Optical and Photonic Glasses

Lecture 3:

Kinetics and Nucleation

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C) **Kinetic theory** of glass formation

The basic postulate is that (in principle) any material can be made from the melt into as glass, if quenched quickly enough.

It is sufficient that the melt is cooled below T_g so quickly that crystallization is prevented (kinetic control).

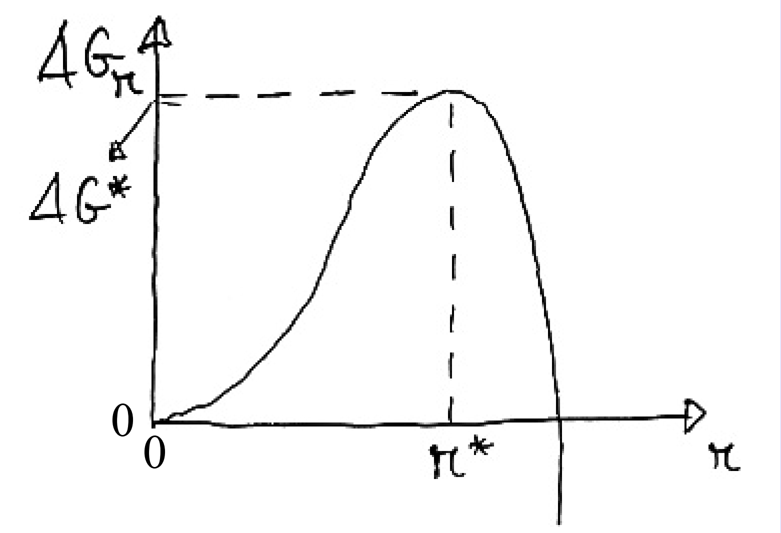
A determination of the **rates of nucleation** and **crystallization from the melt** will lead to an estimate of a *critical cooling rate* necessary for glass formation in each case.

Nucleation and crystallization rates from the melt

A)Nucleation (homogeneous)

A liquid matrix/crystal nucleous interface is formed, with interfacial energy γ. For spherical nuclei with a radius r, the change in Gibbs free energy is:

$$\Delta G_r = 4 \pi r^2 \gamma + 4/3 \pi r^3 \Delta G_v \qquad (\Delta G_v \text{ is the volume Gibbs energy change})$$



$T = \text{const.}$ $(< T_f)$

r* is the critical radius (ca. 5 – 10 nm):

$r = r^* \Rightarrow d\Delta G_r/dr = 0 \Leftrightarrow r^* = -2\,\gamma / \Delta G_v$ $(T < T_f \Rightarrow \Delta G_v = G_{nuc} - G_{liq} < 0)$

and the *activation energy for nucleation*:

$$\Delta G^* = 16\,\pi\,\gamma^3 / [3\,\Delta G_v^{\,2}]$$

For a degree of *supercooling* $\Delta T = T_f - T$, it can be shown that:

$$\Delta G^* = 16\,\pi\,\gamma^3\,T_f^{\,2} / [3\,\Delta H_f^{\,2}(\Delta T)^2]$$

Homogeneous nucleation rate

The rate of homogeneous nucleation (or the number of supercritical nuclei formed per unit volume and per unit time) is then:

$$I_v = \nu \; n_s \; n^*$$

frequency of collisions between molecules and nuclei:

$\nu \sim kT/h \exp(- \Delta G_m/RT)$

number of molecules near a critical nucleous

number of critical nuclei per unit volume:

$n^* = n_o \exp(- \Delta G^*/RT)$

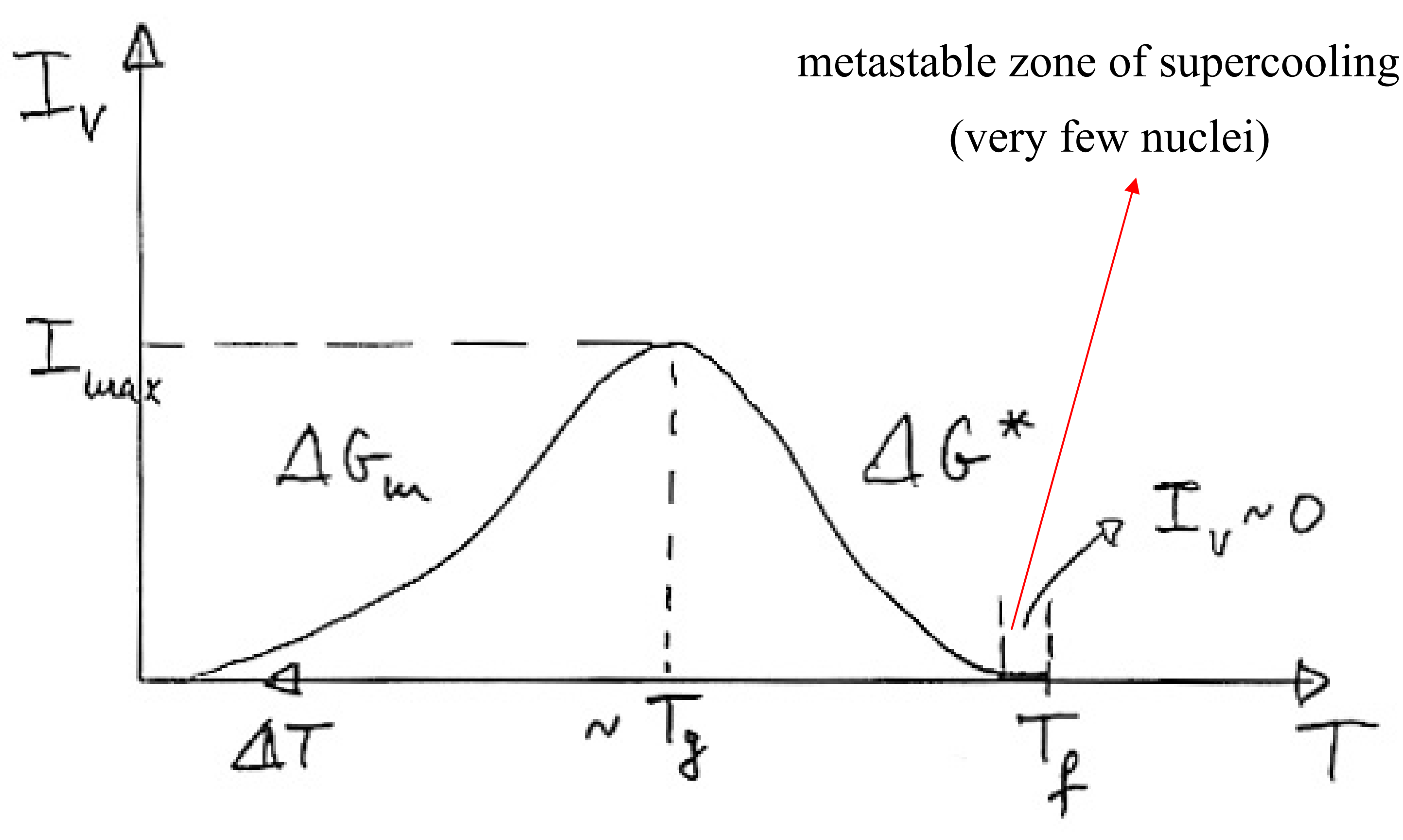
number of molecules per unit volume

Therefore, the rate of homogeneous nucleation is:

$$I_v = I_o \exp\{-16 \pi \gamma^3 T_f^2/[3 RT \Delta H_f^2(\Delta T)^2]\} \exp(- \Delta G_m/RT) \qquad (m^{-3}s^{-1})$$

(This theoretical value of I_v is often << experimentally determined I_v).

This is the typical shape of the homogeneous nucleation rate as a function of temperature. The maximum, I_{max}, occurs at a temperature which, for good glass forming systems (which crystallize incongruently and where *heterogeneous* nucleation is more likely to occur), may be well below T_g. For poor glass formers (which crystallize congruently, like 2 $SiO_2.Li_2O$), I_{max} occurs at ~ T_g.



metastable zone of supercooling

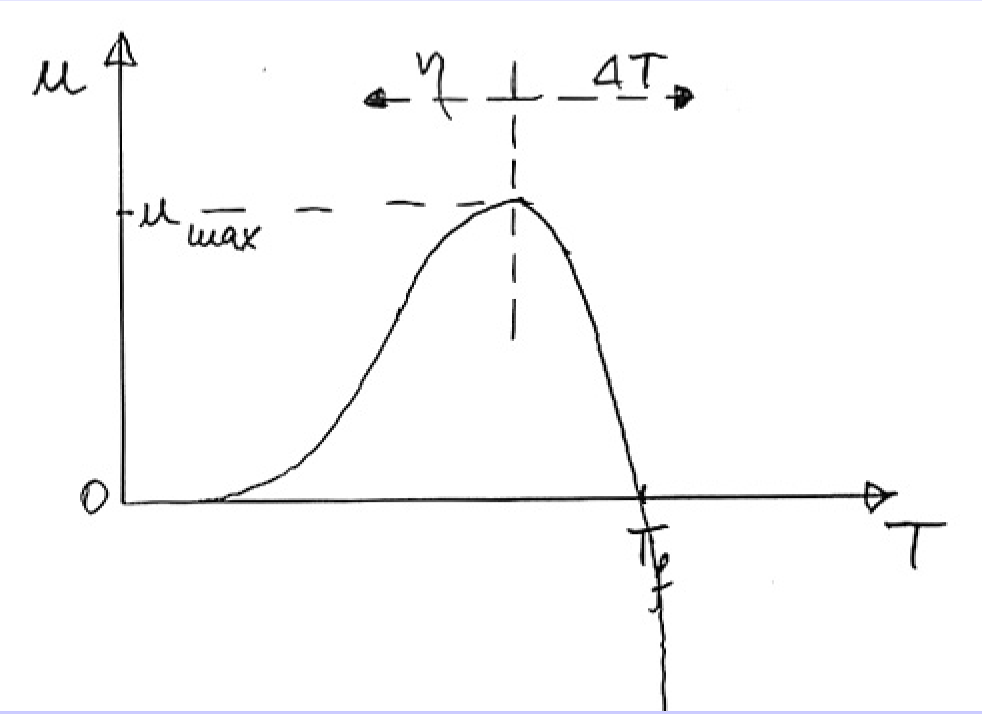
(very few nuclei)

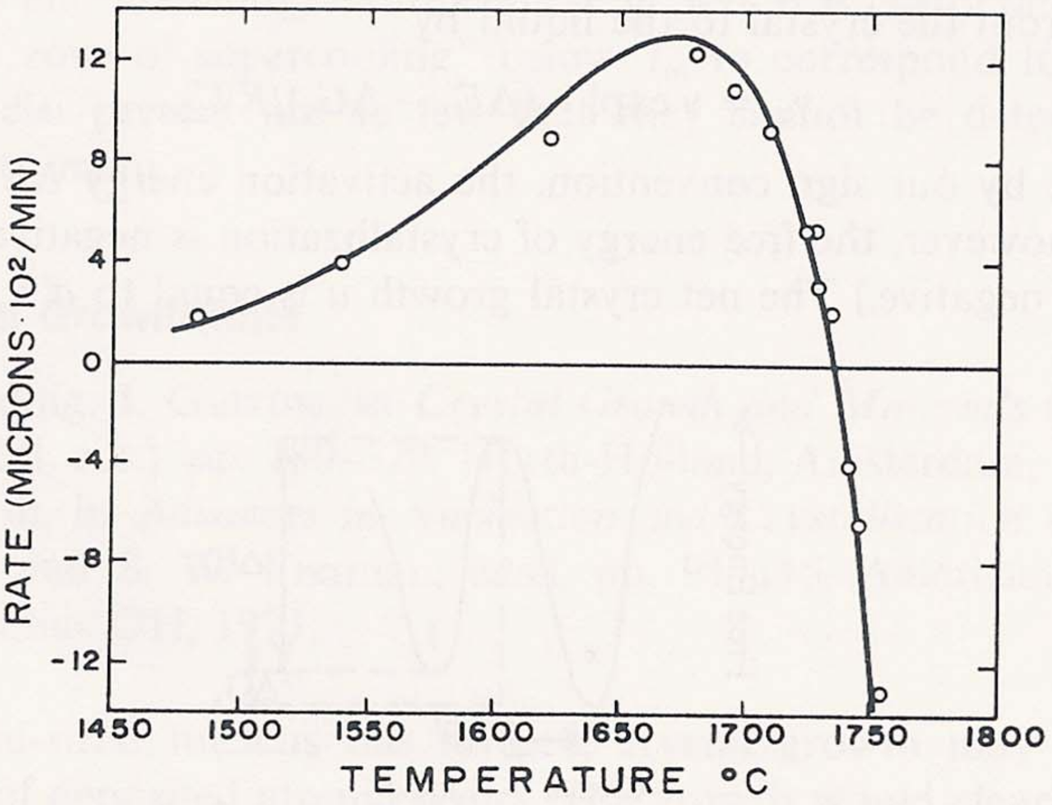
Rate of **crystal growth** from the melt

This is the rate (or velocity) of growth of supercritical nuclei, u:

$$u = \Delta H_f \, \Delta T / 3 \pi \lambda^2 T_f \, \eta \, N_o \qquad (\mathrm{m\ s^{-1}}) \qquad (u \sim \text{const. } \Delta T/\eta)$$

where $\lambda \sim 0.2$ nm.





Experimental Crystal growth rate of cristobalite from fused silica as a function of temperature.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

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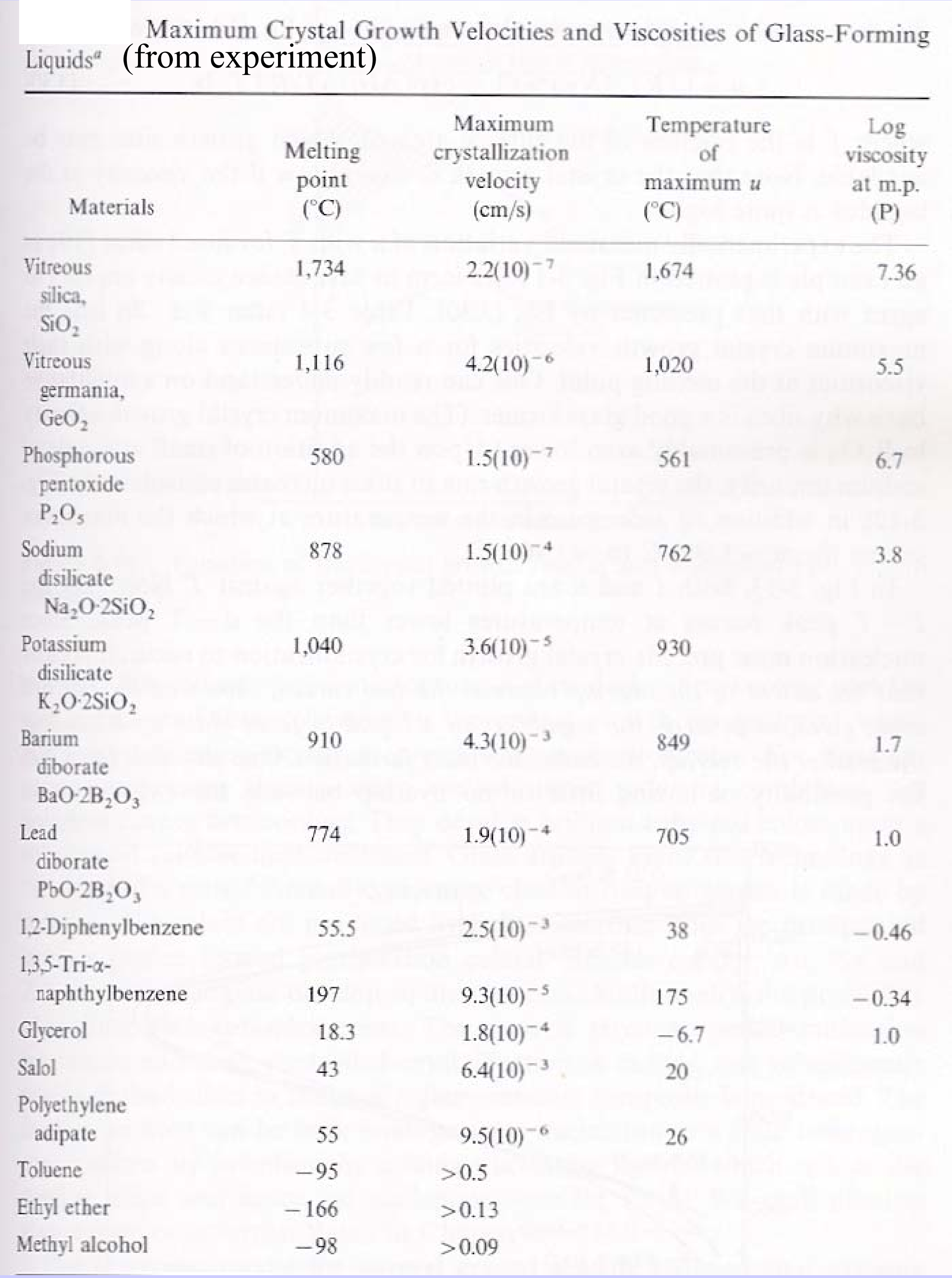


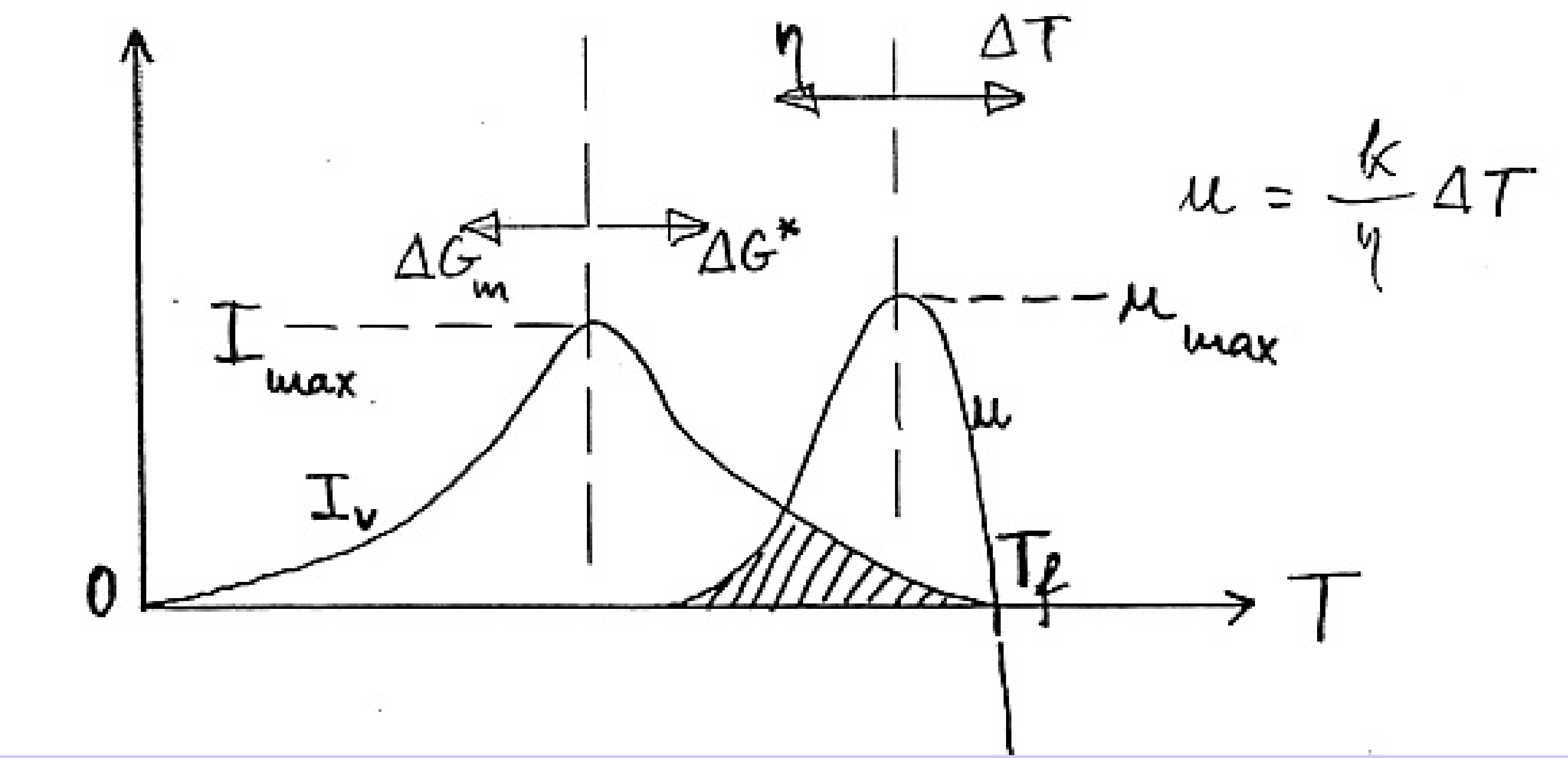
Maximum Crystal Growth Velocities and Viscosities of Glass-Forming Liquids[a] (from experiment)

Materials	Melting point (°C)	Maximum crystallization velocity (cm/s)	Temperature of maximum u (°C)	Log viscosity at m.p. (P)
Vitreous silica, SiO_2	1,734	$2.2(10)^{-7}$	1,674	7.36
Vitreous germania, GeO_2	1,116	$4.2(10)^{-6}$	1,020	5.5
Phosphorous pentoxide P_2O_5	580	$1.5(10)^{-7}$	561	6.7
Sodium disilicate $Na_2O{\cdot}2SiO_2$	878	$1.5(10)^{-4}$	762	3.8
Potassium disilicate $K_2O{\cdot}2SiO_2$	1,040	$3.6(10)^{-5}$	930	
Barium diborate $BaO{\cdot}2B_2O_3$	910	$4.3(10)^{-3}$	849	1.7
Lead diborate $PbO{\cdot}2B_2O_3$	774	$1.9(10)^{-4}$	705	1.0
1,2-Diphenylbenzene	55.5	$2.5(10)^{-3}$	38	−0.46
1,3,5-Tri-α-naphthylbenzene	197	$9.3(10)^{-5}$	175	−0.34
Glycerol	18.3	$1.8(10)^{-4}$	−6.7	1.0
Salol	43	$6.4(10)^{-3}$	20	
Polyethylene adipate	55	$9.5(10)^{-6}$	26	
Toluene	−95	>0.5		
Ethyl ether	−166	>0.13		
Methyl alcohol	−98	>0.09		

(1 Pa.s = 10 P

P → poise)

The combined curves for the rates of homogeneous nucleation and crystal growth from the melt as a function of temperature present two maxima at different temperatures:



In order to obtain a glass, one has to quench the melt below T_f at a **cooling rate** above a **critical** value, such that the supercooled liquid does not have enough time to crystallize. This implies that the temperature range where the crystal growth rate is appreciable has to be crossed quickly enough.

For example, for v-SiO_2, the value of $u_{max} \sim 2.2$ nm/s.

The **critical cooling rate** for a given glass-forming system may be estimated based on the Johnson-Mehl-Avrami theory of crystallization.

The minimum volume fraction of crystals which can be detected in a glass is typically:

$$V \sim 10^{-6}$$

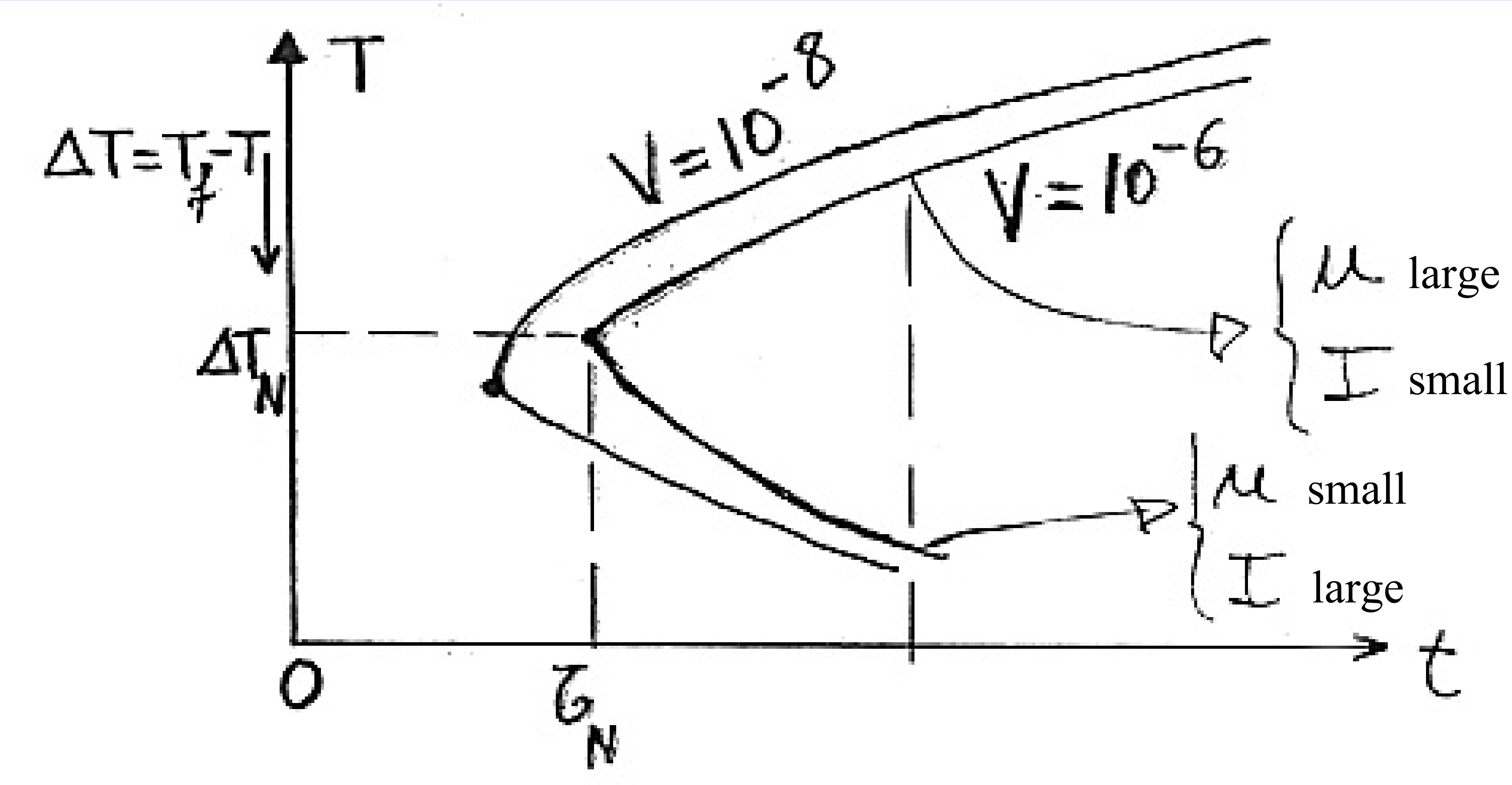
Under isothermal conditions, the Avrami theory yields the following expression for V, as function of time, t:

$$V = 1 - \exp\left[- (\pi/3)\, I_v\, u^3\, t^4\right] \sim (\pi/3)\, I_v\, u^3\, t^4$$

for time-independent, 3-D crystal growth and for short transformation times.

On the basis of this equation, one can construct a so-called T-T-T (time-temperature-% transformation) curve.

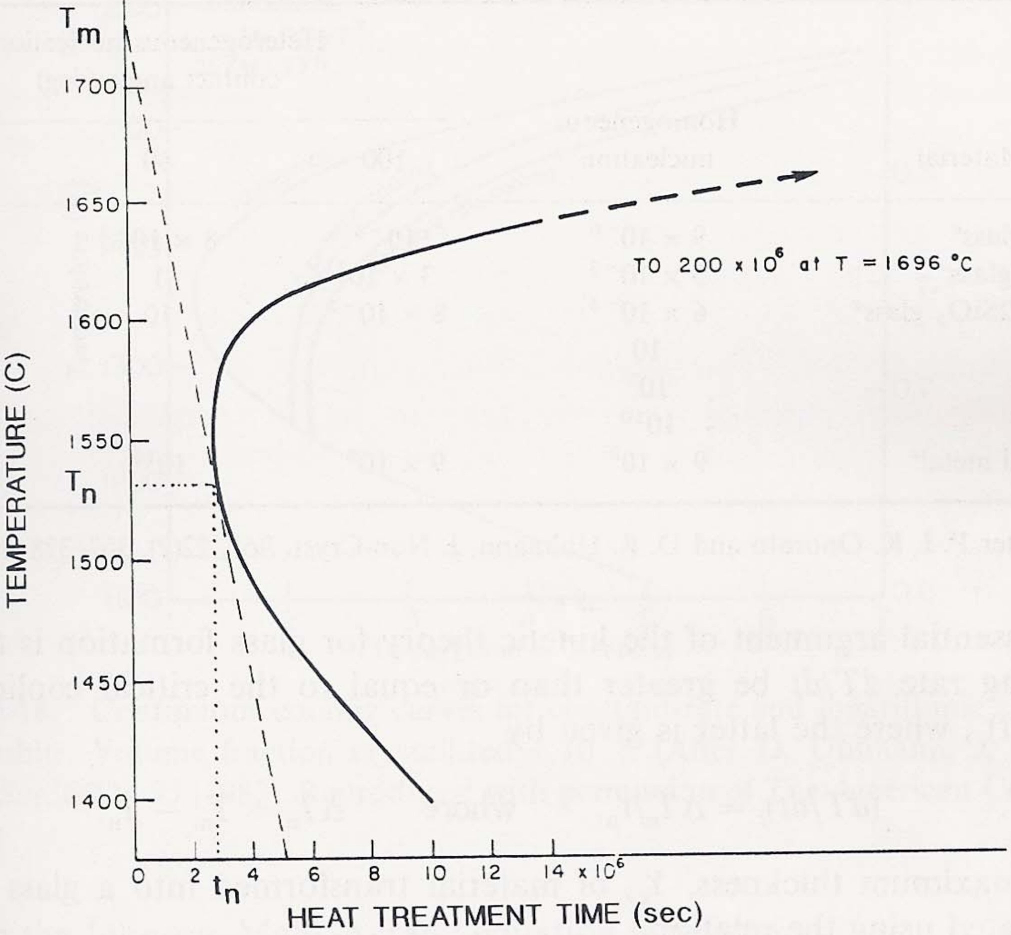
Generic T-T-T curves for melts with nucleation and crystal growth rates I and u, respectively and glasses with maximum volume fractions of crystals V (1 and 0.01 ppm):



(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

T-T-T curve for **silica**

(based on isothermal heat treatments)



Time–temperature–transformation diagram for silica corresponding to a volume fraction crystallized of 10^{-6}. (After D. Uhlmann, *J. Non-cryst. Sol.* **7**, 337 (1972). Reproduced with permission of Elsevier Science Publishers.)

For a given, selected value of V (in fact, it makes little difference whether this is 10^{-6} or 10^{-8}, for example), the T-T-T curve is built by calculating, for each temperature in a range of interest, the time which a fraction V takes to crystallize at a temperature T (at which the nucleation and growth rates are I_v and u, respectively).

The "nose" of the curve, which has the coordinates (t_n, T_n), defines the **critical cooling rate**, $(dT/dt)_c$, as the *slope* of the line drawn between T_m and the "nose":

$$(dT/dt)_c \sim \Delta T_n / t_n$$

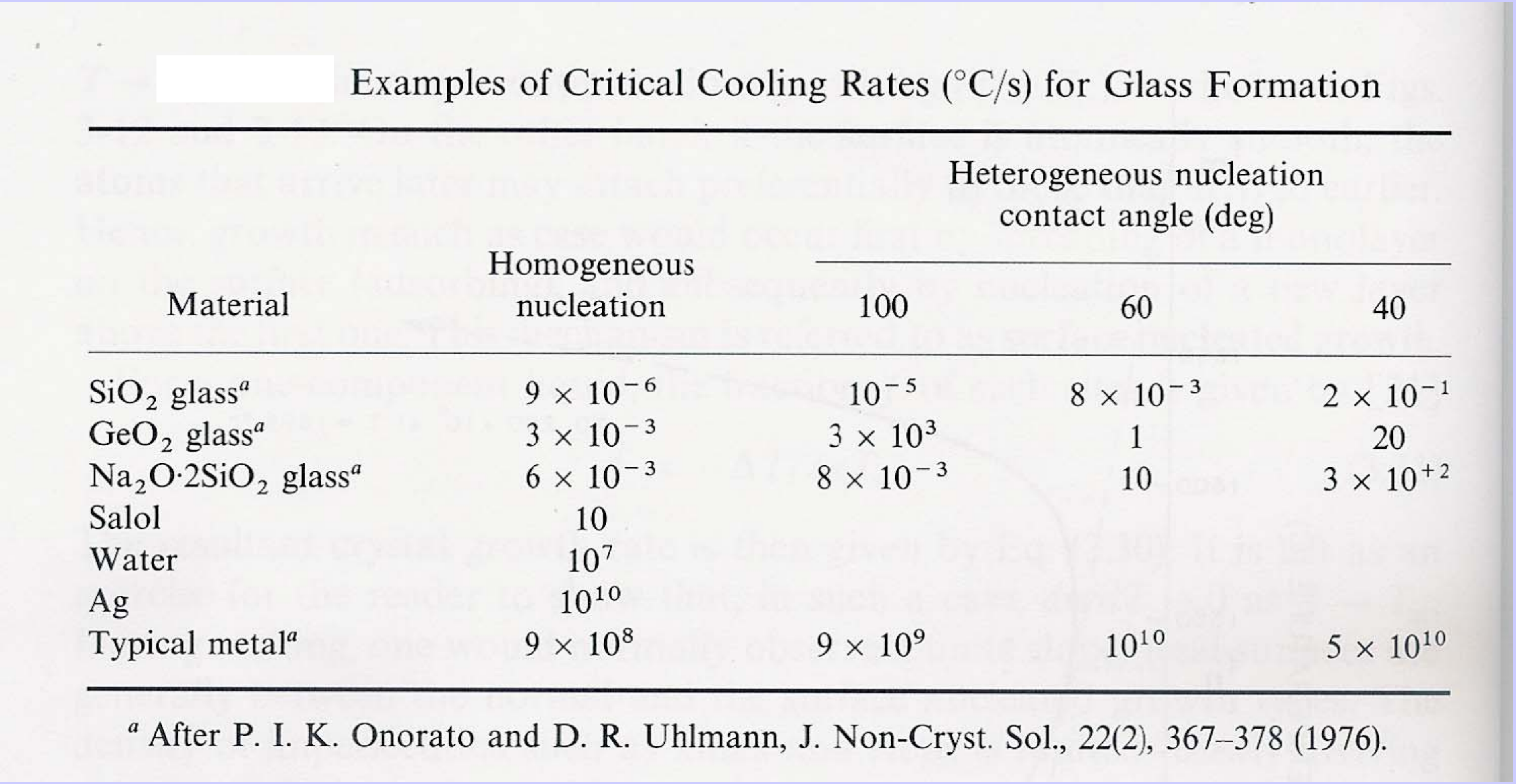
which means that, when the melt reaches T_n after a cooling time t_n ($\Delta T_n = T_m - T_n$), the crystallized fraction will not exceed the chosen value of V. Actual continuous cooling conditions correspond to lower real values of V and easier vitrification.

Another empirical criterion is: $(dT/dt)_c \sim 10^5 / \eta_f \quad (^oC/s)$

where η_f is the melt viscosity at T_m, in Pa.s .

Note that the "melting" temperature, T_m, may actually be well over T_L.

In general, **glass formation** will be favored by: (1) a cooling rate as high as possible; (2) a high viscosity at the nose of the T-T-T curve (and at T_m); (3) absence of heterogeneous nucleation sites; (4) a large liquid-crystal interfacial energy γ; (5) in multicomponent systems, a large compositional change between liquid and crystalline phase formed (in such systems, glass formation is also favored by a *deep eutectic*, at "low T", where the melt viscosity is higher).



Examples of Critical Cooling Rates (°C/s) for Glass Formation

Material	Homogeneous nucleation	Heterogeneous nucleation contact angle (deg)		
		100	60	40
SiO_2 glass[a]	9×10^{-6}	10^{-5}	8×10^{-3}	2×10^{-1}
GeO_2 glass[a]	3×10^{-3}	3×10^{3}	1	20
$Na_2O \cdot 2SiO_2$ glass[a]	6×10^{-3}	8×10^{-3}	10	$3 \times 10^{+2}$
Salol	10			
Water	10^{7}			
Ag	10^{10}			
Typical metal[a]	9×10^{8}	9×10^{9}	10^{10}	5×10^{10}

[a] After P. I. K. Onorato and D. R. Uhlmann, J. Non-Cryst. Sol., 22(2), 367–378 (1976).

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)