Advanced Physical Metallurgy
"Amorphous Materials"

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Fragility

~ **ability of the liquid to withstand changes in medium range order with temp.**
~ **extensively use to figure out liquid dynamics and glass properties corresponding to "frozen" liquid state**
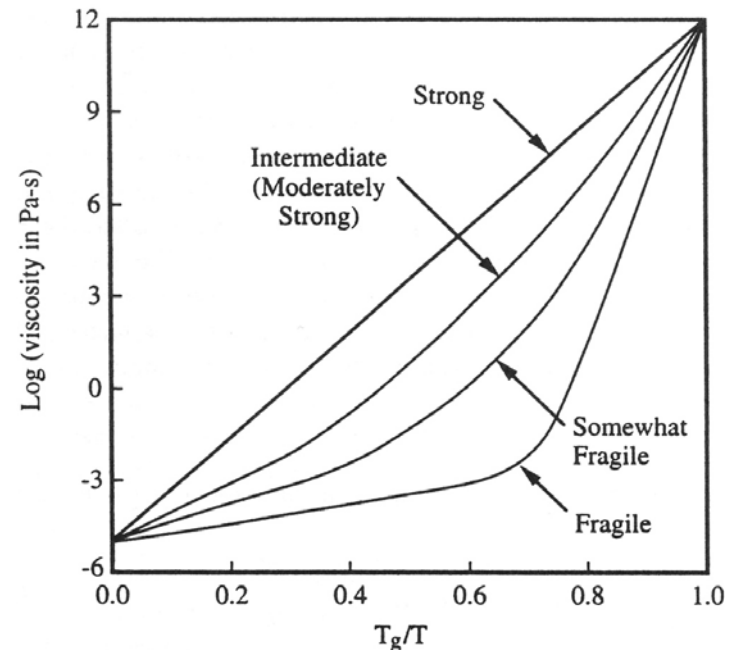
Strong liquid vs. Fragile liquid

• *Strong glass forming liquid*

⟶ **covalent bond of SiO_2**

⟶ **small difference of C_p between SCL and glass at T_g**
(*small difference of structure*)

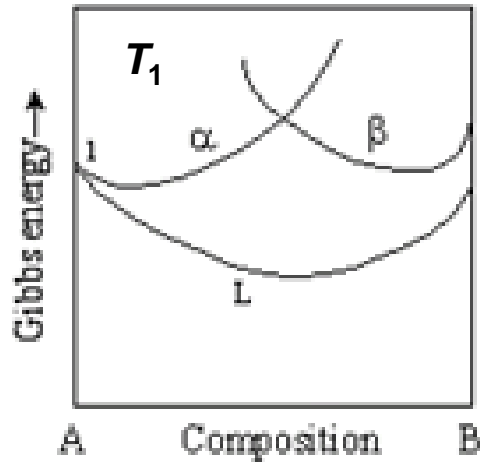⟶ **SCL: relatively low entropy**

• *fragile glass forming liquid*

⟶ **non-directional bonding**
(*Van der waals bonding*)

⟶ **large difference of C_p at T_g**
(*relatively large free volume*)
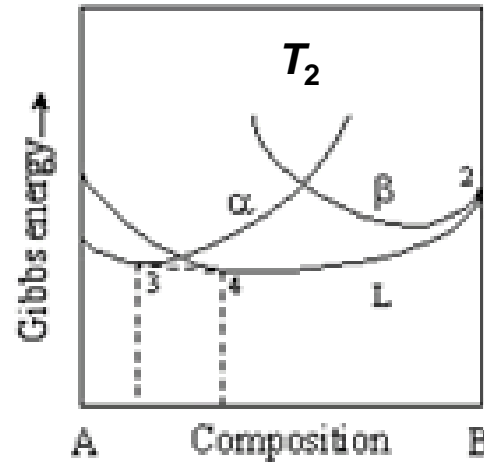
⟶ **SCL: relatively high entropy**

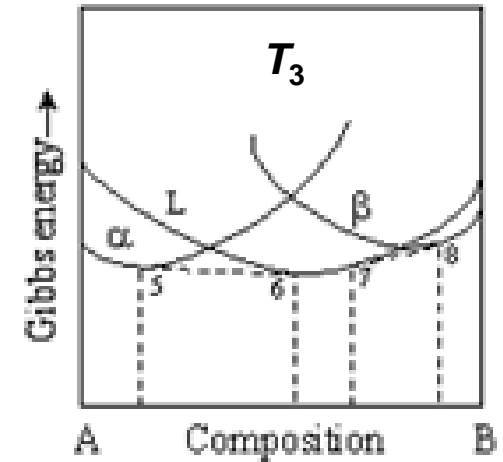**Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g**

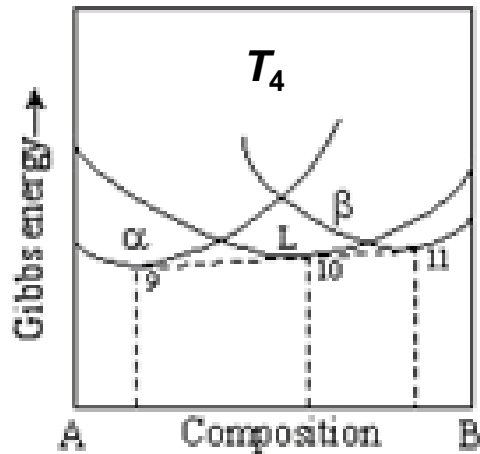**Use of Gibbs energy curves to construct a binary phase diagram of the eutectic type.**
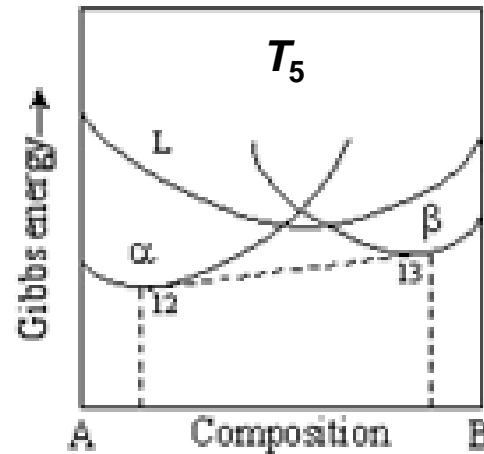

High temperature

low temperature

Liquid: metastable ⟶ glass

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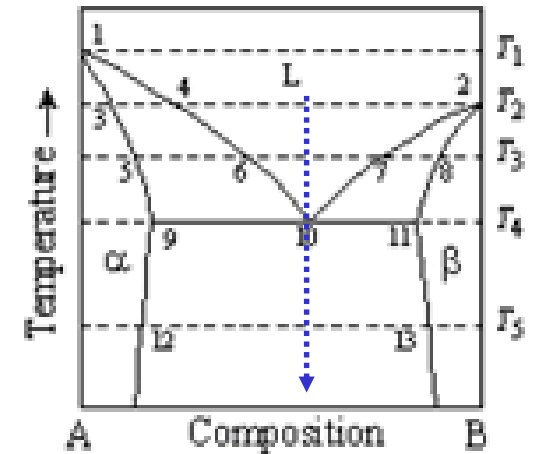
< Thermal map >
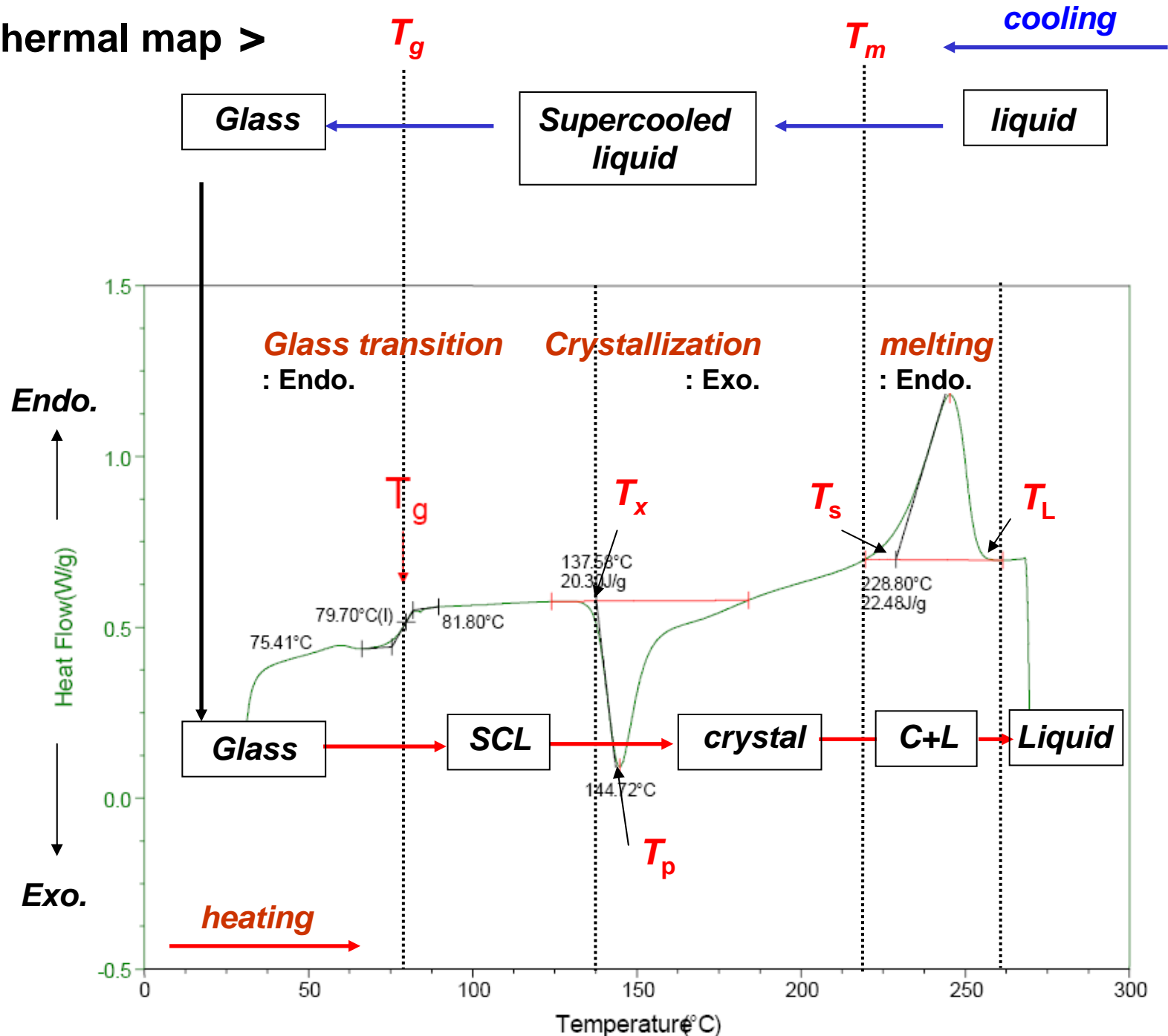
< Characteristics of metallic glass >

Critical cooling rate: several hundreds K/s

Reversible ↔   Irreversible →

| Amorphous phase (Solid) | Supercooled liquid state | Crystal phase (Solid) | Liquid phase |

Room temperature   Glass transition temperature: Tg   Crystallization temperature: Tx   Melting point: Tm   High temperature

High strength
High elastic limit
High hardness

Viscous flow
Viscosity$<10^{12}$Pa·s
⇩
New micromachining at supercooled liquid region

Brittleness

Theories for the glass transition

- *4 viewpoints for Glass transition*

Viscosity

Entropy

Free volume

Relaxation behavior

Kinetic variables
depending on time
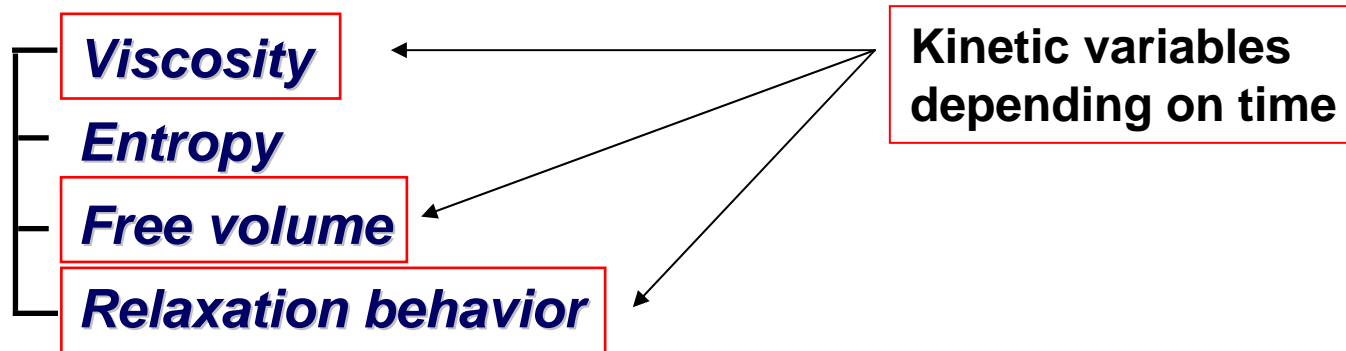
➡ **by thermodynamic origin, 2nd order transition**

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

→ **glass transition can be realized by evaluating one of factors.**

Theories for the glass transition

A. Thermodynamic phase transition

- ### *Glass transition*

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

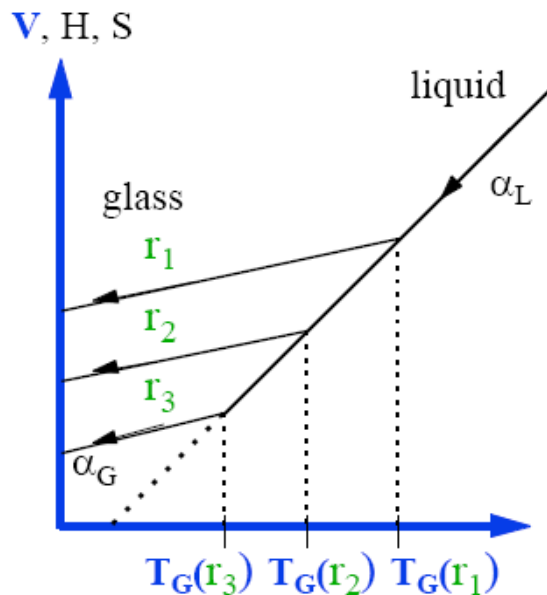→ **by thermodynamic origin, 2nd order transition**

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

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

V, H, S

liquid

glass　α_L

r_1

r_2

r_3

α_G

$T_G(r_3)$ $T_G(r_2)$ $T_G(r_1)$

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

V, H, S

liquid

glass α_G　α_L

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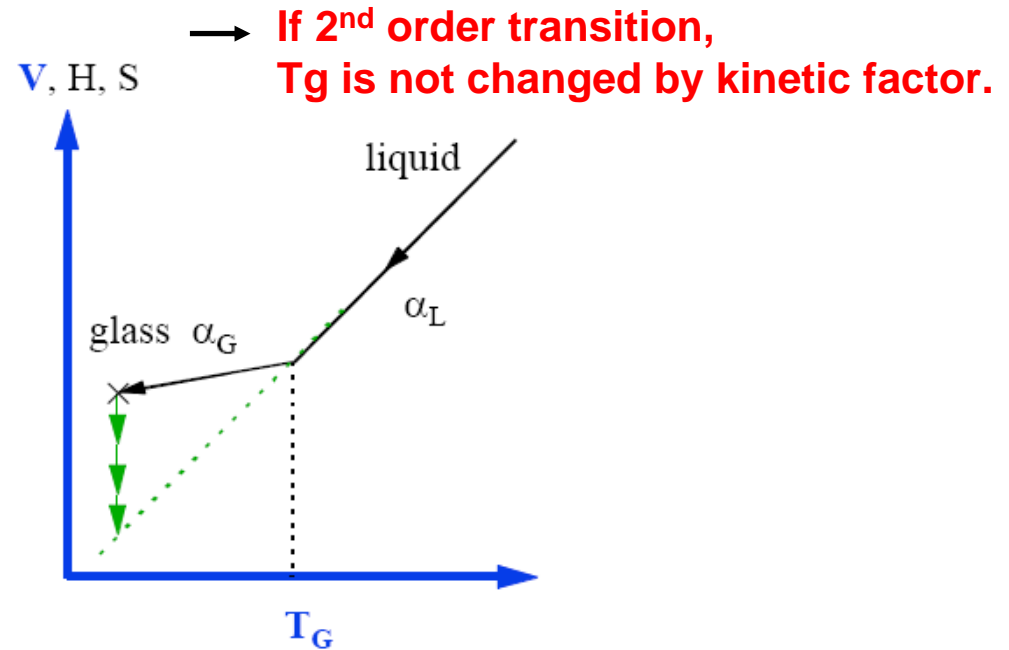
Specific Volume (density)
of the glass depends on the
time at a given $T < T_g$

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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

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

Theories for the glass transition

$$\longrightarrow \quad \frac{C_{p_1}}{T}dT + V\alpha_{T1}dP = \frac{C_{p2}}{T}dT - V\alpha_{T2}dP$$

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

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

measureable

But, *2) Thermodynamic consideration*

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

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

(b) continuity of V

$$V_1 = V_2 \quad \& \quad dV_1 = dV_2$$

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

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

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

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

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

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Contents for previous class

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

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 :** $\dfrac{dT_g}{dP} < \dfrac{\Delta\kappa_T}{\Delta\alpha_T}$

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

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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 $\left(\dfrac{dP}{dT}\right) = \dfrac{\Delta S}{\Delta V} = \dfrac{\Delta H}{T\Delta V}$

- 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.

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

$$\Longrightarrow \quad \left(\frac{dP}{dT}\right) = \frac{\Delta C_p}{VT\Delta\alpha}$$

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

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

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

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

$\Longrightarrow$ Prigogine Defay Ratio:R

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

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

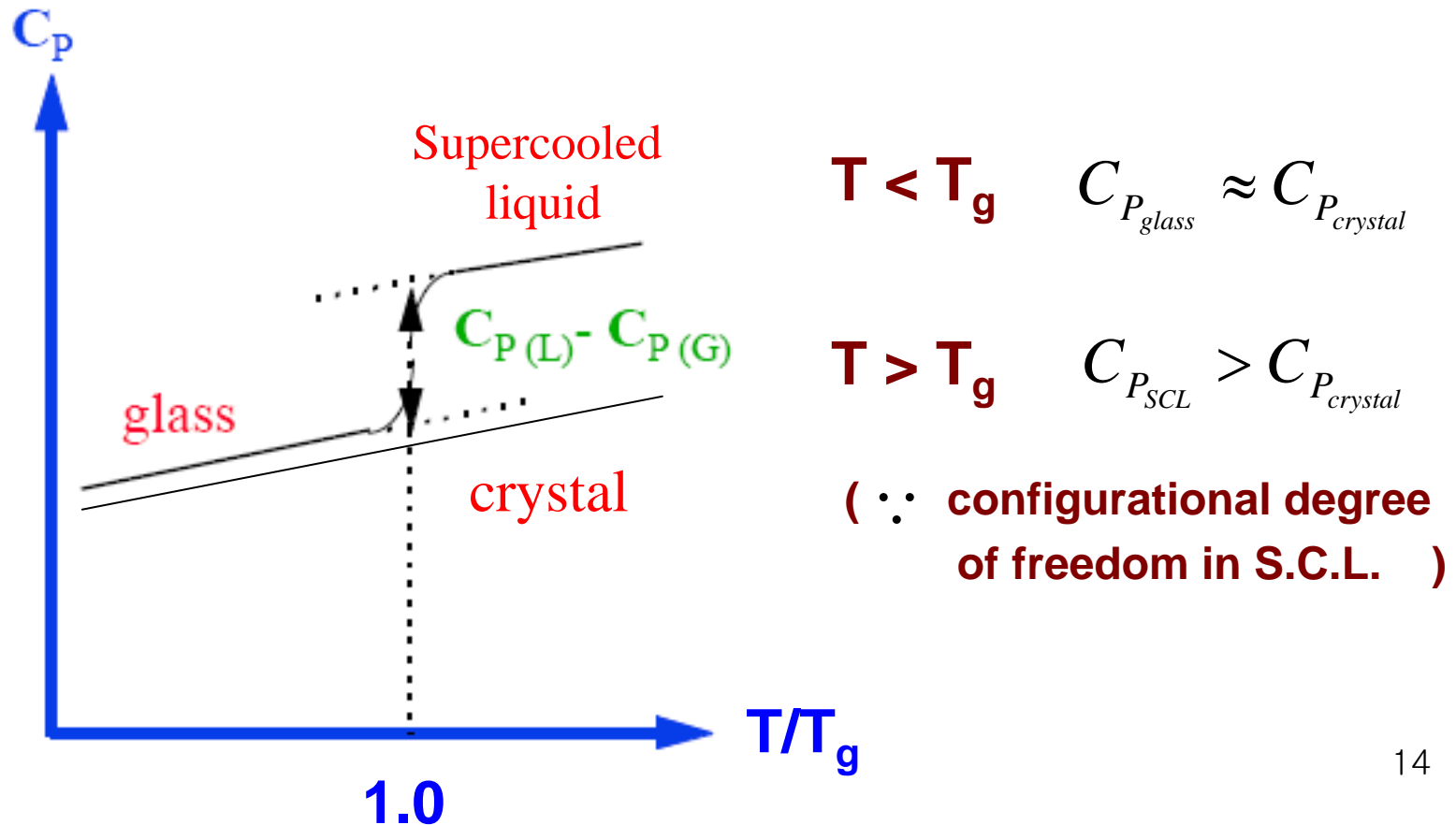**Additional consequence of the experimental verification,**

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

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Theories for the glass transition

B. Entropy

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

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

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

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

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

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**

Glasses

Entropy of fusion
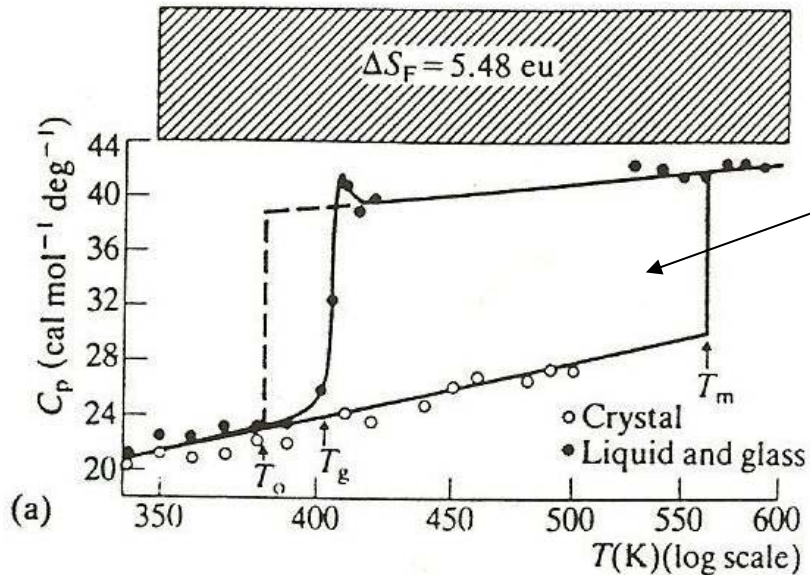
$$S = \int C_P d \ln T$$

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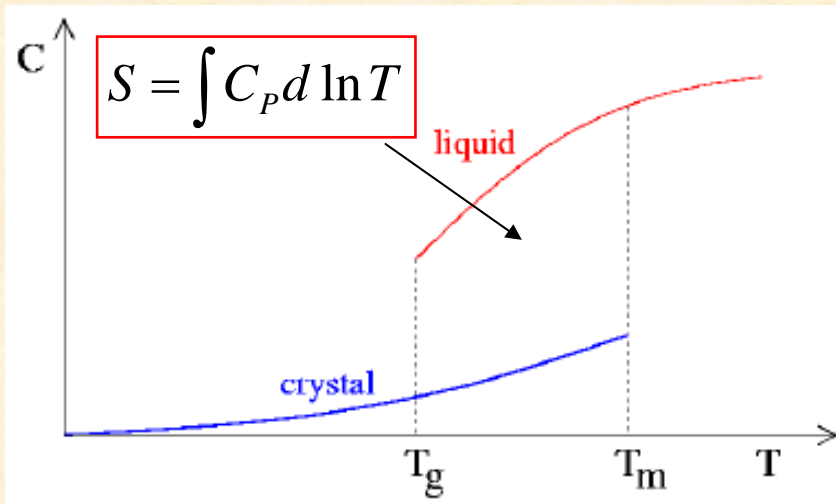
Heat capacities of glassy, liquid and crystalline phases of lithium acetate

Theories for the glass transition

B. Entropy

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

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

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

liquid

crystal

T_g T_m T

Kauzmann (1948) extrapolates the specific heat data below melting

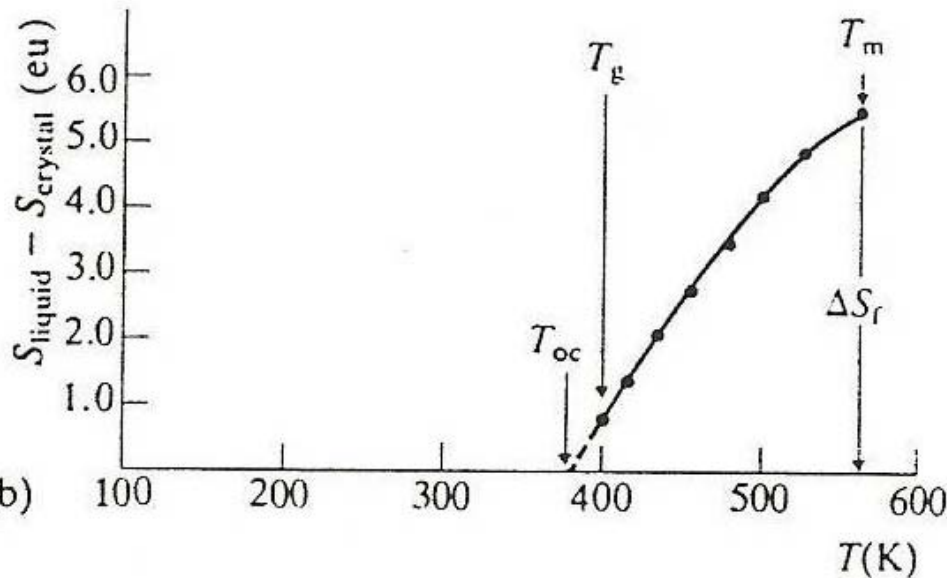$$s_\alpha(T_m) = s_\alpha(T) + \int_T^{T_m} \frac{c_\alpha}{T} dT \quad \alpha \in \{\text{liquid, crystal}\}$$

$c_{\text{liquid}} > c_{\text{crystal}}$ **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

(b)

The difference in entropy between liquid and crystalline phases as a function of temperature
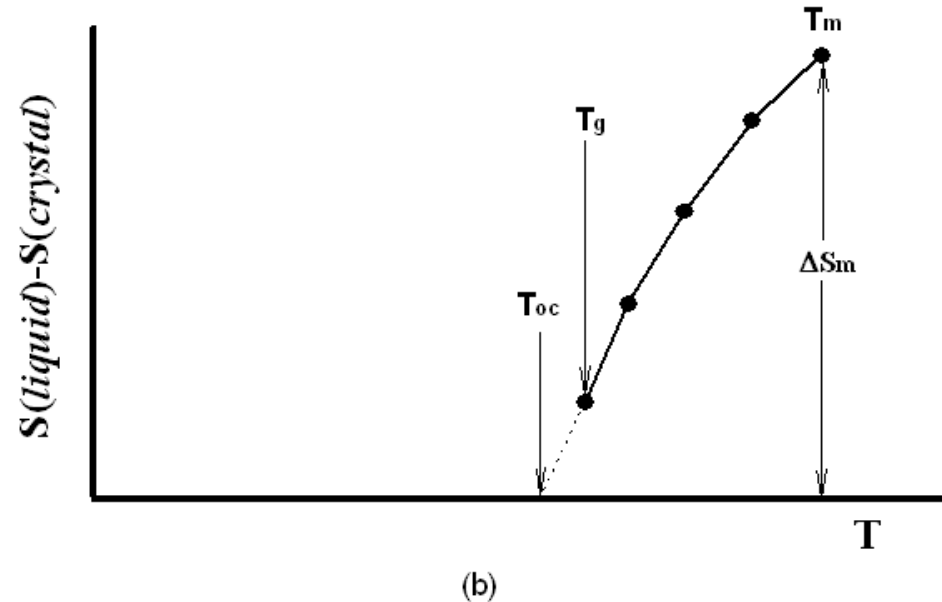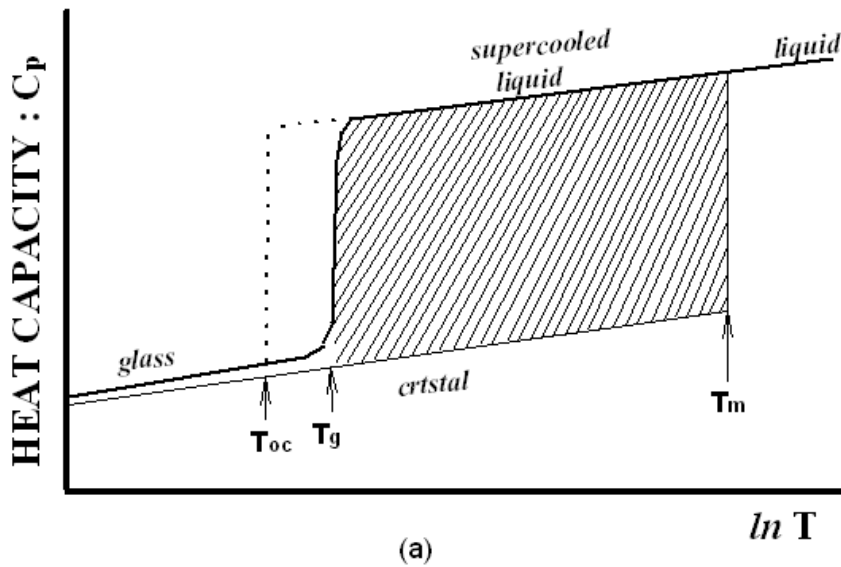
The vanishing excess entropy temperature Is termed the "ideal' glass transition temp. T_{oc} (Wong and Angell 1976)
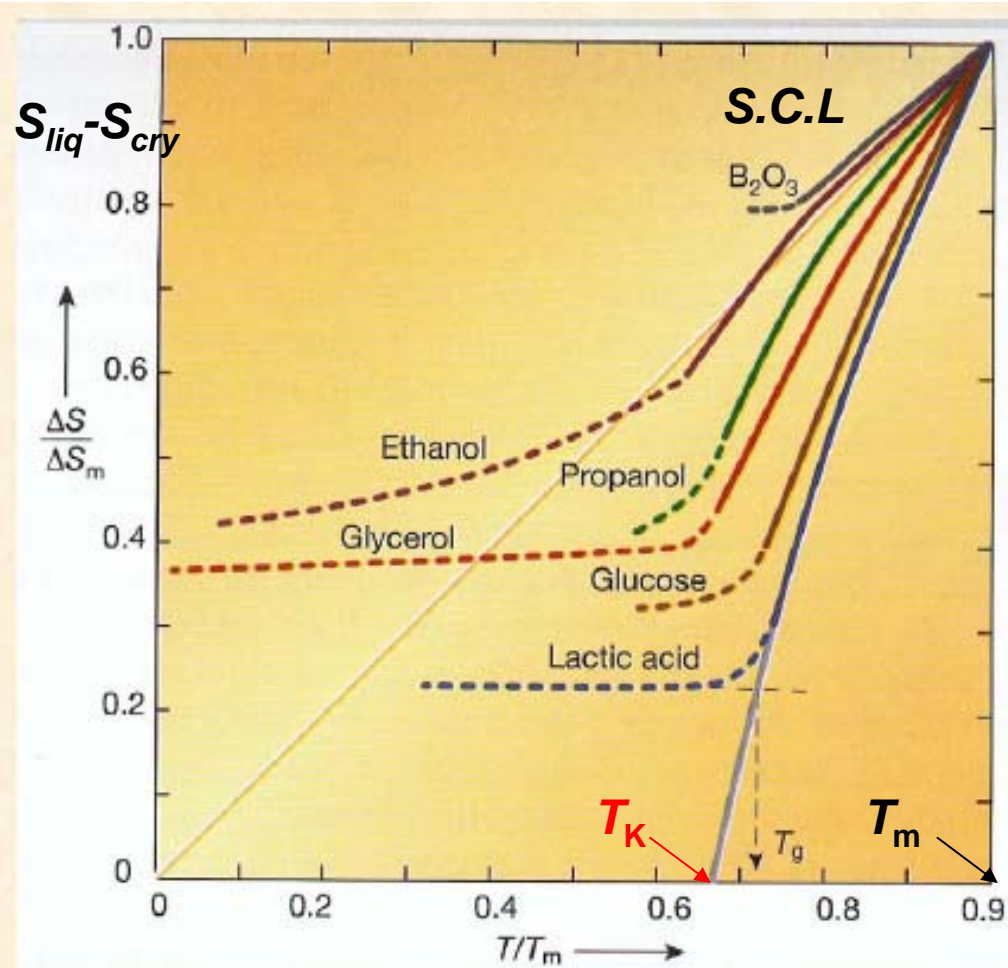
➡️ *Not satisfied with third law of thermodynamics*

• 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.**

$S_{liq} - S_{cry}$

$\frac{\Delta S}{\Delta S_m}$

S.C.L

B_2O_3

Ethanol

Propanol

Glycerol

Glucose

Lactic acid

T_K T_g T_m

T/T_m

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**

Controversies in Amorphous Solids: The Kauzmann Paradox

If we extrapolate the specific volume of the liquid from above T_M to temperatures much below T_G, one must accept that at some temperature T_K well above 0 K, the specific volume, the enthalpy and the entropy of the equilibrium liquid would become lower than that of the crystal... Since the above statement is not possible (Kauzmann paradox) , two solutions are possible:

1) at some temperature (T_K), there is a true 2nd order phase tansition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!
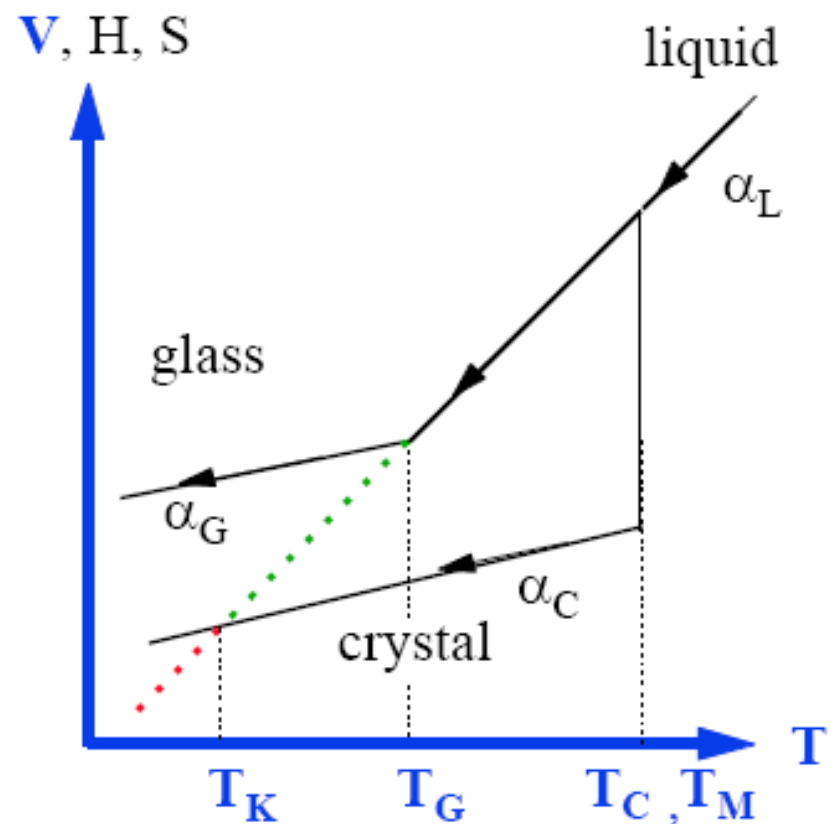
Thermodynamics

; the investigation of energy transformations
that accompany physical and chemical changes in matter

; use to evaluate the flow and interchanges of matter and energy

"[Thermodynamics] is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never be overthrown." — Albert Einstein

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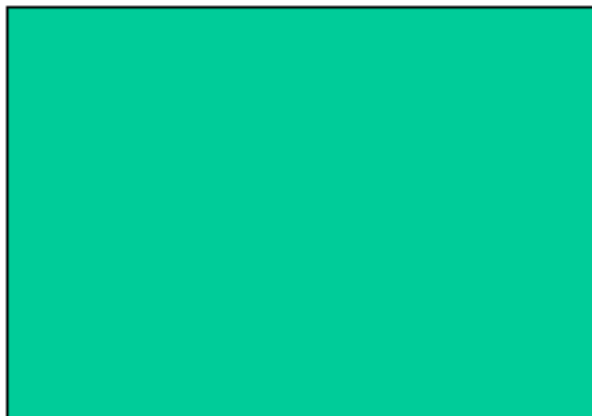
**The existence of a thermodynamic driving force does not mean that the reaction will necessarily occur!!!**

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.

Classical or statistical thermodynamics?
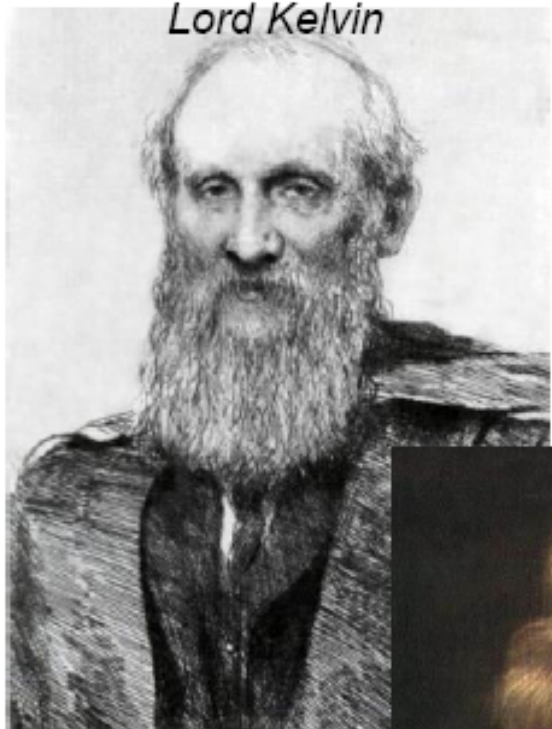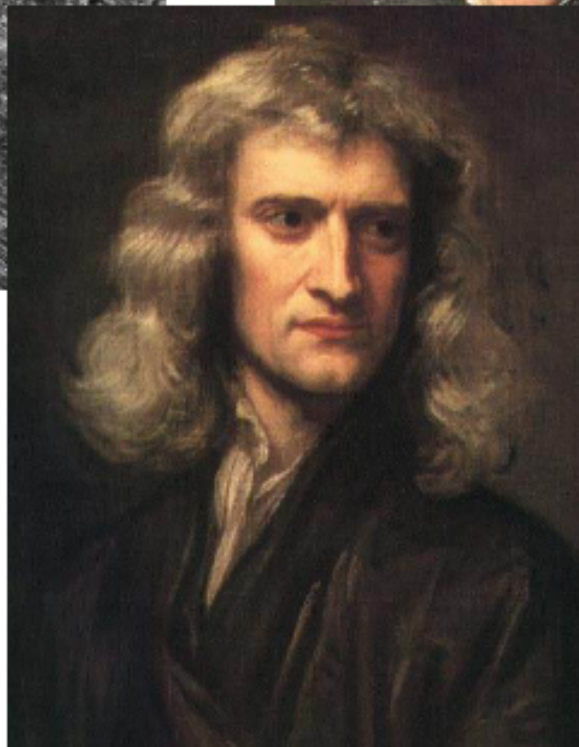# What's the difference?

A macroscopic model
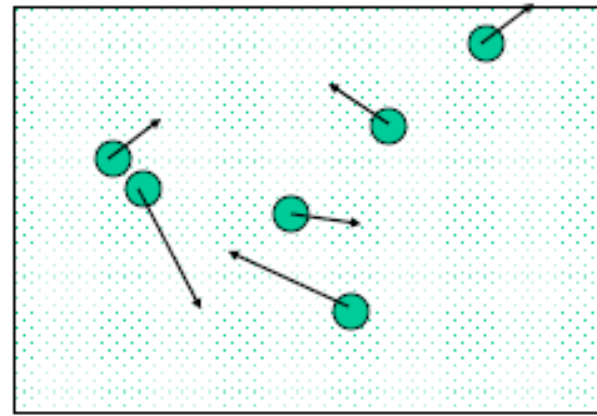
A microscopic model

Lord Kelvin

Carnot

Joule

Newton

Thermodynamics
has always been confusing…

About the thermodynamical laws :-)
(According to P.W. Atkins "*The Second Law, Energy Chaos, and Form*".)

- There are four laws.

- The third of them, the *Second Law*, was recognized first.

- The first, the *Zeroth Law*, was formulated last.

- The *First Law* was second.

- The *Third Law* might not even be a law in the same sense as the others.

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

$$S = \frac{q}{T}$$
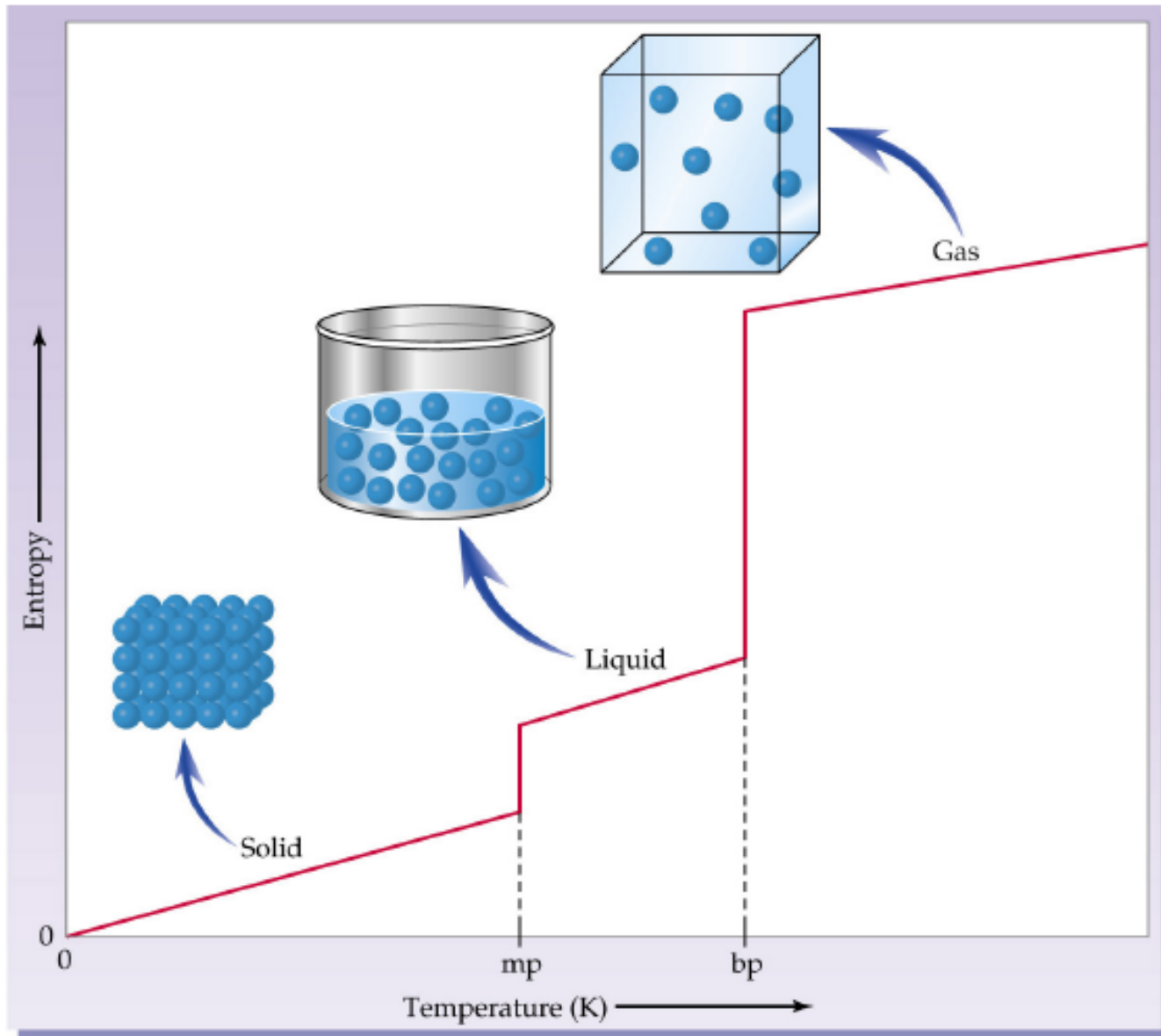
    ; The disorder of the universe always **increase**

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

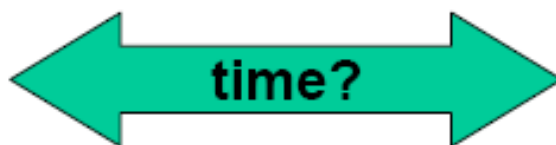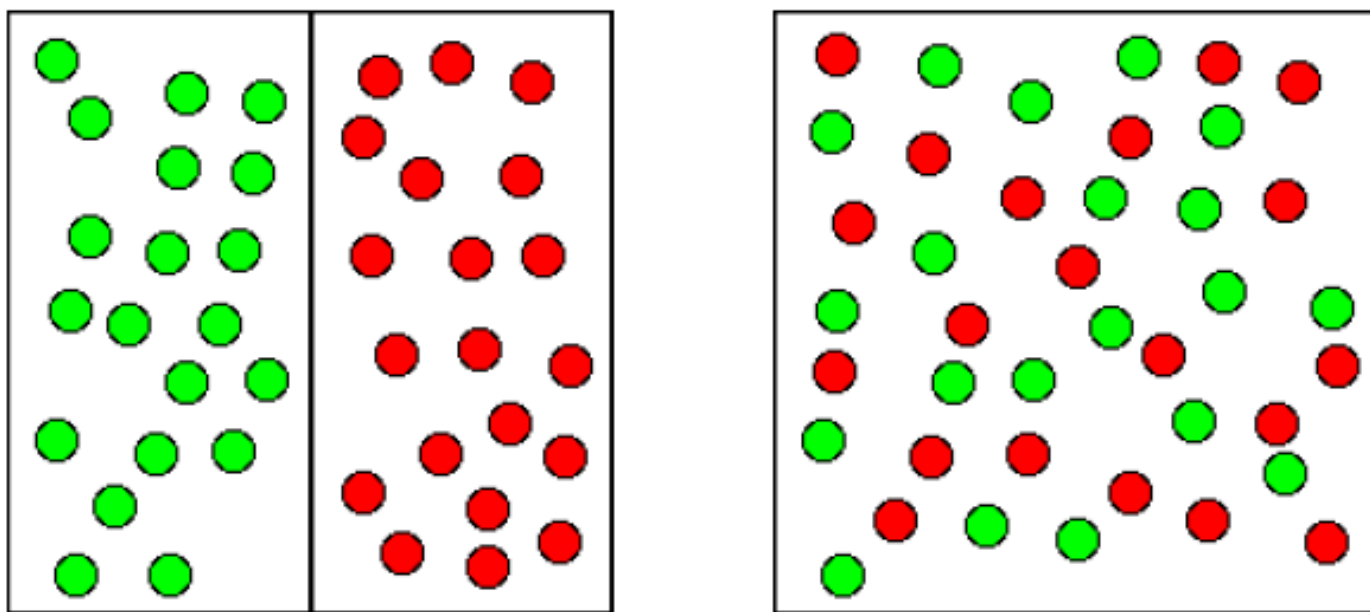"SPONTANEOUS" REACTION
as time elapses

ORGANIZED EFFORT REQUIRING ENERGY INPUT

Gas

Liquid

Solid

Entropy

0

0

mp

bp

Temperature (K)

probability

time?

Entropy

For each of your Permanent events in play that you discard, you may cancel and discard one event with a Permanent duration in play that is owned by an opponent.

All good things must come to an end.

EVENT

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ENTROPY

- A THEORETICAL MEASURE OF ENERGY THAT CANNOT BE TRANSFORMED INTO MECHANICAL WORK IN A THERMODYNAMIC SYSTEM.

- The total amount of entropy in a system always goes up.

- No thermodynamic process can occur without some losses.

- A MEASURE OF DISORDER
  - always growing in our universe

- "THE END OF THE UNIVERSE IS UPON US"

THE SECOND LAW OF THERMODYNAMICS

(1) All energy received as heat by a heat engine cycle cannot be converted into work (This means that no cycle can have a thermal efficiency of 100%)

(2) The transformation of heat to work is dependent of a temperature difference and on the flow of heat from a high temperature reservoir to a low temparature reservoir to a low temperature reservoir. (In other word heat must flow from hot to cold)

(3) It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the transfer of heat from a low temperature reservoir to a hight temperature reservoir.

FIRST LAW OF THERMODYNAMICS

Energy can be neither created nor destroyed but only transformed

; but it can be transformed from one into another.

; The total amount of energy in the universe is constant
for any physical and chemical change.

THE GENERAL ENERGY EQUATION

Energy In = Energy Out

or

$$U_2 - U_1 = Q - W$$

where

U_1: internal energy of the system at the beginning

U_2: internal energy of the system at the end

Q : net heat flow into the system

W : net work done by the system

$$dE = \delta Q - \delta w + d(\sum \mu_i N_i)$$

The third law of thermodynamics

- The **third law of** thermodynamics is an axiom of nature regarding entropy and the impossibility of reaching absolute zero of temperature. The most common enunciation of third law of thermodynamics is:

- "As a system approaches absolute zero of temperature, all processes cease and the entropy of the system approaches a minimum value.

- In brief, this postulates that entropy is temperature dependent and leads to the formulation of the idea of absolute zero.

Thermodynamic Equilibrium
(Zeroth Law)

Object # 1
(Thermometer)
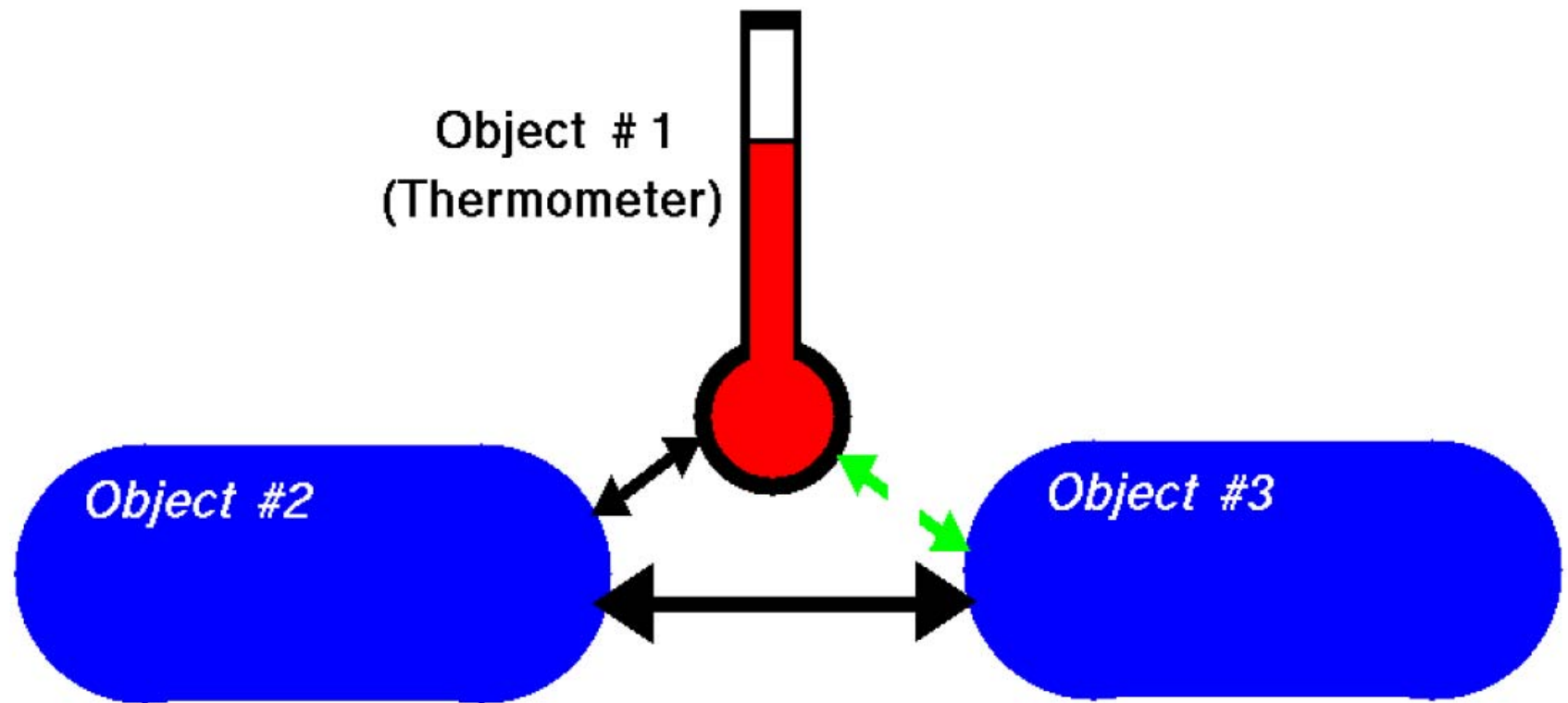
Object #2

Object #3

When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

Objects in thermodynamic equilibrium have the same temperature.