Landscape Approach to Glass Transition and Relaxation

Lecture # 4, April 1 (last of four lectures)

Relaxation in the glassy state

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Review paper: A Heuer, " Exploring the potential energy landscape of glass forming systems", J. Phys (Cond. Matt.) 20 (2008) 373101.

1. Landscape view of glassy state (Review)

2. Basic concepts of relaxation.

3. Landscape view of relaxation kinetics.

4. Non-exponential relaxation

5. Non-Arrhenius T-dependence of relaxation kinetics

6. Home Work Problems (Due on Tuesday, April 6, 2010)

Review: Landscape view of glassy state

1. Liquid state [equilibrium state, high T or large t_{OBS} ($\to\infty$)] :

• All inter-basin transitions are active. The system is ergodic (i.e., is able to sample the entire landscape).

• Liquid state properties have two parts: vibrational (arising from intra-basin transitions) and configurational (arising from inter-basin transitions).

• The intra-basin (vibrational) transitions are extremely fast at all temperatures. The system remains in thermal equilibrium with and follows the temperature of heat bath at all times.

• The inter-basin transitions are relatively slow and slow down rapidly (in an Arrhenius manner) upon cooling but remain ergodic in the liquid state.

Review: Landscape view of the glassy state (contd.)

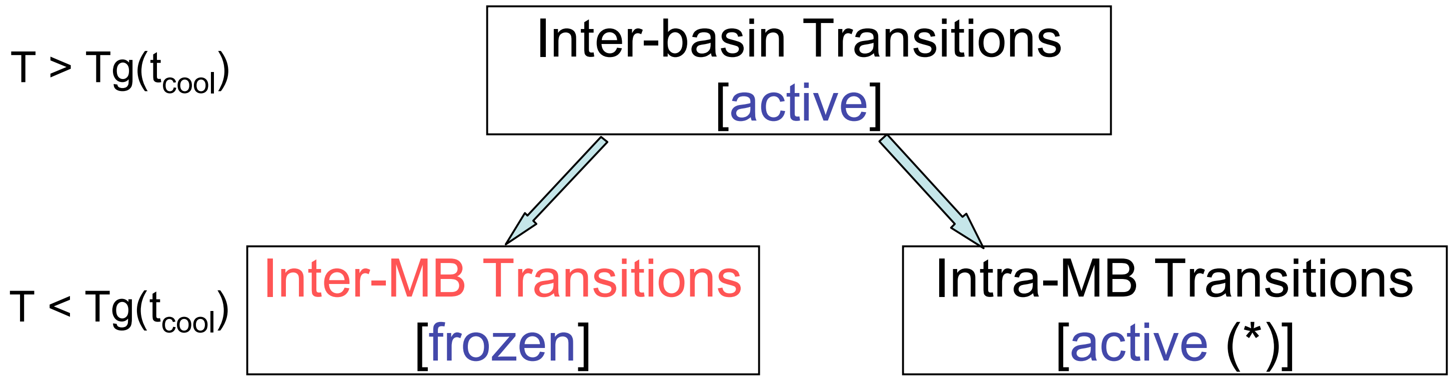
3. The glass transition:

- On cooling, at a fixed observation time, t_{cool}, freezing of the inter-basin transitions begins with the slowest transitions (corresponding to highest barriers) followed sequential freezing of transitions with lower barrier heights.

- When sufficient number of inter-basin transitions are frozen, the configuration space partitions into a set of meta-basins (MBs) such that there are no inter-MB transitions. The temperature corresponding to this partitioning is the glass transition temperature,Tg. Below Tg, the glassy state is a broken-ergodic state (with a partitioned configurational space).

- As a consequence of freezing of inter-MB transitions at Tg, there is a loss of configurational contribution to properties such as entropy and heat capacity in going from liquid to glass.

Freezing of Inter -MB transitions at $Tg(t_{cool})$ (**)



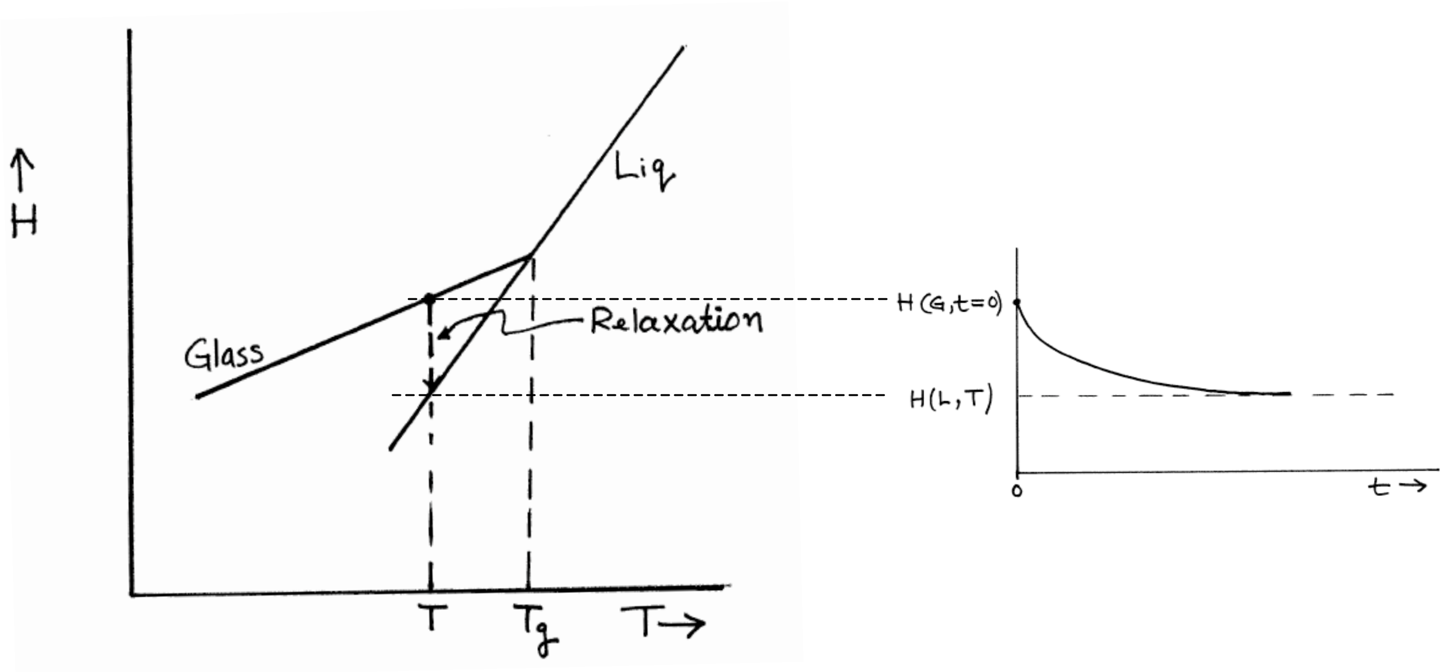
(*) For simplicity, we will assume no secondary partitioning of MBs at lower temperatures.

(**) For clarity, from now on, we use t_{cool} to denote the observation time during the cooling the liquid.

Basic concepts of glassy state relaxation:

Consider a glass, freshly formed by cooling a liquid, held at some temperature T below Tg.

Even though the glass is below Tg, the properties of the glass change with time as shown below:

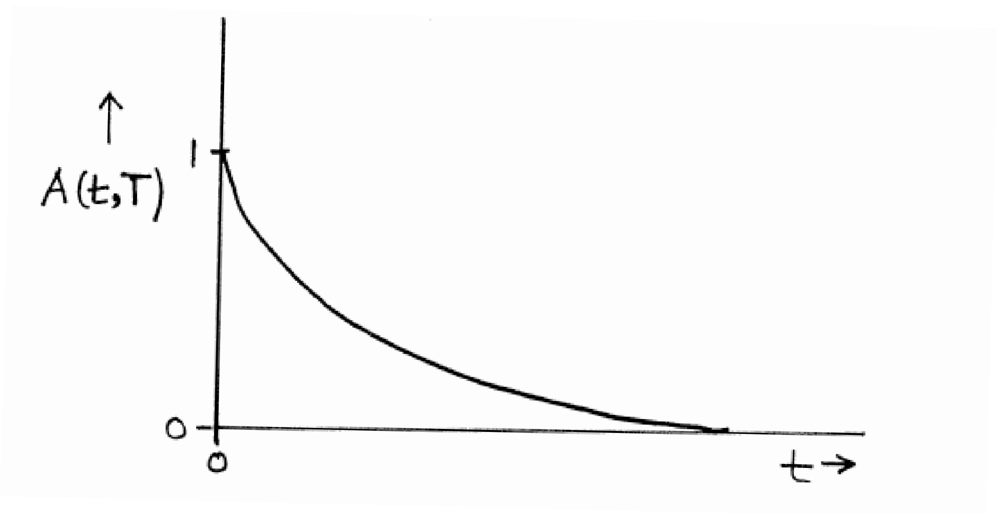


The relaxation function, $A_Q(t,T)$

The isothermal change in a property Q is normally represented in terms of a relaxation function $A_Q(t,T)$ as defined below:

$$A_Q(t,T) \equiv \frac{Q(t) - Q(\infty)}{Q(0) - Q(\infty)}$$

Thus by definition $A(0) = 1$ and $A(\infty) = 0$.



Non-exponential relaxation function:

A(t) is non-exponential and is frequently dscribed by the "stretched exponential" function (or KWW function):

$$A(t,T) = \exp[-(\frac{t}{\tau_A(T)})^{b_A(T)}]$$

Here τ_A is the KWW-relaxation time and the stretching parameter b_A lies in the range $0 < b_A < 1$.

When $b_A = 1$, the KWW-function becomes a single exponential.

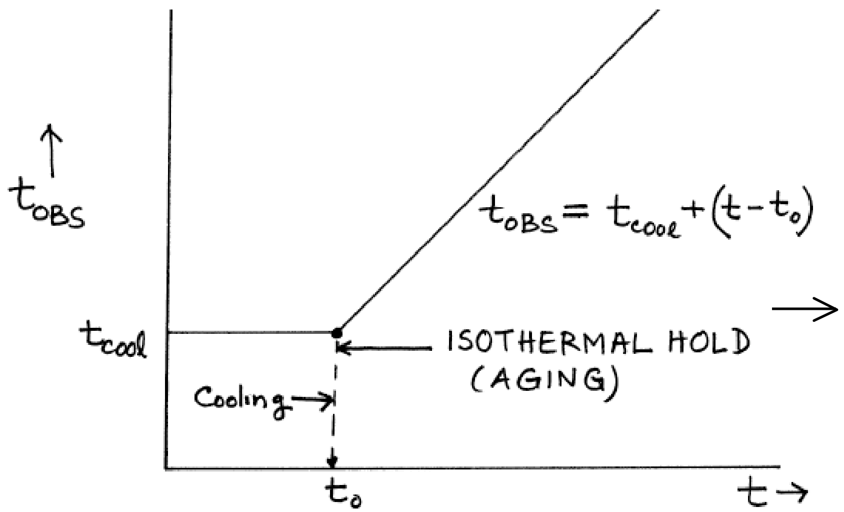
Why does a glass relax below Tg ?

• Relaxation occurs because the definition of the observation time, t_{OBS},changes:

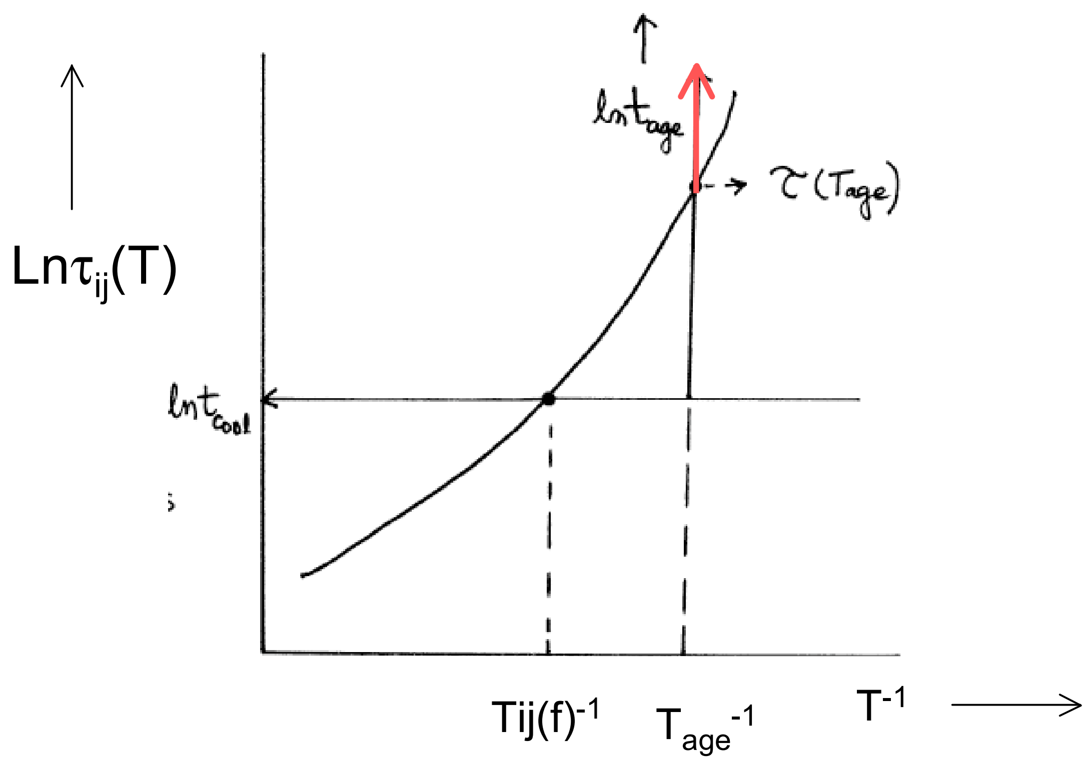
During glass formation (cooling the liquid): $t_{OBS} = t_{cool}$ (constant)

During isothermal hold at T < Tg (called aging):

t_{OBS} = t (clock time) [not constant]



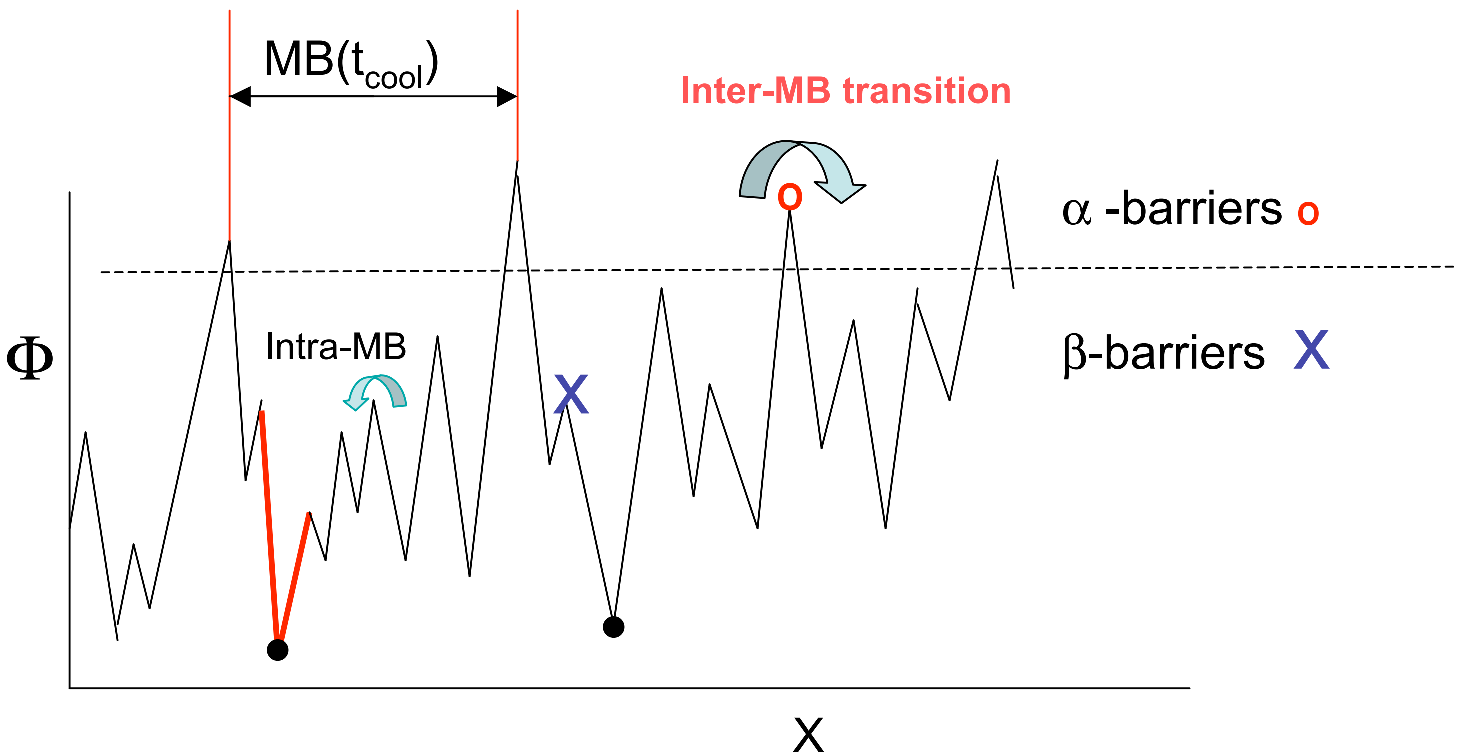
Unfreezing of a transition with time at sub-Tg temperatures



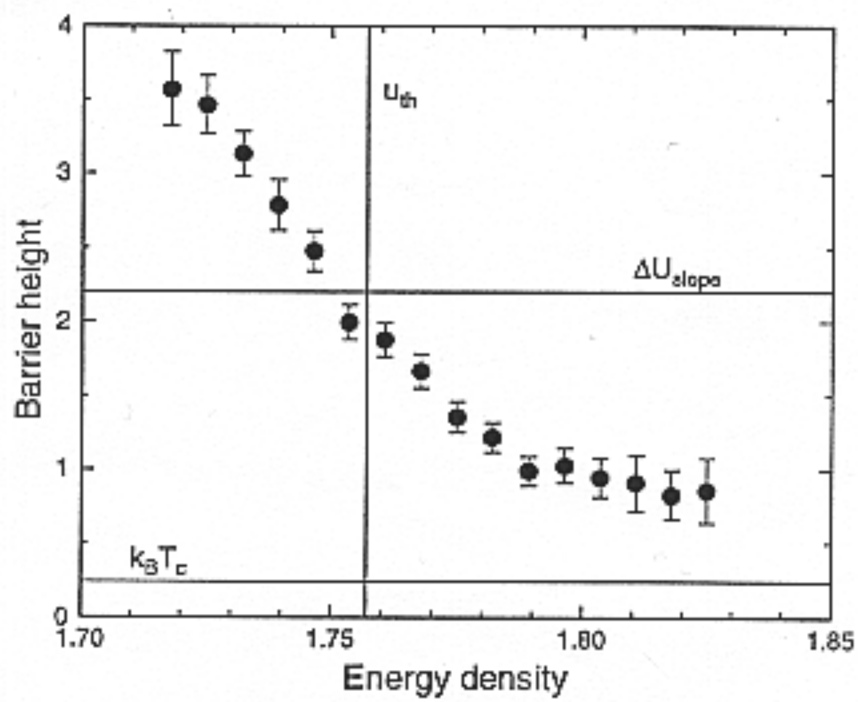
3. Energy Landscape View of relaxation

α (primary) relaxation ≡ inter-MB transitions [$\tau_\alpha(T)$]

β (secondary) relaxation ≡ intra-MB transitions



Distribution of Barrier Heights



Fragile soft Sphere system

Av. barrier height

Energy density of the adjacent IS.

[T. Grigera et al, Phys Rev Lett, 88 (2002) 055502.]

Why non-exponential relaxation?

• During liquid to glass transition, a range of transitions are frozen before partitioning occurs at Tg. The range of frozen barrier heights (B) is: B(min) ≤ B ≤ B(max).

Here B(max) is the largest and the first to freeze on cooling. B(min) is the smallest and the last barrier to freeze before the partitioning of the configuration space at Tg:

$$B(\min) = k_B T_g Ln(\nu t_{cool})$$

• During relaxation (or aging) of glass, the smallest of the frozen barriers (i.e., B(min)) is the first to unfreeze (thaw) and the largest barrier (i.e.,B(max)) is the last to thaw. Thus, during aging, one observes a distribution of relaxation times that corresponds to the range of frozen-in α-barriers during cooling.

Inter-MB relaxation rates W_{ab} (T,T_g)

$$W_{ab}(T,T_g) = \nu_a n_{IS}(a,T_g)\exp[-\frac{B_{ab}(T_g)}{kT}]$$

Here $n_{IS}(a)$ is the number of basins in the a-th MB. This is related to the configurational entropy of the MB:

$$S_{conf}^{MB}(a,T_g) = k_B Ln[n_{IS}(a,T_g)]$$

$$W_{ab}(T,T_g) = \nu_a \exp[\frac{S_{Conf}^{(MB)}(a,T_g)}{k}]\exp[-\frac{B_{ab}(T_g)}{kT}]$$

Average inter-MB relaxation time, $\tau_\alpha(T,Tg)$

$$[\tau_{ab}(T,T_g)]^{-1} = W_{ab}(T,T_g)$$

$$\tau_{ab}(T,T_g) = \nu_a{}^{-1}\exp[-\frac{S_{Conf}^{(MB)}(a,T_g)}{k}]\exp[\frac{B_{ab}(T_g)}{kT}]$$

Using similar reasoning, it follows that the average inter- MB relaxation time, $\tau_\alpha(T,Tg)$ can be expressed as :

$$\tau_\alpha(T,T_g) = \nu^{-1}\exp[-\frac{S_{Conf}^{(MB)}(T_g)}{k}]\exp[\frac{B(T_g)}{kT}]$$

High temperature limit, $\tau_\alpha(\infty)$:

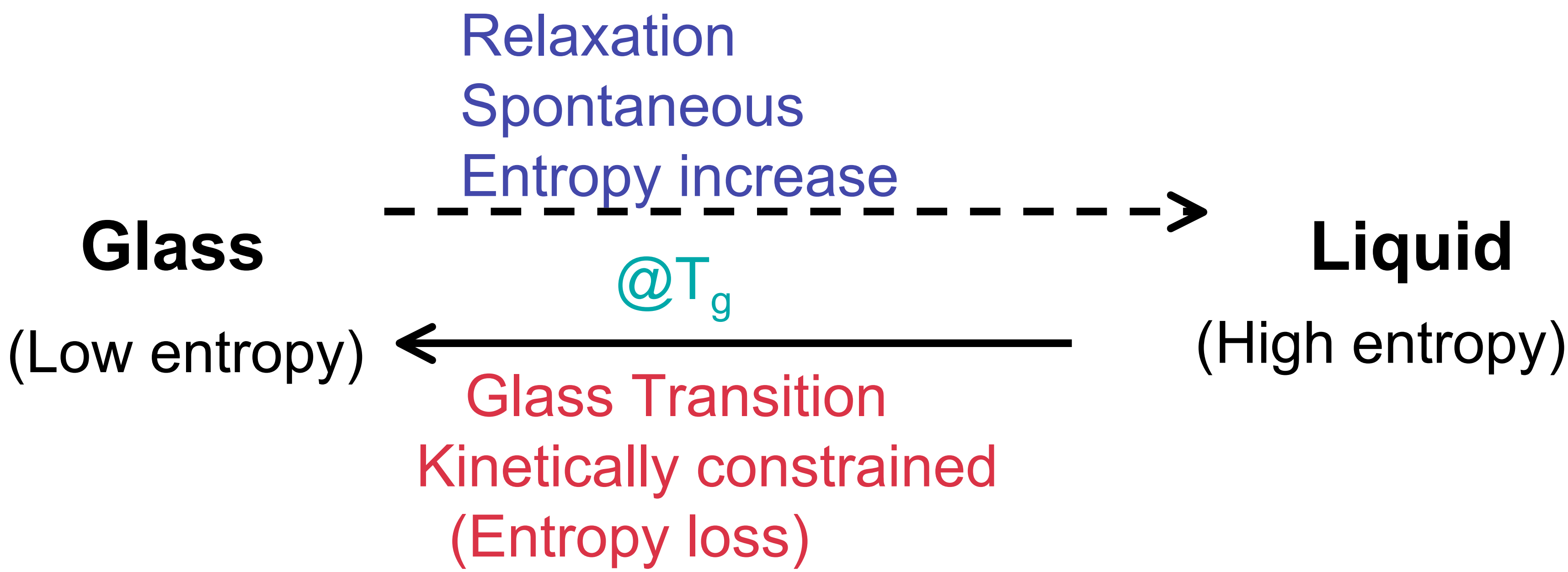
$$\tau_\alpha(\infty) = \frac{1}{\nu}\exp\left(-\frac{S_{conf}^{MB}(T_g)}{k_B}\right)$$

- Recall that $\nu^{-1} \sim 10^{-13}$s. A value of $\tau_\alpha(\infty)$ less than 10^{-13}s indicates the effect of configurational entropy of MBs. Values less than 10^{-13} s. As low as 10^{-37} s has been reported.

Since the configurational entropy of the glass,

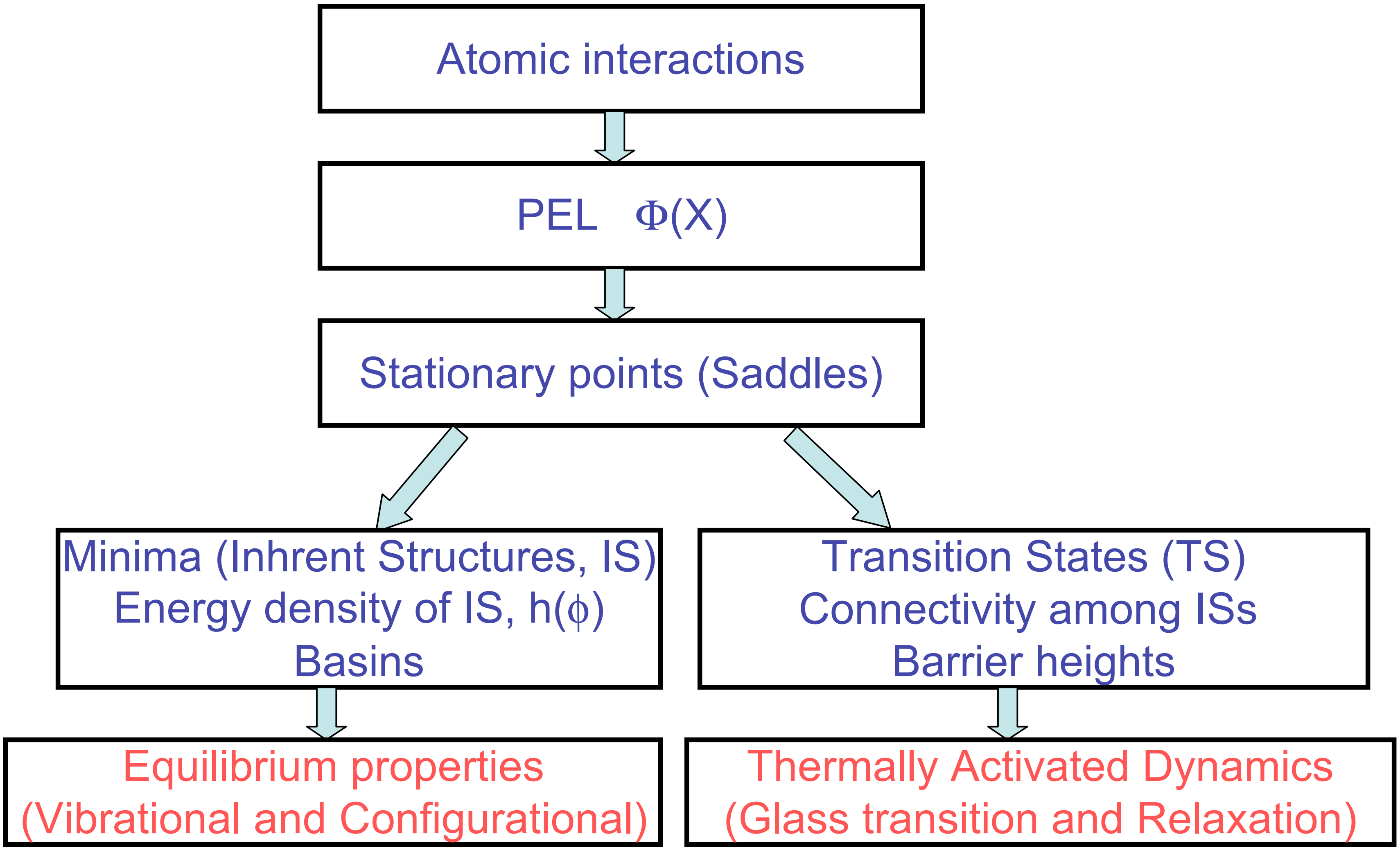
$$S_{conf}(G, Tg) = \langle S_{conf}(MB) \rangle \approx - k_B \, Ln\, [\nu\tau_\alpha(\infty)]$$

Glass Transition and Relaxation



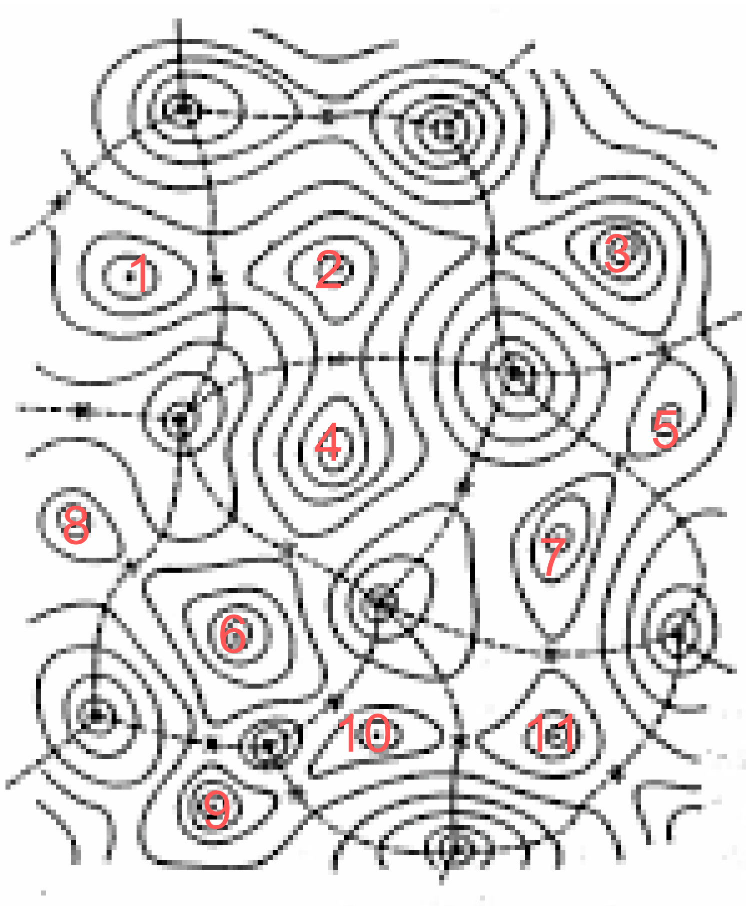
(Transition and relaxation is purely entropic at Tg. However, there will be enthalpy effects at $T \neq$ Tg).

Summary of the PEL approach



Home Work Problems (Due April 6, 2010)

Prob # 1: Consider the following landscape.



a) Identify the IS with the lowest energy.

b) Identify the transition state with the lowest barrier height.

c) What is the connectivity of ISs # 2, 4, 7 and 10?

Home Work Problems (Due April 6, 2010)

Problem # 2:

Consider the Gaussian landscape given by the top eqn on p 19 (lecture #2). Derive the following two equations (on the same page) for the average IS energy and the configurational entropy.