

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

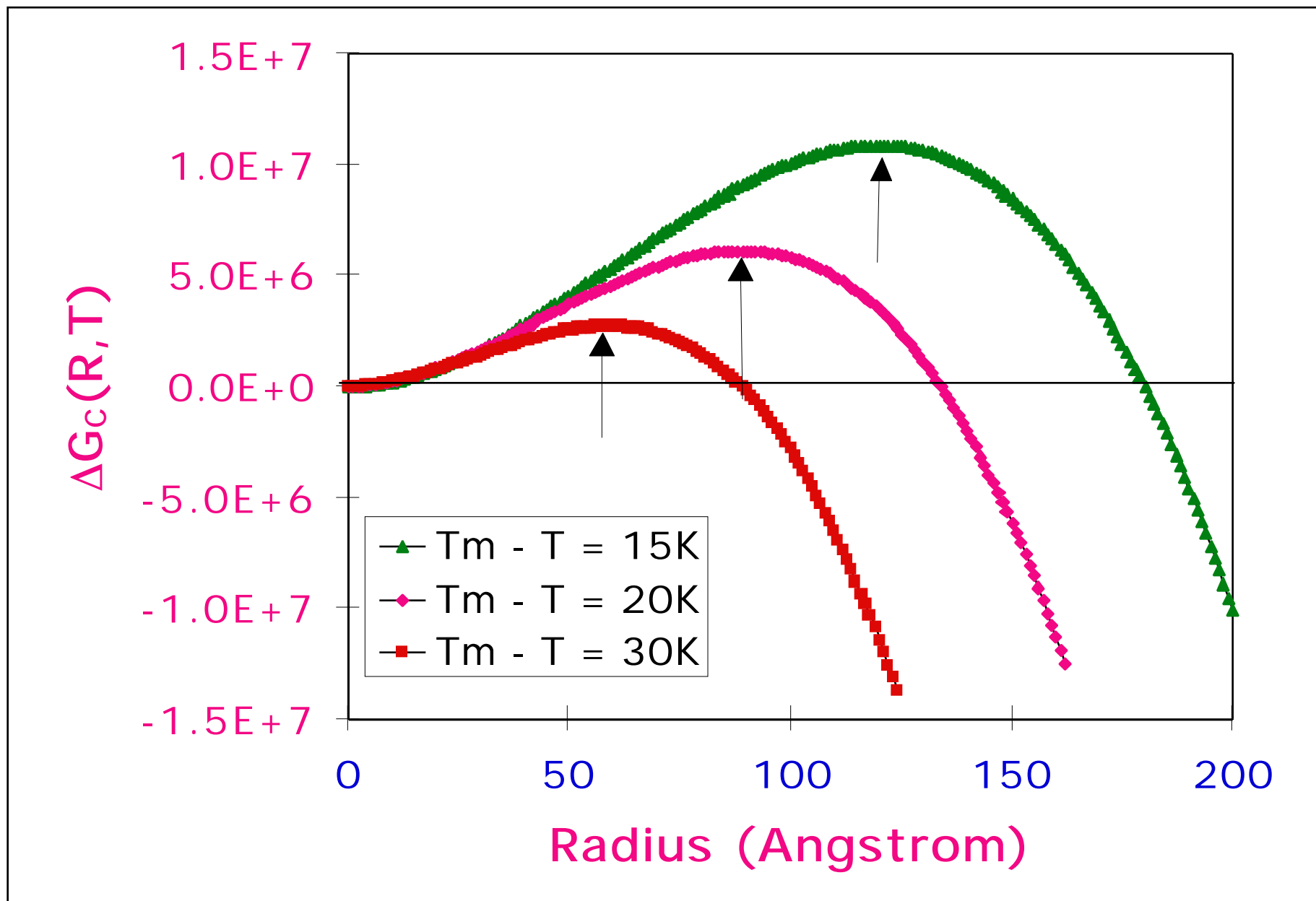
The maximum in the free energy barrier can be obtained by differentiation of  $G_C(R, T)$  with respect to  $R$  and finding the zero of that derivative.

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

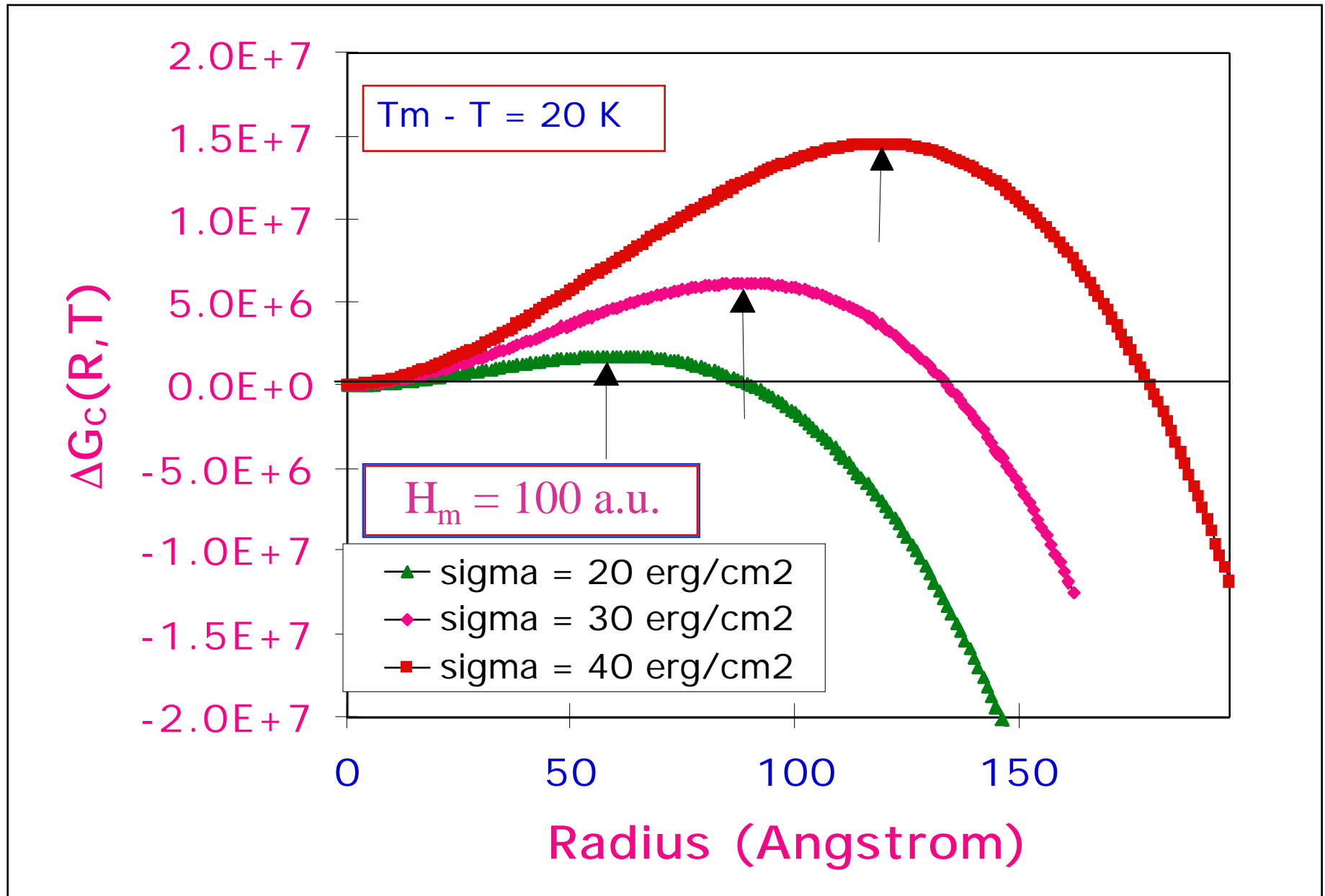
$$R^* = \frac{2\sigma T_m}{H_m T} \quad G_C(R^*, T) = \frac{16\pi\sigma^3}{3} \frac{T_m^2}{H_m T}$$

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.

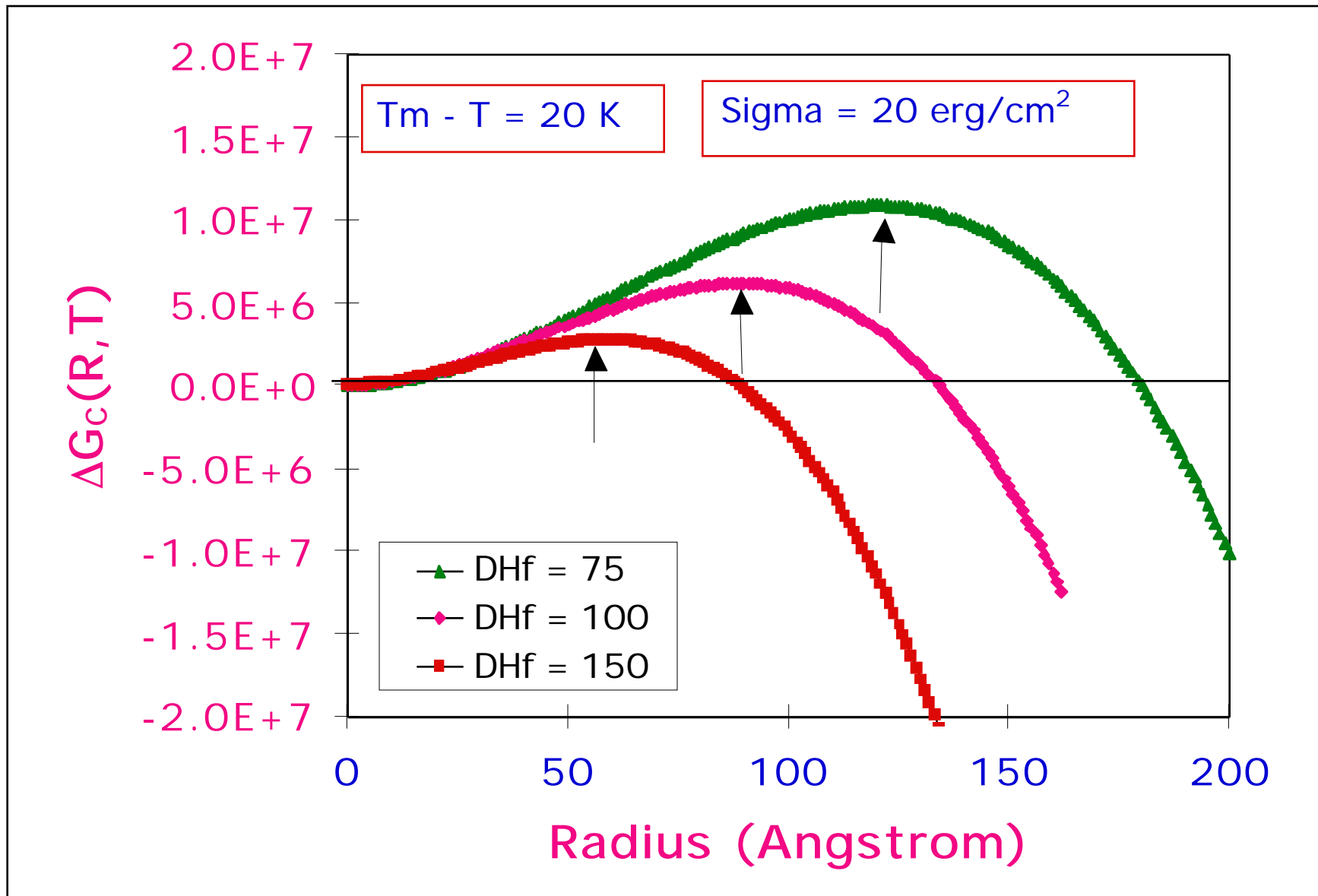
# Free Energy of Nucleation vs. Radius and Undercooling



# Effect of Surface Energy on the Free Energy of Nucleation

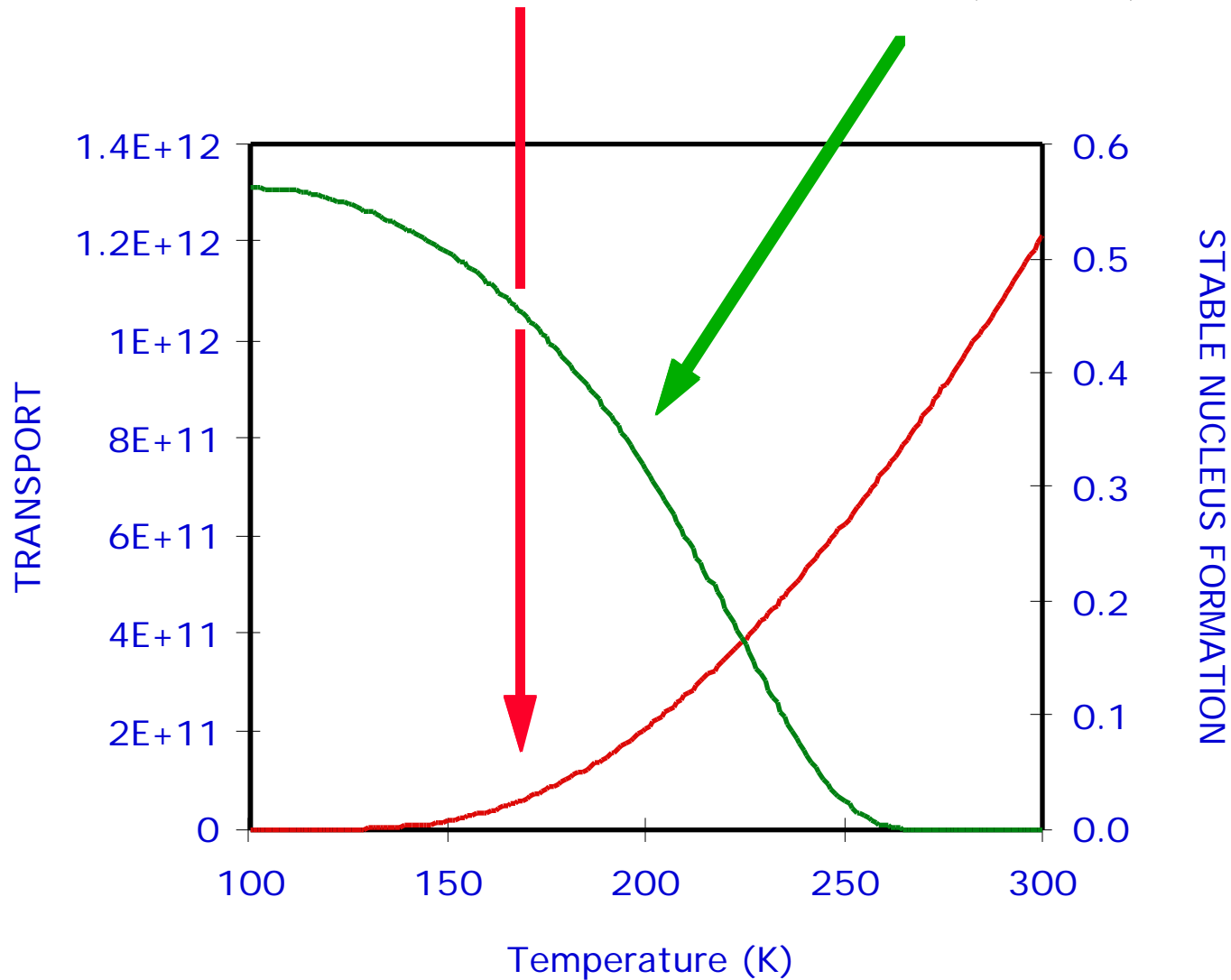


# Effect of Enthalpy of Crystallization on the Free Energy of Nucleation

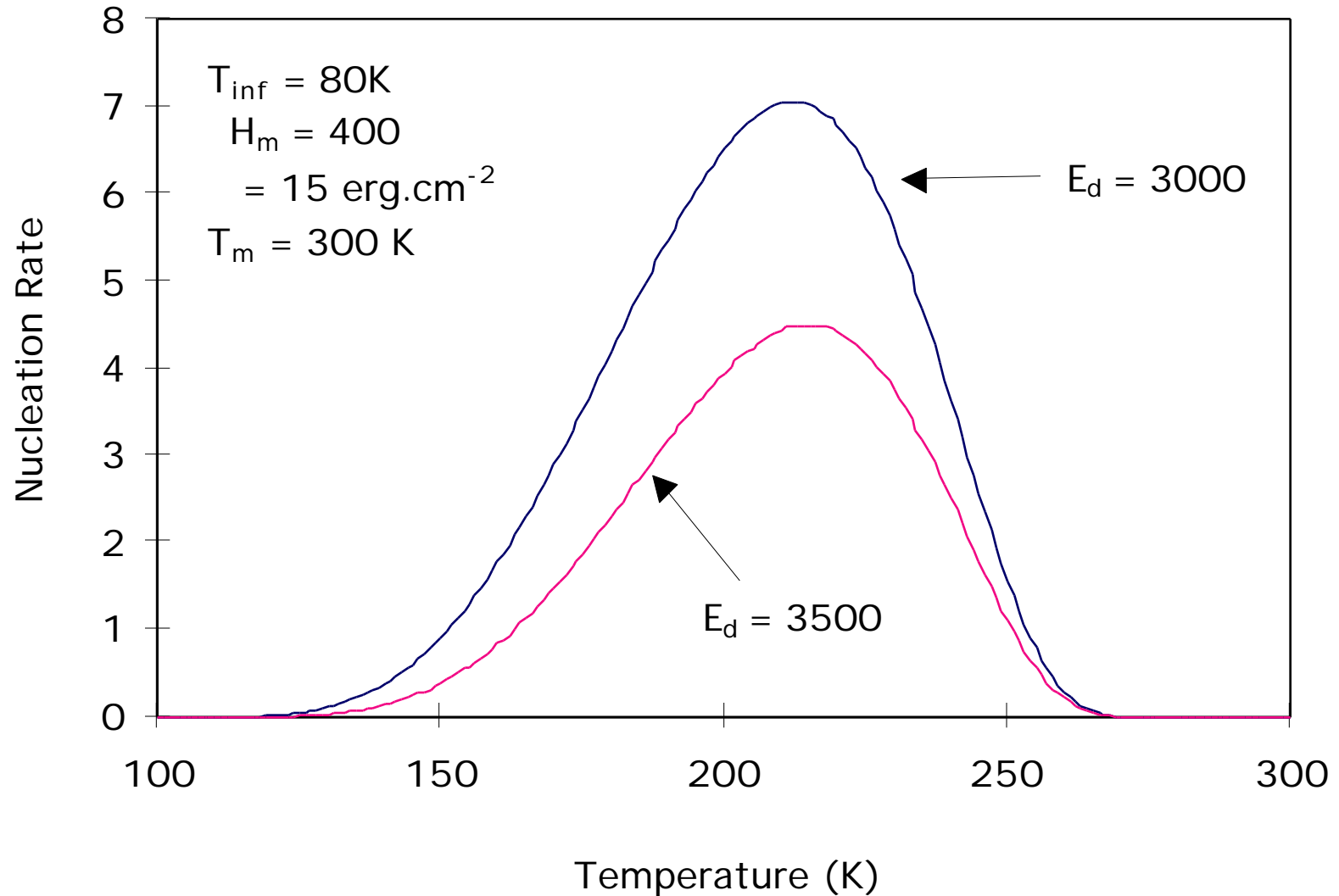


# Temperature Dependence of the Nucleation Rate

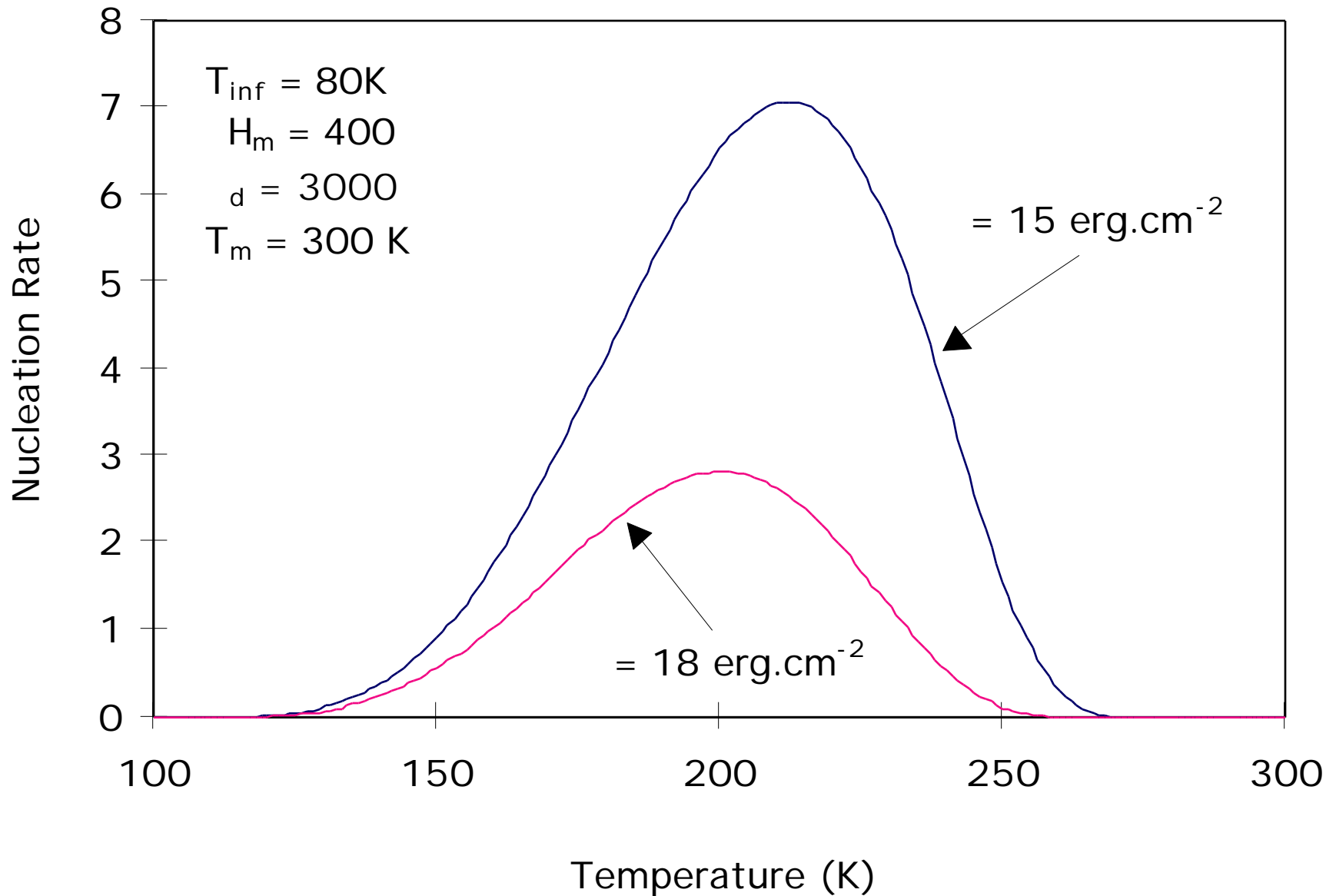
$$\frac{dN}{dt} = \frac{kT}{h} \exp\left(\frac{-B}{R(T - T_m)}\right) \exp\left(\frac{-16\pi\sigma^3 T_m^2}{3kT H_m^2 (T_m - T)^2}\right)$$



# 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



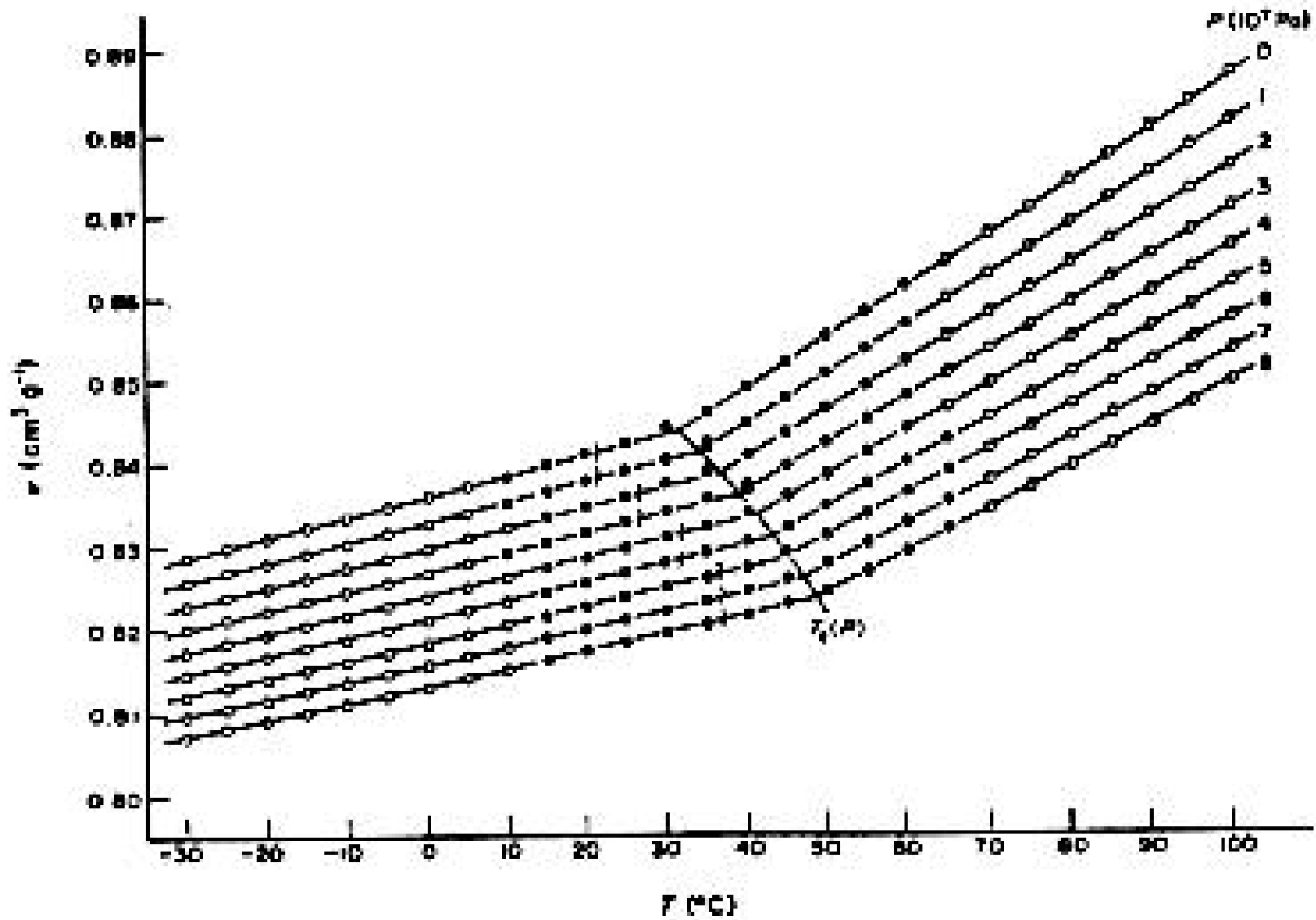
## Glass Formation vs. Crystallization: Quenching

- 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.

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

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

# Effect of Pressure on the Glass Transition Temperature

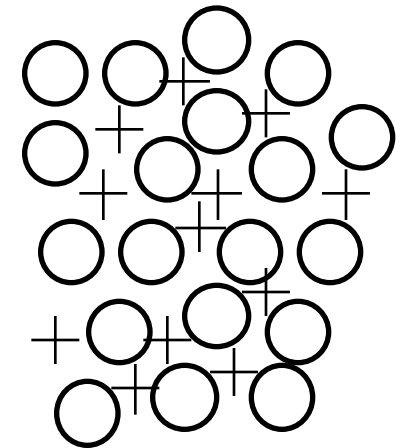


## Glass Formation vs. Crystallization: Pressurization

- 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.



+ Free Volume Site  
○ Molecule

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

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

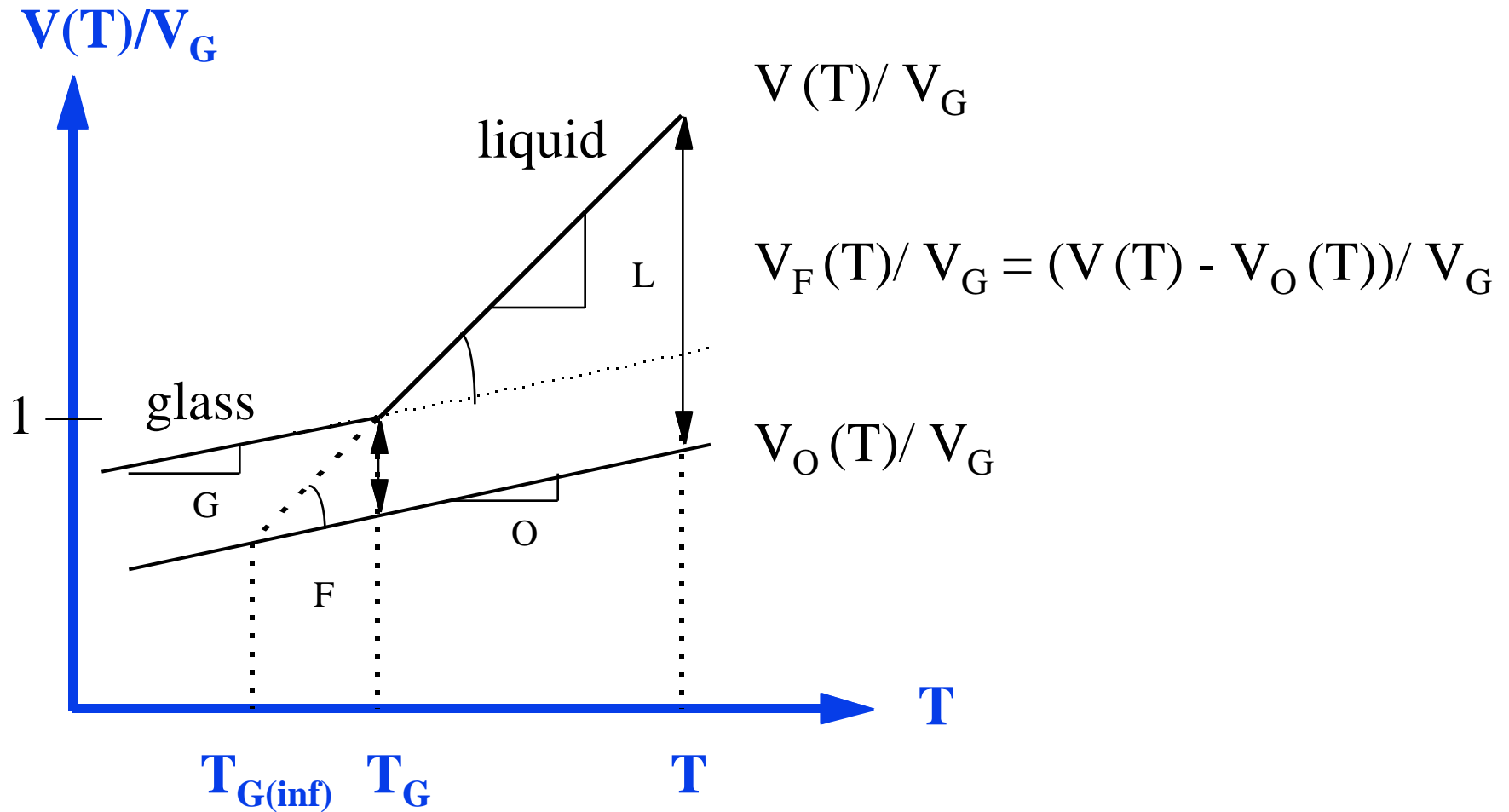
where  $a$  and  $b$  are constants,  $V$  is the material's specific volume and  $V_0$  is the occupied specific volume.

- 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:

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

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

where  $\alpha_F$  is the isobaric coefficient of thermal expansion of the free volume.



- One should realize that  $\alpha_O$ ,  $\alpha_G$  and  $\alpha_C$  are of the same order of magnitude. The small values of  $\alpha_G$  and  $\alpha_C$  are associated with the anharmonicity of the dependence of the potential energy on interatomic distances. The higher value of  $\alpha_L$  is associated with the formation of additional free volume with increase in  $T$ .

## Vogel-Fulcher-Tamman-Hesse Law

- The fractional free volume  $f$  can then be written as :

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

which leads to an expression for  $\ln(\eta)$

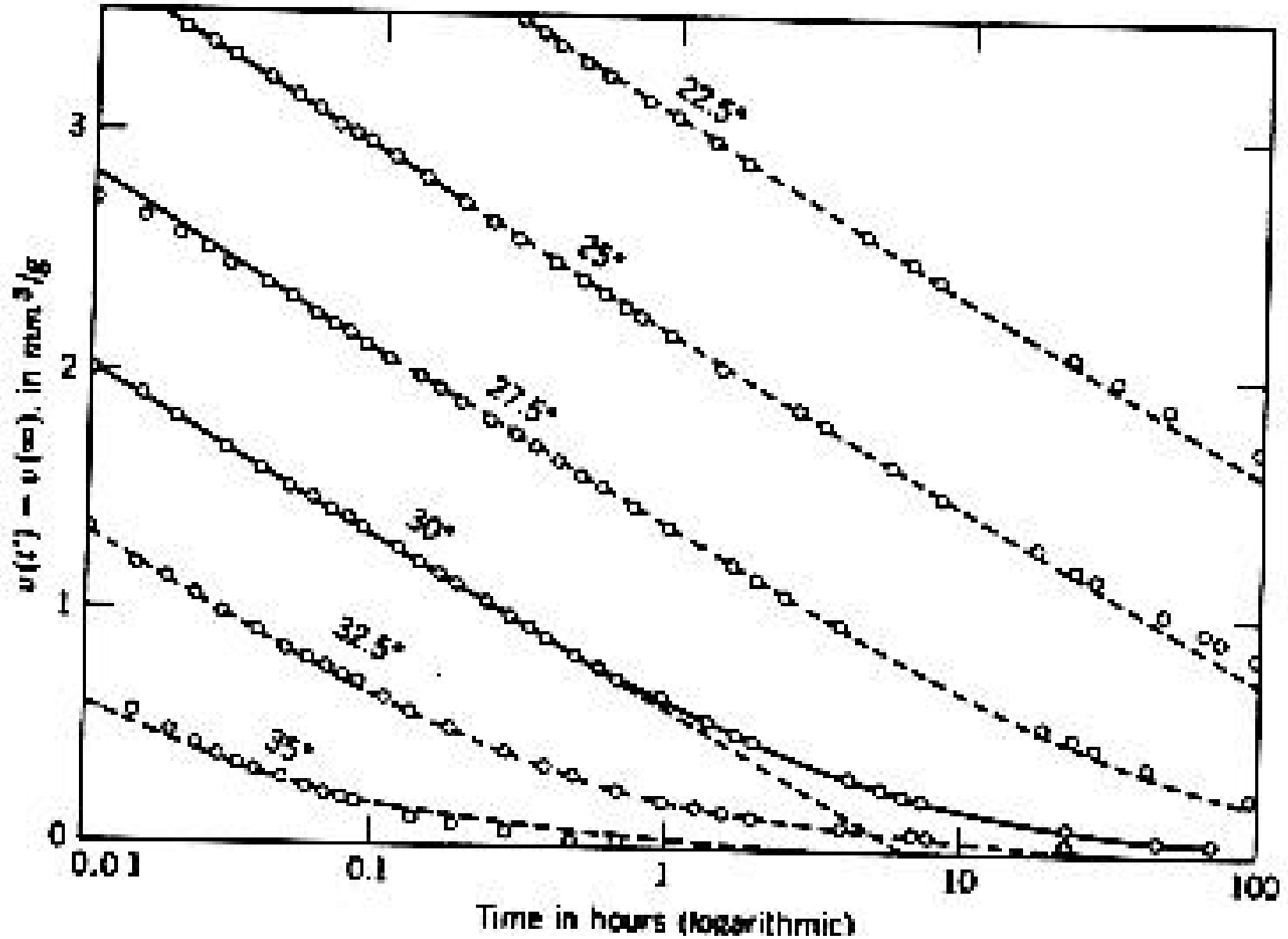
$$\ln(\eta) = a + \frac{b}{\alpha_F (T - T_G)} \quad \text{Fulcher-Tamman-Hesse Law}$$

$$\ln(\eta) = A + \frac{B}{(T - T_G)} \quad \text{Vogel Law (empirical)}$$

$T_{Ginf}$  is the glass transition temperature extrapolated to zero free volume (infinitely slow cooling). It has also often be associated with the Kauzmann temperature or the  $T_2$  temperature in the Gibbs-DiMarzio theory where configurational entropy vanishes

- 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)



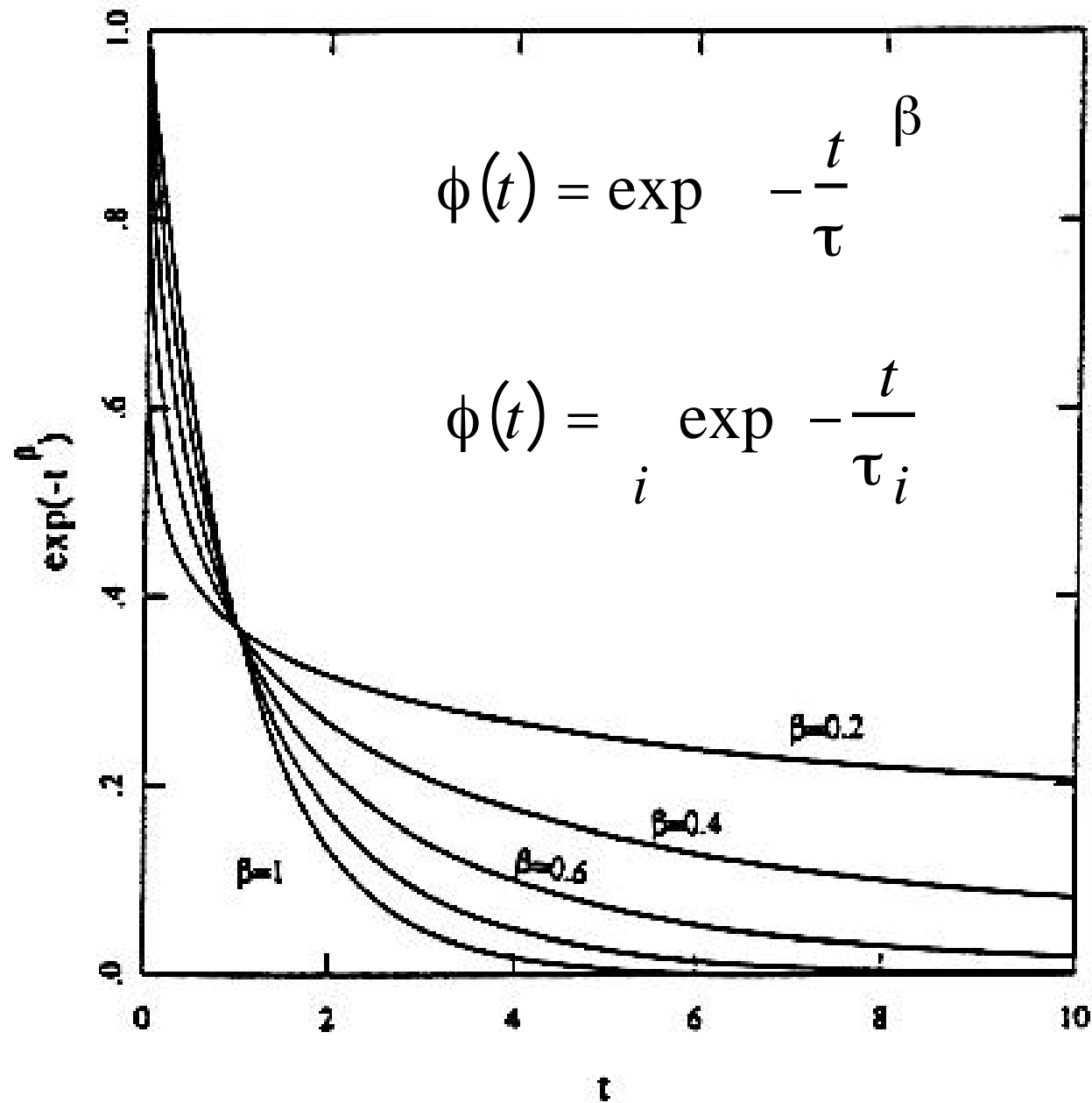
## Time Dependent Properties in the T<sub>g</sub> Region

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<sub>G</sub>. The time scale over which they reach their equilibrium value in the T<sub>G</sub> 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,  $\tau_i$ .

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

**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	$\text{SiO}_2$	S, Se, Polymers, Organic