LECTURE 11 : GLASSY DYNAMICS

- Intermediate scattering function
- Mean square displacement and beyond
- Dynamic heterogeneities
- Isoconfigurational Ensemble
- Energy landscapes

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A) INTERMEDIATE SCATTERING FUNCTION

Instead of considering correlations in space, one can perform a study in reciprocal space, i.e. in Fourier components.

❑ **The intermediate scattering function** is defined as the Fourier transform of the Van Hove function:

$$F(\mathbf{k},t) = \int d\mathbf{k} G(\mathbf{r},t) e^{-i\mathbf{k}.\mathbf{r}t}$$

out of which, can be defined a self and a distinct part:

$$F_s(\mathbf{k},t) = \int d\mathbf{k} G_s(\mathbf{r},t) e^{-i\mathbf{k}\mathbf{r}t}$$

$$F_d(\mathbf{k},t) = \int d\mathbf{k} G_d(\mathbf{r},t) e^{-i\mathbf{k}\mathbf{r}t}$$

Instead of Fourier transform, these functions can be also directly computed from the atomic trajectories.

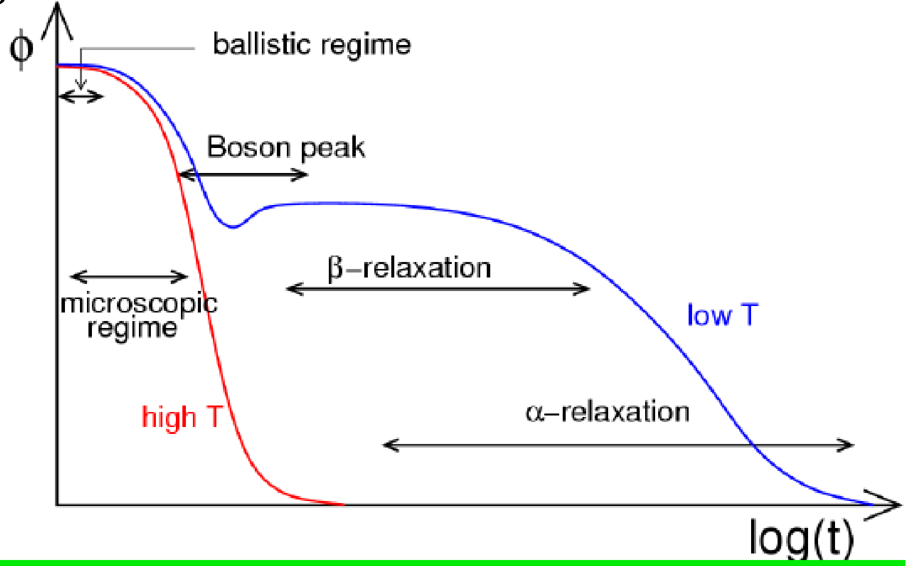
$$F_s(\boldsymbol{k},t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp[i\boldsymbol{k}.(\boldsymbol{r}_j(t) - \boldsymbol{r}_j(0)]\right\rangle \qquad F_d(\boldsymbol{k},t) = \frac{1}{N}\sum_{k=1}^{N}\sum_{j=1}^{N}\langle \exp[i\boldsymbol{k}.(\boldsymbol{r}_j(t) - \boldsymbol{r}_k(0)]\rangle$$

1. Self part (incoherent intermediate scattering function):

$$F_s(\boldsymbol{k},t)=\frac{1}{N}\left\langle\sum_{j=1}^{N}\exp[i\boldsymbol{k}.(\boldsymbol{r}_j(t)-\boldsymbol{r}_j(0))]\right\rangle$$

- $F_s(k,t)$ can be directly compared to experiments from inelastic neutron or X-ray scattering.

- $F_s(k,t)$ characterizes the mean relaxation time of the system (area under $F_s(k,t)$ can be used to define a relaxation time). Spatial fluctuations of Fs(k,t) provides information on dynamic heterogeneities.



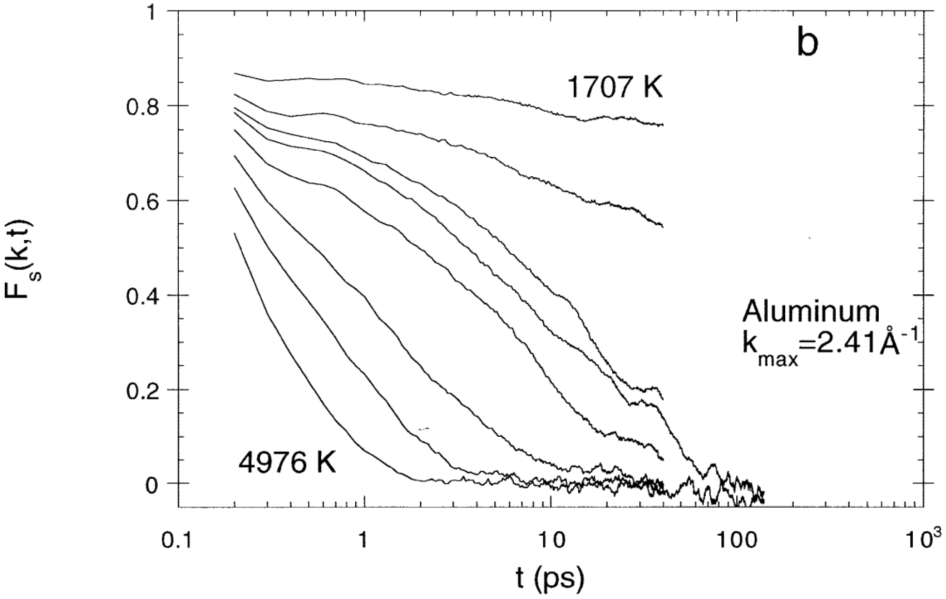
- **Short times :** balistic régime

- **Intermediate times:** cage motion (β relaxation)

- **Long times:** Particles leaving cages. Kohlrausch (stretched exponential) behavior.

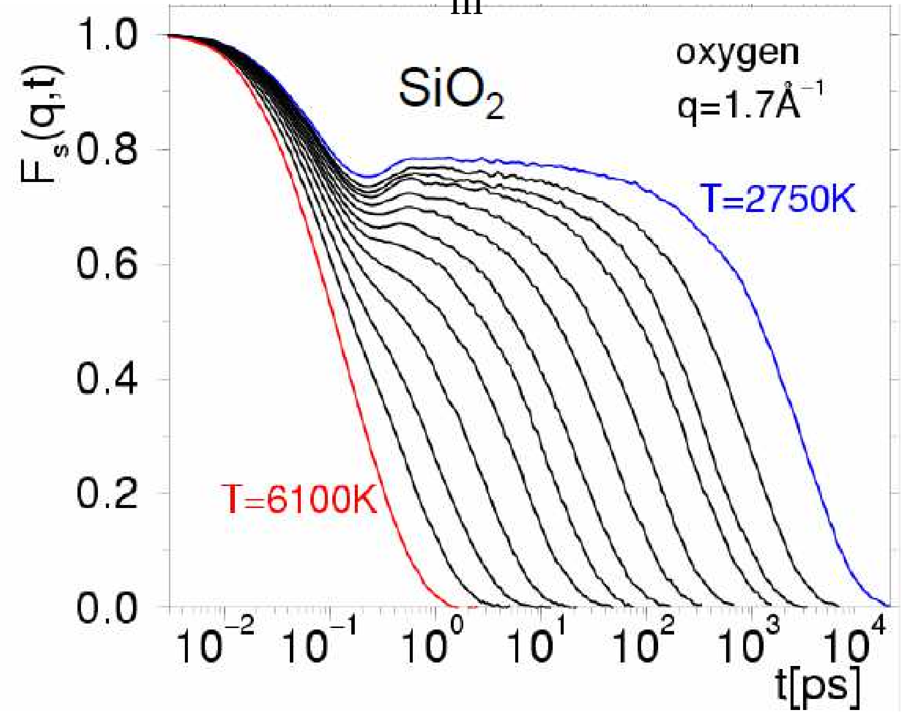
Examples :

$CaAl_2SiO_8$



Morgan and Spera, GCA 2001

T_m=2000 K



Cage motion (β régime) extends to long times at low T

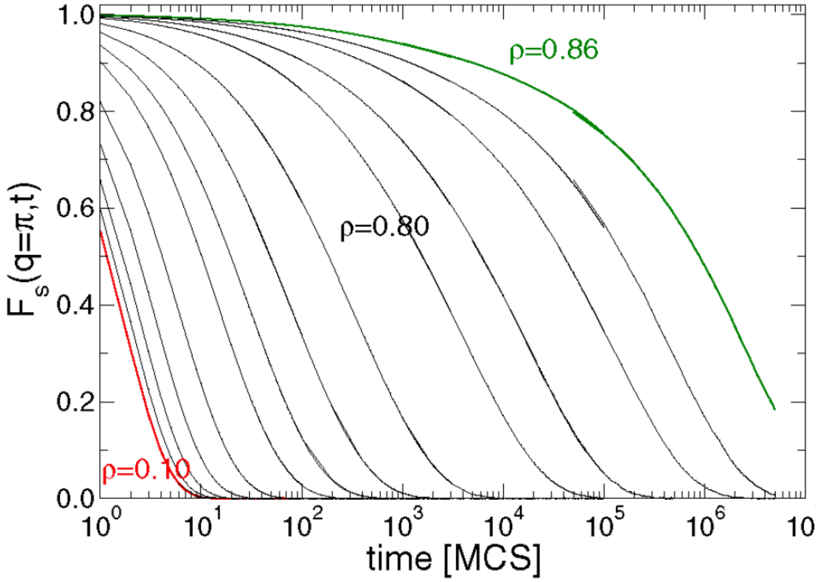
Horbach, Kob PRB 1999

Slowing down of the dynamics: a more universal behavior…

Experiments on bidimensional granular packing

MD simulation of hard spheres

Effet of density



Chaudhuri et al. AIP Conf. 2009

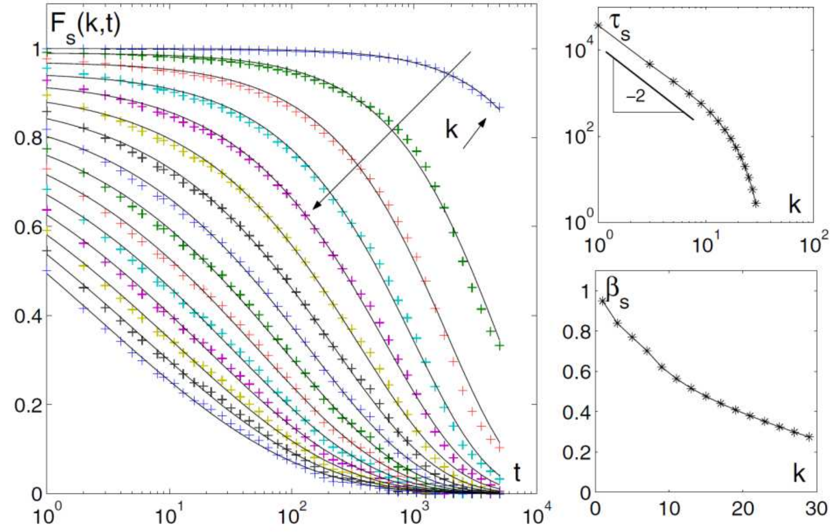


FIG. 1 (color online). On the left: $F_s(k,t)$ as a function of time for different odd values of the wave vector $k = 1, 3, \ldots, 29$ from top to bottom (as indicated by the arrow and the increasing $k \nearrow$). The black lines are fits of the form $\exp[-(t/\tau(k))^{\beta(k)}]$. On the right: $\tau(k)$ (top) and $\beta(k)$ (bottom) as a function of k.

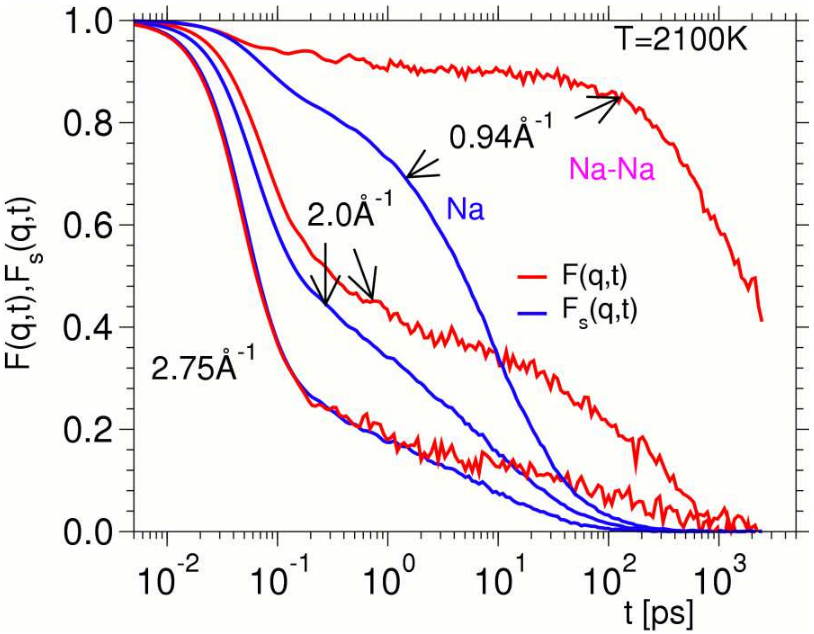
Dauchot et al. PRL 2006

2. Distinct part (coherent intermediate scattering function):

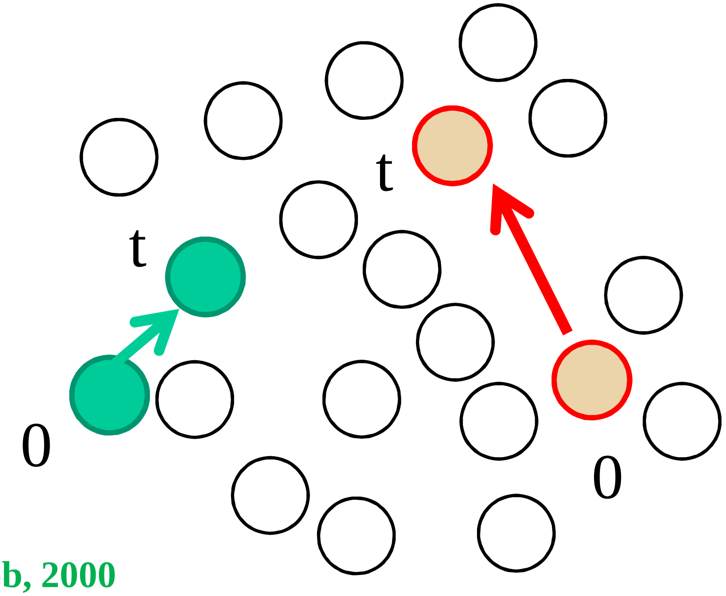
$$F_d(\boldsymbol{k},t) = \frac{1}{N}\sum_{k=1}^{N}\sum_{j=1}^{N}\langle \exp[i\boldsymbol{k}.(\boldsymbol{r}_j(t) - \boldsymbol{r}_k(0)]\rangle$$

- $F_d(k,t)$ can be measured in coherent inelastic neutron or x-ray scattering experiments ($k=k_{initial}-k_{final}$).

- Fluctuations of $F_d(k,t)$ give information about dynamical heterogeneities.



Kob, 2000



B) MEAN SQUARE DISPLACEMENT AND BEYOND

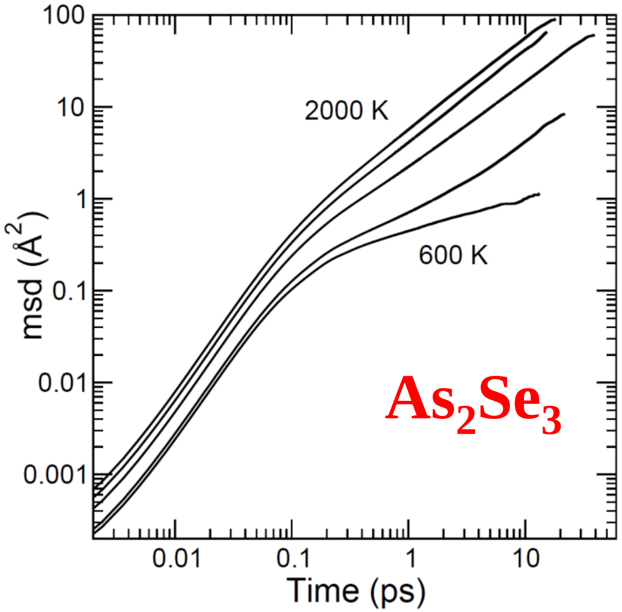
Remember: The mean square displacement is defined as

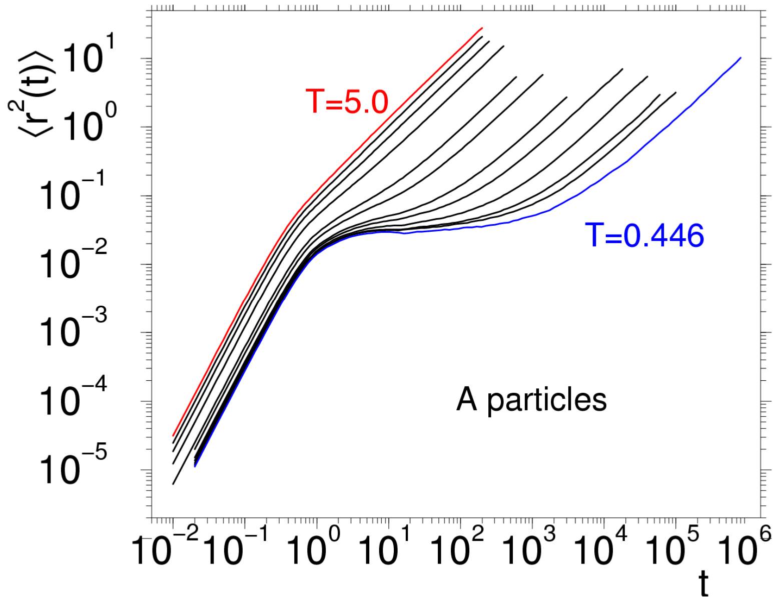
- performed in NVE or NVT.
- do not use periodic boundary conditions

$$\langle[\Delta\mathbf{r}_i(t)]^2\rangle = \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha}\langle|r_i(t)-r_i(0)|^2\rangle,$$

Gives a direct description of the dynamics.

A-B Lennard-Jones liquid



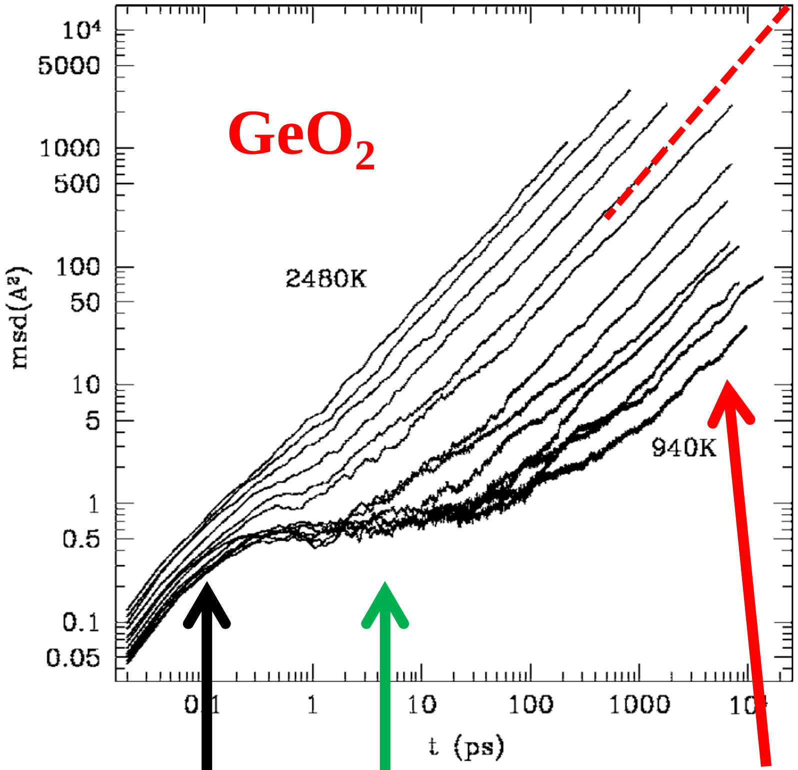


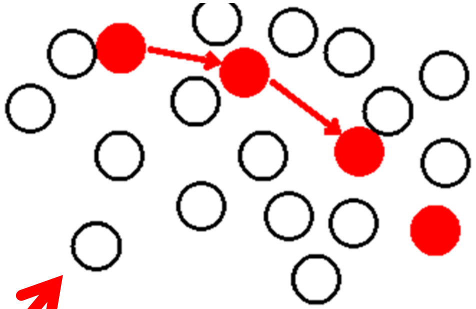
Bauchy et al., PRL 2013

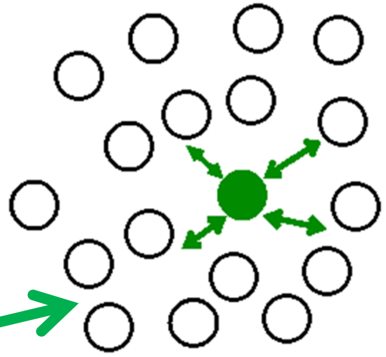
Kob PRE 2000

B) MEAN SQUARE DISPLACEMENT AND BEYOND

$$D = \lim_{t\to\infty} \frac{1}{6}\frac{\mathrm{d}}{\mathrm{d}t}\langle[\Delta \mathbf{r}_i(t)]^2\rangle$$







Diffusive régime
Long times

Ballistic régime
msd~t^2
Short time

Caging régime (LT)

B) MEAN SQUARE DISPLACEMENT AND BEYOND

Remember: The diffusion constant (Einstein relation) is defined as:

$$D = \lim_{t\to\infty} \frac{1}{6}\frac{\mathrm{d}}{\mathrm{d}t}\langle[\Delta \mathbf{r}_i(t)]^2\rangle$$

or from the velocity auto-correlation functions: $D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(0)\cdot\mathbf{v}_i(t)\rangle\,\mathrm{d}t$

Interesting alternative: $D = \lim_{t\to\infty} \frac{1}{3}\langle \mathbf{v}_i(0)\cdot\Delta\mathbf{r}_i(t)\rangle.$

- ❑ Diffusion constant measures the extent to which a particle's initial velocity vi(0) biases its longtime displacement Δr_i in the same direction.
- ❑ For an isotropic medium (liquids), can be written as the integral of a joint probability distribution of initial velocity and final displacement.
- ❑ Diffusion can be written as $D = \lim_{\Delta t\to\infty}\int\int v_0\cdot\Delta x\cdot P(v_0,\Delta x)\,\mathrm{d}v_0\,\mathrm{d}\Delta x$

and computed over MD time intervals

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A) MEAN SQUARE DISPLACEMENT AND BEYOND

$$D = \lim_{\Delta t \to \infty} \int \int v_0 \cdot \Delta x \cdot P(v_0, \Delta x)\, \mathrm{d}v_0\, \mathrm{d}\Delta\, x$$

- ❑ At short times (hot liquid), the ballistic motion of particles is not spatially correlated (Maxwell-Boltzmann distribution f(v)).

- ❑ At very long times (low temperature), particles lose memory of their original positions and velocities, and any spatial heterogeneity in the displacements is simply averaged out.

- ❑ The presence of dynamic heterogeneity implies the existence of an intermediate time scale, dependent on the temperature, which reveals clustering in terms of particle mobility.

- ❑ For purely random diffusion, one has (solution of Fick's law):

$$P(\Delta \mathbf{r}_i) = \frac{1}{8(\pi D \Delta t)^{3/2}} \exp\left(\frac{-|\Delta \mathbf{r}_i|^2}{4 D \Delta t} \right)$$

B) MEAN SQUARE DISPLACEMENT AND BEYOND

$$P(\Delta\mathbf{r}_i) = \frac{1}{8(\pi D\Delta t)^{3/2}} \exp\left(\frac{-|\Delta\mathbf{r}_i|^2}{4D\Delta t}\right)$$

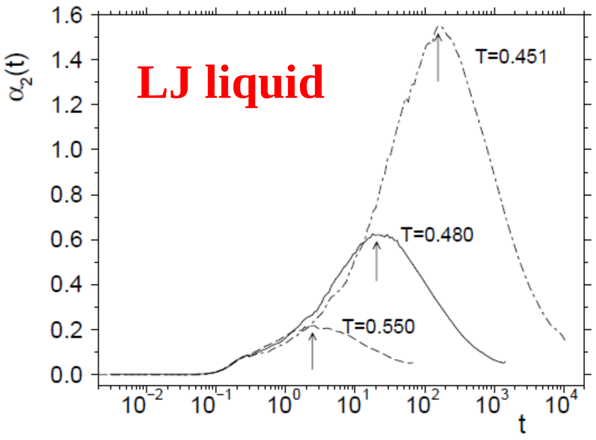
- At short times (hot liquid), since one has a Maxwell-Boltzmann distribution f(v) and also $\Delta\mathbf{r}_\mathbf{i}=\mathbf{v}_\mathbf{i}\Delta t$, P is also Gaussian.

$$P(\Delta\mathbf{r}_i) = \left(\frac{m}{2\pi k_\mathrm{B}T(\Delta t)^2}\right)^{3/2} \exp\left(\frac{-m|\Delta\mathbf{r}_i|^2}{2k_\mathrm{B}T(\Delta t)^2}\right)$$

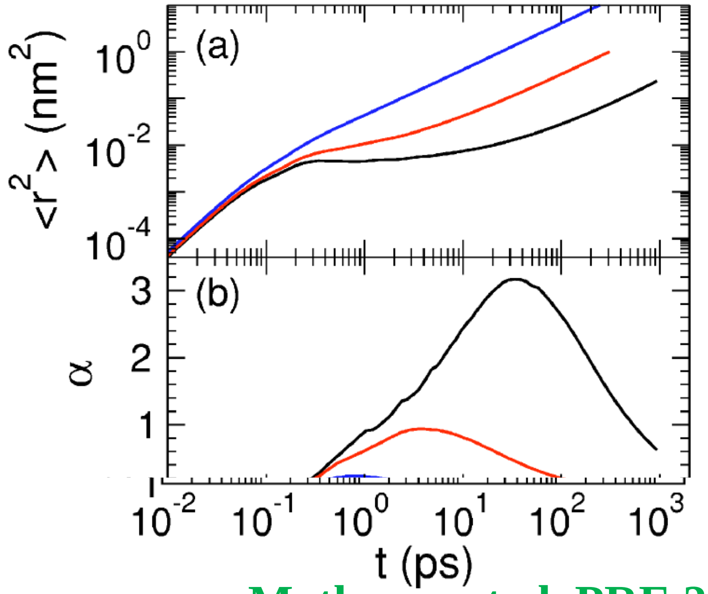
- For moderate to deeply supercooled liquids, the intermediate-time behaviour of *P* becomes substantially non-Gaussian, reflecting the effects of ‘caged’ particles and the presence of dynamic heterogeneity.
- Reflected in a **non-Gaussian parameter** $\alpha_2(\Delta t) = \frac{3\langle\Delta r(\Delta t)^4\rangle}{5\langle\Delta r(\Delta t)^2\rangle^2} - 1$
- For a truly Gaussian distribution in $\mathbf{r}_i$, $\alpha_2 = 0$
- $\alpha_2(0)=0$ and for $\Delta t \rightarrow \infty$

B) MEAN SQUARE DISPLACEMENT AND BEYOND

- On the time scale at which the motion of the particles is ballistic,
  $\alpha_2 = 0$
- Upon entering the intermediate time scales (β-relaxation), α_2 starts to increase.
- On the time scale of the α-relaxation, α_2 decreases to its long time limit, zero.
- The maximum value of α_2 increases with decreasing T. Evidence that the dynamics of the liquid becomes more heterogeneous with decreasing T.



Kob et al. PRL 1997

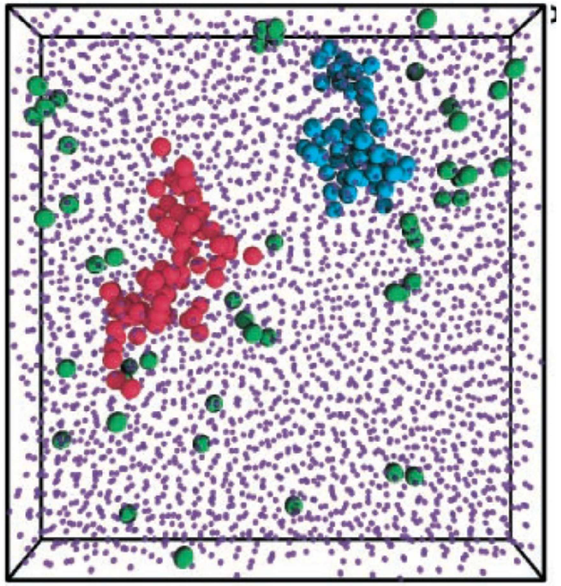


Matharoo et al. PRE 2006

C) DYNAMIC HETEROGENEITIES

- ☐ **Observation:** Particles in deep supercooled liquids behave very differently at the same time.
  - Most of the particles are characterized by a extremely slow evolution.
  - A small part evolves more rapidly.
  - Do these “rapid” regions have a collective behavior ?
  - Seen experimentally in colloidal hard sphere suspension (most mobile particles highlighted)

E. Weeks et al. Science 2000



C) DYNAMIC HETEROGENEITIES

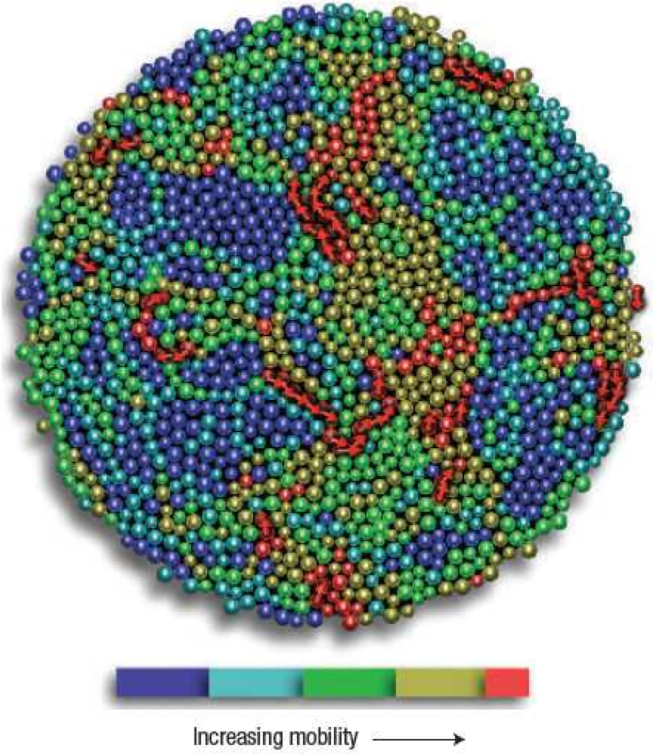
- ☐ Other example: Granular fluid of beads showing different mobilities

- ☐ The characterization of **Dynamical Heterogeneities** shows evidence of a **collective** behaviour

- ☐ Needs to build more suitable correlation functions. No signature of heterogeneous dynamics from g(r) or S(k) or even the msd.

- ☐ Consider the liquid of N particles occupying volume V with density

$$\rho(\mathbf{r},t)=\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i(t))$$



Keys et al. Nature Phys. 2007

C) DYNAMIC HETEROGENEITIES

- ❑ Measure of the number of "*overlapping*" particles in two configurations separated by a time interval *t (*time-dependent order parameter):

$$Q_p(t) \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1,0)\rho(\mathbf{r}_2,t)\,\delta(\mathbf{r}_1-\mathbf{r}_2)$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r}_i(0)-\mathbf{r}_j(t)),$$

out of which can be defined a fluctuation (time-dependent order parameter χ_4(t):

$$\chi_4^p(t) = \frac{\beta V}{N^2}[\langle Q_p^2(t)\rangle - \langle Q_p(t)\rangle^2]$$

which expresses with a four-point time-dependent density correlation function $\mathcal{G}_4$(r$_1$,r$_2$,r$_3$,r$_4$,t):

$$\chi_4^p(t) \equiv \frac{\beta V}{N^2}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \mathcal{G}_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,t)$$

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C) DYNAMIC HETEROGENEITIES

$$\chi_4^p(t) \equiv \frac{\beta V}{N^2} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \mathcal{G}_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,t)$$

☐ Four-point time dependent density correlation :

$$\begin{aligned}
&\mathcal{G}_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,t)\\
&\quad \equiv \langle \rho(\mathbf{r}_1,0)\rho(\mathbf{r}_2,t)\delta(\mathbf{r}_1-\mathbf{r}_2)\rho(\mathbf{r}_3,0)\rho(\mathbf{r}_4,t)\delta(\mathbf{r}_3-\mathbf{r}_4)\rangle\\
&\qquad -\langle \rho(\mathbf{r}_1,0)\rho(\mathbf{r}_2,t)\delta(\mathbf{r}_1-\mathbf{r}_2)\rangle\\
&\qquad \times\langle \rho(\mathbf{r}_3,0)\rho(\mathbf{r}_4,t)\delta(\mathbf{r}_3-\mathbf{r}_4)\rangle,
\end{aligned}$$

which can be reduced (isotropic media) to a function $\mathcal{G}_4(r,t)$.

☐ **Meaning of $\mathcal{G}_4(r,t)$:** Measures correlations of motion between 0 and t arising at two points, 0 and r.

☐ **Meaning of the dynamic susceptibility $\chi_4(t)$:** Typical number of particles involved in correlated motion (volume of the correlated clusters)

C) DYNAMIC HETEROGENEITIES

- ☐ Critical phenomena language: assuming the existence of a single dominant length scale ξ_4, one expects for large distances to have :

$$G_4(r;t) \approx A(t)[\exp(-r/\xi_4(t))]/r^p,$$

or, in Fourier space (more convenient, simulation cell size limitation) using a four-point structure factor:

$$S_4(q;t) = \int d^d\mathbf{r}\, \exp(\mathrm{i}\, \mathbf{q}\cdot\mathbf{r}) G_4(r;t)$$

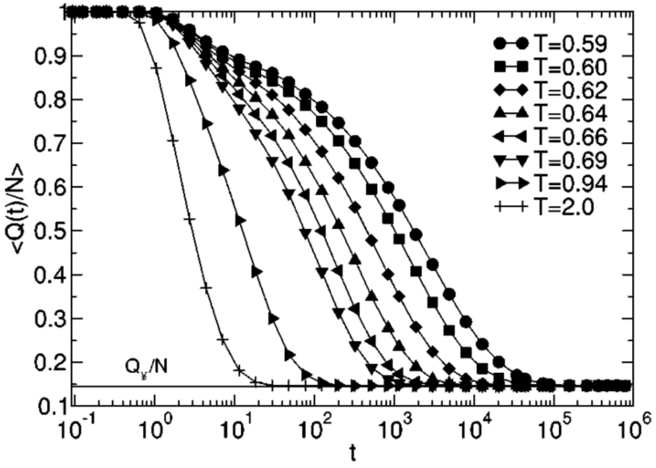
which can be fitted at low q (Ornstein-Zernike functional form of critical phenomena) involving a correlation length.

$$S_4(q,t) = \frac{S_4(0)}{(1+(q\xi_4(t))^2)}$$

C) DYNAMIC HETEROGENEITIES

Lacevic et al. JCP 2003

Going through the functions for a LJ liquid



- Overlap order parameter Q(t)

$$Q_p(t) \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1,0)\rho(\mathbf{r}_2,t)\delta(\mathbf{r}_1-\mathbf{r}_2)$$

Two-step relaxation (transient caging) similar to the behavior of the intermediate scattering function F(k,t). Decays to Q_{inf}, random overlap, fraction of the volume occupied by particles at any given time.

- Sample to sample fluctuation:

$$\chi_4^p(t) = \frac{\beta V}{N^2}[\langle Q_p^2(t)\rangle - \langle Q_p(t)\rangle^2]$$

Growth of correlated motion between pairs of particles. At long times, diffusion thus χ_4(t)=0.

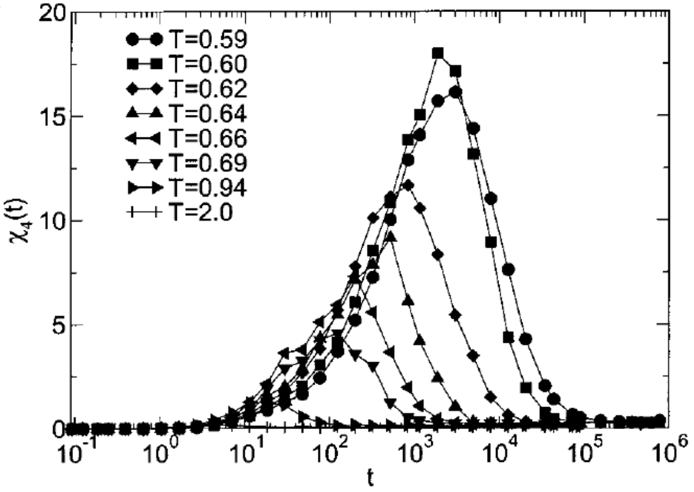


FIG. 6. Time and temperature dependence of $\chi_4(t)$. As T decreases, the peak in $\chi_4(t)$ monotonically increases and shifts to longer time. We define the time at which $\chi_4(t)$ is maximum as $t_4^{\max}$.

C) DYNAMIC HETEROGENEITIES

Lacevic et al. JCP 2003

Going through the functions for a LJ liquid

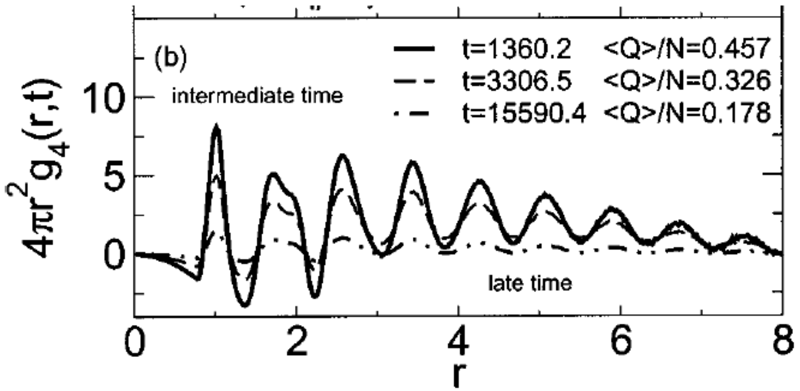
☐ Radial correlation function $\mathcal{G}_4(r,t)$.

$$g_4(r,t) \equiv \left\langle \frac{Q(t)}{N} \right\rangle^2 g(r) - 1$$

- At small times (ballistic), <Q(t)>=1 so that g4=g(r)-1.
- Deviates when <Q(t)> deviates from unity and $\chi_4(t)$ becomes non-zero.

☐ Four point structure factor

$$S_4(q;t) = \int d^d\mathbf{r} \exp(\mathrm{i}\,\mathbf{q}\cdot\mathbf{r}) G_4(r;t)$$



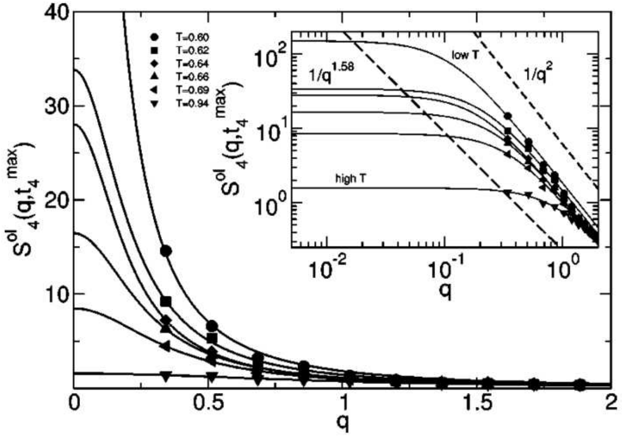


FIG. 12. Small q behavior of $S_4^{ol}(q,t_4^{\max})$. Inset shows a log–log plot of $S_4^{ol}(q,t_4^{\max})$ vs q. The lines in both figures are fits to the data using Eq. (30). The second lowest temperature $T=0.60$ is difficult to fit because of the large uncertainty in $S_4^{ol}(0,t)$ at times in the vicinity of $t_4^{\max}$ (see text for further discussion).

C) DYNAMIC HETEROGENEITIES

Lacevic et al. JCP 2003

Going through the functions for a LJ liquid

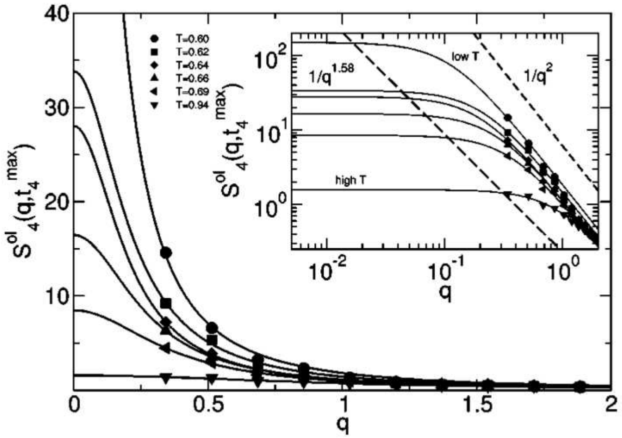
- ☐ Fitting using the Ornstein-Zernike theory

$$S_4^{ol}(q,t)=\frac{S_4^{ol}(0)}{(1+(q\xi_4(t))^2)}$$

  - ➢ Allows determining correlation length ξ4(t) as a function of temperature.

- ☐ Correlation length ξ4(t)

  - ➢ Qualitatively similar to χ_4(t)
  - ➢ Increase of ξ4(t) as T decreases.



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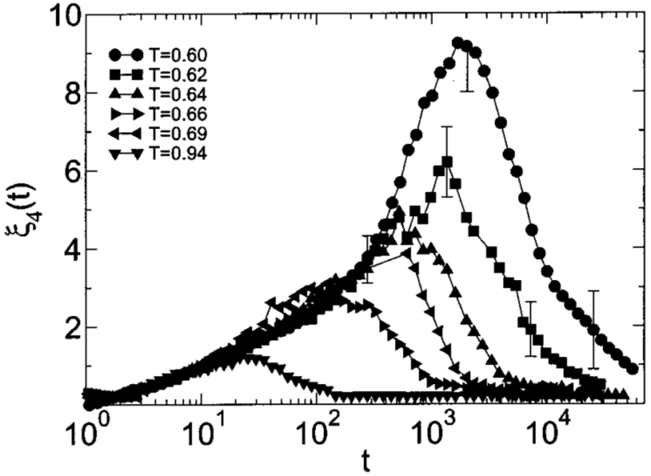


C) DYNAMIC HETEROGENEITIES

- **Experimental and theoretical evidence:** Growing dynamic length scale in molecular liquids and colloidal suspensions.

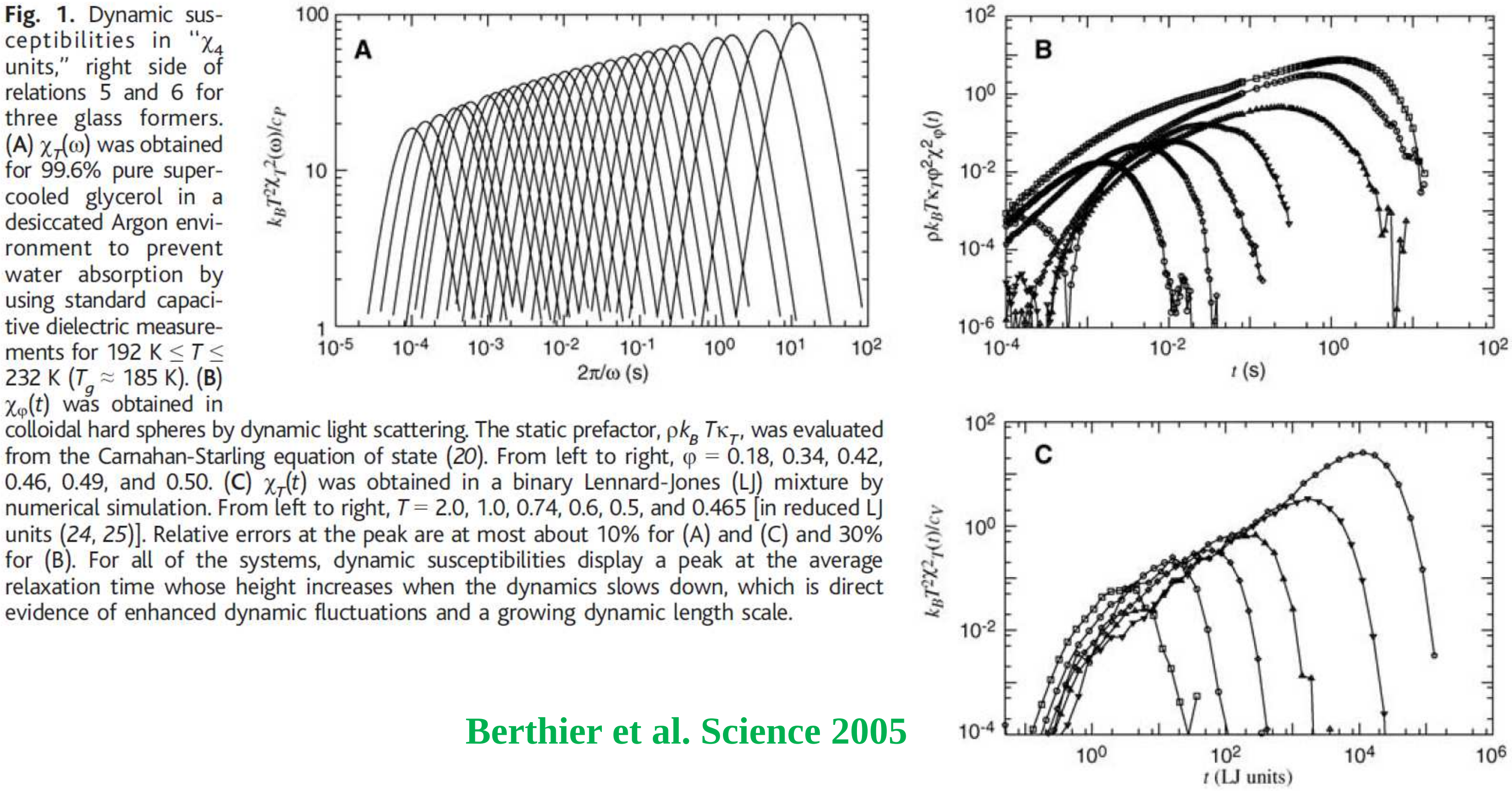
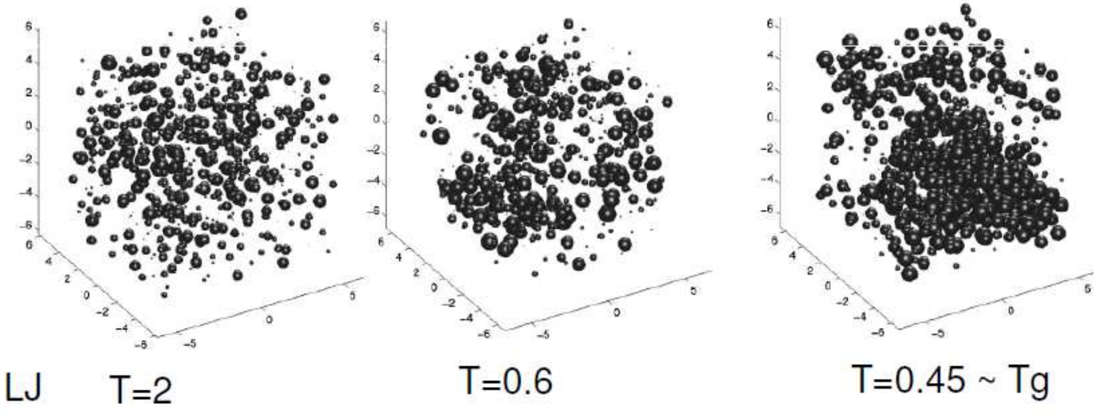


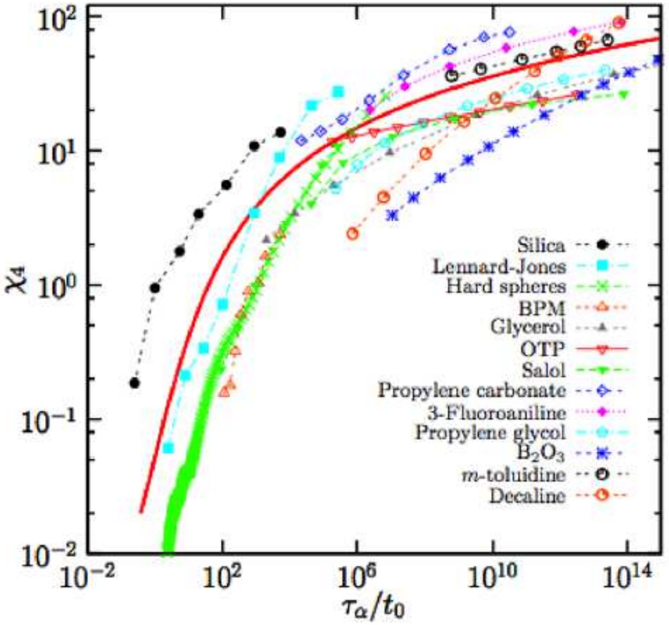
Fig. 1. Dynamic susceptibilities in "χ_4 units," right side of relations 5 and 6 for three glass formers. (**A**) $\chi_T(\omega)$ was obtained for 99.6% pure supercooled glycerol in a desiccated Argon environment to prevent water absorption by using standard capacitive dielectric measurements for 192 K $\leq T \leq$ 232 K ($T_g \approx$ 185 K). (**B**) $\chi_\varphi(t)$ was obtained in colloidal hard spheres by dynamic light scattering. The static prefactor, $\rho k_B T\kappa_T$, was evaluated from the Carnahan-Starling equation of state (*20*). From left to right, φ = 0.18, 0.34, 0.42, 0.46, 0.49, and 0.50. (**C**) $\chi_T(t)$ was obtained in a binary Lennard-Jones (LJ) mixture by numerical simulation. From left to right, T = 2.0, 1.0, 0.74, 0.6, 0.5, and 0.465 [in reduced LJ units (*24*, *25*)]. Relative errors at the peak are at most about 10% for (A) and (C) and 30% for (B). For all of the systems, dynamic susceptibilities display a peak at the average relaxation time whose height increases when the dynamics slows down, which is direct evidence of enhanced dynamic fluctuations and a growing dynamic length scale.

Berthier et al. Science 2005

C) DYNAMIC HETEROGENEITIES

Experimental and theoretical evidence: Growing dynamic length scale in molecular liquids and colloidal suspensions.





- ☐ Number of dynamically correlated particles (peak height of χ_4) increases as temperature decreases (or relaxation time τ_α increases).
- ☐ Dynamical fluctuations and correlation length scales increase as one approaches Tg.

D) ISOCONFIGURATIONAL ENSEMBLE

- ❑ A. Widmer-Cooper, P. Harrowell, PRL 2004, Bertier and Lack, PRE 2007
- ❑ **Idea:** Study of the **role of local structure** when approaching the glass transition. As T is lowered, it becomes harder to sample all the phase space.
- ❑ Initial positions of particles are held fixed, but **N dynamical trajectories** are independent through the use of random initial velocities. **N MD runs**
- ❑ Define $C_i(t)$ a general dynamic object attached to particle i such as:

$$f_i(t) \equiv \cos\{\boldsymbol{k}\cdot[\boldsymbol{r}_i(t)-\boldsymbol{r}_i(0)]\}$$

- ❑ Isoconfigurational average $\langle \cdots \rangle_{\text{iso}}$
- ❑ Equilibrium Ensemble averages $\mathbb{E}[\cdots]$
- ❑ Dynamic propensity $\langle C_i(t) \rangle_{\text{iso}}$ e.g. displacement

D) ISOCONFIGURATIONAL ENSEMBLE

☐ Allows disentangling structural and dynamical sources of fluctuations through the definition of 3 variances over the quantity of interest C:

$$\delta_C(t) = \mathbb{E}[\langle C_i(t)\rangle_{\text{iso}}^2] - \mathbb{E}^2[C_i(t)],$$

Structural component of the fluctuations (particle-to-particle fluctuation of Ct(t)

$$\Delta_C^{\text{iso}}(t) = \mathbb{E}[\langle C_i^2(t)\rangle_{\text{iso}} - \langle C_i(t)\rangle_{\text{iso}}^2]$$

Fluctuations of C between different runs (**dynamics**)

$$\Delta_C(t) = \mathbb{E}[\langle C_i^2(t)\rangle_{\text{iso}}] - \mathbb{E}^2[C_i(t)]$$

Total amount of fluctuations.

and: $\Delta_C(t) = \Delta_C^{\text{iso}}(t) + \delta_C(t)$

D) ISOCONFIGURATIONAL ENSEMBLE

Matharoo et al. PRE 2006

Example: Dynamic propensity in liquid water.

- Make M IC copies of a N component water system.
- Define for e.g. an O atom the squared displacement $r^2(i,k,t)$
- The system-averaged and IC-ensemble averaged msd is:

$$\langle r^2\rangle=(NM)^{-1}\Sigma_{i=1}^{N}\Sigma_{k=1}^{M}r^2(i,k,t)$$

- Dynamic propensity of each molecule is:

$$\boxed{\langle r_i^2\rangle_{\rm ic}=M^{-1}\Sigma_{k=1}^{M}r^2(i,k,t)}$$

- Potential propensity

$$\boxed{\langle u_i\rangle_{\rm ic}=M^{-1}\Sigma_{k=1}^{M}u(i,k,t)}$$

$$u_i=\Sigma_{j=1}^{N}\phi_{ij}$$

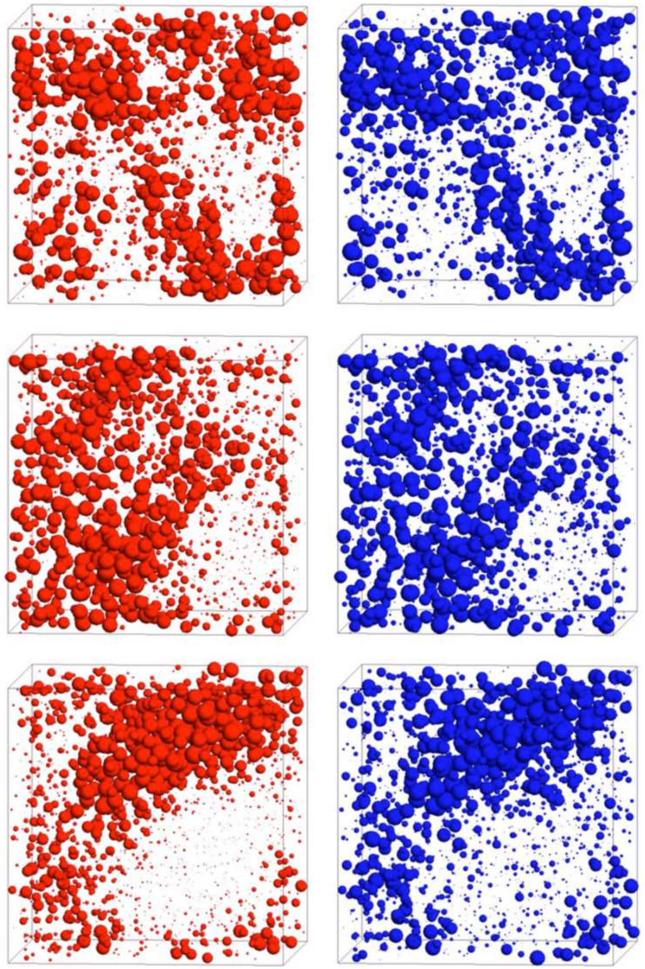


FIG. 3. (Color online) Dynamical heterogeneity (left panels) and structural heterogeneity (right panels) in the initial configuration at $T=350$ K (top panels), 290 K (middle panels), and 270 K (bottom panels). To make each panel, the values of $\langle r_i^2\rangle_{\rm ic}$ (or $\langle u_i\rangle_{\rm ic}$), evaluated at the time of the maximum of S_u, are assigned to each molecule in the initial configuration. These values are sorted

D) ISOCONFIGURATIONAL ENSEMBLE

$\langle r_i^2\rangle_{\rm ic}$:

$\langle n_i\rangle_{\rm ic}$

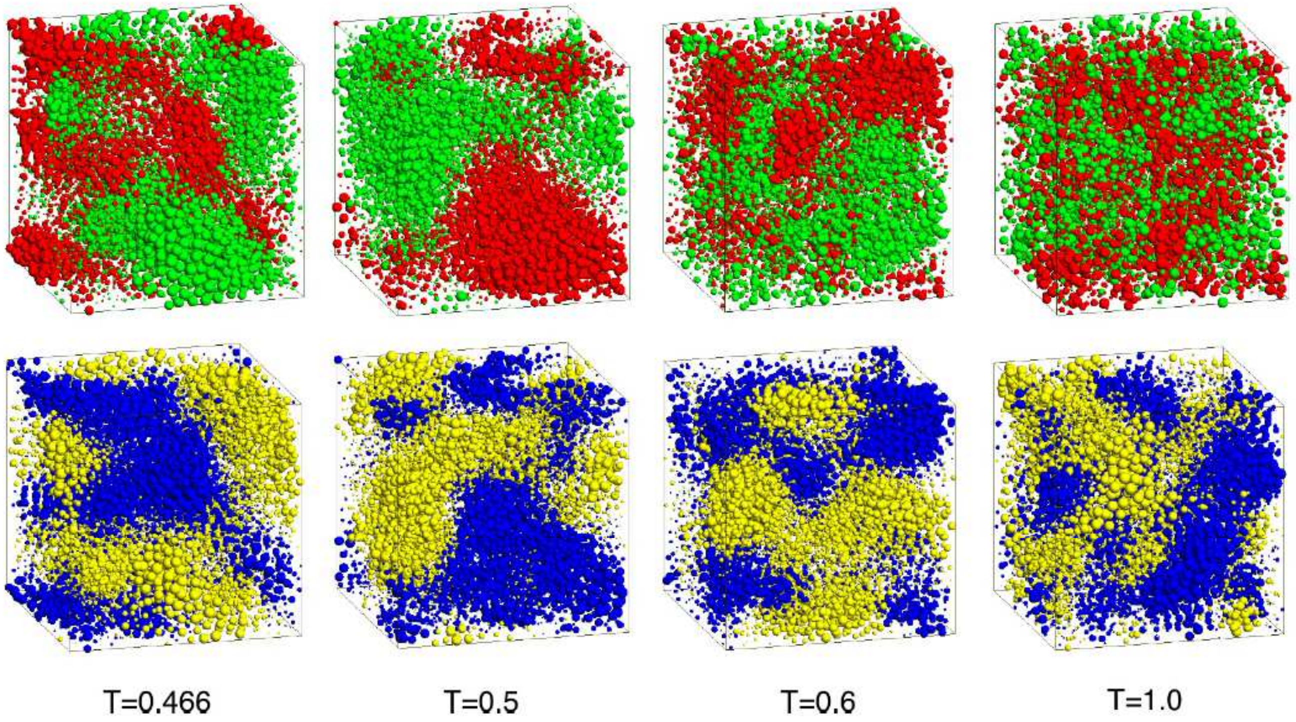


FIG. 10: Spatial variation of $\langle r_i^2\rangle_{\rm ic}$ (top panels) and $\langle n_i\rangle_{\rm ic}$ (bottom panels) at each T. To make each top panel, the values of $\langle r_i^2\rangle_{\rm ic}$, evaluated at the time of the maximum of S_M, are assigned to each A particle at its position in the initial configuration of the IC ensemble. These values are sorted and assigned an integer rank R_i from 1 to N, from smallest to largest. Each A particle is then plotted as a green sphere of radius $\sigma = R_{\rm min}\exp\{[(R_i - N)/(1-N)]\log(R_{\rm max}/R_{\rm min})\}$, where $R_{\rm max} = 0.5$ and $R_{\rm min} = 0.01$. The ranks R_i are then reversed (i.e. assigned from largest to smallest), and each A particle is also plotted as a red sphere of radius σ. The color observed for each particle therefore indicates which of the green or red spheres is larger. The result presents the rank of $\langle r_i^2\rangle_{\rm ic}$ on an exponential scale, such that the largest green spheres represent the most mobile A particles, and the largest red spheres the most immobile. The bottom panels are created in exactly the same way as the top panels, but with $\langle r_i^2\rangle_{\rm ic}$ replaced by $\langle n_i\rangle_{\rm ic}$, and where the time is chosen to be the maximum of S_L at each T. In the bottom panels, the largest yellow spheres represent the A particles with the lowest B coordination, and the largest blue spheres the A particles with the highest B coordination.

Lennard-Jones liquid

Razul et al., JPCM (2011).

E) ENERGY LANDSCAPE

- ☐ **Definition**: Potential energy landscape (**PEL**) is V($\mathbf{r}^N$) of a system of N particles.

  Stillinger and Weber, 1982

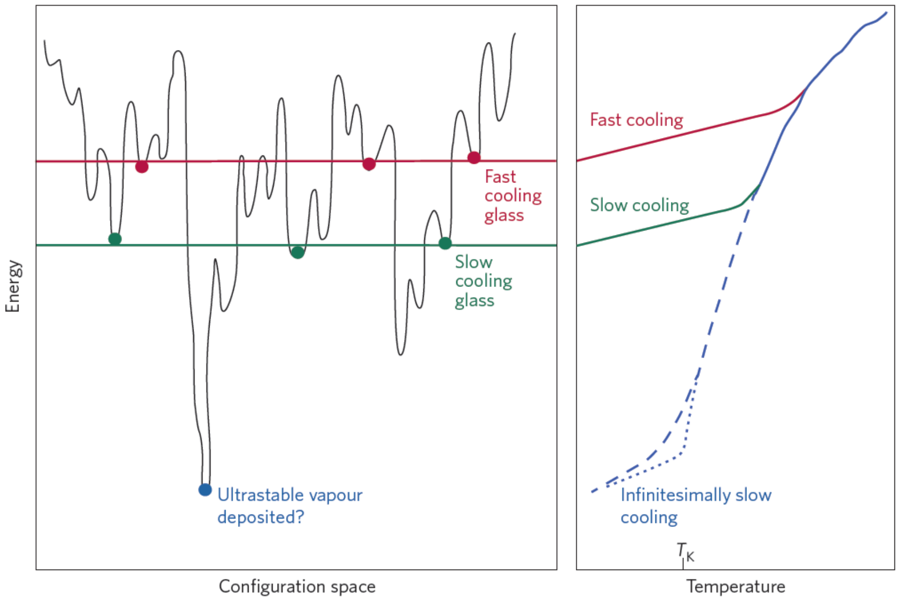
- ☐ While PEL does not depend on T, its exploration does.

- ☐ The PEL of glasses is made of
  - ➢ **Distinct basins with local minima** (**inherent structures**) of the PE.
  - ➢ Saddles, energy barriers

- ☐ Decreasing temperatures reduces the possibility to explore parts of the PEL.

  Barriers of increasing heights

  Too much time spent in basins



Parisi and Sciortino, Nature 2013

E) ENERGY LANDSCAPE

- The partition function *Z* of a system of *N* particles interacting via a two-body spherical potential is :

$$Z(T,V) = \frac{1}{N!\lambda^{3N}} Q(V,T) \qquad Q(V,T) = \int_V \mathrm{e}^{-\beta V(\vec{r}^N)}\,\mathrm{d}\vec{r}^N$$

- Configuration space can be partitioned into basins. Partition function becomes a sum over the partition functions of the individual distinct basins *Qi*

$$Q(T,V) = \sum_i{}' Q_i(T,V)$$

- Partition function averaged over all distinct basins with the same

e_{IS} value as

$$Q_i(T,V) = \mathrm{e}^{-\beta e_{\mathrm{IS}_i}} \int_{\mathrm{basin}\ i} \mathrm{e}^{-\beta\Delta V(\vec{r}^N)}\,\mathrm{d}\vec{r}^N$$

$$Q(e_{\mathrm{IS}},T,V) = \frac{\sum_i \delta_{e_{\mathrm{IS}_i},e_{\mathrm{IS}}} Q_i(T,V)}{\sum_i \delta_{e_{\mathrm{IS}_i},e_{\mathrm{IS}}}}$$

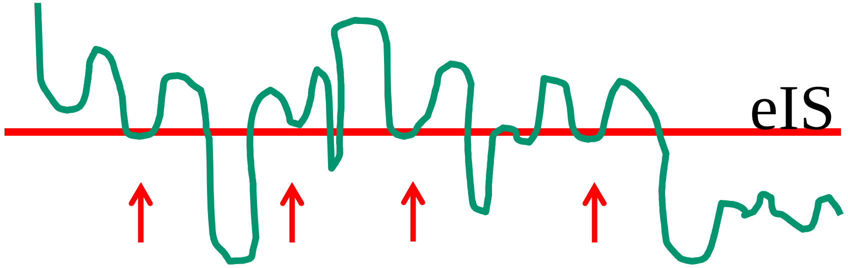
and associated average basin free energy as $-\beta f_{\mathrm{basin}}(e_{\mathrm{IS}},T,V) \equiv \ln\left[\frac{Q(e_{\mathrm{IS}},T,V)}{\lambda^{3N}}\right]$

E) ENERGY LANDSCAPE

- ☐ The partition function of the system then reduces to a sum of the IS:

$$Z(T,V) = \sum_{e_{\mathrm{IS}}} \Omega(e_{\mathrm{IS}}) \mathrm{e}^{-\beta f_{\mathrm{basin}}(e_{\mathrm{IS}},T,V)}$$

$\Omega(e_{IS})$ is the **number** of basins of depth e_{IS}.



- ☐ This defines the configurational entropy :

$$S_{\mathrm{conf}}(e_{\mathrm{IS}}) \equiv k_{\mathrm{B}} \ln[\Omega(e_{\mathrm{IS}})]$$

$$Z(T,V) = \sum_{e_{\mathrm{IS}}} \mathrm{e}^{-\beta[-TS_{\mathrm{conf}}(e_{\mathrm{IS}})+f_{\mathrm{basin}}(e_{\mathrm{IS}},T,V)]}$$

E) ENERGY LANDSCAPE

- **Basin free energy from harmonic approximation**:

$$V(\vec{r}^N) \approx e_{\mathrm{IS}} + \sum_{i,j,\alpha,\beta} H_{i\alpha j\beta}\,\delta r_i^\alpha \delta r_j^\beta$$

- With $H_{i\alpha j\beta}$ the 3N Hessian matrix: $H_{i\alpha j\beta} = \left.\dfrac{\partial^2 V(\vec{r}^N)}{\partial r_i^\alpha \partial r_j^\beta}\right|_{\mathrm{IS}}$

- The partition function, averaged over e_{IS}, can be written, with ωj the 3N eigenvalues associated with e_{IS}

$$Z(e_{\mathrm{IS}}, T, V) = \mathrm{e}^{-\beta e_{\mathrm{IS}}} \left\langle \prod_{j=1}^{3N} [\beta \hbar \omega_j (e_{\mathrm{IS}})]^{-1} \right\rangle_{e_{\mathrm{IS}}}$$

$\uparrow$ vibrations

- This allows separating the vibrational part of the basin free energy $-\, k_B T \ln Z$.

E) ENERGY LANDSCAPE

- ☐ **A simple example** : one dimensional PEL defined between 0 and L made of n basins, each with e_{IS}= - 1 and size L/n: $V(x) = V_o \cos[(2\pi n/L)x]$

- ☐ Stilinger-Weber formalism will give:

$$Q = \int_0^L \mathrm{e}^{-\beta V(x)}\,\mathrm{d}x = \sum_{i=0}^{n-1} Q_i$$

$$Q_i = \int_{i(L/n)}^{(i+1)(L/n)} \mathrm{e}^{-\beta V(x)}\,\mathrm{d}x$$

- ☐ All the basins have the same depth: $Q = nQ_0$

$$F = -T\ln[n] + f_{\text{basin}} \qquad -\beta f_{\text{basin}} = \ln[Q_0]$$

E) ENERGY LANDSCAPE

- **BKS silica**: IS energies and configurational energies

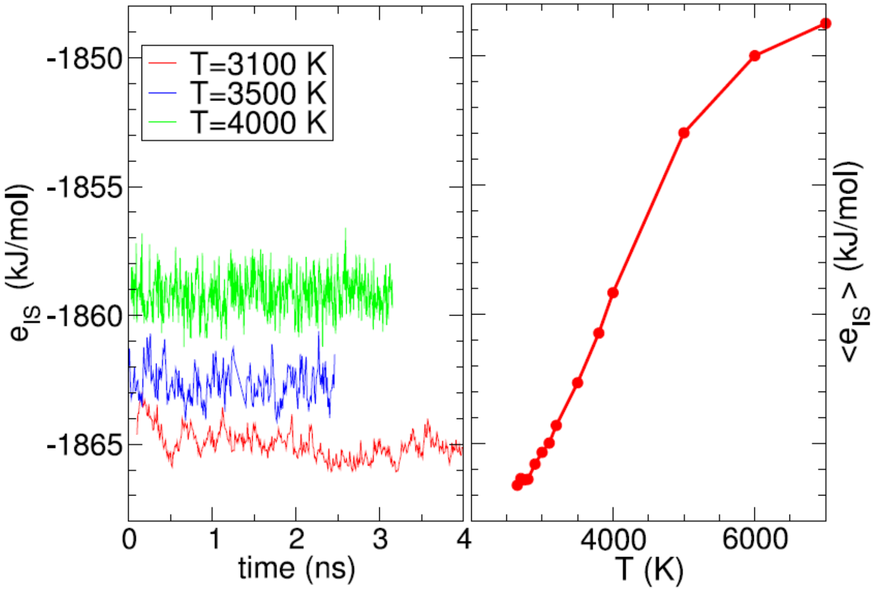


Figure 2. Left: time dependence of $e_{\rm IS}$ for the BKS model for silica in a 999-ion system for three different temperatures. Note that at each T, a different set of $e_{\rm IS}$ values is sampled. Right: T dependence of $\langle e_{\rm IS}\rangle$ for the same model.

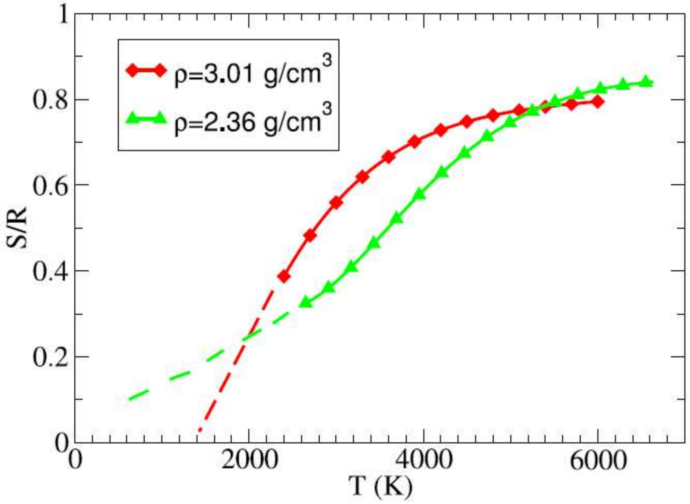


Figure 12. T dependence of $S_{\rm conf}$ for BKS silica at $\rho = 2.36$ and 3.01 g cm^{-3}. Note that in this model, at the lowest density, $S_{\rm conf}$ does not appear to vanish at a finite T. Dashed lines represent possible extrapolations. Redrawn from [62].

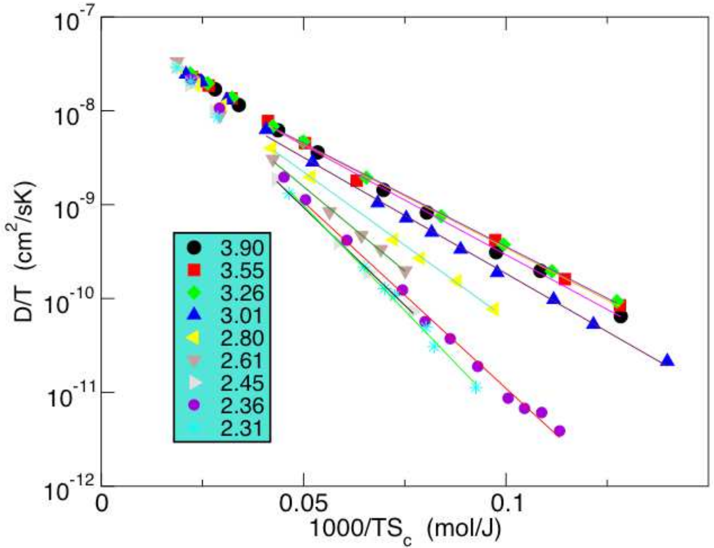
F. Sciortino, J. Stat. Mech. 2005

E) ENERGY LANDSCAPE

- ❑ Simultaneous calculation of D (diffusivity) and S_{conf} (from PEL) shows Arrhenius behavior.

- ❑ Numerical validation of the Adam-Gibbs relationship

$$\boxed{\tau(T) \propto \exp\left[\frac{C}{TS_{conf}}\right]}$$



Sakai-Voivod, Nature 2001

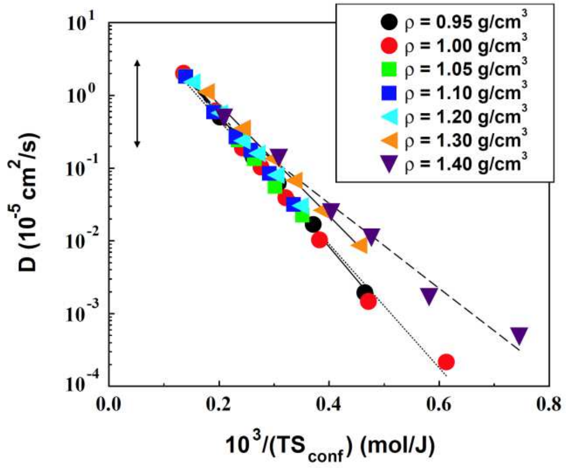


Fig. 5. Test of the Adam-Gibbs relation in SPC/E water. For all the densities studied the diffisivity follows the Adam-Gibbs law, for about four decades in diffusivity. The arrow indicates the range of diffusivity values accessible to experiments. Redrawn from reference [18].

Sciortino et al. Eur. Phys. J. E 2002

Conclusion:

- Dynamics of glass-forming systems can be followed with numerous tools using computer simulations.
- Functions quantify the slowing down of the dynamics.
- Heterogeneous dynamics sets in: Non-Gaussian parameter, Four-point correlation functions, Isoconfigurational Ensemble
- Energy landscapes provides a thermodynamic view that connects back to the simple Adam-Gibbs relationship.

Next lecture (12): Ab initio simulations…a survey