

Only the single particle *local stability* is simply and directly related to the linear stability analysis. Local stability means that each junction is in a stable position when all the other junctions are kept fixed. For the site i this means that the d eigenvalues κ_i^ν of the local matrix $\boldsymbol{K}_{ii}$ of Eq. (7.10)

$$\|\boldsymbol{K}_{ii}\|\boldsymbol{u}_i^\nu = \kappa_i^\nu \boldsymbol{u}_i^\nu \tag{7.16}$$

are all positive

$$\kappa_i^\nu > 0\,, \quad \nu = 1,\dots,d\,. \tag{7.17}$$

The condition for the *local stability* of all the N sites of a network is that all these local force constants are positive so that the inequality (7.17) applies at all the sites. This is a much weaker condition than (7.14).

On the other hand the answer to the question whether a model is *macroscopically floppy* depends on the distribution of bonds in the floppy network. For a network which is MF *macroscopic stability* then depends on the actual distribution of the stabilizing initial stresses. We shall return to this problem in Sections 12 and 13.

Both the macroscopic stability of the network as a whole and the local stability of all junctions, condition (7.17), follow from the condition that the network is stable – Eq. (7.14). The converse is not true. The stability of the whole network configuration $\{\boldsymbol{R}\}$, the inequality (7.14), does not follow from the local stability condition (7.17).

8. Examples of macroscopically floppy networks

Our purpose in this chapter is largely heuristic. We want to discuss some specific examples of networks which are floppy and to show how geometrical and dynamical floppiness are related. This seems useful as an introduction to the general formal discussion of geometrically floppy networks in Section 9 and of their dynamic stability in Section 10.

The intuitively most obvious manifestation of insufficient bonding is that a network becomes *macroscopically* floppy and does not retain its shape. This means that it can be deformed without changing the lengths of any of its bonds. When the physical models described by these networks are also dynamically floppy the macroscopic floppiness appears in the continuum limit as a property of the elastic constant tensor of the model. Some of the elastic constants then vanish.

It is useful to illustrate this first on some specific simple examples where the fact that the networks are floppy is intuitively obvious. The examples we shall discuss are simple periodic lattices – mainly Bravais lattices – with nearest neighbor bonds. They can therefore be analyzed fairly easily using simple heuristic arguments.[29] We shall look at the geometric floppiness of the networks and – using the results of Section 5 – also at their elastic constants. When this is easy we also indicate the effect of the floppiness on the phonon spectrum. In some cases, we shall also show how elastic shear rigidity reappears for geometrically floppy networks when they are stressed.

Only very few Bravais lattices with nearest neighbor bonds are rigid. The only two-dimensional Bravais lattice which is rigid with nearest-neighbor interactions is the *triangular lattice*. A tiling of triangles in the plane is obviously rigid.

8.1. The square lattice

8.1.1. The unstressed square lattice

We have already discussed the *geometrical* floppiness of the square lattice in Section 7.3.1 of Section 7. The square lattice with nearest neighbor bonds can be sheared without changing the length of any bond – as we indicated in Fig. II.1. It is obvious from the figure that the lattice can be sheared continuously until it eventually collapses into a line while keeping all bond lengths constant. A finite shear, say $\partial_y u_x \neq 0$, transforms the square lattice into a rhombic lattice.

So far we have not discussed *dynamic flexibility*, i.e., the appearance of *linear* eigenmodes with no restoring forces – Eq. (7.15). It can be seen in Fig. II.4 that the square lattice has soft shear lines perpendicular to the bonds. If one shears the square lattice along these lines the relative deviations

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[29] For periodic lattices the linear eigenmodes are all phonons and can often be calculated explicitly. We shall do this for the honeycomb lattice in Section 11.

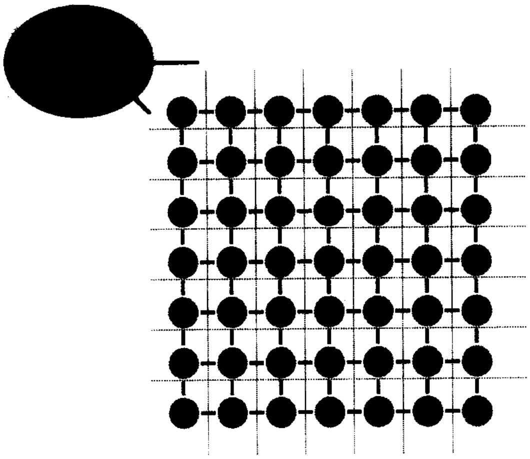

Fig. II.4. The soft shear lines of the square lattice.

of the bonded neighbors are all perpendicular to the bonds. Only $u_{ij}^{\perp}$ appear. It follows that the shear modulus of the unstressed square lattice for these shears, $\boldsymbol{D}^{xyxy}$, must vanish. There are elastic constants for an isotropic volume change, $\partial_x u_x = \partial_y u_y$, and for the planar strain at constant volume – $\partial_x u_x = -\partial_y u_y$ – but there are no elastic constants for the shear strains – $\partial_x u_y$, $\partial_y u_x$.

Using Eq. (5.24)

$$\boldsymbol{D}^{\alpha\beta,\gamma\delta}_{\text{Cauchy}} \propto \frac{1}{2}\sum_i \mathscr{K}_{ij}\frac{X_{ij}^{\alpha}\cdot X_{ij}^{\beta}\cdot X_{ij}^{\gamma}\cdot X_{ij}^{\delta}}{R_{ij}^2}$$

to calculate the elastic constants we do indeed find for the square lattice

$$\boldsymbol{D}^{xxxx} = \boldsymbol{D}^{yyyy} \propto \mathscr{K}\cdot a^2 \neq 0\,, \qquad \boldsymbol{D}^{xxyy} = \boldsymbol{D}^{xyxy} = 0 \tag{8.1}$$

because the bonds, $\hat{\boldsymbol{R}}_{ij}$ are all either in the x or in the y directions.

From the fact that there is a separate soft line between every two lattice lines it is also evident that *all* the transverse acoustic modes with wave vectors along the x or y directions have zero frequency.[30]

8.1.2. The dynamic floppiness of the family of the square lattice

The square lattice is geometrically floppy and belongs to a floppy manifold, a family of equivalent configurations which can be obtained by continuously deforming the square lattice. All the configurations in this family, $(\{\boldsymbol{R}\}_{\text{bond}})$, are geometrical realizations of the same bonded network and have identical bonded distances – $\{R\}_{\text{bond}}$. Because of this these configurations also have identical energies, $\mathscr{E}(\{R\}_{\text{bond}})$ and they can all, in principle, serve as reference states for an expansion.

The expansions in the changes in the bonded distances, δr_{ij},

$$\mathscr{E}(\{r\}) - \mathscr{E}(\{R\}) = \sum_{\text{bonds}} \mathscr{T}_{ij}\,\delta r_{ij} + \frac{1}{2}\sum_{\text{bonds}} \mathscr{K}\,\partial r_{ij}^2 + \cdots,$$

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[30] For this simple model it is easy to confirm this by calculating the eigenmodes explicitly.

Eq. (3.18), and their formal expression in terms of $u_{ij}^{\prime\prime}$ and $u_{ij}^{\perp}$ upon substitution of Eq. (3.21)

$$\delta r_{ij} = u_{ij}^{\prime\prime} + (u_{ij}^{\perp})^2/2R_{ij} + \text{h.o.t}$$

in this expansion are also all identical for all the reference states belonging to the family:

$$\mathscr{E}(\{r\}) - \mathscr{E}(\{R\}) = \sum_{\text{bonds}} \mathscr{T}_{ij} u_{ij}^{\prime\prime} + \frac{1}{2} \sum_{\text{bonds}} (\mathscr{T}_{ij}/a) u_{ij}^{\perp 2} + \mathscr{K} u_{ij}^{\prime\prime 2} + \cdots . \tag{8.2}$$

For an unstressed network for which $\mathscr{T}_{ij} \equiv 0$, the harmonic energy then looks completely identical

$$\frac{1}{2} \mathscr{K} \sum_{\text{bonds}} u_{ij}^{\prime\prime 2} \tag{8.3}$$

for the expansion around any of these reference configurations. The difference in the reference states only shows up when we express this in terms of the single particle deviations in space $\boldsymbol{u}_i, \boldsymbol{u}_j$ using

$$u_{ij}^{\prime\prime} = (\boldsymbol{u}_i - \boldsymbol{u}_j) \cdot \hat{\boldsymbol{R}}_{ij} . \tag{8.4}$$

Because the vectors $\hat{\boldsymbol{R}}_{ij}$ are different for different configurations the explicit form of the expansion on the right

$$\frac{1}{2} \mathscr{K} \sum_{\text{bonds}} u_{ij}^{\prime\prime 2} = \frac{1}{2} \mathscr{K} \sum_{i,j,\alpha\beta} u_i^{\alpha} u_i^{\beta} \hat{X}_{ij}^{\alpha} \hat{X}_{ij}^{\beta} - \frac{1}{2} \mathscr{K} \sum_{i,j,\alpha\beta} u_i^{\alpha} u_j^{\beta} \hat{X}_{ij}^{\alpha} \hat{X}_{ij}^{\beta} \tag{8.5}$$

depends explicitly on the form of the reference state around which one is expanding.

The square lattice has the highest symmetry among all the configurations in its family. Because of this the dynamic floppiness of the square lattice is intuitively obvious. The floppiness can be attributed completely to the soft shear lines shown in Fig. II.4 and the floppy zero-frequency modes are the transverse acoustic modes along the axis. In general, the other configurations in the family have no obvious geometrical symmetry. In general, they also have no straight soft-shear lines and the eigenmodes of Eq. (8.5) can no longer be determined from translation symmetry. They are, in general, complicated modes and not phonons. Nevertheless, all the reference states in the family are dynamically floppy and Eq. (8.5) always has the same number of floppy zero frequency modes as the square lattice.[31] The zero-frequency eigenmodes for the expansion around a general reference configuration are complex and, in general, have no simple spatial interpretation.

These considerations apply only when there are no stresses. One cannot make any similar general statements about the dynamical modes of the stressed network. This is mainly because of the appearance of the transverse deviations $u_{ij}^{\perp}$ in Eq. (8.2). In addition, the bond tensions, $\mathscr{T}_{ij}$, are constrained by the equilibrium conditions

$$\sum_j \mathscr{T}_{ij} \hat{\boldsymbol{R}}_{ij} = 0 ,$$

Eq. (3.23), which are different for different reference configurations.

It is instructive to single out the square lattice and investigate the effect of stresses on its floppiness.

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[31] We shall prove this in Section 10.

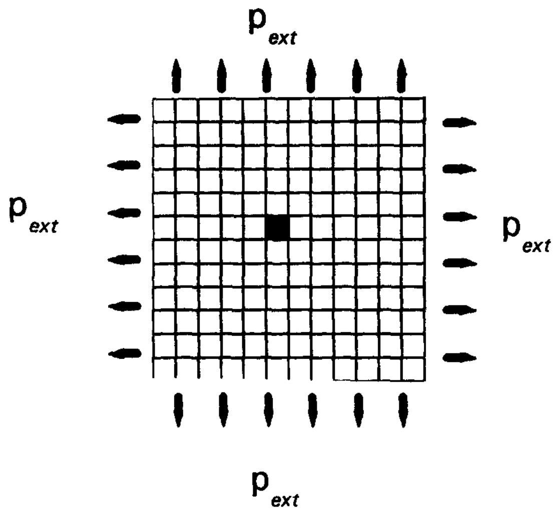

Fig. II.5.

8.1.3. *The stretched square foam*

If we want to retain the spatial symmetry of the square lattice the only choice of bond tensions is

$$\mathscr{T}_{ij} \equiv \mathscr{T} . \tag{8.6}$$

This means that the lattice exerts an isotropic stress, a "network" pressure

$$p_{\mathrm{net}} = -\mathscr{T}/a \tag{8.7}$$

or, equivalently, a normal force of this magnitude per unit length on its boundaries.

Consider the situation depicted in Fig. II.5. A negative external pressure, p_{ext}, exerts forces on the outer boundaries of the square lattice in the direction shown. In equilibrium this will set up a positive tension $\mathscr{T}$ (>0) in the bonds which will exert an opposite force on the boundaries. Equivalently, the internal network pressure p_{net}, created by the tension in the stretched springs is equal to the external pressure

$$p_{\mathrm{net}} = p_{\mathrm{ext}} < 0 . \tag{8.8}$$

The pressure inside the net, the pressure which acts on some internal boundary inside the net, p_{int}, is then

$$p_{\mathrm{int}} = p_{\mathrm{net}} = p_{\mathrm{ext}} . \tag{8.9}$$

In this scenario the internal stress is balanced by the external pressure on the boundaries. This is the situation one thinks of intuitively. The network is stressed because of external forces.

Alternatively one could think of a foam. No external pressure is then required to maintain mechanical equilibrium for a stressed net.

Let the pressure of a fluid trapped in the squares of the square net be p_{fluid}. The forces exerted by this fluid on the external boundaries are exactly the same as those which would be exerted by an external pressure $-p_{\text{fluid}}$ $(=p_{\text{ext}})$ acting on the outside. The same equilibrium tension, $\mathcal{T}$, is set up in the bonds of the network by p_{fluid} and by an external pressure of the opposite sign.

But the total internal pressure is different because both the network pressure p_{net} and the fluid pressure p_{fluid} act on any internal boundary. Thus

$$p_{\text{int}} = p_{\text{net}} + p_{\text{fluid}} \tag{8.10}$$

inside the foam. If, in particular, there is no external pressure then the total internal pressure must vanish

$$p_{\text{int}} = p_{\text{net}} + p_{\text{fluid}} = 0\,. \tag{8.11}$$

There is no real external pressure, no force on the external boundaries but the *network* is nevertheless stressed.

Consider now the effect of the network pressure on the rigidity. The part of the mechanical energy which depends on the pressures can be written

$$\mathscr{E}^{\text{elastic}}_{\text{scalar}}/V = p_{\text{fluid}}(\delta V/V)_{\text{fluid}} + p_{\text{net}}\cdot e^1_{\text{iso}} + p_{\text{net}}\cdot e^2_{\text{iso}}\,, \tag{8.12}$$

where

$$e^1_{\text{iso}} = \operatorname{div}\boldsymbol{u} = (\delta^1 V/V)_{\text{net}}\,.$$

Equilibrium with respect to the simultaneous volume change of the two components

$$(\delta V/V)_{\text{fluid}} = (\delta^1 V/V)_{\text{net}} \tag{8.13}$$

requires Eq. (8.11) as an equilibrium condition when there is no external pressure.

The network pressure, p_{net}, is then responsible for a term in the elastic energy

$$\tfrac{1}{2}p_{\text{net}}[(\partial_x u_y)^2 + (\partial_y u_x)^2] \tag{8.14}$$

which is the only term which makes the network rigid for shears along the soft lines, $\partial_x u_y$ and $\partial_y u_x$, for which there are no proper elastic constants – Eq. (8.1). Thus the foam, or the stressed network is no longer dynamically floppy.

8.2. The three-dimensional cubic Bravais lattice

In *three dimensions* only the close-packed *face centered cubic* (FCC) and the *trigonal* (HCP) Bravais lattices, both with 12 nearest neighbors, are rigid. In particular the nearest-neighbor *simple cubic* (SC) lattice with 6 neighbors and even the *n.n. body centered cubic* (BCC) lattice with a coordination of 8 can be deformed continuously without changing the nearest neighbor distances.

8.2.1. The simple cubic lattice

For a cubic lattice there are always three elastic constants – two of them relevant to shear, μ_{T} and μ_{E} – Eq. (5.53). As we saw in Section 5.3.3.2 this is not changed by the Cauchy relations. One

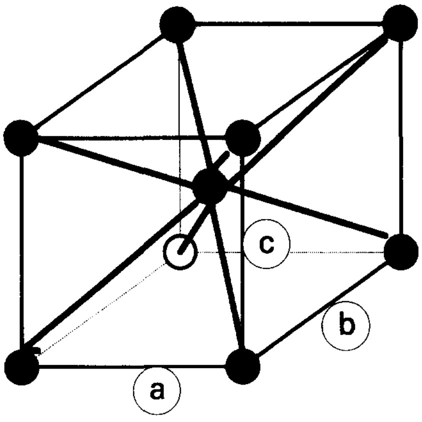

Fig. II.6. The BCC unit cell can be distorted by changing the lengths of the three edges without changing the distance from the center to the corners of the cell.

of these constants can vanish because of floppy binding. We consider the nearest neighbor cubic lattices in detail to show how the softness is related to the elastic constant tensor.

There is no shear rigidity in the 100 planes of an *SC* lattice with *n.n.* bonds because the bonds cutting these planes are perpendicular to them. This is completely analogous to the situation for the square lattice which we illustrated in Fig. II.4. Using Eq. (5.21) we can calculate the elements of the fourth rank elasticity tensor. All the bonds are along the 1 0 0 directions so that the only non-vanishing elements are

$$\boldsymbol{D}^{xxxx} = \boldsymbol{D}^{yyyy} = \boldsymbol{D}^{zzzz} \neq 0 . \tag{8.15}$$

All the other elements of the tensor $\|\boldsymbol{D}\|$ vanish in close analogy to the square lattice – Eq. (8.1).

In the notation of Eq. (5.56) this means that one of the three elastic constants for a cubic lattice – namely μ_{T}, the coefficient of $(e_{xy}^2 + e_{yz}^2 + e_{zx}^2)$ – vanishes

$$\mu_{\mathrm{T}} = 0 , \qquad \mu_{\mathrm{E}}, K \propto \boldsymbol{D}^{xxxx} \neq 0 . \tag{8.16}$$

It follows that the velocity of sound for transverse modes vanishes along the 1 0 0 directions.

It is straightforward to see that for this model the vibration spectrum is unusual. One can describe the vibration spectrum by three acoustic bands, each of them polarized along one of the three axes with frequencies

$$(\omega_{\mathrm{q}}^{\alpha})^2 \propto 1 - \cos q_a , \quad \alpha = x, y, z , \tag{8.17}$$

where we have taken the lattice constant as 1. It can be seen that the frequency of the vibrations polarized in the α direction vanishes in the whole plane $q_\alpha = 0$ and not only along the other two axes – $\alpha' \neq \alpha$ – for which it is transverse. The number of zero frequency modes is therefore proportional to $V^{2/3}$ and not to $V^{1/3}$ as one would predict from the number of obvious soft shear planes.

8.2.2. *The body centered cubic lattice*

The unit cell of the *n.n. body centered cubic* BCC lattice can be distorted without changing the distance from the center to its bonded neighbors. Any transformation into an orthorhombic, or tetragonal unit cell, with translations a, b and c along the axis and obeying the constraint

$$a^2+b^2+c^2=1 \tag{8.18}$$

does this (see Fig. II.6).

This distortion also implies a *volume* change because there are no solutions to

$$a\cdot b\cdot c=1 \tag{8.19}$$

which also obeys the constraint (8.18).

For BCC the bonds are all along the 1 1 1 directions. Thus, from (5.23),

$$\boldsymbol{D}^{\alpha\alpha\alpha\alpha}=\boldsymbol{D}^{\alpha\alpha\beta\beta}=\boldsymbol{D}^{\alpha\beta\alpha\beta}\,, \qquad \alpha,\beta=x,y,z \tag{8.20}$$

so that

$$\mu_{\mathrm{E}} \propto \boldsymbol{D}^{\alpha\alpha\alpha\alpha}-\boldsymbol{D}^{\alpha\alpha\beta\beta}=0\,, \qquad \mu_{\mathrm{T}}, K \propto \boldsymbol{D}^{\alpha\alpha\alpha\alpha}\neq 0\,. \tag{8.21}$$

Thus the pure elongational shears along the cubic axis

$$\begin{aligned} &\partial_\alpha u_\alpha=-\partial_\beta u_\beta\,, \quad \alpha\neq\beta\,,\\ &\tfrac{1}{2}\partial_\alpha u_\alpha=-\partial_\beta u_\beta=-\partial_\gamma u_\gamma\,, \quad \alpha\neq\beta\neq\gamma \end{aligned} \tag{8.22}$$

have no restoring elastic constant but the *n.n.* BCC lattice is rigid with respect to a transverse shear

$$\partial_\alpha u_\beta\,, \quad \alpha\neq\beta$$

and with respect to volume changes

$$\partial_\alpha u_\alpha=\partial_\beta u_\beta=\partial_\gamma u_\gamma\,.$$

Finally for the *n.n.* FCC lattice the bonds are in the 1 1 0 directions and therefore

$$\boldsymbol{D}^{\alpha\alpha\alpha\alpha}=2\boldsymbol{D}^{\alpha\alpha\beta\beta}=2\boldsymbol{D}^{\alpha\beta\alpha\beta}\,, \quad \alpha\neq\beta \tag{8.23}$$

so that

$$\mu_{\mathrm{E}} \propto \boldsymbol{D}^{\alpha\alpha\alpha\alpha}-\boldsymbol{D}^{\alpha\alpha\beta\beta}\neq 0\,, \qquad \mu_{\mathrm{T}} \propto \boldsymbol{D}^{\alpha\beta\alpha\beta}\neq 0\,, \qquad K \propto \boldsymbol{D}^{\alpha\alpha\alpha\alpha}+\boldsymbol{D}^{\alpha\alpha\beta\beta}\neq 0\,. \tag{8.24}$$

In agreement with the symmetry analysis.

8.3. Lattices with complex unit cells

8.3.1. The honeycomb lattice

For the *honeycomb lattice* there are soft shear lines perpendicular to the three bond directions. We show this in Fig. II.7.

Evidently there are no harmonic restoring forces for shear along the directions of the lines shown in the figures because the bonds cutting these lines are all perpendicular to the lines. Shear on these lines amounts to a rotation of the bonds and there are no restoring forces. Since all lines of the types shown in the figures have no restoring force the transverse acoustic phonons along the bond directions have zero frequency and the transverse velocity of sound must vanish in these directions.

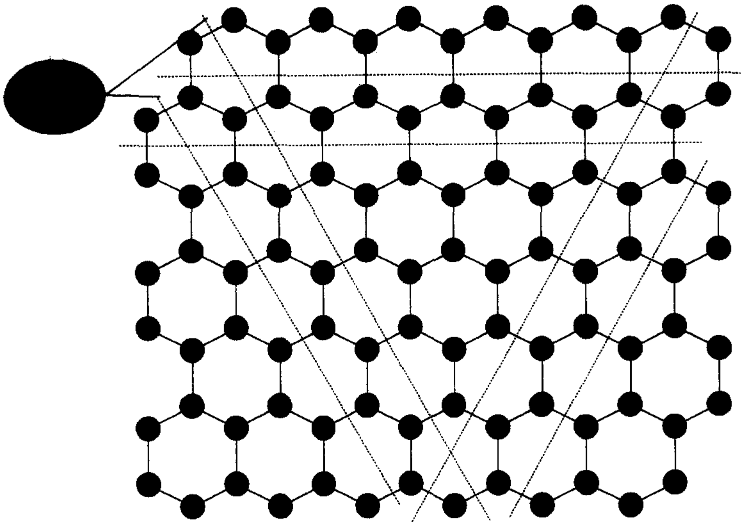

Fig. II.7. The obvious soft shear lines of the honeycomb lattice.

We shall discuss the mechanical properties of the unstressed honeycomb lattices in Section 11. We shall show there that this lattice is not only macroscopically floppy but microscopically floppy in spite of the fact that it is locally rigid. We shall also show there that there is no shear rigidity in any direction which is not obvious from the above.

8.3.2. *The diamond lattice*

It is easy to see that the nearest-neighbor *diamond* lattice has no shear rigidity in the 1 1 1 planes. To see this it is convenient to think of the diamond lattice planes as an AABBCC stacking of triangular planes perpendicular to the 111 direction – similar to the usual description of the FCC closed packing of spheres. Since the bonds between pairs of identical planes, AA, BB or CC, are along the 1 1 1 direction and therefore perpendicular to the planes – they have no shear rigidity. Evidently the same applies to the directions of the other body diagonals.

We will show later that this by no means exhausts the floppiness of this lattice. We will show that this lattice is microscopically floppy and has no shear rigidity in any direction.

8.3.3. *The hydrogen peroxide lattice*

Something similar happens for the H_2O_2 (gyroid) lattice for which all the nearest neighbor bonds are in the 1 1 0 directions and some of the 1 1 0 planes are cut only by bonds perpendicular to them. Because of the relative complexity of these structures this is a little more difficult to visualize. There is no shear rigidity in the 1 1 0 directions and the velocity of sound in these directions vanishes (Alexander Bruinsma and Hilfer, 1989).

8.3.4. *Complex unit cells*

We note that the *honeycomb* lattice, the *diamond* lattice and the H_2O_2 lattice all have complex unit cells. There are two vertices per cell for both the *honeycomb* and the *diamond* lattices and four (or even eight) for the H_2O_2 lattice. This has to be incorporated into the *microscopic* computation of the elastic constants. One cannot simply use Eq. (5.23) to calculate $\boldsymbol{D}$ when the unit cell is complex.[32]

If one were to ignore the complexity of the unit cell one would conclude from Eq. (5.23) that there is no difference between the elastic constants of the honeycomb and triangular lattices and of the diamond and BCC lattice, respectively, because for each pair the bonds are in the same directions. For H_2O_2 the conclusion would be that it is equivalent to FCC – Eq. (8.24). This is evidently wrong. When one investigates this in detail one can see that Eq. (5.24) is not valid for these lattices because the affinity criterion – Eq. (5.36) – is violated for the bonds connecting the different sites in the unit cell of the floppy lattices – honeycomb, diamond and H_2O_2.[33] The use of Eq. (4.6) to obtain the continuum limit is therefore not justified. For these geometrically floppy models the relative motion inside the unit cell, the relative motion of the different atoms in the cell, is correlated and very different from the average strain. This results in a dramatic reduction of some of the elastic constants. Because of this we cannot evaluate the explicit microscopic expression for the elements of the elasticity tensor using the standard expressions. We note that these are very simple examples where the *non-affinity* of the short range deformations, in response to imposed stresses, is important. In these simple situations this is an effect inside the respective unit cells.

9. The bond counting inequality

In Sections 3 and 7 we defined bonded networks and related them to the mechanical model which describes a physical system. This allowed us to introduce two distinct definitions of rigidity. Geometrical rigidity (GR) in Section 7.2 and dynamical stability (DS) in Section 7.4. GR is a property of the graph, the bonded network. A bonded network is geometrically rigid if it becomes completely rigid when its bonds are made into rigid links. A bonded network which is not geometrically rigid is a geometrically floppy network (GFN).

The precise criteria for the *geometric rigidity* of a bonded network are complicated and depend on the detailed structure of the network when it is embedded in d-dimensional space – see, e.g., Dewdney (1991).[34] In this chapter we shall use some very general considerations to derive a very simple but general inequality for the number of bonds in a rigid bonded network. This inequality, the *bond counting inequality* (BCI), is a *necessary* condition for geometrical rigidity. Networks with more bonds than required by the BCI may or may not be rigid – depending on their detailed structure but the bonding of networks which violate the BCI is always inadequate. Such networks cannot be GR. They are always GFN and have free degrees of freedom (FDOF) which allow them to deform continuously without changing the length of any of their bonds. We will then show that BCI is violated for many connected networks.

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[32] We note that the two 3-D networks also have no center of symmetry and the symmetry analysis of the elastic constants in Section 4.3.3.2 is therefore incomplete. There are additional elastic constants.

[33] We shall show how this happens for the honeycomb lattice in Section 11.

[34] See also Sen et al. (1985) and numerous publications by Thorpe with collaborators.

9.1. Counting degrees of freedom and counting bonds

9.1.1. The free degrees of freedom of floppy bonded networks

One can always parametrize an N-point configuration $\{\boldsymbol{r}\}$ in terms of the distances between the points. We discussed this in Section 3. One then needs

$$n_{\text{int}} = d(N - \tfrac{1}{2}(d+1)) \approx dN \tag{9.1}$$

distances, r_{ij}, to fix the relative positions of all N junctions in d dimensions. One can also say that n_{int} is the number of internal DOF for a configuration of N points in d dimensions. To fix the configuration uniquely any set of n_{int} geometrically independent distances is *sufficient*. In d dimensional space all the $\frac{1}{2}N(N-1)$ distances between N points are determined and can be calculated once n_{int} independent distances, $\{r\}_{\text{ind}}$, are fixed. n_{int} independent distances are also *necessary*. A smaller number of distances, smaller than n_{int}, cannot determine the configuration of N points in d dimensions completely. This is a purely geometrical statement.

The number of bonds in a specific bonded network, n_{b}, is the number of different distances which are needed to specify the energy and therefore appear in the set $\{r\}_{\text{bond}}$. Since a network of N points can accommodate $\frac{1}{2}N(N-1)$ bonds, n_{b} can obviously be larger than n_{int} (when $N > d+1$). Since $N-1$ $(< n_{\text{int}})$ bonds are sufficient to connect N points the number of bonds in a connected bonded network can also be much smaller than n_{int}. The configuration of N vertices, $\{\boldsymbol{r}\}$, is determined by the n_{b} bonds when the set of bonded distances, $\{r\}_{\text{bond}}$, – Eq. (7.4) – contains a subset of n_{int} independent distances $\{r\}$. The remaining distances which appear in $\{r\}_{\text{bond}}$ are then determined uniquely by these distances.

A necessary condition for the existence of such a subset is obviously that the total number of bonds, n_{b}, is *at least* equal to the geometrically required minimum number

$$n_{\text{b}} \geq n_{\text{int}} . \tag{9.2}$$

We shall call this inequality the *bond counting inequality* (BCI). It is a *necessary* condition for the geometrical rigidity of a bonded network.[35]

A bonded network is always geometrically *floppy* when the BCI is violated

$$n_{\text{b}} < n_{\text{int}} . \tag{9.3}$$

The network then always has free distances, DOF which are not determined by the bonded distances. When the number of bonds n_{b} is too small the set of bonded distances

$$\{r\}_{\text{bond}} = \{r_{12}, r_{13}, \ldots, r_{ij}, \ldots\}_{\text{bond}}$$

cannot determine the geometric configuration completely. To parametrize a definite configuration the bonded distances in $\{r\}_{\text{bond}}$, have to be supplemented by

$$n_{\text{free}} \geq n_{\text{int}} - n_{\text{b}} \tag{9.4}$$

additional distances

$$\{r\}_{\text{free}} = \{r_f^1, r_f^2, \ldots, r_f^{\nu}, \ldots, r^{n_{\text{free}}}\} \tag{9.5}$$

---

[35] We note that Eq. (9.2) is not a sufficient condition for geometric rigidity because the n_{b} bonded distances can depend on each other.

which do not correspond to bonds. These additional distances are needed to specify the configuration completely but are not bonds of the bonded network. The geometric configuration of the N atoms is only specified fully by $\mathscr{n}_{\rm int}$ independent distances

$$\{r\} = \{\{r\}_{\rm bond}; \{r\}_{\rm free}\} = \{r^1, r^2, \ldots, r^\nu, \ldots, r^{\mathscr{n}_{\rm int}}\} \tag{9.6}$$

but of these only the $\mathscr{n}_{\rm b}$ distances $\{r\}_{\rm bond}$ correspond to bonds of the network and appear as arguments in the energy.[36]

The $\mathscr{n}_{\rm int}$ independent distances, $\{r\}$, which describe an N-point configuration cannot determine each other. It follows that each of the $\mathscr{n}_{\rm free}$ "free" distances in $\{r\}_{\rm free}$ can be changed *continuously* over a finite range while keeping the $\mathscr{n}_{\rm b}$ bonded distances in $\{r\}_{\rm bond}$ and the $\mathscr{n}_{\rm free} - 1$ other free distances in $\{r\}_{\rm free}$ – fixed.[37] This means that when $\mathscr{n}_{\rm b}$ is smaller than $\mathscr{n}_{\rm int}$ there exists an $\mathscr{n}_{\rm free}$ dimensional *continuum* of configurations for every value of the energy. Holding all the bonded distances in $\{r\}_{\rm bond}$ fixed defines an $\mathscr{n}_{\rm free}$ dimensional surface $\mathscr{s}(\{r\}_{\rm bond})$ in the space of configurations. $\mathscr{s}(\{r\}_{\rm bond})$ is obtained by changing the free distances $\{r\}_{\rm free}$ while keeping all the bonded distances $\{r\}_{\rm bond}$ fixed. A freely linked bonded network with rigid links will then be floppy and $\mathscr{s}(\{r\}_{\rm bond})$ describes the range of configurations into which it can be deformed.

Since the energy only depends on the bonded distances which are held fixed

$$\mathscr{E}(\{r\}) = \mathscr{E}(\{r\}_{\rm bond})$$

the energy is of course also the same for all the configurations on the surface $\mathscr{s}(\{r\}_{\rm bond})$.

9.2. Relating the bond counting inequality to the coordination

One can relate the BCI for the whole network, the inequality (9.2), to the local coordination at the bonded junctions.

Let b_i be the number of bonds connected to junction i – its coordination number. The total number of bonds in the net, $\mathscr{n}_{\rm b}$, is related to the coordination numbers b_i, and to the average coordination number, $\langle b\rangle$, through

$$\sum_{i=1}^{N} b_i = N\langle b\rangle = 2\mathscr{n}_{\rm b}\,. \tag{9.7}$$

The factor 2 on the right appears because each bond is counted twice in the sum over junctions at its two ends.

Combining Eq. (9.7) with the BCI, the inequality (9.2), and using Eq. (9.1) one can relate the BCI to the local coordination. $\mathscr{n}_{\rm b}$ bonds can determine the configuration of N junctions in d dimensions only when the average coordination number is large enough:

$$\langle b\rangle \geq 2d \tag{9.8}$$

which is another form of the BCI.[38]

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[36] In this equation and below we implicitly assume in our notation that the bonded distances are geometrically independent. This is just to avoid repetition of the distinction between the bonded distances and their independent subset.

[37] The range is determined by geometrical constraints – which can be expressed as inequalities between the distances.

[38] For macroscopic systems the number of rigid-body degrees of freedom, $\mathscr{n}_{\rm rig}$ $(= \frac{1}{2}d(d+1))$, is a small number compared to Nd and can therefore be neglected.

These elementary geometric considerations tell us that in three-dimensions one needs at least *six* bonds per junction, on the average, and in two-dimensions at least *four* bonds per junction to determine the equilibrium configuration, $\{\boldsymbol{R}\}$.

When the average number of bonds per site, $\langle b\rangle$, is smaller than required by the inequality (9.8) the network is always geometrically floppy. The reference configuration $\{R\}$ (or, equivalently, $\{\boldsymbol{R}\}$) then also belongs to a *continuum* of equivalent equilibrium configurations all having the same bonded distances $\{R\}_{\mathrm{bond}}$. There exists a continuous $\mathscr{n}_{\mathrm{free}}$ dimensional manifold of configurations $\mathscr{A}(\{R\}_{\mathrm{bond}})$ which all have the same energy and the same bonded distances and are therefore in a sense equivalent – but are nevertheless different configurations, $\{R\}$, $\{\boldsymbol{R}\}$, of the network.

The fraction of DOF which is free in a floppy network is

$$\mathscr{C}_{\mathrm{free}} \geq \mathscr{n}_{\mathrm{free}}/\mathscr{n}_{\mathrm{c}} \geq 1 - (\langle b\rangle/2d)\,. \tag{9.9}$$

This means that the number of FDOF, $\mathscr{n}_{\mathrm{free}}$, becomes large and extensive – proportional to N – when the average coordination, $\langle b\rangle$, is smaller than $2d$. For macroscopic systems, in the limit $N \to \infty$, there is then a finite fraction of FDOF. This implies that such a network is necessarily microscopically floppy.

9.3. Locally rigid floppy networks

9.3.1. Definition

It is easy to visualize the high concentrations of FDOF predicted by Eq. (9.9) when the network is not locally rigid so that the position of some atoms is not fully determined by the rest of the bonded network. The tree depicted in Fig. II.3 has many singly connected dead-ends which obviously have some free atomic DOF. In three-dimensional space an atom in a linear chain (Fig. II.2) is also insufficiently bound and can move freely in the direction perpendicular to the plane of its two bonds.[39] A finite concentration of such local FDOF can appear in many different ways and is almost trivial. It is therefore important to show that the BCI is a much stronger condition than this and can be violated even when all the atoms are in locally rigid positions.

The inequality (9.8), the local form of the BCI is in a way a strange result and seems counter-intuitive. In d dimensions each vertex, i, has only d DOF and *local* rigidity therefore requires only d bonds at a site

$$b_i \geq d \quad \text{for all } i\,. \tag{9.10}$$

In d dimensions the position of a point is fully determined by its distances from d other points to which it is directly bonded. Eq. (9.10) is the condition that the *local* coordination is sufficient for this. Because of this the local equilibrium conditions at a site, Eq. (3.29) amounted to d equations per site – rather than $2d$ – and the *local* stability requirement – Eq. (7.17) – also involves only d equations.

The fact that $2d$ bonds are needed at each vertex, on the average, is a *collective*, global requirement and not a local one. Any specific single site can be in a rigid position when it is connected by only d bonds but the whole N-particle configuration cannot be geometrically rigid if the average number of bonds at a site is less than $2d$.

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[39] Such atomic freedom occurs for singly bonded sites in both two and three dimensions and for sites with only two bonds in three dimensions. The insufficiently coordinated atom then has some freedom to change its position without changing any of the bonded distances.

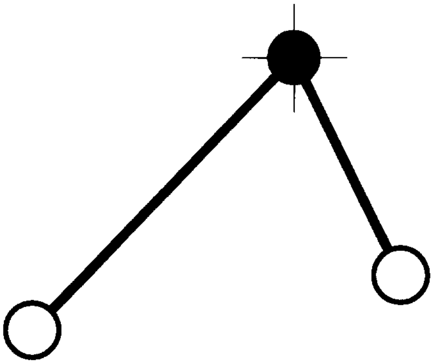


Fig. II.8. The position of the central black atom in the plane is determined by the positions of its two bonded neighbors.

The BCI is violated for many connected network structures which are locally rigid. For such networks there are enough bonds for local rigidity at all the junctions, Eq. (9.10), but the average coordination is still too low for the BCI rigidity criterion for the whole network – Eq. (9.8) – so that

$$2d > \langle b \rangle . \tag{9.11}$$

We shall call networks for which the two inequalities (9.10) and (9.11) hold simultaneously as *locally rigid floppy networks* (*LRFN*). The FDOF for LRFN are all *collective*. No single atom is free to move alone. The network has only collective free DOF which require the coordinated motion of many atoms. Some LRFN are very familiar.

9.3.2. Locally rigid floppy networks with d bonds

d is obviously the absolute minimum for the average coordination in a locally rigid network. When the positions of all the neighbors to which a junction is connected are fixed d bonds are sufficient to determine a rigid position. d bonds can fix all the d DOF of the junction. d dimensional networks with this minimal coordination number at all their vertices

$$b_i \equiv d \tag{9.12}$$

exist. They even appear naturally in many models for rubbers and gels. Thus, e.g., the natural coordination for percolation is three and one does not require a higher multiplicity for the branching of a chemical gelation process in 3-D.

9.3.2.1. Doubly coordinated LRFN in two-dimensions

If a junction is connected by only *two* ($= d$) bonds in *two dimensions* its position, $\boldsymbol{R}_i$ is fixed by the bonds. The junction is at the apex of a triangle – Fig. II.8.

Clearly the black atom is in a locally rigid position. Its position is fixed if the bonds are rigid.

We just note that the conditions for simultaneous dynamical stability and equilibrium are marginal for such local configurations. One has to satisfy two sets of conditions – d equilibrium conditions

$$\sum_j f_{ij} = 0$$

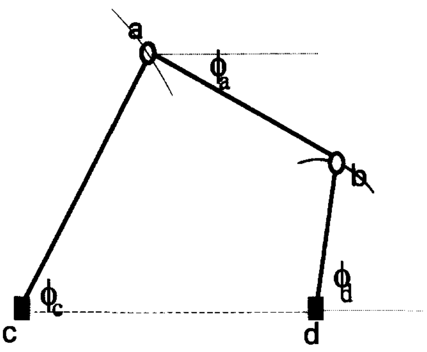


Fig. II.9. Collective freedom of a locally stable configuration.

and d local stability conditions – Eq. (7.16). When the two bonds are not collinear one can only have mechanical *equilibrium* when the bond tensions in the two consecutive bonds, $\boldsymbol{R}_{ij}$ and $\boldsymbol{R}_{jk}$ vanish. When there is any stress the bonds have to be collinear but then one cannot satisfy the d local stability conditions in the transverse direction.[40]

The only connected network one can construct with the bonding condition

$$\langle b\rangle = b_i = 2$$

is a freely linked linear chain as in Fig. II.2. Such a chain can be folded to cover the plane. Because

$$\langle b\rangle = 2 < 4$$

the linear chain is obviously floppy. Thus the linear chain in the plane is a LRFN.[41]

The freely linked linear chain with rigid links is obviously not geometrically rigid in the plane. It can be deformed without changing the lengths of any of its bonds. Since the chain is locally rigid the deformations must all be collective. It provides an extreme, and rather trivial illustration of a LRFN.

The smallest free DOF of the linear chain involves four points. This is the correlated motion of two consecutive vertices when all other vertices, and all bond-lengths, are kept fixed. We describe this in Fig. II.9.

Assume the vertices “c” and “d” are fixed. The remaining two vertices, “a” and “b”, are both in *locally* stable positions in the plane. If we fix “b” the position of “a” is fixed and vice versa. There is however one collective FDOF which keeps the three distances [ac], [ab], and [bd] fixed. In this collective mode the points “a” and “b” move *together* along the indicated arcs which are centered at the points “c” and “d”, respectively – while keeping their distance, [ab] fixed.

It is easy to see that this collective freedom is that of a quadrilateral in the plane. For a quadrilateral $d = 2$ and $N = 4$ so that

$$n_{\mathrm{int}} = 2 \cdot 4 - 3 = 5\,.$$

---

[40] The generalization to three-dimensions is obvious.

[41] Intuitively one would probably not think of the linear chain as a proper two-dimensional network suitable for describing a rigid solid. We note however that in many contexts in polymer physics freely linked random-walk chains do behave as rigid bodies – not only in two-dimensions but also in 3-D.

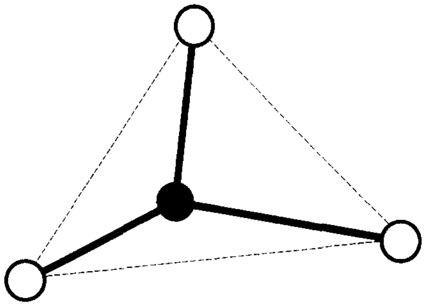


Fig. II.10. Minimally coordinated locally stable position in three-dimensions.

One needs five distances to fix the configuration of the four points "a", "b", "c", "d". There is therefore one FDOF when only four distances ([ab], [bd], [dc], [ca]) are specified so that $n_{\mathrm{b}} = 4$.

9.3.2.2. *Three-coordinated LRFN in three dimensions*

A three-coordinated junction i can only be in a locally rigid position in 3-D at the apex of a triangular pyramid formed by the three bonds – Fig. II.10.

The linear chain seemed rather artificial as a network describing a solid. In contrast to this, three-dimensional lattices with a bonding coordination of 3 can be constructed and some of them are even observed.

Several periodic cubic space groups suggest structures with this coordination. In the cubic space groups No. **198** ($P2_13$, T^4), **199** ($I2_13$, T^5), **205** ($Pa3$, T_h^6), **206** ($Ia3$, T_h^7) and **230** ($Ia3d$, O_h^{10}) the Wyckoff points in the unit cell with the highest symmetry have a single 3-fold axis (Henry and Lonsdale, 1952). All these space groups therefore allow one to construct lattices – bonded networks with 3-fold coordination – by connecting each of these high symmetry Wyckoff points to three symmetrically located neighbors of the same type. A fairly common example which appears in various contexts in the real world is the hydrogen-peroxide, H_2O_2 structure (space-group 230) which consists of two interpenetrating three-coordinated cubic networks related by an inversion. For the lattices of this type whose observation we are aware of the three bonds connected to any specific junction are coplanar, and these are also the structures one constructs naturally from the space-groups – or otherwise (Alexander et al., 1989). One notes that while such structures are locally rigid they are not linearly stable when the bonds are not stretched in the reference state. Perpendicular to the plane of bonds the leading restoring potential is fourth-order.

9.3.2.3. *d-Coordinated LRFN in d dimensions cannot support stresses unless they are pre-stressed*

We note an amusing dynamic peculiarity of locally stable networks with the minimum coordination d – in any dimension.

For a coordination of d in d-dimensions there is a problem in reconciling the local equilibrium conditions with the local linear stability.

(a) Local stability requires that the d bonds point in d linearly independent directions. This is necessary if one wants the matrix $\boldsymbol{K}_{ii}$ defined in Eq. (7.10) to have d non-vanishing eigenvalues.

(b) This geometry is consistent with *mechanical equilibrium* at the same junction *only* when there is no tension in the bonds. One cannot satisfy the d-dimensional vectorial zero-force condition of Eq. (3.29)

$$\sum_j \mathscr{T}_{ij} \cdot \hat{\boldsymbol{R}}_{ij} = 0$$

at a vertex connected by bonds in d linearly independent directions unless all the bond tensions vanish

$$\mathscr{T}_{ij} \equiv 0 \,.$$

Thus the linearly stable structures of d bonds in d dimensions cannot maintain stresses.

When there is tension in any of the bonds the vectorial equilibrium requirements can be satisfied only when the directions of the d bonds are *not* linearly independent. The bonds must then be collinear in 2-D or coplanar in 3-D. But stresses will always appear when external forces are applied. There must then be tension in some bonds. The implication is that some pyramids must *collapse* into coplanar or collinear configurations. Even an isotropic compression – a uniform dilatation of all the bonds – is not consistent with local mechanical equilibrium.

In defining the Born–Huang approximation we did of course neglect the bond tensions, Eq. (5.3). But one would like to regard this as a convenient approximation rather than as a structural requirement. The above argument shows that BH unstressed LRFN with the minimum coordination d are not really consistent stable mechanical networks.

9.3.3. LRFN with $d+1$ bonds – the Hilbert networks

Networks with

$$b_i \equiv d + 1 \tag{9.13}$$

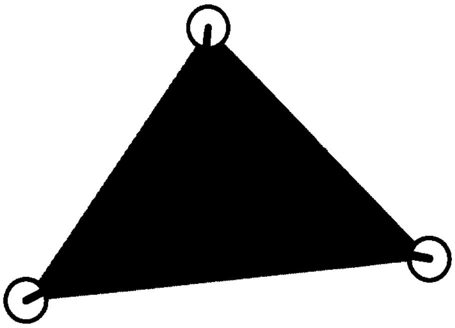
are much more common and well known. In many physically important situations one is also interested in binary interactions with no minimum for which one cannot set the bond tensions to zero. Examples of this are bonding by polymeric chains which are *attractive* at all distances – as in polymeric networks; electrostatic interactions – as for example in Wigner lattices and ionic crystals and "packing" problems with purely repulsive short range interactions. In all these cases the bond tensions cannot vanish and one needs at least $d+1$ "bonds" to allow the simultaneous establishment of local equilibrium and local stability.

The local coordination condition – Eq. (9.13) – is known as the *loosest packing* condition of Hilbert. It was invoked by Hilbert for the study of the dilute packing of spheres. In this context the implications have been studied extensively (Hilbert and Cohen-Vossen, 1932, 1952; Heesch and Laves, 1933; Melmore, 1942, 1948).[42]

In two dimensions a junction *inside* a triangle and bonded to the three neighbors at the vertices of the triangle is in a locally rigid position in the plane – Fig. II.11.

---

[42] These papers search for dilute packings which satisfy the Hilbert local stability requirement at all sites. The possibility that such packings could still be collectively floppy is not discussed. It is evident from our discussion that all the packings generated (and referenced above) are LRFN, i.e., they are all floppy packings. This has interesting implications for the loose packing problem which we shall discuss elsewhere.



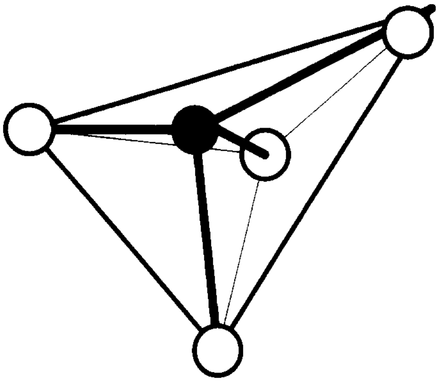


Fig. II.11. Locally stable Hilbert position in 2-D.

Fig. II.12. Hilbert position in 3-D.

The same holds, in three dimensions for a junction inside a triangular pyramid and bonded to its four vertices. We illustrate this in Fig. II.12.

Locally stable extended structures with $d+1$ bonds per atom for all junctions are quite common and familiar in both two and three dimensions. The simplest and most symmetric illustrations of such structures are the honeycomb lattice with nearest neighbor bonds in two-dimensions and the diamond lattice in three dimensions. In both two and three dimensions one can construct an infinite number of other less symmetric arrangements even if one insists on the strong constraint $b_i \equiv d+1$ for all sites. One can, e.g., introduce dislocation pairs – rings with less and more than six junctions into the honeycomb lattice. This keeps the coordination number but requires a distortion of the bond lengths and of the angles between bonds.

Here we shall only discuss the geometric floppiness of the honeycomb lattice which is relatively easy to visualize.

9.3.4. *The geometric floppiness of the honeycomb lattice*

The honeycomb lattice is an example of a $d+1$ coordinated LRFN in d dimensions. It has a coordination of 3 ($=d+1$) at all its vertices. Having a coordination of 3, instead of the BCI requirement 4 ($=2d$), means that one misses $\frac{1}{2}$ a degree of freedom per site. One quarter of the DOF are free.

Consider the network in Fig. II.13. We construct the nearest neighbor honeycomb lattice by successively adding vertical columns as indicated by the numbering in the figure. Constructing each column amounts to adding "dumbbells" attached at the relevant positions in the previous column. In constructing such a column each "dumb-bell" – indicated by the color scheme and heavy connecting line – separately has the 4-point collective freedom we described in Fig. II.9. It can be shifted and rotated over a considerable range without changing the lengths of the two bonds connecting it to the previous column. Thus, having fixed column n there is still one FDOF for each dumbbell in the next column $n+1$. This amounts to one FDOF for every 2 points as required by the BCI.

In general the collective degrees of freedom corresponding to the FDOF of LRFN can be very complex. It is therefore difficult to visualize them even for simple periodic lattices like the diamond

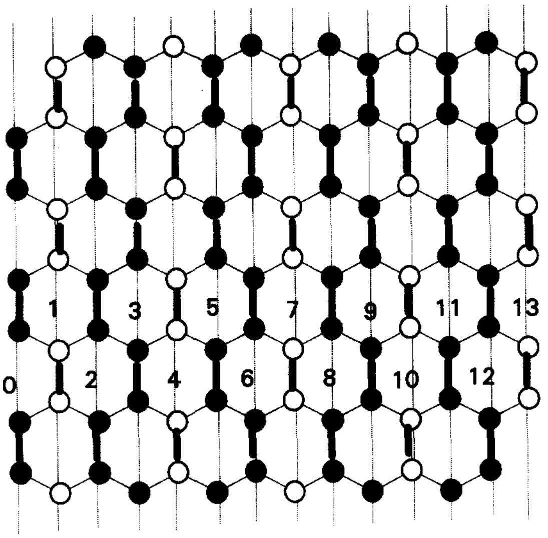


Fig. II.13. Microscopic freedom in constructing the honeycomb network by rows.

lattice and certainly in general. The violation of the BCI proves that they must be there even when this is not intuitively obvious.

9.4. Marginal bonding and macroscopic floppiness

In Section 8 we described some examples of networks which were only macroscopically floppy – the nearest neighbor square lattice in two dimensions and the simple and body centered cubic lattices. The only floppiness of these lattices is the floppiness of their macroscopic boundaries. The boundaries can be deformed freely over a considerable range without changing the lengths of any bonds but this exhausts their floppiness. Once the form of the boundary is fixed the network becomes completely rigid and *all* positions are determined by the bonds.

We called this purely *macroscopic floppiness.*

Macroscopic floppiness is not just a peculiarity of these very symmetric and almost trivial floppy networks. One expects it to be a fairly general property of bonded network with the marginal coordination required by the BCI.

For simplicity consider an infinite bonded network constructed with the marginal coordination for rigidity

$$b_i = 2d \tag{9.14}$$

at all sites. We also assume that this network is embedded in space uniformly so that the bonds are all reasonably short range. We now make a finite network by cutting out a piece of this infinite network. We cut all the bonds which cross the boundaries and connect the finite network to the rest of the infinite network. This creates sites with a coordination smaller than $2d$ near the boundaries. Like the simple examples of Sections 8.1.1 and 8.2.1 such a network has a number $\propto N^{1-(1/d)}$ of free DOF and it becomes completely rigid when the positions of the boundary atoms are fixed. Thus all the floppy modes must be macroscopic collective modes.

Our argument shows that macroscopic floppiness is closely related to marginal bonding and seems to follow from it at least qualitatively. The number of FDOF is then proportional to the surface area.

10. The free eigenmodes of floppy networks

10.1. The harmonic energy of floppy networks

The energy of a bonded network depends only on the bonded distances $\{r\}_{\text{bond}}$

$$\mathscr{E}(\{r\}) = \mathscr{E}(\{r\}_{\text{bond}})\,.$$

The energy can therefore be expanded in the deviations of the bonded distances $\{\delta r\}_{\text{bond}}$, from their reference values $\{R\}_{\text{bond}}$

$$\mathscr{E}(\{r\}_{\text{bond}}) - \mathscr{E}(\{R\}_{\text{bond}}) = \sum_{\text{bonds}} \left[\frac{\partial \mathscr{E}}{\partial r_{ij}}\right] \delta r_{ij} + \frac{1}{2} \sum_{\text{bonds}} \left[\frac{\partial^2 \mathscr{E}}{\partial r_{ij} \partial r_{lk}}\right] \delta r_{ij}\, \delta r_{lk} + \cdots\,. \tag{10.1}$$

This differs from Eq. (3.18) only in the restriction of the summation to bonded distances.

Only n_{b} $(< n_{\text{int}})$ independent variables appear in the expansion of the energy $\mathscr{E}(\{r\})$ – the changes in the n_{b} *bonded* lengths, $\{\delta r\}_{\text{bond}}$. This is equivalent to saying that in the space of distances $[\mathscr{R}]$ – as functions of the n_{ind} independent distances $\{r\}$ which determine the configurations – the expansion of the energy is confined to the subspace spanned by the bonded distances $[\mathscr{R}]_{\text{bond}}$. The expansion Eq. (10.1) has no components in the complementary free space $[\mathscr{R}]_{\text{free}}$ with coordinates $\{r\}_{\text{free}}$ on which the energy does not depend.

The changes in the bonded distances, δr_{ij}, are however not the variables one really wants. We have to map the expansion in $[\mathscr{R}]$, Eq. (10.1), into the *Nd* dimensional space of single particle deviations, $[\mathscr{U}]$, defined in Eq. (7.8) and this mapping is nonlinear. One has, as in Eq. (3.21)

$$\delta r_{ij} \cong u^{\parallel}_{ij} + \frac{(u^{\perp}_{ij})^2}{2R_{ij}} + \text{h.o.t.}$$

The $u^{\parallel}_{ij}$ are the lowest order terms in this expansion. As we saw in Section 5 this means that in the Born–Huang approximation, when there are no stresses, the harmonic, second order expansion of the energy in the components of the $\boldsymbol{u}_i$ can be written as an expansion in the $u^{\parallel}_{ij}$ only. Thus the harmonic Cauchy energy becomes

$$\mathscr{C}^{\text{h}} = \frac{1}{2} \sum_{\text{bonds}} \left(\tfrac{1}{2} \mathscr{K}_{ij} \cdot u^{\parallel 2}_{ij}\right) \tag{10.2}$$

and in general

$$\mathscr{E}^{\text{h}}_{\text{BH}} = \frac{1}{2} \sum_{\text{bonds}} \left(\tfrac{1}{2} \mathscr{K}_{ij} u^{\parallel 2}_{ij} + \mathscr{K}_{i,jk} u^{\parallel}_{ij} u^{\parallel}_{ik} + \tfrac{1}{4} \mathscr{K}_{ij,kl} u^{\parallel}_{ij} u^{\parallel}_{kl}\right) \tag{10.3}$$

which differs from Eqs. (5.8), (5.11) and (5.13) only in the restriction of the summation to bonded distances. The mapping of the expansion of the energy from the expansion in distances, that is in

$\{\mathscr{R}\}$, Eq. (10.1), to the expansion in the vector deviations $\boldsymbol{u}_i$ in the space $\{\mathscr{U}\}$, Eq. (10.3) is then linear to the order required

$$\delta r_{ij} \;\Rightarrow\; u_{ij}^{\prime\prime} = \boldsymbol{u}_i \cdot \boldsymbol{R}_{ij} - \boldsymbol{u}_j \cdot \boldsymbol{R}_{ij}\,. \tag{10.4}$$

When there are no stresses the nonlinearities in the expansion of the δr_{ij}, Eq. (3.21), do not show up in the construction of the harmonic expansion in the components of the $\boldsymbol{u}_i$. The $\mathscr{n}_{\mathrm{b}}$ variables $u_{ij}^{\prime\prime}$ simply replace the $\mathscr{n}_{\mathrm{b}}$ variables δr_{ij}. The result is that the expansion in the space $[\mathscr{U}]$ is confined to an $\mathscr{n}_{\mathrm{b}}$ dimensional subspace of $[\mathscr{U}]$, $[\mathscr{U}]_{\mathrm{b}}$ defined by the $u_{ij}^{\prime\prime}$ via Eq. (10.4). The complementary subspace of $[\mathscr{U}]$, $[\mathscr{U}]_{\mathrm{free}}$ describes free eigenmodes with no restoring force, Eq. (7.15). We want to show this by constructing the subspace $[\mathscr{U}]_{\mathrm{b}}$ and its complementary subspace $[\mathscr{U}]_{\mathrm{free}}$.

10.2. Decomposing the vector space $[\mathscr{U}]$

10.2.1. The bonded subspace $[\mathscr{U}]_{\mathrm{b}}$

Define the Nd dimensional vector $(\hat{\boldsymbol{R}}_{ij}]$

$$(\hat{\boldsymbol{R}}_{ij}] = (0,0,\dots,\hat{\boldsymbol{R}}_{ij},0,\dots,-\hat{\boldsymbol{R}}_{ij},0,\dots] \tag{10.5}$$

so that the unit vectors $\hat{\boldsymbol{R}}_{ij}$ and $-\hat{\boldsymbol{R}}_{ij}$ appear in the positions i and j respectively.[43] We can then write the longitudinal deviations $u_{ij}^{\prime\prime}$ as

$$(\boldsymbol{u}][\hat{\boldsymbol{R}}_{ij}) = \boldsymbol{u}_i \cdot \hat{\boldsymbol{R}}_{ij} - \boldsymbol{u}_j \cdot \hat{\boldsymbol{R}}_{ij} = u_{ij}^{\prime\prime}\,. \tag{10.6}$$

Using this notation the harmonic Cauchy energy $\mathscr{C}^{\mathrm{h}}$, Eq. (10.2), can be written

$$\mathscr{C}^{\mathrm{h}} = \frac{1}{2}\sum_{\text{bonds}} \mathscr{K}_{ij}((\boldsymbol{u}][\hat{\boldsymbol{R}}_{ij}))^2 = \tfrac{1}{2}(\boldsymbol{u}\|\boldsymbol{K}_{\mathrm{C}}\|\boldsymbol{u})\,, \tag{10.7}$$

where the Cauchy dynamic matrix is

$$\|\boldsymbol{K}_{\mathrm{C}}\| = \sum_{\text{bonds}} \mathscr{K}_{ij}\|[\hat{\boldsymbol{R}}_{ij}) * (\hat{\boldsymbol{R}}_{ij}]\|\,. \tag{10.8}$$

More generally, from Eq. (10.3) the general Born–Huang dynamical matrix is

$$\boldsymbol{K}_{\mathrm{BH}} = \sum_{\text{bonds}} (\mathscr{K}_{ij}[\hat{\boldsymbol{R}}_{ij}) * (\hat{\boldsymbol{R}}_{ij}] + \tfrac{1}{2}\mathscr{K}_{i,jk}[\hat{\boldsymbol{R}}_{ij}) * (\hat{\boldsymbol{R}}_{ik}] + \tfrac{1}{2}\mathscr{K}_{ij,kl}[\hat{\boldsymbol{R}}_{ij}) * (\hat{\boldsymbol{R}}_{kl}])\,. \tag{10.9}$$

There are $\mathscr{n}_{\mathrm{b}}$ vectors $(\hat{\boldsymbol{R}}_{ij}]$ in $[\mathscr{U}]$ defined by the $\mathscr{n}_{\mathrm{b}}$ vectors $\boldsymbol{R}_{ij}$ $(=\boldsymbol{R}_i - \boldsymbol{R}_j)$ for all the bonds $[ij]$ in the realization $\{\boldsymbol{R}\}$ of the bonded network which serves as a reference configuration. The $\mathscr{n}_{\mathrm{b}}$ vectors $(\hat{\boldsymbol{R}}_{ij}]$ span a linear subspace of the Nd dimensional space $[\mathscr{U}]$ – the *bonded subspace* $[\mathscr{U}]_{\mathrm{b}}$. The dimension of this subspace is at most $\mathscr{n}_{\mathrm{b}}$. It has this maximum dimension when all the vectors $(\hat{\boldsymbol{R}}_{ij}]$ are linearly independent in $[\mathscr{U}]$.[44]

---

[43] We note that the vectors $[\hat{\boldsymbol{R}}_{ij})$ for different bonds are not orthogonal to each other when the bonds have a common vertex because $(\hat{\boldsymbol{R}}_{ij}][\hat{\boldsymbol{R}}_{ik}) = \hat{\boldsymbol{R}}_{ij} \cdot \hat{\boldsymbol{R}}_{ik}$ which, in general, does not vanish.

[44] In general the vectors $[\hat{\boldsymbol{R}}_{ij})$ are all linearly independent in $[\mathscr{U}]$ when the $\mathscr{n}_{\mathrm{b}}$ distances R_{ij}, are geometrically independent distances. Exceptions to this are singular reference states of the type we discussed in Section 5.2.3.1 for which the dimension of $[\mathscr{U}]_{\mathrm{b}}$ is reduced.

It follows from the form of the dynamical matrix, Eq. (10.9), that it only has elements between vectors belonging to the subspace $[\mathcal{U}]_\mathrm{b}$. $\boldsymbol{K}_\mathrm{BH}$ operates only *inside* the bonded subspace $[\mathcal{U}]_\mathrm{b}$ or, equivalently the harmonic expansion of the energy is defined completely in this n_b dimensional subspace. The rank of the dynamic matrix $\boldsymbol{K}_\mathrm{BH}$ is n_b and it therefore cannot have more than n_b eigenvectors with non-vanishing eigenvalues, κ^α.

10.2.2. The free subspace $[\mathcal{U}]_\mathrm{free}$

Consider the vectors $[\boldsymbol{u}_\mathrm{free})$ in $[\mathcal{U}]$ which are orthogonal to all the bonded vectors $(\hat{\boldsymbol{R}}_{ij}]$. These vectors are defined by the n_b equations

$$(\hat{\boldsymbol{R}}_{ij}][\boldsymbol{u}_\mathrm{free})=0 \tag{10.10}$$

for all the bonds. The solutions of these equations are

$$n_\mathrm{free} \geq n_\mathrm{int} - n_\mathrm{b} \tag{10.11}$$

linearly independent vectors $[\boldsymbol{u}^\nu_\mathrm{free})$ which define a linear subspace $[\mathcal{U}]_\mathrm{free}$ of $[\mathcal{U}]$. This subspace is complementary to $[\mathcal{U}]_\mathrm{b}$:

$$[\mathcal{U}]=[\mathcal{U}]_\mathrm{b} \times [\mathcal{U}]_\mathrm{free} .$$

It follows from Eq. (10.10) and the definition of $\boldsymbol{K}_\mathrm{BH}$, Eq. (10.9), that

$$\boldsymbol{K}_\mathrm{BH}[\boldsymbol{u}_\mathrm{free}) \equiv 0 \tag{10.12}$$

for all the free vectors $[\boldsymbol{u}^\nu_\mathrm{free})$ which satisfy Eq. (10.10). All the deviations described by vectors in $[\mathcal{U}]_\mathrm{free}$ are eigenvectors of $\boldsymbol{K}_\mathrm{BH}$ with zero eigenvalue and there are n_free such eigenmodes.

We can make this somewhat more intuitive. A vector in $[\mathcal{U}]_\mathrm{free}$ describes a deformation mode for which

$$u^{\prime\prime}_{ij} \equiv 0 \tag{10.13}$$

for all bonds. The *relative* deviation of the two ends of a bond in a free mode, $[\boldsymbol{u}_\mathrm{free})$, is perpendicular to the direction of the bond

$$\boldsymbol{u}^\mathrm{free}_{ij} \cdot \boldsymbol{R}_{ij}=0 \tag{10.14}$$

so that

$$\boldsymbol{u}^\mathrm{free}_i \cdot \boldsymbol{R}_{ij}=\boldsymbol{u}^\mathrm{free}_j \cdot \boldsymbol{R}_{ij} , \quad \boldsymbol{u}^\mathrm{free}_i=\boldsymbol{u}^\mathrm{free}_j+\boldsymbol{u}^\perp_{ij} , \tag{10.15}$$

where $\boldsymbol{u}^\mathrm{free}_i$ is the deviation of site i in the free mode, $[\boldsymbol{u}_\mathrm{free})$.

This means that each bond can undergo a rigid translation and a rotation described by a transverse relative deviation. This is of course just the requirement that the lengths of the bonds do not change to lowest order. Our argument demonstrated that for floppy networks one can indeed construct n_free such modes.

We have thus shown that for unstressed floppy networks there are always (at least) $n_\mathrm{int}-n_\mathrm{b}$ $(\leq n_\mathrm{free})$ independent free eigenmodes with no restoring forces. By Eq. (9.8) this means that there are at least $\frac{1}{2}(2d-\langle b\rangle)$ free modes per junction.

10.3. The free eigenmodes

10.3.1. The linear stability of the free modes

We defined the free subspace $[\mathscr{U}]_{\text{free}}$ from the requirement that for functions belonging to this space the $u^{\parallel}_{ij}$ vanish for all bonds, Eq. (10.13). For a BH reference state modes defined by vectors in this subspace are all degenerate and have no restoring forces, Eq. (10.12). The motion of a *bond* in a free mode is always a combination of a rigid translation of the bond and a transverse relative motion of the two ends $u^{\perp}_{ij}$. When

$$u^{\perp}_{ij} \equiv 0$$

for all the bonds the “free” mode reduces to a rigid translation of the whole network.

This immediately shows that the modes are no longer free when the network is stressed. We saw in Section 6 that when there are stresses in the reference state a stress induced contribution

$$\mathscr{E}^{\text{str}}(\{\boldsymbol{R}\}) = \sum_{\text{bonds}} \frac{\mathscr{T}_{ij}(\{R\})}{R_{ij}}(u^{\perp}_{ij})^2 \tag{10.16}$$

appears in the harmonic expansion in addition to the BH terms derived from the dynamic matrices (10.8) and (10.9). The stress induced terms will of course affect all the eigenmodes but they are completely dominant in the free subspace. For modes in this subspace the harmonic force constant κ^{free} vanishes with the bond tensions $\mathscr{T}_{ij}$

$$\kappa^{\text{free}} = \kappa^{\text{free}}(\{\mathscr{T}_{ij}\}), \quad \kappa^{\text{free}}(\{0\}) = 0\,. \tag{10.17}$$

The force constants for the free modes, $\kappa^{\text{free}}(\{\mathscr{T}_{ij}\})$, all vanish for a Born–Huang reference state – i.e., when there are no bond tensions. When the network is stressed the initial bond tensions can remove the degeneracy of the free modes. In general, some of them will end up as stable modes with positive force constants

$$\kappa(\{\mathscr{T}\}) > 0$$

while for others

$$\kappa(\{\mathscr{T}\}) < 0$$

so that the modes become linearly unstable and will tend to buckle.

10.3.2. Anharmonic terms

The transverse deviations of the bonds, $u^{\perp}_{ij}$, also appear when one goes beyond the harmonic expansion – in the anharmonic terms – even when there are no stresses. There are, e.g., anharmonic terms in the expansion of the BH energy in which $u^{\perp}_{ij}$ appears, such as

$$\mathscr{K}_{ij}\delta r^2_{ij} \cong \mathscr{K}_{ij}\left(u^{\parallel}_{ij} + \frac{{u^{\perp}_{ij}}^2}{2R_{ij}}\right)^2 = \mathscr{K}_{ij}u^{\parallel 2}_{ij} + \frac{\mathscr{K}_{ij}}{R_{ij}}u^{\parallel}_{ij}{u^{\perp}_{ij}}^2 + \frac{\mathscr{K}_{ij}}{4R^2_{ij}}{u^{\perp}_{ij}}^4\,. \tag{10.18}$$

Like the stress induced terms in Eq. (10.16) the anharmonic terms in Eq. (10.18) also appear because the expansion of the δr_{ij} is nonlinear and not because of intrinsic nonlinearities of the interactions.[45] These terms all result from the mapping of the harmonic, second order terms in the expansion in the bond lengths – Eq. (10.1).

Thus the "free" subspace $[\mathscr{U}]_{\text{free}}$, is only linearly free even when there are no stresses. There are no harmonic restoring forces for the free modes in the BH approximation when there are no stresses. The dynamics in this subspace is dominated by stresses, Eq. (10.16), or by anharmonic terms, Eq. (10.18), even when their coefficients are small. The free modes of geometrically floppy bonded networks can be stabilized (or destabilized) by stresses and are always bounded as anharmonic modes.

10.3.3. *An example of a collective free mode*

We illustrate the nature of these collective free modes by considering the free mode of the four-point configuration of Fig. II.9.

The deviation of the point $\boldsymbol{a}$ has to be normal to the vector $(\boldsymbol{ca})$ and therefore of the form

$$\boldsymbol{u}_a = u_a \begin{pmatrix} \sin\phi_c \\ -\cos\phi_c \end{pmatrix} \tag{10.19a}$$

and similarly

$$\boldsymbol{u}_b = u_b \begin{pmatrix} \sin\phi_d \\ -\cos\phi_d \end{pmatrix} \tag{10.19b}$$

using the notation of this figure. To assure that the collective mode does not change the distance between the points $\boldsymbol{a}$ and $\boldsymbol{b}$ the components of these translations parallel to the vector $(\boldsymbol{ab})$

$$u_a^{\prime\prime} = u_a \sin(\phi_c + \phi_a)\,, \qquad u_b^{\prime\prime} = u_b \sin(\phi_d + \phi_a) \tag{10.20}$$

have to be equal to each other

$$u_a^{\prime\prime} = u_b^{\prime\prime}\,, \qquad \frac{u_a}{u_b} = \frac{\sin(\phi_d + \phi_a)}{\sin(\phi_c + \phi_a)}\,. \tag{10.21}$$

A mode of the form (10.19) with the relation (10.21) between the two amplitudes has only second order effects on the three lengths. The mode is therefore linearly free when the bonds are not stressed.

10.4. *Geometrical description*

We can express this in a more general formal way.

In Section 9.1 we defined the $\mathscr{n}_{\text{b}}$ dimensional manifold of bonded configurations $\mathscr{A}(\{r\}_{\text{bond}})$ in the space of configurations $\{\mathscr{R}\}$ by the requirement that the bonded distances $\{r\}_{\text{bond}}$ are the same for all the configurations belonging to the manifold $\mathscr{A}(\{r\}_{\text{bond}})$. In particular the reference configuration $\{R\}$ then belongs to a bonded manifold $\mathscr{A}(\{R\}_{\text{bond}})$ defined by the parametrization

$$\{r\} = \{\{R\}_{\text{bond}};\ \{r\}_{\text{free}}\}\,. \tag{10.22}$$

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[45] But they obviously appear even when there are no stresses.

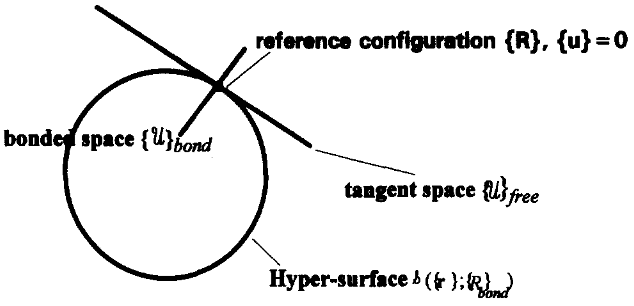

Fig. II.14. The hyper-surface $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$ and its linear tangent space at $\{\boldsymbol{R}\}$ – $[\mathcal{U}]_{\mathrm{free}}$.

In the physical space of *vectorial* deviations around the reference state $\{\boldsymbol{R}\}$ – the space $[\mathcal{U}]$, Eq. (7.8) – the bonded distances $\{R\}_{\mathrm{bond}}$ define an n_{b} dimensional hyper-surface $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$ by the equations

$$\{r\}_{\mathrm{bond}}(\{\boldsymbol{R}\}) = \{r\}_{\mathrm{bond}}(\{|\boldsymbol{R}+\boldsymbol{u}|\}) = \{R\}_{\mathrm{bond}} \tag{10.23}$$

or explicitly as an expansion at $\{\boldsymbol{R}\}$

$$(\boldsymbol{R}_{ij}+\boldsymbol{u}_{ij})^2 - R_{ij}^2 = 2R_{ij}u_{ij}^{\parallel} + u_{ij}^{\parallel 2} + u_{ij}^{\perp 2} = 0\,. \tag{10.24}$$

Each point on the hyper-surface $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$ describes a different configuration[46] of the N vertices. All these states have the same bonded distances and identical energies. The specific configuration $\{\boldsymbol{R}\}$ – the specific reference state we have selected for our expansion is described by the point

$$\{\boldsymbol{r}\} = \{\boldsymbol{R}\}\,, \quad \boldsymbol{u} = 0$$

on $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$.

The condition that the bonded distances do not change to first order, Eq. (10.14)

$$\boldsymbol{u}_{ij}^{\mathrm{free}} \cdot \boldsymbol{R}_{ij} = 0$$

defines $[\mathcal{U}]_{\mathrm{free}}$ as the linear space tangent to the *curved* hyper-surface $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$ at the point $\{\boldsymbol{R}\}$ $(\{\boldsymbol{u}\}=0)$. We illustrate this schematically in Fig. II.14.

It is evident from Eq. (10.24) which defines the surface $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$ that the $u_{ij}^{\parallel}$ correspond to deviations which are normal to the surface and the $u_{ij}^{\perp}$ to deviations tangential to it. Thus the condition (10.14) which defines the free subspace $[\mathcal{U}]_{\mathrm{free}}$, can also be considered as defining the tangent space to $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$ at $\{\boldsymbol{R}\}$. This is a direct generalization of the description of the effects of rotational invariance on the single spring in Appendix B, Fig. B.1. In that case the surface $\mathcal{S}(\{\boldsymbol{r}\};\{R\}_{\mathrm{bond}})$ reduces to the hyper-cylinder

$$(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2 = r^2 = \mathrm{const}\,.$$

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[46] This includes the trivial states related to $\{\boldsymbol{R}\}$ by the *global* rigid-body translation–rotation symmetry. But $\mathcal{S}(\{\boldsymbol{R}\};\{r\}_{\mathrm{bond}})$ also describes the effect of the large group of *local* gauge symmetries of the geometrical floppiness.

The unstressed harmonic expansion at $\boldsymbol{R}$ is an expansion in u'' and is therefore confined to the normal for every point on the hyper-cylinder. The components in the direction of the tangent, $u_{ij}^{\perp}$, are free. They only appear in the harmonic expansion of the energy when the spring is stressed, Eq. (10.16), and in the anharmonic higher order terms in the expansion, Eq. (10.18).

For a single spring the "free modes" are of course simply the "rigid body" modes related to the overall translation–rotation symmetry of the pair. The generalization to a tenuous net of N particles is more subtle and is not related to any such simple symmetry. Our derivation shows however that the appearance of free modes in floppy networks is just another aspect of the same type of symmetry. One could say that for floppy nets the underlying gauge symmetry, the product of the translation–rotation symmetries of the separate bonds is not fully suppressed by the interconnections. This quasi-rotational symmetry disappears when the network is stressed.

11. The vibrations of the nearest neighbor honeycomb lattice

Our results in Section 10 were quite general. We showed that geometrically floppy networks must have free eigenmodes when they are not stressed. It is useful to show how these predictions are confirmed in a specific but not quite trivial example. Showing this is quite straightforward for simple networks which are periodic lattices. For such networks one can use the periodicity to solve Eq. (10.10) and thus compute the free eigenmodes explicitly. We shall demonstrate this for the honeycomb lattice with nearest neighbor interactions. Since the coordination of this lattice is three one misses half a degree of freedom per site and this is therefore the number of free eigenmodes one predicts.

11.1. The free librations of hexagons

Because of the simple geometry it is easy to visualize free eigenmodes for the honeycomb lattice. We have indicated a free mode – the torsional motion of a rigid hexagon – in Fig. II.15.

All the atomic motions of the torsional libration are transverse to the bonds connecting the hexagon to the rest of the lattice while the bonds belonging to the hexagon itself experience a motion which is a combination of a translation and a rotation. Thus the change in the energy of an unstressed bond in the libration is purely anharmonic because for all bonds

$$u''_{ij}=0 \quad \text{and therefore} \quad \delta\mathscr{V}_{ij}=\mathscr{K}_{ij}\delta r_{ij}^{2}=\mathscr{K}_{ij}\frac{(u_{ij}^{\perp})^{4}}{4R_{ij}^{2}}+\text{h.o.t}\,.$$

for the libration. There are no harmonic restoring forces for these librations in the unstressed network so that the librations are free eigenmodes. We note that the anharmonicity is a geometric effect. We have only expanded the potentials $\mathscr{V}_{ij}$ to second order around their equilibrium separation. It is only the fact that the network is floppy which causes the librational modes to become anharmonic. When there is stress a harmonic term

$$\mathscr{T}_{ij}\delta r_{ij}\cong\mathscr{T}_{ij}\cdot\frac{(u_{ij}^{\perp})^{2}}{2R_{ij}}$$

appears in the bond energy.

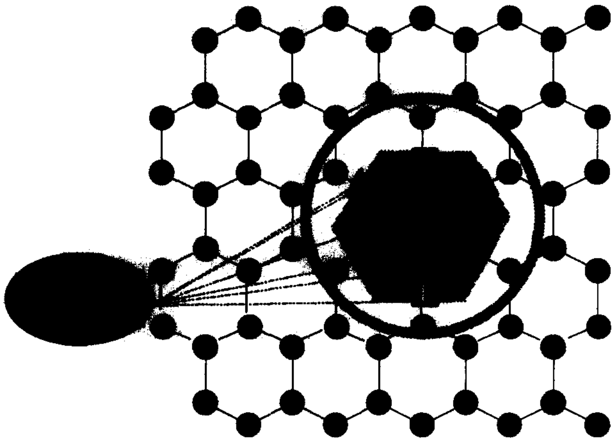

Fig. II.15. The free librations of the honeycomb lattice.

It is easy to see that the librations of different hexagons are not mutually orthogonal eigenmodes. They are however linearly independent and their number is the number of FDOF. Each atom belongs to three hexagons and there is therefore half a hexagon – and consequently half a libration – per site in the honeycomb lattice.

11.2. The dynamical matrix

Because of the high degeneracy of the free vibrations their description as librations of hexagons is of course not unique. Instead of looking at the librations we can calculate the free eigenmodes of the honeycomb lattice directly in the usual way by Fourier transformation. The free eigenmodes must then appear in the calculation as zero-frequency vibrations.

We shall show that for each wave-vector $\boldsymbol{q}$ in the Brillouin zone there is one free mode. This is the difference between the number of DOF in the unit cell – four – and the number of bonds in the unit cell – 3.[47]

There are three types of bonds in the honeycomb lattice,

$$\boldsymbol{b}_1 = (0, -1), \qquad \boldsymbol{b}_2 = (\tfrac{\sqrt{3}}{2}, \tfrac{1}{2}), \qquad \boldsymbol{b}_3 = (-\tfrac{\sqrt{3}}{2}, \tfrac{1}{2}), \tag{11.1}$$

and two sites per unit cell marked "+" and "−" in Fig. II.16. We have chosen the vectors in Eq. (11.1) so that the $\boldsymbol{b}_\lambda$ always point from a site of type "+" to a site of type "−".

We write for the four-dimensional vector of amplitudes belonging to the wave vector $\boldsymbol{q}$

$$[\boldsymbol{u}_q) = [\boldsymbol{u}_q^+, \boldsymbol{u}_q^-), \tag{11.2}$$

where

$$\boldsymbol{u}_q^\nu = (\xi_q^\nu, \eta_q^\nu), \qquad \nu = +, - \tag{11.3}$$

is a two-dimensional polarization vector for the site ν.

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[47] This result applies to any periodic but geometrically floppy lattice.

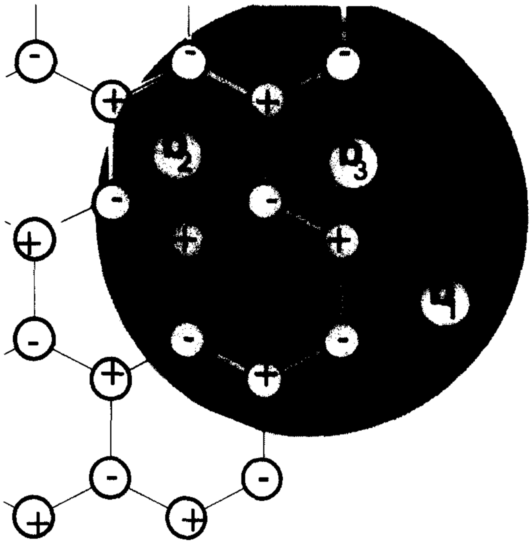

Fig. II.16. The three bonds $\boldsymbol{b}_1, \boldsymbol{b}_2$, and $\boldsymbol{b}_3$, and the two sites + and − in the unit cell of the honeycomb lattice.

The vectors $\boldsymbol{u}_{\boldsymbol{q}}^{v}$ are defined as

$$\boldsymbol{u}_{\boldsymbol{q}}^{v} = \left(\frac{1}{N}\right) \sum_{i} \boldsymbol{u}^{i,v} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}^{i,v}} , \tag{11.4}$$

where $\boldsymbol{R}^{i,v}$ is the position of the vertex (i, v) in the cell i. They are related to the deviations at the sites by

$$\boldsymbol{u}^{i,v} = \sum_{\boldsymbol{q}} \boldsymbol{u}_{\boldsymbol{q}}^{v} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}^{i,v}} . \tag{11.5}$$

Thus one has

$$u''^{\lambda}_{\substack{ij\\+,-}} = (\boldsymbol{u}_{+}^{i} - \boldsymbol{u}_{-}^{j}) \cdot \boldsymbol{b}_{\lambda} = \sum_{\boldsymbol{q}} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}^{i}} [\boldsymbol{u}_{\boldsymbol{q},f}^{\lambda} \cdot \boldsymbol{b}_{\lambda}] , \tag{11.6}$$

where $[{}^{i}_{+}]$ and $[{}^{j}_{-}]$ are the two ends of a bond

$$\boldsymbol{R}_{+}^{i} = \boldsymbol{R}^{i} , \qquad \boldsymbol{R}_{-}^{j} = \boldsymbol{R}^{i} + \boldsymbol{b}_{\lambda} \tag{11.7}$$

and the complex vector

$$\boldsymbol{u}_{\boldsymbol{q}}^{\lambda} = \boldsymbol{u}_{\boldsymbol{q}}^{+} - \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{b}_{\lambda}} \boldsymbol{u}_{\boldsymbol{q}}^{-} \tag{11.8}$$

describes the deviation across the bond λ. For the whole lattice this gives

$$\sum \left(u''^{\lambda}_{\substack{ij\\+,-}} \right)^{2} = \sum_{\boldsymbol{q}} [\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}}^{\lambda} \cdot \boldsymbol{b}_{\lambda}] [\boldsymbol{u}_{-\boldsymbol{q},\mathrm{f}}^{\lambda} \cdot \boldsymbol{b}_{\lambda}] . \tag{11.9}$$

In analogy to the definition of the vectors $(\hat{\boldsymbol{R}}_{ij}]$ in Eq. (10.6) we define the three four-dimensional vectors $(\boldsymbol{b}_\lambda^{\boldsymbol{q}}]$

$$(\boldsymbol{b}_\lambda^{\boldsymbol{q}}] = (\boldsymbol{b}_\lambda, -\mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{b}_\lambda}\boldsymbol{b}_\lambda]\,, \quad \lambda = 1,\ldots,3 \tag{11.10}$$

which gives Eq. (10.7) as a sum

$$\sum_i \sum_\lambda \left(u''^{\lambda}_{\substack{ij\\+,-}} \right)^2 = \sum_{\boldsymbol{q}} \sum_\lambda (\boldsymbol{u}_{-\boldsymbol{q}}]\|[\boldsymbol{b}_\lambda^{-\boldsymbol{q}}) * (\boldsymbol{b}_\lambda^{\boldsymbol{q}}]\|[\boldsymbol{u}_{\boldsymbol{q}}) \tag{11.11}$$

where $[\boldsymbol{b}_\lambda^{-\boldsymbol{q}})$ is the Hermitian conjugate of $(\boldsymbol{b}_\lambda^{\boldsymbol{q}}]$. The dynamical matrix for $\boldsymbol{q}$ can be written in this notation as

$$\|\boldsymbol{K}_{\boldsymbol{q}}\| = \sum_{\lambda=1}^{3} \|[\boldsymbol{b}_\lambda^{-\boldsymbol{q}}) * (\boldsymbol{b}_\lambda^{\boldsymbol{q}}]\| = \sum_{\lambda=1}^{3} \begin{Vmatrix} \tilde{\boldsymbol{b}}_\lambda * \boldsymbol{b}_\lambda & -\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{b}_\lambda}\tilde{\boldsymbol{b}}_\lambda * \boldsymbol{b}_\lambda \\ -\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{b}_\lambda}\tilde{\boldsymbol{b}}_\lambda * \boldsymbol{b}_\lambda & \tilde{\boldsymbol{b}}_\lambda * \boldsymbol{b}_\lambda \end{Vmatrix}, \tag{11.12}$$

where the vectors $\boldsymbol{b}_\lambda$ are defined in Eq. (11.1). Explicitly this gives

$$\|\boldsymbol{K}_{\boldsymbol{q}}\| = \begin{Vmatrix} \frac{3}{2} & 0 & \alpha & \gamma^* \\ 0 & \frac{3}{2} & \gamma^* & \beta \\ \alpha^* & \gamma & \frac{3}{2} & 0 \\ \gamma & \beta^* & 0 & \frac{3}{2} \end{Vmatrix}, \tag{11.13}$$

where we have defined

$$\begin{gathered} \alpha = -\tfrac{3}{2}\mathrm{e}^{-1/2\mathrm{i}q_y} \cos \tfrac{\sqrt{3}}{2} q_x\,, \qquad \beta = -(\mathrm{e}^{\mathrm{i}q_y} + \tfrac{1}{2}\mathrm{e}^{-1/2\,\mathrm{i}q_y} \cos \tfrac{\sqrt{3}}{2} q_x)\,, \\ \gamma = -\mathrm{i}\tfrac{\sqrt{3}}{2}\,\mathrm{e}^{1/2\,\mathrm{i}q_y} \sin \tfrac{\sqrt{3}}{2} q_x\,. \end{gathered} \tag{11.14}$$

11.3. The free eigenmodes

The free eigenmode $[\boldsymbol{u}_{\boldsymbol{q}})_{\text{free}}$ are defined as the solutions of

$$\|\boldsymbol{K}_{\boldsymbol{q}}\|[\boldsymbol{u}_{\boldsymbol{q}})_{\text{free}} = 0\,. \tag{11.15}$$

Using Eq. (11.10) it follows that one can instead solve the three equations

$$(\boldsymbol{b}_\lambda^{\boldsymbol{q}}][\boldsymbol{u}_{\boldsymbol{q}})_{\text{free}} = \boldsymbol{b}_\lambda \cdot \boldsymbol{u}^{\lambda}_{\boldsymbol{q},\mathrm{f}} = 0\,. \tag{11.16}$$

One finds an explicit form for the free modes

$$[\boldsymbol{u}_{\boldsymbol{q}})_{\text{free}} = \left[\begin{matrix} \xi^{+}_{\boldsymbol{q},\mathrm{f}} \\ \eta^{+}_{\boldsymbol{q},\mathrm{f}} \\ \xi^{-}_{\boldsymbol{q},\mathrm{f}} \\ \eta^{-}_{\boldsymbol{q},\mathrm{f}} \end{matrix} \right), \tag{11.17}$$

where

$$\xi^{\pm}_{\boldsymbol{q},\mathrm{f}} = \pm A\mathrm{i}\,(\cos(\tfrac{\sqrt{3}}{2} q_x) - \mathrm{e}^{\pm\mathrm{i}\,\frac{3}{2} q_y})\,, \qquad \eta^{\pm}_{\boldsymbol{q},\mathrm{f}} = A\sqrt{3}\,\sin(\tfrac{\sqrt{3}}{2}\, q_x)\,. \tag{11.18a,b}$$

In general the real and imaginary parts of the polarization vectors point in different directions so the polarization is elliptical. Moreover, the polarization rotates in opposite directions at the "+" and "−" sites.

The meaning of these solutions is more translucent if we write the explicit expressions for the relative deviations of the two ends of a bond by substituting into the expression (11.6). This gives

$$\begin{aligned} {}^1\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}} &= \mathrm{i}A\,(\cos(\tfrac{3}{2}q_y) - \cos(\tfrac{\sqrt{3}}{2}q_x))\hat{\boldsymbol{b}}^1\,, \\ {}^2\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}} &= A\,\sin(\tfrac{\sqrt{3}}{2}q_x)(\exp[-\mathrm{i}(\tfrac{\sqrt{3}}{2}q_x + \tfrac{3}{2}q_y)] - 1)\hat{\boldsymbol{b}}^2\,, \\ {}^3\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}} &= A\,\sin(\tfrac{\sqrt{3}}{2}q_x)(\exp[\mathrm{i}(\tfrac{\sqrt{3}}{2}q_x - \tfrac{3}{2}q_y)] - 1)\hat{\boldsymbol{b}}^3\,, \end{aligned} \tag{11.19}$$

where we have introduced the unit vectors normal to the bonds

$$\hat{\boldsymbol{b}}^1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \hat{\boldsymbol{b}}^2 = \begin{pmatrix} -\frac{1}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix}, \qquad \hat{\boldsymbol{b}}^3 = \begin{pmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix} \tag{11.20}$$

defined so that

$$\boldsymbol{b}_\lambda \cdot \hat{\boldsymbol{b}}^\lambda = 0\,. \tag{11.21}$$

The ${}^\lambda\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}}$ are thus always orthogonal to the respective bonds.

11.4. The transverse acoustic modes are the free modes

11.4.1. The small q limit

In the small q limit the polarization vectors $\boldsymbol{u}^+_{\boldsymbol{q},\mathrm{f}}$ and $\boldsymbol{u}^-_{\boldsymbol{q},\mathrm{f}}$ we computed in Eq. (11.18) become transverse and real

$$\left.\begin{aligned} \xi^\pm_{\boldsymbol{q},\mathrm{f}} &\approx -\tfrac{q_y}{q} = -\sin\varphi \\ \xi^\pm_{\boldsymbol{q},\mathrm{f}} &\approx \tfrac{q_x}{q} = \cos\varphi \end{aligned}\right. , \quad \boldsymbol{q}\cdot\boldsymbol{u}^\pm_{\boldsymbol{q},\mathrm{f}} = 0 + \mathrm{i}\,\mathrm{O}(q) \tag{11.22}$$

and are to this order the same for the two types of sites.

Thus the free modes are the phonons of the transverse acoustic branch. The fact that they are free means that the transverse velocity of sound vanishes in all directions

$$c^2_{\mathrm{trans}} = 0\,, \qquad \mu = 0 \tag{11.23}$$

which also shows that the shear modulus, μ, vanishes.[48]

This also means that the shear modulus cannot be computed using the techniques of Section 5.4. If one uses Eq. (5.24) to compute the shear modulus the result is the same as that for the triangular lattice except for a factor of 2. This predicts, in particular, that

$$\mu \propto K \neq 0 \tag{11.24}$$

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[48] There is only one shear modulus for the 2-dimensional hexagonal point symmetry of the honeycomb lattice.

which we have just shown to be wrong. The procedure of Eq. (5.18) breaks down for the honeycomb lattice because the unit cell is complex – there are two sites per cell – and the deformations inside the unit cell are nonaffine.

11.4.2. The atomic motions in the transverse acoustic band

In a free mode the relative deviation of the two ends of a bond must always be *transverse* to the bond. This is true for all the free modes, Eq. (11.19). The simplest way to assure this is of course when the deviations themselves are transverse to the bonds

$$\boldsymbol{u}_{i+}^{\boldsymbol{q},\mathrm{f}} \cdot \boldsymbol{b}_\lambda = \boldsymbol{u}_{j-}^{\boldsymbol{q},\mathrm{f}} \cdot \boldsymbol{b}_\lambda = 0 \tag{11.25}$$

as for the librations of the hexagons. We have however found in Eq. (11.22) that in the small q limit the *polarizations* are normal to the *wave vector*

$$\boldsymbol{u}_{i+}^{\boldsymbol{q},\mathrm{f}} \cdot \boldsymbol{q} = \boldsymbol{u}_{j-}^{\boldsymbol{q},\mathrm{f}} \cdot \boldsymbol{q} = 0 \tag{11.26}$$

which is obviously inconsistent with Eq. (11.25) for at least two of the three bond directions, λ. The deviations cannot simultaneously be orthogonal to $\boldsymbol{q}$ and to the three vectors $\boldsymbol{b}_\lambda$. This means that while the "+" and the "−" sub-lattices *separately* are described by transverse waves with wave vector $\boldsymbol{q}$ the *relative* motion of the two sites is correlated in a non-trivial way so that Eq. (11.26) becomes consistent with

$$\boldsymbol{b}_\lambda \cdot (\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}}^{+} - \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{b}_\lambda} \cdot \boldsymbol{u}_{\boldsymbol{q},\mathrm{f}}^{-}) = 0 \tag{11.27}$$

– Eq. (11.16). We want to see how this comes about.

11.4.3. Shears along the bonds

Consider first a wave along a bond direction

$$q_x = 0\,, \qquad q_y \neq 0\,. \tag{11.28}$$

Substitution into Eq. (11.19) gives

$${}^2\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}} = {}^3\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}} = 0 \tag{11.29}$$

exactly. Thus there is shear only across the "1" bonds – ${}^1\boldsymbol{u}_{\boldsymbol{q},\mathrm{f}} \neq 0$. This is exactly what one expects from the soft-shear lines we showed in Fig. II.7. The bi-layers connected by the "2" and "3" bonds move rigidly and all the shear appears in the soft layers of "1" bonds. We discussed the same effect of soft shear lines for shear perpendicular to the axis of the square and simple cubic lattices in Section 8. Checking Eqs. (11.19) one finds such "soft line" modes also for shears perpendicular to the two other bond directions as required by the symmetry of the lattice.

11.4.4. Shears normal to the bonds

Consider the phonons propagating in the x direction

$$q_x \neq 0\,, \qquad q_y = 0\,. \tag{11.30}$$

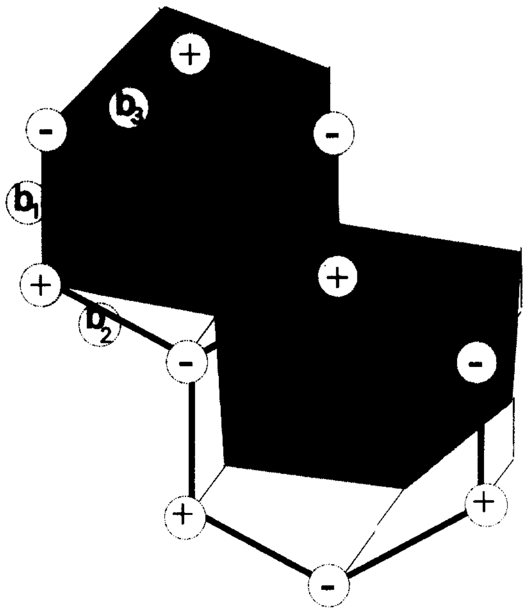

Fig. II.17. Schematic drawing of the distortion of 2 hexagons in a free shear. In each hexagon the “1” bonds are sheared rigidly, as indicated, and the “2” and “3” bonds rotate. The sheared pattern is shaded. It can be seen that the distortion of the hexagon is not a simple shear but more complex.

Starting from Eq. (11.19) we can see how the atoms move when the lattice is sheared by adding up the relative deviations of the ends of the bonds. It is convenient to look at the real part of the expressions. (The phase is of course arbitrary.) One finds

$$\mathrm{Re}(\boldsymbol{u}^1_{\boldsymbol{q},\mathrm{f}}) = 0\,, \qquad \mathrm{Re}(\boldsymbol{u}^2_{\boldsymbol{q},\mathrm{f}}) = \varepsilon\,\hat{\boldsymbol{b}}^2\,, \qquad \mathrm{Re}(\boldsymbol{u}^3_{\boldsymbol{q},\mathrm{f}}) = \varepsilon\,\hat{\boldsymbol{b}}^3\,, \tag{11.31}$$

where ε is a constant which depends on the amplitude of the shear.

For this choice of phase the “1” bonds only move rigidly (without rotating) while the two other bonds are sheared. For each hexagon the two bonds parallel to the y axis are sheared with respect to each other. The remaining two vertices then adjust so that all bond distances remain unchanged. We have indicated this in Fig. II.17. It can be seen from the figure that the distortion is a simple shear strain only at large distances. The distortion of a hexagon is not described by a simple shear and is therefore not affine. It can also be seen that the sub-lattices of the “+” and “−” sites separately are also not deformed affinely. This is a result of the fact that for this choice of phase the three types of bonds are not treated symmetrically.

11.4.5. A general shear

But these are special symmetry directions. Eqs. (11.19) show that there are similar correlated soft transverse waves, or equivalently shears, in all directions. This shows that a *macroscopic* shear of the honeycomb lattice *in any direction* can be carried out so that the relative deviation of the two ends of *every nearest neighbor bond* is transverse. We want to see how the atoms actually move for such a general shear.

To leading order in q Eq. (11.19) becomes

$$\begin{aligned} {}^1\boldsymbol{u} &= u(\tfrac{3}{2}\sin^2\varphi - \tfrac{1}{2}\cos^2\varphi)\hat{\boldsymbol{b}}^1 , \\ {}^2\boldsymbol{u} &= u(\cos^2\varphi + \sqrt{3}\sin\varphi\cos\varphi)\hat{\boldsymbol{b}}^2 , \\ {}^3\boldsymbol{u} &= u(-\cos^2\varphi + \sqrt{3}\sin\varphi\cos\varphi)\hat{\boldsymbol{b}}^3 , \end{aligned} \tag{11.32}$$

where

$${}^\lambda\boldsymbol{u} = \boldsymbol{u}_i^+ - \boldsymbol{u}_j^- \quad \text{when} \quad \boldsymbol{R}_-^j - \boldsymbol{R}_+^i = \boldsymbol{b}_\lambda . \tag{11.33}$$

One notes that for any two bonds λ, λ', Eq. (11.32) gives

$$({}^\lambda\boldsymbol{u} - {}^{\lambda'}\boldsymbol{u}) \cdot \hat{\boldsymbol{s}} = 0 , \tag{11.34}$$

where

$$\hat{\boldsymbol{s}} = \begin{pmatrix} \cos\varphi \\ \sin\varphi \end{pmatrix} . \tag{11.35}$$

This shows that the deformation defined by Eqs. (11.32) is a general shear perpendicular to the direction $\hat{\boldsymbol{s}}$. For this shear each of the two sub-lattices – the "+" sub-lattice and the "−" sub-lattice separately – experiences a simple shear

$$(\boldsymbol{u}_i^+ - \boldsymbol{u}_j^+) \cdot \hat{\boldsymbol{s}} = (\boldsymbol{u}_i^- - \boldsymbol{u}_j^-) \cdot \hat{\boldsymbol{s}} = 0 , \qquad \boldsymbol{u}_i^+ - \boldsymbol{u}_j^+ = \boldsymbol{u}_i^- - \boldsymbol{u}_j^- \propto (\boldsymbol{R}_i - \boldsymbol{R}_j) \cdot \hat{\boldsymbol{s}} . \tag{11.36}$$

The overall macroscopic deformation of the honeycomb lattice is thus also a shear in this direction. It is however evident from Eqs. (11.32) that the relative motion of the bonded nearest neighbors is not described by this shear but is always perpendicular to the relevant bonds. One can also say that the deformation *inside* the unit cell – between the "+" and "−" sites in each cell – is non-affine, because it is not described by the affine shear transformation which describes the average deformation of the whole lattice. This non-affine response at short distances reduces the shear modulus, in this case to zero, and are responsible for the fact that one cannot use Eq. (5.24) to calculate the elastic constants of the honeycomb lattice.

11.5. The free vibrations of floppy periodic lattices

The formal procedure we used in Sections 11.2 and 11.3 above can be applied to all periodic bonded lattices. Quite generally a lattice with n atoms in the unit cell has nd DOF per cell and must be floppy when the number of bonds per cell, n_b, is smaller

$$n_\mathrm{b} < nd . \tag{11.37}$$

The dimension of the dynamical matrix for wave vector $\boldsymbol{q}$ – $\|\boldsymbol{K}_{\boldsymbol{q}}\|$ is nd. For a bonded Cauchy network (we assume Cauchy networks for simplicity, as in Eq. (10.8)) this matrix can always be written as a sum over the n_b *different* types of bonds λ:

$$\|\boldsymbol{K}_{\boldsymbol{q}}\| \sum_{\lambda=1}^{n_\mathrm{b}} \mathscr{K}_\lambda \cdot [\boldsymbol{b}_\lambda^{-\boldsymbol{q}}) * (\boldsymbol{b}_\lambda^{\boldsymbol{q}}] , \tag{11.38}$$

generalizing Eq. (11.12) and its rank is therefore at most n_b.

The free modes can be obtained from the solution of the n_b equations:

$$(\boldsymbol{b}_{\lambda}^{\boldsymbol{q}}][\boldsymbol{u}_{\boldsymbol{q}})_{\text{free}} = \boldsymbol{b}_{\lambda} \cdot \boldsymbol{u}_{\boldsymbol{q},\text{f}}^{\lambda} = 0 \tag{11.39}$$

for all the bonds as in Eq. (11.16).

Thus for the nearest neighbor diamond lattice one has two atoms per cell so that the dimension of $\boldsymbol{K}_q$ is 6 but there are only 4 nearest neighbor bonds in the four (1 1 1) directions. The rank of the six-dimensional matrix, $\boldsymbol{K}_q$, is therefore four. Two of the six phonon branches must have frequency zero over the whole Brillouin zone. One can show that these are the two transverse acoustic branches.

PART III. THE ROLE OF STRESSES IN AMORPHOUS SOLIDS

Amorphous solids do not represent global thermodynamic equilibrium. They are only locally stable and are never the global minimum energy states of their constituents. They are formed by processes which thwart the approach to true thermodynamic equilibrium. Because of this the random reference states of amorphous solids are determined by the specific history and are restricted only by local equilibrium and stability. The reference states of amorphous solids therefore tend to be much more tenuous than the tightly bound reference states of crystalline solids. The initial stresses in amorphous solids are also much larger and more ubiquitous.

The basic claim of our discussion in the following is that one cannot understand the mechanical properties of amorphous materials if one does not explicitly take into account the direct effect of stresses. For amorphous solids instabilities induced by stresses are important in the dynamics of the quenching processes which create the random reference state one observes. Stresses in the reference state also play an important role in the stability and nature of the basic vibrational eigenmodes of amorphous solids. This is of course dramatically different from the situation for crystalline solids for which the neglect of the effects of stresses on the linear bulk properties, the BH approximation, is essentially always justified.

We will support this claim by discussing the role of stresses in three main classes of amorphous solids:

1. *Soft matter* – solids which are not rigid at the microscopic molecular levels but only at larger scales in Section 14,
2. *Packings* of hard objects which only become rigid because of externally applied stresses in Section 15 and
3. *Glasses* produced by rapid quenching with purely internal quenched initial stresses in Section 16.

To do this we will use the formalism which we developed in Part I, in particular the distinction between the usual, Born–Huang (BH) terms in the harmonic expansion and elastic energy (Section 5) and the special stress-induced terms which describe the direct effect of stresses which we analyzed in Section 6 and the role of this distinction in the theory of floppy networks which we developed in Part II which gave us the tools for understanding the effects of initial stresses in tenuous solids. *Positive* stresses can *destabilize* sufficiently soft modes and cause structural buckling. On the other hand, *negative* stresses can *stabilize* such modes. However, to make the discussion more readable, we have attempted to make these discussions self-contained so they can be read without continuous reference to the earlier formal discussions.

Before discussing specific physical situations we must first discuss stress fields in solids and stressed reference states in a general way.

The stress fields in a solid are restricted by the conditions of *mechanical equilibrium*. We discuss this in Section 12. We describe the equilibrium conditions on the continuum stress fields in a solid and the microscopic equilibrium conditions on the bond tensions using the results of Sections 3 and 4. We also analyze the special restrictions which mechanical equilibrium imposes on the stressed reference states of floppy network models. We show that the *stressed* reference state of a floppy network is uniquely determined by the external forces and is the only equilibrium state in the geometric manifold to which it belongs.

In addition to requiring mechanical equilibrium we also require that the reference state of a solid is *stable*. In Section 13 we discuss the linear stability of stressed reference states from two points of view. We first discuss the requirement that the microscopic expansion around a stressed reference state is stable. On floppy networks this amounts to conditions on the signs of the bond tensions and of their distribution in the solid which assures that all the BH-free eigenmodes modes are stabilized by the direct effect.

We restrict most of our detailed discussion to the weaker requirement that the stressed solid is *completely rigid* – i.e., that it has shear rigidity everywhere and at all scales. Tenuous solids which do not have *complete* BH shear rigidity in this sense can nevertheless become completely rigid when there are enough negative initial stress fields.

In the rest of Part III we discuss three common classes of amorphous solids for whose mechanical properties the initial stresses are important.

In Section 14 we discuss the general structure of the theory of the mechanical properties of *soft solids* – extending and generalizing our earlier results on rubbers and gels (Alexander 1984, 1985). The main point of this discussion is that the shear rigidity of soft solids is due to negative network stresses and not to a standard BH shear modulus. Soft matter is described by models which are *macroscopically floppy* and can even have no geometric shear rigidity at any length scale. Unstressed reference states would have no significant shear rigidity. The observed macroscopic shear rigidity is due to negative initial stresses. We show that this is possible only because soft solids are free-energy solids. They are not rigid at the atomic level and can be described as solid only at larger scales by a partially averaged parametrized free energy.

The two other situations we discuss are situations where *structural buckling* is important in the evolution of the reference state.

In Section 15 we discuss random packings of rigid objects with purely repulsive interactions. The more obvious realizations are granular materials and models such as the Princen model for bubbles (Levine et al., 1996) and the solidification of hard spheres. Such materials only solidify under positive external pressure and have no static shear modulus when no positive initial stresses are applied. In a packing the BH interactions responsible for its shear modulus are induced by the stress. A packing can have stable shear rigidity only when these induced BH interactions are numerous enough and strong enough to overcome the destabilizing tendency to buckling – the *direct* effect of the same stresses. We discuss the implications of this balance for the structure of the reference state of packings.

In Section 16 we discuss *glasses*. The main point of this discussion is that we treat the low temperature glass as a Cauchy–Born solid whose properties can be described by the expansion around a quenched reference state. We assume that rapid quenching suppresses rearrangements by single particle diffusion states. The dominant restructuring process responsible for the formation of the stable equilibrium reference state of the low-temperature glass is then structural buckling driven by quenched internal stresses. We discuss the implications for the properties of the expansion around a stressed reference state which is produced in this way. We show that some of the most striking universal low temperature peculiarities of glasses appear naturally.

Internal stresses are complex and in amorphous solids it is not practical to try to derive them from structural singularities as commonly done for crystals. We therefore analyze the implications of the mechanical equilibrium conditions for the stresses directly. We derive some important general properties. We also show how dislocations and disclinations appear in this rather unconventional formalism in which the stresses are regarded as the primary fields and the structural strains do not show up. This is the content of Section 17.

12. Equilibrium in stressed reference states

12.1. Initial stresses

12.1.1. Initial network stresses

Following Love (1927) we shall call the stresses in the stressed reference state of a solid *initial network stresses.* They are properties of the expansion of the energy around a stressed reference state. As we showed in Section 4 the *initial network stresses* can be calculated from the initial bond tensions in the reference state just as the elastic constants can be calculated from the coefficients in the BH expansion around it.

Since the network stress is not always the only stress in the volume occupied by a solid we emphasize the distinction between the *network* stresses, which are properties of the reference state and the *total* stress in Part III.

12.1.2. External stresses

Stresses can always be described as the sum of *external* stresses which are induced by *external forces* acting on the solid and disappear when these forces are removed and purely *internal* stresses which cannot be attributed to such forces and are quenched into the reference state by its preparation history. Truely external forces can be the cause of initial stresses. Examples are, gravitational forces, the effect of large external pressures on a solid under geophysical conditions and the forces on the boundaries of a string or drumhead.

The stresses are not always fully described by the network stresses one calculates from the bond tensions. When there are additional contributions to the total stress besides the network stress their effect is external to the network and they generate a *network stress* which is *external* even when there is no external contribution to the total stress. An example is the fluid “osmotic pressure” in a gel which balances the (external) network pressure of the stretched polymeric chains. Another example is the “stretched square foam” model discussed in Section 8.1.3.

12.1.3. Internal stresses

A different type of initial stresses are *internal stresses* (Love, 1927a, Section 75) which do not require any external balancing forces.

The true minimum energy state of a solid is not stressed. The energy of a solid can always be reduced by removing the stresses. Internal stresses are therefore always the result of the specific preparation history of the material. They are almost inevitably related to structural singularities in the reference state and are therefore properties of *quenched reference states.*

Internal stresses are also ubiquitous.

Even single crystals to which no external forces are applied have complex internal stress fields associated with the defects in their periodic structure. There are the internal stress fields of point defects – vacancies, interstitials, etc.; the internal stress fields of the Frank network of dislocations (Friedel, 1964, ch. VIII; Landau and Lifshitz, 1970, ch. IV) and those due to planar defects – grain boundaries and twinning planes.[49]

In amorphous non-crystalline solids the internal stresses cannot be related to structural defects in such a straightforward way but the actual equilibrium states are also stressed. This is particularly true for glasses because quenching plays an essential role in the preparation of their reference states.

12.2. Equilibrium conditions for the stress field

An initial stress field, $\sigma(\boldsymbol{r})$, is subject to the requirement that the stressed reference state is an equilibrium state. It must satisfy the requirements of mechanical equilibrium in the bulk

$$\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\boldsymbol{r})=-\boldsymbol{f}_{\mathrm{bulk}}(\boldsymbol{r})\,,\qquad \sum_{\alpha}\partial_{\alpha}\sigma_{\alpha\beta}=-f_{\beta}\,, \tag{12.1}$$

where $\boldsymbol{f}_{\mathrm{bulk}}(\boldsymbol{r})$ is the external force density per unit volume acting at the point $\boldsymbol{r}$ in the bulk. It must also satisfy the boundary conditions

$$\hat{\boldsymbol{n}}(\boldsymbol{r}_{\mathrm{b}})\cdot\boldsymbol{\sigma}(\boldsymbol{r}_{\mathrm{b}})=-\boldsymbol{f}_{\mathrm{bound}}(\boldsymbol{r}_{\mathrm{b}})\,,\qquad \sum_{\alpha}n_{\alpha}(\boldsymbol{r}_{\mathrm{b}})\sigma_{\alpha\beta}(\boldsymbol{r}_{\mathrm{b}})=f_{\beta}(\boldsymbol{r}_{\mathrm{b}})\,, \tag{12.2}$$

where $\boldsymbol{n}(\boldsymbol{r}_{\mathrm{b}})$ is an outward pointing unit vector normal to the boundary and $\boldsymbol{f}(\boldsymbol{r}_{\mathrm{b}})$ the force per unit area acting on the boundary at the point $\boldsymbol{r}_{\mathrm{b}}$ on the boundary.[50]

As equations for determining the stress field, the equilibrium conditions (12.1) and (12.2) are incomplete. They do not fully determine the stress field. There are only d equations (and d boundary conditions) for the $\frac{1}{2}d(d+1)$ components of the stress tensor in d dimensions. The equations are only completed when one adds the material properties, typically via the stress–strain relations,

$$\sigma^{\alpha\beta}(\boldsymbol{r})=\boldsymbol{K}^{\alpha\beta\gamma\delta}(\boldsymbol{r})\cdot e^{\gamma\delta}(\boldsymbol{r}) \tag{12.3}$$

to the equations for the stress.

One result of this is that the homogeneous equations

$$\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}^{\mathrm{int}}(\boldsymbol{r})=0 \tag{12.4a}$$

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[49] Friedel (1964, ch. 2, Section 2.2) shows that the internal stresses can be related to a distribution of dislocations when the stress–strain relations are added to close the equations.

[50] For simplicity we omit the equilibrium conditions for the torques which should be added to (12.2).

in the bulk and

$$\hat{\boldsymbol{n}} \cdot \boldsymbol{\sigma}^{\mathrm{int}}(\boldsymbol{r}) = 0 \tag{12.4b}$$

on the surface have a family of non-trivial solutions which describe *internal* stresses.

Since the equilibrium equations are linear their solutions can always be written as the sum of a regular special solution which satisfies the inhomogeneous equations (12.1) and (12.2) and an *internal* stress field which satisfies (12.4).

12.3. The microscopic equilibrium conditions

The equilibrium conditions for the stress field, Eqs. (12.1) and (12.2), are the continuum limit of the local microscopic equilibrium conditions

$$\sum_j \frac{\mathscr{T}_{ij}}{|\boldsymbol{R}_i - \boldsymbol{R}_j|} (\boldsymbol{R}_i - \boldsymbol{R}_j) = -\boldsymbol{f}_i^{\mathrm{ext}} \tag{12.5}$$

at all sites i (Eq. (3.23)). Both the bulk continuum equations (12.1) and the bulk boundary conditions (12.2) arise from the continuum limit of Eqs. (12.5).

Like the continuum equations for the stress fields the discrete microscopic equations are also incomplete. For N particles the Nd equations (12.5) cannot determine both the $\mathscr{n}_{\mathrm{b}}$ bond tensions, $\mathscr{T}_{ij}$, and the Nd components of the positions, $\boldsymbol{R}_i$. One gets a complete set of defining equations only when one supplements Eqs. (12.5) by the $\mathscr{n}_{\mathrm{b}}$ defining equations for the bond tensions, Eqs. (3.28)

$$\mathscr{T}_{ij}(\{\boldsymbol{R}\}) = \mathscr{T}_{ij}(\{\boldsymbol{R}_{\mathrm{bond}}\}) = \left[\frac{\partial \mathscr{E}(\{\boldsymbol{r}\})}{\partial \boldsymbol{r}_{ij}}\right]_{\{R_{\mathrm{bond}}\}} \tag{12.6}$$

which also relate the same variables. In general the solution of this combined set of equations is unique.

In this form this is quite general. In the continuum theory of elasticity one achieves the same result by "closing" the continuum equations by adding the linear stress–strain relations, Eq. (12.3). In contrast to Eqs. (12.6) this procedure assumes an unstressed underlying reference state with respect to which the strains and elastic constants can be defined. Our microscopic formulation is not subject to such restrictions.

12.4. Uniqueness of stressed equilibrium states of floppy networks

We saw that for models defined on floppy networks all the states belonging to the manifold of free DOF, $\mathscr{A}(\{R_{\mathrm{bond}}\})$, have the same energy, $\mathscr{E}(\{R\}_{\mathrm{bond}})$. They also all have the same bond tensions for all the bonded pairs $[ij]$. One can therefore define a set of *initial* bond tensions

$$\{\mathscr{T}_{\mathrm{ini}}\} = \{\ldots, \mathscr{T}_{\mathrm{ini}}^{ij}, \ldots\} = \{\mathscr{T}_{\mathrm{ini}}\}(\{R\}_{\mathrm{bond}}) \tag{12.7}$$

which is *common* to the whole manifold $\mathscr{A}(\{R_{\mathrm{bond}}\})$. Different points of $\mathscr{A}(\{R_{\mathrm{bond}}\})$ describe different geometrical states of the network but the bond tensions are the same for all of them.

This result holds for any manifold. It applies to stressed manifolds for which $\mathscr{T}_{ij} \neq 0$ for some of the bonds just as it applies to unstressed BH manifolds for which the bond tensions all vanish:

$\mathcal{T}_{ij} \equiv 0$. In this sense all the states which are consistent with the bonded distances, $\{R_{\text{bond}}\}$, are always equivalent and this equivalence is not affected by the fact that the initial bond lengths describe a stressed state for which the tensions do not vanish. But this does not mean that the states of the manifold are all equilibrium states.

12.4.1. Unstressed BH reference state are degenerate

For an unstressed BH manifold, $\mathcal{A}^{\text{BH}}(\{R_{\text{bond}}\})$, the mechanical equilibrium conditions, Eq. (12.5), are trivial. By definition there are no external forces and no bond tensions in $\{\boldsymbol{R}\}_{\text{BH}}$ and therefore, in equilibrium, no forces on the particles.

$$\mathcal{T}_{ij} \equiv 0 \Rightarrow f_{ij} \equiv 0 ; \qquad f_i^{\text{ext}} \equiv 0 .$$

All the states belonging to a BH manifold are automatically equilibrium states.

All the states in a BH manifold can therefore, in principle, appear as reference states. As we have shown in Section 10 they can also transform into each other freely via the free eigenmodes of the unstressed floppy network which correspond to its geometrical FDOF. Because of this the properties of such reference states can be quite strange. They do not even necessarily describe microscopically rigid solids – this depends on the specifics of the problem and on the anharmonicities.[51]

12.4.2. Stressed equilibrium states are unique

The equivalence of all the states on the manifold $\mathcal{A}(\{R_{\text{bond}}\})$ disappears when one considers the mechanical equilibrium conditions of stressed states.

For stressed manifolds mechanical equilibrium is no longer automatic. When there are initial bond tensions the general condition for mechanical equilibrium is that there are no net forces at any site. All atoms must be in equilibrium – Eq. (12.5). This is a set of N vectorial equations which depends on the specific vectors $\boldsymbol{R}_{ij}$ and therefore on the specific arrangement of the N points in space, $\{\boldsymbol{R}\}$. This arrangement is different for each state in $\mathcal{A}(\{R_{\text{bond}}\})$. The external forces $\boldsymbol{f}_i^{\text{ext}}$ which, for a given set of bond tensions $\{\mathcal{T}_{\text{bond}}\}$, assure equilibrium for the state $\{\boldsymbol{R}\}$ will, in general, not assure equilibrium for another state which belongs to the same manifold $\{\boldsymbol{R}'\}$. The fact that $\{\boldsymbol{R}'\}$ and $\{\boldsymbol{R}\}$ belong to the same manifold $\mathcal{A}(\{R_{\text{bond}}\})$ and therefore have the same bond tensions $\{\mathcal{T}_{\text{bond}}\}$ is not sufficient to assure that they are both equilibrium states.

The external forces are

$$\{\boldsymbol{f}^{\text{ext}}\} = \{\boldsymbol{f}_1^{\text{ext}}, \boldsymbol{f}_2^{\text{ext}}, \ldots, \boldsymbol{f}_i^{\text{ext}}, \ldots, \boldsymbol{f}_N^{\text{ext}}\} . \tag{12.8}$$

We assume that the network is in equilibrium in the reference state $\{\boldsymbol{R}\}$ so that

$$\sum_{\text{bonds}} \frac{\mathcal{T}_{ij}}{R_{ij}} \boldsymbol{R}_{ij} = -\boldsymbol{f}_i^{\text{ext}} , \quad \boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j \tag{12.9}$$

for all i. If another equilibrium state say $\{\boldsymbol{R}'\}$ is also an equilibrium state the equilibrium conditions

$$\sum_{\text{bonds}} \frac{\mathcal{T}_{ij}}{R_{ij}} \boldsymbol{R}'_{ij} = \sum_{\text{bonds}} \frac{\mathcal{T}_{ij}}{R_{ij}} (\boldsymbol{R}_{ij} + \boldsymbol{u}_{ij}) = -\boldsymbol{f}_i^{\text{ext}} \tag{12.10}$$

---

[51] Depending on the detailed structure unstressed floppy reference states can, e.g., have a secondary non-linear buckling instability with respect to the formation of internal stress fields. Alternatively a macroscopically floppy network can also describe a rheological fluid which utilizes "free" collective shear modes to flow in response to applied shear stresses.

must also hold. If $\{\boldsymbol{R}'\}$ belongs to the same manifold it has the same bonded distances and therefore also satisfies

$$|\boldsymbol{R}'_{ij}| = |\boldsymbol{R}_{ij} + \boldsymbol{u}_{ij}| = |\boldsymbol{R}_{ij}| = R_{ij} \tag{12.11}$$

for all the $\mathscr{n}_{\mathrm{b}}$ bonded pairs.

Since

$$\boldsymbol{u}_{ij} = \boldsymbol{u}_i - \boldsymbol{u}_j$$

Eqs. (12.10) and (12.11) can be written as a set of $Nd + \mathscr{n}_{\mathrm{b}}$ homogeneous equations for the Nd components of the $\boldsymbol{u}_i$. Subtracting Eq. (12.9) from Eq. (12.10) gives Nd equations

$$\sum_j \frac{\mathscr{T}_{ij}}{R_{ij}} \boldsymbol{u}_{ij} = 0 \tag{12.12}$$

– the conditions that $\{\boldsymbol{R}\}$ and $\{\boldsymbol{R}'\}$ $(=\{\boldsymbol{R}+\boldsymbol{u}\})$ are both equilibrium states for the same set of external forces.[52] In addition Eqs. (12.11) amount to $\mathscr{n}_{\mathrm{b}}$ non-linear homogeneous equations

$$(2\boldsymbol{R}_{ij} + \boldsymbol{u}_{ij})\boldsymbol{u}_{ij} = 0 \tag{12.13}$$

one for each bond. Altogether there are thus

$$\mathscr{n}_{\mathrm{b}} + Nd \tag{12.14}$$

homogeneous equations, (12.12) and (12.13), for the Nd components of the $\boldsymbol{u}_i$. This over-determined set of homogeneous equations can have non-zero solutions only in exceptional cases.

We have thus demonstrated that, in general, the equilibrium state is unique. The set of external forces $\{\boldsymbol{f}_i^{\mathrm{ext}}\}$ picks out a *unique* state $\{\boldsymbol{R}\}$ which is the only equilibrium state on the manifold, $\mathscr{A}(\{R_{\mathrm{bond}}\})$ for this particular choice of forces. The other states which belong to the same manifold $\mathscr{A}(\{R_{\mathrm{bond}}\})$ have the same energy

$$\mathscr{E}(\{\boldsymbol{R}'\}) = \mathscr{E}(\{\boldsymbol{R}\}) = \mathscr{E}(\{R_{\mathrm{bond}}\})$$

but are not equilibrium states. One needs a *different* set of forces $\{\boldsymbol{f}'^{\mathrm{ext}}\}$ to assure equilibrium in each state of the manifold, $\{\boldsymbol{R}'\}$. Thus the high degeneracy which characterized the reference states of floppy bonded networks disappears when the reference state is stressed.

We have not explicitly distinguished external and internal stresses in the above discussion but, obviously, the argument also applies when the external forces, $\{\boldsymbol{f}^{\mathrm{ext}}\}$, all vanish and the stress field is therefore purely internal but does not vanish.

To avoid misunderstanding we emphasize that this result does not imply that the internal stress field itself is unique. Different solutions of the continuum equations (12.1) and (12.2) with the same boundary conditions and the same external forces correspond to different solutions of the microscopic equations (12.5). All we have shown is that these different stress fields not only differ in their equilibrium configurations but *always* also in their bonded equilibrium distances

$$\{\boldsymbol{R}\} \neq \{\boldsymbol{R}'\}, \qquad \{R_{\mathrm{bond}}\} \neq \{R'_{\mathrm{bond}}\}. \tag{12.15}$$

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[52] Evidently the $\boldsymbol{u}_i$ are not necessarily small in these equations which relate any two equilibrium states on the manifold.

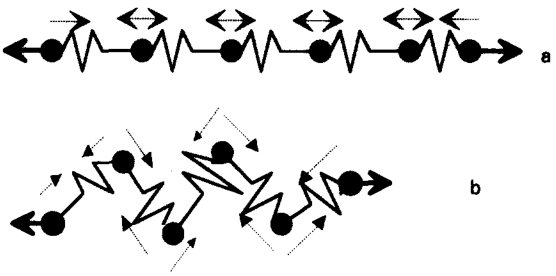

Fig. III.1. The two configurations shown have the same elastic energy $\mathscr{E}(\{r\})$ and the same bond tensions, $\mathscr{T}_{ij}$ but only the stretched configuration, *a*, is an equilibrium configuration.

They therefore belong to different manifolds even when the external forces $\{f'^{\text{ext}}\}$ and the energy $\mathscr{E}(\{r\})$ are identical. We have shown that on each of the (microscopic) manifolds, $\{R_{\text{bond}}\}, \{R'_{\text{bond}}\}, \ldots$ there is a unique equilibrium reference state.

12.4.2.1. Examples. A simple example is a linear chain of springs as in Fig. III.1. When forces are applied at the ends of the straight chain, as in III.1.a in the figure, all the separate springs are stretched and aligned. This is obviously an equilibrium configuration.

The energy of this equilibrium state is the sum of the energies of the separate springs, and therefore depends only on the distances between their ends $r_{i,i+1}$. In configuration III.1.b these distances remain the same and the energy is thus not changed.

The configurations *a* and *b* belong to the same manifold as *a* and have the same energies and the same bond tensions. However, obviously, *b* does not describe an equilibrium state when the strings are stretched and exert forces at their ends. The two configurations are equivalent equilibrium configurations only in the unstretched BH limit.

We have seen another somewhat less trivial example of this in our discussion of the square foam in Section 8.1. As discussed in detail in Section 8.1.3 the "external forces" in this example are the forces exerted by the pressure of the fluid in the cells on the outer vertices of the lattice. The network energy, the energy of the springs which constitute the network, is the same for all the continuum of configurations in the manifold of the square lattice but the internal pressure, the volume constraint, picks out the square lattice in which all the cells have their maximum volume. This is the unique reference state in the manifold[53] which minimizes the total energy – the energy of the stressed network plus the energy of the compressed fluid in the cells.

Something similar happens in other cases. Thus Panyukov and Rabin (1996) find by an explicit analysis of random polymeric network gel models that the reference state is uniquely determined by the chemically quenched crosslinking structure of the network.[54]

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[53] We note that in this example the origin of the "external" forces is internal – the pressure of the fluid in the cells. As a result one retains translation–rotation symmetry for the stressed reference states.

[54] I am grateful to Drs. Panyukov and Rabin for making me aware of this result and explaining it to me.

13. Stress-induced stability of floppy networks

We now want to discuss the linear stability of the reference state. If we assume, as usual, that the BH dynamical matrix is stable this becomes a condition on the stress field which can destabilize soft, or free modes or, if the network is floppy, stabilize the free modes. This obviously depends on the way the stress field is related to the BH rigidity of the reference state.

In the following we shall only discuss the effects of stresses on the free modes of floppy networks. We believe this is more translucent and focuses attention on the importance of soft collective modes in tenuous solids.[55]

We saw in Section 10 that the floppy eigenmodes have no harmonic force constants in the BH approximation, that is as long as the direct effect of the stresses on the harmonic expansion is neglected. The stability of the vibrational modes which correspond to the FDOF of a geometrically floppy network is determined by the initial stresses. The force constants of these modes are determined completely by the relevant initial bond tensions. The linear stability of the stressed reference state is a requirement on the initial bond tensions, $\mathscr{T}_{ij}^{\text{ini}}$, and on the way they are related to the reference state – separate from the equilibrium conditions – Eqs. (12.5).

We want to discuss these conditions.

13.1. Stability of the microscopic free modes

The special stress induced contribution to the harmonic expansion which describes the direct effect of the stresses is

$$\mathscr{P}_{\text{scalar}} = \frac{1}{4}\sum_{ij}\frac{\mathscr{T}_{ij}}{R_{ij}}u_{ij}^2 \tag{13.1}$$

– Eq. (6.13). The continuum limit of (13.1) is the contribution of the second order strain, $e_{\alpha\beta}^2 = -\frac{1}{2}\sum_\gamma \partial_\alpha u_\gamma \partial_\beta u_\gamma$, to the elastic energy

$$\mathscr{P}^{\text{elastic}} = -\frac{1}{4}\int d\boldsymbol{r}\cdot\sum_{\alpha\beta\gamma}\sigma_{\text{ini}}^{\alpha\beta}(\boldsymbol{r})\cdot\partial_\alpha u_\gamma(\boldsymbol{r})\cdot\partial_\beta u_\gamma(\boldsymbol{r}) \tag{13.2}$$

– Eq. (6.20).

Eqs. (13.1) and (13.2) describe the terms in the expansion around a stressed reference state which are qualitatively different. These terms are responsible for the effects of the stresses on the linear stability of the stressed reference state.

Eq. (13.1) can be written in the form

$$\mathscr{P}_{\text{scalar}} = (\boldsymbol{u}]\|\boldsymbol{K}^{\mathscr{P}}(\{\mathscr{T}\})\|[\boldsymbol{u})\,. \tag{13.3}$$

We saw in Section 10 that when $\boldsymbol{K}^{\mathscr{P}}$ is added to the BH dynamical matrix

$$\|\boldsymbol{K}^{\text{BH}}\| \Rightarrow \|\boldsymbol{K}\| = \|\boldsymbol{K}^{\text{BH}}\| + \|\boldsymbol{K}^{\mathscr{P}}(\{\mathscr{T}\})\| \tag{13.4}$$

---

[55] The question when a realistic model can be adequately approximated by a floppy network, how one should check this and how one should go about the construction of such a floppy network goes beyond the scope of our discussion here.

the geometrically free degrees of freedom of floppy networks are no longer dynamically free. When the stresses are neglected the force constants, κ_{free}, which correspond to the free DOF of the floppy network must vanish. When the reference state is stressed they can be finite and, moreover, can have either sign. The stressed reference state is stable when

$$\kappa^{\alpha}_{\text{free}} > 0 \tag{13.5}$$

for all the free eigenmodes. We are interested in the conditions which assure this.

The reason for the qualitative change when the direct effect of the initial stresses is included is that the projection of $\boldsymbol{K}^{\mathscr{P}}(\{\mathscr{T}\})$ into the free subspace, $[\mathscr{U}]_{\text{free}}$,

$$\|\boldsymbol{K}_{\text{free}}\| = \|\boldsymbol{K}^{\mathscr{P}}_{\text{free}}\|(\{\mathscr{T}\}) \tag{13.6}$$

does not vanish. These are the only terms of the total dynamical matrix in this subspace.

For small bond tensions it is sufficient to consider the eigenvalue equation in the free subspace[56]

$$\|\boldsymbol{K}_{\text{free}}\|[\boldsymbol{u}^{\alpha})_{\text{free}} = \kappa^{\alpha}_{\text{free}}[\boldsymbol{u}^{\alpha})_{\text{free}}\,. \tag{13.7}$$

The force constants of the free modes, $\kappa^{\alpha}_{\text{free}}$, the eigenvalues of $\boldsymbol{K}_{\text{free}}$, depend on the specific set of bond tensions $\{\mathscr{T}\}_{\text{bond}}$. In particular their signs depend on the signs of the $\mathscr{T}_{ij}$. If we change the signs of all the bond tensions

$$\{\mathscr{T}\}_{\text{bond}} \Rightarrow -\{\mathscr{T}\}_{\text{bond}}$$

then the signs of the $\kappa^{\alpha}_{\text{free}}$ will also reverse.

$$\kappa^{\alpha}_{\text{free}}\{\mathscr{T}\} = -\kappa^{\alpha}_{\text{free}}\{-\mathscr{T}\}$$

The limiting cases are simple:

(1) If all the bonds are stretched so that

$$\mathscr{T}_{ij} > 0 \tag{13.8}$$

for all the bonds then all the $\kappa^{\alpha}_{\text{free}}$ are also positive

$$\kappa^{\alpha}(\{\mathscr{T}_{\text{bond}}\}) \geq 0 \tag{13.9}$$

and the stressed reference state is therefore stable.

The inequality (13.8) also implies that the bonds cannot *push* the boundaries. Like stretched strings and drumheads a stretched *three-dimensional bulk solid* exerts a *pull* on all its boundaries. The external forces on the boundaries which balance these network forces, Eq. (12.2), have to be stretching forces directed outward.

Following standard conventions this corresponds to a *negative* network pressure in the continuum limit or, more generally, to negative network stresses[57] for which the principal axis components of the stress are all negative

$$\sigma^{\alpha\alpha} < 0\,. \tag{13.10}$$

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[56] The other parts of $\boldsymbol{K}^{\mathscr{P}}$ only have higher order effects.

[57] We use a sign convention in which the pressure has the same sign as the trace of the stress tensor.

(2) The converse of (13.8) – negative bond tensions

$$\mathcal{T}_{ij} < 0 \tag{13.11}$$

imply instability

$$\kappa^{\alpha}(\{\mathcal{T}_{\text{bond}}\}) \leq 0 \tag{13.12}$$

for *all* the free eigenmodes.

The network stresses are then *positive*

$$\sigma^{\alpha\alpha} > 0 \tag{13.13}$$

and exert forces on the boundaries which are directed outward. For bulk solids this situation is easier to realize. It describes, e.g., situations where a *positive* external compressing stress is applied.

13.2. General stability conditions

In principle one would like to determine the conditions on the microscopic set of initial bond tensions $\{\mathcal{T}_{\text{bond}}\}$ or on the stress fields, which assure that all the eigenmodes in the stressed reference state are stable. It is however difficult to formulate any general conditions for stability in terms of the $\mathcal{T}_{ij}$ themselves.

The inequality (13.8) is *sufficient* to assure stability but is much too restrictive. To see this we note that a floppy network need not be floppy everywhere. The network can be floppy and still contain parts which, on their own, are BH rigid and can therefore support considerable negative bond tensions and positive stresses. The network can nevertheless contain other regions which are floppy. Thus, in general, the overall stability of a floppy network is consistent with having some negative bond tensions. The argument shows that a full stability criterion must depend on the detailed bond structure and on the actual distribution of the bond tensions in the network. It cannot simply be a condition on the numbers of positive and negative tensions.

Instead of attempting to analyze this very complex problem we will discuss the direct effect of the stresses from a continuum point of view. We shall look for criteria which assure that all regions of the solid have shear rigidity on their own. For regions which have no BH shear rigidity this requires suitable negative stabilizing stresses. Implicitly this assumes averaging over regions which are large enough so that one can define smooth position dependent stresses and elastic constants and that the expansion in the shears, $\partial_{\alpha}u_{\beta}$, the gradient expansion in the deviations, makes sense. Roughly this means that we will loose the information on very local floppiness – on scales comparable to the lengths of the bonds.

13.3. Stress-induced macroscopic shear rigidity

We first consider solids which are described by macroscopically floppy networks and have macroscopic shear rigidity which the unstressed network does not have. We called this macroscopic floppiness in Section 7. We described several examples in Section 8.

13.3.1. Macroscopic floppiness

In Section 7.3.2 we defined macroscopic floppiness (MaF) as a property of floppy networks. A solid which is described by a MaF network has no shear rigidity in the BH approximation.[58] It can only exhibit macroscopic shear rigidity when there are initial stresses. A familiar example of such a network is the square lattice – Section 8.1. We want to formulate this a little more precisely.

Macroscopic shear rigidity describes the response of the elastic energy to deformations which shear the boundary of the solid. Two points on the boundary, $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, move so that

$$u_\beta(\boldsymbol{r}_1) - u_\beta(\boldsymbol{r}_2) = \sum_\alpha (\boldsymbol{r}_1 - \boldsymbol{r}_2)_\alpha \cdot \overline{\partial_\alpha u_\beta}\,, \tag{13.14}$$

where $\overline{\partial_\alpha u_\beta}$ is the average shear

$$\overline{\partial_\alpha u_\beta} = \frac{1}{V}\int \mathrm{d}\boldsymbol{r} \cdot \partial_\alpha u_\beta(\boldsymbol{r})\,. \tag{13.15}$$

The average linear strain and the average second order strain which are relevant to the macroscopic rigidity are both defined in terms of these average shears

$$\overline{e^1_{\alpha\beta}} = \tfrac{1}{2}\left(\overline{\partial_\alpha u_\beta} + \overline{\partial_\beta u_\alpha}\right), \tag{13.16}$$

$$\overline{e^2_{\alpha\beta}} = \frac{1}{2}\sum_\gamma \overline{\partial_\alpha u_\gamma} \cdot \overline{\partial_\beta u_\gamma}\,. \tag{13.17}$$

When a solid is macroscopically floppy and has no macroscopic BH shear rigidity this means that the coefficients in the expansion in the average shears

$$\bar{\mu} \cdot \overline{e^1_{\alpha\beta}}^{\,2} = \tfrac{1}{4} \cdot \bar{\mu} \cdot \left(\overline{\partial_\alpha u_\beta} + \overline{\partial_\beta u_\alpha}\right)^2 \tag{13.18}$$

must vanish

$$\bar{\mu} = 0\,. \tag{13.19}$$

Eq. (13.19) defines macroscopic floppiness (MaF).

We recall that the coefficient in (13.18), the macroscopic shear modulus $\bar{\mu}$, is not the volume average of the local shear modulus. In general

$$\bar{\mu} \le \langle \mu \rangle = \frac{1}{V}\int \mathrm{d}\boldsymbol{r} \cdot \mu(\boldsymbol{r})\,.$$

Equality holds only when the deformation is uniform:

$$\partial_\alpha u_\beta(\boldsymbol{r}) = \overline{\partial_\alpha u_\beta} \tag{13.20}$$

which requires that $\mu(\boldsymbol{r})$ is constant. For a macroscopically floppy network this can happen only when the solid is uniformly floppy so that

$$\bar{\mu} = \langle \mu \rangle = \mu(\boldsymbol{r}) \equiv 0\,. \tag{13.21}$$

---

[58] For convenience we only mention the transverse shears which clearly distinguish solids from fluids. In considering the longitudinal strains $\partial_\alpha u_\alpha$, one obviously has to distinguish between the volume change and the traceless shear strains.

13.3.2. Affine shears

If we shear a uniformly floppy solid affinely, Eq. (13.20), then the stress-induced macroscopic elastic energy is

$$\mathscr{E} = -\mathscr{V} \sum_{\alpha\beta} \overline{\boldsymbol{\sigma}}_{\text{ini}}^{\alpha\beta} \sum_{\gamma} \overline{\partial_\alpha u_\gamma} \cdot \overline{\partial_\beta u_\gamma} \tag{13.22}$$

or, in the principal axis system of the average stress

$$\mathscr{E} = -\mathscr{V} \sum_{\alpha} \overline{\boldsymbol{\sigma}}_{\text{ini}}^{\alpha\alpha} \sum_{\gamma} (\overline{\partial_\alpha u_\gamma})^2 \,. \tag{13.23}$$

The condition for stress-induced stability of the macroscopic shears is obviously

$$\overline{\boldsymbol{\sigma}}_{\text{ini}}^{\alpha\alpha} < 0 \,. \tag{13.24}$$

More precisely, if a shear normal to the α direction, say $\partial_\alpha u_\gamma$, is BH floppy

$$\overline{D^{\alpha\gamma\alpha\gamma}} = 0$$

then the linear stability of these shears in the stressed state requires that the component of the initial stress in this direction, $\overline{\boldsymbol{\sigma}}_{\text{ini}}^{\alpha\alpha}$, is negative. If any component of the average stress – say $\overline{\boldsymbol{\sigma}}_{\text{ini}}^{\beta\beta}$ – is positive then the coefficient of $\overline{\partial_\beta u_\gamma}^2$ in Eq. (13.23) is negative and the shears $\overline{\partial_\beta u_\gamma}$ are destabilized by the stress. If the BH shear modulus for these shears vanishes then they are linearly unstable in the stressed state.

If, in particular, the solid has no BH shear rigidity at all, Eq. (13.19), then the stressed reference state is macroscopically stable only if the inequality (13.24) holds for all principal axis components of the average stress. This is a condition on the average stress. All the principal axis components of the average stress must be *negative*. We shall call such a stress a *negative* stress.

A negative stress cannot be a pure traceless, shear stress because

$$\operatorname{Tr} \sigma = \sum \overline{\boldsymbol{\sigma}^{\alpha\alpha}} = 0$$

implies that at least one principal axis component is positive. The inequality (13.24) implies a negative initial network pressure

$$\overline{p}_{\text{net}} = \frac{1}{d} \sum \overline{\boldsymbol{\sigma}_{\text{ini}}^{\alpha\alpha}} < 0 \tag{13.25}$$

which is large enough to assure that (13.24) holds for all components.

The normal force exerted by a stress on a surface is

$$\boldsymbol{f} \cdot \boldsymbol{n} = \sum_{\alpha} \boldsymbol{\sigma}^{\alpha\alpha} \cdot \hat{n}_\alpha^2 \,,$$

where $\hat{\boldsymbol{n}}$ is the outward pointing unit vector normal to the surface. A negative average network stress exerts an inward pull on all the boundaries of the solid. Since these pulling forces must be balanced in equilibrium one needs some external forces, distinct from those exerted by the network itself, for mechanical equilibrium. These forces can either pull on the boundaries, from *outside*, or push on them from *inside*. A macroscopically floppy network can have stress induced rigidity only when it is exposed to such stretching forces. The external forces which act across the boundary determine the average stress

$$\bar{\boldsymbol{\sigma}}_{\text{ini}} = \left(\frac{1}{2\mathscr{V}}\right) \int_{\text{boun}} [\boldsymbol{f}_{\text{ini}}(\boldsymbol{r}) * \boldsymbol{r} + \boldsymbol{r} * \boldsymbol{f}_{\text{ini}}(\boldsymbol{r})]\,\mathrm{d}s \tag{13.26}$$

as in Eq. (4.12).

13.3.3. Non-affine shears

When the solid is not homogeneous fluctuations can be important. These show up in Eq. (13.2) in two ways:

(a) The initial stress field need not be uniform

$$\boldsymbol{\sigma}_{\text{ini}}(\boldsymbol{r}) = \bar{\boldsymbol{\sigma}}_{\text{ini}} + \delta\boldsymbol{\sigma}_{\text{ini}}(\boldsymbol{r}) \tag{13.27}$$

In addition

(b) the response to deformations of the boundary need not be affine

$$\partial_\alpha u_\beta(\boldsymbol{r}) = \overline{\partial_\alpha u_\beta} + \delta_{\alpha\beta}(\boldsymbol{r})\,. \tag{13.28}$$

Substitution into (13.2) gives the corrections to the affine elastic energy (13.23)

$$\delta\mathscr{E} = -\sum \bar{\boldsymbol{\sigma}}_{\text{ini}}^{\alpha\alpha} \int \delta_{\alpha\gamma}^2\,\mathrm{d}\boldsymbol{r} - \sum \overline{\partial_\alpha u_\gamma} \int \delta\boldsymbol{\sigma}_{\text{ini}}^{\alpha\beta}\delta_{\beta\gamma}\,\mathrm{d}\boldsymbol{r} - \int \mathrm{d}\boldsymbol{r} \sum \delta\boldsymbol{\sigma}_{\text{ini}}^{\alpha\beta}\delta_{\alpha\gamma}\delta_{\beta\gamma} \tag{13.29}$$

which determines the deviation field $\delta_{\alpha\beta}(\boldsymbol{r})$. Evidently a uniform initial stress

$$\boldsymbol{\sigma}_{\text{ini}}(\boldsymbol{r}) = \bar{\boldsymbol{\sigma}}_{\text{ini}}\,, \qquad \delta\boldsymbol{\sigma}_{\text{ini}}(\boldsymbol{r}) \equiv 0 \tag{13.30}$$

implies affinity

$$\delta_{\alpha\beta}(\boldsymbol{r}) = 0\,. \tag{13.31}$$

Eq. (13.23) describes the elastic energy correctly as long as the stress is uniform because the response is then affine. When there are fluctuations in the initial stress field they generate non-affine fluctuations in the shear which are correlated with the fluctuations in the initial stresses. This always reduces the elastic energy compared to the affine value – Eq. (13.23) – for the same average shear. The expression (13.23) is thus an upper bound on the elastic energy and is a necessary condition for stability.[59]

13.3.4. Anisotropic floppiness

It is by no means necessary that a network is simultaneously floppy with respect to all the nine strains $\partial_\alpha u_\beta$ which appear in the summation (13.23). A network can very well be floppy for some shears and, at the same time, remain rigid for others. This happens when some but not all of the average BH elastic moduli vanish.

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[59] We believe that the corrections can probably only reduce the magnitude of the shear rigidity but cannot reverse the sign of the coefficient in the elastic energy. We are however unable to prove this.

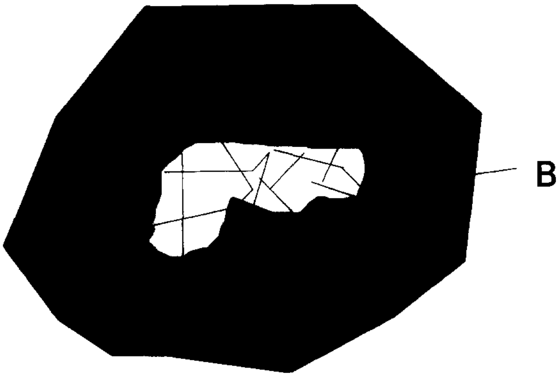

Fig. III.2.

For an isotropic material the BH shear modulus, μ, can vanish, while the bulk modulus, K, remains finite. This means that the pure traceless shears are BH floppy but the simple longitudinal strains $\partial_\alpha u_\alpha$ are not because they are also affected by the bulk modulus.

One can also have situations where only the shears perpendicular to one axis, say

$$\partial_z u_x\,, \qquad \partial_z u_y$$

are free. It is then sufficient for stability to have a negative uniaxial stress

$$\sigma^{zz} < 0\,.$$

Shear rigidity in the plane perpendicular to z is then assured by

$$-\sigma^{zz}[(\partial_z u_x)^2 + (\partial_z u_y)^2]\,. \tag{13.32}$$

The signs of the other components of the stress tensor are not important as long as they are not large enough to overcome the BH shear rigidity for the corresponding shears. An example is a hexagonal lattice consisting of rigid triangular planes stacked on top of each other – with nearest neighbor interactions. Another example is a smectic B mesophase.

13.4. Homogeneously rigid networks

13.4.1. The shear rigidity of a region

The stability condition on the macroscopic stress which we derived above, the inequality (13.24), applies to any floppy network which is macroscopically floppy (MaF). One can therefore also apply it locally, to networks which describe parts of a solid.

Consider the part of a solid which is enclosed by the boundary, B – Fig. III.2. If the network formed by the internal bonds in this region is not geometrically rigid in the sense of Section 7.3.2 then this internal network is MaF and has no average BH shear modulus:

$$\bar{\mu}_{\mathrm{B}} = 0 \tag{13.33}$$

in complete analogy to (13.19). When (13.33) holds the network in B is macroscopically floppy.

The stability of the shears of this region then depends on the average stress in B. The network in B has shear rigidity only when the configuration of the bonds, the distances $\{r_{ij}\}$, describe a stressed state and the average stress in B satisfies the inequality (13.24), i.e.,

$$\bar{\sigma}_{\mathrm{B}}^{\alpha\alpha} = \langle \sigma^{\alpha\alpha} \rangle_{\mathrm{B}} < 0 . \tag{13.34}$$

We can use this to define a local floppiness.

13.4.2. Homogeneous shear rigidity

We define a *homogeneously rigid solid* (HRS) as a solid which has shear rigidity at all scales. Every part of such a solid, separately, has shear rigidity.

Proper tightly bound solids are HRS. The elastic constants in their BH energy

$$\int \mathrm{d}\boldsymbol{r} \sum_{\alpha\beta\gamma\delta} \boldsymbol{D}^{\alpha\beta,\gamma\delta}(\boldsymbol{r}) \cdot \boldsymbol{e}^{1}_{\alpha\beta}(\boldsymbol{r}) \cdot \boldsymbol{e}^{1}_{\gamma\delta}(\boldsymbol{r}) \tag{13.35}$$

are such that any part of the solid has shear rigidity even if all the bonds which connect it to the rest of the solid are disconnected. For any region B the average elastic constants one calculates from (13.35) are such that all the average shears in

$$\sum_{\alpha\beta\gamma\delta} \overline{\boldsymbol{D}_{\mathrm{B}}^{\alpha\beta,\gamma\delta}} \cdot \langle \partial_\alpha u_\beta \rangle_{\mathrm{B}} \langle \partial_\gamma u_\delta \rangle_{\mathrm{B}} \tag{13.36}$$

are stable.[60] Most ordinary solids are homogeneously rigid in this sense. Evidently this requires that

$$\bar{\mu}_{\mathrm{B}} > 0 .$$

There are no floppy regions in a homogeneously rigid solid.

If there are floppy regions then the shear modes of these regions are only rigid if they are stressed. Stability then requires that the average stresses in any region which has no BH rigidity is negative – Eq. (13.34). This assures that the stressed floppy solid has shear rigidity everywhere and is therefore homogeneously rigid only when one adds (13.2) to the ordinary elastic energy, Eq. (13.35).

The requirement that a solid should be homogeneously rigid is obviously closely related to the microscopic linear stability requirements but the two conditions are probably not completely equivalent.

13.5. Homogeneously floppy networks

If a network is sufficiently floppy then all the separate pieces into which it can be divided are separately floppy with respect to shears. This is the reverse situation from that which we considered in defining homogeneously rigid solids. We shall call such a network a *homogeneously floppy network* (HFN). A HFN is geometrically floppy and has no BH shear rigidity on any scale. Every piece of a HFN separately is also MaF.

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[60] As in our discussion above the shears in (13.36) are the averages one sees at the boundaries but the average coefficients $\overline{\boldsymbol{D}_{\mathrm{B}}^{\alpha\beta,\gamma\delta}}$ have to be determined by minimizing (13.35).

HFNs have no shear moduli of the ordinary BH type

$$\mu(\boldsymbol{r}) \equiv 0$$

down to some microscopic cutoff scale. If they have shear rigidity it must be stress induced in all directions and at all scales. The only term in the elastic energy responsible for the shear rigidity of a HFN is the term in which the initial stress multiplies the second order strain – Eq. (13.2).

Since the shear rigidity of a HFN is stress induced at all scales the stability of the reference state requires that the stress field satisfies the continuum limit of (13.34)

$$\sigma^{\alpha\alpha}(\boldsymbol{r}) < 0 \tag{13.37}$$

everywhere. We will call such stress fields *homogeneously negative stress fields* (HNSF).

The average of a HNSF over a region is obviously also negative. A HNSF always exerts a pull on all boundaries – including the external boundaries of the solid

$$f_n = \sum \overline{\sigma^{\alpha\alpha}\hat{n}_\alpha}^2 .$$

In mechanical equilibrium these forces have to be balanced by external forces. This amounts to a very serious limitation on HFN models which describe real solids. An intrinsic mechanism which can stretch the boundaries and cancel the forces exerted by the negative network stresses is an essential ingredient for such models. This requirement and the fact that the shear rigidity has the form (13.2) and cannot be written as an expansion in the linear strains are peculiarities of HFN solids.

HFN describe a large class of materials. An example of HF networks are the polymeric networks which appear in the standard Flory models for rubbers and gels. These networks are floppy at all scales down to the mesh size. Other "soft" solids are also, almost always, described by HFN models. We will discuss the mechanical properties of soft matter from this point of view in Section 14 mainly emphasizing the origin of the negative stresses and the peculiarities. Our analysis generalizes the ideas we presented a long time ago (Alexander, 1984, 1985) and puts them in a wider context.

14. Soft solids

Most of the solids one ordinarily thinks of are solid down to the molecular level and have rigid reference states in which the atoms have fixed positions. Our discussion above, and in particular Section 2, assumed or at least suggested this picture. There are other types of solids. In particular there exists a large class of materials, soft solids, which are not rigid at the molecular level and which can nevertheless be described by a CB expansion at a larger scale. Soft solids also seem to be the only three-dimensional materials whose macroscopic shear rigidity is predominantly due to a stabilizing initial network stress and not to a standard BH shear modulus.

14.1. Between liquids and solids

Nature confronts us with large classes of materials which are somehow intermediate between regular solids and fluids. As macroscopic matter they behave as solids but they are definitely not solid at the molecular level.

A piece of rubber, a boiled egg, a cup of custard and a piece of biological tissue can all be classified as macroscopic solids. They all have shear rigidity and develop restoring forces when externally applied forces deform them. These solids are however quite different from ordinary solids – metals, ionic crystals, minerals or even glasses. Their most obvious peculiarity as solids is that they are soft. They are easier to deform and require smaller stresses for a given strain. Typically they can also sustain much larger strains reversibly and also before they break.

The origin of the difference between these soft solids and other solids is microscopic. In all the cases we have mentioned the soft solids are not completely rigid in the sense that they are not rigid down to the microscopic molecular level. One cannot define a rigid molecular reference state for any of the soft solids we have mentioned.

One distinguishes between solids and liquids as condensed states of interacting atoms. In a tightly bound solid the positions of the atoms are fixed – there exists a rigid atomic reference configuration which describes the equilibrium state of the solid. This makes it possible to disregard most entropy considerations and to describe their mechanical properties by a Cauchy–Born expansion. There is no such reference configuration for the atomic positions in a liquid. One describes a fluid in terms of averaged quantities, like the particle density, which involve statistical averaging over the atomic positions. A static liquid can sustain a stress, pressure, and also has a static elastic constant, a compressibility. But they cannot be related to deviations from a rigid atomic reference configuration.

Soft solids are in a way intermediate between liquids and solids. They are solids from a macroscopic point of view because they have shear rigidity but are not solid at the atomic level. A rigid *atomic* reference frame does not exist – the fluctuations in the atomic positions are very large. This is similar to what one finds in liquids. One can, however, define a rigid reference frame at a larger scale after some partial statistical averaging. The reference frame which is responsible for the shear rigidity is defined a posteriori after this averaging over the positions – in terms of the positions of the *cross-linking junctions* in the polymeric network and not in terms of the positions of the monomers and of the solvent molecules in a gel.

The correctness of this description is most clearly seen in the actual theories one uses in describing the mechanical properties of specific soft solids. One thinks, in particular of the classical Flory–Graessley–Edwards theory of rubber elasticity (Flory, 1953, 1976; Graessley, 1975; Pearson, 1977; Deam and Edwards, 1976) and of the "infinite cluster" percolation theory of gelation of Stockmayer (1943, 1944; Zimm and Stockmayer, 1949) and its generalization by Stauffer (1976) and deGennes (1976). We also mention a very recent development of these theories (Panyukov and Rabin, 1996) which greatly enhances the sophistication of the statistical analysis.

These theories use models which incorporate a lot of physical insight and also have a lot of predictive power. They use explicit "network" models which ascribe shear rigidity to a bonded network which permeates space. They also contain very successful schemes for calculating the shear modulus and other quantities. They are however constructed in a way in which the relationship to the general CB theory and even the need for a rigid reference frame is not obvious.[61]

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[61] We single out these theories because they are capable of explicit predictions of *shear rigidity*. Along a different line one has less explicit theories, such as the Flory mean field theory (James and Guth, 1943; Flory and Rehner, 1943; Flory, 1953) and its development in the deGennes "c* theorem" description (deGennes, 1979b) which in essence identify the shear modulus with the bulk modulus (compressibility) and avoid any explicit mechanical evaluations.

The models describe, in one way or another, the geometry of the "networks" and it is obvious that they are floppy and cannot have any significant BH shear rigidity. Thus, e.g., the Flory theory of rubber elasticity (Flory and Rehner, 1943; James and Guth, 1943) incorporates large fluctuations in the positions of the monomers. These unquenched fluctuations are implicitly important in the theory in defining the so-called "*osmotic pressure*" and in allowing one to treat the polymer chains between the crosslinks as Gaussian and therefore as *entropic* – rather than mechanical – springs. This would not be consistent if the monomer positions were fixed in a rigid CB reference state and the positional fluctuations of the monomers were therefore quenched.

These theories describe solids in terms of homogeneously floppy networks which, as we have shown in detail above and already in Alexander (1984, 1985), can only develop shear rigidity when their bonds are stretched. We will argue in the following that the fact that they are more or less fluid at the molecular level is essential because it is the source of their negative network stresses.

14.2. The Lindemann ratio

One analyzes the mechanical properties of solids by studying the CB expansion of their mechanical energy around a microscopic reference configuration. The consistency of this expansion procedure is not obvious. When it is applied one assumes, at least implicitly, that fluctuations – both the thermal fluctuations and those appearing in macroscopic shears – are small enough. We have already discussed this in Section 2.3. One can regard the requirement that the fluctuations calculated from the harmonic expansion are small as a consistency criterion which checks the consistency of the CB expansion procedure.

The need for consistency is of course quite general. It turns out however that for solids with reference states which are rigid at the atomic level consistency is assured in a fairly trivial way by the Lindemann melting criterion because such solids melt before the fluctuations become large. Thus the incorporation of fluctuations into the theory has no dramatic effects.

As we will show large ergodic fluctuations are an essential ingredient of the description of *soft solids*. Under the conditions one envisages in the description of soft solids the interatomic interactions do not fix all the atomic positions but the macroscopic properties are nevertheless those of a solid. It is therefore necessary to discuss carefully how this is possible.

14.2.1. The general rigidity criterion

The *Cauchy–Born* procedure, the expansion in positional deviations, $\{\boldsymbol{u}\}$, from a reference state, $\{\boldsymbol{R}\}$, does not make sense as a mathematical procedure when the reference configuration $\{\boldsymbol{R}\}$ is not well defined. The fluctuations around the reference state must be so small that the reference state retains its microscopic structure in the presence of fluctuations. This means that the fluctuations in the distances between the particles must be small:

$$\left|\frac{\langle \delta r_{ij}^2\rangle}{R_{ij}^2}\right| \ll 1\,, \tag{14.1}$$

Eq. (2.4), so that the reference configuration defined by $\{\boldsymbol{R}\}$ remains reasonably well defined. It is natural to formulate this in terms of the *Lindemann ratio*

$$\mathscr{L}_{ij} = \langle \boldsymbol{u}_{ij}^2\rangle / R_{ij}^2 \tag{14.2}$$

which compares the fluctuations of atoms i and j relative to each other, $\langle \boldsymbol{u}_{ij}^2 \rangle$, to the equilibrium separation of these atoms in the reference configuration R_{ij}.[62]

The general criterion for the rigidity of the reference state $\{\boldsymbol{R}\}$ in the presence of fluctuations is that the Lindemann ratio which one calculates from the harmonic expansion is small for *all* the $\frac{1}{2}N(N-1)$ pairs $[ij]$

$$\mathscr{L}_{ij} \ll 1 . \tag{14.3}$$

This *general rigidity criterion* (GRC) assures that the microscopic reference configuration $\{\boldsymbol{R}\}$ is rigid and describes the reference state of the solid adequately.

As we explained in Section 2 the formal CB theory of the mechanical properties of solids which we described in Part I assumes a rigid reference configuration and therefore assumes, at least implicitly, that the inequality (14.3) holds. If this inequality does not hold for all pairs one cannot be sure that the expansion of the energy in the deviations from the reference configuration $\{\boldsymbol{R}\}$ is indeed a convergent expansion. One can therefore regard the inequality (14.3) as a *formal* criterion for the possibility of describing the mechanical properties by a *Cauchy–Born* expansion.

In the following it will be convenient to regard the Lindemann ratio as a function of the distance. We shall therefore write

$$\mathscr{L}(r) = \langle \mathscr{L}_{ij} \rangle \, \delta(r - R_{ij}) , \tag{14.4}$$

where the brackets indicate averaging over the pairs $[ij]$.

14.2.2. The short range limit of the Lindemann ratio

The reference configuration $\{\boldsymbol{R}\}$ defines a microscopic minimal distance a. The general rigidity criterion (14.3) implies that the Lindemann ratio has to be small down to this scale

$$\mathscr{L}(a) \ll 1 . \tag{14.5}$$

In many cases a is also comparable to the range of the interactions.

As a criterion for the validity of the expansion procedure the inequality (14.5) is the most important part of the general inequality (14.3). It does not make sense to describe an interaction of range a by the leading terms in its expansion around a configuration with an equilibrium separation comparable to a if the inequality (14.5) does not hold.

The meaning of the short range rigidity criterion (14.5) is of course simply that the material is rigid at the atomic level. Ordinary solids do indeed represent rigid arrangements of their constituents and it therefore seems almost obvious intuitively that the neighboring atoms in a solid must be strongly bound to each other.[63] From this point of view it is therefore somewhat surprising to notice that (14.5) is quite dramatically violated at the atomic or molecular level, i.e., at scale a, for large classes of materials which have shear rigidity and are therefore macroscopic solids – namely for soft solids.

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[62] We call the quantity defined in Eq. (14.2) the *Lindemann ratio* because of its obvious relation to the Lindemann melting criterion (Lindemann, 1910).

[63] See, e.g., Peierls (1954, p. 53). *Note added in proof.*

14.2.3. Macroscopic rigidity

The *short range* rigidity – the inequality (14.5) – is not *formally* necessary to assure shear rigidity.

A material is conceived as solid if it has macroscopic shear rigidity. This is a macroscopic requirement. The condition that a solid has shear rigidity must also be macroscopic. It is a requirement on what happens at large, macroscopic length-scales. Fluctuations in the relative positions of particles separated by *macroscopic* distances, L

$$L/a \gg 1$$

have to be small if the reference configuration is to describe a solid. The macroscopic rigidity of a solid depends on the long range limit of the Lindemann ratio, Eq. (2.5),

$$\lim_{L\to\infty} \mathscr{L}(L) = 0\,. \tag{14.6}$$

One cannot conceive a solid for which this does not hold. We can even regard this *macroscopic rigidity criterion* (MRC) as a general formal *definition* of a solid which more or less coincides with one's intuitive concept of a solid. It is evident that the macroscopic fluctuations of a solid can only be small when the shear modulus, μ, does not vanish. Because of this the inequality (14.6) is equivalent to the requirement that there is a finite shear rigidity.[64]

One can be a little more specific without loss of generality. The long range fluctuations in a solid are dominated by acoustic phonons with a linear dispersion and are therefore universal. This follows from translational invariance. The standard calculation gives for a d-dimensional solid

$$\mathscr{L}(L) \propto (kT/\mu)(a/L)^d \tag{14.7}$$

which uses

$$\langle u(0)u(L)\rangle \approx \frac{a^d}{L^{d-2}} \int (qL)^{d-1}\,\mathrm{d}(qL)\,\frac{1-\cos(qL)}{(qL)^2} \propto \frac{a^d}{L^{d-2}}\,. \tag{14.8}$$

It follows from (14.7) that the Lindemann ratio is small at macroscopic distances for *all* solids. This does not assume the microscopic inequality (14.5) and does not depend on it. The fluctuations at scale a can be large.

14.2.4. Long range order

The MRC is a very weak criterion for a solid.

Solid state physics texts usually define a solid by *long-range-order* (LRO) which compares the long-range fluctuations, $\langle u(0)u(L)\rangle$, to the minimal atomic separation, a. Thus LRO requires that

$$\frac{\langle(\boldsymbol{u}(0)-\boldsymbol{u}(L))^2\rangle}{a^2} \ll 1 \tag{14.9}$$

for macroscopic distances L. From Eq. (14.8) one finds

$$\frac{\langle(\boldsymbol{u}(0)-\boldsymbol{u}(L))^2\rangle}{a^2} = \left(\frac{L}{a}\right)^2 \mathscr{L}(L) \propto \left(\frac{a}{L}\right)^{d-2}\,. \tag{14.10}$$

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[64] One could also say that the fluctuation in (14.6) are related to the shear modulus by the fluctuation dissipation theorem.

Thus LRO is a much more stringent condition then the MRC which we defined above. One notes:

1. LRO is not consistent with large fluctuations in the atomic positions.

Long range correlations in the fluctuations are small so that

$$\langle (\boldsymbol{u}(0)-\boldsymbol{u}(L))^2\rangle \approx 2\,\langle \boldsymbol{u}^2\rangle \tag{14.11}$$

and the inequality (14.9) therefore implies

$$\frac{\langle \boldsymbol{u}^2\rangle}{a^2} \ll 1\,, \tag{14.12}$$

where $\langle \boldsymbol{u}^2\rangle$ is the mean square fluctuation in the position of a single atom.

Macroscopic rigidity is not restricted in this way. It is consistent with fluctuations which are large compared to the interatomic distances, a, but still not macroscopic

$$L^2 \gg \langle \boldsymbol{u}^2\rangle \gg a^2 \tag{14.13}$$

which is consistent with (14.6) but not with (14.9).

2. LRO is also a much more stringent criterion for a solid in a universal and deeper sense which we mention for completeness even though it is not really relevant to our discussion.

One knows (and teaches) that one-dimensional and two-dimensional crystals are impossible because their fluctuations are too large so that they have no LRO (Peierls, 1934; Landau, 1937a; see Eq. (14.10) above). This is taken to mean that there are no solids for these dimensions. This is however a question of the definition of a solid. There is obviously no restriction on the dimensionality of a solid if one is satisfied with the weaker MRC, Eq. (14.6). One- and two-dimensional crystals are solids according to this weaker criterion because, obviously, for $d<2$.

$$(a/L)^d \ll 1 \quad \text{but} \quad (a/L)^{d-2} \gg 1\,.$$

LRO appears naturally as a criterion in the theoretical discussion of *crystalline* solids. It expresses the requirement that the periodicity of the crystal is maintained over long distances. Formally LRO can also be defined for amorphous solids which have no crystalline periodicity. One can always compare the fluctuation in R_{ij} to the microscopic length-scale a as in (14.9). In this context the meaning of this comparison is however less evident. It is not clear why one should require that the fluctuations at the *macroscopic* scale L, should be small compared to the *microscopic* length a. This length plays no obvious role in the macroscopic behavior when there is no periodicity. It is even difficult to construct an experiment which would detect the presence, or absence, of LRO in an amorphous solid. For crystals the shape of the Bragg peaks is a clear indication of periodicity. Detecting the effect of fluctuations on the speckle pattern is a much more delicate thing.

It is therefore not obvious that one should require LRO in this context. We believe that for most purposes the MRC is a more meaningful general definition of a solid than LRO, especially when one is interested in amorphous solids.

14.2.5. Consistency and the Lindemann melting criterion

The short and long range inequalities for the Lindemann ratio – Eqs. (14.5) and (14.6) – and LRO – Eq. (14.9) – all follow from the familiar Lindemann criterion for the melting of a solid

(Lindemann, 1910)

$$\frac{\langle \boldsymbol{u}^2\rangle_{\mathrm{T}}}{a^2} < 0.1\,, \quad T < T_{\mathrm{m}}\,, \tag{14.14}$$

where $\langle \boldsymbol{u}^2\rangle_{\mathrm{T}}$ is the *single particle* mean square deviation calculated from the harmonic expansion at temperature T and T_{m} is the melting temperature.

It is well known that the Lindemann (1910) melting criterion, the inequality (14.14), implies LRO because long range correlations in the fluctuations are weak, Eq. (14.11). The microscopic inequality (14.5) follows, a forteriori, because the nearest neighbor motion is strongly correlated below the melting temperature so that

$$\langle \boldsymbol{u}_{ij}^2\rangle_{R_{ij}\approx a} = 2\left(\langle \boldsymbol{u}^2\rangle - \langle \boldsymbol{u}_i\cdot \boldsymbol{u}_j\rangle_{R_{ij}\approx a}\right) \ll 2\,\langle \boldsymbol{u}^2\rangle\,. \tag{14.15}$$

It follows that for most solids the Lindemann melting criterion assures that all the consistency criteria we have discussed are satisfied throughout the existence range of the solid. If one uses the harmonic expansion to calculate the fluctuations of a solid at high temperatures

$$T > T_{\mathrm{m}}$$

one can of course formally find arbitrarily large fluctuations. For solids which obey the Lindemann melting criterion this does not mean that one is dealing with large fluctuations in the solid state. It simply means that one is using the wrong theoretical approach. One is trying to describe a liquid as though it were solid – by expanding around a reference state which does not really exist. Formally this is of course possible. The energy $\mathscr{E}(\boldsymbol{r})$ which describes an ice cube also describes the liquid formed by the same molecules and therefore can define an apparent equilibrium state $\{\boldsymbol{R}\}$ around which one can formally expand. But this expansion does not describe the mechanical properties of the melt.

Fluctuations are never large for solids for which the Lindemann melting criterion holds. Because of this the need for using the Lindemann ratio explicitly as a consistency check for the expansion procedure does not arise when this melting criterion applies.

The Lindemann melting criterion applies to most solids and describes their melting quite accurately. It is, however, not useful in describing soft solids. It is obvious that soft solids can often have fluctuations in the atomic positions which are much larger than the nearest neighbor separations as in Eq. (14.13). In general soft solids do not melt and they also do not obey the Lindemann melting criterion when they are solid.

The physical reason for this difference between soft and rigid solids is model dependent. Soft solids are complex materials with a hierarchy of different interactions. Thus, e.g., polymeric networks are not rigid at the monomer level because the intermolecular interactions between monomers belonging to different chains are relatively weak above the glass temperature. This only changes at the glass temperature which can be considered as a "melting temperature" for the inter-chain nearest-neighbor interactions between monomers. At high temperatures these interactions induce no strong short distance correlations in position. Only the strong chemical interactions inside the polymer chains and at the crosslinks have to be considered when one wants to describe rubbers.

For wet gels the solvent is liquid and the solvent molecules obviously also have no fixed reference positions.

In simpler materials which do not have such complex internal structures and such radically different types of interactions one can almost always identify local atomic rigidity with the appearance of macroscopic solid properties.

14.3. The parametrized free energy

We recall that we introduced the general rigidity criterion (14.2) initially as a purely formal criterion for the applicability of the CB expansion technique. We argued that one can describe the mechanical properties consistently by expanding the many particle energy $\mathscr{E}(\{\boldsymbol{r}\})$ around a reference state only when one can find a reference state, $\{\boldsymbol{R}\}$, which is rigid. This means, in particular, that the short range criterion (14.5) must hold at the minimum distance of $\{\boldsymbol{R}\}$. If one cannot find such a reference state then it is not possible to construct the theory in this way by a CB expansion around $\{\boldsymbol{R}\}$.

This by no means always implies that the model cannot describe a solid at larger scales. It may be possible to coarse-grain the model and thus obtain a formulation for which one can define a consistent CB reference state.

14.3.1. The averaging procedure

When the direct expansion of the energy $\mathscr{E}(\{\boldsymbol{r}\})$ shows large fluctuations at the initial atomic level one has to perform some prior statistical averaging, prior to the definition of a reference frame. This averaging replaces the microscopic energy $\mathscr{E}(\{\boldsymbol{r}\})$ by an averaged functional which we will call a *parametrized free energy* (PFE) (Alexander, 1985).

We only write schematically

$$\begin{aligned}&\mathscr{F}(\{\boldsymbol{x}\};\ T,V,\dots)\\&\quad = kT\log\left(\int D\{\boldsymbol{r}\}\cdot \Pi\delta(\boldsymbol{x}_i-\boldsymbol{x}_i(\{\boldsymbol{r}\}))\exp-\frac{1}{kT}[\mathscr{E}(\{\boldsymbol{r}\})-p\cdot V,\dots]\right).\end{aligned} \tag{14.16}$$

Like the usual definition of a free energy this describes statistical averaging subject to thermodynamic constraints designated $T, V, \dots$. We call it a parametrized free energy because of the extensive set of M microscopic constraints

$$\boldsymbol{x}_i=\boldsymbol{x}_i(\{\boldsymbol{r}\}) \tag{14.17}$$

which define the positions of M new reference points $\{\boldsymbol{x}\}$, which remain as parameters, and are defined as functions of the N positions of the original particles $\{\boldsymbol{r}\}$.

The parametrized free energy, $\mathscr{F}(\{\boldsymbol{x}\};\ T,V,\dots)$ is a thermodynamic potential in that it results from a statistical averaging process and depends explicitly on thermodynamic variables $T, V, \dots$. The statistical averaging is however only partial. The parametrized free energy, $\mathscr{F}(\{\boldsymbol{x}\};\ T,V,\dots)$, is also a function of the M microscopic positions

$$\{\boldsymbol{x}\}=\{\boldsymbol{x}_1,\dots,\boldsymbol{x}_\alpha,\dots,\boldsymbol{x}_M\}\,. \tag{14.18}$$

One can consider the averaging process (14.16) as a decimation process on the original microscopic variables

$$\{\boldsymbol{r}\}\ \Rightarrow\ \{\boldsymbol{x}\}\,,\qquad \mathscr{E}(\{\boldsymbol{r}\})\ \Rightarrow\ \mathscr{F}(\{\boldsymbol{x}\};\ T,V,\dots)\,. \tag{14.19}$$

The number M, the number of entities whose position are the $\boldsymbol{x}_\alpha$, is an extensive quantity proportional to the volume like the number of atoms, N. In this process the number of microscopic degrees of freedom is reduced from N to M.

The purpose of this reduction in the number of degrees of freedom is to construct a function for which a CB expansion can be carried out consistently. The basic assumption of this procedure is that the $N-M$ degrees of freedom which are eliminated by the averaging procedure, (14.16), are ergodic and therefore have to be treated by ensemble averages as in the statistical description of a liquid. Only the remaining variables can be considered as labeled particles in a CB expansion.

An example is the replacement of the N monomer positions, denoted by $\{\boldsymbol{r}\}$, by the positions of the M cross-linking junctions, $\{\boldsymbol{x}\}$, in polymeric network models. One (implicitly) averages over the positions $\{\boldsymbol{r}\}$ using the positions $\{\boldsymbol{x}\}$ as constraints on the averaging process. Discussing the mechanical properties of rubbers and gels in terms of the positions of the cross-linking junctions, $\{\boldsymbol{x}\}$, rather than in terms of the positions of the monomers and solvent molecules, $\{\boldsymbol{r}\}$, means, in this terminology, that one is constructing a theory based on a parametrized free energy $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$ rather than in terms of an energy $\mathscr{E}(\{\boldsymbol{r}\})$.

14.3.2. Consistency conditions on the expansion of PFE

The purpose of the prior averaging was to obtain a function – the PFE, $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$ – which can be expanded consistently. The derivation of a parametrized free energy necessarily involves averaging over some internal modes or DOF. These modes contribute to the large fluctuations in the expansion of the energy $\mathscr{E}(\{\boldsymbol{r}\})$ but do not appear as fluctuating modes in the expansion of the parametrized free energy $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$. This reduces the fluctuations in the expansion of $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$ in comparison to those in the expansion of the energy $\mathscr{E}(\{\boldsymbol{r}\})$. If one has performed enough prior averaging so that the fluctuations in the expansion of $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$ are small than one can use the CB expansion of this function consistently.

We can make this explicit.

The parametrized free energy $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$ determines an equilibrium state

$$\{\boldsymbol{X}\} = \{\boldsymbol{X}_1, \ldots, \boldsymbol{X}_\alpha, \ldots, \boldsymbol{X}_M\} \tag{14.20}$$

from

$$\left[\frac{\partial}{\partial \boldsymbol{x}_\alpha} \mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)\right]_{\{X\}} + \boldsymbol{f}_\alpha^{\text{ext}} = 0 \tag{14.21}$$

for all the M sites α. $\{\boldsymbol{X}\}$ is a microscopic equilibrium state of $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$, exactly as $\{\boldsymbol{R}\}$, Eq. (3.12), is defined as a microscopic equilibrium state of $\mathscr{E}(\{\boldsymbol{r}\})$ by Eq. (3.13).

The expansion of the parametrized free energy $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$ around the equilibrium reference state $\{\boldsymbol{X}\}$ can be carried out exactly like the expansion of the energy $\mathscr{E}(\{\boldsymbol{r}\})$ described in Part I. In analogy to the consistency requirement (14.3) for the expansion of the energy one requires for the consistency of the expansion of $\mathscr{F}(\{\boldsymbol{x}\};\ T, V, \ldots)$ around $\{\boldsymbol{X}\}$ that

$$\mathscr{L}_{\alpha\beta} = \langle \boldsymbol{u}_{\alpha\beta}^2 \rangle / X_{\alpha\beta}^2 \ll 1 \tag{14.22}$$

for all pairs $[\alpha\beta]$.

The inequality (14.22) is a consistency requirement on the expansion around $\{\boldsymbol{X}\}$. It can also be considered as a condition on the amount of statistical averaging which was necessary in deriving the function $\mathscr{F}(\{x\}; T, V, \ldots)$. In the context of the transformation, Eq. (14.19), this is a condition on the functional form of the constraints $\boldsymbol{x}_\alpha = \boldsymbol{x}_\alpha(\{\boldsymbol{r}\})$ and on their number, M.

14.3.3. The Born–von Kármán rigidity length

The averaging which replaces the N atoms with positions $\boldsymbol{r}_i$ by the M new particles at the positions $\boldsymbol{x}_\alpha$ can be regarded as a coarse-graining process. We have eliminated some degrees of freedom by the averaging process so that

$$M/N \ll 1 .$$

Thus the density of the new points is lower. This defines a coarse-graining length which we have called the Born–von Kármán length (BvKl), ξ_{BvK} (Alexander, 1984, 1985). The parametrized free energy is defined so that

$$\mathscr{L}(\xi_{\mathrm{BvK}}) < 1 \tag{14.23}$$

when the fluctuations are computed from the expansion of $\mathscr{F}(\{x\}; T, V, \ldots)$ around $\{X\}$.

The model does not describe a solid on smaller scales:

$$a < r < \xi_{\mathrm{BvK}} . \tag{14.24}$$

Conceptually one can think about this as a crossover. The Born–von Kármán length is a crossover length. Relative fluctuations are large locally, at scale a, but become small when one averages over regions larger than the BvKl. A piece of material larger than ξ_{BvK}, will be rigid and its shape will only exhibit small fluctuations. On the other hand, small pieces of the same material, smaller than ξ_{BvK}, are not rigid. The interactions internal to such a small region do not create a rigid configuration. Their mechanical properties can therefore not be treated by techniques and concepts which assume the existence of a rigid reference frame. These small scale properties can only be analyzed by statistical averaging techniques which do not require a rigid reference configuration.

14.4. The special features of a parametrized free energy

We have made a considerable effort to discuss the formal meaning of a parametrized free energy $\mathscr{F}(\{x\}); T, V, \ldots)$ and of its derivation from the bare energy $\mathscr{E}(\{r\})$. We justified this by pointing out that soft solids cannot be described by expanding their "bare" energy, $\mathscr{E}(\{r\})$, around an atomic reference configuration $\{\boldsymbol{R}\}$. They can only be described as solids by the CB expansion of a statistically averaged quantity, the parametrized free energy $\mathscr{F}(\{x\}; T, V, \ldots)$, around the reference configuration $\{X\}$. This is of course just a formal description of what one does conventionally in the Flory theory and in other microscopic models for soft solids.

The purpose of this detailed discussion was not to construct a formal averaging procedure. The motivation for discussing the distinction between an energy and a parametrized free energy is to emphasize the real differences, the real effects of the prior averaging process which make soft solids different. We want to emphasize the qualitative theoretical differences between soft solids, described by a PFE and tightly bound solids which can be modeled directly by the expansion of their atomic energy.

14.4.1. Similarity of the expansion

In a general theory one is interested in the most general formal expansions.

At first sight it would therefore seem that the distinction between "*parametrized free energy*" soft solids and tightly bound "*energy*" solids cannot be very important. The free energy $\mathscr{F}(\{x\};\ T, V, \ldots)$ is a translation–rotation invariant function of the positions $\{x\}$ and this determines the general form of its expansion in these variables – just as translation–rotation invariance determines the most general form of the expansion of $\mathscr{E}(\{r\})$ in $\{r\}$. Everything we did in Parts I and II applies to the expansion of $\mathscr{F}(\{x\};\ T, V, \ldots)$, when considered as a function of the positions $\{x\}$, just as it does to the expansion of $\mathscr{E}(\{r\})$ as a function of $\{r\}$. It therefore does not seem to matter very much if one calls the function one is expanding an *energy*, $\mathscr{E}(\{r\})$, or a *parametrized free energy*, $\mathscr{F}(\{x\};\ T, V, \ldots)$. Certainly the general form of the expansion of the energy $\mathscr{E}(\{r\})$ in the $\boldsymbol{u}_i$ and $\boldsymbol{u}_{ij}$, will not look different from the expansion of the parametrized free energy $\mathscr{F}(\{x\};\ T, V, \ldots)$ in the respective variables $\boldsymbol{u}_\alpha$ and $\boldsymbol{u}_{\alpha\beta}$. The form of this expansion will not allow one to make any distinction.

14.4.2. Network and non-network stresses

The most important difference between an energy and a PFE is the dependence of $\mathscr{F}(\{x\};\ T, V, \ldots)$ on thermodynamic variables.

The dependence of the energy $\mathscr{E}(\{r\})$ on the atomic positions $\{r\}$ describes the mechanical properties of the system of N particles completely. Because of this the CB expansion of the energy around the reference configuration, $\{\boldsymbol{R}\}$, gives a complete description. It defines the microscopic dynamics, the stresses in the reference state and the elastic constants.

The CB expansion of the parametrized free energy $\mathscr{F}(\{x\};\ T, V, \ldots)$ also describes the mechanical properties of an N-particle system but, because it also depends on thermodynamic variables, this is not a complete description. We have indicated this by including the volume, V, as an explicit variable in (4.16).

The network stresses are determined by the procedure we described in Section 4. The expansion of $\mathscr{F}(\{x\};\ T, V, \ldots)$ around $\{X\}$ defines stress tensors at the sites exactly as in Eq. (4.11)

$$\bar{\sigma}_\alpha = -\frac{1}{\mathscr{V}_i}\sum_\beta \mathscr{T}_{\alpha\beta}\frac{(\boldsymbol{X}_{\alpha\beta} * \boldsymbol{X}_{\alpha\beta})}{X_{\alpha\beta}}\,, \tag{14.25}$$

where the bond tensions are defined by the derivatives

$$\mathscr{T}_{\alpha\beta} = \left[\frac{\partial\mathscr{F}(\{x\};\ T, V, \ldots)}{\partial x_{\alpha\beta}}\right]_{\{X\}} \tag{14.26}$$

as in Eq. (3.27). The bond tensions appear in the harmonic energy, Eq. (6.11), and the site stresses define a *network* stress field, $\boldsymbol{\sigma}^{\mathrm{net}}(\boldsymbol{x})$. This *network* stress is uniquely determined by the expansion of the parametrized free energy $\mathscr{F}(\{x\};\ T, V, \ldots)$ around the reference state $\{\boldsymbol{X}\}$. In the continuum limit the network stress multiplies the first and second order network strain in the elastic energy exactly as in Sections 4 and 6. Similarly the network elastic constants $D_{\mathrm{net}}^{\alpha\beta\gamma\delta}$ are defined by the second derivatives of the parametrized free energy $\mathscr{F}(\{x\};\ T, V, \ldots)$ with respect to the distances $x_{\alpha\beta}$ exactly as in Eqs. (5.23) and (5.26). But these are only the *network* contributions to the stresses and to the elastic constants.

Because the PFE depends explicitly on thermodynamic variables there are additional contributions. There are additional, liquid-like contributions to the stress and compressibility

$$p^{\text{liq}} = \frac{\partial \mathscr{F}(\{\boldsymbol{x}\};\, T, V, \ldots)}{\partial V}\,, \qquad K^{\text{liq}} = \frac{\partial^2 \mathscr{F}(\{\boldsymbol{x}\};\, T, V, \ldots)}{\partial V^2} \tag{14.27}$$

which are separate from the network contributions – the network pressure p^{net}, and the *network* bulk modulus, $\boldsymbol{K}^{\text{net}}$.[65]

The *total* pressure, p^{tot}, the isotropic part of the total stress in the soft solid is therefore a sum

$$p^{\text{tot}} = p^{\text{net}} + p^{\text{liq}}\,. \tag{14.28}$$

p^{tot} is the pressure which exerts a force on the external boundaries and has to be balanced by external forces, but only the network pressure p^{net} multiplies the second order strain – a term

$$p^{\text{net}} \sum (\partial_\alpha u_\beta)^2 \tag{14.29}$$

in the elastic energy. Because of this the second order strain can appear in the bulk elastic energy of soft solids which are not stressed by any external forces. We have thus shown that a soft solid can have stress-induced shear rigidity even when the average *total* stress vanishes.

$$p^{\text{tot}} = 0 \tag{14.30}$$

does not imply that the network pressure vanishes but only that there are no forces on the boundaries and

$$p^{\text{liq}} = -p^{\text{net}}\,.$$

We discussed an example, the square foam, in Section 8.1.3.

Because of these intrinsic network stresses stable soft solids can be described by HFN.

The total bulk modulus is of course also a sum of two contributions:

$$K = \kappa^{\text{net}} + \kappa^{\text{liq}}\,. \tag{14.31}$$

This means that the bulk modulus can be very different from the elastic constants which determine the shear rigidity which is often observed. But these are only quantitative effects.

14.5. Entropic interactions

The interactions which appear in the expansion of $\mathscr{F}(\{\boldsymbol{x}\};\, T, V, \ldots)$ result from statistical averaging and can have entropic contributions. This means that they can look very different from the microscopic bare interactions between atoms.

We are interested in polymeric network models. The entropic interactions there are described by flexible polymeric chains which can be elongated by large factors compared to their equilibrium separation. Because of this the internal stresses in rubbers and gels can become much larger compared to the BH interactions than in tightly bound solids with microscopic atomic interactions.

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[65] The argument can of course be generalized to situations where there are other liquid stresses besides the pressure. An example could be a gel in a nematic solvent.

One has to compare the coefficients in the stress-induced terms

$$\frac{\mathscr{T}_{ij}^{\mathrm{ini}}}{R_{ij}}(u_{ij}^{\perp})^2 \tag{14.32}$$

– Eq. (6.9) – to the coefficients in the unstressed harmonic terms

$$\mathscr{K}_{ij}(u_{ij}^{\prime\prime})^2 \tag{14.33}$$

as in Eq. (5.5). The dimensionless ratio of the coefficients in these expressions

$$\frac{\mathscr{T}_{ij}^{\mathrm{ini}}}{R_{ij}\cdot\mathscr{K}_{ij}} = \eta_{ij}^{\mathrm{ini}} \tag{14.34}$$

can be interpreted as an effective bond strain

$$\eta_{ij}^{\mathrm{ini}} = \frac{\delta_{ij}^{\mathrm{ini}}}{R_{ij}}\,, \tag{14.35}$$

where $\delta_{ij}^{\mathrm{ini}}$ is the elongation of the bond $[ij]$ required to give the initial tension $\mathscr{T}_{ij}^{\mathrm{ini}}$.

The quantum mechanical interactions responsible for binding in tightly bound solids are asymmetrical and have relatively large anharmonic terms. They become soft for large elongations so that the maximum elongation they can sustain is relatively small

$$\eta_{ij}^{\mathrm{ini}} \ll 1\,. \tag{14.36}$$

Thus when the interactions are atomic *positive* bond tensions cannot become large enough to be important in the harmonic energy compared to the Born–Huang terms.[66]

In contrast one can very easily have large bond tensions for Gaussian chains because

$$\frac{\mathscr{T}_{ij}^{\mathrm{ini}}}{R_{ij}} = \mathscr{K}_{ij} = \frac{k_{\mathrm{B}}T}{N} \tag{14.37}$$

so that

$$\eta_{ij}^{\mathrm{ini}} \approx 1\,. \tag{14.38}$$

The stress-induced terms in the harmonic expansion can therefore become large and important.

The fact that Gaussian chains can be stretched by a large factor, which we used in (14.38), explains that the large elastic range observed in rubber elasticity is familiar. We invoke the same property of polymeric chains here to show that the internal stresses in polymeric networks can potentially become large. This means that the stress-induced terms in the harmonic expansion can become important for rubbers while they are never really important for the bulk properties of tightly bound solids.

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[66] Atomic interactions are very asymmetric and large destabilizing *negative* bond tensions are certainly possible as in the materials in geophysical conditions under large external pressures. We shall discuss this in detail in Section 15.

15. Random packing and structural buckling

15.1. Positive stresses

15.1.1. The nature of positive initial stresses

For a number of reasons the role of positive initial stresses in a solid is very different from that of negative stresses.

In the context of our discussion in Sections 13 and 14 the most obvious of these is that the direct effect of positive stresses is destabilizing. For this reason the magnitude of the stresses in open structures is limited by *structural buckling*. If the positive stresses become too large any open structure will buckle to a denser structure which can support the stresses.

On the other hand, there is no real limitation on the magnitude of positive stresses at the microscopic level. For this reason compact structures can support very large stresses. Large positive stresses are also relatively easy to produce by external or internal compressional forces.

This means that positive stresses are not compatible with tenuous or floppy structures – they can only appear in stable reference states in structures which have a BH rigid bond structure.

Since positive stresses can be large one also cannot neglect the induced indirect effect of the stresses, Section 6.1.1, on the BH coefficients and elastic constants. As we will show this effect tends to be stabilizing and, moreover, is much larger than the destabilizing direct effect of the same stresses.

One therefore expects positive stresses to have two important functions:

1. When solidification occurs initially in relatively tenuous, floppy structures stress-induced structural buckling will dominate the process leading to the final stable reference state.
2. For sufficiently large stresses the BH interactions are predominantly due to the indirect effect of stresses on the repulsive cores.

To show how this works we will discuss the mechanical properties of packings of rigid particles with contact interactions. For simplicity we will also assume that the stresses are purely external, imposed stresses.

As formulated this is directly relevant to the description of granular matter – e.g. sand – from a microscopic point of view. We just note that geometrical packing considerations of atoms with reasonably well-defined atomic radii are also central to the interpretation of structural information even in crystallography (see, e.g., Evans, 1966, in particular Section 3.10 and ch. 9) and that attractive interactions are often of much longer range than the repulsive interactions. For this reason similar considerations can be applied in many other contexts.

15.1.2. Structural buckling

When the initial stresses are all positive their direct effect is destabilizing – Section 13.2. Because of this floppy networks cannot support positive stresses. Solids can only sustain destabilizing stresses when the destabilizing effects of the stresses are weaker than the BH terms which stabilize the same deformations. The most familiar example of this effect is the Euler buckling of loaded columns (Euler, 1755; Landau Lifshitz, 1970, Section 21).

For three-dimensional structures the analogous effects mean that the structure becomes linearly unstable for some limiting stresses. This instability sets a limit to the positive stresses which the structure can sustain. When the stresses exceed this limit some deformational modes become unstable.

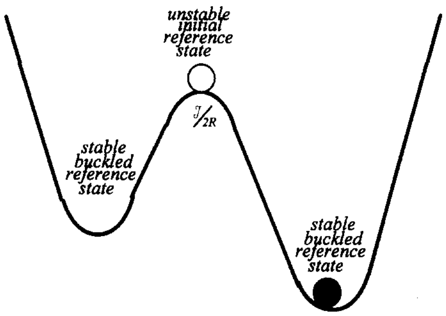

Fig. III.3. Structural buckling in a double well potential.

The structure buckles to a different structure which is stronger and is stable at the given stresses. It is natural to call this instability *structural buckling.*

A network which is macroscopically floppy, i.e., not completely rigid, cannot support *any* positive stresses. The free shears of such a network become unstable in the presence of positive stresses. As soon as one applies stresses the floppy modes of the network buckle. The result of the buckling must be a new structure which is BH rigid and not floppy. We describe a simple example in Appendix E.

15.1.3. Double-well buckling – an example

The simplest example of structural buckling are transverse modes with negative tension – e.g., the librational modes of a hexagon in the honeycomb model of Section 11. As a function of distances the energy is

$$\mathcal{T}_{ij}\,\delta r_{ij} + \mathcal{K}_{ij}\,\delta r_{ij}^2 + \cdots .$$

For a transverse mode we substitute

$$\delta r_{ij} \cong (u_{ij}^{\perp})^2/2R_{ij}$$

which gives a double well potential

$$\frac{\mathcal{T}_{ij}}{2R_{ij}}(u_{ij}^{\perp})^2 + \frac{\mathcal{K}_{ij}}{4R_{ij}^2}\,u_{ij}^{\perp 4}$$

when the bond tension is negative. The equilibrium at $u_{ij}^{\perp} = 0$ is then unstable and the mode buckles to one of the minima. See Fig. III.3.

This is of course schematic and oversimplified. One does however expect that, quite generally, some stabilizing anharmonic terms will eventually dominate. It is, e.g., easy to see that for the free torsional mode of a hexagon which we considered in Section 11.1 – Fig. II.15 – the anharmonic terms we included will limit the torsional amplitudes and make the torsional potential into a double well potential.

15.1.4. The buckling edge

Assume one starts from a floppy network state with large BH interactions. Even small stresses will cause buckling which will continue until a geometrically rigid reference state is reached. This follows from our analysis in Section 10 because all, or at least most of the free DOF will disappear by buckling. One therefore expects that a state which is just barely rigid will be reached. Such a state is in a way critical because it represents a balance between the stress induced destabilizing effects and the stabilizing BH interactions. We call this a stress-induced structural buckling edge. At the buckling edge one expects that the destabilizing effect of the positive stresses, Eq. (13.23),

$$-\overline{\boldsymbol{\sigma}}^{\alpha\alpha}(\overline{\partial_\alpha u_\beta})^2$$

is approximately equal to the stabilizing effects of the BH interactions for the same reference configuration

$$\overline{\mu(\sigma)}(\overline{\partial_\alpha u_\beta}+\overline{\partial_\beta u_\alpha})^2\,,\quad \text{i.e.,}\quad \overline{\boldsymbol{\sigma}}\approx\overline{\mu}(\{\boldsymbol{R}\}_\sigma)\,,$$

where $\{\boldsymbol{R}\}_\sigma$ is the new BH rigid reference state, the final state of the buckling process.

This is quite general. In the following we shall discuss structural buckling and the rigidity of the stable reference state for a specific model – the packing of rigid particles. We emphasize the peculiarities of a reference state which results from a structural buckling process.

15.2. The packing model

We consider the most simple mechanical model.

The particles are assumed to be in contact – both before and after the buckling. All "free volume" and rearrangement entropies are neglected. The interparticle forces are all repulsive contact interactions. The particles interact only through the energies of their stressed contacts. The arrangement of the particles and their contacts defines a reference state for the elastic properties.

Since there are no attractions the initial stresses in the reference state are homogeneously positive. We shall call such a model a *packing.*

15.3. Geometrical rigidity of a packing

The interactions in a packing vanish with the external forces. In the zero stress limit the reference state becomes a purely geometrical packing of the constituent particles which are considered as hard objects having their unperturbed shapes. The unstressed limit of the reference state is a packing of these hard objects with unstressed contacts. Because there are no forces the contacts are point contacts. The rigidity of this unstressed packing is a purely geometrical problem.

In Sections 7 and 9 we defined the geometrical rigidity of a graph, a bonded network of point objects. A bonded network is geometrically rigid if it cannot be deformed without changing the length of any bond. In analogy one can define the geometrical rigidity of a packing of hard, undeformable objects. One can ask if the packing can be deformed continuously by rotating and translating the constituent grains without deforming any of them and without *breaking* the contacts between any two grains. A packing is *geometrically rigid* if it cannot be deformed subject to these conditions. This defines the rigidity of a packing as a purely geometrical property of the arrangement of rigid particles and is a generalization of the definition of geometrical rigidity in Section 7.2.

The geometrical rigidity of a packing depends only on the shapes of the packed hard objects and on the arrangement of their contact points.

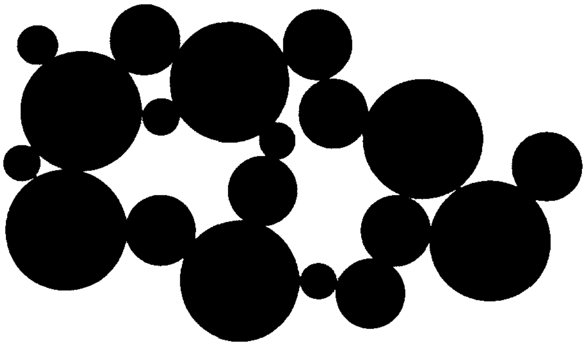

Fig. III.4. A packing of discs and the bonded network of their centers.

15.4. Geometrical rigidity of packings of spheres

We consider the packing of hard spheres first.

15.4.1. Packing constraints

Quite generally we can describe a packing of spheres by the positions of the centers of the spheres $\boldsymbol{r}_i$. When the spheres i and j are in contact one must have

$$(\boldsymbol{r}_i - \boldsymbol{r}_j)^2 = (\rho_i + \rho_j)^2 , \tag{15.1}$$

where ρ_i and ρ_j are the radii of the sphere i and j, respectively. This is the condition that the two spheres are in contact. A packing of spheres must satisfy an equation like this for every contact point between spheres.

Since the spheres are hard they cannot overlap and one must also satisfy the inequalities

$$(\boldsymbol{r}_i - \boldsymbol{r}_j)^2 > (\rho_i + \rho_j)^2 \tag{15.2}$$

for *all* pairs $[ij]$ which are not in contact.

Any solution of Eq. (15.1) which also satisfies the inequalities (15.2) describes a possible configuration of the packing of spheres.

15.4.2. Mapping on a bonded network

The solutions of Eq. (15.1) describe the configurations of the centers of the spheres

$$\{\boldsymbol{r}\} = \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i, \ldots, \boldsymbol{r}_j, \ldots, \boldsymbol{r}_N\} . \tag{15.3}$$

The graph of the centers of the spheres connected across the contact points is a bonded network with a "bond" of length

$$R_{ij} = \rho_i + \rho_j \tag{15.4}$$

associated with each contact point $[ij]$. We illustrate this in Fig. III.4.

The geometrical rigidity of this bonded network is a *necessary* condition for the rigidity of the packing. If the bonded network is not geometrically rigid, then the packing cannot be rigid. The packing can then be deformed continuously without changing the set of contact points, $\{[ij]\}$,

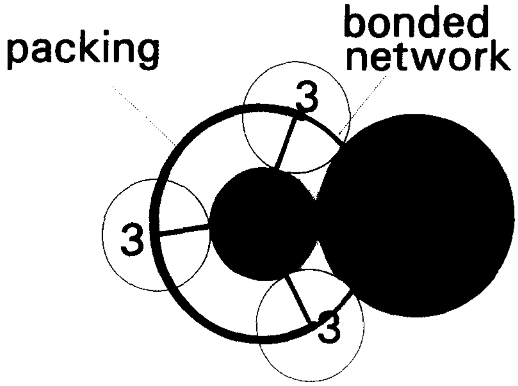

Fig. III.5. Restriction on the freedom of three discs with two contact points.

also satisfy the excluded volume inequalities. For the rest of the circle the discs 1 and 3 overlap and the inequality

$$r_{13} > \rho_1 + \rho_3$$

is violated.

This effect always amounts to restrictions on the deformations of the packing. Some of the bonded-network solutions of (15.1) cannot be realized as packings. The excluded volume restrictions can even become so severe that none of the solutions of (15.1) satisfies all the inequalities (15.2). When solutions exist the floppiness of the bonded-network always implies the floppiness of the packing. When the network is floppy the packing must also be floppy over some finite range – if it exists.

The number of bonds in a bonded network is fixed – by definition. The number of contact points of the packing remains fixed for the whole range of allowed deformations which satisfy Eqs. (15.1) in the open range defined by the inequalities (15.2).[67]

15.4.4. Decreasing the number of contact points

The second difference between the rigidity of packings and the rigidity of bonded networks concerns a decrease in the number of contact points.

The bonded network describes deformations in which spheres in contact move around each other. It does not describe normal displacements in which the number of contact points is decreased because the centers of the spheres move away from each other.

Deformations which *decrease* the number of contact points

$$|\boldsymbol{r}_i - \boldsymbol{r}_j| = \rho_i + \rho_j \;\Rightarrow\; |\boldsymbol{r}_i - \boldsymbol{r}_j| > \rho_i + \rho_j \qquad (15.7)$$

are not allowed by the bonded network constraints (15.1) but are allowed by the packing conditions – the excluded volume constraints:

$$|\boldsymbol{r}_i - \boldsymbol{r}_j| \geq \rho_i + \rho_j \,. \qquad (15.8)$$

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[67] New contact points are of course formed on the boundaries of the excluded volume region where some of the inequalities (15.2) become equalities.

following the deformations of the bonded network until one reaches the boundaries defined by the excluded volume inequalities (15.2), where spheres start to overlap. On these boundaries new contacts are formed.

The FDOF of the bonded network describe deformations in which the centers of the spheres move and the contact point between any two spheres slides on their surfaces. In such a deformation the positions of the spheres change but no 2-sphere contacts are broken. Any two spheres which are in contact remain in contact. It follows that one can apply the rigidity considerations of Section 9 to the geometrical rigidity of packings of spheres. In particular the "bond counting inequality" on the average number of bonds per vertex, Eq. (9.8), becomes a condition on the average number of contact points per sphere

$$\langle n_{\mathrm{cp}} \rangle \geq 2d \,. \tag{15.5}$$

This *contact point counting inequality* (CPCI) is a *necessary* condition for the geometric rigidity of the packing just as the BCI, Eq. (9.8), was a necessary condition for the rigidity of a bonded network. When there are fewer contact points

$$\langle n_{\mathrm{cp}} \rangle < 2d \tag{15.6}$$

the packing must be floppy.

There are however two important differences between the rigidity of a packing of hard spheres and the rigidity of the corresponding bonded network.

15.4.3. Excluded volume inequalities

The first is rather obvious and concerns the role of the excluded volume inequalities (15.2).

When the bonded network is geometrically floppy, Eqs. (15.1) define a hypersurface

$$\mathcal{S}(\{\boldsymbol{r}\};\ \{[ij]\},\{\rho_i\})$$

in the Nd dimensional space spanned by the positions of the centers as discussed in Section 10.4. All points on this surface describe allowed configurations of the bonded network of centers for which the "bonds" across the contact points have the lengths required by (15.1). The other distances between centers vary on the surface $\mathcal{S}(\{\boldsymbol{r}\};\ \{[ij]\},\{\rho_i\})$.

The hypersurface $\mathcal{S}(\{\boldsymbol{r}\};\ \{[ij]\},\{\rho_i\})$ consists of parts of the "bonded-network" surface $\mathcal{S}(\{\boldsymbol{r}\};\ \{R_{ij}\}_{\mathrm{bond}})$ defined by the bond lengths (15.4). In general some of the excluded volume inequalities (15.2) are violated for the configurations described by large parts of the "bonded-network" surface. These configurations of the bonded network cannot be realized by the centers of the spheres in a packing of spheres because some spheres overlap. The range in which one can deform a packing of spheres is much more restricted than the range of deformation of the corresponding bonded network.

We illustrate this for a simple example in Fig. III.5.

The drawing shows three discs – 1,2,3 – with two contact points [12] and [23]. This corresponds to two distances for the bonded network of the three centers. For the bonded network the center of the third disc, the open circle 3, can be moved over a whole circle keeping the two distances r_{12} and r_{23} constant. In contrast only the marked arc describes possible states of the packing of discs which

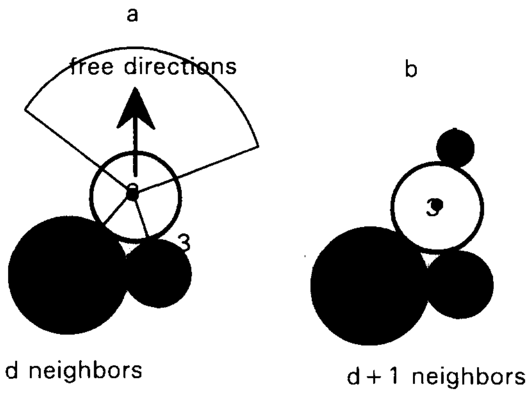

Fig. III.6. Freedom in the packing of discs, the Hilbert condition.

R_{ij} is not a proper "bond" whose length cannot be changed. The two hard spheres can be moved away from each other, disconnecting the contact $[ij]$ if this is possible without violating any of the excluded volume inequalities (15.2).

The most familiar manifestation of this is the Hilbert local rigidity condition for a single sphere in a packing (Hilbert and Cohen-Vossen, 1952, which we discussed in detail in Section 9.3.3 above)

$$n_{\mathrm{cp}} \geq d+1 . \tag{15.9}$$

In d-dimensional space d bonds are sufficient to determine the position of a junction when the positions of all the other junctions are fixed but one needs $d+1$ contact points to fix the position of a single sphere when the rest of the packing is fixed. One needs the "last" $(d+1)$th contact to prevent free motions of the sphere which break contacts.

We illustrate this in Fig. III.6.

The two "bond lengths" r_{13} $(=\rho_1+\rho_3)$ and r_{23} $(=\rho_2+\rho_3)$ fix two distances and therefore the position of the center of the disc 3 in the plane. In the packing problem one only has the inequalities (15.8). The packing of Fig. III.6a is not rigid when $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are fixed even though the corresponding bonded network is rigid.

In our discussion below we will assume that the packings are also rigid in this additional sense. This means that the Hilbert conditions are satisfied for all spheres and that the generalization of these conditions to the rigid motion of clusters of spheres is also assured.

15.5. Geometrical rigidity for grains of general shape

The generalization of the above consideration to the packing of particles of arbitrary shape complicates the detailed geometrical considerations considerably. The differences concern the effect of the orientational degrees of freedom of a rigid object of general shape on the rigidity of the packing.[68]

Formally one can generalize the BCI argument:

A rigid body has $d(d+1)/2$ degrees of freedom in d dimensional space. Of these d-DOF describe its position, say the position of its center of mass $\boldsymbol{r}_i$. The remaining $d(d-1)/2$ degrees of freedom

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[68] The orientation of a sphere obviously drops out of the rigidity considerations. Only the positions matter.

are orientational – ϕ. In a rigid configuration all these degrees of freedom must be fixed by the contact points.[69]

The position and orientation of particle i are described by

$$[\boldsymbol{x}_i) = [\boldsymbol{r}_i, \phi_i) \tag{15.10}$$

and the shapes of the particles by functions which describe their boundaries

$$|\boldsymbol{r}(\psi) - \boldsymbol{r}_i| = \rho_i(\psi)\,, \tag{15.11}$$

where ψ_i describes the $d(d-1)/2$ angular coordinates of the boundary point $\boldsymbol{r}(\psi_i)$ in an internal coordinate system of the particle i.

The condition that the two particles i and j are in contact is, in general, some function of the vector connecting their centers, $\boldsymbol{r}_i - \boldsymbol{r}_j$, of their orientations in space, ϕ_i, ϕ_j and of their shapes $\rho_i(\psi)$ – say

$$\Psi[\boldsymbol{r}_i - \boldsymbol{r}_j, \phi_i, \phi_j;\ \rho_i(\psi_i), \rho_i(\psi_i)] = 0 \tag{15.12}$$

which replaces the inequality (15.1) for spheres. This has to be supplemented by the excluded-volume inequalities

$$\Psi(\boldsymbol{r}_i - \boldsymbol{r}_j;\ \phi_i, \rho_i(\phi_i);\ \phi_j, \rho_j(\phi_j)) > 0 \tag{15.13}$$

which replace (15.2).

There is one condition of the type (15.12) per contact point and one therefore requires, in general,

$$\langle n_{\mathrm{cp}} \rangle \geq d(d+1) \tag{15.14}$$

contact points to determine all the rigid-body DOF of the particles.

Because of the additional orientational degrees of freedom one requires more contact points – *at least* 6 contact points per grain in two dimensions and 12 contacts in three dimensions. This replaces the much weaker BCI condition for spheres – 4 contacts in 2-D and 6 contacts in 3-D – the inequality (15.5).

The very large number of contact points which is *necessary* for the rigidity of a packing of anisotropic objects is somewhat surprising. Nevertheless, we do not see how one can avoid the conclusions of the elementary argument above.

15.5.1. The Hilbert condition for general shapes

The generalization of the local Hilbert argument to general rigid bodies is a little easier to visualize and seems to agree with the simple "counting" philosophy of the above.

One requires 4 (=3 + 1) contacts to fix the three DOF – the position and the orientation – of an ellipse in the plane (see Fig. III.7). This suggests that the trivial generalization of (15.9) to general shapes

$$n_{\mathrm{cp}} \geq \tfrac{1}{2} d(d+1) + 1 \tag{15.15}$$

is valid as a generalized local rigidity condition.

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[69] Contacts on whole lines or surfaces are also possible for some particle shapes.

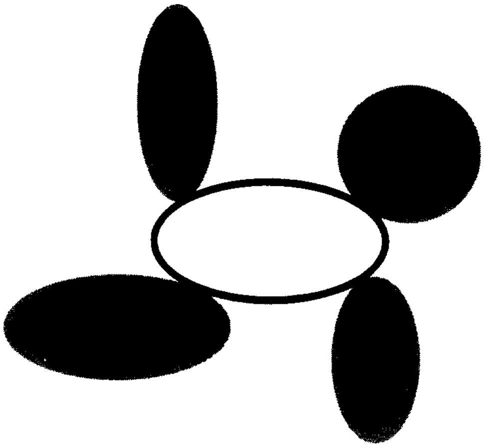

Fig. III.7. Hilbert local rigidity condition for ellipses.

15.6. Stressed packings of spheres

As we saw in Section 15.4 an unstressed packing of spheres can be mapped on the bonded networks of their centers. We will assume that the dominant interactions in the packing can be described by the two-body interactions of the bonded network.

This neglects many-body interactions, which is probably not always justified, but is reasonable for the Hertzian contacts of elastic spheres at small pressures. It also neglects tangential friction – a problem to which we shall return.

We describe the energy as a function of the distances between the centers as we did in our discussion of bonded networks in Section 10. Under stress the spheres are deformed and the distance between their centers decreases. The distance between the centers of two touching spheres in the stressed reference state is no longer given by Eq. (15.4) but is smaller:

$$R^{\mathrm{s}}_{ij} = \rho_i + \rho_j - \delta_{ij} \,. \tag{15.16}$$

The stressed reference state is described by the R^{s}_{ij} or equivalently by the δ_{ij}.

In the equilibrium reference state the two spheres exert a repelling force on each other

$$\boldsymbol{f}_{ij} = \mathscr{T}_{ij} \cdot \hat{\boldsymbol{R}}_{ij}$$

whose magnitude is given by the negative bond tension in the stressed reference state.

$$\mathscr{T}_{ij} = \mathscr{T}_{ij}(\delta_{ij}) < 0 \,.$$

We expand the energy around the stressed state

$$\mathscr{E}(\{r\}) = \mathscr{E}(\{\delta + \eta\}) \,, \qquad r_{ij} = \rho_i + \rho_j - \delta_{ij} - \eta_{ij} \tag{15.17}$$

so that

$$\mathscr{E} = \mathscr{E}(\{\delta\}) + \sum \mathscr{T}_{ij}(\{\delta\}) \cdot \eta_{ij} + \frac{1}{2} \sum \mathscr{K}_{ij}(\{\delta\}) \cdot \eta^2_{ij} + \cdots \,. \tag{15.18}$$

We note that the expansion around the unstressed state

$$\delta_{ii} \equiv 0$$

is restricted to positive deviations $\eta_{ij} \geq 0$ and is therefore irregular. There is no formal problem with the expansion around any stressed reference state. In particular the unstressed limit

$$\{\delta\} \to 0$$

of the expansion coefficients is well defined:

$$\mathcal{T}(\delta) \propto -\delta^{1+\varsigma}\,, \qquad \mathcal{K}(\delta) = -\frac{\partial \mathcal{T}(\delta)}{\partial \delta} \propto \delta^{\zeta} + \text{h.o.t.}\,, \tag{15.19}$$

where the index ζ depends on the elastic properties of the particle. One expects the spring constant to increase with the pressure and therefore

$$\zeta \geq 0\,. \tag{15.20}$$

An example are Hertzian contacts between elastic spheres for which

$$\mathcal{T} \propto -\mu\, \rho^{1/2}\, \delta^{3/2}$$

which means $\zeta = \frac{1}{2}$.

The leading terms in the expansion of the energy around the stressed equilibrium reference states are

$$\frac{\mathcal{T}_{ij}(\delta)}{2R_{ij}} (u_{ij}^{\perp})^2 + \mathcal{K}_{ij}(\delta)\, (u_{ij}^{\prime\prime})^2\,, \tag{15.21}$$

where the first term is the destabilizing direct contribution of the stresses and the second term is the BH contribution. It follows that for small compressions for which

$$\delta/\rho < 1$$

the coefficients of the stress induced-destabilizing terms are small compared to the coefficients of the two-body BH terms

$$\left| \frac{\mathcal{T}}{\mathcal{K}\rho} \right| \approx \frac{\delta}{\rho} \ll 1\,. \tag{15.22}$$

It follows that the BH interactions are always larger. The destabilizing effect of the stresses is therefore only important in tenuous configurations – for anomalously soft or free modes. Any geometrically rigid reference state of the stressed packing is stable. In particular, increasing the stresses cannot make such a state unstable or cause structural buckling from one rigid state to another because the stress-induced destabilizing terms remain small when the stresses are increased.[70]

15.7. Structural buckling

15.7.1. The buckling instability

Any packing of spheres which is not geometrically rigid becomes unstable when a positive stress is applied.

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[70] This assumes that the deformations δ/ρ remain small.

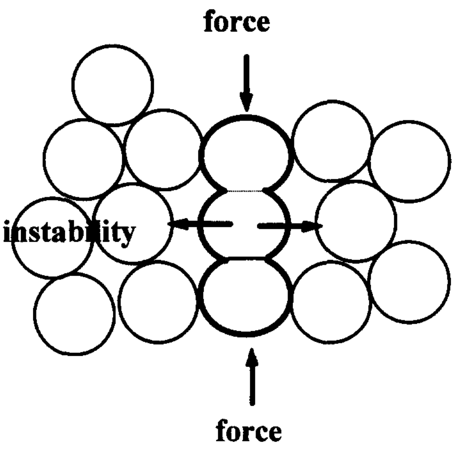

Fig. III.8. Instability of a column of three spheres under uniaxial stress.

The instability can be removed only by a structural buckling process which creates *new* contact points. The end result of this structural buckling process is a state of the packing which is stable. This is illustrated by the simple example in Fig. III.8.

Assume that the initial packing is floppy so that the final state is reached by a structural buckling process. The buckling continues until the packing becomes geometrically rigid and therefore stable. The packing of spheres which results from the buckling process describes a new structure which must be geometrically rigid. This means that it has enough contact points and also that their arrangement assures stability. A necessary condition for this is the contact point counting inequality (15.5)

$$\langle n_{\mathrm{cp}} \rangle \geq 2d\,.$$

The rigid state reached by buckling under stress remains stable when the stress is increased. Increasing the stress does not generate new instabilities because, as we saw in Eq. (15.22), the destabilizing effects of the stress for a geometrically rigid packing are always small.

Evidently this does not mean that increasing the applied stresses has no effect. But this is no longer a linear instability under stress which, in principle, can occur for arbitrarily small stresses. For finite stresses the deformations of the spheres are finite and this can cause structural changes. The point we want to emphasize is that this is a qualitatively different process from the structural buckling process.

15.7.2. The rigidity threshold state

The structural buckling process we described does not depend on the magnitude of the stress. The stable state reached by the structural buckling process in the small stress limit

$$\sigma^{\alpha\alpha} \to 0^{+} \tag{15.23}$$

is special.

This state is a property of the geometrical packing of hard spheres itself and is reached by a continuous process which only involves linear instabilities and the hard core repulsions between spheres. This defines a unique *rigidity threshold state* (RTS). The RTS depends only on the geometry of the initial state from which the system buckled.

We conjecture that for the RTS the CPC inequality, (15.5), becomes an equality

$$\langle n_{\mathrm{cp}}\rangle^{\mathrm{RTS}} \cong 2d \tag{15.24}$$

and that the RTS describes a "critical" state of the packing. We also suggest that the RTS has no macroscopic shear rigidity.

Note. We described the RTS as a *unique* well-defined state.

Our discussion above assumed that a specific realization of the configuration of the particles was the initial preparation state. It also assumed that this initial state determines a unique structural buckling process and therefore a unique final state.

The first of these assumptions means that buckling starts in a quenched state which is unstable but in which the liquid like mixing dynamics is already suppressed. This raises no serious problems.

The second assumption is clearly untenable if taken literally. A large random packing can obviously not be specified so accurately that a complex structural buckling process will lead to a unique final state. Even for a specific realization of the initial state of the random packing the structural buckling process is a quenching process which more or less randomly selects one out of a very large number of possible RT states.

15.8. Shear modulus near the rigidity threshold

In the model we have described the shear rigidity near the RTS depends on an applied external pressure for two reasons – the dependence of a typical BH force constant on the applied pressure[71]

$$\tilde{\mathscr{K}} \propto p^{w} \tag{15.25}$$

and the effect of the stress on the reference state itself.

For a definite reference state, ϕ, one can write

$$\mu_{\phi} \propto \mathscr{A}_{\phi}\,\mathscr{K}\,, \tag{15.26}$$

where $\mathscr{A}_{\phi}$ is a constant which can in principle be calculated from the geometry of the hard spheres packing, ϕ, and $\mathscr{K}$ is a typical BH force constant as in (15.25).

Near a rigidity threshold the reference packing depends on the pressure. If the RTS is indeed critical one expects

$$\mathscr{A}(p) \propto p^{s}\,, \qquad \mathscr{A}_{\mathrm{RTS}} = \mathscr{A}(0) = 0\,. \tag{15.27}$$

One therefore predicts

$$\mu(p) \propto p^{s} \cdot p^{w}\,. \tag{15.28}$$

One should be able to check this with experiments or simulations.

There exist quite accurate estimates of w for different models in the literature, e.g., Levine (1997) and deGennes (loc. cit.). We are not aware of attempts to study the GRS in detail.

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[71] An example is the discussion of packings of grains with Hertzian contacts in deGennes (1996).

15.9. *The role of friction*

We have neglected friction completely in our discussion. We assumed that linearly unstable modes amount to mechanical instabilities which are realized. This was the essence of the structural buckling process which we described. For macroscopic grains the main limitation of this argument is that it neglects the role of friction in the structural buckling process. Solid friction has no effect on intrinsic stability of a configuration. Its main effect is to inhibit the dynamics and thus increase the range of stability. Friction can clearly inhibit the structural buckling process. As a result the packing can get stuck in states which are not stable, the route of the buckling process can change and the final state of the buckling can be a state which is not critical RTS. Just how important this is depends on the specific situation.

We have discussed the description of the mechanical properties of packings of bubbles from a similar point of view in detail in Levine and Alexander (1997) and in Alexander (1997).

16. Glasses – solids with quenched reference states

16.1. *General approach*

We want to describe glasses as solids, i.e., in terms of a *Cauchy–Born* expansion around a rigid reference state. The reference state for the CB expansion in the glass is the outcome of the quenching process which produces the glass. This means that it is not a global minimum of the energy but also not an arbitrarily disordered random state. It must be a realization of the random quenching process which produces the glass from the liquid.

Every realization of the reference state of the glass must be a stable equilibrium state of the interaction energy, $\mathscr{E}(\{\boldsymbol{r}\})$, down to the atomic level. In this sense the molecular configuration in the glass is qualitatively different from the arrangement of the same molecules in the liquid from which the glass emerged. We want to try to understand the properties of amorphous glasses as the properties of an expansion around such a reference state in the same sense in which one understands ordered crystalline solids in Born–von Karman lattice dynamics without worrying about the way a liquid actually freezes.

The most important new, and presumably controversial point in our description is the emphasis on the role of stresses in the quenching process which produces the reference state of the glass and in the "lattice dynamics" of the glass. We will argue that one cannot understand what happens in a rapid quench and the nature of the reference state of the glass which it produces without taking into account the role of structural buckling caused by internal stresses in the dynamic restructuring process which produces the reference state. We also claim that one has to take into account the role of the internal stresses in the eventual reference state of the glass if one wants to understand the peculiarities of this reference state which distinguish glasses from other solids.

16.1.1. *Treating glasses as solids*

From a phenomenological point of view the motivation for treating glasses as solids is fairly obvious. As we explained in Section 2 glasses are solids according to any reasonable criteria for defining what a solid is. The mechanical properties of glasses are the mechanical properties of solids and not of fluids. Glasses are *macroscopic* solids. They have a static zero-frequency shear modulus which describes their elastic response in exactly the same sense in which crystalline solids have such a modulus. Glasses are also *microscopic* solids and have reasonably rigid microscopic reference states which define the atomic positions in the glass. Like all other solids glasses do of course "flow" to some degree but their "fluid" properties like irreversible changes in shape in response to applied forces and microscopic molecular self-diffusion are not dramatically different from what they are in crystalline solids.[72]

This means that it must be possible to derive the properties of glasses from a consistent CB expansion around a microscopic reference state in the sense of the consistency conditions which we discussed in Section 2. As in the description of crystalline solids the deviations from this atomically rigid picture in glasses can be treated as a relatively small correction which does not change the basic picture.

If this is true then the numerous and important differences between the mechanical and thermodynamic properties of amorphous glasses and those of crystalline solids must reflect the difference between their respective reference states. They should be explained by the difference between the CB expansion around a "typical" realization of the isotropic and random reference state of a glass and the expansion around the ordered periodic reference state of a crystalline solid.

16.1.2. The quenched reference state of the glass and the internal stresses

The essence of the microscopic theory of glasses which we will describe is that the reference state of the glass cannot be regarded simply as an arbitrary random state. The reference state has very special properties because it is produced by a glass-forming quench. The reference state of the glass is a stable equilibrium state which is produced by the rapid quenching of a liquid. Rapid quenching suppresses single particle rearrangements. We therefore claim that the *dominant* restructuring process which creates the reference state of the glass is a hierarchy of solid-like structural buckling processes controlled by the internal stress fields in the glass. The distinguishing feature of the reference states of the glass is in the role of buckling in producing them and in the presence of tenuous, or even floppy inclusions.

This scenario predicts very special reference states for the glass in which the internal stresses are correlated with the local structure in a non-trivial way. It predicts that the quenched reference state of the glass is very different from the "random medium" which one obtains by simply introducing a large amount of uncorrelated disorder into a homogeneous medium and in which one can neglect the effect of stresses. For this reason the properties of the expansion around such a quenched reference state are also predicted to be very different from those of the CB expansion around a BH "random medium".[73]

The essence of the difference between glasses and other solids is in the role of stresses in the process which creates the reference state of glasses and in its stability.

16.1.3. The initial stresses in a glass are internal stresses

As we saw in Sections 14 and 15 the initial stresses are also important in understanding other types of amorphous matter. In *soft solids* – Section 14 – we saw that the shear rigidity is

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[72] This is certainly true at low temperatures but also, though perhaps less dramatically, fairly close to the glass transition.

[73] Studied, e.g., by John et al. (1983), Grest and Webman (1984), Webman and Grest (1985) and much earlier in the pioneering work of Thouless.

dominated by the negative average stresses and for *random packings* we found – in Section 15 – that the direct effect of the positive stresses is responsible for the structural buckling which produces the eventual stable structure. Glasses differ from this because there are no "external forces". The initial stresses in glasses must be internal stresses with a zero average. The stresses in a glass are therefore *stabilizing* in some regions, or for some modes when the relevant stresses are negative and destabilizing in other regions and for other deformational modes for which the relevant stresses are positive. This combination of structural buckling similar to that we discussed for packings which is induced by the positive parts of the internal stresses and stress-stabilization by the negative parts of the same internal stress produces a very peculiar reference state for the glass. After deriving the properties of such a reference state we will then analyze the properties of the expansion around such a state.

16.1.4. Some special properties of glasses which appear naturally

The results of this analysis of the glassy state are very encouraging. As we will show some of the most puzzling universal properties of the glassy state appear naturally from this microscopic description when one thinks about the reference state in this way. In particular we shall discuss three well-known peculiarities of glasses which are particularly striking and universal and which we believe to be most important:

1. The microscopic origin of the large excess of soft modes in glasses which is responsible for the T^3 specific heat anomaly and for the "boson-peak" observed in neutron scattering – discussed and described extensively in Karpov et al. (1983), Karpov and Parshin (1983), Il'in et al. (1987), Buchenau et al. (1991), Buchenau et al. (1992), Parshin et al. (1993), Gurevich et al. (1993), mostly in the context of phenomenological "soft-potential" models.
2. The microscopic origin of the anomalously strong phonon scattering in amorphous materials whose most thoroughly studied manifestation is the "plateau" in the heat conductivity of glasses (Alexander and Orbach, 1982; Alexander, 1984b, 1986). Using general dimensional and scaling considerations inspired by the fracton model (Alexander and Orbach, 1982; Alexander, 1984a), we (Alexander et al., 1983) have suggested in the past that this is an effect of anomalously strong elastic scattering which is also reflected in the very large Joffe–Regel localization length.

This picture is confirmed by the microscopic model we present below.

3. The microscopic origin of the *two-level* systems which dominate the low temperature specific heat and long wavelength phonon scattering (Anderson et al., 1972).

All these well-known and universal properties of glasses are usually discussed in the framework of phenomenological models, e.g., in the references we have just cited, but are not really related to any microscopic description. We will show that they appear naturally as properties of the expansion around a quenched reference state produced in the way we described above.

We will discuss this model of glasses in this chapter.

The fact that the stresses in a glass are purely internal plays a crucial role in this analysis. Since we are also not aware of an adequate discussion of the structure of internal stress fields we will discuss the internal stresses in an elastic continuum in some detail and in a very general way in Section 17 in a form which seems convenient for describing amorphous materials. We do this in a somewhat unusual way which avoids the usual emphasis on structural defects and the associated linearity assumptions.

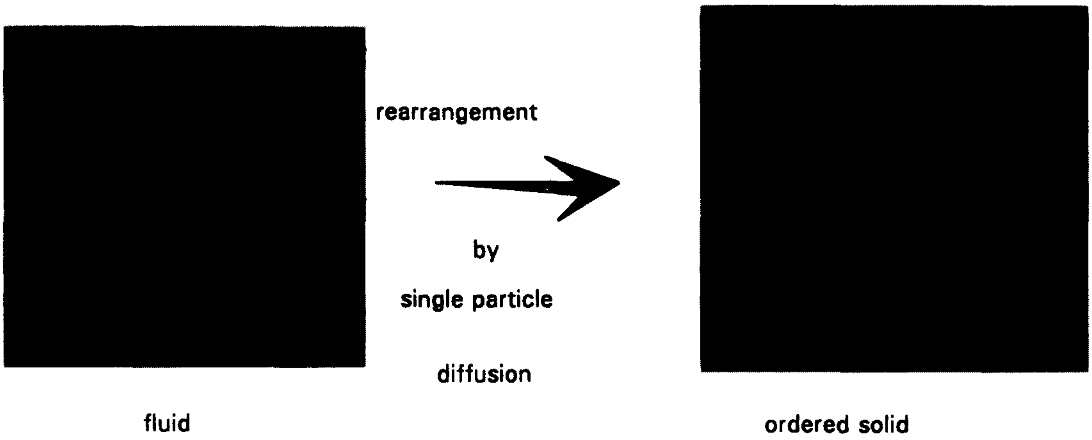

Fig. III.9. Crystallization involves major rearrangement which requires single particle diffusion.

16.2. Making a glass

Glasses are produced by rapid quenching from the liquid. The main effect of the rapid cooling is to suppress the single-particle diffusion processes. This is possible because the diffusion constants decrease rapidly with temperature – typically

$$D \propto \mathrm{e}^{-E/T} .$$

Sufficiently rapid quenching not only suppresses the ongoing rapid rearrangement of the molecules in the liquid state but also blocks the route to crystallization (see Fig. III.9) by nucleation and growth and even by spinodal instabilities. The atomic configurations in the liquid and in the periodic solid are, in general, so different that the transition cannot occur without major rearrangements which require diffusion at the single particle level.

16.2.1. The "snapshot state" is not the reference state of the glass

Sufficiently rapid quenching blocks the route from the liquid to the true global energy minimum which is presumably ordered and crystalline and tends to freeze-in the instantaneous configuration of the molecules in the liquid. The fact that the reference state is random must be a reflection of the randomness of the molecular arrangement in the liquid which is conserved in freezing into the glassy state. Ideally, for sufficiently rapid cooling rates, one might think that one could really freeze-in a "snapshot" of the instantaneous molecular configuration in the liquid at the time of the quench.

The fact that elastic scattering of X-rays from fluids and glasses gives fairly similar structure factors demonstrates that this picture of the quenched reference state of the glass cannot be dramatically wrong. It shows that

$$\{\boldsymbol{R}\}_{\text{glass}} \approx \{\boldsymbol{r}\}_{\text{snap}} = \{\boldsymbol{r}(t_{\text{que}})\}_{\text{liquid}} ,$$

where $\{\boldsymbol{r}(t_{\text{que}})\}$ describes the atomic positions in the liquid at the time of the quench, and $\{\boldsymbol{R}\}_{\text{glass}}$ is the reference state of the quenched glass.

The large "missing" low temperature entropy one observes for glasses also supports this picture. But this cannot be quite correct.

The reference state of a glass is the reference state of a solid and therefore must obey the standard equilibrium conditions

$$\sum_j \frac{\mathcal{T}_{ij}}{|\boldsymbol{R}_i - \boldsymbol{R}_j|}(\boldsymbol{R}_i - \boldsymbol{R}_j) = 0$$

– Eq. (12.5) and the linear stability conditions for such a reference state, Eqs. (13.5) which we discussed in detail in Sections 10 and 13.

These are conditions on the expansion of the potential energy, $\mathscr{E}(\{\boldsymbol{r}\})$, around $\{\boldsymbol{R}\}_{\text{glass}}$. Since kinetic energy and entropy play an important role in the liquid, a representative configuration of the liquid, $\{\boldsymbol{r}(t)\}$, is obviously not a configuration in which the potential energy, $\mathscr{E}(\{\boldsymbol{r}\})$, is in stable equilibrium. Thus the "snapshot" state does not satisfy the equilibrium and stability conditions which one requires for the reference state of the solid glass. To become a stable equilibrium reference state $\{\boldsymbol{r}\}_{\text{snap}}$ must undergo a restructuring process which removes the instabilities and the deviations from equilibrium – no matter how fast and efficient the quenching is. We can write for this restructuring process:

$$\{\boldsymbol{r}\}_{\text{snap}} \Rightarrow \{\boldsymbol{R}\}_{\text{glass}} = \{\boldsymbol{R}\}_{\text{glass}}(\{\boldsymbol{r}\}_{\text{snap}}), \qquad \mathscr{E}(\{\boldsymbol{r}\}_{\text{snap}}) \Rightarrow \mathscr{E}(\{\boldsymbol{R}\}_{\text{glass}}) \tag{16.1}$$

which emphasizes the distinction between the "snapshot" state and the stable equilibrium reference state of the glass $\{\boldsymbol{R}_{\text{glass}}\}$.

One can also say this differently. One expects the snapshot state to be an open tenuous configuration with fairly large "bond-tensions" $\mathcal{T}_{ij}$, and therefore interatomic forces and internal stresses. Even when one has suppressed single particle diffusion such a state is still unstable and will restructure in a relatively rapid relaxational process.

16.2.2. What happens in the ideal "infinitely fast" quench

In describing the restructuring during the quench one has to distinguish between two distinct processes:

1. the diffusive single particle motion which the quenching inhibits and
2. the relaxation of the potential energy to a stable equilibrium state.

Ideally – for an "infinitely fast" quench – the diffusive processes would be completely suppressed. This leaves a solid-like relaxation process in which the snapshot state, $\{\boldsymbol{r}\}_{\text{snap}}$, relaxes to a specific stable equilibrium reference state $\{\boldsymbol{R}\}_{\text{glass}}$. The restructuring process then consists of continuous deformations of the many particle configuration $\{\boldsymbol{r}\}$ on the potential energy surface $\mathscr{E}(\{\boldsymbol{r}\})$.

One can regard this as the relaxation of a "solid" from the initial distorted state $\{\boldsymbol{r}\}_{\text{snap}}$, to the ideal reference state $\{\boldsymbol{R}\}_{\text{ideal}}$, which is a stable equilibrium state. In this process the potential energy $\mathscr{E}(\{\boldsymbol{r}\})$ decreases from to its value in the liquid state $\{\boldsymbol{r}\}_{\text{snap}}$, to that in the reference state of the ideal glass $\{\boldsymbol{R}\}_{\text{ideal}}$. We call this idealized process the *ideal quench* and the state which results from it the *ideal reference state.*

The distinction between the ideal quench and a real quench can be seen clearly if we assume, e.g., that the interactions are short range so that the snapshot state can be represented by a well-defined bonded network. The ideal quench is then a relaxation of the way this network is embedded in space. The positions of the particles change but the bonded network remains the network defined in the snapshot state. Diffusion moves the particles and changes the bonded network. It cuts “bonds” and produces new bonds.

The ideal quench is of course an idealization. It corresponds to an infinitely fast quench. It differs from any real quench because diffusion plays no role whatsoever. The rate of a real quench is of course always finite and the state which is actually reached then depends on the actual quenching process which is more or less well approximated by the ideal quench.

The ideal quench is a relaxation process which realizes the transition from the snapshot state, $\{\boldsymbol{r}\}_{\text{snap}}$, to the ideal reference state of the glass, $\{\boldsymbol{R}\}_{\text{ideal}}$ – Eq. (16.1).

The dynamic processes in the ideal quench are collective deformations driven by the forces on the atoms

$$\{f\}_{\{r\}} = \{f_1, f_2, \ldots, f_i, \ldots, f_N\}_{\{r\}}\,, \qquad f_i = \nabla_i \mathscr{E}(\{\boldsymbol{r}\})\,. \tag{16.2}$$

These forces vanish in equilibrium

$$f_i(\{\boldsymbol{r}^{\text{equ}}\}) \equiv 0 \tag{16.3}$$

but are finite for non-equilibrium configurations. In a continuum limit the discrete forces $\{\boldsymbol{f}\}_{\{r\}}$ are replaced by a continuum field, $\boldsymbol{f}(\boldsymbol{r};\ \{\boldsymbol{r}\})$ which depends on $\boldsymbol{r}$ but also, implicitly, on the specific configuration of all the atoms $\{\boldsymbol{r}\}$. This continuum force field is related to the tensorial stress field at $\boldsymbol{r}$ for the same atomic configuration, $\sigma(\boldsymbol{r};\ \{\boldsymbol{r}\})$, through

$$\boldsymbol{f}(\boldsymbol{r};\ \{\boldsymbol{r}\}) = \nabla \cdot \sigma(\boldsymbol{r};\ \{\boldsymbol{r}\})\,. \tag{16.4}$$

For an equilibrium configuration, $\{\boldsymbol{r}\}_{\text{equ}}$, one requires

$$\boldsymbol{f}(\boldsymbol{r};\ \{\boldsymbol{r}\}_{\text{equ}}) = 0\,. \tag{16.5}$$

But this is clearly not enough.

Most of the equilibrium states – the extrema of $\mathscr{E}(\{\boldsymbol{r}\})$ in the Nd dimensional space spanned by $\{\boldsymbol{r}\}$ – are saddle points which are stable in some directions and unstable with respect to collective structural buckling instabilities in other directions in this space. These saddle points determine the route by which the glass evolves during the ideal quench from its specific initial state – the snapshot state $\{\boldsymbol{r}\}_{\text{snap}}$ – to a stable equilibrium state, the specific “ideal” reference state of the glass which is realized – $\{\boldsymbol{R}_{\text{ideal}}\}(\{\boldsymbol{r}_{\text{snap}}\})$. Qualitatively one can therefore think of the relaxation process (16.1) as a sequence of structural buckling instabilities which successively restructure the microscopic configuration until a stable reference state is reached. This is described schematically in Fig. III.10.[74]

This “ideal” scenario treats the glass as a solid throughout the quenching process. The snapshot state is regarded as the distorted state of a solid which then relaxes to its stable equilibrium reference state $\{\boldsymbol{R}\}_{\text{ideal}}$. The solid is assumed to relax more or less smoothly from the distorted state

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[74] This should of course not be taken too literally. In general the relaxation route will not go exactly through the equilibrium saddle points themselves. It only passes close to some of them.

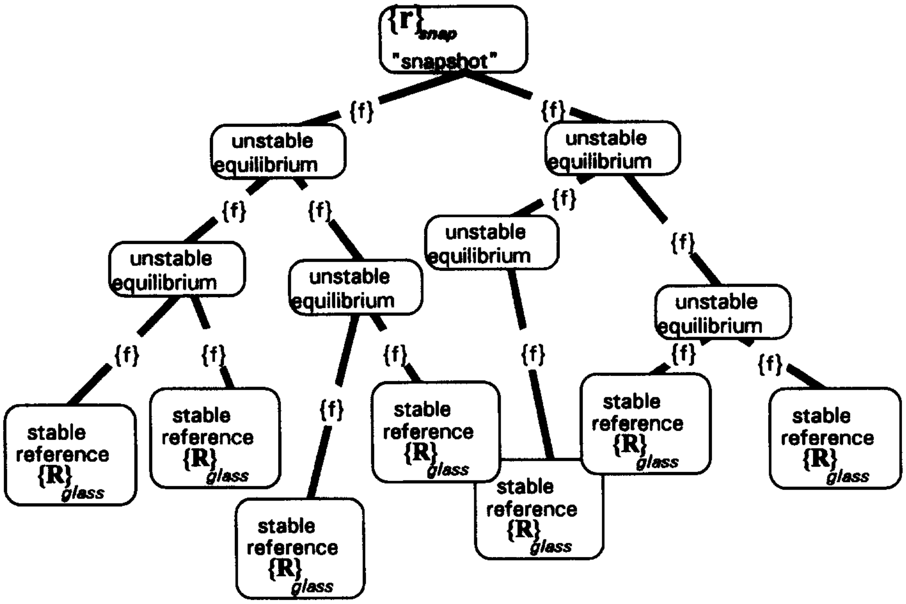

Fig. III.10. The "ideal" route from the "liquid" snapshot state $\{\boldsymbol{r}\}_{\text{snap}}$ to the stable equilibrium reference state of the glass $\{\boldsymbol{R}\}_{\text{glass}}$. The branching tree structure is meant to indicate that there are many possibilities and the choice can depend on very small changes.

$\{\boldsymbol{r}\}_{\text{snap}}$, along a path determined by the structural instabilities which it encounters. We describe this schematically in Fig. III.10.

The ideal, infinite-rate quench is obviously an approximate and incomplete description of the real physical situation. The important points which this limit emphasizes are the distinction between the snapshot state, $\{\boldsymbol{r}\}_{\text{snap}}$, and the reference state of the glass which it produces, $\{\boldsymbol{R}\}_{\text{glass}}$, which must be a stable equilibrium state and the nature of the process which restructures the glass. Since the snapshot state cannot describe a solid this restructuring must always occur no matter how rapid the quench.

We believe that this idealized picture describes the essence of the quenching process which produces the glass. In particular it focuses attention on the distinction between the snapshot state, an arbitrary configuration of the molecules in the liquid, and the final stable equilibrium state $\{\boldsymbol{R}\}_{\text{glass}}$. The reference state of the glass, $\{\boldsymbol{R}\}_{\text{glass}}$, is a random state which "remembers" the quenched random arrangement of the atoms in the fluid. But the atomic positions have been modified by collective restructuring. In the reference state they are correlated with the interatomic forces and local stresses to assure stable equilibrium.

16.3. Restructuring in internal stresses

To make this more specific we need a more formal formulation. It will be convenient to do this in a continuum description. In essence we will do this along the lines of the arguments we described in detail in Sections 13.4 and 15.

16.3.1. *The elastic energy which drives the restructuring*

The stability of a configuration, $\{\boldsymbol{r}\}$, with respect to deformations, $\boldsymbol{u}(\boldsymbol{r})$, depends on the balance between the BH elastic energy of the system,

$$E^{\mathrm{BH}}(\{\boldsymbol{r}\}) = \int \mathrm{d}\boldsymbol{r} \sum K^{\alpha\beta,\gamma\delta}(\boldsymbol{r};\ \{\boldsymbol{r}\})\,(\partial_\alpha u_\beta + \partial_\beta u_\alpha)(\partial_\gamma u_\delta + \partial_\delta u_\gamma) \tag{16.6}$$

and the stress induced energy

$$E^{\mathrm{dir}}(\{\boldsymbol{r}\}) = -\int \mathrm{d}\boldsymbol{r} \sum_\alpha \sigma^{\alpha\alpha}(\boldsymbol{r}, \{\boldsymbol{r}\}) \sum_\beta (\partial_\alpha u_\beta)^2\,. \tag{16.7}$$

This means that the spatial correlations between the BH elastic constants and the stress in the same vicinity are important. Positive stresses in the region around $\boldsymbol{r}$ imply a local buckling instability unless the configuration $\{\boldsymbol{r}\}$ is such that the elastic constants at $\boldsymbol{r}$, $\boldsymbol{K}(\boldsymbol{r};\ \{\boldsymbol{r}\})$, are large enough and have the right structure to prevent the buckling.[75] The effect of the restructuring during the quench is to create such a situation. The reference state $\{\boldsymbol{R}\}_{\mathrm{glass}}$ must be stable. Where $\sigma^{\alpha\alpha}(\boldsymbol{r};\ \{\boldsymbol{r}\})$ is positive and large enough buckling instabilities will modify the structure so as to increase its BH stability. In the final stable reference state positive $\sigma^{\alpha\alpha}(\boldsymbol{r};\ \{\boldsymbol{R}\}_{\mathrm{glass}})$ are always correlated with rigid structures such that near $\boldsymbol{r}$ the $\boldsymbol{K}(\boldsymbol{r};\ \{\boldsymbol{R}\}_{\mathrm{glass}})$ are large enough to assure stability. Tenuous regions whose BH rigidity is small can survive in such a restructuring process only if they are correlated with stabilizing negative stresses.

16.3.2. *Internal stresses*

To make this more specific we have to consider the stress field in more detail.

In contrast to the situations we considered in Sections 14 and 15, there are no external forces acting on the glass in the configuration $\{\boldsymbol{R}\}_{\mathrm{glass}}$ – the stresses in the glass are purely internal.[76] It follows that the average stress in the glass vanishes

$$\langle\sigma\rangle_V = \frac{1}{V}\int_V \mathrm{d}\boldsymbol{r}\cdot\sigma(\boldsymbol{r}) = 0 \tag{16.8}$$

which implies that the sign of the stresses must change sign. In particular the pressure changes sign and the zero pressure surfaces

$$p(\boldsymbol{r}) = \frac{1}{d}\sum \sigma^{\alpha\alpha}(\boldsymbol{r};\ \{\boldsymbol{r}\}) = 0 \tag{16.9}$$

divide the solid into compressed regions where the pressure is positive and stretched regions where it is negative.

The tensorial components of the stress, $\sigma^{\alpha\beta}(\boldsymbol{r};\ \{\boldsymbol{r}\})$, and its principal axis components $\sigma^{\alpha\alpha}(\boldsymbol{r};\ \{\boldsymbol{r}\})$, which determine the stability of the elastic energy, also change sign.

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[75] As in Section 13.4 we assume that the BH elastic energy is always stable. This is convenient and is usually justified. We only note that it is a somewhat stronger assumption here because it implicitly assumes that the BH energy is stable for all the unstable equilibrium configurations which determine the quenching path.

[76] This not only applies to the eventual stable reference state of the glass $\{\boldsymbol{R}\}_{\mathrm{glass}}$, but also to all the intermediate unstable equilibrium states which control the structural buckling route from the snapshot state.

These properties of internal stress fields are quite general. In Section 17 we shall derive them, and some other general properties of internal stress fields, from the mechanical equilibrium conditions for the stress.

16.3.3. The correlation length of the random internal stresses in glasses

The changes in the sign of the stress follow from the fact the average stress of the whole solid vanishes. In itself this tells us relatively little about the detailed structure of the field. We will assume that the alterations in sign of the random stress field $\sigma(\boldsymbol{r}; \{\boldsymbol{R}\}_{\text{glass}})$ can be described by a correlation length, ξ, such that the stresses average out when they are averaged over larger distances – say

$$\langle\sigma\rangle_L \propto \frac{1}{L^d}\int_L \mathrm{d}\boldsymbol{r}\cdot\sigma(\boldsymbol{r}) \approx \left(\frac{\xi}{L}\right)^{d/2}, \quad \frac{\xi}{L} \ll 1 . \tag{16.10}$$

We believe that in glasses the correlation length ξ is a microscopic distance. This, obviously, does not follow from the fact that the macroscopic average of the stress vanishes, Eq. (16.8), which would be consistent with sign-changes on macroscopic scales. It does however seem very plausible and almost inevitable for a stress field produced by a rapid quench.

In the snapshot state the internal stresses should reflect the correlation length of the fluctuations in the liquid. This means that one expects ξ, to start out in $\{\boldsymbol{r}\}_{\text{snap}}$ as a relatively small microscopic length. In the restructuring process the stress presumably undergoes some coarsening which increases ξ. It is difficult to see how this increase could become very dramatic for a rapid quench. This would predict a correlation length for the stresses in glass which is comparable to that in the supercooled liquid which is quenched. This means a correlation length which is larger than the interatomic nearest neighbor distance but still microscopic. Say

$$\xi/a \approx 3\text{–}10 \tag{16.11}$$

just to make this more definite.

We believe that this must be at least qualitatively correct but this is of course just a tentative guess. To the best of our knowledge there are no measurements which check the variations in the internal stresses down to such small distances directly. We will discuss some indirect evidence for (16.11) below.

We will now try to draw some conclusions about the reference state of the glass from the general considerations we have listed.

16.4. The quenched reference state is composite

16.4.1. The buckled rigid scaffolding and the soft inclusions

The quenched reference state of the glass must have macroscopic BH rigidity. Since the average of the internal stress vanishes, Eq. (16.8), the internal stresses cannot contribute to the overall macroscopic shear rigidity. It follows that the macroscopic elastic moduli which one measures, and which appear in the sound velocities, must be proper BH shear moduli. Contrary to the situation in soft solids which we considered in Section 14 they cannot be due to the direct effect of the stresses. This is not a trivial result.

The conclusion that the reference state of the glass $\{\boldsymbol{R}_{\text{glass}}\}$ must have proper macroscopic BH elastic moduli implies that the reference state must contain a connected BH-rigid scaffolding which

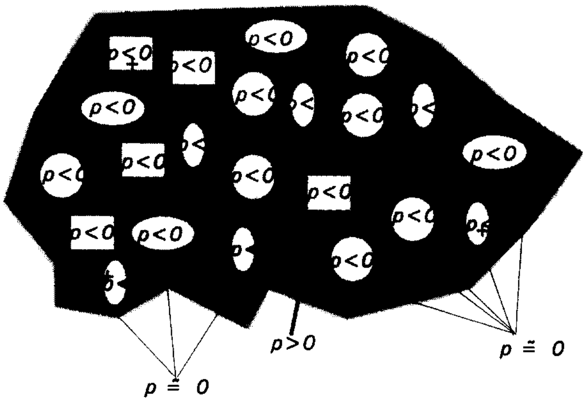

Fig. III.11. Schematic description of a 2-D quenched reference state. The stress in the soft white regions is negative. Forces on the boundaries of these regions are supported by the BH rigid scaffolding (light gray) which is responsible for the macroscopic rigidity. The stresses in the dark gray boundary regions are small.

is sufficiently rigid to generate this shear rigidity. Moreover, the BH-rigid solid material which forms this scaffolding must be rigid enough to overcome the destabilizing effects of positive stresses – the remnants of the stresses which caused the structural buckling and thus created this BH rigid material. Embedded in this scaffolding one can still have relatively soft regions which have not buckled and are correlated with the negative parts of the internal stresses.

In general such a structure can be very complicated. It is essential that the rigid scaffolding should be connected. Moreover, the mesh size of this scaffolding should be the correlation length of the stress, ξ. One can also say that the size of the soft negative stress regions is expected to be ξ.

Fig. III.11 illustrates schematically what this model implies for the structure of the reference state. The rigid scaffolding, colored light gray, is responsible for the BH macroscopic rigidity of the glass. It supports all the destabilizing positive stresses. The white enclosures are soft and are stabilized by negative stresses. This picture makes several simplifying assumptions. It implicitly identifies the sign of the pressure with the sign of the stress. This ignores the complications which can occur because of anisotropy when the principal axis components do not all have the sign of the pressure. The drawing also assumes that the soft regions are confined to closed inclusions in the scaffolding. This is a geometrical necessity in two dimensions. In three dimensions one can of course have bicontinuous geometries where both the rigid scaffolding and the soft negative-stress regions are macroscopically continuous.

16.4.2. Describing the glass as a composite

This amounts to a description of the glass as a composite. The glass consists of two types of solid materials which together constitute the glass.

a. *The BH-rigid buckled material* which forms the rigid continuous scaffolding.

b. *The soft unbuckled solid* in the inclusions. The stresses in these regions have to be negative and are important for their shear rigidity.

The two regions are coupled through the stresses. The forces exerted by the negative stresses in the soft regions on their boundaries have to be supported by the BH-rigid scaffolding.

One also notes that the strength of the couplings across the boundaries between the two regions define a limit on the magnitude of the negative stresses which they cannot exceed. Because the average stress vanishes this is automatically also a limit on the positive stresses in the buckled regions.

16.5. Predictions and comparison to experiment

16.5.1. Propagating sound, Rayleigh scattering and heat conduction

If the reference state of the glass has the structure we have suggested then it is obvious that the bulk elastic moduli, in particular the bulk shear modulus, are properties of the rigid scaffolding. Sound propagates on the scaffolding and for small wave vectors

$$q\cdot\xi<1 \tag{16.12}$$

is relatively insensitive to the soft inclusions.[77]

Sound is scattered from the soft inclusions of size ξ which means that elastic Rayleigh scattering is anomalously strong

$$q\,\lambda_{\mathrm{R}}(q)\propto(q\xi)^{-3} \tag{16.13}$$

in three dimensions. Because of the high power on the r.h.s this is a fairly dramatic effect. The predicted scattering is much stronger than the scattering from disorder at the atomic level, a. In the range we have suggested, (16.11), it amounts to an increase of 1–2 orders of magnitude.

In particular one predicts that there will be a qualitative change in the nature of the eigenmodes when one extends the phonon branches beyond a cross-over frequency

$$\Omega\approx c/\xi\,,\qquad q_{\Omega}\cdot\xi=1\,. \tag{16.14}$$

This seems to agree qualitatively with the "plateau" in the heat conductivity observed in glasses, with measurements of the scattering length and even with specific heat measurements – see, e.g., Alexander et al. (1983) and Alexander (1986).

16.5.2. Soft modes

It is well known that an excess of soft modes is observed in glasses. This shows up as an excess in the T^3 contribution to the specific heat and in the Boson peak observed in neutron scattering. Our model for the reference state predicts such an excess because of the vibrations of the "soft" and stressed unbuckled regions of size ξ which we predict.

16.5.3. Unharmonic two-level systems

We have distinguished between a region where buckling has occurred because the stresses are positive and large enough and a soft region which has not buckled because the stresses are negative and stabilizing. On the boundary between these two regions, say the dark gray region in Fig. III.11, the stresses are small and anharmonic terms are important. The effective potential for a vibrational eigenmode in this region would have the "canonical" form for 2-level systems as in Fig. III.12.

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[77] On the very qualitative level of the analysis it does not make sense to discuss the distinction between longitudinal and transverse modes.

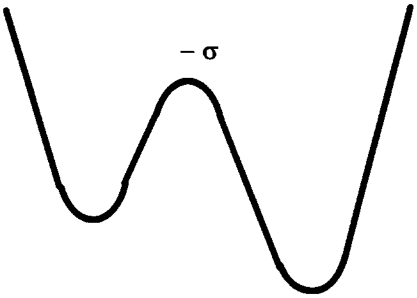

Fig. III.12. A small positive stress creates anharmonic two-level states.

17. Internal stresses

The fact that the stresses in the glass are purely internal so that their average must vanish and their signs have to change played a crucial role in our analysis in Section 16. In this discussion we used a very rough qualitative picture of the stress field. To extend this analysis and make it more detailed and realistic one obviously needs a better understanding of the stresses. Our purpose here is to present some general results in this direction. We do this here because we are not aware of any detailed analysis of internal stress fields which is appropriate for the description of such stresses in glasses and in other amorphous solids. Even though we do not use them explicitly the results we derive here can be regarded as a background for the picture described in Section 16. They can also be regarded as a preliminary, introductory step in the development of a more detailed theory of glasses along the lines we have indicated.

17.1. The description of internal stresses in crystals and in amorphous materials

In the physics literature internal stress fields are usually derived from the structural defects which produce them rather than on their own. There are extensive discussions of the structural defects of crystalline solids in the literature, see, e.g., Friedel (1964), Landau and Lifshitz (1970, ch. IV) and Kleman (1977). In these monographs the defects are classified according to the structural singularities from which they arise – which perturb the discrete translation–rotation space group symmetry of the periodic crystal. Familiar examples are line defects like dislocations and disclinations and point defects like vacancies and interstitials.

In this description the structural defects are the primary objects. When required one then calculates the stress fields associated with them from the strains assuming linear stress–strain relations. In this way the locations of the singularities of the structural defects – the defect lines or points – also appear as singularities of the internal stress fields they produce.

While this procedure is most familiar nowadays in the discussion of crystalline solids it actually originated in continuum elasticity and therefore, implicitly, in the description of the internal stresses in isotropic amorphous solids. Internal stress fields were first analyzed by Volterra (1907) and then by Love (1927a, #156A) in the context of purely continuum elasticity long before they were applied to periodic lattices. The standard types of defects can all be generated from an unstressed solid medium by variants of the operational Volterra construction – making cuts and repairing them.[78] Even the global, integral conditions on the strains are essentially the same.[79] The term "dislocation" was originally coined by Love (1927a) to describe continuum defects. Nevertheless, we believe that it is better to discuss the internal stresses in an amorphous solid directly, regarding the stresses themselves as the primary object, rather than to try to relate them to structural defects and strains. There are three main reasons for this:

1. One is intuitive and fairly obvious.

In a periodic lattice a structural defect has a clear and fairly obvious geometric meaning. The dislocation line in a lattice is, e.g., a well defined object and can be found by suitable microscopic inspection of the atomic arrangement. In contrast one cannot really imagine or describe what a dislocation line in an amorphous solid would look like. Even conceptually the only reliable way for finding such a line is to measure the stress field.

2. The second reason for preferring a description in which the stresses themselves are the primary objects is that in this way one does not need to refer to a "true" unstressed BH reference state. For an amorphous glass the definition of a "true" reference configuration with respect to which one can define strains is quite difficult and ambiguous and not even obviously meaningful.

Another way of saying this is that in an amorphous solid the deviations from an unstressed state can be very large – making the expansion in strains meaningless. On the other hand, as we demonstrated in Section 3, one can define the stresses unambiguously for any configuration. The fact that the solid is amorphous does not matter.

3. The most important manifestation of the difference between the internal stress fields of crystalline and amorphous materials is in the nature of the cores. In crystals a defect usually has a well-defined structural core at the microscopic level. The "core" region of a crystalline defect is strongly strained and therefore cannot be described by the periodic lattice which describes the crystal far from the core. The core region is then qualitatively different from the bulk of the same crystal which is only weakly strained.

This does not carry over to structural defects in amorphous solids, where, in general, no "cores" can be identified. The strongly stressed material near the singularity of a Volterra construction can simply rearrange itself into a different and non-singular configuration of the amorphous solid with no obvious distinguishing features. Thus the cores which mark the dislocation lines in crystals will in general not show up in amorphous materials.

For all these reasons, and also because disordered amorphous solids are often much more deformed internally than crystals the internal stress fields in amorphous materials can be very complex even more complex than, say, the stress field of a Frank network of dislocations. It is therefore useful to study them in the most general way possible. It turns out that one can actually say some very general things about these fields.

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[78] The generation of line singularities, dislocations and disclinations, by gluing cuts is discussed in all texts. The creation of point singularities by the action of point sources or sinks is a little less familiar but not really very different.

[79] To avoid confusion we note that the continuum "*Burgers vector*" of a dislocation has a continuous, rather than discrete set of values.

17.2. The equilibrium conditions

The microscopic form of the equilibrium conditions for a solid are Eqs. (12.5)

$$\sum_j \frac{\mathcal{T}_{ij}}{|\boldsymbol{R}_i - \boldsymbol{R}_j|}(\boldsymbol{R}_i - \boldsymbol{R}_j) = 0 .$$

The continuum form of these equations are the homogeneous mechanical equilibrium conditions for the stress field in the bulk – Eqs. (12.4a)

$$\nabla \cdot \sigma^{\mathrm{int}}(\boldsymbol{r}) = 0 \tag{17.1}$$

and the zero force boundary conditions – Eqs. (12.4b)

$$\hat{\boldsymbol{n}}(\boldsymbol{r}^{\mathrm{b}}) \cdot \sigma^{\mathrm{int}}(\boldsymbol{r}^{\mathrm{b}}) = 0 , \tag{17.2}$$

where $\hat{\boldsymbol{n}}(\boldsymbol{r}^{\mathrm{b}})$ is the normal at the point $\boldsymbol{r}^{\mathrm{b}}$ on the boundary.

Since internal stresses exert no forces on the boundaries the *average* internal stress must vanish

$$\langle \sigma^{\mathrm{int}} \rangle = \frac{1}{V} \int_V \mathrm{d}\boldsymbol{r} \cdot \sigma^{\mathrm{int}}(\boldsymbol{r}) \equiv 0 . \tag{17.3}$$

17.3. The effect of the boundary conditions

We first consider the implications of the fact that the average internal stress must vanish – Eq. (17.3).

17.3.1. The pressure and the pure shear stress

We divide the stress tensor, $\sigma(\boldsymbol{r})$, into its scalar part, the pressure

$$p(\boldsymbol{r}) = d^{-1}\,\mathrm{Tr}\,\sigma(\boldsymbol{r}) = d^{-1} \sum_\alpha \sigma_{\alpha\alpha}(\boldsymbol{r}) \tag{17.4}$$

and a traceless irreducible second rank tensor – the pure shear stress, $\sigma^{\mathrm{she}}(\boldsymbol{r})$:

$$\sigma^{\alpha\beta}(\boldsymbol{r}) = p(\boldsymbol{r})\,\delta(\alpha\beta) + \sigma^{\mathrm{she}}{}_{\alpha\beta}(\boldsymbol{r}) . \tag{17.5}$$

The average pressure, $\langle p \rangle$, and the average traceless shear stress tensor, $\langle \sigma^{\mathrm{she}} \rangle$ cannot cancel each other. It therefore follows from (17.3) that their averages have to vanish separately:

$$\langle p \rangle = V^{-1} \int \mathrm{d}\boldsymbol{r} \cdot p(\boldsymbol{r}) = 0 , \tag{17.6}$$

$$\langle \sigma^{\mathrm{she}} \rangle \propto \int \mathrm{d}\boldsymbol{r} \cdot \sigma^{\mathrm{she}}(\boldsymbol{r}) = 0 . \tag{17.7}$$

If the average pressure vanishes the pressure must change sign. The zero-pressure surfaces defined by

$$p(\boldsymbol{r}) = 0 \tag{17.8}$$

divide space into regions in which the pressure is positive

$$p(\boldsymbol{r})>0 \tag{17.9}$$

which, in general, one expects to be compressed and stretched negative-pressure regions for which

$$p(\boldsymbol{r})<0\,. \tag{17.10}$$

Since the average shear stress also vanishes, (17.7), it follows that the average of each component of the shear stress must vanish separately

$$\langle\sigma^{\alpha\beta}_{\mathrm{she}}\rangle \propto \int \mathrm{d}\boldsymbol{r}\cdot\sigma^{\alpha\beta}_{\mathrm{she}}(\boldsymbol{r})=0\,. \tag{17.11}$$

17.3.2. *The principal axis components of the internal stress change sign*

As we saw in Section 13.4 the effect of the stresses on stability is seen most clearly when we write the stress in its principal axis system. The contribution of the stresses to the energy density at $\boldsymbol{r}$ is

$$-\sum_{\alpha}\boldsymbol{\sigma}^{\alpha\alpha}_{\mathrm{ini}}(\boldsymbol{r})\cdot\sum_{\gamma}(\partial_{\alpha}u_{\gamma}(\boldsymbol{r}))^2$$

which is stabilizing when $\sigma^{\alpha\alpha}(\boldsymbol{r})$ is negative and destabilizing when it is positive.

The fact that the average pressure vanishes, Eq. (17.6), implies that the principal axis components $\sigma^{\alpha\alpha}(\boldsymbol{r})$ cannot all have the same sign.

When the pressure vanishes

$$p(\boldsymbol{r})\propto\sum\sigma^{\alpha\alpha}=0\,,$$

the stress is a pure shear stress and one must have diagonal components of both signs.

If the pressure is not everywhere zero it must change sign. In the positive pressure regions, (17.9), all components of the stress can be positive but, in any case, there are positive $\sigma^{\alpha\alpha}(\boldsymbol{r})$ whose sum is larger than the sum of the negative $\sigma^{\alpha\alpha}(\boldsymbol{r})$ – everywhere in this region. The reverse is true for the negative pressure regions, $p(\boldsymbol{r})<0$, for which the negative principal axis components of the stress, $\sigma^{\alpha\alpha}(\boldsymbol{r})<0$, dominate.

We have thus shown that both signs of the principal axis components of the stress appear for any internal stress field. Internal stresses therefore always have both stabilizing and destabilizing effects for different shears or in different regions.

17.4. *Effect of the equilibrium conditions*

17.4.1. *The principal axis components rotate*

We have discussed the properties of the stress field which follow from the fact that the average internal stress vanishes. An internal stress field also has to satisfy the bulk equilibrium conditions (17.1)

$$\boldsymbol{f}(\boldsymbol{r})=\nabla\sigma(\boldsymbol{r})=0\,,\qquad \sum_{\alpha}\partial_{\alpha}\sigma^{\alpha\beta}(\boldsymbol{r})=0\,. \tag{17.12}$$

When the principal axes do not rotate – the orientation of the axes of the stress field is the same everywhere and (17.12) becomes

$$\partial_\alpha \sigma^{\alpha\alpha}(\boldsymbol{r}) = 0$$

which implies

$$\sigma^{\alpha\alpha}(\boldsymbol{r}) = \text{const}\,. \tag{17.13}$$

This generalizes Archimedes law of liquid hydrostatics:

$$p = \text{const}\,.$$

An internal stress field which exerts no force on the boundaries and whose principal axes are fixed in space must vanish identically.

17.4.2. *Classification of the singularities of the stress field*

Naturally, as one expects, this last result implies that internal stress fields can be classified in a way which is closely related to the topological classification of structural defects. In particular, one can classify dislocations and disclinations, the "first homotopy group" topological singularities of the stress field (Toulouse and Kleman, 1976; Kleman, 1977, ch. 10) according to the rotations of the principal axis system of the stress along closed paths.

There are however two reservations to this general statement.

- First is that the stress field or just some of its components can vanish. This is fairly obvious but it can restrict the power of the topological classification.
- The second point is that the correspondence between the usual structural classification and the classification of the stress is not simple.

Since this is an interesting point we want to show how the stress fields of edge dislocations and of disclinations created by Volterra constructions show up in this description.

17.5. *The stress fields of dislocations and disclinations*

We consider internal stress fields with cylindrical symmetry.

From the symmetry we can then write

$$\sigma(\boldsymbol{r}) = p(r) + \sigma(r)\cdot \tilde{O}(\varphi)\,, \tag{17.14}$$

where the pressure $p(r)$ and the magnitude of the shear stress, $\sigma(r)$, depend only on the radial distance, r.

We start by assuming that the tensor $\tilde{O}(\varphi)$ can be written in the general form

$$\tilde{O}_n(\varphi) = \begin{vmatrix} \cos n\varphi & \sin n\varphi \\ \sin n\varphi & -\cos n\varphi \end{vmatrix} \tag{17.15}$$

which assures periodicity around the circle. Substituting Eqs. (17.14) and (17.15) into Eqs. (17.1) one derives for the force

$$\boldsymbol{f}(\boldsymbol{r}) = p'(r)\cdot \begin{vmatrix} \cos\varphi \\ \sin\varphi \end{vmatrix} + \left(\sigma'(r) + \frac{n\sigma(r)}{r}\right) \begin{vmatrix} \cos(n-1)\varphi \\ \sin(n-1)\varphi \end{vmatrix} = 0\,. \tag{17.16}$$

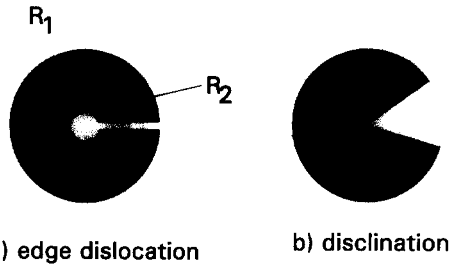

Fig. III.13. The Volterra construction for (a) an *edge dislocation*: and (b) for a simple *disclination*. The structural singularity is generated by closing the respective gaps and then gluing the flat surfaces together.

In general this can be interpreted as a balance between three forces

- The radial force exerted by the gradient of the pressure: $p'(r)\left|\begin{matrix}\cos\varphi\\ \sin\varphi\end{matrix}\right|$;
- The force exerted by the gradient of the shear stress: $\sigma'(r)\left|\begin{matrix}\cos(n-1)\varphi\\ \sin(n-1)\varphi\end{matrix}\right|$;
- A "curvature" term which describes the effect of the rotation of the stress as φ changes:[80] $\dfrac{2\sigma(r)}{r}\left|\begin{matrix}\cos(n-1)\varphi\\ \sin(n-1)\varphi\end{matrix}\right|$.

Evidently the scalar pressure only contributes when the shear stress tensor performs one full 2π rotation around the circle, i.e., for $n=2$ when the full cylindrical symmetry is maintained. Eq. (17.16) becomes

$$\delta(n-2)\,p'(r)+\sigma_n'(r)+\frac{2\sigma_n(r)}{r}=0 \tag{17.17}$$

with the boundary conditions

$$\delta(n-2)\,p(r)+\sigma_n(r)=P_r \tag{17.18}$$

on a circular boundary of radius r where P_r is the external pressure.

The stresses for both edge dislocations and for the simple bending disclinations of Fig. III.13 must be solutions of Eqs. (17.17) for $n=2$.

17.5.1. The stress of an edge dislocation

For large r, in the linear regime, the shear stress of an edge dislocation (Fig. III.13(a)) must be proportional to the shear strain and therefore consistent with the $1/r$ dependence of the transverse contraction. This is assured by setting

$$p'(r)=\sigma_2'(r) \tag{17.19}$$

in Eq. (17.17) which gives

$$\sigma_2(r)=\sigma(r_0)\frac{r_0}{r}\,,\qquad p(r)=a+\sigma_2(r)\,. \tag{17.20}$$

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[80] This is analogous to the normal force exerted by a curved stretched membrane.

On the outside boundary one requires

$$a + 2\sigma_2(r_0)r_0/R_2 = 0 \tag{17.21}$$

which fixes a. On a circle enclosing the core one finds

$$2\sigma(r_0)r_0\left(\frac{1}{R_1} - \frac{1}{R_2}\right) = P_{\rm core}\,, \tag{17.22}$$

where $P_{\rm core}$ is the pressure exerted by the material in the core on its outside boundary. We note that the form of the stresses in the core does not matter. A purely hydrostatic, compressed or extended core can generate the stresses outside the core.

17.5.2. Stress of a disclination

We compare with a disclination.

The shear strain of a disclination is constant, independent of r as can be seen for example in Fig. III.13(b). It follows that one is looking for solutions of Eq. (17.17) for which the shear stress is constant

$$\sigma'(r) = 0\,, \qquad \sigma(r) = \sigma\,. \tag{17.23}$$

Only the scalar pressure is singular

$$p(r) = 2\sigma\log(r_0/r) \tag{17.24}$$

and the boundary conditions are

$$1 + 2\log(r_0/R_2) = 0\,, \qquad 2\sigma\log(R_2/R_1) = P_{\rm core}\,. \tag{17.25}$$

One notes that the solutions are quite different. Both types of solutions, and many others, can be generated by the same core pressure because the equations for the stress on their own are of course not closed.

Acknowledgements

Over the years I have tried to explain what I was doing and the problems I was worried about in discussions with many people and I have certainly benefited greatly from their comments and advice.

I particularly want to thank three colleagues and friends Dov Levine, Zeev Olami and Yitzhak Rabin who, patiently and separately, spent a lot of valuable time in long discussions, keeping in touch with my slow progress and even managed to sound interested. Their help has been invaluable. Many of the ideas I develop originated in these discussions or are related to their work or to collaborations with them on a variety of topics. The discussion of soft matter in Sections 12–14, owes much to the work of Yitzhak Rabin and his collaborators on gels (Panyukov and Rabin, 1996; Rabin and Bruinsma, 1992, 1993, 1994; Alexander and Rabin, 1990). Dov Levine introduced me to the problems of granular matter and our collaboration on these problems (Levine et al., 1995; Levine and Alexander, 1996; Alexander, 1996a) is undoubtedly the origin of my understanding of structural buckling and its role in packings which I describe in Section 15. I discussed most of this work with Zeev Olami when in progress and many of his suggestions and ideas have been incorporated in it. In particular, our discussions and collaboration had a very large impact on the development of the theory of glasses described in Section 16.

In this context I want to thank P.G. deGennes, who introduced me to soft matter and from whom I have learned so much; and also for telling me, many years ago, that he liked what I did in Alexander (1985a) and understood why I did it. This was a great help. He has also listened patiently and commented on my descriptions on many later occasions.

I also want to thank Itamar Proccacia for encouragement and for many discussions.

I gratefully acknowledge support from the Minerva Foundation for several years.

Finally, finishing something of this length gives me the opportunity to thank my wife, Esther, whose encouragement and support have been invaluable. This does of course hold for most of the other things I have done over the years, certainly for all those I managed to conclude successfully, but for some reason it is only customary to acknowledge this sort of debt when one writes something which is at least 200 pages long. Looking for an opportunity to thank Esther has probably been the main factor which prevented me from giving up an effort which turned out to be much longer and harder than I had anticipated and was often discouraging.

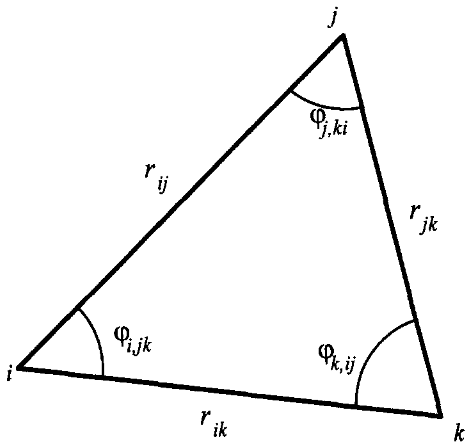
Appendix A. Description of the many-body interactions as angular and twist energies

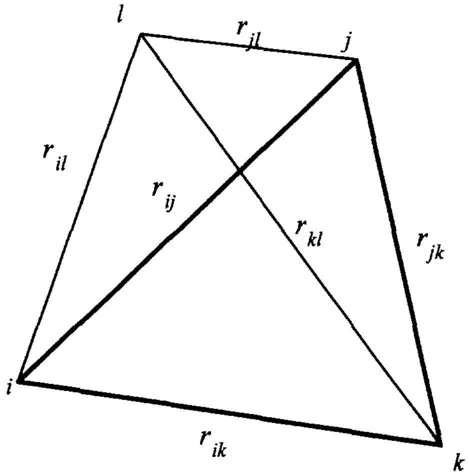
The expressions we derived in Section 5.2.3 for the many-body interactions, Eqs. (5.11) and (5.13), are in terms of the *longitudinal* deviations, $u_{ij}^{\prime\prime}$. This is convenient because it emphasizes the distinction between these terms and the stress-induced terms in Section 6 which cannot be written in this way. Writing the non-Cauchy interactions in this way is also convenient for the discussion of the continuum limit in Section 5.4. We want to show that angular (bending) and twist energies can indeed be written in this somewhat unusual way. We do this for completeness and also to assure the reader that the somewhat unconventional description in Section 5.2.3 is quite general.

Rotationally invariant three-body interactions can only depend on the shape of the triangle $[ijk]$ – Fig. A.1 – and rotationally invariant four-body interactions on the shape of the triangular pyramid $[ijkl]$ – Fig. A.2. We consider the three-body interactions in detail.

The harmonic expansion of the interactions between the three particles i, j and k is an expansion in the nine components of the deviations $\boldsymbol{u}_i$, $\boldsymbol{u}_j$ and $\boldsymbol{u}_k$ in three dimensions (or 6 in 2-D). But the rotationally invariant interaction energy $\mathscr{E}(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k)$ is completely determined by the triangle $[ijk]$, Fig. A.1, which, for any dimension, is determined by three parameters. To derive the rotationally invariant expansion one can choose any three parameters which determine the triangle. This can be done in different ways and leads to harmonic expansions which *look* different. In particular the explicit many-body terms can be chosen in different ways. The final expansion in the components of the $\boldsymbol{u}_i$ which one derives is of course independent of the parameters chosen to describe the triangle. In this final form of the expansion the rotational invariance and the distinction between two-body and three-body interactions is however no longer manifest.

If we parametrize the triangle $[ijk]$ in terms of the *three distances* r_{ij}, r_{ik} and r_{jk} this leads to an expansion in terms of two-site interactions of the form of Eq. (5.8) and three-site terms of the





A.1. The triangle $[ijk]$.

A.2. The pyramid $[ijkl]$.

form (5.11). The most general harmonic expansion is

$$\mathscr{A}'_{ijk} = \mathscr{K}'_{ij} u''^2_{ij} + \mathscr{K}'_{jk} u''^2_{jk} + \mathscr{K}'_{ki} u''^2_{ki} + \mathscr{K}_{i,jk} u''_{ij} \cdot u''_{ik} + \mathscr{K}_{j,ki} u''_{jk} u''_{ji} + \mathscr{K}_{k,ij} u''_{ki} u''_{kj} \tag{A.1}$$

which can of course be rewritten explicitly in terms of the components of the $\boldsymbol{u}_i$.

Alternatively one can describe *the same triangle* in terms of the distances r_{ij}, r_{ik} and r_{jk}, and of the angles $\varphi_{i,jk}$, $\varphi_{j,ki}$, $\varphi_{k,ij}$, (see Fig. A.1). If one uses this parametrization the explicitly three-body terms in the harmonic expansion appear as angular interactions

$$\left[\frac{\partial^2 \mathscr{E}}{\partial \varphi^2_{i,jk}}\right]_{\{R\}} (\delta\varphi_{i,jk})^2 = \mathscr{B}_{i,jk}\,\delta\varphi_i^2\,, \tag{A.2}$$

where $\delta\varphi_{i,jk}$ is the change in the angle $\varphi_{i,jk}$. One can thus write the harmonic energy of the triangle as the sum of angular and Cauchy terms

$$\mathscr{A}''_{ijk} = \mathscr{K}''_{ij} u''^2_{ij} + \mathscr{K}''_{ik} u''^2_{ik} + \mathscr{K}''_{jk} u''^2_{jk} + \mathscr{B}_{i,jk}\delta\varphi^2_{i,jk} + \mathscr{B}_{j,ki}\delta\varphi^2_{j,ki} + \mathscr{B}_{k,ij}\delta\varphi^2_{k,ij}\,. \tag{A.3}$$

Eventually, to write the expansion in the positional deviations, $\boldsymbol{u}_i$, one then has to express the $\delta\varphi_{i,jk}$ in the components of the $\boldsymbol{u}_i$. It is natural to do this using

$$\delta\varphi_{i,jk} \approx \frac{u^\perp_{ij}}{R_{ij}} - \frac{u^\perp_{ik}}{R_{ik}}\,. \tag{A.4}$$

The resulting expression must be equivalent to Eq. (A.1). The two explicit expressions, $\mathscr{A}'_{ijk}$ (Eq. (A.1)) and $\mathscr{A}''_{ijk}$ (Eq. (A.3)) can differ only in anharmonic terms in the components of the $\boldsymbol{u}_i$.

We want to show explicitly that the angular expansion $\mathscr{A}''_{ijk}$ can be rewritten as an expansion in the u''_{ij} that is in the form of Eq. (A.1). To be explicit we expand the angular bending energy Eq. (A.2).

We use

$$\cos\varphi_{i,jk} = -\frac{r_{jk}^2 - r_{ij}^2 - r_{ik}^2}{2\, r_{ij}\, r_{ik}} \tag{A.5}$$

to derive an explicit expression for the expansion of $\delta\varphi_{i,jk}$ in the δr_{ij}:

$$\begin{aligned} 2\sin\Phi_{i,jk}\,\delta\varphi_{i,jk} = {} & \left(\frac{R_{ij}}{R_{ik}} + \frac{R_{ik}}{R_{ij}} - 2\cos\Phi_{i,jk}\right)\left(2\frac{\delta r_{jk}}{R_{jk}} - \frac{\delta r_{ij}}{R_{ij}} - \frac{\delta r_{ik}}{R_{ik}}\right) \\ & - \left(\frac{R_{ij}}{R_{ik}} - \frac{R_{ik}}{R_{ij}}\right)\left(\frac{\delta r_{ij}}{R_{ij}} - \frac{\delta r_{ik}}{R_{ik}}\right) . \end{aligned} \tag{A.6}$$

It can be seen that this substitution behaves properly except for the singular situations when $\sin\Phi_{i,jk}$ vanishes. One can substitute $\delta\varphi_{i,jk}$ from Eq. (A.6) into Eq. (A.2) and then replace the δr_{ij} by the u''_{ij}. The expression becomes simpler and somewhat more translucent if we set $R_{ij} = R_{ik} = R$ in the reference state. Eq. (A.6) can then be written in a more explicit form

$$\delta\varphi_{i,jk} = \tan(\Phi_{i,jk}/2)\left(2\,\frac{\delta r_{jk}}{R_{jk}} - \frac{\delta r_{ij} + \delta r_{ik}}{R}\right) . \tag{A.7}$$

Finally, using

$$\delta r_{ij} \approx u''_{ij}$$

in Eq. (A.7) and substituting in Eq. (A.2) one gets the angular contribution to the harmonic expansion in explicit form

$$\left[\frac{\partial^2\mathscr{E}}{\partial\varphi_{i,jk}^2}\right]_{\{R\}} \delta\varphi_{i,jk}^2 = \left[\frac{\partial^2\mathscr{E}}{\partial\varphi_{i,jk}^2}\right] \tan^2(\Phi_{i,jk}/2)\left(2\frac{u''_{jk}}{R_{jk}} - \frac{u''_{ij} + u''_{ik}}{R}\right)^2 . \tag{A.8}$$

We have thus transformed the angular terms in Eq. (A.2) into an expansion of the form (A.1).

Using the general form (A.6) instead of (A.7) gives more complicated expressions but has no qualitative effects.

The analysis of the four-body interaction, $\mathscr{W}$, Eq. (3.13), can be done in a similar way. The intuitive four-body interaction is a *twist*. Four points $[ijkl]$ form a triangular pyramid as depicted in Fig. A.2. One has two-body interactions along the six edges, three-body angular interactions in each of the four triangular faces and finally explicit four-body interactions between the four vertices. This explicit four body component can be described as a twist

$$\mathscr{W}''_{ijkl} = \left[\frac{\partial^2\mathscr{E}}{\partial\varphi_{ij,kl}^2}\right]_{\{R\}} \delta\varphi_{ij,kl}^2 + \left[\frac{\partial^2\mathscr{E}}{\partial\varphi_{ik,jl}^2}\right]_{\{R\}} \delta\varphi_{ik,jl}^2 + \left[\frac{\partial^2\mathscr{E}}{\partial\varphi_{il,kj}^2}\right]_{\{R\}} \delta\varphi_{il,kj}^2 , \tag{A.9}$$

where $\delta\varphi_{ij,kl}$ is the twist angle. We shall not describe the trivial and tedious algebra which shows that this can indeed be written in the form implied by (3.13), i.e., as a combination of contributions to the six two-body interactions along the edges, to the four three-body interactions on the faces and six four point interaction terms.

Appendix B. How rotational invariance is maintained for stressed springs

Consider the expansion of the two-point interaction potential $\mathscr{V}(r)$ around its value at equilibrium when $r=R$

$$R \to R + \delta r \,. \tag{B.1}$$

Expanding $\mathscr{V}(r)$ in δr one has, to second order in δr,

$$\mathscr{V}(R+\delta r) - \mathscr{V}(R) = \left[\frac{\mathrm{d}\mathscr{V}(r)}{\mathrm{d}r}\right]_{r=R} \delta r + \frac{1}{2}\left[\frac{\mathrm{d}^2\mathscr{V}(r)}{\mathrm{d}r^2}\right]_{r=R} \delta r^2 + \mathrm{O}(\delta r^3)\,. \tag{B.2}$$

In general the “equilibrium” distance R will not correspond to the minimum of $\mathscr{V}(r)$ so that

$$\mathscr{T} = \left[\frac{\mathrm{d}\mathscr{V}(r)}{\mathrm{d}r}\right]_{r=R} \neq 0 \tag{B.3}$$

and one therefore has to keep the term linear in δr in Eq. (B.2).

So far rotational invariance is manifest because only the changes in the distance r, δr, appear in the expansion (B.2). For the harmonic expansion we have to rewrite this expansion in terms of the components of the relative deviation of the two end points

$$\boldsymbol{u} = \boldsymbol{u}_1 - \boldsymbol{u}_2 \,. \tag{B.4}$$

Now to second order in these components

$$\delta r = \delta^1 r + \delta^2 r + \mathrm{O}(u^3)\,, \qquad \delta^1 r = u''\,, \qquad \delta^2 r = (u^{\perp})^2/2R \tag{B.5}$$

as illustrated in Fig. B.1.

The second-order contribution to δr, namely $\delta^2 r$, is the *difference* between the transverse deviation, $u^{\perp}$, and the rotation $\delta\varphi$. A purely transverse $\boldsymbol{u}$

$$u^{\perp} \neq 0\,, \qquad u'' = 0 \tag{B.6}$$

implies a second order *change* in r, namely $\delta^2 r$, while the rotation, $\delta\varphi$, obviously does not change r to any order.

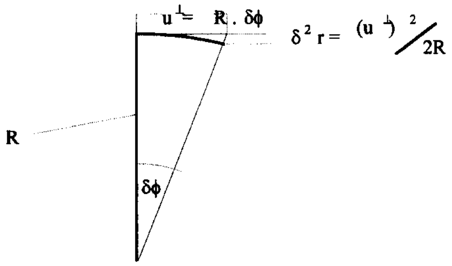


Fig. B.1.

Substituting δr from Eq. (B.5) into Eq. (B.2) gives, to *second* order in the components of $\boldsymbol{u}$, the *rotationally invariant* expression for the change in energy

$$\mathscr{V}(R+\delta r) - \mathscr{V}(R) = \mathscr{T} u'' + \mathscr{T}\frac{(u^{\perp})^2}{2R} + \frac{1}{2}\mathscr{K}(u'')^2 + \mathrm{O}(u^3)\,, \tag{B.7}$$

where

$$\mathscr{K} = \left[\frac{\mathrm{d}^2\mathscr{V}(r)}{\mathrm{d}r^2}\right]_{r=R}\,. \tag{B.8}$$

The first term on the right-hand side of Eq. (B.7) is the term we considered in the first order expansion in Section 4 – Eq. (4.1). The third term gives rise to the harmonic Cauchy energy – Eq. (5.8). The second term on the right in Eq. (B.7) is the origin of the tension induced terms in the harmonic energy, $\mathscr{P}$ – Eq. (6.11). One notes that these are contributions to the δr_{ij} which are *quadratic* in the components of the $\boldsymbol{u}_{ij}$ – $\delta^2 r_{ij}$, Eq. (B.5). It is evident that this does not violate rotational invariance. Quite to the contrary, these terms have to be included in the harmonic expansion if one wants to maintain rotational invariance consistently to second order in the components of $\boldsymbol{u}_i$.

We note that this is the only contribution of $\delta^2 r$ to the energy in the harmonic approximation. When $\delta^2 r$ is included in the $(\delta r)^2$ terms in Eq. (B.2) it only contributes to the anharmonicities, to third and fourth order in the components of the $\boldsymbol{u}_i$.

We want to mention two more points

1. The first concerns *equilibrium*. In equilibrium the forces $\boldsymbol{f}_{ij}$ on any single atom, i, must cancel each other

$$\Delta\mathscr{E} = \boldsymbol{f}_i\cdot\boldsymbol{u} = \sum_j \boldsymbol{f}_{ij}\cdot\boldsymbol{u}_i = 0 \tag{B.9}$$

– Eq. (3.29). This is a condition on terms in the expansion which are linear in the $\mathscr{T}_{ij}$ but also *linear* in the components of the $\boldsymbol{u}_i$. The terms linear in the $\boldsymbol{u}_i$ must cancel. There is however no cancellation for terms which are linear in the $\mathscr{T}_{ij}$, but *quadratic* in the components of the $\boldsymbol{u}_i$. In the stressed equilibrium state there is a restoring force for the transverse deviations of a single atom when there is tension.

2. The second point concerns *anharmonicity*. In (B.2) we expand around an equilibrium separation R which, obviously, cannot be the separation for which the potential $\mathscr{V}(r)$ has its minimum. In this expansion one evidently does not want any terms corresponding to higher powers of δr. Assume however that $\mathscr{V}(r)$ has a minimum

$$\left.\frac{\partial\mathscr{V}}{\partial r}\right|_{r=R_0} = 0 \tag{B.10}$$

so that

$$\mathscr{T} = \left.\frac{\partial\mathscr{V}}{\partial r}\right|_R = \delta R\left.\frac{\partial^2\mathscr{V}}{\partial r^2}\right|_{R_0} + \frac{1}{2}\delta R^2\left.\frac{\partial^3\mathscr{V}}{\partial r^3}\right|_{R_0} + \cdots\,, \qquad \left.\frac{\partial^2\mathscr{V}}{\partial r^2}\right|_R = \left.\frac{\partial^2\mathscr{V}}{\partial r^2}\right|_R + \delta R\left.\frac{\partial^3\mathscr{V}}{\partial r^3}\right|_{R_0} + \cdots\,, \tag{B.11}$$

where

$$\delta R = R - R_0\,. \tag{B.12}$$

Evidently the anharmonicities in the expansion of $\mathscr{V}(r)$ around its minimum do show up. They are of course related to the non-linear terms in the "unstressed" elasticity. These terms may or may not be important numerically. It is however evident that they are not needed to generate the tension $\mathscr{T}$.

The example demonstrates that the tension induced terms are distinct from the anharmonicities one would expect in strained samples or – more precisely – that one has to define accurately what one means by these terms.

Appendix C. The second order strain and the second order volume change

It is instructive to look at the microscopic origin of the stabilization by stresses for one square. A pure shear of magnitude

$$\partial_y u_x = 2u \tag{C.1}$$

distorts a square of unit magnitude and unit area. This is described in Fig. C.1. The two vertical edges are elongated by

$$\delta^2 r = 2u^2 \tag{C.2}$$

but the area is clearly unchanged:

$$\delta S = \delta^2 S \equiv 0\,. \tag{C.3}$$

For a *pure shear* the second order strain tensor has only one element

$$e^2_{yy} = \tfrac{1}{2}(\partial_y u_x)^2 = 2u^2\,. \tag{C.4}$$

Thus the isotropic part of the second order strain which multiplies the isotropic pressure

$$e^2_{\text{iso}} = e^2_{yy} = 2u^2 \tag{C.5}$$

does not vanish.

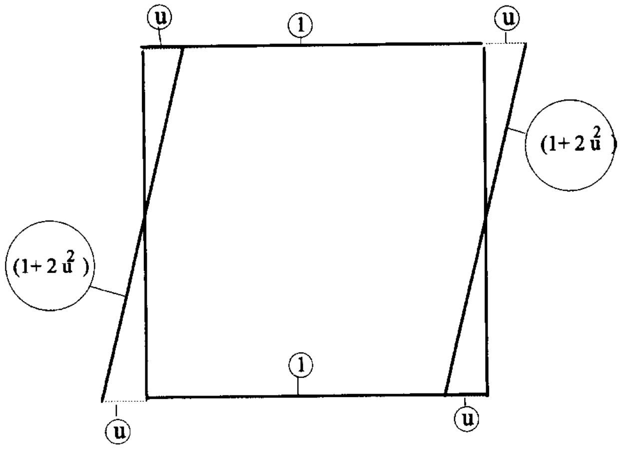


Fig. C.1.

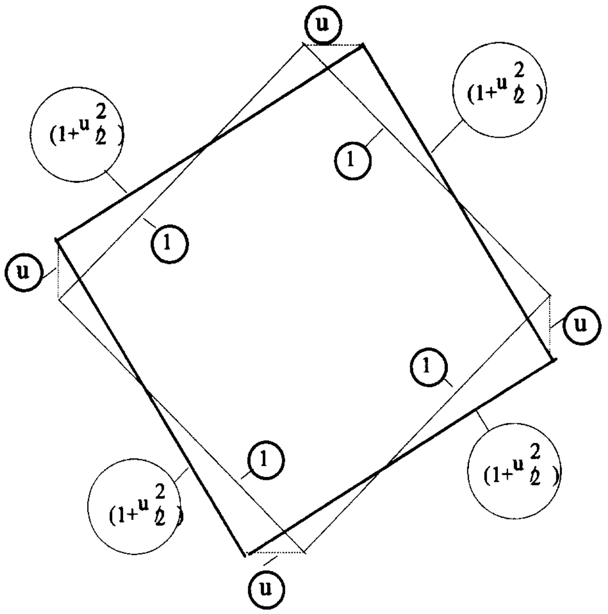


Fig. C.2.

Evidently this means that there is now a restoring force for the shear with a coefficient which is the network pressure:

$$\mathscr{P}^{\text{elastic}}_{\text{scalar}}/V = \tfrac{1}{4}\, p_{\text{net}}\,(\partial_y u_x)^2\,. \tag{C.6}$$

This describes a term in the elastic energy which is *isotropic* but for which the deformation which multiplies the pressure does not describe a volume change to any order.

In Fig. C.2 the deformation of the same square is

$$\partial u_x/\partial y = -\partial u_y/\partial x = \sqrt{2}\,u \tag{C.7}$$

so that

$$e^2_{xx} = e^2_{yy} = -e^2_{xy} = u^2\,. \tag{C.8}$$

This is an element of the antisymmetric part of the deformation tensor – the z component of rot $\boldsymbol{u}$ and describes a rotation.

Again, as in Eq. (C.5) the isotropic part of the second order strain does not vanish:

$$e^2_{\text{iso}} = \tfrac{1}{2}[(\partial_x u_y)^2 + (\partial_y u_x)^2] = 2u^2\,. \tag{C.9}$$

But, somewhat paradoxically, there is also a second order volume change associated with this first order rotation

$$\delta^2 V/V = u^2\,. \tag{C.10}$$

In both cases the second order strain contributes to the shear rigidity.

For this simple example one can also see the meaning of this directly. Assume the mechanical properties are described by a Cauchy model with nearest neighbor interactions. The unstressed square then has no linear shear rigidity. When there is tension in the bonds $\mathcal{T}$ the lattice is stressed. The stress is isotropic and amounts to a negative network pressure

$$p_{\mathrm{net}} = -\mathcal{T} \tag{C.11}$$

in units in which the lattice constant is 1. The lattice stress exerts the force of one bond, $\mathcal{T}$, on a surface of unit area. Consider now the effect of the shear described in Fig. C.2. There is an increase in energy

$$\delta f = 2u^2\mathcal{T} = -2u^2 p_{\mathrm{net}} \tag{C.12}$$

due to the shear. This results in a restoring force which stabilizes the nearest neighbour square lattice against shear.

Appendix D. Double-well buckling – an example

Evidently the simplest example of structural buckling is a single bond with negative tension. Using only the inevitable anharmonic terms of Eq. (10.18) one gets

$$-\left|\frac{\mathcal{T}_{ij}}{2R_{ij}}\right|(u_{ij}^{\perp})^2 + \frac{\mathcal{K}_{ij}}{4R_{ij}^2}\, u_{ij}^{\perp 4} \tag{D.1}$$

– a double-well potential. The equilibrium at $u_{ij}^{\perp} = 0$ is unstable and the mode buckles to one of the minima. See Fig. D.1.

This is of course schematic and oversimplified. One does however expect that, quite generally, some stabilizing anharmonic terms will eventually dominate. It is, e.g., easy to see that for the free torsional mode of a hexagon which we considered in Section 11.1 – Fig. II.16 – the anharmonic terms we included in Eq. (D.1) limit the torsional amplitudes and make the torsional potential into a double well potential.

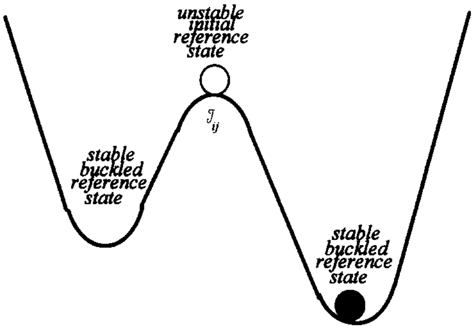


Fig. D.1.

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