Thermodynamic fluctuations in model glasses

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Coworkers

- With:

D. Coslovich (Montpellier)

R. Jack (Bath)

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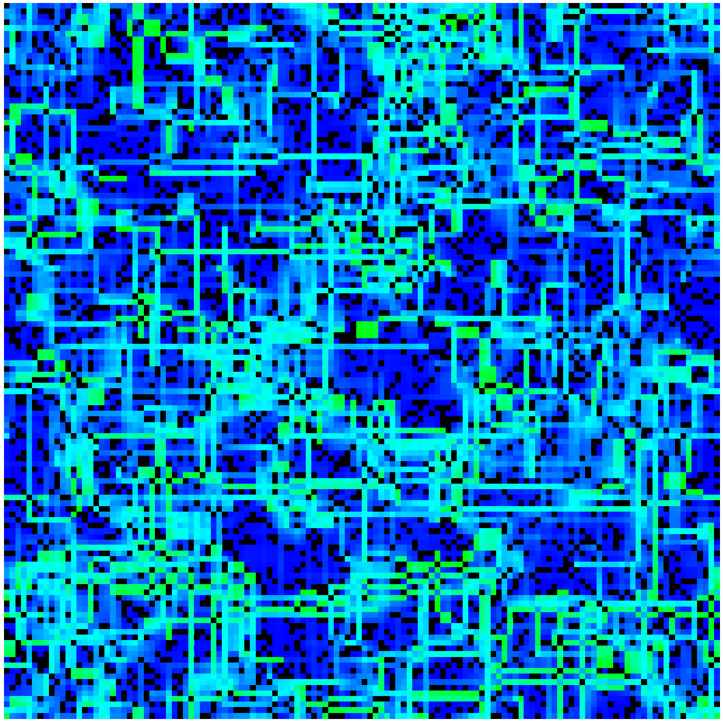
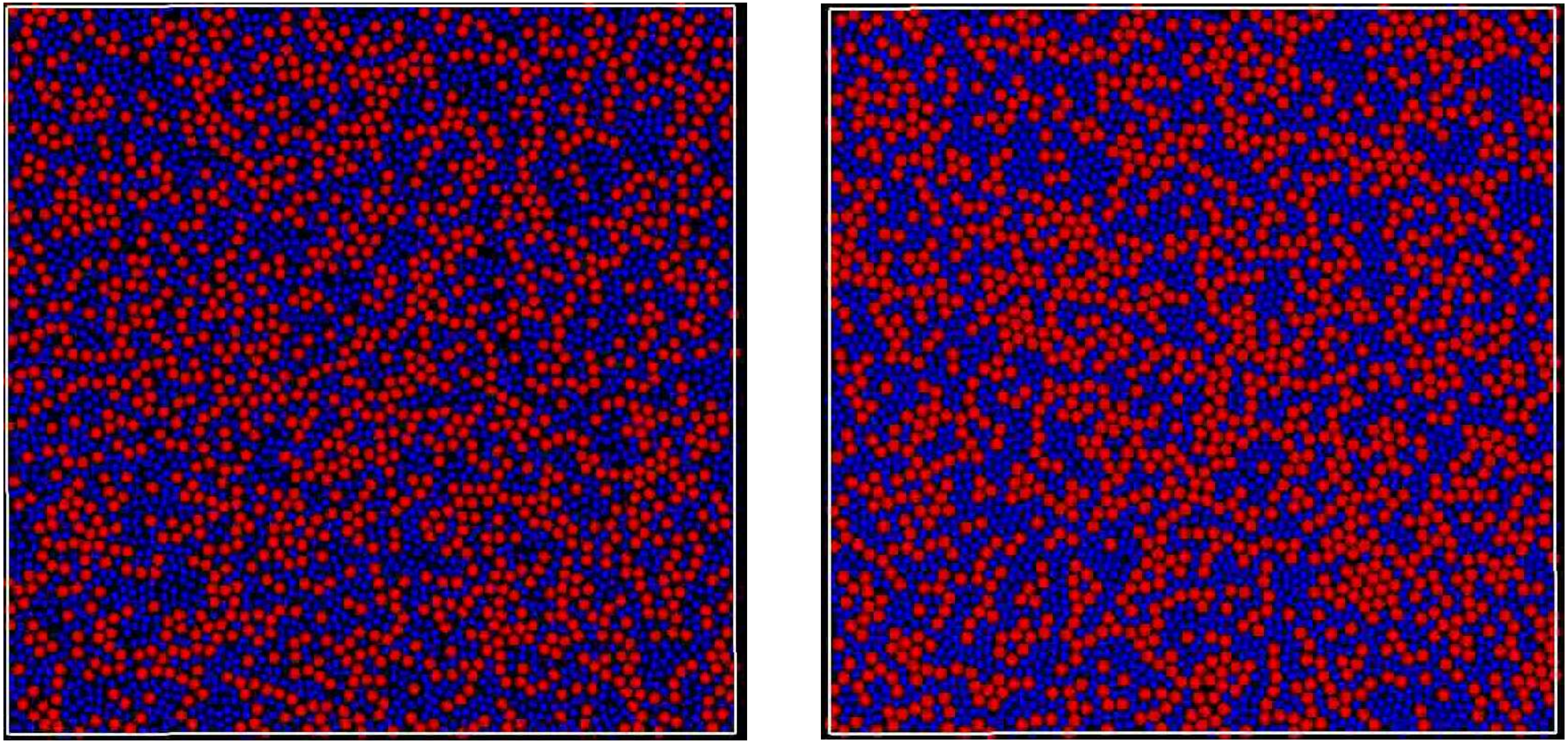


The glass “transition”

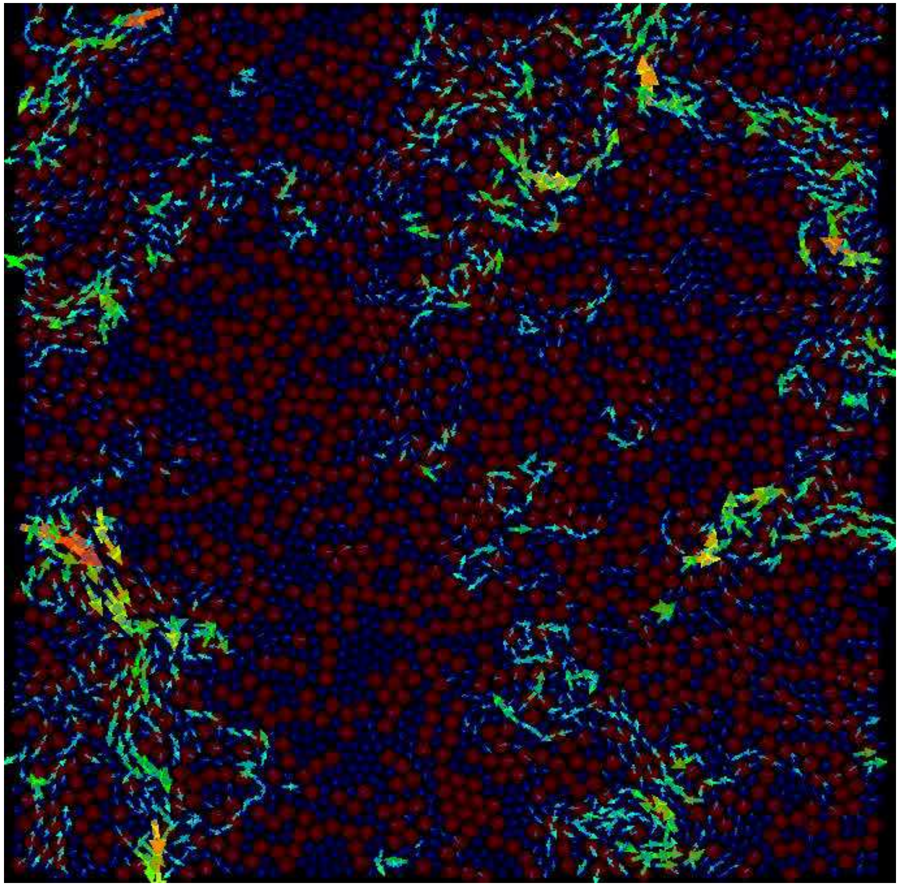


Fluid *Glass*

- Activated dynamics: “super-Arrhenius” growth of viscosity.
- “No change of structure” accompanying dynamic arrest.

Dynamic heterogeneity

- Growth of spatio-temporal correlations. fast

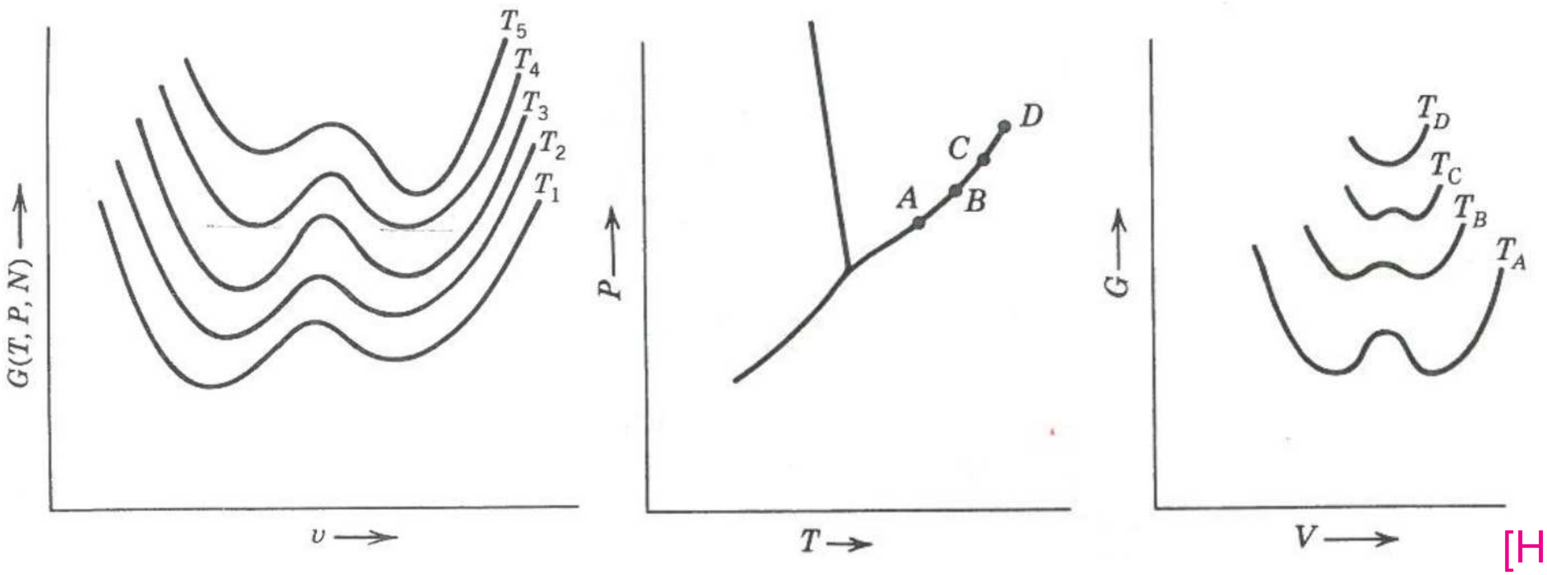


["Dynamical heterogeneities in glasses, colloids and granular materials", Oxford, 2011]

- Major puzzle: Link with static length scales? Statics vs. dynamics.

Lessons from a simpler problem

- Liquid-gas transition: First-order transition ending at a critical point.



[H. Callen]

- Van der Waals (1873): Mean-field equation of state predicts nature of phase transition, and a simple "landscape" with (only) 2 states.

- Missing in mean-field: Nucleation ('27-'60) and critical fluctuations ('75).
  - -Convex free energy (interfaces); super-activated dynamics from CNT.
  - -Non-trivial finite d exponents, mean-field valid for $d \geq 4 (\gtrsim d = 3)$.

Less simple problems: disorder

- Random field Ising model (Imry-Ma '75): $H = -J \sum_{ij} S_i S_j - \sum_i h_i S_i$.
- Edwards-Anderson spin glass model ('75): $H = -\sum_{ij} J_{ij} S_i S_j$.
- Some lessons:

- RFIM: Super-Arrhenius dynamics ($T = 0$ critical point), non-trivial exponents for the barriers, nonperturbative treatment needed for $d < 6$.

- SG: Mean-field solution using replica symmetry breaking (Parisi '79-'83), encoding hierarchical free energy landscape.

- Below $d = 6$: Mean-field results vs. phenomenological 'droplet' (low dimensional excitations) theory? Unsolved to this day.

- Numerical studies of critical properties and low-temperature phases notoriously difficult (e.g. AT line...). Multiple models useful.

- Decisive experiments are difficult.

Structural glasses

• Hard spheres as a canonical glass model (Pusey - van Megen '86).

• Mean-field thermodynamic solution $d \to \infty$ established in 2013. Solution confirms density functional theory, Bethe lattice, etc.

[Kurchan, Parisi, Zamponi '13-'14]

• Universality class identified earlier using models such as p-spin model.

$$H = -\sum_{i_1 \cdots i_p} J_{i_1 \cdots i_p} S_{i_1} \cdots S_{i_p}.$$

[Kirkpatrick, Thirumalai, Wolynes '87-'89]

• Mean-field dynamics unsolved to this day. This is probably not Götze's mode-coupling theory.

• Lessons learnt from earlier problems:

- Well-defined path (vdW $\to$ Wilson)... possibly incorrect!
- Non-trivial critical fluctuations below $d = 8$ (or 6?) $\gg d = 3$;
- Difficulty of numerical simulations;
- Experiments not always decisive.

RFOT

• Random First Order Transition (RFOT) theory is a theoretical framework constructed over the last 30 years using a diverse set of analytical techniques. [*Structural glasses and supercooled liquids*, Wiley '12]

• Mean-field character now fully understood. Complex free energy landscape gives rise to sharp transitions ('guessed' in experimental data):

- Onset (apparition of metastable states);

- "Mode-coupling" singularity (long-lived metastable states, $\mathcal{N} \sim e^{N\Sigma}$);

- Entropy crisis ($\Sigma = \frac{1}{N} \ln \mathcal{N} \to 0$).

• Ideal glass $=$ zero configurational entropy, replica symmetry breaking.

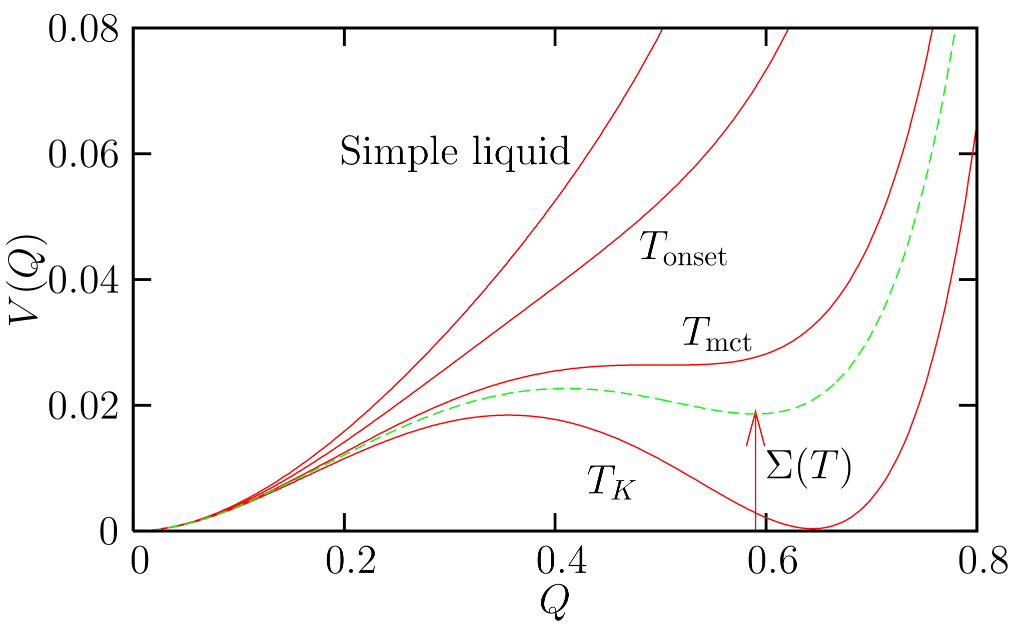
• Proliferation of 'states' identified by density profiles. Overlap between (coarse-grained) density profiles is the order parameter:

$$Q_{12} = \frac{1}{N} \sum_{i,j=1}^{N} \theta(a - |\mathbf{r}_{1,i} - \mathbf{r}_{2,j}|), \text{ with } a \approx 0.3\sigma.$$

Landau free energy

• Effective potential $V(Q)$ is the free energy cost to have 2 configurations at fixed overlap Q_{12}: [Franz & Parisi, PRL '97]

$$V(Q) = -(T/N) \int d\mathbf{r}_2 e^{-\beta H(\mathbf{r}_2)} \log \int d\mathbf{r}_1 e^{-\beta H(\mathbf{r}_1)} \delta(Q - Q_{12})$$



• 'van der Waals' picture of the glass transition.

• Large Q metastable state has infinite lifetime in mean-field.

• First-order jump at T_K, when 'driving force' $\Sigma \to 0$.

• Finite d implies convex $V(Q)$: Surface tension between 'metastable' states appears. Suggests to interpret relaxation as nucleation process driven by entropic forces (super-Arrhenius). [KTW, '89]

Direct $3d$ measurement?

• $V(Q)$ is a 'large deviation' function, mainly studied in mean-field RFOT limit: $P(Q) = \overline{\langle \delta(Q - Q_{12}) \rangle_T} \sim \exp[-\beta N V(Q)]$.

• Principle: Take two equilibrated configurations 1 and 2, measure their overlap Q_{12}, record the histogram of Q_{12}.

• Problems:

- $T > T_K$: typical configurations have $Q_{12} \ll 1$.
- Thermalizing near/below T_K?
- Translational/rotational invariance: $Q_{12} \ll 1$ even in ideal glass.

• A possible solution: Seek large deviations using umbrella sampling techniques for coupled copies with $\epsilon \to 0$: [e.g. Frenkel & Smit]

- Biased sampling using $W_i(Q_{12}) = k_i(Q_{12} - Q_i)^2$ to explore $Q_{12} \approx Q_i$.
- Vary (k_i, Q_i) to explore entire Q_{12}-range with careful thermalization.
- Reconstruct $P(Q)$ using histogram reweighting techniques.

Free energy measurements

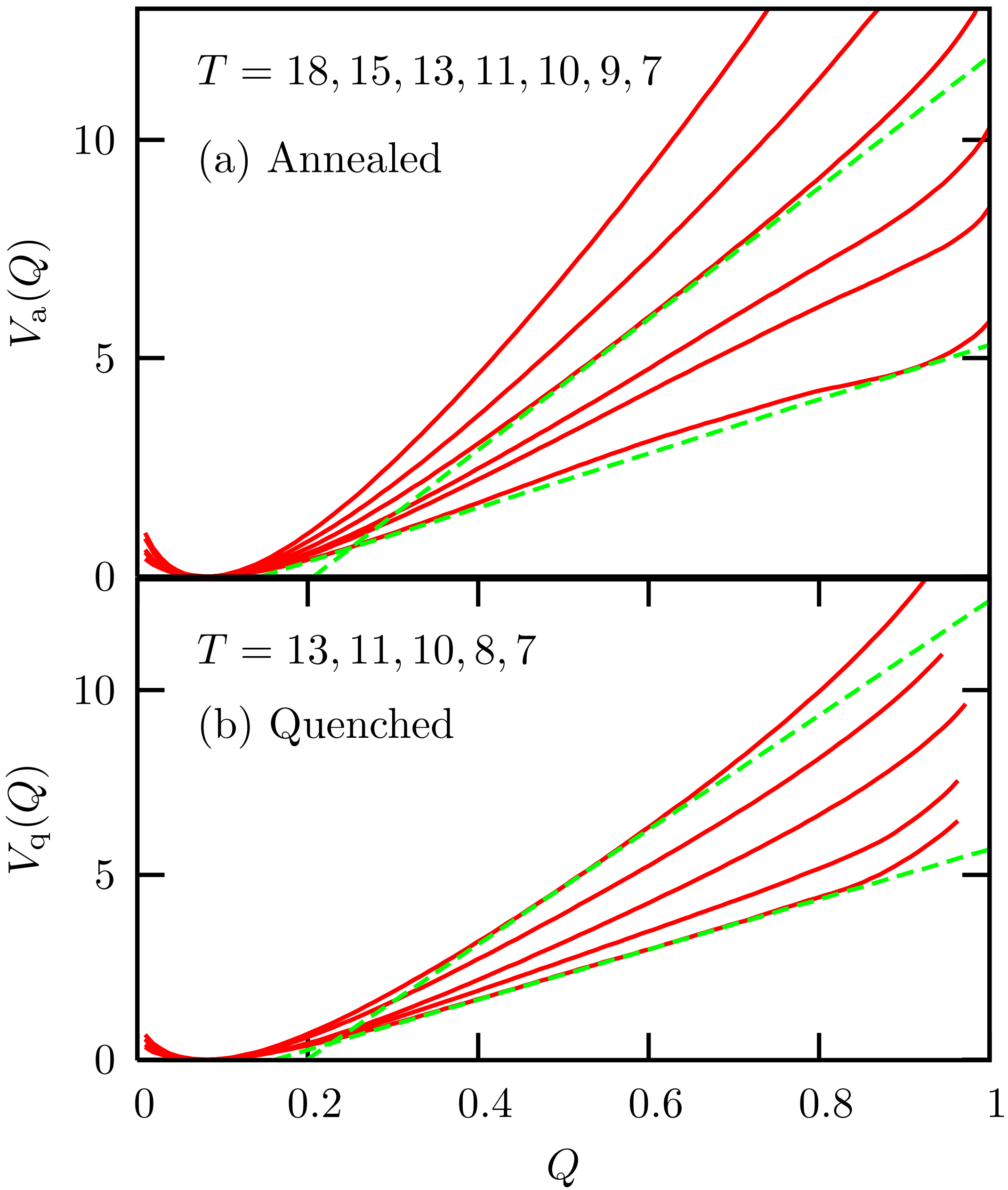
- Thermalized MD simulations of harmonic spheres with $N = 108$; $T_{\rm onset} \approx 12$.

- Linear part below $T_{\rm onset}$: phase coexistence between multiple metastable states in $3d$ bulk liquid.

- Non trivial thermodynamic fluctuations accompany slow dynamics.

- The 'structure' changes dramatically with T – just not $g(r)$. Mirrors dynamical large deviations.

[Berthier, PRE '13]

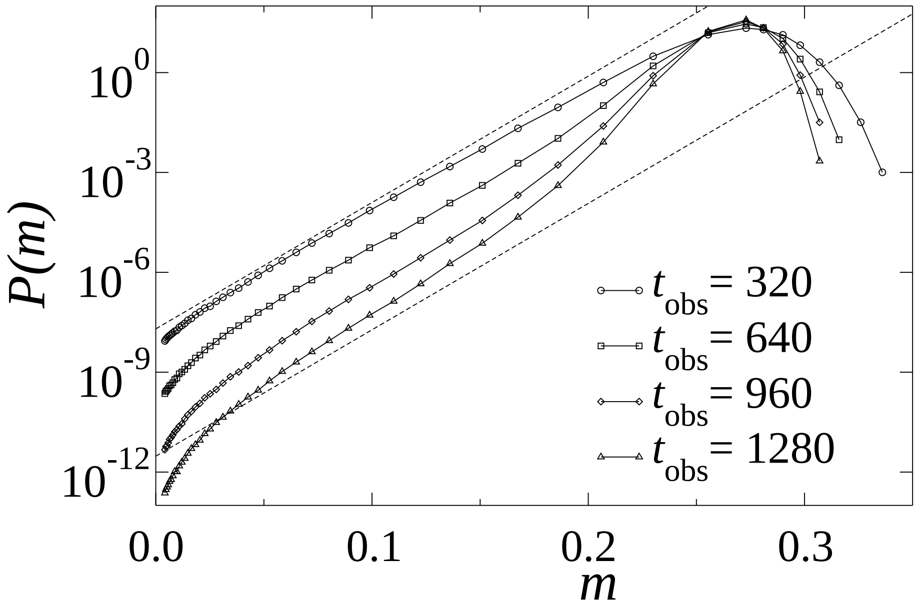


Link with dynamic heterogeneity

• Large deviations of global fluctuations of local activity $m_t = \int dx \int_0^t dt' m(x;t',t'+\Delta t)$: $P(m) = \langle \delta(m - m_t) \rangle \sim e^{-tN\psi(m)}$.

• Dynamic heterogeneity seen as exponential tail in $P(m)$.

• Phase coexistence in $(d+1)$ dimensions: High and low activity phases.



[Jack *et al.*, JCP '06]

• Equivalently, a field coupled to local dynamics induces a nonequilibrium first-order phase transition in the "s-ensemble". [Garrahan *et al.*, PRL '07]

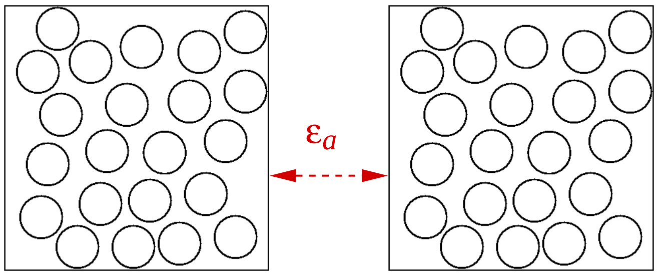
• Also seen within mean-field RFOT [Jack & Garrahan, PRE '10].

• Global thermodynamic and dynamic fluctuations behave very similarly.

Equilibrium phase transitions

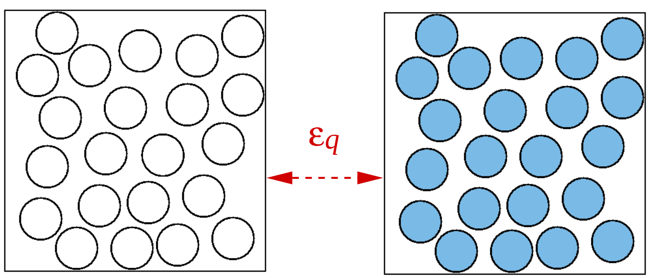
• Non-convex $V(Q)$ implies that an equilibrium phase transition can be induced by a field conjugated to Q. [Kurchan, Franz, Mézard, Cammarota, Biroli...]

• Annealed: 2 coupled copies.

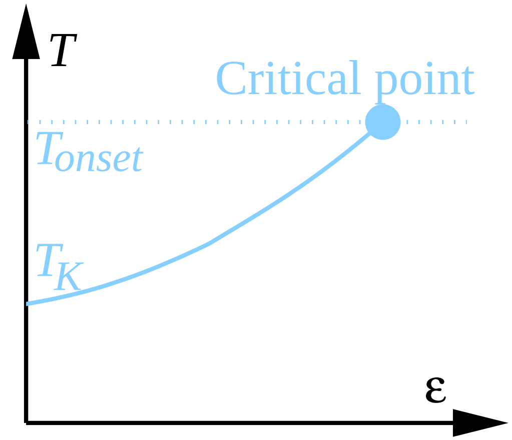


$$H = H_1 + H_2 - \epsilon_{\rm a} Q_{12}$$

• Quenched: copy 2 is frozen.



$$H = H_1 - \epsilon_{\rm q} Q_{12}$$



• Within RFOT: Different universality classes for quenched and annealed.
[Biroli *et al.*, Franz & Parisi, ’14]

• First order transition emerges from T_K, ending at a critical point near $T_{\rm onset}$.

• Extended phase diagrams as useful probe of RFOT/glass physics.

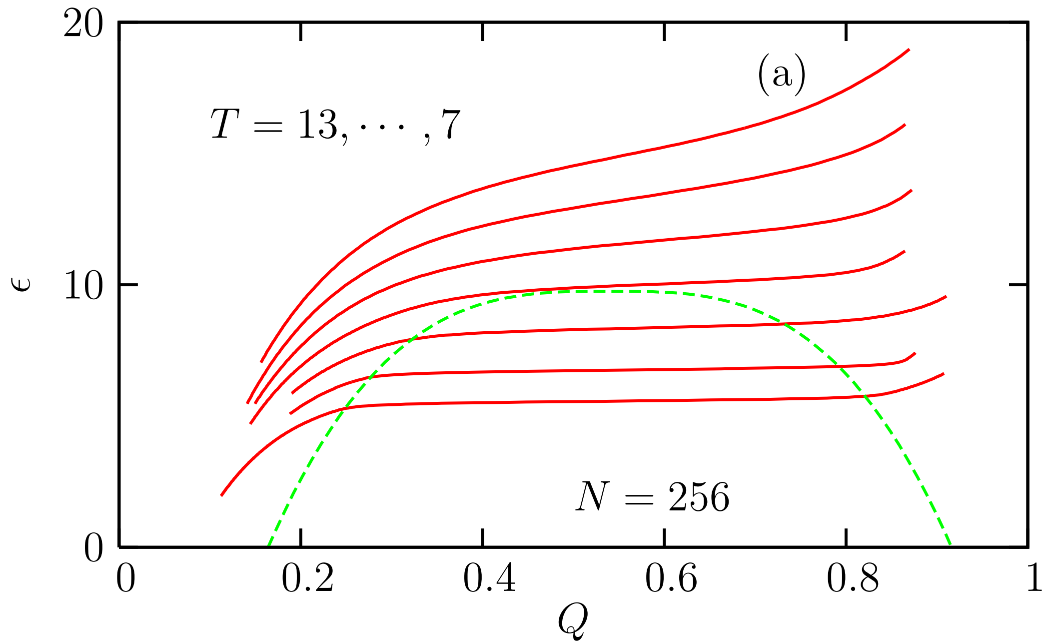
Numerical evidence in $3d$ liquid

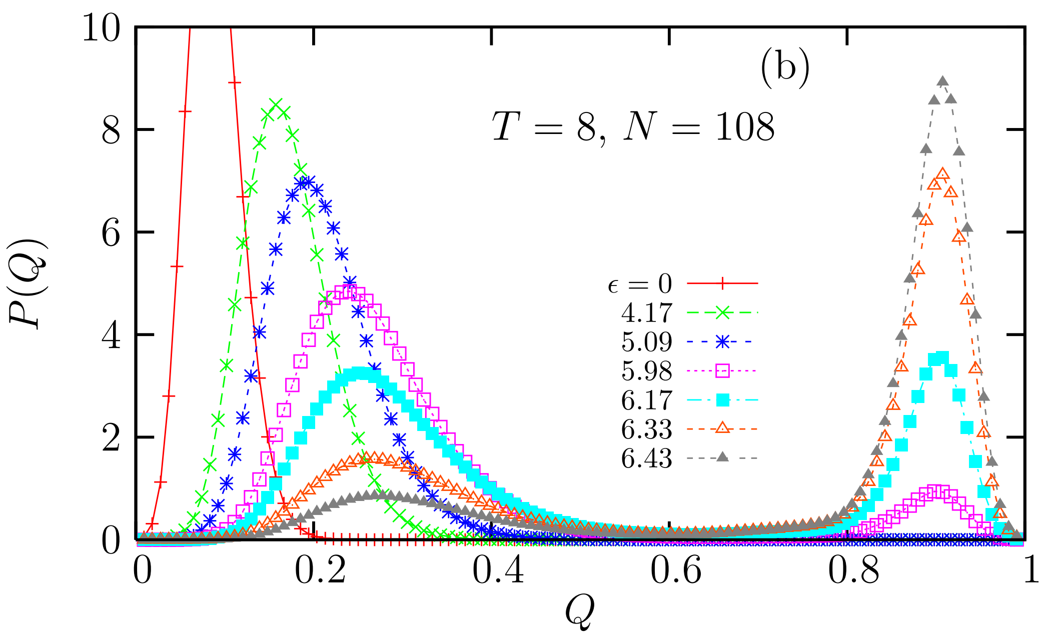
- (T, ϵ) plan for annealed case.

[Berthier, PRE '13]

- Sharp jump of the overlap below $T_{\text{onset}} \approx 10$.

- Suggests coexistence region ending at critical point.





- $P(Q)$ bimodal for finite N.

- Bimodality and static susceptibility enhanced at larger N for $T \lesssim T_c \approx 9.8$.

→ Equilibrium first-order phase transition, Ising criticality.

[see also: Parisi & Seoane, PRE '14]

Spin plaquette models

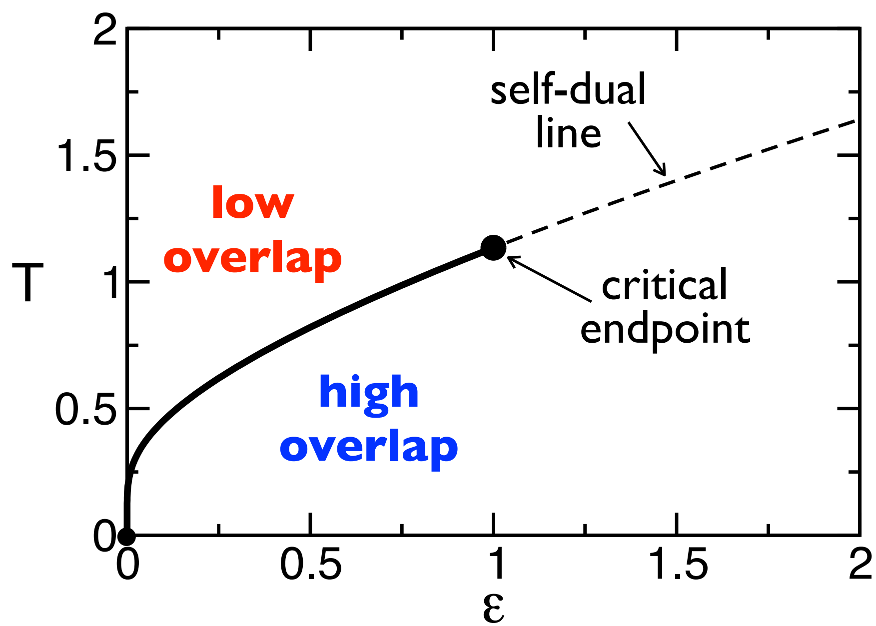
• Plaquette models are spin models intermediate between KCM and spin glass RFOT models: statics not fully trivial, localized defects and facilitated dynamics. E.g. in $d = 2$ on square lattice: $E = -\sum_{\square} s_1 s_2 s_3 s_4$.

• Plausible scenario for emergence of facilitated dynamics out of interacting Hamiltonian with glassy dynamics. [Garrahan, JPCM '03]

• Dynamic heterogeneity similar to standard KCM. [Jack *et al.*, PRE '05]

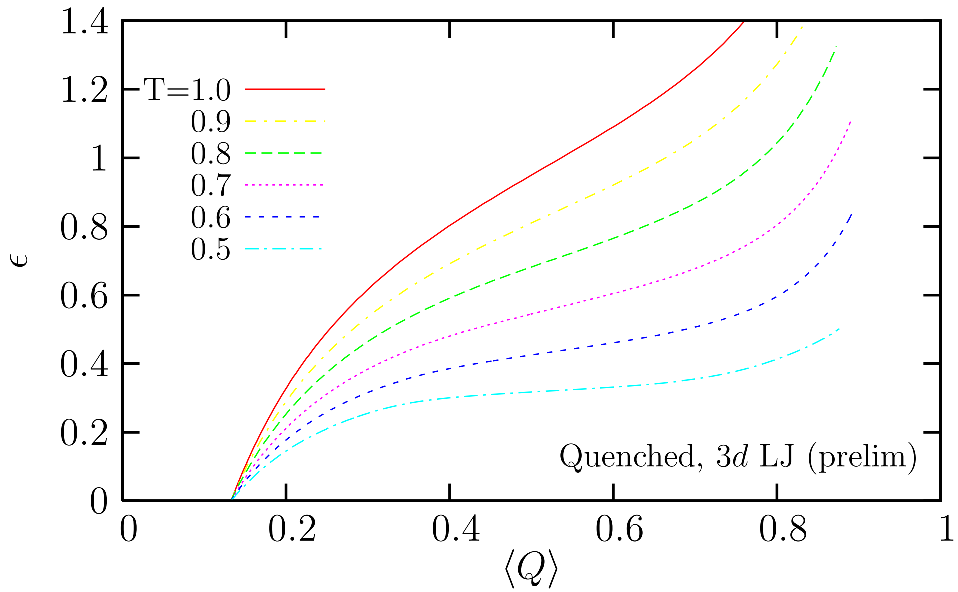
• "High-order" or "multi-point" static correlations develop without finite T phase transitions.

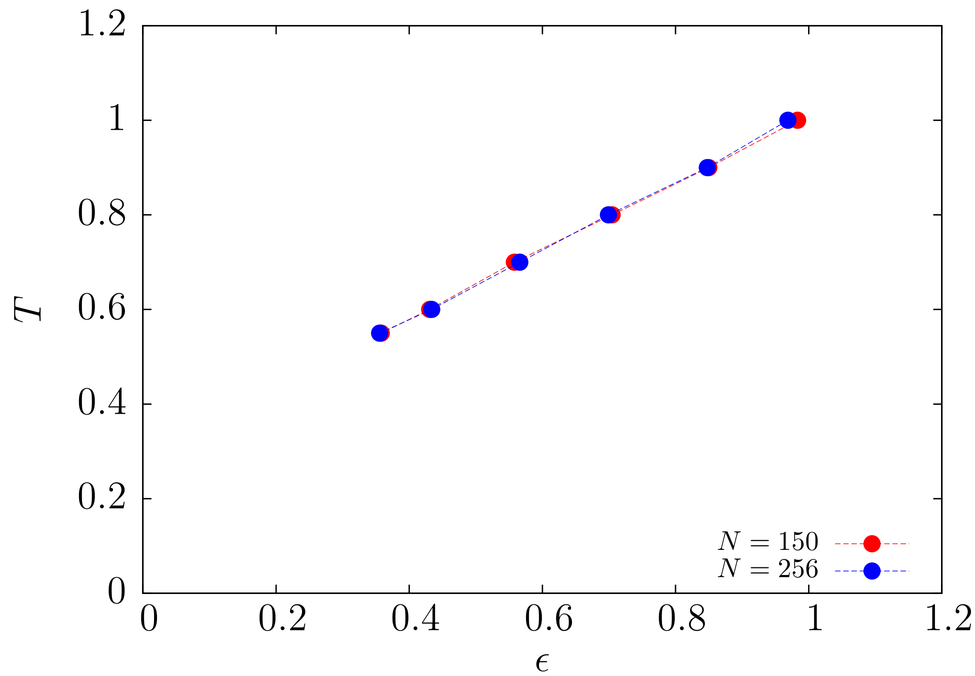
• Triangular plaquette model, annealed transition occurs [Garrahan, PRE '14]. No quenched?



Quenched transition

- Important because transition not seen in lattice glass models or spin plaquette models, but predicted within RFOT: Deep link with Kauzmann transition? Several on-going works by Garrahan/Jack, Hukushima, etc.





- Confirms smaller system size results for harmonic spheres.

- Naive first estimate for $d = 3$ Lennard-Jones binary mixture: $T_c \lesssim 0.6$.

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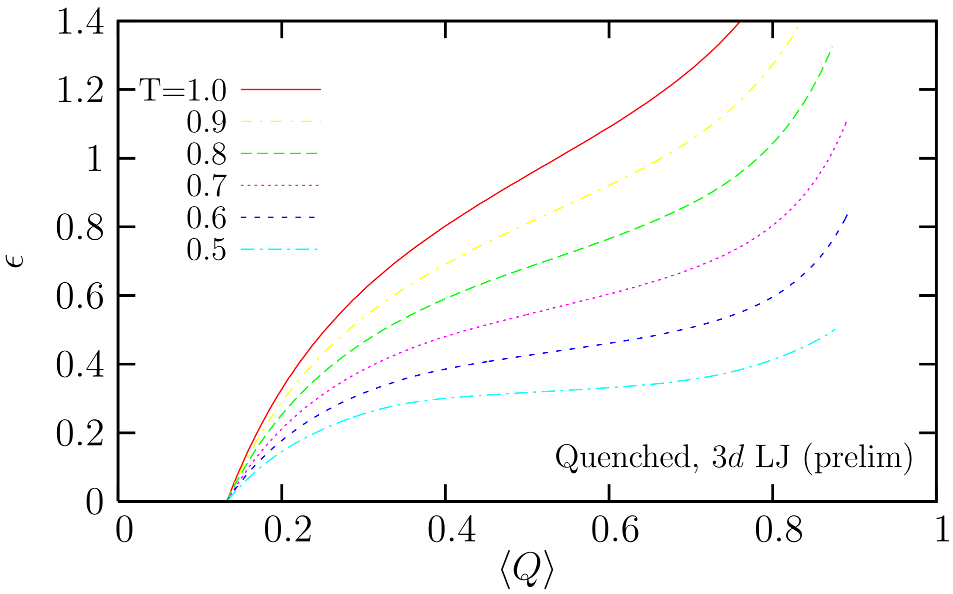

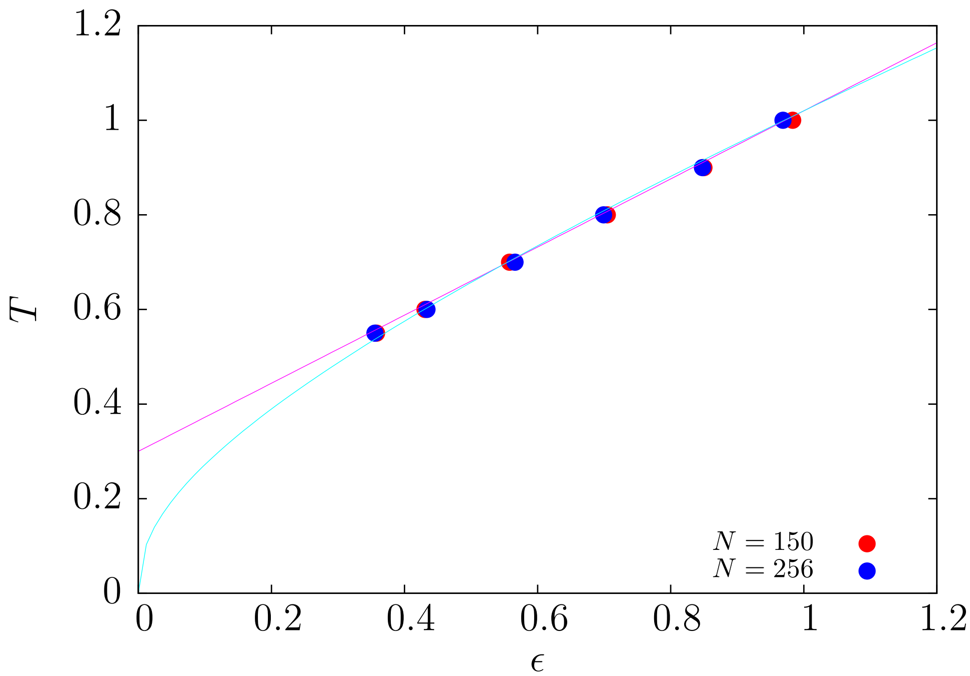

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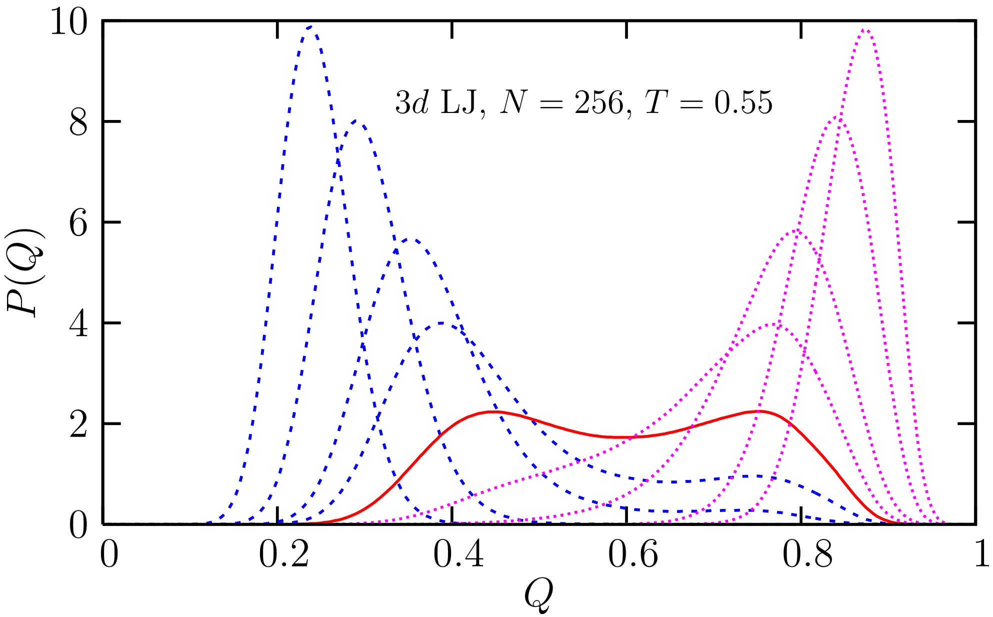
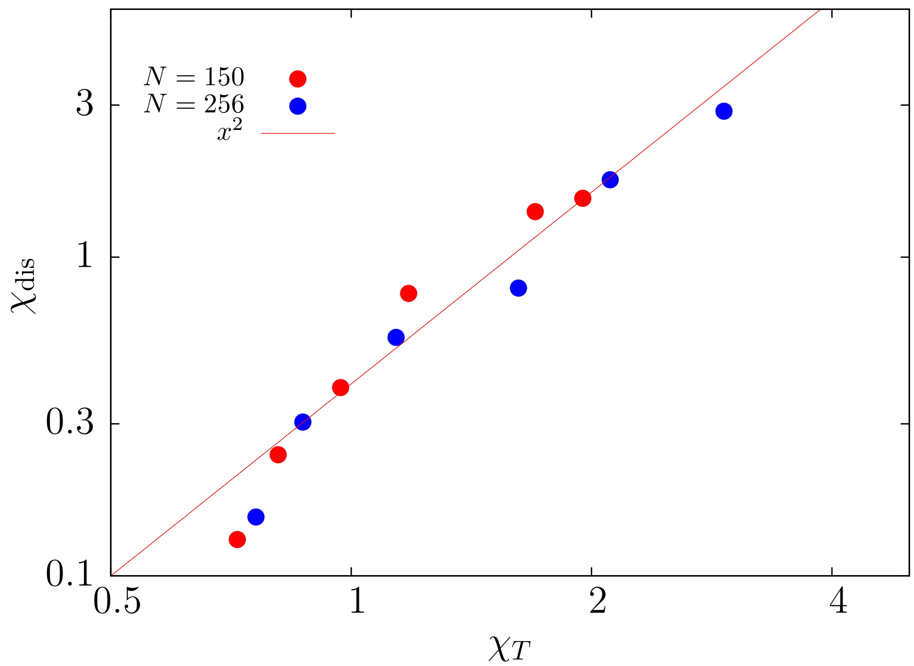
Overlap fluctuations

- Overlap distributions are Gaussian at $T > T_c$, look "critical" at T_c, and become bimodal at $T \lesssim T_c$.





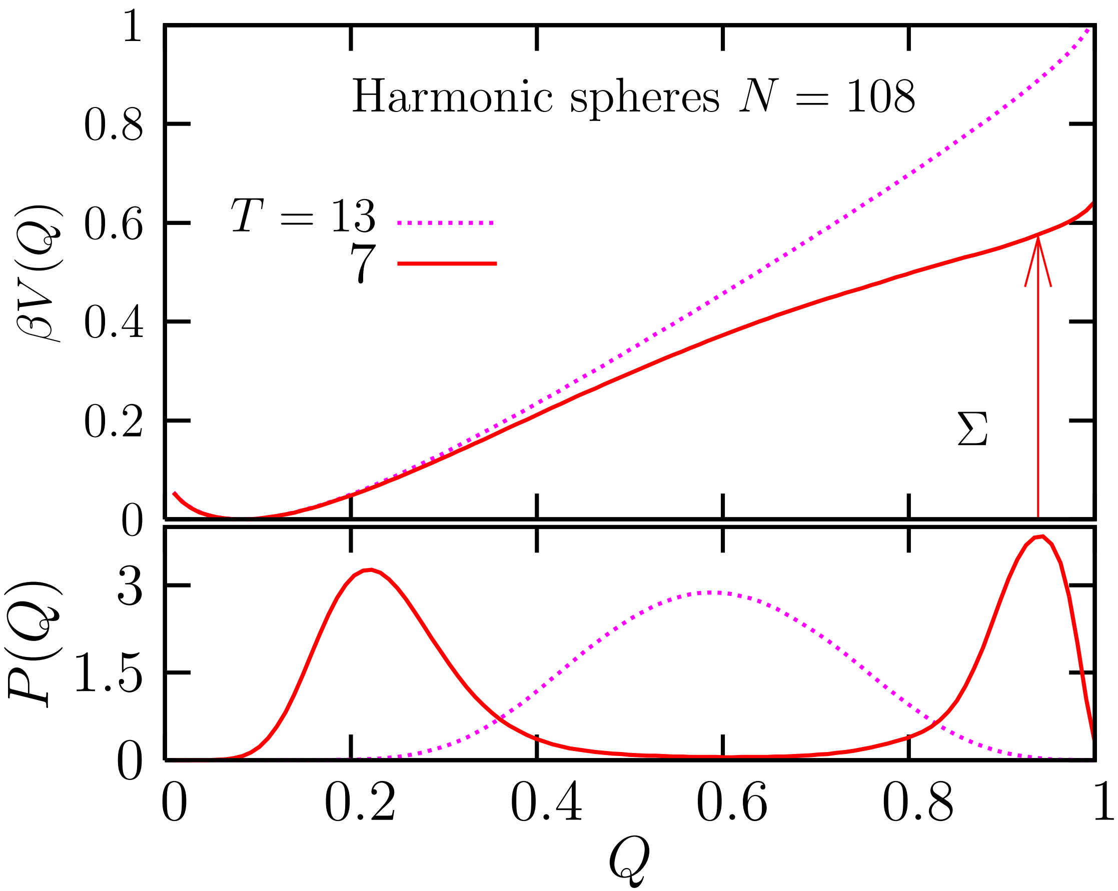
- Two types of fluctuations: $\chi_T = \overline{\langle Q^2\rangle_T - \langle Q\rangle_T^2}$ and $\chi_{\rm dis} = \overline{\langle Q\rangle_T^2} - \overline{\langle Q\rangle_T}^2$. Simulations indicate $\chi_{\rm dis} \approx \chi_T^2$: Critical point is controlled by disorder.

- (Much) more work needed for exponents...

Configurational entropy $\Sigma(T)$

- $\Sigma = \frac{k_B}{N} \log \mathcal{N}$ signals entropy crisis. Problem when $d < \infty$, because metastable states cannot be (rigorously) defined.

- Experiments and simulations use approximations: $\Sigma \approx S_{\rm tot} - S_{\rm vib}$.



- Sensible estimate:
$\Sigma \approx \beta[V(Q_{\rm high}) - V(Q_{\rm low})]$

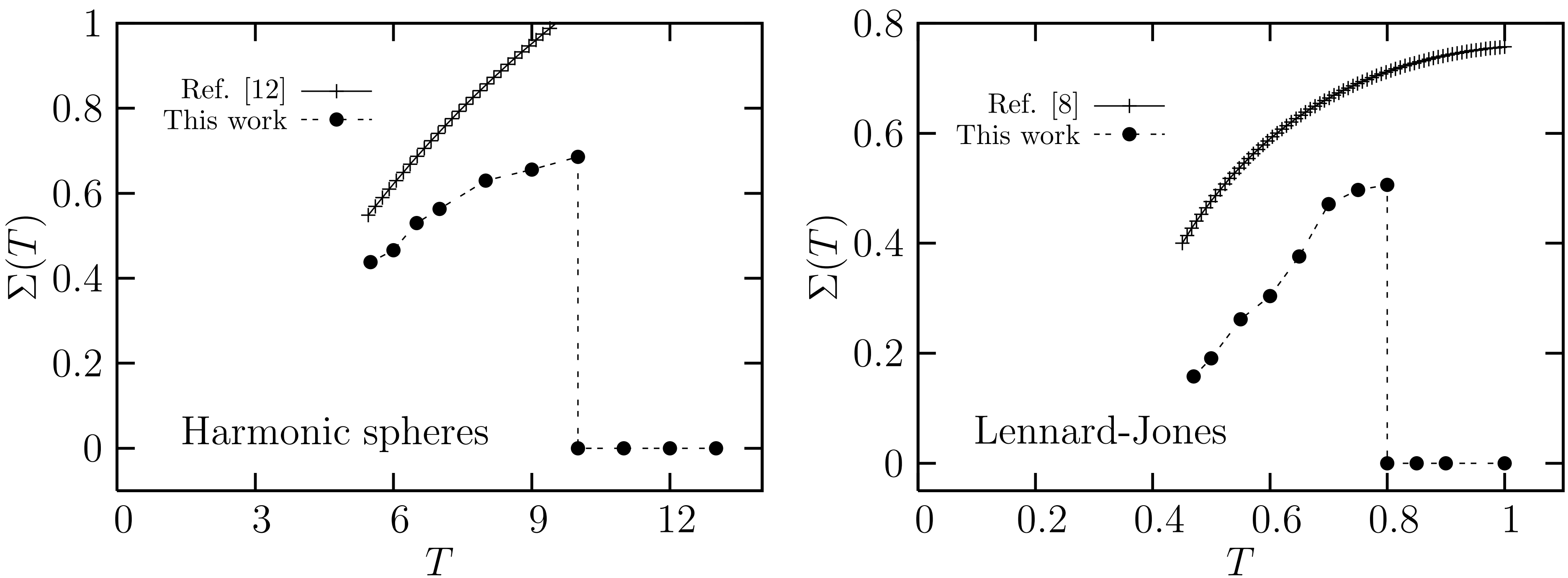
- Free energy cost to localize the system 'near' a given configuration.

- Well-defined in finite d ($T < T_c$), consistent with mean-field.

- Definition of 'states', 'vibrations', exploration of energy landscape not needed.

[Berthier & Coslovich, PNAS '14]

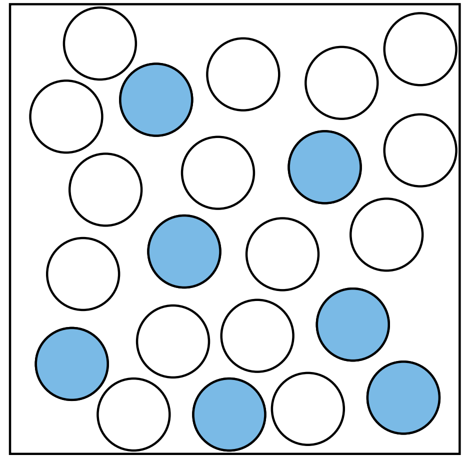
Results for two liquids



- Configurational entropy not defined in high-T liquid.
- Discontinuous emergence of $\Sigma(T)$ at T_c signals slow dynamics.
- Strong temperature dependence, qualitatively correlated with dynamics.
- $\Sigma(T)$ can be used to study T_K directly in bulk systems.

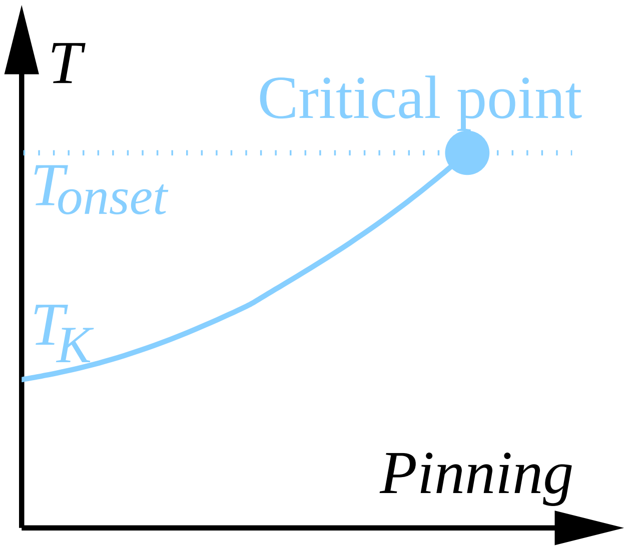
More ideal glass transitions

- Random pinning of a fraction c of particles: unperturbed Hamiltonian.



- Slowing down observed numerically.

[Kim, Scheidler... '00's]



- Within RFOT, ideal glass transition line extends up to critical point.

[Cammarota & Biroli, PNAS '12]

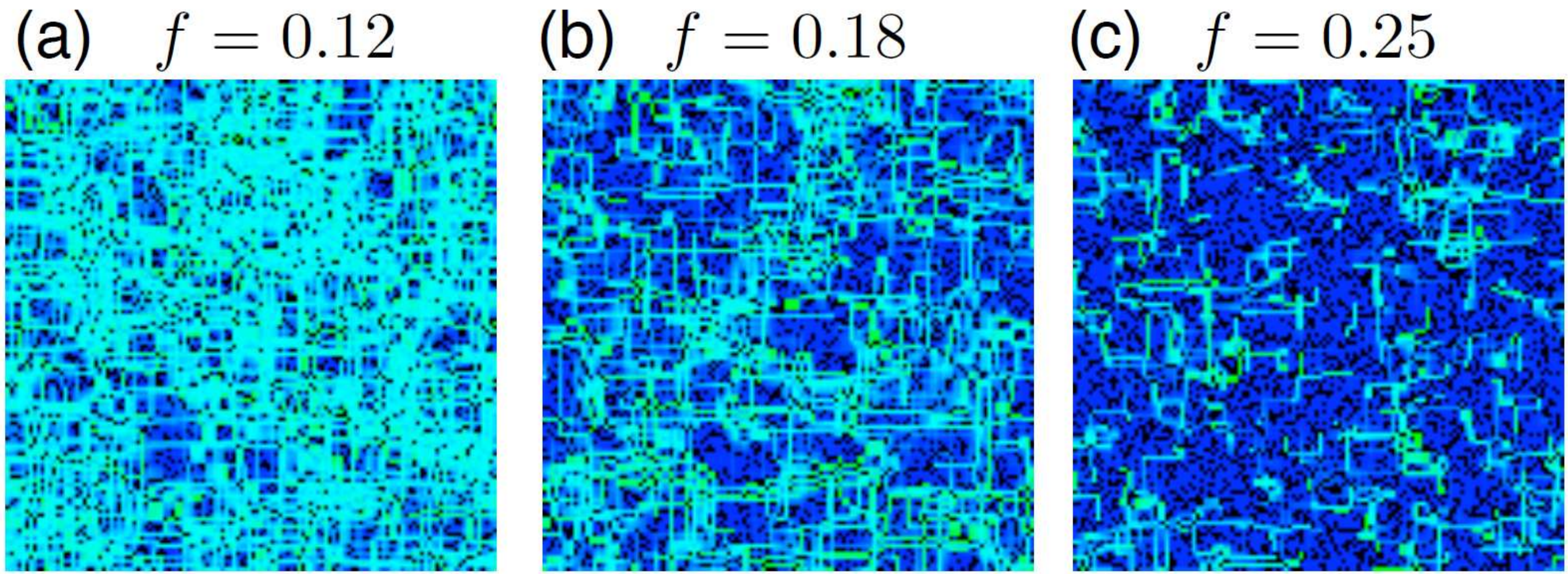
- Pinning reduces multiplicity of states, i.e. decreases configurational entropy: $\Sigma(c,T) \simeq \Sigma(0,T) - cY(T)$. Equivalent to $T \to T_K$.

- Ideal glass transition with quenched disorder - overlap can be used.

Pinning in plaquette models

• Random pinning studies in spin plaquette models offer an alternative scenario to RFOT. [Jack & Berthier, PRE '12]

• Crossover $f^\star(T)$ from competition between bulk correlations and random pinning: directly reveals growing static correlation lengthscale.



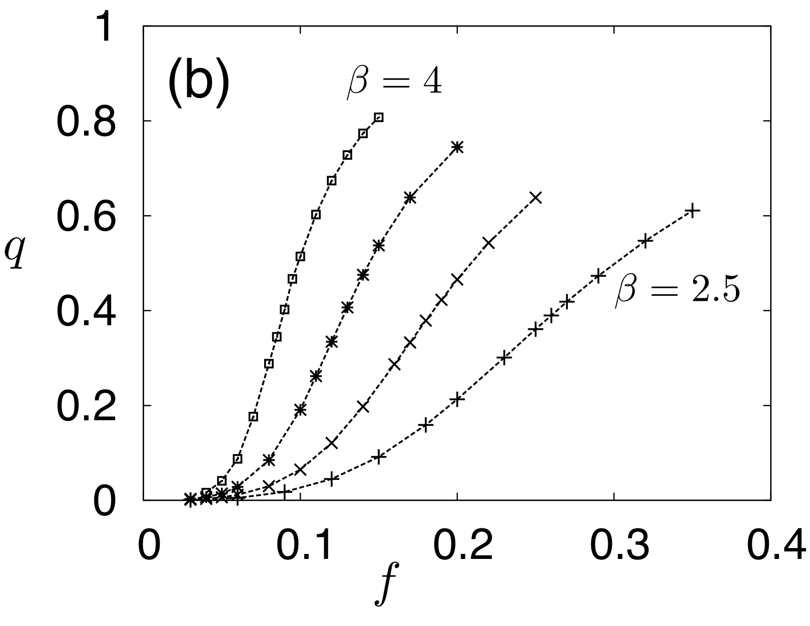
Light blue: mobile. Deep blue: frozen. Black: pinned.

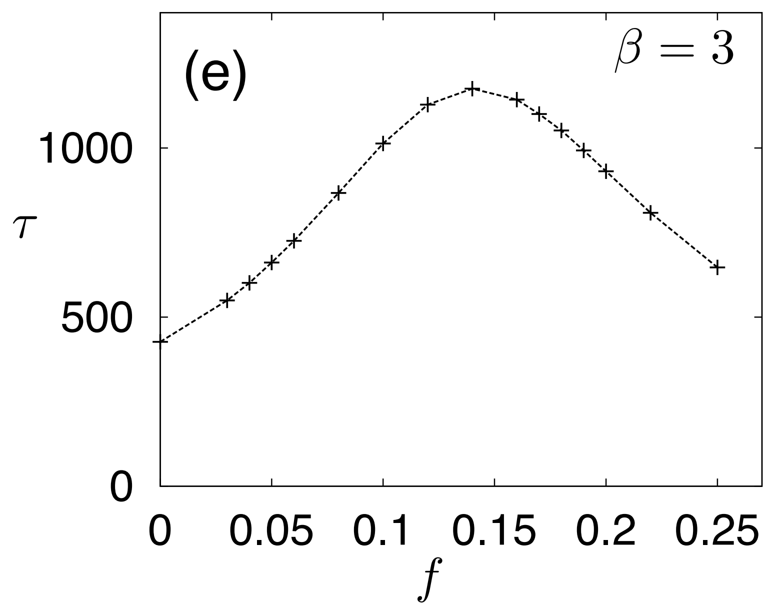
Smooth crossover

- Static overlap q increases rapidly with fraction f of pinned spins, crossover $f^\star = f^\star(T)$, but no phase transition.

- Overlap fluctuations reveal growing static correlation length scale, but susceptibility remains finite as $N \to \infty$.

- Dynamics barely slows down with f, unlike atomistic models.

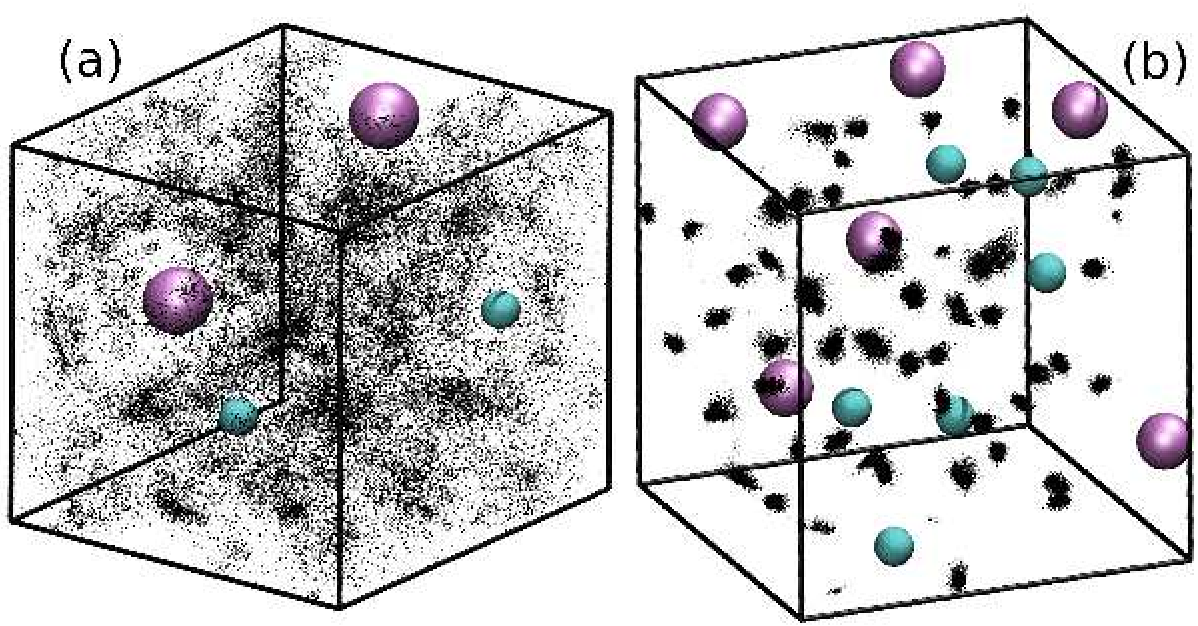




Random pinning in $3d$ liquid

• Challenge: fully exploring equilibrium configuration space in the presence of random pinning: parallel tempering. Limited (for now) to small system sizes: $N = 64, 128$. [Kob & Berthier, PRL '13]

Low-c fluid



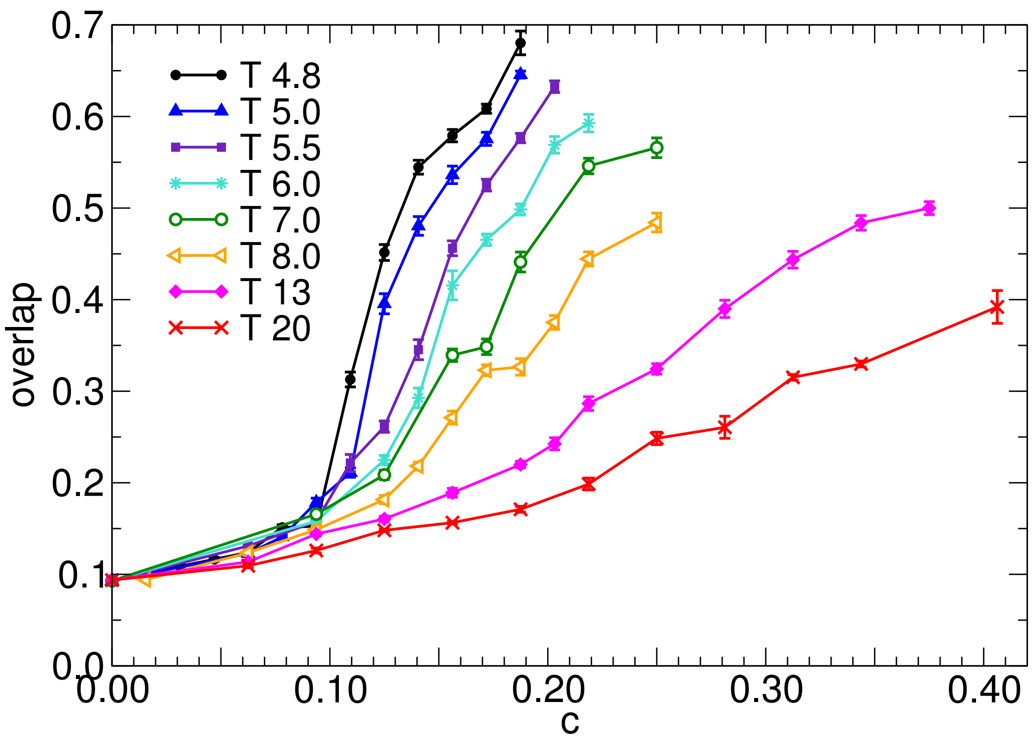
High-c glass

• From liquid to equilibrium glass: freezing of amorphous density profile.

• We performed a detailed investigation of the nature of this phase change, in fully equilibrium conditions.

Order parameter

• We detect this 'glass formation' using an equilibrium, microscopic order parameter: The global overlap $Q = \langle Q_{12} \rangle$.

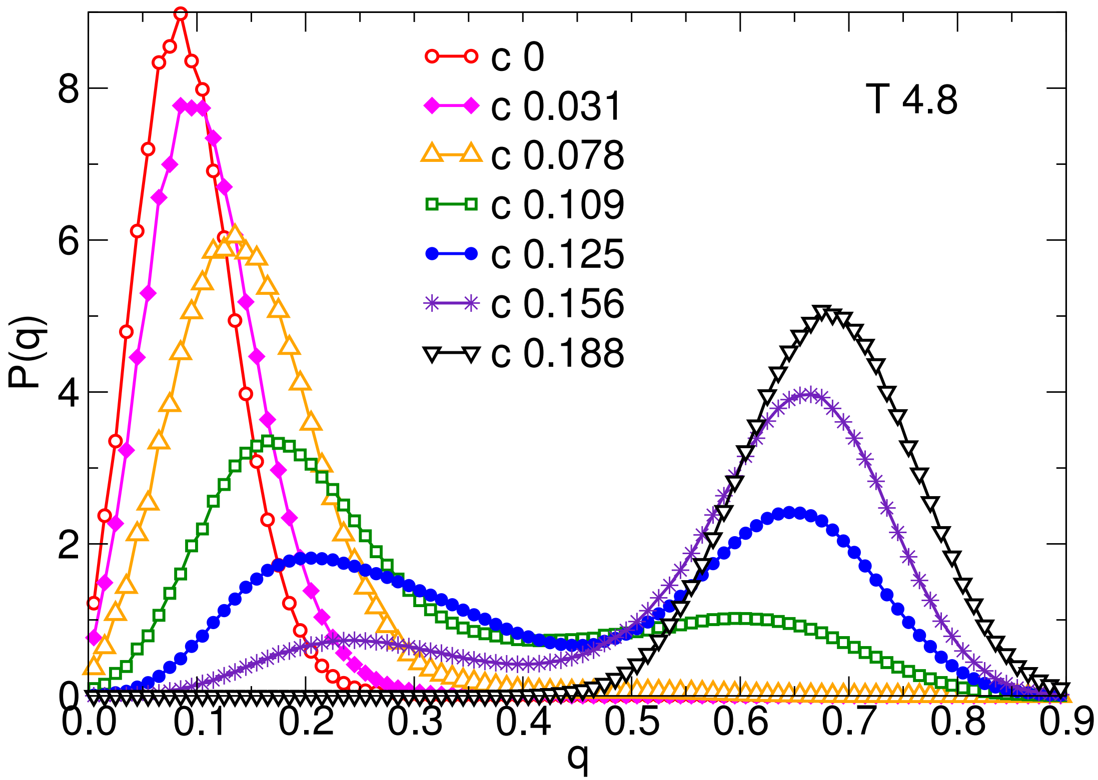


$N = 64$

• Gradual increase at high T to more abrupt emergence of amorphous order at low T at well-defined c value. First-order phase transition or smooth crossover?

Fluctuations: Phase coexistence

- Probability distribution function of the overlap: $P(Q) = \overline{\langle \delta(Q - Q_{12}) \rangle}$.

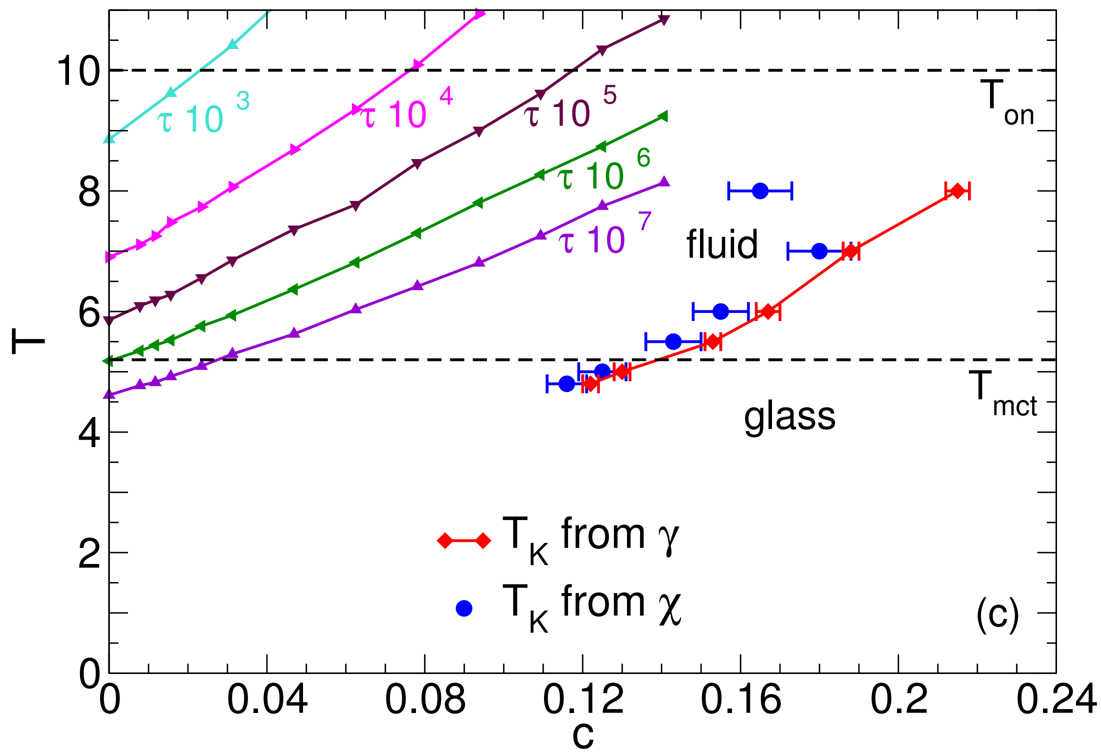


$N = 64$

- Bimodal distributions appear at low enough T, suggestive of phase coexistence at first-order transition, rounded by finite N effects. More work needed to study $N \to \infty$...

Equilibrium phase diagram

- Location of the transition from liquid-to-glass determined from equilibrium measurements of microscopic order parameter on both sides.



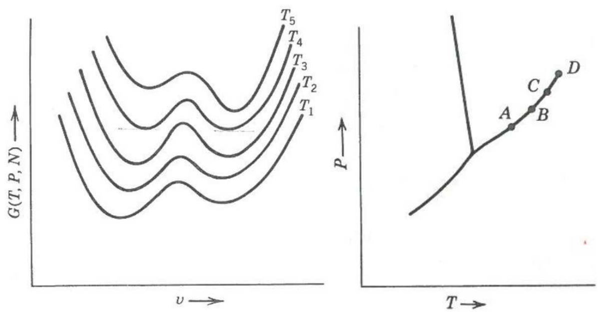
- Glass formation induced by random pinning has clear equilibrium thermodynamic signatures which can be studied directly.
- Results compatible with Kauzmann transition – this can now be decided.

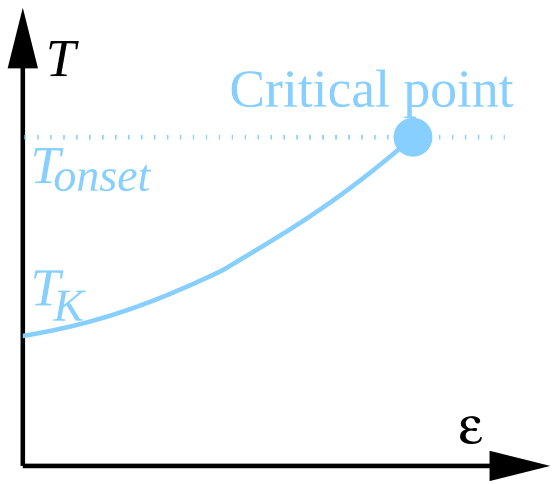
Conclusion

- Non-trivial thermodynamic fluctuations of the overlap in $3d$ bulk supercooled liquids: non-Gaussian $V(Q)$ losing convexity below $\approx T_{\mathrm{onset}}$.

- Statics and dynamics seem to go hand in hand.

- Adding a thermodynamic field can induce equilibrium phase transitions.





- Theory: Mean-field limit well understood at thermodynamic level, finite d (i.e. $d = 3$) will be difficult. Dynamics?

- Simulations have entered a new phase: equilibrium phase transitions, microscopic order parameters.

- A genuine glass transition may exist, and its existence can be studied directly.

May 4-7, 2015

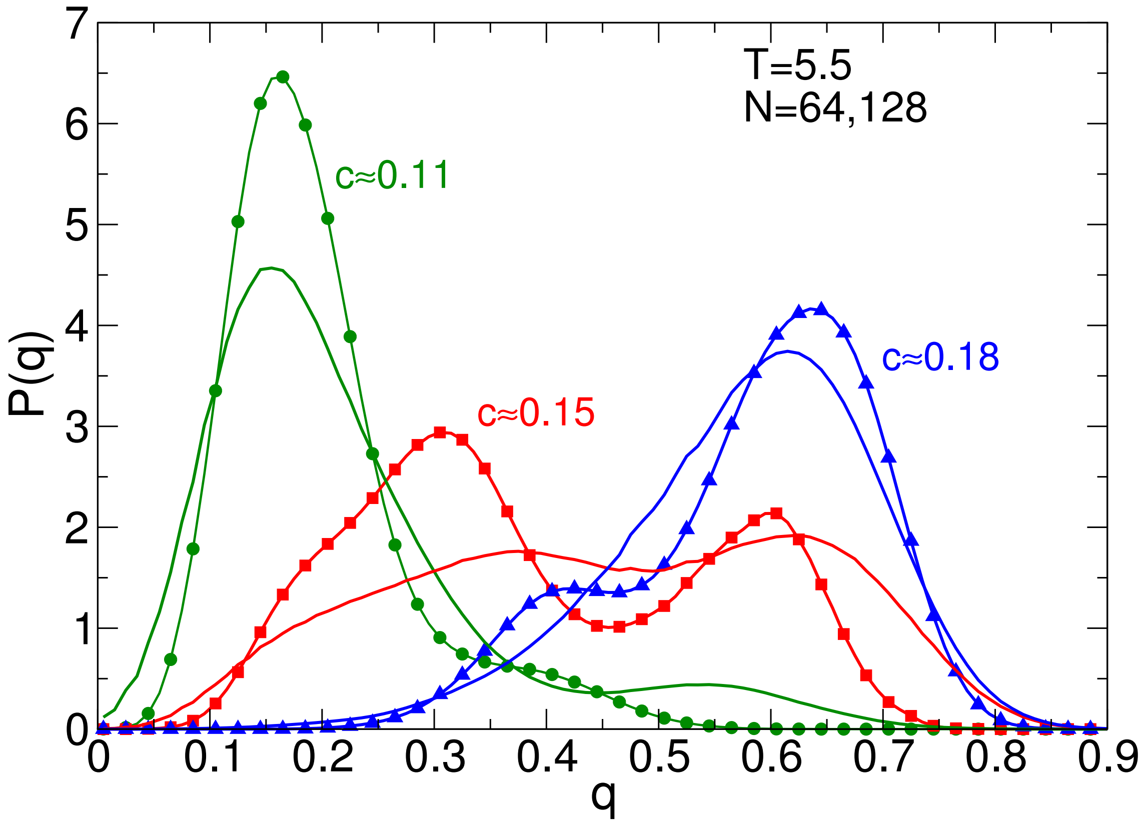
http://www.viscous-liquids.de/2015/

Liquids, colloids, glasses, gels, active & living matter, melts, grains...

No invited speaker: Apply and get selected!

Thermodynamic limit?

• Phase transition can only be proven using finite-size scaling techniques to extrapolate toward $N \to \infty$.



• Limited data support enhanced bimodality and larger susceptibility for larger N. Encouraging, but not quite good enough: More work needed.