Landscape Approach to Glass Transition and Relaxation

(Lecture # 2, March 25)

Basic Concepts (contd.)

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Review of Lecture # 1

1. Potential energy landscape (PEL):
   - microscopic state (X),
   - configuration space (Ω)
   - potential energy surface, $\Phi(X)$

2. Important geometric features of PEL:
   - inherent structures (IS) and basins
   - density of ISs $h(\phi)$
   - transition states (TS)

3. important topological features:
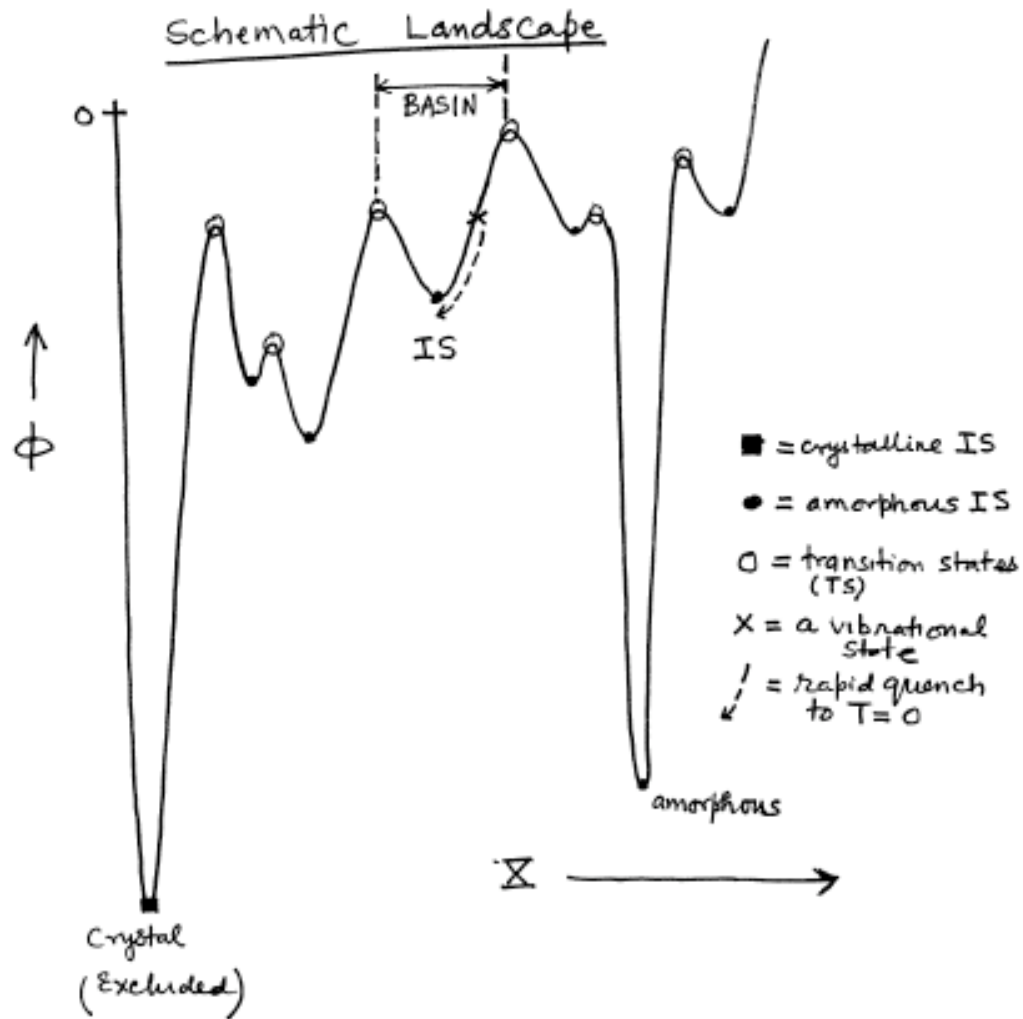   - degree of connectivity of inherent structures.

4. clean separation of vibrational and configurational (IS) states in a basin
   - all states of a basin (except the IS) are vibrational states.
   - The IS is the only configurational state in a basin.

5. PEL of a super-cooled liquid (SCL):
   - PEL(SCL) = Total PEL - PEL (crystal).

Review (Contd.):

Schematic Landscape

BASIN

IS

■ = crystalline IS

● = amorphous IS

O = transition states (Ts)

X = a vibrational state

↙ = rapid quench to T = 0

amorphous

X ⟶

Crystal (Excluded)

Landscape dominated regime:

$$U = \Phi + (3/2)Nk_B T$$

• At high tempertures, the kinetic energy, $(3/2)\,Nk_B T$, is sufficiently large that the representative point of the system moves freely over the PEL. In other words, at such temperatures the motion is not influenced by the features (such as mountain tops and barriers) of the landscape.

• As the temperature is reduced, the features of the landscape - local minima, maxima, transition states, etc., - begin to influence the dynamics of the system. Below a certain temperature, called the cross-over temperature, T_C, the dynamics is becomes dominated by the landscape features. This low T-regime is called the "landscape dominated regime".

• Since $T_c > T_g$, it is the 'landscape dominated regime' that is of interest to understanding the behavior of deeply super-cooled liquids and glasses. From now on, we will only consider this regime.

Dynamics in a deeply super-cooled liquid

• There are two kinds of configurational changes (or transitions):

  a) Intra-basin transitions ≡ Vibrational changes

  b) Inter-basin transitions ≡ Transitions from one basin to a different basin.

The representative point of the system spends lot of time exploring the vibrational states within a basin and only rarely makes a transition to another nearby basin. Inter-basin transitions lead to a new basin and a new IS. Because there is a change in IS, the inter-basin transitions imply a change in the structure (atomistic configuration) of the system.

Inter-basin transitions constitute the process of structural change or relaxation.

"Thermally activated" inter-basin transition rates

Initial IS $\longrightarrow$ Final IS
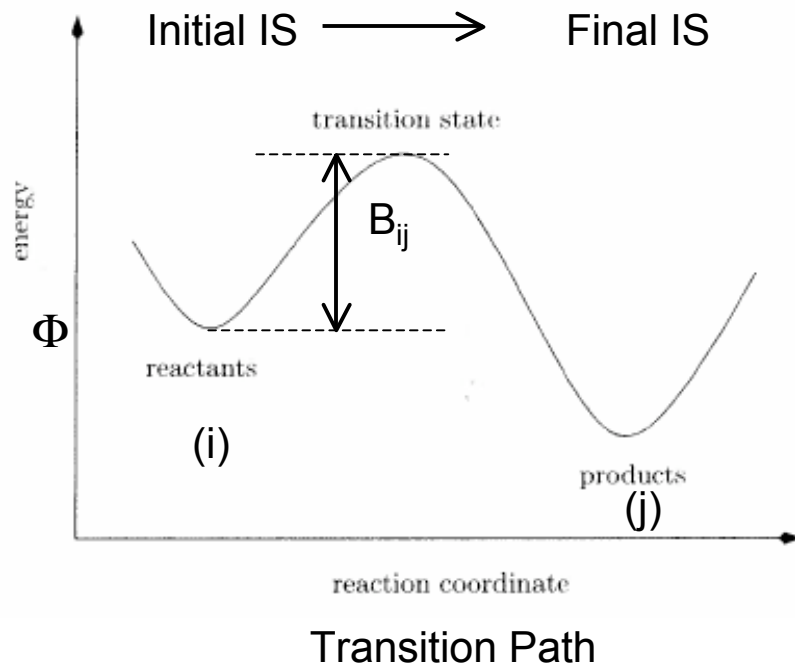
Transition Path

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

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

ν_I = attempt frequency

B_{ij} = barrier energy

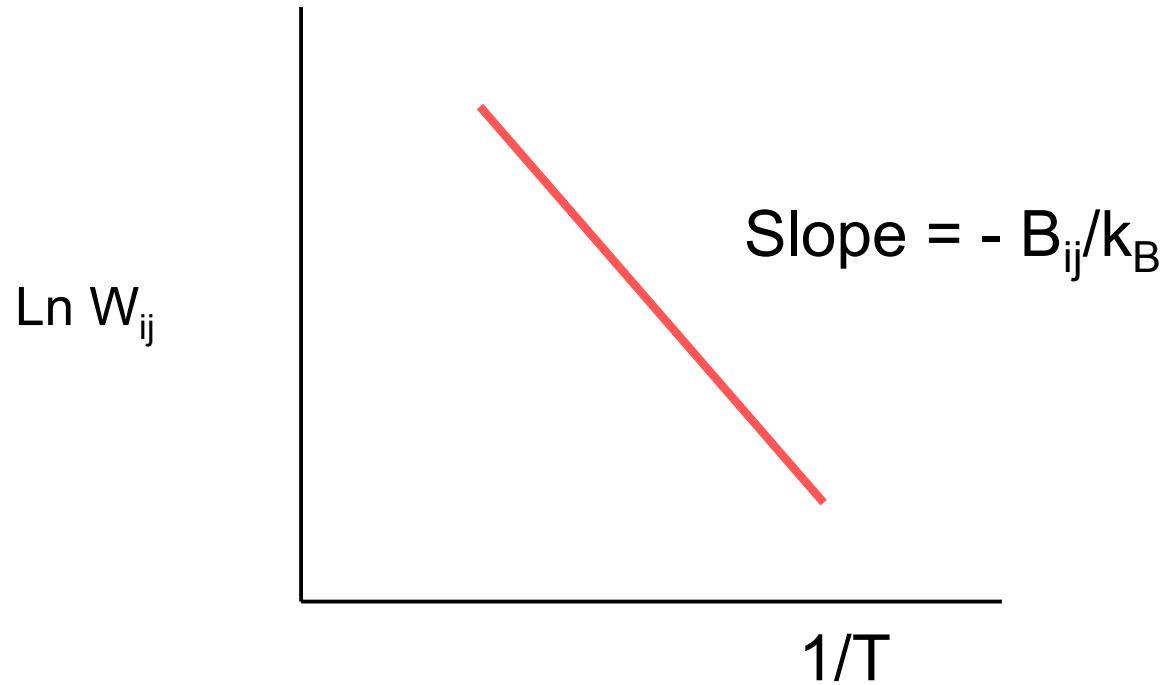$$B_{ij} = \Phi_{ij}(TS) - \Phi_i(IS)$$

(TS = transition state)

Note that $W_{ij} \neq W_{ji}$.

Inter-basin transition rates W_{ij} are strongly T- dependent

• Arrhenius T-dependence.

Slope = $- B_{ij}/k_B$

Ln W_{ij}

1/T

• Transition rates decrease rapidly with decrease in T.

Inter-basin transition time, $\tau_{ij}(T)$:

τ_{ij} = average time for one transition from IS(i) to IS(j).

$$\tau_{ij}(T) \equiv \frac{1}{W_{ij}(T)}$$

$$\tau_{ij}(T) = v^{-1} \exp[\frac{B_{ij}}{k_B T}]$$

The observation time, t_{OBS} :

• The time of observation (also known as the 'experimental time scale' or 'external time scale') is a very important concept (especially when discussing glass transition).

• A precise definition of t_{OBS} depends on the experiment. However, every experiment contains a measure of t_{OBS}.

Consider two examples:

i) In experiments measuring the frequency(ω) dependent response of a system, t_{OBS} is given by $$t_{OBS} = \omega^{-1}$$

ii) During cooling a system, one may define:

$$t_{OBS} = [\frac{\partial LnT}{\partial t}]^{-1}$$

The observation of an inter-basin transition during t_{OBS}:

• Whether a transition appears inactive or frozen (rate = 0) or active (rate > 0) during t_{OBS}, depends on the relative values of the transition time, τ_{ij}, and the observation time, t_{OBS}.

$$\tau_{ij} < t_{OBS} \quad \text{(active)}$$

$$\tau_{ij} > t_{OBS} \quad \text{(frozen, inactive, rate = 0)}$$

Observation time and the vibrational (or thermal) equilibrium

- It seems reasonable to assume that for most experiments
    minimum $t_{OBS} \approx 10^{-9}$ s (~ a nanosecond)
    maximum $t_{OBS} \approx 10$ years (~ 10^8 s).

• Since vibrational times (typically < 10^{-12} s) are much less than the minimum t_{OBS}, vibrational states are always observed at all times in equilibrium with the thermal reservoir (or heat bath).

This implies that during all processes involving structural changes (such as glass transition and relaxation), a system remains in thermal (i.e. temperature) equilibrium with the heat bath at all times.

Basin probabilities (p$_i$)

• Microscopically, at any instant of time, the representative point of the system is only in one basin. However, one does not know exactly which basin the system is in.

• It is natural to use probabilistic description. In other words, one only knows that, at some time t, the system is in the basin i with a probability p$_i$(t).

• Of course, from the definition of probabilities, it follows that:

$$\sum_i p_i(t) = 1$$

and p$_i$(t) ≥ 0 (for all i).

Structural relaxation:

• The process of achieving equilibrium among different basins (i.e., inter-basin transitions) is called the structural relaxation process. We will refer to it simply as the relaxation process.

The relaxation process is complex involving a distribution of inter-basin transitions rates. One may define the average structural relaxation time (or the relaxation time), $\tau(T, t)$, simply as follows

$$\tau^{-1}(T,t) = \sum_i p_i(T,t) \sum_j W_{ij}(T)$$

Here, $p_i(T,t)$ is the probability of the system point being in the i-th basin at time t.

The equilibrium (or the super-cooled liquid) state

• Because we have excluded all crystalline ISs from the PEL, the super-cooled liquid state (L) is the equilibrium state.

• The system is in equilibrium when the "ergodicity condition" is satisfied:

$$t_{OBS} >> \tau_{ij} \qquad \text{(for all i and j)}$$

• In equilibrium, the basin probabilities do not change with time even though the inter-basin transitions are continuously taking place. This is because the system is in a dynamic equilibrium.

In equilibrium: $p_i(T,t) = p_i(eq,T)$ or $p_i(L,T)$

The equilibrium probability distribution, $p_i(L,T)$

• The equilibrium probability distribution is given by the
  Boltzmann distribution:

$$p_i(L,T,V,N) = \frac{\exp[-\beta\{\phi_i(IS) + f_i(Vib,T)\}]}{Z[T,V,N]} \equiv p_i(L,T)$$

where $\quad \beta \equiv \dfrac{1}{k_B T} \quad$ and $\quad Z(T,V,N) = \sum_i \exp[-\beta\{\phi_i(IS) + f_i(Vib,T)\}]$

$$Z(T,V,N) = \exp[-\beta N f(T)] \qquad , f = \text{free energy per atom}$$

(From now on, we will suppress the variables V and N.)

Equilibrium statistical thermodynamics

- Average IS (or configurational) energy, $\phi_{IS}(L,T)$
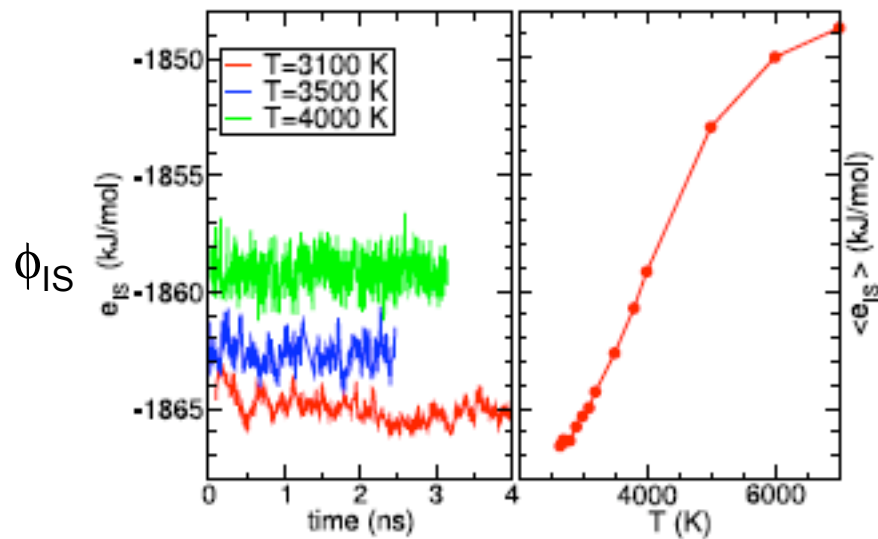
$$\phi_{IS}(L,T) = \sum_i \phi_i p_i(L,T)$$

- Configurational (or inherent) entropy, $S_c(L,T)$:

$$s_C(L,T) = -k_B \sum_i p_i Ln p_i = k_B \sigma[\phi_{IS}(T)]$$

Molecular Dynamics (MD) simulations:

MD run at constant T $\rightarrow$ Energy minimization $\rightarrow$ IS sampling

ϕ_{IS}

Figure 2. Left: time dependence of e_{IS} for the BKS model for silica in a 999-ion system for three different temperatures. Note that at each T, a different set of e_{IS} values is sampled. Right: T dependence of $\langle e_{IS} \rangle$ for the same model.

[F Sciortino, J. Stat. Mech:Theory and Experiment, (2005) P05015]

ϕ_{IS}
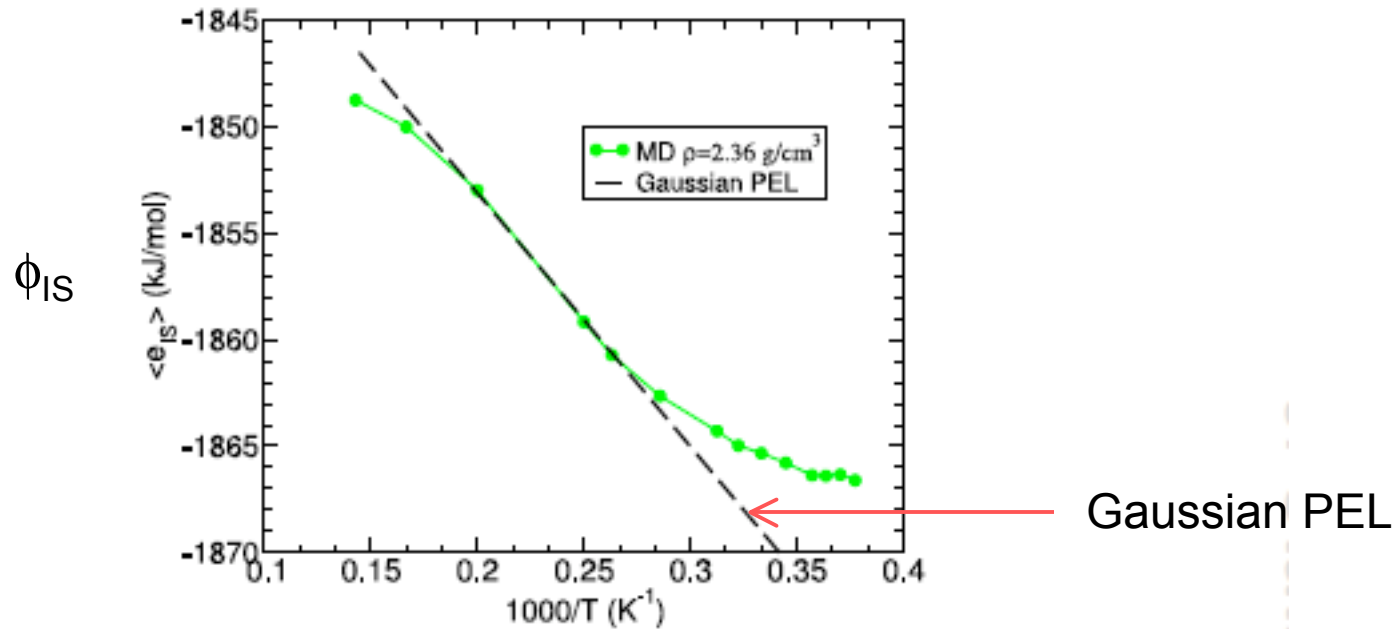
Figure 11. Temperature dependence of $\langle e_{IS} \rangle$ for BKS silica. The $1/T$ law characteristic of Gaussian landscapes is observed only in a restricted region of temperatures. Redrawn from [62].

[F. Sciortino, J. Stat. Mech. Exp & Theory, P05105 (2005)]

Gaussian landscape

• IS energy distribution h(ϕ) is Gaussian:

$$h(\phi) = e^{\alpha N} \left[\frac{e^{-(\phi - \phi_o)^2 / 2\mu^2}}{(2\pi\mu^2)^{1/2}} \right]$$
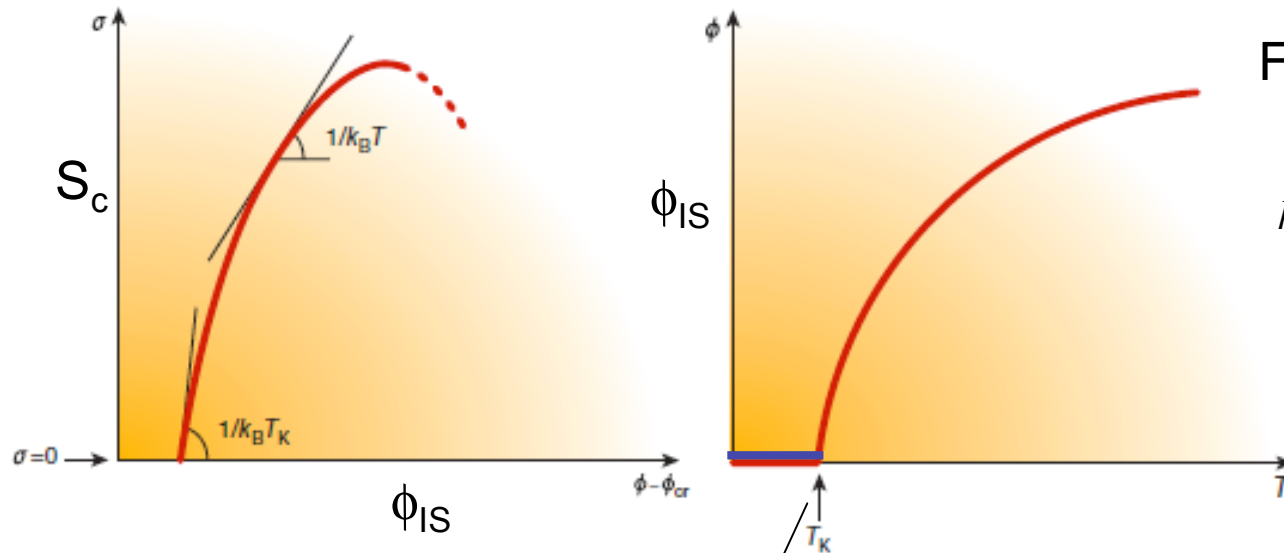
Here α, μ, and ϕ_o are constants.

$$\phi_{IS}(T) = [\phi_o - b\mu^2] - [\mu^2 / k_B T]$$

Here, b is a constant related to vibrational frequency.

$$S_c(T) / k_B = \alpha N - \left[\frac{(\phi_{IS} - \phi_o)^2}{2\mu^2} \right]$$

Kauzmann Temperature (T_K)

$$S_c(T_K) \equiv 0$$

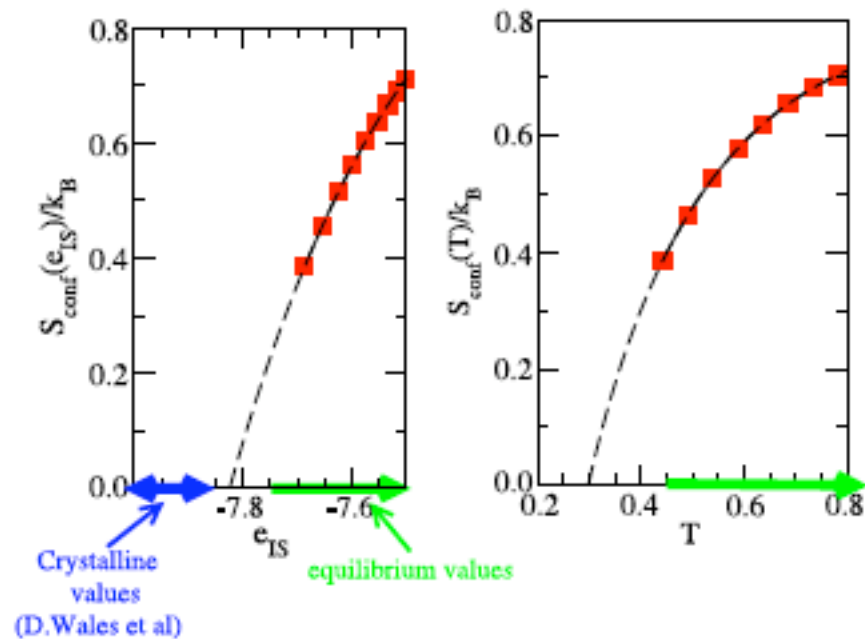$$\frac{\partial S_c}{\partial \phi_{IS}} = \frac{1}{T}$$

For Gaussian model:

$$k_B T_K = [\sqrt{\frac{2\alpha N}{\mu^2}} - b]^{-1}$$

$$\phi_K = \phi_o - (\sqrt{2\alpha N})\mu$$

[PG Debenedetti, FH Stillinger, Nature, 410(2001) 262].

• Ideal glass (transition at T_K).

BMLJ= Binary mixture of Lennard Jones potentials

Figure 8. IS energy (left) and temperature (right) dependences of the configurational entropy for the BMLJ model. The full lines extrapolate to $S_{conf} = 0$ at the Kauzmann energy e_K and the Kauzmann temperature T_K. The arrow indicates the range of energy values of the crystal [49, 50].

[F. Sciortino, J. Stat. Mech. Exp & Theory, P05105 (2005)]

$S_c(T)$
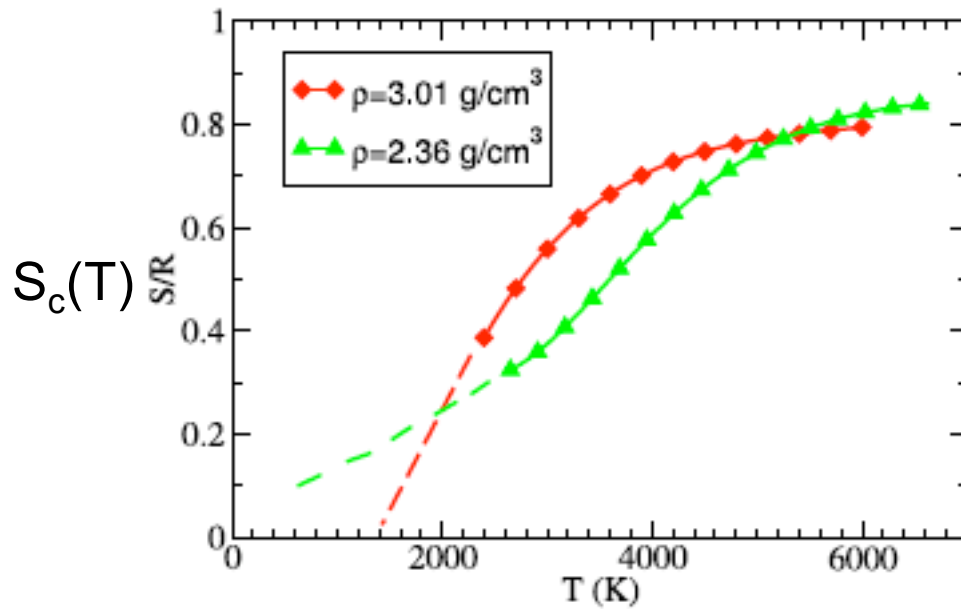
Figure 12. T dependence of S_{conf} for BKS silica at $\rho = 2.36$ and 3.01 g cm^{-3}. Note that in this model, at the lowest density, S_{conf} does not appear to vanish at a finite T. Dashed lines represent possible extrapolations. Redrawn from [62].

[F. Sciortino, J. Stat. Mech. Exp & Theory, P05105 (2005)]

Summary
1.   Inter-basin transitions = structural relaxation
      Intra-basin transitions = vibrational changes.
2.   Inter-basin transitions are thermally activated.
3.   Transition rates, transition times, and the observation time.
4.   Vibrational states are in equilibrium during all observation times.
5.   Ergodicity <=> Equilibrium   (t_{OBS} > max τ_{ij})
6.   Equilibrium state is the super-cooled liquid (L) state.
7.   Equilibrium basin probabilities, p_i(L,T), are the basic parameters.
8.   Knowing the density distribution of ISs, h(ϕ), one can calculate all
  p_i(L,T) and all thermodynamic properties such as the average IS
  energy ϕ_{IS}(T), configurataional entropy S_c(T), heat capacity, etc.
9.   The T-dependence of the average IS energy ϕ_{IS}(T) - sometimes
  called the excitation profile - has a flat top and a flat bottom.
10. At the Kauzmann temperature, $S_c(T_K)$ = 0.
11. If T_K can be reached, then a thermodynamic "ideal glass
transition" will tale place at T_K.
12. A Gaussian PEL shows a finite T_K.