

$$G_c(R, T) = 4\pi R^2 \sigma - \frac{4}{3}\pi R^3 H_M^0(T_M) \frac{T}{T_M}$$

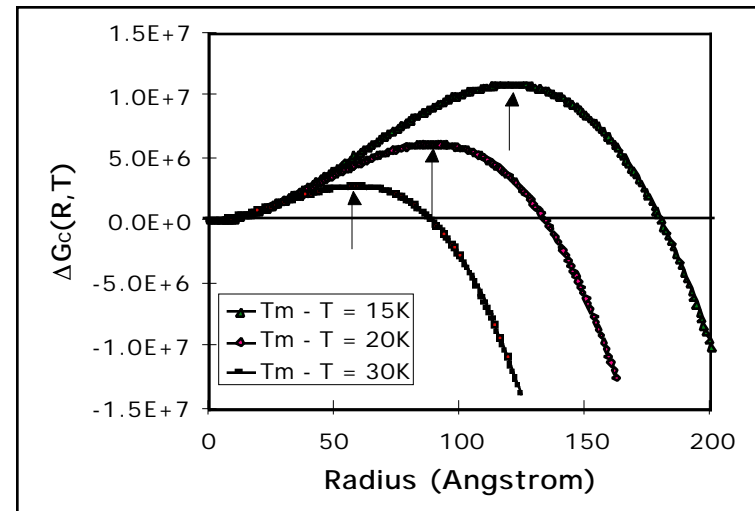
The maximum in the free energy barrier can be obtained by differentiation of $G_c(R, T)$ with respect to R and finding the zero of that derivative.

$$\frac{\partial (G_c(R, T))}{\partial R} = 8\pi R \sigma - 4\pi R^2 H_M^0(T_M) \frac{T}{T_M} = 0$$

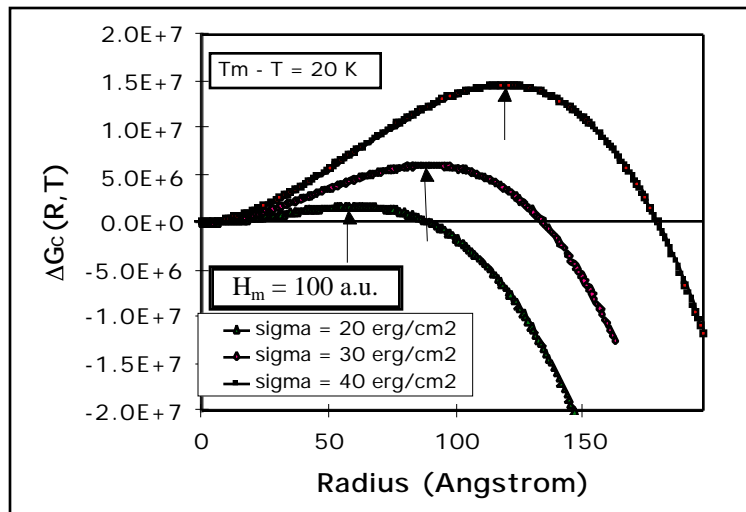
$$R^* = \frac{2\sigma T_m}{H_m T} \quad G_c(R^*, T) = \frac{16\pi\sigma^3}{3} \frac{T_m}{H_m T}^2$$

The activation free energy for formation of a crystalline nucleus increases with increasing melt - crystal interfacial free energy, decreasing enthalpy of fusion, and decreasing undercooling.

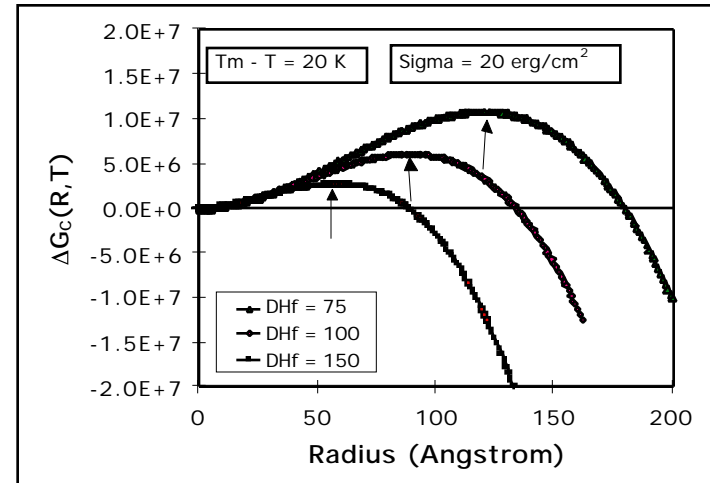
Free Energy of Nucleation vs. Radius and Undercooling



Effect of Surface Energy on the Free Energy of Nucleation

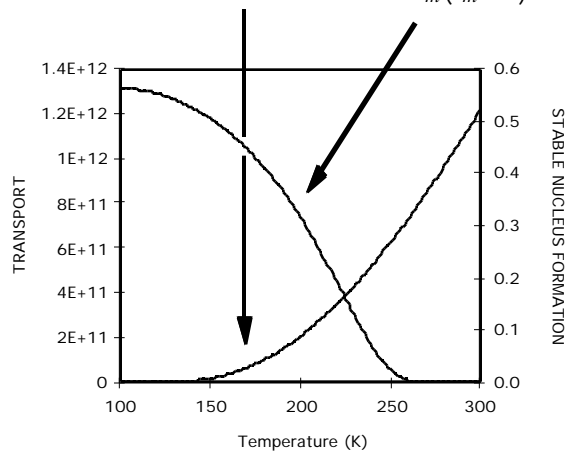


Effect of Enthalpy of Crystallization on the Free Energy of Nucleation

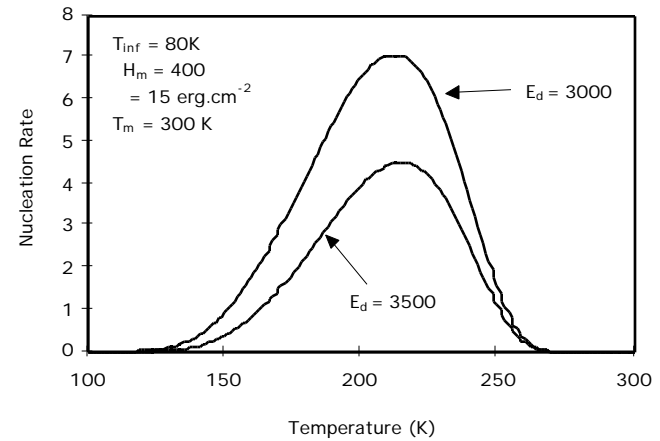


Temperature Dependence of the Nucleation Rate

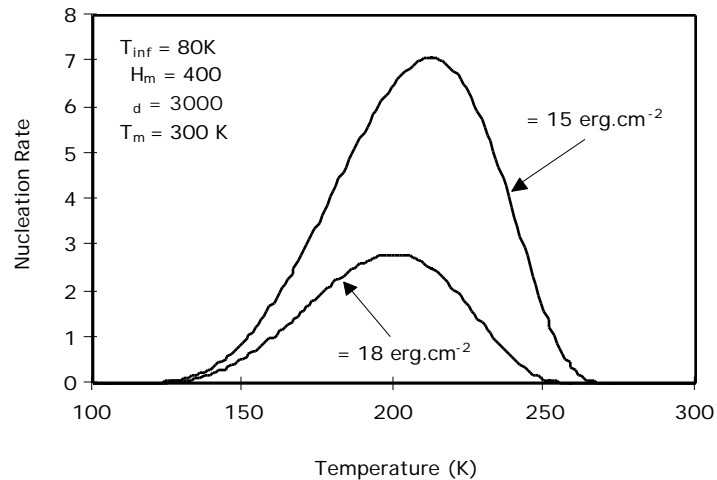
$$\frac{dN}{dt} = \frac{kT}{h} \exp \frac{-B}{R(T - T^*)} \exp \frac{-16\pi\sigma^3 T_m^2}{3kT H_m^2 (T_m - T)^2}$$



Temperature Dependence of the Rate of Nucleation of the Crystal Phase From the Liquid Phase: Effect of E_d



Temperature Dependence of the Rate of Nucleation of the Crystal Phase From the Liquid Phase: Effect of



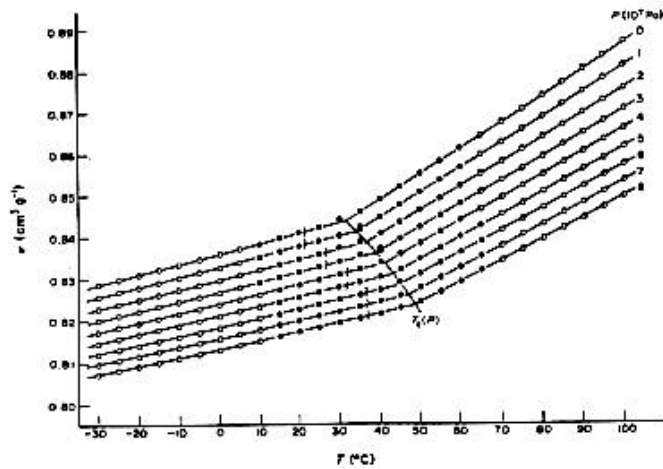
Glass Formation vs. Crystallization: Quenching

- To form a glass instead of a crystalline material by cooling a liquid, one must suppress crystallization (which is the thermodynamically favored process below T_m). One must prevent thermodynamic control and use kinetics to trap the system in a state of lower stability (glass). This can be achieved by cooling sufficiently fast the liquid so that no nucleation event takes place during cooling between T_m and T_g . Once the temperature reaches the “ T_g ” of the system, no crystallization can occur and the material is trapped in the glassy state.

$$N_T = \int_{\text{during cooling}} \frac{dN}{dt} dt = \int_{T_M}^{T_G} \frac{dN}{dT} \frac{dT}{dt} dT = \frac{1}{|C|} \int_{T_M}^{T_G} \frac{dN}{dT} dT$$

C, the cooling rate (dT/dt), was assumed independent of T

Effect of Pressure on the Glass Transition Temperature

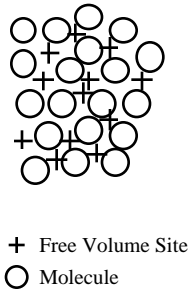


Glass Formation vs. Crystallization: Pressurization

- Glasses can also be formed in some cases by a rapid increase in pressure. The pressure both elevates the glass transition temperature (Prigogine-Defay) and the melting temperature (Clapeyron Equation). If the pressure can be applied very quickly, the glass transition rises, the melting temperature rises. The latter effect can be seen to be identical to a rapid decrease, because at a given T_x and increase in T_m leads to an increase in $T_m - T_x$ which is equivalent to cooling.

Free Volume Theories

- Proposed one of the earliest concepts to explain the glass transition behavior and the change in viscosity as the temperature is lowered.
- According to Free Volume Theories, the transport properties of the liquid are controlled by a parameter called the free volume
- Free Volume = Volume of the Material - Volume Occupied by Molecules. Note that the occupied specific volume also includes the volume associated with thermal vibrations.
- These theories state that when the free volume drops below a small value near zero, the glass transition occurs. More specifically, for flow to occur, there must be some “empty sites” or “free volume sites” in the liquid for molecules to move into.



- Doolittle was the first to propose an empirical free volume expression (1951) relating the liquid viscosity, η , to the fractional free volume, $f = (V - V_0)/V_0$.

$$\ln(\eta) = a + \frac{b}{f} = a + \frac{bV_0}{V - V_0}$$

where a and b are constants, V is the materials specific volume and V_0 is the occupied specific volume.

- If one assumes that the free volume fraction varies linearly with T above T_g and is constant below T_g and that the occupied volume varies linearly with temperature T at all temperatures, then:

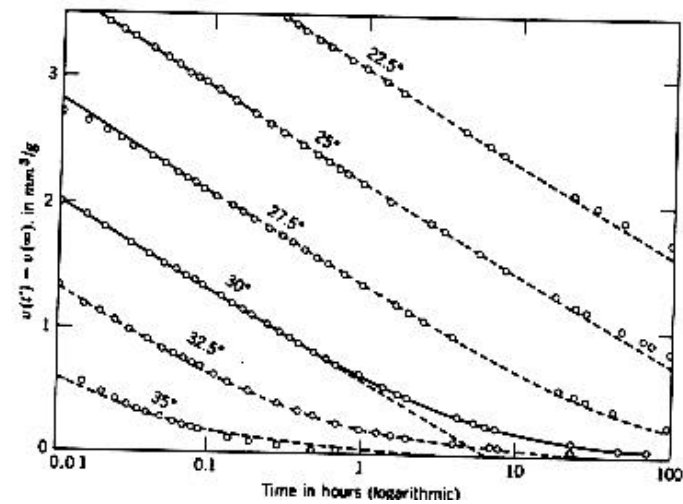
$$f = f_G + \alpha_F (T - T_G) \text{ for } T > T_G$$

$$f = f_G \text{ for } T < T_G$$

where α_F is the isobaric coefficient of thermal expansion of the free volume.

- A lowering of temperature at high temperatures where Brownian motion is rapid is accompanied by a collapse of free volume as molecular rearrangements can take place for the experimental time scale associated with the cooling. At lower temperatures (where T_g is detected), cooling is no longer accompanied by a collapse in free volume as internal rearrangements cannot take place on the experimental time scale.
- To show that the time scale for molecular rearrangements is very strongly dependent on the temperature near T_g , we can examine volumetric data obtained by rapid quenching from $T \gg T_g$ to a temperature T' near T_g . If we denote by $v(\infty)$ the specific volume of the sample after it has reached equilibrium and $v(t)$ the volume of the sample at time t , a plot of $v(t) - v(\infty)$ versus time will show the temperature dependent volume relaxation and the associated time scale for molecular rearrangements.

Volume Relaxation in the Vicinity of T_g (25-33°C)



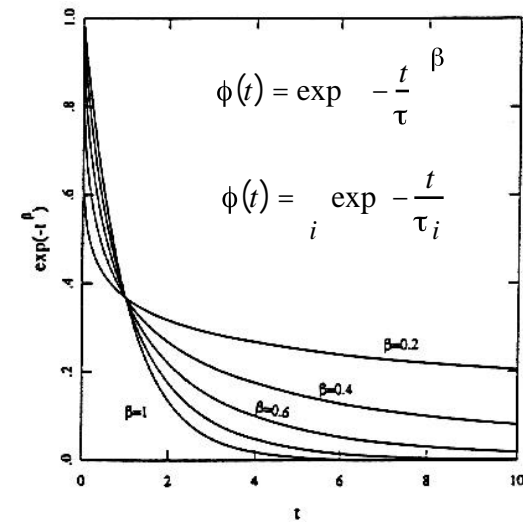
Time Dependent Properties in the T_G Region

Properties such as the volume, the enthalpy, the creep compliance, stress relaxation, polarization, non-linear optical properties rapidly reach their equilibrium values in the liquid state far above T_G. The time scale over which they reach their equilibrium value in the T_G region parallels what was discussed in the case of the volumetric data. This characteristic time dependence can be expressed by the Kohlraush-Williams-Watts function or stretched exponential. This function is mathematically equivalent to a series of single exponentials having different relaxation times, τ_i .

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right)^\beta \qquad \phi(t) = \sum_i \exp\left(-\frac{t}{\tau_i}\right)$$

KWW

Kohlraush-Williams-Watts Stretched Exponential



Classification of Liquids as they Approach Equilibrium

- Liquids are classified as “Strong” or “Fragile” depending on a number of experimental observations:

Strong Liquids

Fragile Liquids

Kauzmann Paradox	No	Yes
Relaxation	Single Exponential	Stretched Exp close to T_G Single Exp at High Temperature
T Dependence	Arrhenius	VFTH close to T_G Arrhenius at High Temperature
Examples	SiO_2	S, Se, Polymers, Organic