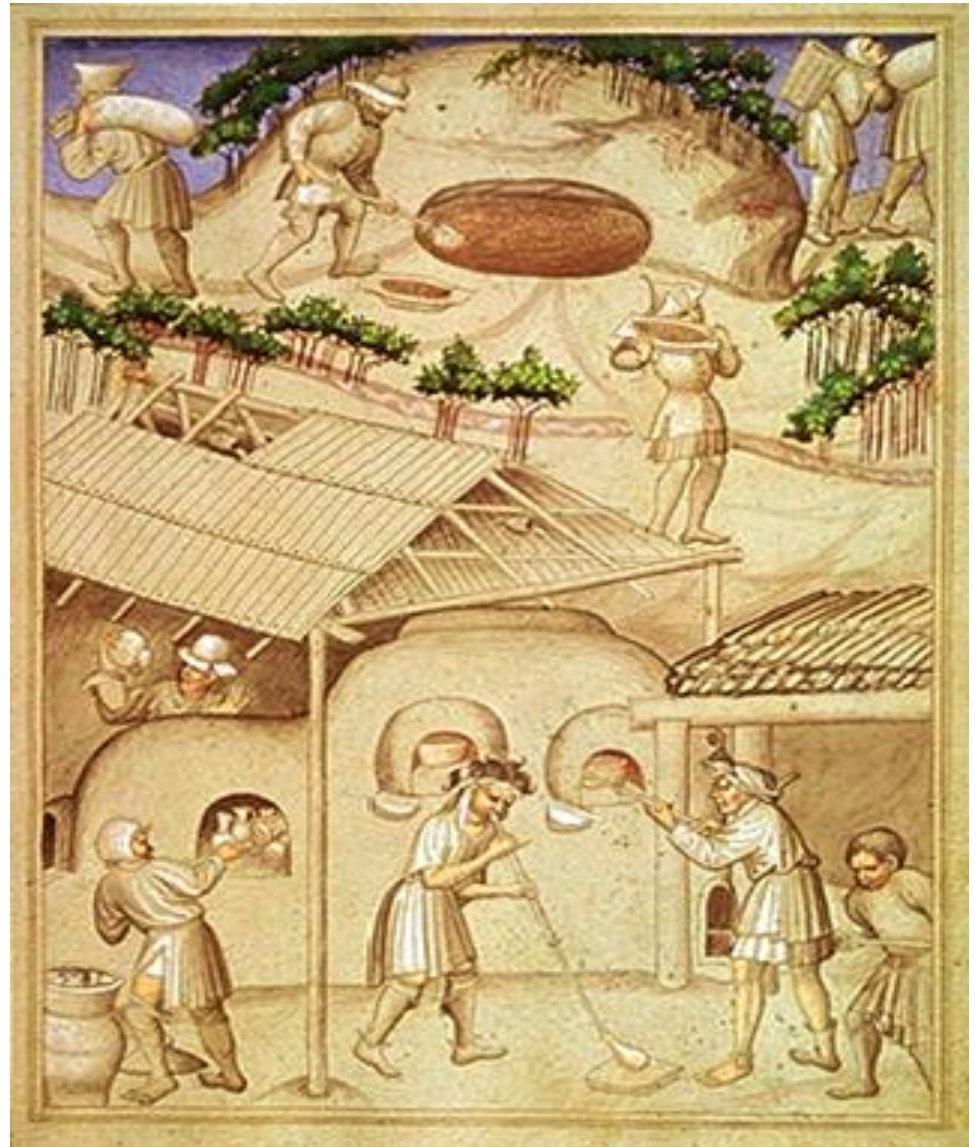


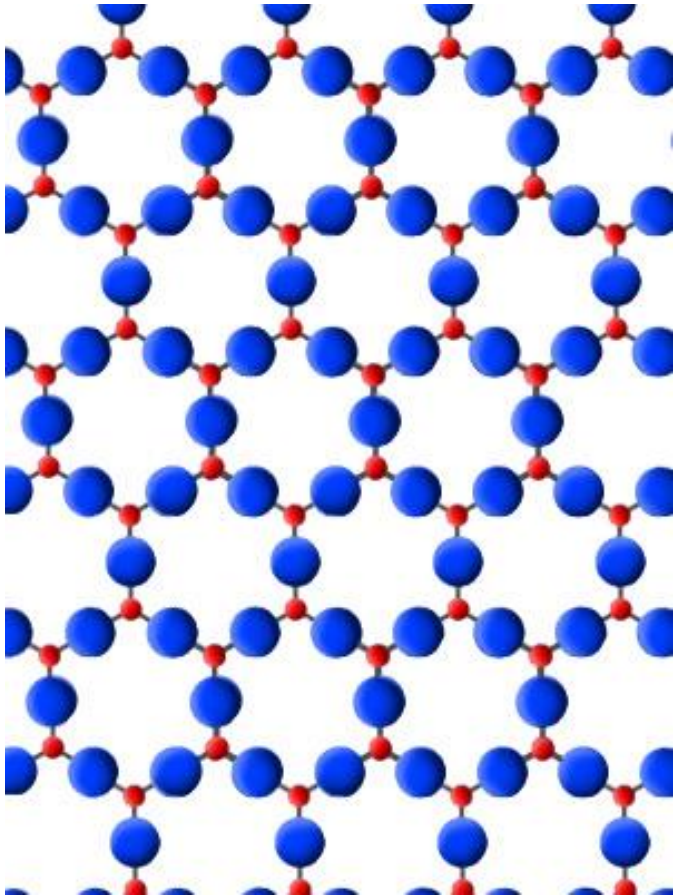
Estrutura de vidros

Prof. Dr. Eduardo Bellini Ferreira
PPG-CEM
USP – São Carlos



O que é o vidro?

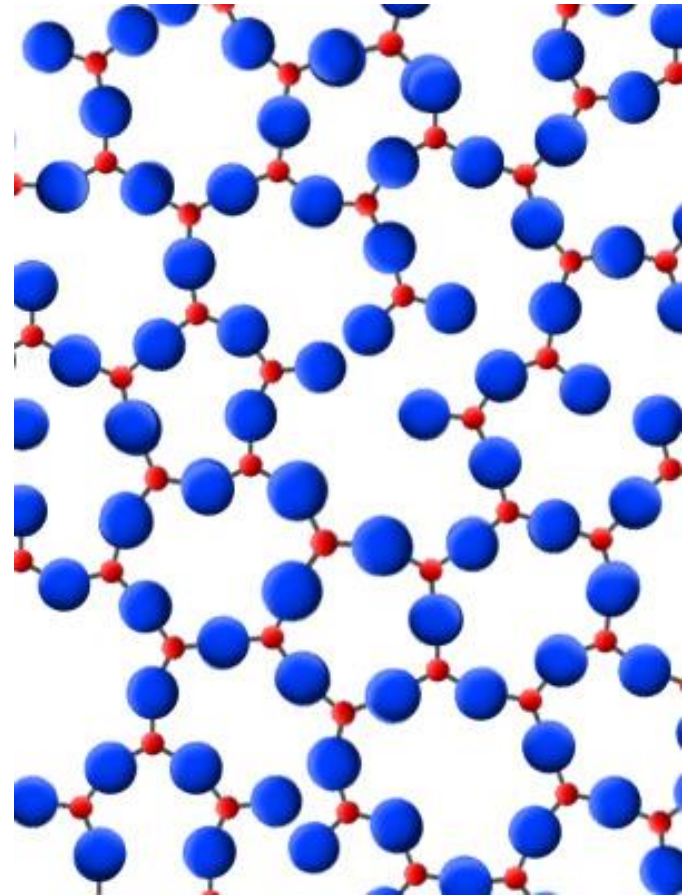
Vidro: material “sólido” não-cristalino que apresenta o fenômeno da transição vítrea.



Legenda:

● Silício

● Oxigênio

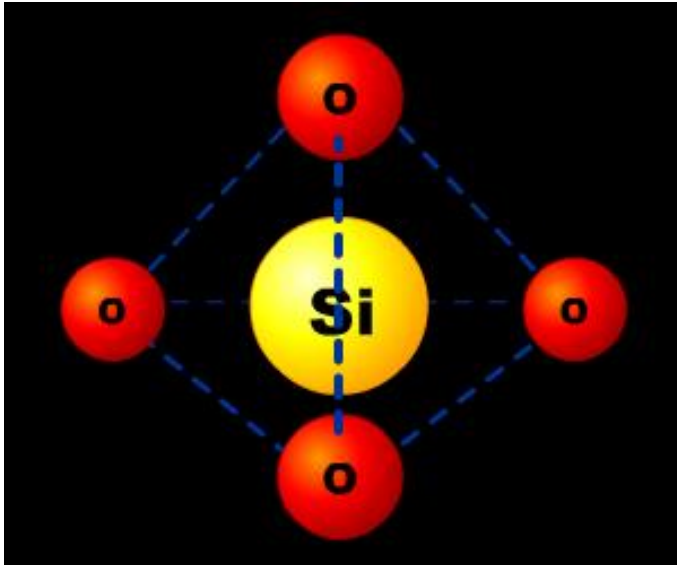


Sílica cristalina (Quartzo, Areia)

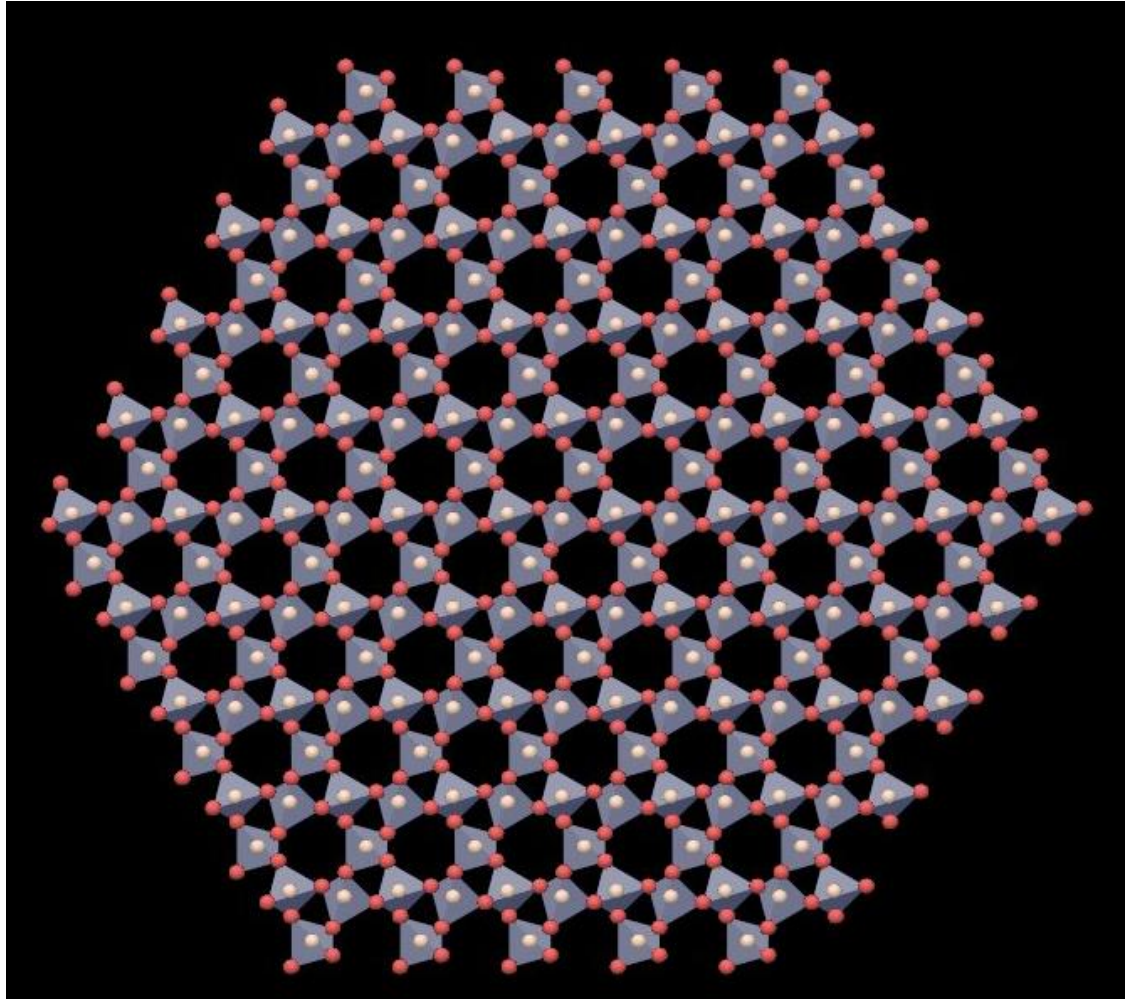
Sílica vítrea (Vidro)

Cristal x Vidro

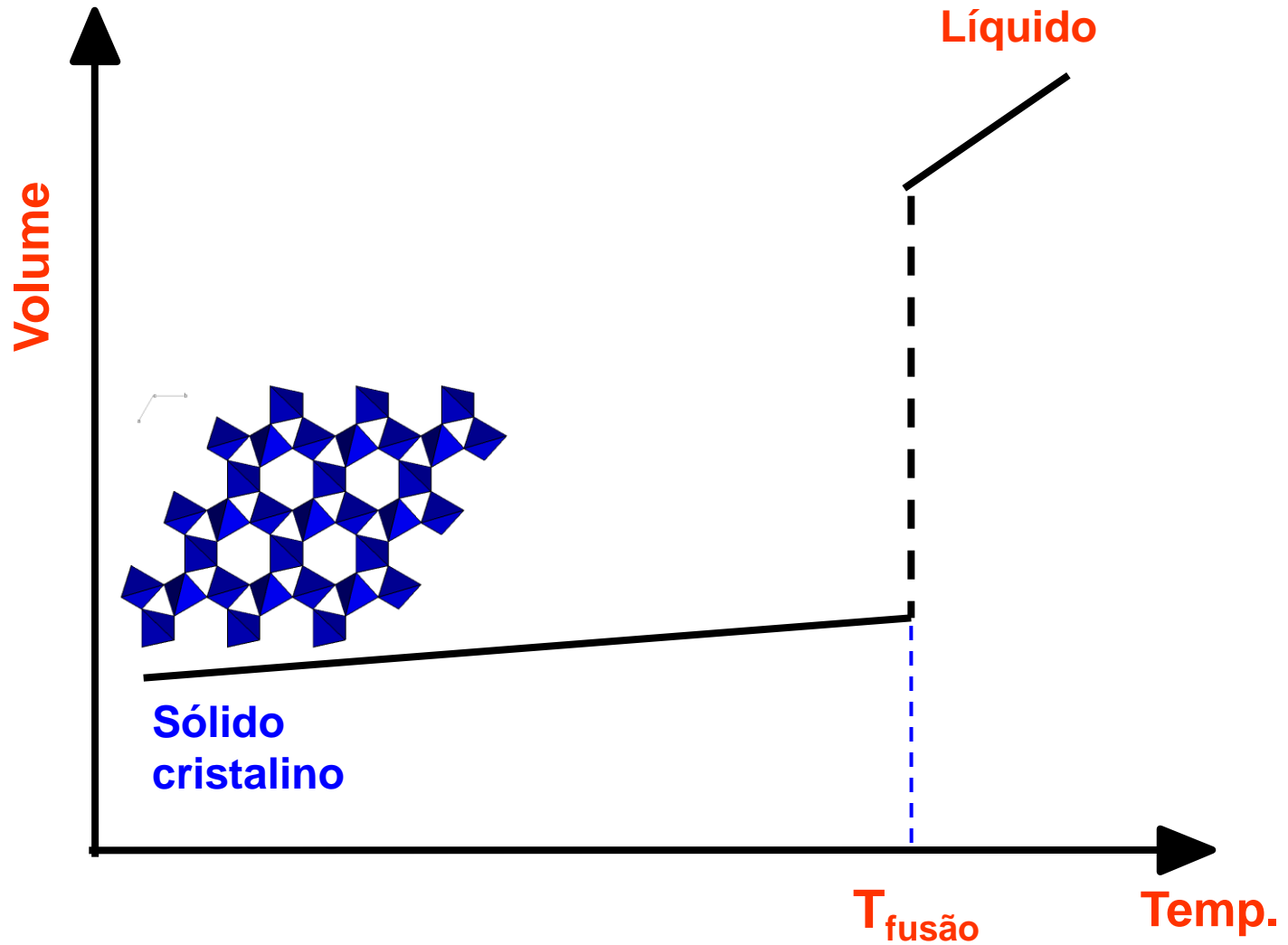
Tetraedro de
 SiO_2



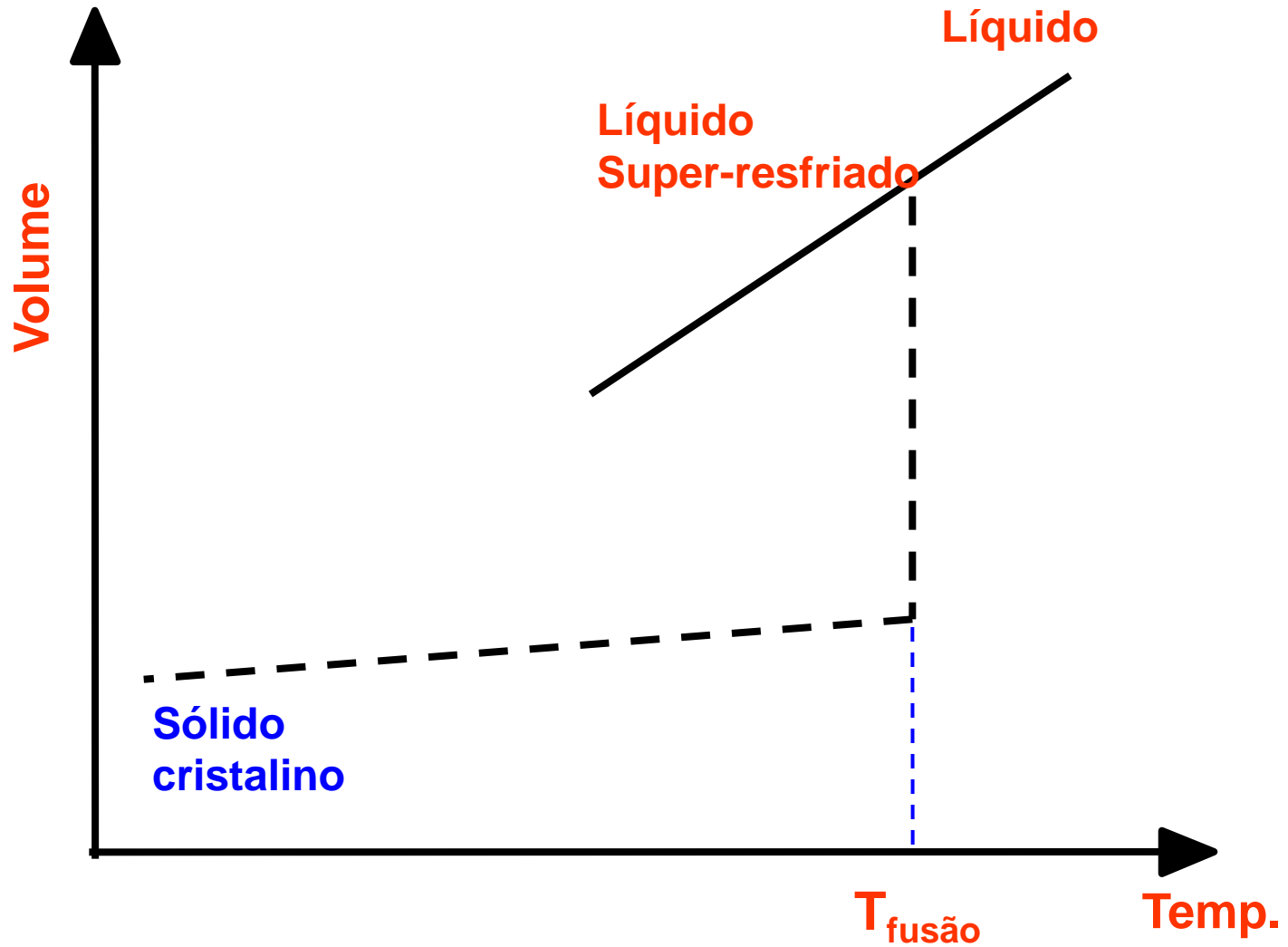
Quartzo



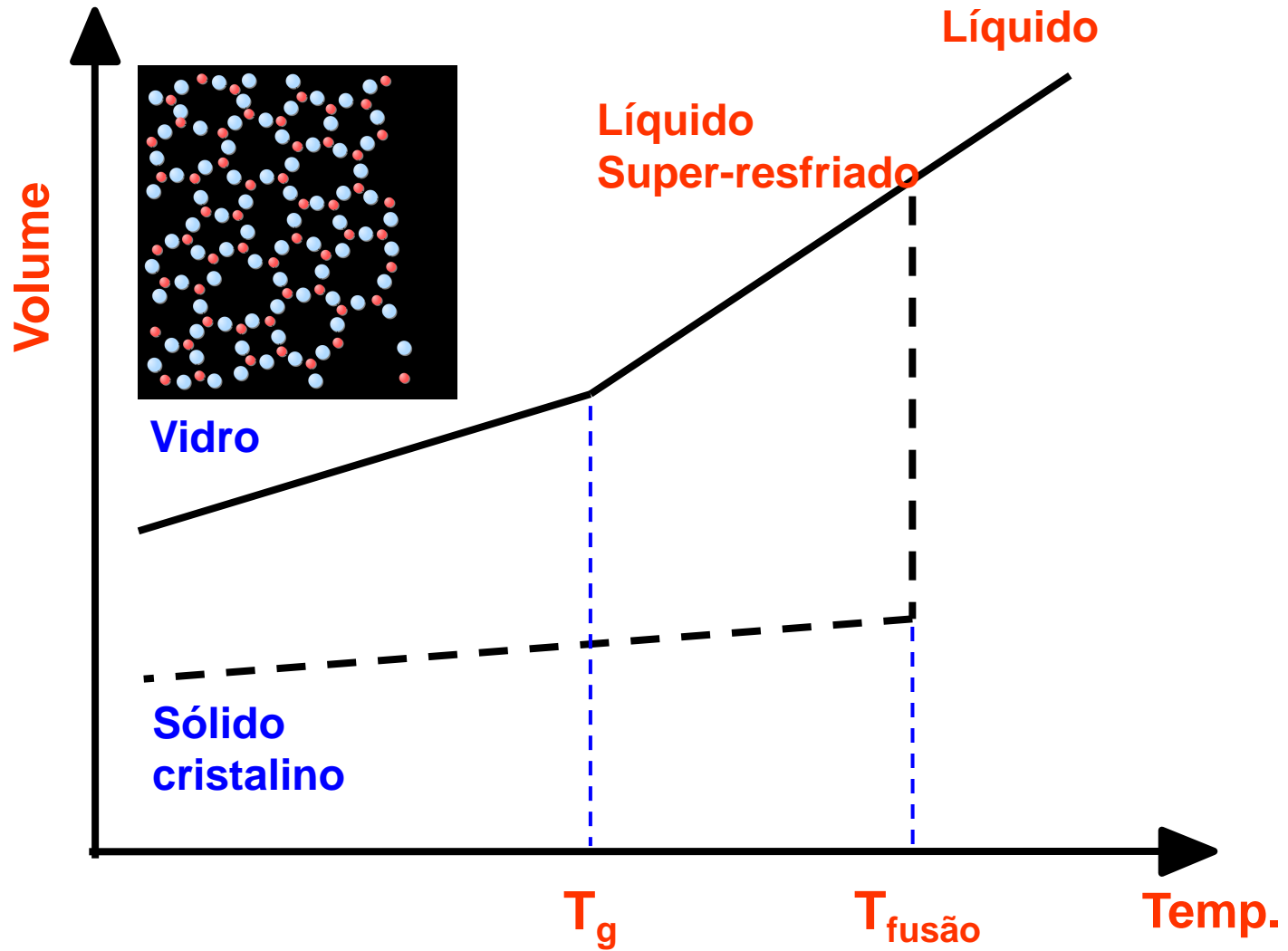
Resfriamento lento de um líquido



Resfriamento rápido de um líquido



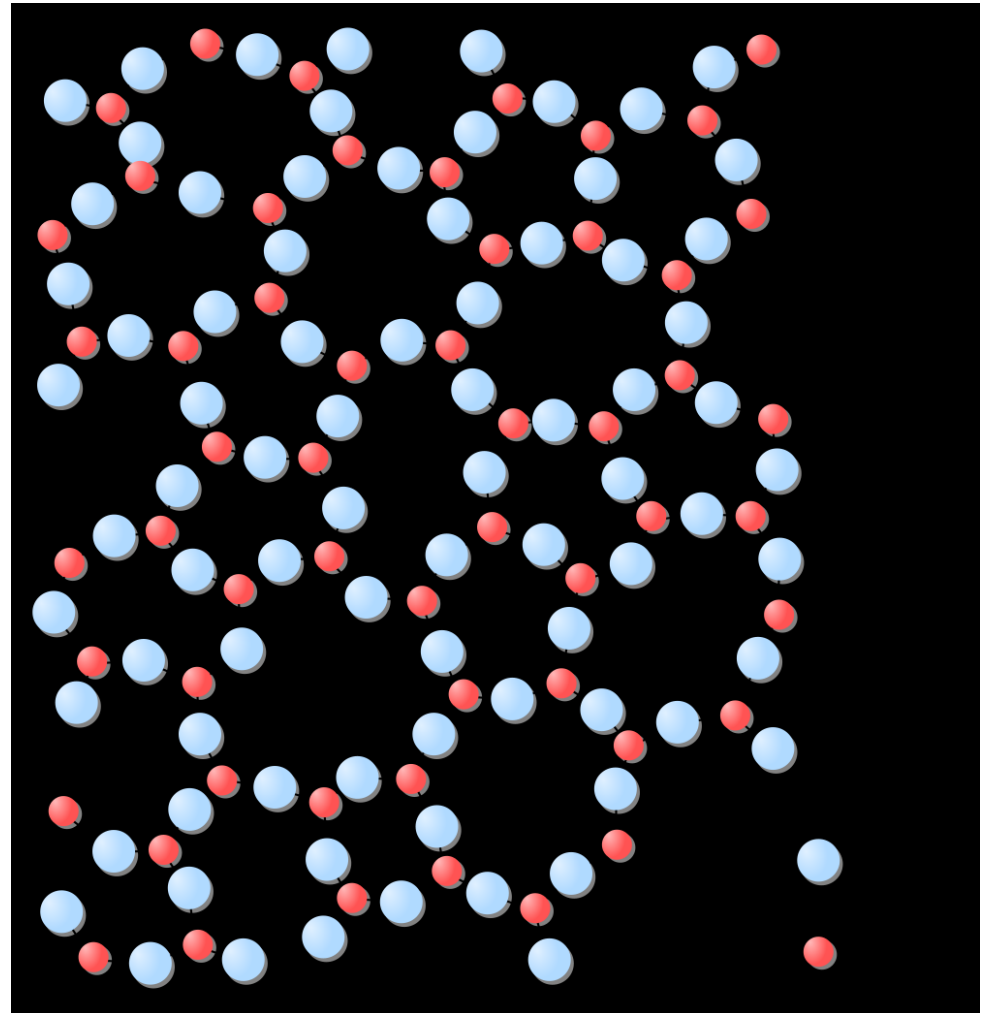
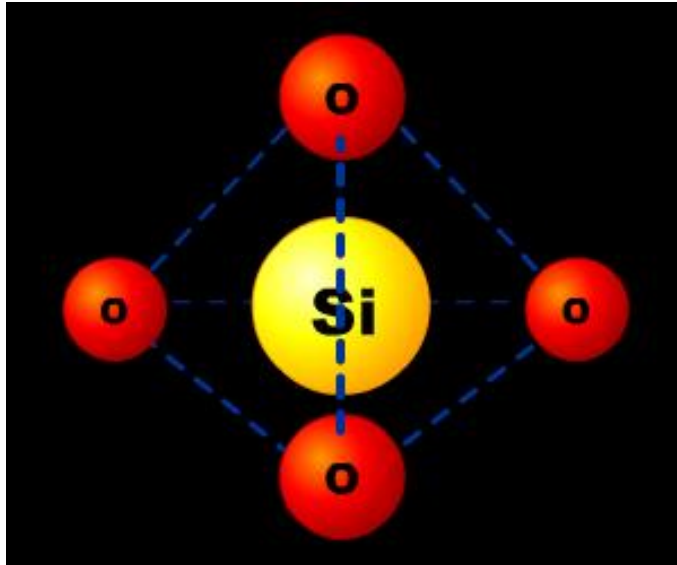
Resfriamento rápido de um líquido



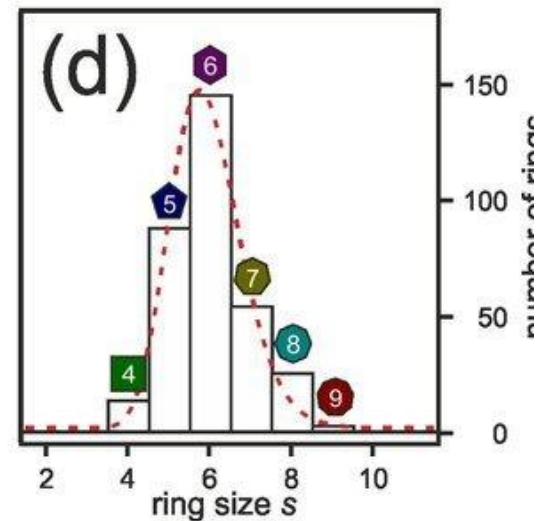
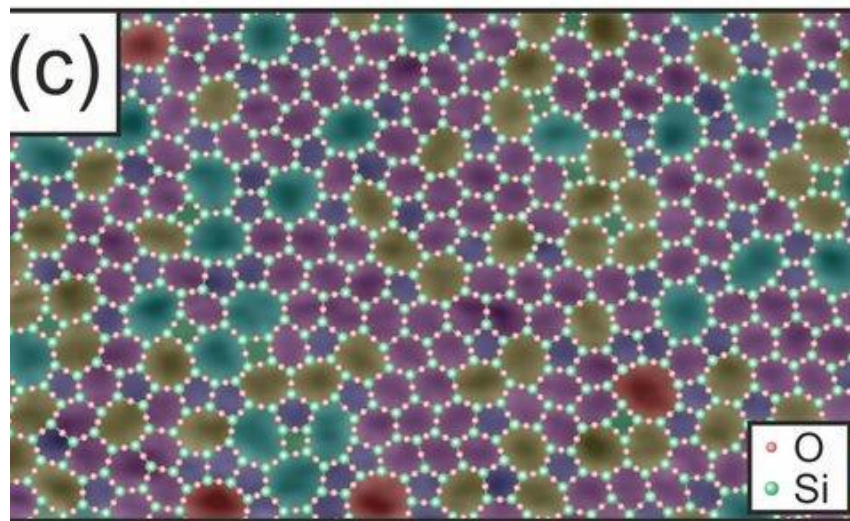
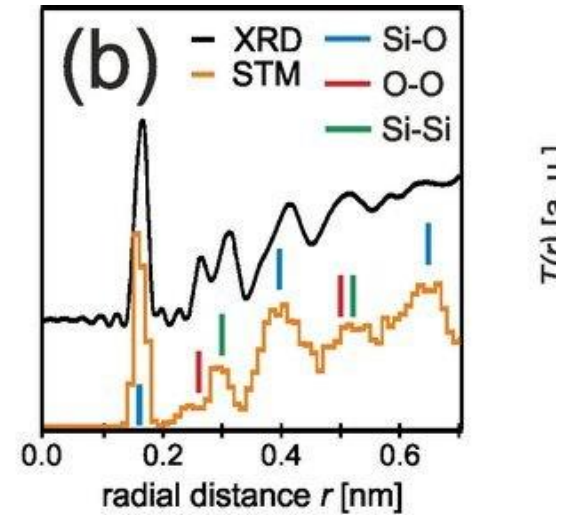
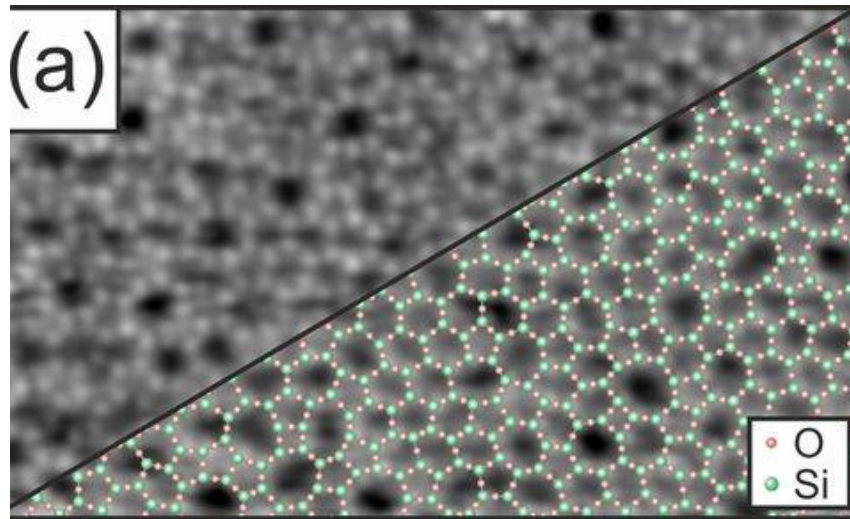
Cristal x Vidro

Vidro de sílica – SiO_2

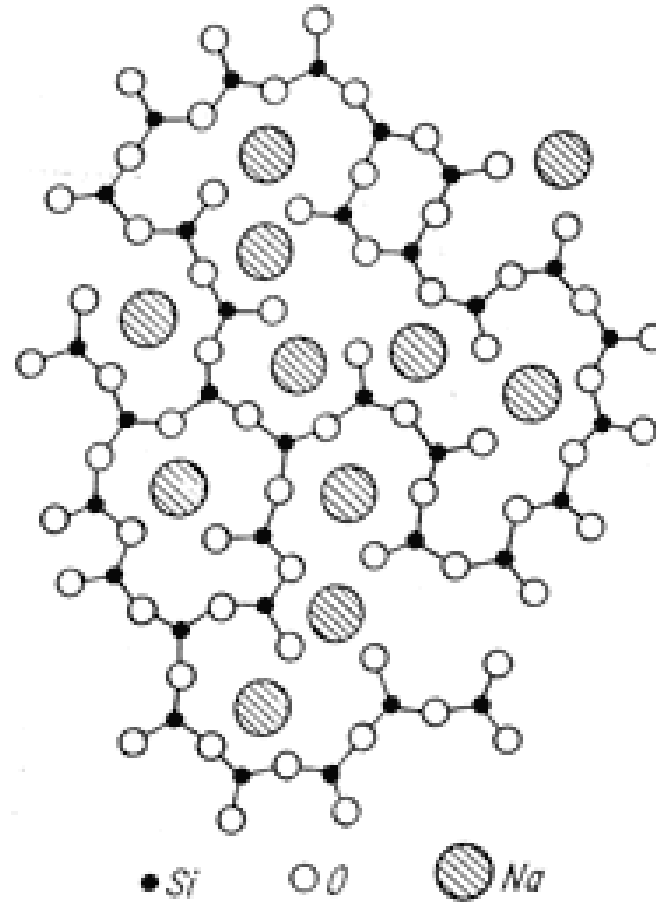
Tetraedro de SiO_2



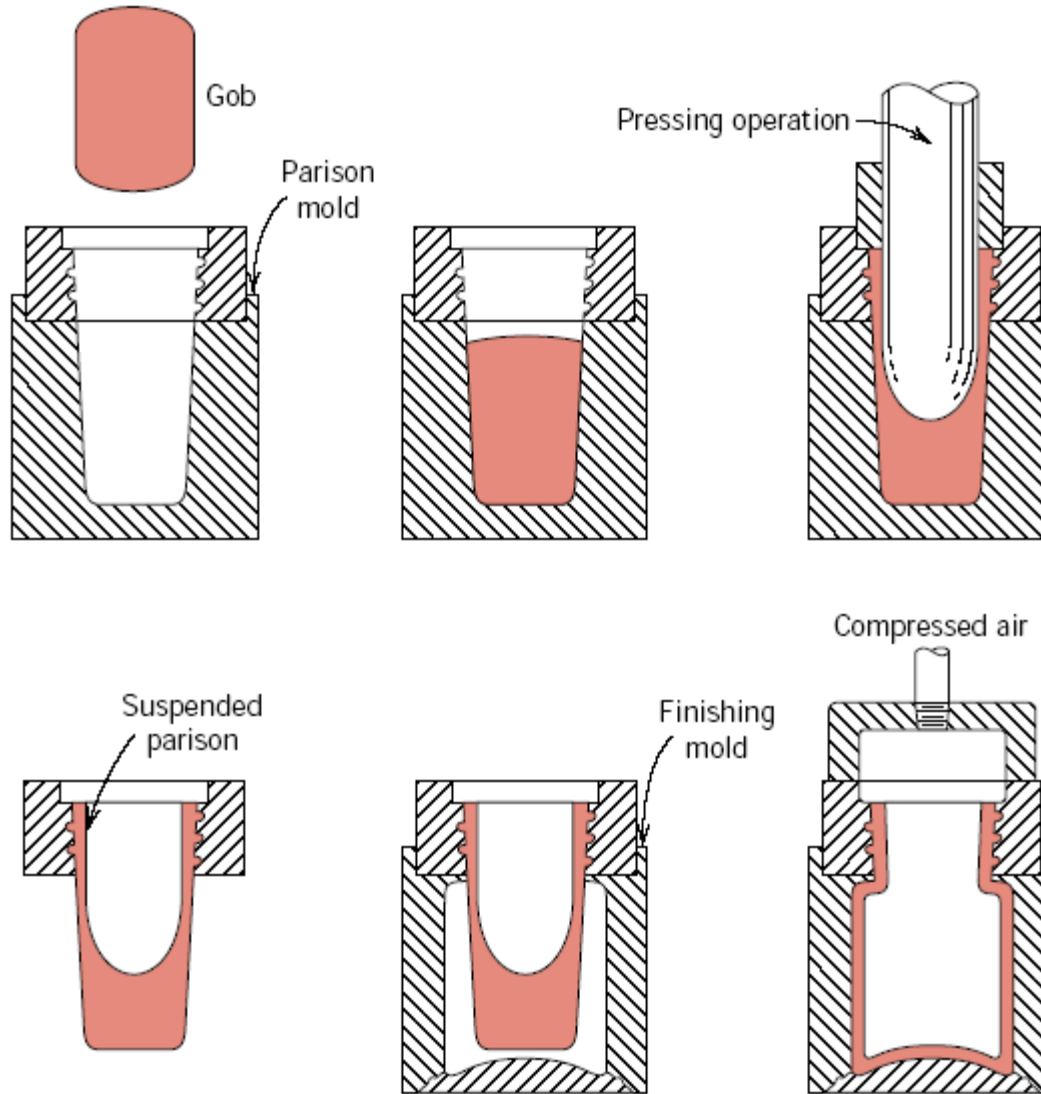
Comprovação experimental



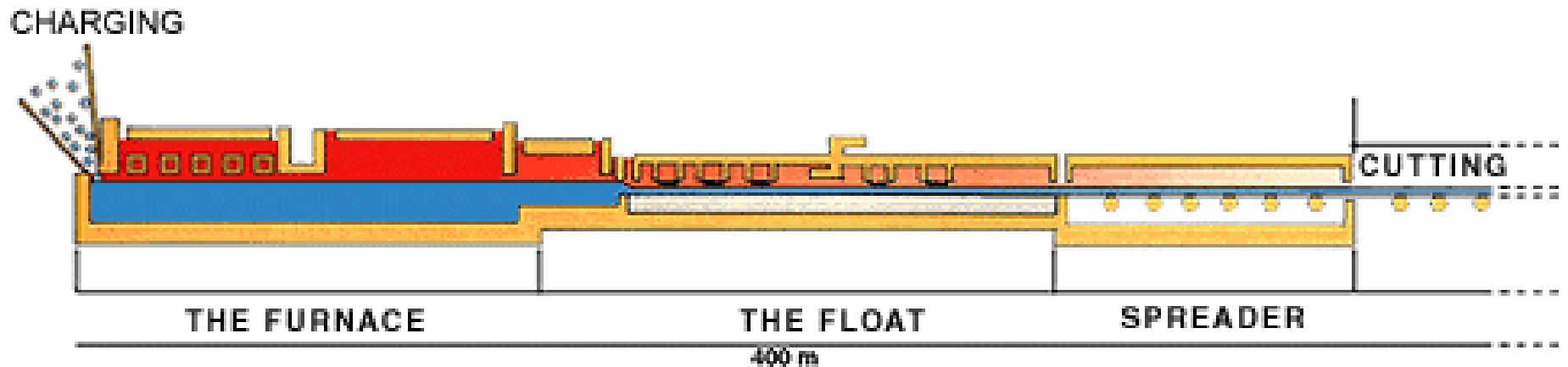
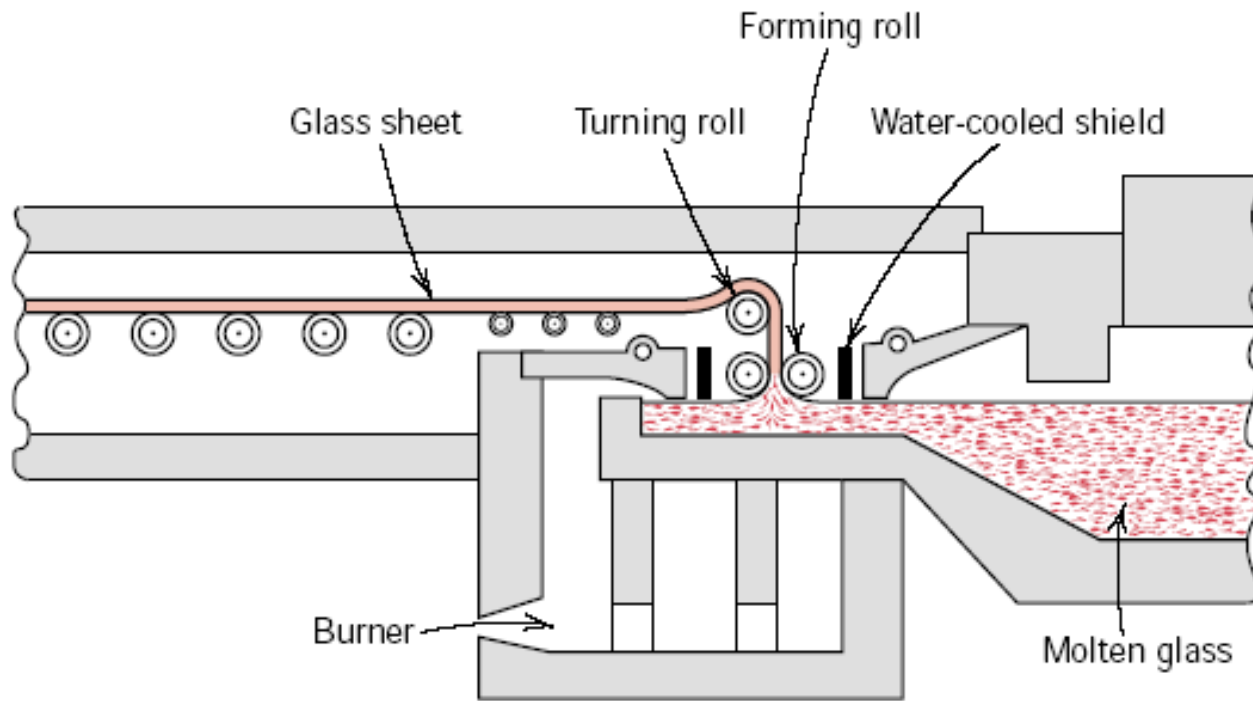
Efeito modificadores



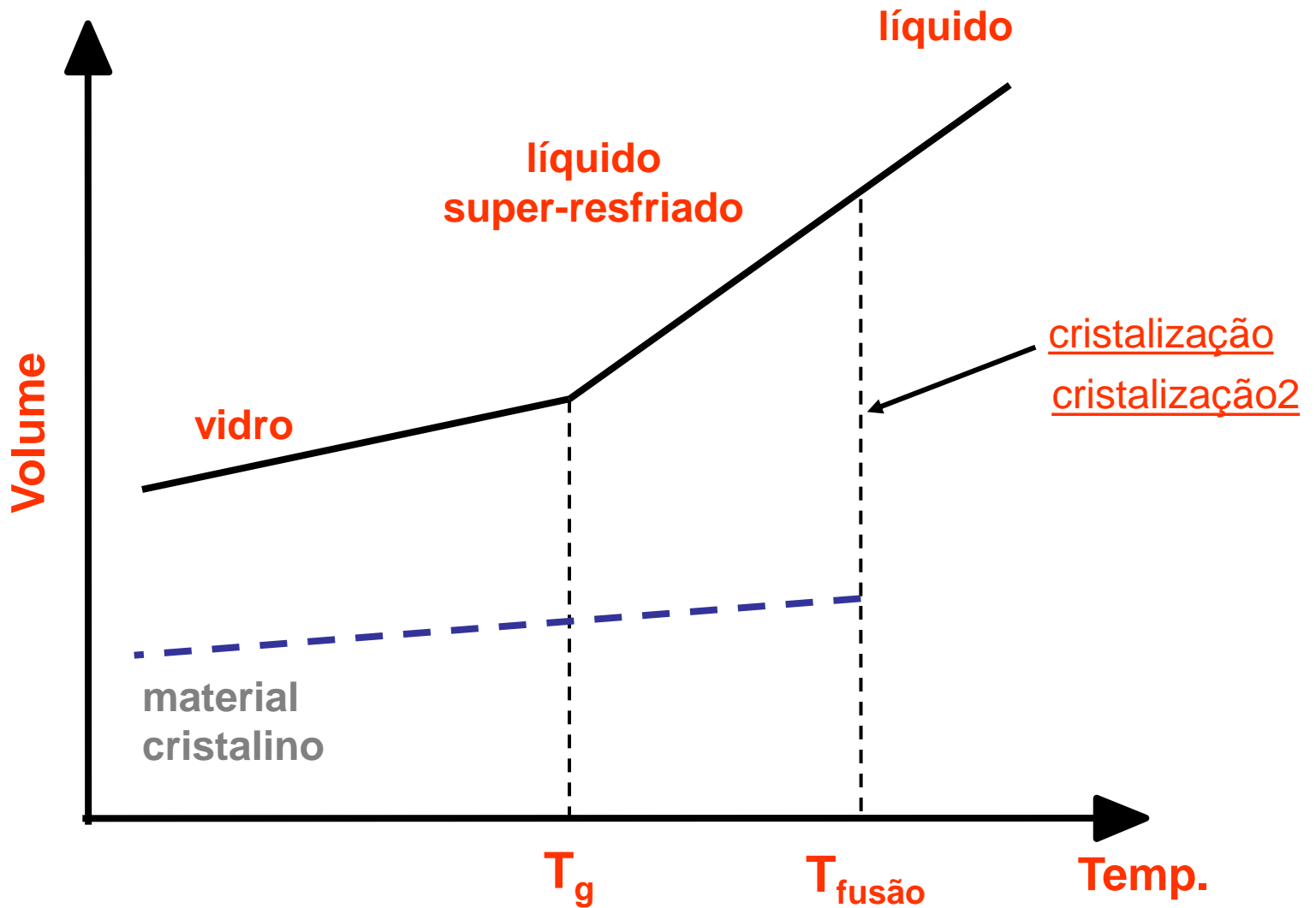
Técnicas de fabricação – vidros



Técnicas de fabricação – vidros



Transição Vítrea – T_g



Relaxação estrutural e temperatura fictícia

- Relaxação estrutural – a mudança no valor de qualquer propriedade com o tempo, após uma perturbação qualquer.
- Temperatura fictícia – temperatura que corresponde ao equilíbrio da estrutura congelada do vidro.

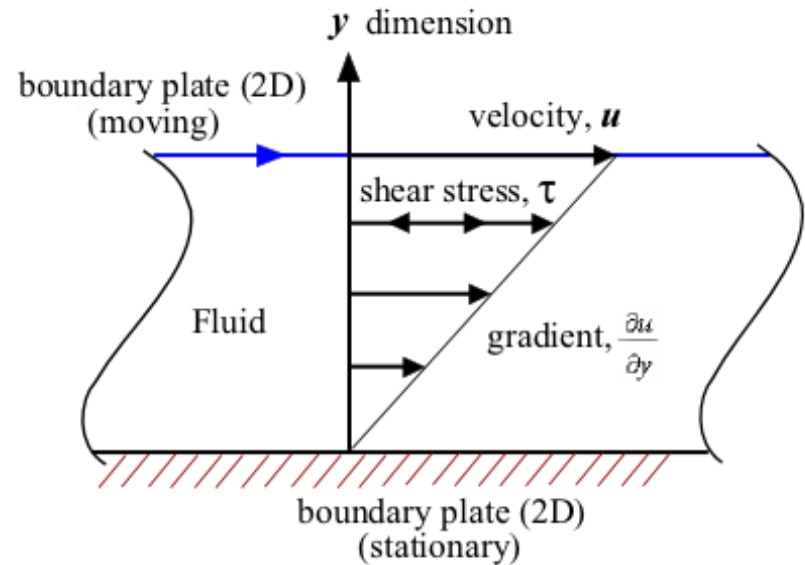
Na lousa!

Características dos vidros

- Não têm um ponto de fusão (ou liquidus) verdadeiro.
- Isotrópicos – as propriedades são não dependem da direção.
- Viscosidade, coeficiente de expansão térmica, volume específico, índice de refração, etc. variam linearmente com a composição química.

Viscosidade

- Resistência de um líquido à deformação causada por uma tensão cisalhante
- Unidades:
 - Poise (P) (CGS)
 - $\eta_{\text{água}} = 1\text{cP}$
 - Pa.s (SI)
 - $1\text{cP} = 1\text{mPa.s}$
 - $1\text{P} = 10^{-1}\text{Pa.s}$
- Quanto maior a viscosidade, maior a resistência ao escoamento



Viscosidade

- Uma das propriedades mais importantes do ponto de vista do processo de fabricação de vidros
- Muda dramaticamente com a mudança da temperatura
- Pode variar 20 ordens de magnitude
- A viscosidade da água a 20 °C é muito próxima de 1 centipoise (1 cP; valor exato: 1,002 cP)

Viscosidade de líquidos (a 20 °C) (Pa·s)

- álcool etílico $0,248 \times 10^{-3}$
- acetona $0,326 \times 10^{-3}$
- metanol $0,597 \times 10^{-3}$
- álcool propílico $2,256 \times 10^{-3}$
- benzeno $0,64 \times 10^{-3}$
- **água** **$1,0030 \times 10^{-3}$**
- nitrobenzeno $2,0 \times 10^{-3}$
- mercúrio $17,0 \times 10^{-3}$
- ácido sulfúrico 30×10^{-3}
- óleo de oliva 81×10^{-3}
- óleo de rícino 0,985
- glicerol 1,485
- polímero derretido..... 10^3
- piche 10^7
- vidro 10^{40}

A viscosidade determina

- as condições de fusão
- a homogeneidade do vidro
- o regime de temperaturas para
 - Conformação
 - Recozimento
 - Têmpera térmica
- a máxima temperatura para se evitar a devitrificação

Um processo industrial pode ser associado ao seu gradiente de velocidade

Processo	Gradiente de velocidade (s ⁻¹)
Moldagem	0,1-10
Extrusão	10 ² -10 ³
Estiramento de fibra	10 ⁴ -10 ⁶

Pontos de viscosidade importantes para os fabricantes de vidro

Tab. 6.2 Reference temperatures and viscosity regime⁸⁾.

Practical melting temperature is not the melting temperature associated with the crystal–liquid phase transition (Chapter 5) but the working temperature.

Reference temperature	Viscosity (Pa s)
Practical melting temperature	1–10
Working point	10^3
Littleton softening point	$10^{6.6}$
Annealing point	$\sim 10^{12}$
Glass transition	$\sim 10^{12} - 10^{12.5}$
Strain point	$\sim 10^{13.5}$

- **Pontos de viscosidade importantes para os fabricantes de vidro**

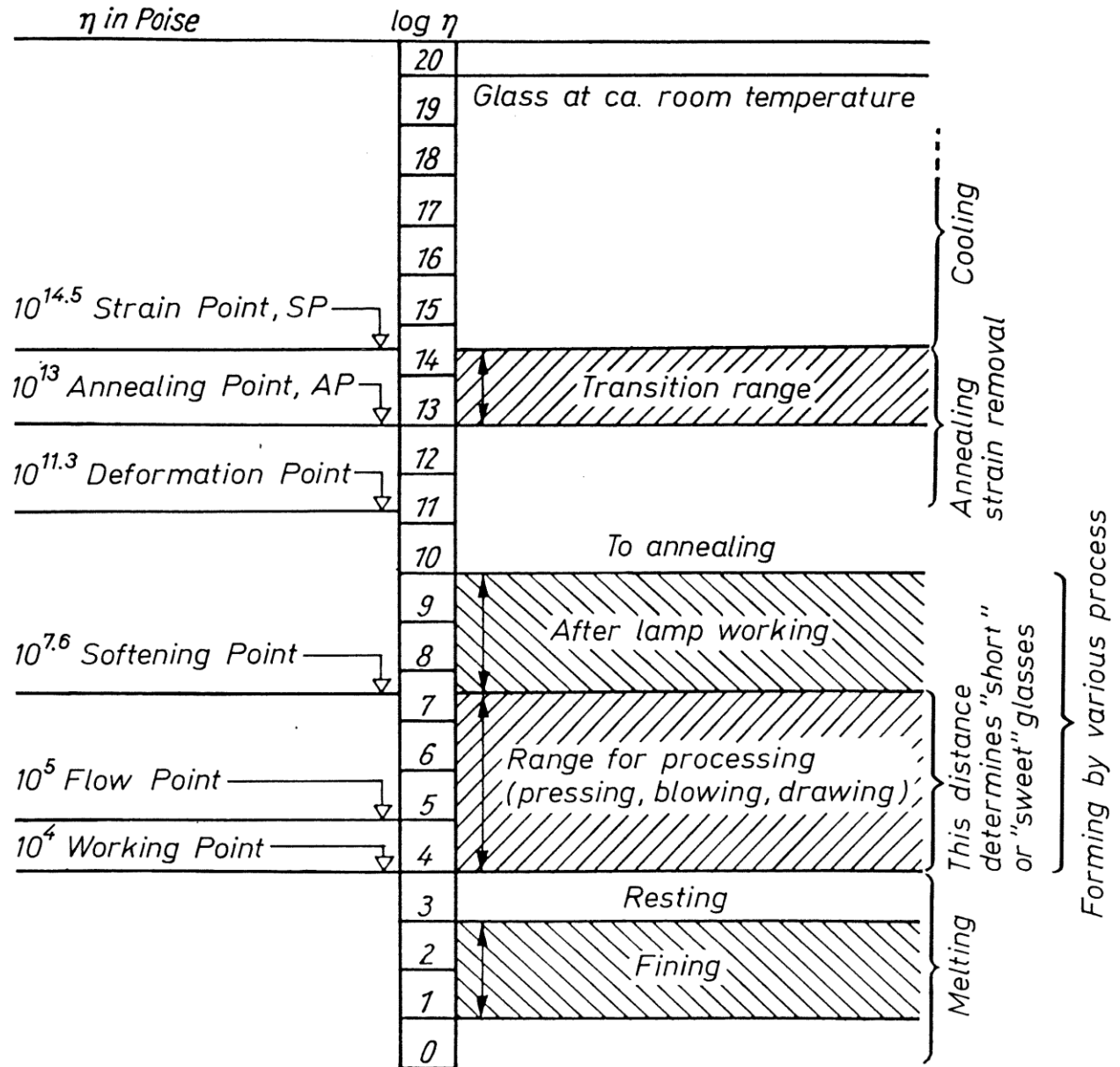


Fig. 2.9. Fix points in the entire viscosity range (after Lindig [20]). 1 poise = 10^{-1} Pa·s

Métodos de medida de viscosidade

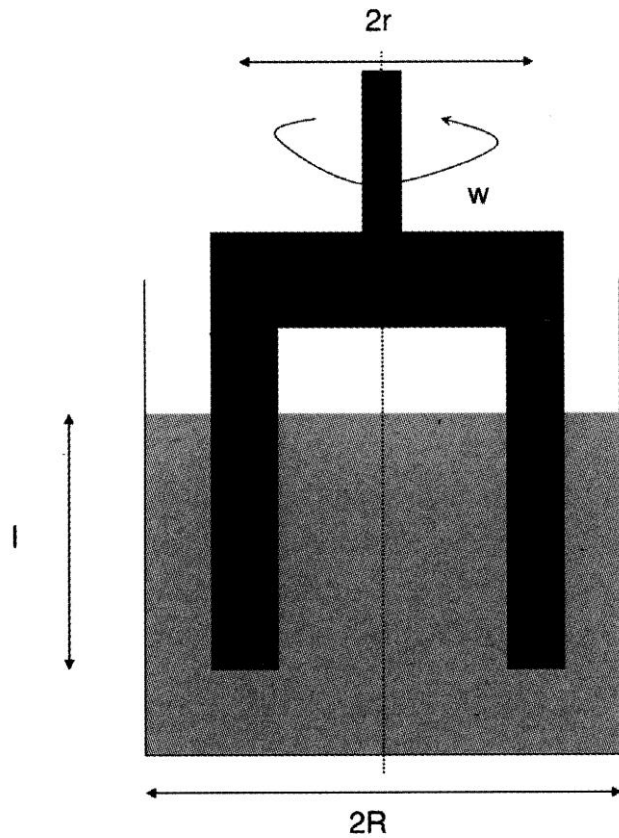


Fig. 6.3 Rotation viscometer principle.

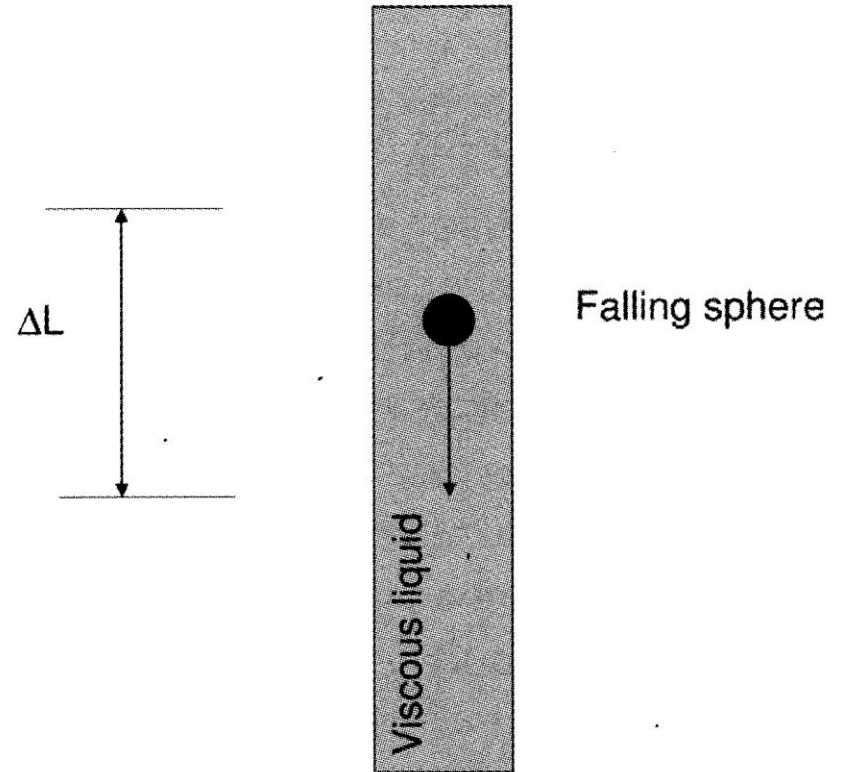


Fig. 6.4 Falling sphere viscometer.

Métodos de medida de viscosidade

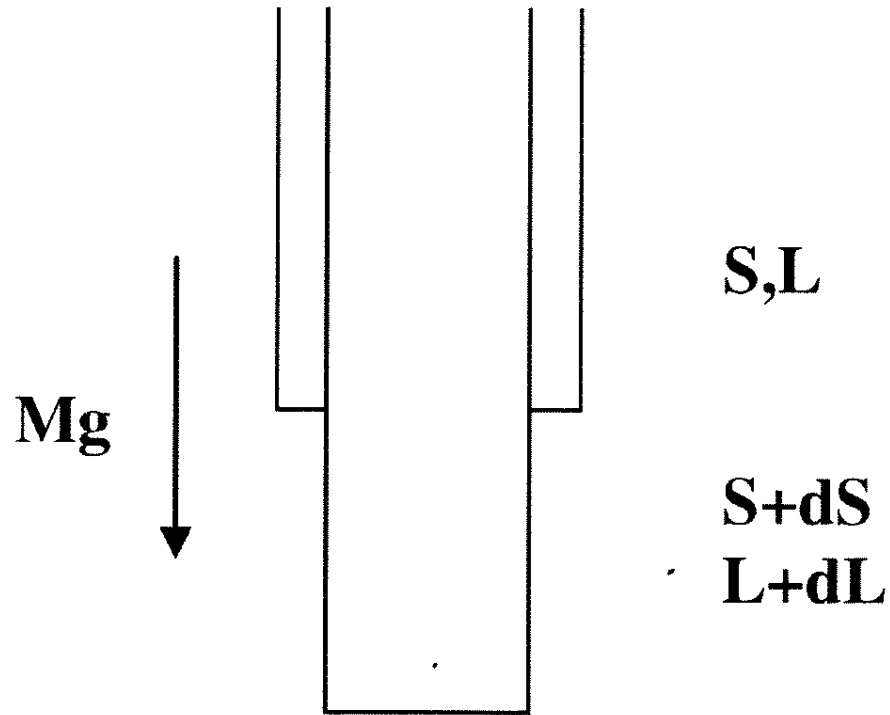


Fig. 6.5 Fibre elongation viscometer principle.

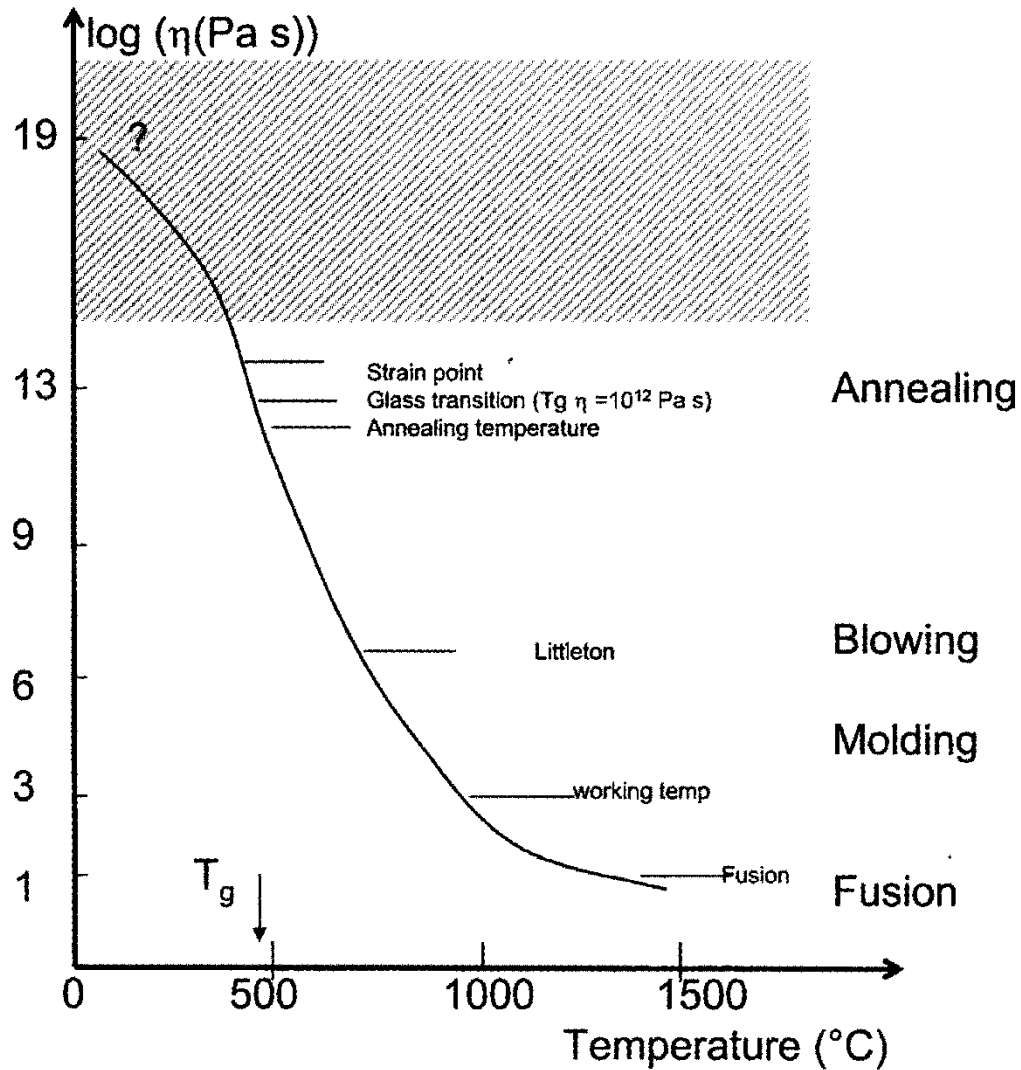


Fig. 6.6 Viscosity as a function of temperature below and over transition temperature (according to Zarzycki, 1982).

Tipos de vidros

Table 13.10 Compositions and Characteristics of Some of the Common Commercial Glasses

<i>Glass Type</i>	<i>Composition (wt%)</i>						<i>Characteristics and Applications</i>
	<i>SiO₂</i>	<i>Na₂O</i>	<i>CaO</i>	<i>Al₂O₃</i>	<i>B₂O₃</i>	<i>Other</i>	
Fused silica	>99.5						High melting temperature, very low coefficient of expansion (shock resistant)
96% Silica (Vycor)	96				4		Thermally shock and chemically resistant—laboratory ware
Borosilicate (Pyrex)	81	3.5		2.5	13		Thermally shock and chemically resistant—ovenware
Container (soda–lime)	74	16	5	1		4MgO	Low melting temperature, easily worked, also durable
Fiberglass	55		16	15	10	4MgO	Easily drawn into fibers—glass–resin composites
Optical flint	54	1				37PbO, 8K ₂ O	High density and high index of refraction—optical lenses
Glass–ceramic (Pyroceram)	43.5	14		30	5.5	6.5TiO ₂ , 0.5As ₂ O ₃	Easily fabricated; strong; resists thermal shock—ovenware

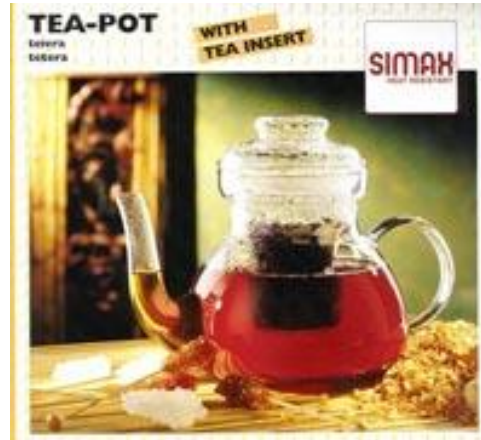
Vidro soda-cal-sílica



Vidros ao chumbo (“*cristais*”)



Vidros borosilicatos



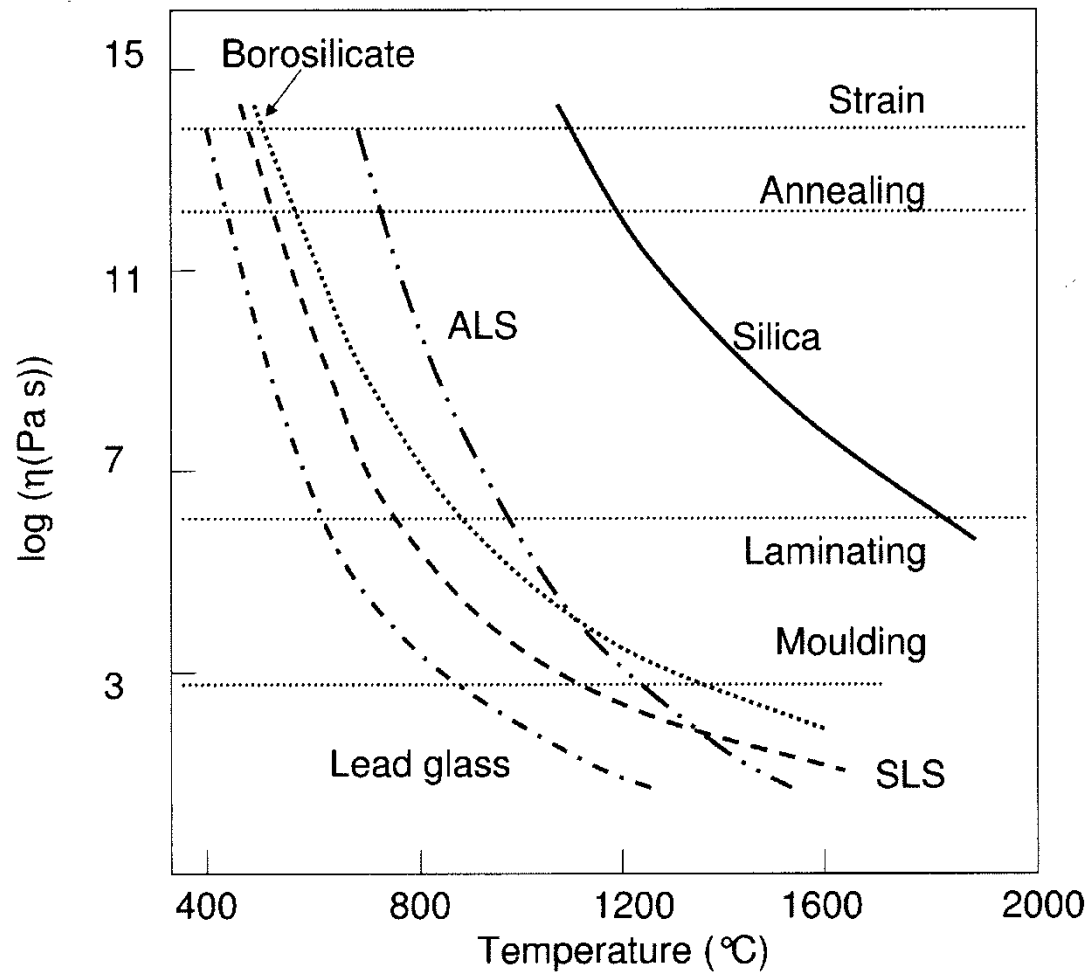
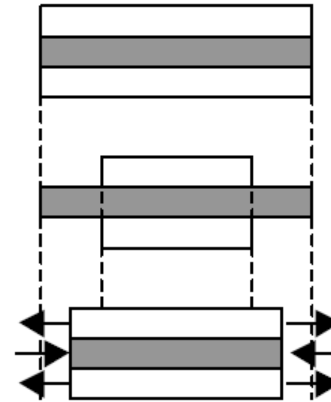
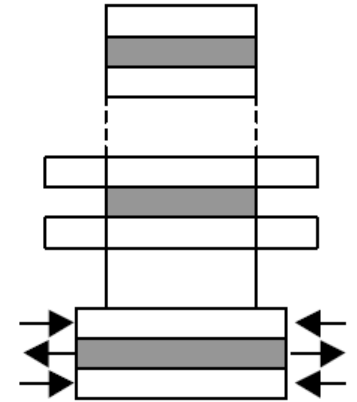


Fig. 6.2 Viscosity variations with temperature and composition (SLS, soda-lime-silica glass; ALS, aluminosilicate glass; according to Zarzycki, 1982).

Tensões residuais vs. Recozimento

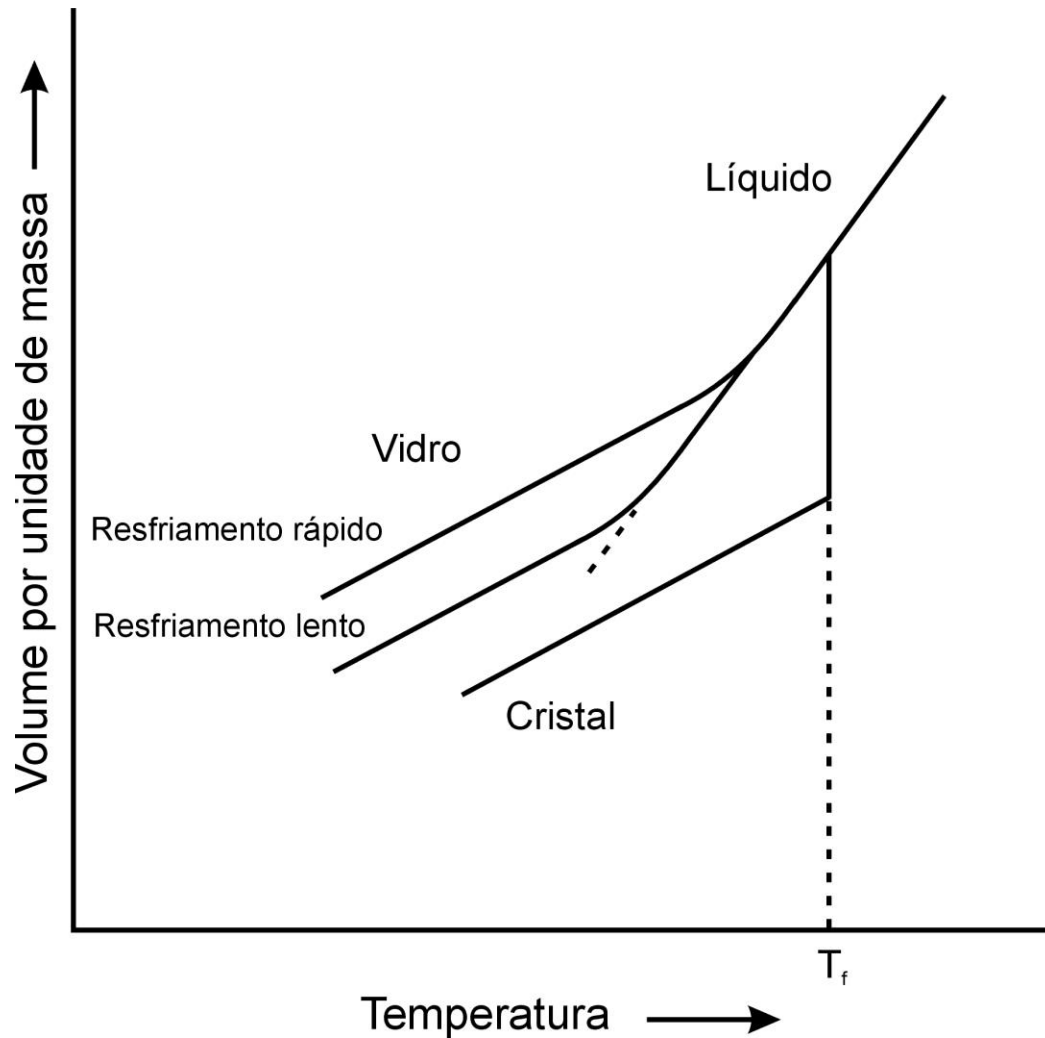


resfriamento



aquecimento

Dependência da taxa de resfriamento



Recozimento

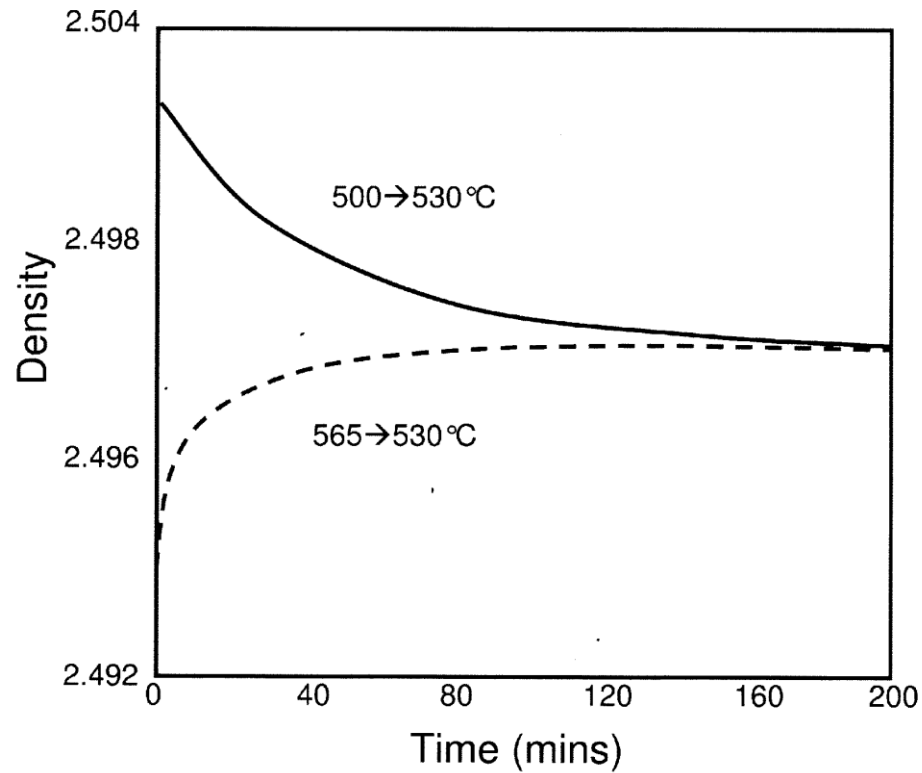


Fig. 6.29 Structural relaxation of two pieces of glass stabilized at two different temperatures (according to Moynihan, 1996).

Recozimento

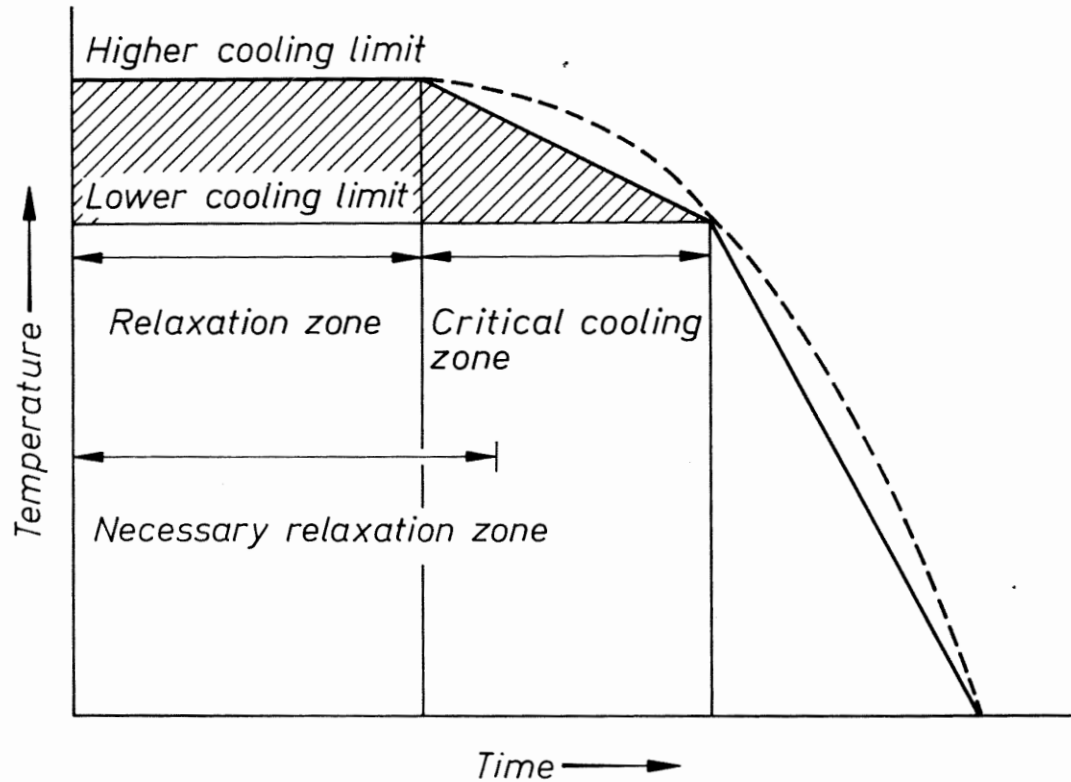


Fig. 2.10. Schematic representation of the theoretically calculated and the practically adjustable cooling curve of a glass according to Günther and Meister [22]. --- theoretical cooling curve; . . . experimental cooling curve

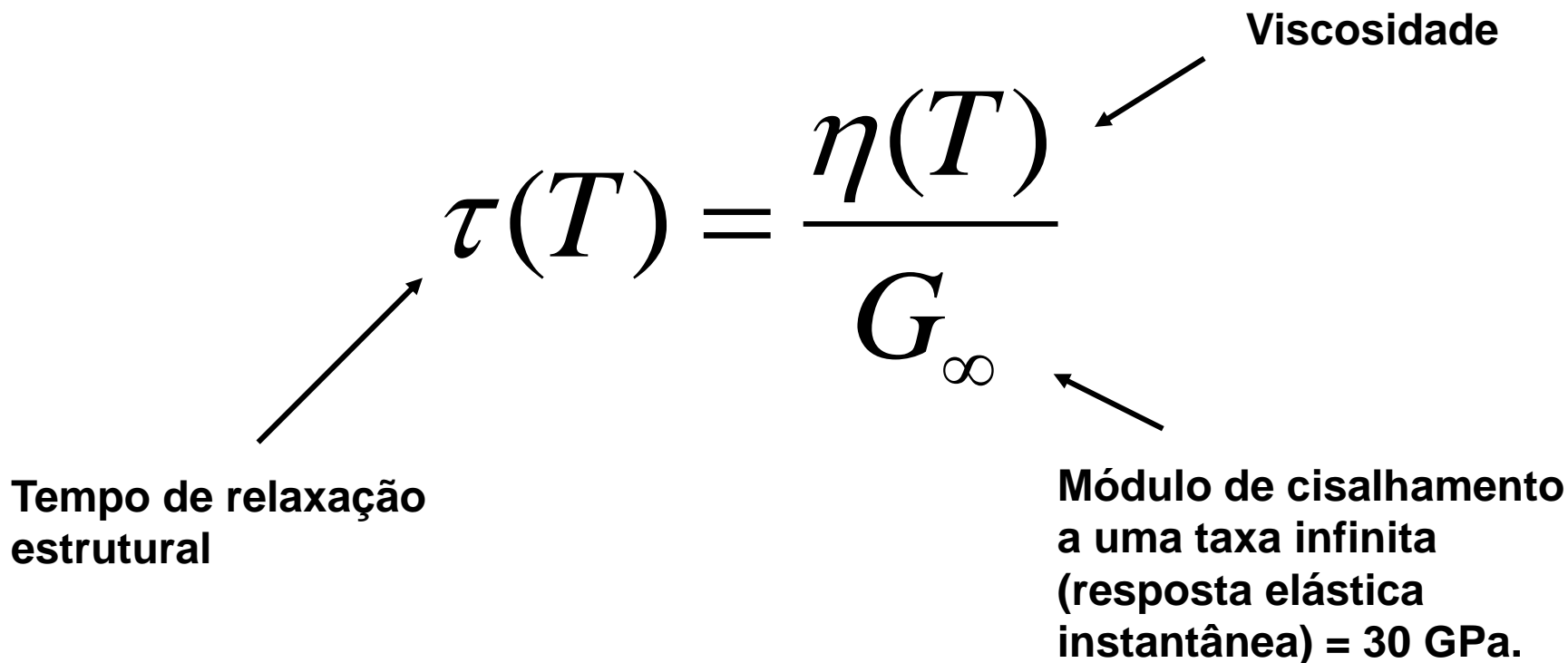
Viscosidade versus Tempo de relaxação estrutural

$$\tau(T) = \frac{\eta(T)}{G_{\infty}}$$

Tempo de relaxação estrutural

Viscosidade

Módulo de cisalhamento a uma taxa infinita (resposta elástica instantânea) = 30 GPa.

The diagram features the equation $\tau(T) = \frac{\eta(T)}{G_{\infty}}$ centered on the page. Three arrows point from text labels to parts of the equation: one from the bottom-left to the symbol $\tau(T)$, one from the top-right to the numerator $\eta(T)$, and one from the bottom-right to the denominator G_{∞} . The labels are: 'Tempo de relaxação estrutural' (bottom-left), 'Viscosidade' (top-right), and 'Módulo de cisalhamento a uma taxa infinita (resposta elástica instantânea) = 30 GPa.' (bottom-right).

Viscosidade versus Tempo de relaxação estrutural



Vidros fluem à temperatura ambiente?

$$\tau(T) = \frac{\eta(T)}{G_{\infty}}$$

Em $\eta(T_g) = 10^{12}$ Pa.s

$T_g = 816$ K

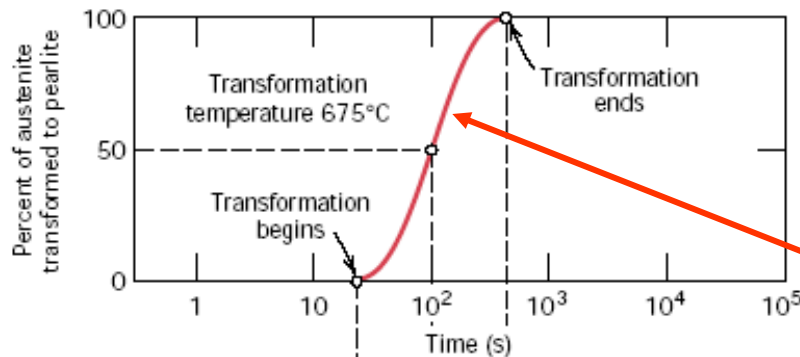
$\tau(T_g) = 2 \times 10^{23}$ anos

Ou seja, muito maior que a unidade do Universo $\sim 10^{10}$ anos!

Zanotto, E. D. "Do cathedral glasses flow?" Am. J. Phys. 66 (1998) 392-395

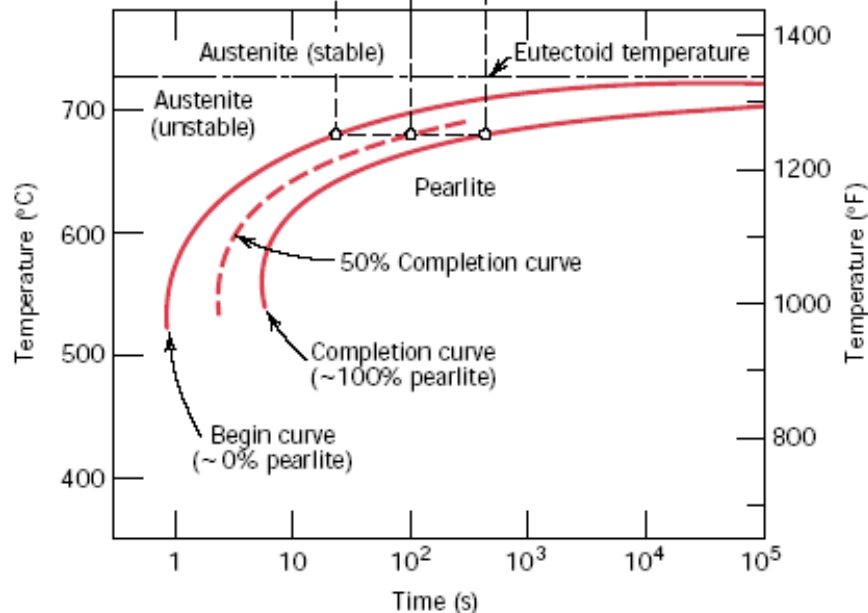
Zanotto, E. D. & Gupta, P. K. "Do cathedral glasses flow?—Additional remarks" 67 (1999) 260-262

A cristalização acima de T_g ocorre a uma dada taxa...



Cinética de transformação de fases de acordo com Johnson, Mehl, Avrami e Kolmogorov:

$$\alpha(t) = 1 - \exp\left[-\frac{4\pi}{3} Iu^3 t^4\right]$$



$\alpha(t)$ = fração volumétrica cristalizada

I = taxa de nucleação

u = taxa de crescimento

t = tempo

Cinéticas calculada versus experimental

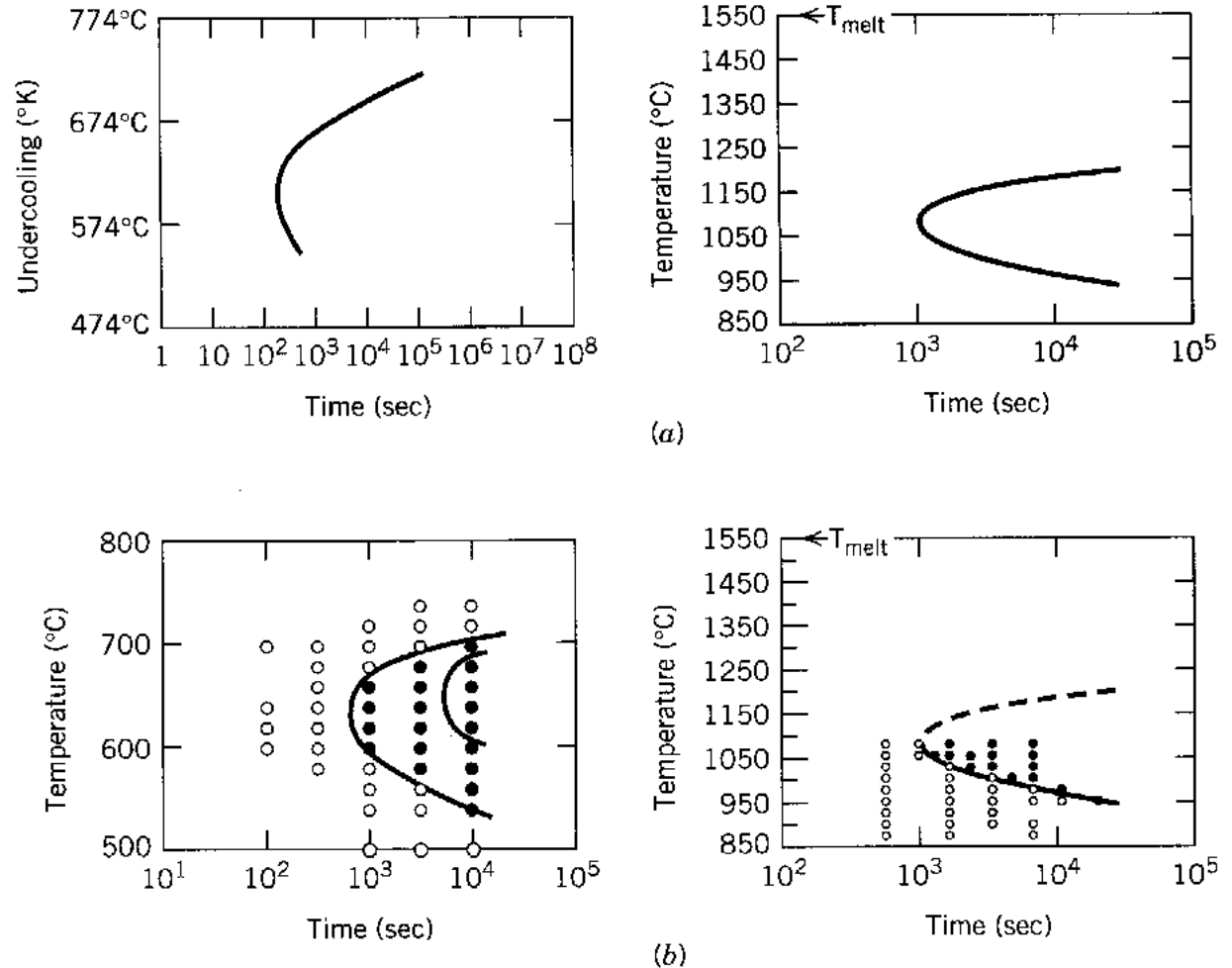


Fig. 5.71 (a) Calculated TTT curves for $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ at $V_c/V = 10^{-6}$ and $\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (anorthite) at $V_c/V = 10^{-3}$. (b) Experimental observations of crystallized (closed symbols) and glassy (open symbols) samples. (From G.S. Meiling and D.R. Uhlmann, *Phys. Chem. Glasses*, **8**, 62 (1967), D. Cranmer, R. Salomaa, H. Yinnon, and D.R. Uhlmann, *J. Non-Cryst. Solids*, **45**, 127, 1981, and H. Yinnon and D.R. Uhlmann, in *Glass: Science and Technology*, Vol. 1, D.R. Uhlmann and N.J. Kreidl, Editors, Academic Press, 1983.)

Critério para formação de vidros

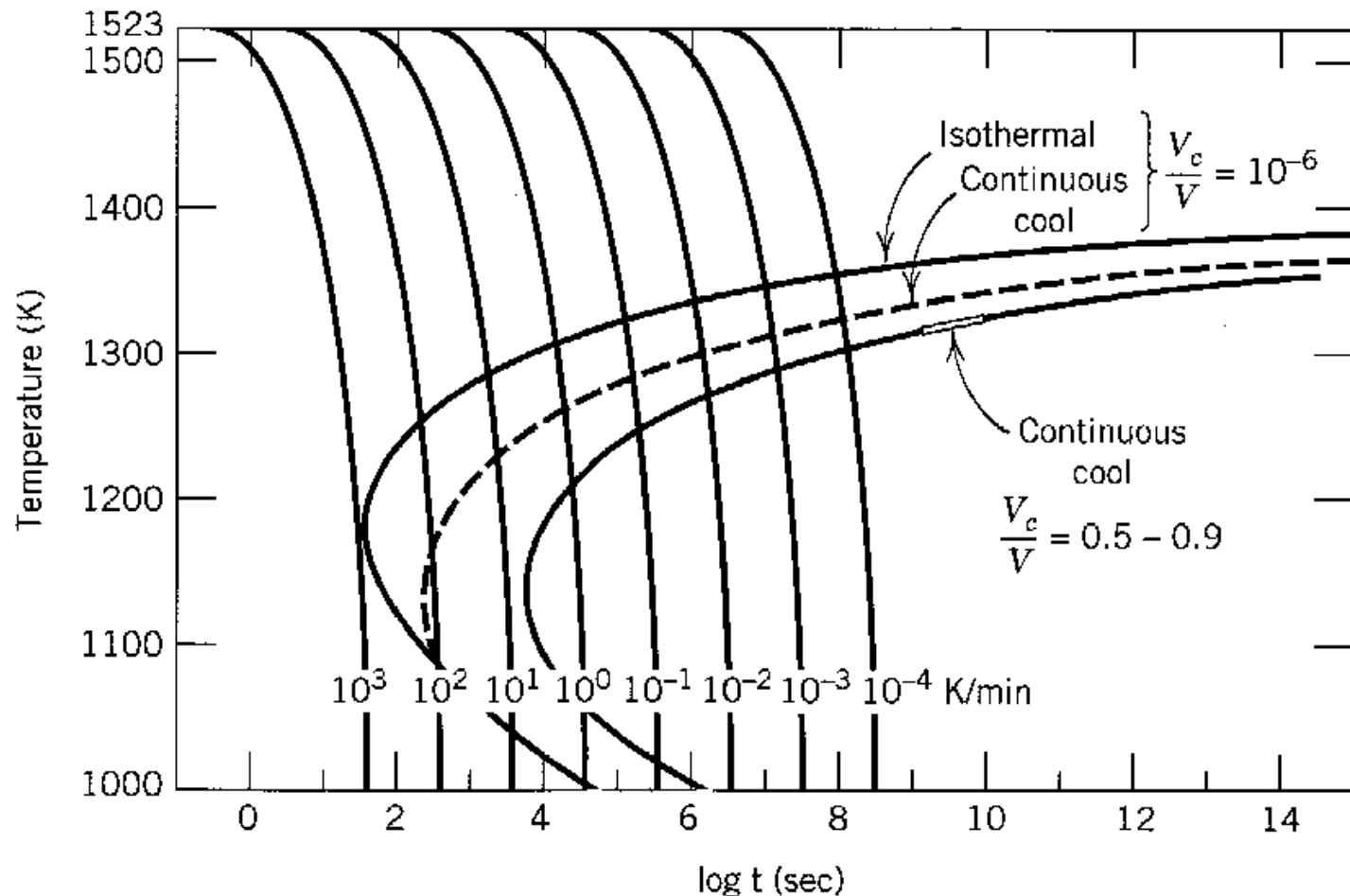
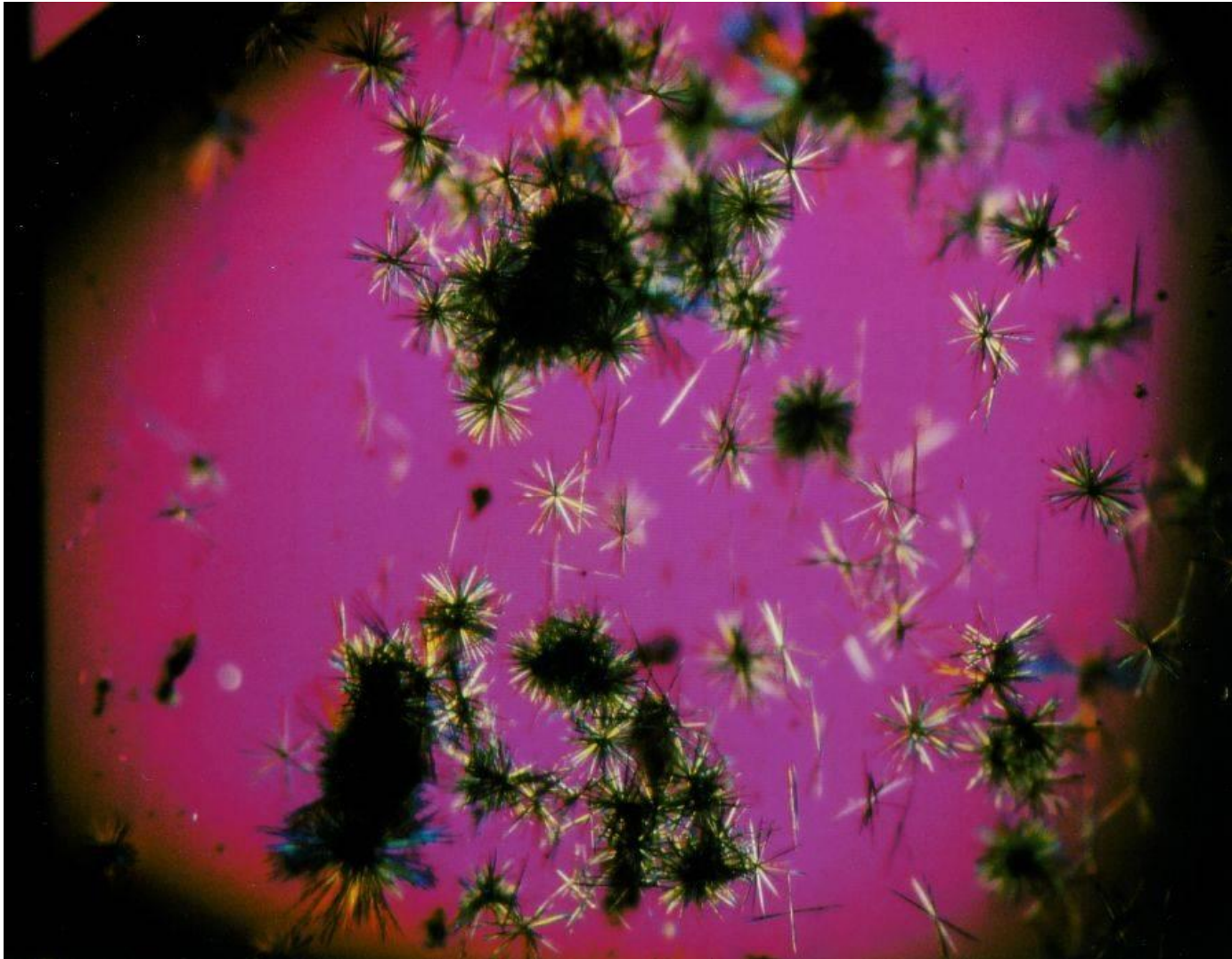
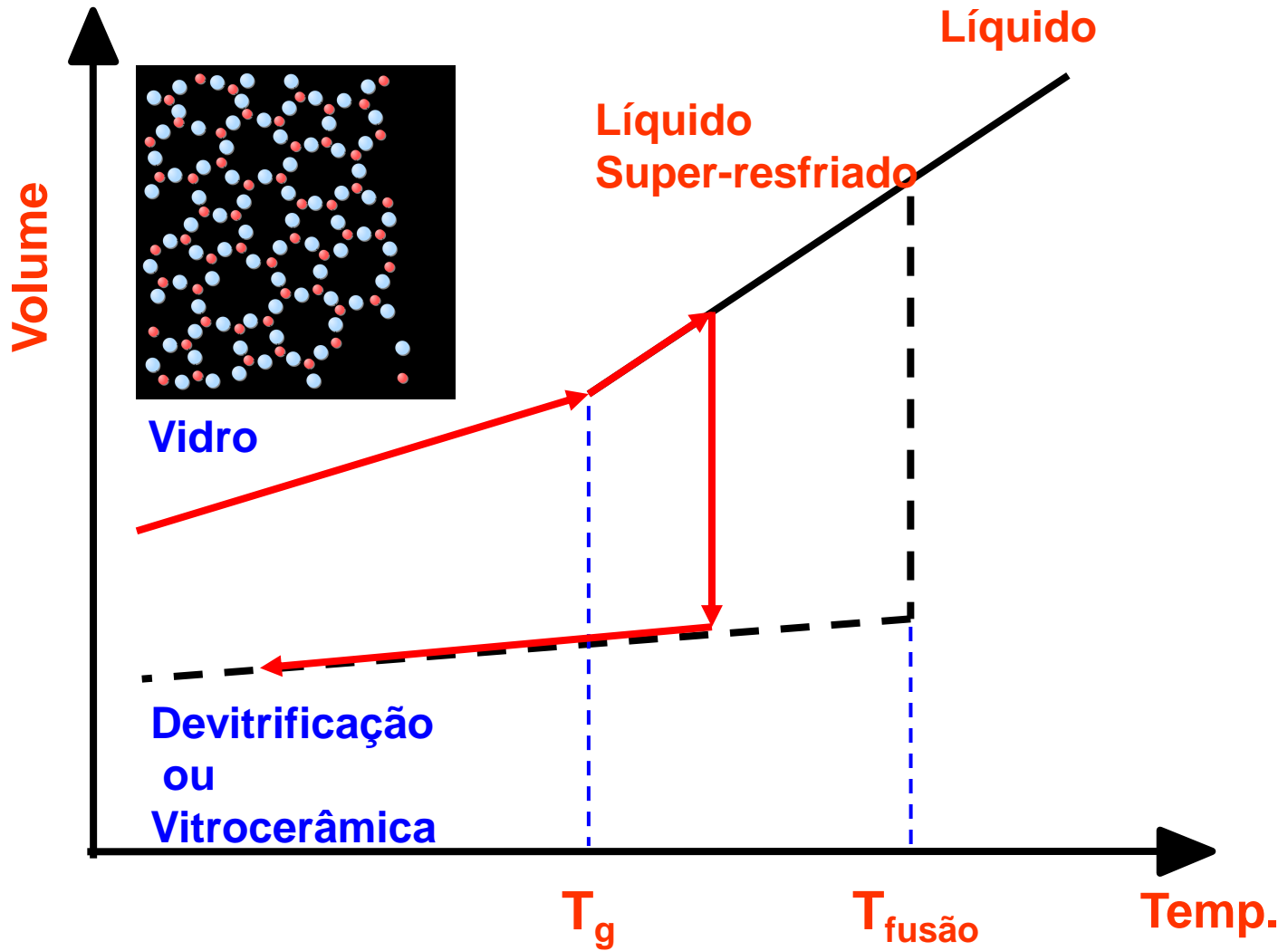


Fig. 5.72 Isothermal and constant-rate cooling TTT curves corresponding to $V_c/V = 10^{-6}$ for lunar glass. (From H. Yinnon and D.R. Uhlmann, in *Glass: Science and Technology*, Vol. 1, D.R. Uhlmann and N.J. Kreidl, Editors, Academic Press, 1983.)

Devitrificação (cristalização descontrolada)



Cristalização do vidro



Vitrocerâmicas

- Cerâmicas obtidas a partir da cristalização controlada de vidros
- Nucleação e crescimento

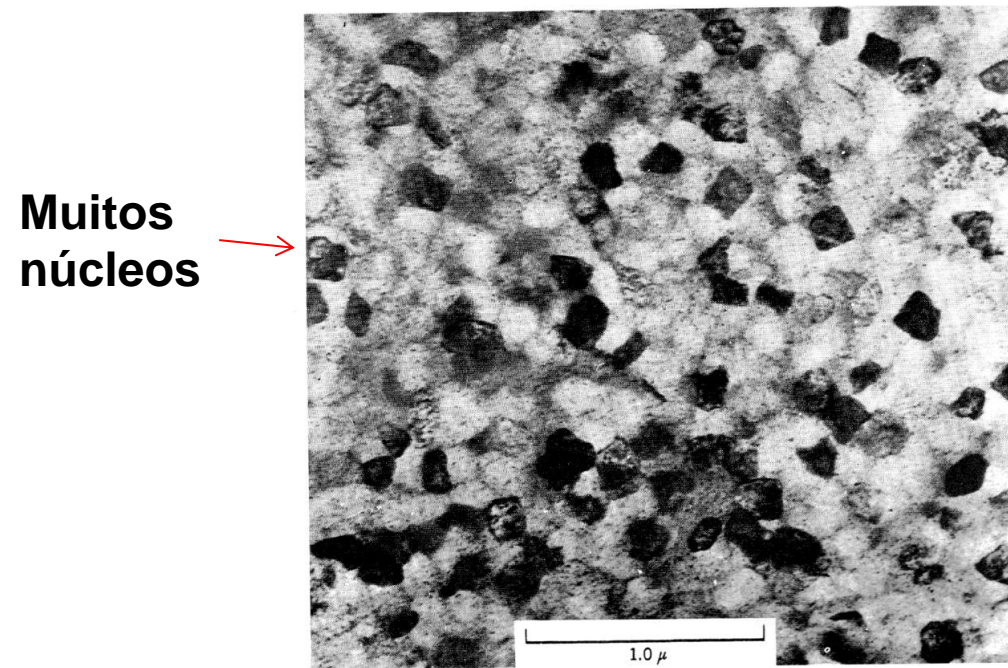


Fig. 5.76 (a) Microstructure in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass ceramic held at 775°C for 2 h, before heating to 975°C for 2 min.

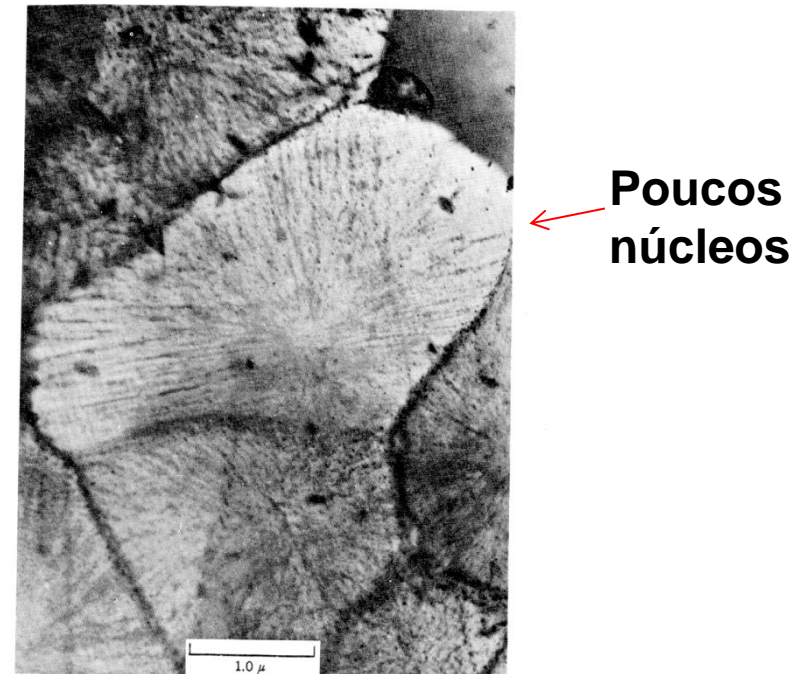
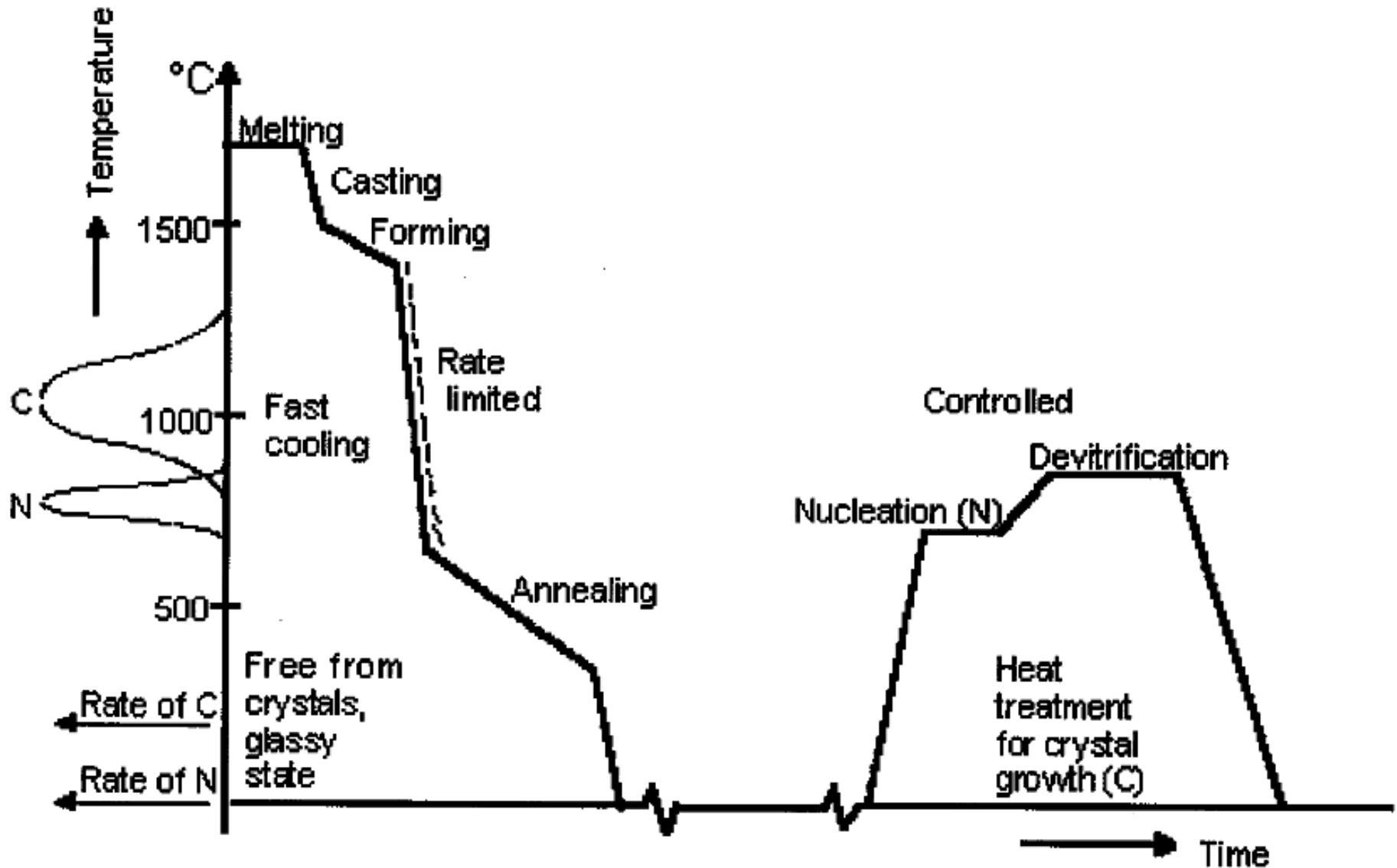
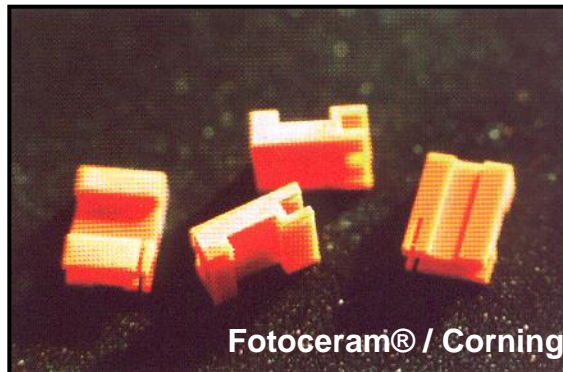
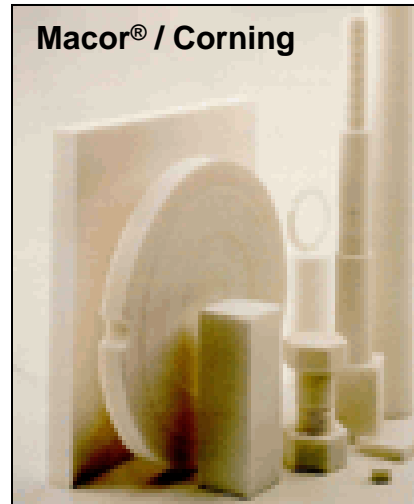


Fig. 5.76 (b) Identical composition heated rapidly to 875°C and held for 25 min. (From P.E. Doherty in R.M. Fulrath and J.A. Pask, Eds., *Ceramic Microstructures*, John Wiley and Sons, New York, 1968, pp. 161-185.)

E se controlarmos a cristalização...



Exemplos de Vitrocerâmicas



β -Quartz_{SS} – (Li,R)O.Al₂O₃.nSiO₂ onde R = Mg²⁺, Zn²⁺ e n = 2 a 10

- Vision®
- Zerodur®, Ceram® e Robax ®
- Narumi® e Neoceram®
- Keraglas® e Eclair ®

Corning – EUA

Schott – Alemanha

NEG – Japão

Eutokera – Corning/St. Gobain



VLT telescope in Chile (8.2 m mirrors with adaptive optics)

Dr. Mark J. Davis



Mirror fabrication
in Mainz, Germany

(www.eso.org)

On the road to Cerro
Paranal, Chile



Neoparies™ - Nippon Electric Glass Co.,Ltd.



Clínica Kaneko - Tóquio (Japão)

Airside Terminal A
Tampa International Airport, U.S.

