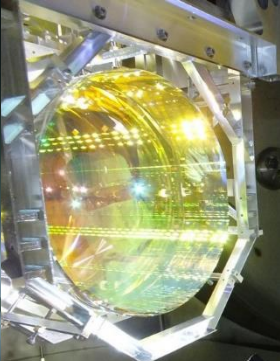
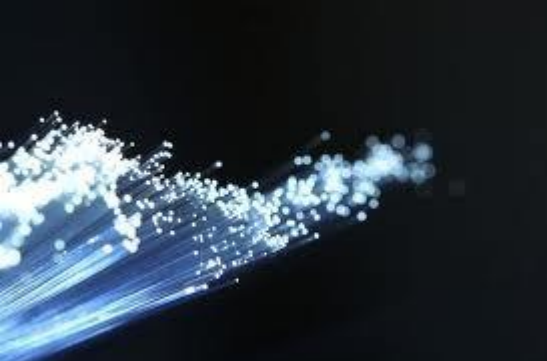


Le Matériau « Verre »

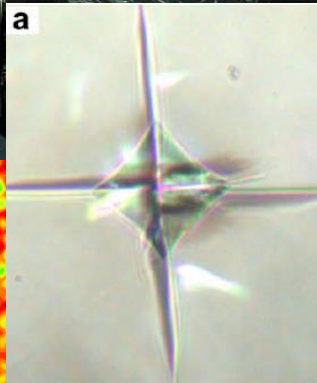
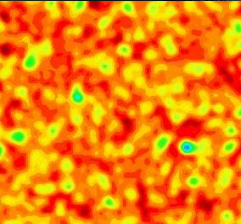
Anne Tanguy

Anne.Tanguy@insa-lyon.fr

Examen Vendredi 15 Mars 2024 14h-16h

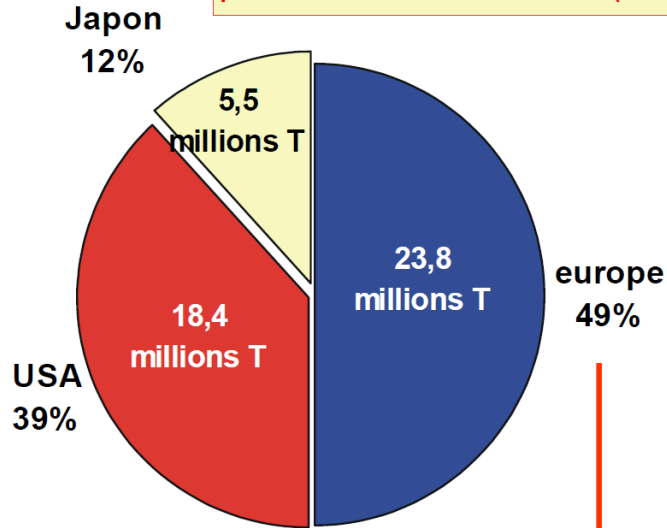


Verres



Verres minéraux

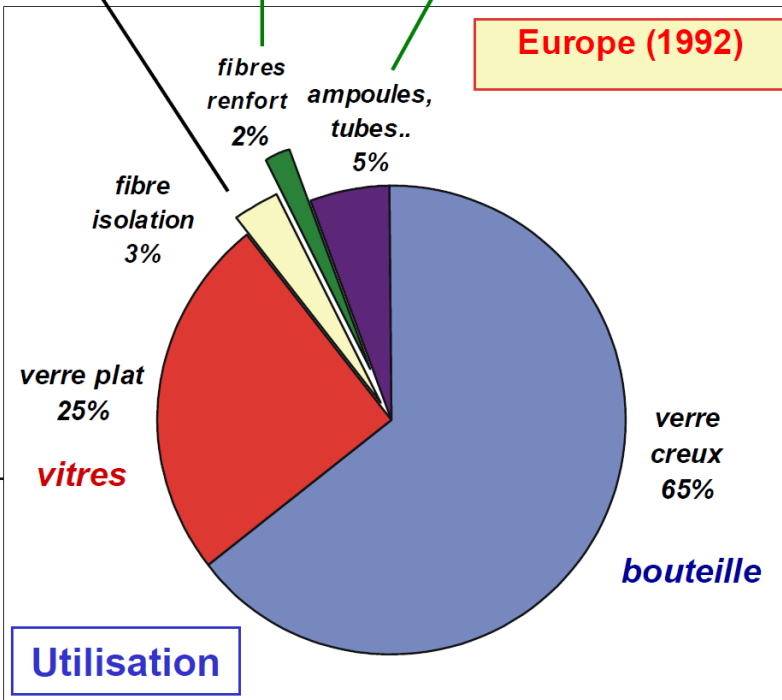
production mondiale de verre (1992)



Production

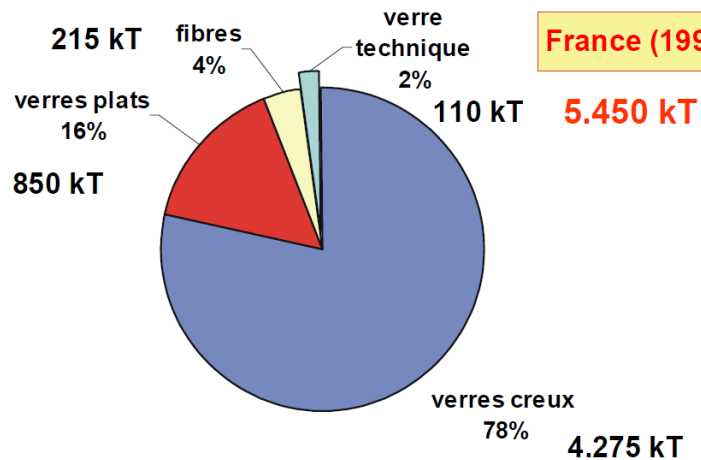
laine de verre
composites
verre technique

Europe (1992)



Utilisation

France (1998)



1er producteur mondial : St Gobain
(120.000 personnes, CA 117 milliards de Frs)

Définition Grand Public (pas exacte scientifiquement):

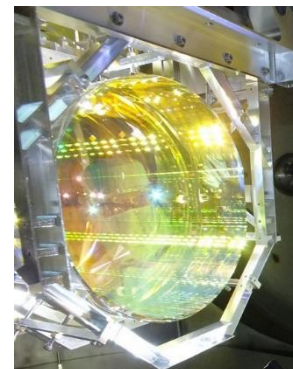
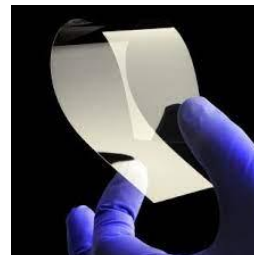
Verre: Substance ~~minérale, dur, cassant, transparente~~ et isotrope

www.larousse.fr, 2023

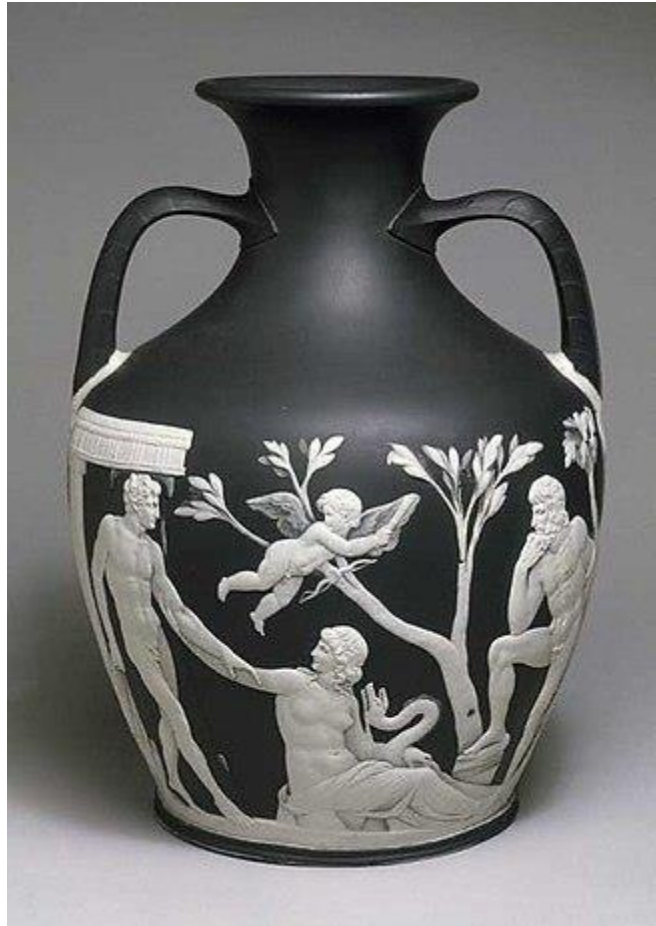
Quelques jalons historiques

Verres

- Obsidienne = Verre naturel
- -5 000 émaillage
- -3 000 1ers objets en verre moulé (Mésopotamie – Irak)
- 1^{er} siècle apr. JC, verre soufflé romain (syro-palestinien)
- XV^{ème} siècle, verre vénitien, renaissance, gentilhommes verriers
- 1627 verre cristal, XVIII^{ème} siècle, cristal de Bohême puis verre flint
- 1835 fabrication industrielle de miroirs argentés
- 1960 « verre métallique », 1990 « verre métallique massif »
- XX^{ème} siècle: fibre optique, verres techniques, téléphone, pare-balle, ...



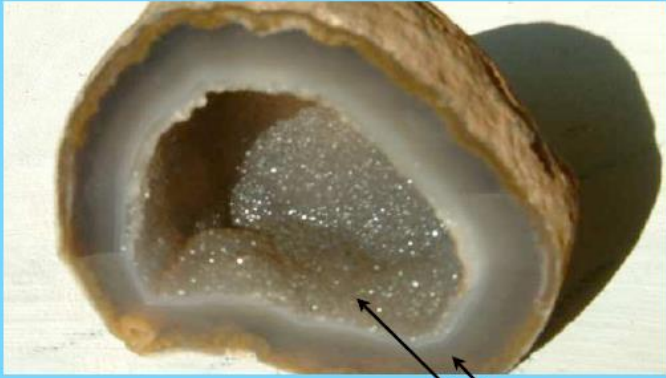
©Ligo



Vase de Portland (verre camée)
1er siècle avant J.-C.



Ancienne maison de
Gentilhomme verrier
Forêt de la Grésigne (XVIème siècle)



Géode :
 refroidissement rapide → verre
 refroidissement lent → cristal

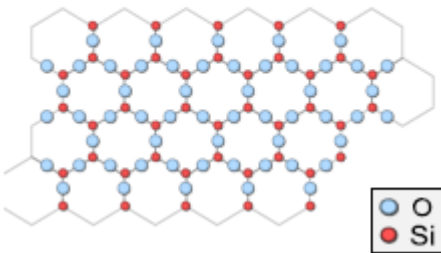


Amphores romaines du 6^e siècle

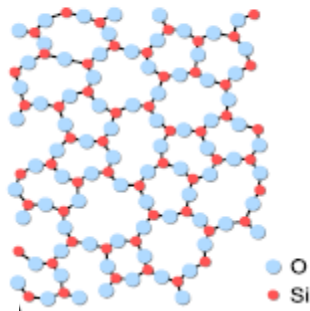


Vase tulipe
 (Daum)
 1900

Quartz $\rho=2.65$

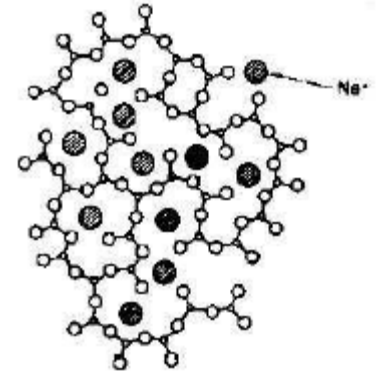


Silice $\rho \sim 2.2$



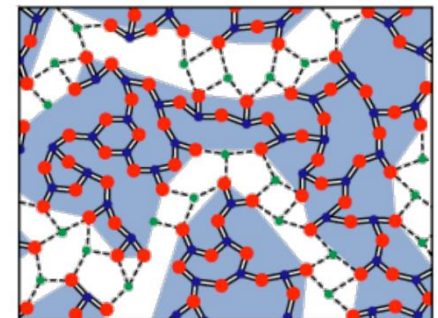
Modèle de Zachariasen
 (1932)

Verres Sodo-Silicates
 $(1-x) \text{SiO}_2 + x \text{Na}_2\text{O}$



Modèle de Greaves
 (1985)

Canaux de sodium



Une première classification

Classification basée sur les procédés:

Famille de céramiques	1 ^{ère} étape	2 ^{ème} étape	3 ^{ème} étape
Céramiques Traditionnelles & Techniques	Poudre	Mise en forme	Traitement T
Verres	Poudre	Traitement T	Mise en forme
Bétons / Ciments	Traitement T	Poudre	Mise en forme

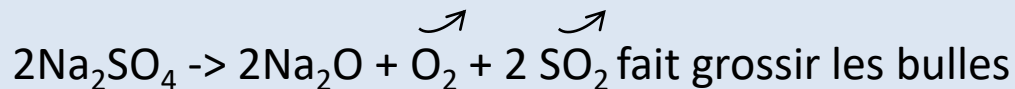
Des ingrédients

Qu'est-ce qui compose un Verre ?

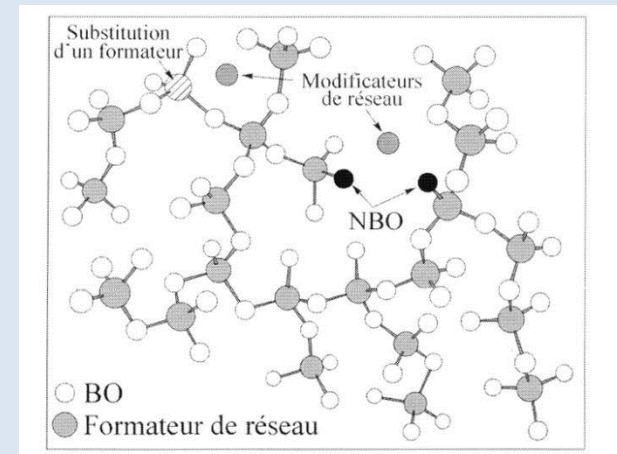
Un verre est un matériau amorphe obtenu par refroidissement à partir de l'état **liquide**.
A l'origine, mélange de sable (silice) et de cendres (soude ou oxyde de sodium)

De manière générale, un verre est obtenu par mélange de:

- ✓ **Vitrifiants** conférant la structure:
par ex. silice SiO_2 ou GeO_2 et ions intermédiaires Al, Ti, Zr, B, P... formateurs de réseau
- ✓ **Fondants** permettant de diminuer la viscosité, ainsi que la température de fusion et la température de solidification T_g (température de transition vitreuse): oxydes alcalins / alcalino-terreux K_2O , Na_2O , MgO , CaCO_3 , Na_2CO_3 fournissant les modificateurs de réseau mais aussi du CO_2
- ✓ **Stabilisants**, permettant d'assurer la stabilité du verre fondu et de limiter la cristallisation: oxydes alcalino-terreux Al_2O_3 , CaO , MgO , PbO , ZnO , TiO_2 , Fe_2O_3 ,...
- ✓ **Affinants**, facilitant l'élimination des gaz. Ex. Na_2SO_4



- ✓ Colorants: oxydes de Fe, Mn (MnO_2 décolorant), Li, Cu...
- ✓ Opalisants: F, P...
- ✓ Verres au Plomb (Cristal) $> 24\% \text{ PbO}$ $n_{\text{optique}} > 1.545$



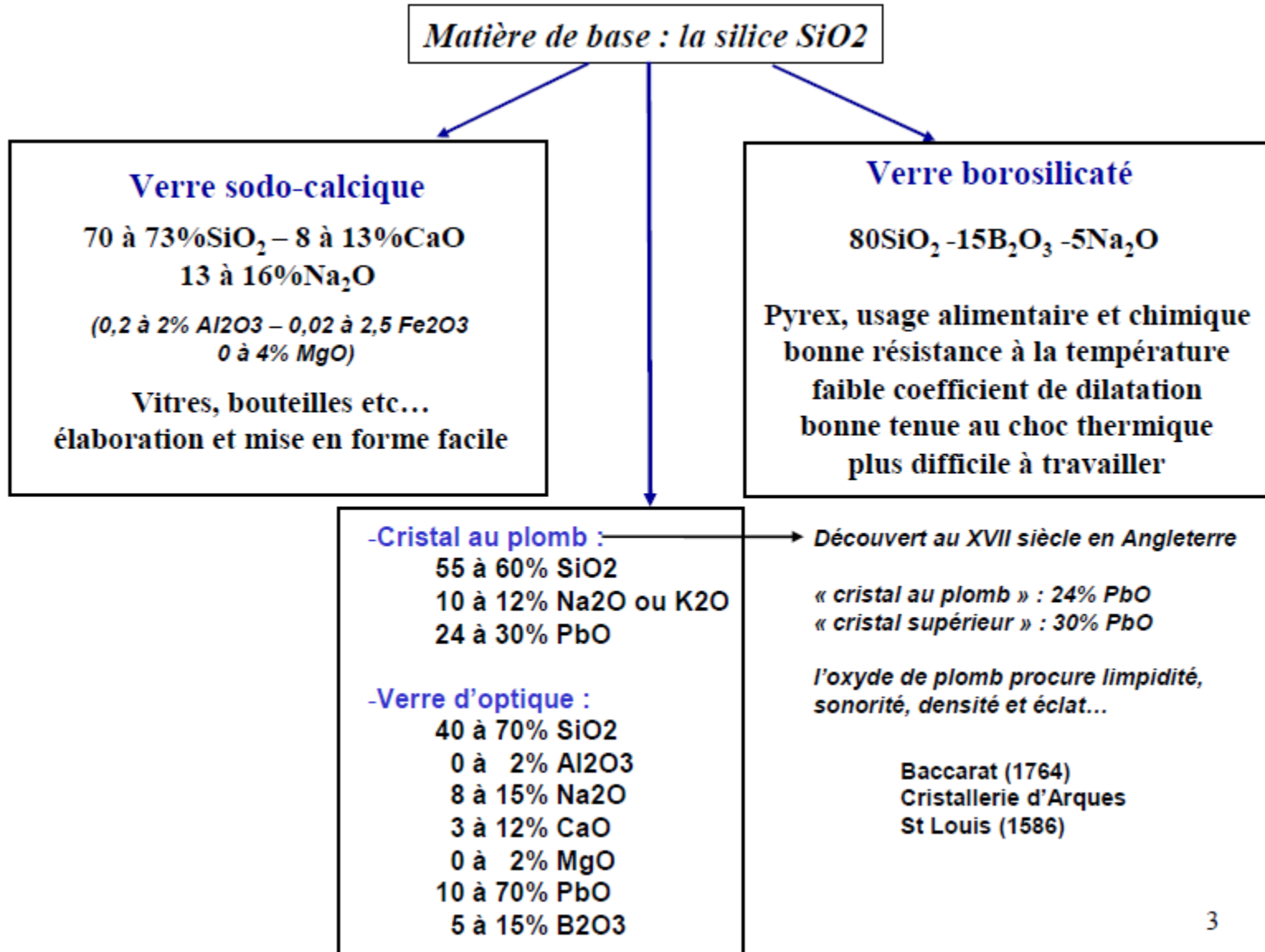
Exemple 1: Verre ordinaire

Base : silice SiO_2 (70% de la croûte terrestre...) et chaux CaO

Verre ordinaire sodo-calcique	Verre boro-silicaté
70% SiO_2 + 10% CaO + 15% Na_2O	80% SiO_2 + 15% B_2O_3 + 5% Na_2O
Vitres, bouteilles	Alimentaire ou chimique : Pyrex [®]

Na_2O est l'agent fondant (800° au lieu de 1650°)
Mais aussi Al_2O_3 (fibres) K_2O et PbO (cristal)...

Exemple 2: Verres Silicates

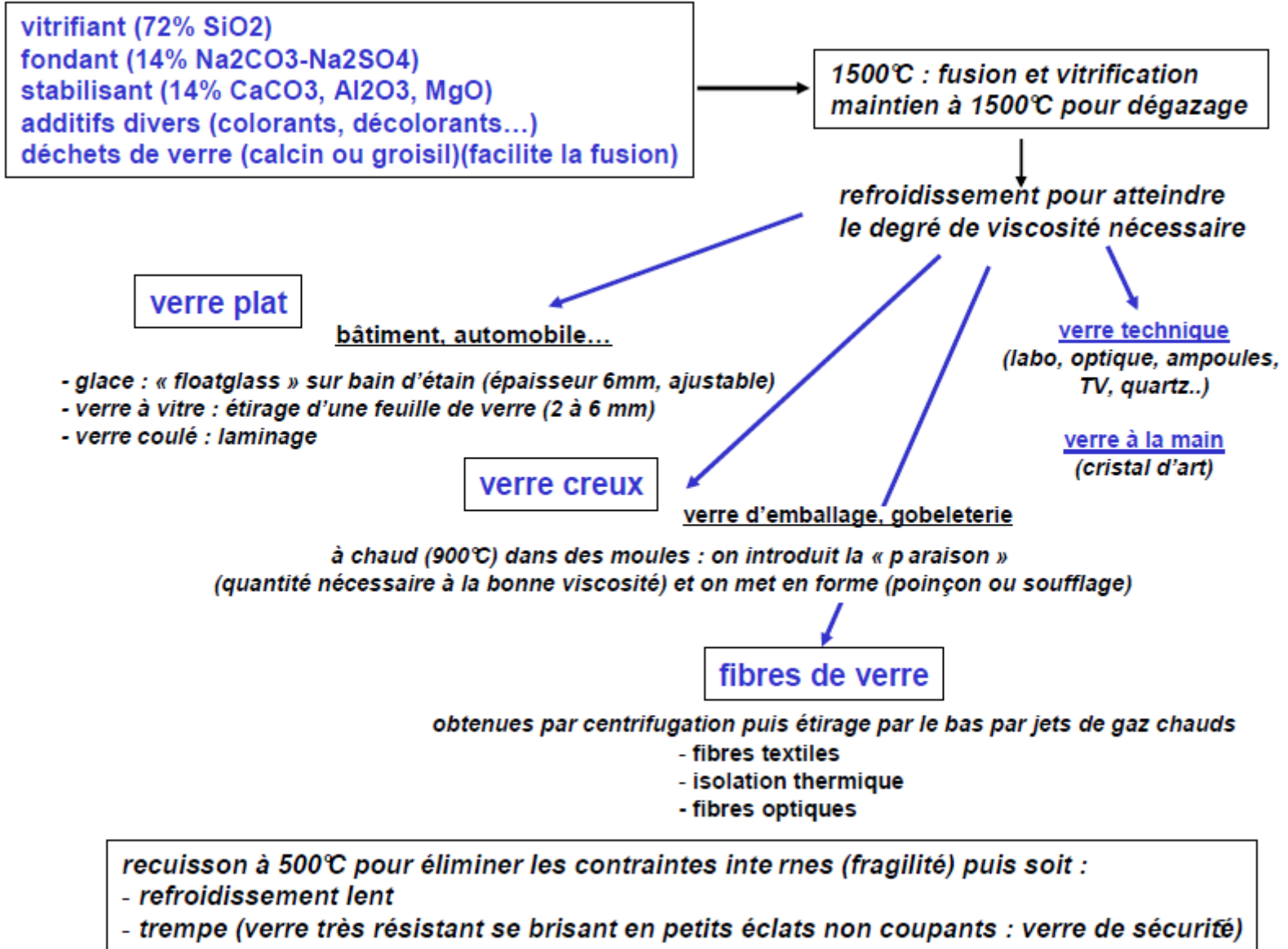


Verres Silicates

TABLE 1: Commercial oxide glass compositions.

Glass family (application)	Oxide, mass %									
	SiO ₂	Na ₂ O	CaO	Al ₂ O ₃	MgO	B ₂ O ₃	BaO	PbO	K ₂ O	ZnO
<i>Vitreous silica</i>										
(Furnace tubes, Si melting crucibles)	100									
<i>Soda-lime silicate:</i>										
Window	72.0	14.2	10.0	0.6	2.5		trace		0.6	
Container	74.0	15.3	5.4	1.0	3.7				0.6	
Bulb and tube	73.3	16.0	5.2	1.3	3.5					
Tableware	74.0	18.0	7.5	0.5						
<i>Sodium borosilicate:</i>										
Chemical glassware	81.0	4.5		2.0		12.0				
Waste immobilisation	43–53	6–24	0–14	3–19	0–5.3	8–17	misc.	misc.	misc.	misc.
<i>Lead-alkali silicate:</i>										
Lead “crystal”	59.0	2.0		0.4				25.0	12.0	1.5
Television funnel	54.0	6.0	3.0	2.0	2.0			23.0	8.0	
<i>Aluminosilicate:</i>										
Halogen lamp	57.0	0.01	10.0	16.0	7.0	4.0	6.0		trace	
Fibreglass “E”	52.9		17.4	14.5	4.4	9.2			1.0	
<i>Optical (crown)</i>	68.9	8.8				10.1	2.8		8.4	1.0

Verres Silicates



Exemple 3: Verres Chalcogénures

Mélange d'éléments du groupe VI (S,Se,Te) avec groupes IV (Ge, Si) ou V (Sb, As) ou halogénés
 Grande pureté requise

— Chalcogènes
 — Éléments associés

Periodic table showing the periodic table with elements highlighted in red (Chalcogènes) and blue (Éléments associés). The red elements are S, Se, and Te. The blue elements are Ge, Si, Sb, and As.

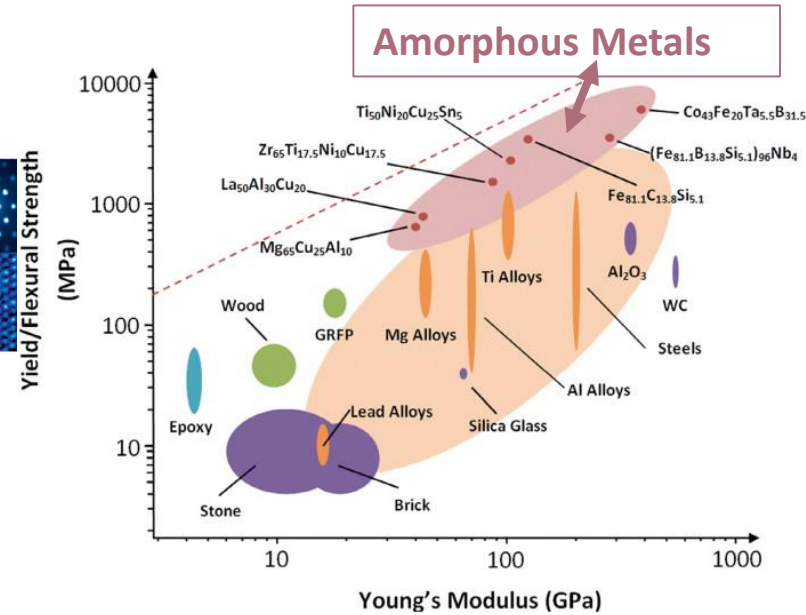
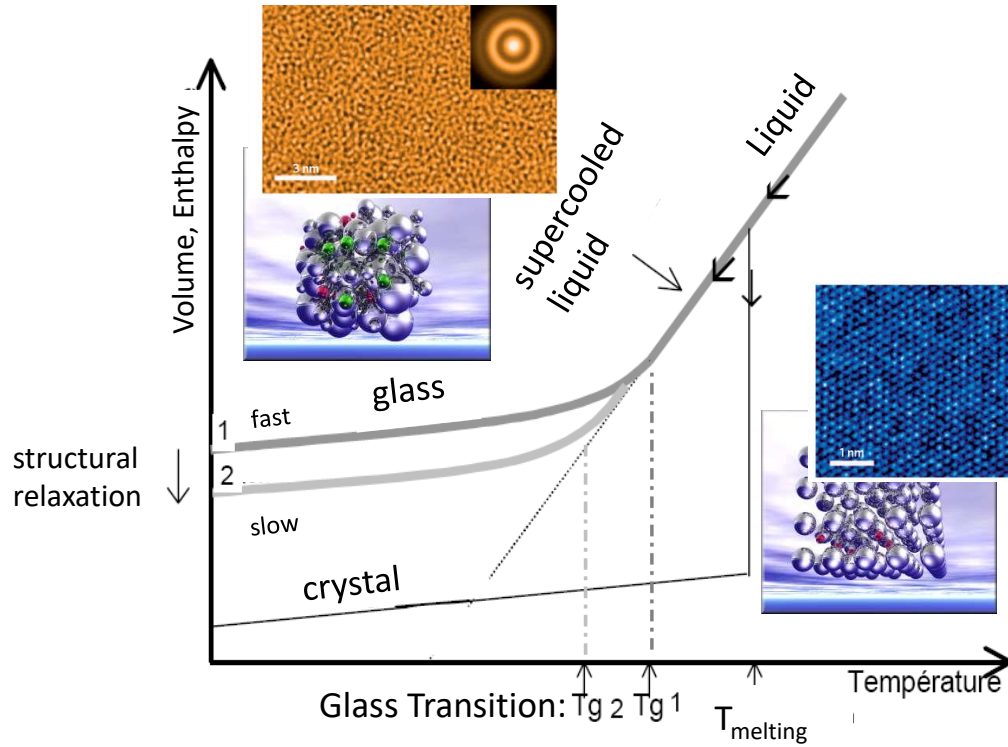
Famille	Nom du verre	Composition
Verres de sulfure	GLS	70 Ga ₂ S ₃ —30 La ₂ S ₃
	GNS	66 Ga ₂ S ₃ —34 Na ₂ S
	GGSSb	Ge ₂₀ Ga ₅ Sb ₁₀ S ₆₅
Verres de chalcogénure	2SG	Sb—Se—Ge—Ga
	TeXAs	Te ₂ Se ₃ lAs ₄

Optiques Transparentes aux Infra-Rouges

Transformation cristal <-> amorphe facile



Exemple 4: Verres Métalliques



Metallic glasses, Vitreloy

Alloy name	At% Zr	At% Ti	At% Cu	At% Ni	At% Be	At% Al
Vit 1	41.2	13.8	12.5	10.0	22.5	
Vit 4	46.8	8.2	7.5	10.0	27.5	
J'35	50.0	5.0	22.0	13.0		10.0
D'35	52.5	2.5	22.0	13.0		10.0

Exemples d'objets en verre métallique:

Articles de sport



Bijouteries



Coques portables



Autres exemples de Verres

Composition	Liaisons	T_f (K)	T_g (K)
SiO ₂	covalentes	1996	1473
GeO ₂	covalentes	1386	900
B ₂ O ₃	covalentes	723	521
BeF ₂	ioniques	1076	580
ZnCl ₂	ioniques	591	375
Au ₈₀ Si ₂₀	métalliques	636	290
Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	métalliques	804	572
Se	polymériques	491	303
polypropylène	polymériques	449	259
polyéthylène	polymériques	483	163
glycérol	Van der Waals	291	178
éthanol	Van der Waals	156	93
eau	Van der Waals	273	140

Cependant, en général **la composition ne suffit pas**
à distinguer les matériaux

Exemple de Matériaux à base d'Alumine:

Monocristal

Verre

Céramique

Cér. vitreuse

SiO_2



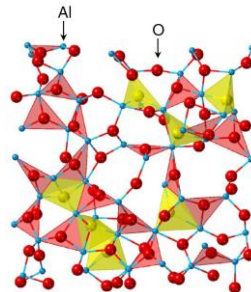
Quartz, améthyste...



Al_2O_3



Rubis, saphir,
topaze...



Verre d'alumine
(2004)

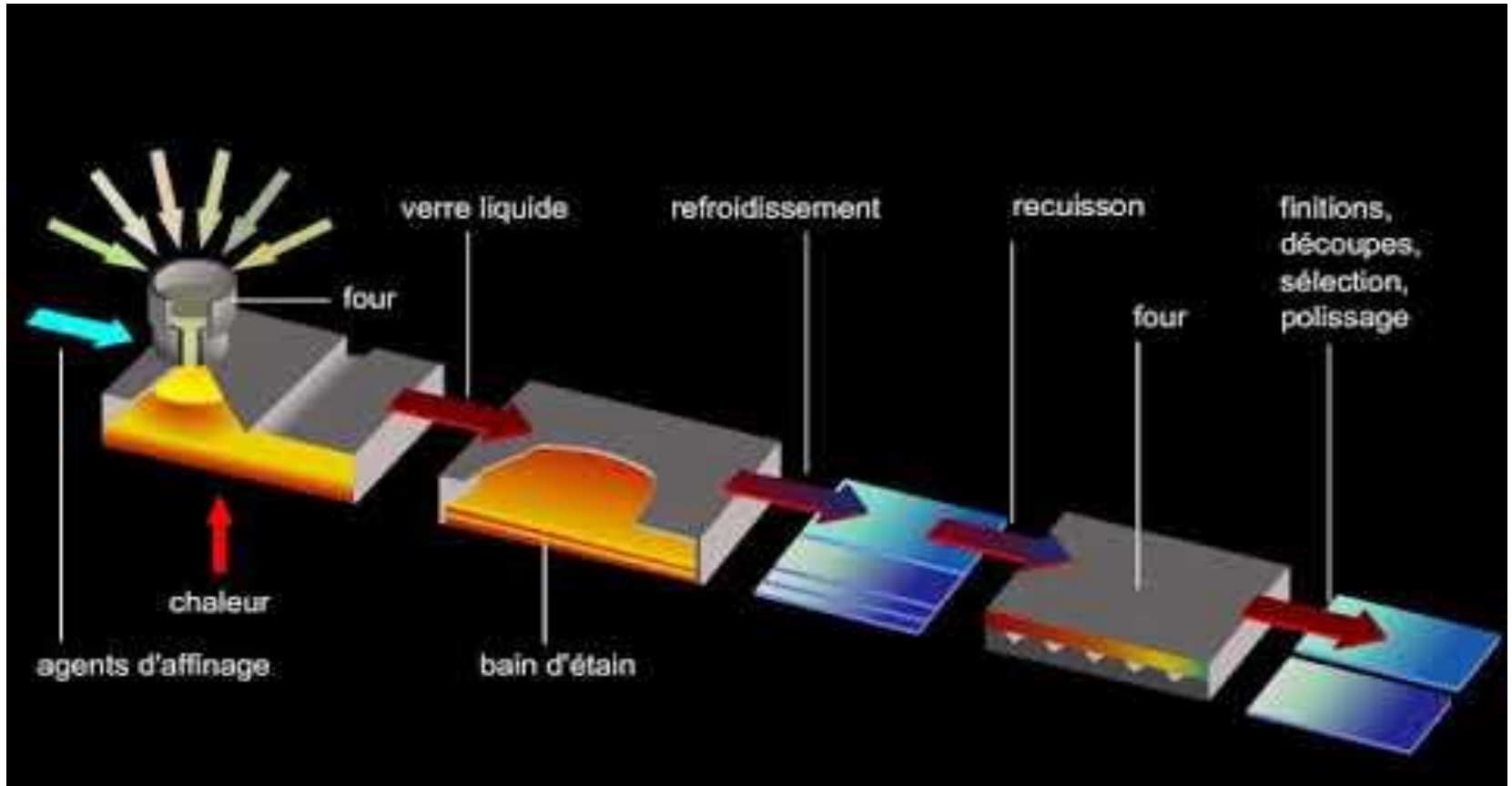


Alumine

Alumine vitreuse
(expérimental)

Des procédés de Fabrication

Verre



Mélange



Chauffage (liquide visqueux)



Mise en Forme



Refroidissement



Recuit



Finition

1) **Choix des Matières Premières**

Permettant un mélange et un refroidissement efficaces –
Tous types de liaisons

2) **Fusion** puis Transition Vitreuse

3) **Mise en forme** après chauffage

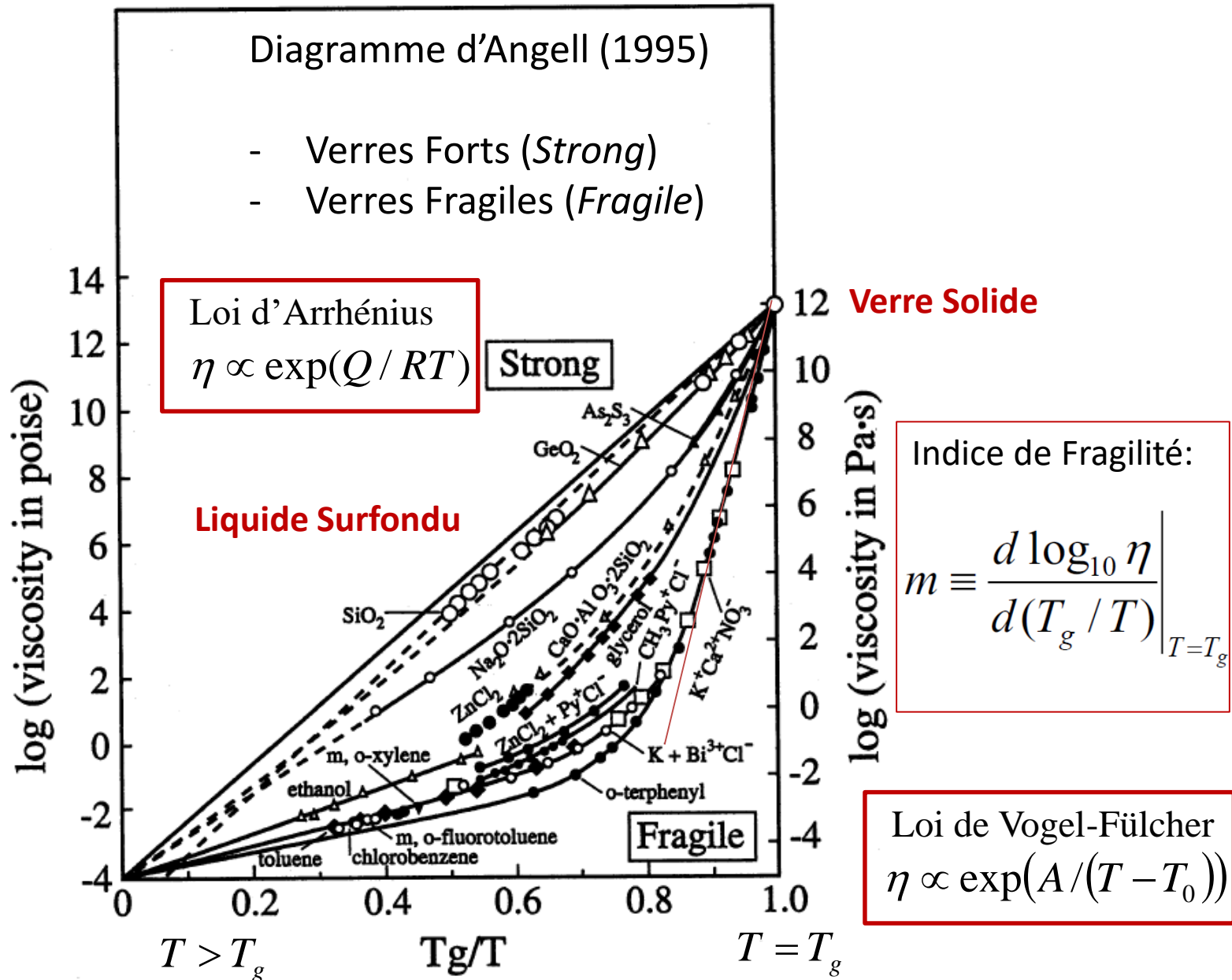
4) Finition

Essais de Classification des Verres

Classification des verres en fonction de la composition

- ✓ Verres d'oxydes (à base de SiO_2 , B_2O_3 , P_2O_5 , GeO_2 , As_2O_3 , Sb_2O_3 , TeO_2 , ...)
- ✓ Verres de chalcogénures (S, Se, Te + Ge, Si + Sb, As + ...)
- ✓ Verres de chlorures (ZnCl_2 , CdCl_2 - BaCl_2 - NaCl , BiCl_3 - KCl , ...)
- ✓ Verres de fluorures (BeF_2 , 53ZrF_4 - 20BaF_2 - 4LaF_3 - 3AlF_3 - 20NaF , ...)
- ✓ Verres Métalliques (métal/métalloïde $\text{Pd}_{80}\text{Si}_{20}$, $\text{Ni}_{80}\text{P}_{20}$, $\text{Cu}_{50}\text{Zr}_{50}$, $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, ...)
- ✓ ...

Classification des verres en fonction du comportement à la Transition Vitreuse



Classification des verres d'optique

Classification Internationale: basée sur la norme militaire MIL-G-174B pour normaliser la dénomination des verres d'optique à partir de leurs propriétés (code à 6 chiffres)



Famille du verre	Indice de réfraction n_d	Nombre d'Abbe V_d	Codification internationale MIL-G-174-B	Codifications des principaux producteurs								
				Schott	Pilkington	Hoya	Ohara	Sumita	Corning	CDGM	Nikon-Hikari	Potapenko
Crown borosilicate	1.5168	64.17	517-642	BK7	BSC517642	BSC7	S-BSL7	K-BK7	B16-64	D/H-K9L	J-BK7	K8 (516-610)
Baryum crown	1.5688	56.05	569-561	BaK4	MBC569561	BAC4	S-BAL14	-	B69-56	H-BaK7	J-BAK4	BF6 (569-494)
Crown dense	1.6204	60.32	620-603	SK16	DBC620603	BACD16	S-BSM16	K-SK16	C20-60	H-ZK9 A	J-SK16	TK20 (622-567)
Lanthane flint	1.7439	44.85	744-448	LaF2	LAF744447	LaF2	S-LAM2	K-LaF2	D44-45	H-LaF3	J-LAF2	CTK19 (744-504)
Flint dense	1.7847	25.76	785-258	SF11	DEDF785258	FD11	S-TIH11	K-SFLD11	D85-26	ZF51	J-SF11	TF12 (785-256)

Indice de réfraction $n_d = c_{\text{vide}}(\text{lumière}) / c_{\text{matériau}}$

Nombre d'Abbe $v_d = (n(589,3 \text{ nm}) - 1) / (n(486,1 \text{ nm}) - n(656,3 \text{ nm}))$

Synthèse et Mise en Forme des Verres

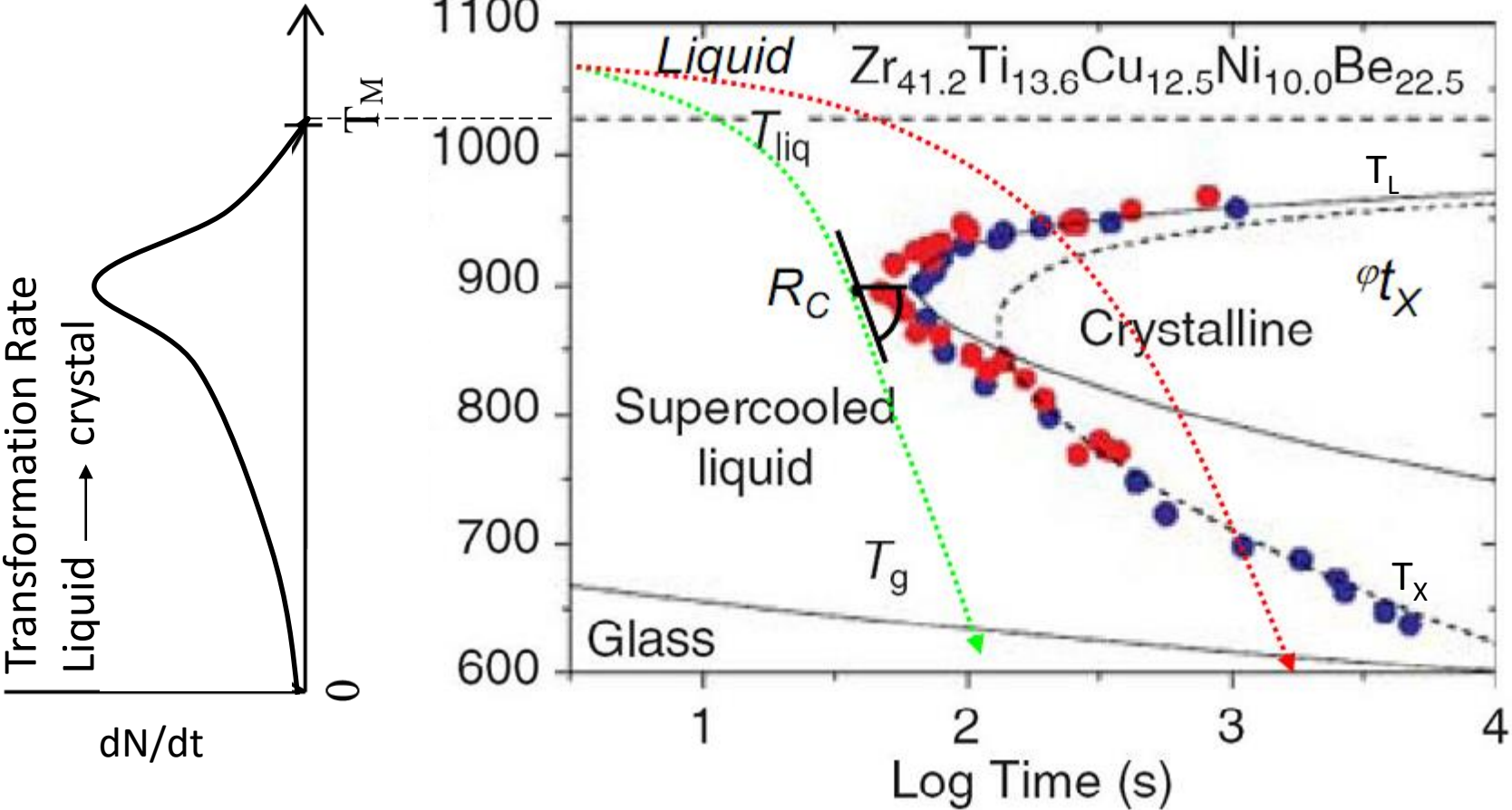
Verre

- ✓ Choix des **Matières premières** : vitrifiants, fondants, stabilisants, affinants, ...
- ✓ **Chauffage** et **Mélange** dans un four
- ✓ **Mise en Forme** en une ou plusieurs étapes à partir du liquide surfondu
- ✓ **Refroidissement** (selon la méthode $1\text{K/s} < dT/dt < 10^6 \text{K/s}$)
- ✓ **Finition**: recuits, ponçage, thermoformage, découpe ...
 - Transition Vitreuse
 - Microstructure d'un Verre

Comprendre la **Transition Vitreuse**

Cinétique de cristallisation

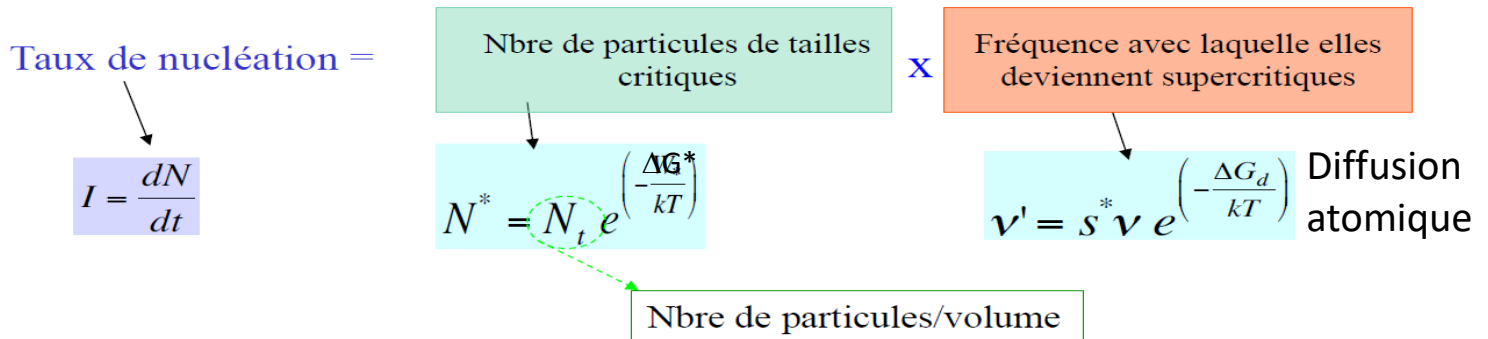
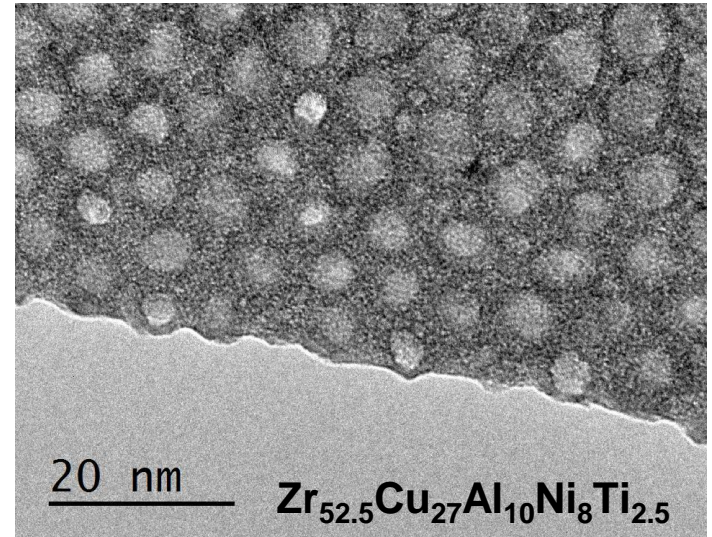
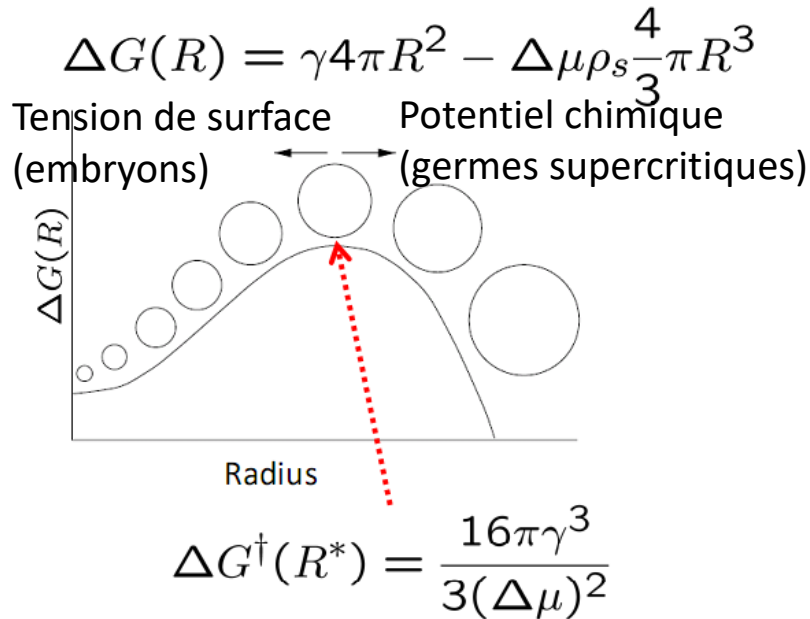
Diagramme TTT (Transformation-Temps-Température)



Comprendre la **Transition Vitreuse**

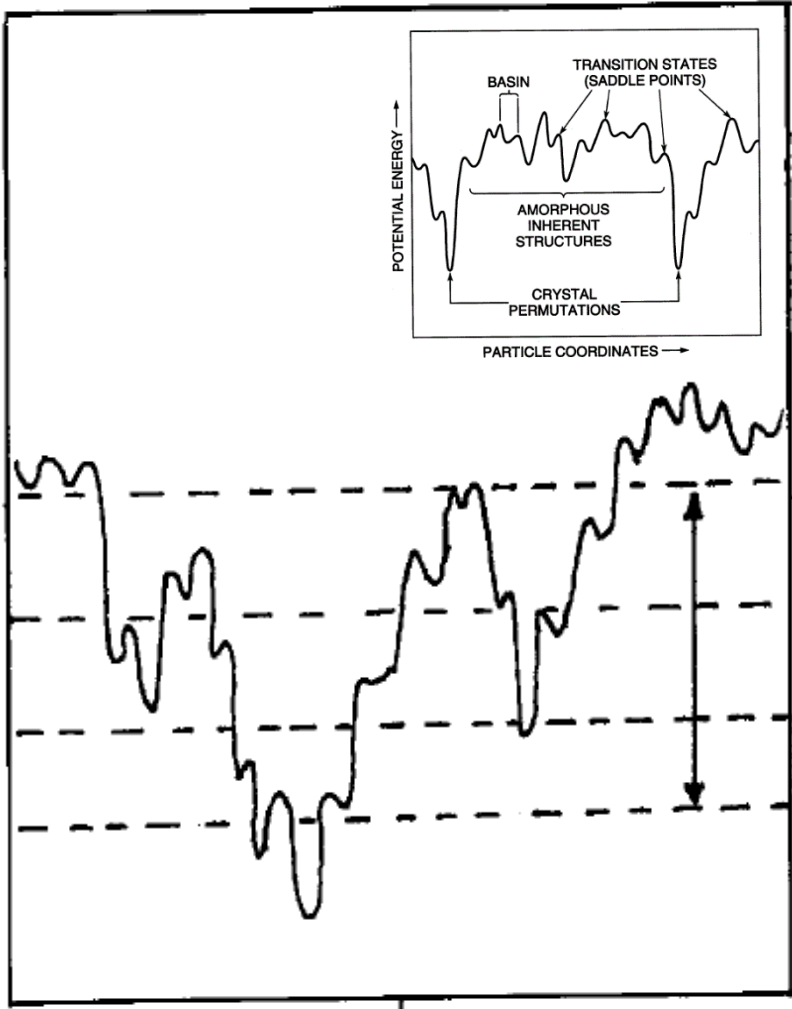
Cas d'une vitro-céramique:

2 étapes: Nucléation d'un crystallite, puis croissance

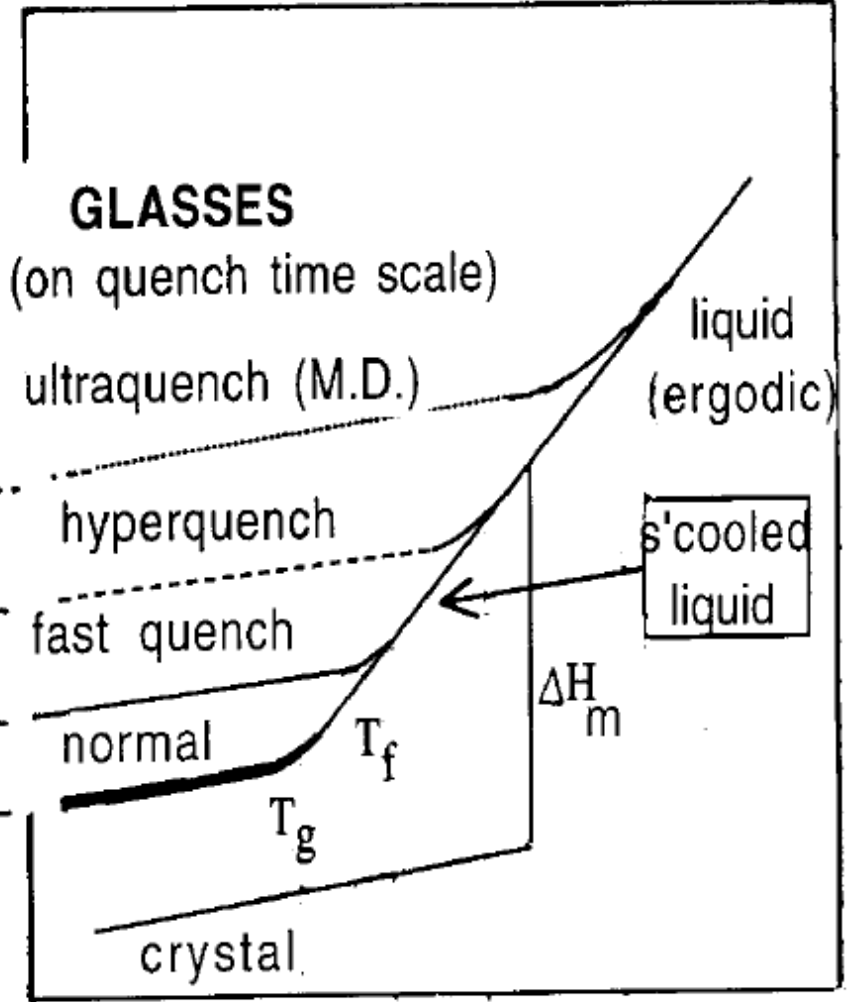


Comprendre la Transition Vitreuse

ENERGY

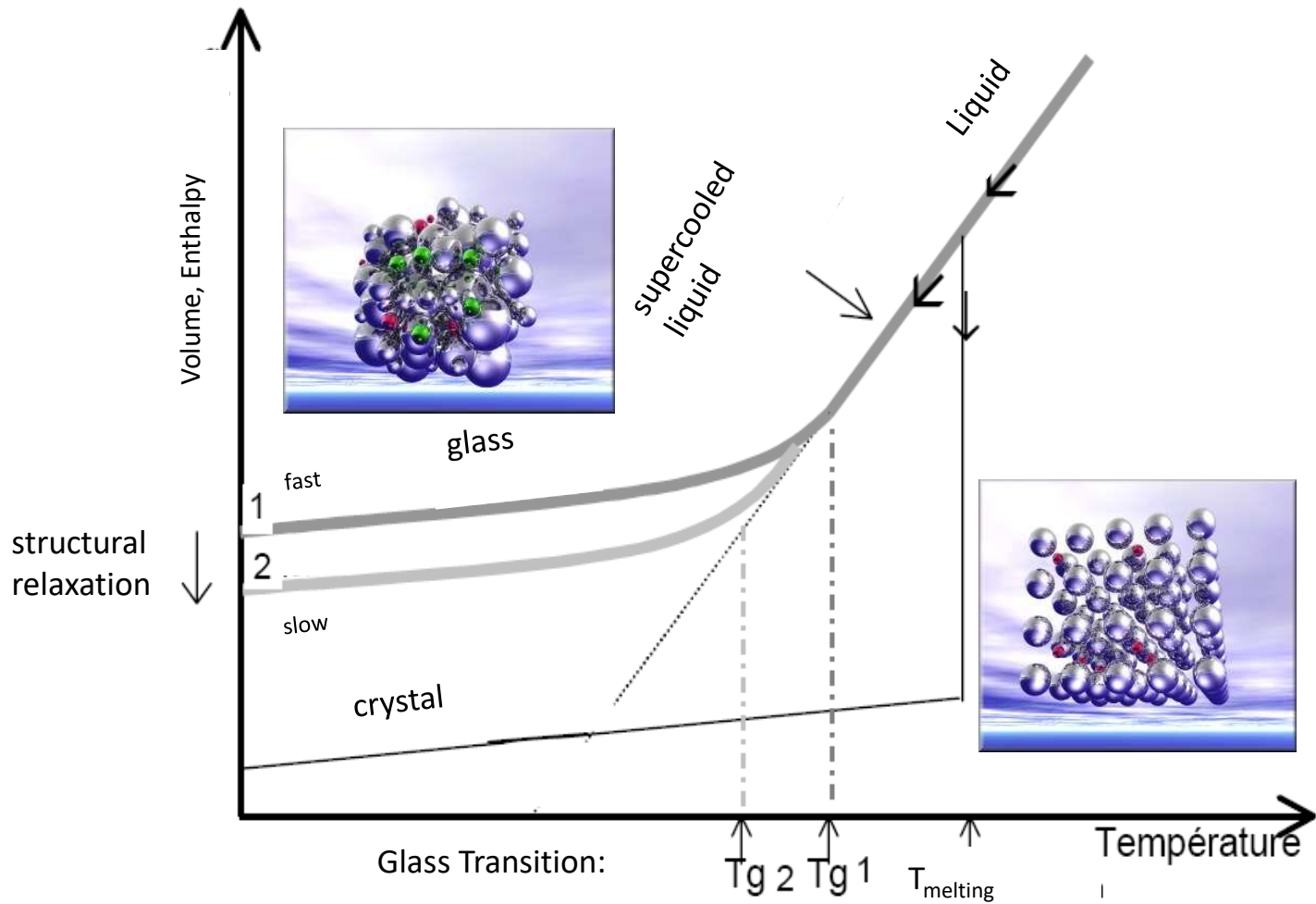


Z^*

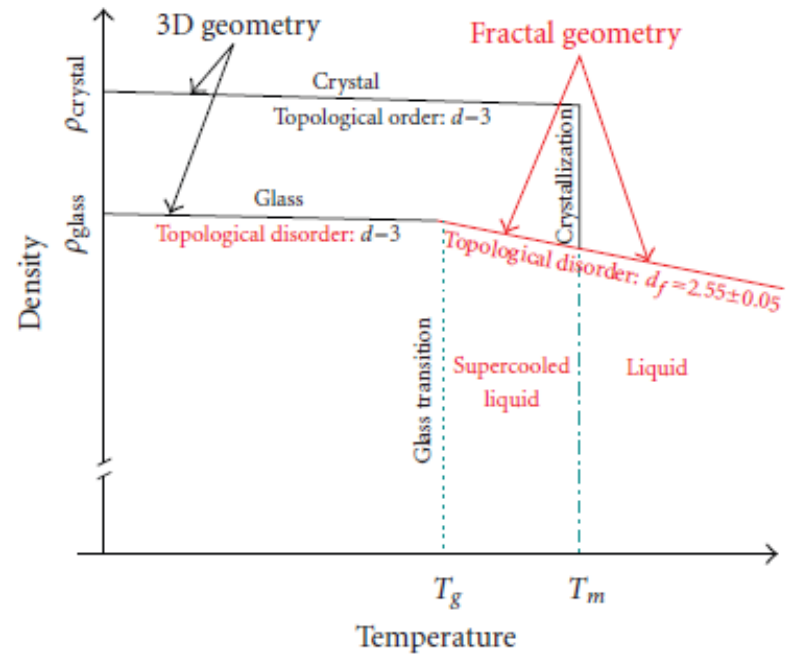
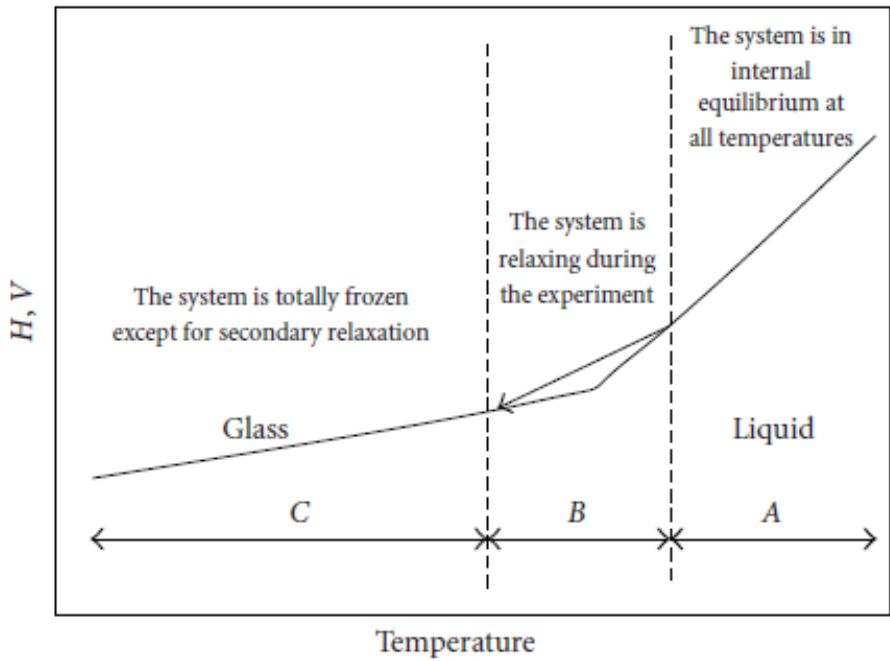


T / K

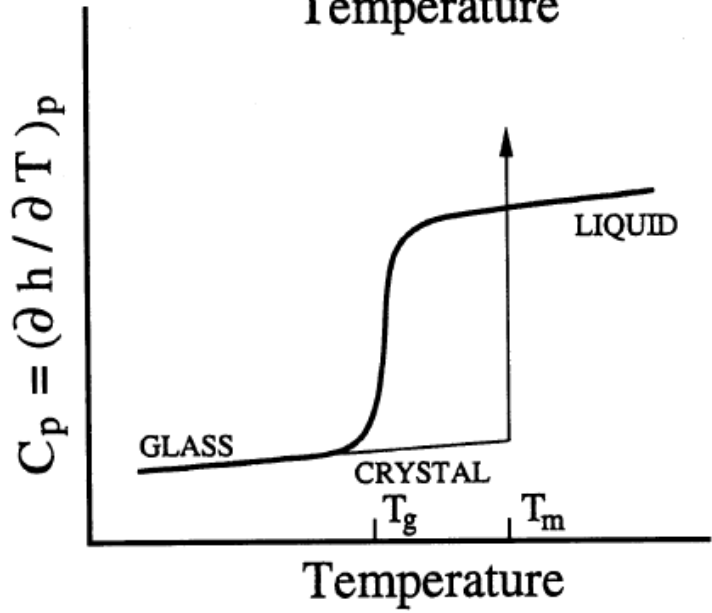
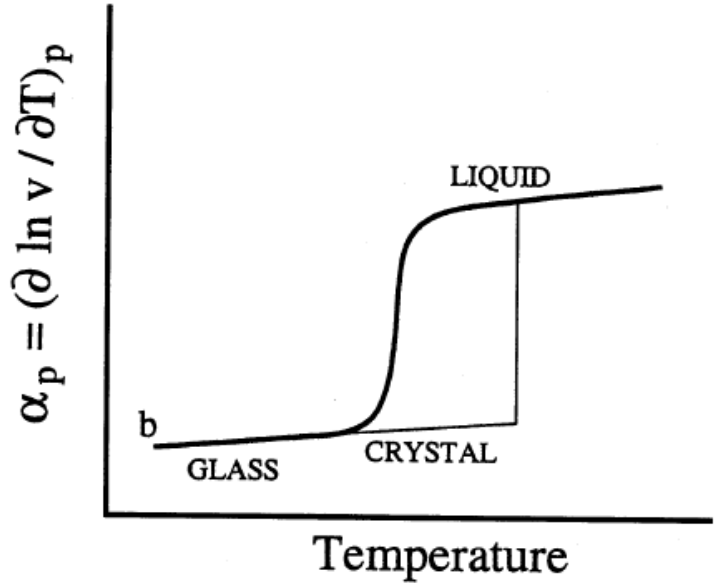
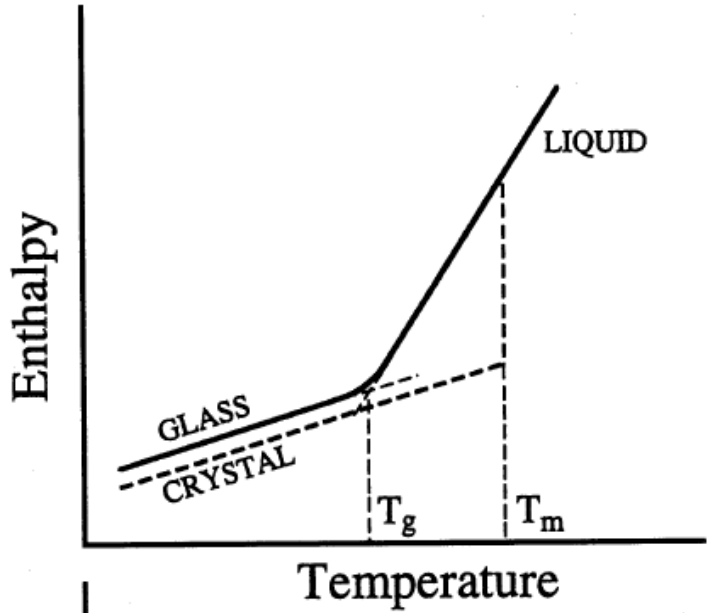
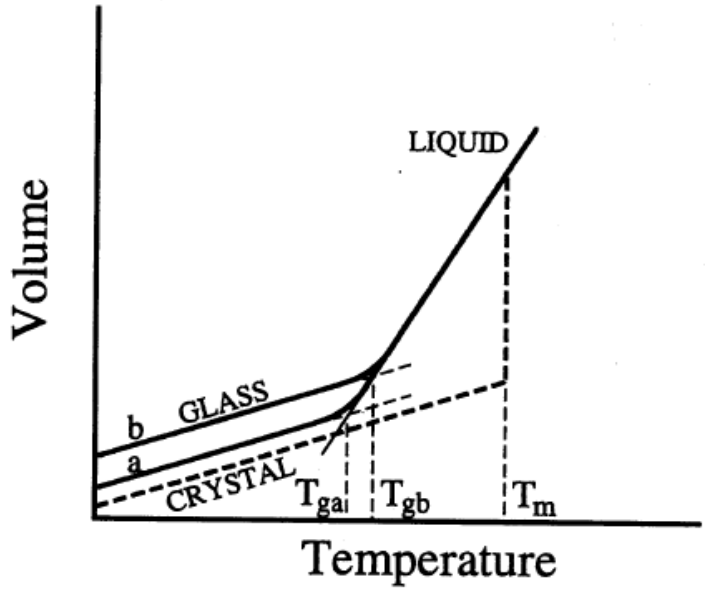
Comprendre la Transition Vitreuse



Comprendre la Transition Vitreuse

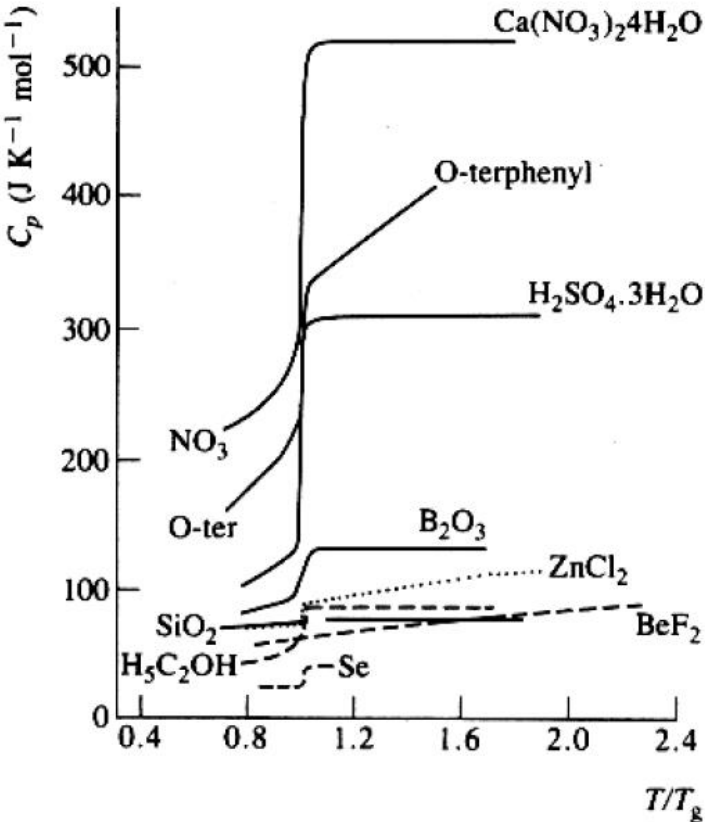
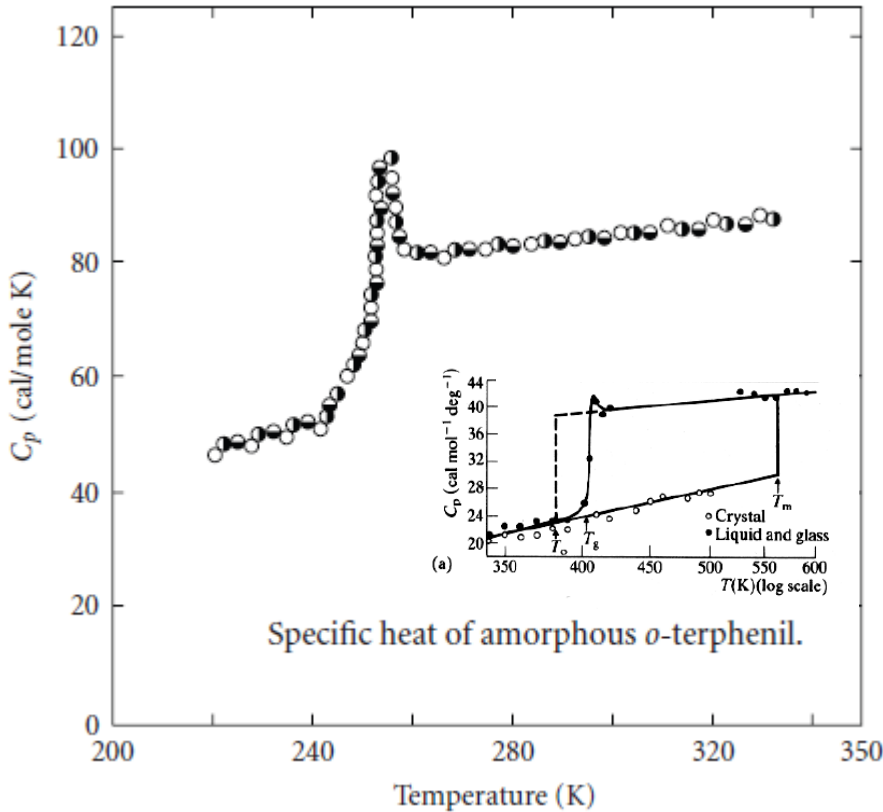


Comprendre la Transition Vitreuse



Comprendre la Transition Vitreuse

Mesures de Capacité Calorifique Isobarique



Comprendre la **Transition Vitreuse**

Mesures de Calorimétrie Différentielle

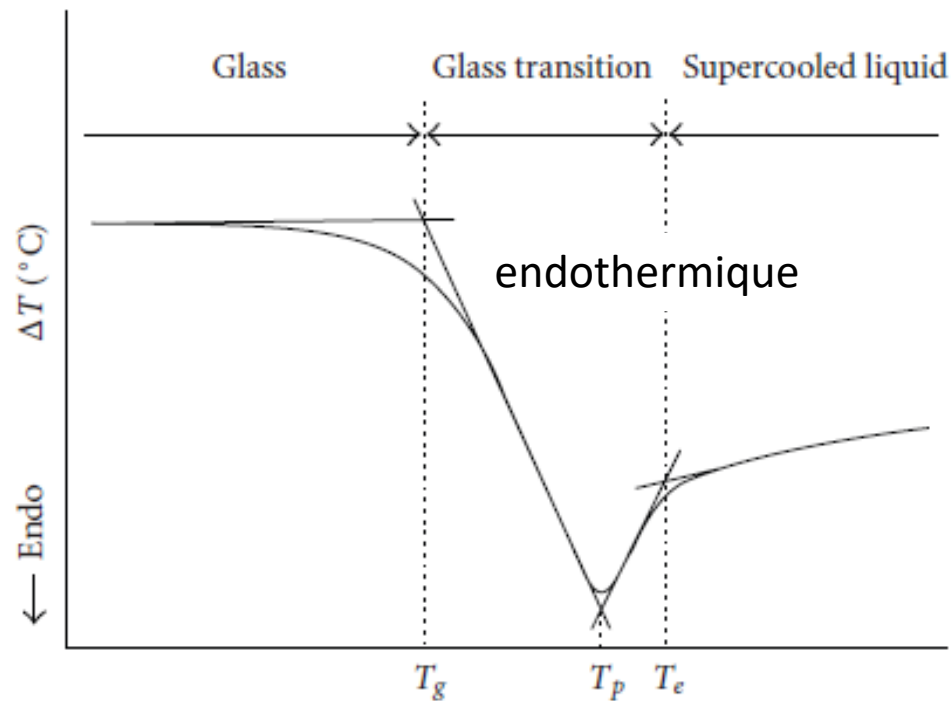
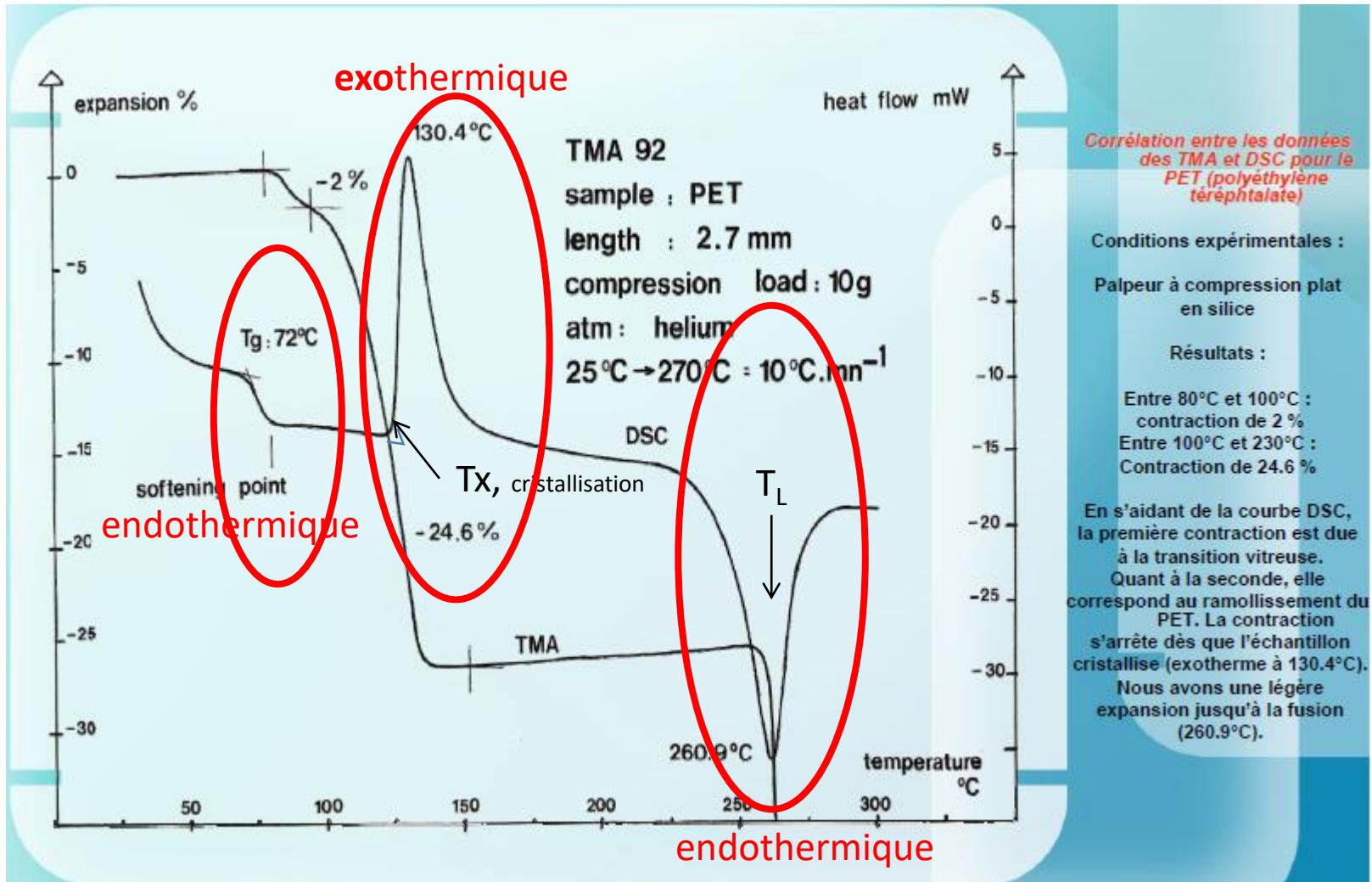


FIGURE 2: Determination of glass transition temperature T_g based on differential temperature analysis (DTA), below the T_g the material is glassy whereas above the T_e the material is liquid (after [32]).

Comprendre la Transition Vitreuse

Mesures de Calorimétrie Différentielle



Analyse Enthalpique Différentielle (DSC) vs. Analyse Thermo-mécanique (TMA)

Comprendre la Transition Vitreuse

Mesures de Viscosité

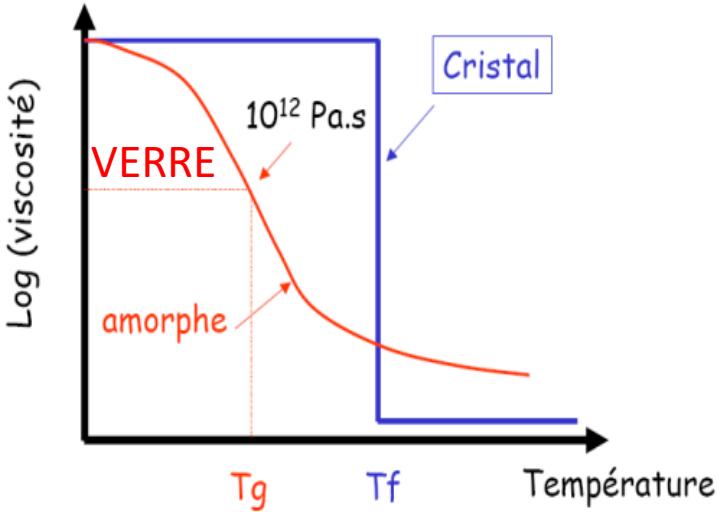
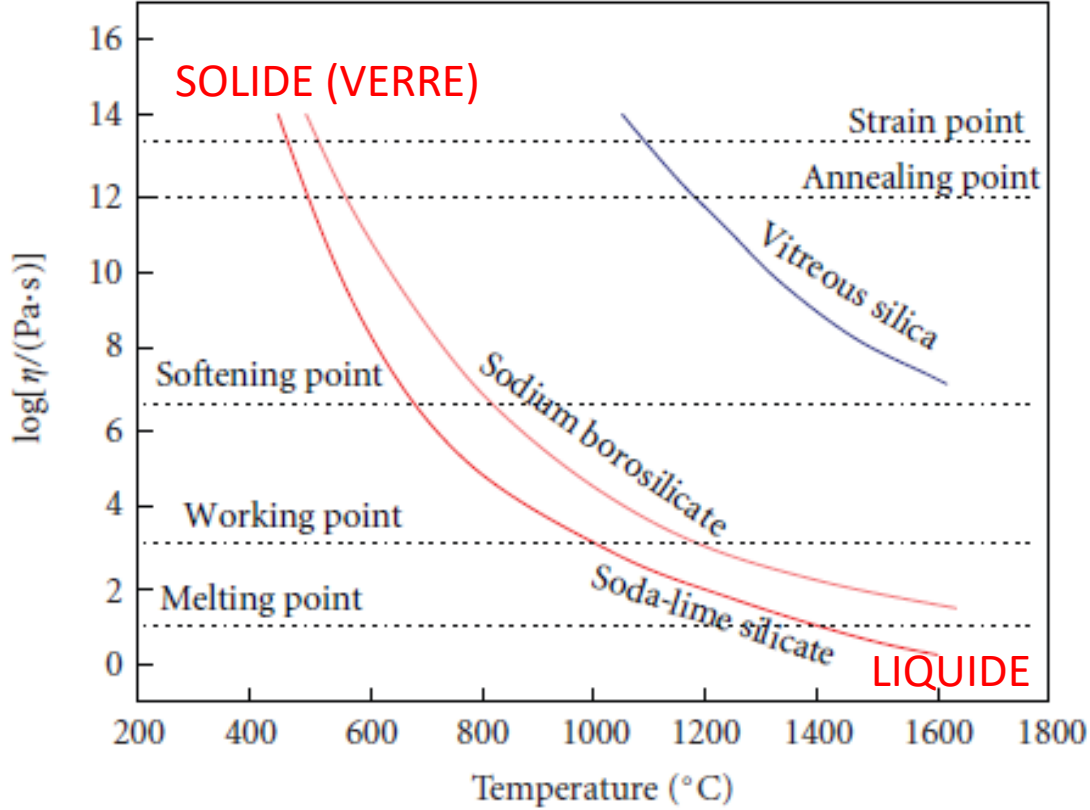
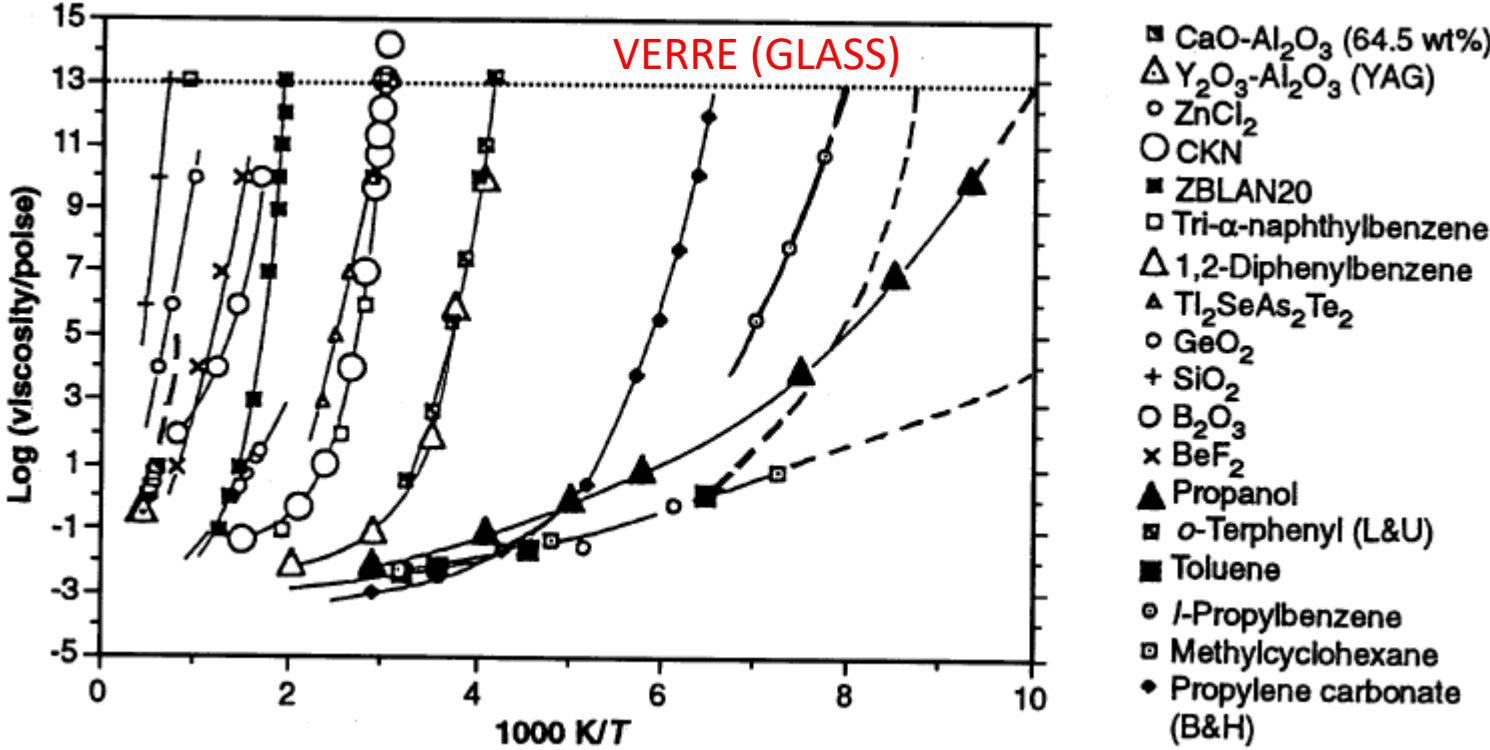


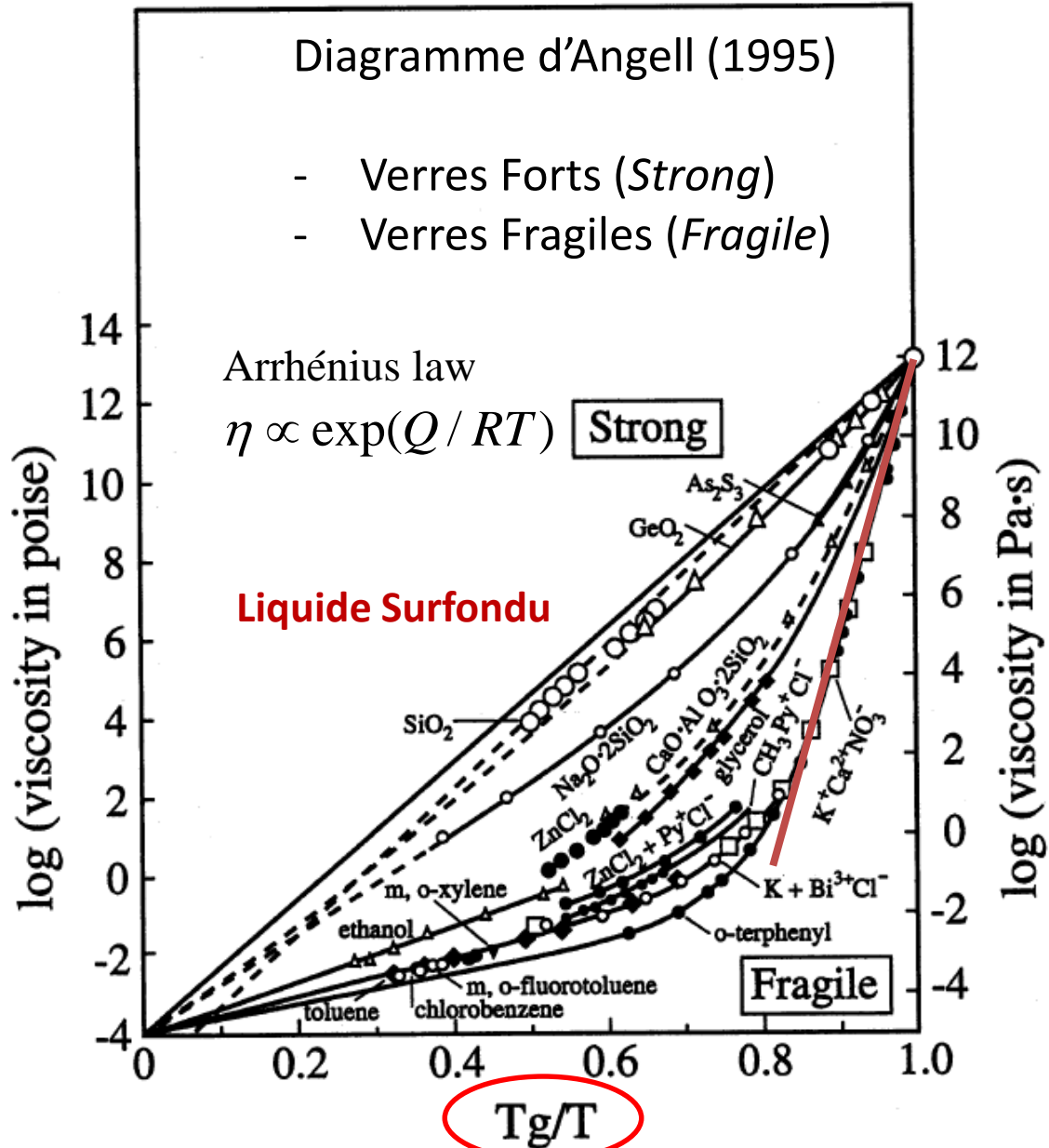
FIGURE 4: Viscosity of amorphous silicates and important technological points in glass manufacture industry (after [49]).

Comprendre la Transition Vitreuse

Mesures de Viscosité



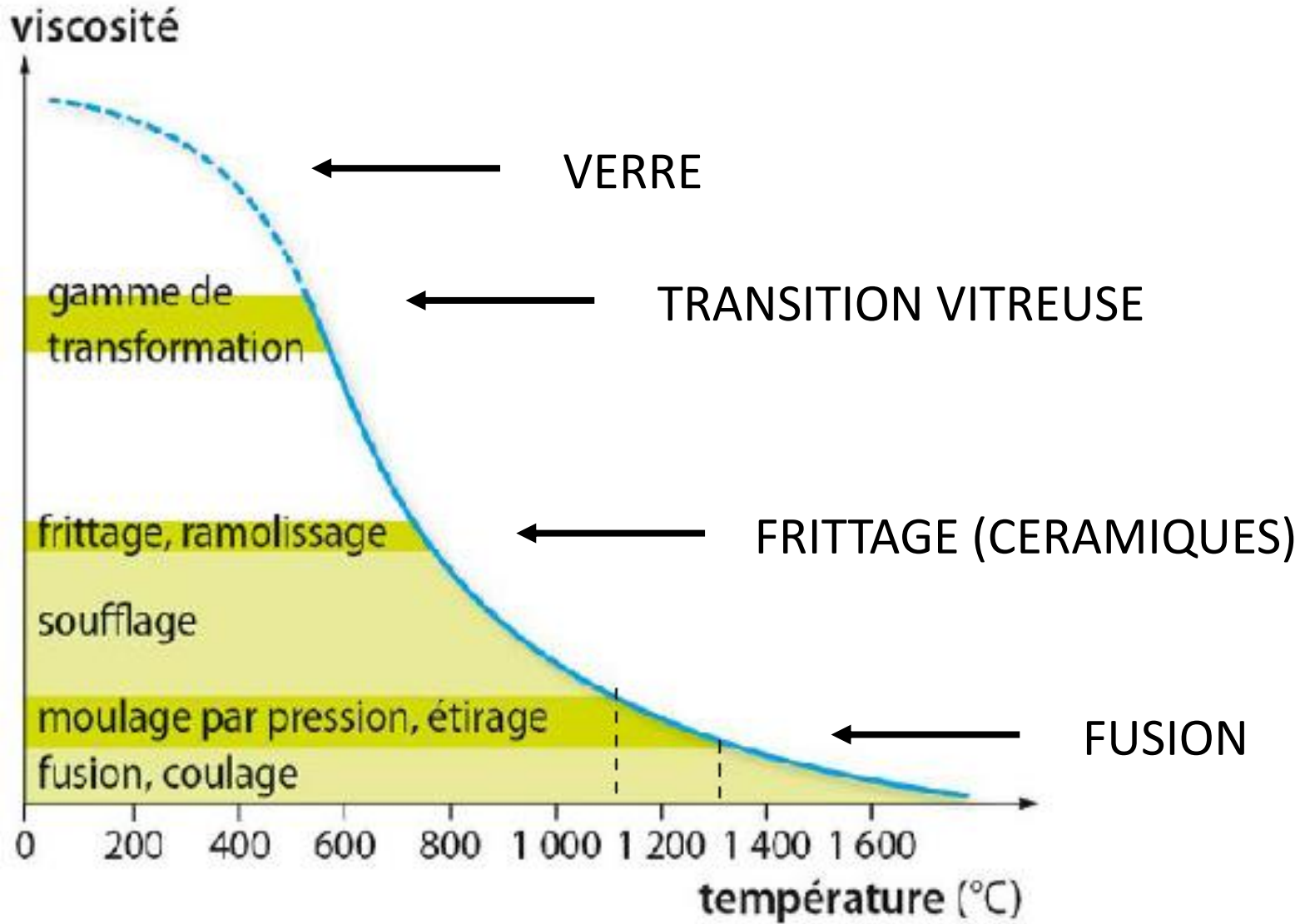
Comprendre la Transition Vitreuse



Indice de Fragilité :

$$m \equiv \left. \frac{d \log_{10} \eta}{d(T_g / T)} \right|_{T=T_g}$$

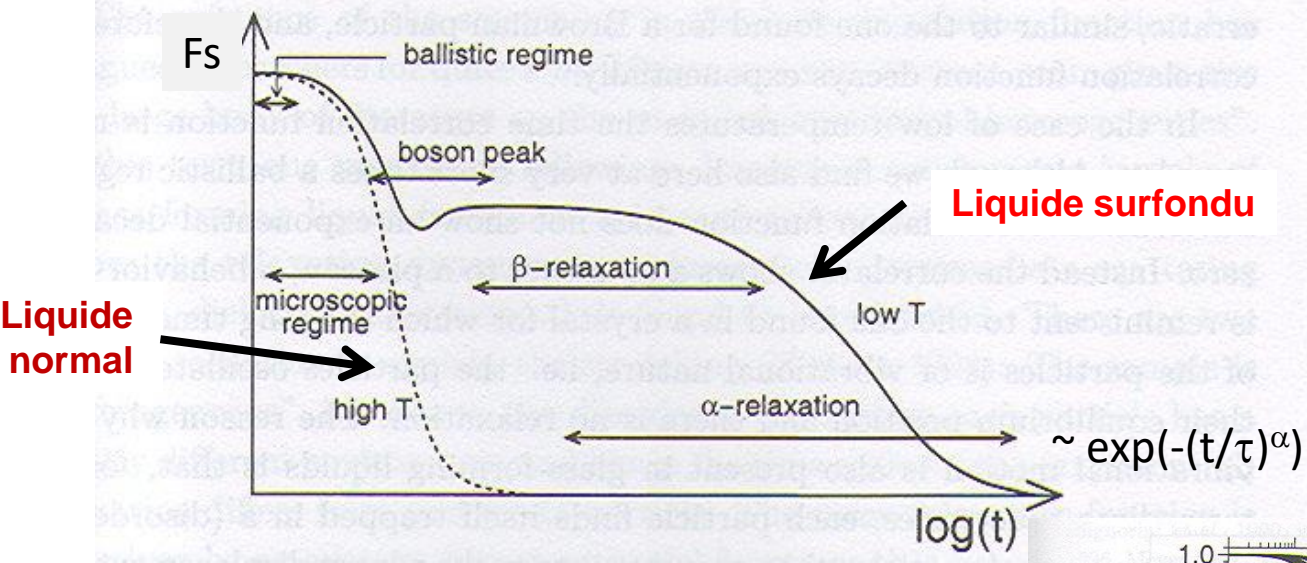
Comprendre la Transition Vitreuse



Comprendre la Transition Vitreuse

Relaxation lentes, avec **plusieurs temps de relaxation**:

Dépendance temporelle typique d'une fonction de corrélation:

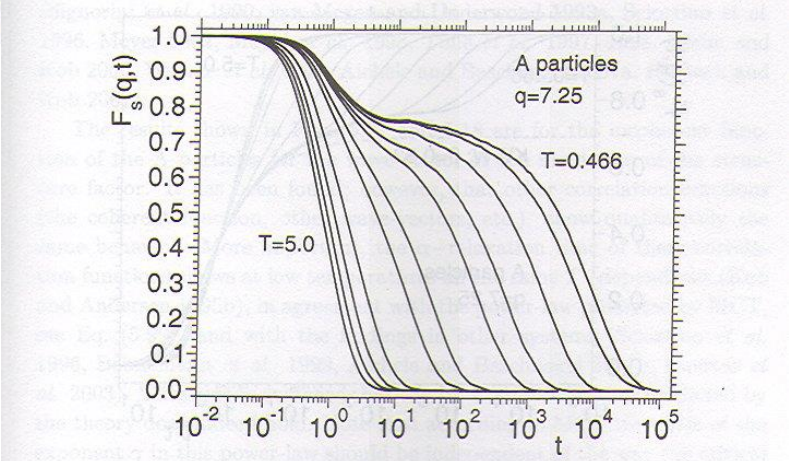


β -relaxation: rapide
 α -relaxation: lente

Exemple: Fonctions de corrélation dynamiques:

$$F_s(\vec{q}, t) = \frac{1}{N} \sum_j \langle \exp\{i\vec{q} \cdot [\vec{r}_j(0) - \vec{r}_j(t)]\} \rangle$$

$$S(\vec{q}, \omega) = \frac{1}{2\pi} \int dt. \exp(i\omega t). F_s(\vec{q}, t)$$



Comprendre la Transition Vitreuse

PHYSICAL REVIEW E

VOLUME 61, NUMBER 6

JUNE 2000

Cooperativity and spatial correlations near the glass transition: Computer simulation results for hard spheres and disks

B. Doliwa* and A. Heuer

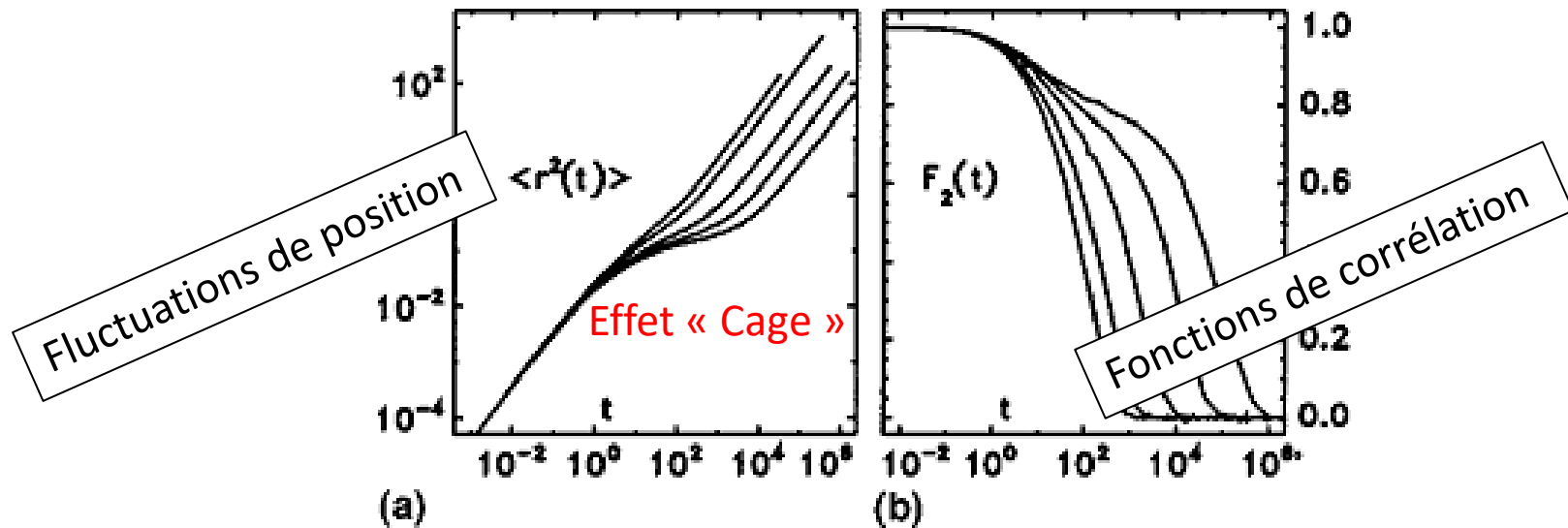


FIG. 1. One-particle, two-time quantities for the 3d packing fractions $\varphi_{3d} = 50\%$, 53% , 56% , 57.3% , and 58% , from left to right. The system sizes are $N \approx 1000$. (a) The mean squared displacement $\langle r^2(t) \rangle$ and (b) the incoherent scattering function $F_2(\mathbf{k}_{\max}, t)$.

Comprendre la Transition Vitreuse

Fluctuations de Position

Molecular Dynamics Simulations on poly (methyl methacrylate)
Tsige (2002)

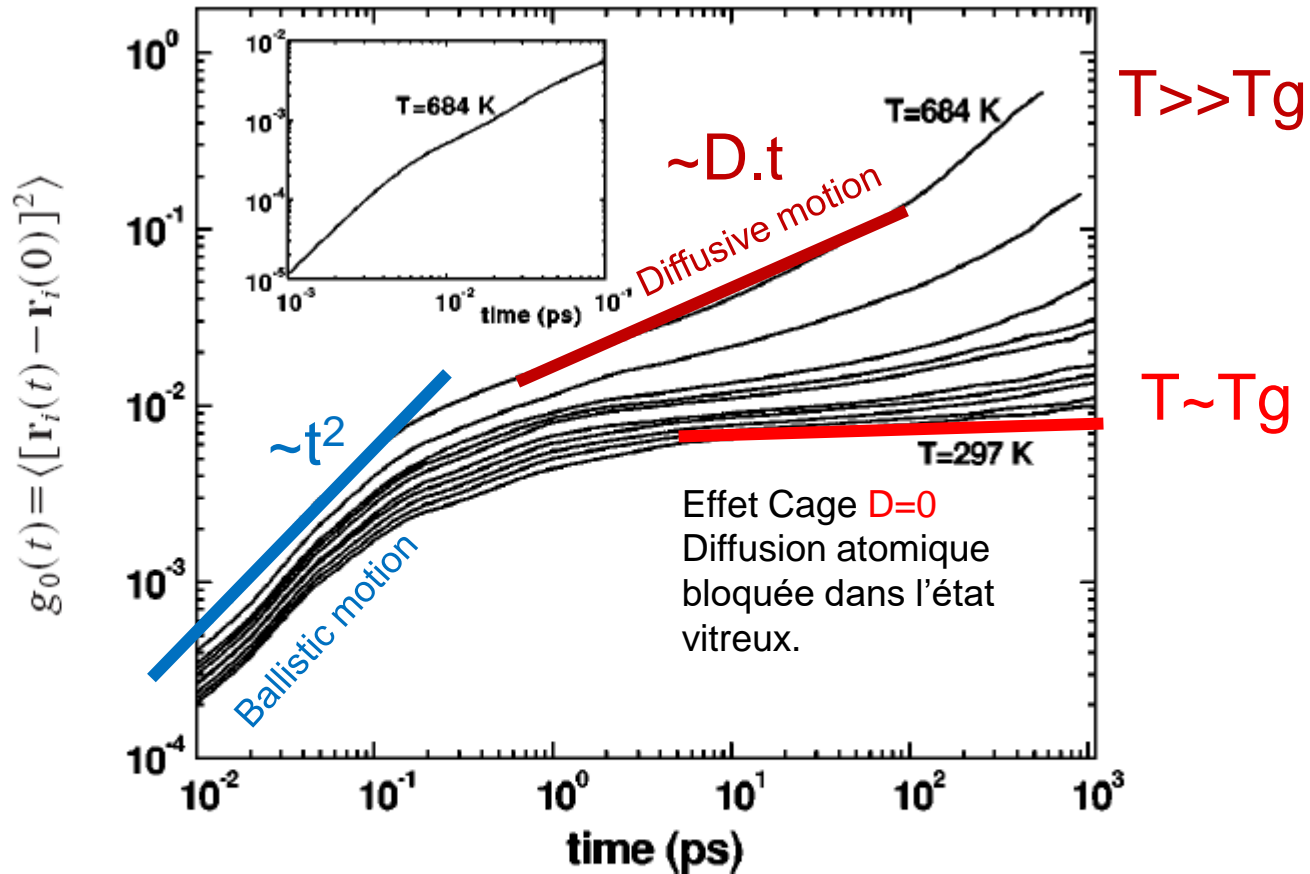
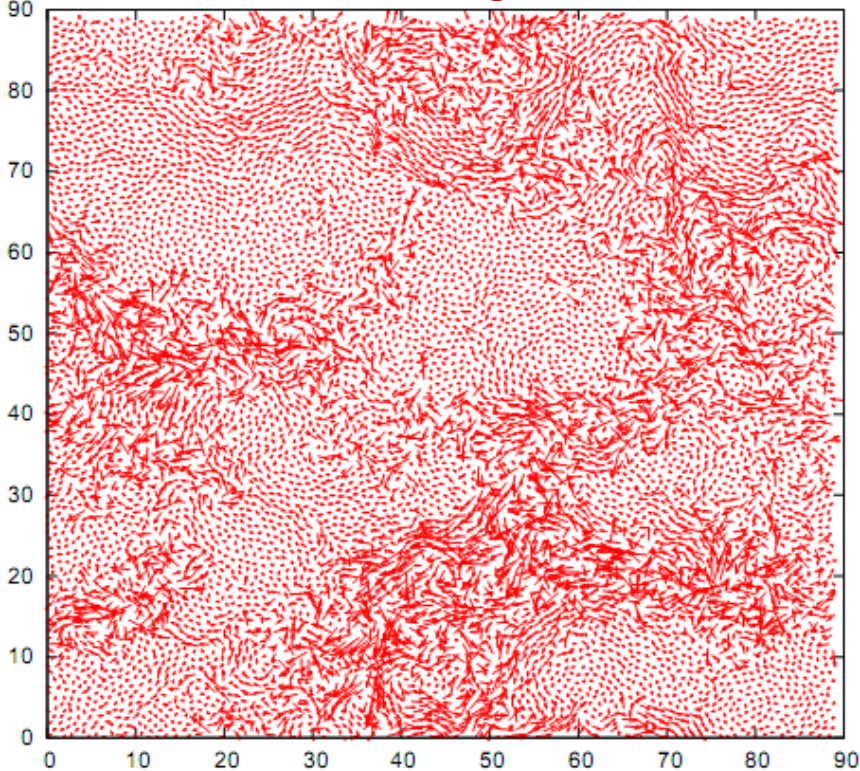


FIG. 1. Atomic mean squared displacement evaluated at ten different temperatures (297, 324, 346, 396, 415, 436, 472, 509, 599, and 684 K). Inset: same quantity at the highest temperature studied but with time starting from 1 fs to show the ballistic region clearly.

Comprendre la **Transition Vitreuse**

Dynamique Locale des atomes

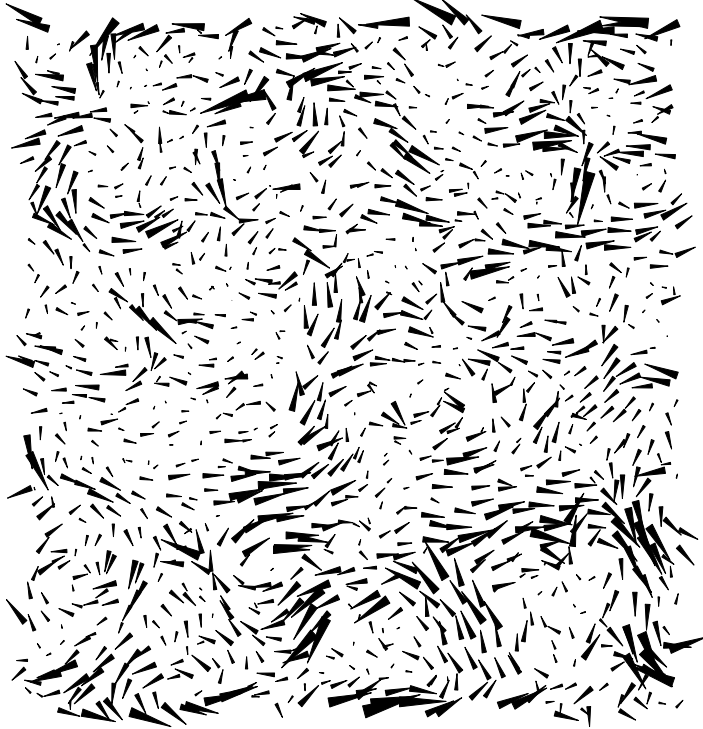
$T \geq T_g$



L. Berthier at al. (2004)

Déplacements dans l'état
Liquide Surfondu à $T \sim T_g$

$T \leq T_g$

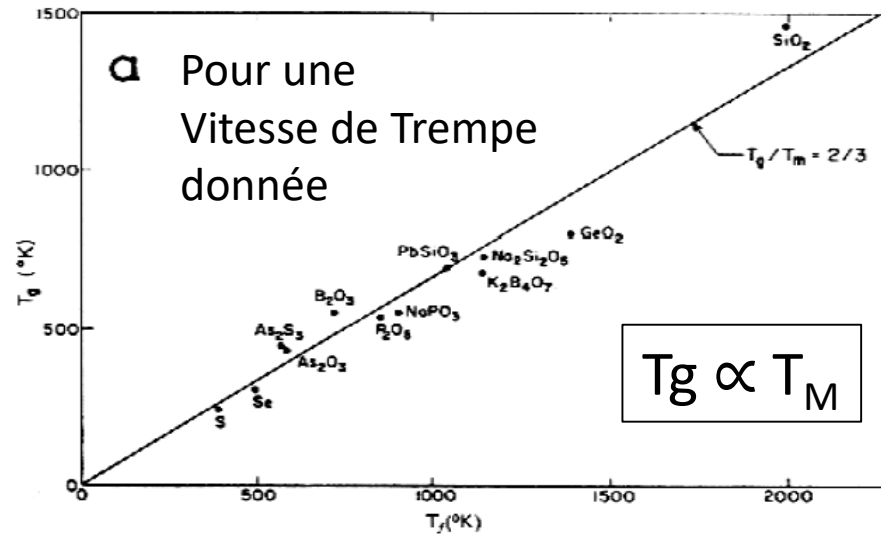


A. Tanguy at al. (2002)

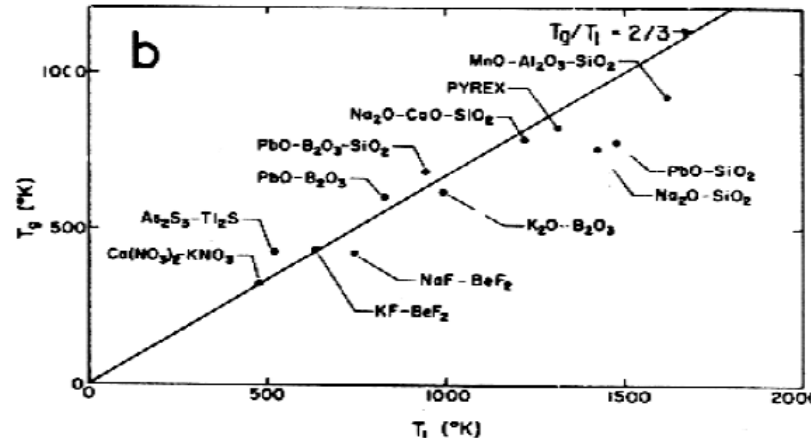
Déplacement Non-Affines ($\times 10^3$)
dans le Solide amorphe

Température de Transition Vitreuse et Facilité à former un verre (Glass Forming Ability GFA)

Température
Transition Vitreuse

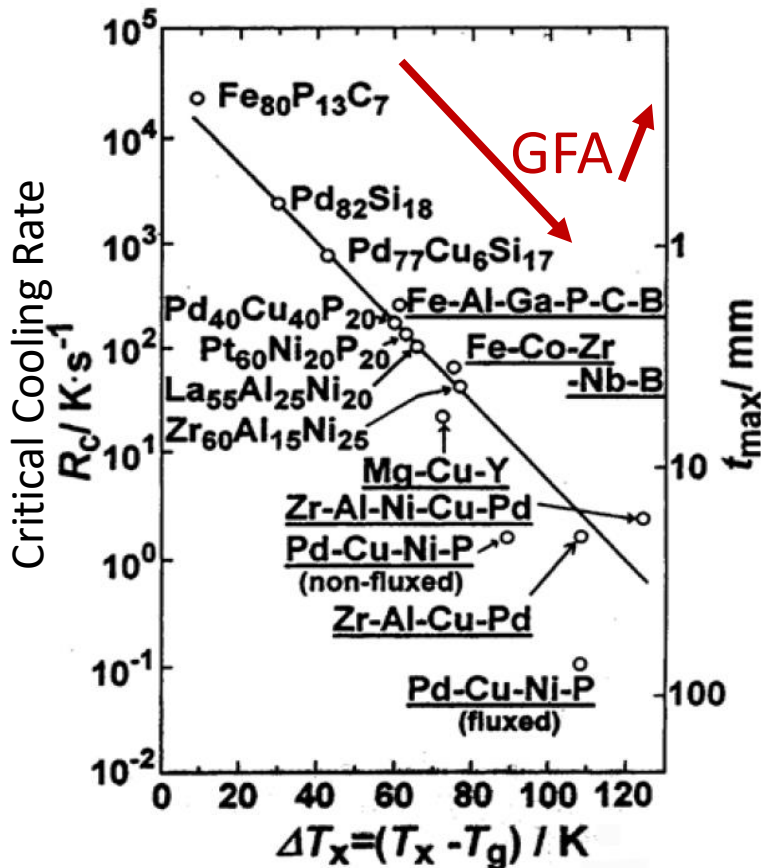


Température
de Fusion



Température de Transition Vitreuse et Facilité à former un verre (Glass Forming Ability GFA)

1970's Indicateurs: températures caractéristiques



Région de liquide surfondu $\Delta T_x = T_x - T_g$
 T_x cristallisation, T_g transition vitreuse

Autres indicateurs envisagés:

$$T_{rg} = T_g / T_L \text{ (liquidus) } 0.66 < T_{rg} < 0.69$$

$$\gamma = T_x / (T_g + T_L)$$

$$\alpha = T_x / T_L$$

$$\phi = T_{rg} \cdot (\Delta T_x / T_g)^{0.143}$$

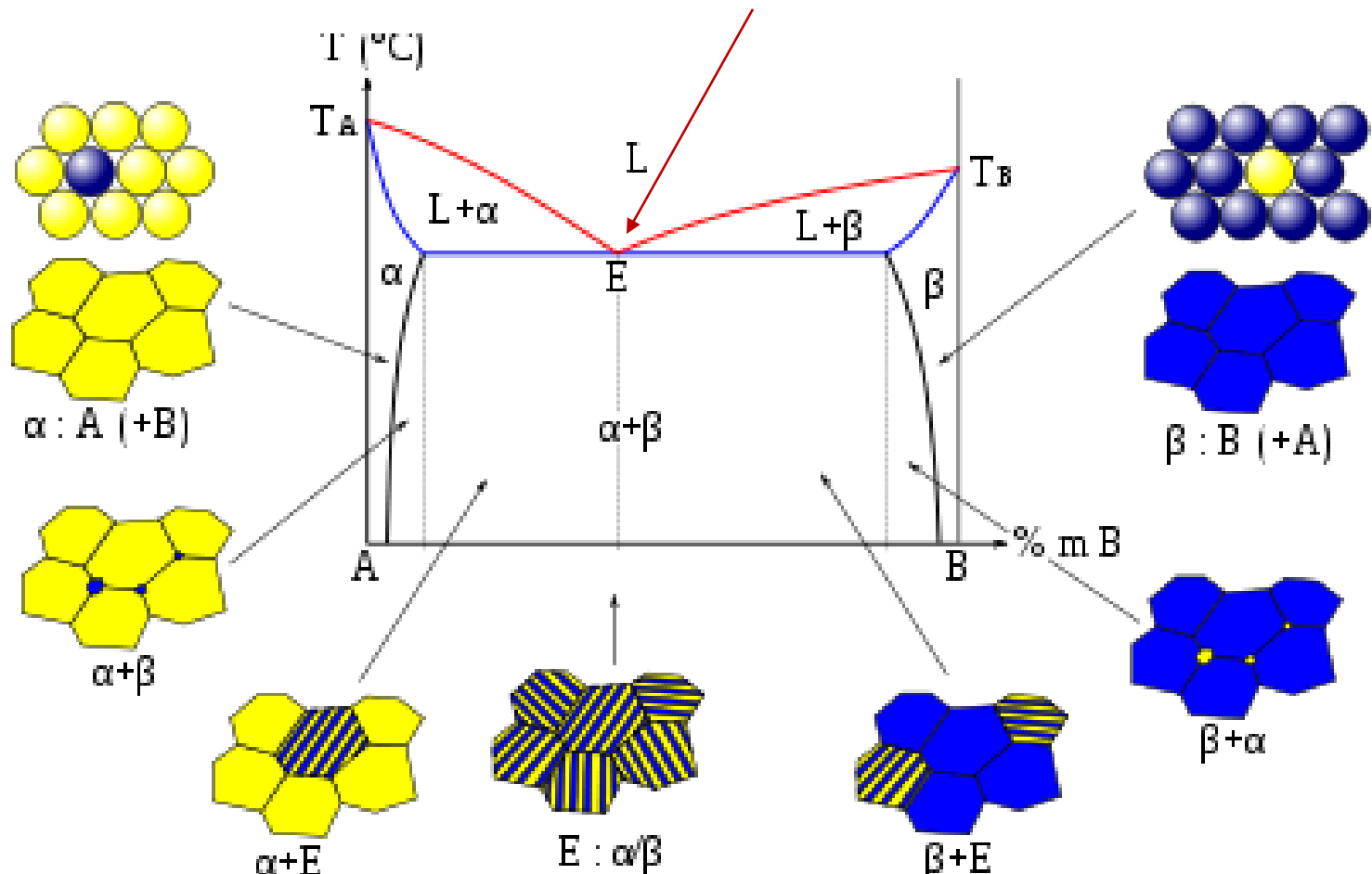
$$\delta = T_x / (T_L - T_g)$$

$$\beta = T_x \cdot T_g / (T_L - T_x)^2 \dots$$

ΔT_x élevé permet d'obtenir un verre avec
un **taux de refroidissement** plus bas

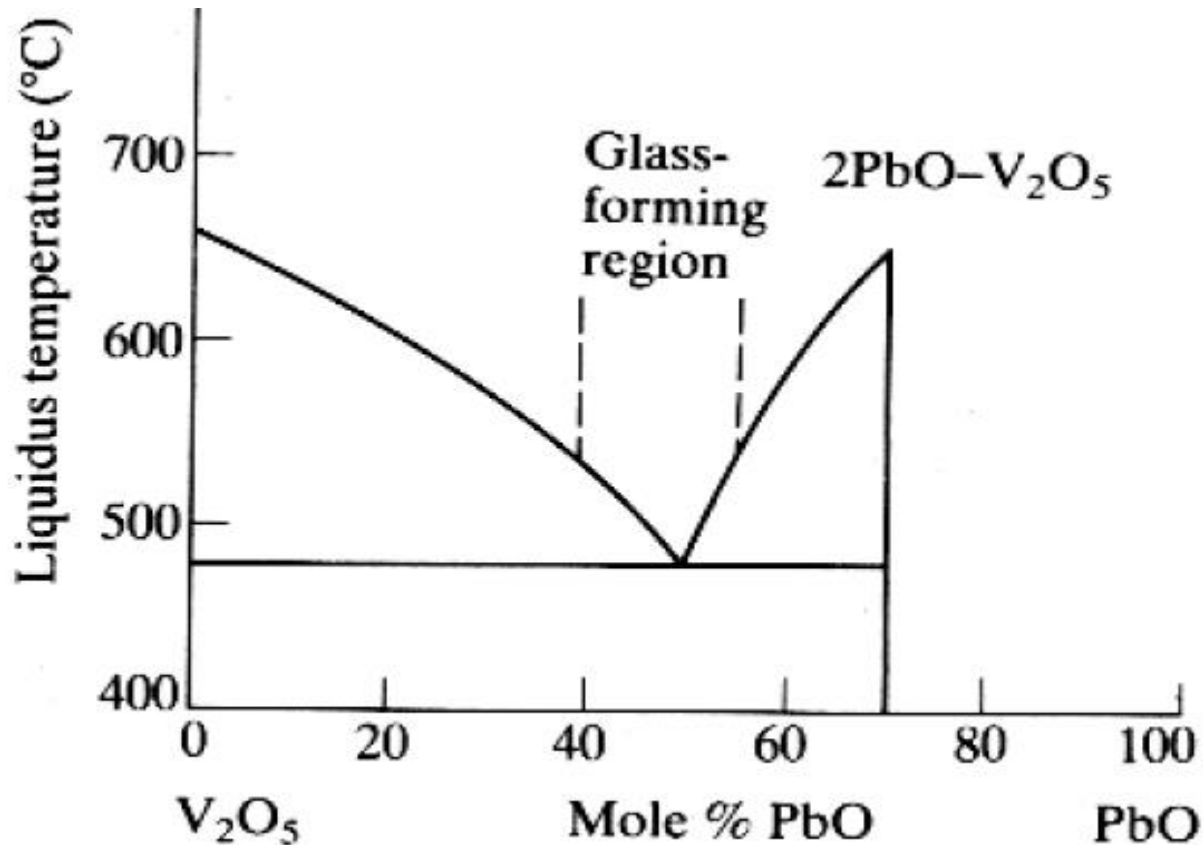
Diagrammes de Phase et **Facilité à former un verre** (Glass Forming Ability GFA)

L'état Amorphe serait favorisé par
la **frustration cinétique** et un point **Eutectique** profond

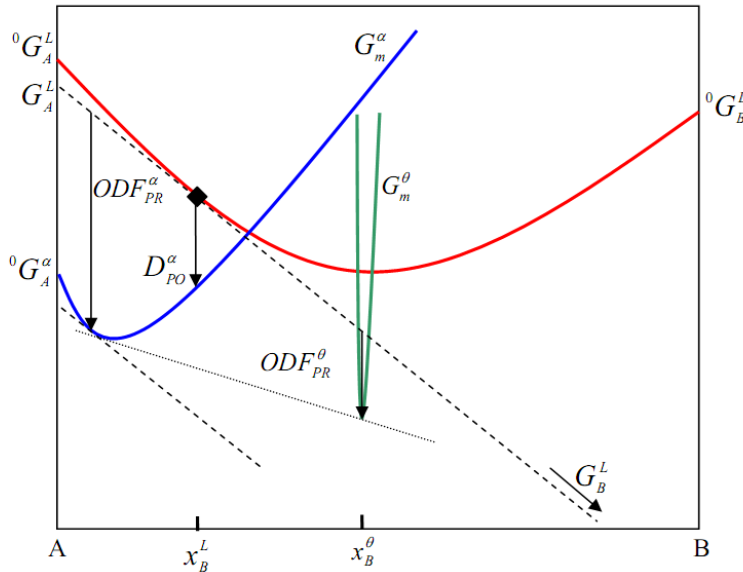


Diagrammes de Phase
et **Facilité à former un verre**
(Glass Forming Ability GFA)

L'état Amorphe serait favorisé par
la **frustration cinétique** et un point **Eutectique** profond

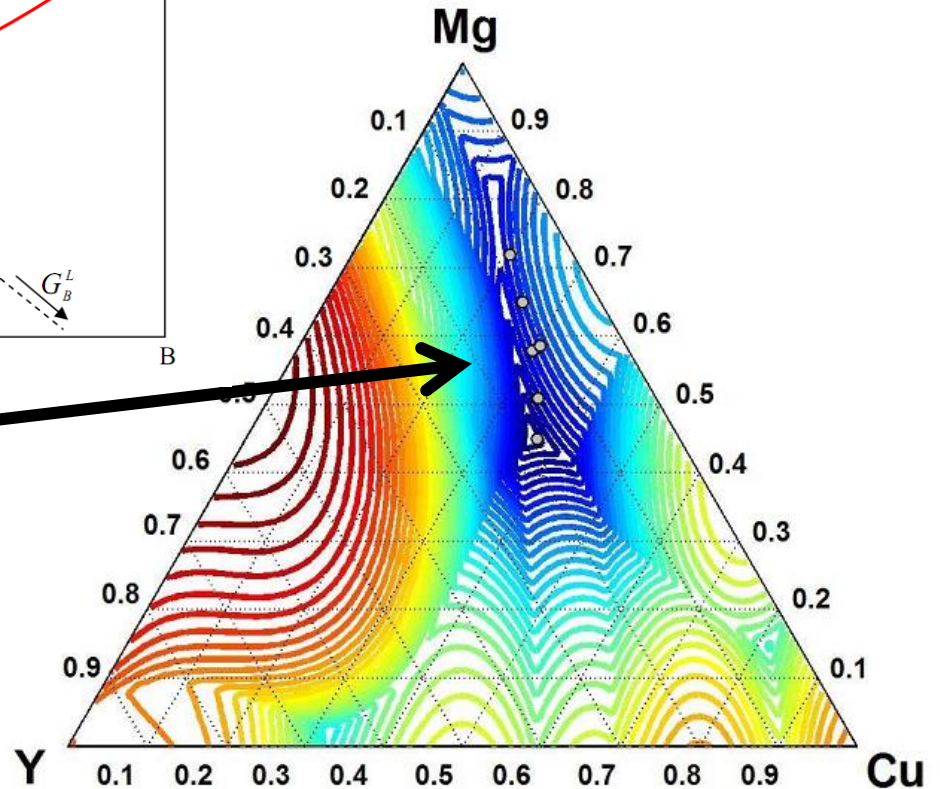


Diagrammes de Phase et Facilité à former un verre (Glass Forming Ability GFA)



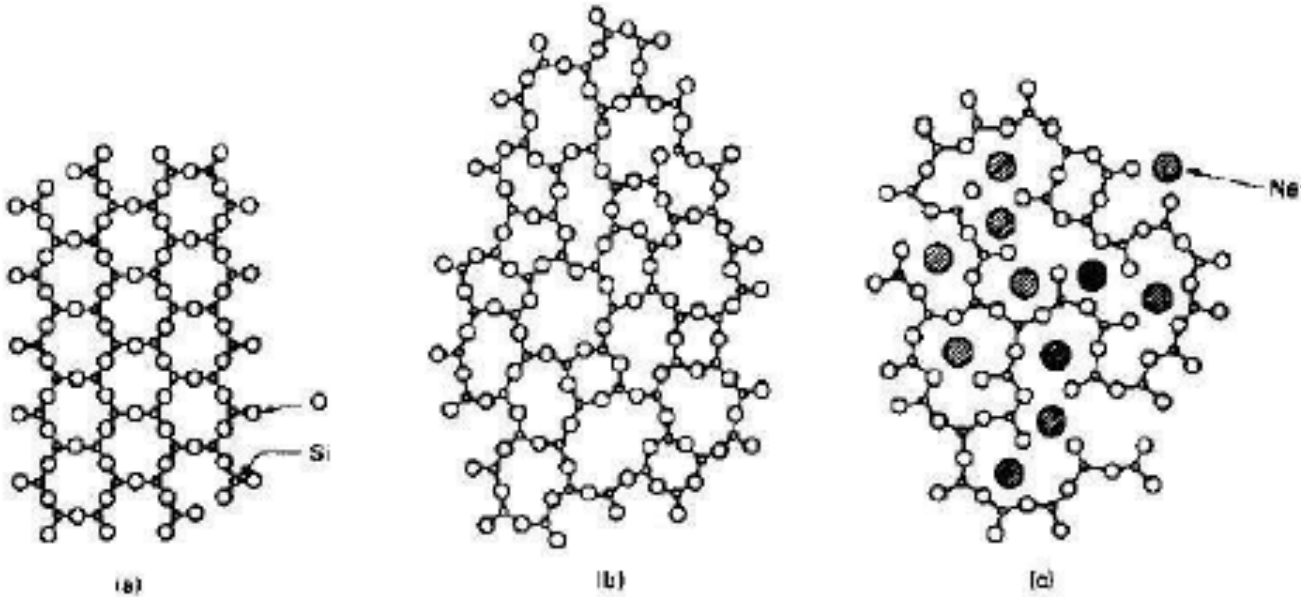
Etat amorphe

Force motrice d'initiation
pour la cristallisation $\propto \Delta\mu$
(Energie de Gibbs-Duhem)



Microstructure d'un Verre

Modèle Structural de Zachariasen (1932)



**Réseau régulier
de silice**

*Structure
cristalline*

**Réseau aléatoire
de silice**

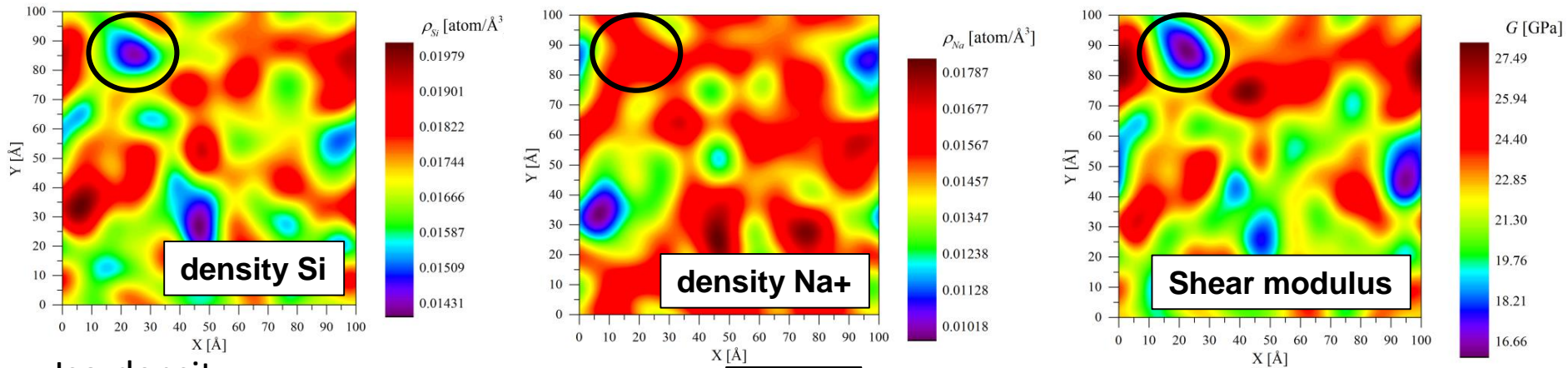
*Structure
amorphe*

**Incorporation d'agent
modificateurs (Na_2O)
qui brise la continuité
du réseau**

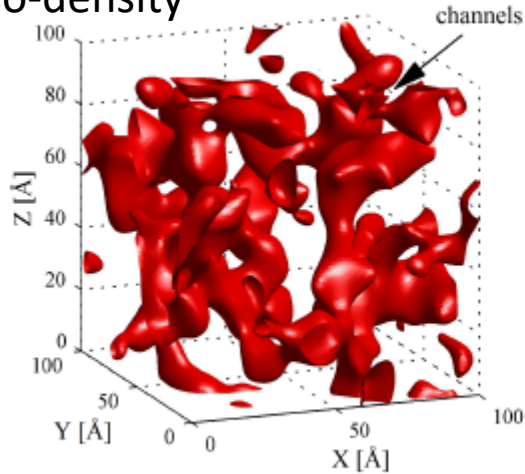
———— vitrification —————>

Microstructure d'un Verre

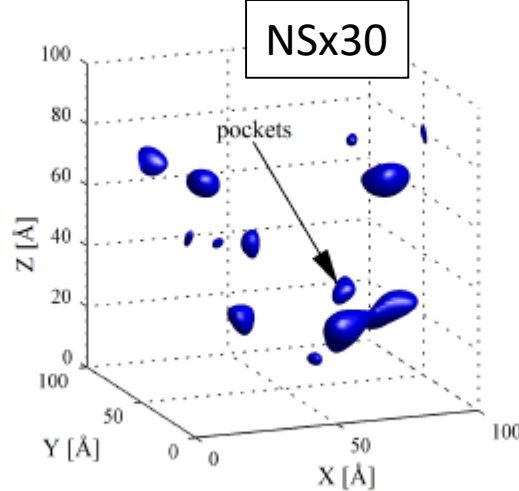
Simulation de Dynamique Moléculaire Verre Sodo-silicate (1-x)SiO₂ + xNa₂O



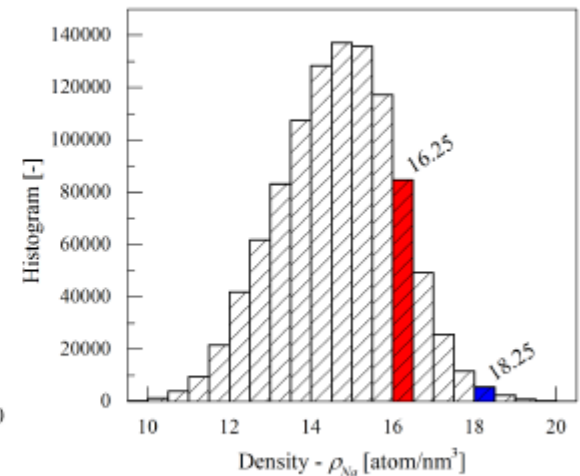
Iso-density



(a) $\rho_{Na} = 16.25 \text{ atom/nm}^3$.



(b) $\rho_{Na} = 18.25 \text{ atom/nm}^3$.



(c) Histogram.

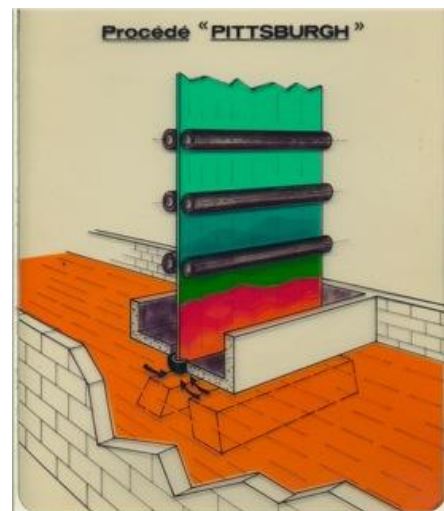
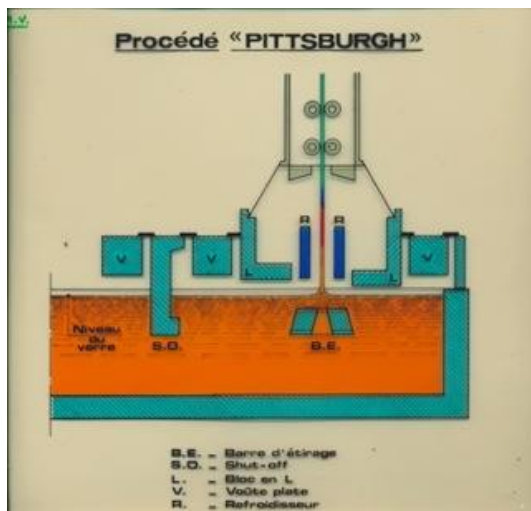
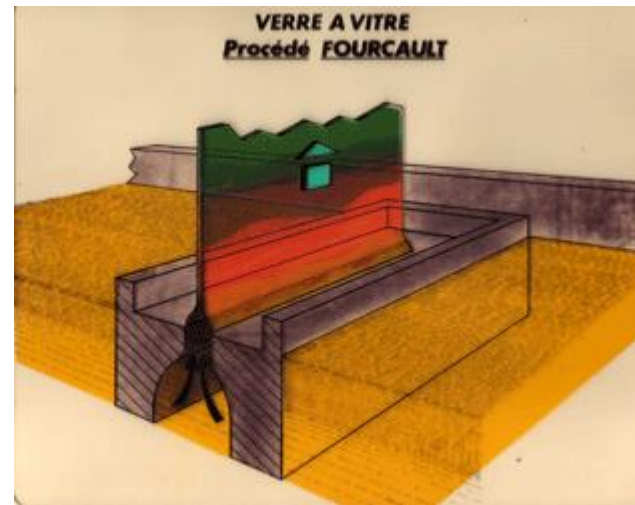
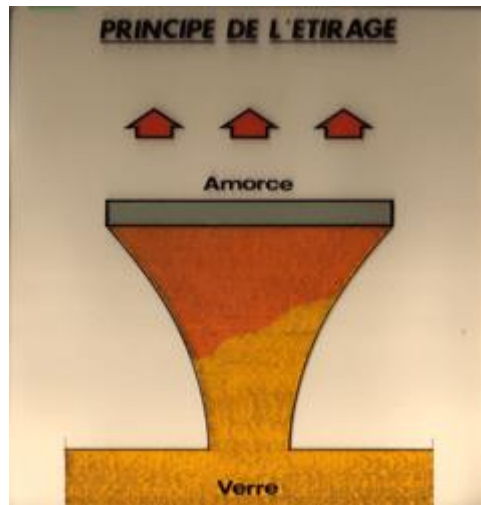
Définition d'un Verre

Un verre est un solide résultant du piégeage d'un liquide dans un état solide non cristallin.

Un verre possède une **température de transition vitreuse**.

Procédés de Mise en Forme

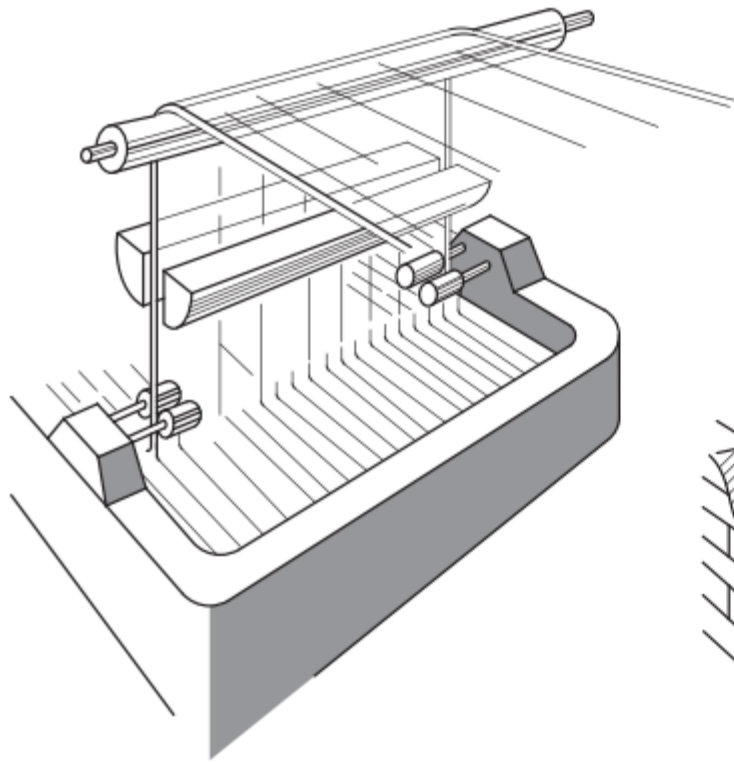
Verre Plat



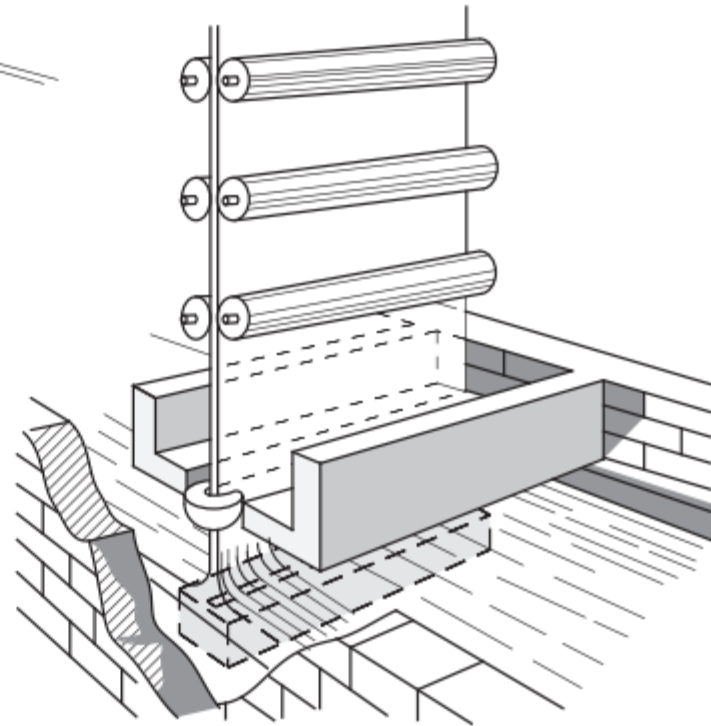
Procédés de Mise en Forme

Verre Plat

A. PROCÉDÉ LIBBEY-OWENS

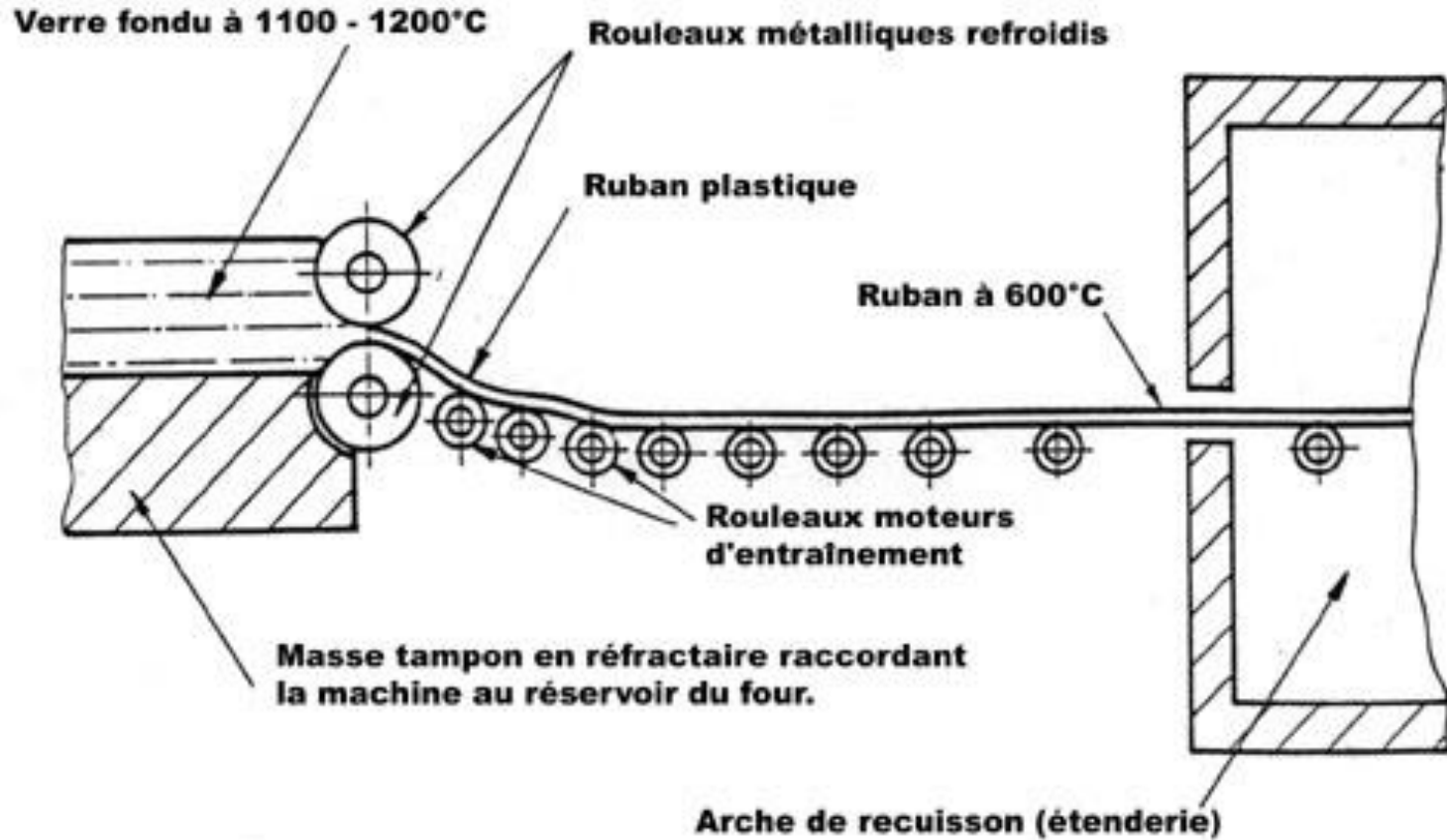


B. PROCÉDÉ FOURCAULT EN
PITTSBURGH



Procédés de Mise en Forme

Verre Plat

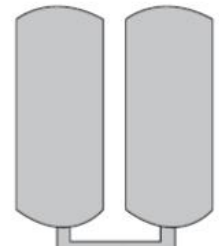


FORMATION DU VERRE LAMINE

Procédés de Mise en Forme

Verre Flotté (« Float ») - 1959

1 Enfournement

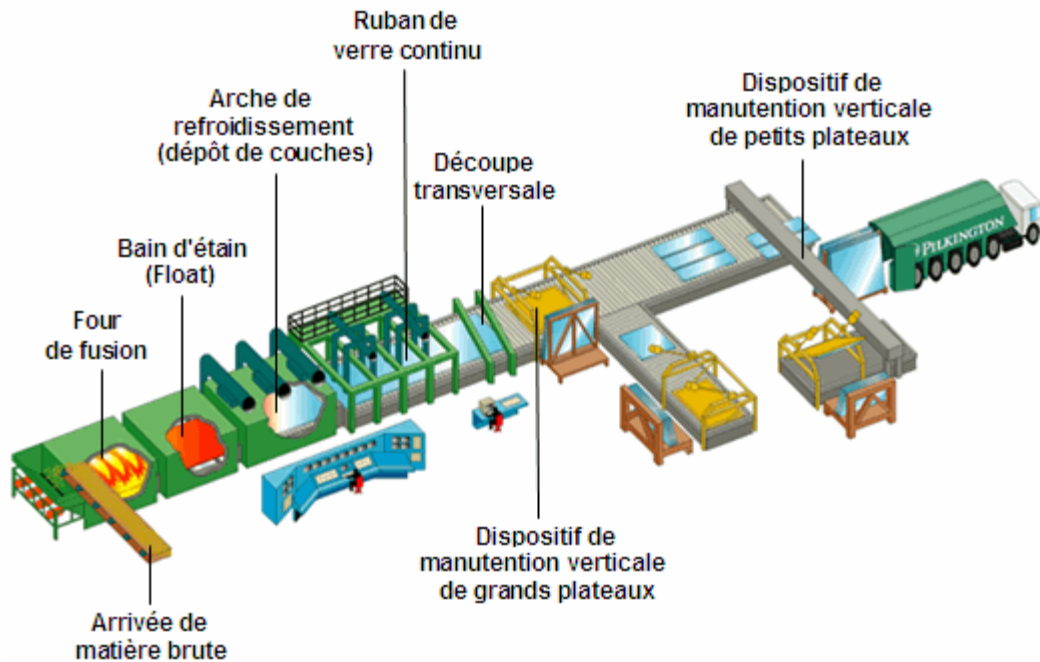
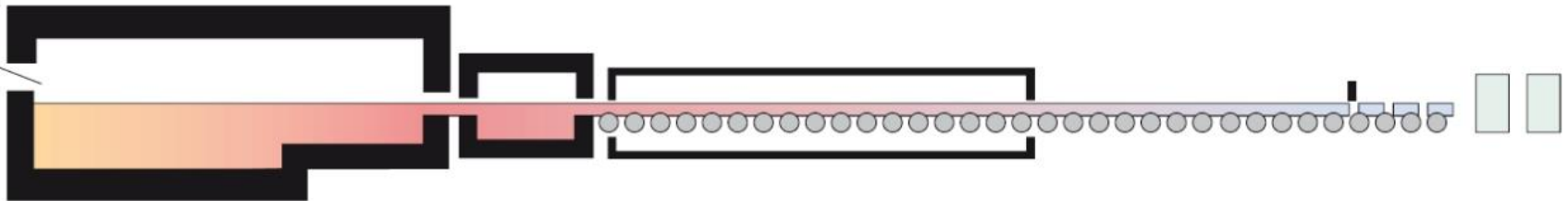


2 Cuve de fusion
env. 1550° C

3 Bain de
flottage

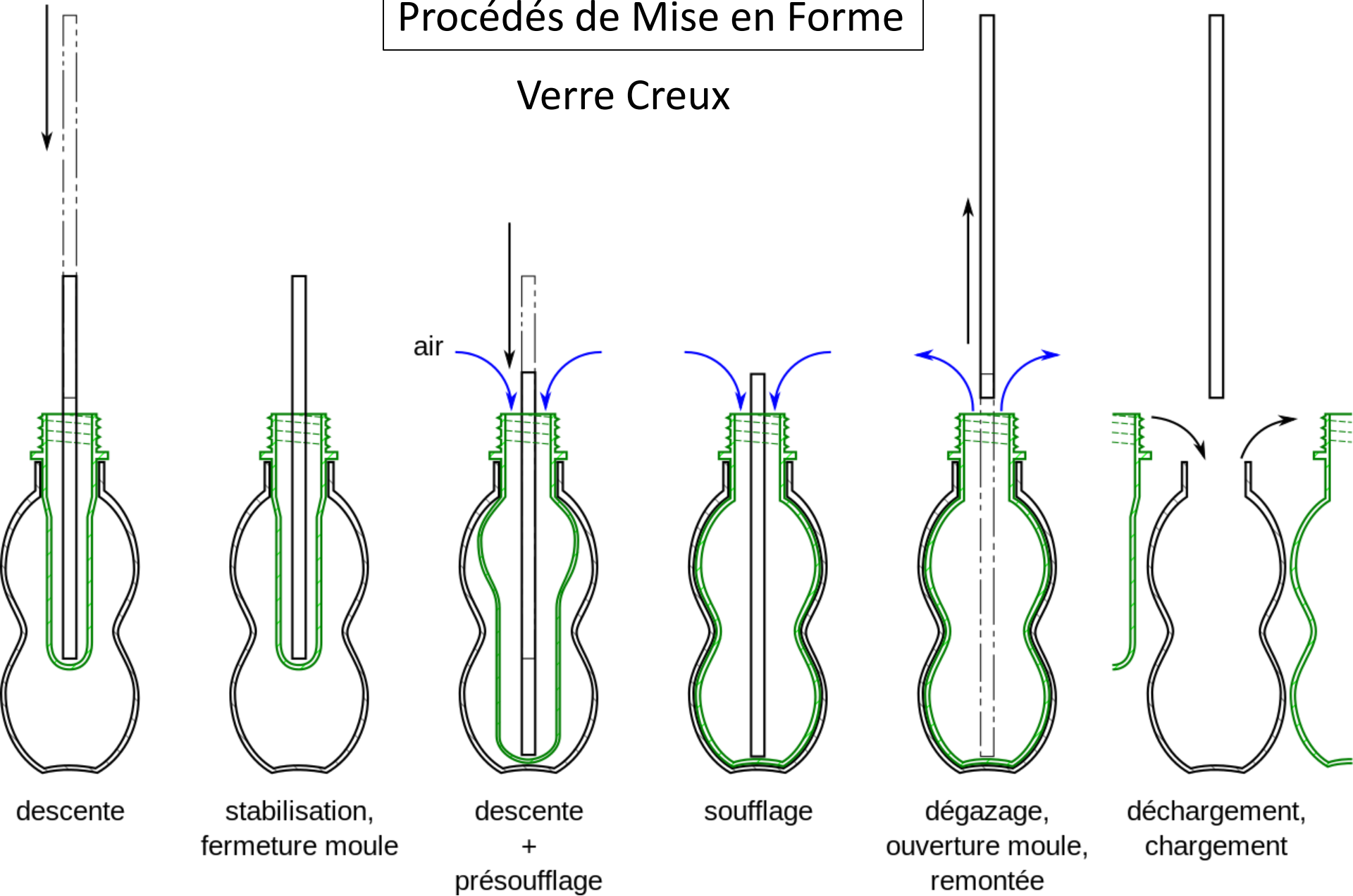
4 Zone de
refroidissement

5 Découpe



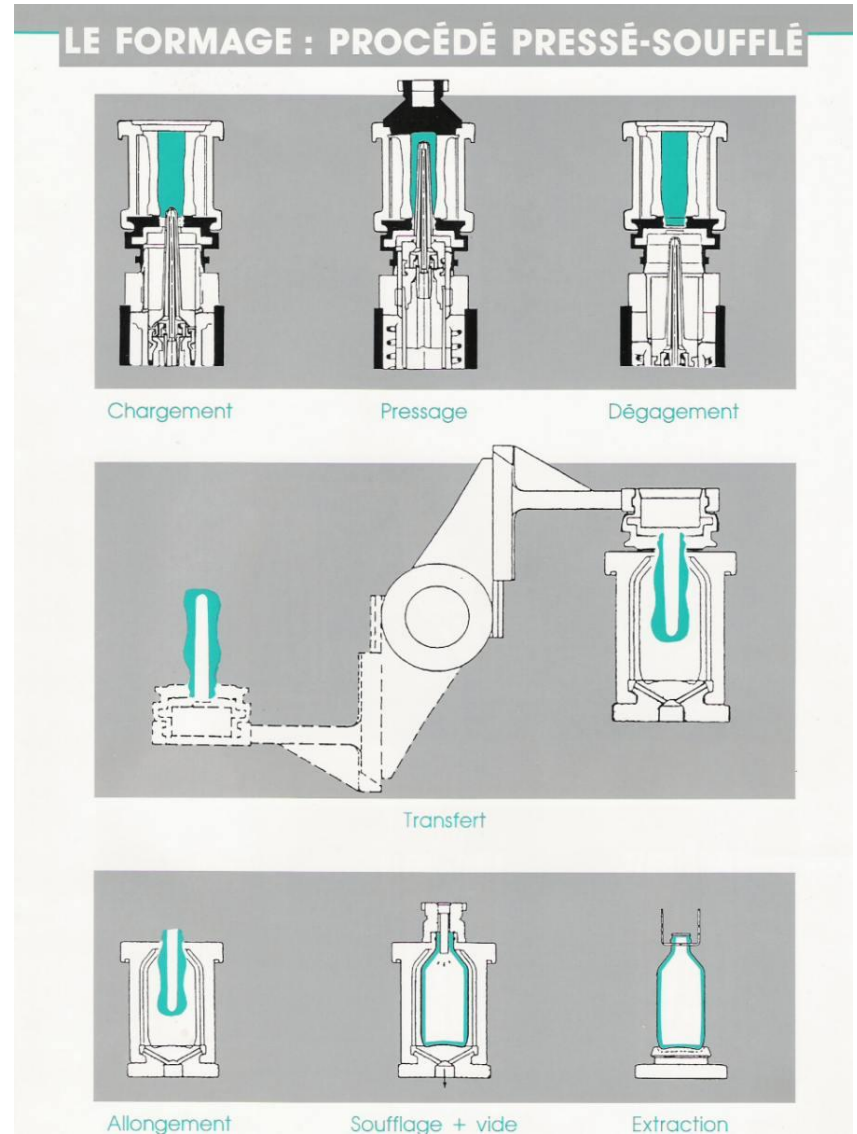
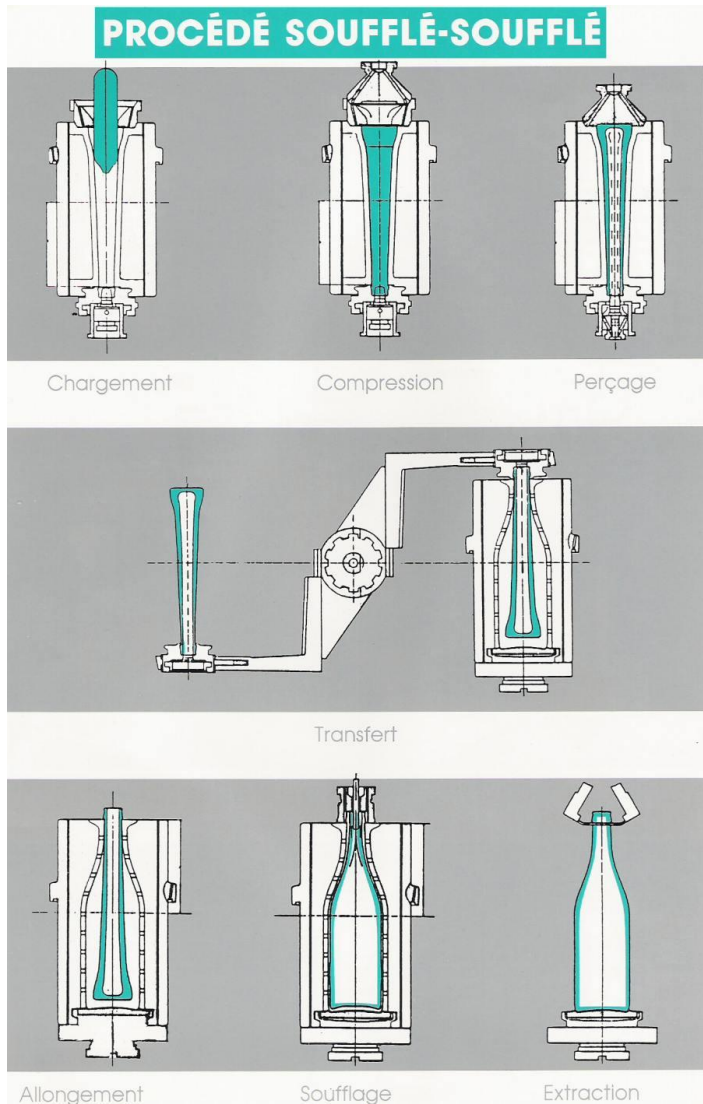
Procédés de Mise en Forme

Verre Creux



Procédés de Mise en Forme

Verre Creux



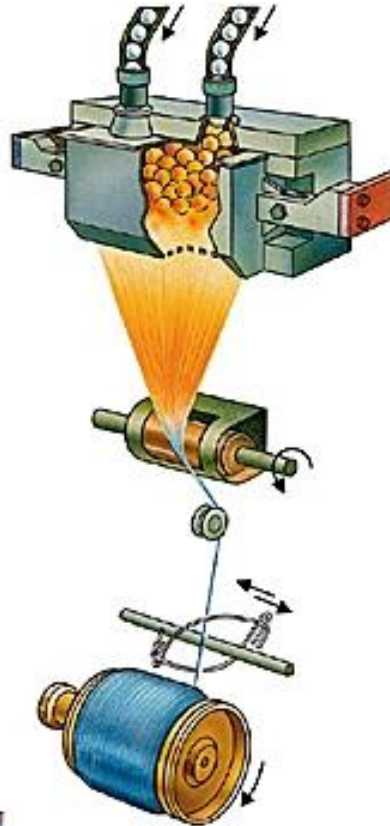
Procédés de Mise en Forme

Verre Technique

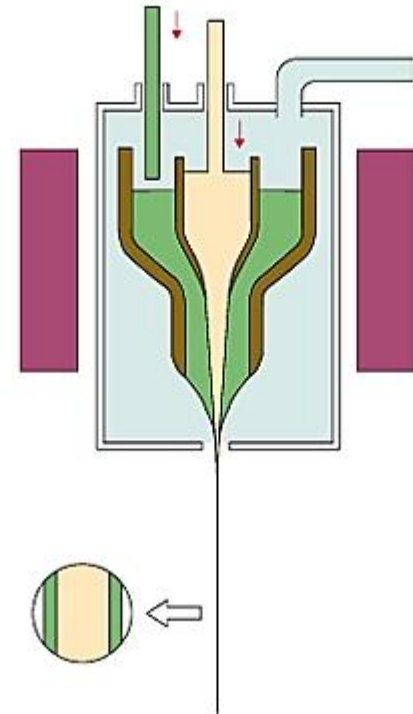
Etirage à la Vapeur



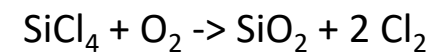
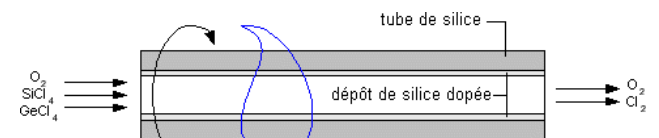
Fibrage Mécanique



Double Creuset

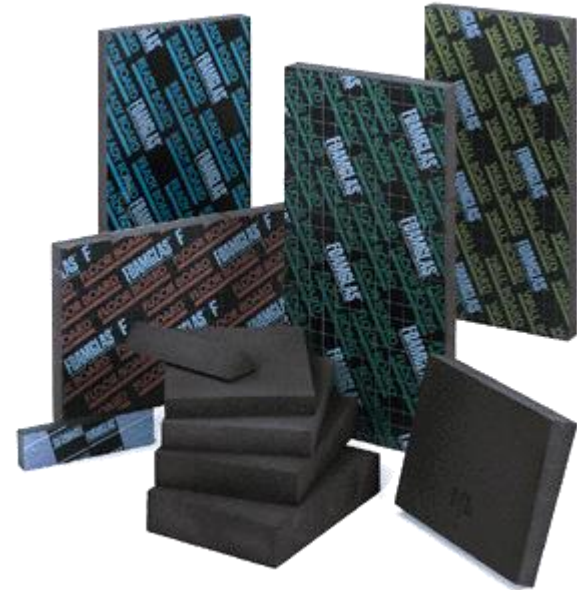
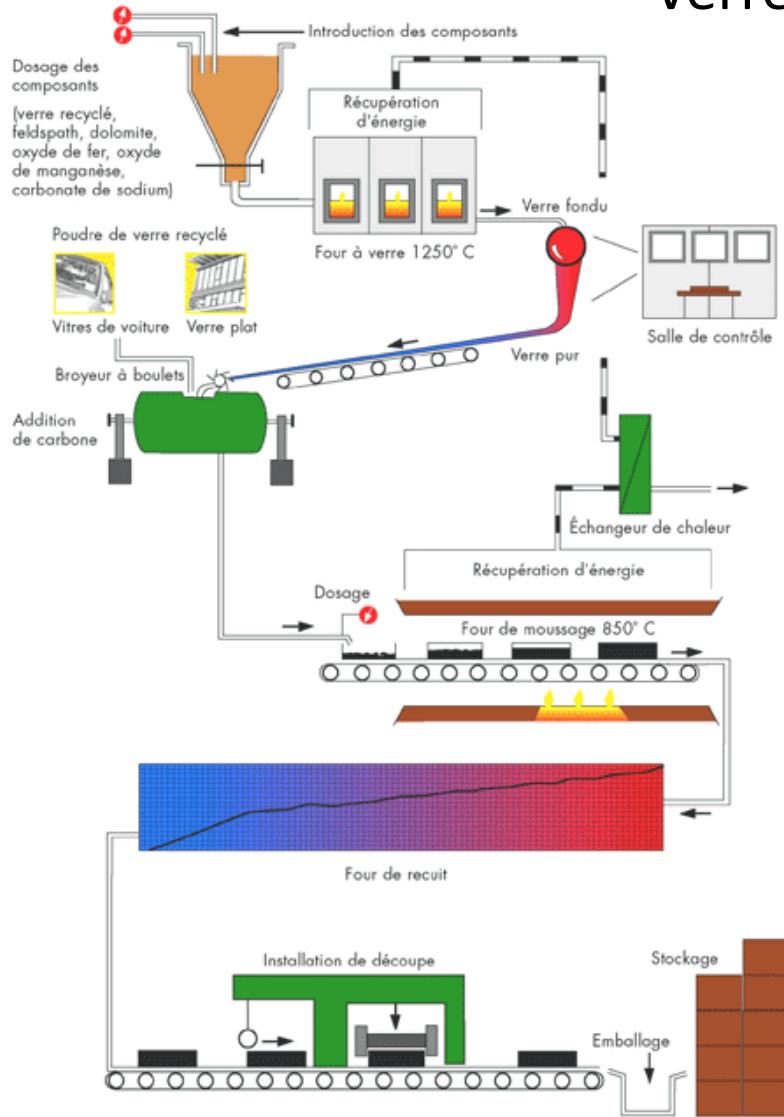


Préforme:



Procédés de Mise en Forme

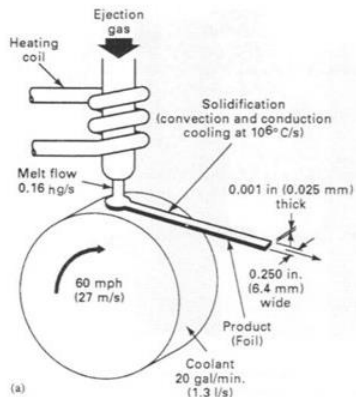
Verre Cellulaire



Procédés de Mise en Forme

Verres Métalliques

Trempe sur roue:



Metallic Glass
Splat quenching of ribbons

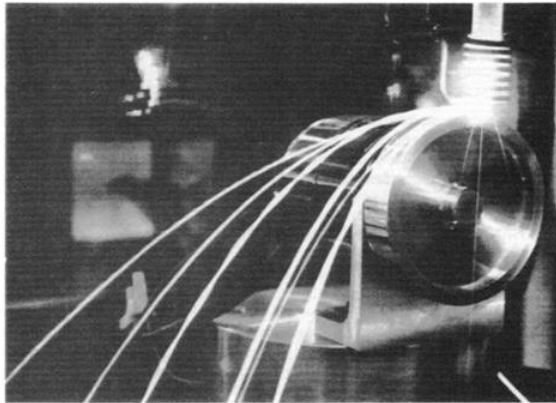
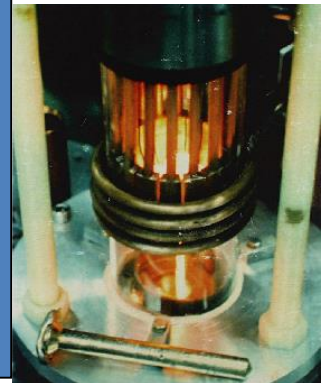
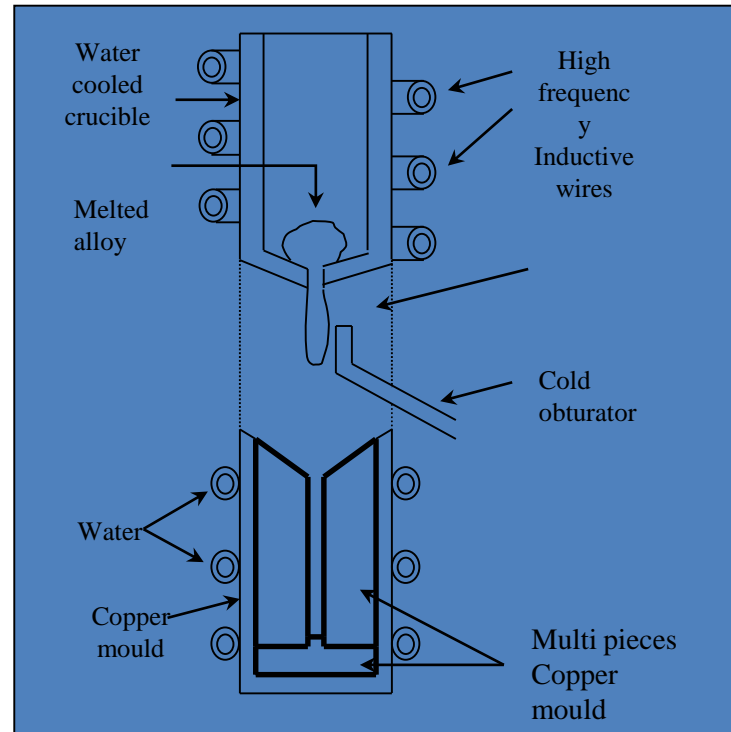


Figure 3-63 (a) A jet of molten metal is solidified rapidly when it strikes a liquid-cooled rotating drum. (b) This striking photo shows a melt-spinning device at the National Institute of Standards and Technology. Glowing metal, melted by coils at top right, hits a whirling wheel and flies off as rapidly solidified ribbon. Time photography produced multiple images. (Photo courtesy of NIST)

$$dT/dt = 10^6 \text{°C/s}$$

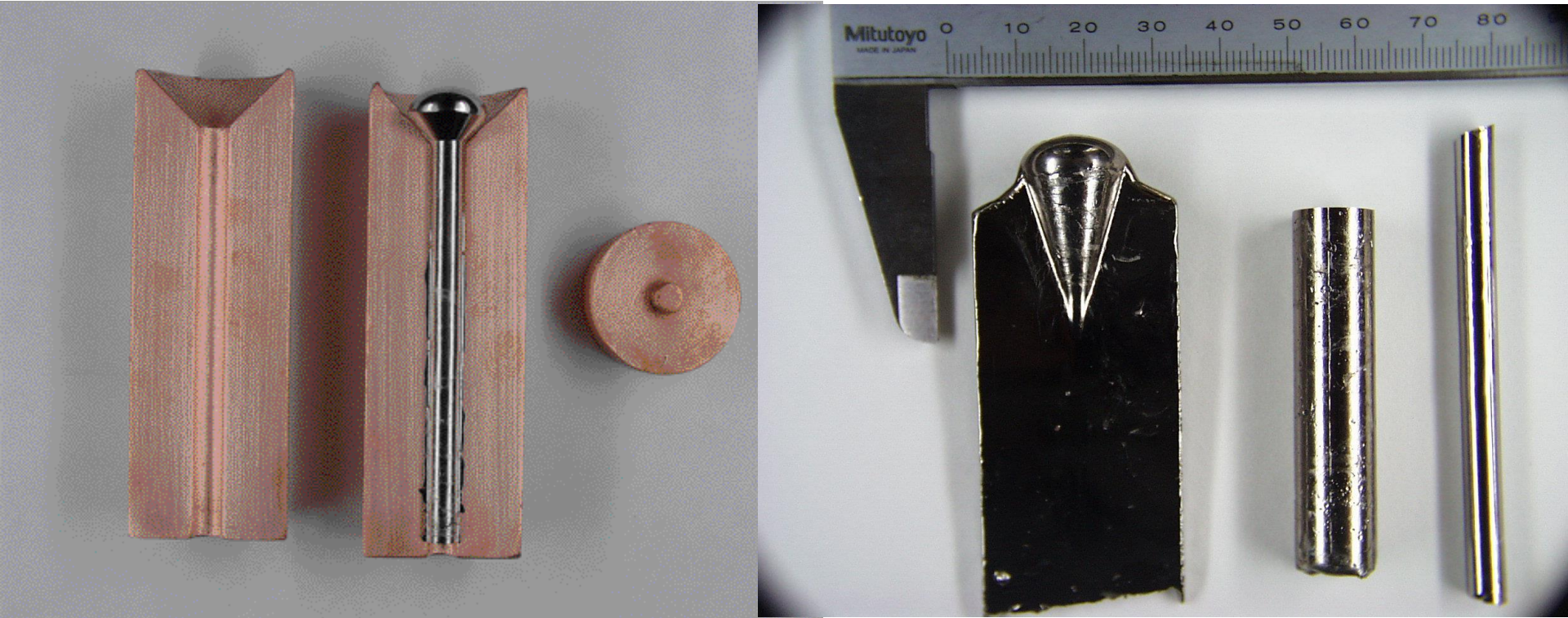
Synthèse par fusion HF des métaux purs, sous Argon:



$$dT/dt \approx 10 \text{°C/s}$$

Procédés de Mise en Forme

Différentes formes peuvent être obtenues en fonction des moules. Des échantillons jusqu'à 12 mm ont été obtenus pour l'alliage vitreloy 4

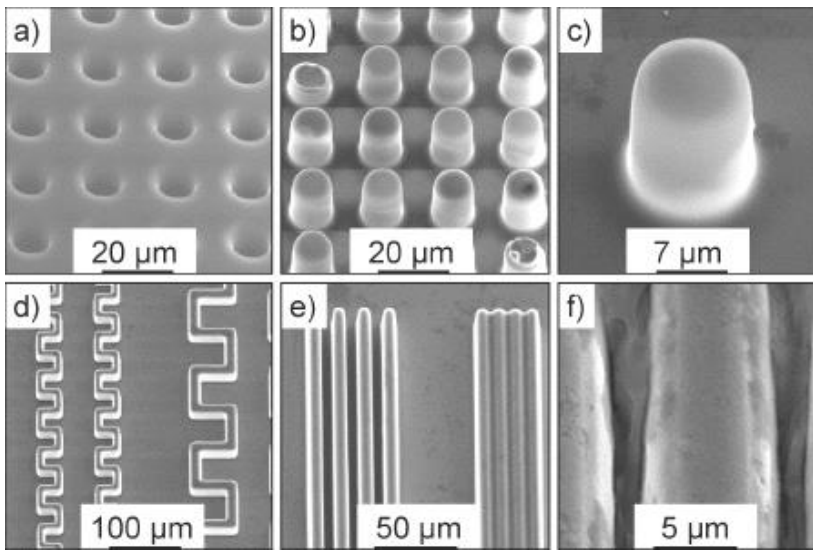
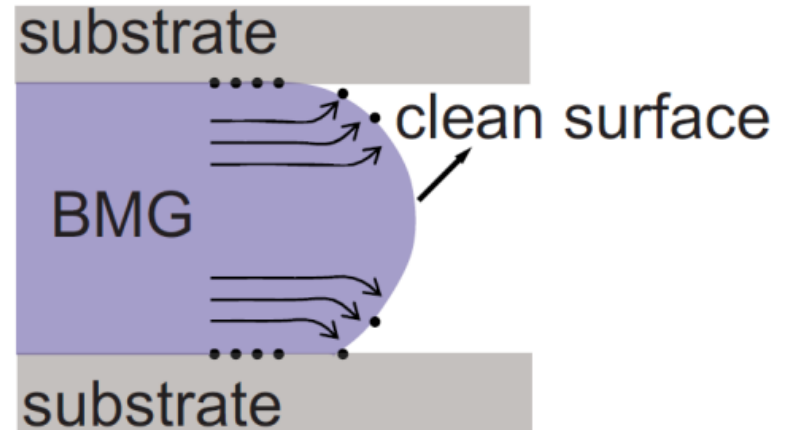
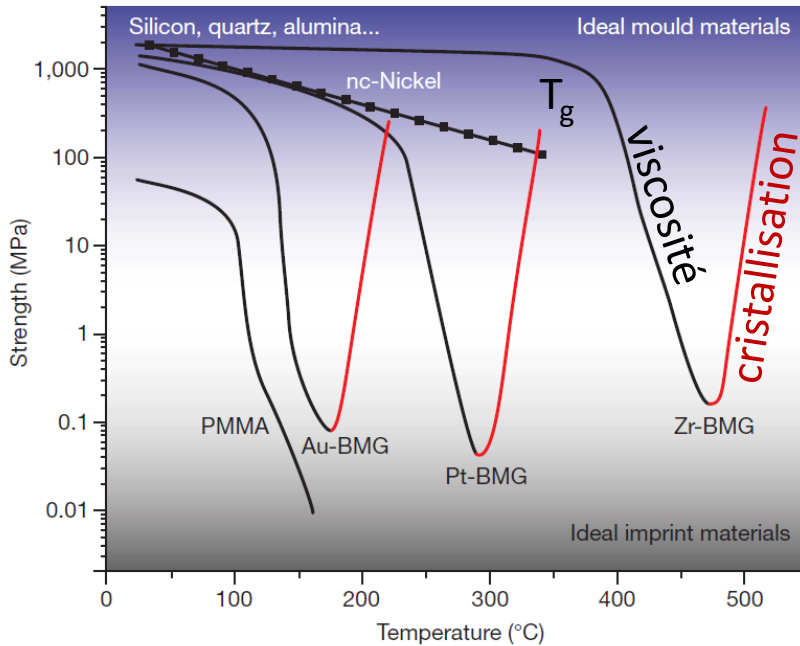


Glass Forming Ability (règles empiriques):

- 3 types d'atomes différents au moins
- différence de taille de au moins 15% entre les atomes
- enthalpie de mélange entre certaines espèces doit être négative.

Procédés de Mise en Forme

Mise en forme par Formage Thermo-Plastique:

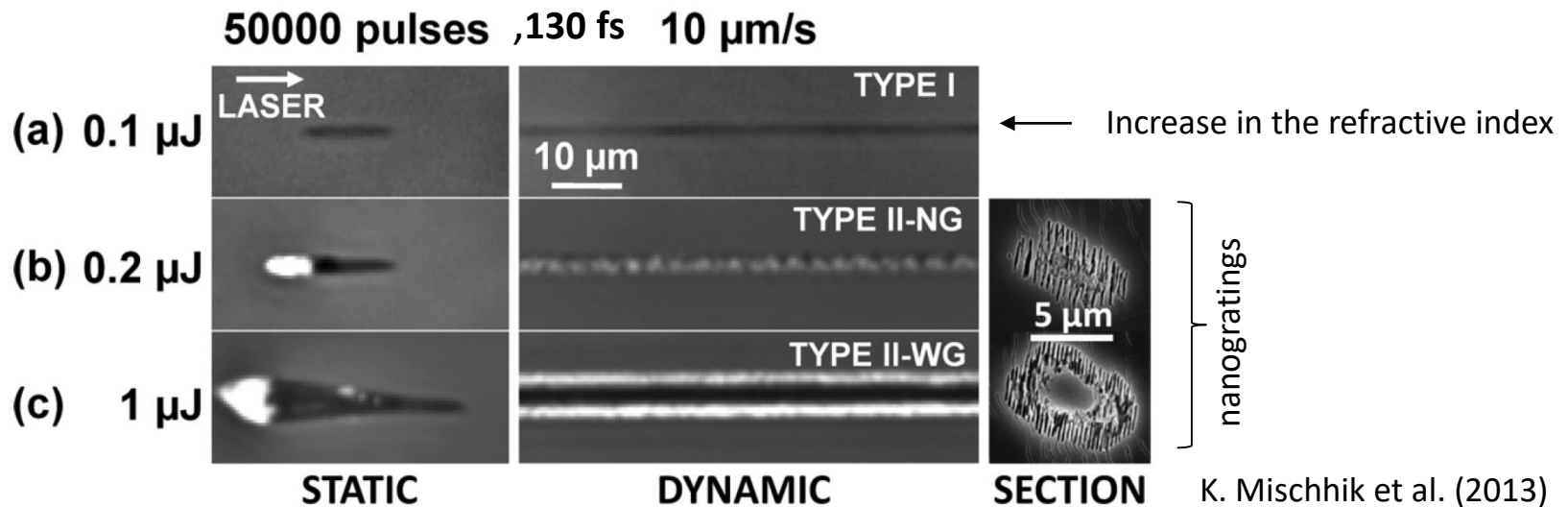
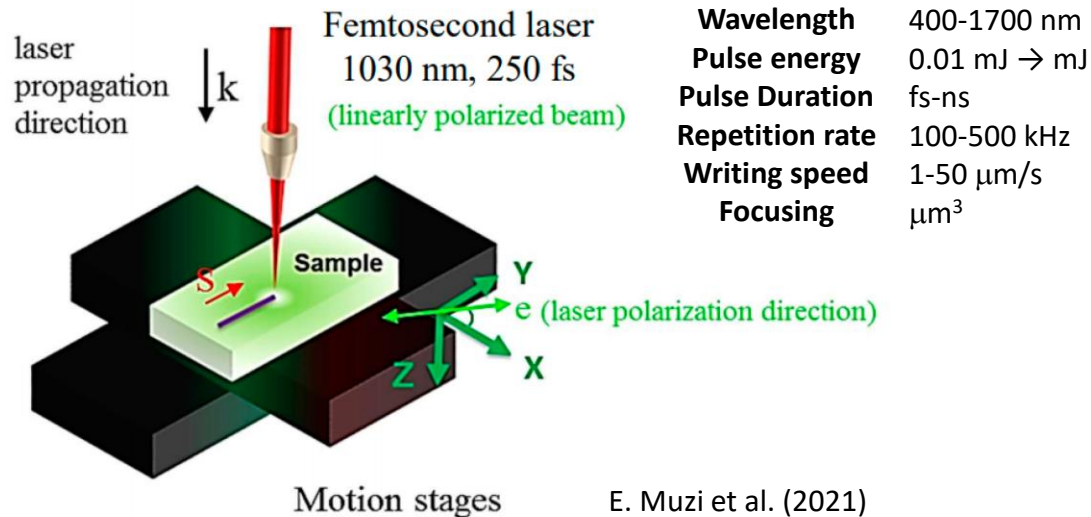


Details of test structures replicated into bulk metallic glass
(alloy: $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$).

a) silicon mold and **b)** its replication in bulk metallic glass with **c)** a detail. Pins of 10 μm in diameter and 20 μm height are completely replicated. A protective coating of 1 μm SiO_2 is still present on the metallic glass after removal of the Si wafer by etching. **d)** and **e)** show rims with **f)** a detail of 1 μm spaced rims. The mold did not melt and connect the rims, but the silicon mold between the rims is still present due to a decreased etch rate in narrow channels.

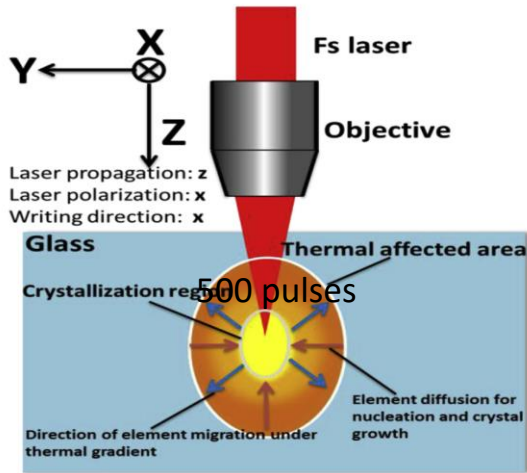
Procédés de Mise en Forme

Structuration des Verres Silicates par Laser Ultra-rapide:

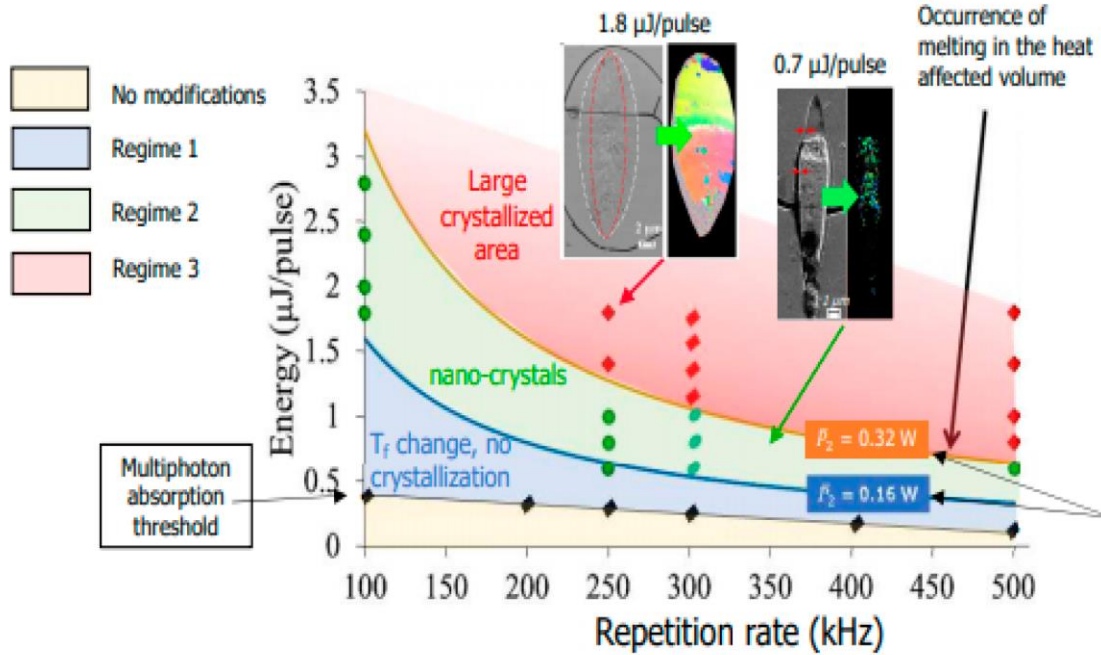


Procédés de Mise en Forme

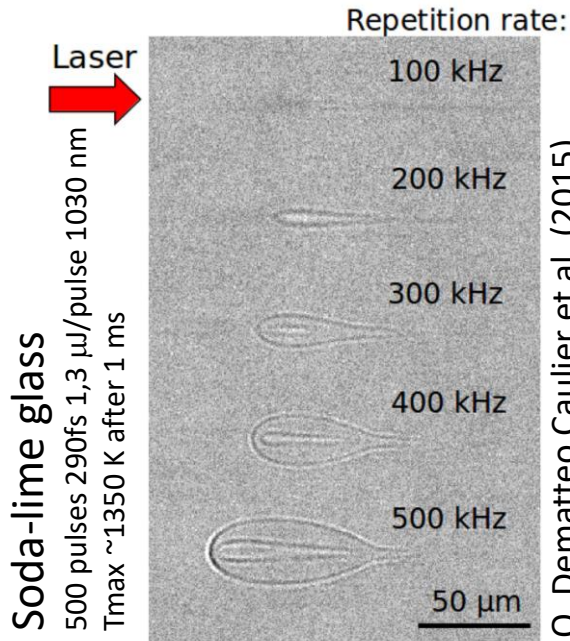
Structuration des Verres Silicates par Laser Ultra-rapide:



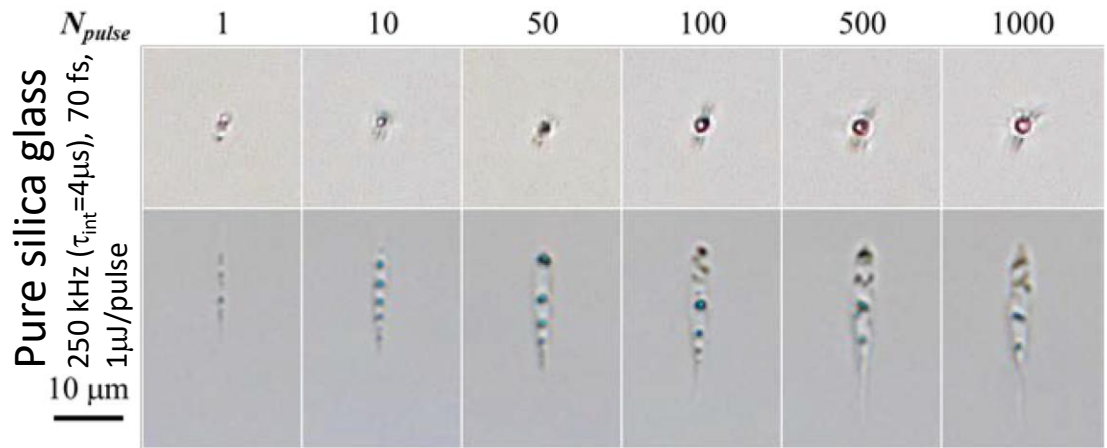
B. Pommellec et al. (2015)



Lithium niobosilicate glass



O. Dematteo Caulier et al. (2015)



Regime II.
Y. Shimotsuma et al. (2011)

Low Thermal expansion in pure Silica glass

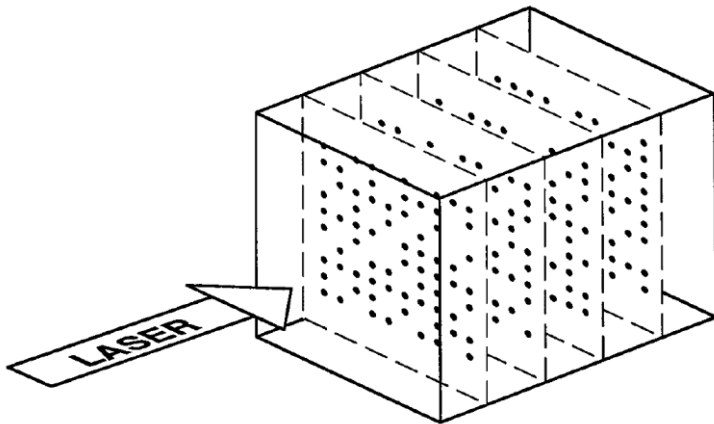
Procédés de Mise en Forme

Structuration des Verres Silicates par Laser Ultra-rapide:

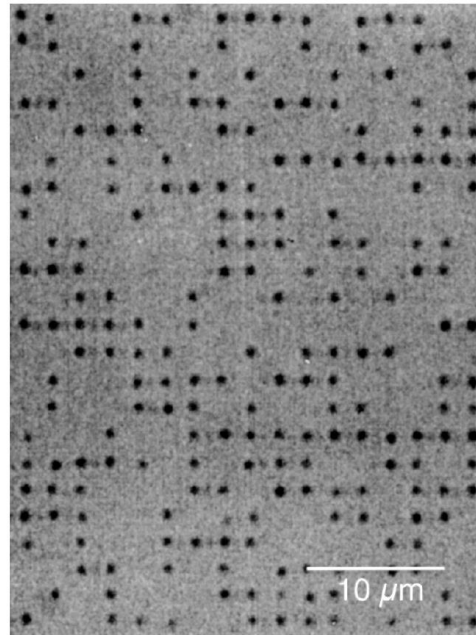
The specific case of **Silica** Glasses: **Single shot** laser ablation

Micro-explosions in regime II, ultra-short laser pulses

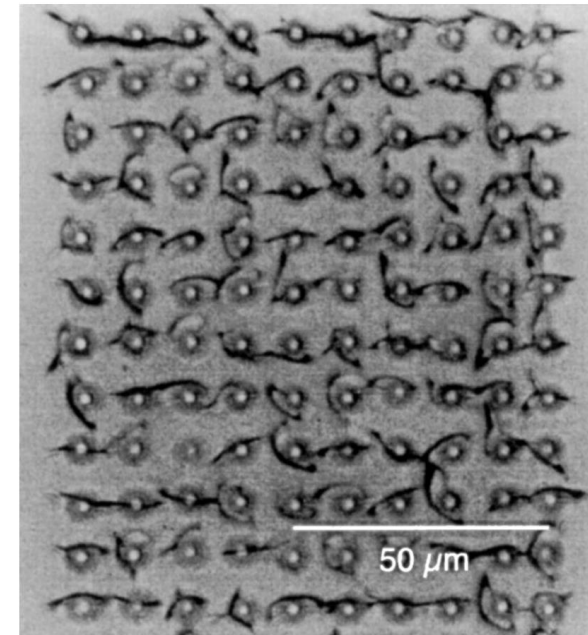
Single pulse $>0.3\mu\text{J}/\text{pulse}$, 750 nm, focused by 65-N.A. microscope objective



E. Glazer et al. (1996)



100 fs, 0.5 μJ pulses



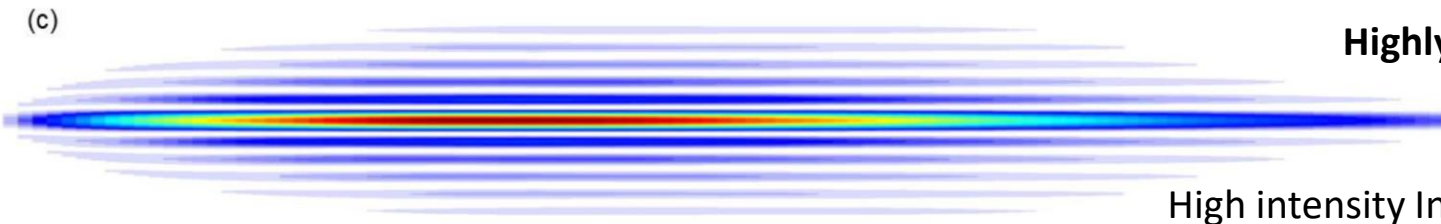
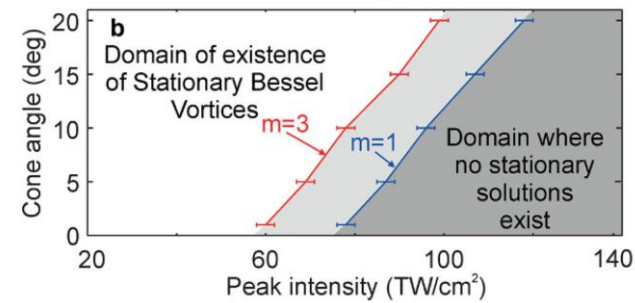
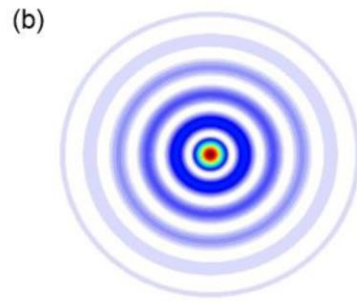
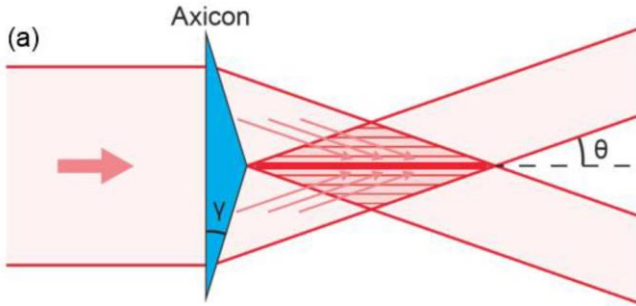
200 ps, 9 μJ pulses

Strong sensitivity of damage to the pulse duration, and imprint dimensions

Procédés de Mise en Forme

Structuration des Verres Silicates par Laser Ultra-rapide:

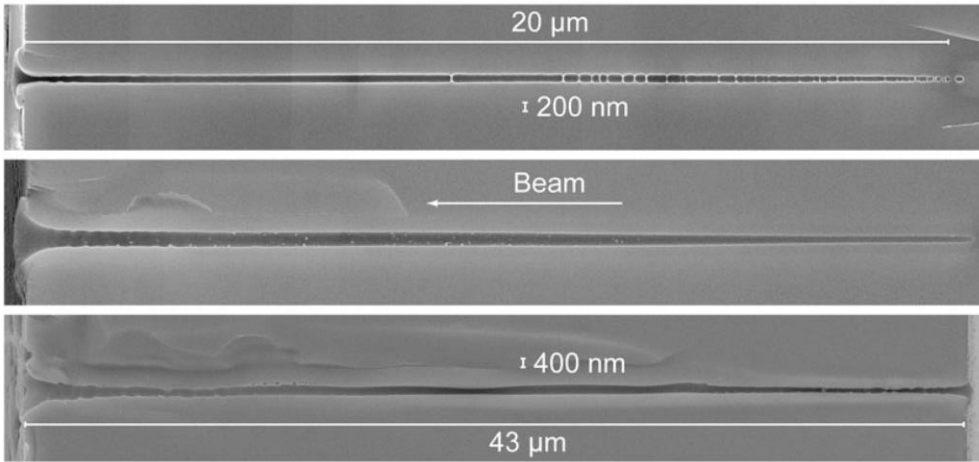
The specific case of **Silica** Glasses: Single-shot Femtosecond **Bessel** Laser Beams



Highly focused beam

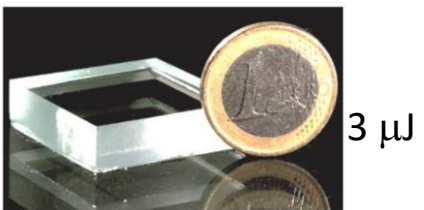
High intensity Interference pattern

800 nm, 230 fs, 0.65 μJ



↕ 0.7 μm (laser pulse stability)

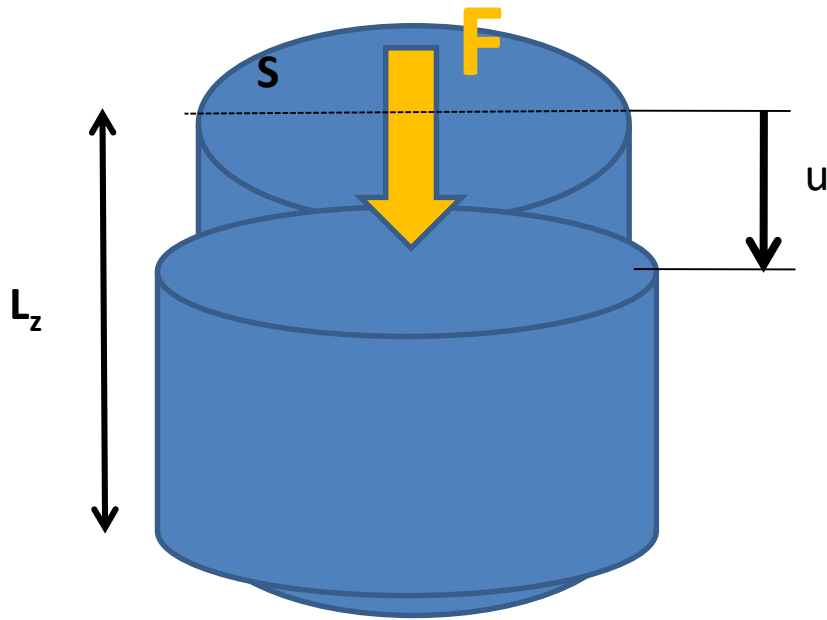
Ultrathin and long imprinted channel



F. Courvoisier et al. (2013)

Propriétés Mécaniques

Réponse Elasto-Visco-Plastique



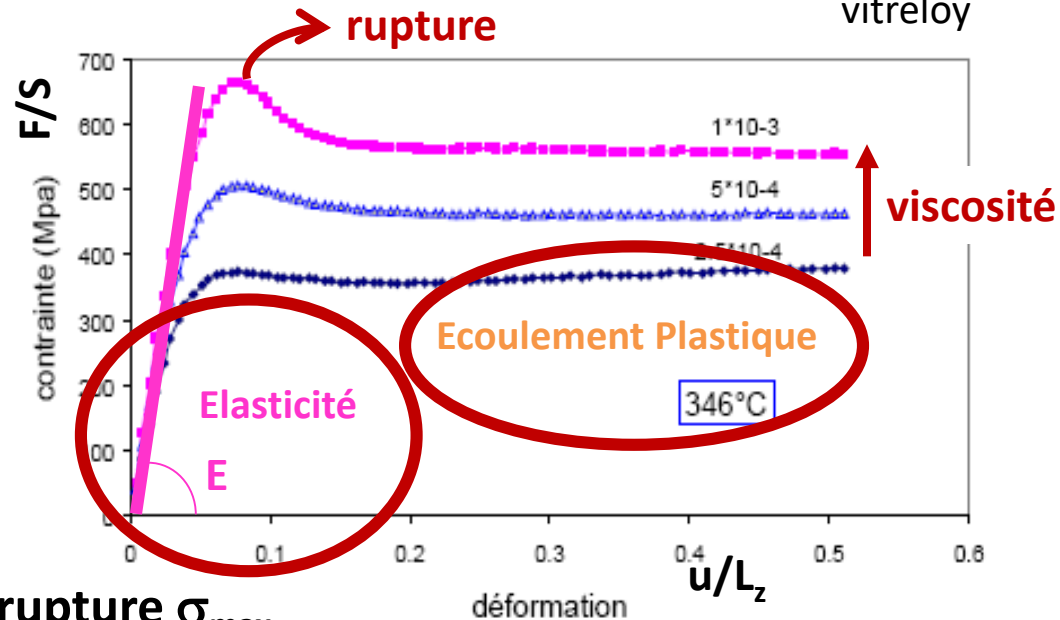
Réponse élastique linéaire (compression)

$$F/S = E \cdot u/L_z$$

Contrainte de compression σ

Module d'élasticité

Déformation ϵ



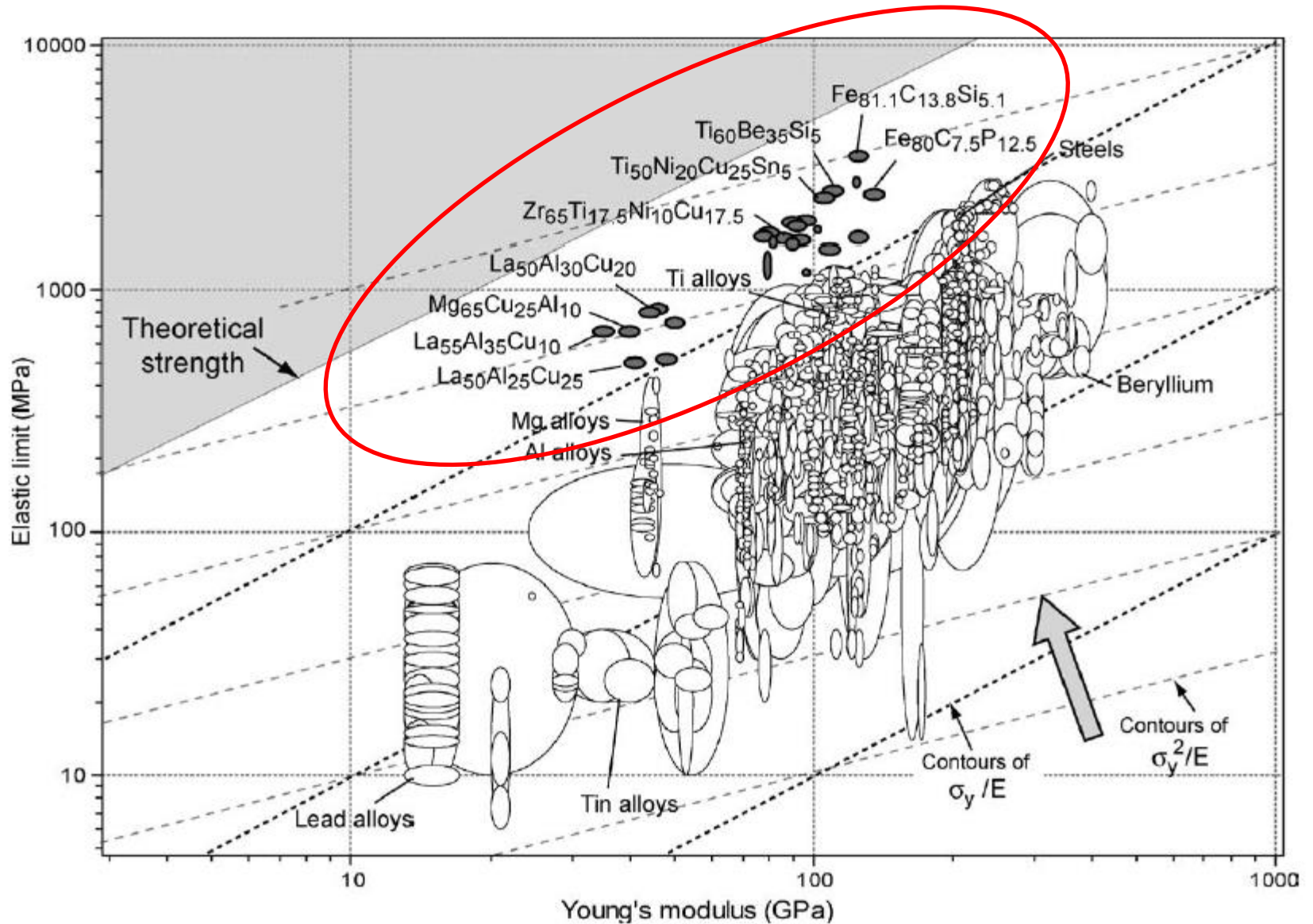
vitreloy

Module d'Young E

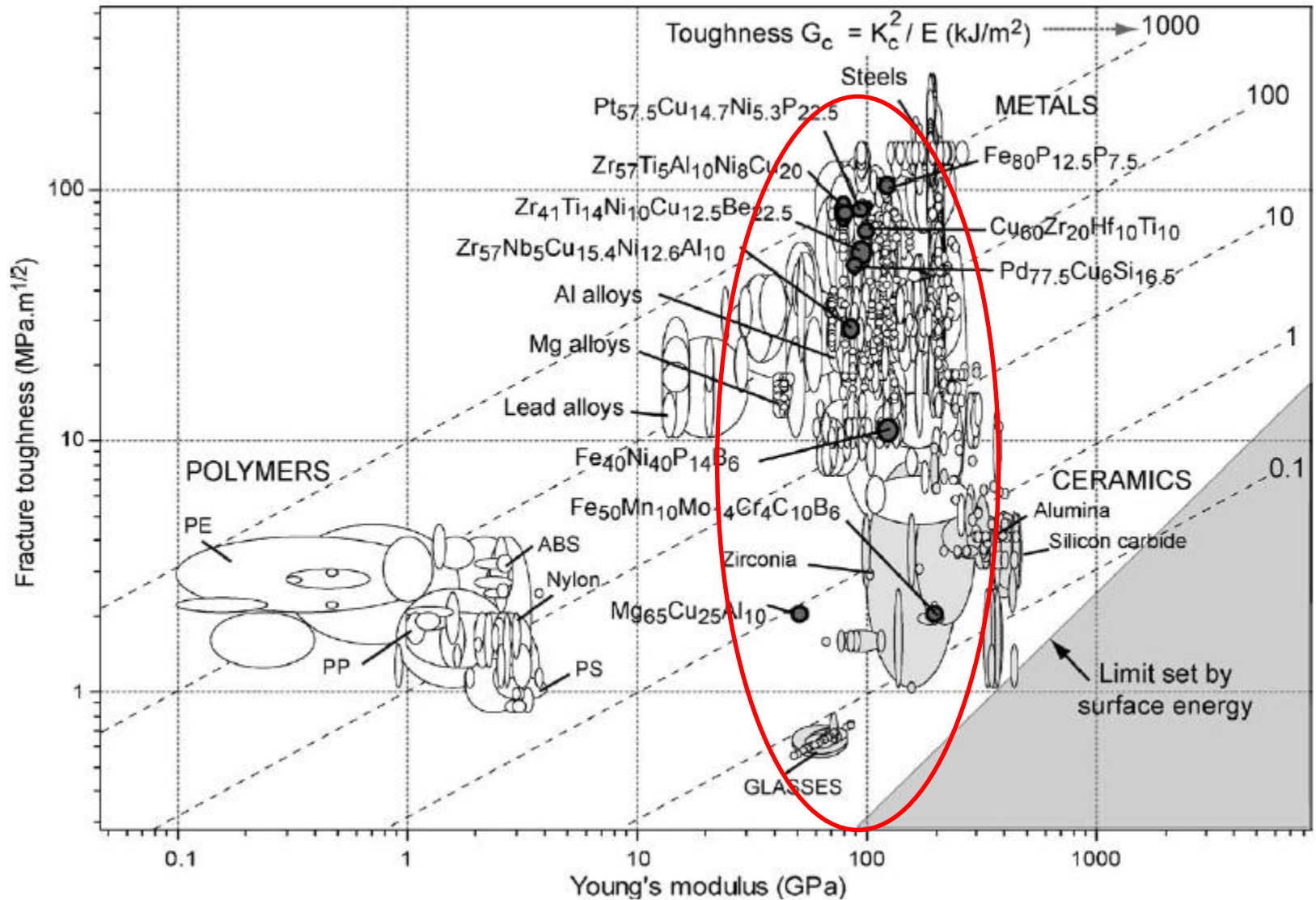
Limite d'élasticité σ_y / Contrainte à la rupture σ_{\max}

Ecoulement Visco-Plastique $\sigma_{\text{flow}} (\delta\epsilon/\delta\tau)$

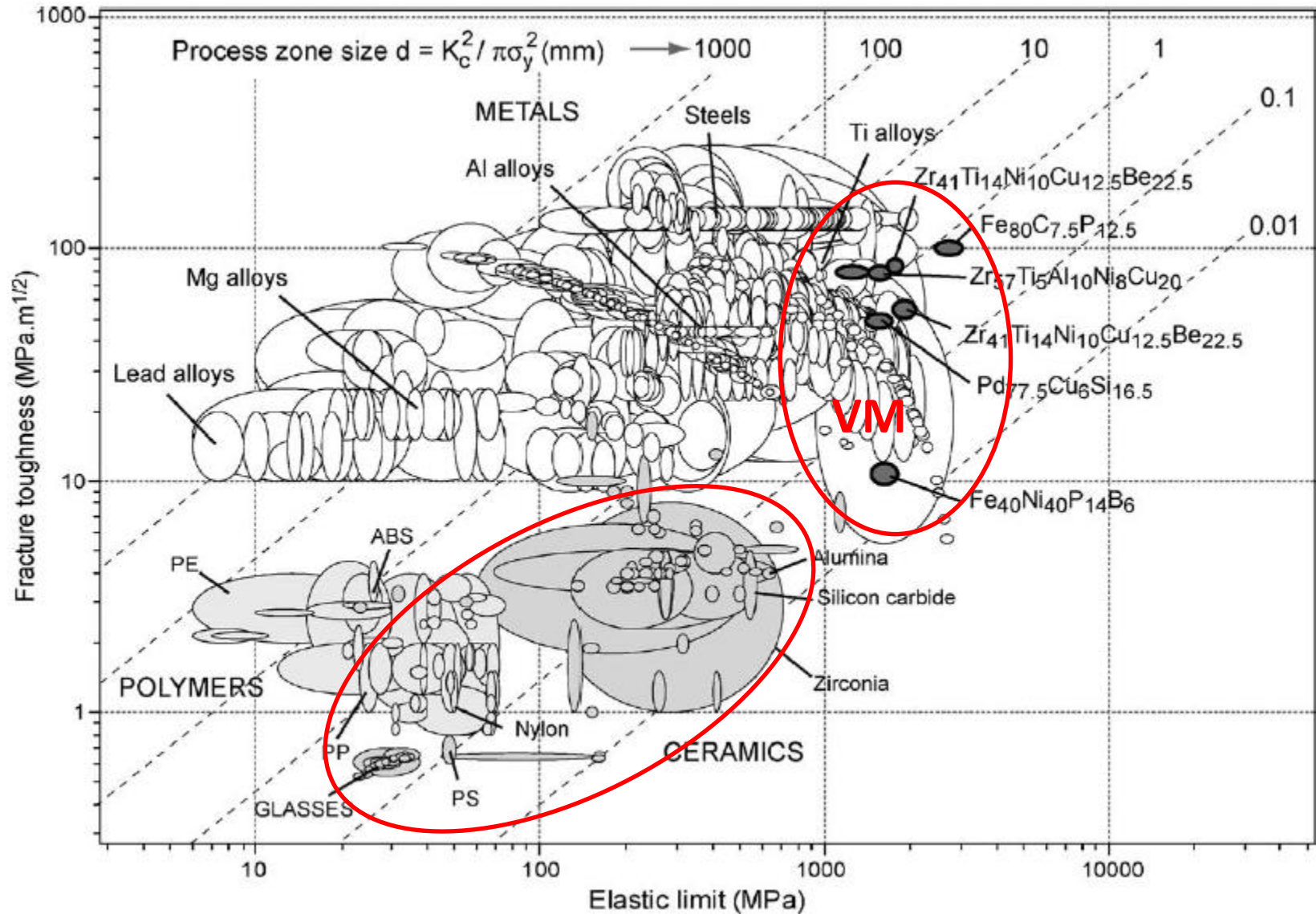
Plasticité: les Verres Métalliques sont Durs



Mécanique de la Rupture: les Verres métalliques ont une ténacité variable



Mécanique de la Rupture: Verres Métalliques vs. Céramiques



Rappels: Elasticité

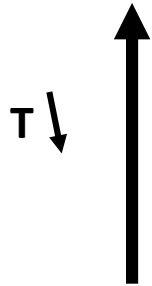
Les 3 équations du mouvement ont **9 inconnues** $\underline{\underline{\sigma}}, \underline{\underline{u}}$

Il est donc nécessaire d'y ajouter des **équations de comportement**

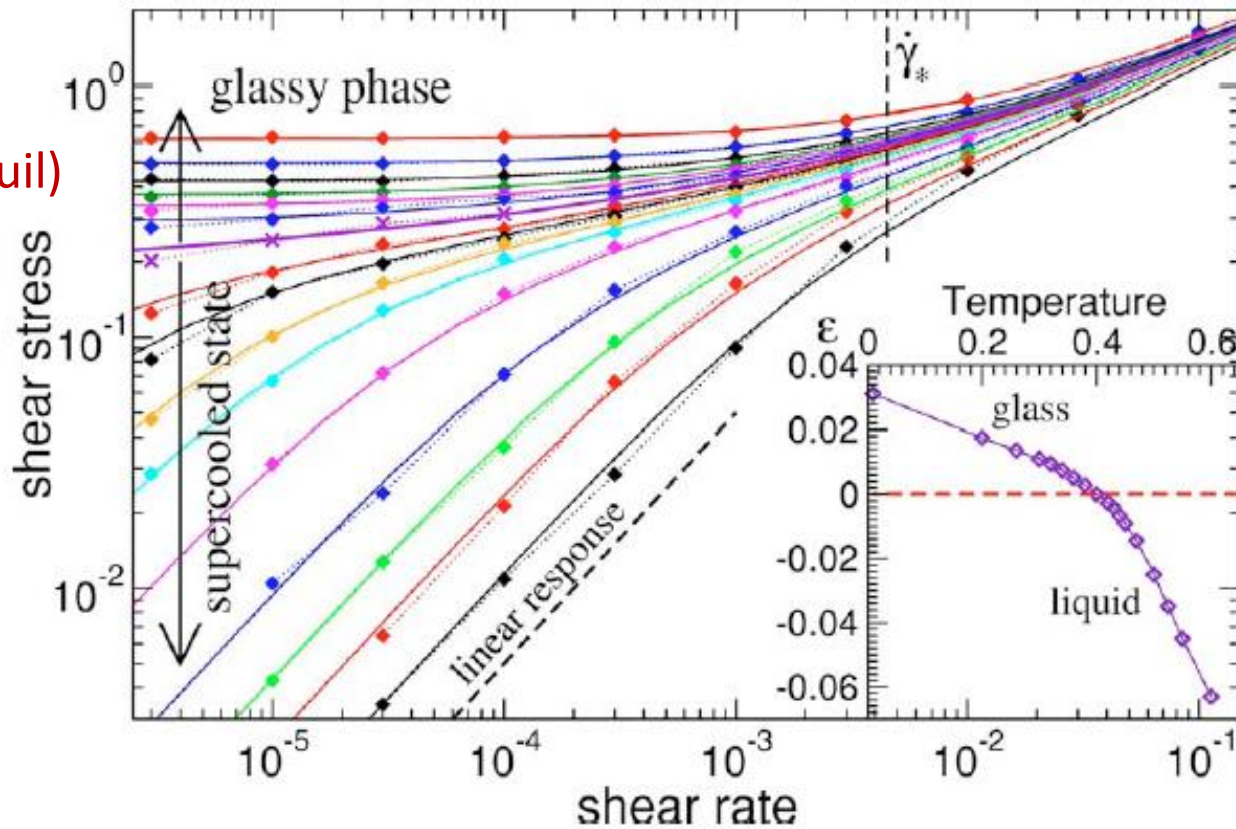
Exemples de Lois de comportement Linéaires en Visco-Elasticité Classique

Exemple de la Transition Vitreuse

Plastique (seuil)

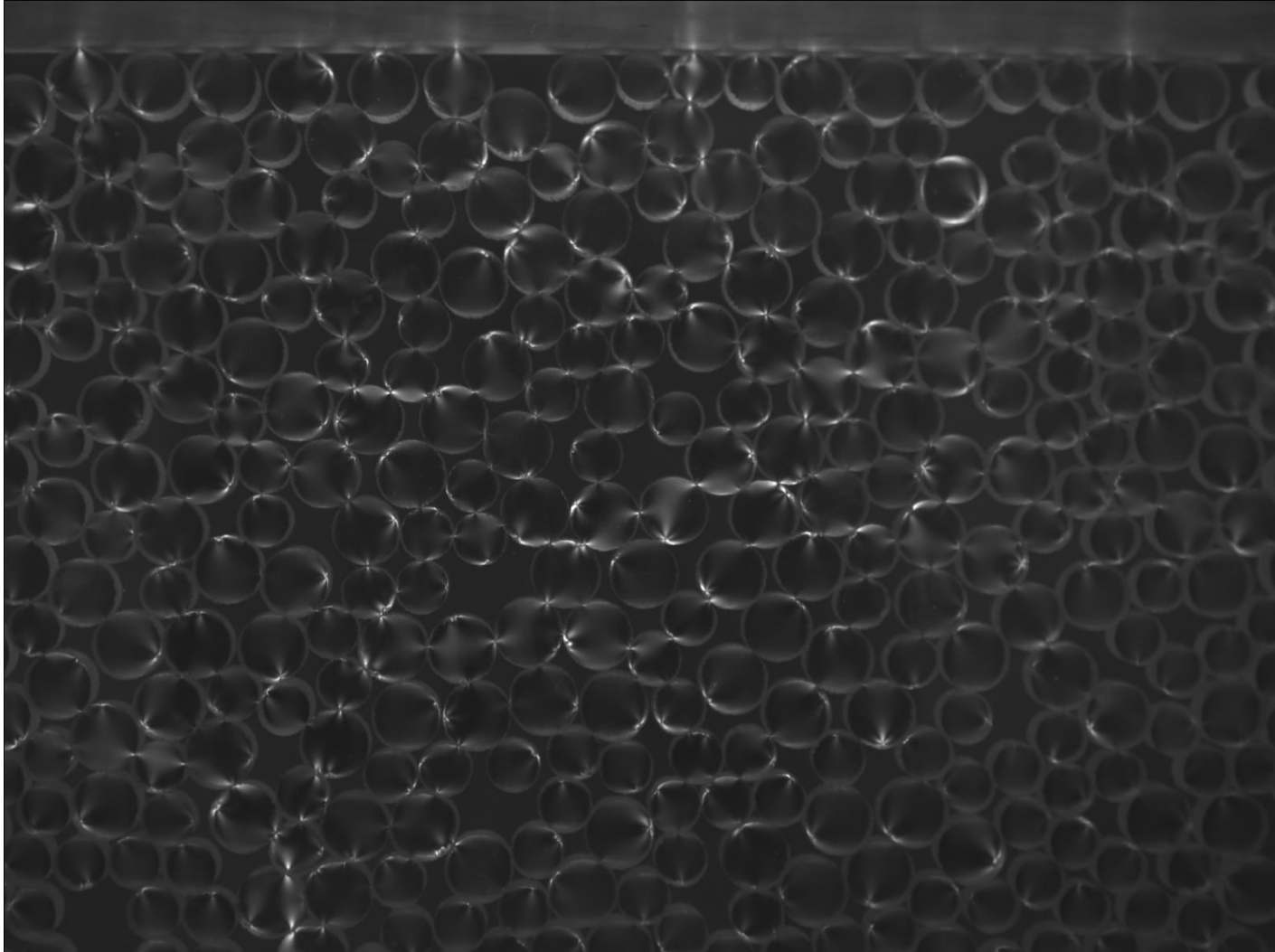


Visqueux



F. Varnik (2006)
3D Lennard-Jones Glass

Hétérogénéité Mécanique

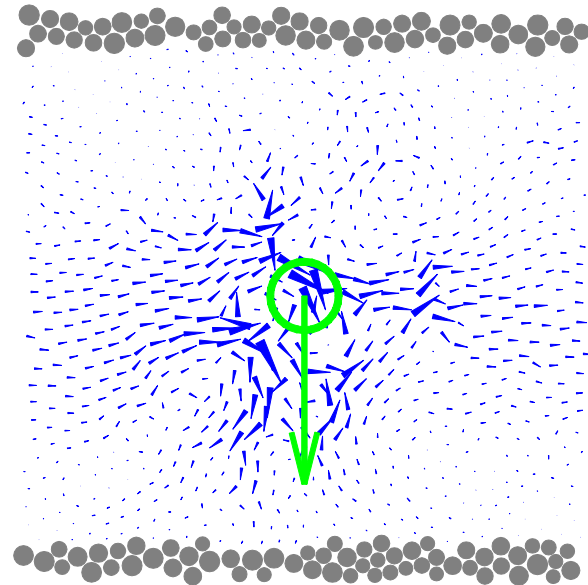
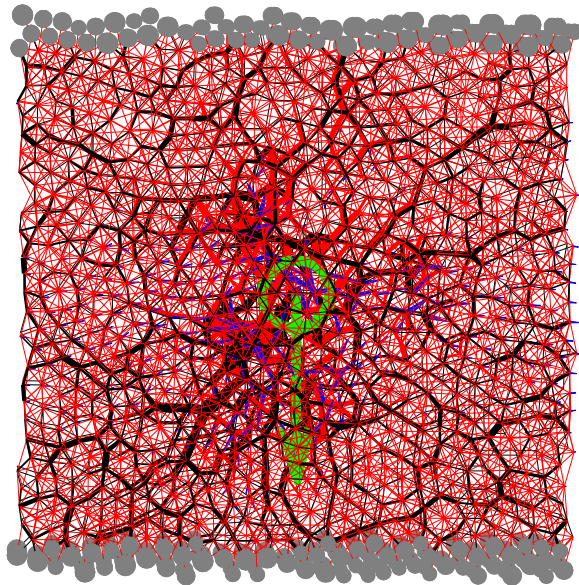


PMMH beads, E. Kolb (2006)

Hétérogénéité Mécanique

Forte Hétérogénéité de la réponse à l'échelle du désordre

Exemple d'une assemblée désordonnée d'atomes:

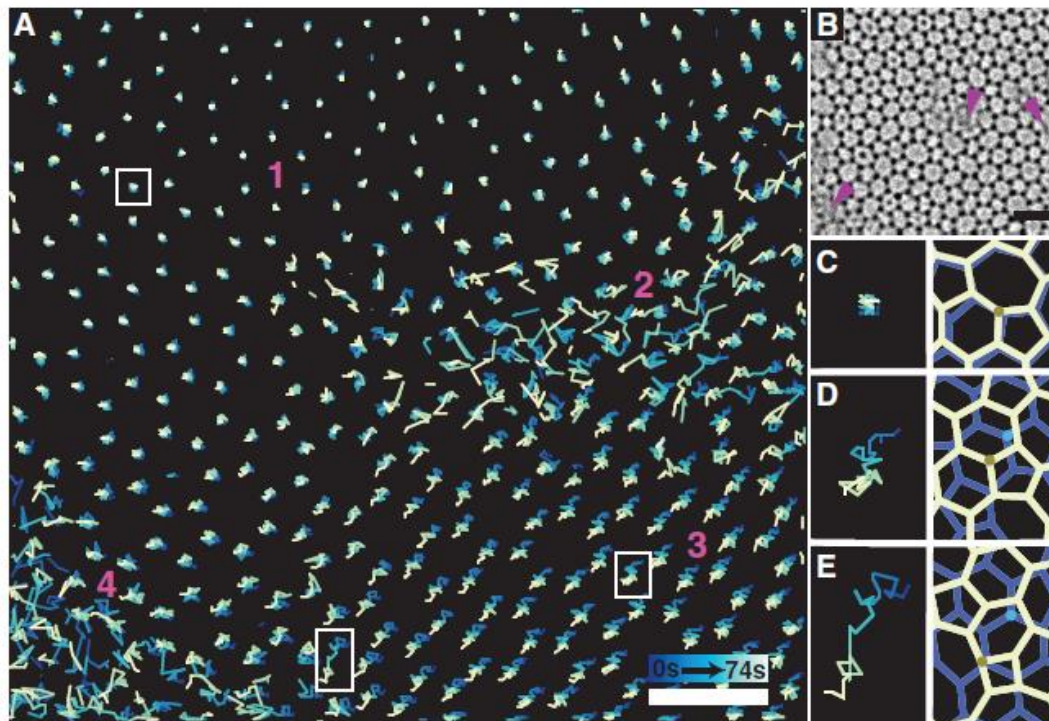


F. Léonforte et al. (2004)

Hétérogénéité Mécanique

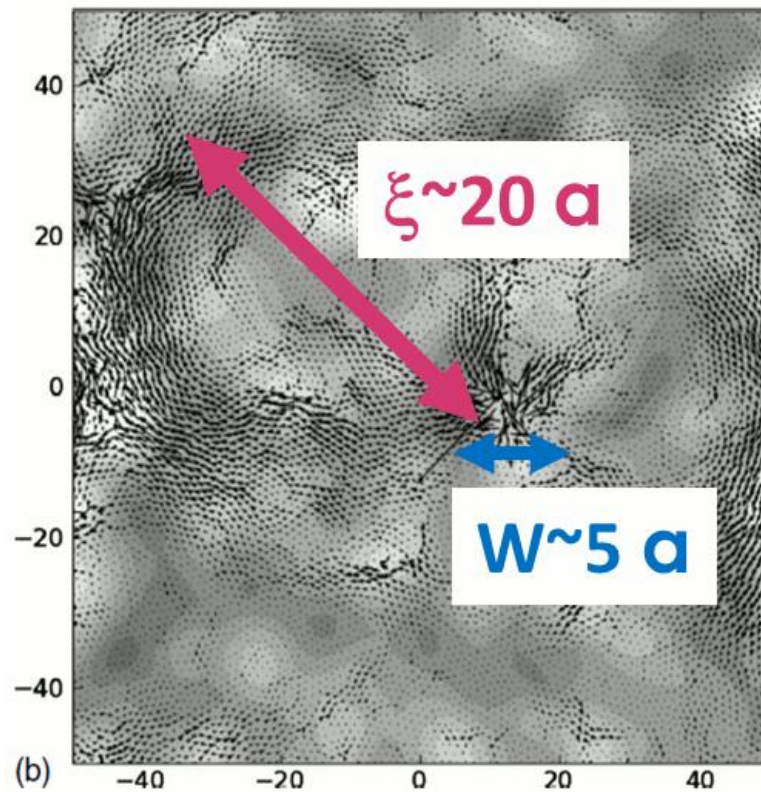
Imaging Atomic Rearrangements in Two-Dimensional Silica Glass: Watching Silica's Dance Science (October 2013)

Pinshane Y. Huang,¹ Simon Kurasch,^{2*} Jonathan S. Alden,^{1*} Ashivni Shekhawat,³
Alexander A. Alemi,³ Paul L. McEuen,^{3,4} James P. Sethna,³ Ute Kaiser,² David A. Muller^{1,4†}



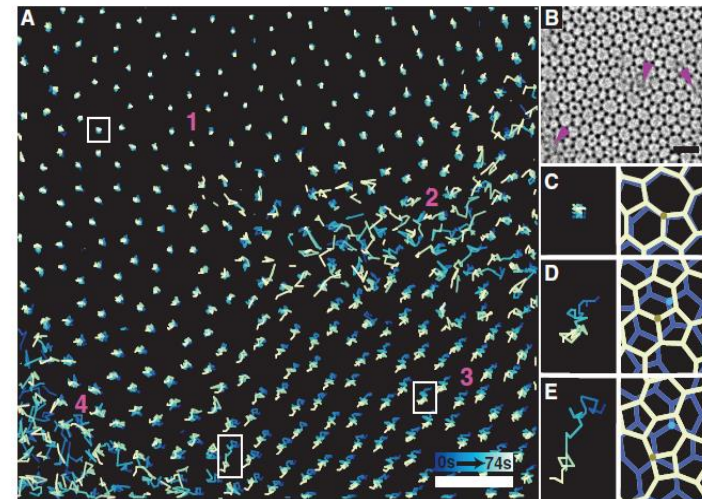
Hétérogénéité Mécanique

Plusieurs échelles caractéristiques:



Imaging Atomic Rearrangements in Two-Dimensional Silica Glass: Watching Silica's Dance

Pinshane Y. Huang,¹ Simon Kurasch,^{2*} Jonathan S. Alden,^{1*} Ashivni Shekhawat,³ Alexander A. Alemi,³ Paul L. McEuen,^{3,4} James P. Sethna,³ Ute Kaiser,² David A. Muller^{1,4†}



Huang et al. Science (October 2013)

Hétérogénéité Mécanique

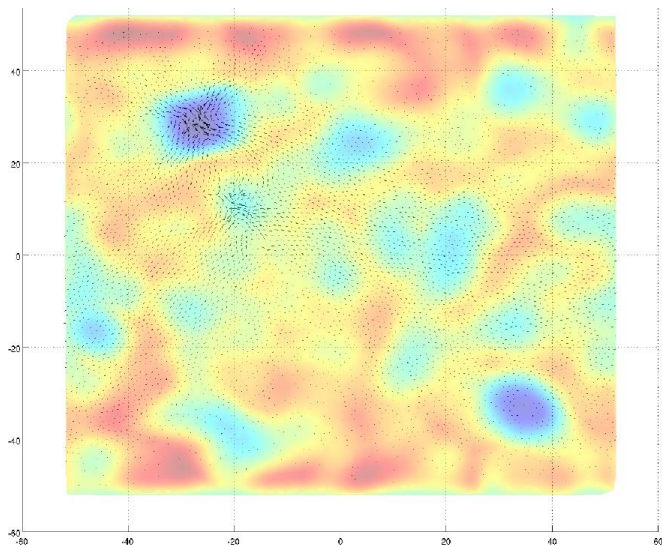
Modules d'Elasticité Locaux

$$\begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \end{bmatrix} = \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1131} & C_{1112} \\ C_{2211} & C_{2222} & C_{2233} & C_{2223} & C_{2231} & C_{2212} \\ C_{3311} & C_{3322} & C_{3333} & C_{3323} & C_{3331} & C_{3312} \\ C_{2311} & C_{2322} & C_{2333} & C_{2323} & C_{2331} & C_{2312} \\ C_{3111} & C_{3122} & C_{3133} & C_{3123} & C_{3131} & C_{3112} \\ C_{1211} & C_{1222} & C_{1233} & C_{1223} & C_{1231} & C_{1212} \end{bmatrix} \cdot \begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2 \varepsilon_{23} \\ 2 \varepsilon_{31} \\ 2 \varepsilon_{12} \end{bmatrix}$$

Loi de Hooke en élasticité linéaire
21 paramètres

Méthode d'optimisation locale
pour différentes échelles
de coarse-graining

Exemple d'un verre modèle de Lennard-Jones:



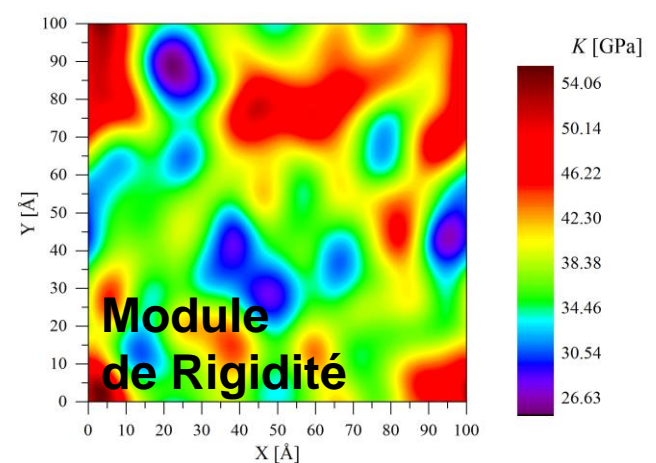
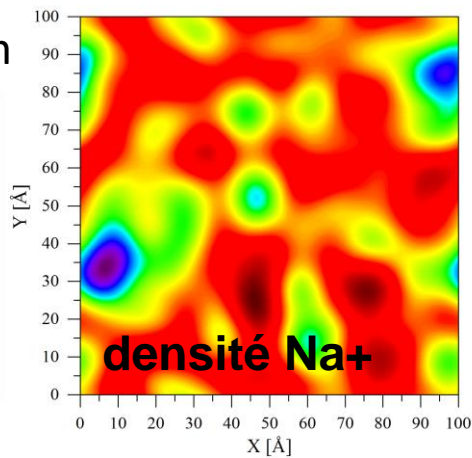
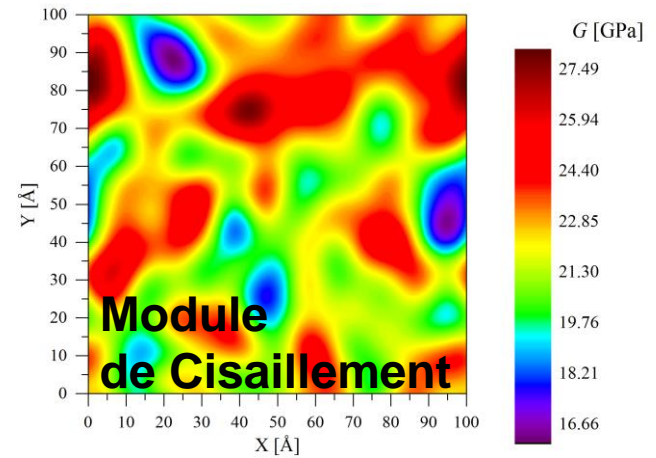
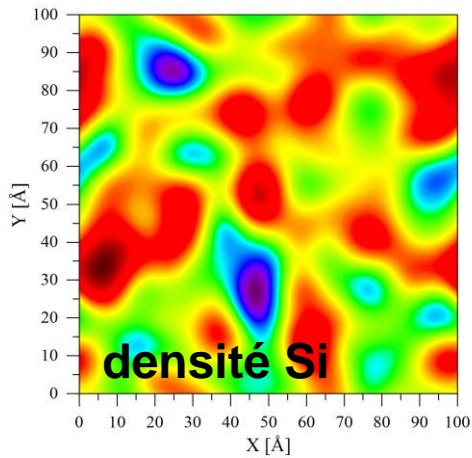
	Linear Elasticity ←				
Coarse Graining Length ω	0	5	10	15	20 a
Hooke's law	NO	YES	YES	YES	YES
Homogeneity $\frac{\langle \varepsilon \rangle \langle \sigma \rangle - 2\mu}{2\mu} < 10\%$	NO	NO	YES	YES	YES
$\frac{\Delta C}{\langle C \rangle} < 10\%$	NO	NO	NO	YES	YES
Isotropy $\frac{\varepsilon_{11} - \varepsilon_{22}}{2\mu} < 10\%$	NO	NO	NO	NO	YES

M. Tsamados et al. (2009)

↑ Isotropic Elasticity

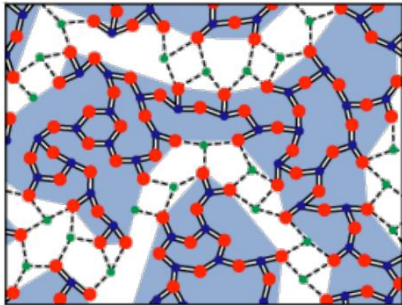
Hétérogénéité Mécanique

Exemple d'un verre sodo-silicate:



Structure en

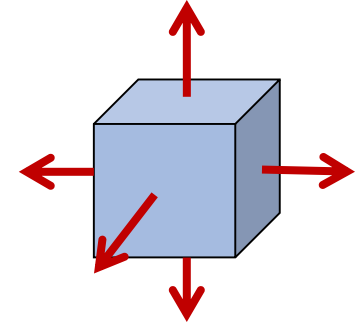
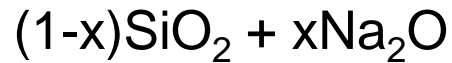
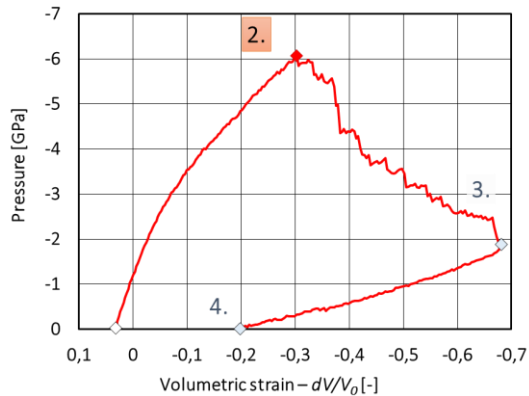
« Canaux » de sodium



Densité Na+ élevée \leftrightarrow Bas Modules d'Elasticité

Hétérogénéité Mécanique

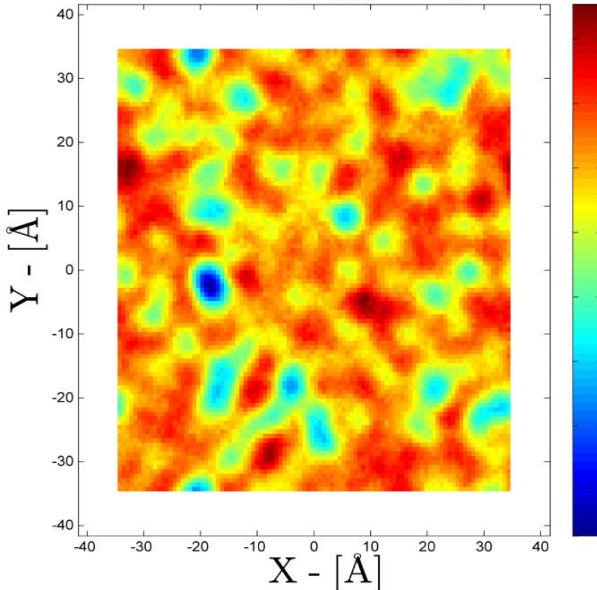
Initiateurs de **fissures** dans un verre sodo-silicate:



Density at step 2.

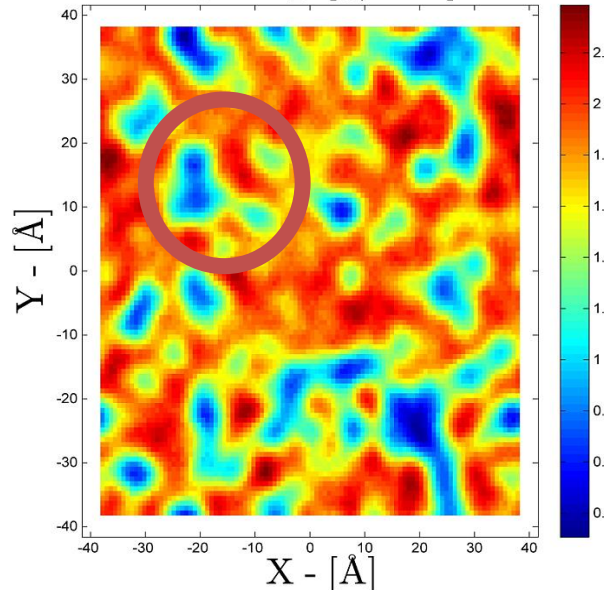
Initial density

Density map [g/cm^3] at $Z = 0 \text{ \AA}$



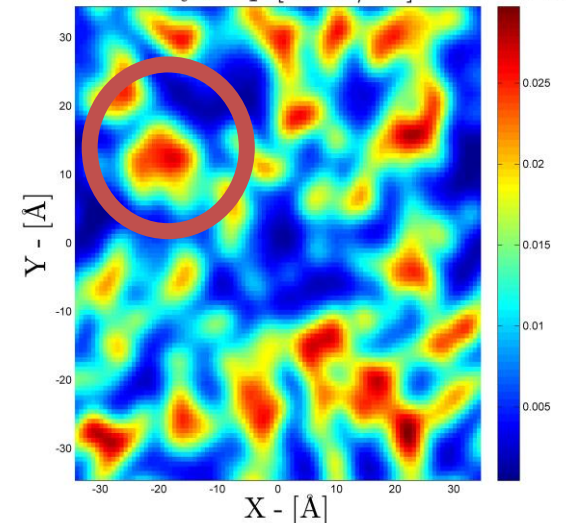
(Crack initiation)

Density map [g/cm^3] at $Z = 0 \text{ \AA}$



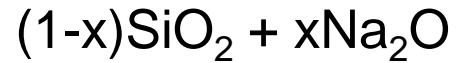
Initial Na density

Density map [$\text{atom}/\text{\AA}^3$] at $Z = 0 \text{ \AA}$

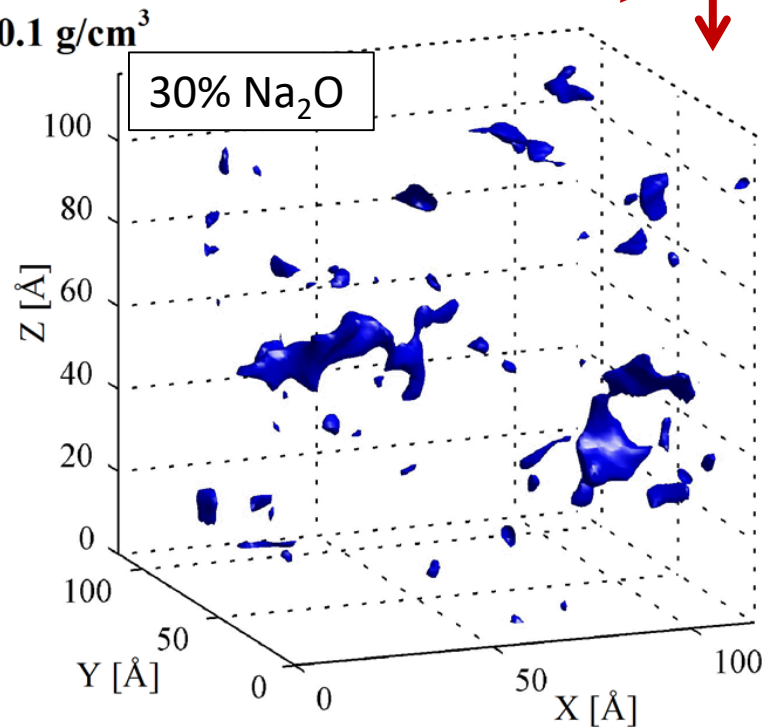
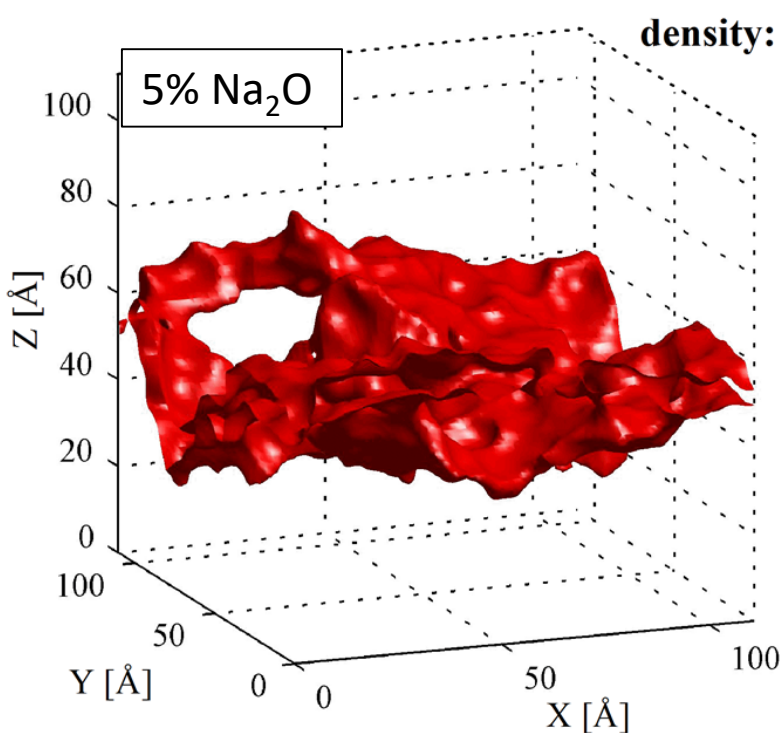
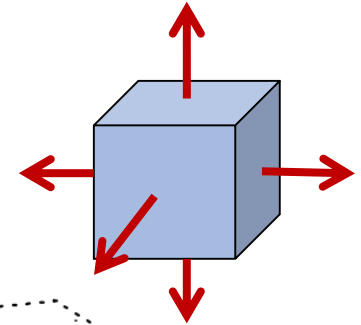


Hétérogénéité Mécanique

Initiateurs de **fissures** dans un verre sodo-silicate:

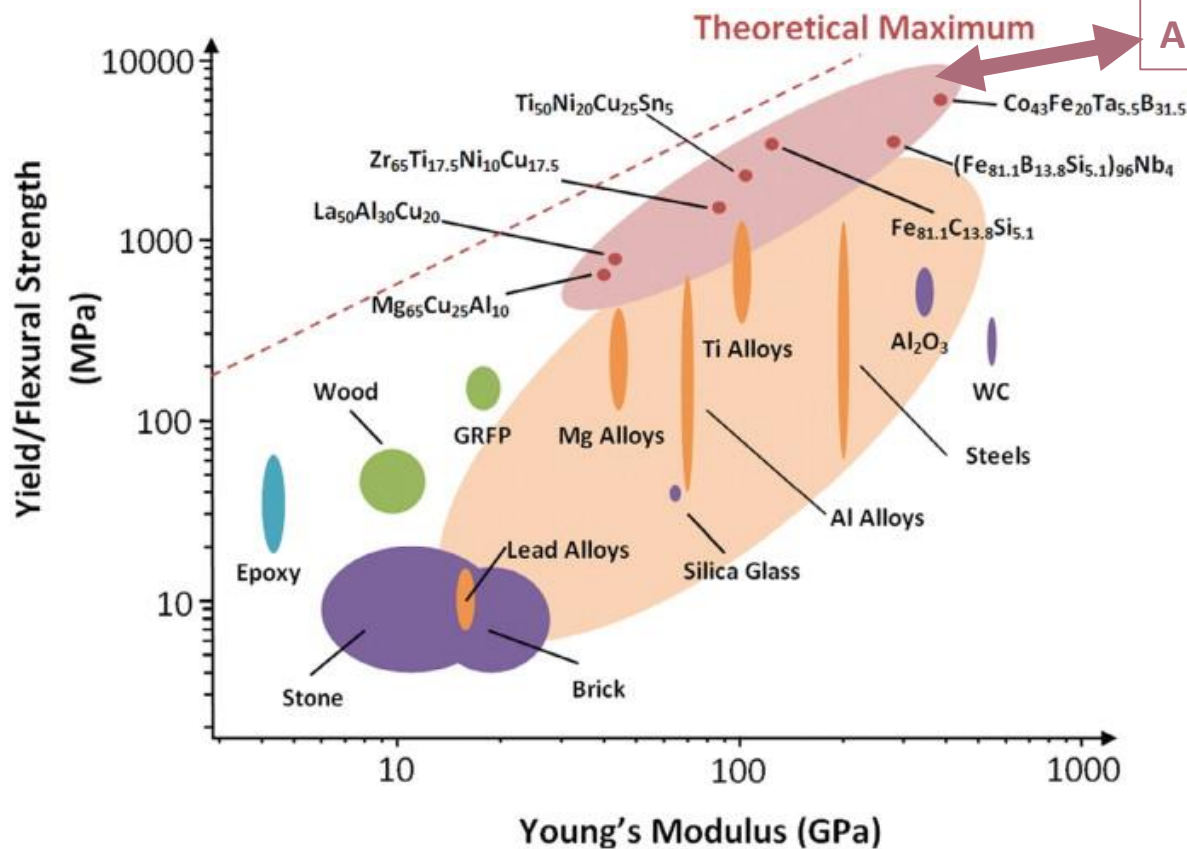


Effet de la composition: profil de densité à la traction max



Plasticité

Les Verres Métalliques sont des matériaux très durs



Amorphous Metals

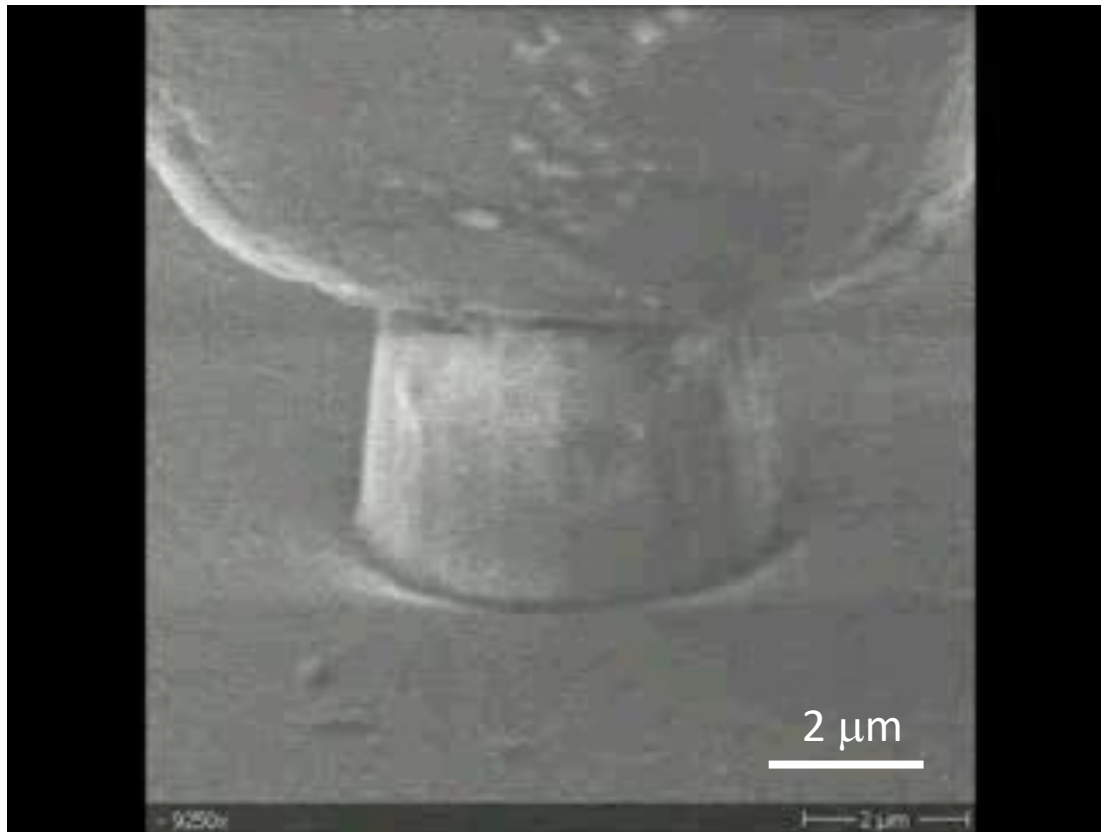
Dur



Fragile ?

Plasticité

Mais ils peuvent être **ductiles** à **petite échelle**




G. Kermouche, E. Barthel (2015)

Micro-pilier en verre de silice pure SiO_2

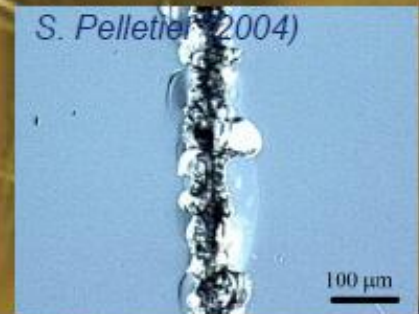
Scratchitti – New York metro
(courtesy of G. Duisit)

N.Y.C.T.A. MATL 3048-89 REV D
HIGH STRENGTH SAFETY GLASS


SAINT-GOBAIN
SULLY

JANUARY 2002 THIS SIDE OUT
PLEASE STOP SCRATCHING THE FUCKING WINDOWS

S. Pelletier (2004)

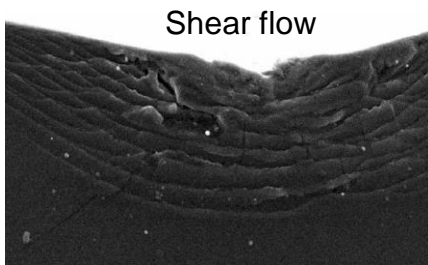



SAINT-GOBAIN

Plasticité

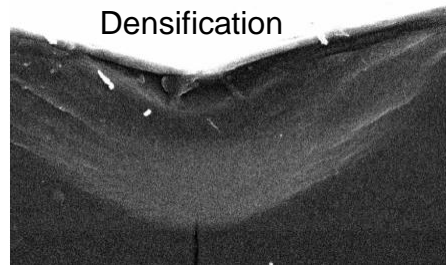
Sensibilité à la **composition** et au **chargement**

Composition



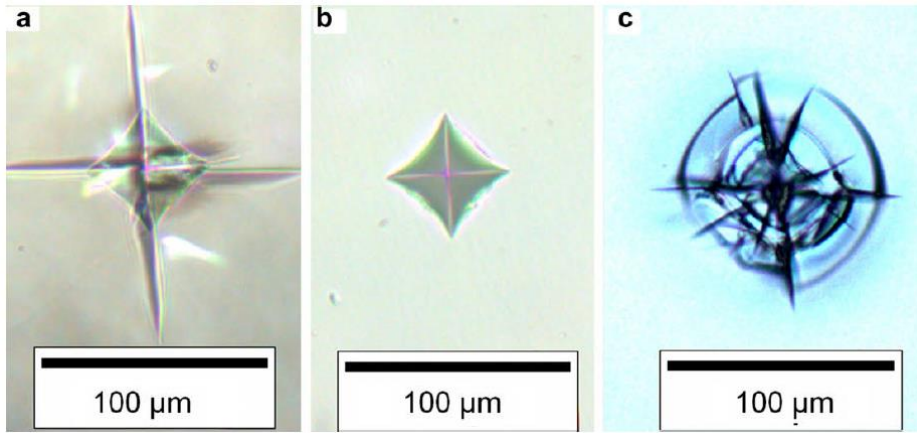
Shear flow

Soda-lime glass



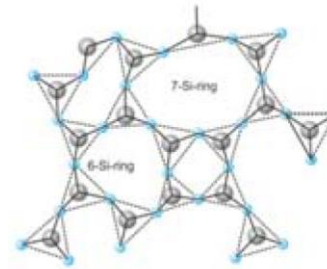
Densification

Anomalous glass

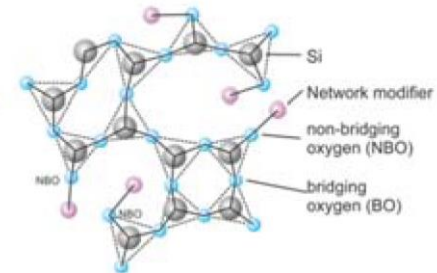


(a) 60% SiO₂ 20% Al₂O₃ 20% CaO; (b) 80% SiO₂ 10% Al₂O₃ 10% CaO; (c) 100% SiO₂

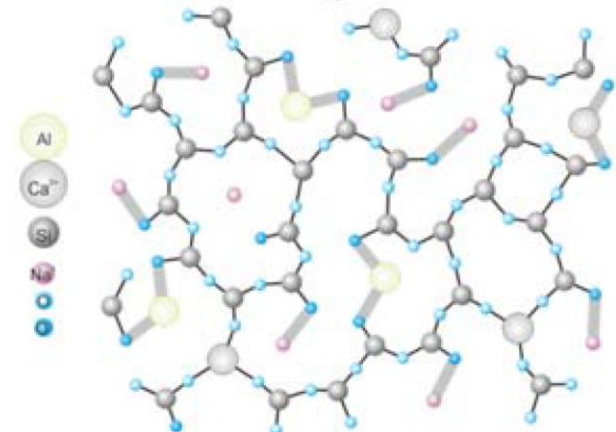
silica glass



sodium silica glass (soluble glass)



soda-lime silica glass

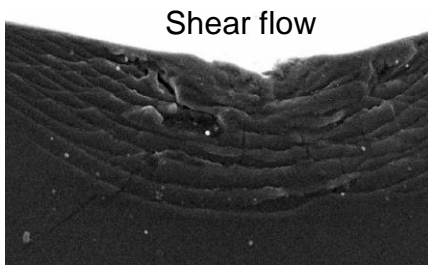


T.M. Gross et al. (2008, 2009)

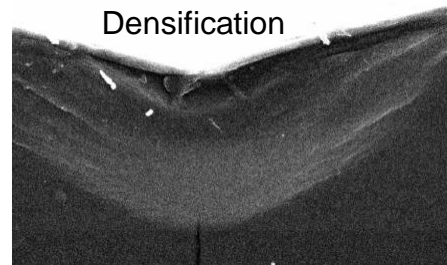
Visco-Plasticité

Sensibilité à la **composition** et au **chargement**

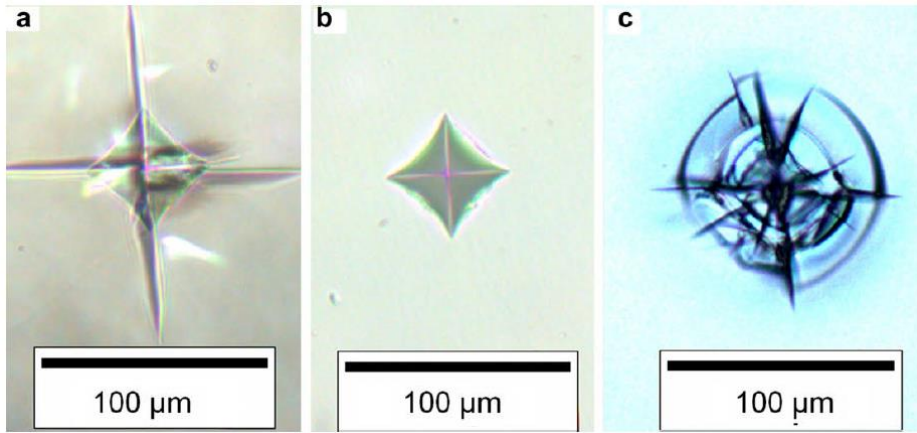
Composition



Soda-lime glass



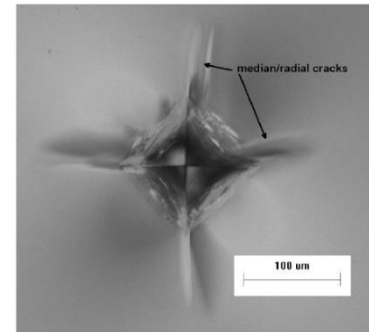
Anomalous glass



(a) 60% SiO₂ 20% Al₂O₃ 20% CaO; (b) 80% SiO₂ 10% Al₂O₃ 10% CaO; (c) 100% SiO₂

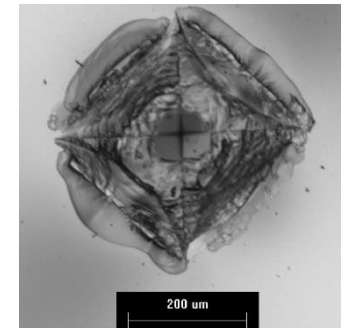
T.M. Gross et al. (2008, 2009)

Quasi-static
indentation
(0.2 mm/mn, 69N)



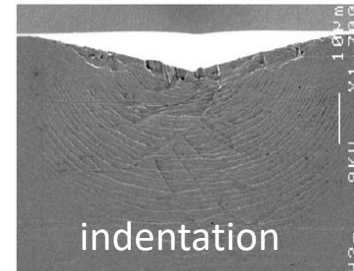
Strain Rate

Impact velocity
(410 mm/s, 562N)

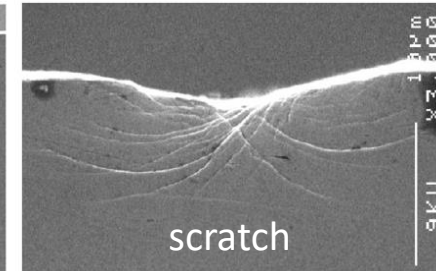


T.M. Gross et al. (2013)

Applied Load



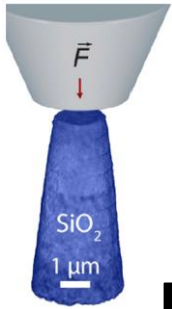
Bulk Metallic Glass



V. Keryvin et al. (2008)

Visco-Plasticité

Sensibilité à la **température** et au **chargement**



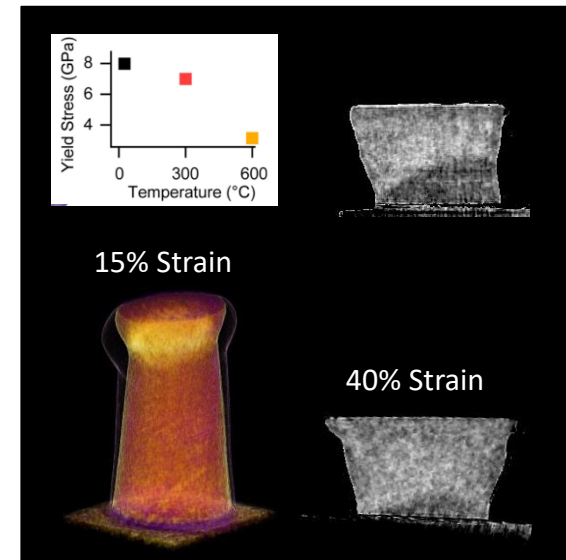
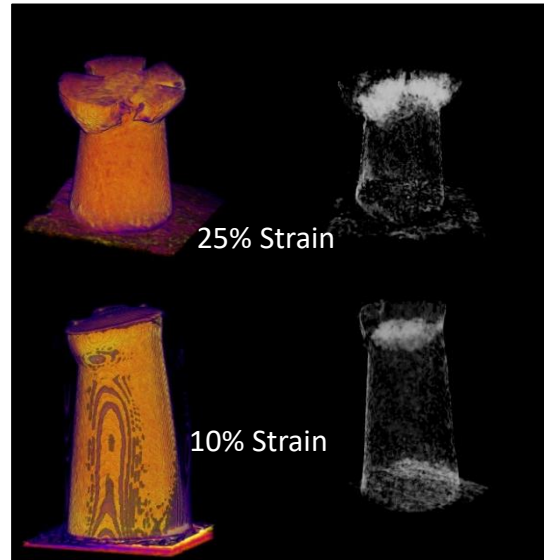
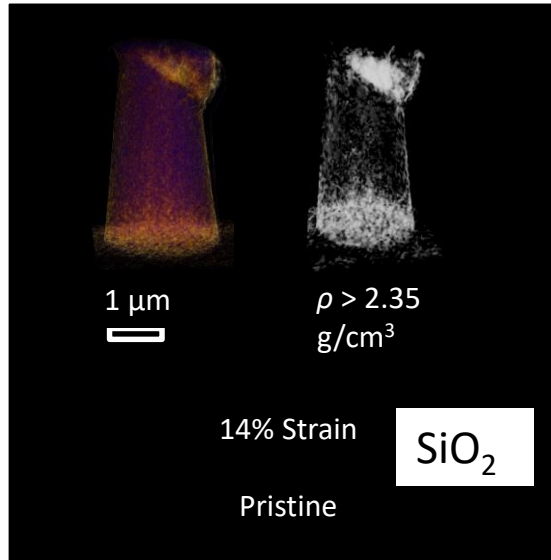
T=25°C

T=300°C

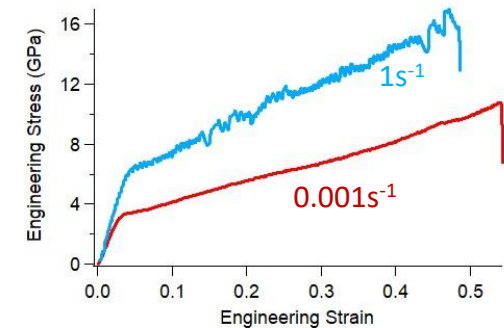
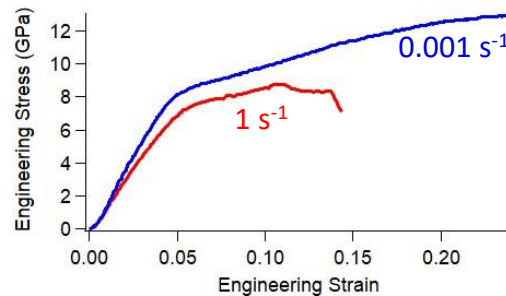
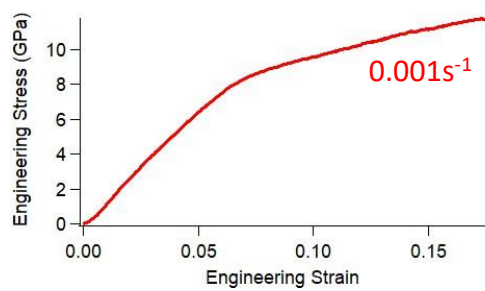
T=600°C

0.001 s⁻¹

1 s⁻¹



R.N. Widmer et al. (2022)



Plasticité

Réarrangement T1 dans un verre de silice 2D

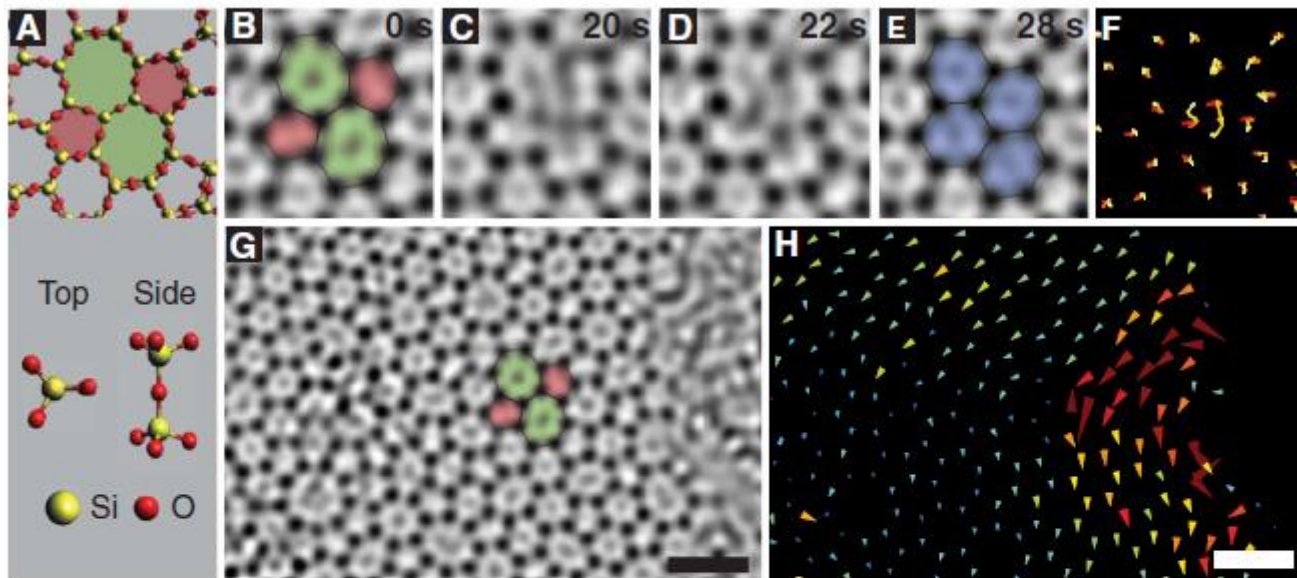
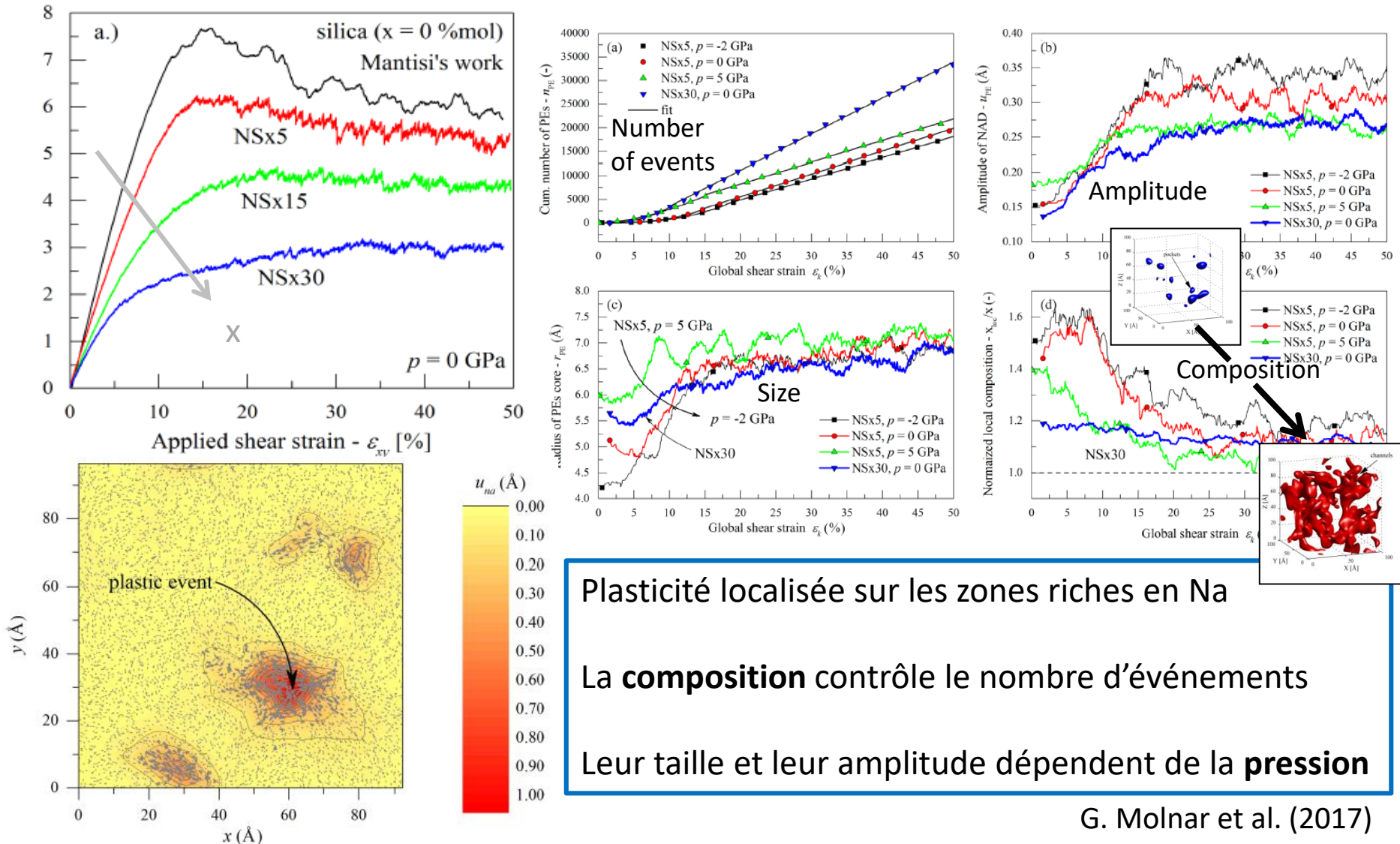


Fig. 1. Elastic and plastic deformation in ring exchange. (A) Cartoon models of the 2D silica structure. (B to E) TEM images showing a ring rearrangement that transforms a 5-7-5-7 cluster into a 6-6-6-6 cluster. The dark spots are Si-O-Si columns that correspond with the top and side views in (A). Images have been smoothed and Fourier-filtered to remove the graphene lattice background [see figs. S2 and S3 and (17)]. (F) A trajectory map of the atomic sites. Color (red to yellow) indicates time of motion. (G) Larger view of the region from (A), and (H) corresponding first-to-last frame displacement map. The arrows have been enlarged $\times 2$ to increase visibility; color indicates size of displacement, from 0 (dark blue) to ≥ 1.3 Å (red). The region between the bond rearrangement and the edge of the sheet exhibits strong local rotation. Scale bars: 1 nm. See also movies S1 and S2.

Plasticité

Dépendance en la **Composition** et la **Pression** dans $(1-x) \text{SiO}_2 + x \text{Na}_2\text{O}$



Plasticité localisée sur les zones riches en Na

La **composition** contrôle le nombre d'événements

Leur taille et leur amplitude dépendent de la **pression**

Plasticité

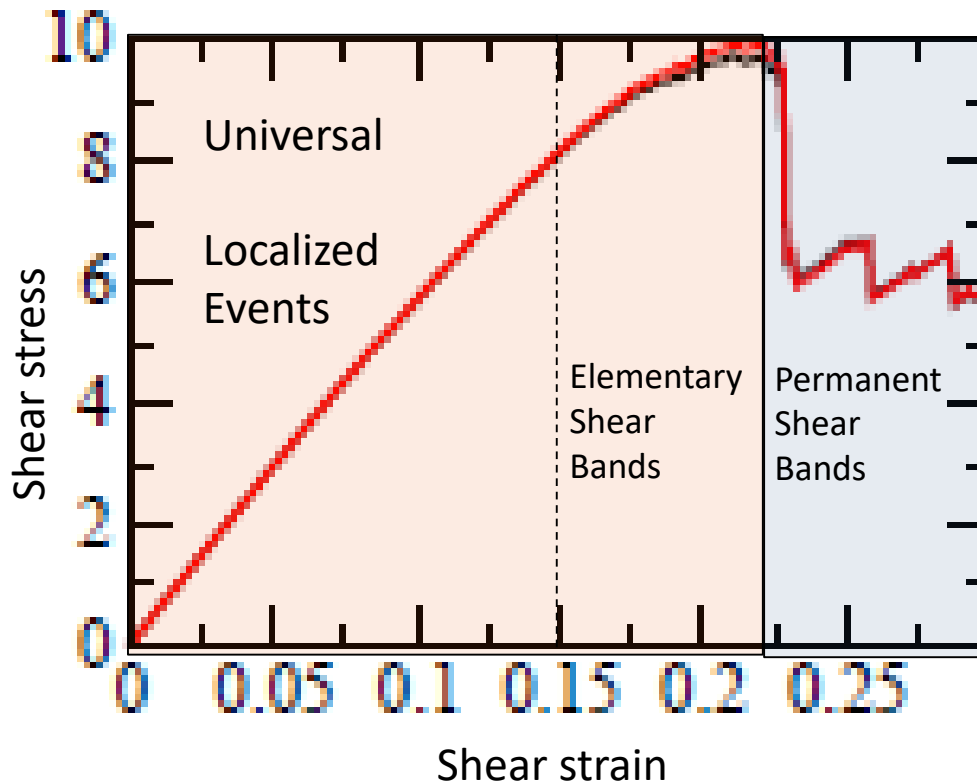
Bandes de Cisaillement

Comportement Général de l'écoulement **Plastique** dans un **matériau amorphe**

Below Global Yield Stress



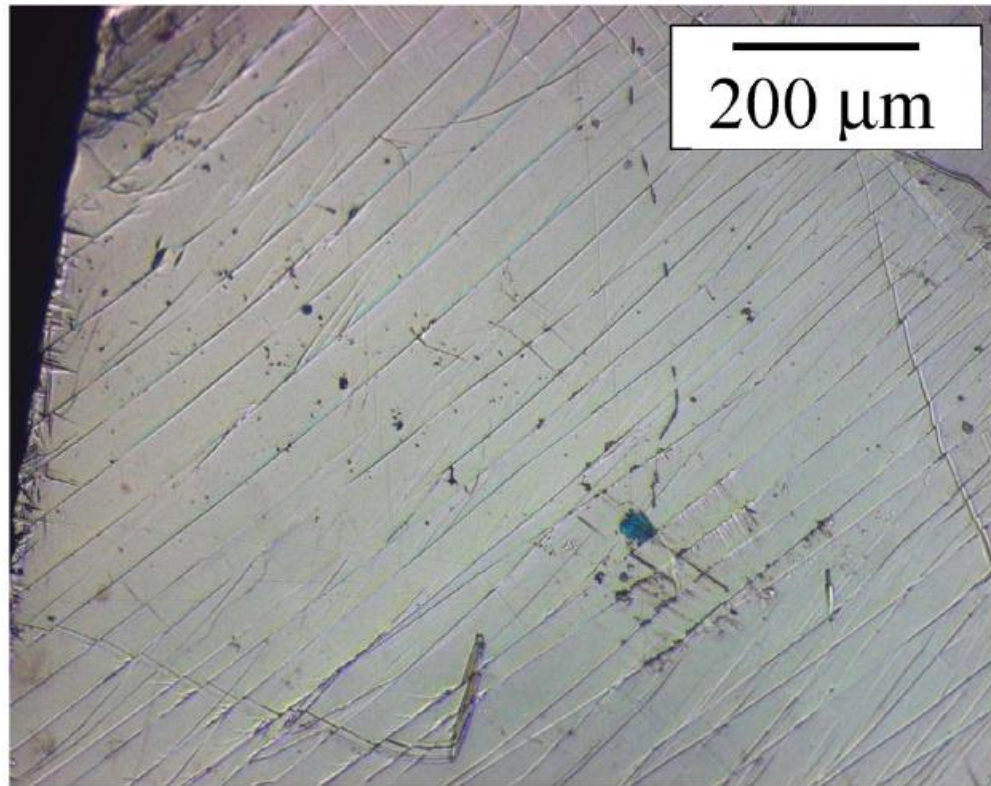
Above Global Yield Stress



Plasticité

Bandes de Cisaillement

Localisation de la déformation (bandes de cisaillement)



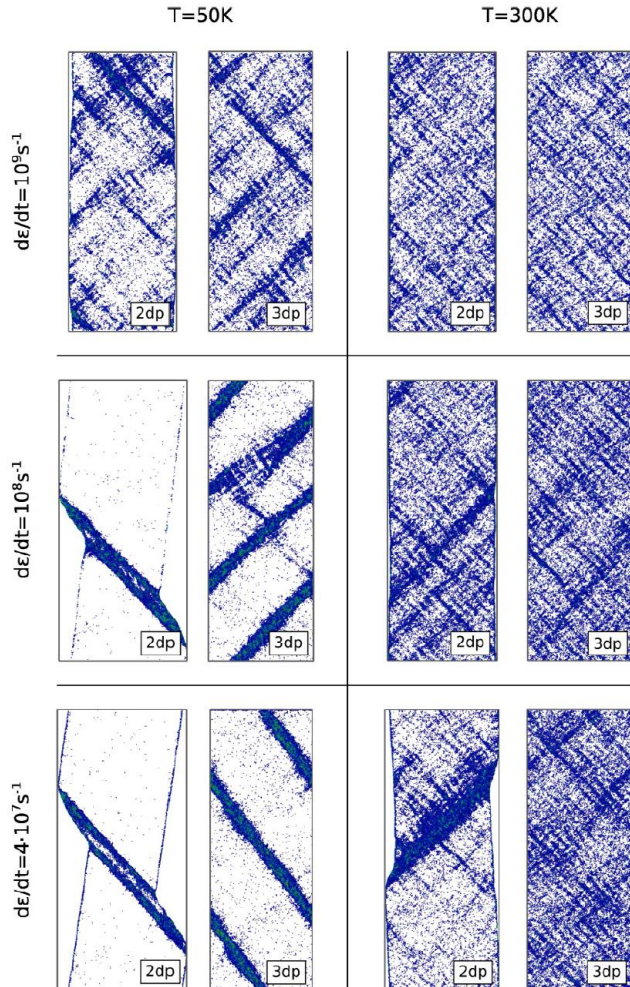
Scroers et Johnson (2004)

$\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$

Plasticité

Bandes de Cisaillement

La permanence des bandes de cisaillement n'est **pas** un mécanisme **universel**



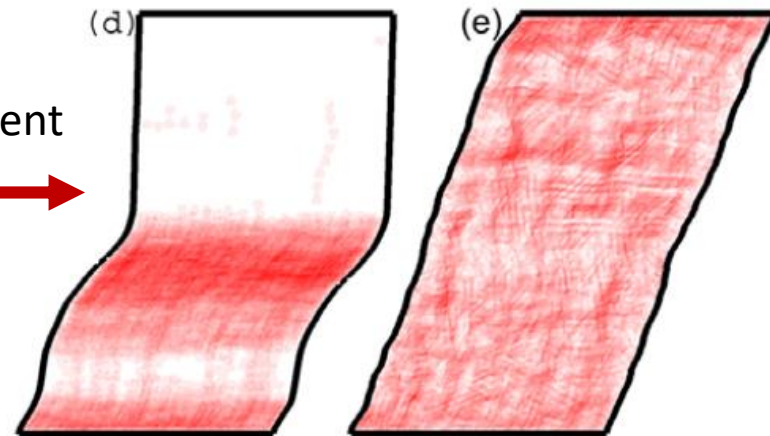
Role de la
Température

Taux de Déformation,
Bords Libres

Mécanisme
Non-universel

← Importance de
l'auto-adoucissement

→ Création de
« Volume Libre »
dans la zone de
plasticité



Plasticité

Bandes de Cisaillement

Applied strain

ductile

brittle

Permanent (mature) shear band

Global localization / Very strong pinning

Elementary (embrionic) shear bands

Percolation / Critical phenomenon / Yielding

Isolated Eshelbys

Reversible elastic

1/P, 1/shear rate, 1/T, aging, damage (defects),
Size L, Free surfaces...

Vibrations

Vibrations du réseau (Modes Propres) dans les Matériaux Amorphes

Exemple du **Silicium Amorphe**

$$m_i \cdot \frac{\partial^2 u_\alpha}{\partial t^2}(\underline{r}_i, t) = - \frac{\partial E_{total}}{\partial r_{i\alpha}} \approx - \sum_j \sqrt{m_i m_j} M_{ij}^{\alpha\beta} \cdot u_\beta(\underline{r}_j, t) + f_\alpha(\underline{r}_i) \quad \text{with } M_{ij}^{\alpha\beta} \equiv \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E_{total}}{\partial r_{i\alpha} \partial r_{j\beta}}$$

$\underline{u}(\underline{r}_i, t) \equiv \underline{r}_i(t) - \underline{r}_i^0 = \underline{U}_i / \sqrt{m_i} \cdot e^{i\omega t}$ Dynamical Matrix: **Eigenvectors** \underline{U} , **eigenvalues** ω^2

soft modes « quasi-localized vibrations »
& **propagons**

(a) $\nu = 0.59$ THz

(b) $\nu = 2.67$ THz

(c) $\nu = 9.95$ THz

(d) $\nu = 17.39$ THz

Strong scattering of Plane Waves and Viscous dynamics

P.B. Allen and
J.L. Feldman (1999)

Most unstable mode

Vibrations

Vibrations du réseau (Modes Propres) dans les **Matériaux Amorphes**

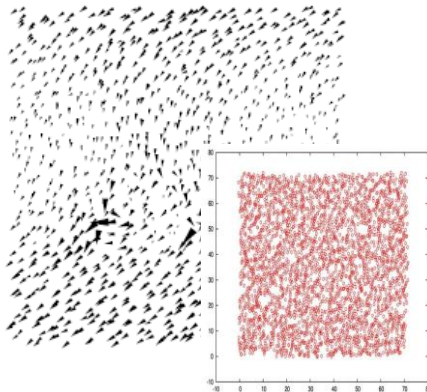
Exemple de la **Silice Amorphe**

$$m_i \cdot \frac{\partial^2 u_\alpha}{\partial t^2}(\underline{r}_i, t) = -\frac{\partial E_{total}}{\partial r_{i\alpha}} \approx -\sum_j \sqrt{m_i m_j} M_{ij}^{\alpha\beta} \cdot u_\beta(\underline{r}_j, t) + f_\alpha(\underline{r}_i) \quad \text{with } M_{ij}^{\alpha\beta} \equiv \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E_{total}}{\partial r_{i\alpha} \partial r_{j\beta}}$$

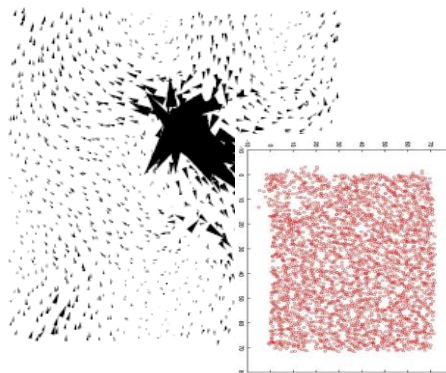
$\underline{u}(\underline{r}_i, t) \equiv \underline{r}_i(t) - \underline{r}_i^0 = \underline{U}_i / \sqrt{m_i} \cdot e^{i\omega t}$ Dynamical Matrix: **Eigenvectors** \underline{U} , **eigenvalues** ω^2

Harmonic approximation of energy

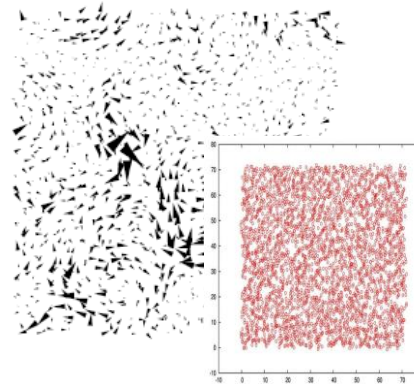
Plane Waves



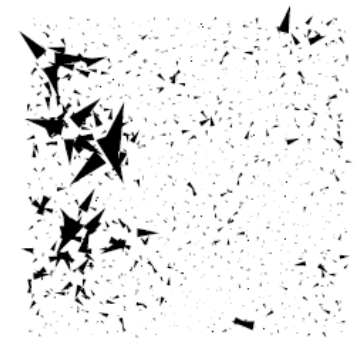
Soft Modes



Diffusons



Locons



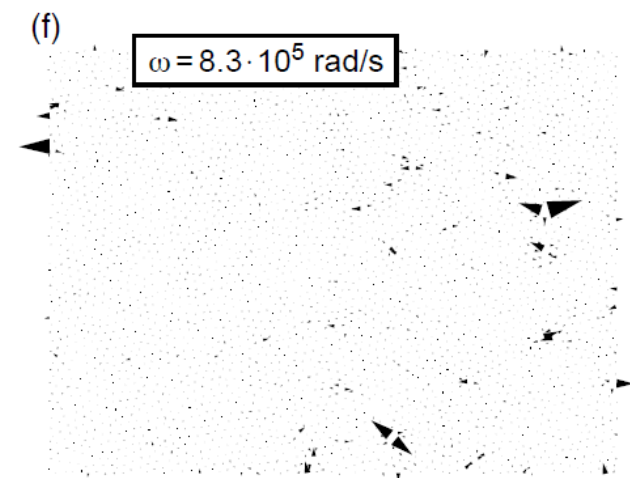
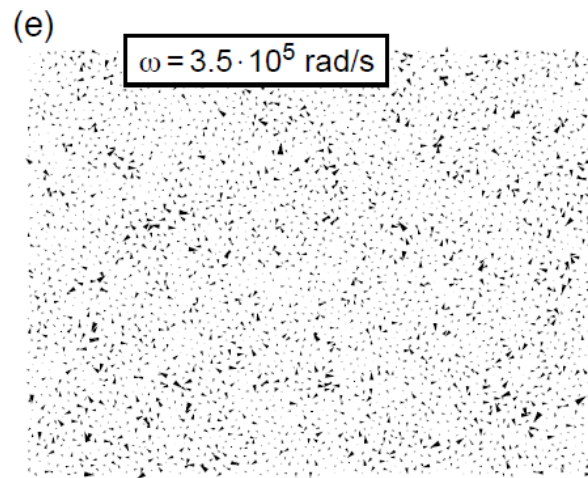
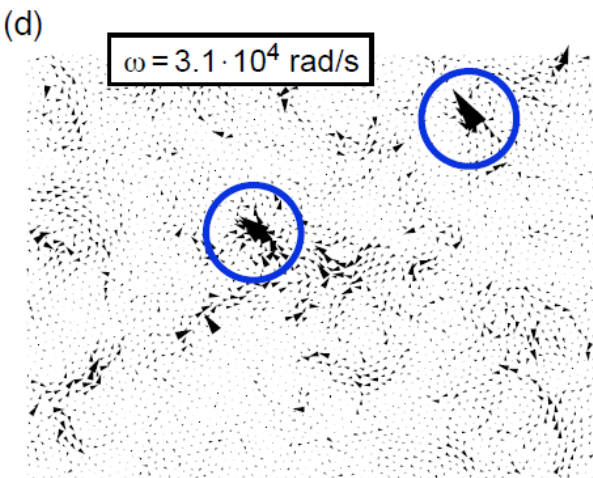
P.B. Allen and
J.L. Feldman (1999)

A.Tanguy et al. (2002)
B. Mantisi et al. (2012)
N. Shcheblanov et al. (2015)

Vibrations

Vibrations du réseau (Modes Propres) dans les **Matériaux Amorphes**

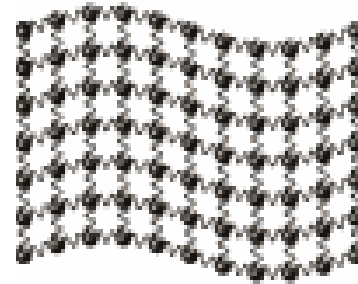
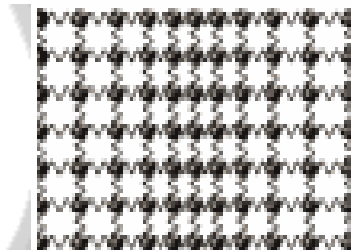
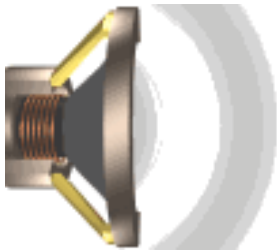
Exemple d'un **Gel Colloïdal mou**



O. Dauchot et al. (2010)

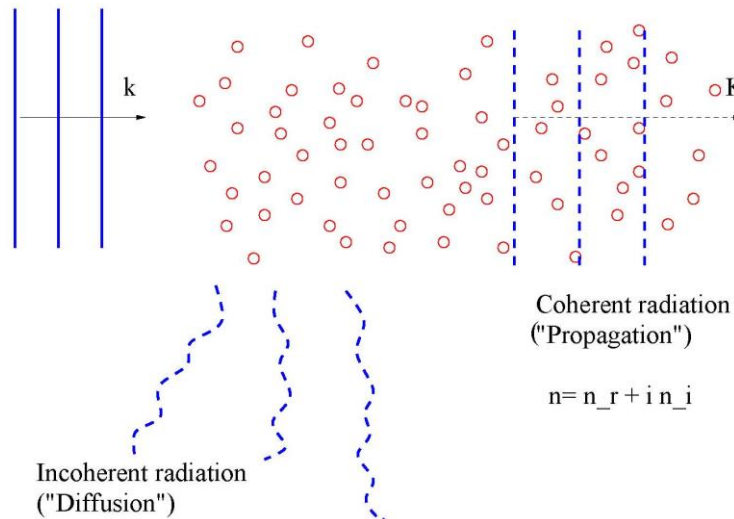
Vibrations

Atténuation Acoustique Apparente dans les Matériaux Amorphes



Cristal

MULTIPLE SCATTERING



Verre (Amorphe)

Incoherent radiation
("Diffusion")

Coherent radiation
("Propagation")

$$n = n_r + i n_i$$

D

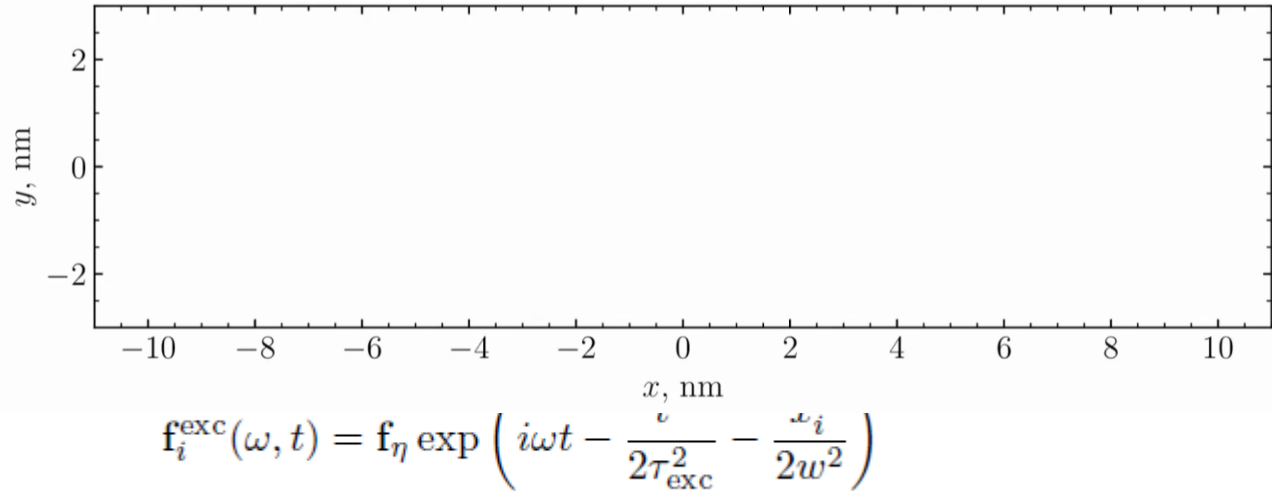
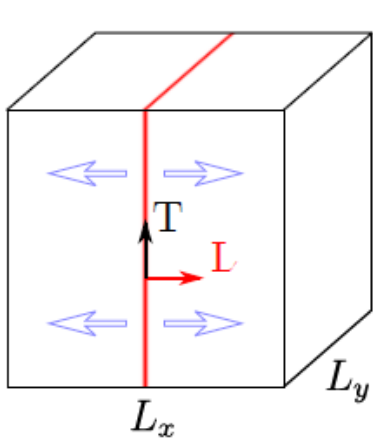
(D=0: "Localization")

F. Lund et al. (2012)

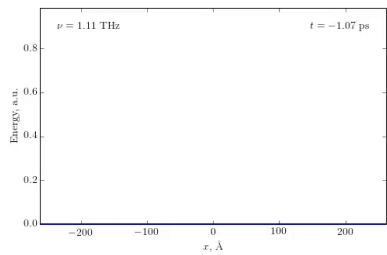
T. Damart et al. (2015)

Vibrations

Dynamique de Paquet d'Onde et Atténuation Acoustique dans a-Si:

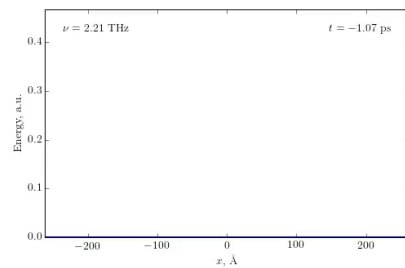


→ $\omega \nearrow$

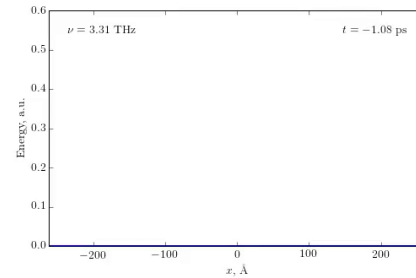


Régime Ballistique
Propagons

$$\omega \ll \omega_{\text{IR}}$$

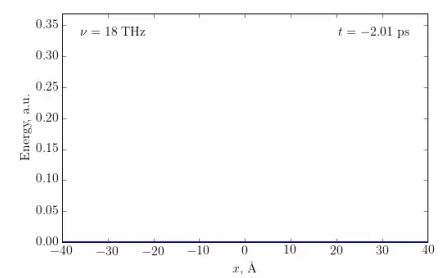


Régime Mixte
(« Pic Boson »)



Régime Diffusif
Diffusons

$$\omega > \omega_{\text{IR}}$$



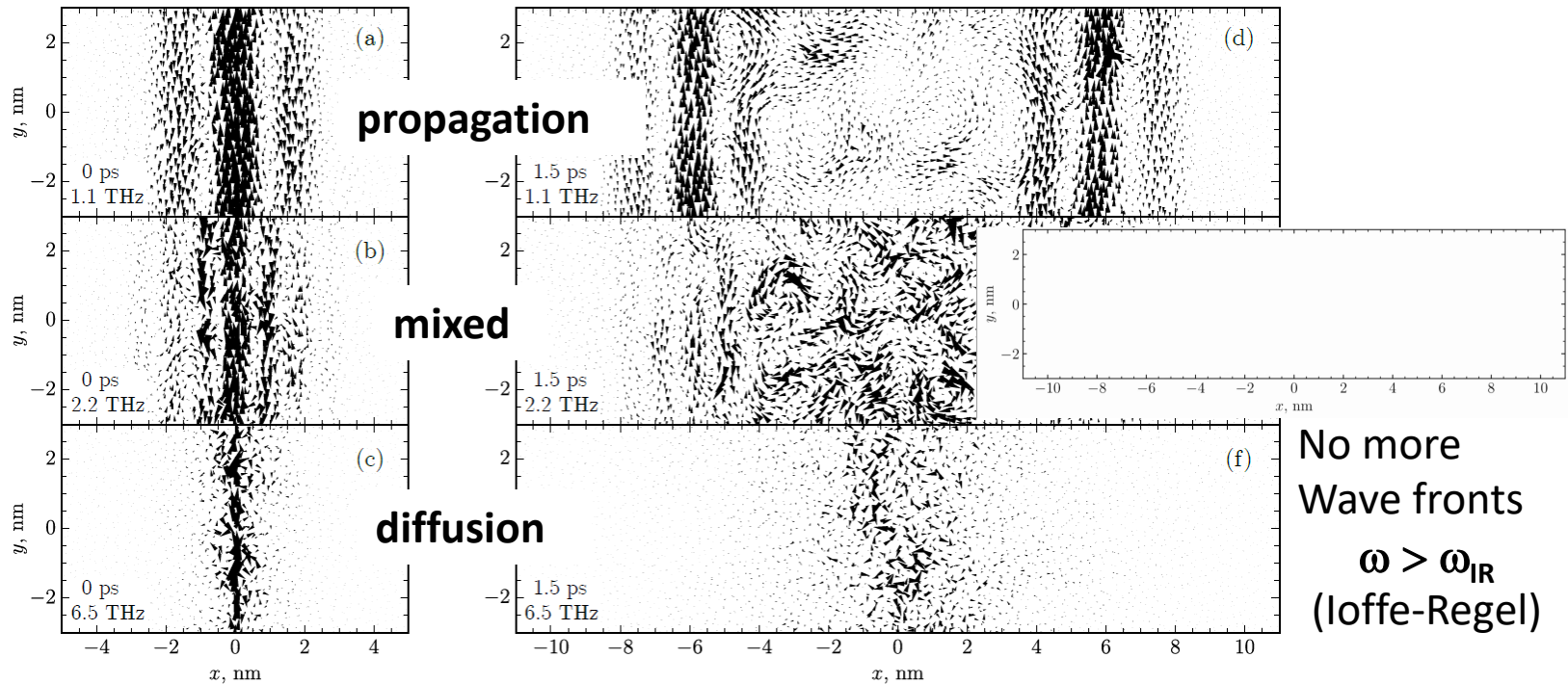
Localisation
Locons

Y. Beltukov et al. (2018)

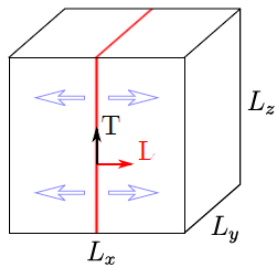
Vibrations

Dynamique de Paquet d'Onde et Atténuation Acoustique dans a-Si:

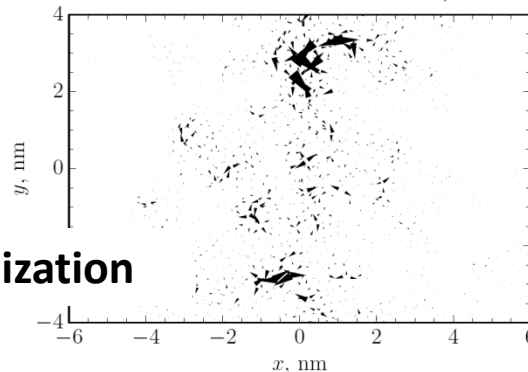
Wave Packet excitation



No more
Wave fronts
 $\omega > \omega_{IR}$
(Ioffe-Regel)



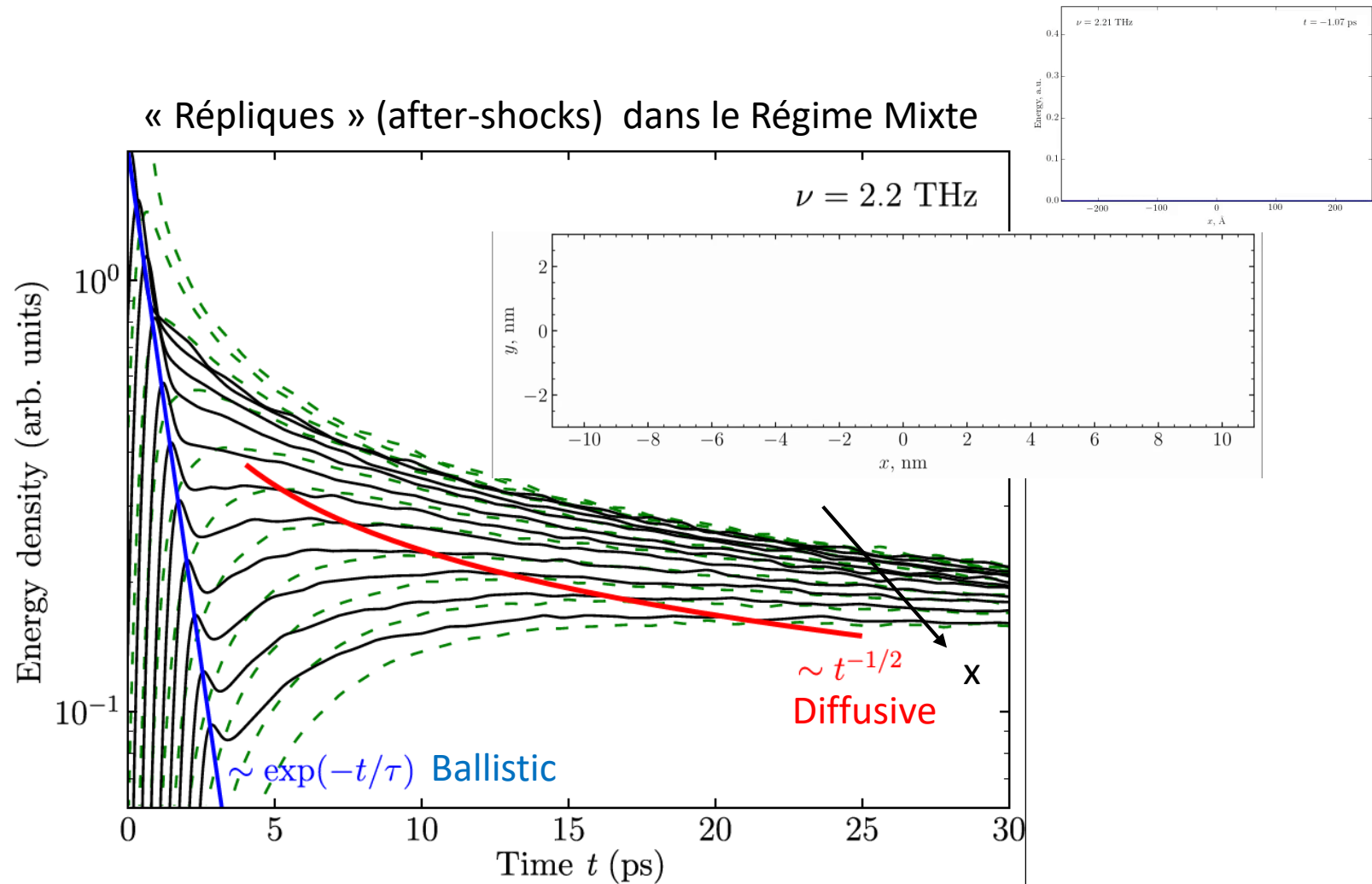
localization



Wave packets are supported by a combination of Normal Modes giving rise to unusual behavior

Vibrations

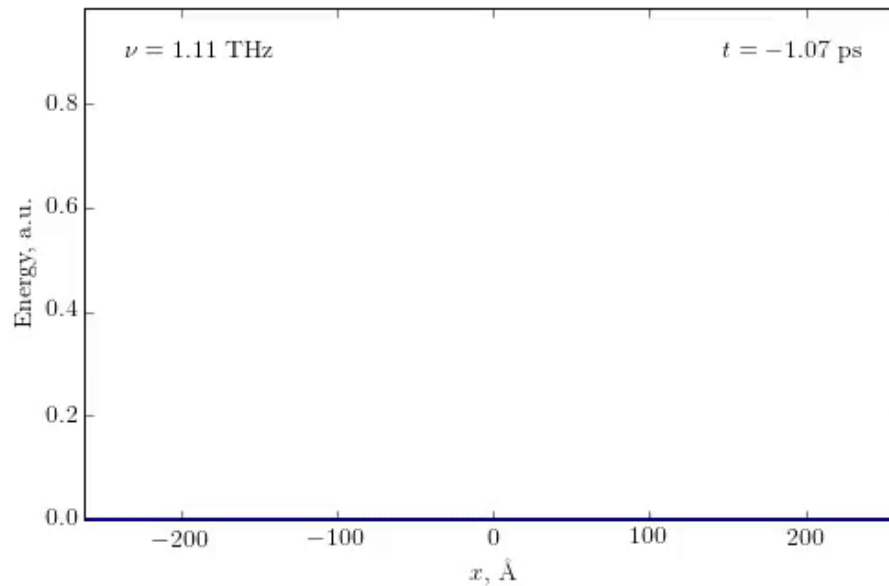
Dynamique de Paquet d'Onde et Atténuation Acoustique dans a-Si:



Vibrations

Rappel

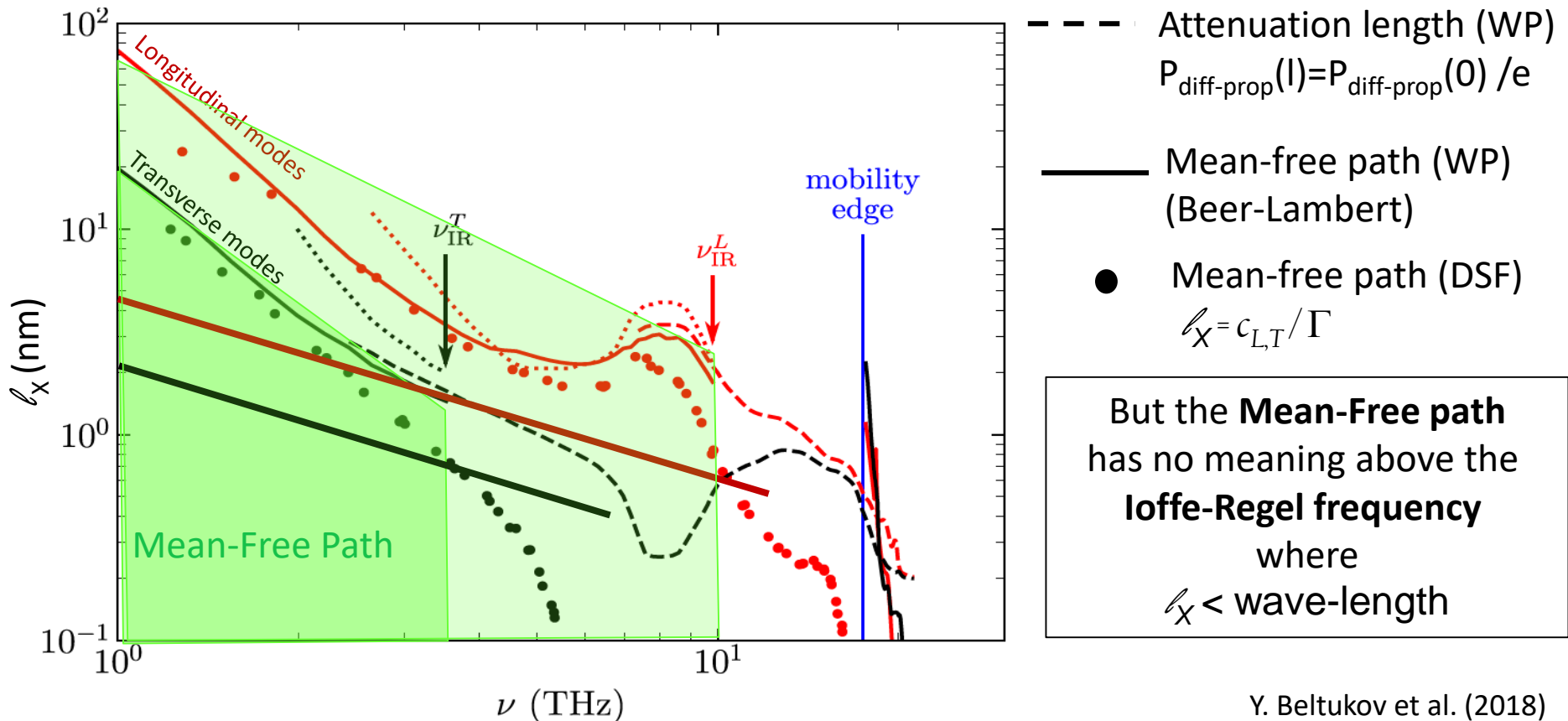
Libre Parcours Moyen dans le régime **Ballistique**



Vibrations

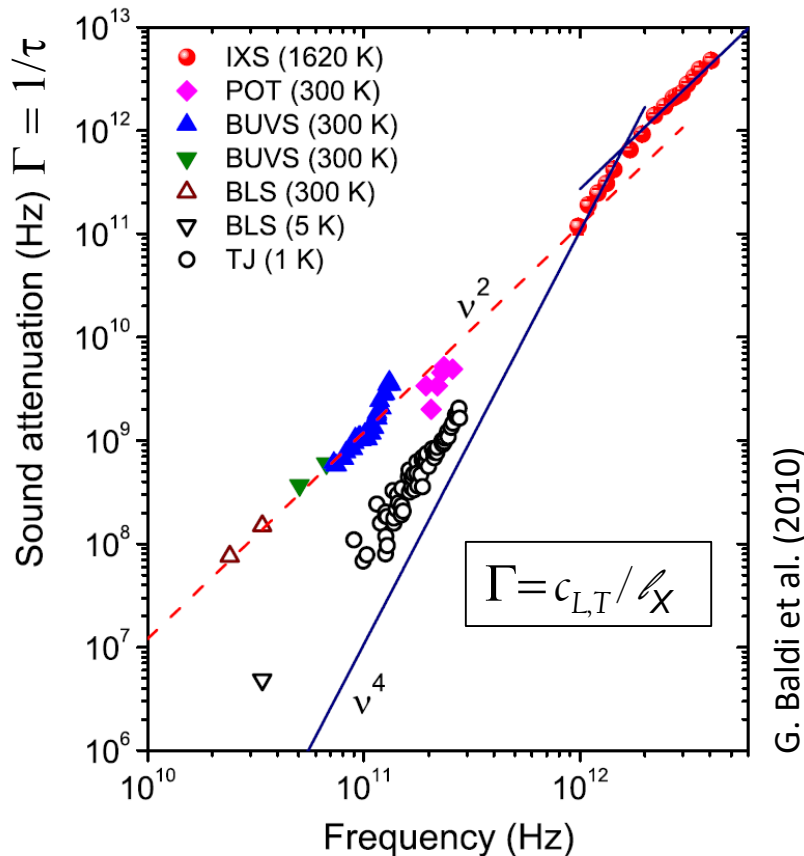
Libre Parcours Moyen dans le régime Ballistique

The **Mean-Free Path** of Wave-Packets in the Propagons regime is identical to that given by **acoustic attenuation** from the **Dynamical Structure Factor**



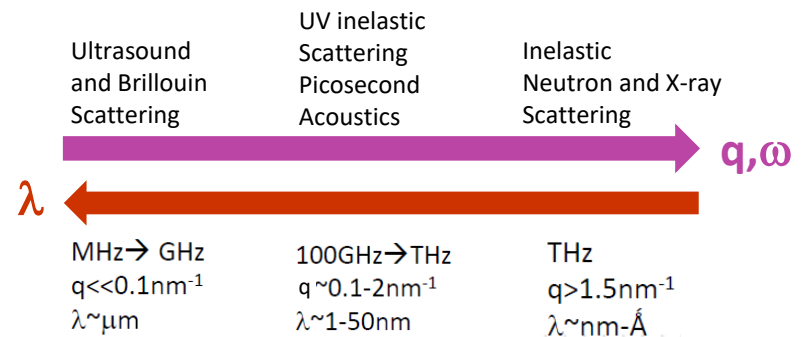
Vibrations

Libre Parcours Moyen dans le régime Ballistique



IXS: Inelastic X-ray Scattering
 POT: picosecond optical technique
 BUVS /BLS: Brillouin Ultraviolet/Light Scattering
 TJ: Tunneling Junction

Experimental Measurements



Inverse Attenuation Time:

$$\Gamma = c_{LT} / \ell_X = 1/\tau \propto \omega^2, \omega^4, \omega^2$$

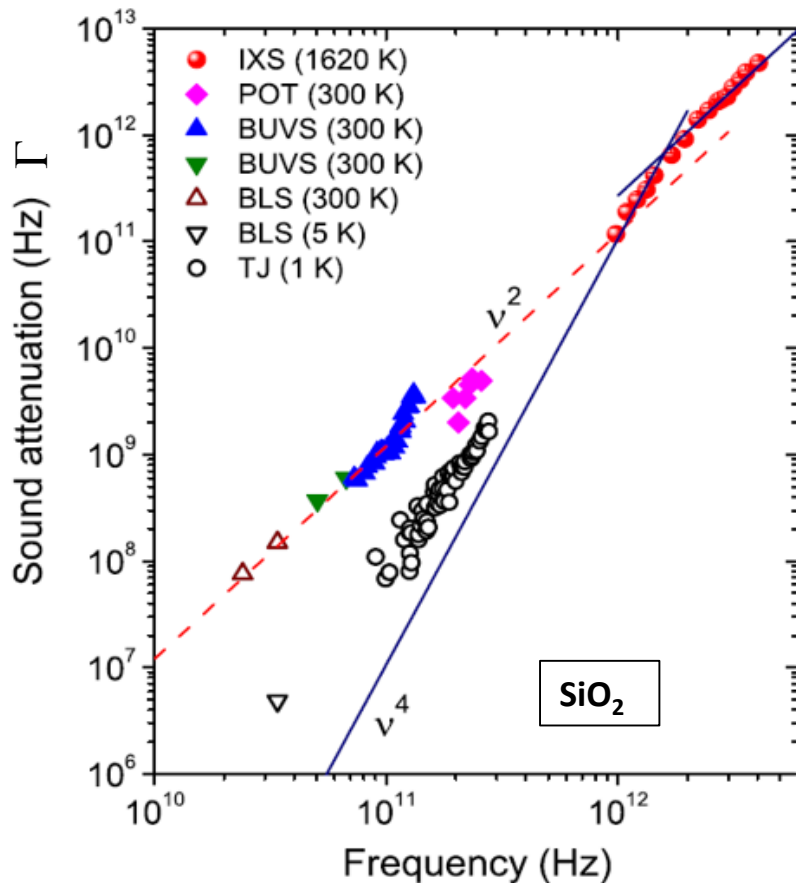
Different **frequency** dependences
of the dissipative term $\Gamma(\omega)$

Vibrations

Libre Parcours Moyen dans le régime Ballistique

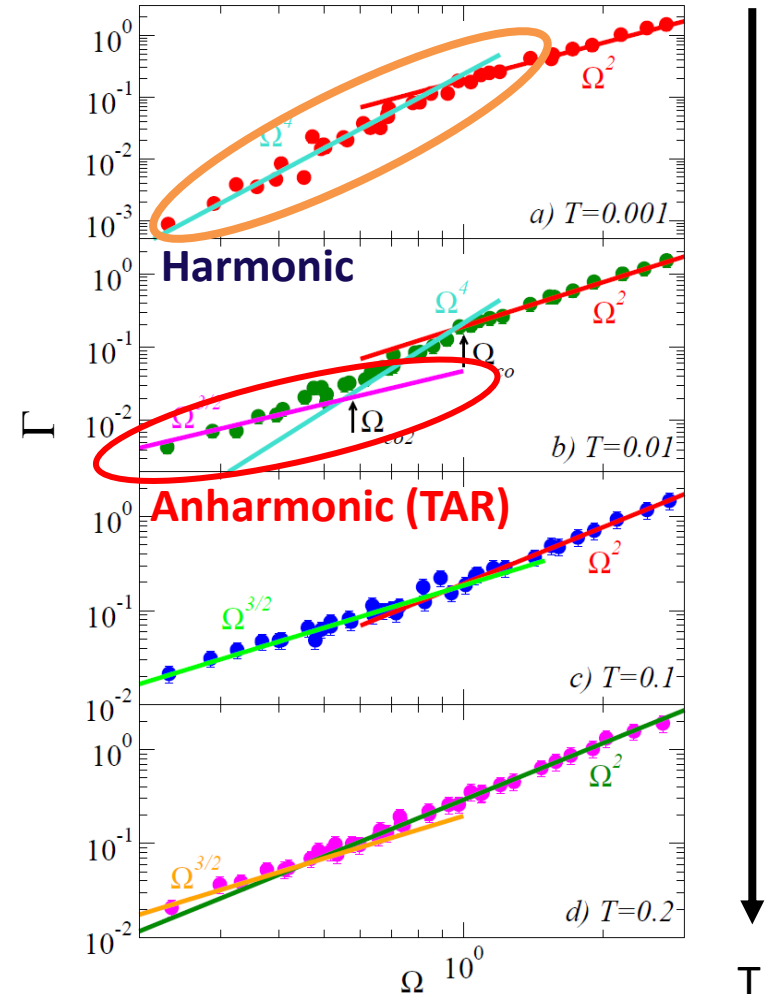
Experimental Results

$$S_{L,T}(q, \omega) = \frac{A}{(\omega^2 - \omega_{L,T}^2(q))^2 + \omega^2 \Gamma^2}$$



G. Baldi et al. (2010)

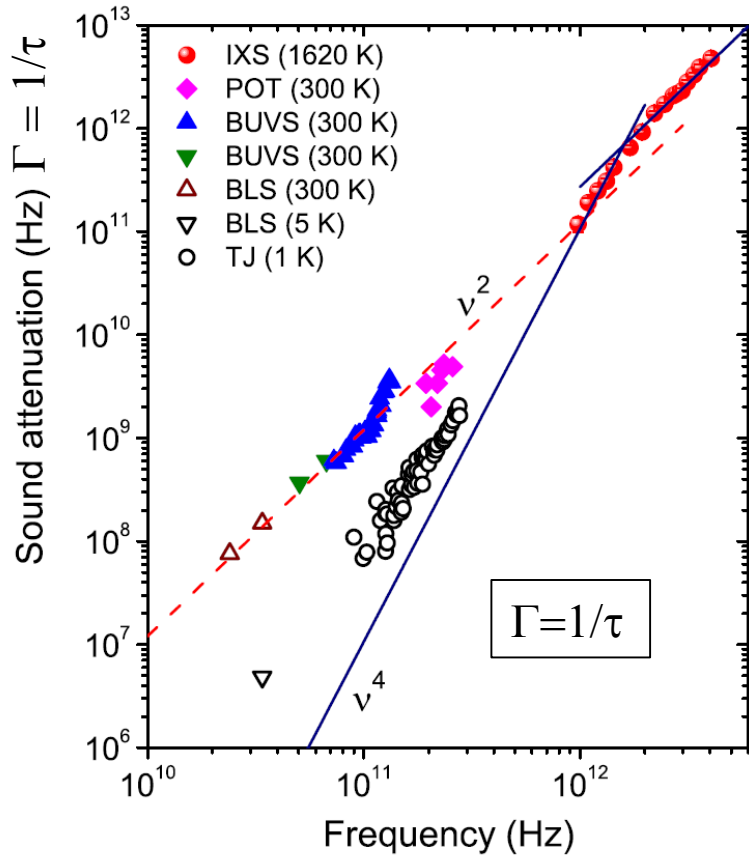
Molecular Dynamics Simulations at different Temperatures



H. Mizuno, et al.(2020)

Vibrations

Modélisation Effective de l'Atténuation Acoustique dans les Verres



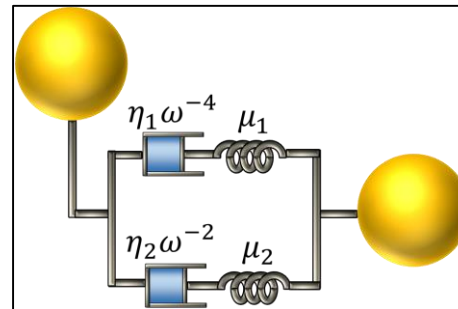
G. Baldi et al. (2010)

IXS: Inelastic X-ray Scattering
 POT: picosecond optical technique
 BUVS /BLS: Brillouin Ultraviolet/Light Scattering
 TJ: Tunneling Junction

Sound attenuation = Inverse Attenuation Time:

$$\Gamma = \frac{1}{\tau} \propto \omega^2; \omega^4; \omega^2$$

Effective modelling: two parallel processes



Quality factor (Q^{-1})

$$\frac{G''}{G'}(\omega) = \Phi(\omega, \alpha, \tau_1, \tau_2)$$

$$\frac{\Gamma}{\omega}(\omega) = \frac{G''}{G'} = Q^{-1}(\omega)$$

3 parameters:

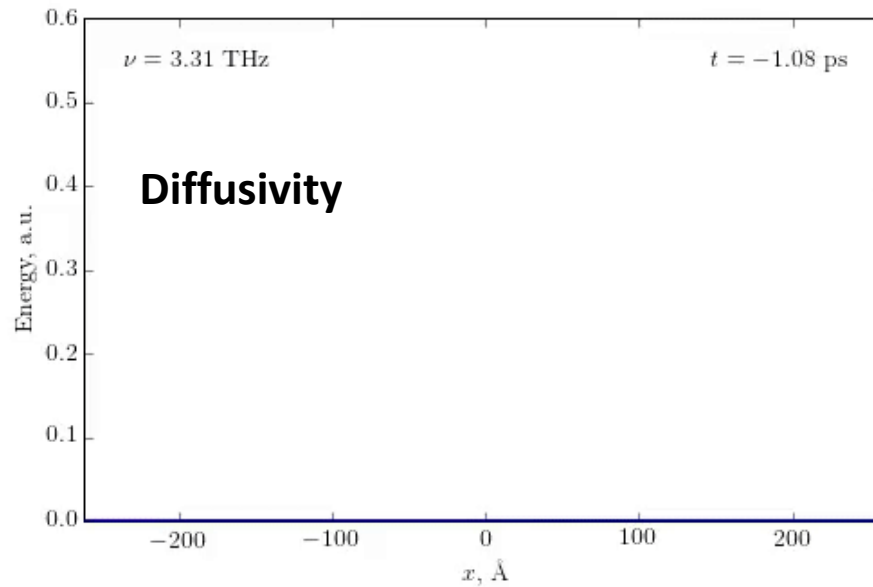
$$\alpha = \frac{\mu_2}{\mu_1}, \tau_1 = \frac{\eta_1}{\mu_1}, \tau_2 = \frac{\eta_2}{\mu_2} \quad \text{with } \alpha(T) \nearrow$$

H. Luo, et al (2021)

Vibrations

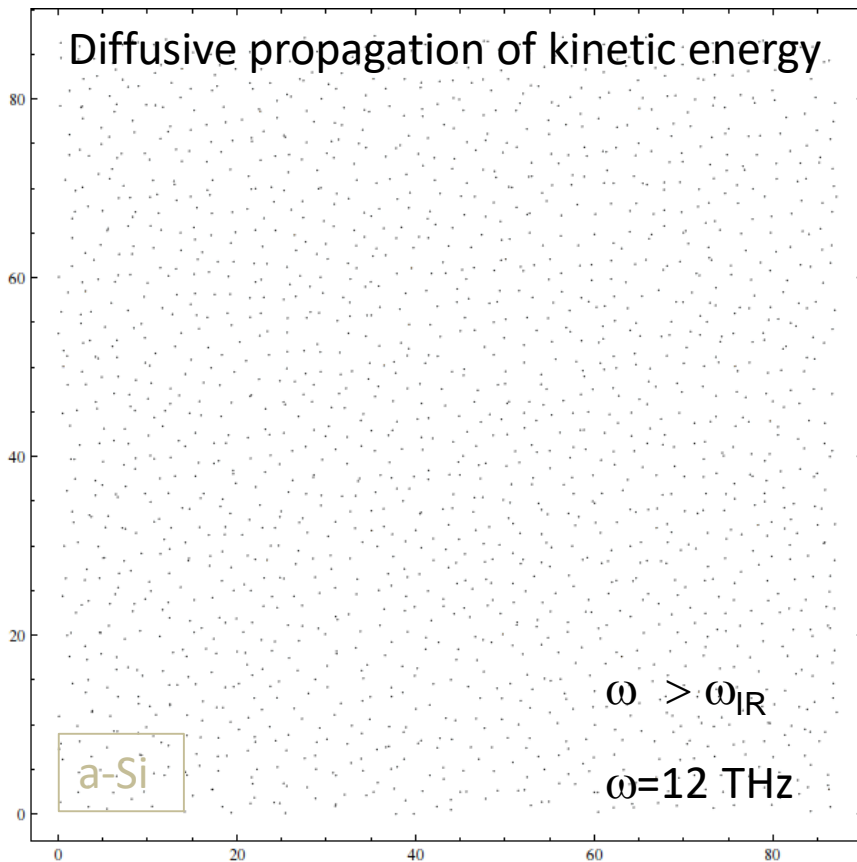
Rappel

Diffusivité dans le régime Diffusif

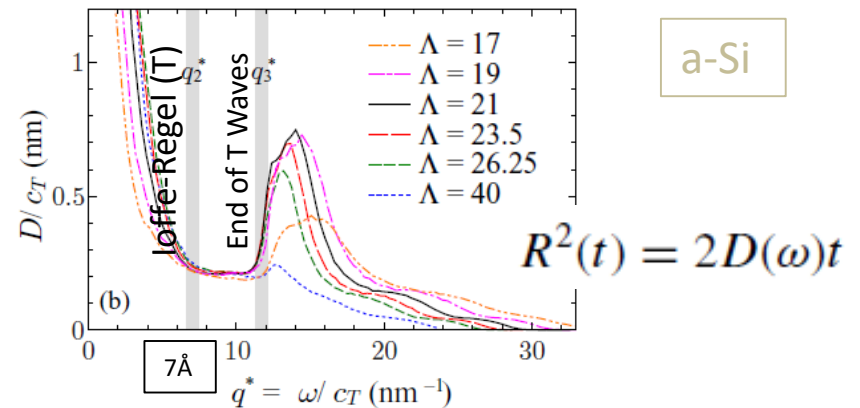
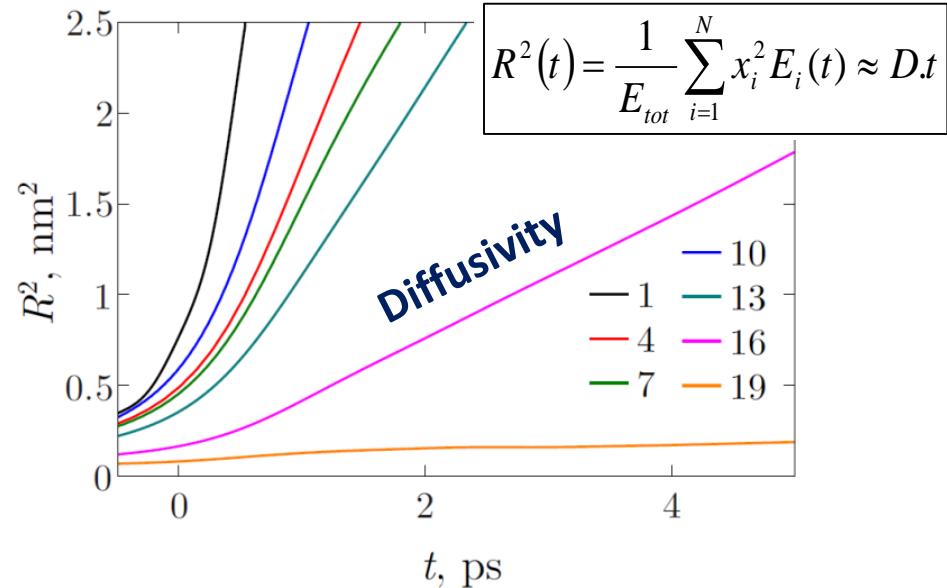


Vibrations

Diffusivité des excitations Acoustiques dans les Verres



Diffusive transport due to the departure from plane waves



Bibliographie:

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J. Barton, C. Guillemet, EDP sciences ed. (2005)

Elasto-plastic behavior of amorphous materials: a brief review

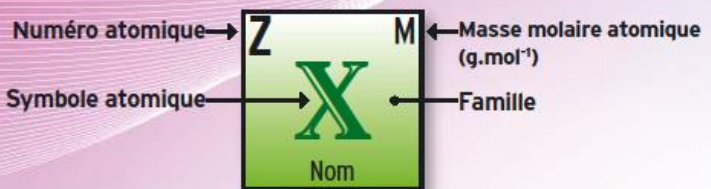
A. Tanguy, CRAS (2021) <https://doi.org/10.5802/crphys.49>

Vibrations and Heat Transfer in Glasses: The Role Played by Disorder

A. Tanguy, CRAS (2023) <https://doi.org/10.5802/crphys.162>

TABLEAU PÉRIODIQUE DES ÉLÉMENTS

Colonne																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 1,0 H Hydrogène																	2 4,0 He Hélium
3 6,9 Li Lithium	4 9,0 Be Béryllium																
11 23,0 Na Sodium	12 24,3 Mg Magnésium																
19 39,1 K Potassium	20 40,1 Ca Calcium	21 45,0 Sc Scandium	22 47,9 Ti Titane	23 50,9 V Vanadium	24 52,0 Cr Chrome	25 54,9 Mn Manganèse	26 55,8 Fe Fer	27 58,9 Co Cobalt	28 58,7 Ni Nickel	29 63,5 Cu Cuivre	30 65,4 Zn Zinc	31 69,7 Ga Gallium	32 72,6 Ge Germanium	33 74,9 As Arsenic	34 79,0 Se Sélénium	35 79,9 Br Brome	36 83,8 Kr Krypton
37 85,5 Rb Rubidium	38 87,6 Sr Strontium	39 88,9 Y Yttrium	40 91,2 Zr Zirconium	41 92,9 Nb Niobium	42 95,9 Mo Molybdène	43 (98) Tc Technétium	44 101,1 Ru Ruthénium	45 102,9 Rh Rhodium	46 106,4 Pd Palladium	47 107,9 Ag Argent	48 112,4 Cd Cadmium	49 114,8 In Indium	50 118,7 Sn Étain	51 121,8 Sb Antimoine	52 127,6 Te Tellure	53 126,9 I Iode	54 131,3 Xe Xénon
55 132,9 Cs Césium	56 137,3 Ba Baryum	57 138,9 La Lanthane	72 178,5 Hf Hafnium	73 180,9 Ta Tantale	74 183,8 W Tungstène	75 186,2 Re Rhénium	76 190,2 Os Osmium	77 192,2 Ir Iridium	78 195,1 Pt Platine	79 197,0 Au Or	80 200,6 Hg Mercure	81 204,4 Tl Thallium	82 207,2 Pb Plomb	83 209,0 Bi Bismuth	84 (209) Po Polonium	85 (210) At Astate	86 (222) Rn Radon
87 (223) Fr Francium	88 (226) Ra Radium	89 (227) Ac Actinium	104 (261) Rf Rutherfordium	105 (262) Db Dubnium	106 (266) Sg Seaborgium	107 (264) Bh Bohrium	108 (269) Hs Hassium	109 (268) Mt Meitnerium	110 (269) Uun Ununnilium	111 (272) Uuu Ununonium	112 (277) Uub Ununbium		114 Uuq Ununquadium		116 Uuh Ununhexium		118 Uuo Ununoctium



Dmitri Ivanovitch Mendeleïev (1834 - 1907) est un chimiste russe connu pour ses travaux sur la classification périodique des éléments. En 1869, il publia une première version de son tableau périodique des éléments appelé aussi tableau de Mendeleïev. Il déclara que les éléments chimiques pouvaient être arrangés selon un modèle qui permettrait de prévoir les propriétés des éléments non encore découverts.

58 140,1 Ce Cérium	59 140,9 Pr Praséodyme	60 144,2 Nd Néodyme	61 (145) Pm Prométhium	62 150,4 Sm Samarium	63 152,0 Eu Europium	64 157,4 Gd Gadolinium	65 158,9 Tb Terbium	66 162,5 Dy Dysprosium	67 164,9 Ho Holmium	68 167,3 Er Erbium	69 168,9 Tm Thulium	70 173,0 Yb Ytterbium	71 175,0 Lu Lutécium
90 232,0 Th Thorium	91 231,0 Pa Protactinium	92 238,0 U Uranium	93 (237) Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Américium	96 (247) Cm Curium	97 (247) Bk Berkélium	98 (251) Cf Californium	99 (254) Es Einsteinium	100 (257) Fm Fermium	101 (258) Md Mendélévium	102 (259) No Nobélium	103 (260) Lw Lawrencium



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des enseignants et des professeurs stagiaires

DÉLÉGATION INTERNET

Élément solide	Élément liquide	Élément gazeux	Élément artificiel
non-métal	métal alcalin	métal alcalin-terreux	métal de transition
		lanthanides	actinides
		métal pauvre	alcoyloxydes
			Co-rare

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