

The potential energy landscape approach to understanding glass forming liquids

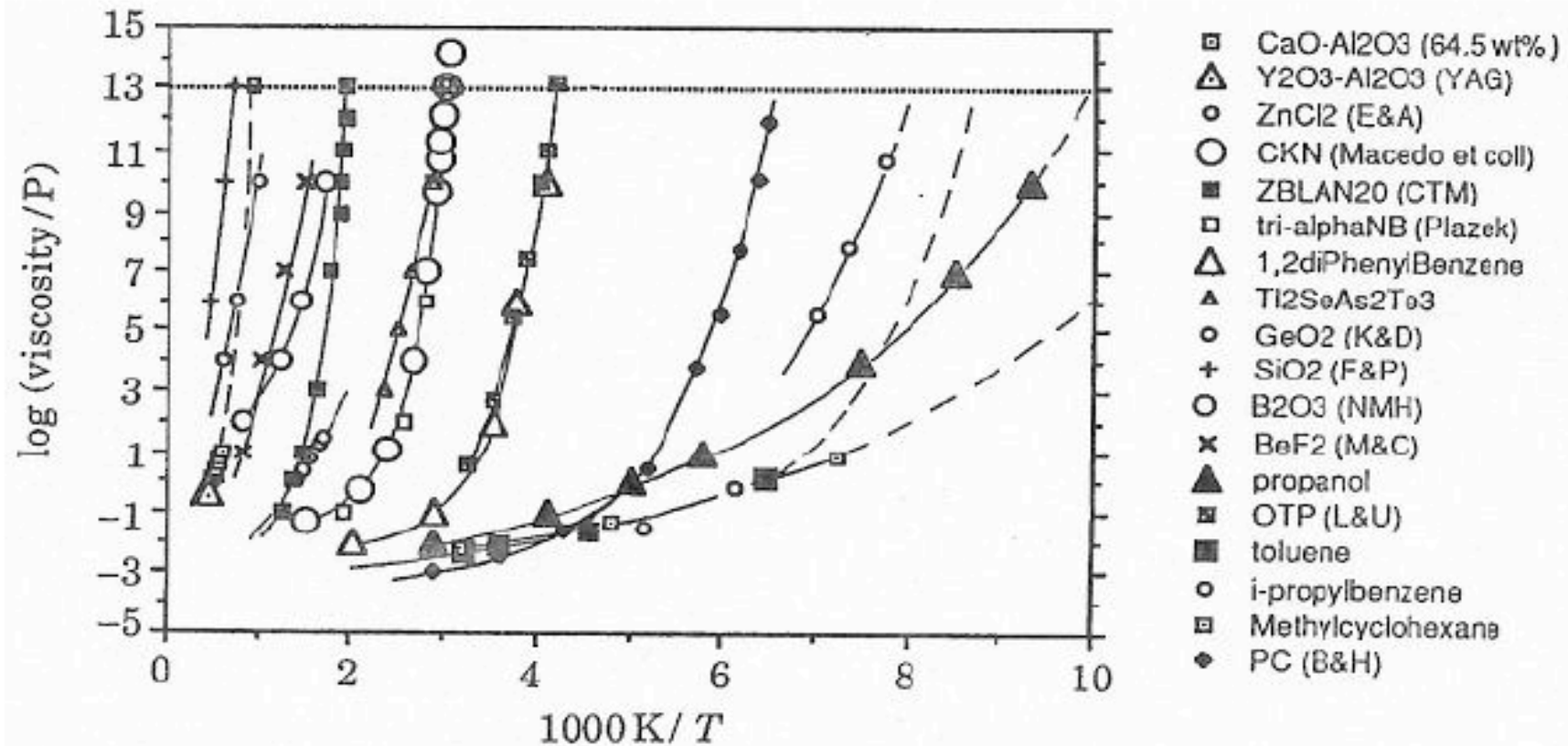


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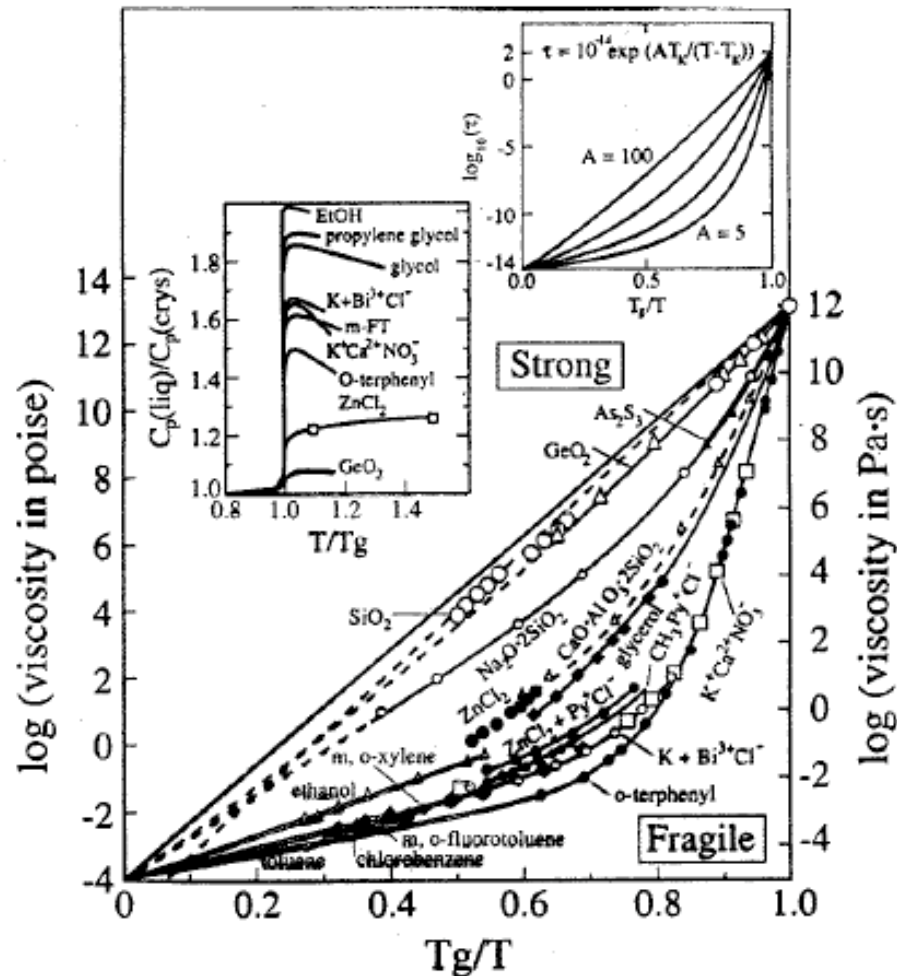
The glass transition



- Fundamental property of liquids -- they flow.
- When viscosity reaches 10^{13} poise, they stop flowing on experimental time scales (relaxation times ~ 100 s)
- “Laboratory glass transition” seen for wide range of substances, and is a *kinetic* effect.

Fragility

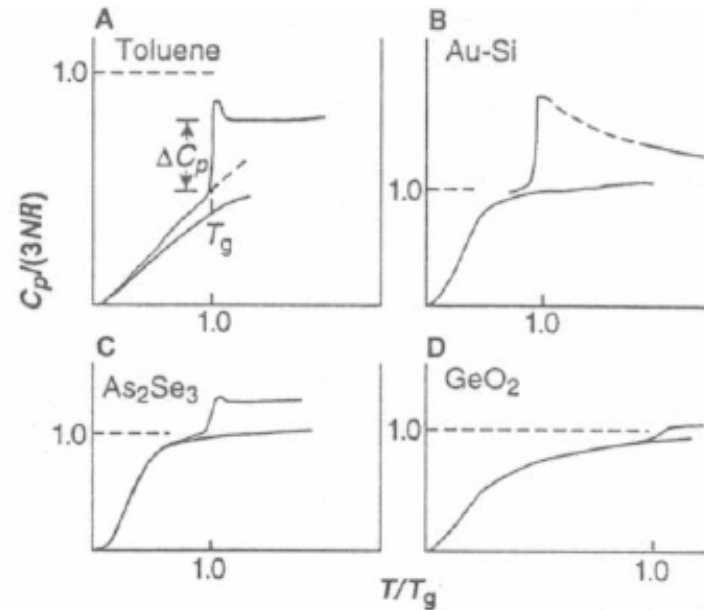
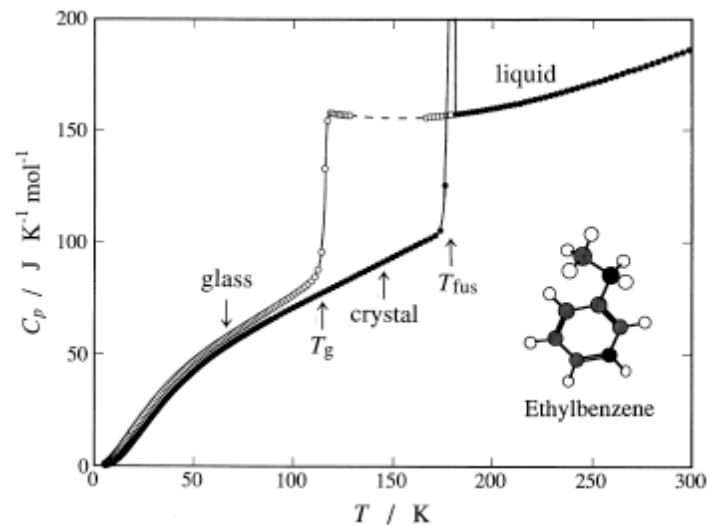
- Data collapse when T scaled with T_g? – No, Instead, a range of behavior.
- How rapidly the viscosity changes is called the fragility of the glass former.
- Well described by the VFT (Vogel Fulcher Tammann) form.



$$\eta = \eta_o \exp \left[\frac{1}{K \left(\frac{T}{T_o} - 1 \right)} \right]$$

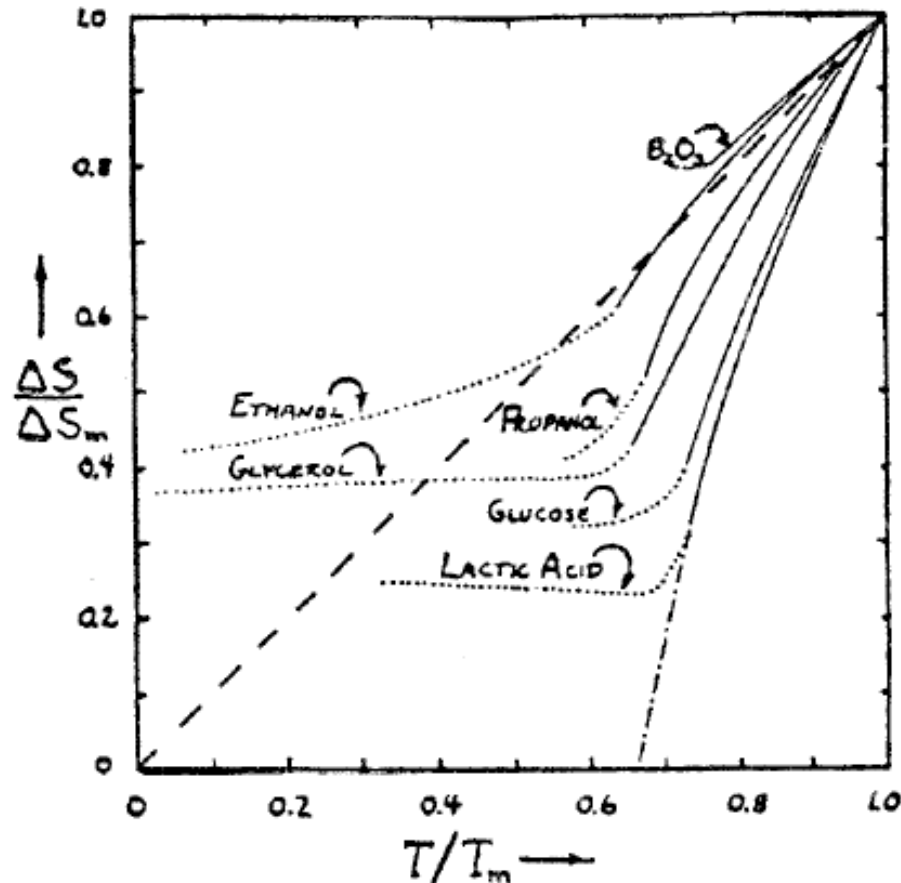
K -- fragility index

Thermodynamics



- Heat capacity also shows a drop.
- Magnitude depends on fragility, location depends on cooling rate.
- Is there an underlying thermodynamic transition?

Kauzmann paradox



- Heat capacity of the liquid higher than crystal.
- By extrapolation, excess entropy of the liquid over crystal appears to vanish at a finite temperature. Paradoxical.
- Resolution in practice -- Glass transition intervenes.
- Resolution in principle -- Entropy vanishing thermodynamic glass transition??
- Meaning of excess entropy? -- Corresponds to multiplicity of distinct *structures* that a liquid can be in.

Adam-Gibbs Theory

- Builds on Gibbs-DiMarzio theory describing the glass transition as an entropy vanishing transition.
- Connection to dynamics.
- Views a liquid as divided into **cooperatively rearranging regions** of size z .
- Probability of rearrangement:

$$p(T) \sim \exp(-\beta \delta \mu z)$$

- Entropy of each CRR roughly constant regardless of size.

- Total entropy of the system $S_c = \frac{N}{z} s_o$

- Results in expression for relaxation times:

$$\tau \sim \exp\left(\frac{\delta\mu s_o}{T s_c}\right)$$

- Tested and found to be a good description of experimental and simulation data.

Results in VFT equation if $\Delta C_p = \frac{K_c}{T}$
since

$$\Delta S = \Delta S(T_K)[= 0] + \int_{T_K}^T \frac{\Delta C_p}{T} dT = \frac{K_c}{T} \left(\frac{T}{T_K} - 1 \right)$$

$$T \Delta S = K_c \left(\frac{T}{T_K} - 1 \right)$$

Plugging into the Adam-Gibbs relation

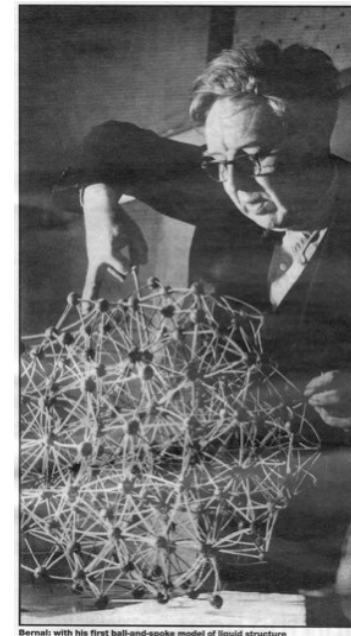
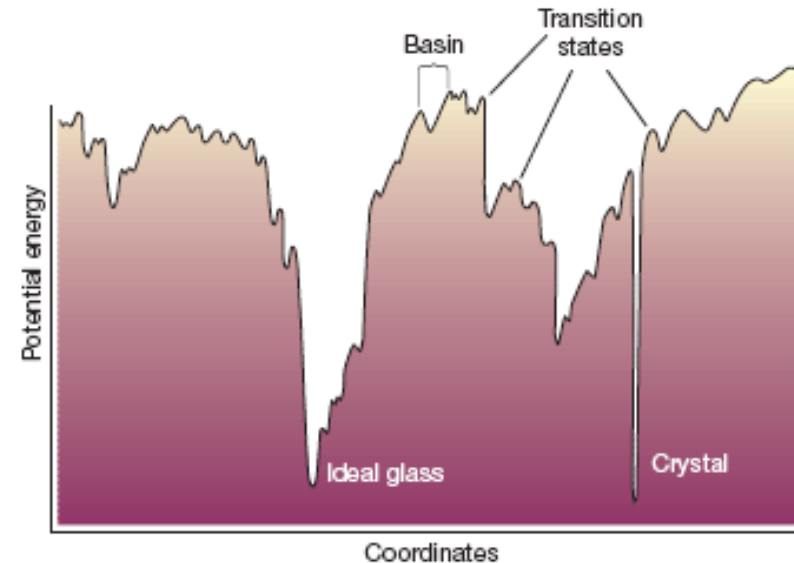
$$\tau \sim \exp \left(\frac{\delta \mu s_o}{K_c \left(\frac{T}{T_K} - 1 \right)} \right)$$

Hence,

$$K_{VFT} = \frac{K_c}{\delta \mu s_o}$$

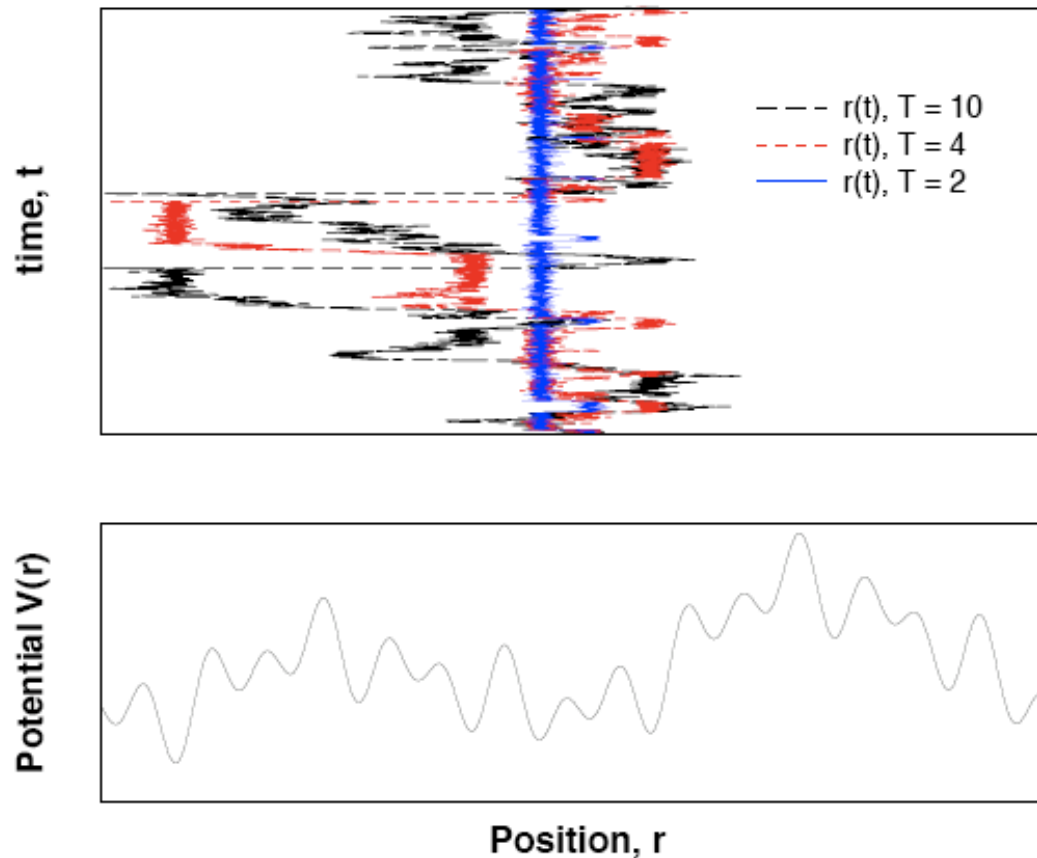
Energy landscape approach: Intuitive picture

- Disordered liquid structure. Potential energy a complicated function of coordinates, with many local energy minima – energy landscape.
- Local minima – many disordered packings of atoms possible in the liquid.
- Premise: disorder and structure of energy landscape play an essential role in the physics of interest.
- Expectation: likely to be true at low temperatures and high densities.
- Lowering temperature, the local minima sampled get deeper, and it gets harder to go from one to the other.
- Increasing relaxation times.
- Local minima: **Inherent structures (Stillinger and Weber)**



Illustration

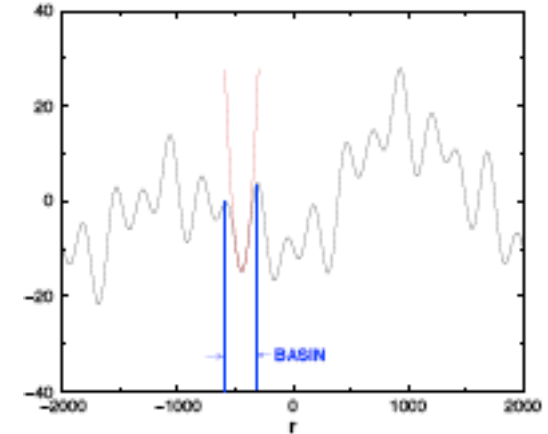
A particle moving in a complicated one dimensional potential



Many local minima of the potential energy – Inherent structures

Some observations:

- Fast equilibration in “basins” of local minima
- Transient localization at intermediate temperatures
- ‘Trapping’ in local minima at low temperatures
- Barrier crossing to explore phase space;
(in higher dimensions) entropic barriers due to connectivity of minima.

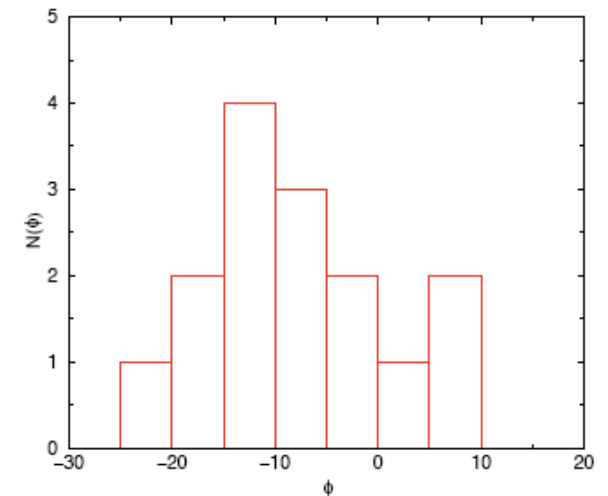


Statistical description of energy landscape:

Distribution of Minima: $N(\Phi)$ = number of minima in $(\Phi, \Phi + \Delta\Phi)$

Configurational Entropy Density = $S_c(\Phi) = k_B \log(N(\Phi))$

Configurational Entropy $S_c(T) = \langle S_c \rangle = S_c(\Phi(T))$



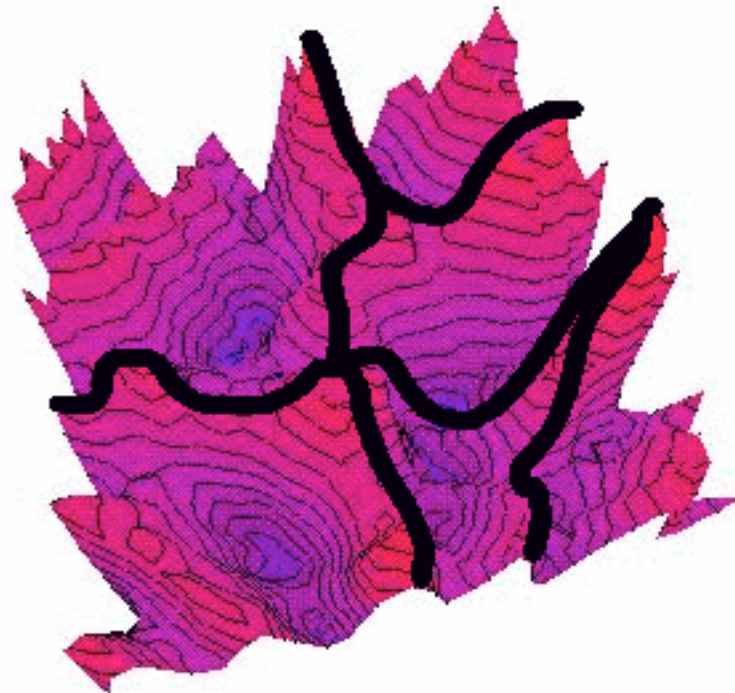
Potential Energy Landscape Picture

Martin Goldstein, Viscous Liquids and the Glass Transition: A Potential Energy Barrier Picture (1969): “...based on the idea that in “viscous” liquids (shear relaxation time 10^{-9} sec) flow is dominated by potential barriers high compared to thermal energies, while at higher temperature, this will no longer be true.”

Stillinger and Weber (1982): Computer simulation studies of local energy minima, termed **Inherent Structures** and the formulation of thermodynamics of liquids in terms of the partitioning of configuration space into basins of inherent structures.

The potential energy of a liquid is a function of $3N$ coordinates of the atoms in the liquid, and forms a surface in $3N+1$ dimensions. For a given liquid, the potential energy surface is temperature independent.

The configuration space can be divided into basins of local energy minima, and the properties of the liquid can be studied by considering the **temperature dependent** sampling of the landscape.



Computer simulations

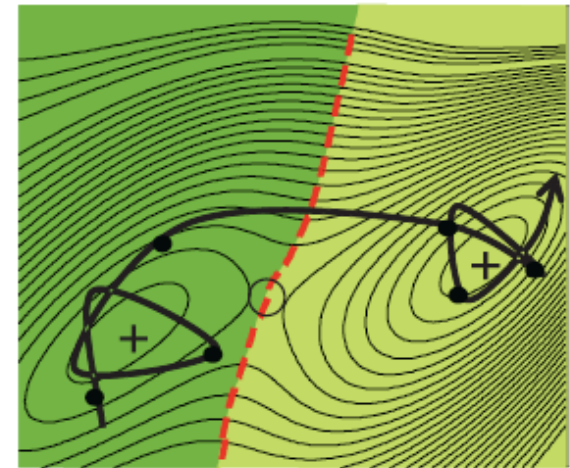
The analysis of the energy landscape has been carried out using computer simulations extensively.

Molecular dynamics simulations to generate trajectory of a collection of interacting particles (atoms) under constant energy or temperature.

A sample of configurations is subjected to local energy minimization to probe the energy landscape sampled by the liquid at the studied state point.

The statistics of energy minima sampled, and properties of such minima are calculated.

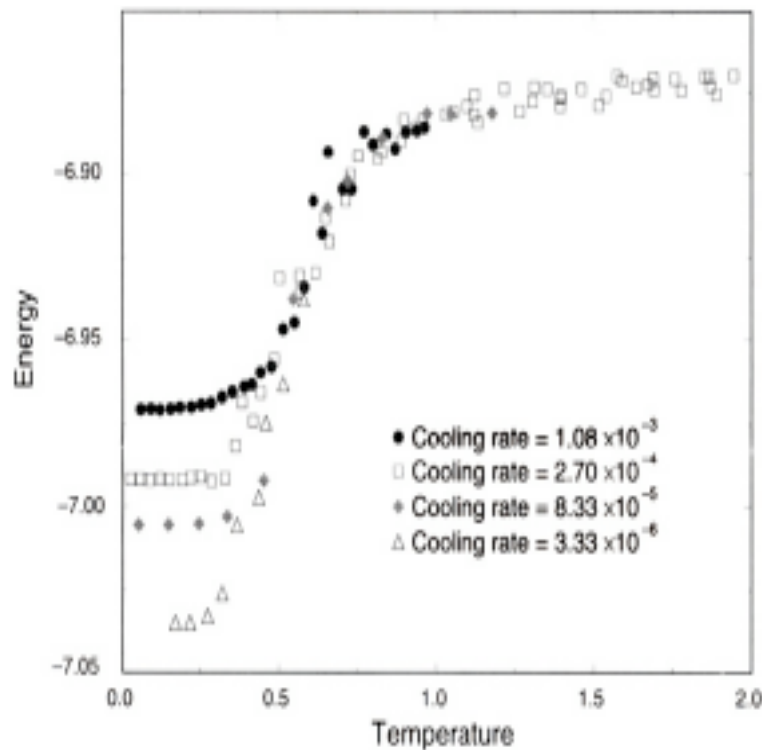
The dynamics of the liquid is probed by the diffusion of particles, density correlation functions, etc.



Average Energy of Inherent Structures

Computer simulation of Kob-Andersen binary LJ mixture:

Liquid simulated at varying cooling rates.



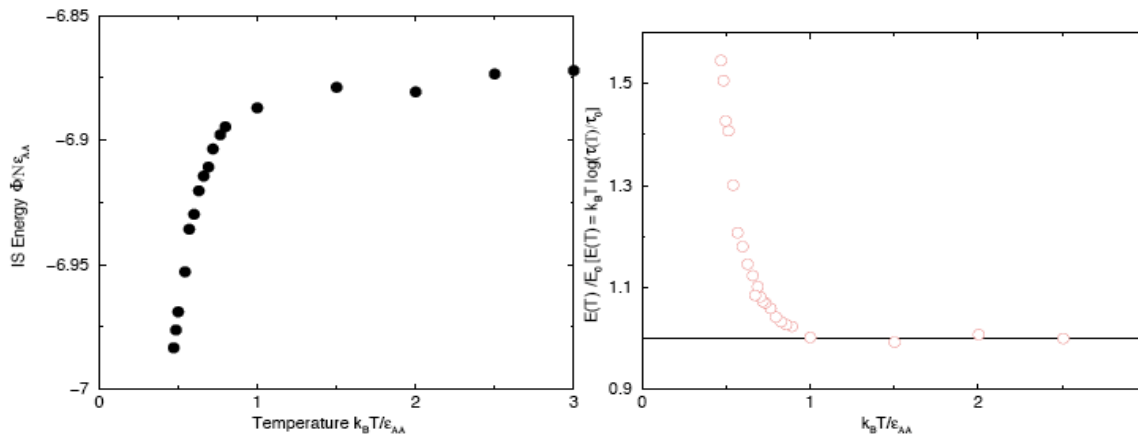
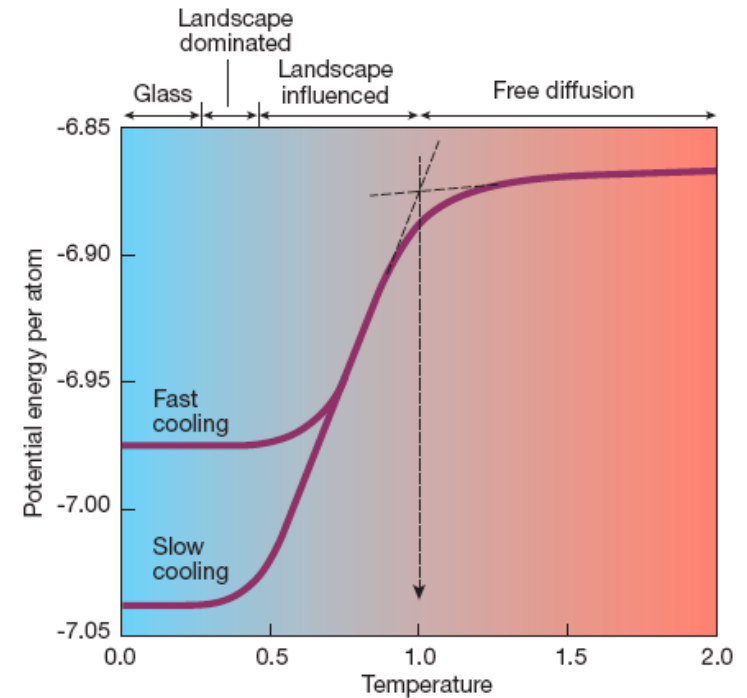
- Nearly constant average energy of inherent structures at high temperature.

- Increasing depth of minima at lower temperatures.

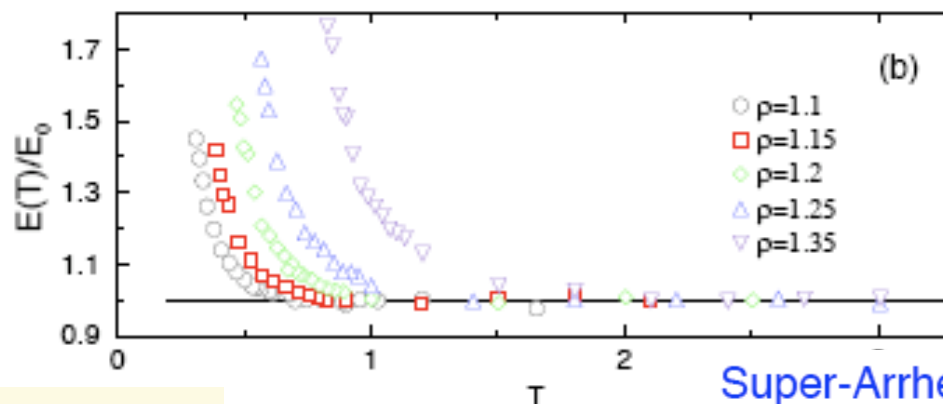
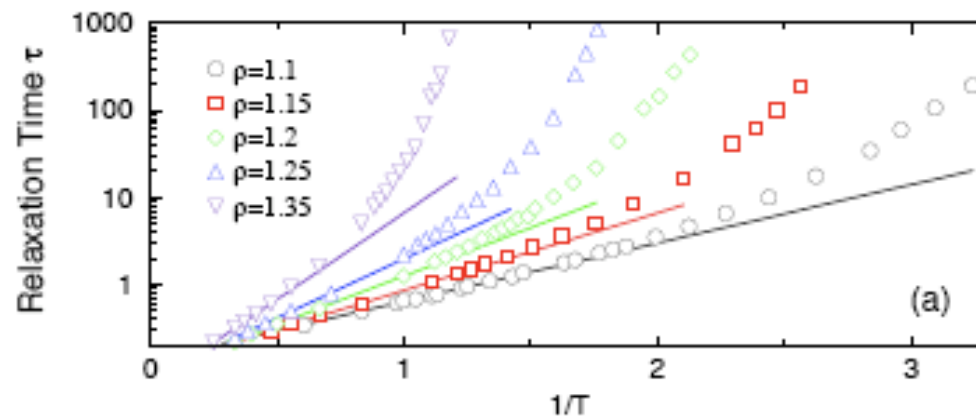
- At the lowest temperatures, liquid gets “stuck” in inherent structures of depth that depends on cooling rate.

Onset Temperature

- Sampling of deeper minima observed in computer simulations
- The temperature below which deeper minima are sampled coincides with the development of non-Arrhenius dependence of relaxation times, and stretched exponential relaxation.
- Relation between energy landscape properties and non-trivial dynamics below onset temperature.



In the temperature range where dynamics of liquids begins to display 'slow dynamics' (super-Arrhenius T dependence, stretched exponential relaxation), one must observe signatures in the energy landscape sampled by the liquid.

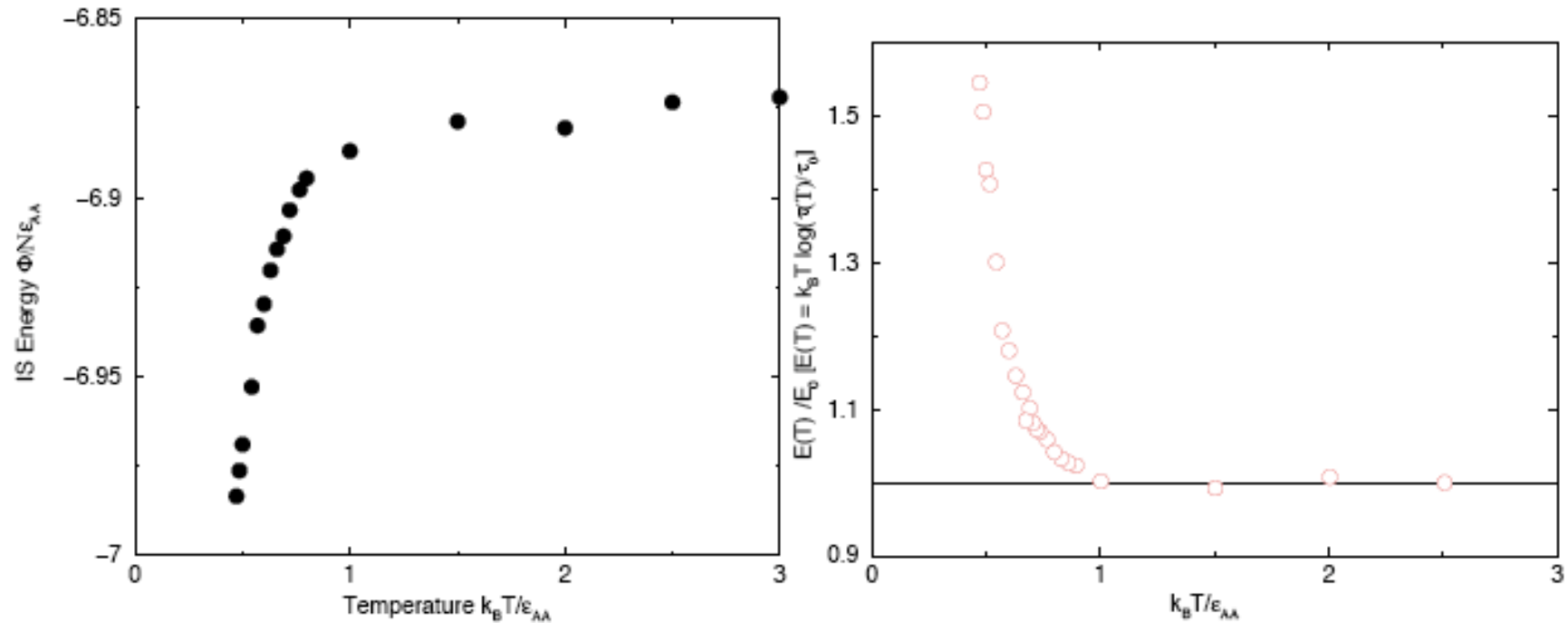


Sastry 2000

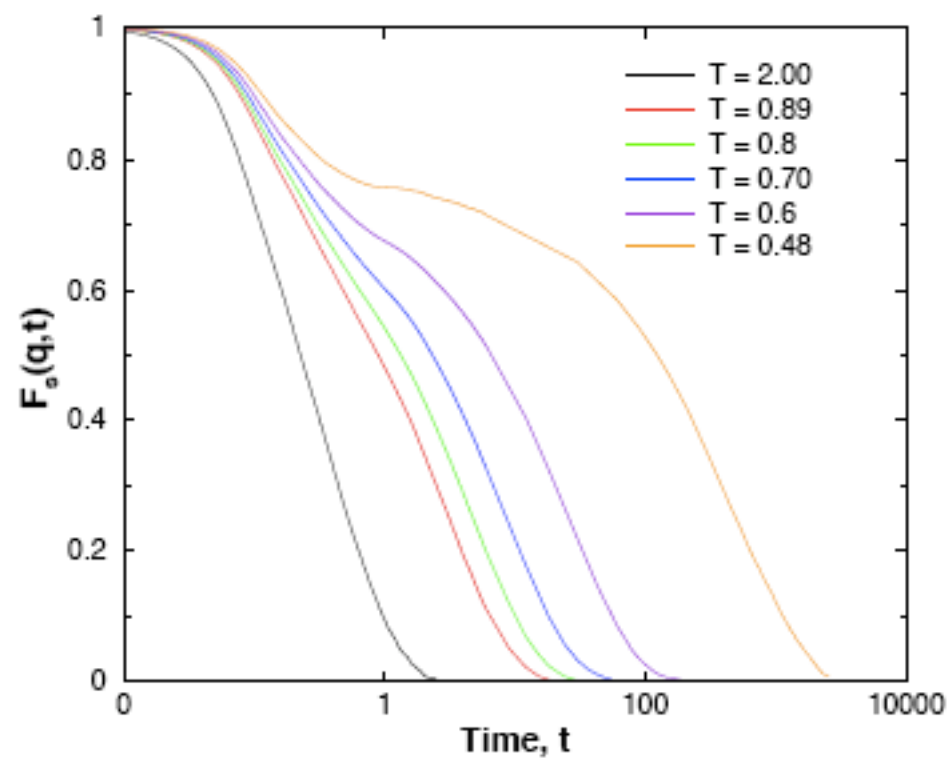
Super-Arrhenius Behaviour at Low Temperatures:
 $E(T) = k_B T \log(\frac{\tau}{\tau_0}) \neq \text{Constant}$.

Sampling of Inherent Structures

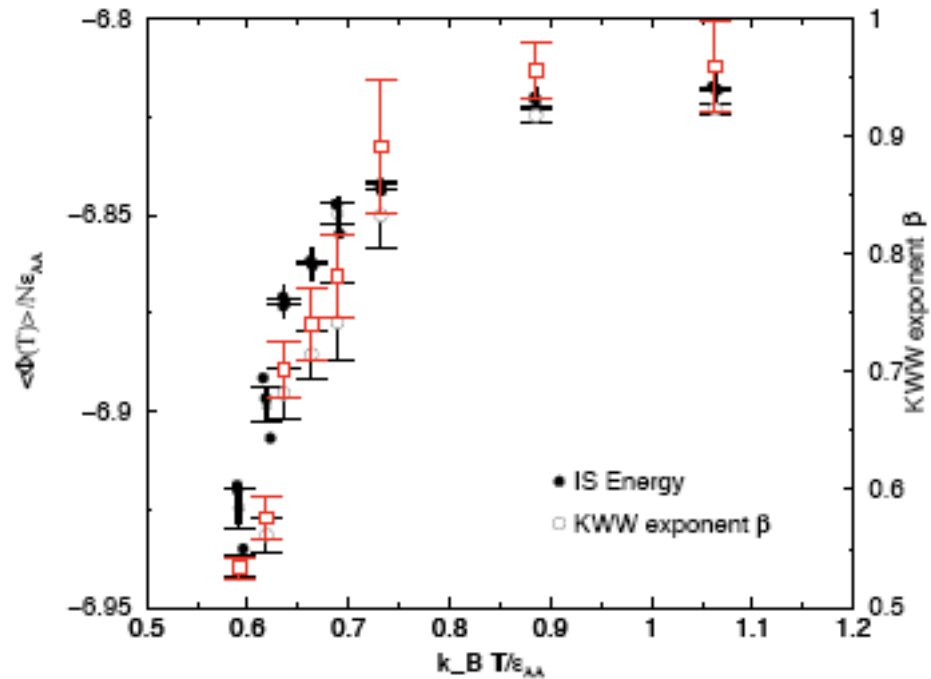
Onset of significant temperature dependence of inherent structure energies coincides with emergence of non-Arrhenius T dependence of relaxation times.



Time dependent correlation functions: Stretched exponential relaxation of density correlation function –



KWW exponent: 50:50 binary mixture, $\rho = 1.296$



Decrease of KWW exponent tracks the sampling of deeper minima

Sastry et al 1999

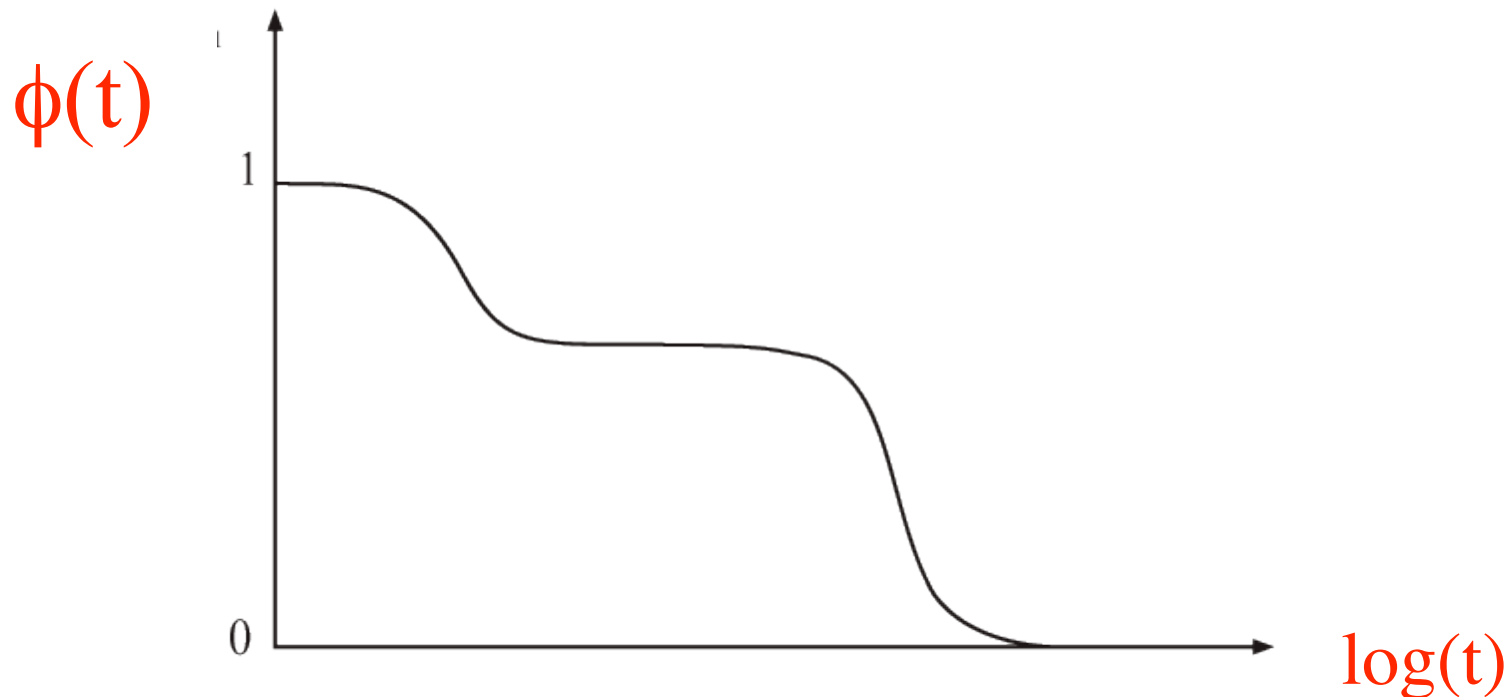
The emergence of interesting dynamics in the liquid is associated with a nontrivial sampling of the potential energy surface.

Goldstein Crossover

Goldstein prediction: Crossover to activated dynamics when relaxation time $\sim 10^{-9}$ sec)

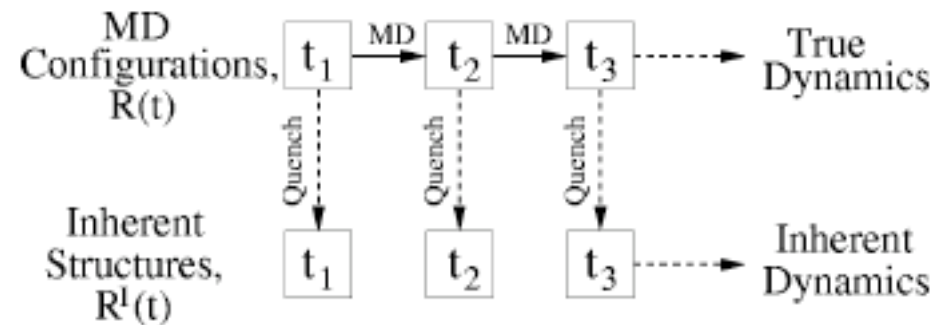
Associated with the mode coupling temperature.

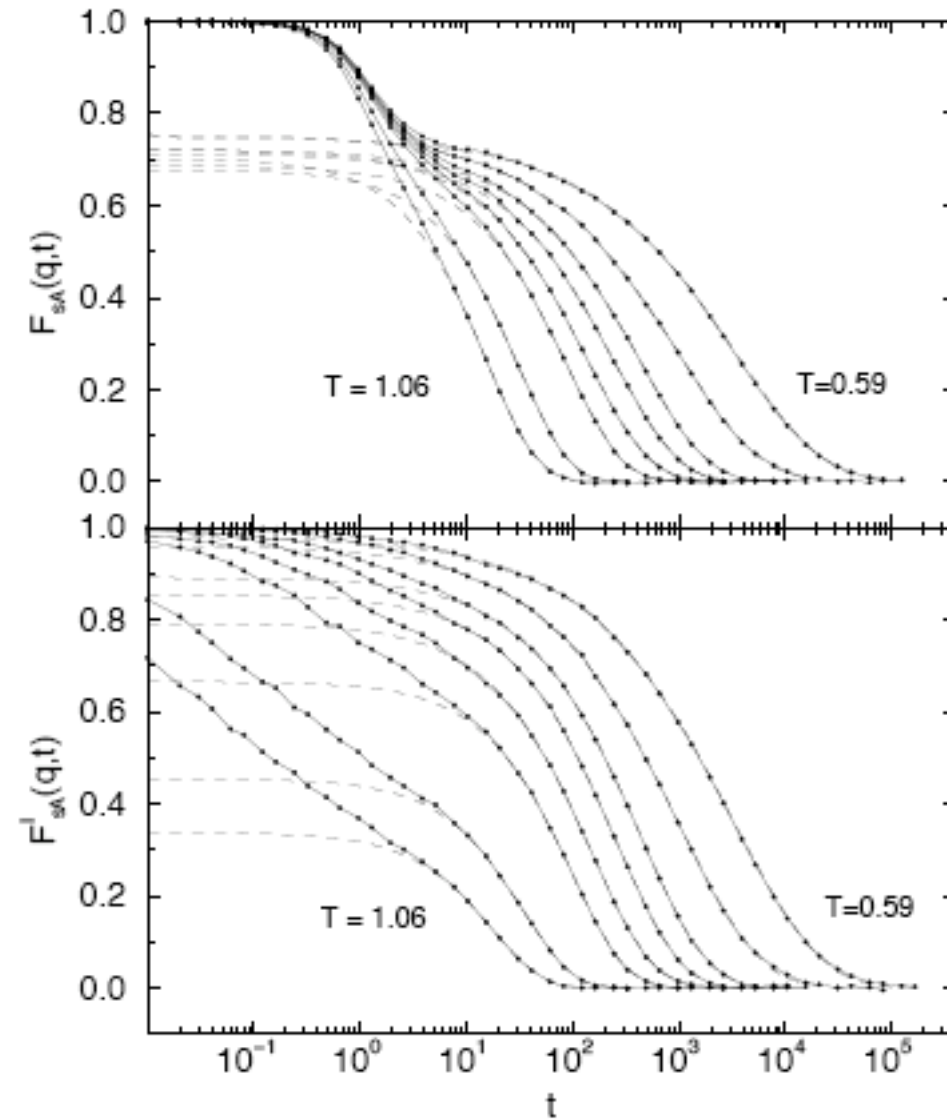
Separation of vibrational and basin hopping times scales.



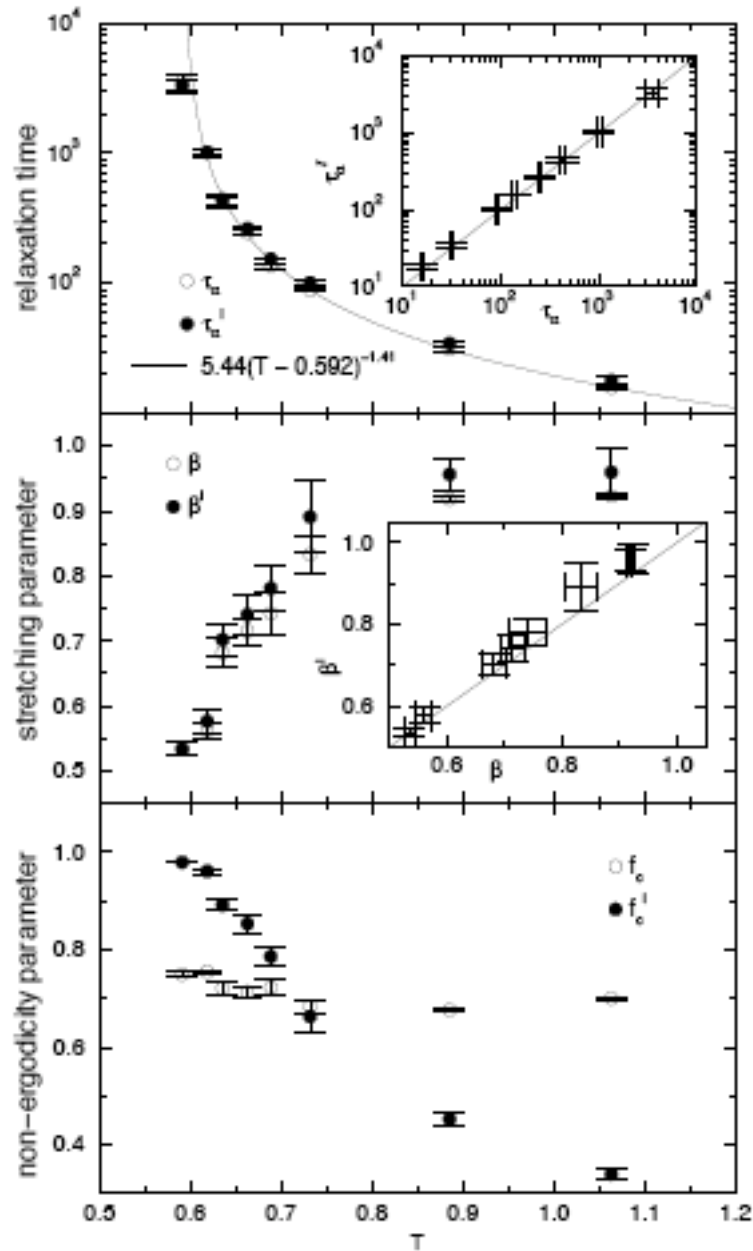
To probe, generate a time series of configurations from molecular dynamics, and a corresponding time series of inherent structures (Schroeder et al 2000).

Calculate time correlation functions for both molecular dynamics and inherent structure trajectory.





Plateau value of inherent structure correlation function approaches 1 as T approaches T_c

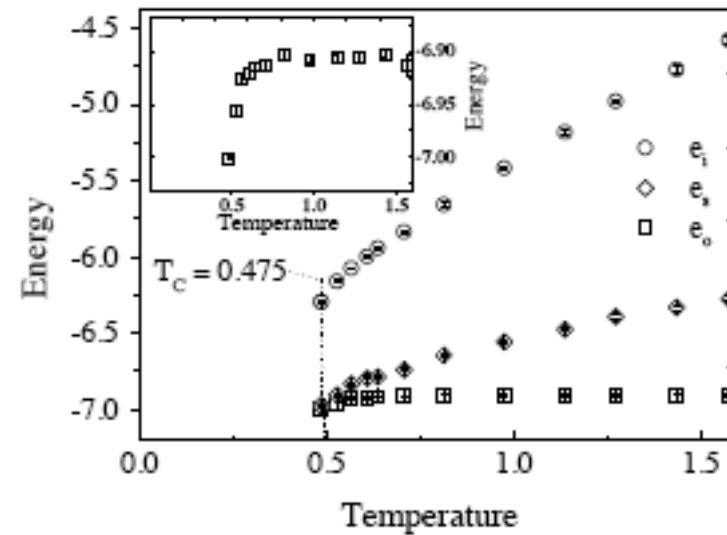
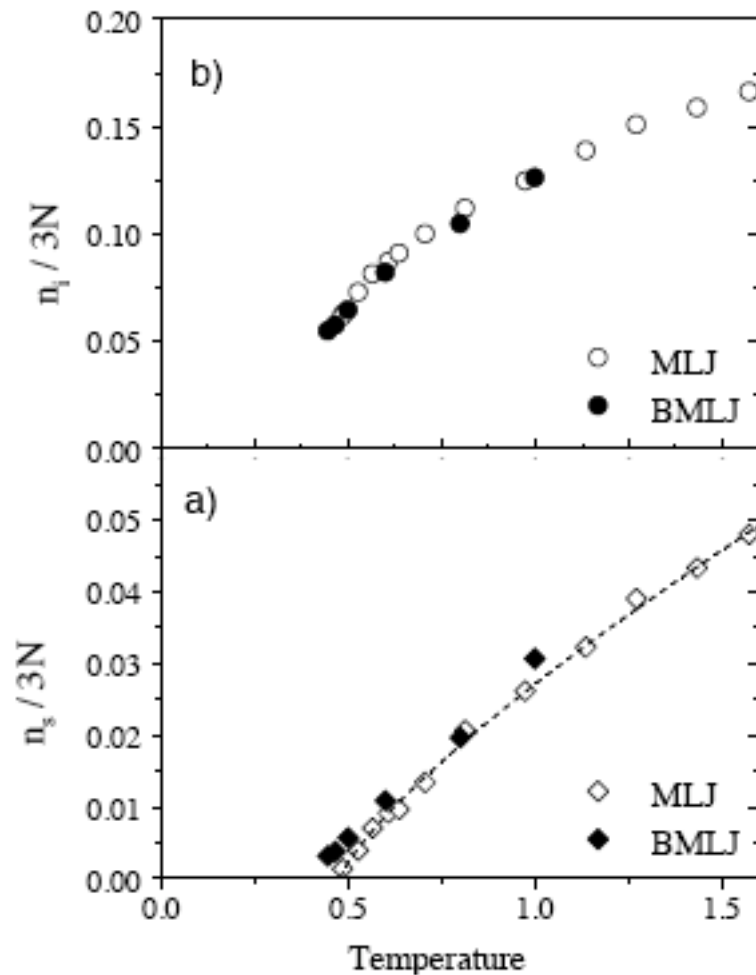


Long time relaxation time and KWW exponent the same for the two trajectories.

Further insights from looking at saddle points in addition to minima.

Map instantaneous configurations to close by saddle points as well as minima.

The order of the saddles vanishes as T_c is approached.



Angelani et al, Broderix et al (2000)

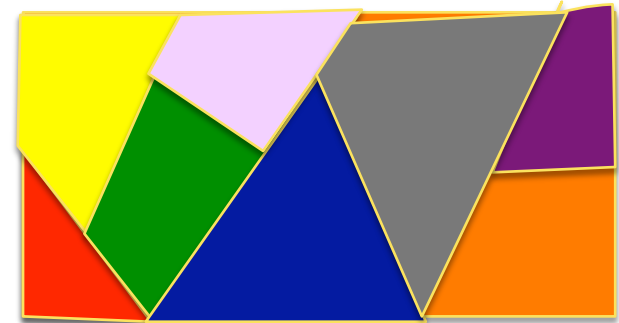
Changes in the nature of dynamics captured by the properties of the sampled energy landscape.

Configurational Entropy from Inherent Structures

The partition function integral can be rewritten in terms of a sum over basins of local minima:

$$Z \propto \int d\mathbf{r}^N \exp(-\beta V)$$

$$Z = \sum_{\alpha} \exp(-\beta \Phi_{\alpha}) \int_{\alpha} d\mathbf{r}^N \exp(-\beta V - \Phi_{\alpha})$$



Defining Basin Free energy: $\exp(-\beta F_{basin \alpha}) \equiv \int_{\alpha} d\mathbf{r}^N \exp(-\beta V - \Phi_{\alpha})$

Approximation: Basin free energy same for minima of same energy: $F_{basin}(\Phi, T)$

The partition function is expressed in terms of the density of states of minima, Ω , and the associated “Configurational Entropy” S_c

$$Z = \sum d\Phi \Omega(\Phi) \exp(-\beta[\Phi + F_{basin}(\Phi, T)])$$

$$Z = \sum d\Phi \exp(-\beta[\Phi + F_{basin}(\Phi, T) - TS_c(\Phi)])$$

- Assumption: Basin free energies same for basins with same energy at the minimum.

- Can we make any simplifying assumptions?

- For not too low temperatures, $\Omega(\Phi)$ should be Gaussian.

- Then, one can write

$$\frac{S_c(\Phi)}{Nk_B} = \alpha - \frac{(\Phi - \Phi_o)^2}{\sigma^2}$$

- α determines total number of energy minima.

- Φ_o – most probable energy of minima.

- σ determines the spread in energies.

- For not too high temperatures, basins can be approximated by harmonic wells.

- Basin free energy is given by:

$$F_{vib} = k_B T \sum_{i=1}^{3N} \ln \frac{h\nu_i}{k_B T}$$

- ν_i – Vibrational frequencies.
- As we expect the basin frequencies to depend on inherent structure energy, a simple approximation is:

$$F_{vib}(\Phi, T) = F_{vib}(\Phi_0, T) - T\delta S(\Phi - \Phi_0)$$

$$F_{vib}(\Phi, T)/k_B T = F_t(T) + F_0(\Phi_0) - \frac{\delta S}{k_B}(\Phi - \Phi_0)$$

- Equivalently

$$S_{vib}(\Phi, T) = S_{vib}(\Phi_0, T) + \delta S(\Phi - \Phi_0).$$

- For these assumptions, the partition function can be solved, and yields

$$\langle \Phi \rangle (T) \equiv e_{IS}(T) = \Phi_0^{eff} - \frac{\sigma^2}{2Nk_B T}, \text{ where } \Phi_0^{eff} = \Phi_0 + \frac{\sigma^2 \delta S}{2Nk_B},$$

$$TS_c(T) = K_{AG}^{PEL}(T)(T/T_K - 1)$$

$$K_{AG}^{PEL}(T) = \left(\frac{\sigma\sqrt{\alpha}}{2} + \frac{\sigma^2 \delta S}{4Nk_B} \right) \left(1 + \frac{T_K}{T} \right) - \frac{\sigma^2 \delta S}{2Nk_B}.$$

- In words:
 - Inherent structure energy must vary at $1/T$.
 - Configurational entropy has nearly the correct form needed to justify VFT relation.
 - Configurational entropy obtained in terms of a few parameters that describe the energy landscape of the liquid: α , σ , Φ_0 and δS .
- We will see later that these predictions hold good.

Equation of state in landscape variables

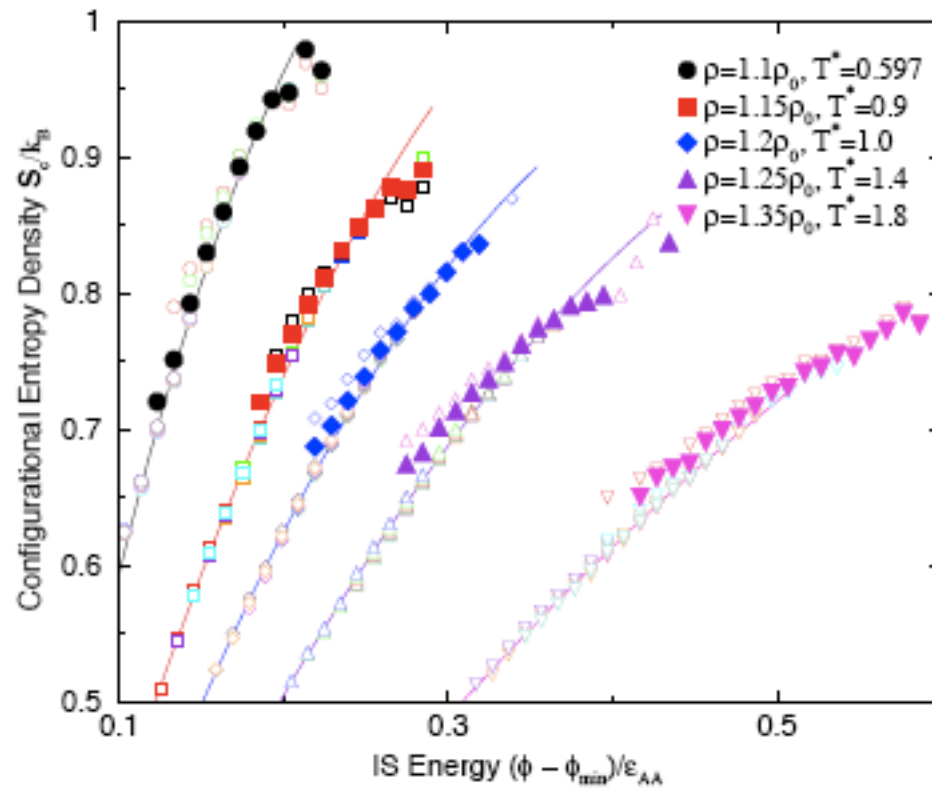
- So far, we have considered only constant density behaviour. To include also the volume, we may write:

$$F(V, T) = \Phi(V, T) - TS_c(\Phi(V, T)) + F_{vib}(\Phi(v, T), V, T)$$

- The volume dependence comes from the volume dependent parameters α , σ , Φ_0 , F_0 and δS .
- The equation of state can be written as
$$P = - \left(\frac{\partial F}{\partial V} \right)_T = P_{IS}(T, V) + P_{vib}(T, V)$$
- The volume derivative applies to landscape parameters.
- $P_{IS}(T, V)$ contains information on the ‘inherent structure’ contribution to the pressure – i.e., the configurational pressure.

Harmonicity of basins:

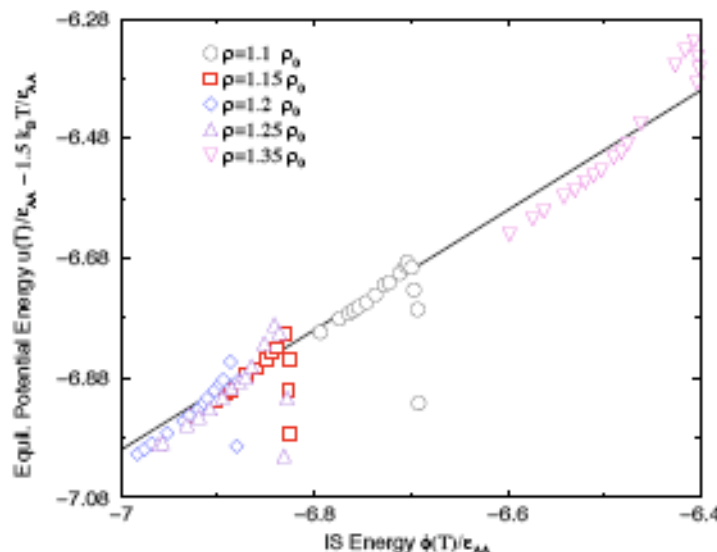
- Distributions of energy minima sampled used to obtain inherent structure density of states.
- Invert $P(\Phi, T) = \exp[-\beta(\Phi + F_{basin}(\Phi, T) - T\mathcal{S}_c(\Phi))]/Q_N(\rho, T)$ to estimate \mathcal{S}_c .
- Assumption of harmonic basins in obtaining $F_{basin}(\Phi, T)$
- Correct procedure must result in consistent \mathcal{S}_c estimates from different T.
- Procedure holds at low T, but breaks down above a ‘crossover’ temperature.



Identify Crossover temperature from deviations

Harmonicity of basins: II

- For harmonic basins, the average ‘instantaneous’ potential energy must be given by $u(T) = \phi(T) + \frac{3}{2}k_B T$.
- At low temperatures $u(T) - \frac{3}{2}k_B T = \phi(T)$, but deviations found at high temperature.
- Deviations permit identification of a crossover temperature

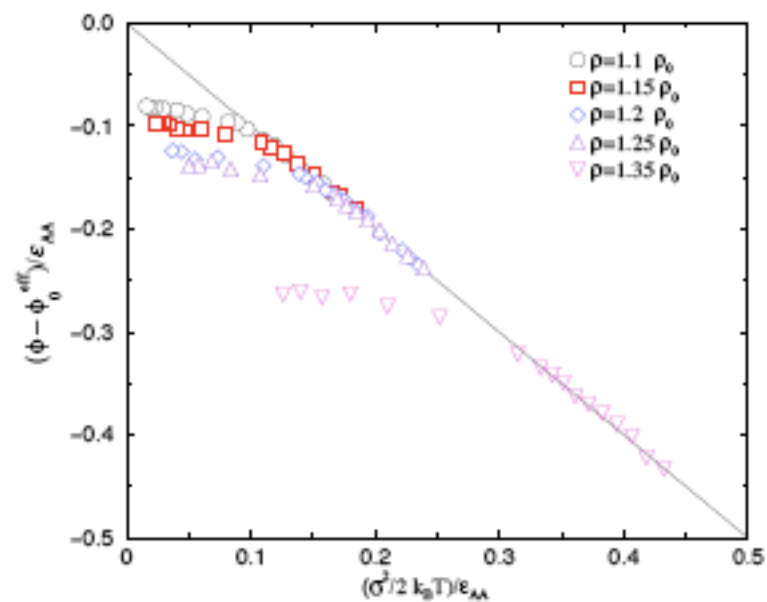


Average energies of local minima

- Assumption of Gaussian configurational DOS, harmonic approximation to basin free energy, permit prediction average inherent structure energy vs. temperature, in terms of landscape parameters:

$$\langle \Phi \rangle (T) \equiv e_{IS}(T) = \Phi_0^{eff} - \frac{\sigma^2}{2Nk_B T}, \text{ where } \Phi_0^{eff} = \Phi_0 + \frac{\sigma^2 \delta S}{2Nk_B}.$$

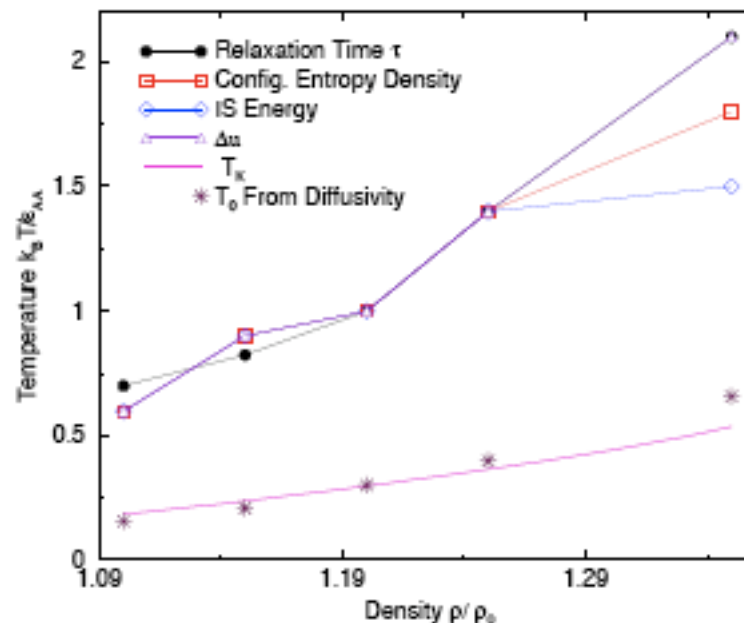
- α, σ, Φ_0 describe Gaussian DOS, and δS the variation of basin entropy with inherent structure energy.



- High temperature deviations from $\frac{1}{T}$ behaviour coincide with onset of slow dynamics.

Crossover temperatures

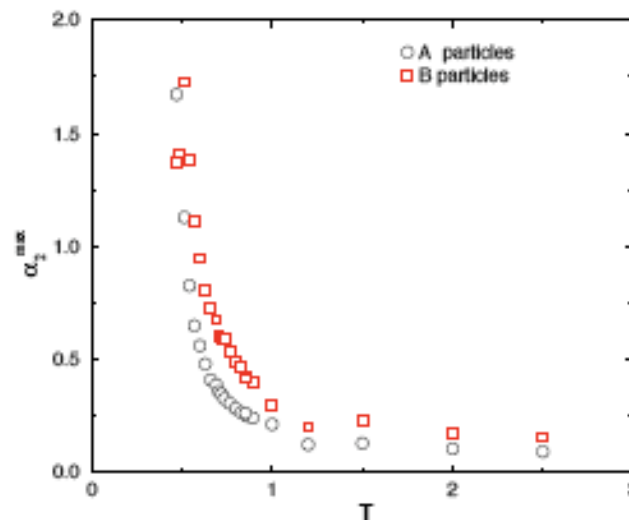
- Crossover temperatures from dynamics and from energy landscape characterization agree for a range of densities of the 80:20 binary mixture.



- Onset of slow dynamics marks a change in qualitative features of the energy landscape sampled by the liquid.

Heterogeneous dynamics

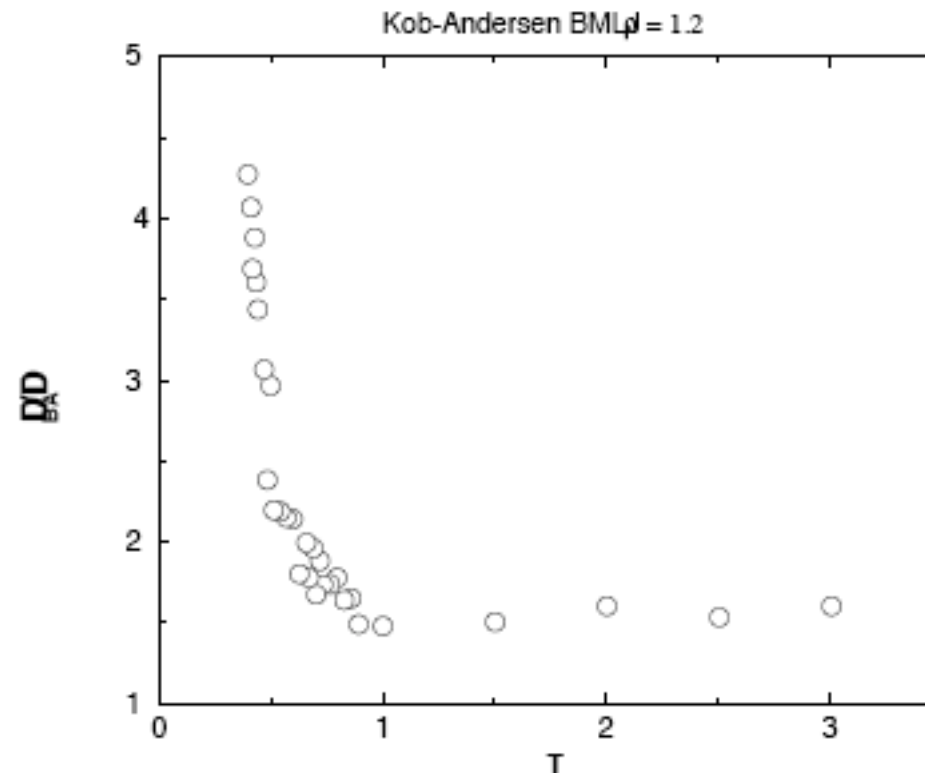
- Non-gaussian parameter α_2 used as an indicator for heterogeneous dynamics. $\alpha_2 = \frac{3\langle r^4 \rangle}{4\langle r^2 \rangle^2} - 1$
- α_2 exhibit maximum value as function of time; maximum value indicative of extent of heterogeneous dynamics.



- α_2^{max} shows marked T dependence below onset temperature

Heterogeneous dynamics

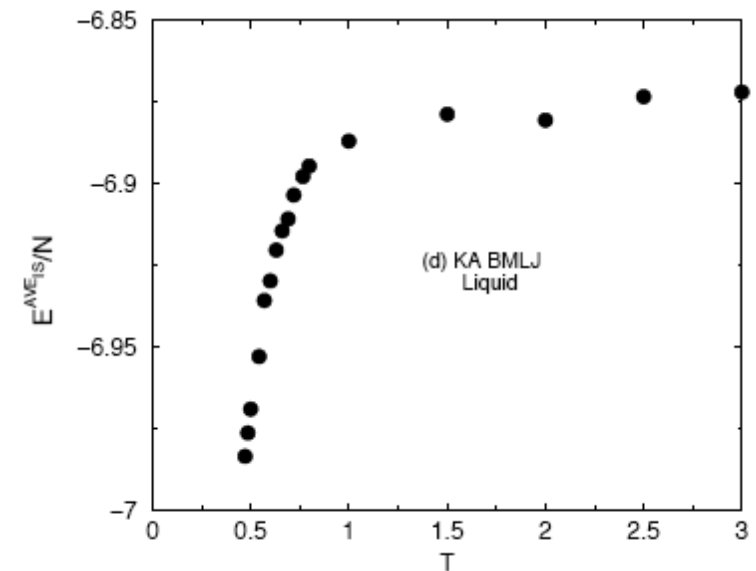
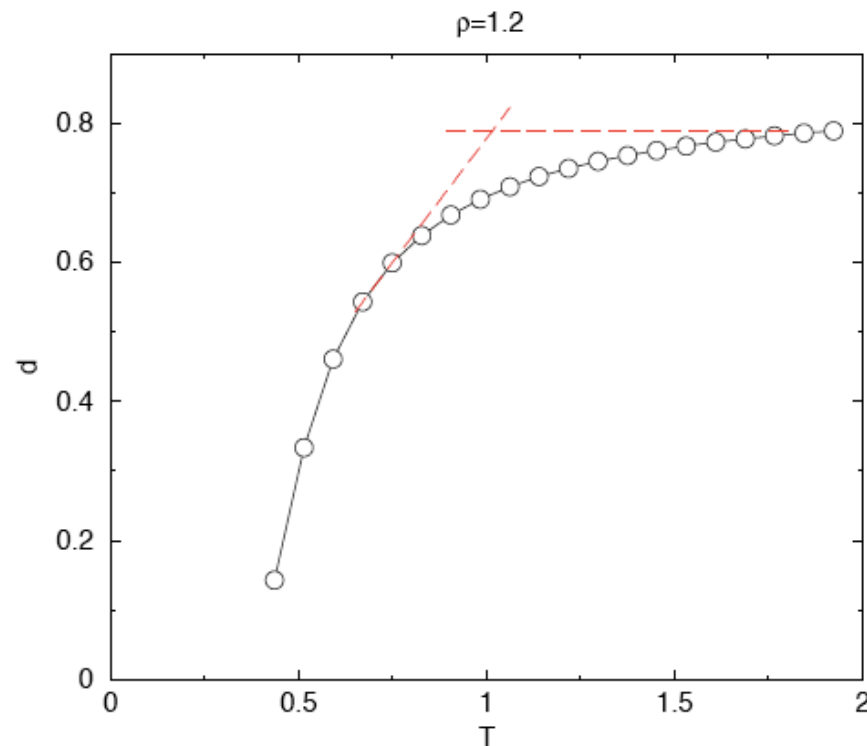
- Ratio of diffusivities of A and B particles shows similar behaviour



- Constant value above onset temperature; strong T temperature dependence below.

Breakdown of Stokes-Einstein relation

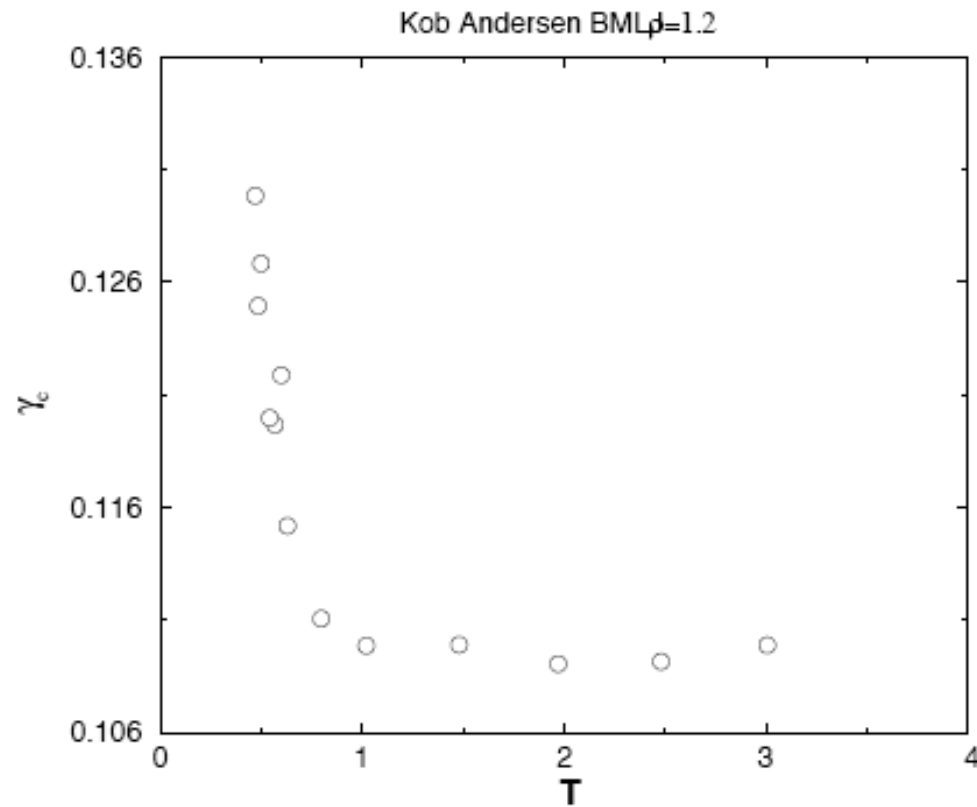
- $D = \frac{k_B T}{3\pi d \eta}$ observed at high T , but breaks down near the glass transition, as observed experimentally.
- $d = \frac{k_B T}{3\pi D \eta}$ a good measure of breakdown.



S S Ashwin, thesis

Response to shear deformation

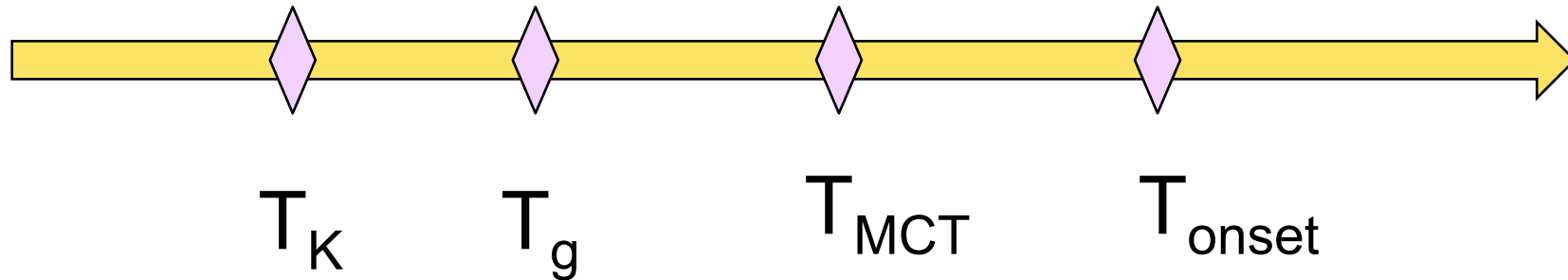
- Other clear-cut correspondence between mechanical properties and dynamics?
- Critical shear strain for inherent structure transitions relates to onset of slow dynamics.
- Deformation: $x_i = x_i + \gamma y_i$
- Find critical γ needed to jump to distinct minimum upon reminimization of energy



γ_c displays significant T dependence below the onset temperature.

Ashwin et al 2004

Significant Temperatures



T_{onset} : Temperature where glassy behavior begins

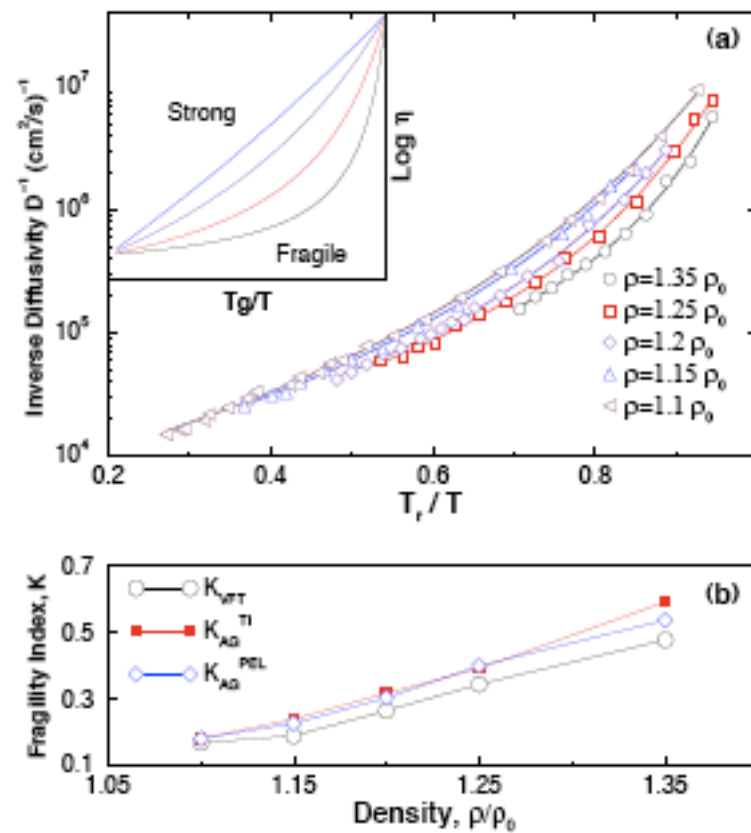
T_{MCT} : Divergence temperature of MCT

T_g : Glass transition temperature

T_K : Kauzmann or ideal glass transition temperature

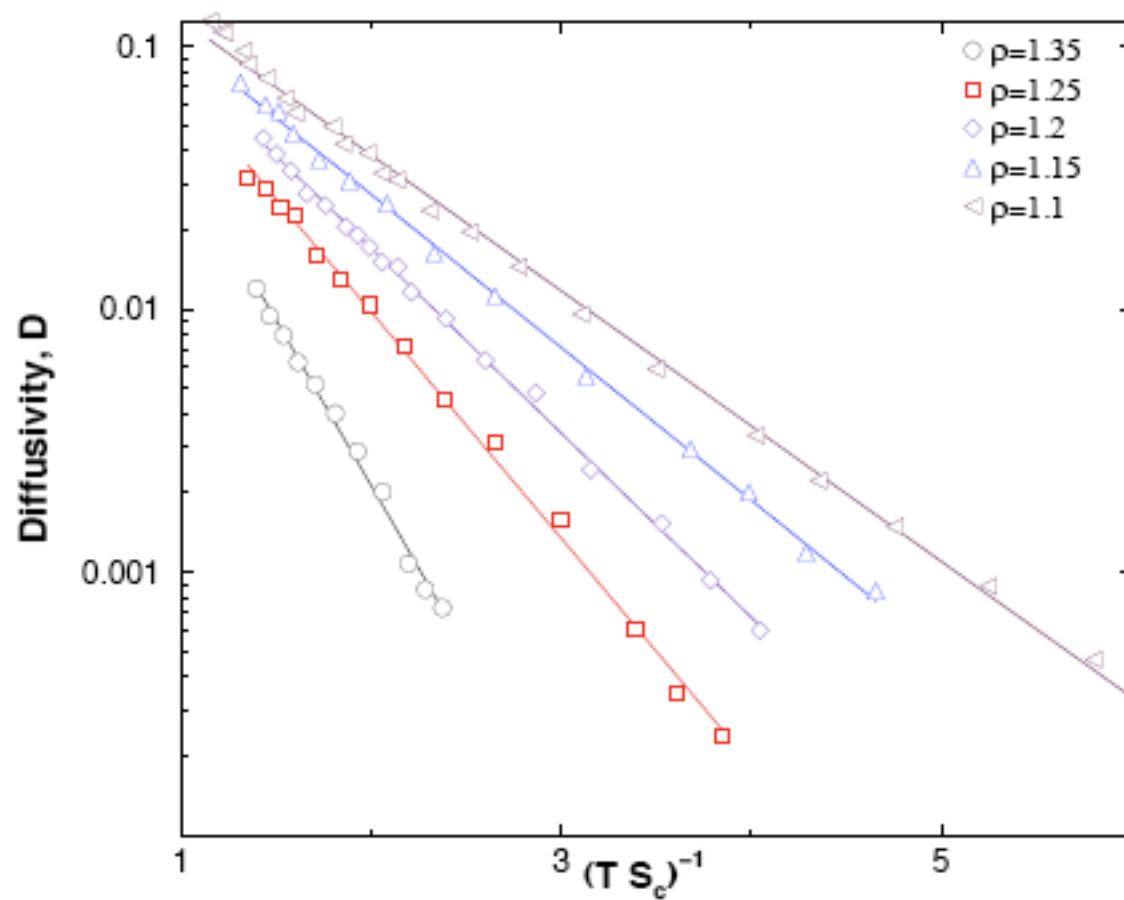
Fragility

Fragility increases with increasing density of the liquid.



Adam-Gibbs Plot

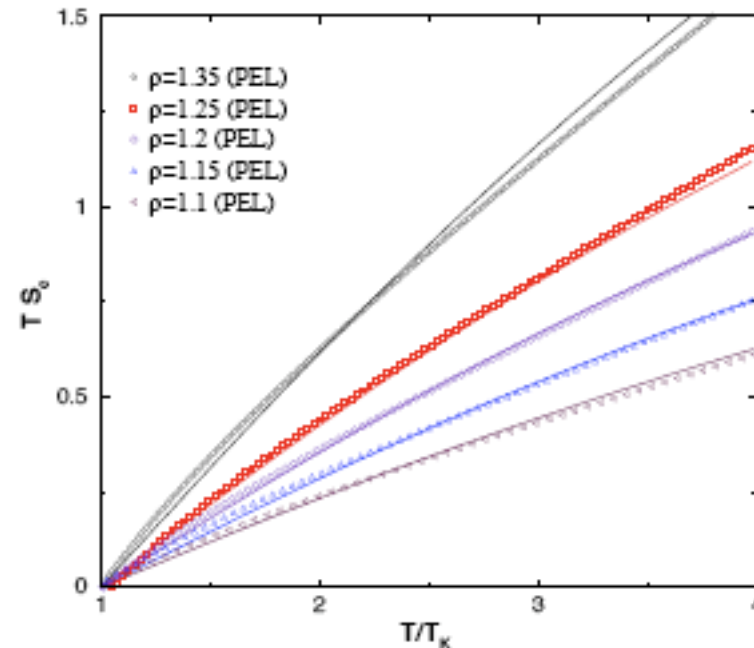
$\log(\text{Diffusivity})$ varies as $(TS_C)^{-1}$ at all densities



T Dependence of S_c

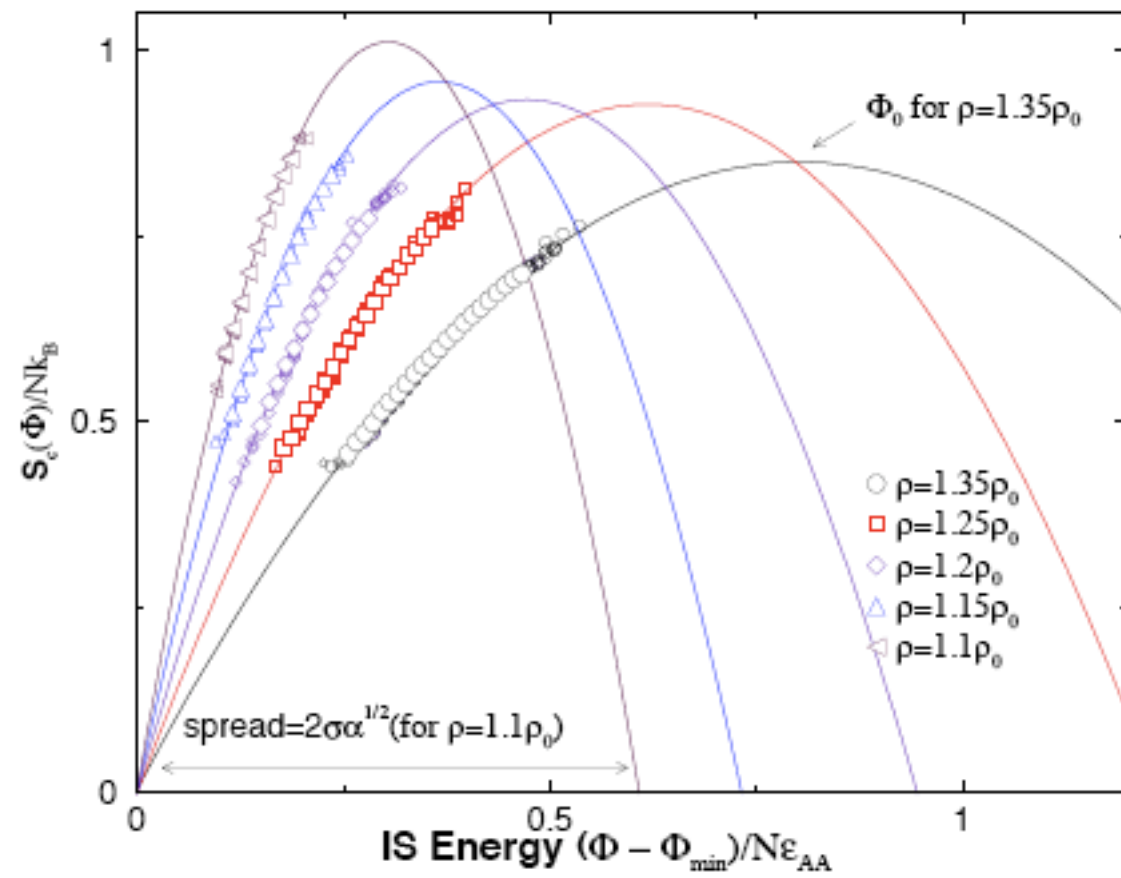
Temperature Dependence of Configurational Entropy:

- TS_c nearly linear with T
- Slope increases with increasing density. Correlates with increase of kinetic fragility.



Inherent Structure Density of States:

- Obtain distributions of energy minima sampled.
- Invert $P(\Phi, T) = \exp[-\beta(\Phi + F_{basin}(\Phi, T) - T\mathcal{S}_c(\Phi))]/Q_N(\rho, T)$ to estimate \mathcal{S}_c .
- DOS assumed to be Gaussian.
- The number of states (α) decreases with density.
- The distribution becomes broader with density.

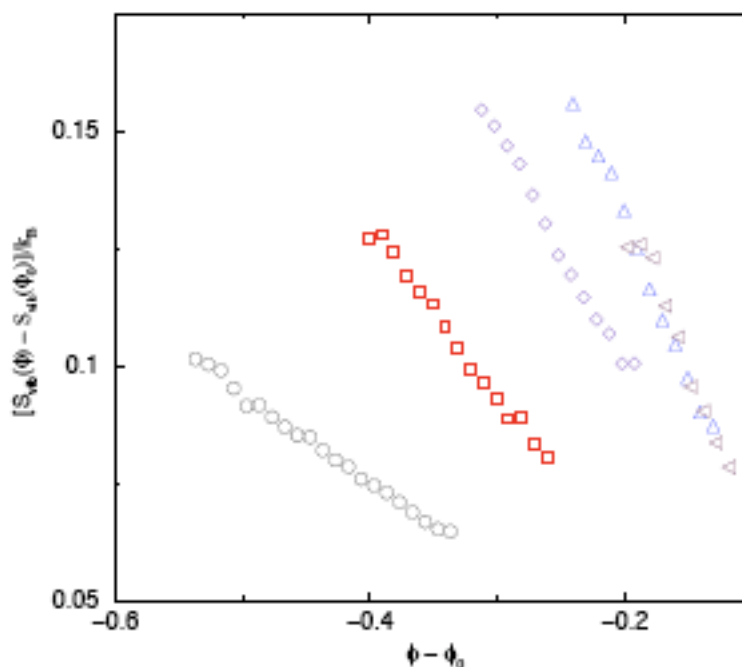


Basin Entropy

- Basin entropies decrease with increasing basin energy:

$$S_{basin} = S_{basin}^0 + \delta S(\Phi - \Phi_0)$$

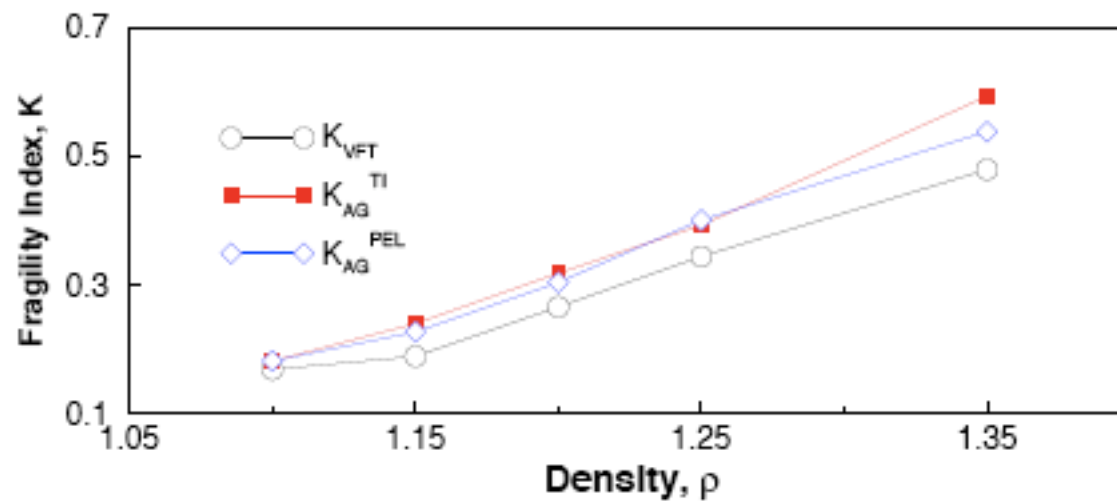
- Rate of change with Φ differs for different densities



Thermodynamic Expression for Fragility

- Configurational entropy obtained in terms of parameters describing the energy landscape:
- $TS_c(T) = K_{AG}^{PEL}(T) (T/T_K - 1)$
- $K_{AG}^{PEL}(T) = \left(\frac{\sigma\sqrt{\alpha}}{2} + \frac{\sigma^2\delta S}{4Nk_B} \right) \left(1 + \frac{T_K}{T} \right) - \frac{\sigma^2\delta S}{2Nk_B}$
- Leads to VFT relation at high temperatures
- When basin entropy changes are negligible, fragility given by breadth of DOS
- Basin entropy changes contribute to fragility
- Common use of ‘excess entropy’ in place of configurational entropy misleading.

Thermodynamic fragility in good quantitative agreement with kinetic fragility.

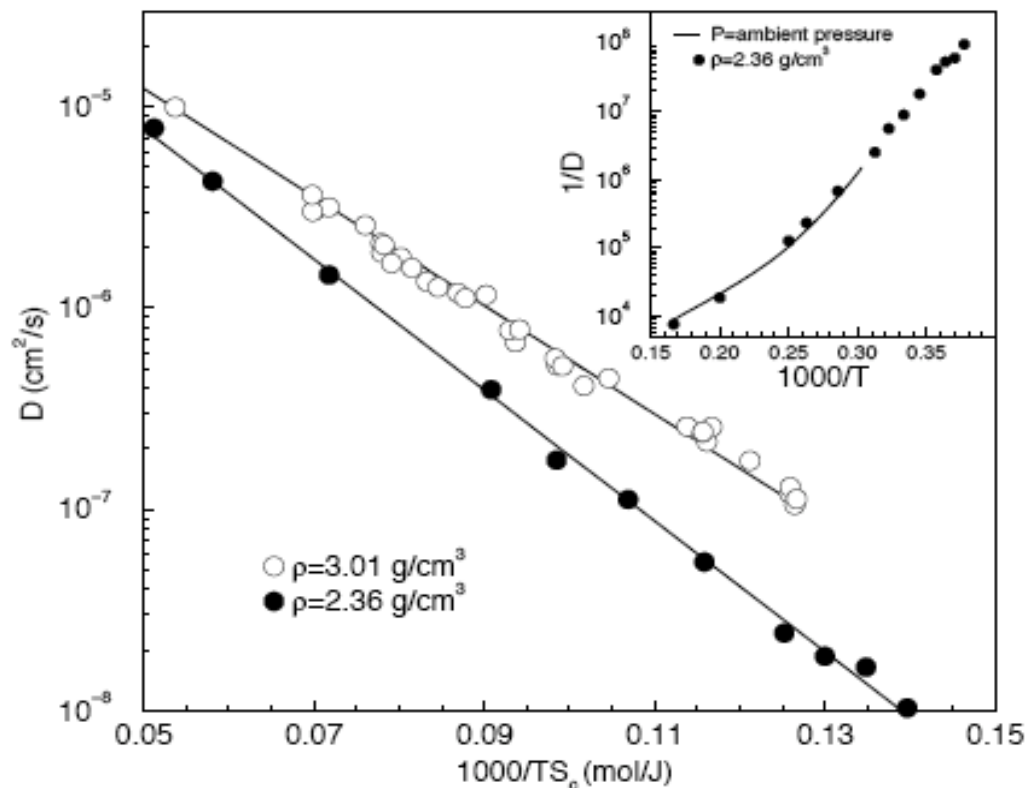


Fragile to Strong crossover

Silica: Archetypal strong liquid.

But shows fragile behavior at high temperatures.

However, diffusivity obeys Adam-gibbs relation.

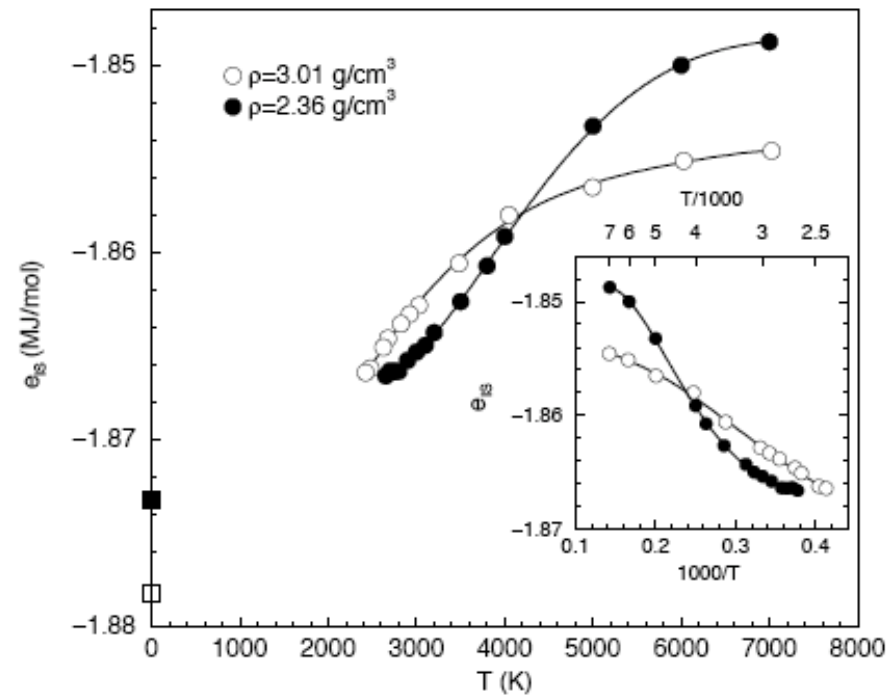


Saika-Voivod 2001

Deviation from $1/T$ dependence of inherent structure energies.

Leveling off of inherent structure energies, leads to strong behavior.

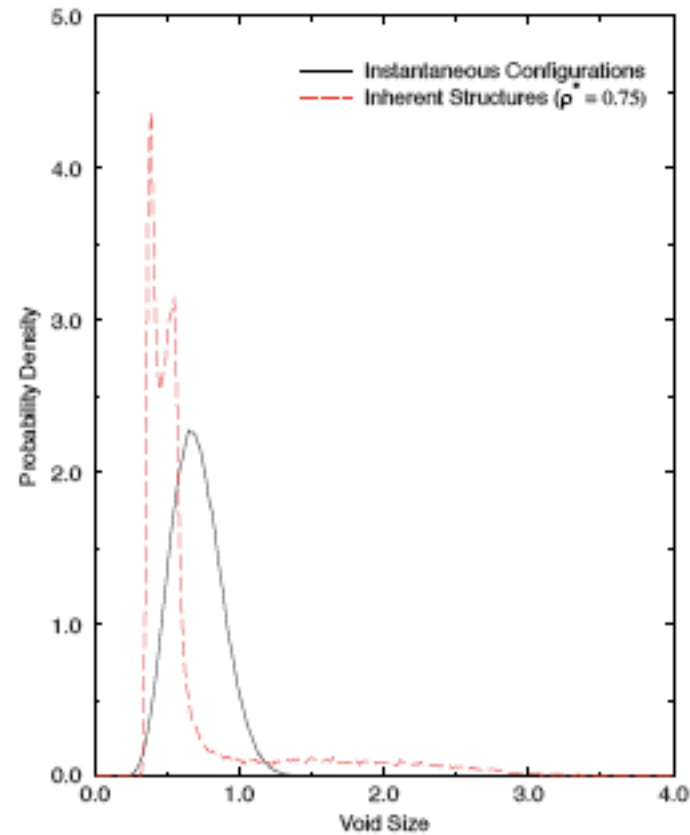
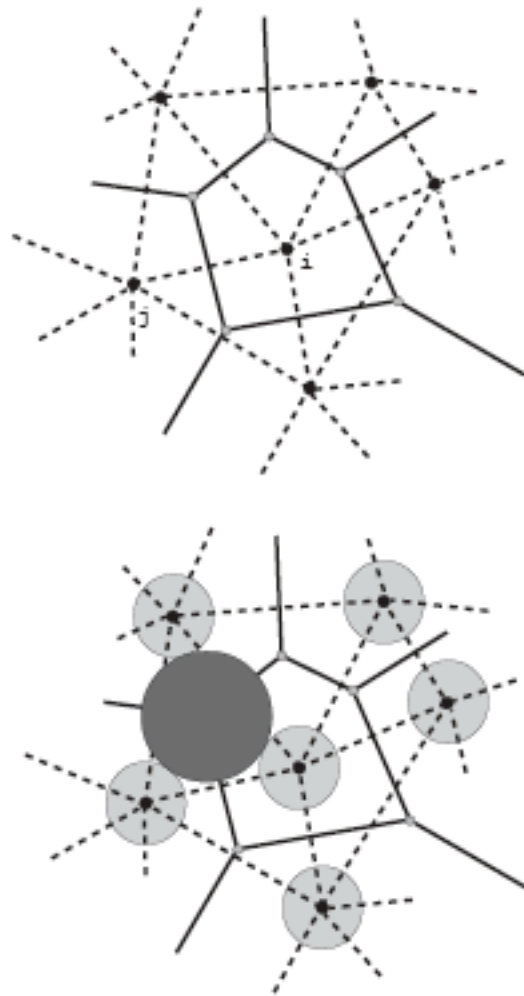
Departure from Gaussian density of states (Saksaengwijit et al 2004)



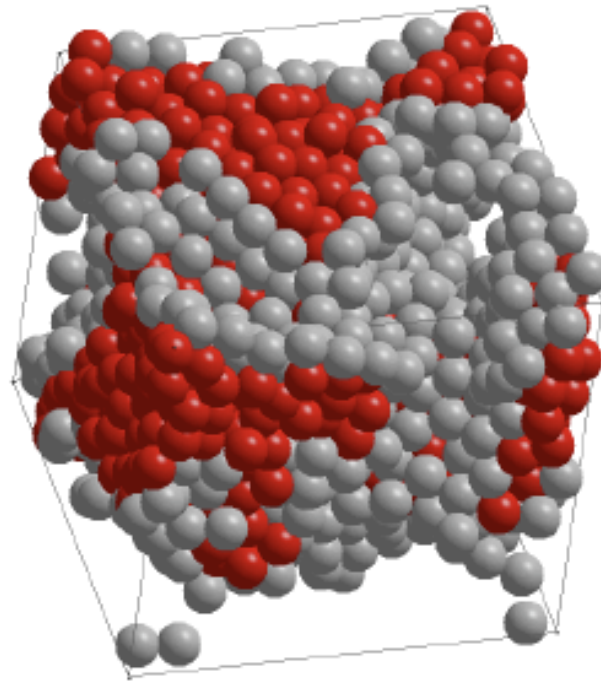
**Liquid limits:
The Glass Transition and Liquid-Gas
Spinodal Boundaries**

Statistical geometry of inherent structures

- Inherent structures (IS) – local energy minimum configurations
- IS for liquids – disordered mechanically stable particle packings
- Statistical geometry through Voronoi analysis – statistics of ‘void sizes’



- Inherent structures display a ‘long tail’ in void size distribution
[Corti et al, 1997; Sastry et al 1997]
- Where does it come from?

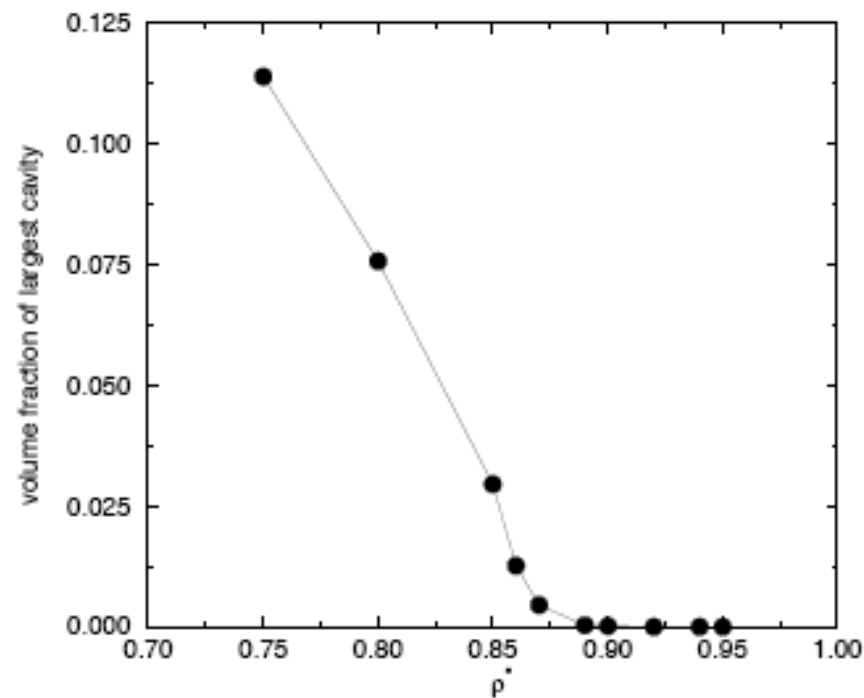


- Heterogeneous or 'fissured' structures
- Red – 'bulk' particles. Grey – 'surface' particles
- Is there a precise way to characterize the structure?

- Algorithm to determine connectivity, cavity volumes etc.

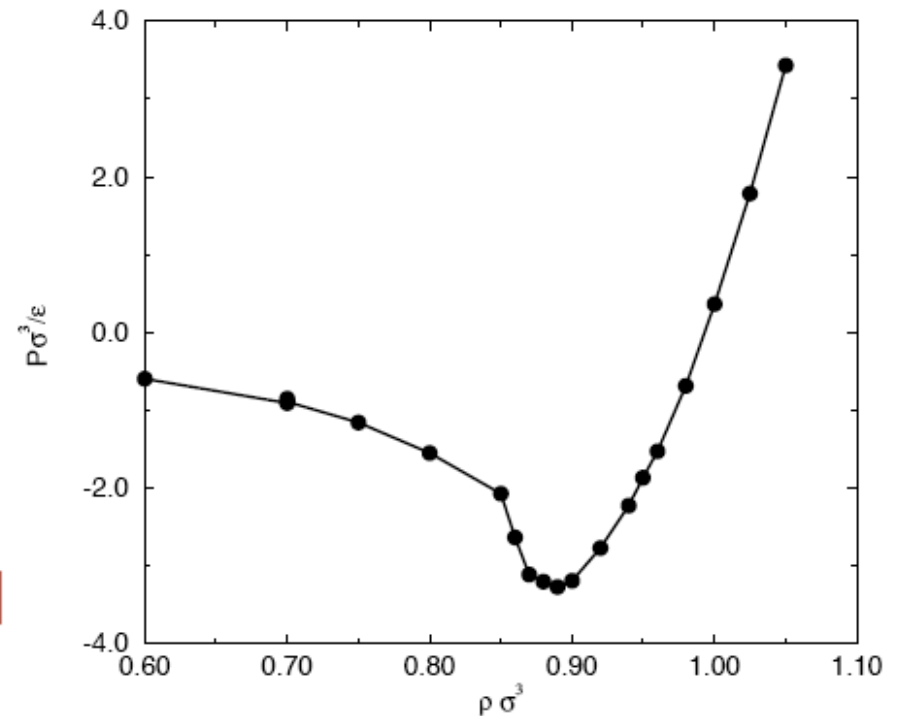
[Sastry et al PRE 56 5524 1997]

- Analysis of inherent structures – bicontinuous structure with ‘system spanning’ cavity below a threshold density $\rho^* \sim 0.89$. Compact structures above.



Inherent structure equation of state

- Calculate the pressure experienced by the inherent structures vs. density
- Non-monotonic pressure dependence.
- Minimum of the pressure at ρ^* !



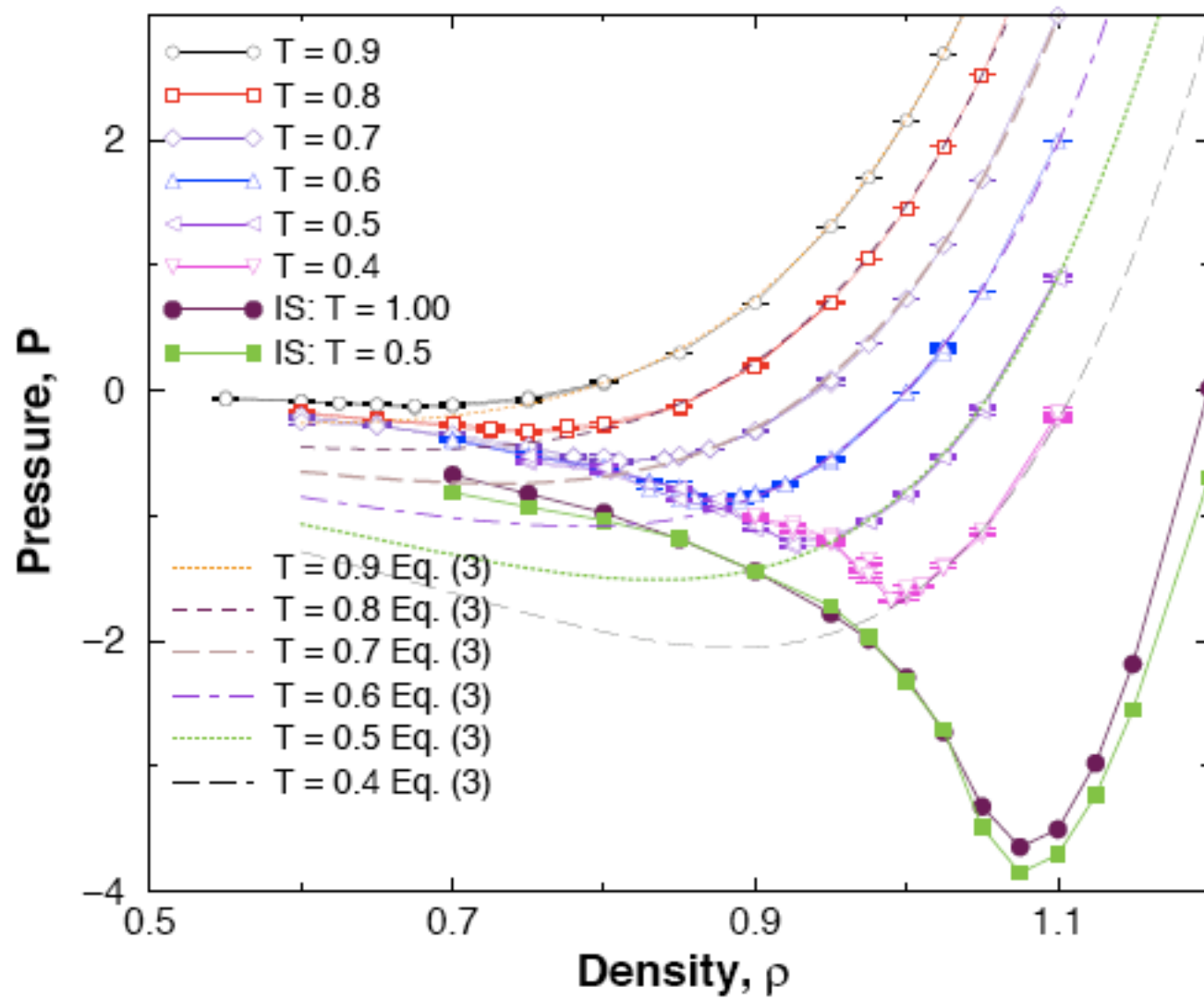
[Sastry et al, PRE 56 5533 1997]

Questions

- Is ρ^* the $T = 0$ limit of the liquid-gas spinodal?
- Does ρ^* define the low density limit to glass formation?
- Do the spinodal and glass transition lines meet at zero or finite T ?

Calculation of the liquid - gas spinodal

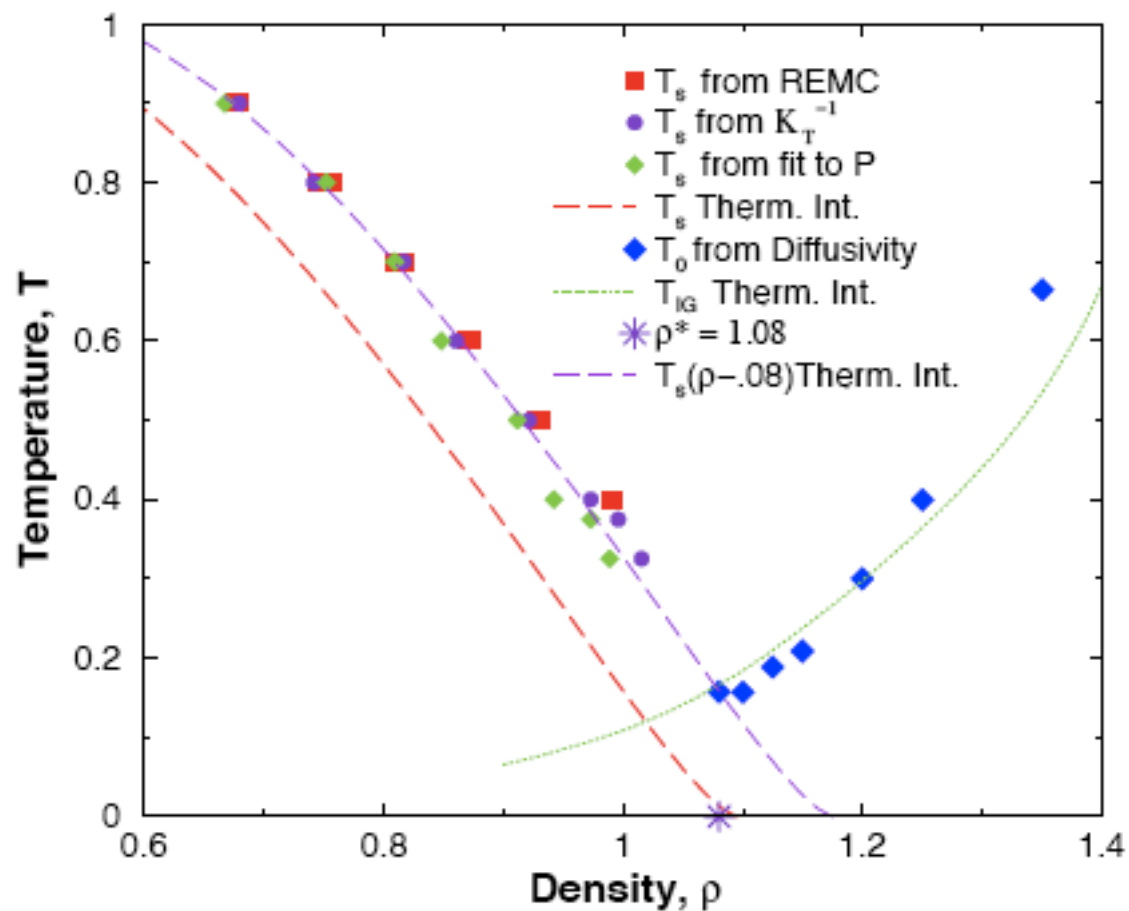
- Simulations for Kob-Andersen binary LJ mixture. $\rho^* = 1.08$.
- 1. Restricted Ensemble Monte Carlo (REMC) [constrain density fluctuations]. Locate pressure minima along isotherms.
- 2. Extrapolate isothermal compressibility from 'normal' MC and MD data.
- 3. Polynomial fits to pressure vs. ρ data. Locate minima.
- 4. Empirical equation of state – liquid free energy from simulation data, via thermodynamic integration, and fits to potential energy of the form $E_0 + E_1 T^{E_2}$ [Rosenfeld and Tarazona prediction of $E_2 = 3/5$]



[Sastry, PRL 85 590 2000]

Calculation of the glass transition line

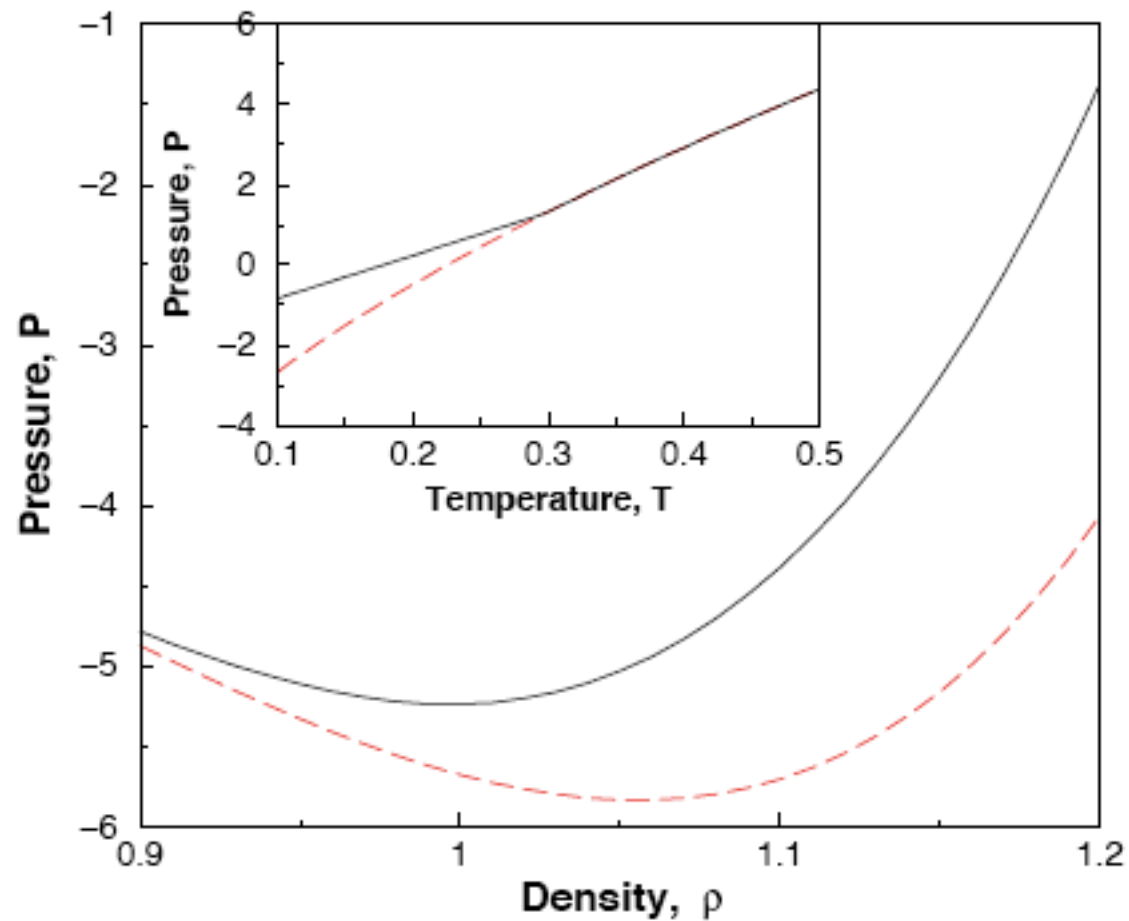
- 1. From VFT extrapolation of diffusivities $D(T) = D_0 \exp(\frac{A}{T-T_0})$.
- 2. Thermodynamic estimate based on inherent structure approach –
- $Q(\rho, T) = \int d\Phi \exp[-\beta(\Phi + F_{basin}(\Phi, T) - TS_c(\Phi))] / Q_N(\rho, T)$
- Total free energy $F(\rho, T) = \Phi + F_{basin} - TS_c$
- At each ρ, T , total free energy from thermodynamic integration.
- Basin free energy from harmonic approximation to minima.
- $S_c(T_K) = S_{total} - S_{basin} = 0$ defines the glass transition line.



Liquid-gas spinodal and glass transition line intersect at finite T !

Behaviour below temperature of intersection

Prediction of Glass-gas limit of mechanical stability.



Integral Equation/Mezard-Parisi method calculation of T_s and T_K

- **Motivation:** Seek support for the simulation based calculations based on calculations by other methods.
- **What we do:** Following Coluzzi *et al* , we perform calculations based on
 - The Zerah-Hansen scheme to solve for the liquid $g(r)$ to obtain the equation of state, and the spinodal line.
 - The Mezard-Parisi method for calculating configurational entropy, and the glass transition line.

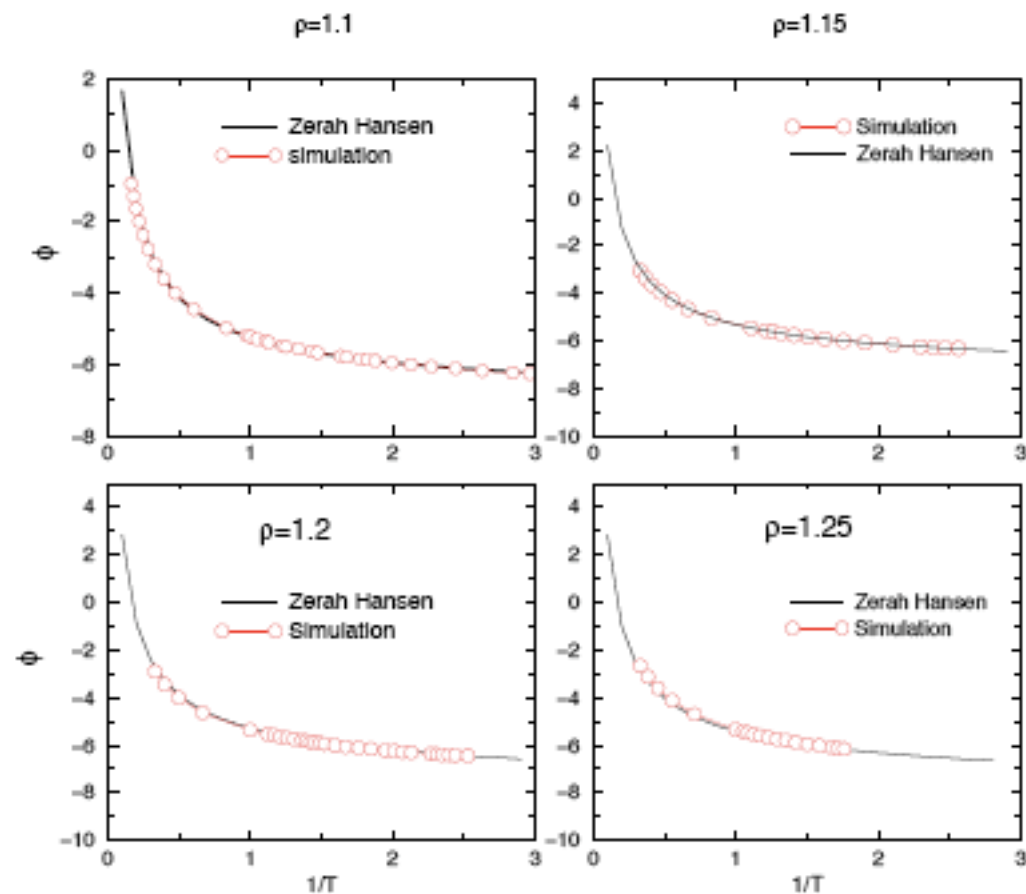
Zerah Hansen liquid state calculation

- Ornstein-Zernicke relation: $h(r) = c(r) + \rho h(r) * c(r)$
- “Exact closure”: $g(r) = \exp[-\beta v(r)] \exp[h(r) - c(r) + B(r)]$
- $B(r) = 0$ – HNC
- $g(r) = \exp[-\beta v(r)] [1 + h(r) - c(r)]$ – PY
- $g(r) = \exp[-\beta v_1(r)] [1 + h(r) - c(r) - \beta v_2(r)]$ – SMSA
- $g(r) = \exp[-\beta v_1(r)] \left(1 + \frac{\exp[f(r)\{h(r) - c(r) - \beta v_2(r)\}] - 1}{f(r)} \right)$ – Zerah-Hansen
- $f(r) = 1 - \exp(-r/k)$ – switching function

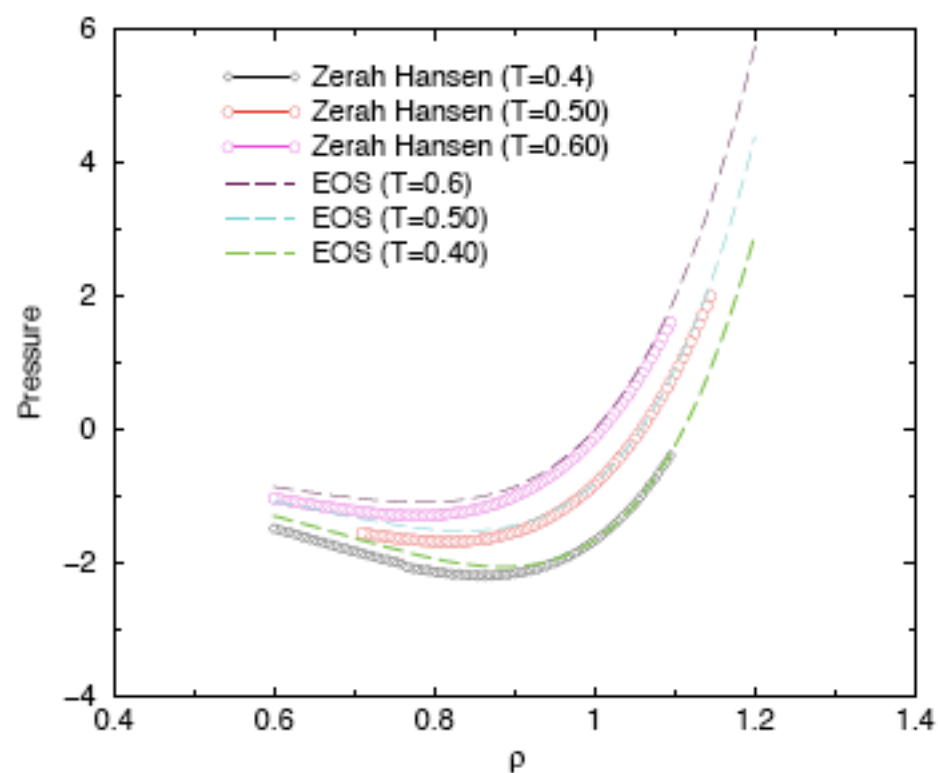
- Switching parameter k interpolates between SMSA ($k \rightarrow \infty$; small distances) and HNC closures ($k \rightarrow 0$; large distances) of Ornstein-Zernicke relation.
- Chosen by Zerah-Hansen to match virial and compressibility EOS.
- We choose $k = 11.17 - 11.7\rho + 6.65\beta$ to match simulation data over some density and temperature range.

Comparison of results

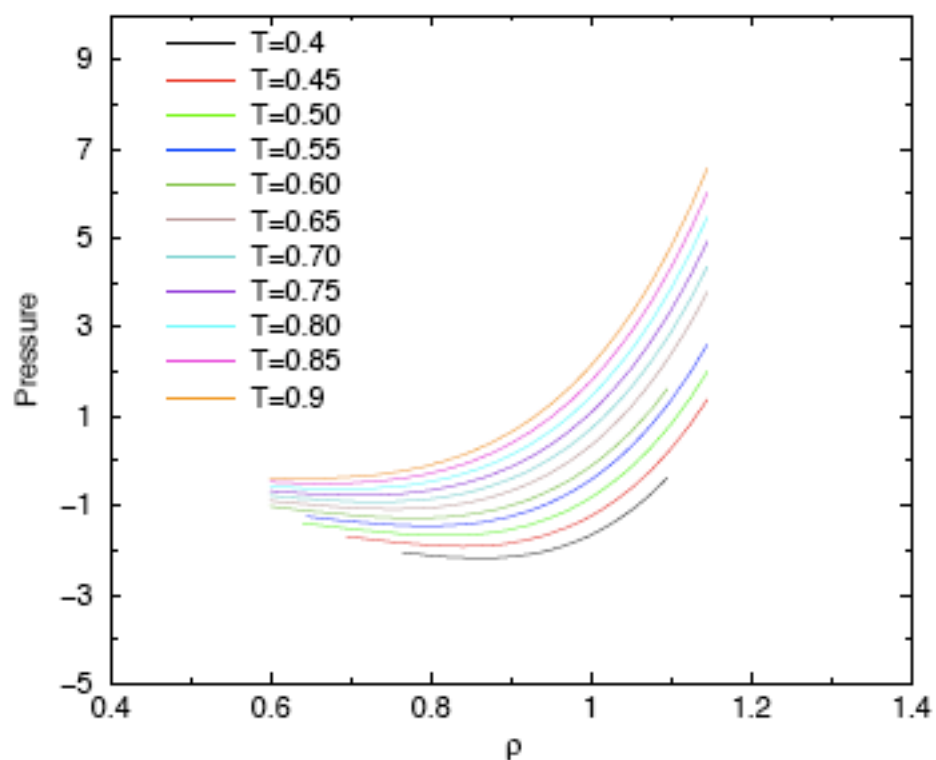
- Good agreement between equation of state and energy vs temperature between simulation and present calculation.



- Pressure not as good, but reasonable. Comparison is with empirical EOS constructed earlier with simulation data.



- Spinodal densities are estimated from the location of the minima of the isotherms.

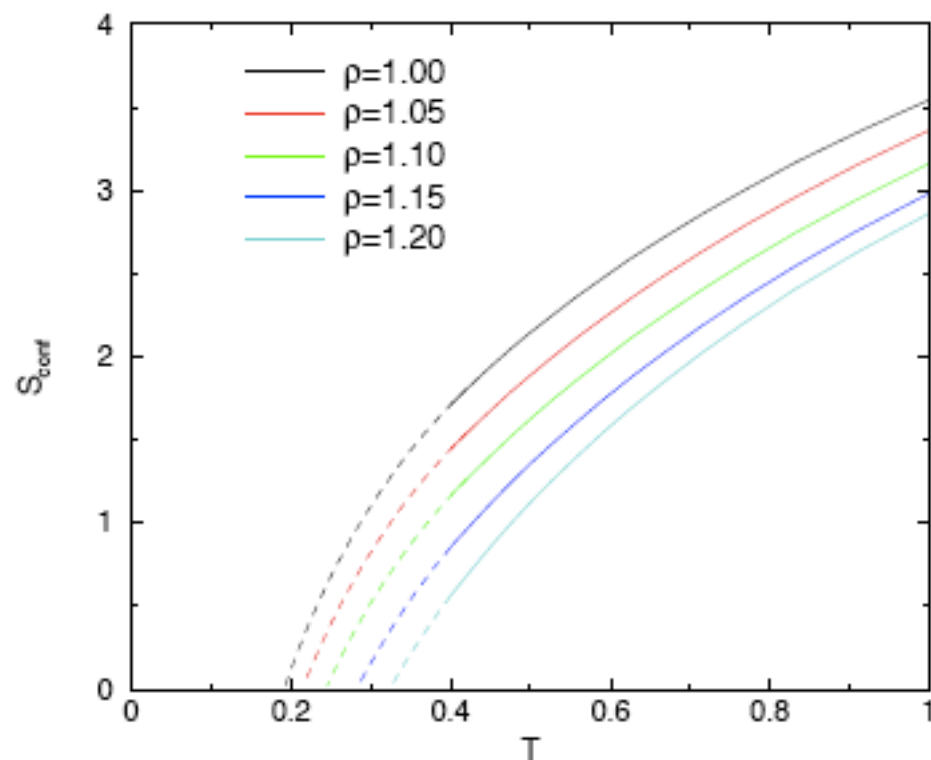


Mezard Parisi Method

- Thermodynamic theory for the glass transition employing a system of m coupled replicas of the liquid.
- Glass transition condition translates to liquid's entropy = "solid entropy" calculated through the curvature matrix.

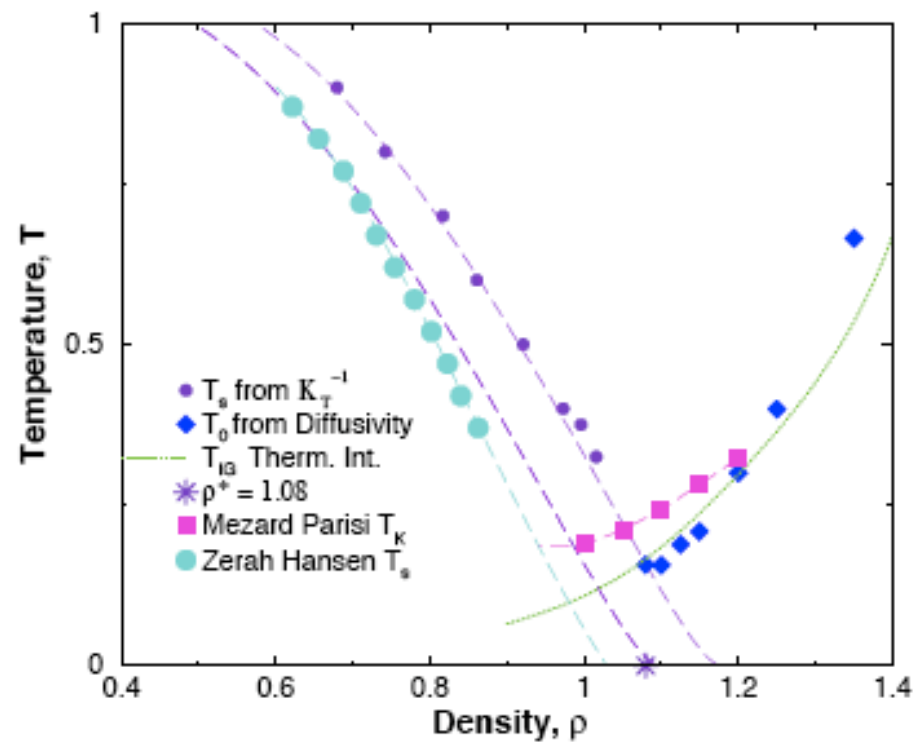
Glass Transition

- Estimates of glass transition by $S_c = 0$ as before.
- ZH equations cannot be solved to the lowest temperatures. We extrapolate with $E \sim T^{3/5}$ as done by Coluzzi *et al* before.



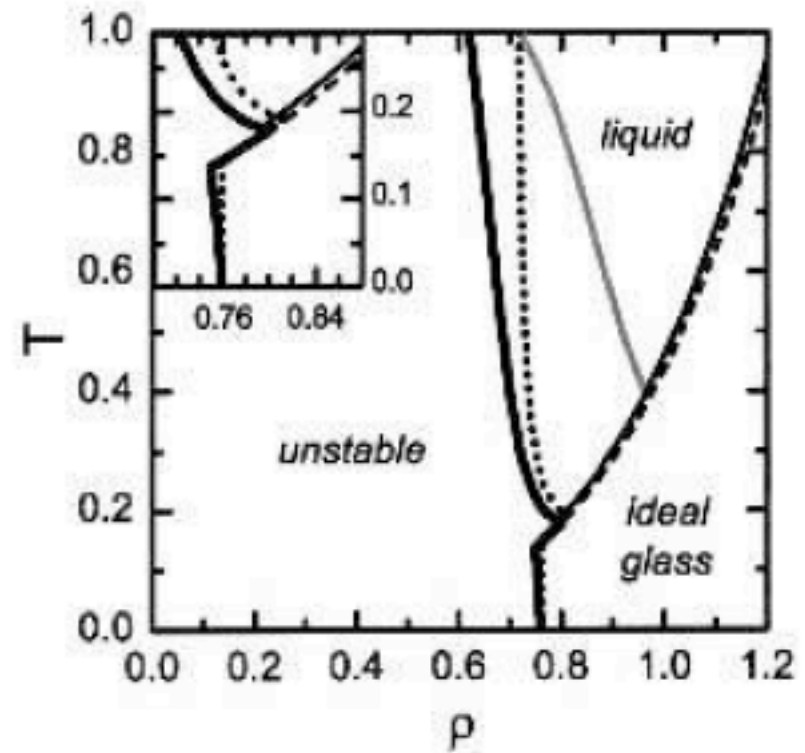
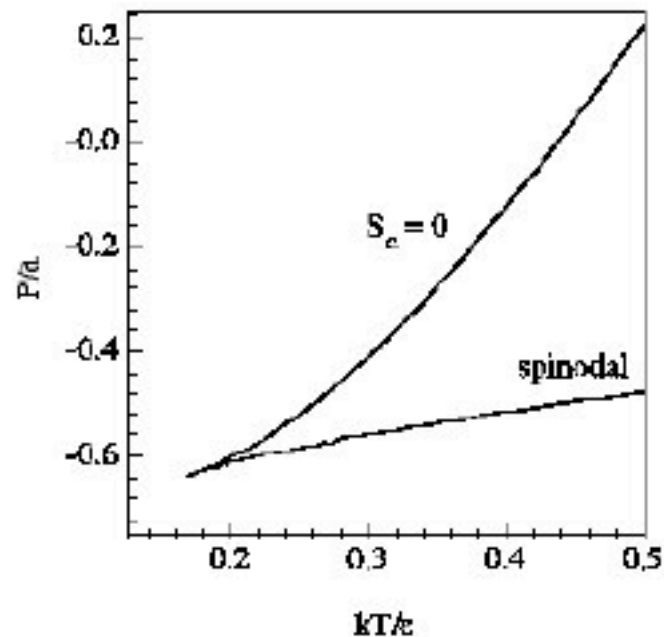
Phase diagram

- Finite T intersection of spinodal and glass transition lines.
- Agreement only qualitative. Location of spinodal, glass transition line shifted by a considerable amount.



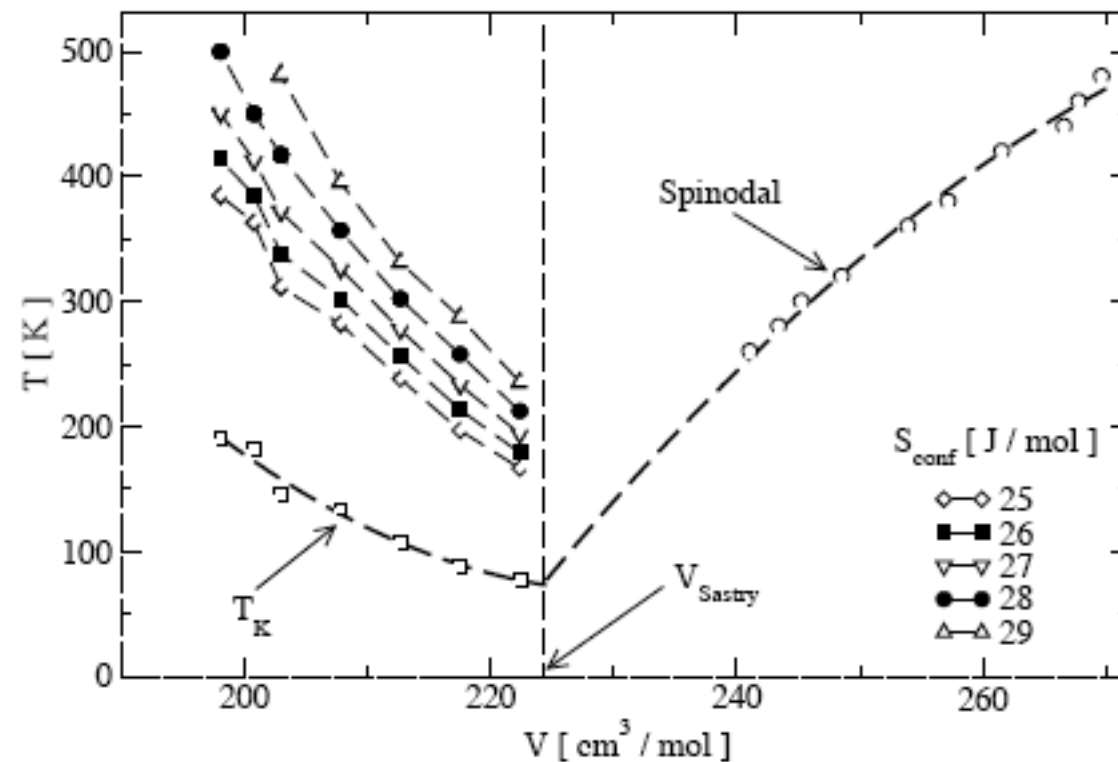
Results from other work

- Calculation for soft spheres (Speedy 2003; Shell and Debenedetti PRE 2004) confirm the same scenario:



Results from other work II

- Simulation study of a model of OTP (La Nave *et al* JCP 2004) also confirm the same scenario:



Summary

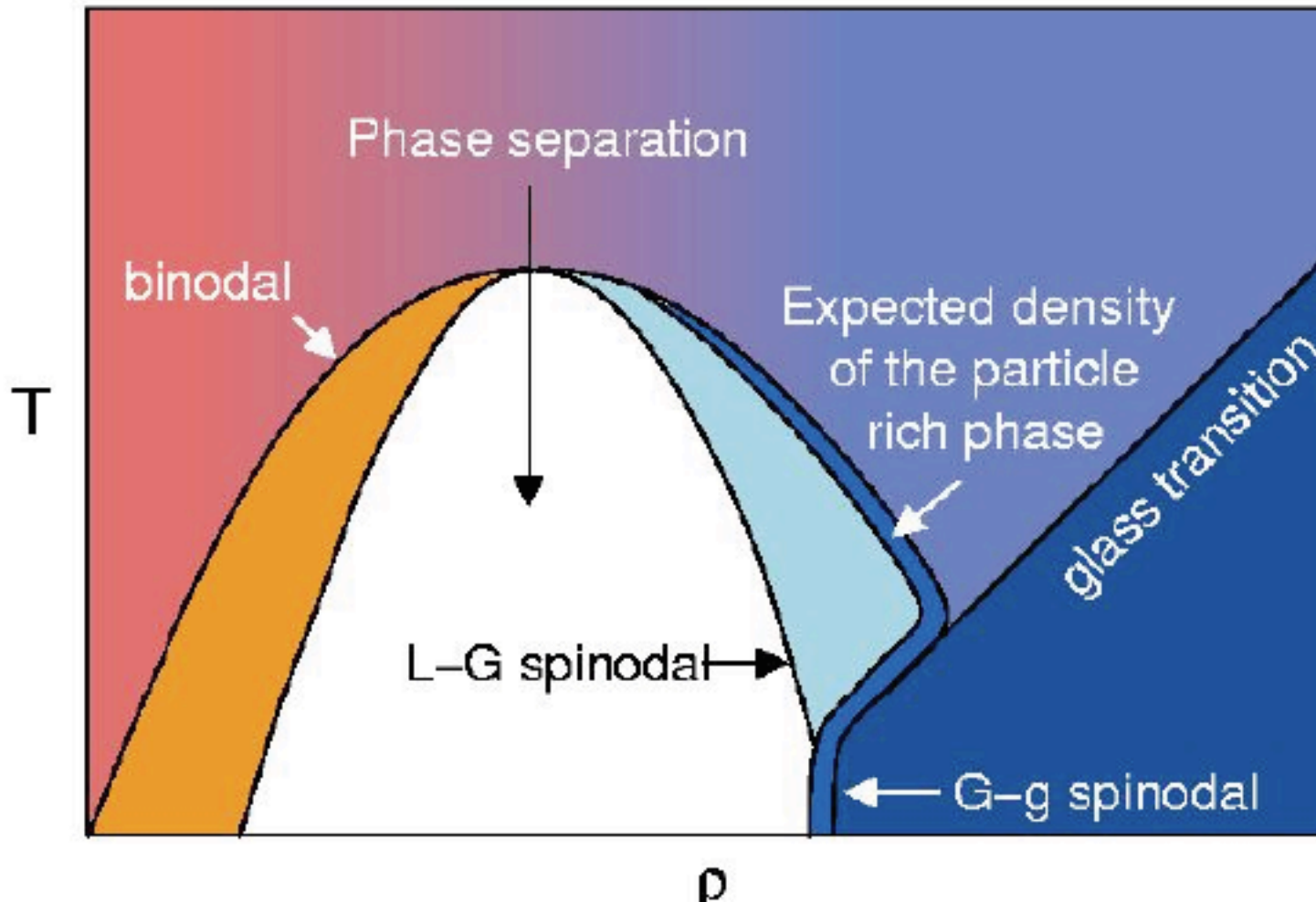
Simulation results and calculations predict a finite T intersection of liquid-gas spinodal and glass transition lines

The intersection occurs at the density where IS pressure displays a minimum.

Glass-gas limit of mechanical stability at low T

Calculations using liquid state theory and the Mezard Parisi approach to the glass transition yield results that are in qualitative, but modest quantitative, agreement.

What to expect from quench into unstable region?



Prediction of intersection of glass transition and spinodal lines relevant for structural arrest during phase separation (gelation)

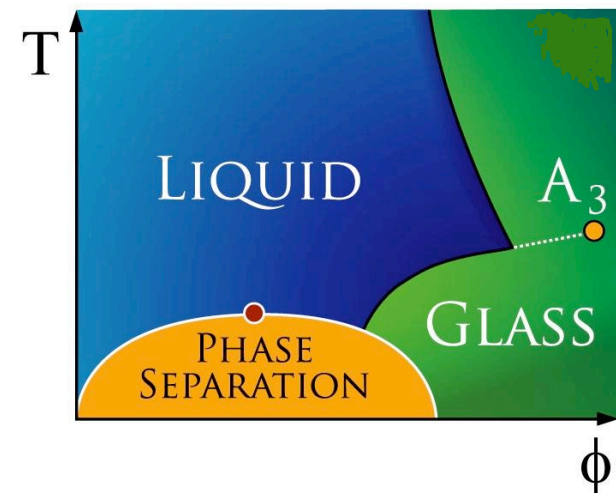
Phase diagram of spherical potentials*

Borrowed from
Sciortino ACS

$$0.13 < \phi_c < 0.27$$



[if the attractive range
is very small ($<10\%$)]

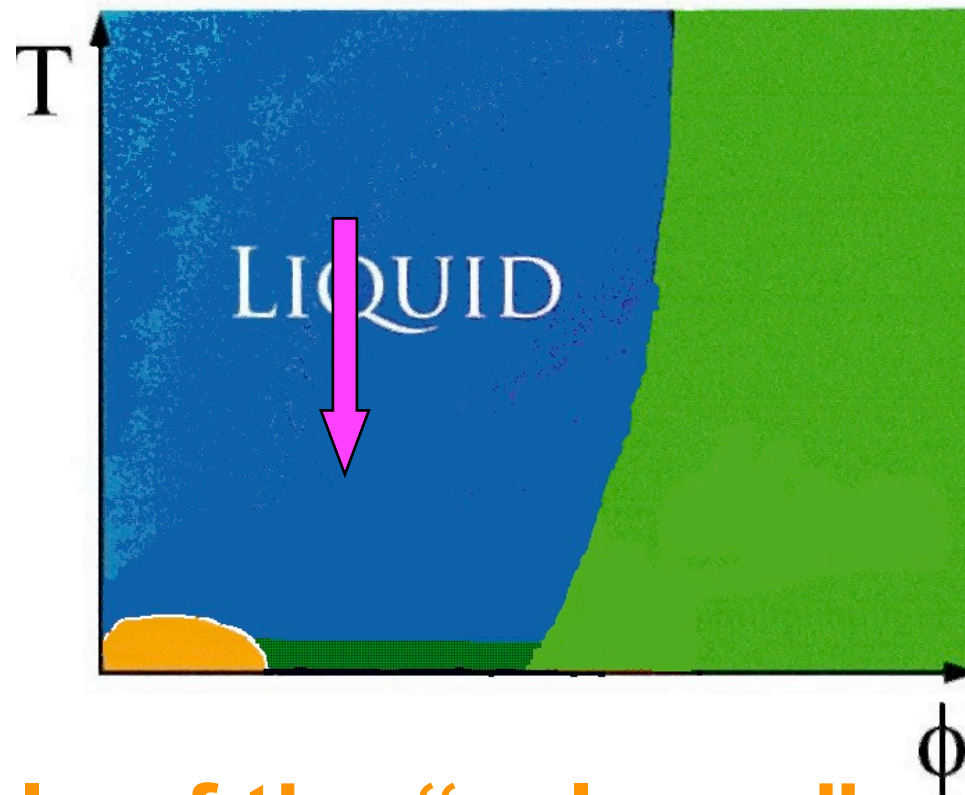


* “Hard-Core” plus attraction

(Foffi et al PRL **94**, 078301, 2005)

How to go to low T at low ϕ
(in metastable equilibrium) ?
Are there other possible scenarios?

How to suppress phase separation ?

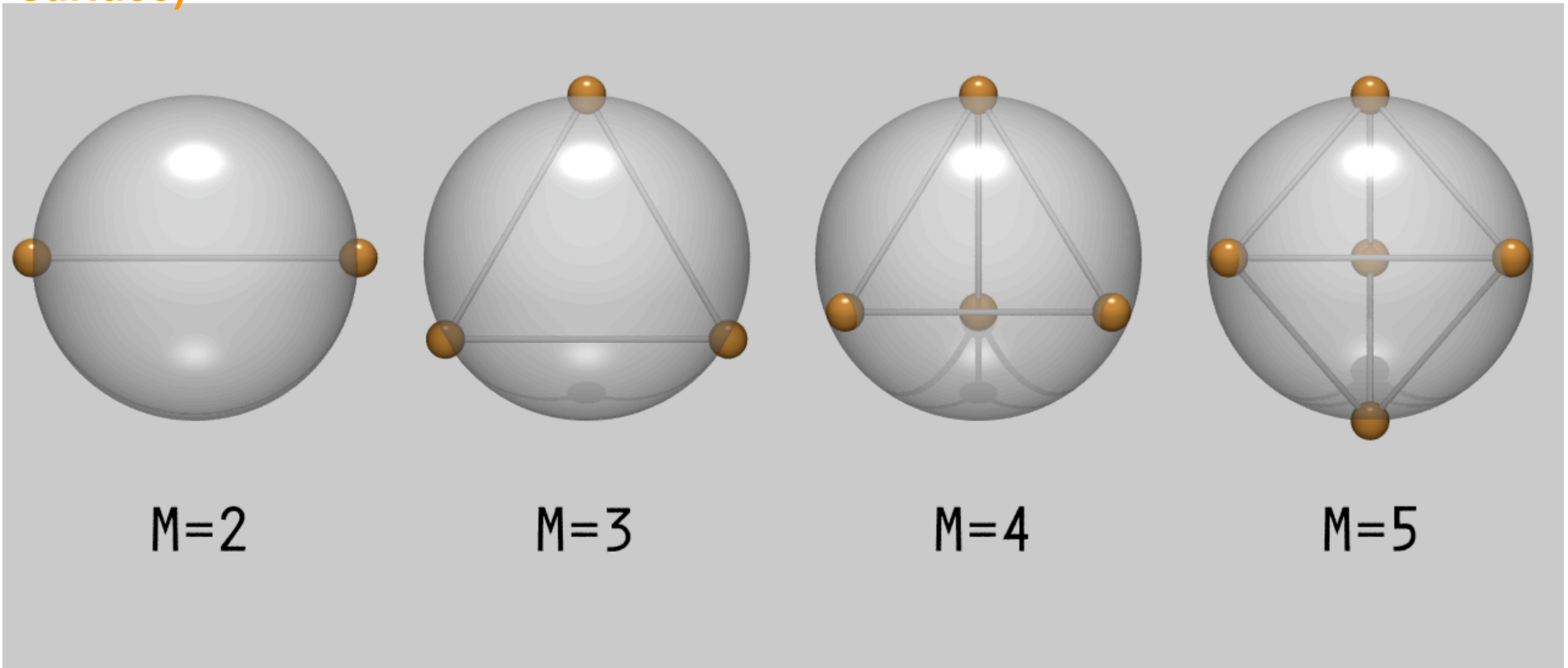


-The role of the “valence”

Borrowed from
Sciortino ACS

Valence-Controlled Patchy particles

maximum # of “bonds”, (as opposed to # patches, fraction of bonding surface)



Hard-Core (gray spheres) Short-range Square-Well (gold patchy sites)

Borrowed from
Sciortino ACS

No dispersion forces
The essence of bonding !!!

Metabasins

Transitions between inherent structure basins are correlated.

One must consider ways of grouping inherent structures so that transitions between them – metabasins – can be analyzed to develop a model of dynamics. [Heuer et al 2003 -]

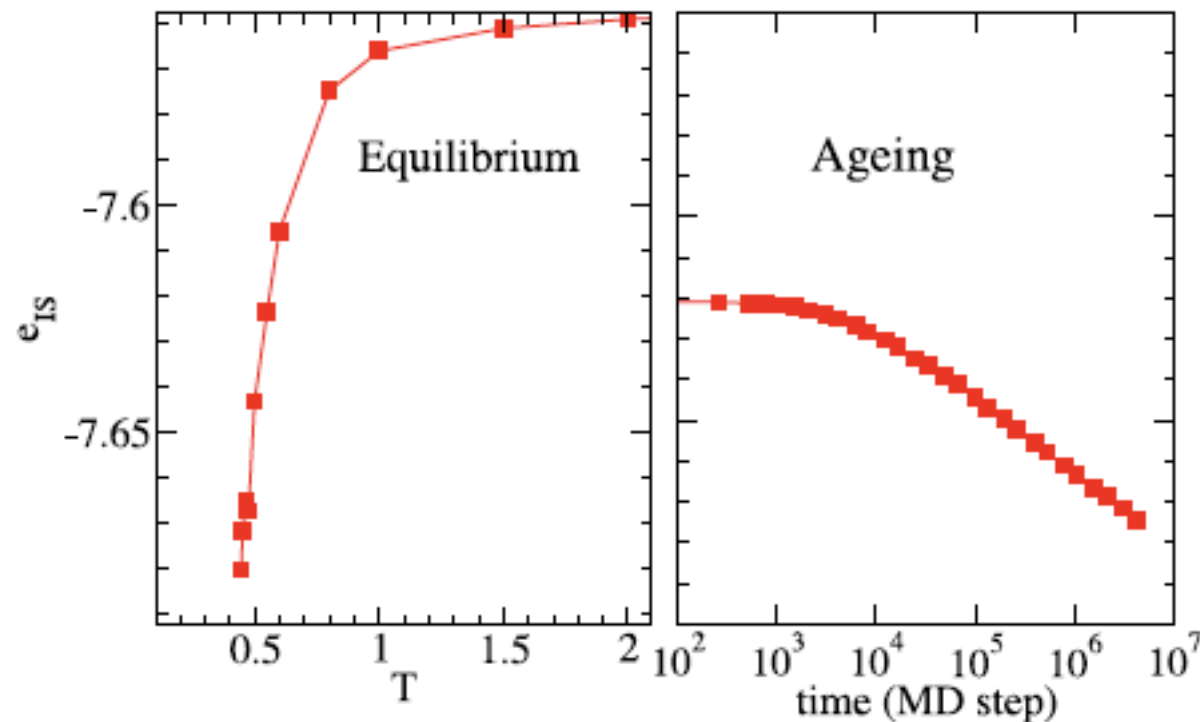
Effective activation energy associated with dynamics.

Description of dynamics in terms of effective activation energies.

Metabasins identified through dynamics of the system [Wales lecture for identification through disconnectivity graphs]

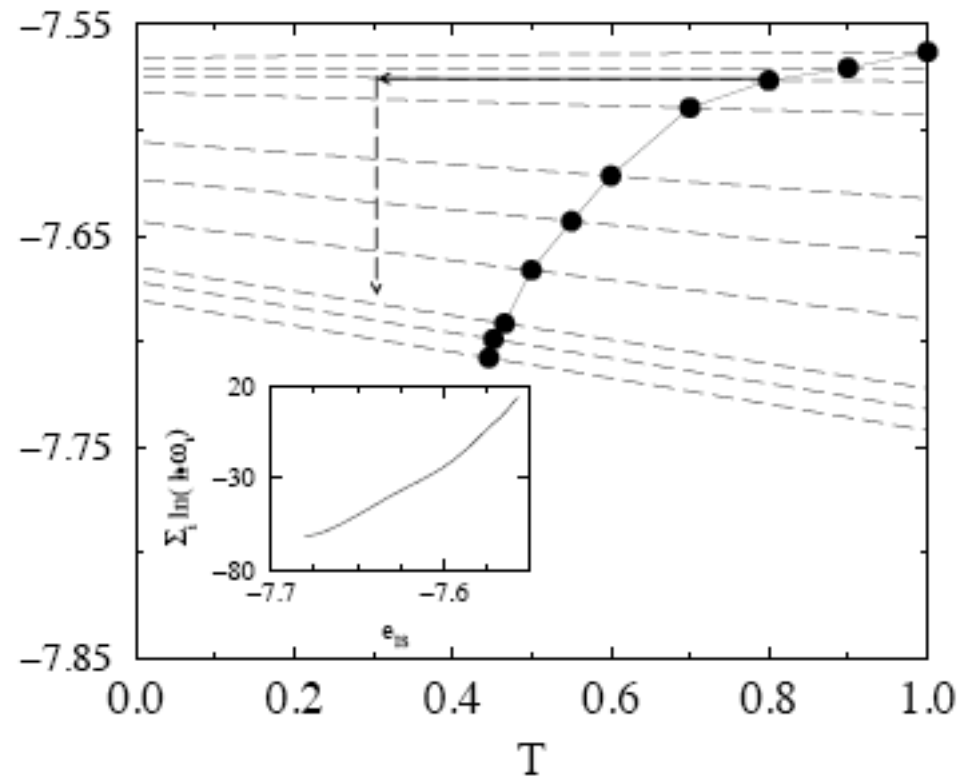
Analysis of aging from energy landscape picture

The separation of time scales between relaxation within basins of a minimum and relaxation from hopping between minima suggests the use of IS energies as a way of identifying the effective temperature experienced by the system.



Sciortino and Tartaglia 2001 and subsequent papers by them with co-workers.

Upon a temperature quench, the system rapidly relaxes within a given basin, and relaxes to an equilibrium sampling of basins on a much longer time scale.



Writing the total free energy of the system as

$$F(T) = -T S_{conf}(e_{IS}(T)) + f_{basin}(T, e_{IS}(T))$$

One can obtain the equilibrium condition by

$$\frac{\partial F}{\partial e_{IS}} = -T_{eq} \frac{\partial S_{conf}(e_{IS})}{\partial e_{IS}} + \frac{\partial f_{basin}(T_{eq}, e_{IS})}{\partial e_{IS}} = 0$$

If e_{IS} does not correspond to the equilibrium value, what are the relevant temperatures?

For the basin free energy it is the equilibrium temperature.

For the first term, assume that this is an 'internal temperature' to be determined by imposing the observed value of e_{IS} :

$$T_{int}(e_{IS}, T_f) = \frac{1 + \frac{\partial}{\partial e_{IS}} f_{vib}(T_f, e_{IS})}{\frac{\partial}{\partial e_{IS}} S_{conf}(e_{IS})}$$

FDT ratio: Test using computer simulation, using perturbation Hamiltonian:

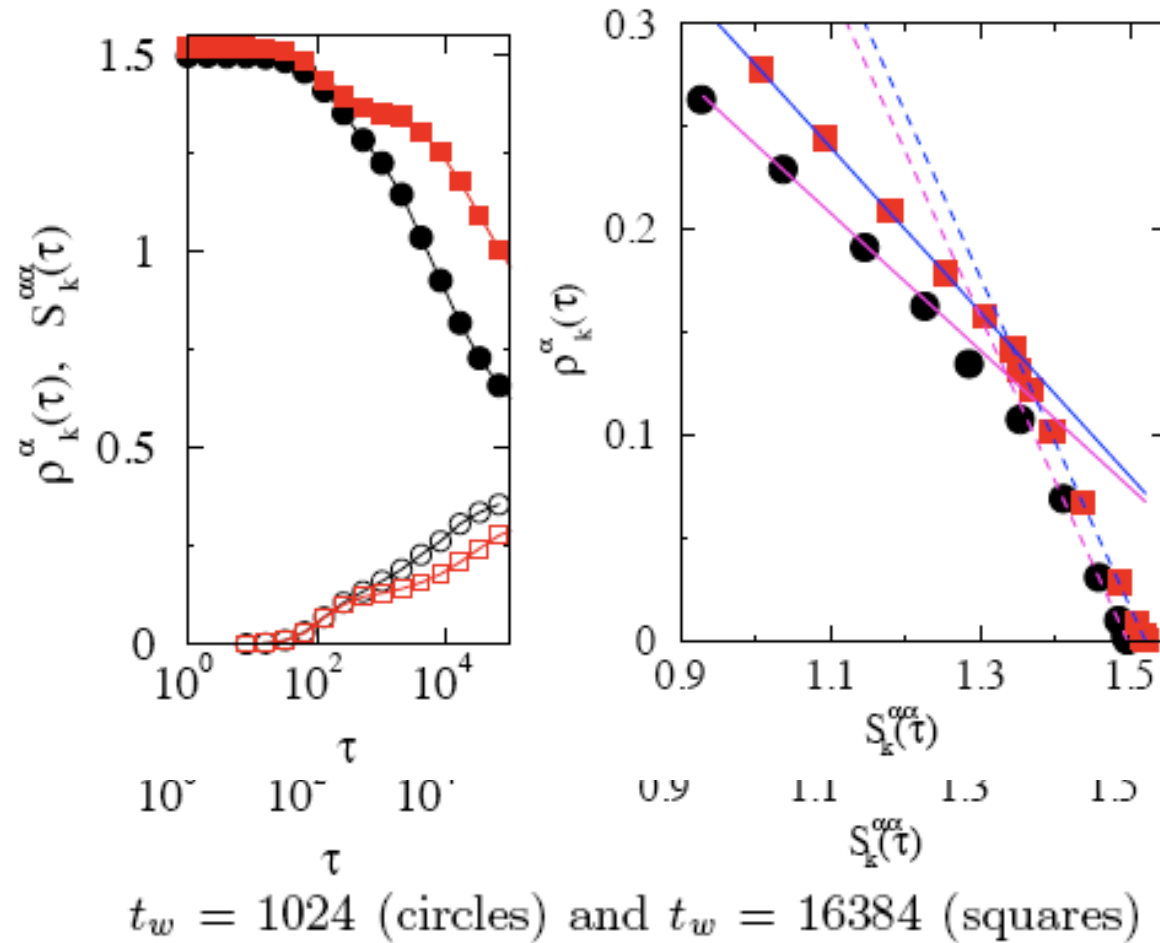
$$H_P = -V_o B(\mathbf{r}^N) \theta(t-t_w)$$

with $A \equiv \rho_{\mathbf{k}}^\alpha$ $B \equiv (\rho_{\mathbf{k}}^\alpha + \rho_{\mathbf{k}}^{\alpha*})$

FDT relation $\langle A(\tau) \rangle = -\frac{V_o}{k_B T} [\langle A(\tau) B(0) \rangle_0 - \langle A(0) B(0) \rangle_0]$

Becomes $\langle \rho_{\mathbf{k}}^\alpha(\tau) \rangle = -\frac{V_o}{k_B T} [S_{\mathbf{k}}^{\alpha\alpha}(\tau) - S_{\mathbf{k}}^{\alpha\alpha}(0)]$

with $S_{\mathbf{k}}^{\alpha\alpha}(t) \equiv \langle \rho_{\mathbf{k}}^\alpha(t) \rho_{\mathbf{k}}^{\alpha*}(0) \rangle_0$



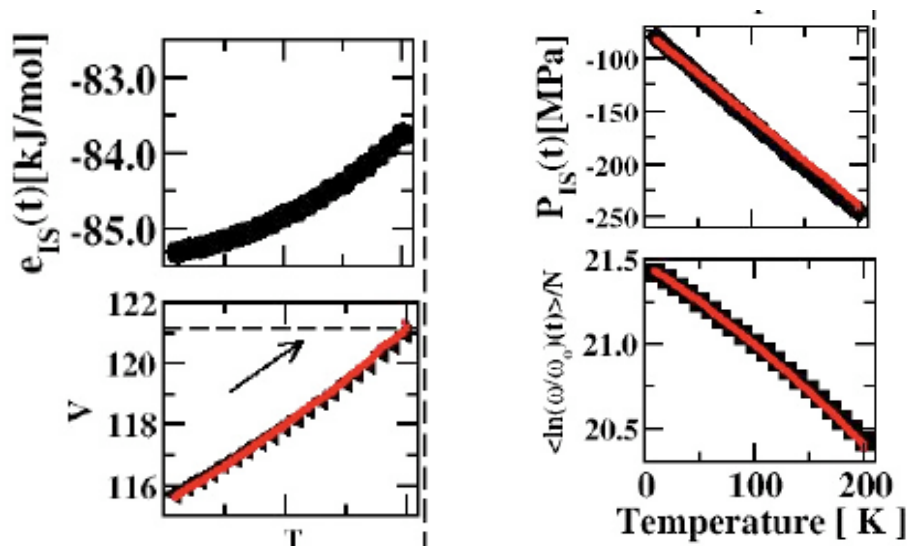
The lines, calculated from the bath and internal temperatures, agree with observed slopes!

Does that mean the the IS energy can be used as a good fictive parameter? One can write a out-of-equilibrium free energy, as

$$F(T_{\text{eff}}, T, V) = -T_{\text{eff}} S_{\text{conf}}(e_{\text{IS}}) + f_{\text{basin}}(e_{\text{IS}}, T, V).$$

And the volume derivative, with a known time dependent e_{IS} as input, should predict, eg, the pressure of an OOE system:

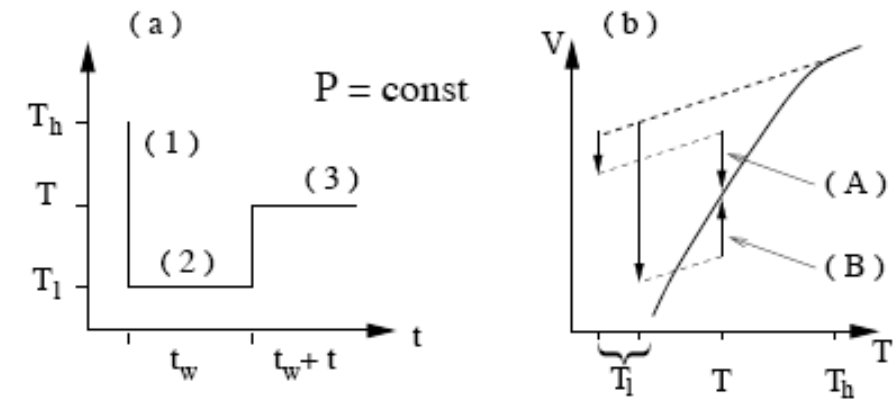
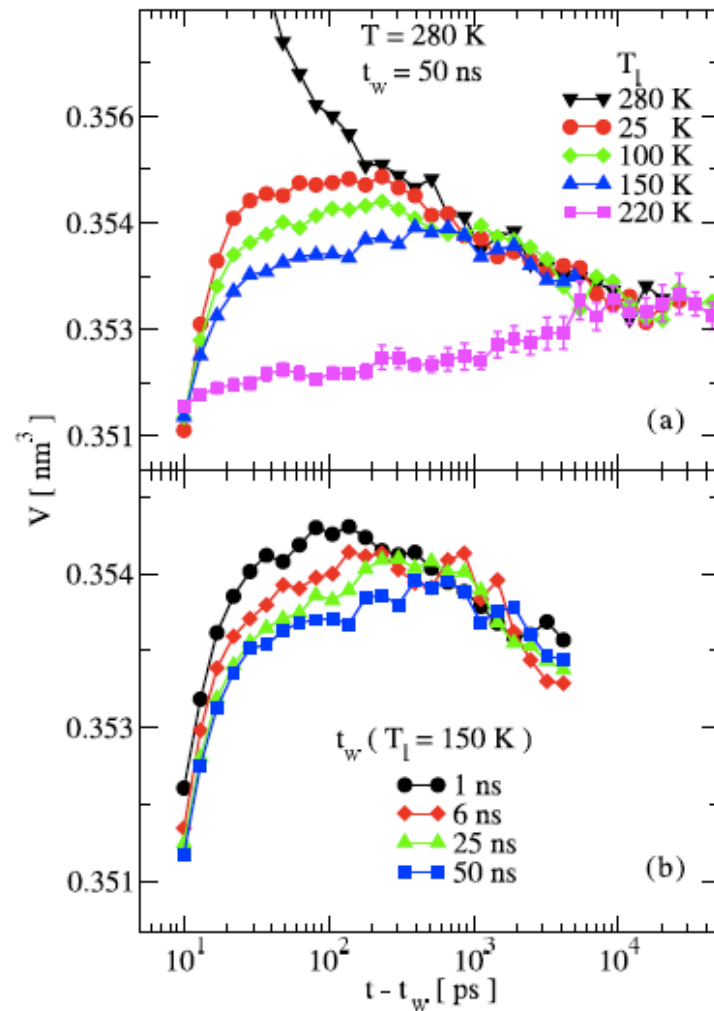
$$P(T_{\text{eff}}, T, V) = T_{\text{eff}} \left. \frac{\partial S_{\text{conf}}(e_{\text{IS}})}{\partial V} \right|_{T, T_{\text{eff}}} - \left. \frac{\partial f_{\text{basin}}(e_{\text{IS}}, T, V)}{\partial V} \right|_{T, T_{\text{eff}}}$$



Works quite well.

Mossa et al 2002 – 04]

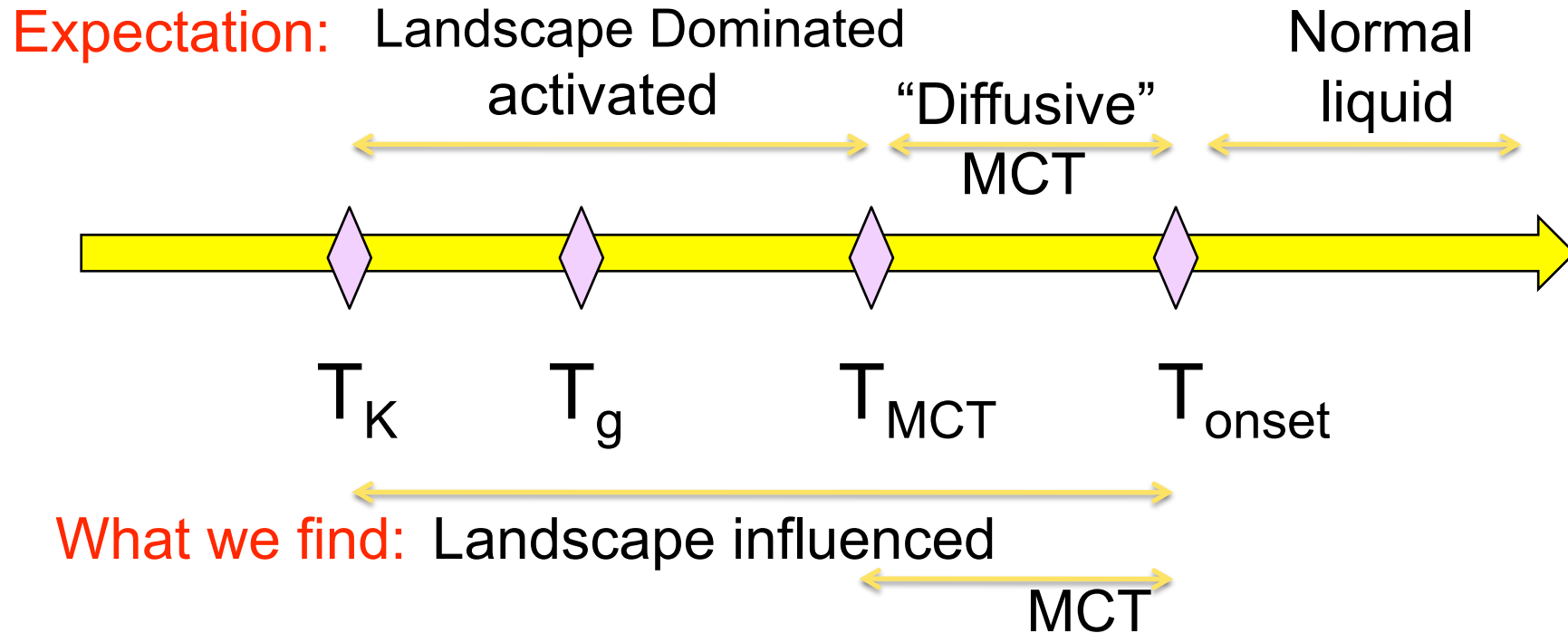
But in general, this should not work, as illustrated by the Kovacs crossover experiment:



At the same T , P , V , the time evolution of the system is history dependent.

Mossa et al 2004]

Another puzzle..



Puzzle: MCT and landscape descriptions appear to apply in the same temperature regime.

Possible solution: Mixing of mechanisms (MCT + hopping)
[Bhattacharyya, Bagchi, Wolynes PNAS 2008]

Outlook

Analysis of dynamics in liquids through the energy landscape provides a useful way of understanding processes leading to relaxation.

However, a satisfactory dynamical description is lacking.

No satisfactory rationalization of Adam-Gibbs relation through this approach yet, though central to many studies.

The observed significance of the sampling of the potential energy landscape to the dynamics of the liquid below the onset temperature, well above the Goldstein crossover is in need of better understanding.

Some reviews and references:

1. F. Sciortino, Lecture notes for the School on ``Unifying Concepts in Glass Physics III'' Bangalore, June 2004, *J. Stat. Mech.*, P05015 (2005)
2. A. Heuer, *J. Phys. Cond. Mat.*, **20**, 373101 (2008)
3. "Energy Landscapes" by D.J. Wales, Cambridge University Press (Cambridge) (2003)
4. D.J. Wales et. al., *Adv. Chem. Phys.*, **115**, 1, (2000)