Thermodynamic fluctuations in glass-forming liquids

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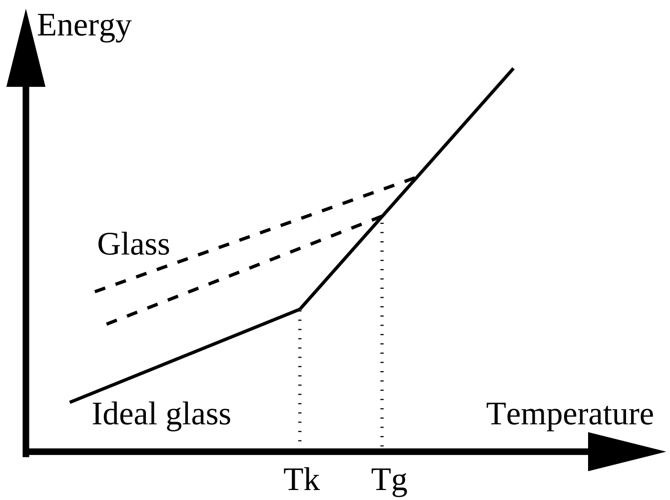
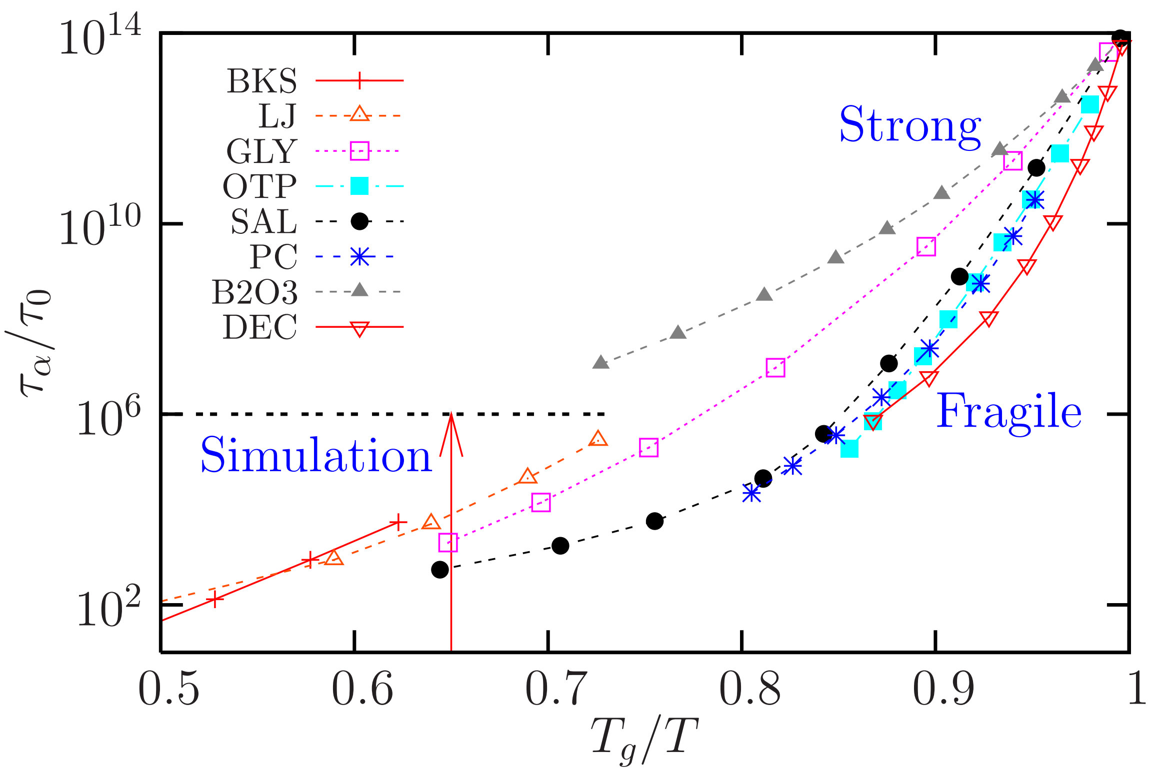
The glass “transition”

- Many materials become glasses (not crystals) at low temperature.





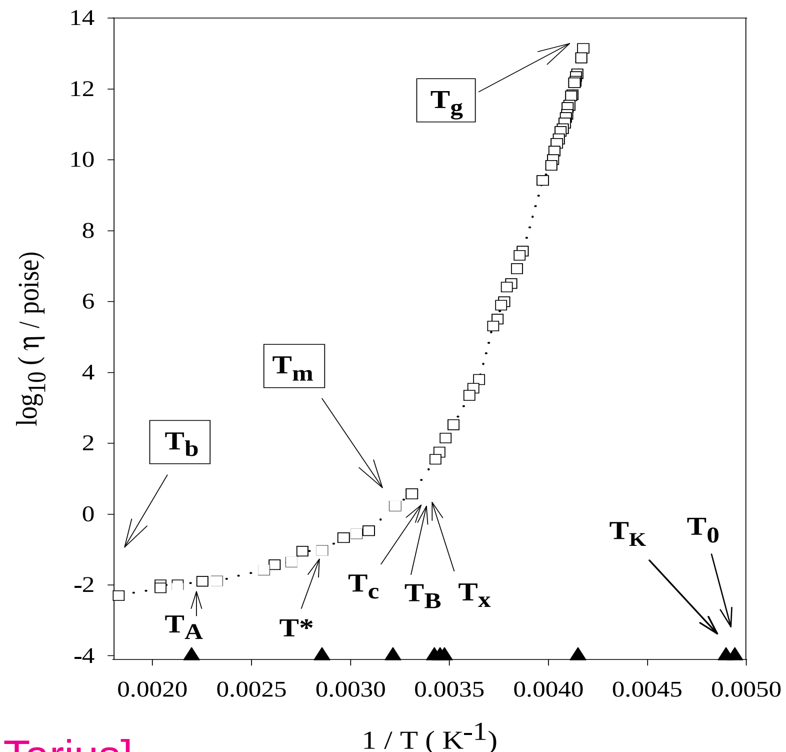
- In practice, glass formation is a gradual process.

- What is the underlying “ideal” glass state?

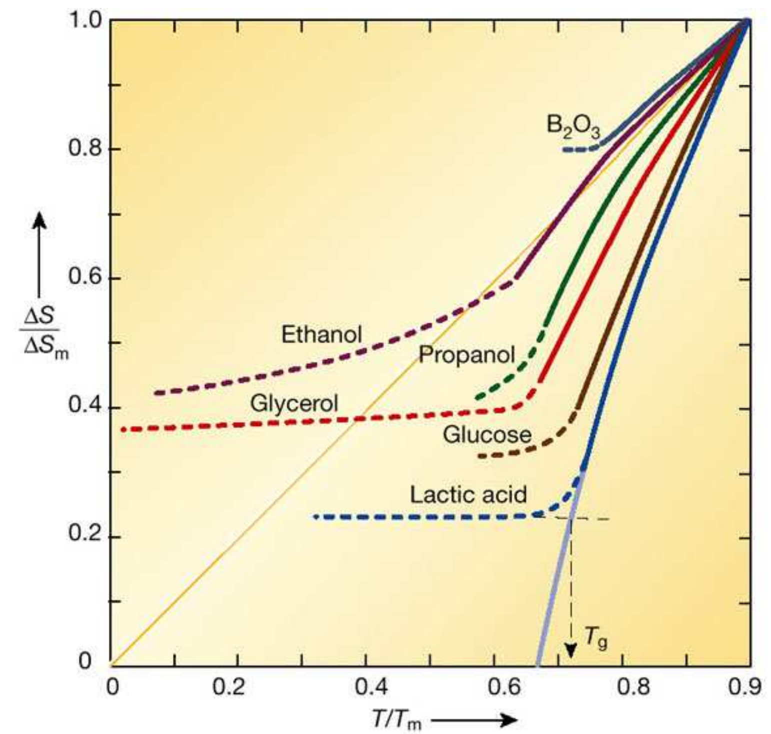
- Existence of many metastable states: glasses are many-body “complex” systems, due to disorder and geometric frustration.

Temperature crossovers

• Glass formation characterized by several “accepted” crossovers. Onset, mode-coupling & glass temperatures: directly studied at equilibrium.



[G. Tarjus]



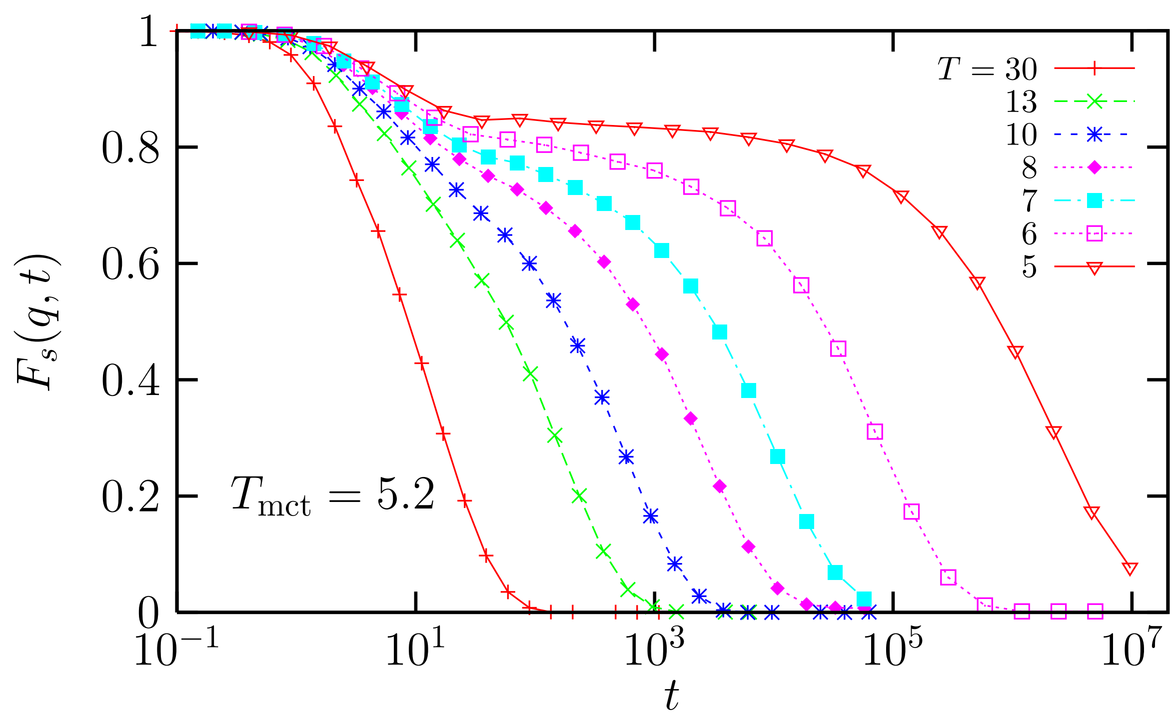
[Debenedetti & Stillinger]

• Extrapolated temperatures for dynamic and thermodynamic singularities: T_0, T_K. Ideal glass transition at the Kauzmann temperature is highly controversial (cf New York Times article in July 2008).

Molecular dynamics simulations

- Pair potential $V(r < \sigma) = \epsilon(1 - r/\sigma)^2$: soft harmonic repulsion, behaves as hard spheres in limit $\epsilon/T \to \infty$.

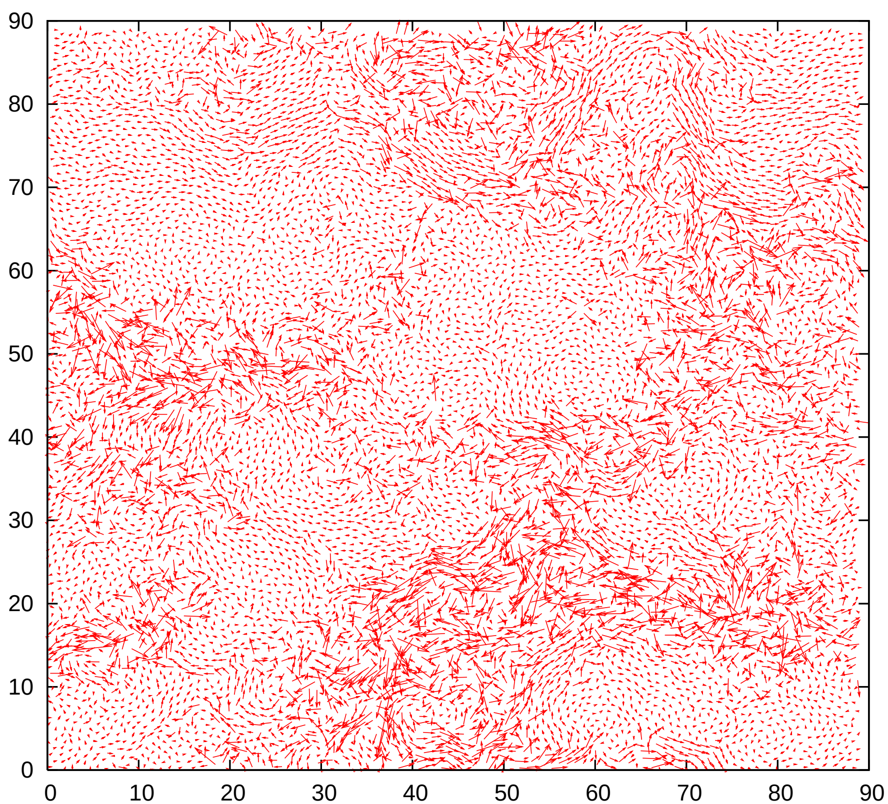
- Constant density, decrease temperature. Dynamics slows down $\to$ computer glass transition. $T_{\text{onset}} \approx 10$, $T_{mct} \approx 5.2$. [Berthier & Witten '09]



- $F_s(q,t) = \dfrac{1}{N}\langle \sum_{j=1}^{N} \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \rangle$

Dynamic heterogeneity

• When density is large, particles must move in a correlated way. New transport mechanisms revealed over the last decade: fluctuations matter.



• Spatial fluctuations grow (modestly) near T_g.

• Clear indication that some kind of phase transition is not far – which?

• Structural origin not established: point-to-set lengthscales, other structural indicators?

[Talks by Tanaka, Gradenigo...]

Dynamical heterogeneities in glasses, colloids and granular materials

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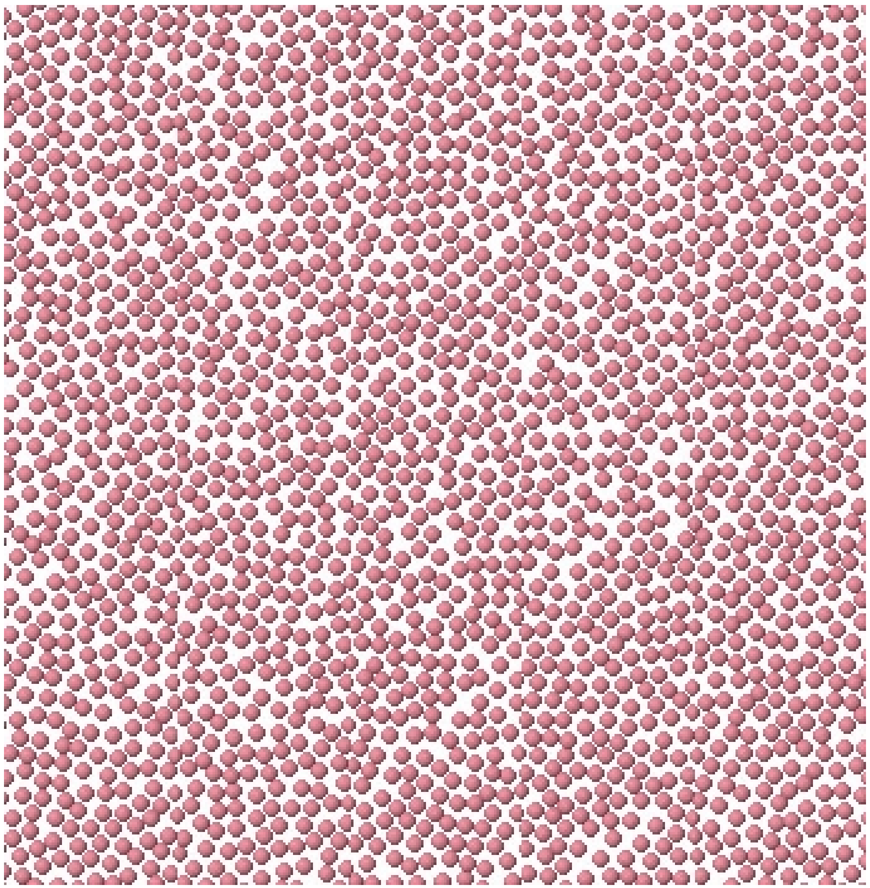

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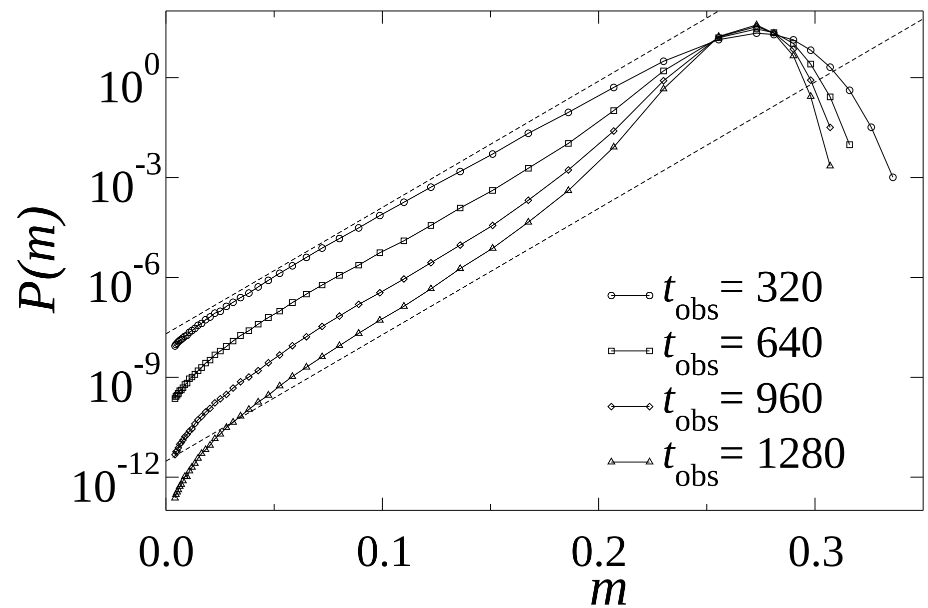
Dynamical view: Large deviations

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

• Exponential tail: direct signature of 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]

• Metastability controls this physics. Complex (RFOT) energy landscape gives rise to same transition, but the transition exists without multiplicity of glassy states [cf Kurchan's talk.] [Jack & Garrahan, PRE '10]

Thermodynamic view: RFOT

- Random First Order Transition (RFOT) theory is a theoretical framework constructed over the last 30 years (Parisi, Wolynes, Götze...) using a large set of analytical techniques.

[*Structural glasses and supercooled liquids*, Wolynes & Lubchenko, '12]

- Some results become exact for simple "mean-field" models, such as the fully connected p-spin glass model: $H = -\sum_{i_1 \cdots i_p} J_{i_1 \ldots i_p} s_{i_1} \cdots s_{i_p}$.

- Complex free energy landscape $\to$ sharp transitions: Onset (apparition of metastable states), mode-coupling singularity (metastable states dominate), and entropy crisis (metastable states become sub-extensive).

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

- Extension to finite dimensions ('mosaic picture') remains ambiguous.

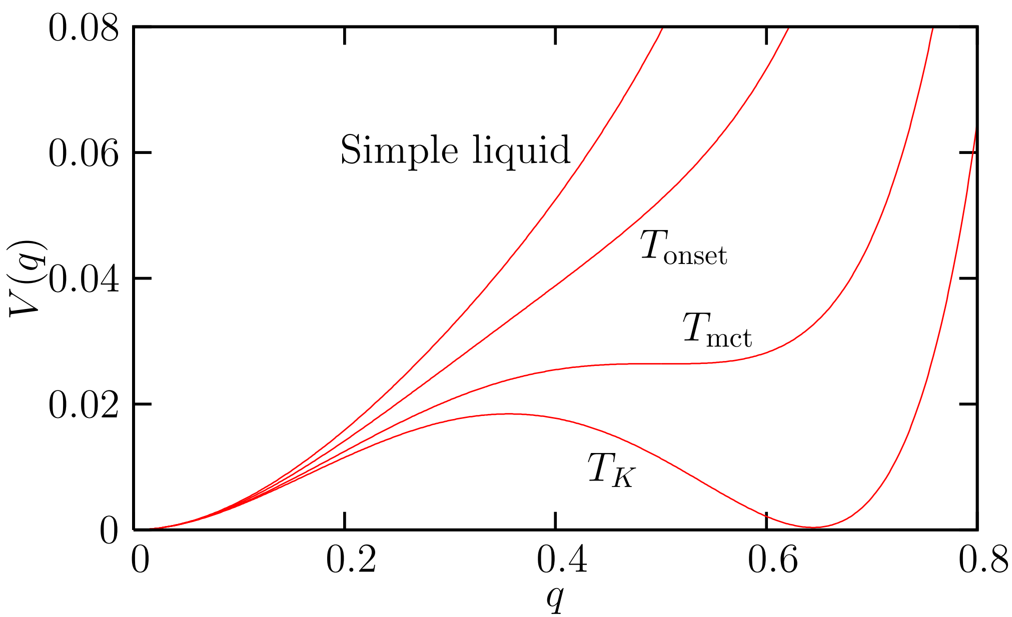
A ‘Landau free energy’

• Complex free energy landscape $\rightarrow$ effective potential $V(Q)$. Free energy cost (configurational entropy) to have 2 configurations at fixed distance Q:

[Franz & Parisi, PRL ’97]

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

where: $Q_{12} = \frac{1}{N} \sum_{i,j=1}^{N} \theta(a - |\mathbf{r}_{1,i} - \mathbf{r}_{2,j}|)$. Quenched vs. annealed approx.



• $V(Q)$ is a ‘large deviation’ function (in d dimensions), mainly studied in mean-field RFOT limit.

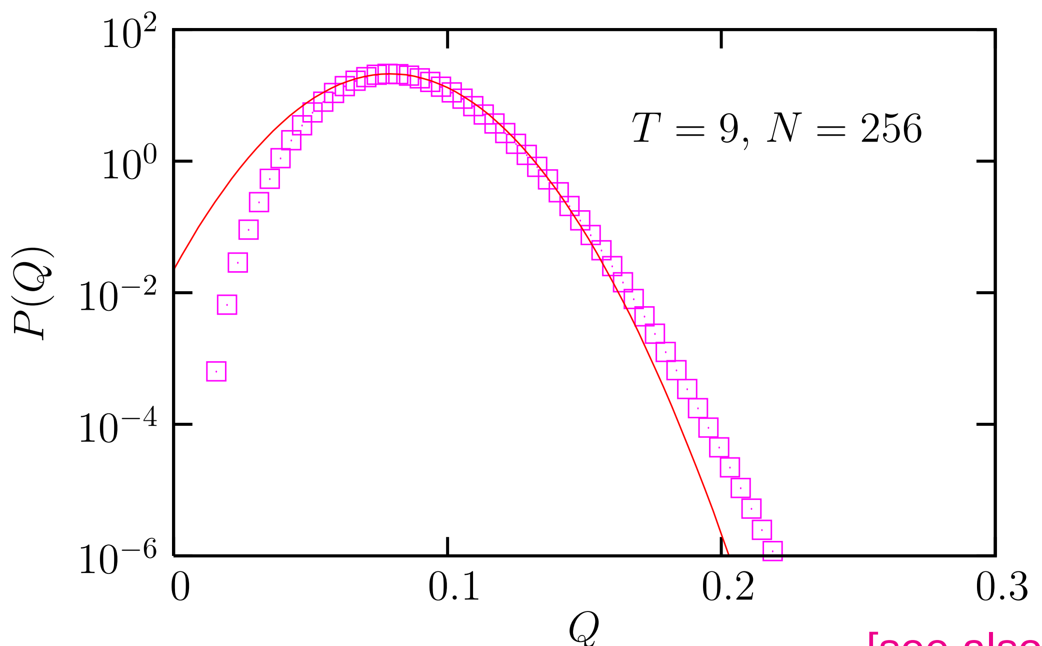
• $$P(Q) = \overline{\langle \delta(Q - Q_{\alpha\beta}) \rangle} \sim \exp[-\beta N V(Q)]$$

• Overlap fluctuations reveal evolution of multiple metastable states. Finite d requires ‘mosaic state’ because $V(Q)$ must be convex: exponential tail.

Direct measurement?

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

• Problem: Two equilibrium configurations are typically uncorrelated, with mutual overlap $\ll 1$ and small (nearly Gaussian) fluctuations.



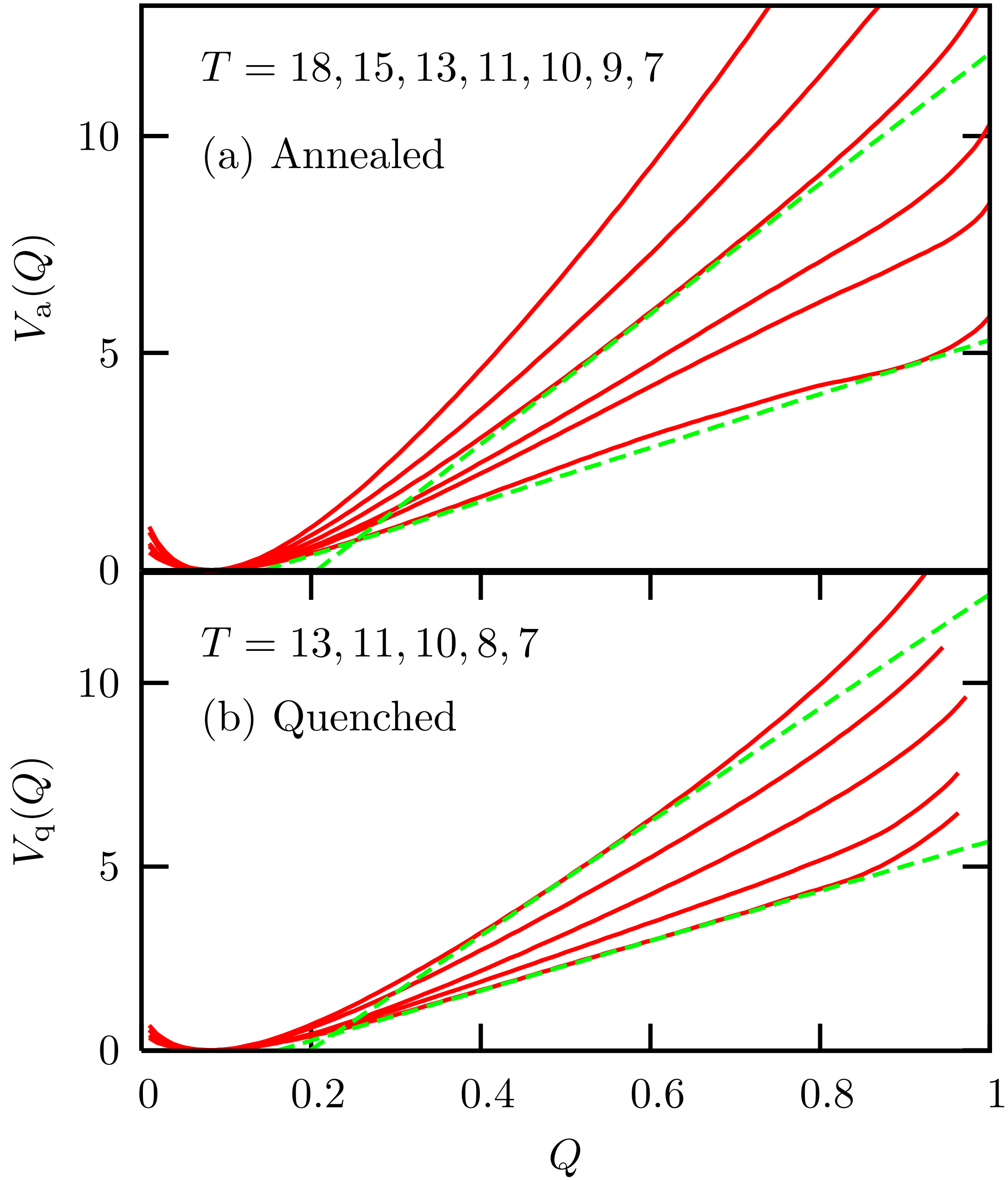
[see also Cammarota *et al.*, PRL ’11]

• Solution: Seek large deviations using umbrella sampling techniques.

[Berthier, arxiv.1306.0425]

Overlap fluctuations: Results

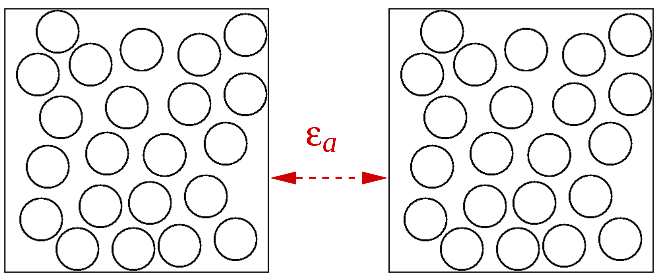
- Idea: bias the dynamics using $W_i(Q) = k_i(Q - Q_i)^2$ to explore of $Q \approx Q_i$.
- Reconstruct $P(Q)$ using reweighting techniques.
- Exponential tail below $T_{\rm onset}$: phase coexistence between multiple metastable states in bulk liquid.
- Static fluctuations control non-trivial fluctuations in trajectory space, and phase transitions in s-ensemble.



Equilibrium phase transitions

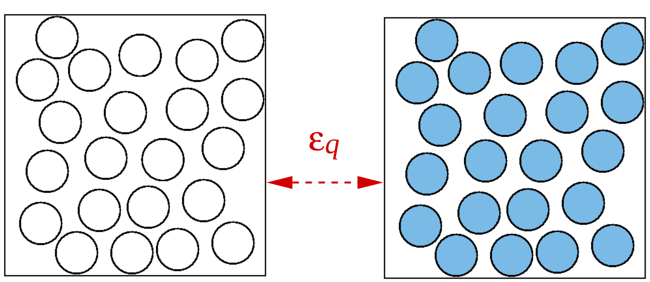
- Non-convex $V(Q)$ implies that an equilibrium phase transition can be induced by a field conjugated to Q. [Kurchan, Franz, Mézard, Cammarota, Biroli...]

- Annealed: 2 coupled copies.

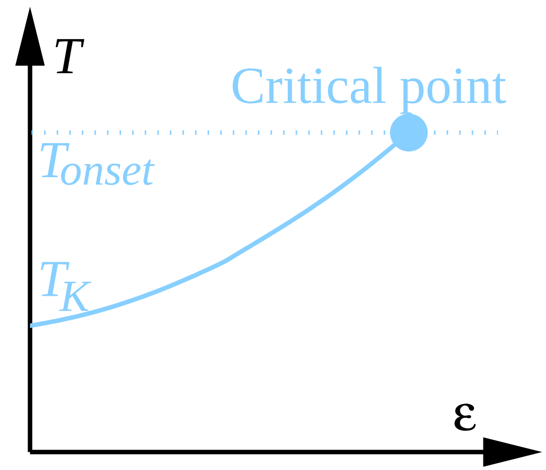


$$H = H_1 + H_2 - \epsilon_{\mathrm{a}} Q_{12}$$

- Quenched: copy 2 is frozen.



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



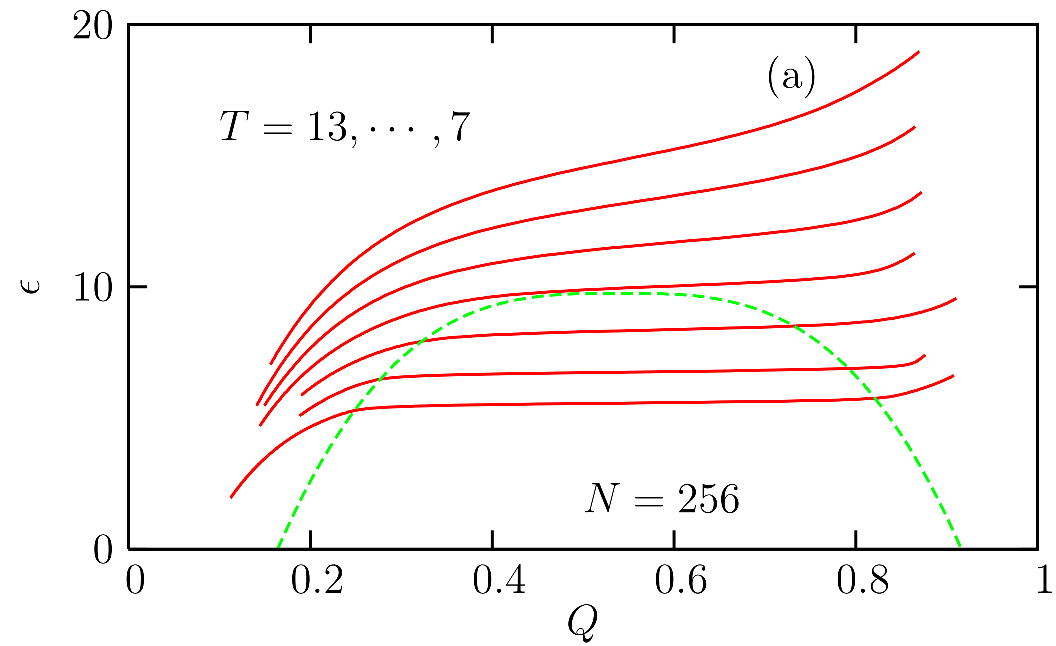
- Within RFOT: Some differences between quenched and annealed cases.

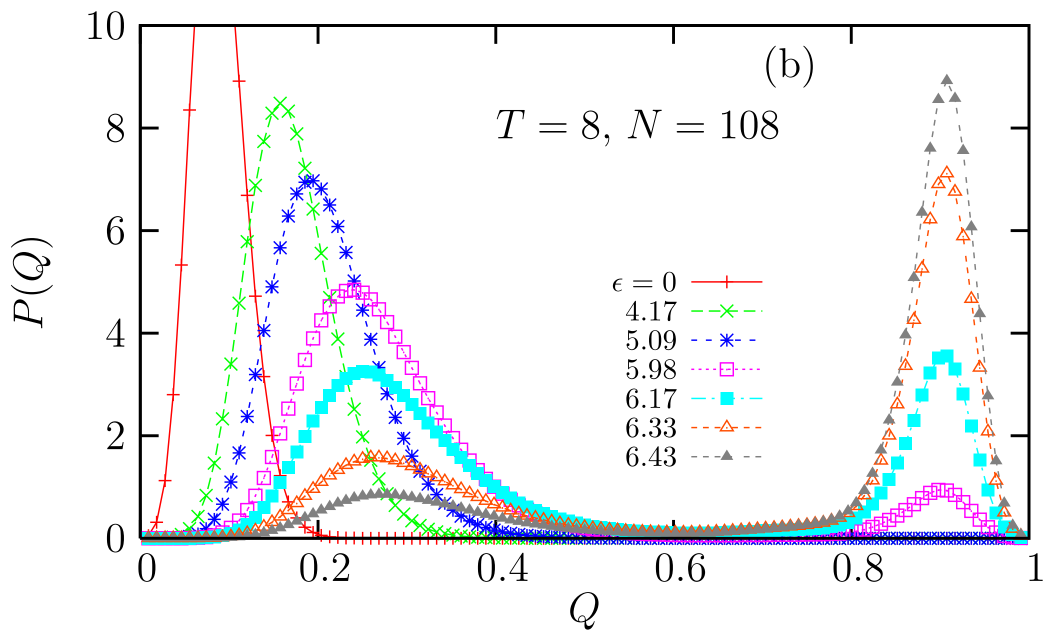
- First order transition emerges from T_K, ending at a critical point near T_{onset}.

- Direct consequence of, but different nature from, ideal glass transition.

Numerical evidence in $3d$ liquid

- Investigate (T, ϵ) phase diagram using umbrella sampling.
- Sharp jump of the overlap below $T_{\mathrm{onset}} \approx 10$.
- Suggests coexistence region ending at a critical point.





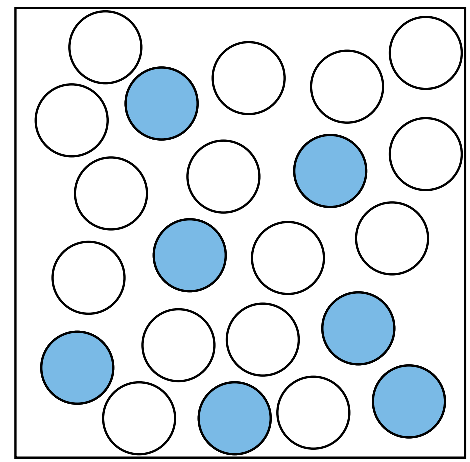
- $P(Q)$ bimodal for finite N.
- Bimodality and static susceptibility enhanced at larger N for $T \lesssim T_c \approx 9.8$.

$\rightarrow$ Equilibrium first-order phase transition.

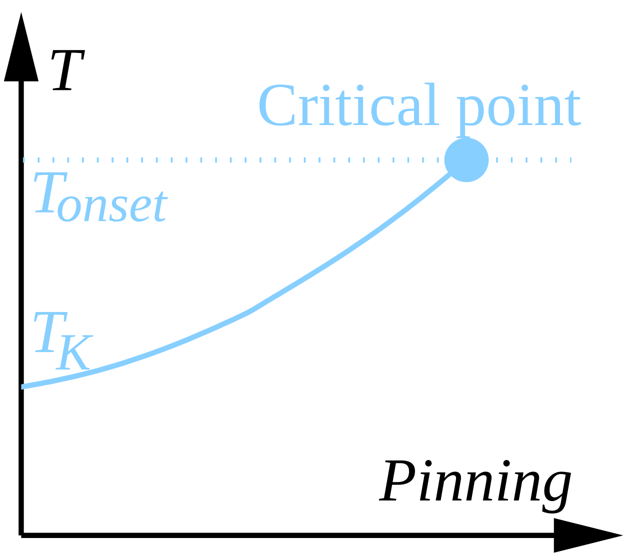
Ideal glass transition?

• ϵ perturbs the Hamiltonian: Affects the competition energy / configurational entropy (possibly) controlling the ideal glass transition.

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



• Dynamical slowing down observed numerically. [Kim, Scheidler, Kuni...]



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

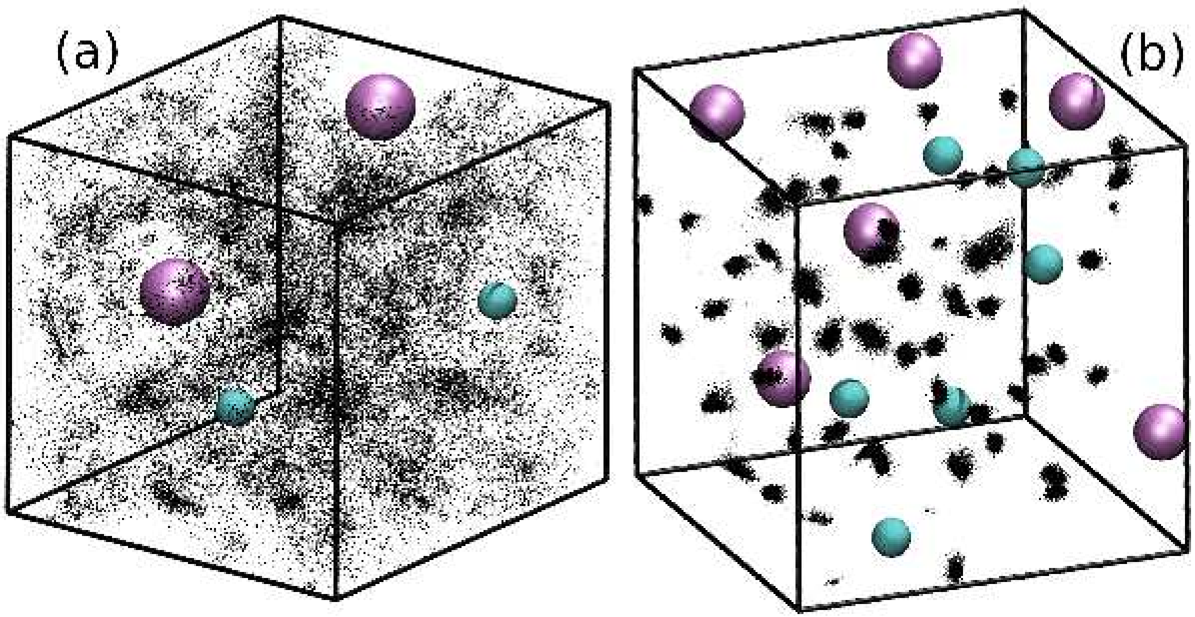
[Cammarota & Biroli, PNAS '12]

• Pinning reduces multiplicity of states, i.e. decreases configurational entropy: $S_{\rm conf}(c,T) \simeq S_{\rm conf}(0,T) - cY(T)$. Equivalent of $T \to T_K$.

Random pinning: Simulations

• 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

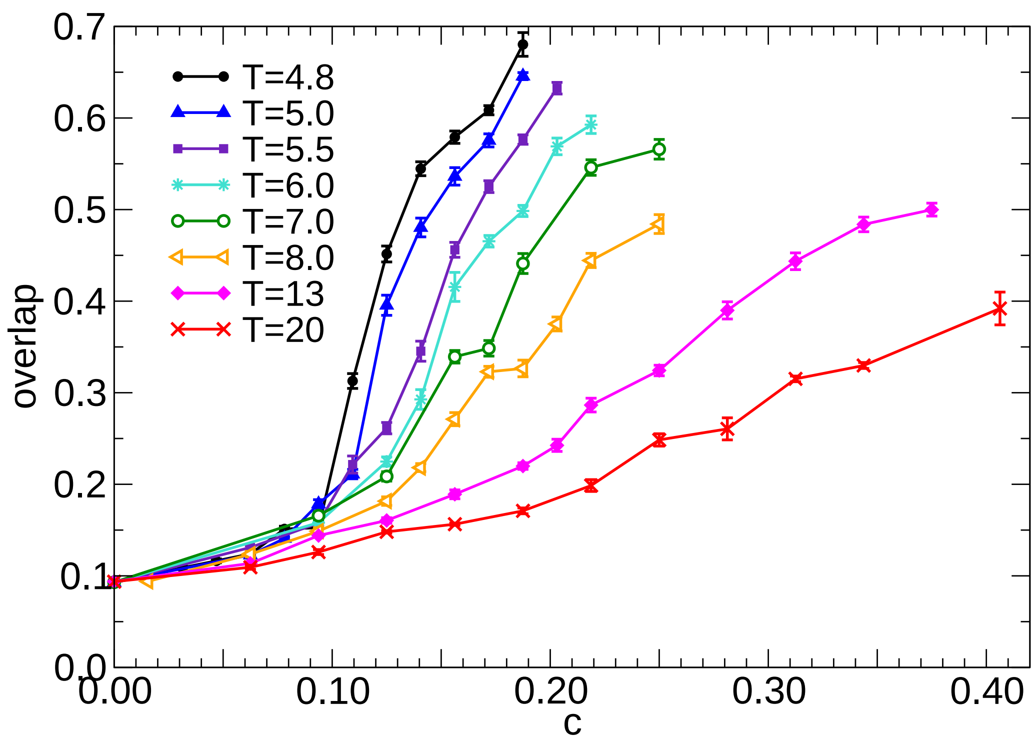
• From liquid to equilibrium glass: freezing of amorphous density profile.

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

Microscopic order parameter

- No configurational entropy, no time scale, no extrapolation, no aging.

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



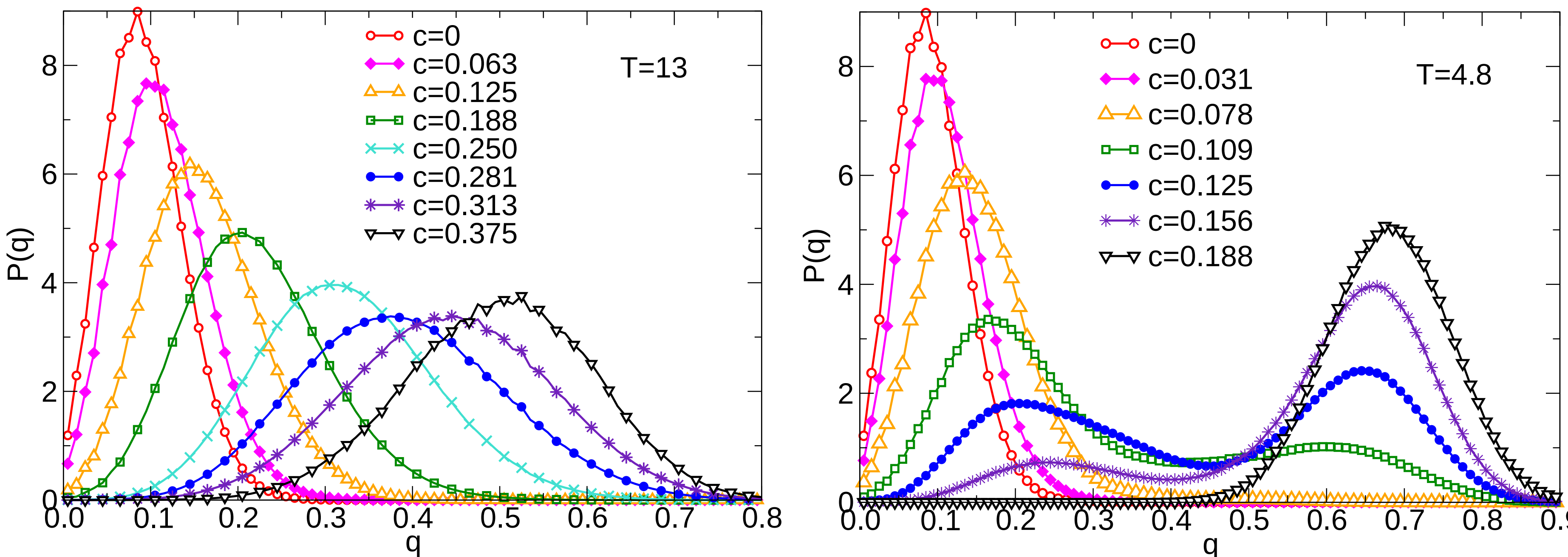
$N = 64$

- Gradual increase at high T to abrupt emergence of amorphous order at low T at well-defined c value. Signature of first-order phase transition?

Fluctuations: Phase coexistence

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

- Numerical measurements using parallel tempering simulations to explore (c, T, N) phase diagram performing thermal and disorder averages.

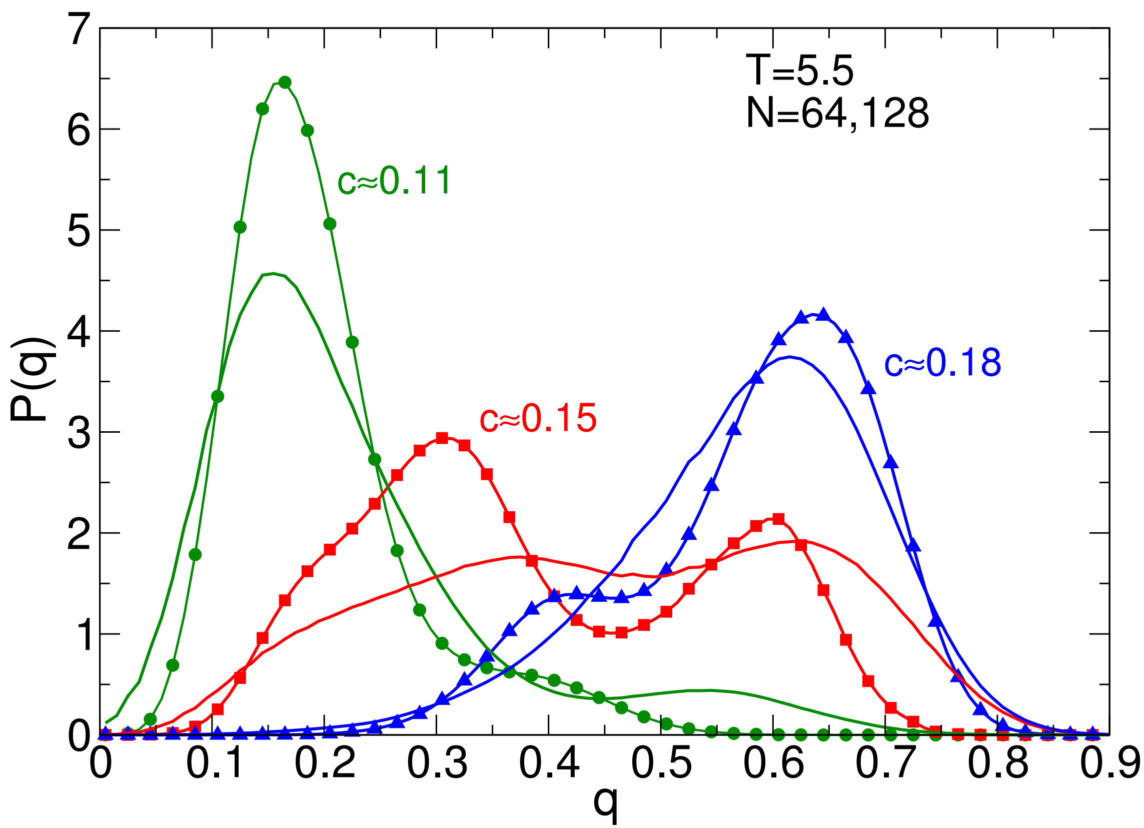


$N = 64$

- Bimodal distributions appear at low enough T, indicative of phase coexistence at first-order transition.

Thermodynamic limit?

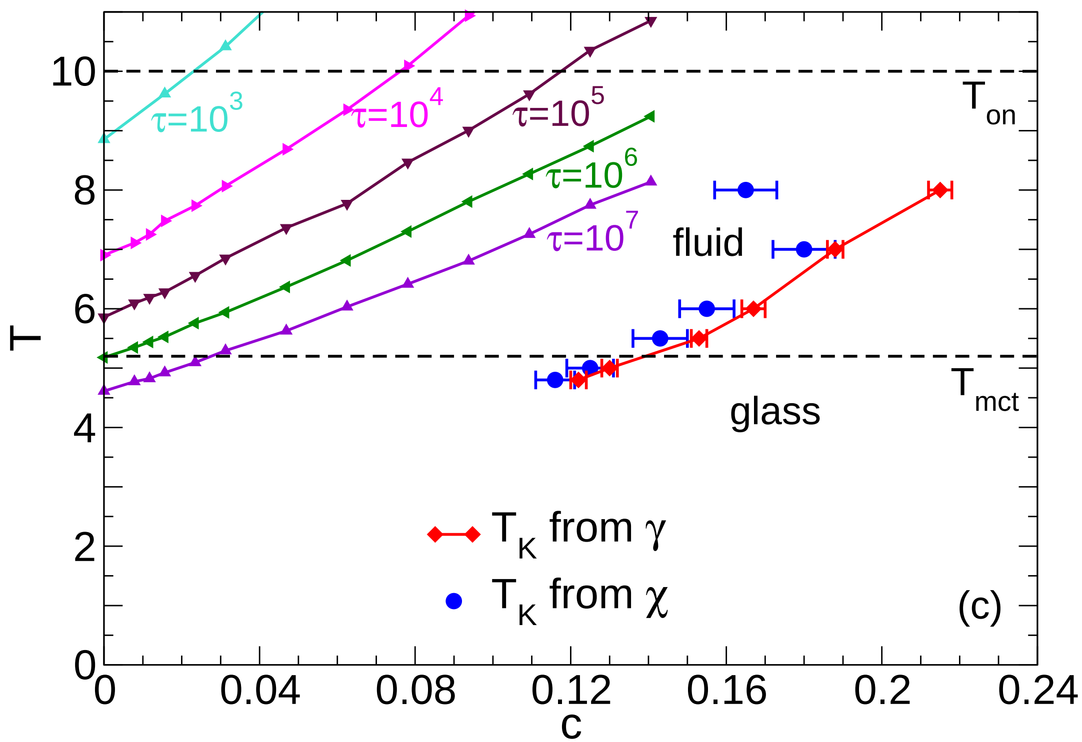
• Phase transition can only be proven using finite-size scaling techniques to extrapolate toward $N \to \infty$.



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

Equilibrium phase diagram

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



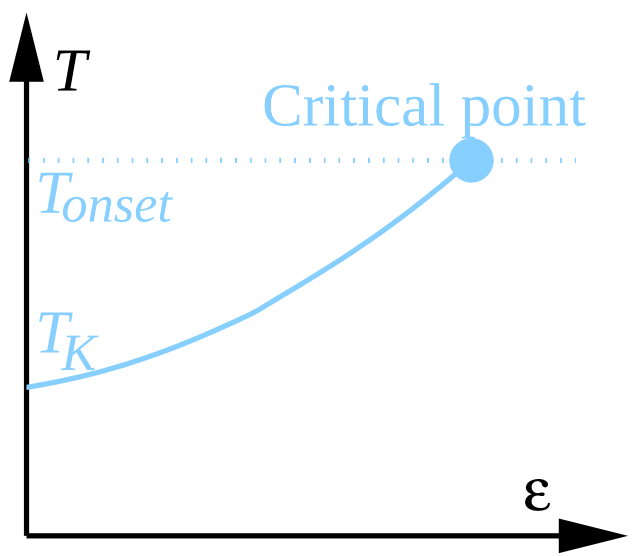
- Glass formation induced by random pinning has clear thermodynamic signatures which can be studied directly.

- Results compatible with Kauzmann transition – this can now be decided.

Summary

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

- Adding a thermodynamic field can induce equilibrium phase transitions.



- Annealed coupling: first-order transition ending at simple critical point.

- Quenched coupling: first-order transition ending at random critical point.

- Random pinning: random first order transition ending at random critical point.

- Direct probes of peculiar thermodynamic underpinnings of RFOT theory.

- A Kauzmann phase transition may exist, and its existence be decided.