Introduction to glass science and technology, 2° ed., J. E. Shelby, The Royal Society of Chemistry, 2005 – Ch. 2

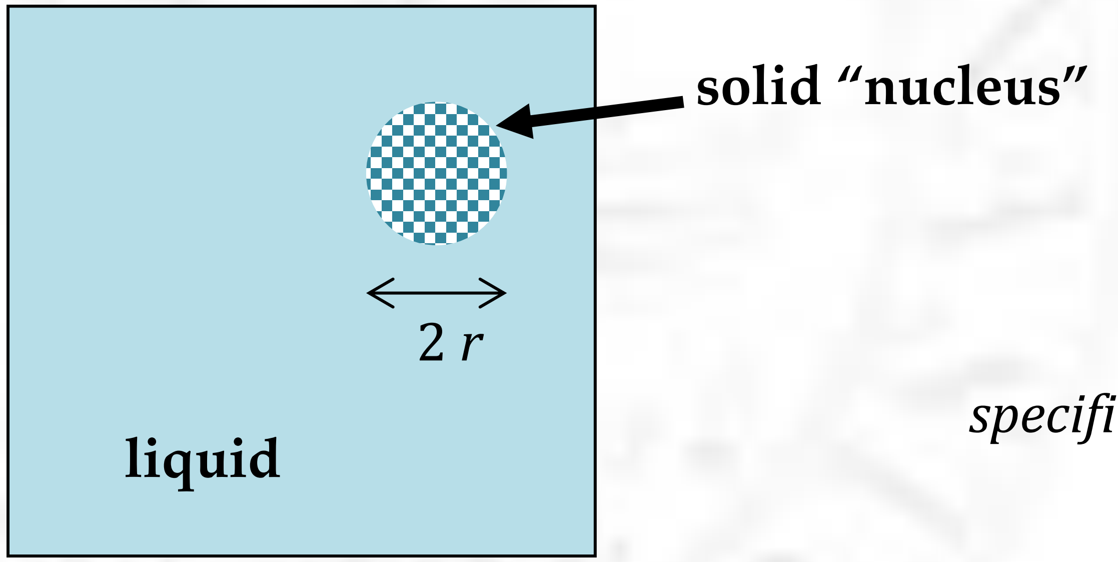
Genesis of glass: *kinetic features*

Solidification: at $T < T_m$ $\Delta G_{solidif} < 0$

nucleation + growth ← *simultaneous movement of atoms* $\Delta S_{solidif} << 0$ *!!*

A. Nucleation

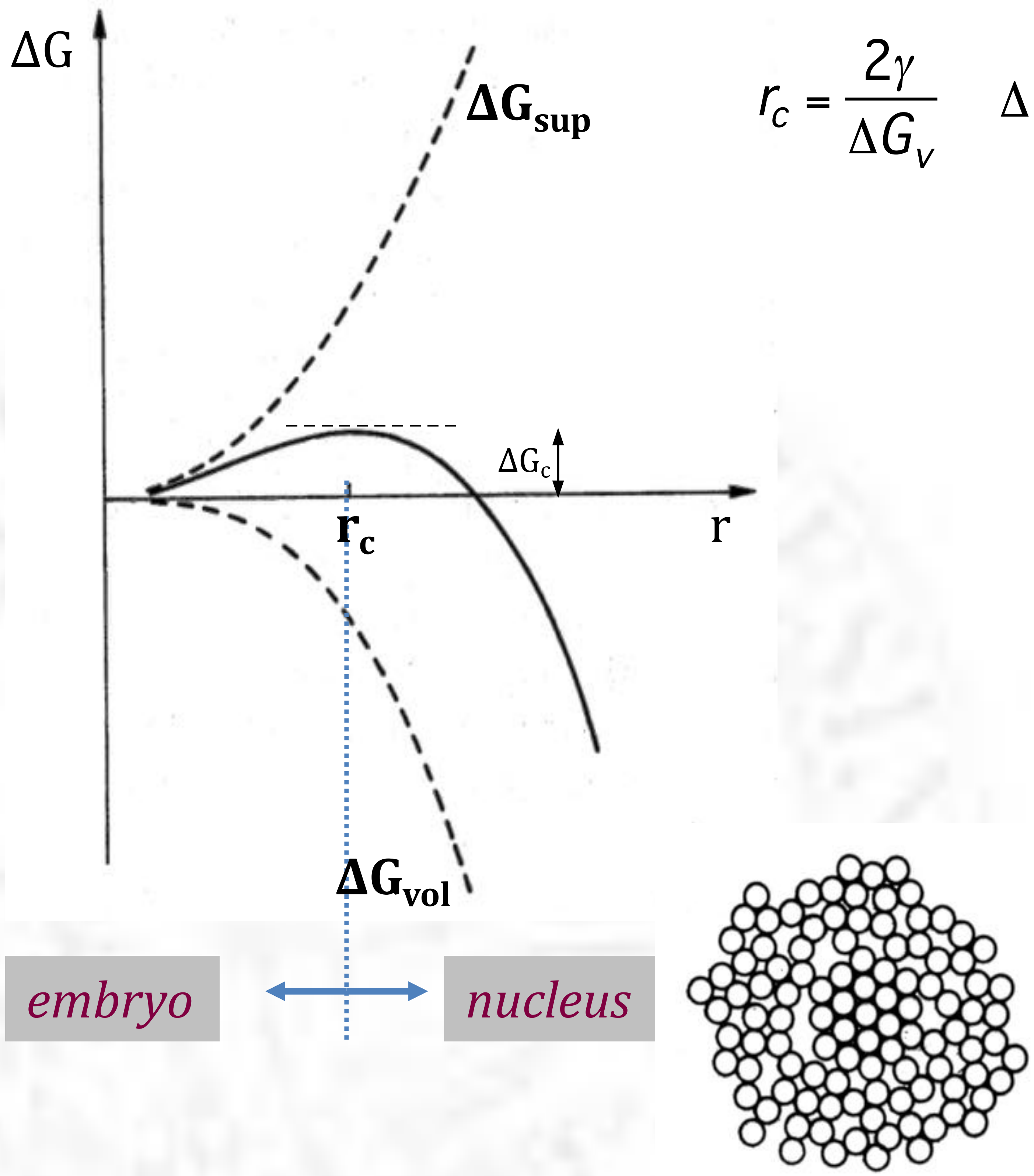
driving force = ΔT (*undercooling*)



$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

specific free energy for solidification (ΔG_v)

surface free energy (γ)



embryo

nucleus

$$r_c = \frac{2\gamma}{\Delta G_v} \qquad \Delta G_c = \frac{16\pi\gamma^3}{3\Delta G_v^2}$$

activation energy (thermodinamic barrier)

number of embryos (*randomly formed*) per unit volume with size i

$$N_i = N_v e^{-\Delta G_i/kT}$$

number of embryos per unit volume with size *c*

$$N_c = N_v e^{-\Delta G_c/kT}$$

number of atoms

Struttura e genesi dello stato vetroso, A. Maddalena, Cleup, 1983

nucleus = embryo + 1 atom

probability to go across the thermodynamic barrier

nucleation frequency: $F_{nucl} = N_v N_s f \varepsilon e^{-C_n/kT} e^{-\Delta G_c/kT}$

number of atoms at the interface

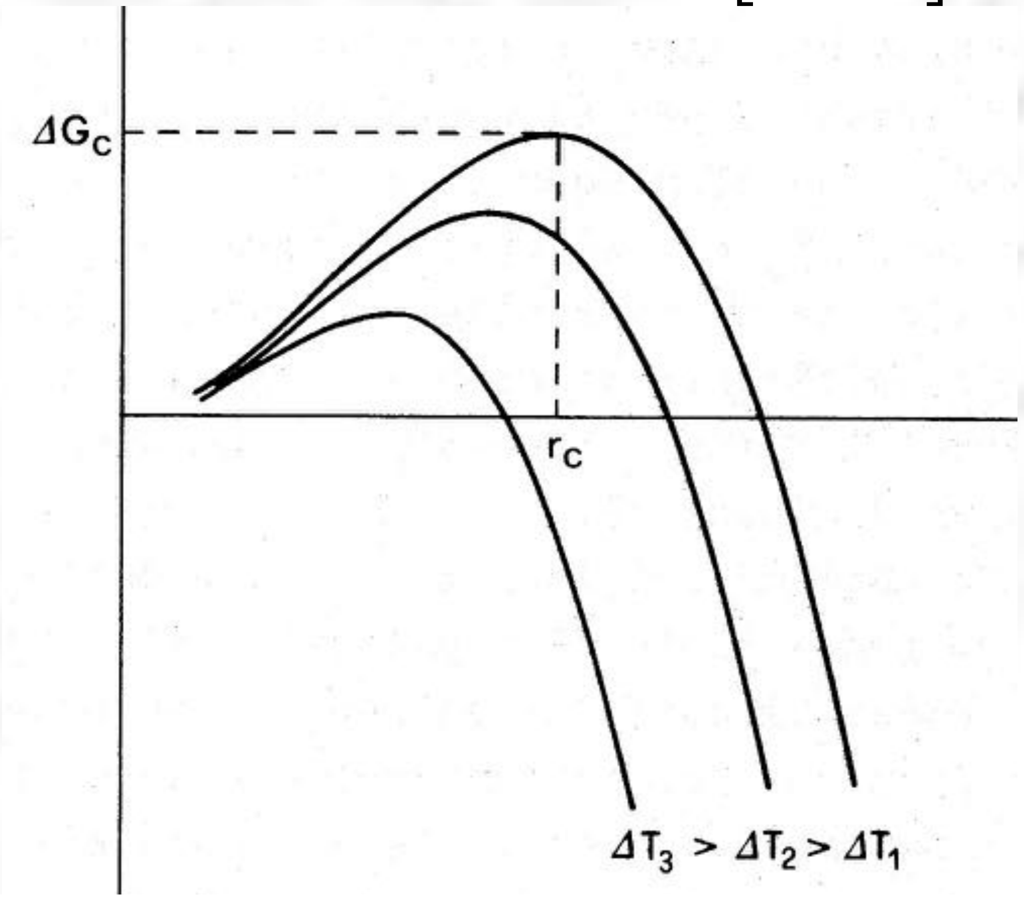
vibration frequency

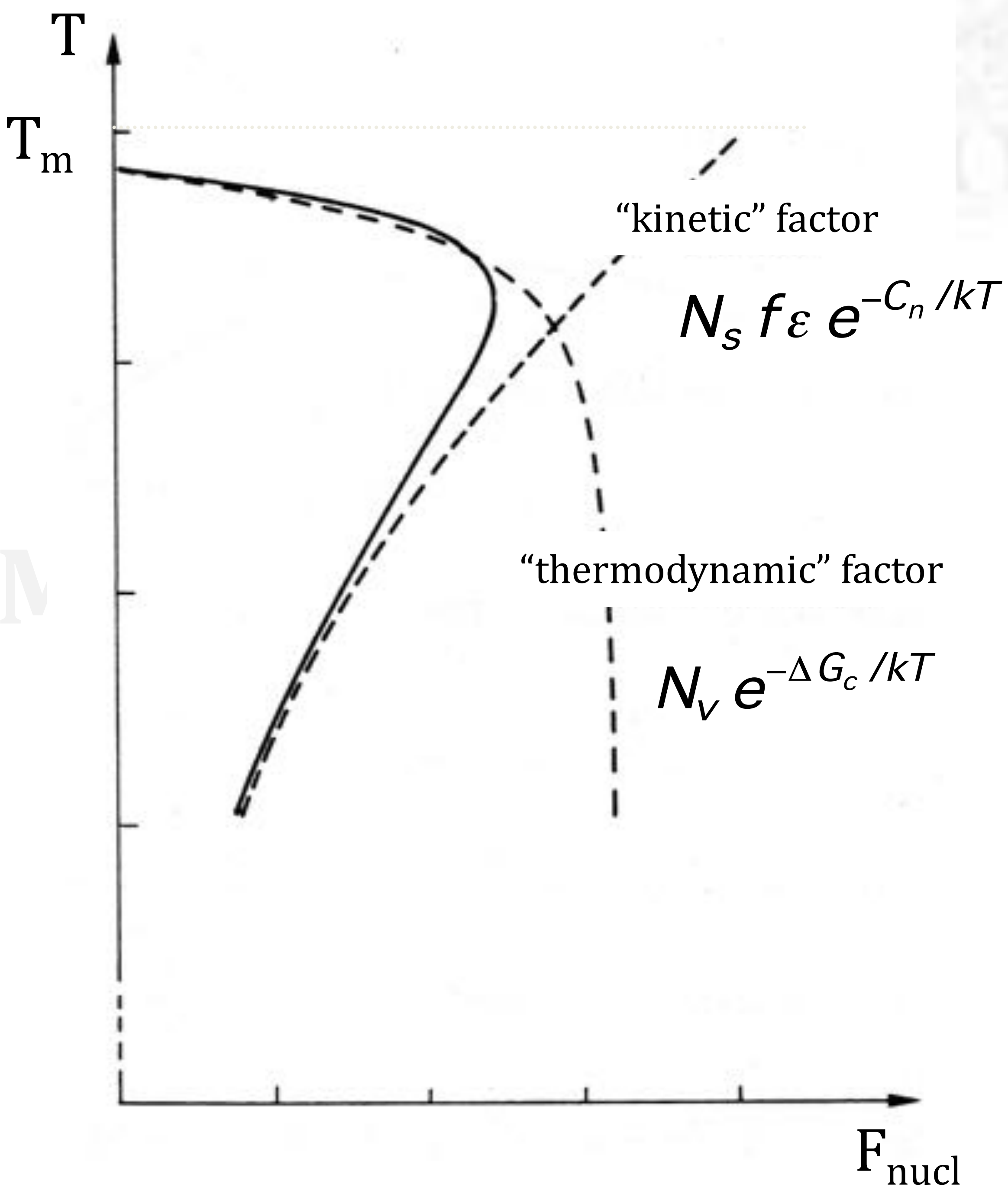
probability of jumping in one direction (= 1/6 ≈ 0.17)

probabilità of success

(movement across the interface)

$$\Delta G_c(T) = \frac{16\pi\gamma^3 T_m^2}{3\Delta H_m^2(T_m)\left[T_m - T\right]^2}$$





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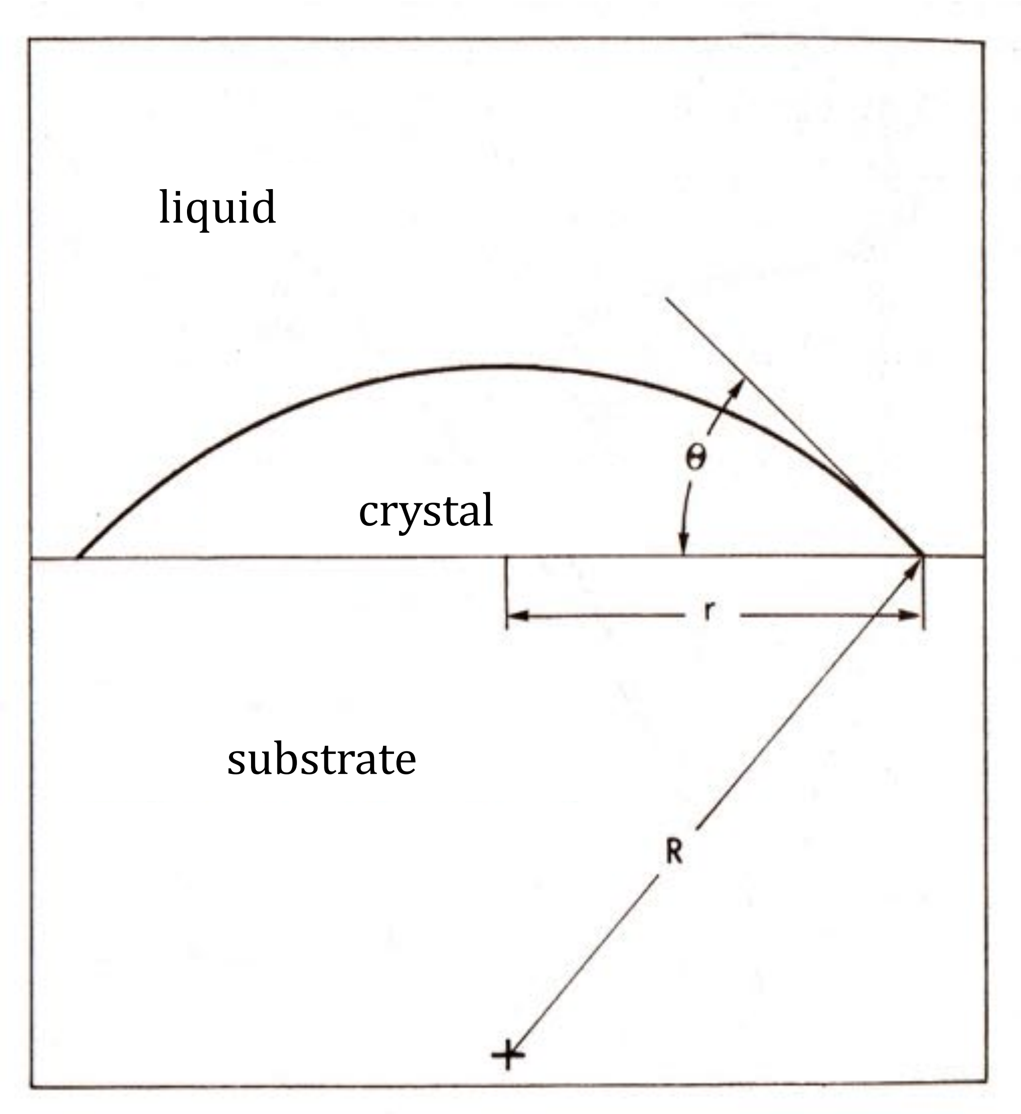
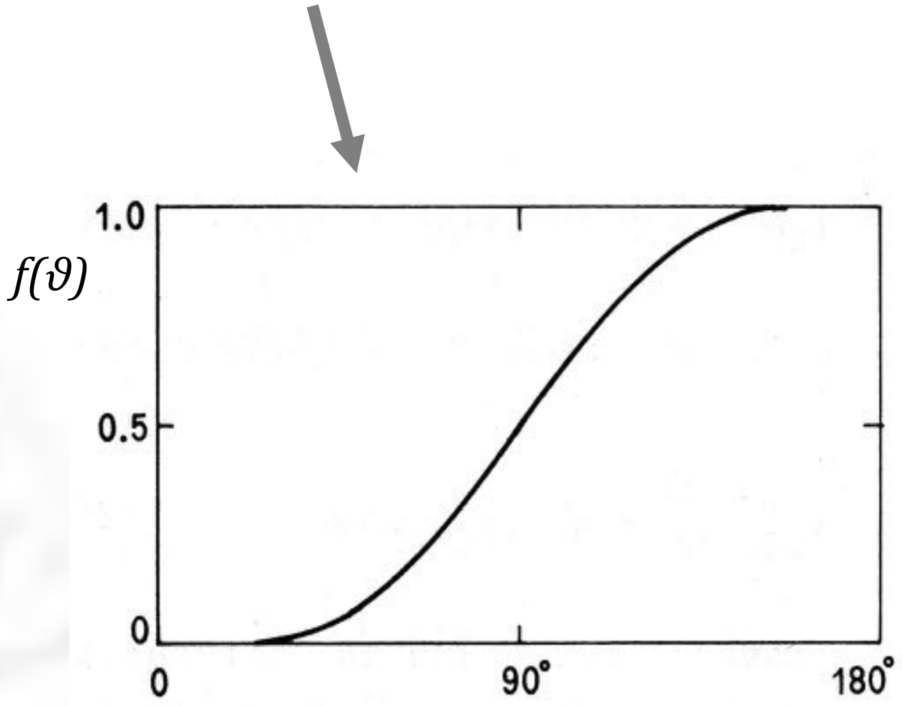
Heterogeneous nucleation



$$\Delta G_c^{het} = \Delta G_c^{hom} f(\vartheta)$$



wettability ➔ more efficient nucleation

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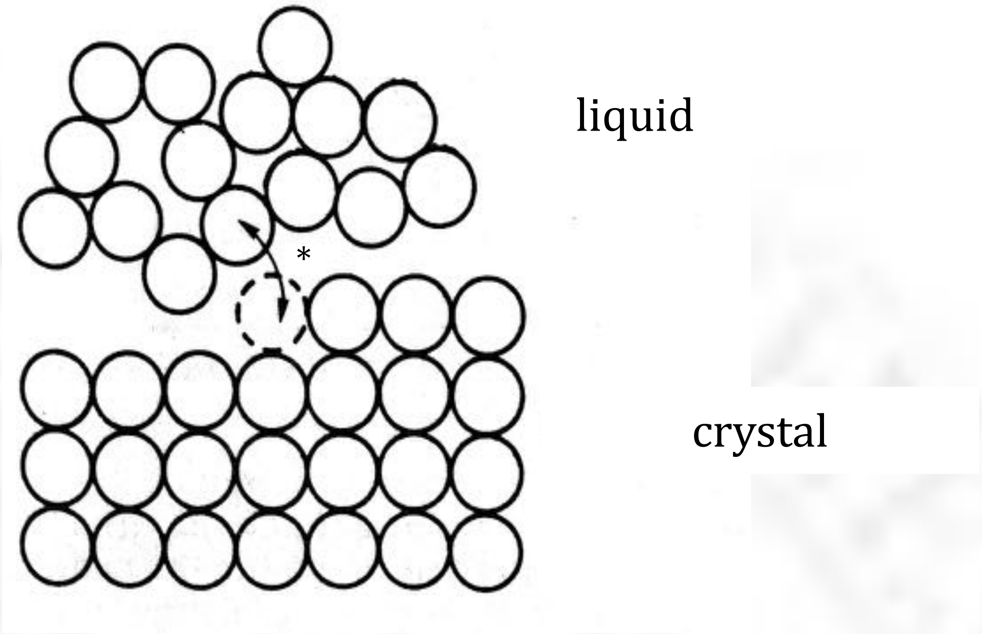
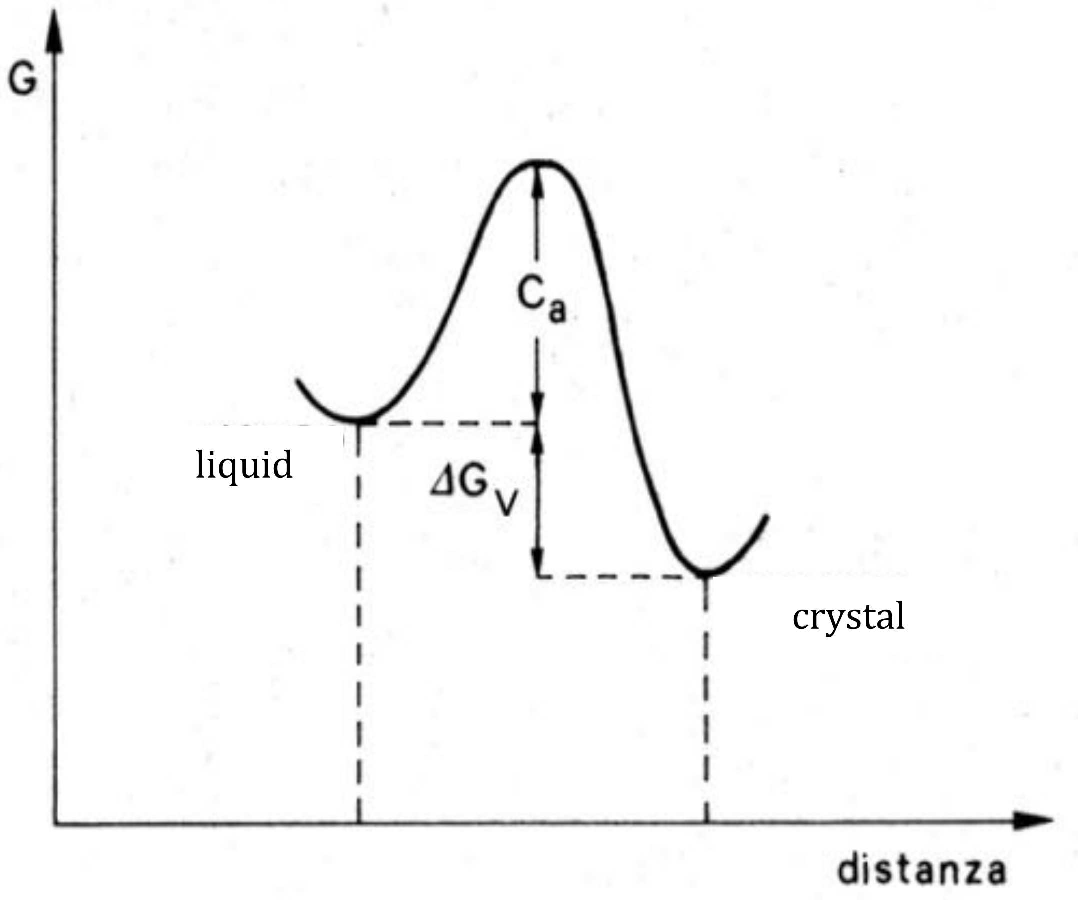
B. Growth





frequency of the liquid-crystal jumps = $\varepsilon f e^{-C_a/kT}$

frequency of the crystal-liquid = $\varepsilon f e^{-(C_a+\Delta G_v)/kT}$

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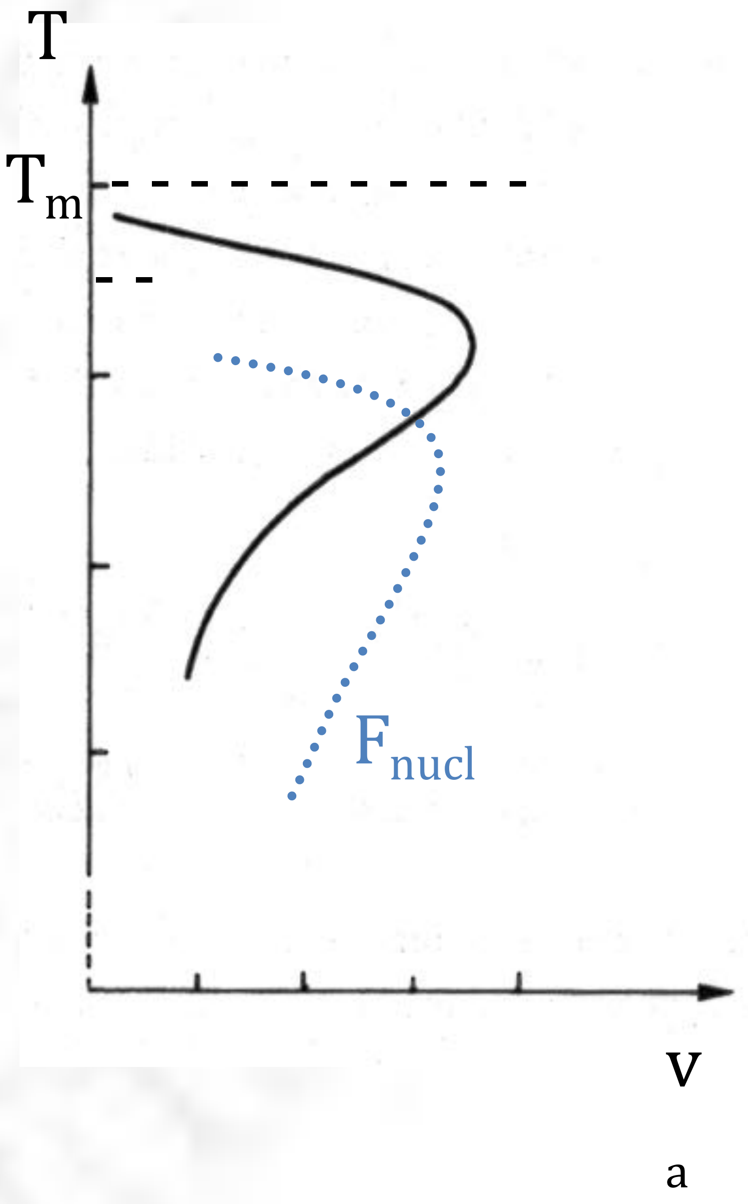
growth rate:

$$v_a = K\, d\, \varepsilon\, f\, \underbrace{e^{-C_a/kT}}_{\text{kinetic term}} \overbrace{\left(1 - e^{-\Delta G_v/kT}\right)}^{\text{thermodynamic term}}$$

"particles" diameter



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Condition for glass formation

1. $F_n < 1$ nucleus/cm^3/s
2. If $F_n \geq 1$ nucleus/cm^3/s @ $T = T'$, $v_a < 10^{-7}$ cm/s for $T < T'$

nucleation frequency:
(must be small)

$$F_{nucl} = N_v N_s f \varepsilon e^{-C_n/kT} e^{-\Delta G_c/kT}$$

≈ *undercooling*

growth rate:
(must be small)

$$v_a = K d \varepsilon f e^{-C_a/kT}\left(1 - e^{-\Delta G_v/kT}\right)$$

➡ $C_n, C_a > 30\,R\,T_m$

limited T_m ➔ *glass*

C_n, C_a ≈ activation energy for viscous flow = C_v

$$\text{viscosity} = \eta = \kappa\, e^{C_v/kT}$$

F_{nucl} e v_a ≈ 1/viscosity

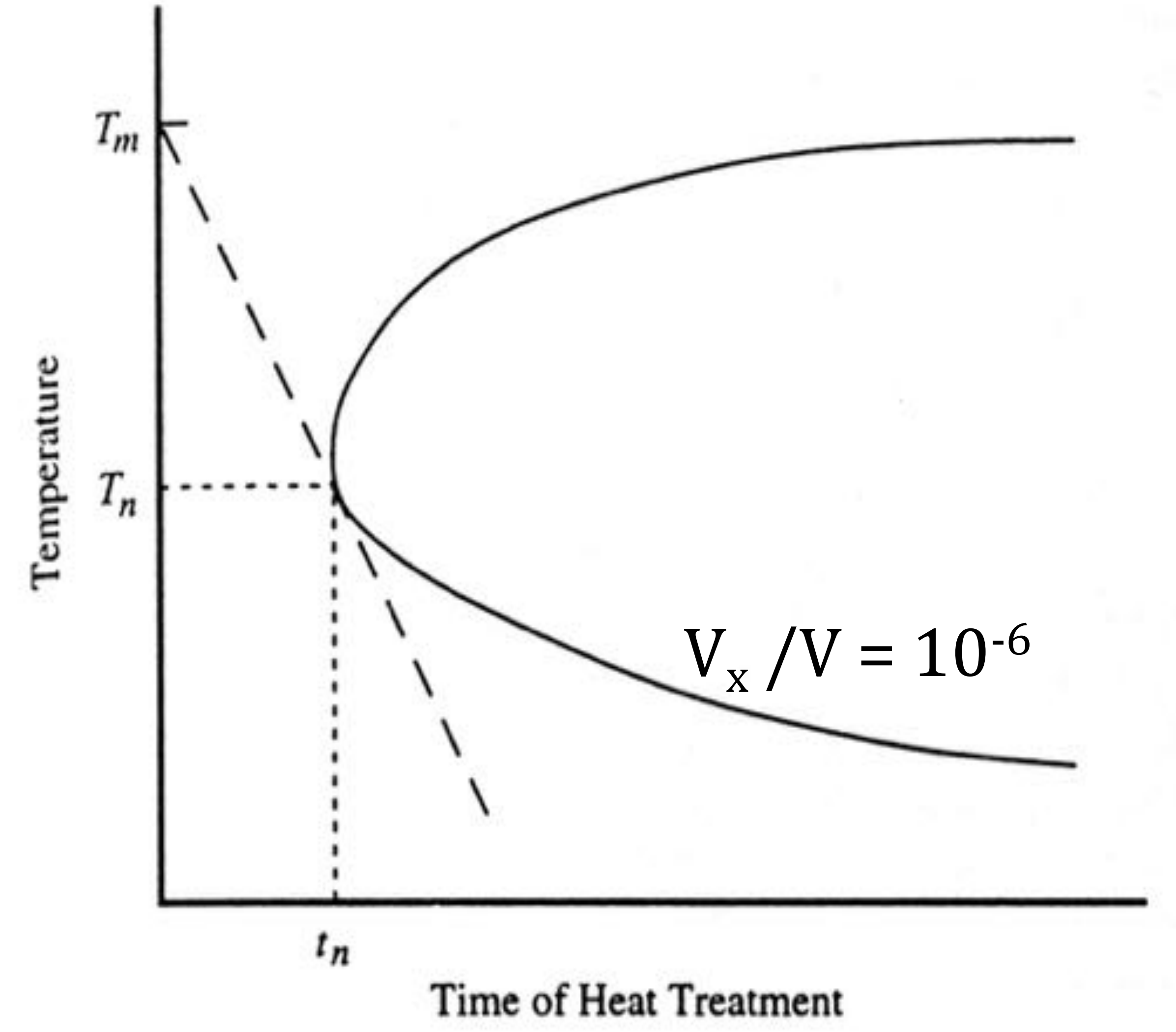
	T_m (°C)	η (poise) @ T_m
SiO_2	1734	2.5×10^{7}
P_2O_5	580	5.0×10^{6}
B_2O_3	450	1.0×10^{5}
Glicerina	18	10
Fe	1530	0.07
Pb	320	0.03
H_2O	0	1.8×10^{-3}

$\left.\begin{matrix} SiO_2 \\ P_2O_5 \\ B_2O_3 \\ \text{Glicerina} \end{matrix}\right\} \Rightarrow$ *glass*

Cooling rate

Crystallized fraction = $$\frac{V_x}{V} = 1 - \exp\left[-\int_0^t F_{nucl}\left(\int_{t'}^t v_a\, d\tau\right)^3 dt'\right]$$

If T = constant $$\frac{V_x}{V} = 1 - \exp\left[-\frac{\pi}{3} F_{nucl}\, v_a^3\, t^4\right]$$



critical cooling rate:

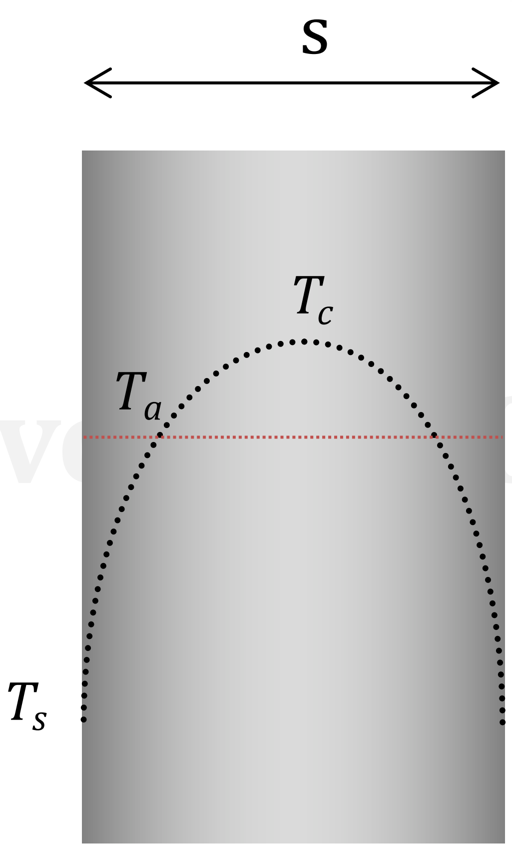
$$\left(\frac{dT}{dt}\right)_c \approx \frac{T_m - T_n}{t_n}$$

Introduction to glass science and technology, J. E. Shelby, The Royal Society of Chemistry, 1997 *critical cooling rate*

thickness that can be produced as a glass

	v_c (°C/s)	s_{max}
SiO_2	2×10^{-4}	400 cm
GeO_2	7×10^{-2}	7 cm
H_2O	10^7	1 µm
Ag	10^{10}	0.1 µm

thermal diffusivity

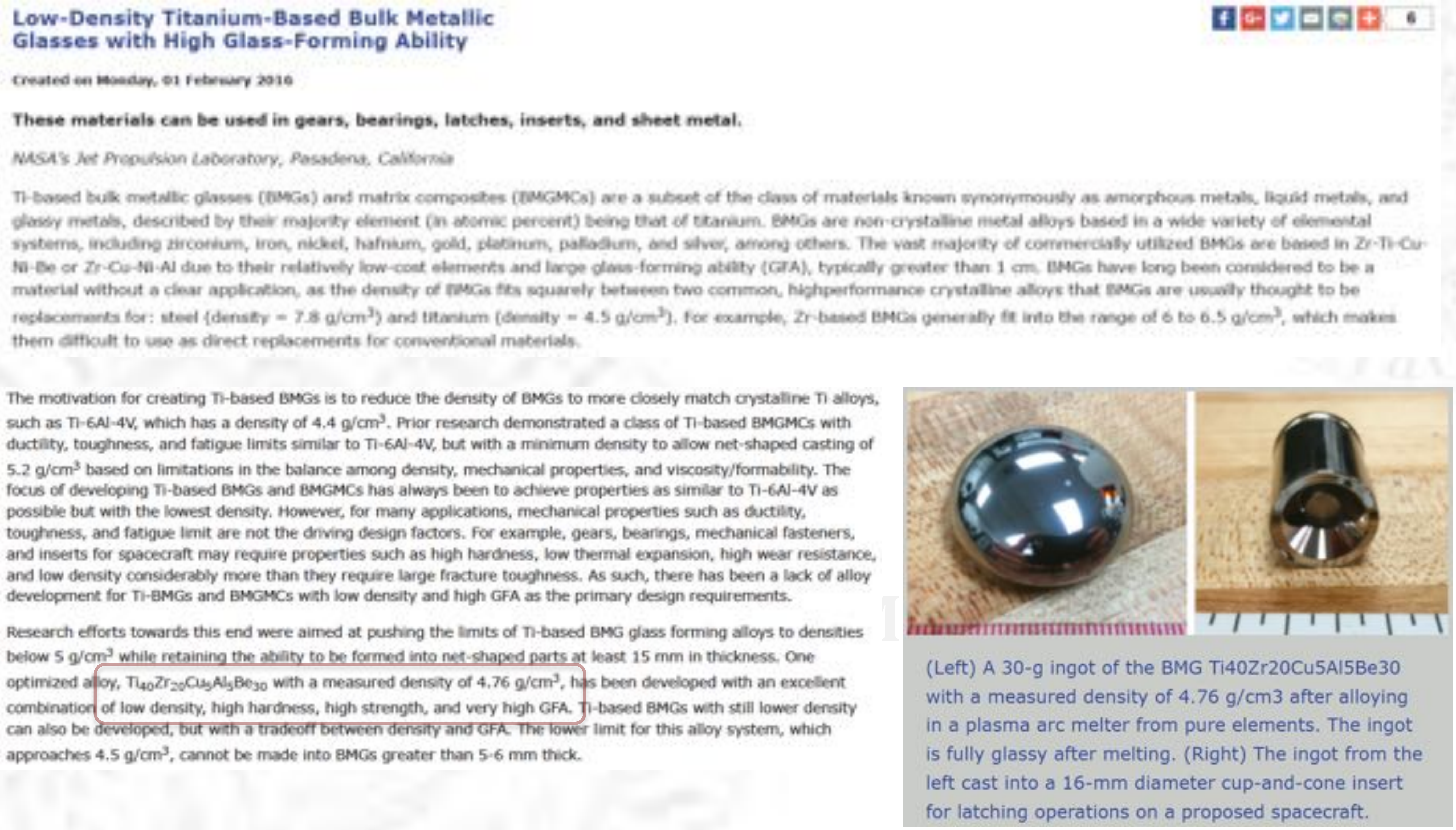


$$T_c - T_s = 0.125\ \phi\ s^2 / (k / \rho\ c_p)$$

ϕ = cooling rate

Synthetic glasses

- **Silicate glasses (**SiO_2**)**
- **Oxide glasses (*alumino-phosphate, alumino-borate, vanadate*)**
- **Chalcogenide glasses (*S, Se, Te*)**
- **Metallic glasses (*Metglas®* -** $Fe_{40}Ni_{40}P_{14}B_6$**, *Vitreloy®* -** $Zr_{41}Ti_{14}Cu_{13}Ni_{10}Be_{22}$**)**
- **Polymers, soaps, waxes**
- **Caramel, cotton candy**



Low-Density Titanium-Based Bulk Metallic Glasses with High Glass-Forming Ability

Created on Monday, 01 February 2016

These materials can be used in gears, bearings, latches, inserts, and sheet metal.

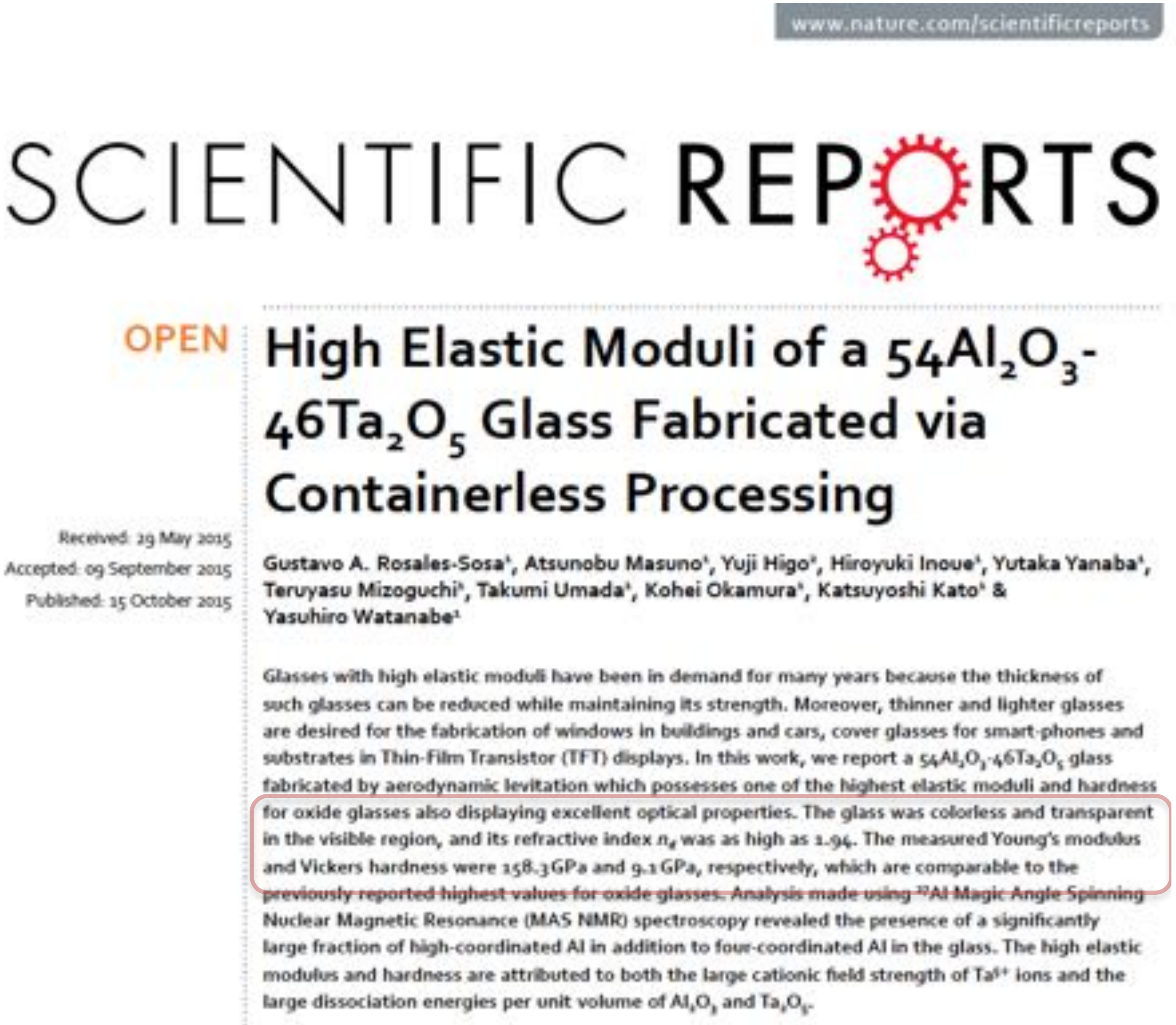
NASA's Jet Propulsion Laboratory, Pasadena, California

Ti-based bulk metallic glasses (BMGs) and matrix composites (BMGMCs) are a subset of the class of materials known synonymously as amorphous metals, liquid metals, and glassy metals, described by their majority element (in atomic percent) being that of titanium. BMGs are non-crystalline metal alloys based in a wide variety of elemental systems, including zirconium, iron, nickel, hafnium, gold, platinum, palladium, and silver, among others. The vast majority of commercially utilized BMGs are based in Zr-Ti-Cu-Ni-Be or Zr-Cu-Ni-Al due to their relatively low-cost elements and large glass-forming ability (GFA), typically greater than 1 cm. BMGs have long been considered to be a material without a clear application, as the density of BMGs fits squarely between two common, highperformance crystalline alloys that BMGs are usually thought to be replacements for: steel (density = 7.8 g/cm^3) and titanium (density = 4.5 g/cm^3). For example, Zr-based BMGs generally fit into the range of 6 to 6.5 g/cm^3, which makes them difficult to use as direct replacements for conventional materials.

The motivation for creating Ti-based BMGs is to reduce the density of BMGs to more closely match crystalline Ti alloys, such as Ti-6Al-4V, which has a density of 4.4 g/cm^3. Prior research demonstrated a class of Ti-based BMGMCs with ductility, toughness, and fatigue limits similar to Ti-6Al-4V, but with a minimum density to allow net-shaped casting of 5.2 g/cm^3 based on limitations in the balance among density, mechanical properties, and viscosity/formability. The focus of developing Ti-based BMGs and BMGMCs has always been to achieve properties as similar to Ti-6Al-4V as possible but with the lowest density. However, for many applications, mechanical properties such as ductility, toughness, and fatigue limit are not the driving design factors. For example, gears, bearings, mechanical fasteners, and inserts for spacecraft may require properties such as high hardness, low thermal expansion, high wear resistance, and low density considerably more than they require large fracture toughness. As such, there has been a lack of alloy development for Ti-BMGs and BMGMCs with low density and high GFA as the primary design requirements.

Research efforts towards this end were aimed at pushing the limits of Ti-based BMG glass forming alloys to densities below 5 g/cm^3 while retaining the ability to be formed into net-shaped parts at least 15 mm in thickness. One optimized alloy, $Ti_{40}Zr_{20}Cu_5Al_5Be_{30}$ with a measured density of 4.76 g/cm^3, has been developed with an excellent combination of low density, high hardness, high strength, and very high GFA. Ti-based BMGs with still lower density can also be developed, but with a tradeoff between density and GFA. The lower limit for this alloy system, which approaches 4.5 g/cm^3, cannot be made into BMGs greater than 5-6 mm thick.

(Left) A 30-g ingot of the BMG Ti40Zr20Cu5Al5Be30 with a measured density of 4.76 g/cm3 after alloying in a plasma arc melter from pure elements. The ingot is fully glassy after melting. (Right) The ingot from the left cast into a 16-mm diameter cup-and-cone insert for latching operations on a proposed spacecraft.



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High Elastic Moduli of a $54Al_2O_3$-$46Ta_2O_5$ Glass Fabricated via Containerless Processing

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Glasses with high elastic moduli have been in demand for many years because the thickness of such glasses can be reduced while maintaining its strength. Moreover, thinner and lighter glasses are desired for the fabrication of windows in buildings and cars, cover glasses for smart-phones and substrates in Thin-Film Transistor (TFT) displays. In this work, we report a $54Al_2O_3$-$46Ta_2O_5$ glass fabricated by aerodynamic levitation which possesses one of the highest elastic moduli and hardness for oxide glasses also displaying excellent optical properties. The glass was colorless and transparent in the visible region, and its refractive index n_d was as high as 1.94. The measured Young's modulus and Vickers hardness were 158.3 GPa and 9.1 GPa, respectively, which are comparable to the previously reported highest values for oxide glasses. Analysis made using ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy revealed the presence of a significantly large fraction of high-coordinated Al in addition to four-coordinated Al in the glass. The high elastic modulus and hardness are attributed to both the large cationic field strength of Ta^{5+} ions and the large dissociation energies per unit volume of Al_2O_3 and Ta_2O_5.