

Winter 1-1-2008

# Lecture 2, Part 2: Sub T<sub>g</sub> relaxation in thin glass - The enthalpy landscape view

Prabhat Gupta  
*Ohio State University*

Follow this and additional works at: <https://preserve.lehigh.edu/imi-tll-courses-usjapanwinterschool>



Part of the [Materials Science and Engineering Commons](#)

---

## Recommended Citation

Gupta, Prabhat, "Lecture 2, Part 2: Sub T<sub>g</sub> relaxation in thin glass - The enthalpy landscape view" (2008). *US-Japan Winter School*. 6.  
<https://preserve.lehigh.edu/imi-tll-courses-usjapanwinterschool/6>

This Video is brought to you for free and open access by the Semester Length Glass Courses and Glass Schools at Lehigh Preserve. It has been accepted for inclusion in US-Japan Winter School by an authorized administrator of Lehigh Preserve. For more information, please contact [preserve@lehigh.edu](mailto:preserve@lehigh.edu).

# Sub - $T_g$ Relaxation in Thin Glass

**Prabhat Gupta**

**The Ohio State University**  
**( Go Bucks ! )**

**Kyoto (January 7, 2008)**

# Outline

1. Phenomenology (Review).
  - A. Liquid to Glass Transition (LGT or GT).
  - B. Structural Relaxation (SR).
2. New developments (Enthalpy landscape view).
3. Size, surface, and interface effects.

# Glass transition phenomena

Liquid to glass transition (LGT)



**Glass**

(Non-equilibrium)

**Liquid**

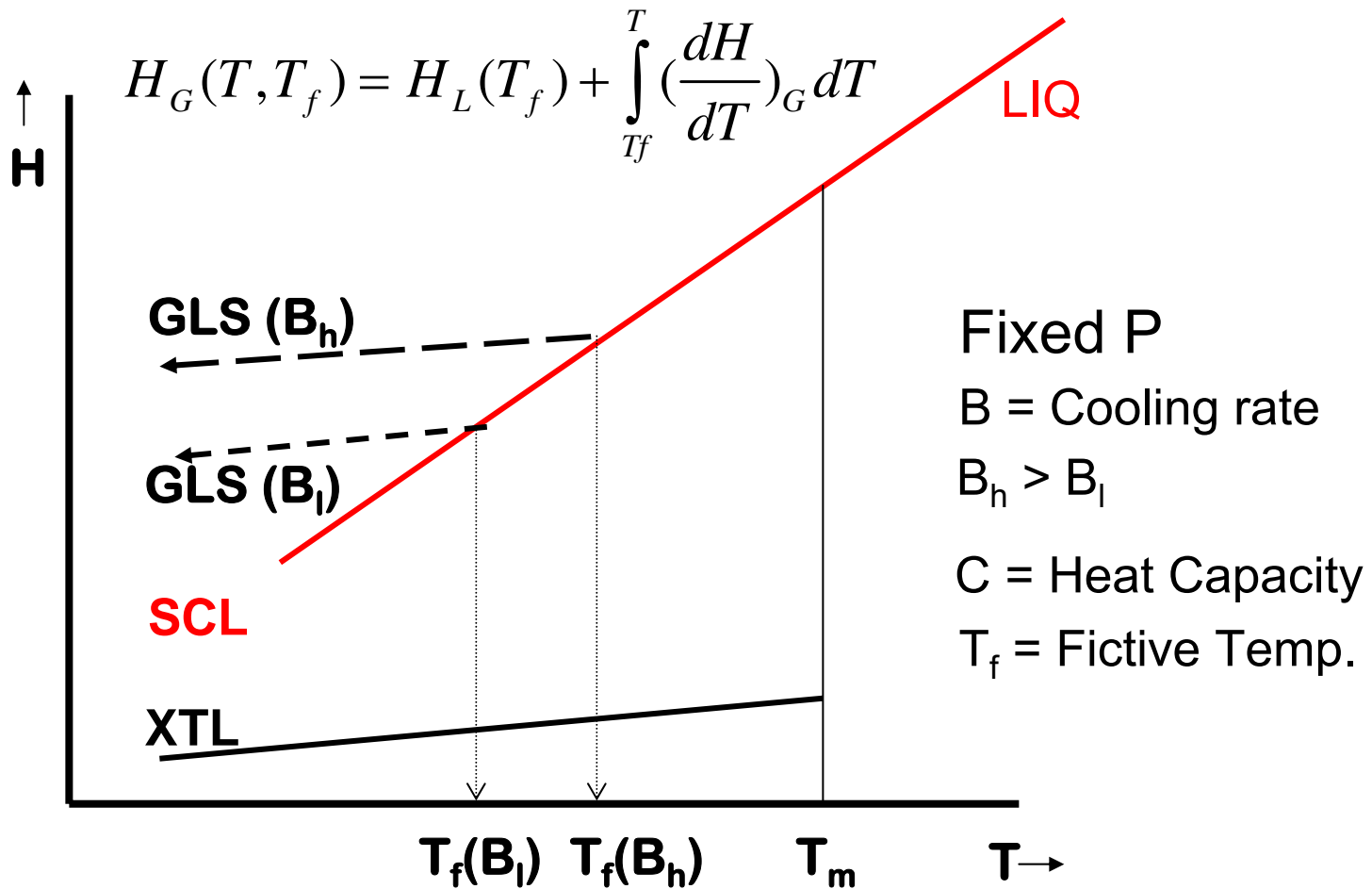
(Equilibrium)



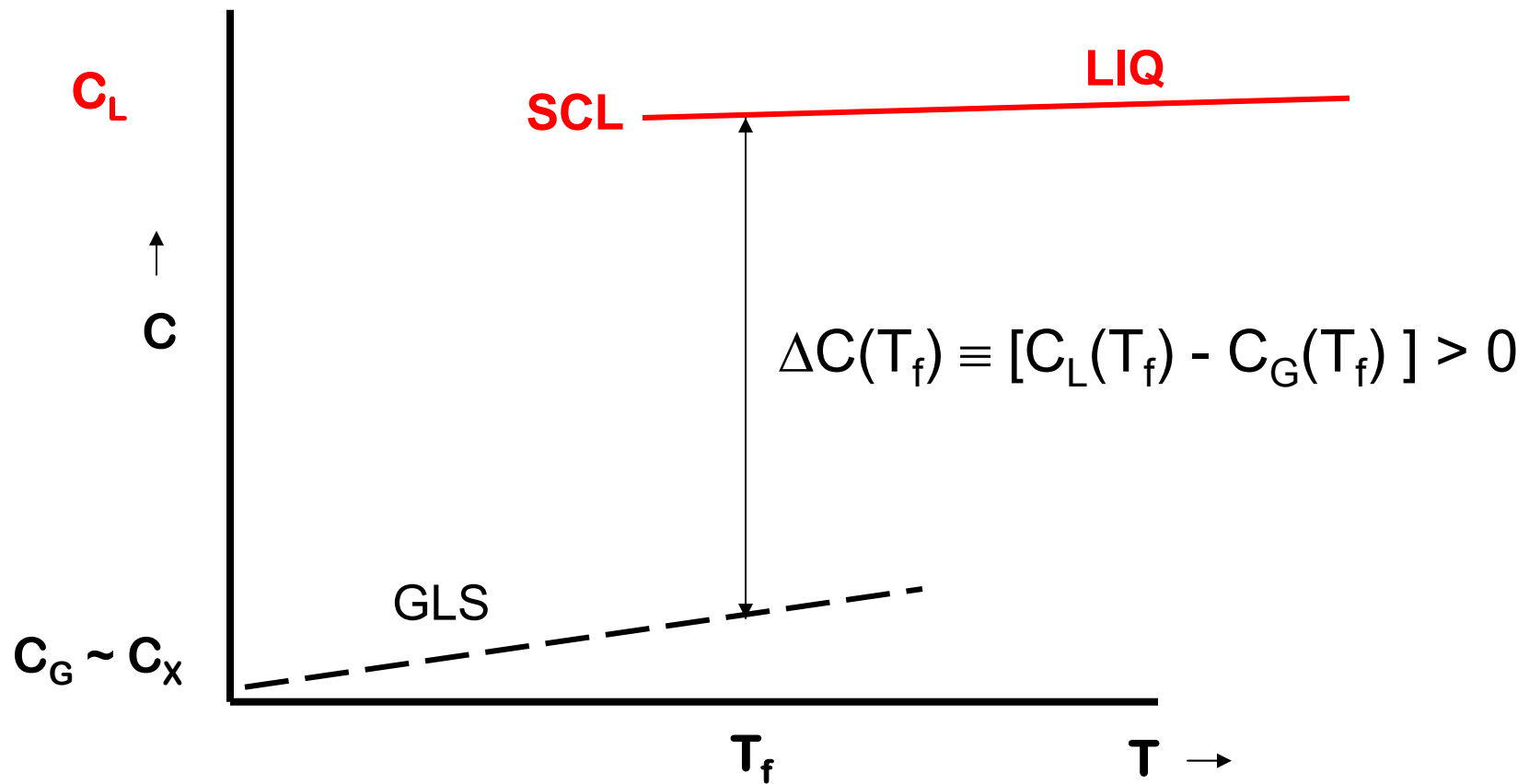
**Structural relaxation (SR)**

# LGT - Phenomenology

# LGT: Enthalpy (H) vs. Temp (T)

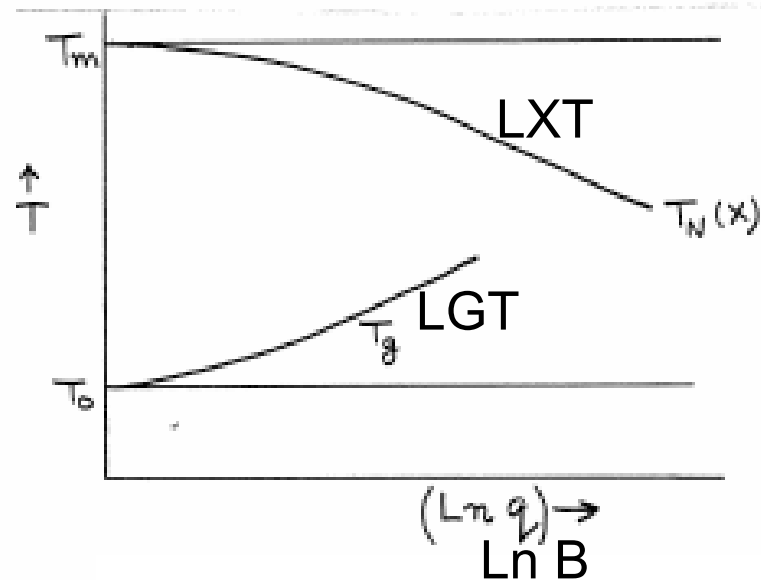
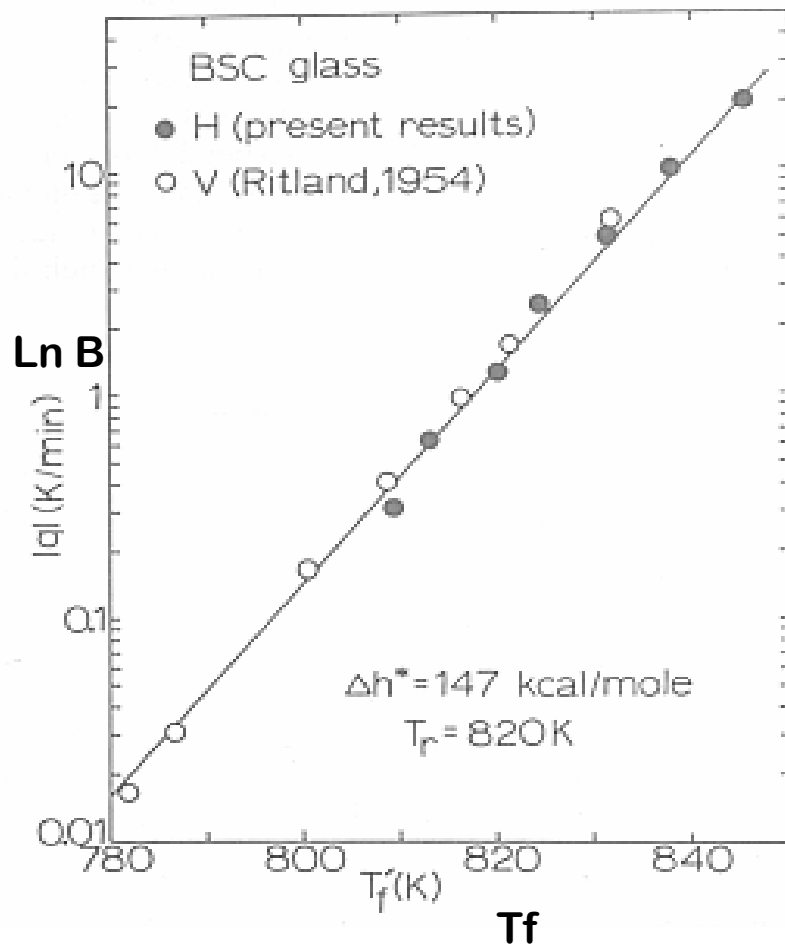


# LGT: Heat Capacity (C) vs. Temp (T)



# LGT: Ergodic (eqbm, liq) to Non-ergodic (frozen, glass)

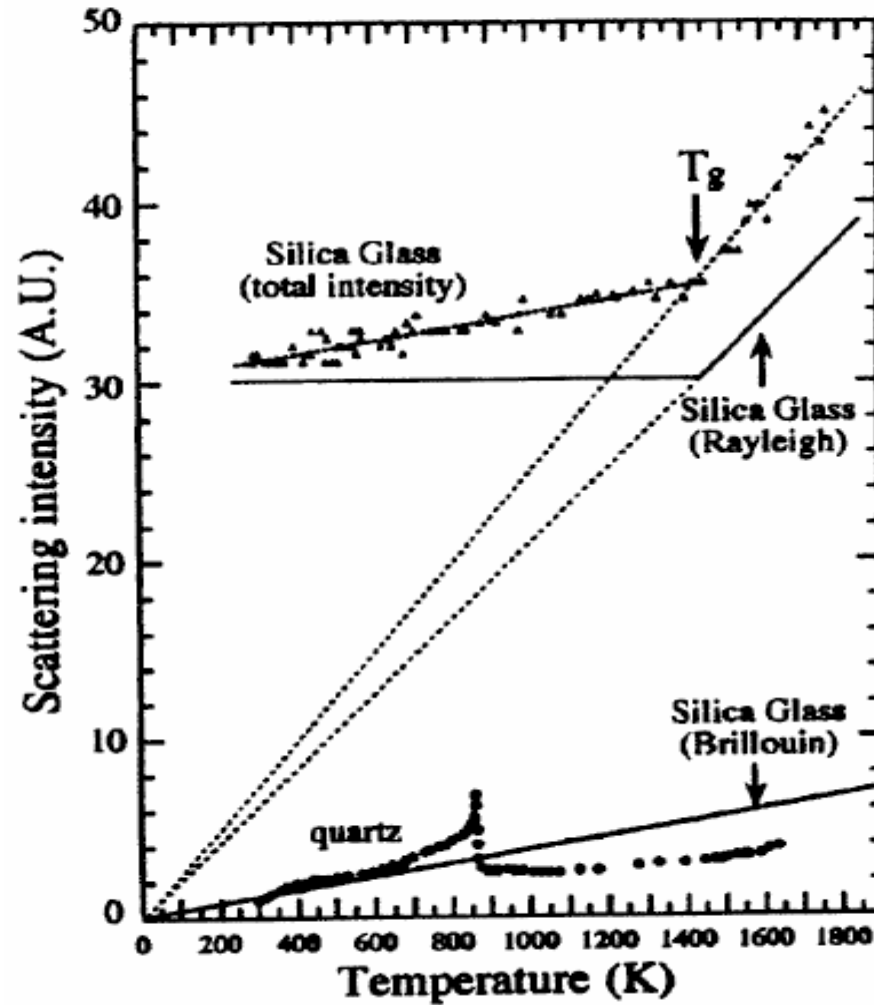
⇒  $T_f$  increases with increase in cooling rate (B).





# Rayleigh Scattering in silica glass

J. Appl. Phys. Rev.: Ikushima, Fujiwara, and Saito  
(2000)



# LGT: Generic Features

- Not a thermodynamic transition.
- Not a spontaneous process.
- $T_f(B) \uparrow$  as  $B \uparrow$ .
- $\Delta V = 0$ ,  $\Delta H = 0$  (*No latent heat !*).
- $\Delta C > 0$ ,  $\Delta \kappa > 0$ ,  $\Delta \beta >, =, < 0$

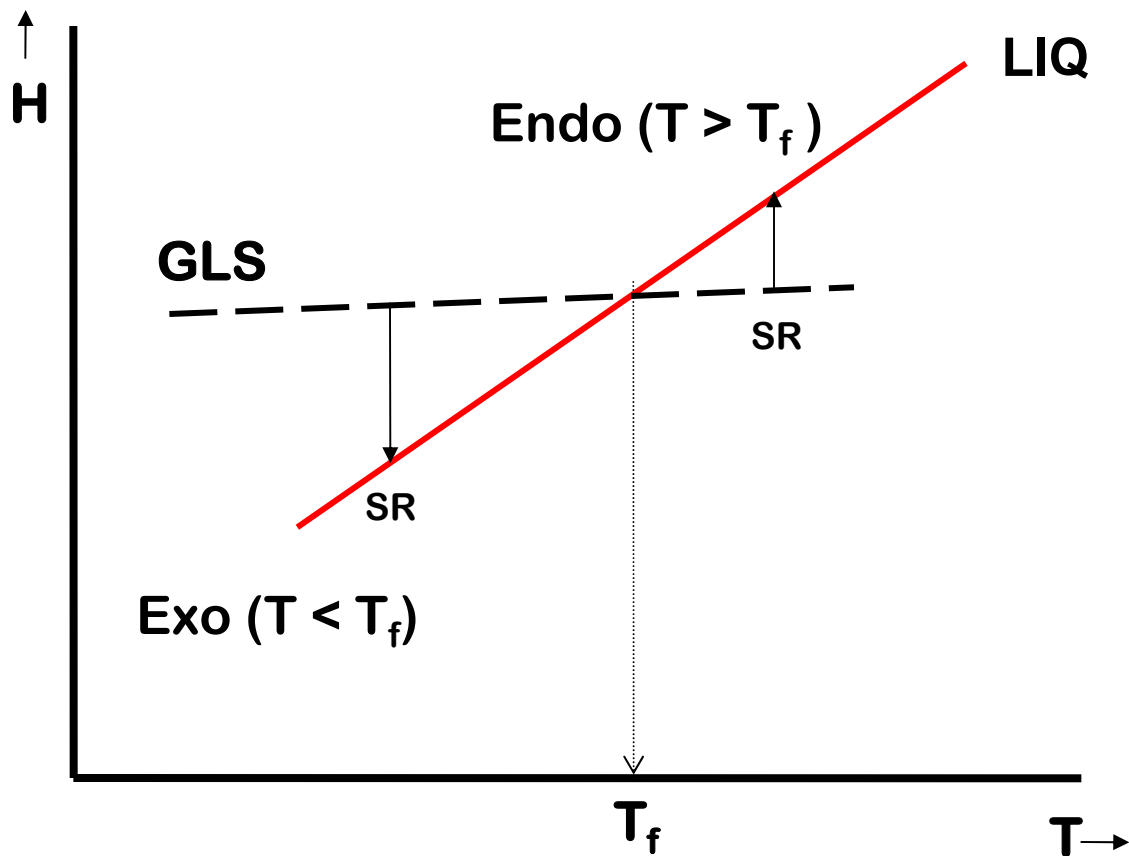
$$PDR \equiv \frac{(\Delta C)(\Delta \kappa)}{TV(\Delta \beta)^2} > 1$$

$$\kappa = -(1/V) \frac{\partial V}{\partial P} \Big|_T, \beta = (1/V) \frac{\partial V}{\partial T} \Big|_P, V = \text{volume}$$

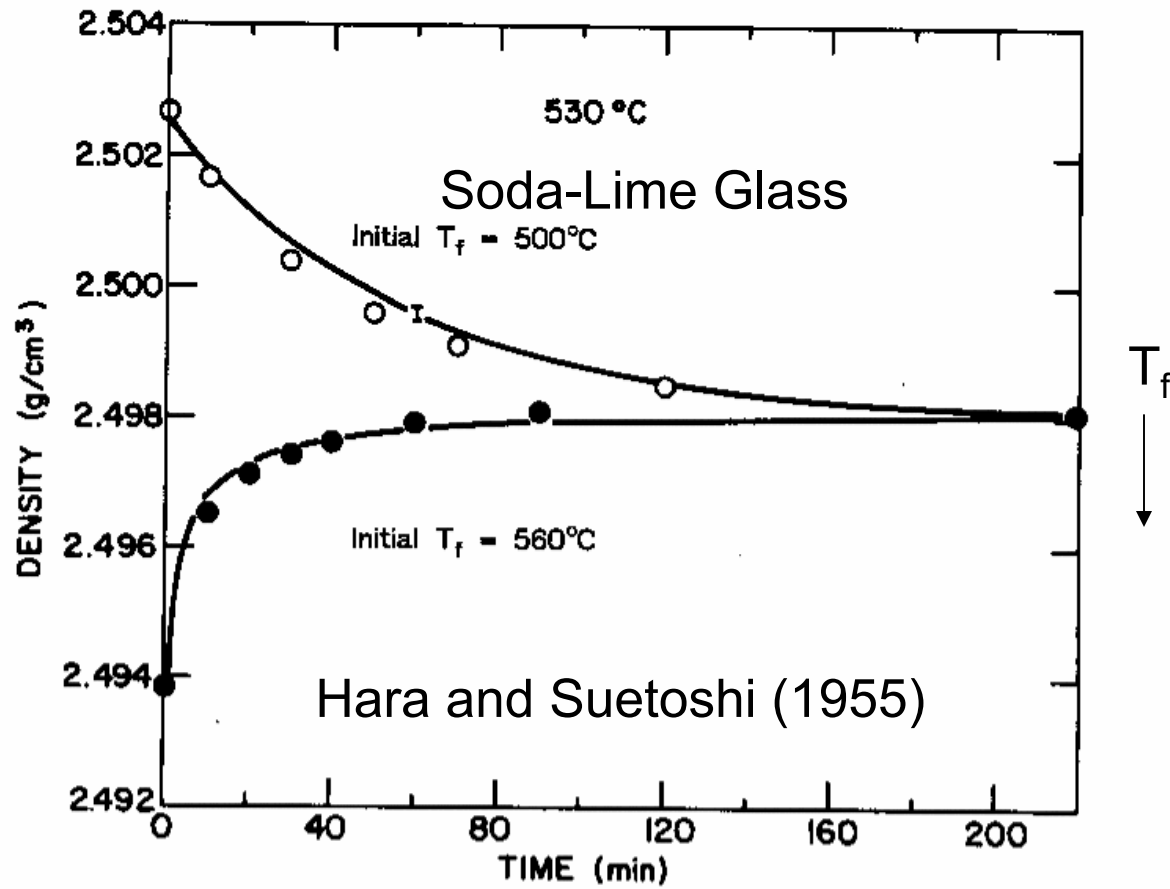
- Glasses have intrinsic nano-scale heterogeneities.

# Relaxation - Phenomenology

# Isothermal SR



# Non-linear Relaxation Kinetics



# Sub-Exponential Relaxation

$M(t,T)$  = Relaxation Function

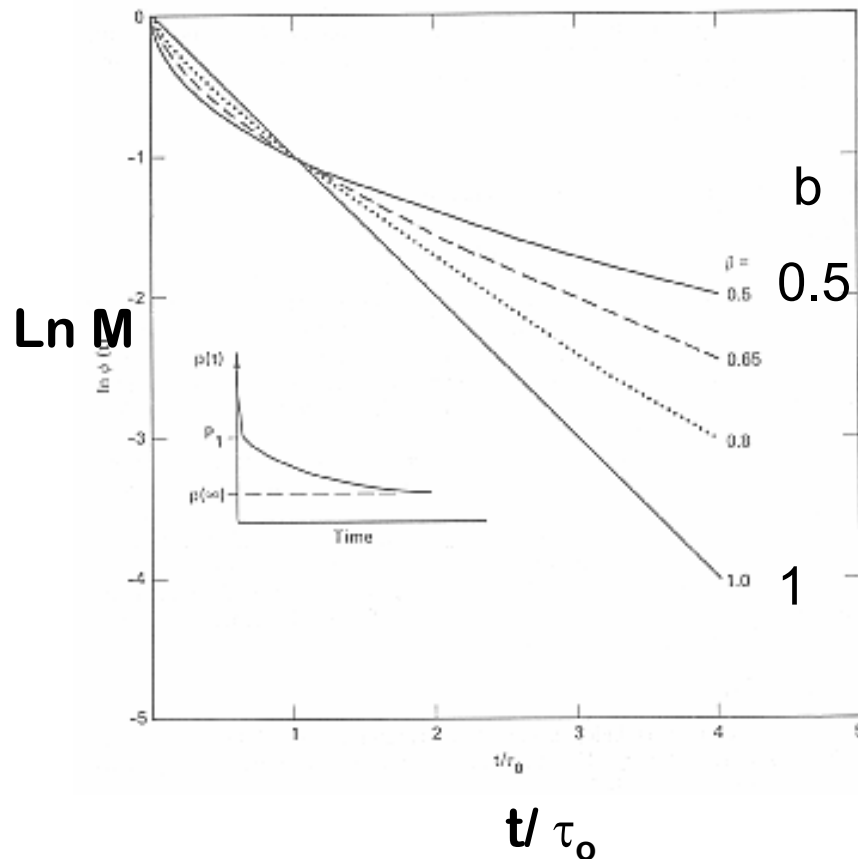
- $M(t,T) \equiv \frac{T_f(t,T) - T}{T_f(0) - T}$

- Stretched Exponential

$$M(t,T) = \exp\left[-\left\{\frac{t}{\tau_o(T,T_f)}\right\}^{b(T)}\right]$$

$$0 < b(T) < 1$$

$$\tau_{av} = (\eta / \text{modulus}) = (\tau_o / b)\Gamma(1/b)$$



# Adam-Gibbs (AG) Model of Viscosity

$$\ln[\eta(T)] = \ln[\eta_\infty] + \left[ \frac{A}{TS_c(T)} \right]$$

$A, \eta_\infty =$  Parameters independent of  $T$ .

$S_c(T) \equiv$  **Configurational entropy** of the liquid

$$\cong \Delta S \equiv S_L(T) - S_G(T).$$

# AG model fits data extremely well !

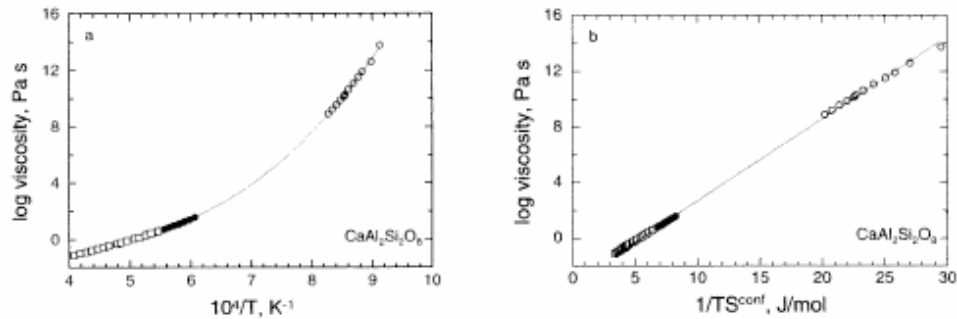


Figure 2.24 - Viscosity of stable and supercooled  $\text{CaAl}_2\text{Si}_2\text{O}_8$  liquid. (a) Against reciprocal temperature. (b) Against  $1/TS^{\text{conf}}$ . Data from Urbain *et al.* [1982; open squares], Scarfe *et al.* [1983; solid circles], and Sipp *et al.* [2001; open circles].

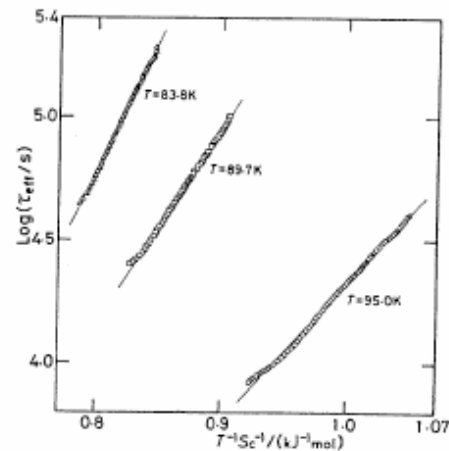


Fig. 4. Test of the Adam-Gibbs equation for the relaxation time of butyronitrile vapor-deposited samples (from [29] by ...)



## SR: Generic features

- SR is spontaneous (irreversible).
- SR is non-linear.
- SR is non-exponential ( $\sim$  stretched exponential).
- Av. relaxation time approximately follows AG theory.
- Deviations from the Arrhenius behavior (fragility) of  $\tau$  correlate with  $\Delta C$ .
- SR can be endothermic (at  $T > T_f$ ).

## What is the entropy change during LGT ?

Entropy change :  $\Delta S(T_f) \equiv S_L(T_f) - S_G(T_f)$

$\Delta S(T_f)$  cannot be measured experimentally *because*

a) Experimental fact: no latent heat ( $\Delta H(T_f) = 0$ ).

*But  $\Delta H(T_f) \neq T_f \Delta S(T_f)$ .*

$$\text{b) } S_L(T_f) = S_X(0) + \int_0^{T_m} \frac{C_X}{T} dT + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_f} \frac{C_L}{T} dT$$

$$S_G(T_f) = S_G(0) + \int_0^{T_f} \frac{C_G}{T} dT \quad [S_G(0) \text{ is not known.}]$$

# The Enthalpy Landscape View

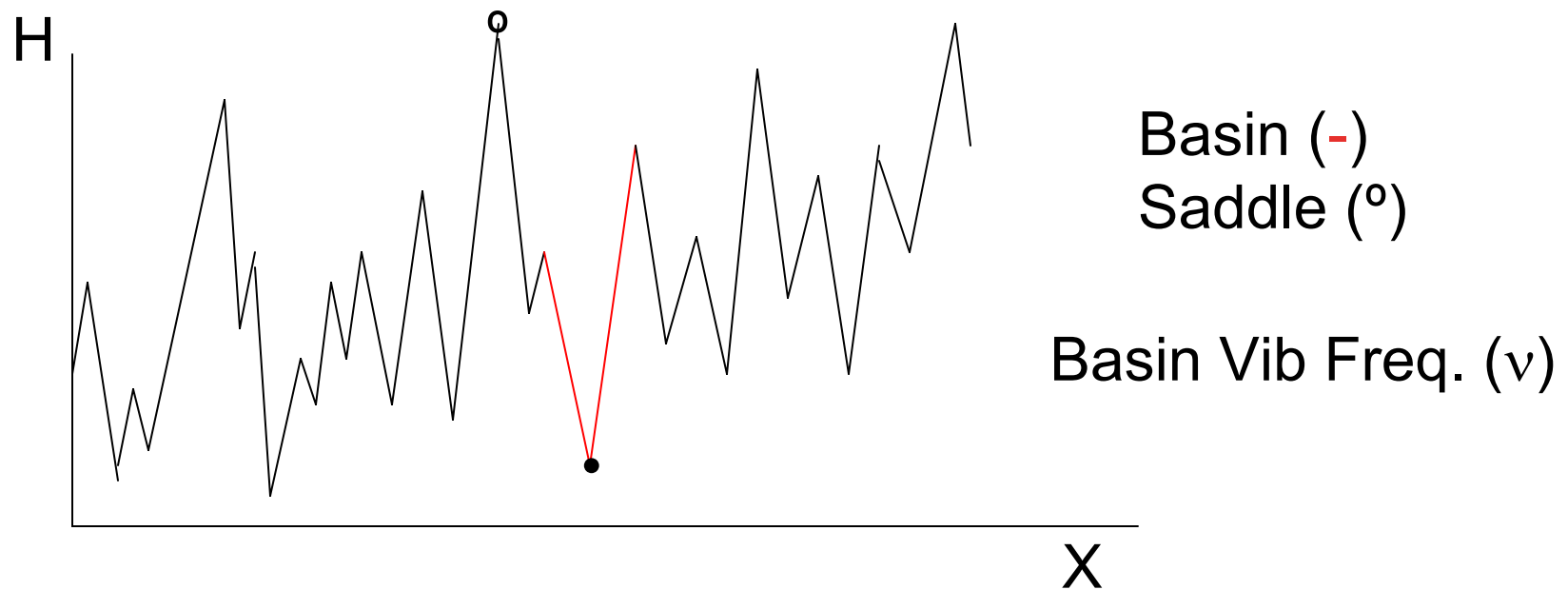
---

Gupta and Mauro, J. Chem. Phys. 126, 224504, (2007)

# Rugged H-Landscape

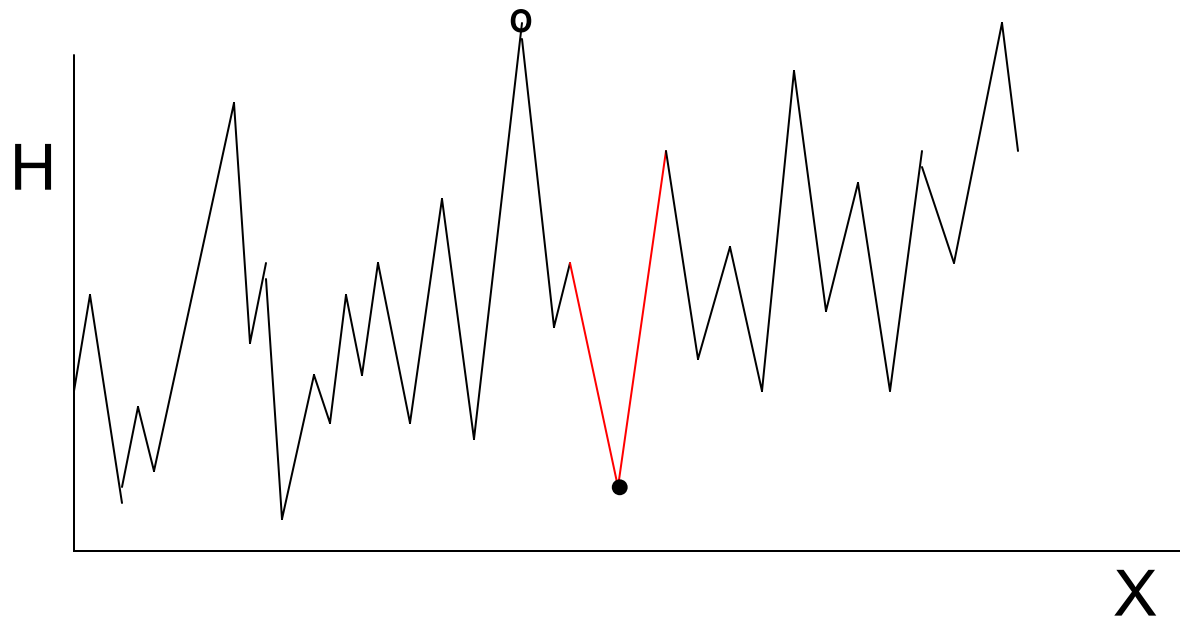
$H=H(3N+1$  dimensional Configuration,  $X$ )

(IS = Inherent states, minima, •)



# Density of Inherent States, $\Omega(H)$

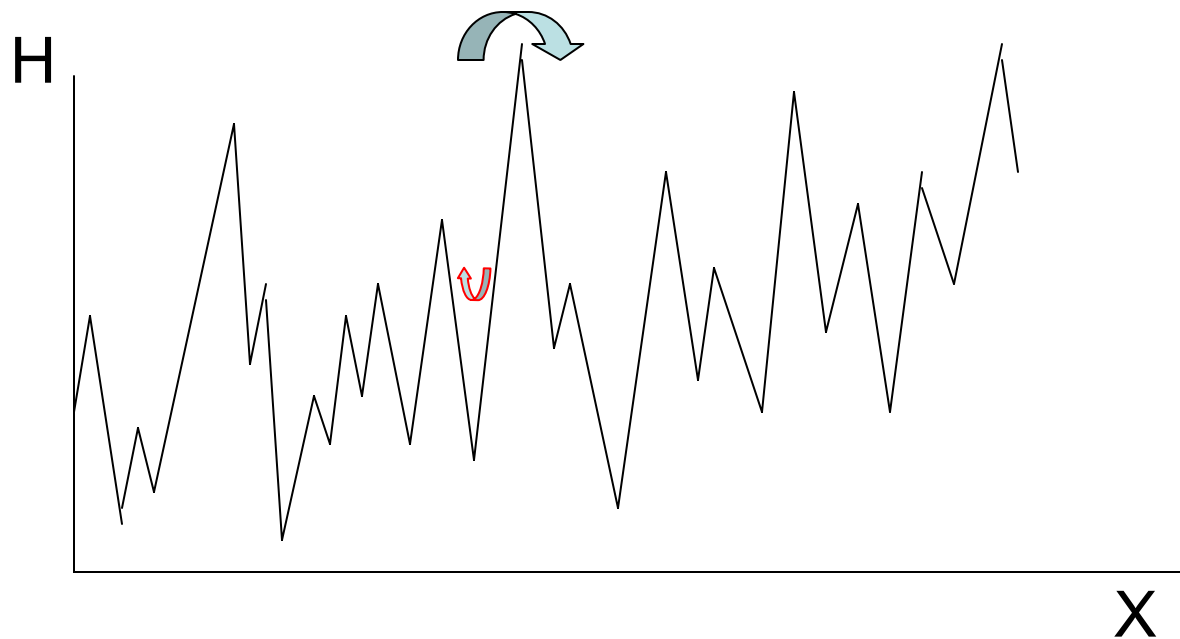
$$\Omega(H) \cong N! \exp[ S_c(H) / k ]$$



# Dynamics in H- Landscape

Intra-basin relaxation: very fast (↻)  
(equilibration of a basin with the heat bath)

Inter-basin transitions: slow (↷)



# Inter-basin transitions

---

An (i→j) transition is *not* allowed at T and  $t_{obs}$  if:

$$t_{obs} < \tau_{ij}(T) \equiv \left(\frac{\varepsilon}{\nu}\right) \exp\left[\frac{F_{ij}^*}{kT}\right]$$

$$F_{ij}^* = H_{ij}^* - kT \ln(n_{ij}^*)$$

$\varepsilon$  = a small constant number

$\nu$  = attempt (vibrational) frequency (~same for all basins)

k = Boltzmann's constant

$H_{ij}^*$  = Barrier enthalpy from basin i to j

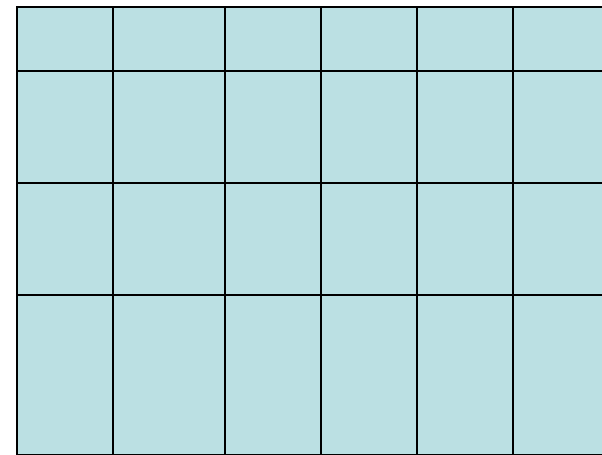
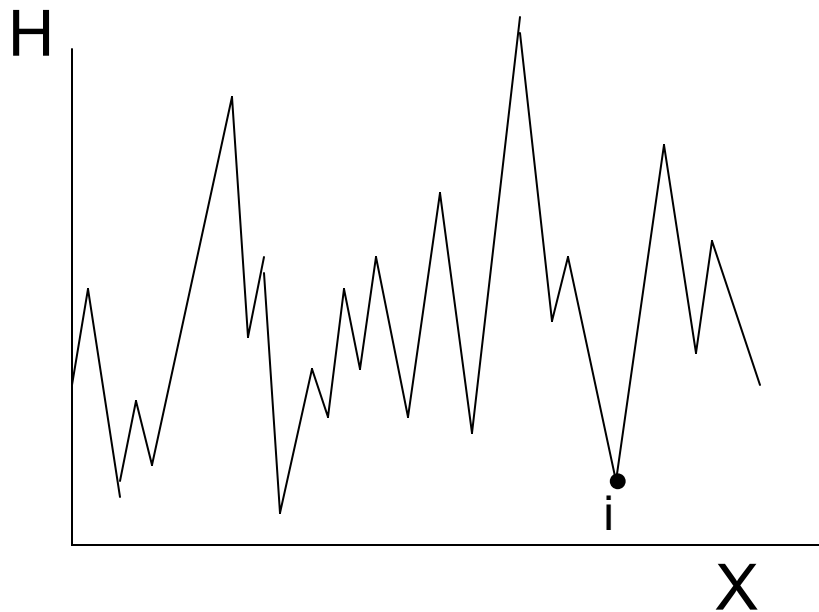
$F_{ij}^*$  = Barrier free energy

$n_{ij}^*$  = Number of transition paths from basin i to j having barrier heights  $H_{ij}^*$ .

# Liquid State

Equilibrium (ergodic) state:  $t_{obs} > \tau_{MAX}(T)$

$$\text{Basin probability, } p_i^L(T) = \frac{\int_{X \in i\text{-basin}} \exp[-H(X)/kT] dX}{\sum_i \int_{X \in i\text{-basin}} \exp[-H(X)/kT] dX}$$



Ergodic ensemble of basins



# Configurational Properties (Liquid)

---

*Enthalpy :*

$$H_C^L(T) = \sum_i^{\Omega} H_i \cdot p_i^L(T)$$

*Configurational Entropy (Gibbs):*

Not a property of a microstate.

$$S_C^L(T) = -k \sum_i^{\Omega} p_i^L(T) \text{Ln}[p_i^L(T)]$$

# Ergodicity Breaking

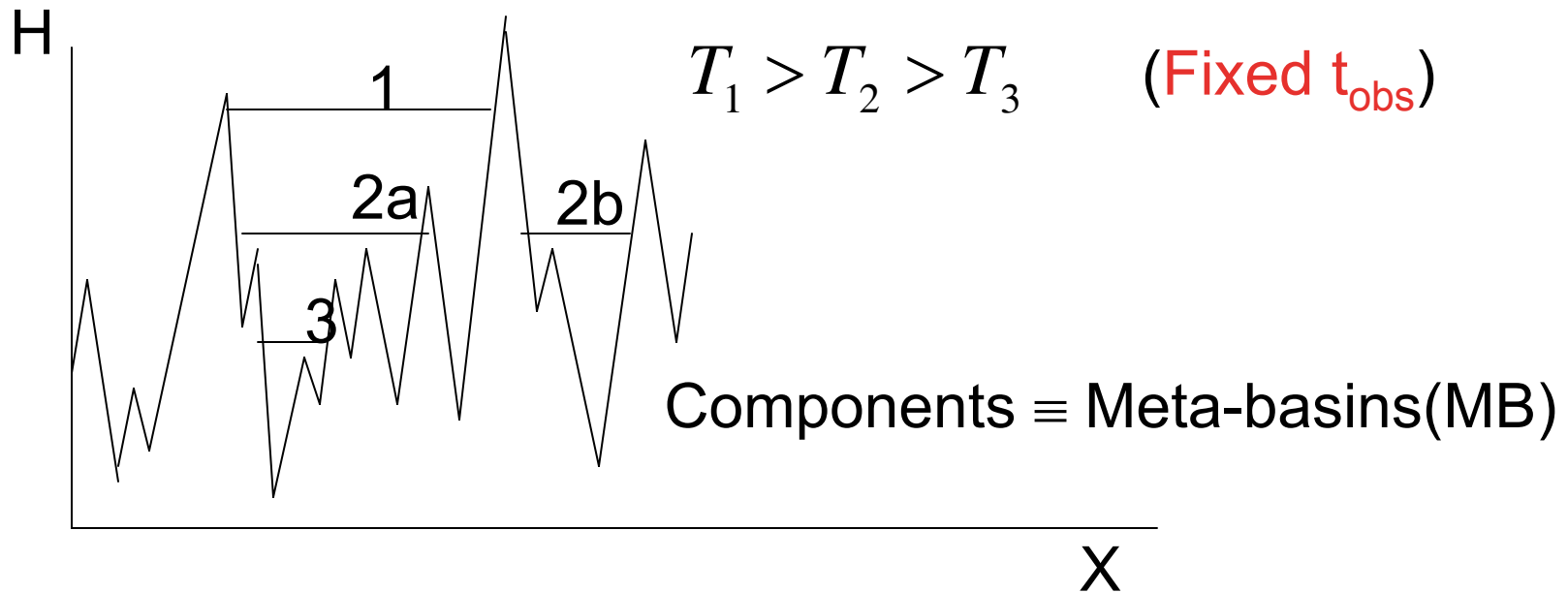
$$kTLn\left(\frac{vt_{obs}}{\varepsilon}\right) < F_{max}^*$$

Partitioning of X-space in to components such that

- no transitions among components
- each component is ergodic in itself.

$$t_{obs(1)} > t_{obs(2)} > t_{obs(3)} \quad (\text{Fixed } T)$$

$$T_1 > T_2 > T_3 \quad (\text{Fixed } t_{obs})$$



# LGT and Broken Ergodicity

At a fixed  $t_{\text{obs}}$  (fixed cooling rate):

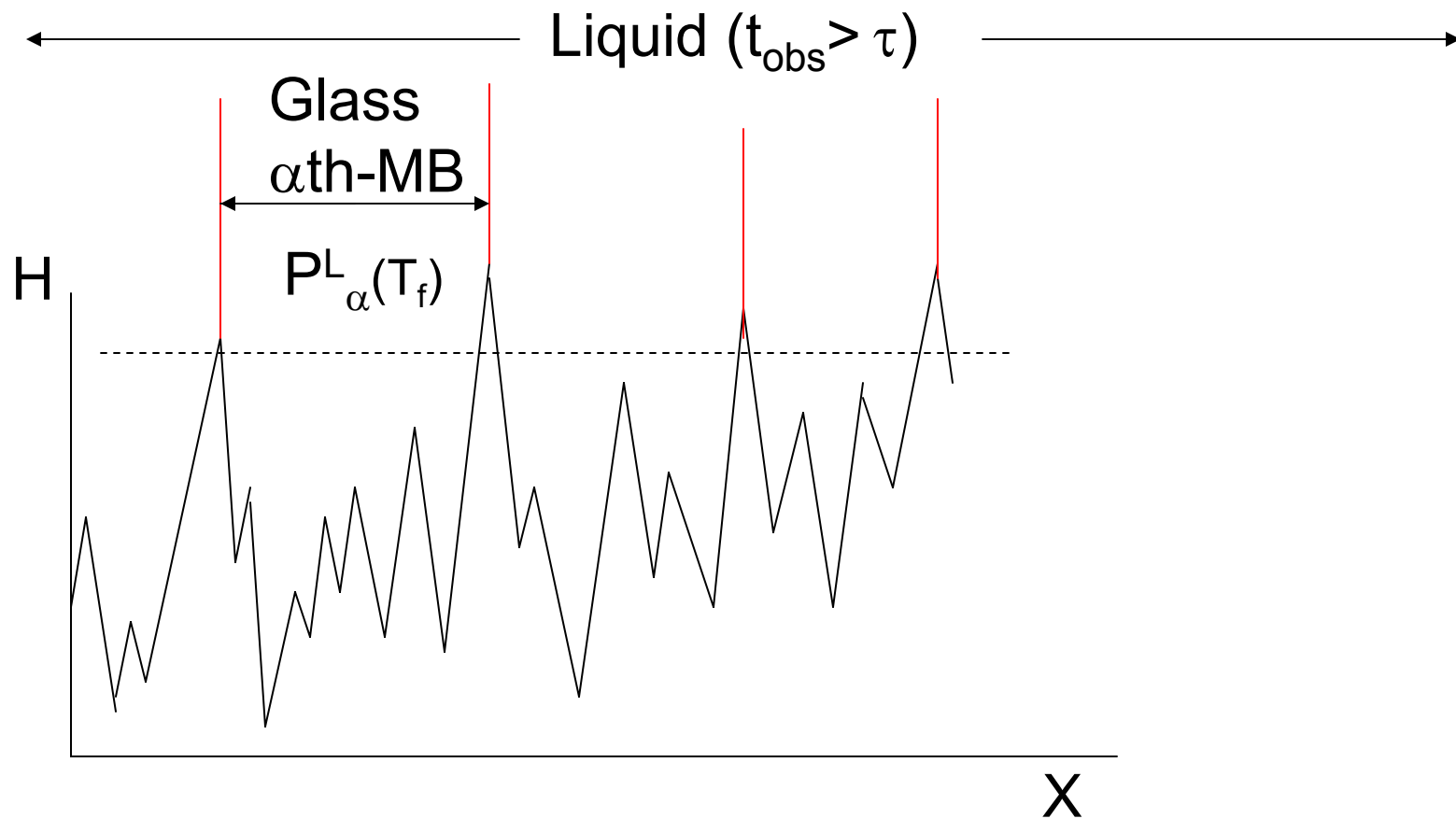
$T > T_f(t_{\text{obs}})$  No partitioning of X-space.  
(Ergodic system = Liquid)

$T = T_f(t_{\text{obs}})$  LGT partition starts.

$T < T_f(t_{\text{obs}})$  X-space is partitioned.  
(Broken ergodic system = glass)  
(System is trapped in a single MB)

## Glass is a constrained liquid!

- Constrained in a single meta-basin.
- The constraint is external:  $t_{\text{obs}} < \tau$ .



# The LGT-partition

---

Total # of MBs =  $M(T_f(t_{\text{obs}}))$  ( $\alpha = 1, \dots, M$ )

Probability of the  $\alpha$ th MB:

$$P_{\alpha}^{MB}(T \leq T_f) = \sum_{i \in \alpha} p_i^L(T_f)$$

Prob. of  $i^{\text{th}}$ -basin:

$$p_i^{\alpha}(T, T_f) = P_{\alpha}^{MB}(T_f) \left[ \frac{\exp(-H_i / kT)}{\sum_{i \in \alpha} \exp(-H_i / kT)} \right]$$

**Glassy State,**  $t_{obs} < \tau_{MAX}(T)$

Broken ergodic (or constrained eqbm) state:

$$Q^G(T, T_f) = \sum_{\alpha} P_{\alpha}^{MB}(T_f) \sum_{i \in \alpha} Q_i p_i^{\alpha}(T, T_f)$$

Q = a measurable property.

## Configurational entropy change during LGT

- $$S_c^L(T) = \sum_{\alpha} P_{\alpha}^{MB}(T) S_c^{\alpha}(T) - k \sum_{\alpha} P_{\alpha}^{MB}(T) \ln(P_{\alpha}^{MB}(T))$$

The first term is the average configurational entropy of the system trapped in a MB.

The second term - called **complexity (I)** - arises from inter-MB transitions.

- $$S_c^G(T, T_f) = \sum_{\alpha} P_{\alpha}^{MB}(T_f) S_c^{\alpha}(T)$$

- $$\Delta S(T_f) = I(T_f) \equiv -k \sum_{\alpha} P_{\alpha}^{MB}(T_f) \ln P_{\alpha}^{MB}(T_f)$$

# $\Delta S$ during LGT

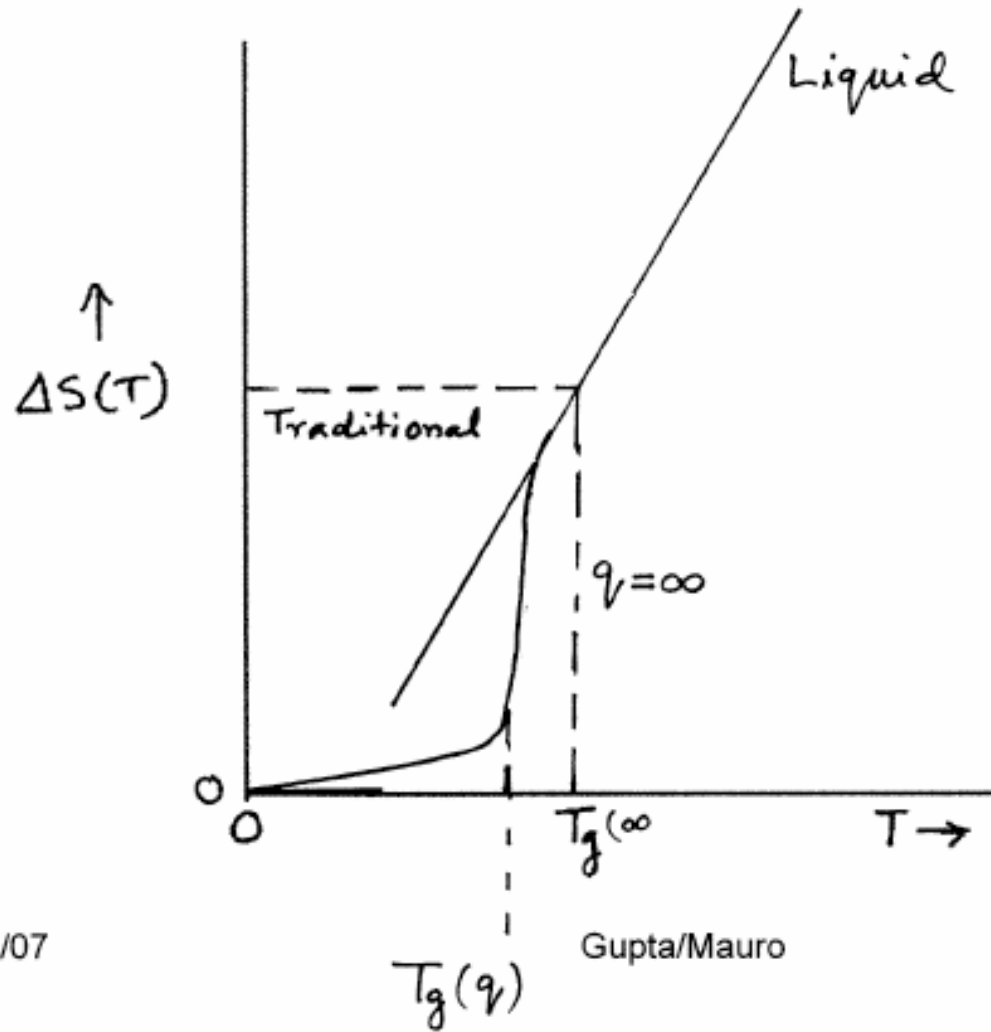
$$\Delta S = 0 \quad (\text{Current View})$$

$$\Delta S = I = -k \sum_{\alpha} P^{\alpha}(T_f) \ln P^{\alpha}(T_f) \quad (\text{New view, } \Delta S > 0)$$

- Entropy loss at  $T_f$  because the inter-MB transitions are frozen in a glass.



# Configurational Entropy of Glass



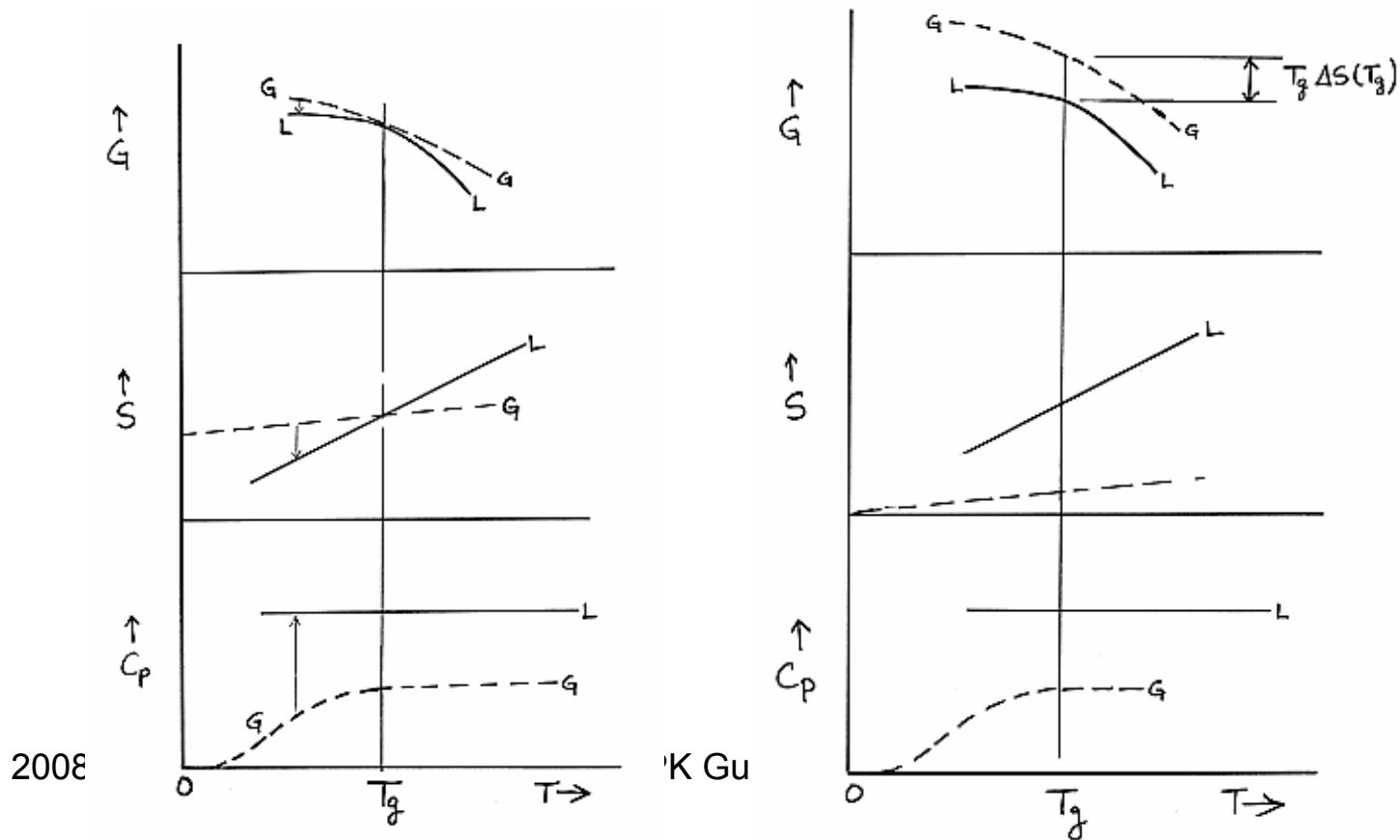
5/24/07

Gupta/Mauro

16

# New View vs. Traditional View

- *How can one distinguish between the two experimentally?*



# Isothermal Relaxation in H-landscape

- SR occurs because time is no longer constrained so that some(or all) of the 'frozen' inter-MB transitions begin to take place again.

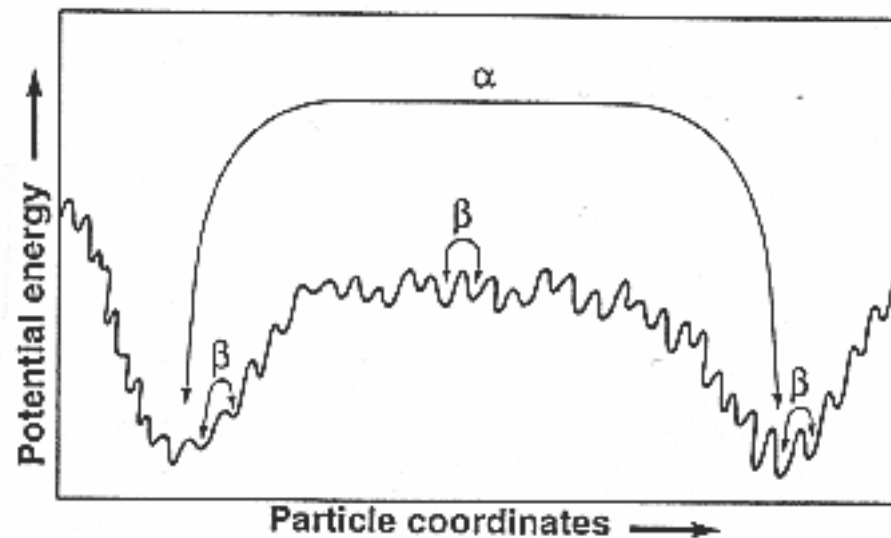
$$t > \tau_{ij}(T) \equiv \left(\frac{\varepsilon}{\nu}\right) \exp[F_{ij}^* / kT]$$

# Relaxation: several time scales !

---

Configurational changes (Inter-basin transitions):

- $\beta$  process (intra-MB transitions)
- $\alpha$  process (inter-MB transitions, slowest)

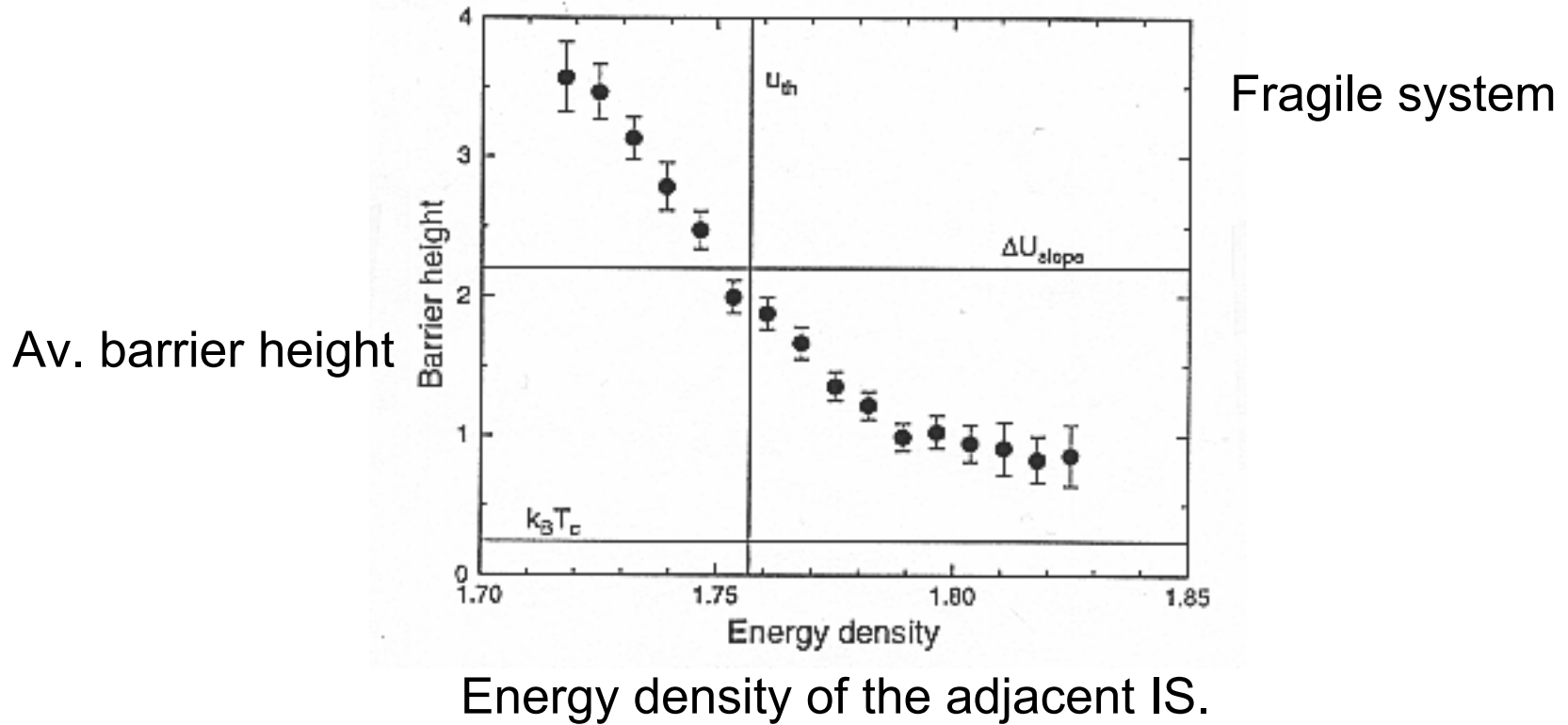


# Hierarchy of Barriers

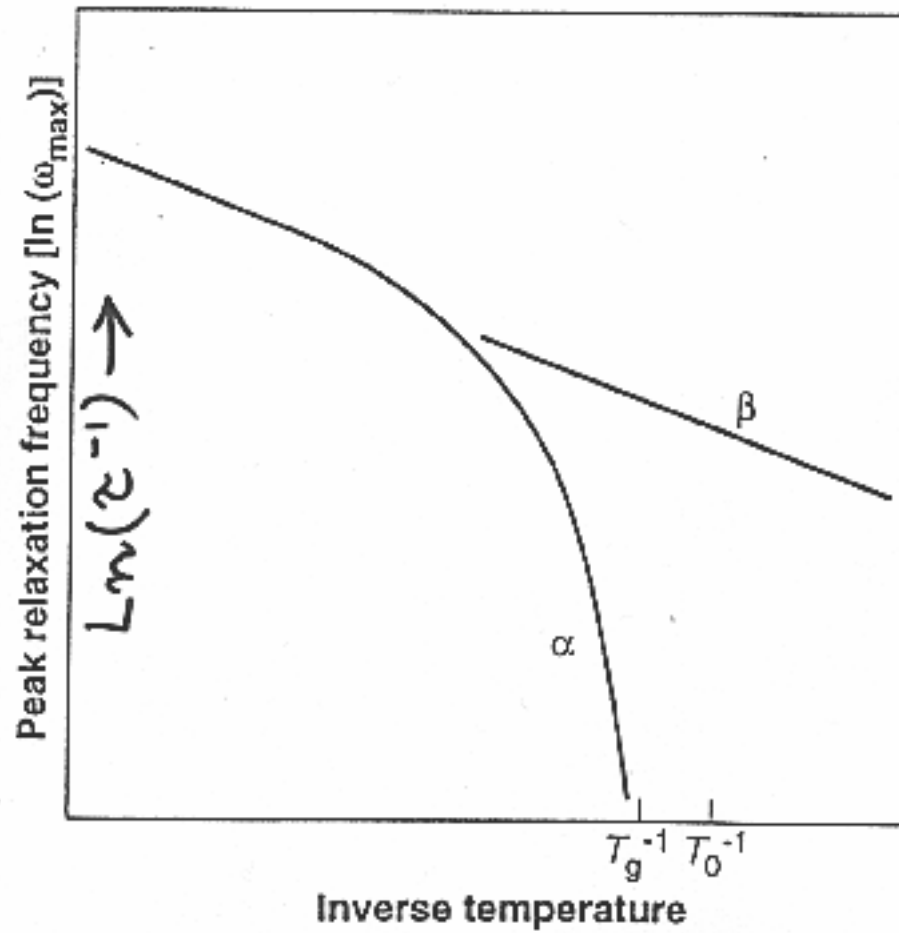
Height	Label	Order of freezing	Order of thawing	T-dependence
Highest	$\alpha$ (Primary)	1st (LGT) ↓	Last ↑	Non-Arrhenius
2nd highest	$\beta$ (Secondary)	2nd ↓	2nd to last ↑	More Arrhenius
3rd highest	$\gamma$	3rd	3rd to last	

Small barriers unfreeze first. Thus relaxation is fast in the beginning and then becomes slower and slower as time increases.

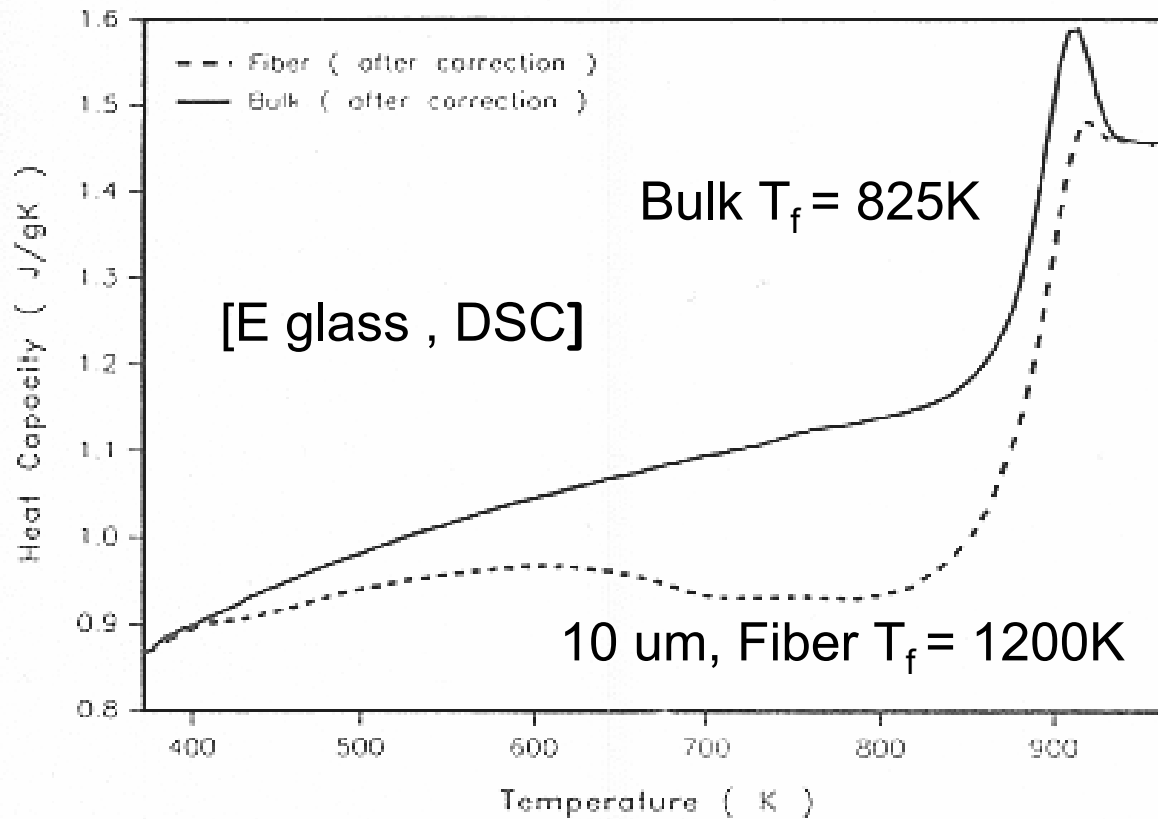
# Barrier Heights (MD simulation)



Parisi et al ( 2002)



# SR: Far from equilibrium (Effect of $T_f$ )



Huang and Gupta, 1992.

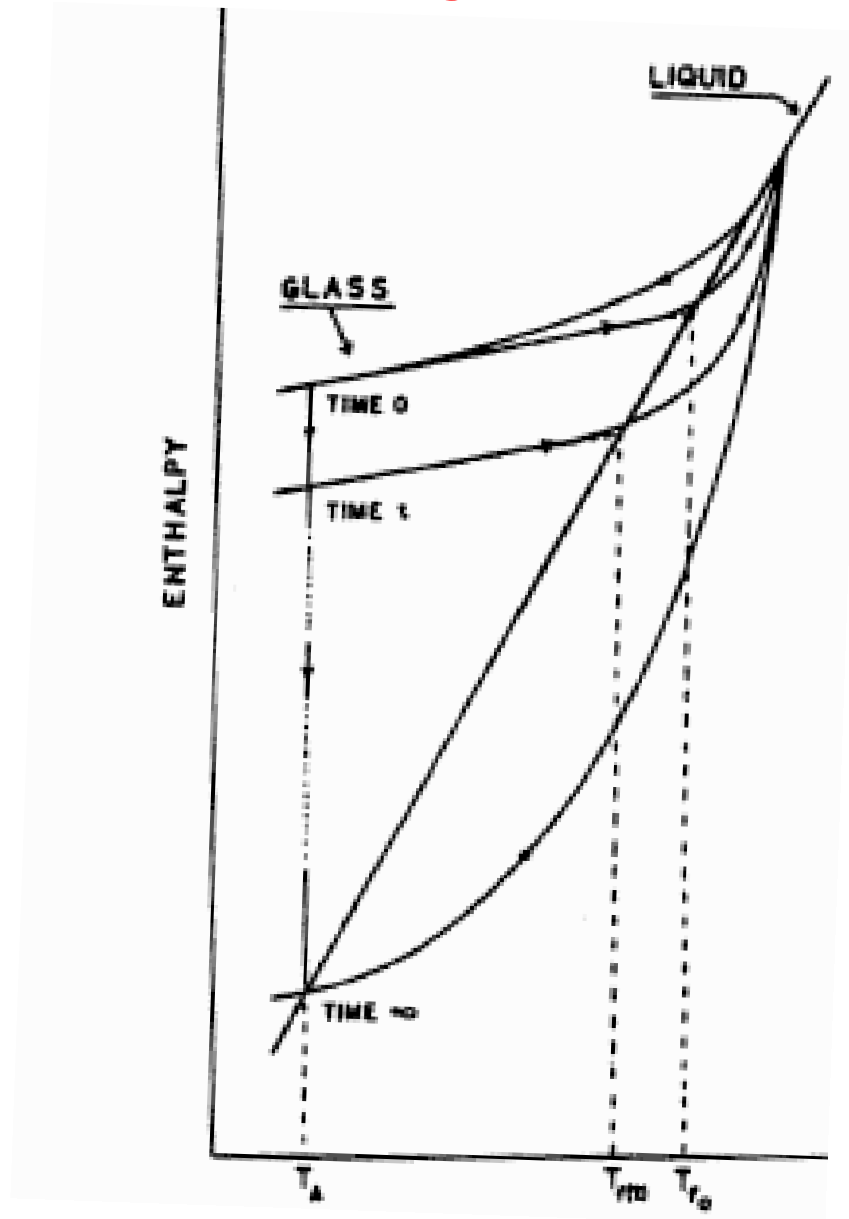


# Sub- $T_g$ Relaxation

$$\delta \equiv \frac{T_g - T}{T_g}$$

- Stabilization ( $\delta < 15\%$ )
- Sub-sub  $T_g$  Relaxation ( $\delta > 15\%$ )

# Effect of sub- $T_g$ isothermal annealing



# Stabilization

C - C(ref)

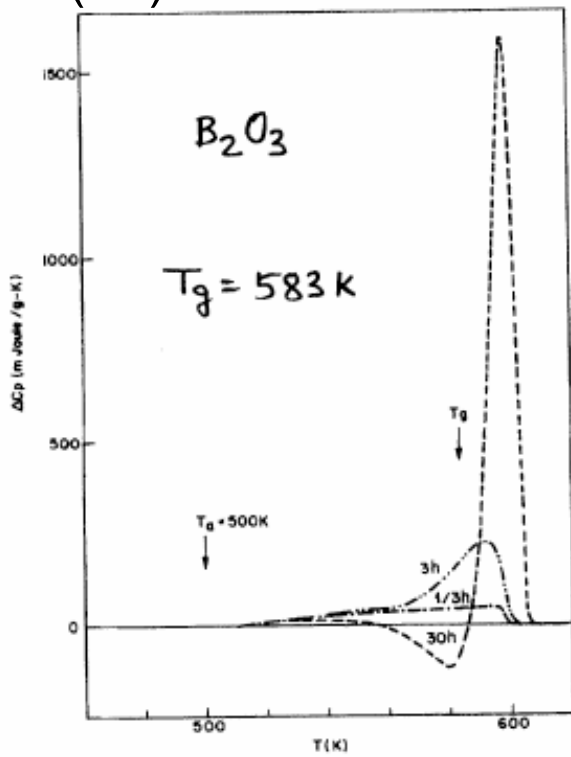


Fig. 9. Evolution of  $\Delta C_p$  at  $T_a=500$  K.

Chen, Kurkjian (1983)

Moynihan et al (1985)

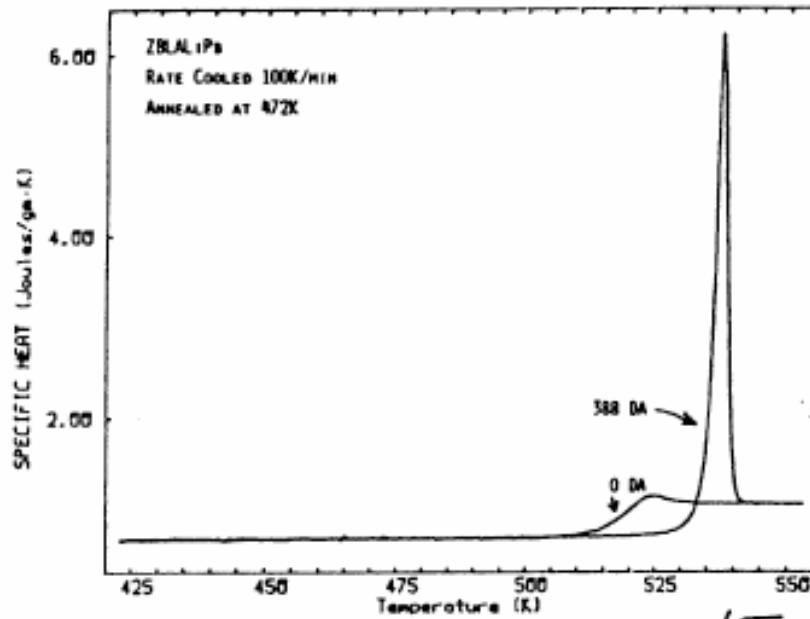


Fig. 2: Specific heat measured at 10 K/min heating rate for ZBLALiPb glass following rate cool and sub- $T_g$  anneal for times shown in figure

( $T_g = 513$  K)

# Sub-sub Tg Relaxation

Sub-Tg peak in C linear heating in DSC.

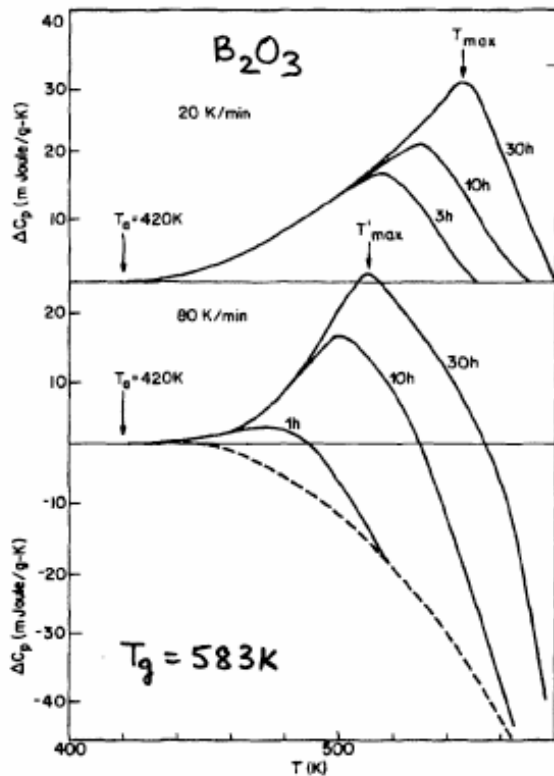


Fig. 6. Difference in specific heat,  $\Delta C_p$ , ( $=C_p - C_{p,0}$ ) of  $B_2O_3$  samples as a function of annealing time,  $t_a$ .

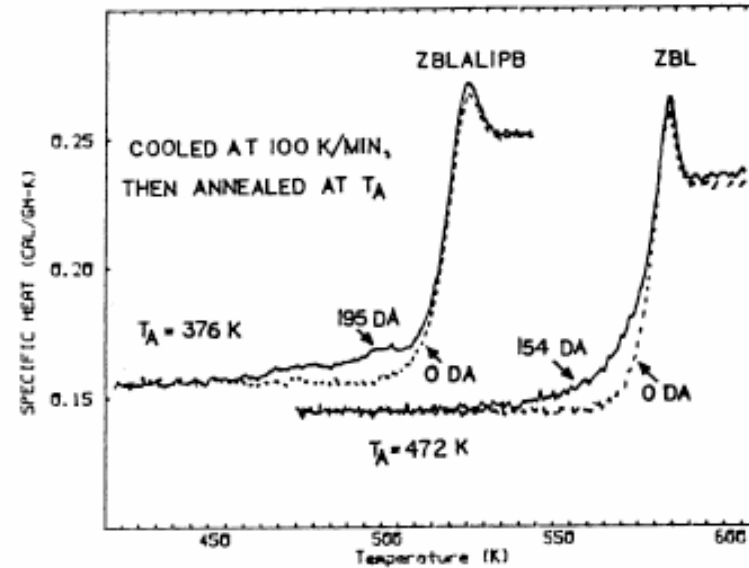


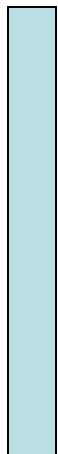
Fig. 3: Specific heat measured at 10 K/min heating rate for ZBL and ZBLALiPB glasses following rate cool and sub-Tg anneal for times shown in figure

$T_g = 574, 513$

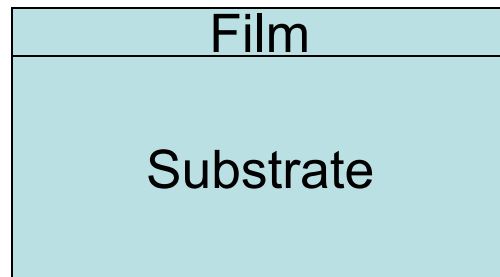
# Size, surface, and interface effects

- Small samples (thin films, fibers, nano-particles) typically - but not always - show a decrease in  $T_f$  (compared to that of the bulk glass).
- The magnitude of the change in  $T_f$  depends on sample size ( $h$ ) *and the nature of confinement* and interfaces.

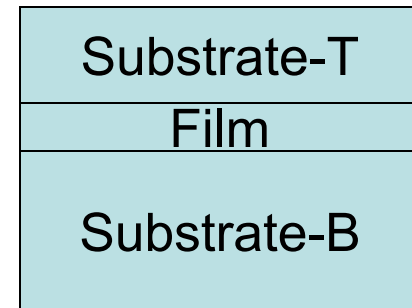
# Nature of confinement (thin film)



Free



Supported



Confined

# Size effect on $T_g$ (supported films)

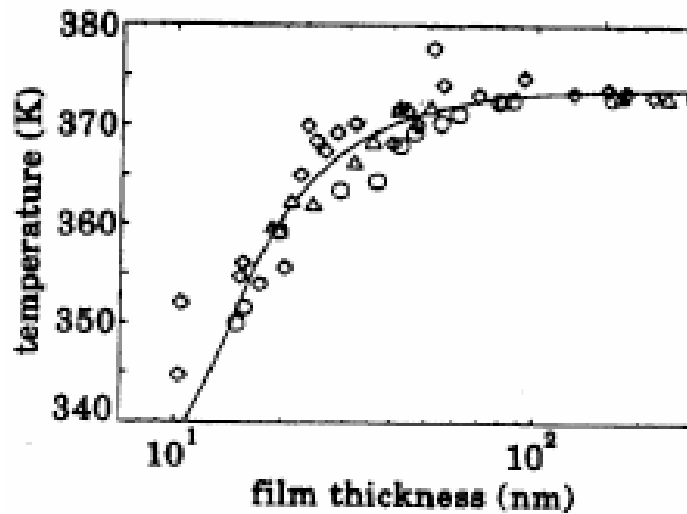


Fig. 3.

Fig. 3. - The glass transition temperature  $T_g$  versus molecular weights. The solid line is a best fit to the data, with  $T_g(\infty) = 373.8$  K,  $A = 3.2$  nm, and  $MW = 2900000$ .

Keddie et al (1994)

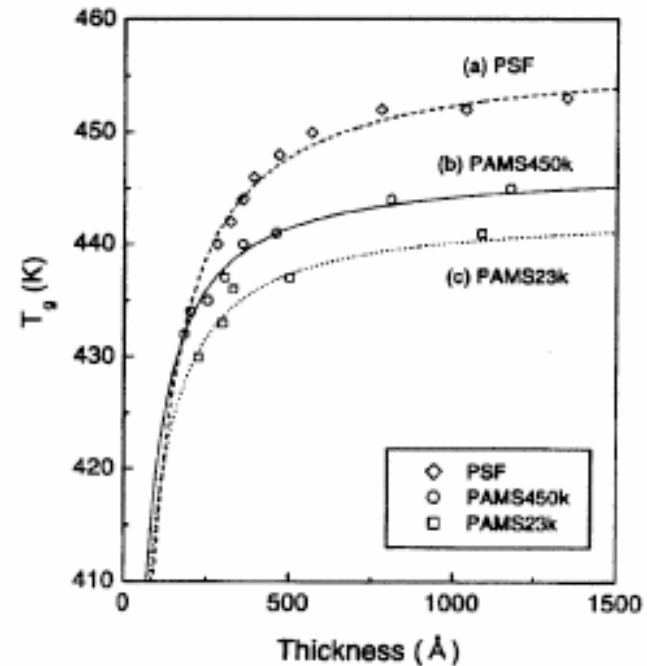


Figure 2. Comparison between the estimated  $T_g$  and the measured  $T_g$  in various thin films. (a) For PSF, the dotted line is  $T_g(\delta)$  curves at  $\xi (=10.3 \text{ \AA})$  and  $T_{g-\infty} (=457 \text{ K})$  and the open diamond is the measured  $T_g$ . (b) For PAMS450k, the solid line is  $T_g(\delta)$  curves at  $\xi (=6.3 \text{ \AA})$  and  $T_{g-\infty} (=447 \text{ K})$  and the open circle is the measured  $T_g$ . (c) For PAMS23k, the dash line is  $T_g(\delta)$  curves at  $\xi (=6.5 \text{ \AA})$  and  $T_{g-\infty} (=443 \text{ K})$  and the open square is the measured  $T_g$ .

Kim et al (2000)

# Sputter deposited silica glass

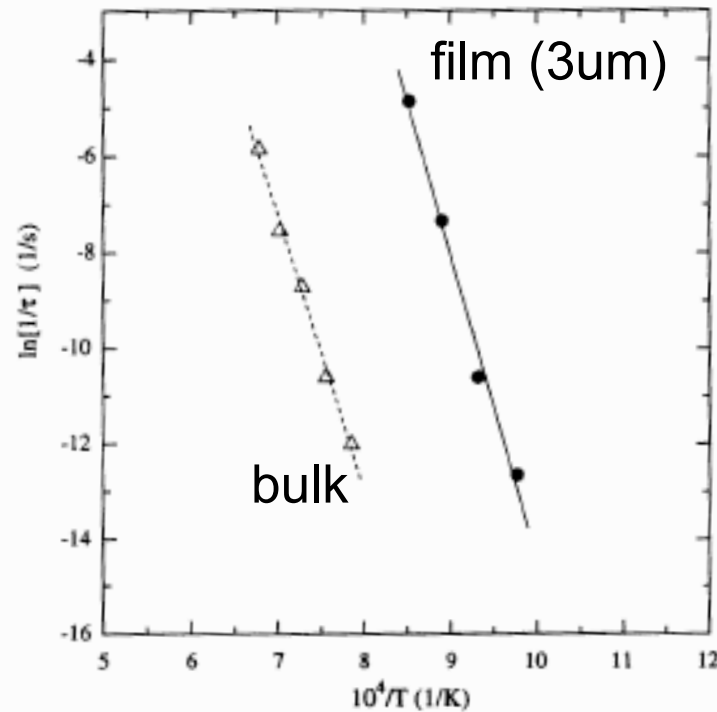


Fig. 7. Structural relaxation times as a function of annealing temperature. Structural relaxation times of the film and the bulk silica glass are plotted. Eq. (3) shows that the relaxation times obey Arrhenius dependence. Triangles and dotted lines show structural relaxation times of the bulk silica glass. Filled dots and solid lines show the structural relaxation times of sputter-deposited silica film. Equations of fitted lines are obtained as  $\frac{1}{\tau} = \exp \left[ (33.1 \pm 1.7) - (5.58 \pm 0.23) \cdot \frac{10^4}{T} \right]$  for bulk silica glass and  $\frac{1}{\tau} = \exp \left[ (49.3 \pm 4.5) - (6.37 \pm 0.49) \cdot \frac{10^4}{T} \right]$  for sputter-deposited silica films.

Hirose, Saito, Ikushima (2006)

PK Gupta(Kyoto)



## 2-dim confined liquids in porous silica

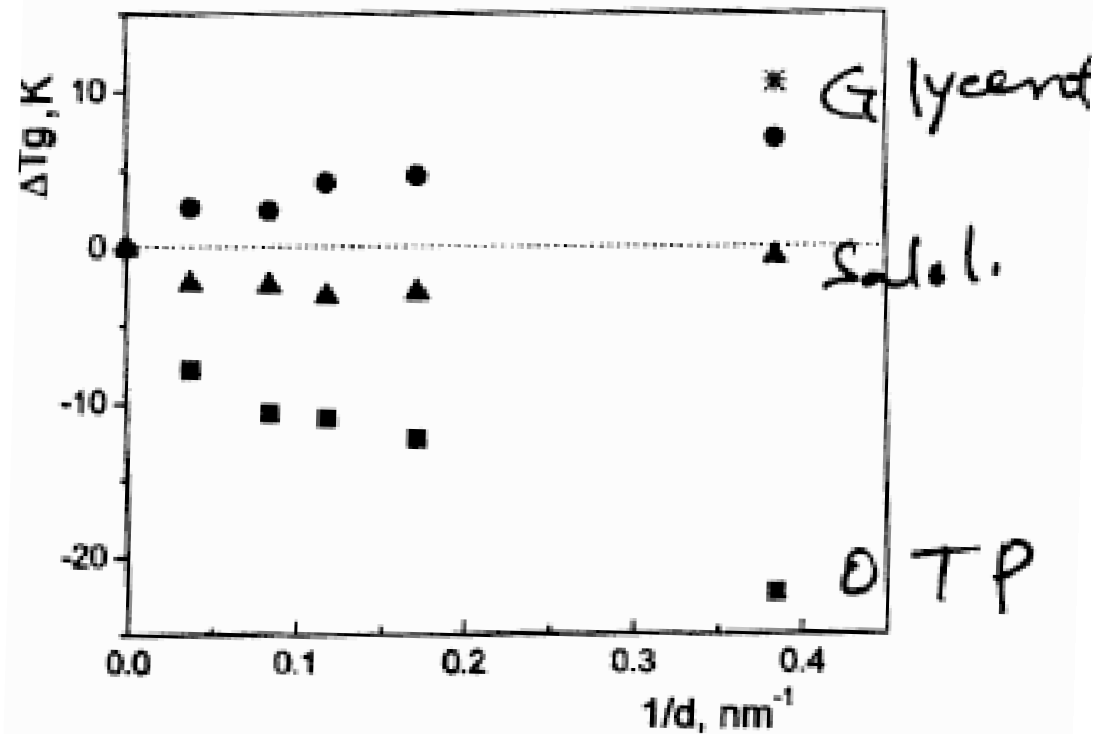
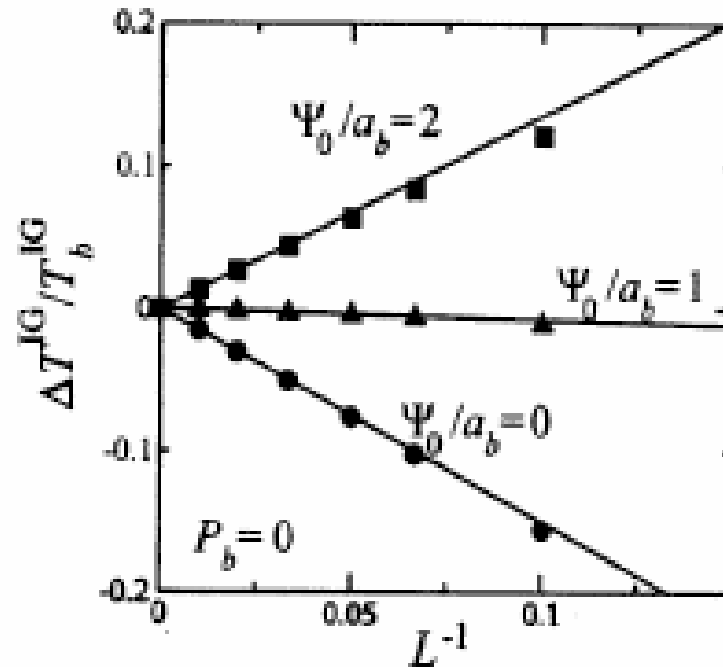


Fig. 3. Master plot of the glass transition change relative to the bulk: ■, P; ▲, salol; ●, glycerol. \*, the same as in Fig. 2. Errors are smaller than size of symbols.

Trofymlyuk, Levchenko, Navrotsky (2005)

# Ideal glass transition $T_K$ in a fluid film model



**Figure 4.** Confinement induced shift in the IG transition of the SSMF relative to that of the bulk system with which it is in equilibrium at pressure  $p_b = 0$ .  $L^{-1}$  is the dimensionless reciprocal film thickness relative to the film particle centers. The solid lines represent the simplification of eq 22, and the symbols are the predictions of the full mean-field model of section II. The relative strength of the film-substrate

Mittal, Shah, and Truskett (2004)  
 (SSMF = Soft sphere/ mean-field)

# Size effect and the AG model

Adam Gibbs Model:  $T_g S_{conf}(T_g) = Cons.$

$$F(T, A, h) = F^B(T) + \gamma(T)A$$

$$S = -\frac{\partial F}{\partial T} = S^B(T) - A \frac{\partial \gamma}{\partial T}$$

$$s \equiv (S / V) = s^B(T) - (1/h)\gamma_T \quad hA = V$$

$$T_f(h) = \frac{T_f^B}{[1 + \{ \frac{-\gamma_T}{hs^B(T_g^B)} \}]}$$

$$\frac{[T_f^B - T_f(h)]}{T_f(h)} = \frac{K}{h} \quad K = -\frac{\gamma_T}{s^B}$$

# AG phenomenological model of size effect

$$\frac{[T_f^B - T_f(h)]}{T_f(h)} = \frac{K}{h}$$

- Eqn same as the theoretical result of the Truskett model (2004).
- Eqn same as the one obtained empirically by Kim et al (2000).
- Typically  $K > 0$  since  $\gamma$  generally decreases with increase in  $T$ .  $K$  can be negative for some systems under certain conditions depending on the nature of the interface.

Thanks and questions.