Landscape Approach to Glass Transition and Relaxation

(Lecture # 3, March 30)

Liquid to Glass Transition

- Instructor: Prabhat Gupta

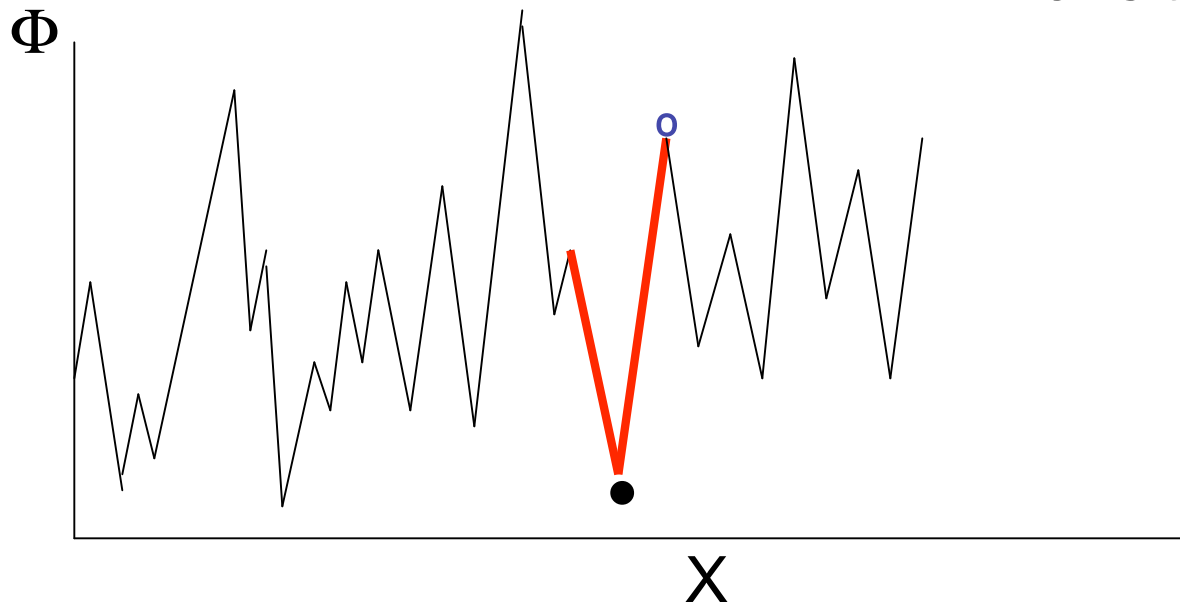 The Ohio State University

  (gupta.3@osu.edu)

Review of Lectures 1 and 2:

- Microscopic configuration (X)
- Configuration space, $\Omega \equiv \{X\}$
- (Total) Potential energy (Φ)
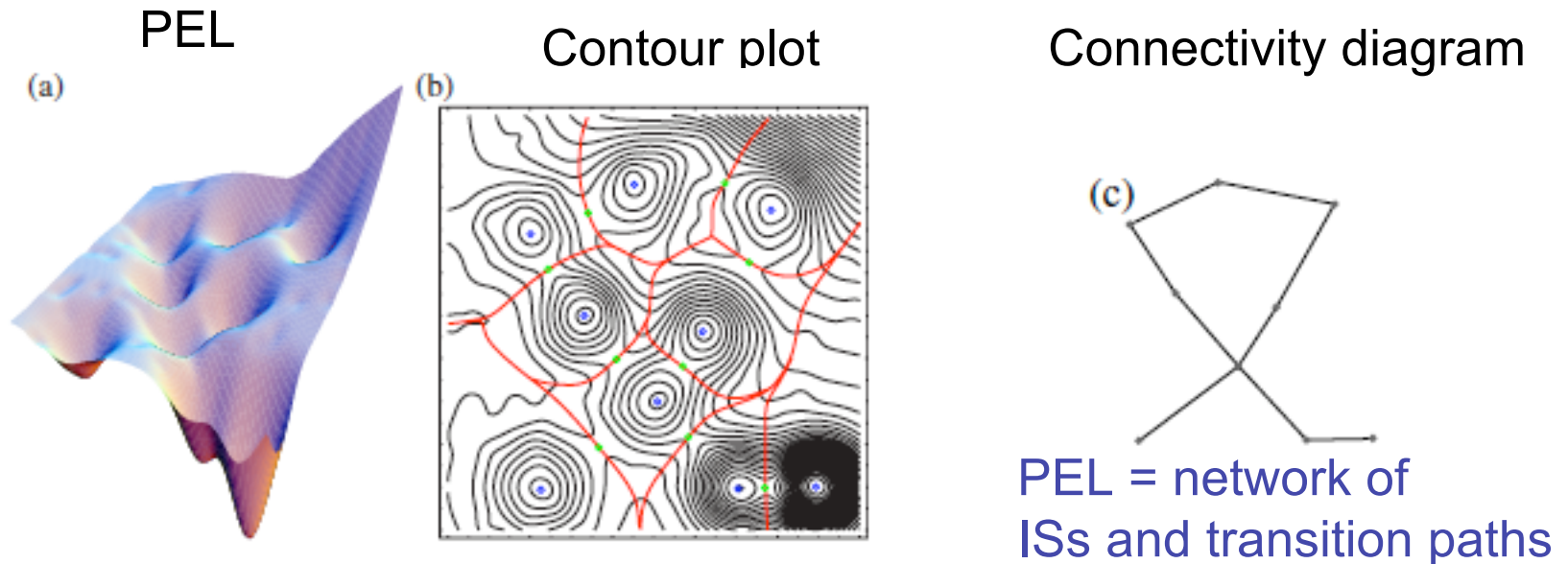- Potential energy landscape, PEL: $\Phi(X)$

2-dimensional schematic of PEL

Most important features:

- Inherent structures (IS)
- Basin
- Transition states

3 dim-schematic of a PEL

PEL   Contour plot   Connectivity diagram

PEL = network of
ISs and transition paths

Inherent Structure (IS) = local minima (blue dots)
Basin of an IS = region separating an IS from other ISs
(shown by red curves)
Transition states = first order saddles (green dots)

[CP Massen and JPK Doye, Phys Rev E 75 (2007) 037101]

Some sources of confusion

1. The terms "configuration" and "configurational"

- The term configuration includes vibrational configurations (generally called vibrational states) and inherent structures (ISs).

- Contributions from IS: Structural or configurational properties

- Contributions from vibrational states : Vibrational properties

Some sources of confusion (contd.)

2. "Energy landscape" (PEL) and "enthalpy landscape" (PHL)

• Potential energy landscape (PEL): refers to a system at constant volume (V). State variables: (N, V, T).

      Frequently used in simulations (virtual experiments).

• Potential enthalpy landscape (PHL): refers to a system at constant pressure (P). State variables: (N, P, T).

      Appropriate for real experiments

• All concepts apply equally well to both. However, it is easier to visualize in terms of PEL. Thus, in these lectures, we mostly use PEL for discussion. But every now and then we generalize results to PHL.

Some sources of confusion (contd.)

3. "Super-cooled liquid" and "deeply super-cooled liquid"

• $T > T_c$ (cross-over temperature): "Hydrodynamic" dynamics

  $T < T_c$: Thermally activated dynamics

  (T_c is called the cross-over temperature.)

• The value of T_c is always greater than Tg ($T_c > $ Tg) but is often less than T_m (the melting point).

• $T < T_c$: SCL is called deeply super-cooled liquid.

In studying glass transition and relaxation, one is only interested in deeply - SCL.
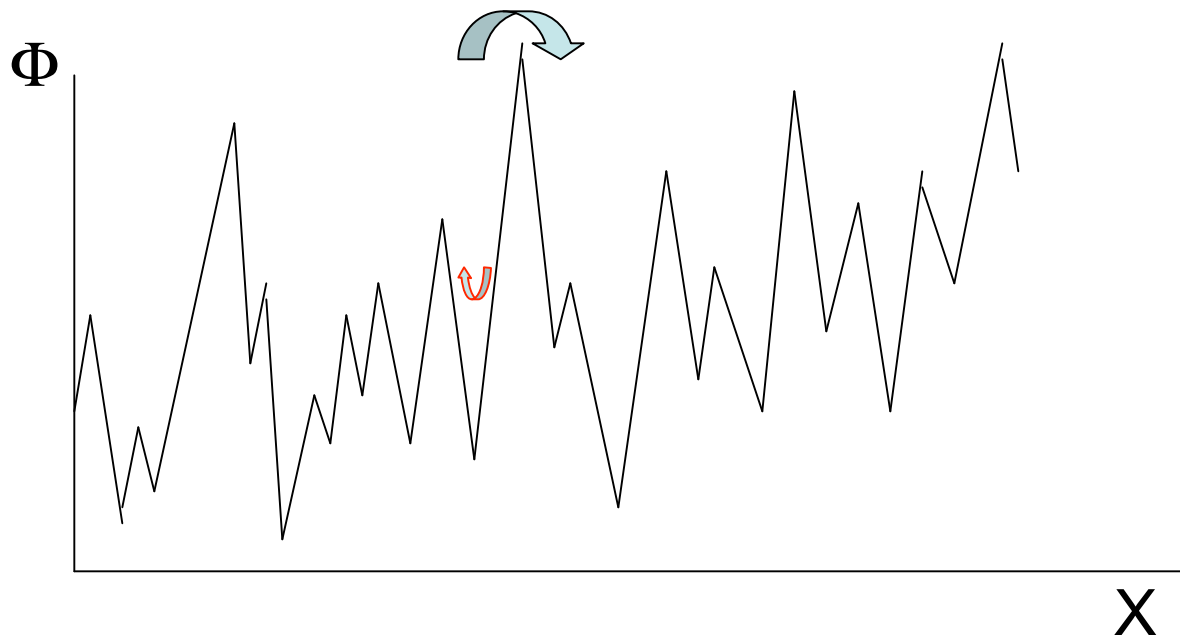
Inherent structures (ISs)

• All ISs of a PEL can be determined. For each one can also determine
        1. potential energy, $\phi_l(IS)$,
        2. vibrational frequencies ($\{\nu_i\}$) and the smallest ν,
        3. its transition states
        4. the smallest barrier state (most probable escape route)
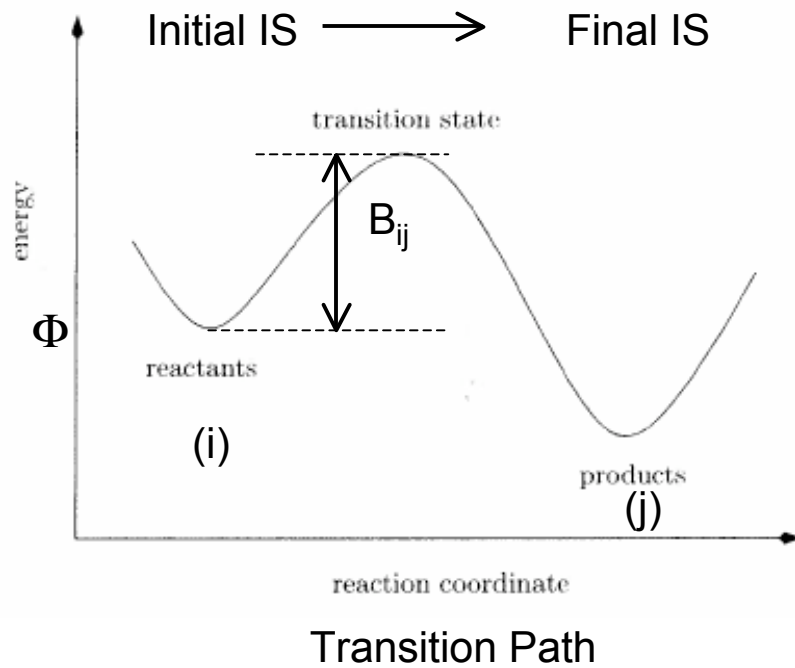   5. its connectivity (k).

Transitions States (TSs)

• All transition states of a PEL can, in principle, be determined for a given landscape. For each transition state, one can also determine

        1. Transition state energy (Φ)
        2. Transition path and associated ISs (i and j)
        3. Barrier heights, Bij, (in the direction $i \rightarrow j$).
        4. Transition rates, Wij (at some specified T)

Transitions in a landscape

- Intra-basin transitions (Vibrational): very fast ($\updownarrow$)
  (equilibration of a basin with the heat bath)

- Inter-basin transitions (configurational change): slow($\curvearrowright$)

Φ

X

"Thermally activated" inter-basin transition rates

Initial IS $\longrightarrow$ Final IS

transition state

B_{ij}

Φ

reactants

(i)

products

(j)

reaction coordinate

Transition Path
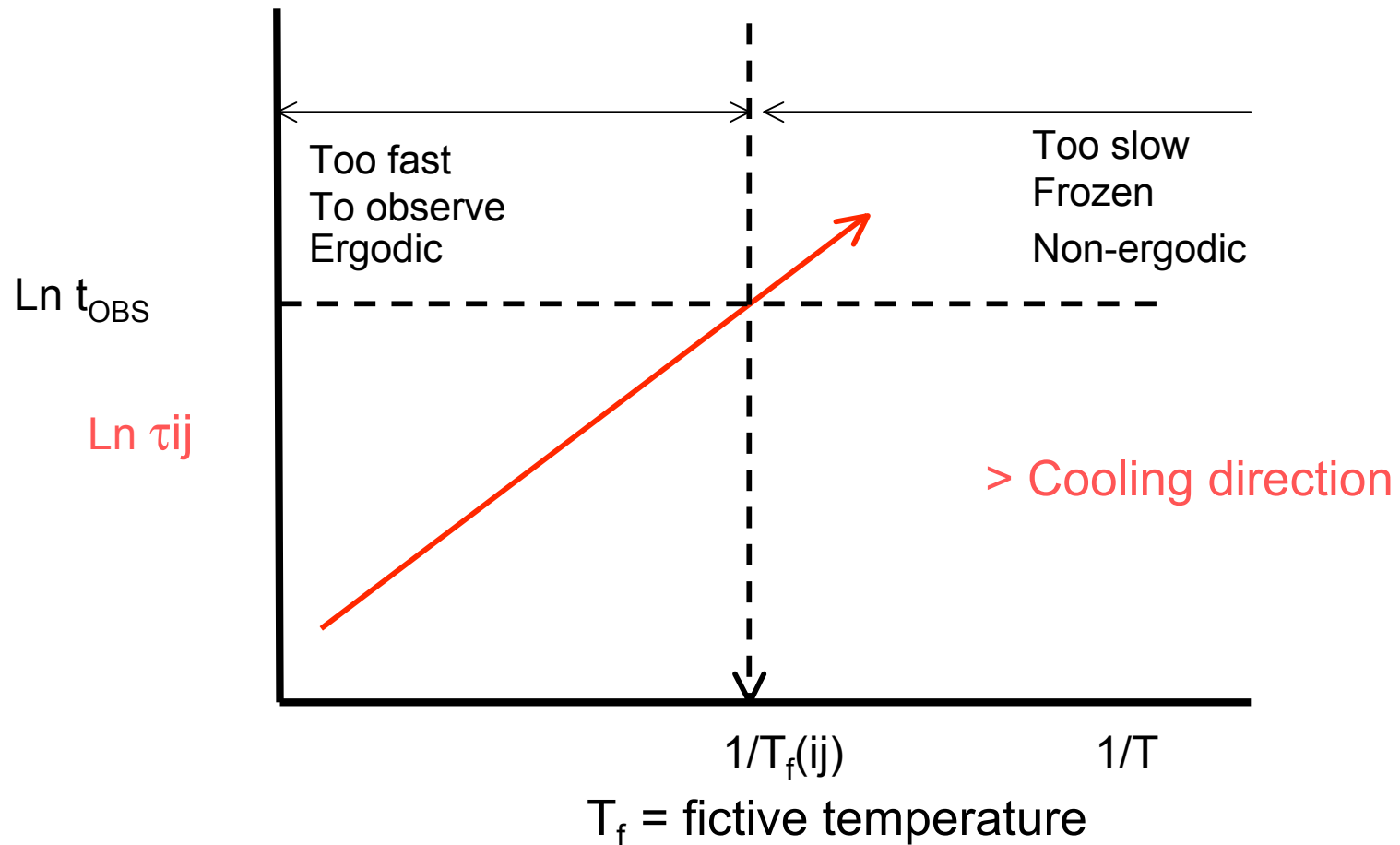
Transition rate, W_{ij}, from i to j :

$$W_{ij}(T) = \nu_i \exp[-\frac{B_{ij}}{k_B T}]$$

$$B_{ij} = \Phi_{ij}(TS) - \Phi_i(IS)$$

Observation Time, t_{OBS}

• A transition (i,j) is not observed when it is too slow [$t_{OBS} < \tau ij$].

Ln t_{OBS}

Ln τij

Too fast
To observe
Ergodic

Too slow
Frozen
Non-ergodic

> Cooling direction

$1/T_f(ij)$ $1/T$

T_f = fictive temperature

Cooling a liquid at a fixed cooling rate (or a fixed t_{OBS})

• At high temperatures, all transitions are very fast, and the system is in equilibrium:

$$\text{All } \tau_{ij}[T > T_f(ij)] \ < t_{OBS} \qquad \text{(ergodic, equilibrium, liquid, L)}$$

• As the liquid is cooled, a temperature is reached when transitions begin to freeze in a sequential manner with the slowest ones freezing first.

Percolation of frozen transitions

T>T*   T<T*

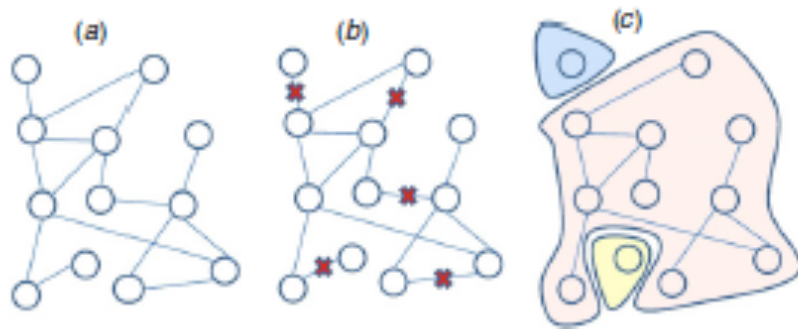Ergodic   broken-ergodic

Figure 5. A schematic of network percolation. (a) The original network. (b) A fraction q = 1/3 (5/15) of the links are removed from the network. (c) The network after removal consists of one large cluster of 10 nodes and two small clusters of one node each.

T* = percolation transition temperature

[S Carmi et al, J. Phys. A, 42 (2009) 105101]

Broken - Ergodic (BE) State (T < T*)

• Configuration space, Ω, is partitioned among components $\{\Omega_a\}$ with following features:

      a) Transitions among components are forbidden.

      b) Transitions within each component remain active.
        (Each component is ergodic within itself).

• Components are called "meta-basins" (MBs).

Broken-ergodic (BE) state and Meta-basins (MB)

$$p_a^{MB}(T < T^*) = \sum_{i \in a} p_i(L, T^*) = p_a^{MB}(eqbm, T^*)$$

- No inter-MB transitions allowed in among MBs.
- All intra-MB transitions are active (each MB is self-ergodic).
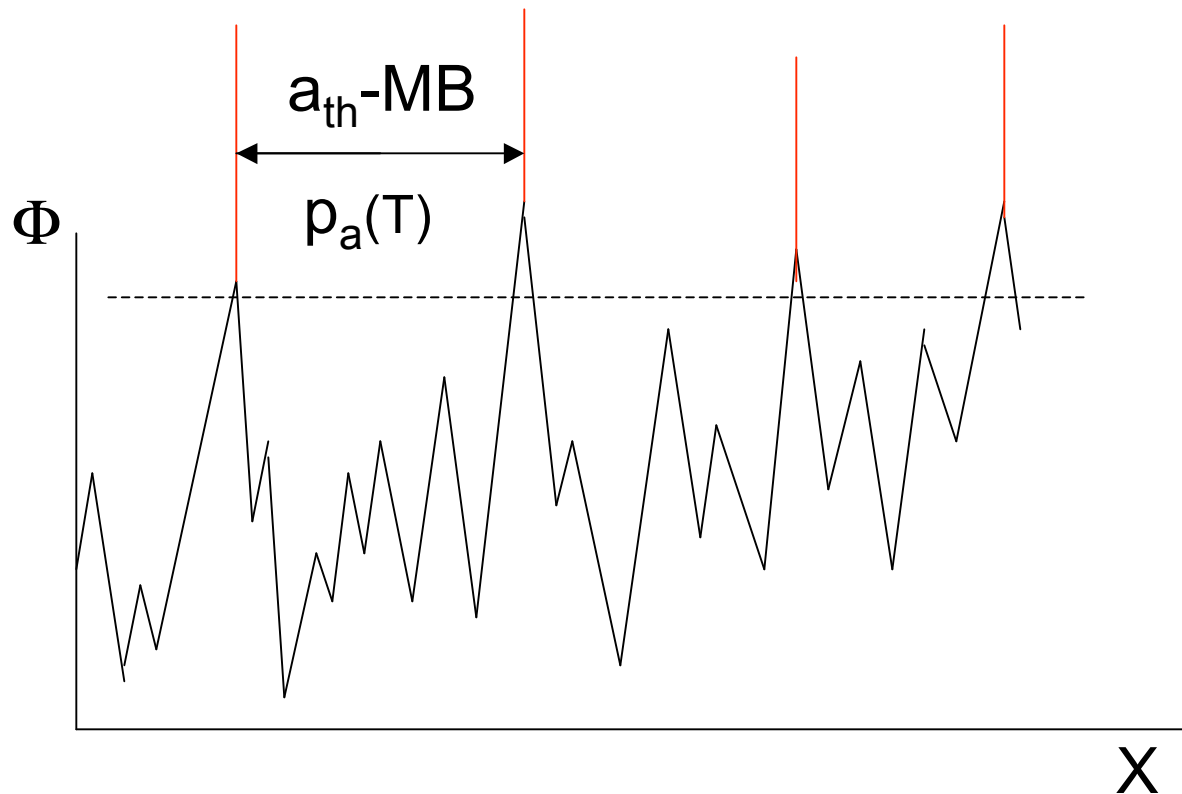
Ergodic to BE Transition @ T*

- All observables $,Q$,remain continuous at T*

$$Q(BE) = \sum p_i(T^*) Q_i = Q(Ergodic)$$

- No latent heat and no change in vibrational properties at T*.

- Loss of Configurational entropy at T* due to freezing of inter-MB transitions:

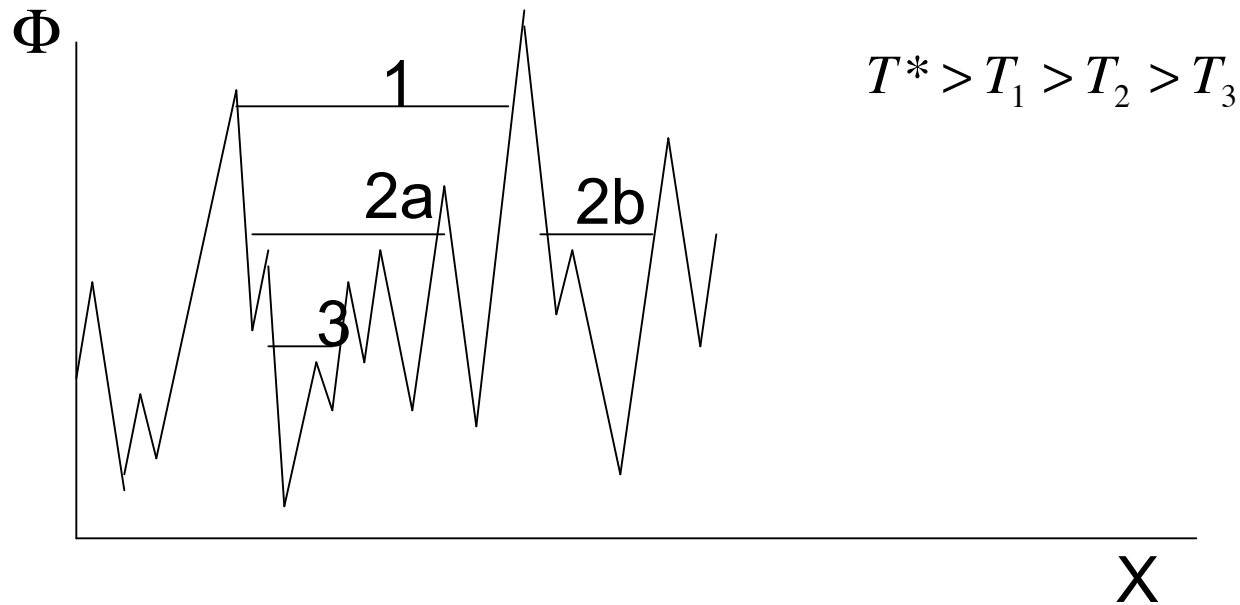 $\Delta S\ (T^*) =\ [\ S(Ergodic) - S(BE)\ ] > 0$

General expression for entropy loss, ΔS

$$\Delta S(T^*) = -k_B \sum_a^M p_a^{MB}(L,T^*) Ln p_a^{MB}(L,T^*) > 0$$

Note that not all configuration entropy is lost at T* but there is a finite loss.

Continued partitioning of the configurational space on cooling below T* at fixed t_{obs}

More configurational entropy is lost on continued cooling.

$$T* > T_1 > T_2 > T_3$$

The Laboratory Glass Transition

Glass transition is the transition from ergodic liquid to broken-ergodic glass state.

At a fixed t_{obs} (~ fixed cooling rate): $T^* \equiv Tg$.

$T > Tg(t_{obs})$ No partitioning of configuration space.
(Ergodic system = Liquid)

$T = Tg(t_{obs})$ Glass Transition (partitioning of Ω) takes place.

$T < Tg(t_{obs})$ Configuration space is partitioned into MBs.
(Glass = Broken ergodic state)

Property changes at Tg

- Definition of Tg: $p_\alpha (G,Tg) = p_\alpha (SCL,Tg)$

- Observables: $Q(G,Tg) = Q(L,Tg)$
(No latent heat, no change in volume, no change in any vibrational property)

- Entropy loss: $S(L,Tg) > S(G,Tg)$

- A glass and the liquid are not the same macro-states at Tg !

Difference between a glass and a liquid at T_g

Liquid @ Tg: All transitions are allowed. [Wij (inter-MB) > 0]

Glass @ Tg: Inter-MB transitions are not allowed.
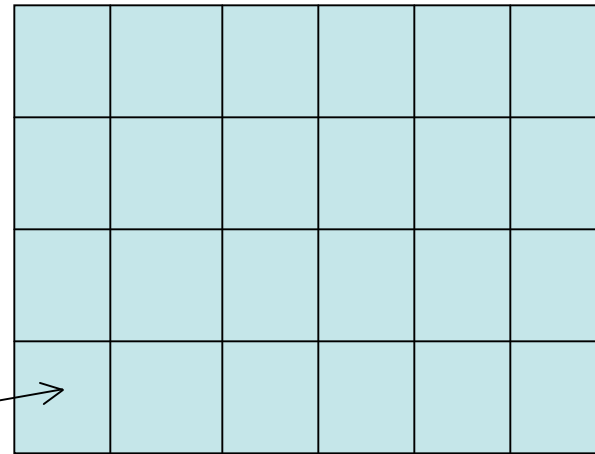(dynamically constrained) [Wij (inter-MB) = 0].

Experimentally, this is supported by the loss of configurational heat capacity on cooling through Tg.

Frozen-in-heterogeneities in glass

• Each subsystem (small but macroscopic) is trapped in a single metabasin (MB) with a probability: $P_a(glass) = P_a(liquid, T_g)$

• A glass is an ensemble of MBs.

• Cooperative region (~ MB)

Landscape view is consistent with the following universal features of glass transition

1. Ergodic (liquid) to broken-ergodic (glass) transition.
   [Tg increases with decrease in t_{OBS}].

2. No change in volume.

3. No change in enthalpy (no latent heat).

4. $C_P(liq) > C_P(glass)$

5. $K_T(liq) > K_T(glass)$ [K_T = Isothermal compressibility]

6. $\dfrac{\Delta C_P \Delta K_T}{TV(\Delta \alpha_P)^2} > 1$ [α_P = isobaric expansion coefficient]

Residual Entropy S(T=0)
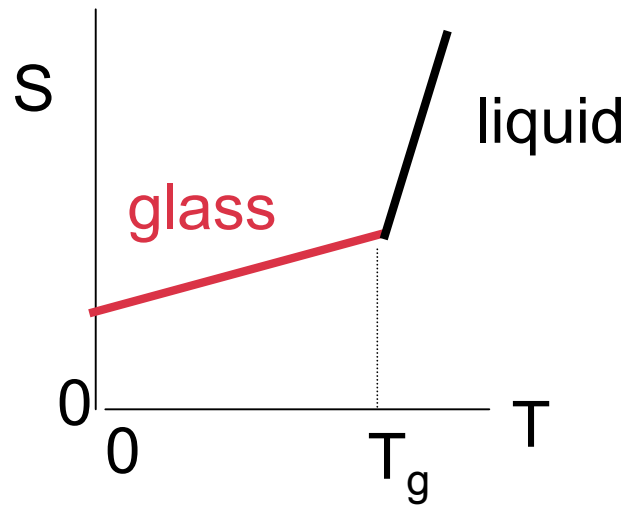
Conventional View
S(0) > 0
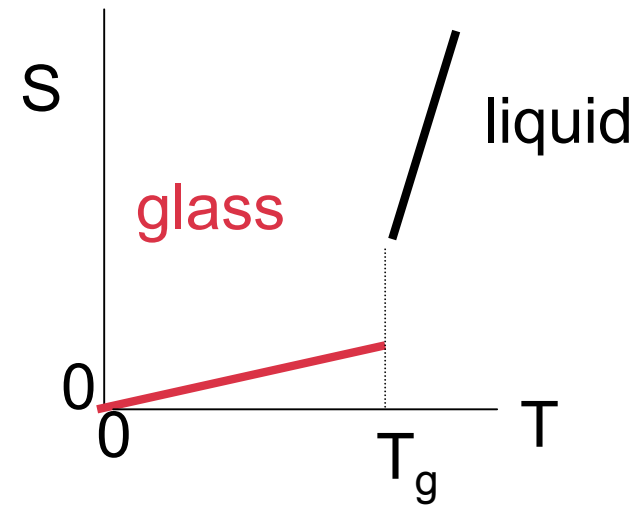
Landscape view
S(0) = 0

$$S_g(0) = S_L(T_g) - \Delta S(Loss, T_g) - \int_0^{T_g} \frac{C_{Pg}}{T} dT$$

QUIZ   ON   APRIL 1 (The last lecture).