Sub -T_g Relaxation in Thin Glass

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(Go Bucks !)**

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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)
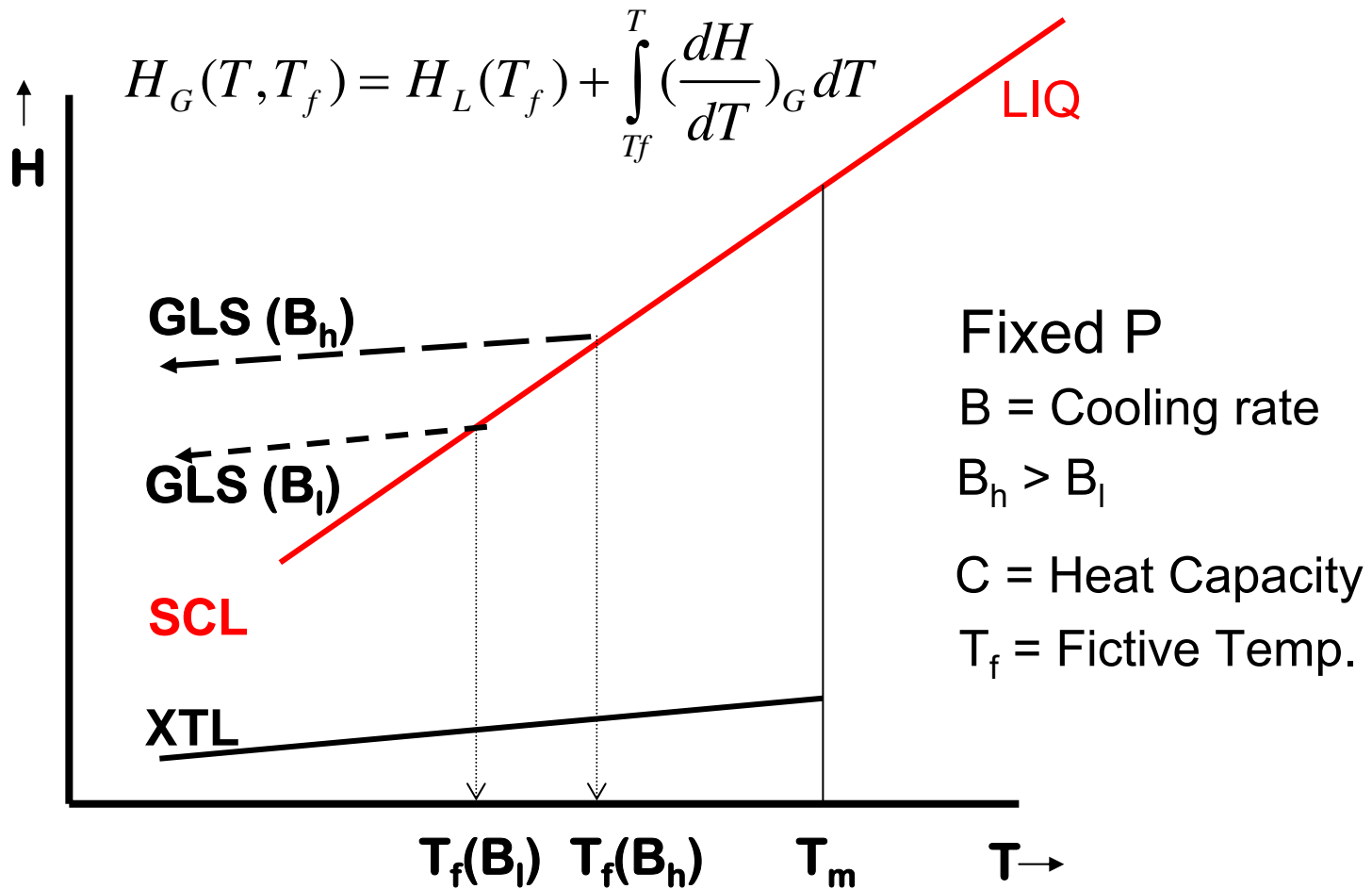
←

Glass   **Liquid**
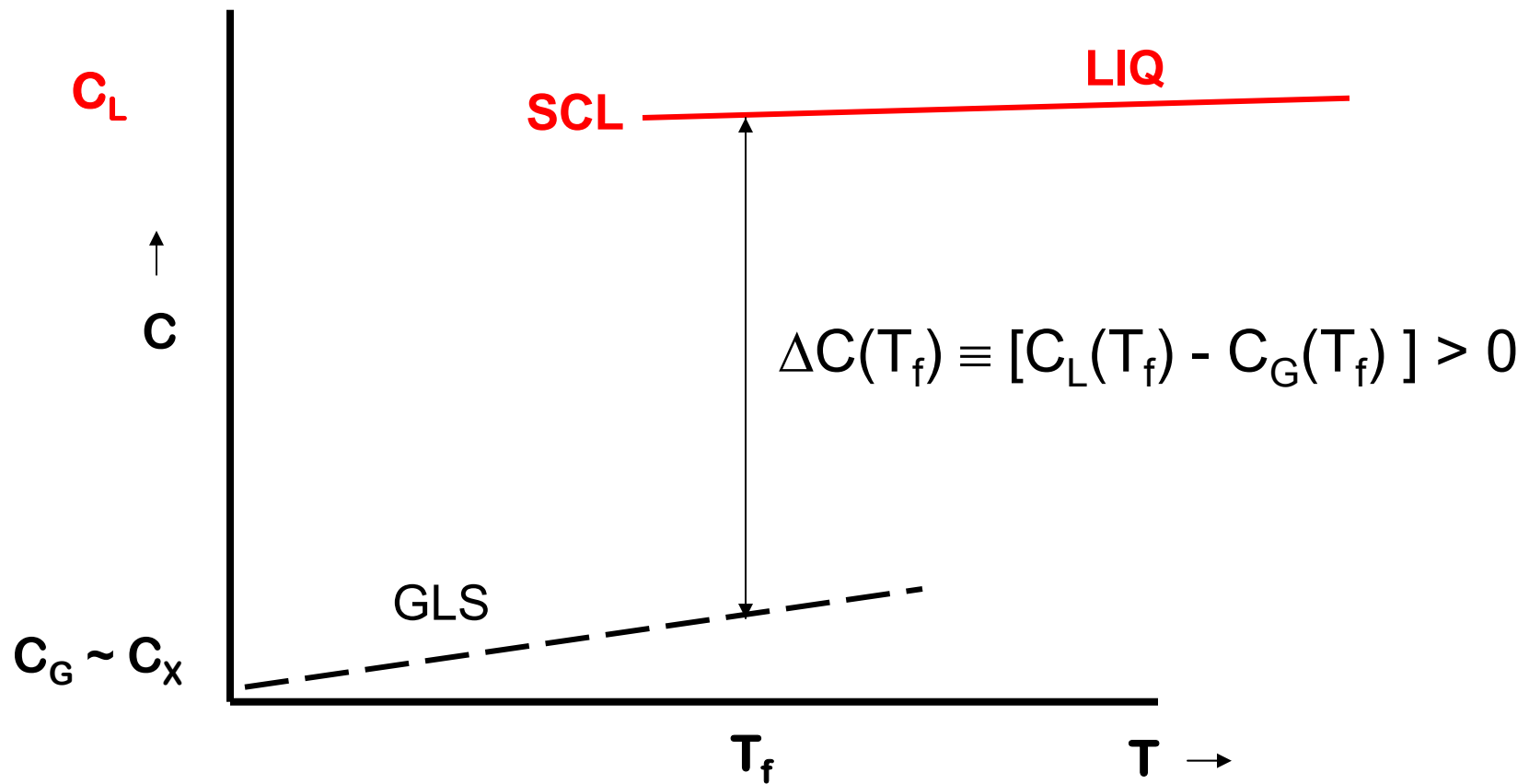
(Non-equilibrium)   **(Equilibrium)**

→

Structural relaxation (SR)

LGT - Phenomenology

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

$$H_G(T, T_f) = H_L(T_f) + \int_{Tf}^{T} \left(\frac{dH}{dT}\right)_G dT$$

LIQ

H ↑

GLS (B_h)

GLS (B_l)

SCL

XTL

$T_f(B_l)$ $T_f(B_h)$ T_m T →

Fixed P

B = Cooling rate

$B_h > B_l$

C = Heat Capacity

T_f = Fictive Temp.

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

C_L

C

$C_G \sim C_X$

LIQ

SCL

$\Delta C(T_f) \equiv [C_L(T_f) - C_G(T_f)] > 0$

GLS

T_f

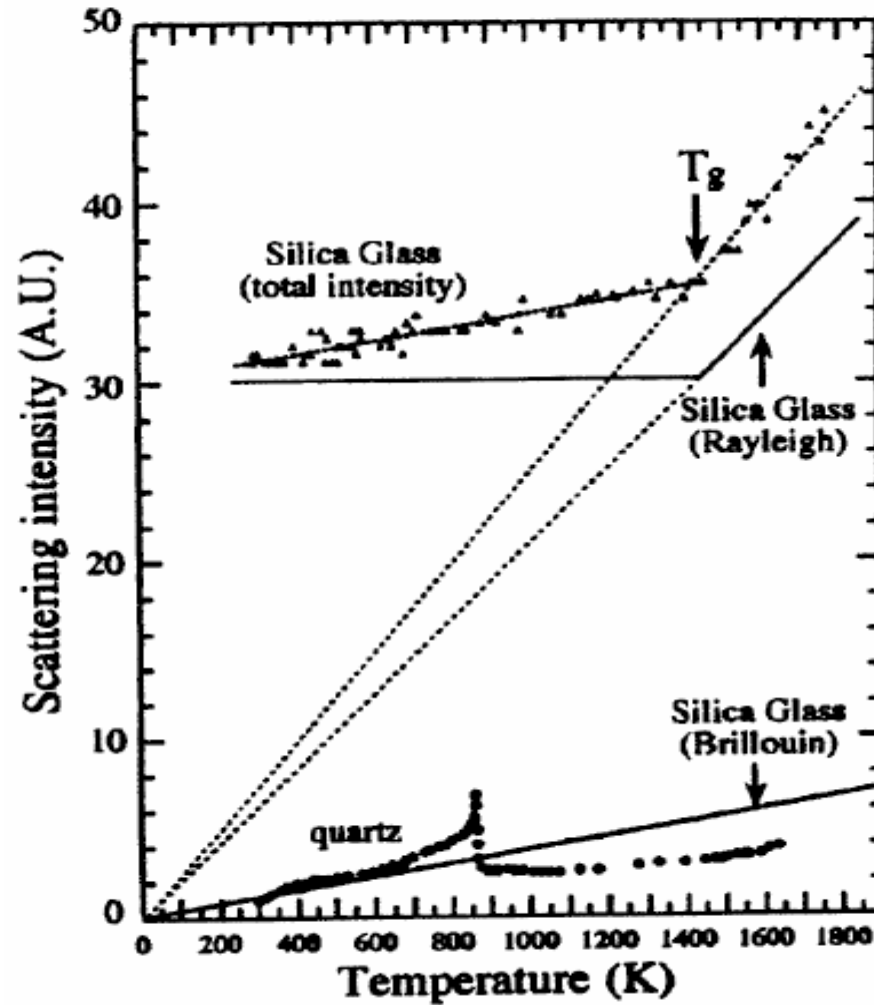$T \rightarrow$

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

⮌T_f increases with increase in cooling rate (B).

Ln B

Tf

Ln B
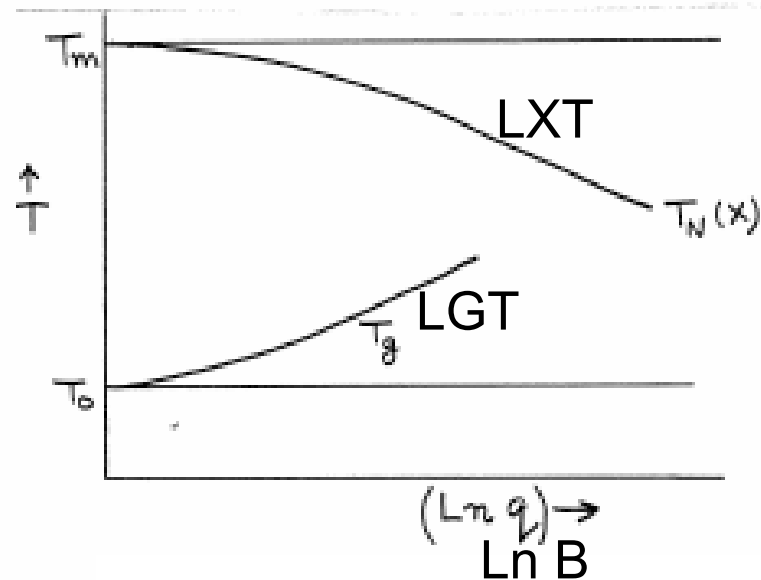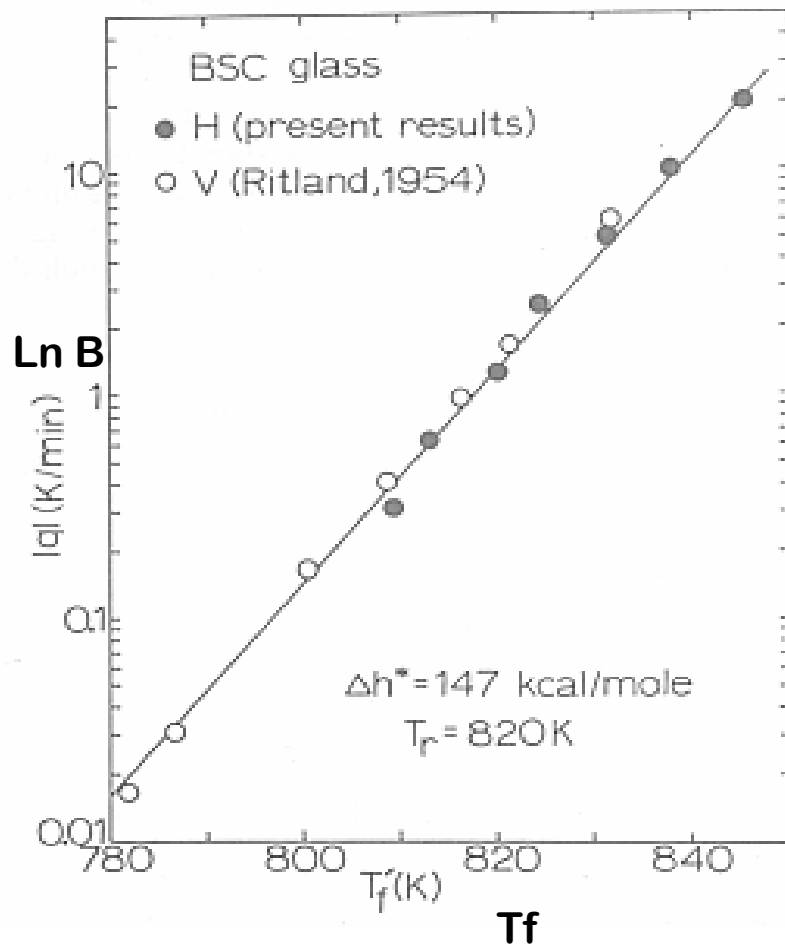
Rayleigh Scattering in silica glass

Γ. 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 !*).
- $\Delta C > 0$, $\Delta \kappa > 0$, $\Delta \beta >,=,< 0$
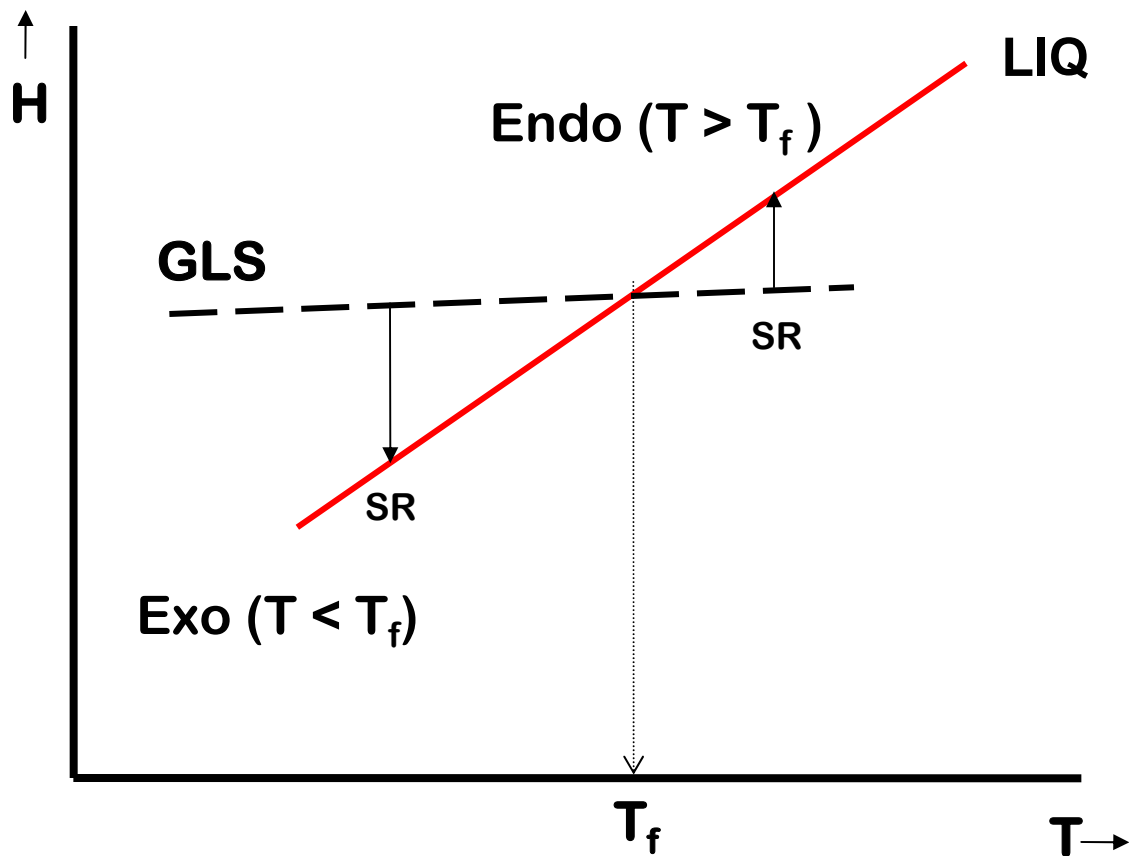
$$PDR \equiv \frac{(\Delta C)(\Delta \kappa)}{TV(\Delta \beta)^2} > 1$$

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

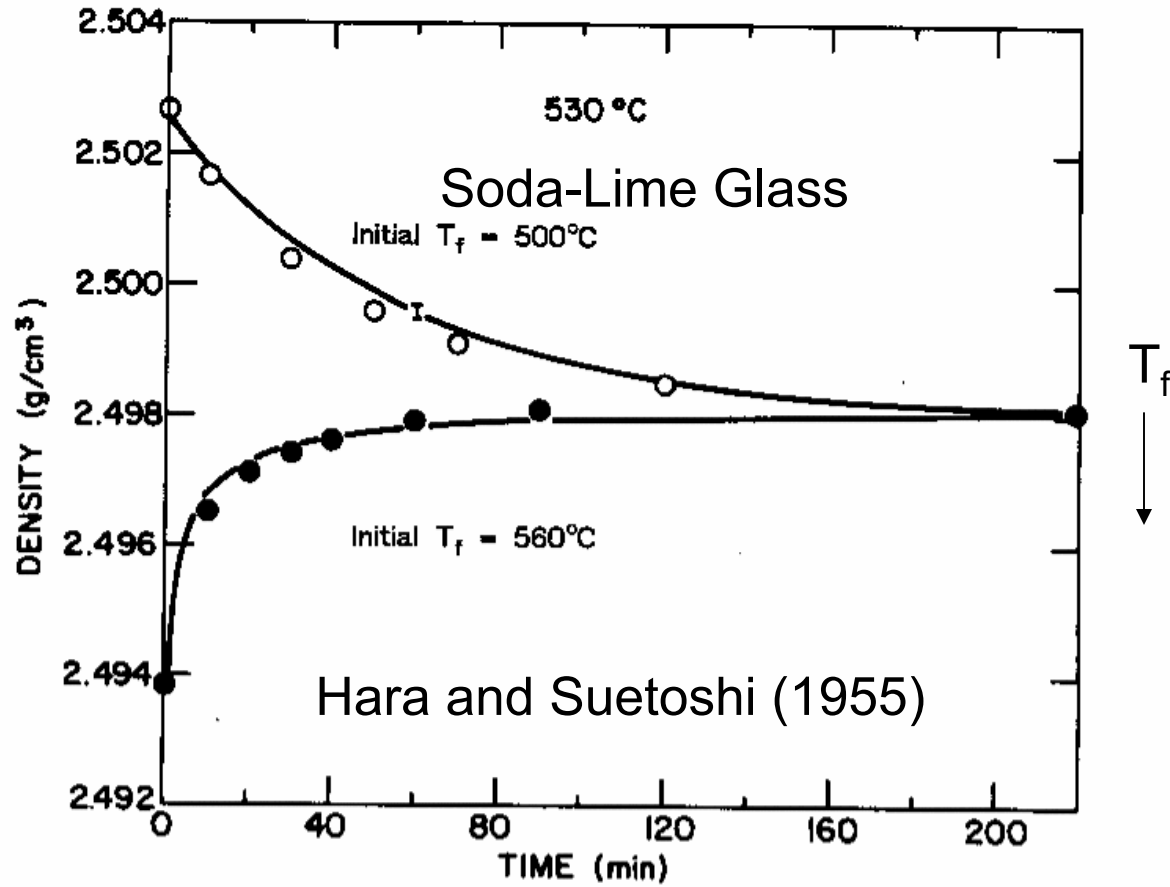- Glasses have intrinsic nano-scale heterogeneities.

Relaxation - Phenomenology

Isothermal SR

Non-linear Relaxation Kinetics

530 °C

Soda-Lime Glass

Initial T_f = 500°C

Initial T_f = 560°C

Hara and Suetoshi (1955)

T_f

Sub-Exponential Relaxation

M(t,T) = Relaxation Function

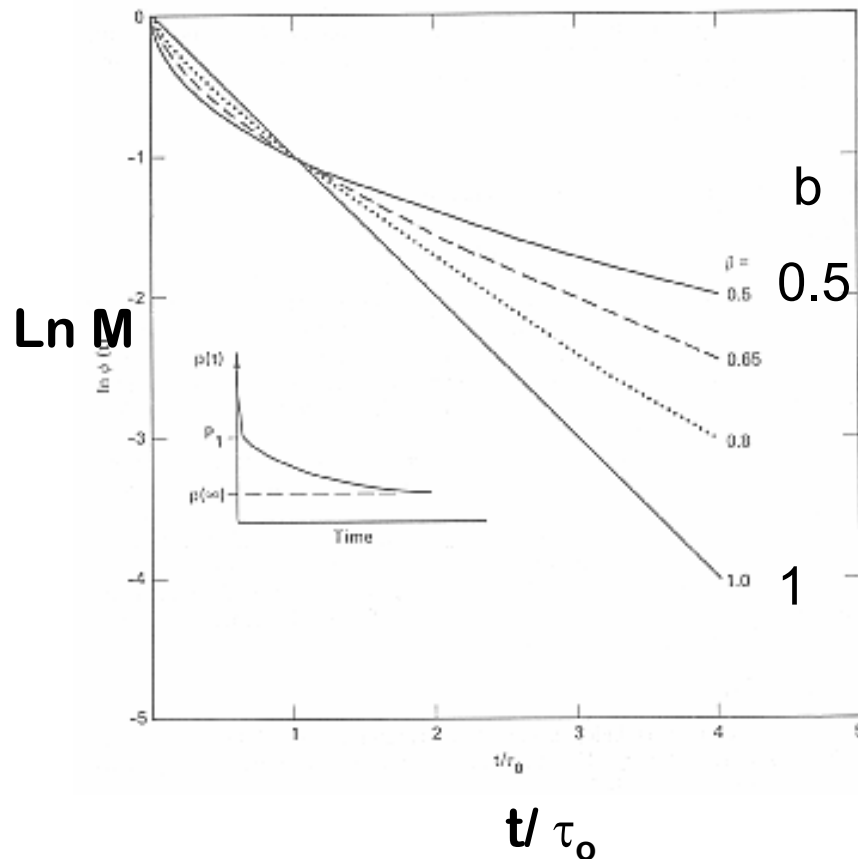- $M(t,T) \equiv \dfrac{T_f(t,T) - T}{T_f(0) - T}$

Ln M

t/ τ_o

- *Stretched Exponential*

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

0 < b(T) < 1

$$\tau_{av} = (\eta / \mathrm{mod}ulus) = (\tau_o / b)\Gamma(1/b)$$

Adam-Gibbs (AG) Model of Viscosity

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

A, η_∞ = Parameters independent of T.

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

$\cong \Delta S \equiv S_L(T) - S_G(T)$.
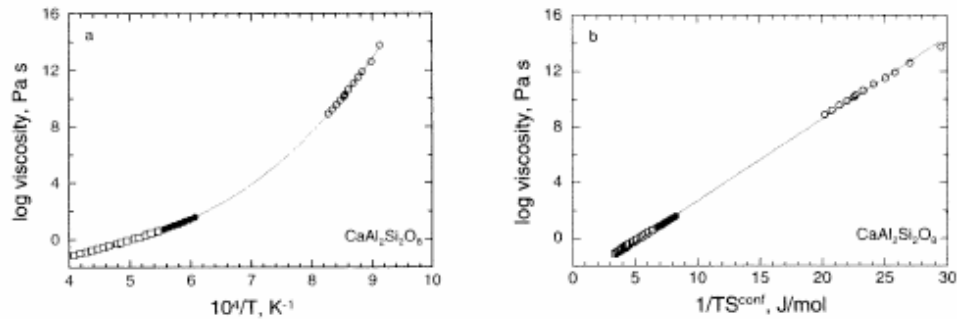
AG model fits data extremely well !

Figure 2.24 - Viscosity of stable and supercooled $CaAl_2Si_2O_8$ liquid. (a) Against reciprocal temperature. (b) Against $1/TS^{conf}$. Data from Urbain et al. [1982; open squares], Scarfe et al. [1983; solid circles], and Sipp et al. [2001; open circles].
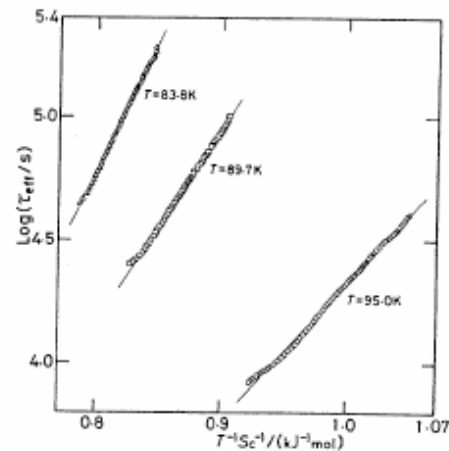

Fig. 4. Test of the Adam–Gibbs equation for the relaxation time of butyronitrile vapor-deposited samples (from [29] by permission).

SR: Generic features

- SR is spontaneous (irreversible).

- SR is non-linear.

- SR is non-exponential (~ stretched exponential).

- Av. relaxation time approximately follows AG theory.

- Deviations from the Arrhenius behavior (fragility) of τ correlate with ΔC.

- 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 $\Delta H(T_f) \neq T_f \Delta S(T_f)$.

b) $S_L(T_f) = S_X(0) + \int\limits_o^{Tm} \dfrac{C_X}{T} dT + \dfrac{\Delta H_m}{T_m} + \int\limits_{Tm}^{Tf} \dfrac{C_L}{T} dT$

$S_G(T_f) = S_G(0) + \int\limits_o^{Tf} \dfrac{C_G}{T} dT$ $[S_G(0)$ is not known.$]$

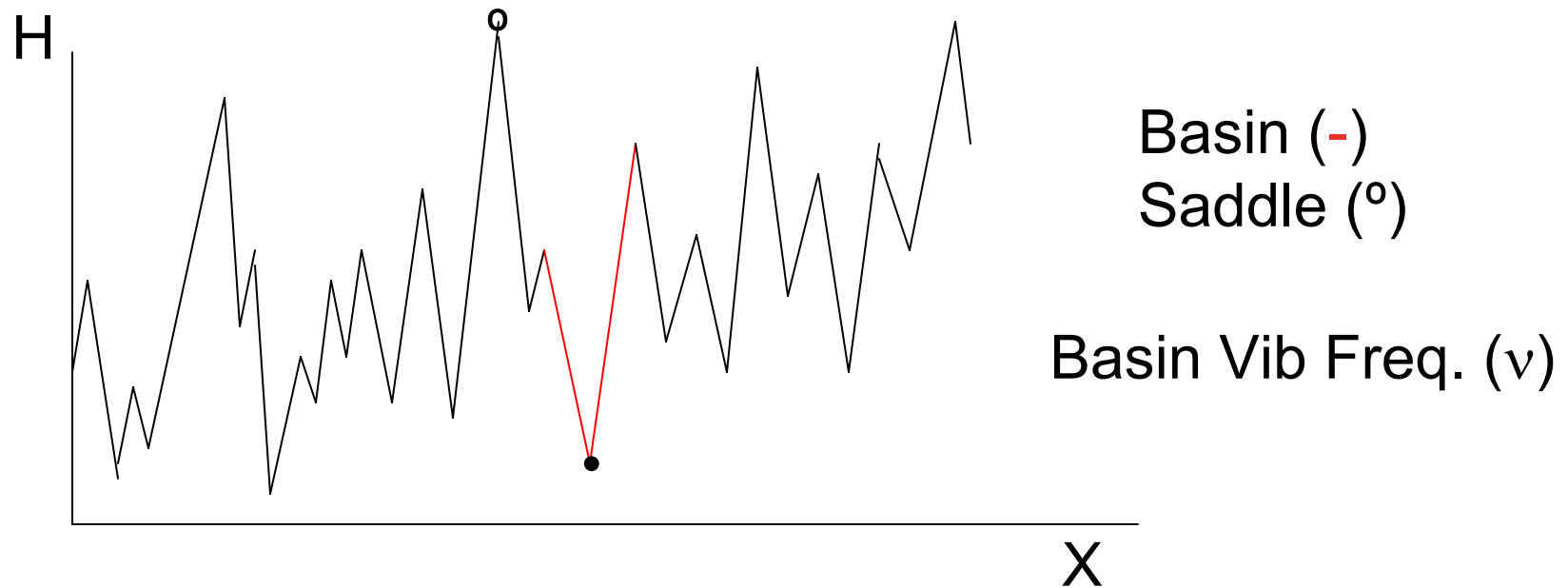# The Enthalpy Landscape View

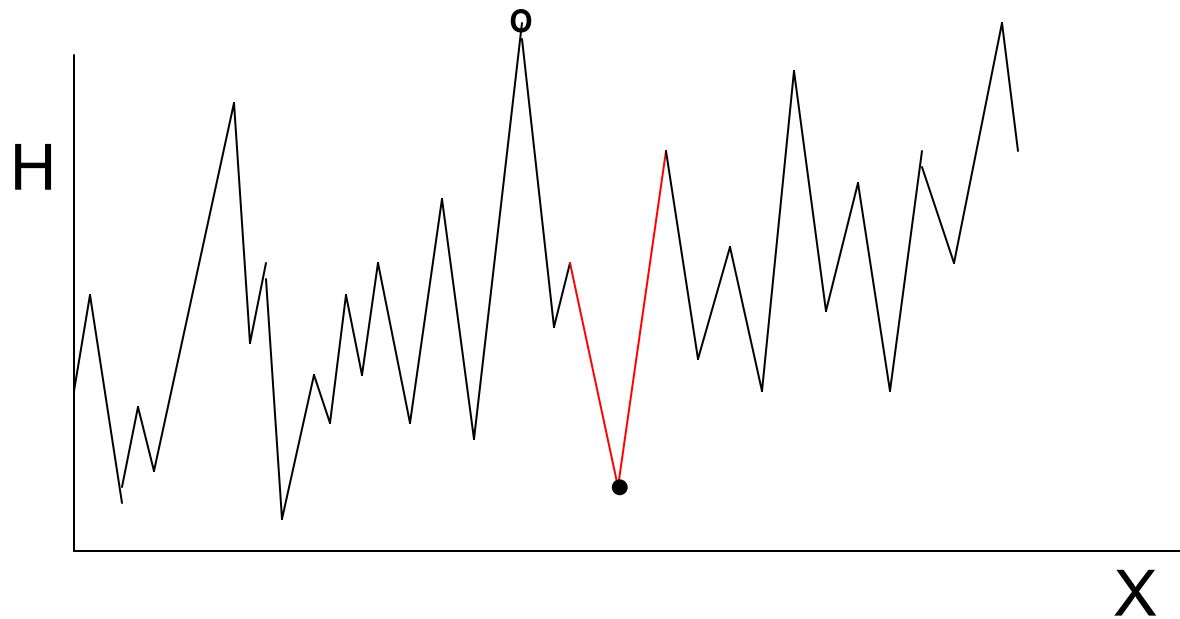Gupta and Mauro,J. Chem. Phys. 126, 224504, (2007)

Rugged H-Landscape

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

(IS = Inherent states, minima, •)

Basin (-)
Saddle (º)

Basin Vib Freq. (ν)
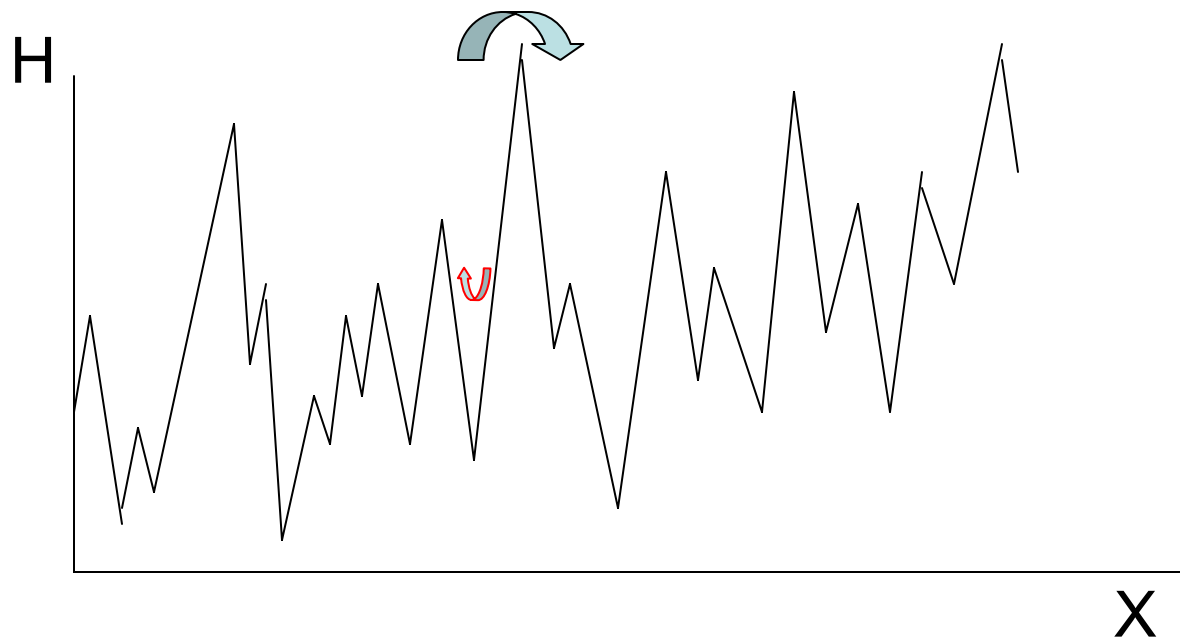
Density of Inherent States, $\Omega(H)$

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

H

X

Dynamics in H- Landscape

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

Inter-basin transitions: slow ( )

H

X

Inter-basin transitions

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

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

$$F_{ij}^* = H_{ij}^* - kTLn(n_{ij}^*)$$

ε = a small constant number

ν = attempt (vibrational) frequency (~same for all basins)

k = Boltzmann's constant

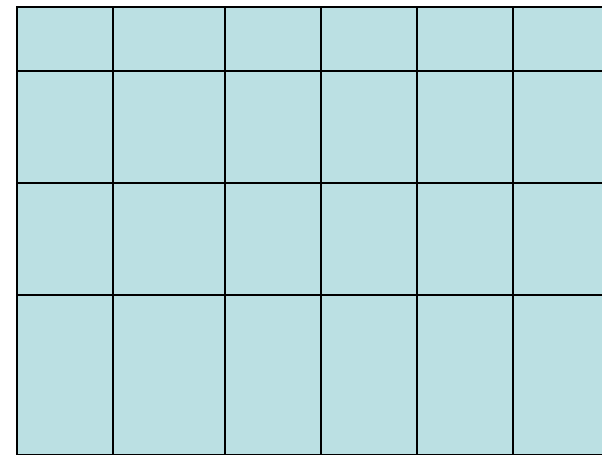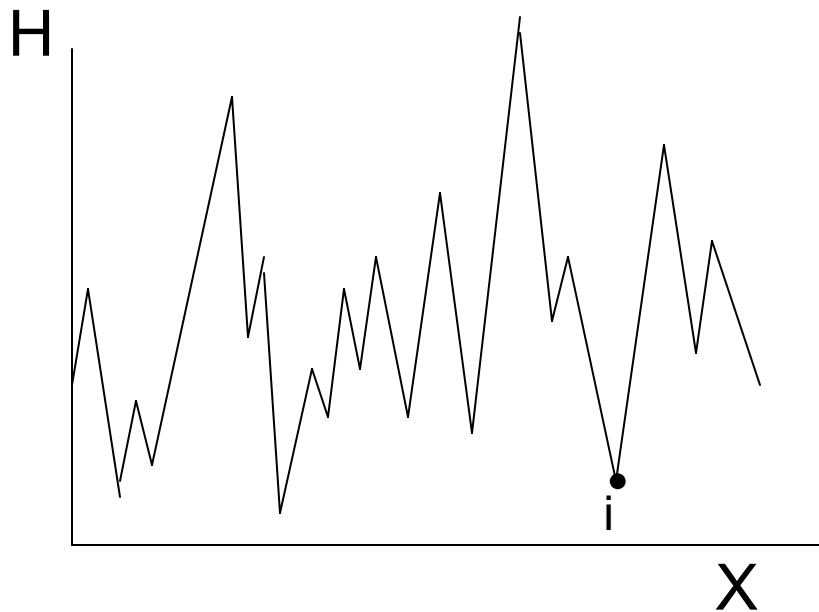H_{ij}^* = Barrier enthalpy from basin i to j

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: $\quad t_{obs} > \tau_{MAX}(T)$

$$Ba\sin probability, p_i^L(T) = \frac{\displaystyle\int_{X \in i-ba\sin} \exp[-\frac{H(X)}{kT}]dX}{\displaystyle\sum_i^{\Omega} \int_{X \in i-ba\sin} \exp[-\frac{H(X)}{kT}]dX}$$

H

i

X

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.

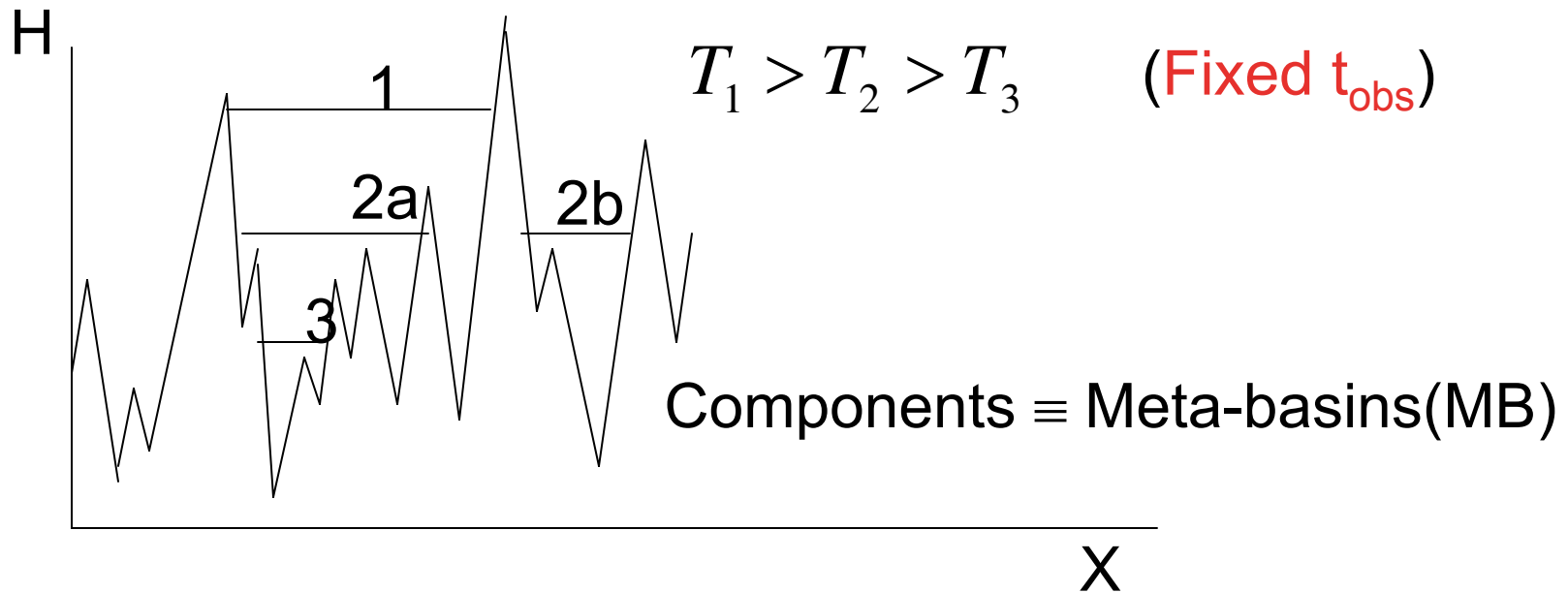$$S_C^L(T) = -k \sum_i^{\Omega} p_i^L(T) Ln[p_i^L(T)]$$

Ergodicity Breaking

$$kTLn(\frac{vt_{obs}}{\varepsilon}) < F^*_{max}$$

Partitioning of X-space in to components such that
- no transitions among components
- each component is ergodic in itself.

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

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

H

1

2a   2b

3

Components $\equiv$ Meta-basins(MB)

X

# LGT and Broken Ergodicity

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

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

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

$T < T_f(t_{obs})$ 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: $t_{obs} < \tau$.

Liquid ($t_{obs} > \tau$)

Glass αth-MB

$P^L_\alpha(T_f)$

H

X
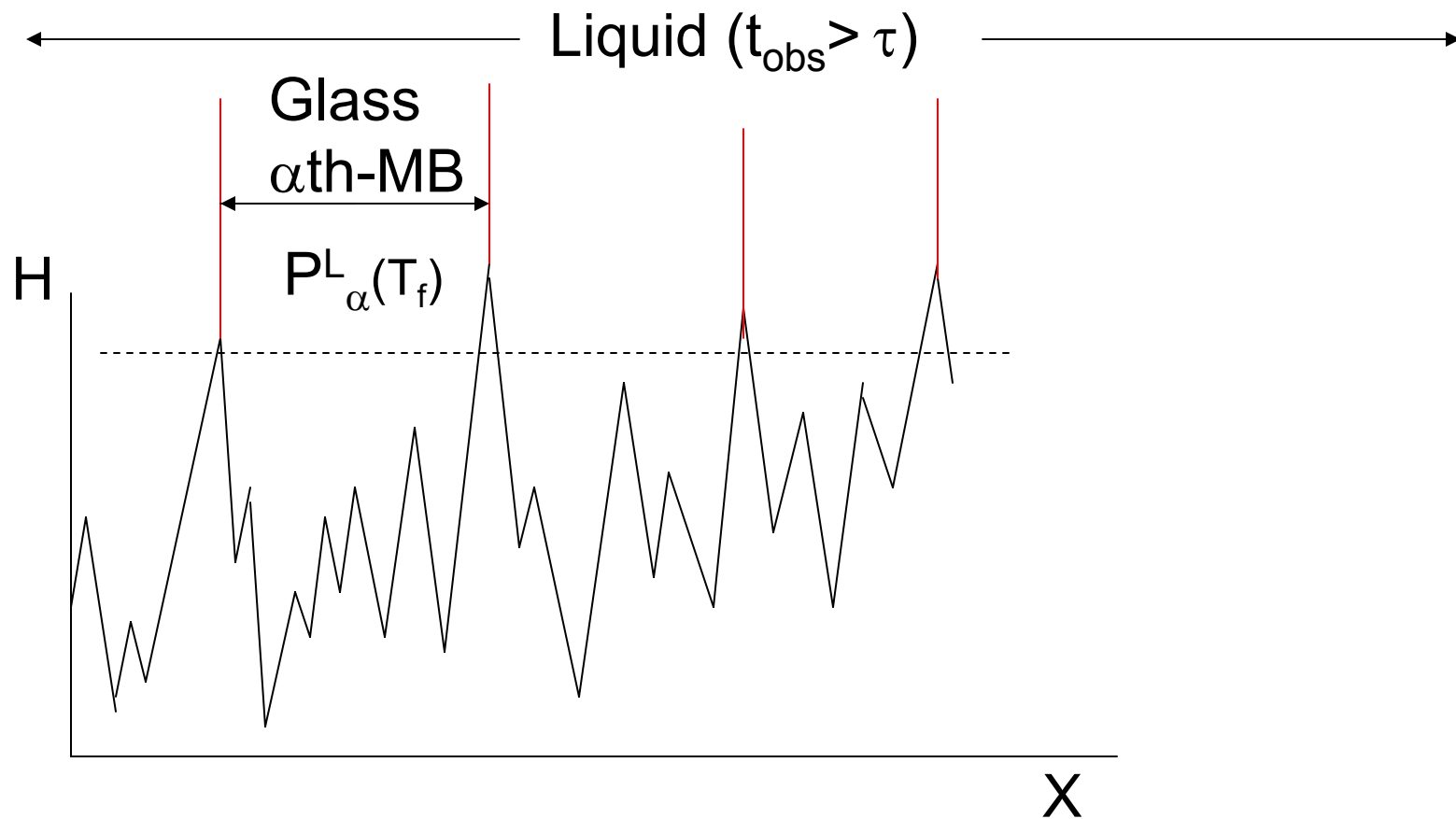
The LGT-partition

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

Probability of the αth MB:

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

Prob. of ith-basin:

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

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

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.

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

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

ΔS during LGT

$\Delta S = 0$ 　　　　　　　(Current View)

$$\Delta S = I = -k\sum_{\alpha} P^{\alpha}(T_f) Ln P^{\alpha}(T_f)$$ 　(New view, ΔS >0)
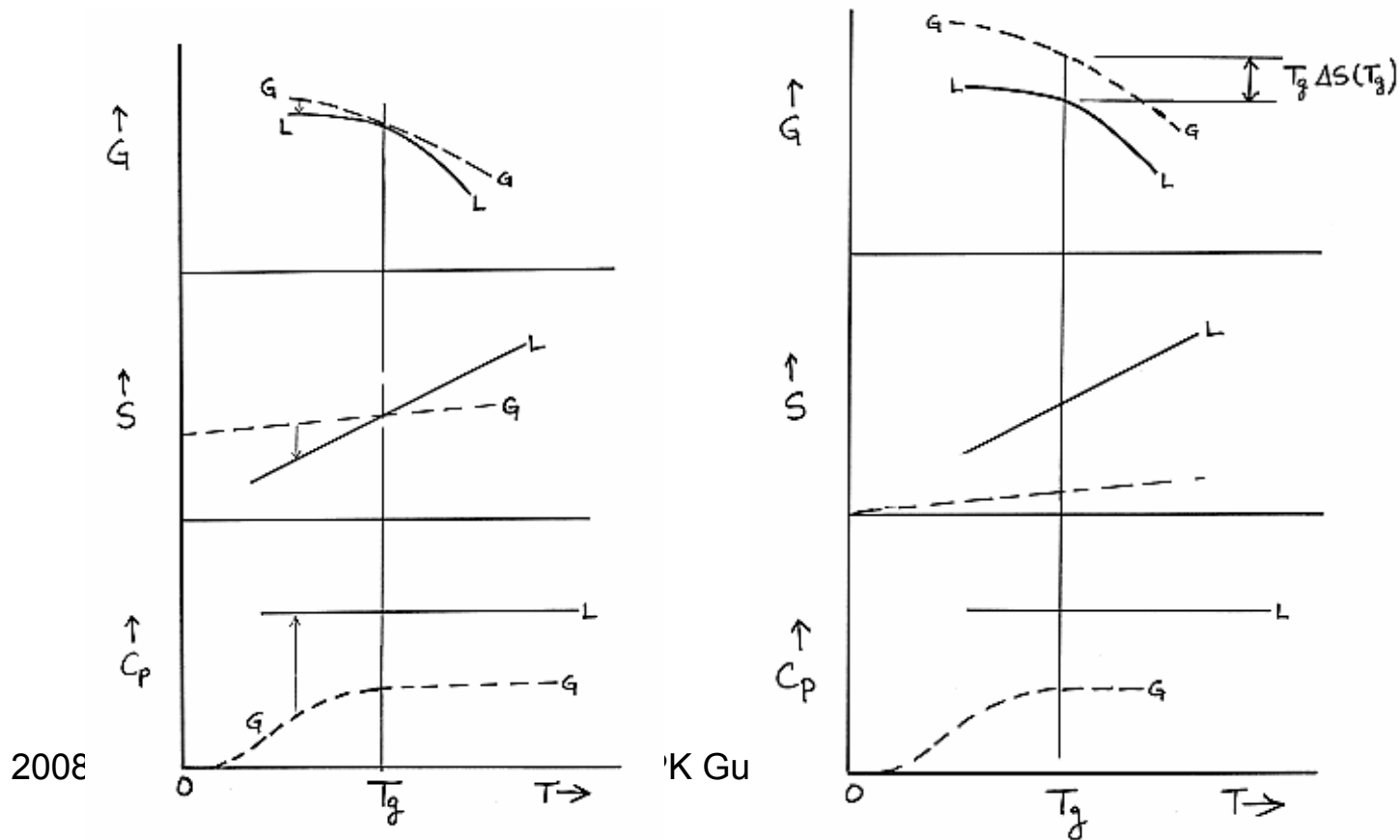
• Entropy loss at T_f because the inter-MB transitions are frozen in a glass.

Configurational Entropy of Glass

Gupta/Mauro
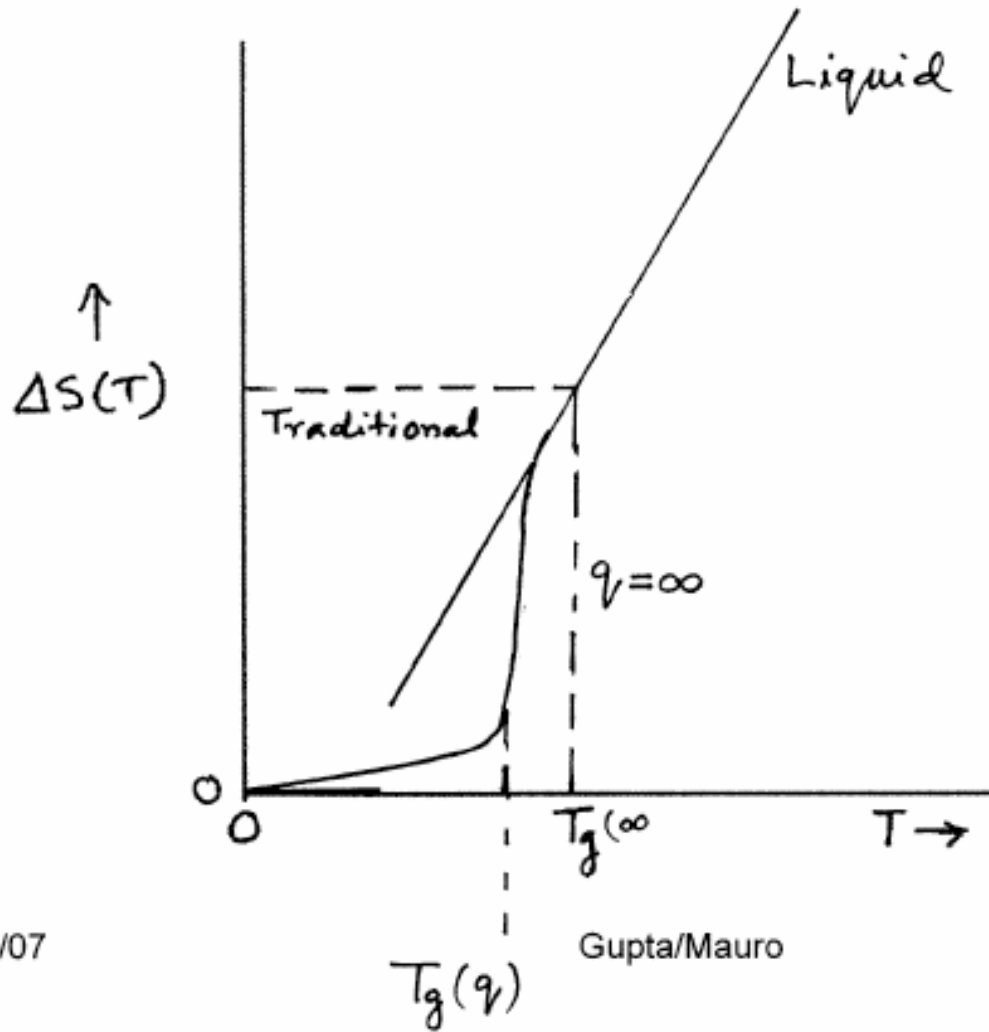
New View vs. Traditional View

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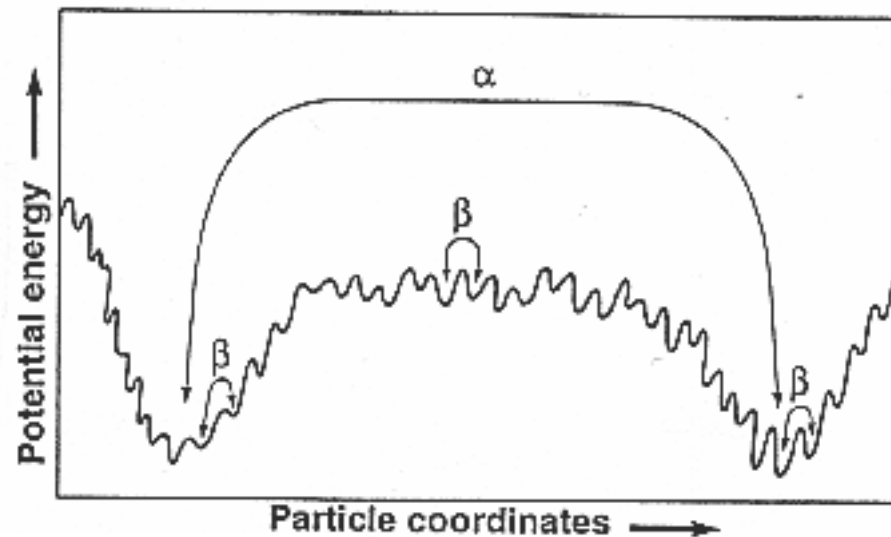

'K Gu

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.

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

Relaxation: several time scales !

Configurational changes (Inter-basin transitions):
- β **process (intra-MB transitions)**
- α **process (inter-MB transitions, slowest)**

Hierarchy of Barriers

Height	Label	Order of freezing	Order of thawing	T-dependence
Highest	α (Primary)	1st (LGT) ↓	Last ↑	Non-Arrhenius
2nd highest	β (Secondary)	2nd ↓	2nd to last ↑	More Arrhenius
3rd highest	γ	3rd	3rd to last	

Small barriers unfreeze first. Thus relaxation is fast in the beginning and then becomes slower and slower as time increases.
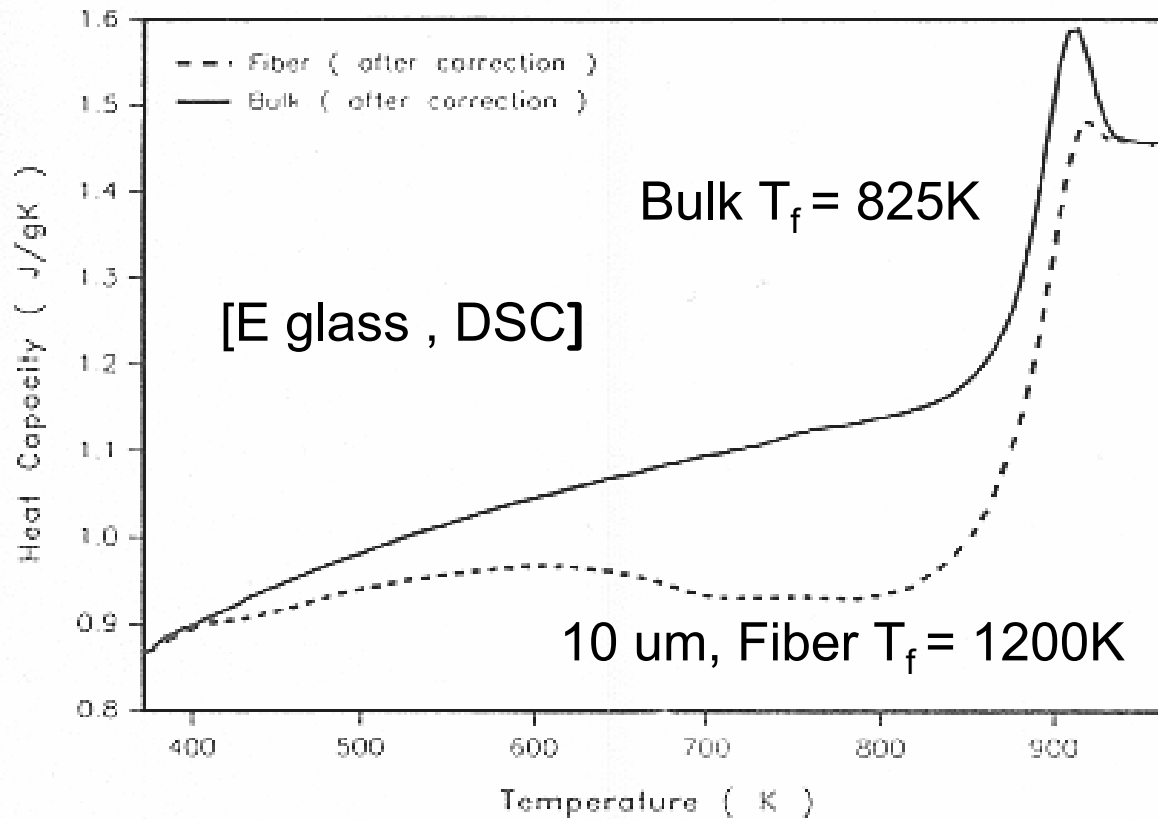
Barrier Heights (MD simulation)

Av. barrier height

Fragile system

Energy density of the adjacent IS.
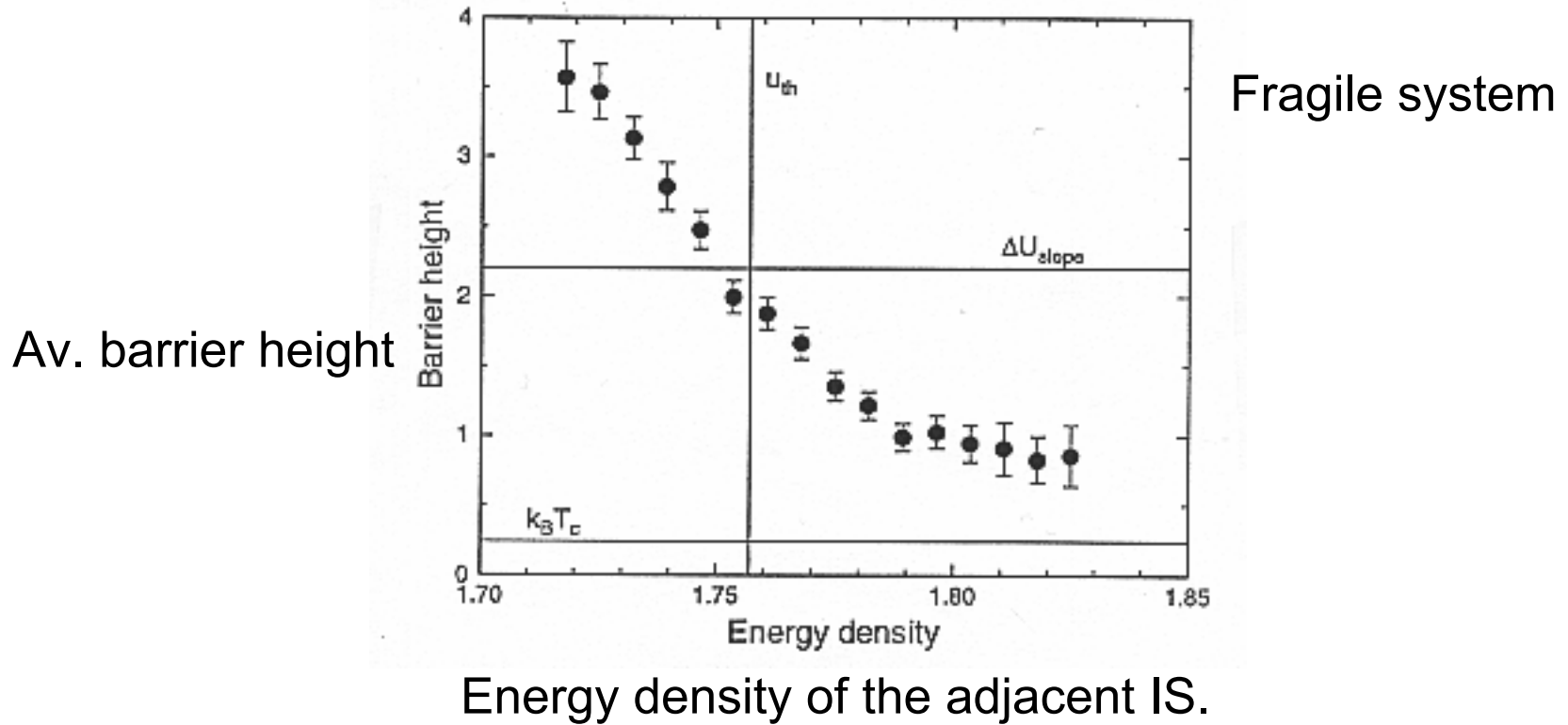
Parisi et al (2002)
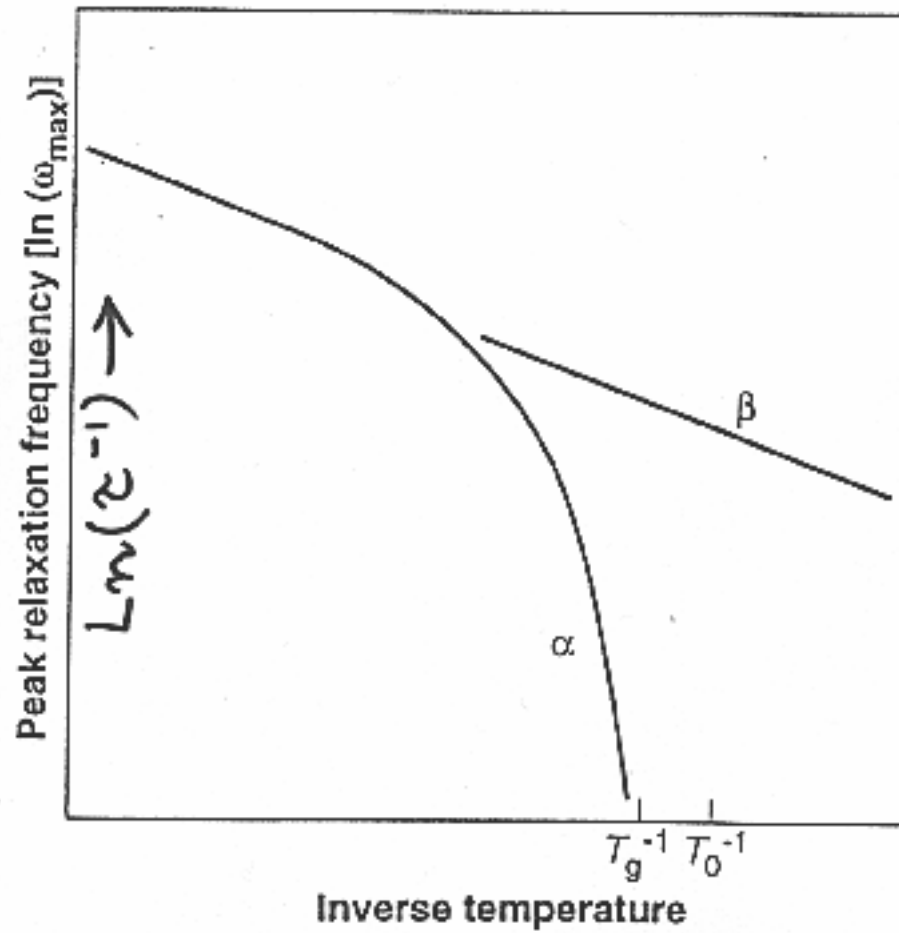
SR: Far from equilibrium (Effect of T_f)

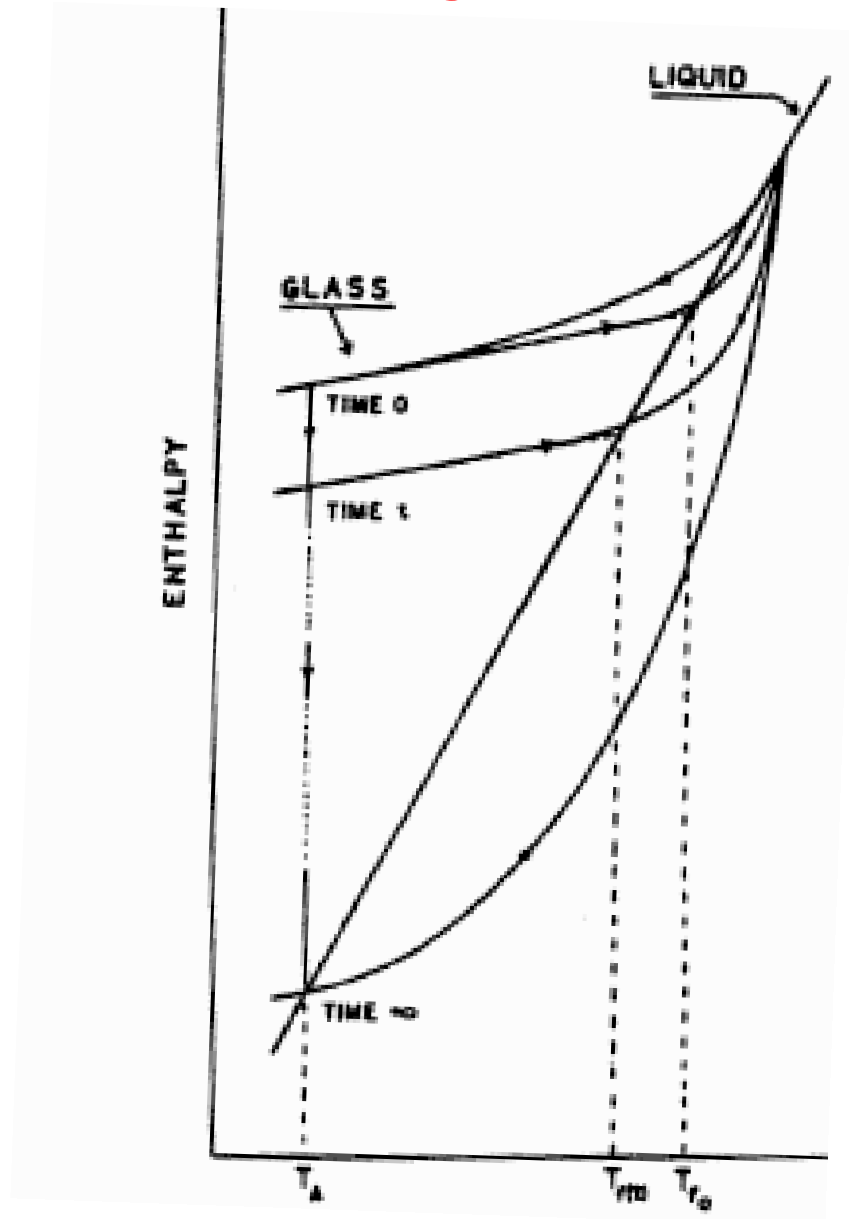
Huang and Gupta, 1992.

Sub-T$_g$ Relaxation

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

- Stabilization (δ < 15 %)

- Sub-sub Tg Relaxation (δ > 15 %)

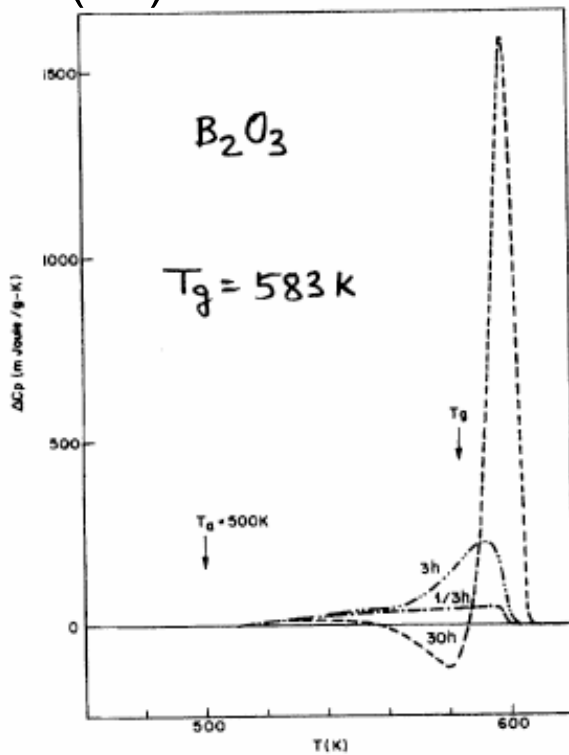# Effect of sub-Tg isothermal annealing

Stabilization

C - C(ref)

Fig. 9. Evolution of ΔC, at T=500 K.
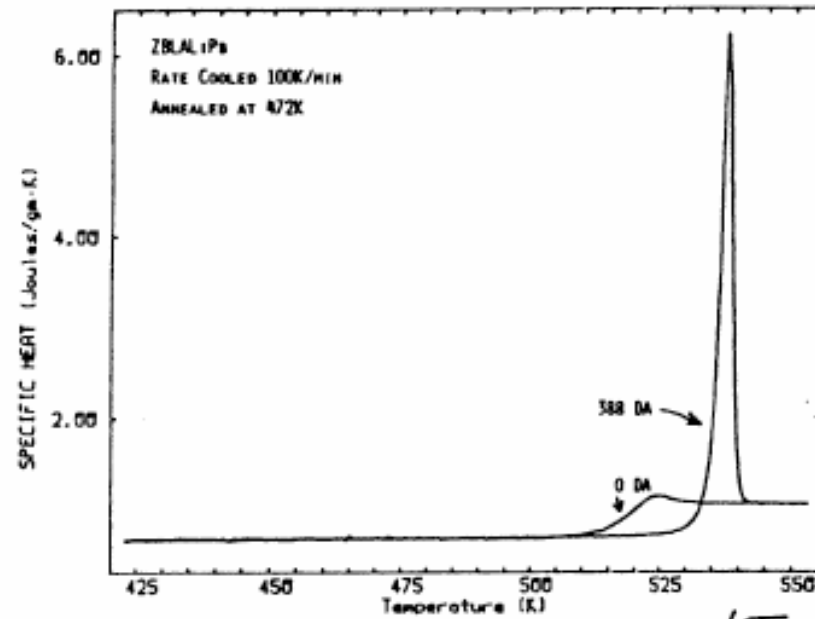
Chen, Kurkjian (1983)

Moynihan et al (1985)

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

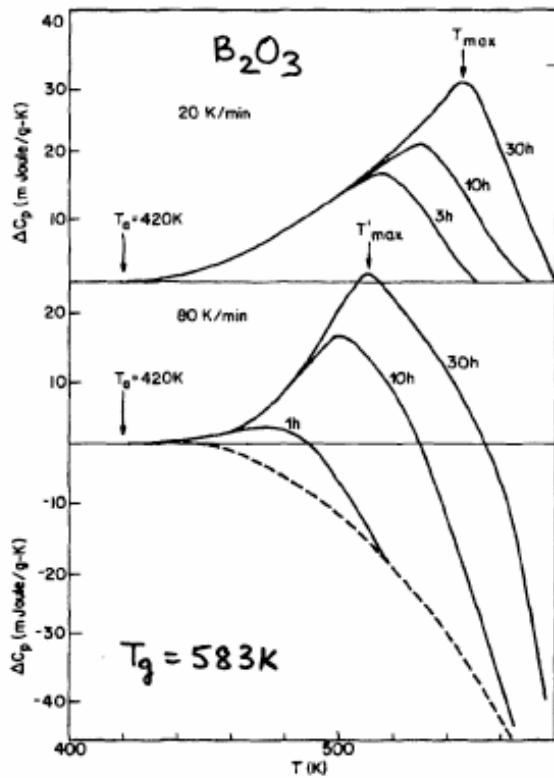# Sub-sub Tg Relaxation

Sub-Tg peak in C linear heating in DSC.

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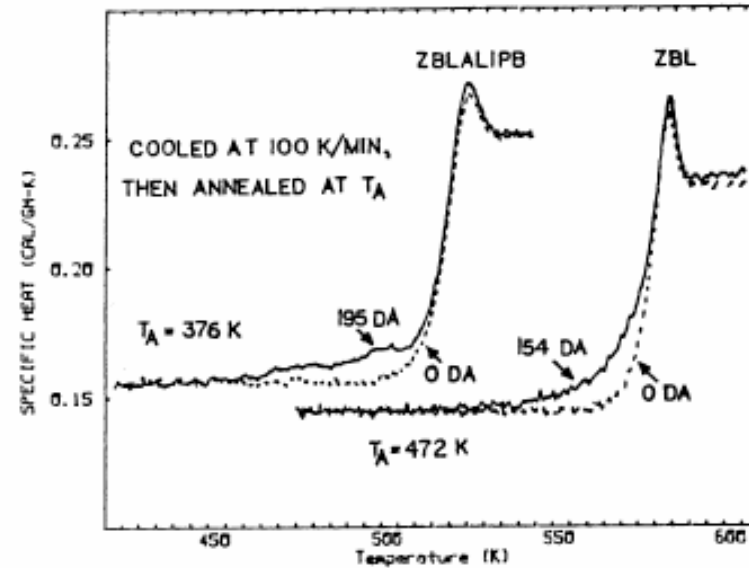

Fig. 3: Specific heat measured at 10 K/min heating rate for ZBL and ZBLALiPb glasses following rate cool and sub-Tg anneal for times shown in figure

$T_g = 574$, 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.
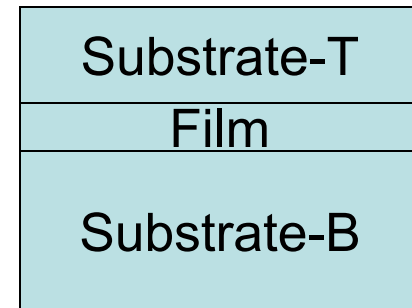
Nature of confinement (thin film)

Free

Film
Substrate

Supported

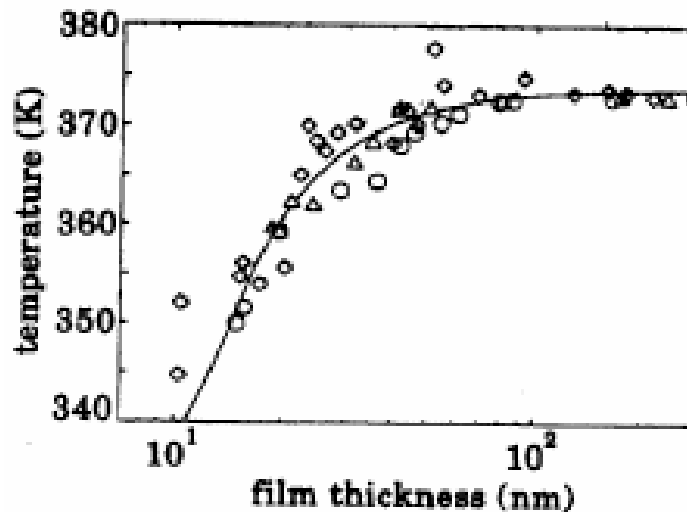| Substrate-T |
| --- |
| Film |
| Substrate-B |
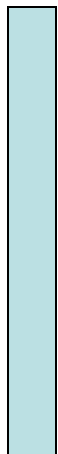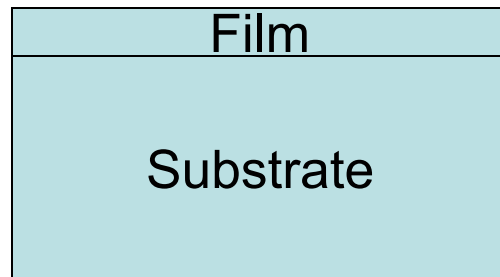
Confined

Size effect on T_g (supported films)

g. 3.

g. 3. – The glass transition temperature T
lecular weights. The solid line is a best
. (1), with $T_g(\infty) = 373.8$ K, $A = 3.2$ n
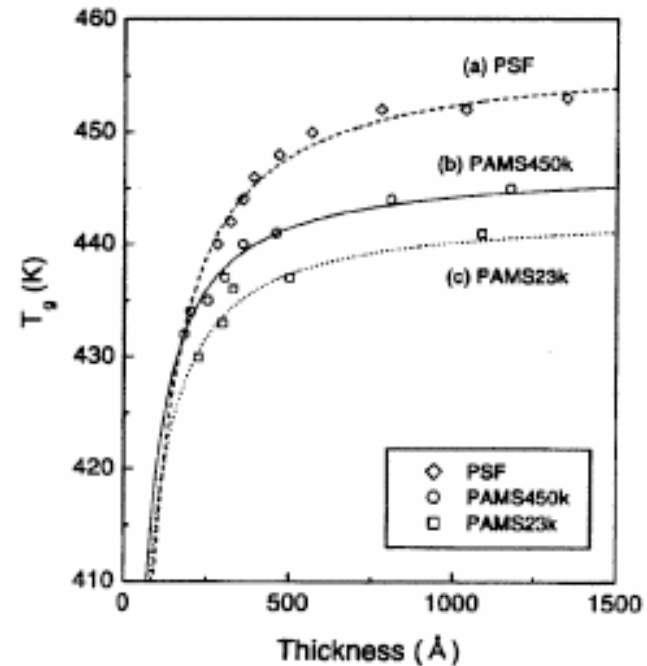MW = 2 900 000.

Keddie et al (1994)

Figure 2. Comparison between the estimated T_g and tl
measured T_g in various thin films. (a) For PSF, the dotted lii
is $T_g(t)$ curves at ξ (=10.3 Å) and $T_{g\infty}$ (=457 K) and the ope
diamond is the measured T_g. (b) For PAMS450k, the solid lii
is $T_g(t)$ curves at ξ (=6.3 Å) and $T_{g\infty}$ (=447 K) and the ope
circle is the measured T_g. (c) For PAMS23k, the dash line
$T_g(t)$ curves at ξ (=6.5 Å) and $T_{g\infty}$ (=443 K) and the open squai
is the measured T_g.

Kim et al (2000)

Sputter deposited silica glass
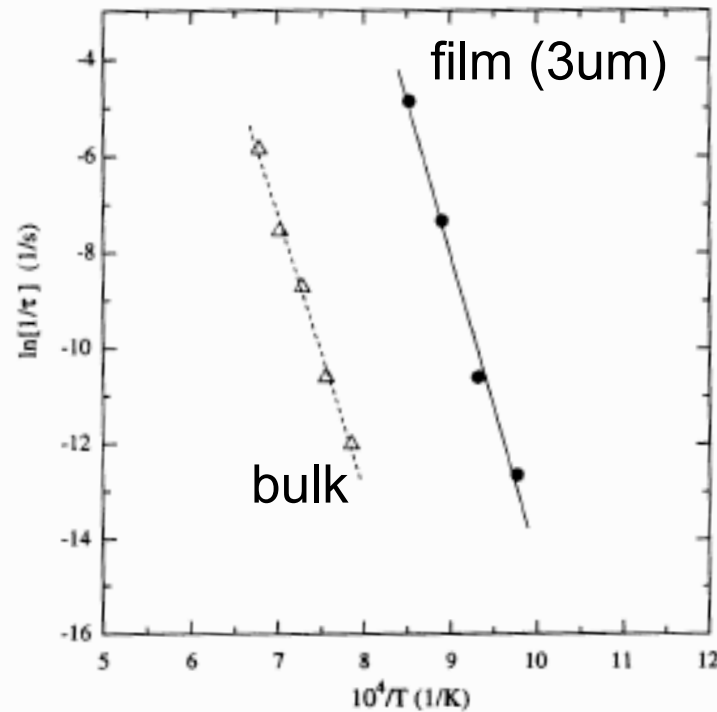

film (3um)

bulk

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

$$\frac{1}{\tau} = \exp\left[(33.1 \pm 1.7) - (5.58 \pm 0.23) \cdot \frac{10^4}{T}\right] \quad \text{for bulk silica glass and}$$

$$\frac{1}{\tau} = \exp\left[(49.3 \pm 4.5) - (6.37 \pm 0.49) \cdot \frac{10^4}{T}\right] \quad \text{for sputter-deposited silica films.}$$

Hirose, Saito, Ikushima (2006)
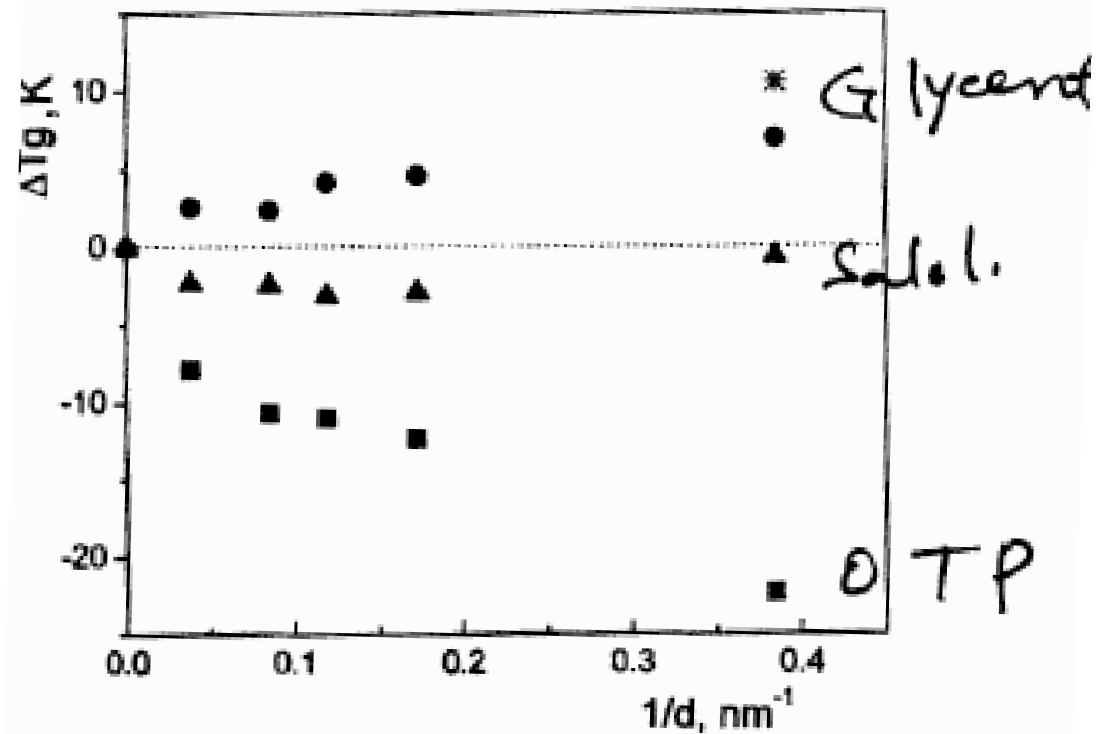
2-dim confined liquids in porous silica

i. 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.

Trofymluk, Levchenko, Navrotsky (2005)
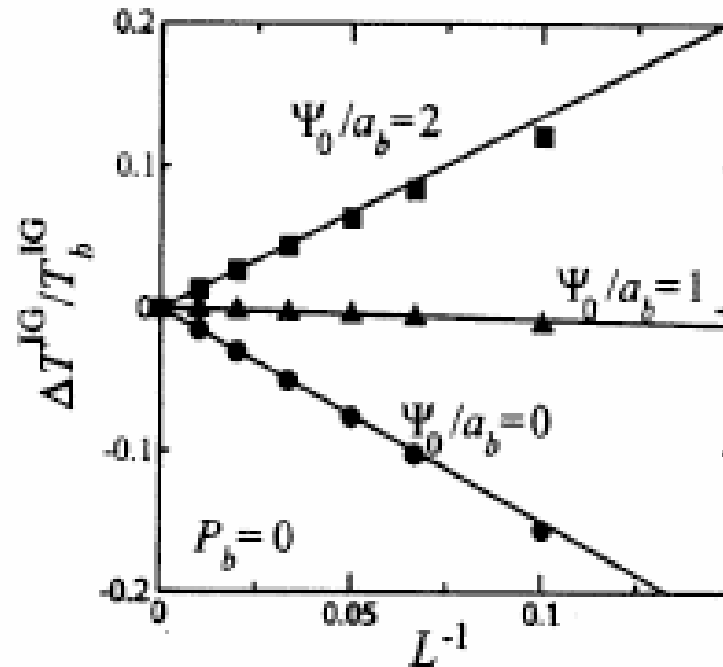
Ideal glass transition T_K in a fluid film model

e 4. Confinement induced shift in the IG transition of the SSMF elative to that of the bulk system with which it is in equilibrium ssure $p_b = 0$. L^{-1} is the dimensionless reciprocal film thickness ible to the film particle centers. The solid lines represent the cimation of eq 22, and the symbols are the predictions of the full ear 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:

$$T_g S_{conf}(T_g) = Cons.$$

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

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

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

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

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

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 γ 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.