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"Amorphous Materials"

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Theories for the glass transition

A. Thermodynamic phase transition

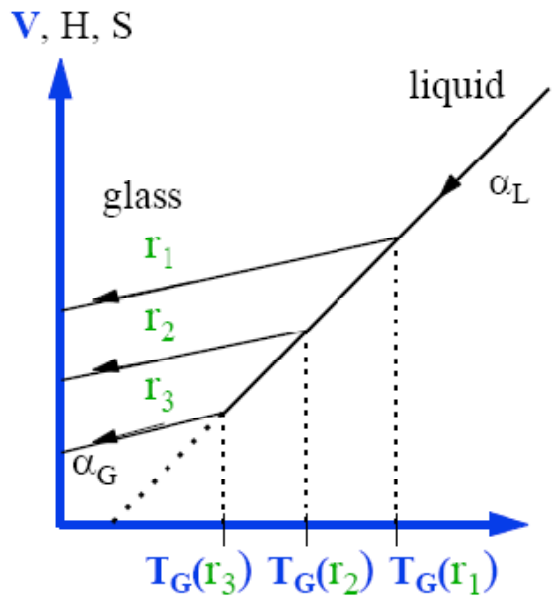
- ***Glass transition***

  H , V , S : continuous ***C_p α_T K_T : discontinuous***

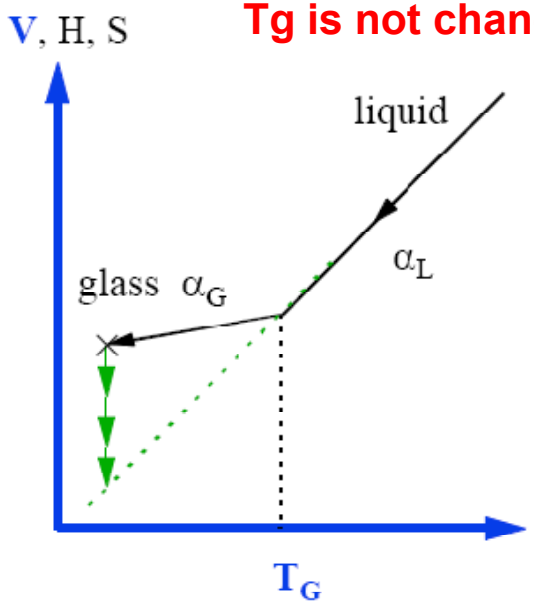
→ **by thermodynamic origin, 2nd order transition**

But, ***1) Tg is dependent on thermal history of sample.***

→ **If 2nd order transition, Tg is not changed by kinetic factor.**



Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$



Specific Volume (density) of the glass depends on the time at a given $T < T_g$

Ehrenfest Classification of Phase Transitions

- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

- Second Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are continuous at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

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  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Value of the Prigogine Defay Ratio: R

- Continuity conditions for G or μ at a first order phase transition allowed us to derive the Clapeyron equation $\left(\frac{dP}{dT}\right) = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$

- If T_G is a second order transition, continuity of V and S at T_G leads to two similar relations between materials parameters and state variables.

$$V_G = V_L \qquad dV_G = dV_L$$
$$dV_G = \alpha_G V_G\, dT - \kappa_G V_G\, dP$$
$$dV_L = \alpha_L V_L\, dT - \kappa_L V_L\, dP$$

$$\Rightarrow \left(\frac{dP}{dT}\right) = \frac{\Delta C_P}{VT\Delta\alpha}$$

$$S_G = S_L \qquad dS_G = dS_L$$
$$dS_G = (C_P^G / T)dT - \alpha_G V_G\, dP$$
$$dS_L = (C_P^L / T)dT - \alpha_L V_L\, dP$$

$$\Rightarrow \left(\frac{dP}{dT}\right) = \frac{\Delta\alpha}{\Delta\kappa}$$

By combining both Ehrenfest equations without invoking a second-order thermodynamic transition,

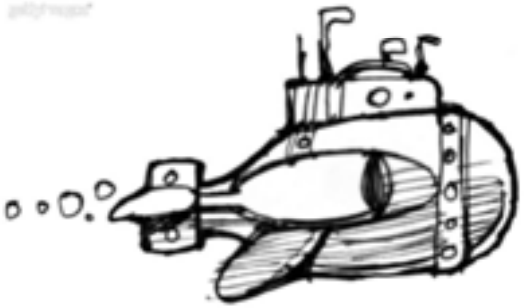
$$R = \frac{\Delta C_P \Delta\kappa}{VT(\Delta\alpha)^2}$$

→ Prigogine Defay Ratio:R

Clausius-Clapeyron Equation in Real Life

❖ Why the bubbles form near the screw of the boat

- When riding a boat, bubbles formed near the screw are seen. Mechanism of bubble formation is closely related to Clausius-Clapeyron equation.



High speed of the screw
→ Velocity of fluid increases $v \uparrow$

↓

Pressure of water near screw decreases $p \downarrow$

↓

Boiling temperature of water decreases $\Delta T < 0$

↓

Water turns into vapor even at low temperature

Bernoulli's Equation

$$\frac{v^2}{2} + gh + \frac{p}{\rho} = \text{constant}$$

Clausius-Clapeyron Equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\,\Delta V}$$

Ref.
두산 엔싸이버 백과 http://www.encyber.com
Wikkipedia http://wiki.answers.com

Value of the Prigogine Defay Ratio: R

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- If T_G is a second order transition, continuity of V and S at T_G leads to two similar relations between materials parameters and state variables.

$$V_G = V_L \qquad dV_G = dV_L$$
$$dV_G = \alpha_G V_G\, dT - \kappa_G V_G\, dP$$
$$dV_L = \alpha_L V_L\, dT - \kappa_L V_L\, dP$$

$$\left(\frac{dP}{dT}\right) = \frac{\Delta C_P}{VT\Delta\alpha}$$

$$S_G = S_L \qquad dS_G = dS_L$$
$$dS_G = (C_P^G / T)dT - \alpha_G V_G\, dP$$
$$dS_L = (C_P^L / T)dT - \alpha_L V_L\, dP$$

$$\left(\frac{dP}{dT}\right) = \frac{\Delta\alpha}{\Delta\kappa}$$

By combining both Ehrenfest equations without invoking a second-order thermodynamic transition,

$$R = \frac{\Delta C_P \Delta\kappa}{VT(\Delta\alpha)^2}$$

→ Prigogine Defay Ratio:R

***Incentive H2: application of R**

Theories for the glass transition

But, *2) Thermodynamic consideration* ***S , V*** **:** ***continuous***

(a) continuity of S

$S_1 = S_2$ *Entropies of the high- and low-temp. forms must be equal at the transition*

⟶ **with respect to temperature and pressure,**

$dS_1 = dS_2$ *in terms of partial derivatives,*

or $$(\frac{\partial S_1}{\partial T})_P dT + (\frac{\partial S_1}{\partial P})_T dP = (\frac{\partial S_2}{\partial T})_P dT + (\frac{\partial S_2}{\partial P})_T dP$$

using one of Maxwell's thermodynamic relations

$$\rightarrow \boxed{C_P = T(\frac{\partial S}{\partial T})_P}, \boxed{(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P}, \boxed{\alpha_T = 1/V(\frac{\partial V}{\partial T})_P}$$

Theories for the glass transition

$$\rightarrow \quad \frac{C_{p1}}{T}dT + V\alpha_{T1}dP = \frac{C_{p2}}{T}dT - V\alpha_{T2}dP$$

$$\rightarrow \quad \frac{1}{T}(C_{P1} - C_{P2})dT = V(\alpha_{T1} - \alpha_{T2})dP$$

$$\therefore \frac{dT_g}{dP} = \frac{TV(\alpha_{T_2} - \alpha_{T_1})}{(C_{P_2} - C_{P_1})} = \frac{TV\boxed{\Delta\alpha_T}}{\boxed{\Delta C_P}} \quad \text{(1)}$$

measureable

$$\frac{\partial^2 G}{\partial P_T^2} = \frac{\partial V}{\partial P_T} = -V\beta(compressibility)$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial V}{\partial T_P} = V\alpha(thermal\ \exp ansion)$$

But, ***2) Thermodynamic consideration***

(b) continuity of V

$V_1 = V_2$ & $d\,V_1 = d\,V_2$

$$(\frac{\partial V_1}{\partial T})_P dT + (\frac{\partial V_1}{\partial P})_T dP = (\frac{\partial V_2}{\partial T})_P dT + (\frac{\partial V_2}{\partial P})_T dP$$

$$\rightarrow \alpha_T = 1/V(\frac{\partial V}{\partial T})_P, \kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_T$$

$$\rightarrow V\alpha_{T1}dT - V\kappa_{T1}dP = V\alpha_{T2}dT - V\kappa_{T2}dP$$

$$\rightarrow (\alpha_{T1} - \alpha_{T2})dT = (\kappa_{T1} - \kappa_{T2})dP$$

$$\therefore \frac{dT_g}{dP} = \frac{\Delta\kappa_T}{\Delta\alpha_T} \qquad \textbf{(2)}$$

$$\therefore \frac{dT_g}{dP} = \frac{TV(\alpha_{T_2} - \alpha_{T_1})}{(C_{P_2} - C_{P_1})} = \frac{TV\Delta\alpha_T}{\Delta C_P} \qquad (1)$$

measureable

$$\therefore \frac{dT_g}{dP} = \frac{\Delta\kappa_T}{\Delta\alpha_T} \qquad (2)$$

→ **Eq. (1) & (2) should be proved experimentally.**

It is found by measuring the discontinuities $\Delta\alpha_T$, ΔC_P, $\Delta\kappa_T$ at the glass transition that Eq. (1) is almost always obeyed within experimental error, but that values for $\Delta\kappa_T/\Delta\alpha_T$ are generally appreciably higher than those of dT_g/dP (Eq. (2)).

→ **Eq. (1) = satisfy** **Eq. (2) = dissatisfy :** $\frac{dT_g}{dP} < \frac{\Delta\kappa_T}{\Delta\alpha_T}$

→ **Therefore, it appears on this evidence that the glass transition is not a simple second-order phase transition.**

If a single ordering parameter determines the position of equilibrium in a relaxing system,

$$R = \frac{\Delta\kappa_T \Delta C_P}{TV(\Delta\alpha_T)^2} = 1$$

If more than one ordering parameter is responsible,

$$R = \frac{\Delta\kappa_T \Delta C_P}{TV(\Delta\alpha_T)^2} > 1$$

➡ **The latter case seems to describe most glasses.**

Goldstein (1973) has suggested that

" The specific volume V_g of the glass depends not only on the temperature, being continuous through the transition, but also on the pressure of formation"

Jäckle (1989) has shown that

$$\frac{dT_g}{dP} = \frac{\Delta\kappa_T}{\Delta\alpha_T} \quad \Rightarrow \quad \frac{dT_g}{dP} = \frac{\Delta\kappa_T + \boxed{\partial(\ln V_g)/\partial p_f}}{\Delta\alpha_T}$$

Additional consequence of the experimental verification,

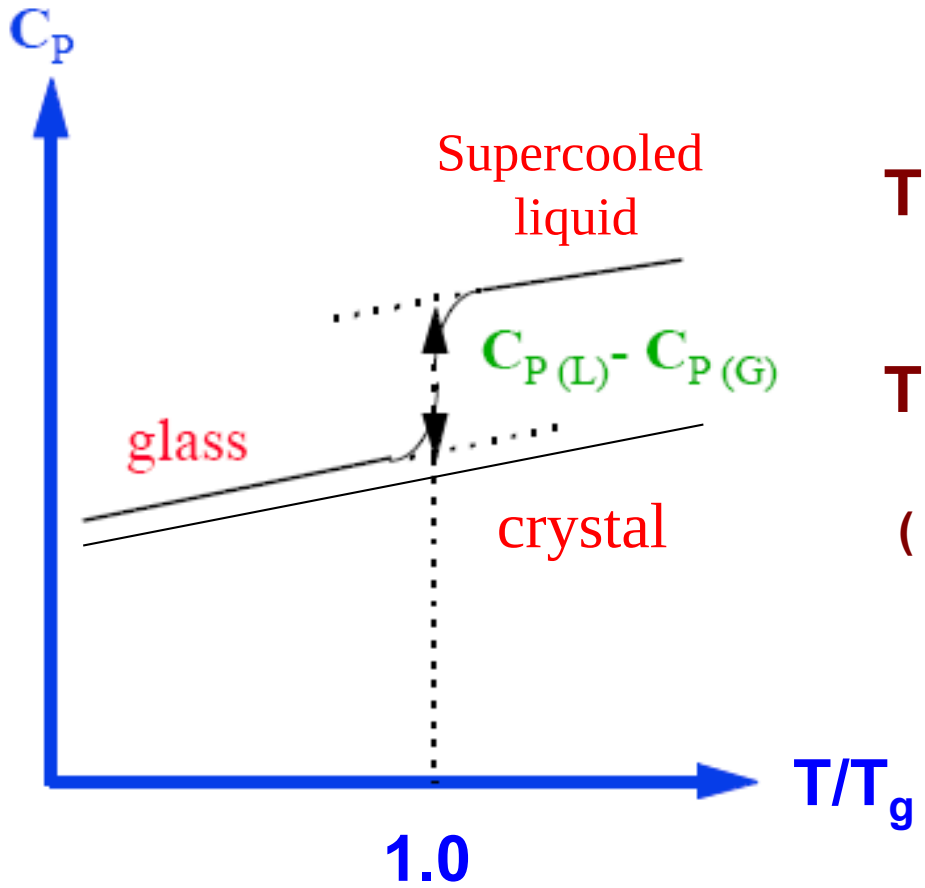
" Glasses prepared under high pressures to have higher than normal densities but normal entropies or enthalpies. "

Theories for the glass transition

B. Entropy $$S = \int C_P d \ln T$$

- ***Description of glass transition by entropy*** **(Kauzmann)**

1) Heat capacity → **dramatic change at Tg**



T < T_g $C_{P_{glass}} \approx C_{P_{crystal}}$

T > T_g $C_{P_{SCL}} > C_{P_{crystal}}$

(∵ configurational degree of freedom in S.C.L.)

Laws of thermodynamics

1) **Zeroth law: thermal equilibrium**
   Objects in thermodynamic equilibrium have the same temperature.

2) **First law: conservation of energy**
   Energy can be neither created nor destroyed but only transformed.

3) **Second law: entropy, $S > 0$**
   The entropy of an isolated system not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium.

3) **Third law: absolute zero**
   As a system approaches absolute zero of temperature, all processes cease and the entropy of the system approaches a minimum value.

- **The *second* law of thermodynamics**

$$S = \frac{q}{T}$$

; The disorder of the universe always increase

; all chemical and physical processes occur spontaneously only when disorder is increased.

Theories for the glass transition

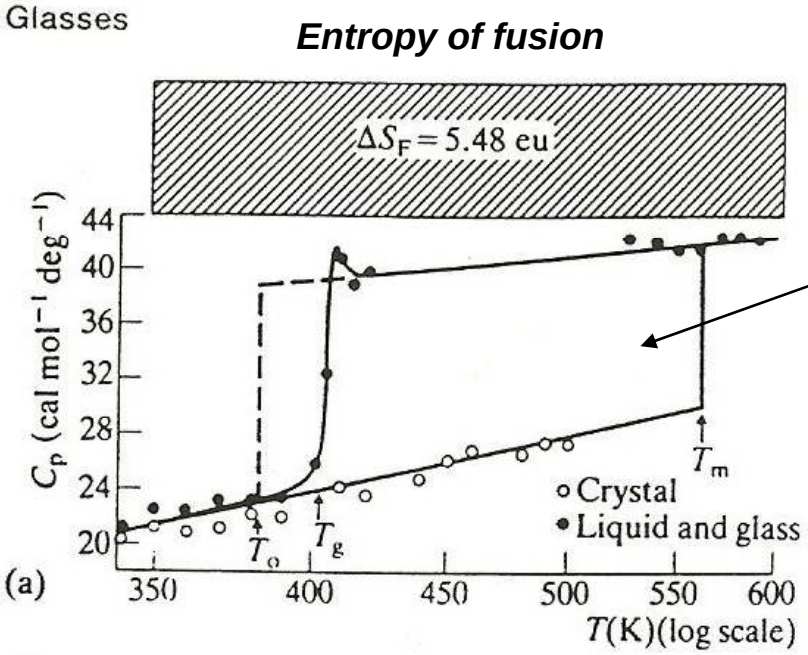
B. Entropy

- ***Description of glass transition by entropy*** **(Kauzmann)**

2) The slow cooling rate, the lower Tg

→ **ideal glass transition temperature exist?**

→ **YES**



$$S = \int C_P d \ln T$$

The data are plotted against ln T so that integrated areas under the curves yield entropies directly, and the entropy of fusion is shown shaded in the upper part of the figure.

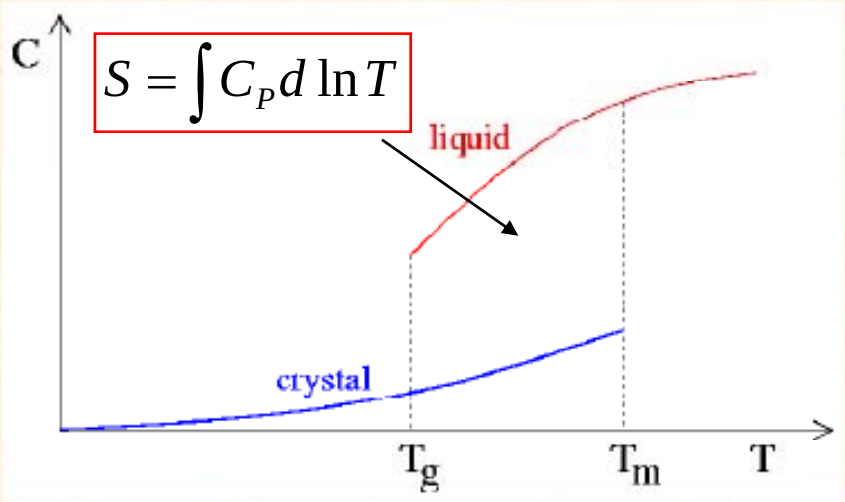
Heat capacities of glassy, liquid and crystalline phases of lithium acetate

Theories for the glass transition

B. Entropy

- ***Description of glass transition by entropy*** **(Kauzmann)**

Entropy of the liquid larger than in the crystal. Typically:



Kauzmann (1948)extrapolates the specific heat data below melting

$$s_\alpha(T_m) = s_\alpha(T) + \int_T^{T_m} \frac{c_\alpha}{T} dT \quad \alpha \in \{\text{liquid, crystal}\}$$

$c_{liquid} > c_{crystal}$ entropy in the liquid decreases faster with T than in the crystal

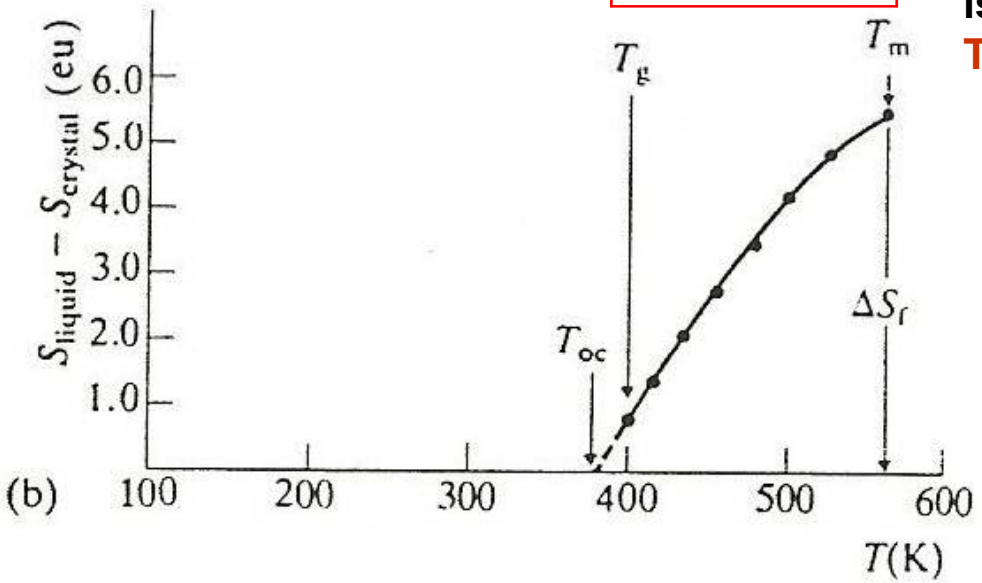
Theories for the glass transition

B. Entropy

- **Description of glass transition by entropy (Kauzmann)**

2) The slow cooling rate, the lower Tg

$$S = \int C_P d \ln T$$



The difference in entropy between liquid and crystalline phases as a function of temperature

The temperature vanishing excess entropy is termed the "ideal' glass transition temp. T_{oc} (Wong and Angell 1976)

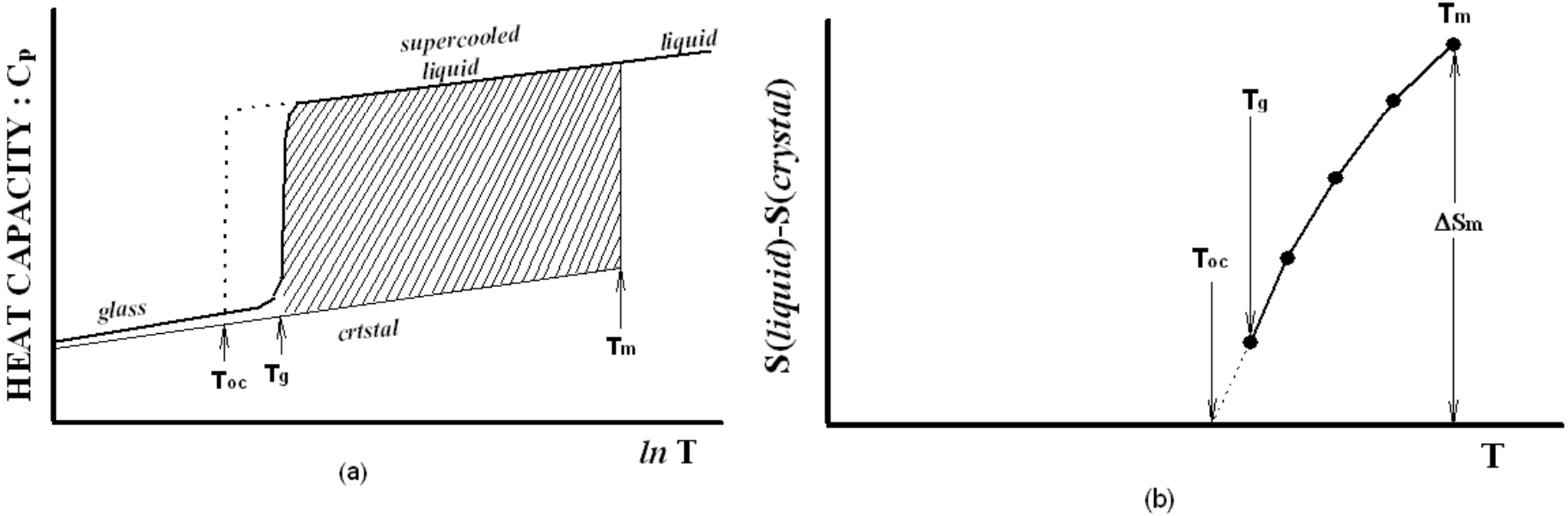
$$T_g \rightarrow T_{0C} \quad as \quad \frac{dT}{dt} \rightarrow 0$$

Not satisfied with third law of thermodynamics

T_{OC}: lower temperature limit to occur glass transition thermodynamically

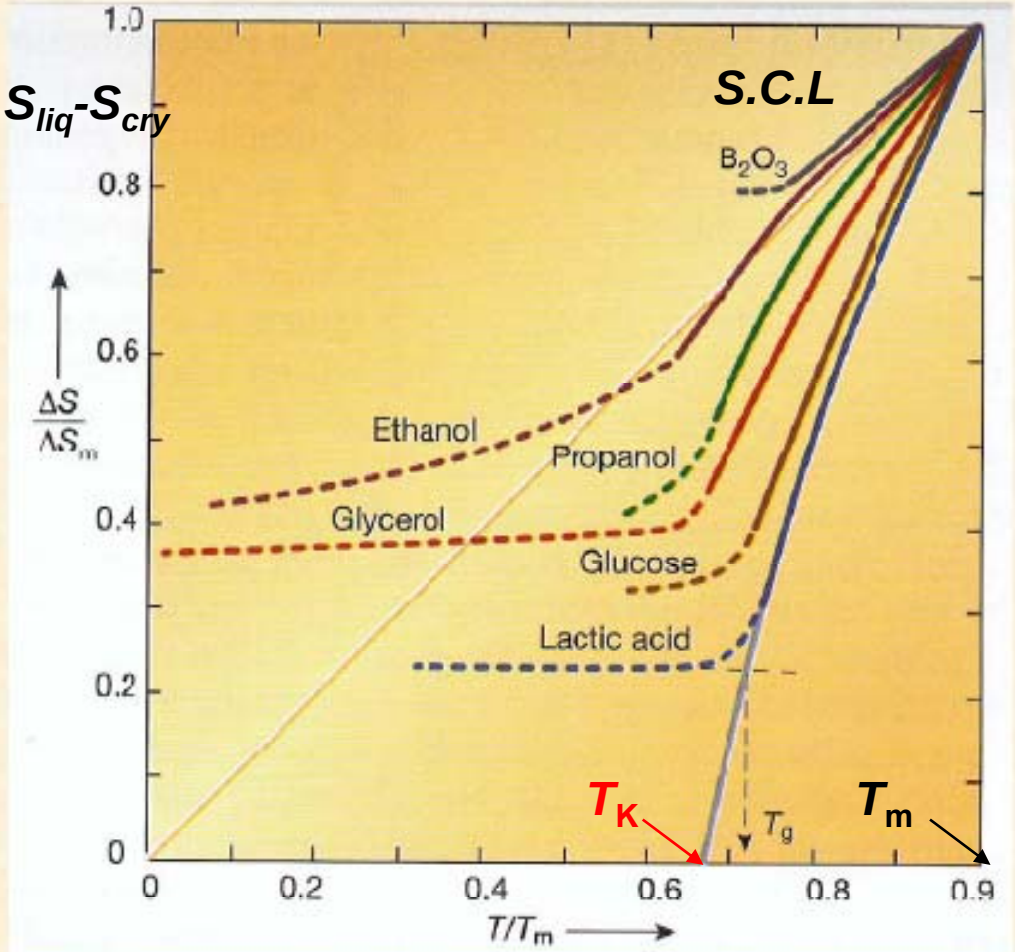
- **Ideal glass transition temperature (T_{oc})**

  : lower temperature limit to occur glass transition thermodynamically



Variation of (a) C_p and (b) excess entropy, S depending on temp. for glass, crystal and liquid. Ideal glass transition temp, T_{oc}. is the temperature when excess entropy is disappeared.

- ***Kauzmann's paradox*** **Thermodynamics: The configurational entropy apparently extrapolates to zero at low temperatures.**



T_K defined by an extrapolation of equilibrium properties. Not really justified. If point defects with finite formation energy are present in a reference configuration, the extrapolation is incorrect (Stillinger).

→ **Measurement of Kauzmann temp. is almost impossible.**

(∵ very slow cooling rate → longer relaxation time → crystallization)

Theories for the glass transition

A. Thermodynamic phase transition

- **Glass transition**

  H , V , S : continuous C_p α_T K_T : discontinuous

→ by thermodynamic origin, 2nd order transition

→ In fact, it appears on some evidences that the glass transition is not a simple second-order phase transition.

B. Entropy

- Heat capacity → dramatic change at Tg
- **Description of glass transition by entropy (Kauzmann)**

$$S = \int C_P d \ln T$$

→ The slow cooling rate, the lower T_g → T_K or T_g^0

→ Measurement of Kauzmann temp. is almost impossible.

(∵ very slow cooling rate → longer relaxation time → crystallization)

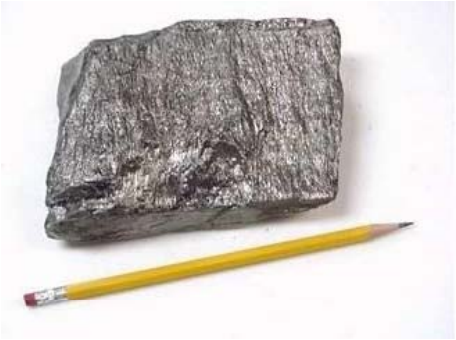
How does thermodynamics different from kinetics?

Thermodynamics ➡ **There is no time variable.**

says which process is possible or not and never says how long it will take.

The existence of a thermodynamic driving force does not mean that the reaction will necessarily occur!!!

⟷



There is a driving force for diamond to convert to graphite but there is (huge) nucleation barrier.

How long it will take is the problem of kinetics.

The time variable is a key parameter. ➡ **Relaxation & Viscosity**