Length and Time Scales in Glass-Forming Fluids

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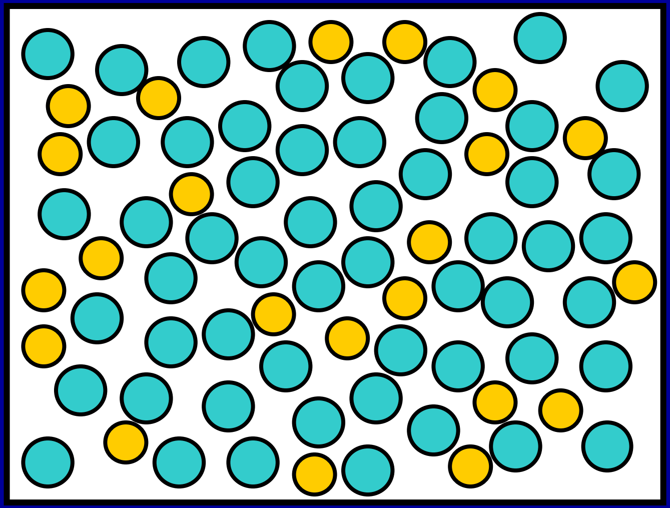


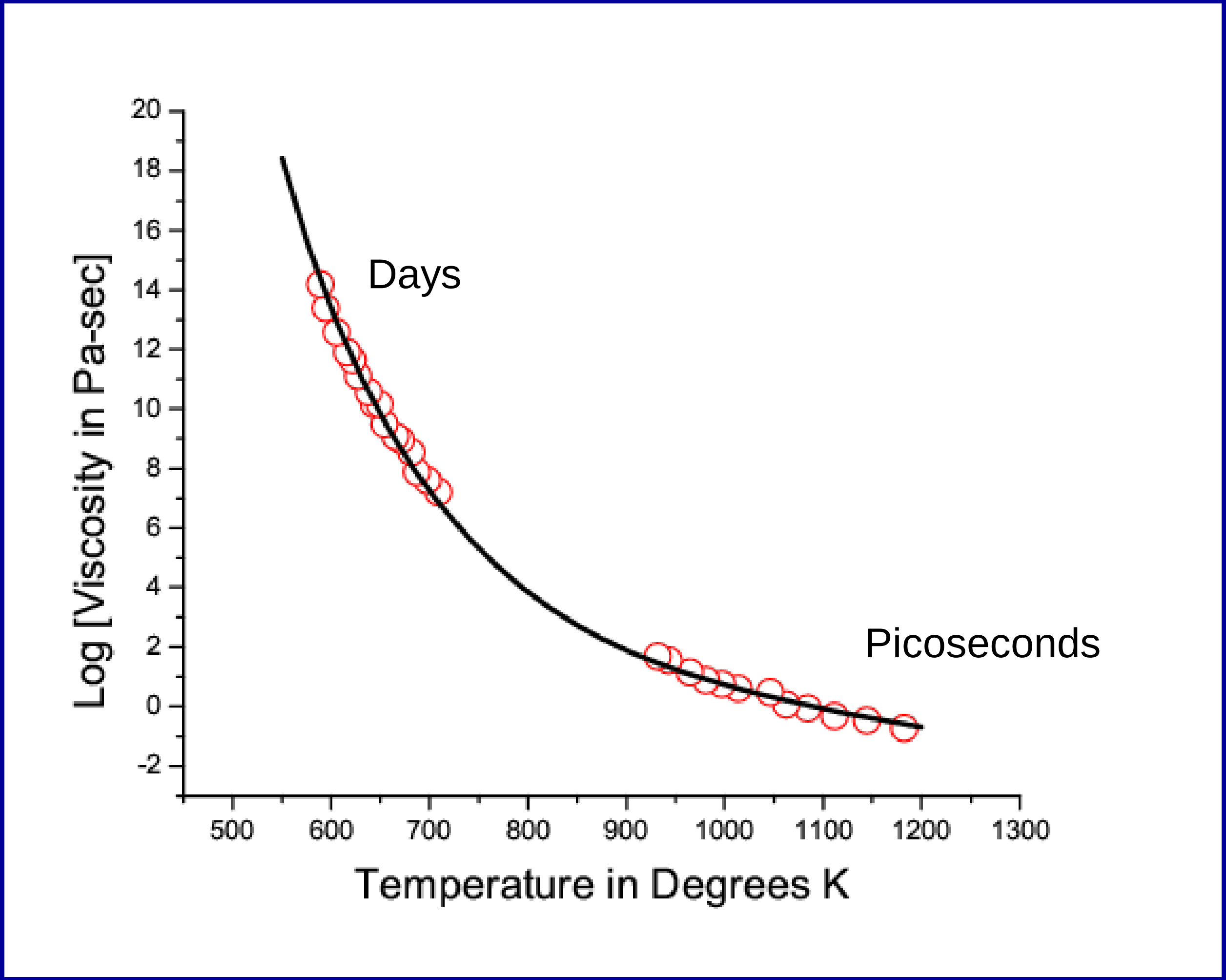
JSL, PRE 88, 012122 (2013);
JSL, Key Issues Review, Rep. Prog. Phys. 77, 042501 (2014)

Main messages:

- Need to focus on simple, realistic models, i.e. systems of particles with finite-range interactions.

- Recent numerical simulations, especially those of Tanaka and coworkers, imply Ising-like universality for fragile glass formers. If so, why ??

The time-scale problem



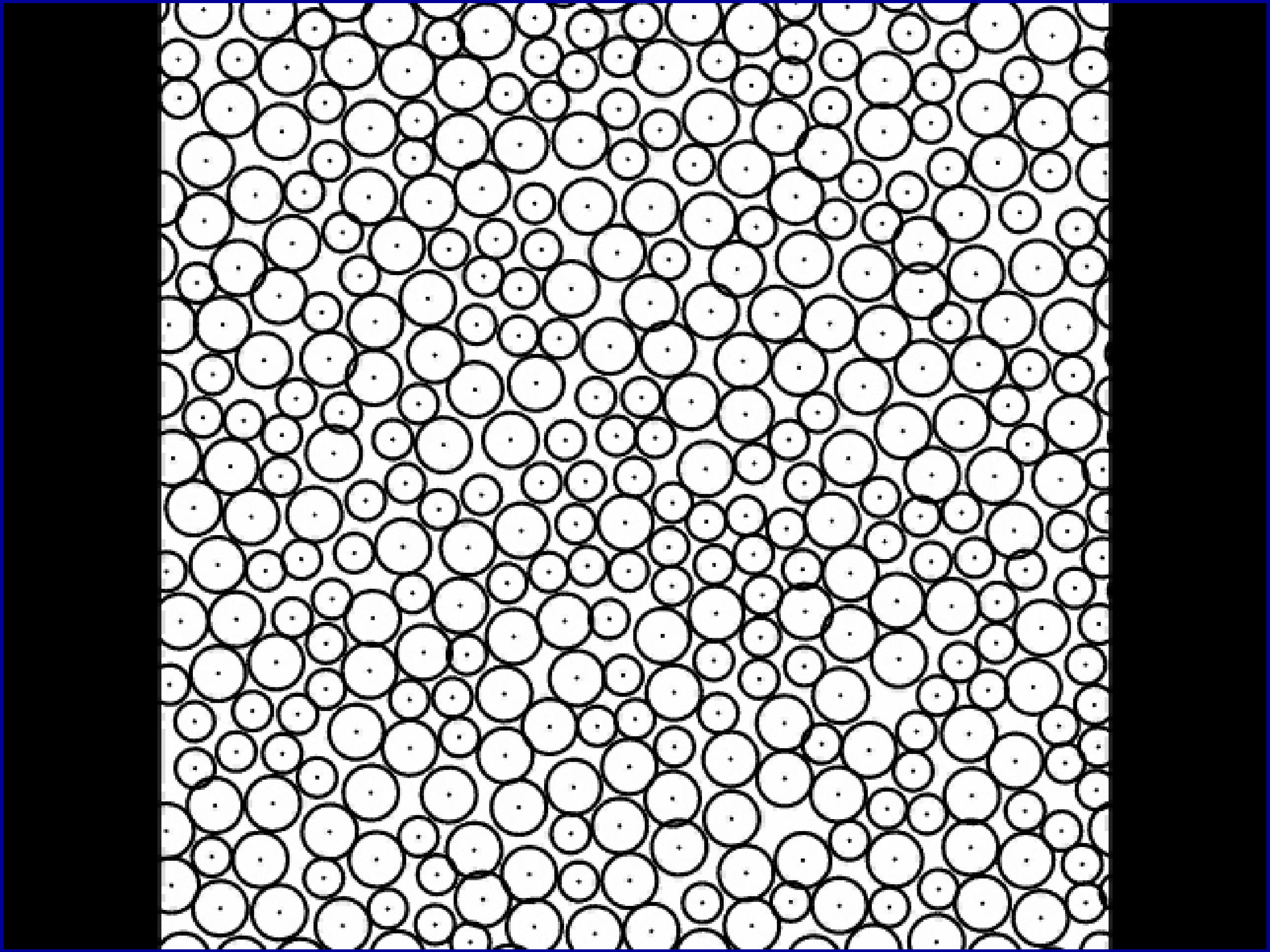
Viscosity of the bulk metallic glass “Vitreloy 1”

Structural relaxation time τ_α

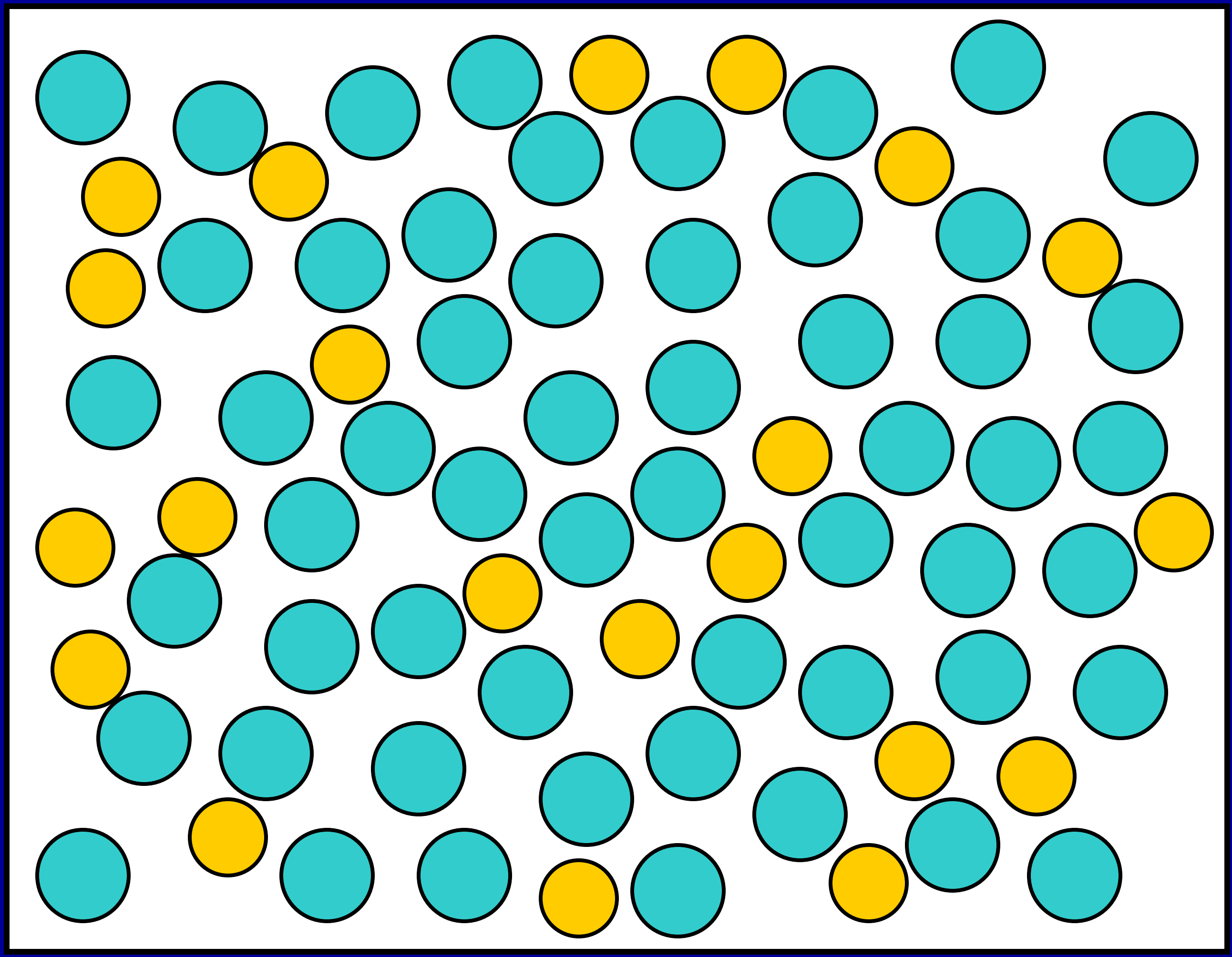
Viscosity $\sim \tau_\alpha$?; Diffusion constant $\sim 1/\tau_\alpha$?

Vogel-Fulcher-Tamann approximation: $\tau_\alpha \sim exp\left(\frac{D\,T_0}{T - T_0}\right)$?

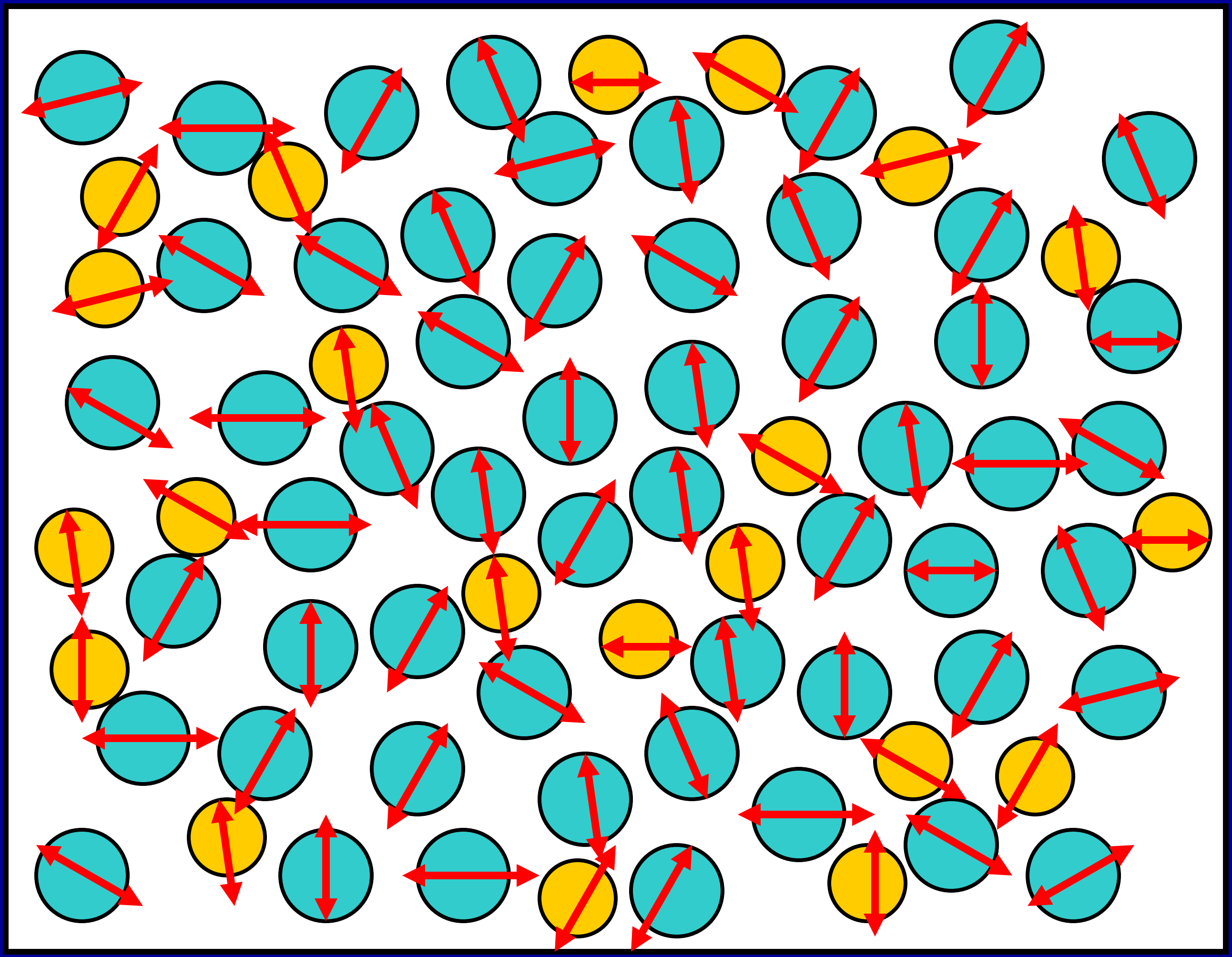
A sharper definition of τ_α must be based directly on the motions of particles



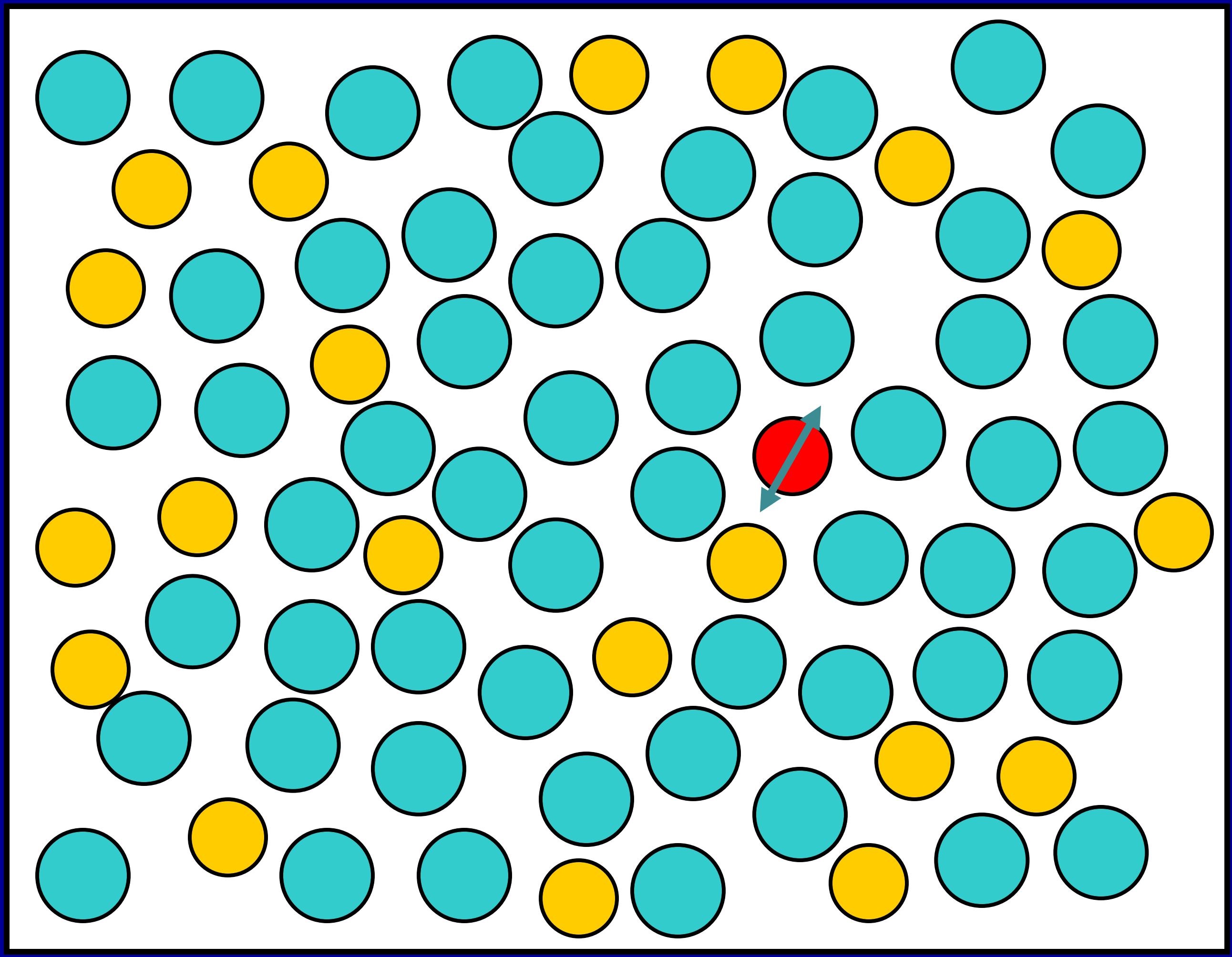
Simulation of a two-dimensional glass forming liquid by T.Haxton and A. Liu, above the glass temperature. Watch occasional irreversible rearrangements.



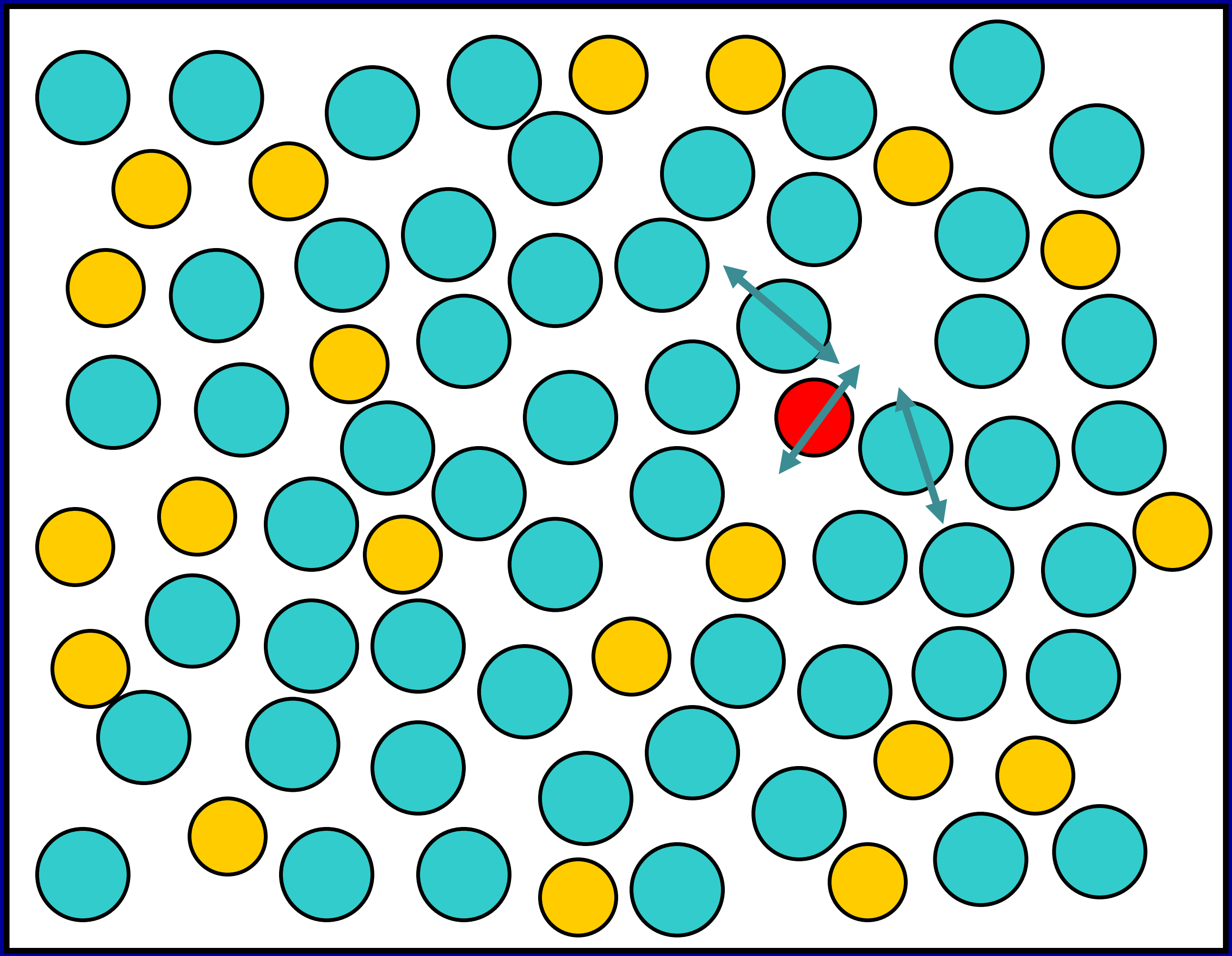
Inherent structure with molecules fixed in a mechanically stable configuration



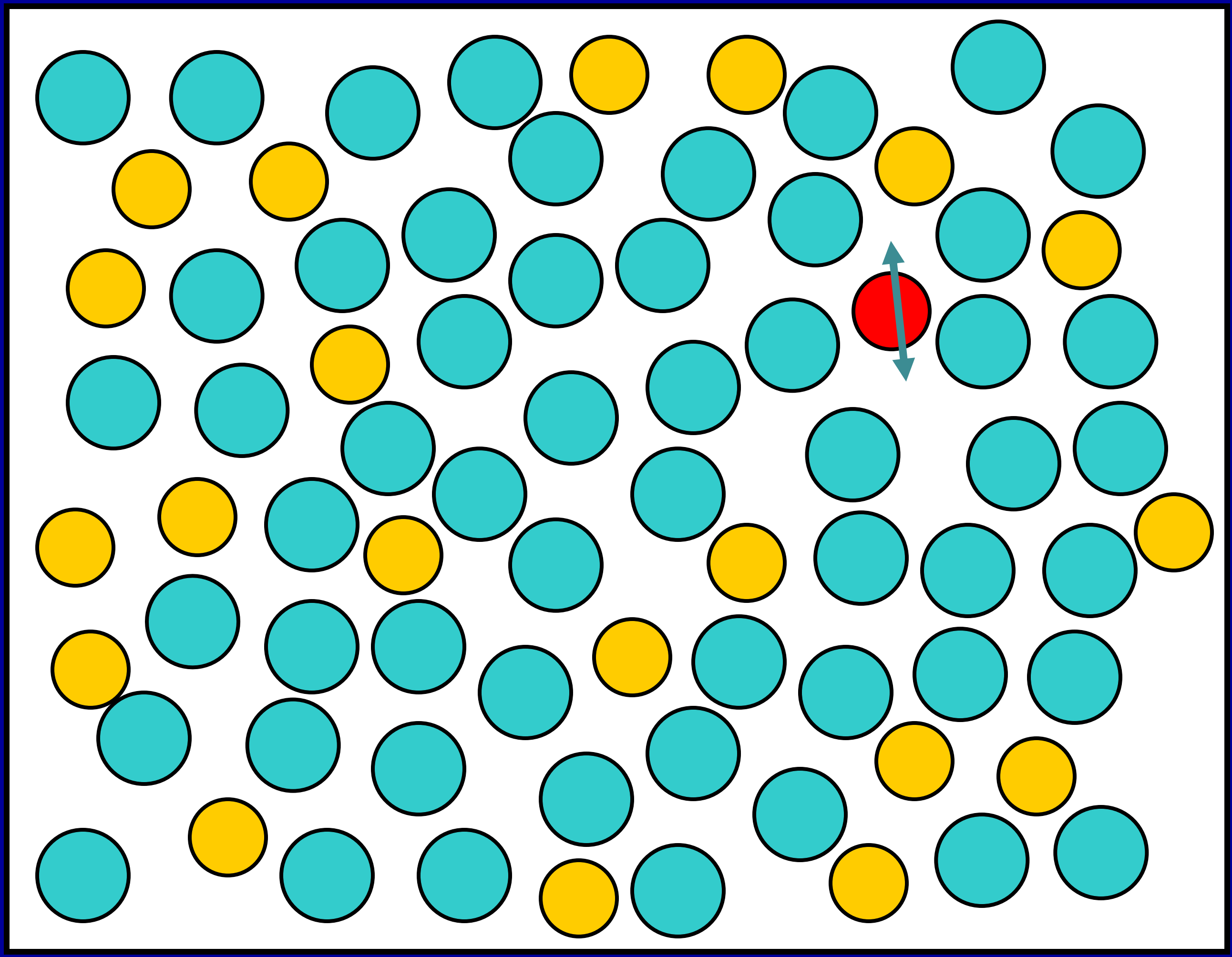
Kinetic/vibrational degrees of freedom superimposed on the inherent structure. In a glassy system, these rapid motions are only weakly coupled to the slow configurational transitions from one inherent structure to another.



Red tagged particle in its “cage”

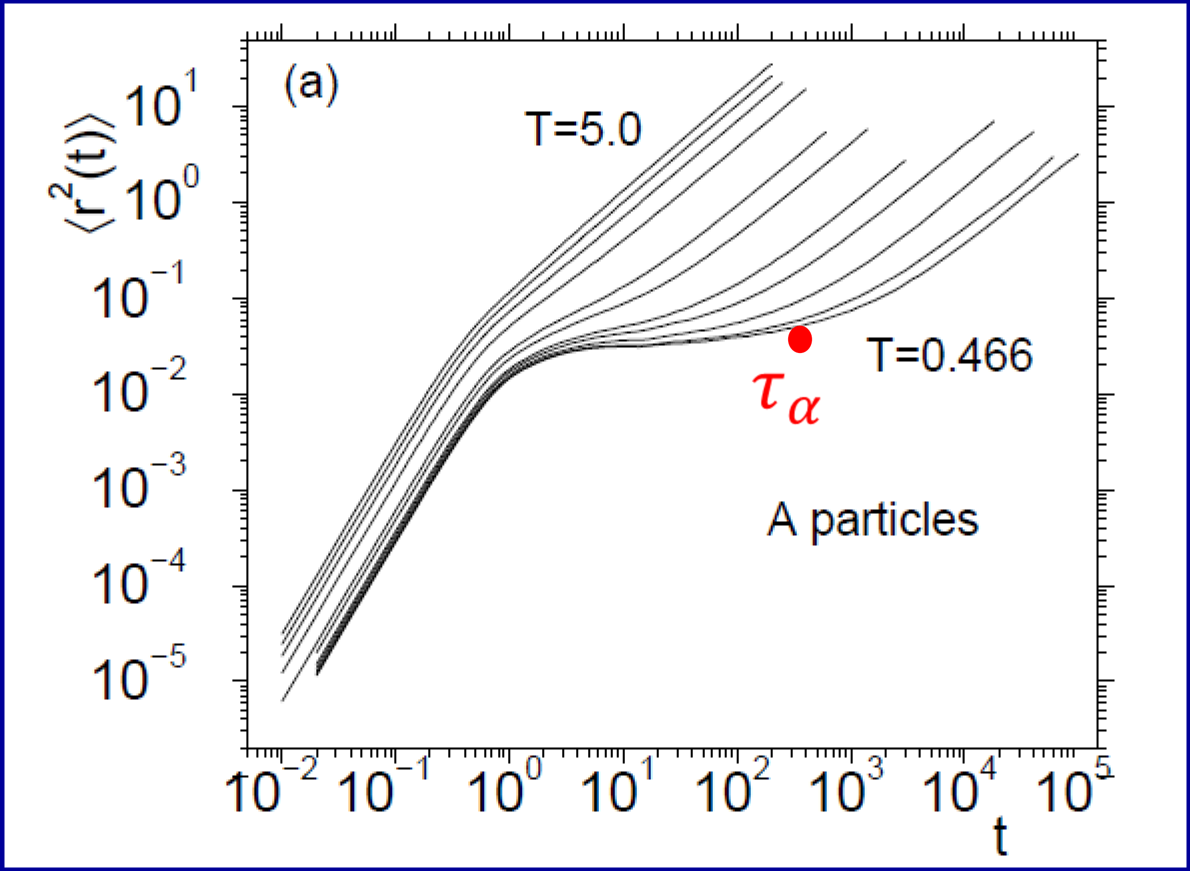


Fluctuation



The tagged particle has escaped from its original cage.
This is a diffusion step to a new inherent structure.
(Equivalently, an elementary shear transformation.)

Structural relaxation time τ_α: Escape from cage

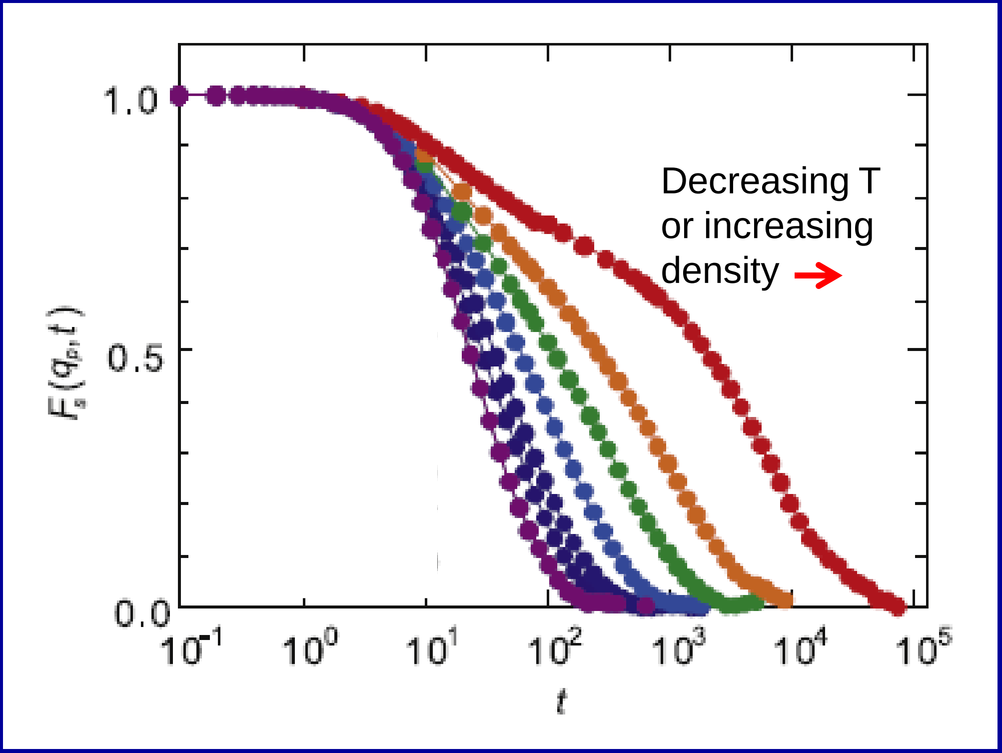


Ballistic motion within cage

$\langle r^2 \rangle \sim t^2$

Diffusion outside cage

$\langle r^2 \rangle \sim t$



Self intermediate scattering function can be used to determine τ_α

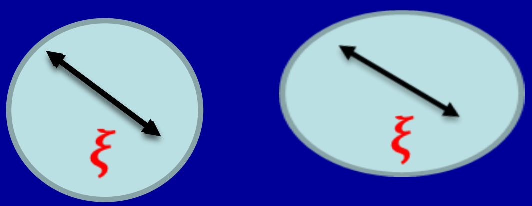
$$F_s(\vec{q}_p, t) = A \exp\left[-\left(\frac{t}{\tau_\alpha}\right)^\beta\right],$$

The length-scale problem

Common sense (a la Montanari and Semergian) implies that a diverging time scale must be related to a diverging length scale.

ξ= longest correlation length; the system consists of independently fluctuating regions of size ξ.

$$\tau_\alpha < exp\left(\frac{\Delta E(\xi)}{k_B T}\right)$$

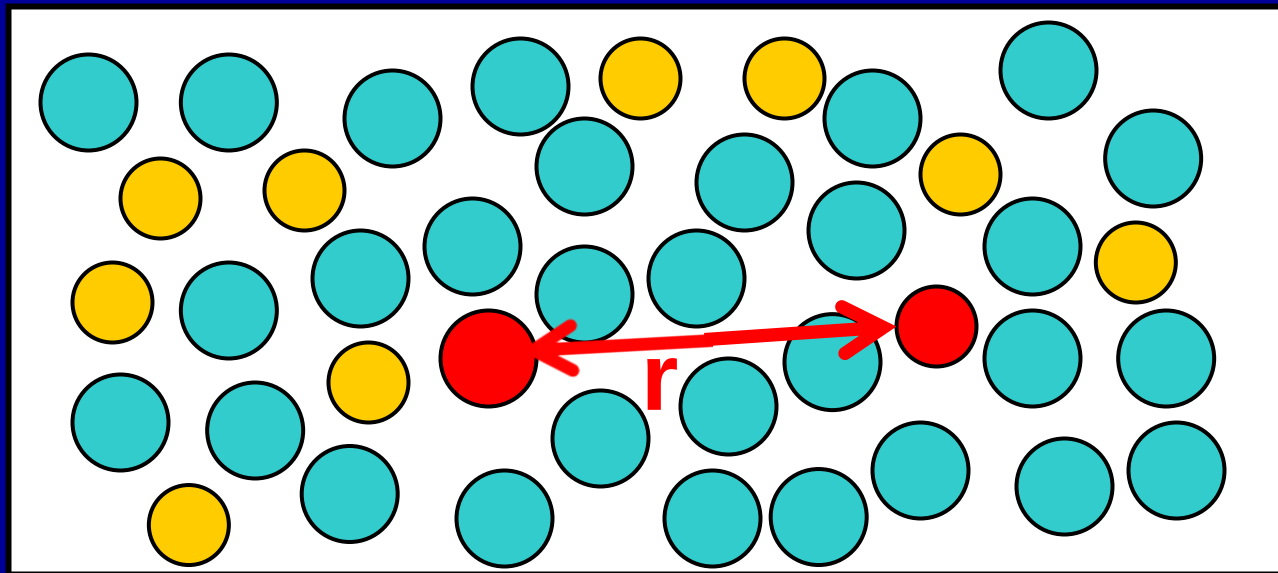


For finite-ranged forces, $\Delta E(\xi) < \xi^d$ (MS limit)

Gaussian fluctuations of the energies or volumes of these correlated regions imply that

$$\Delta E(\xi) \sim \sqrt{N_\xi} \sim \xi^{d/2}$$

which seems to agree with observations. Why? What is ξ?



"Dynamic" correlation length (4-point correlation function)

Two particles in their cages a distance **r** apart.

The probability that they are *both still* in their cages after a time τ_α is proportional to $exp\,(-r/\xi_4)$.

$\xi_4 =$ "dynamic" correlation length (a rigidity length), characterizes the size of "dynamic" heterogeneities.

Must ξ_4 be caused by some kind of structural correlation?

Ising-like scaling relations

Correlation length: $\xi \propto (T - T_0)^{-\nu}$ or $(\varphi_0 - \varphi)^{-\nu}$

Hyperscaling: $\nu = \frac{2}{d} - \alpha \cong \frac{2}{d}$

If $\tau_\alpha \propto exp\left(\frac{\Delta E(\xi)}{k_B T}\right)$ and $\Delta E(\xi) \sim \sqrt{N_\xi} \sim \xi^{d/2}$,

then $\tau_\alpha \sim exp\left(\frac{D\, T_0}{T - T_0}\right)$ (VFT)

Role of τ_α in determining diffusivity, viscosity, etc. ?

JSL, PRE 051507 (2012)

STZ creation rate = $\Gamma \, exp\left(-\, \frac{e_Z}{k_B \, T}\right)$

Attempt frequency: $\Gamma \sim 1/\tau_\alpha$ (a global mechanism)

Thermally activated, local creation and annihilation of STZ's enables particle rearrangements and thus drives diffusion, shear viscosity, etc., but in dynamically different ways.

ARTICLES

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nature materials

Critical-like behaviour of glass-forming liquids

Hajime Tanaka*, Takeshi Kawasaki, Hiroshi Shintani and Keiji Watanabe

"From our simulations and experiments of six different glass-forming liquids, we find that the heterogeneous dynamics is a result of critical-like fluctuations of *static* structural [bond-orientational] order. The static correlation length and susceptibility … show Ising-like power-law divergence towards the ideal glass-transition point…. Our results suggest a far more direct link than thought before between glass transition and critical phenomena. Indeed, the glass transition may be a new type of critical phenomenon where a structural order parameter is directly linked to slowness."

See also Mosayebi, Del Gado, Ilg, and Ottinger, PRL 104, 20574 (2010)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

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Structural signature of slow dynamics and dynamic heterogeneity in two-dimensional colloidal liquids: glassy structural order

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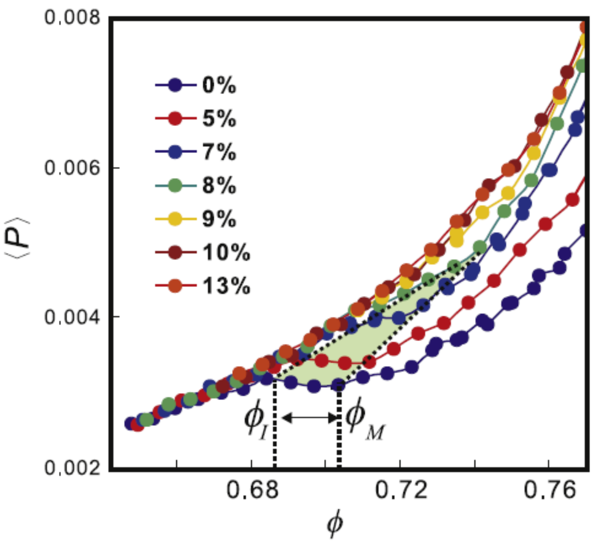


Figure 2. ϕ-dependence of pressure $\langle P \rangle$ for various Δ.

Hard-disk systems for a range of polydispersities, plus one bidisperse system.

Tanaka et al.:

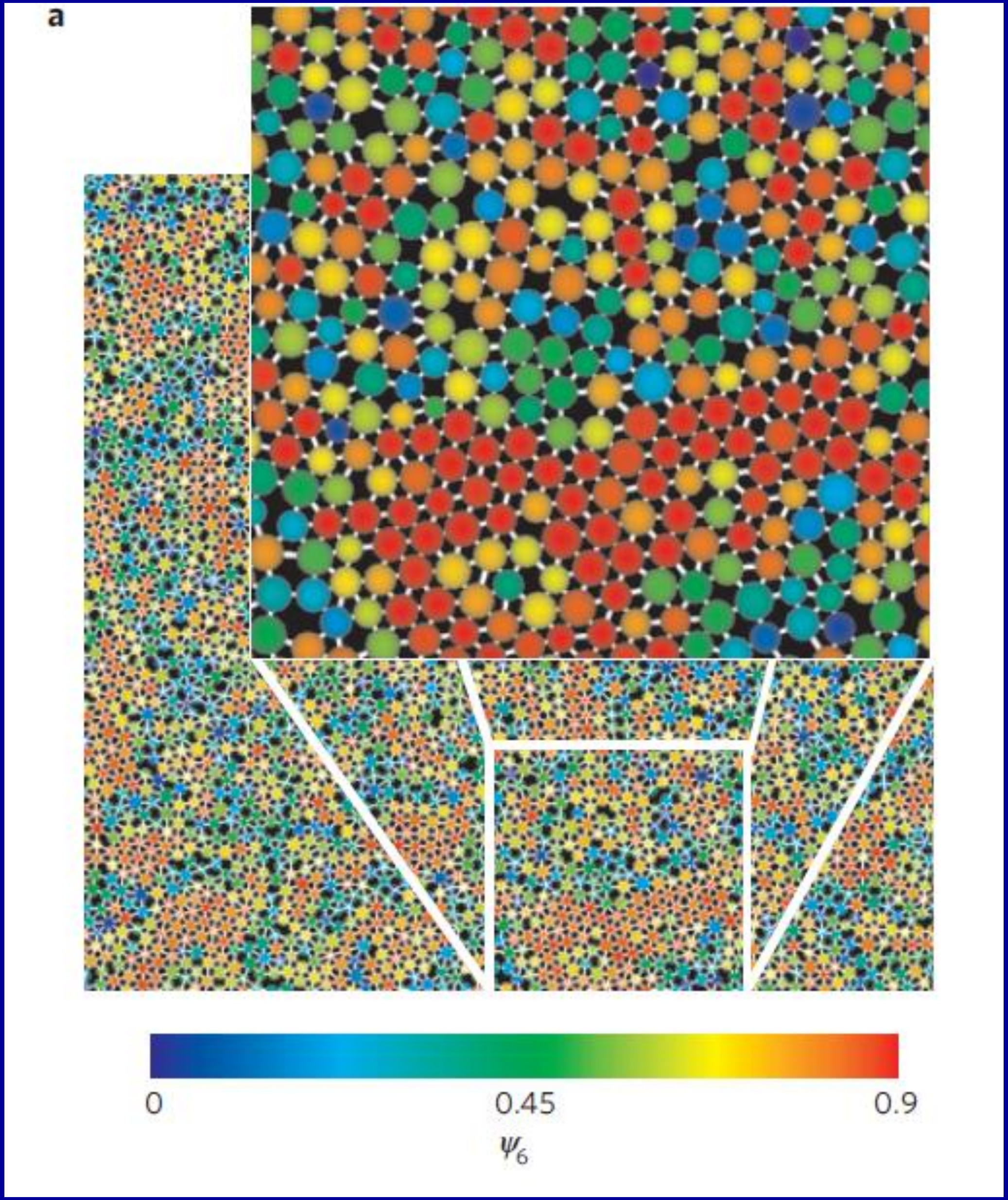
Bond-orientational correlations in moderately polydisperse, hard-core, colloidal suspensions in both two and three dimensions. (Also in some other models)

E.g. two dimensional hexatic order parameter

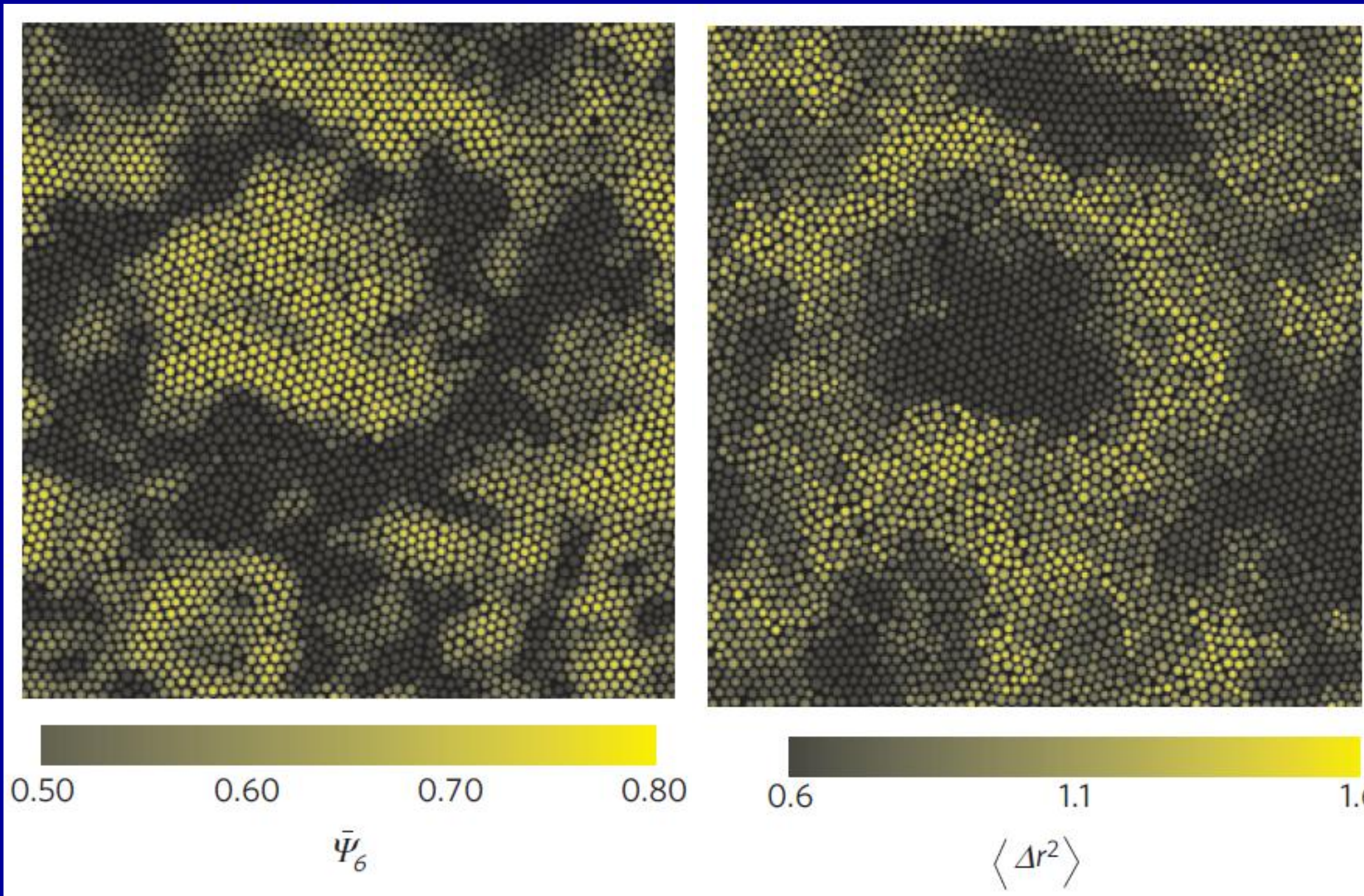
$$\psi_6(j) = \frac{1}{n(j)} \sum_m^{n(j)} exp\,(6\; i\; \theta_m)$$

$$g_6(r) \propto \left\langle \psi_6{}^* \;(r)\;\; \psi_6(0)\right\rangle \propto exp\; \left(-\, {}^{r}/_{\xi_6}\right)$$

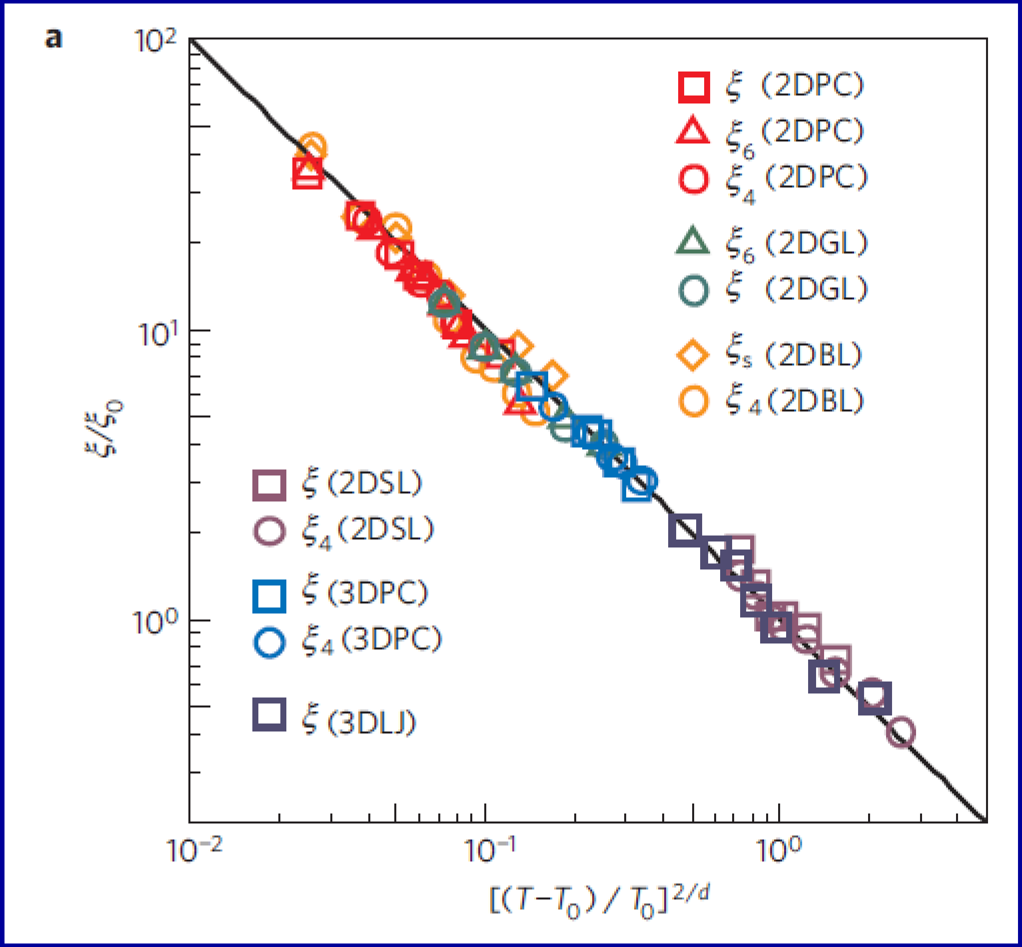
For hard-core systems, measure diverging correlations as functions of increasing packing fraction φ instead of decreasing temperature T.



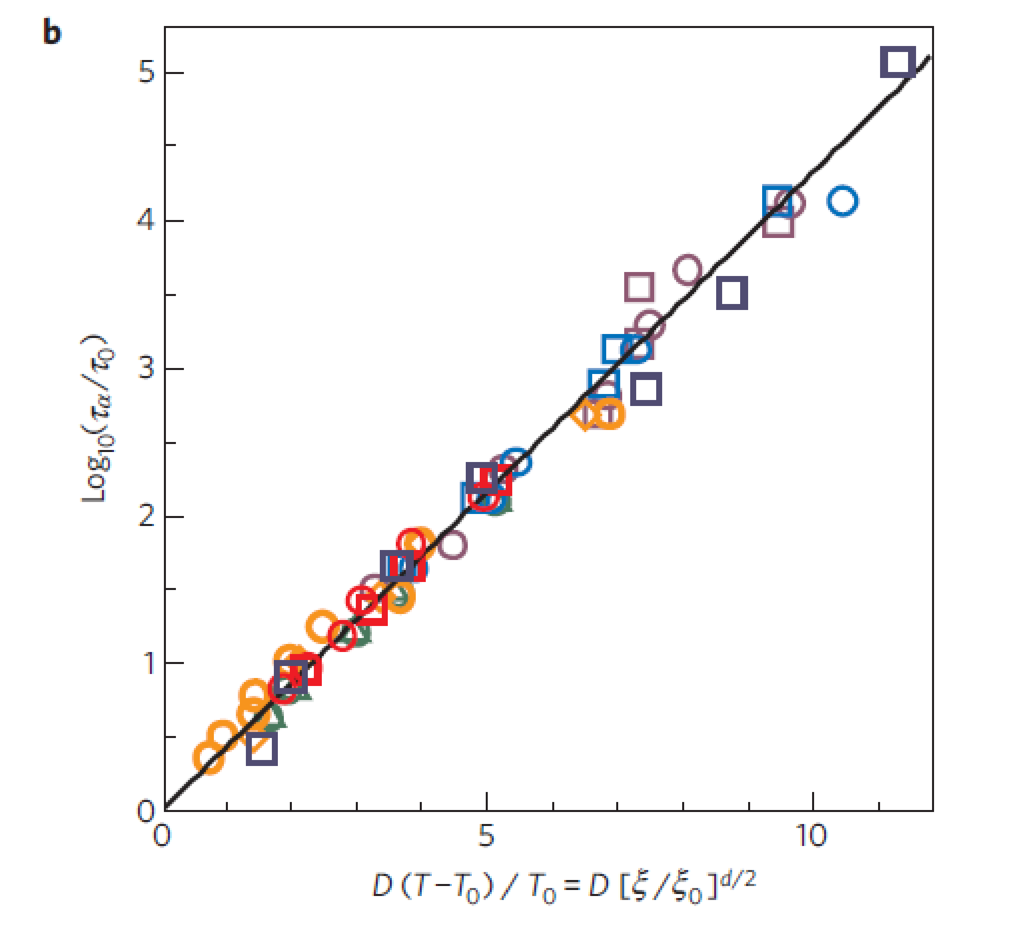
Polydisperse disks: regions of hexatic order (red).



Hexatically ordered (light) regions on the left coincide with the more rigid (dark) regions on the right.



Ising scaling of the correlation length in 2 and 3 dimensions, for several different models of a glass forming liquid. Temperature T is equivalent to inverse packing fraction for hard-core colloidal models (2DPC, 3DPC).



Vogel-Fulcher-Tamann law for structural relaxation time

$$\log \tau_\alpha \sim \frac{D\ T_0}{T - T_0} \ \sim \mathrm{D}\ [\xi/\xi_0]^{d/2}$$

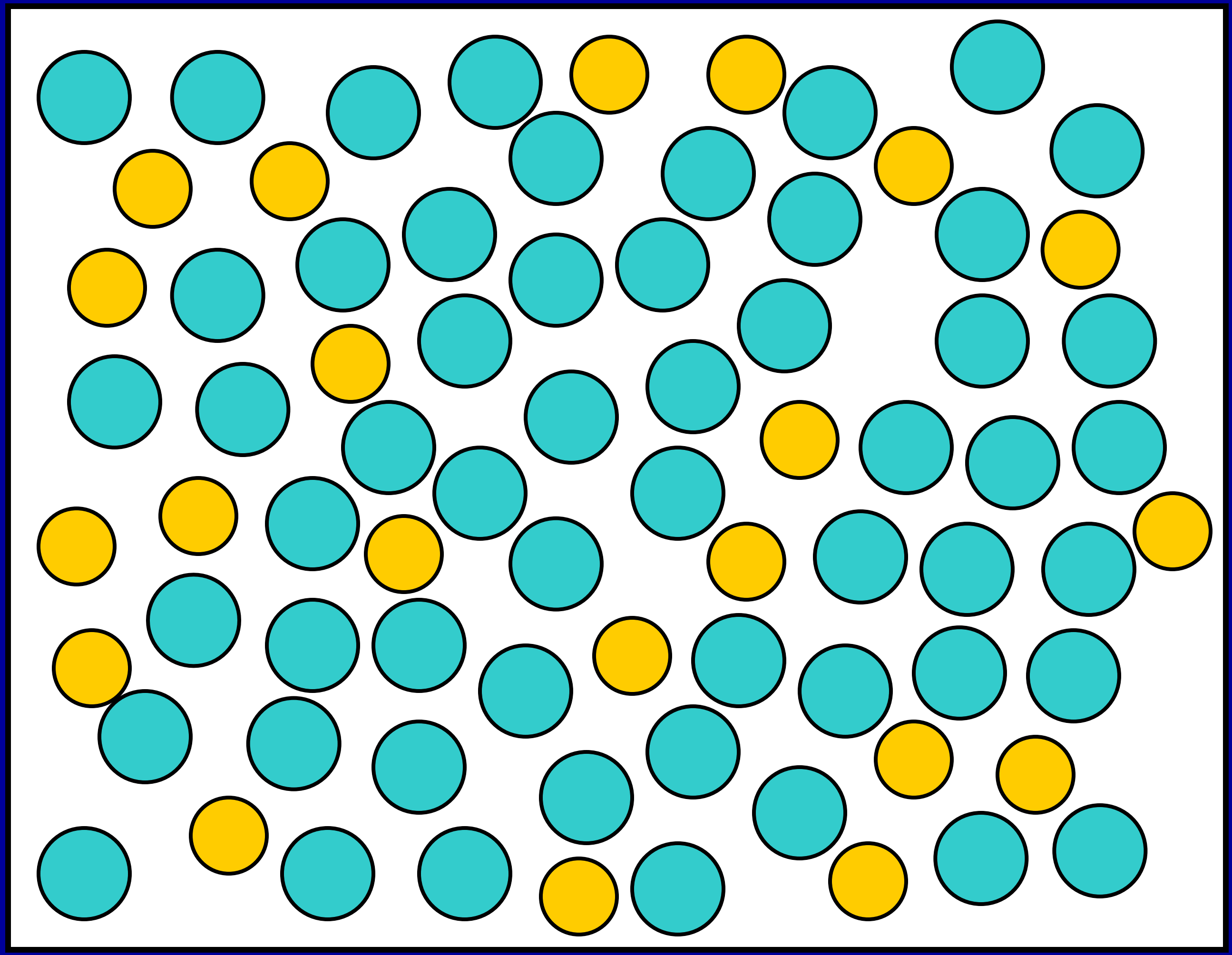
Why Ising symmetry?

Two-state systems:

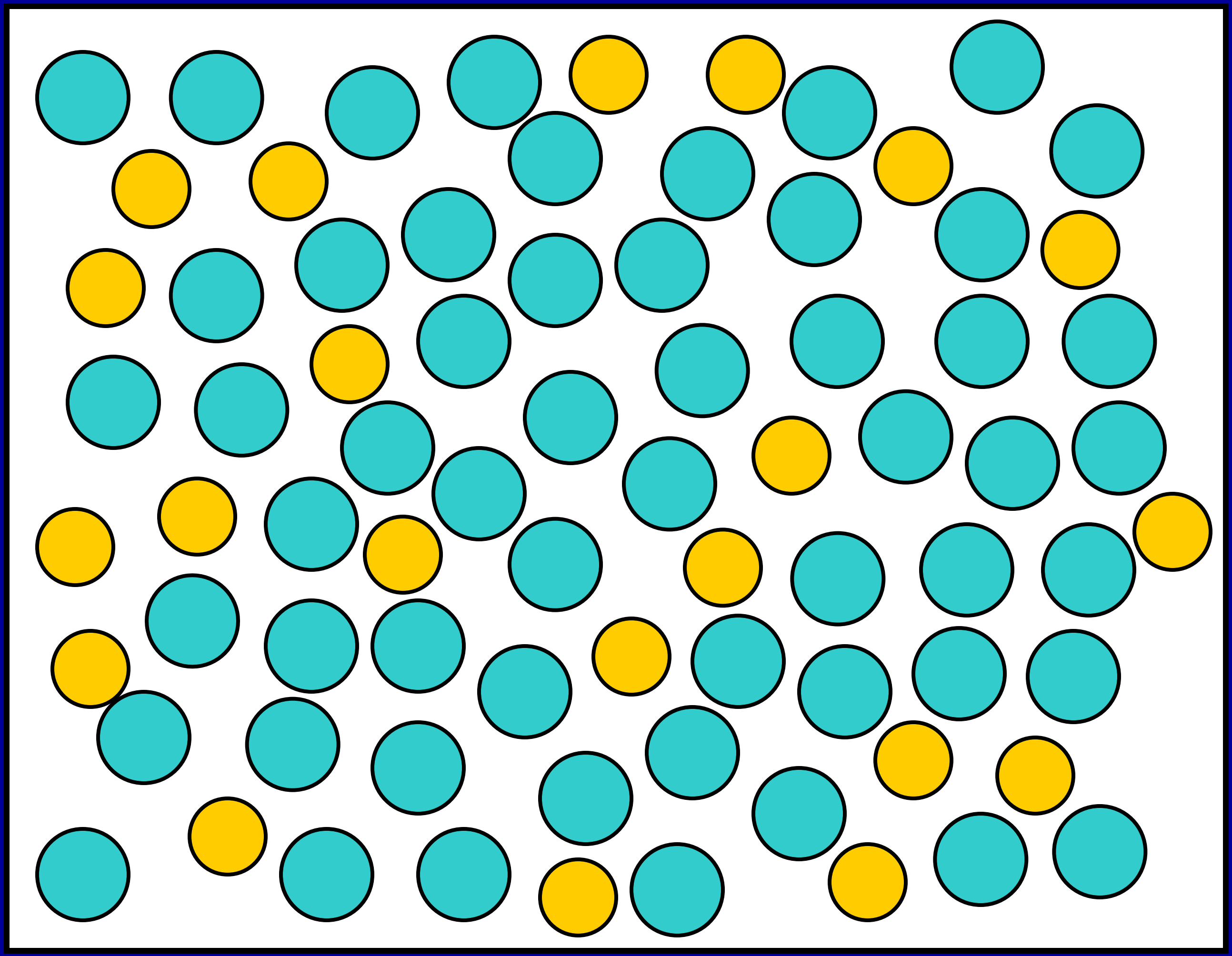
Hypothesized by Anderson, Halperin and Varma (1972) to explain low-temperature glassy behaviors.

Another example: STZ's are two-state flow defects.

If most local configurations in a disordered system are rigid, then the most probable kinds of flexible clusters of particles are those with just two-fold near-degeneracies.



Inherent structure



Inherent structure: second state

Theoretical strategy: JSL PRE 88, (2013)

- Choose statistically relevant internal variables: populations of two-state clusters, plus a population of “voids” that determines the average density of these clusters.

- Write the volume and entropy as functions of these variables.

- Maximize the entropy for fixed volume. The Lagrange multiplier is θ/p , where $\theta = k_B T$ and p is the pressure.

Statistically relevant internal state variables

$N_{\pm}$ = number of +/- two-state clusters

N^* = total number of two-state clusters = $N_+ + N_-$

N_0 = number of "voids"

The volume decreases when clusters of like signs are next to each other. Here is a mean-field approximation for that effect:

$$\mathcal{V} \cong N^* v^* + N_0\, v_0 - \frac{J}{2\,(N^* + N_0)}\,(N_+^2 + N_-^2),$$

J is the analog of the Ising exchange coupling.

More convenient variables are: $m = \frac{N_+ - N_-}{N^*}, \quad \eta = \frac{N^*}{N^* + N_0}.$

m is the analog of the magnetization. η is a measure of how close the system is to jamming. The volume becomes:

$$\frac{\mathcal{V}(m,\eta)}{N^*} = v^* + \left(\frac{1}{\eta} - 1\right) v_0 - \frac{1}{4} J\,\eta\,(1 + m^2).$$

Write the entropy in the form $\mathcal{S}(m,\eta) \cong \mathcal{S}_1(m) + \mathcal{S}_2(\eta).$

$$\frac{\mathcal{S}_1(m)}{N^*} = \ln(2) - \frac{1}{2}(1+m)\ln(1+m) - \frac{1}{2}(1-m)\ln(1-m).$$

= Ising entropy

$$\frac{\mathcal{S}_2(\eta)}{N^*} = -\ln(\eta) + \frac{A}{1-\epsilon}(1-\eta)^{1-\epsilon},$$

= lattice gas for $\epsilon \to 0$;

= van der Waals for $\varepsilon \to 1$

Mean-field equations of state:

Variation with respect to *m:*

$$m = \tanh\left(\frac{p\,J\,\eta\,m}{2\,k_B T}\right).$$

Variation with respect to η :

$$\frac{p}{\theta} = \frac{1}{v_0 + (J/4)\,\eta^2\,(1+m^2)}\left[\eta + \frac{A\,\eta^2}{(1-\eta)^\epsilon}\right].$$

Beyond mean field: *m* undergoes critical fluctuations

$$m \to M(\eta) = \begin{cases} 0, & \text{for } \eta < \eta_c \\ \mu\,[(\eta/\eta_c - 1)]^\beta, & \text{for } \eta > \eta_c\,, \end{cases}$$

$$\eta_c = \frac{2\,\theta}{p_c\,J},$$

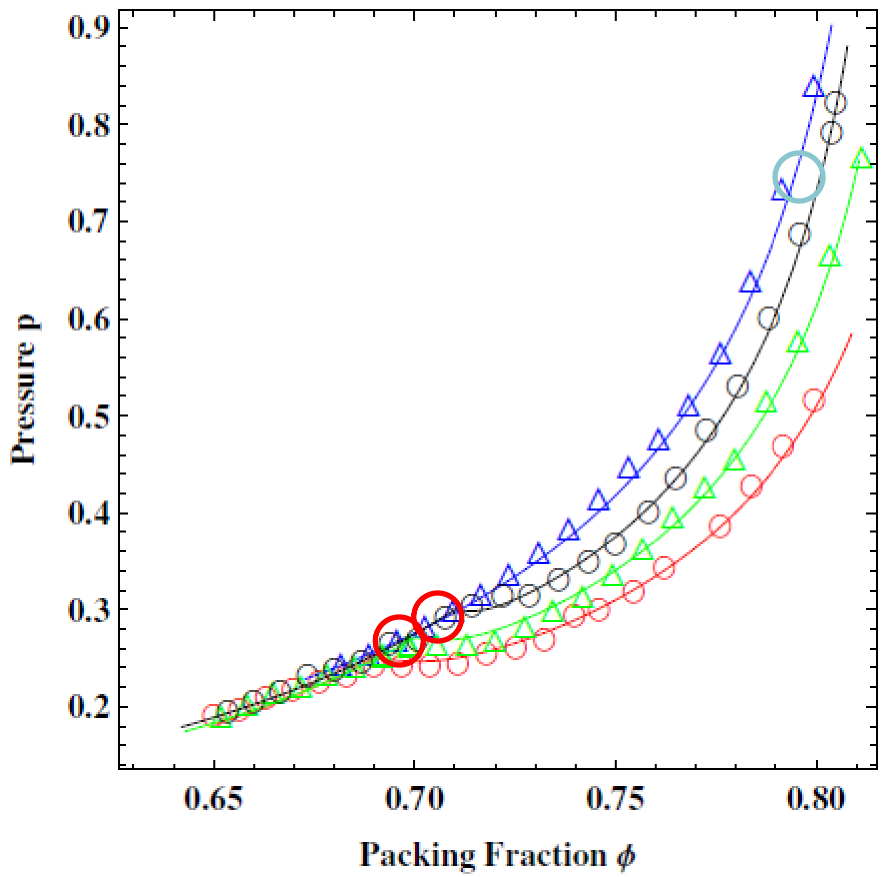


FIG. 2: (Color online) Pressure as a function of packing fraction, from bottom to top, for polydispersties $\Delta = 0\%$ (red circles), 5% (green triangles), 7% (black circles), and 13% (blue triangles).

Kawasaki and Tanaka, 2011

Sequence of liquid-hexatic transitions for small polydispersity Δ < 5%.

Sequence of liquid-glass transitions for Δ > 9%.

Strength D (inverse fragility) increases with increasing Δ and increasing critical packing fraction.

Conclusions: Issues and open questions

- Are glass-forming fluids generally characterized by diverging structural (“static”) correlations? Or does this behavior occur only in special cases?
- Is there always a structural correlation length associated with a dynamical correlation length, i.e. with a dynamical heterogeneity?
- What other mechanisms might be relevant? Rigidity percolation?
- How universal is the Ising-like behavior?