# Thermodynamic fluctuations in model glasses


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Glassy Systems and Constrained Stochastic Dynamics – Warwick, June 11, 2014



D4PARTICLES

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- With:

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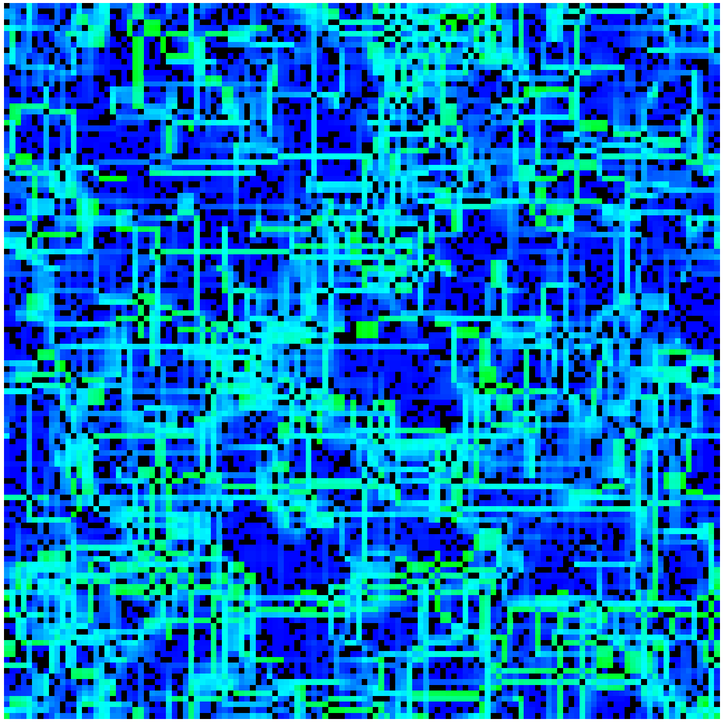
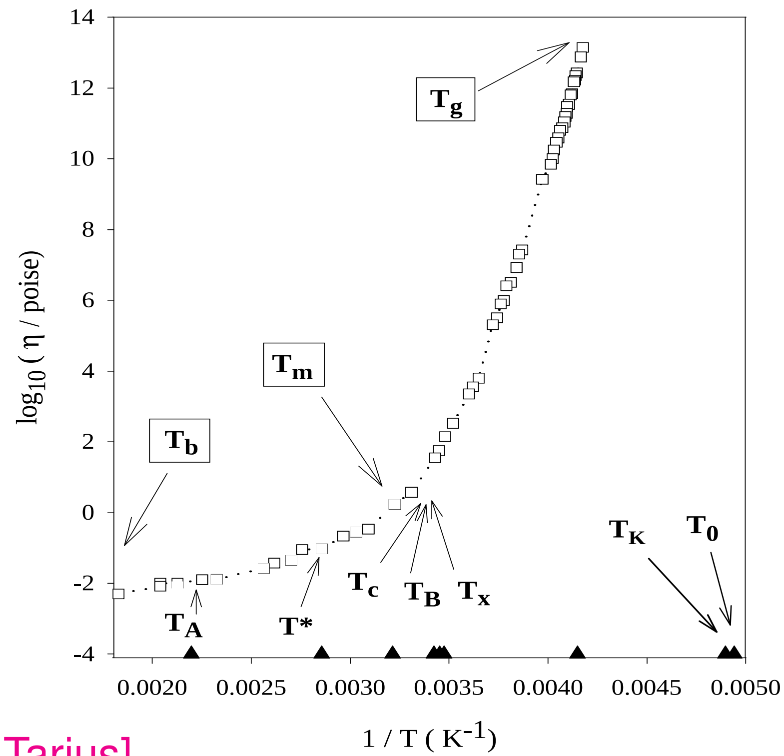
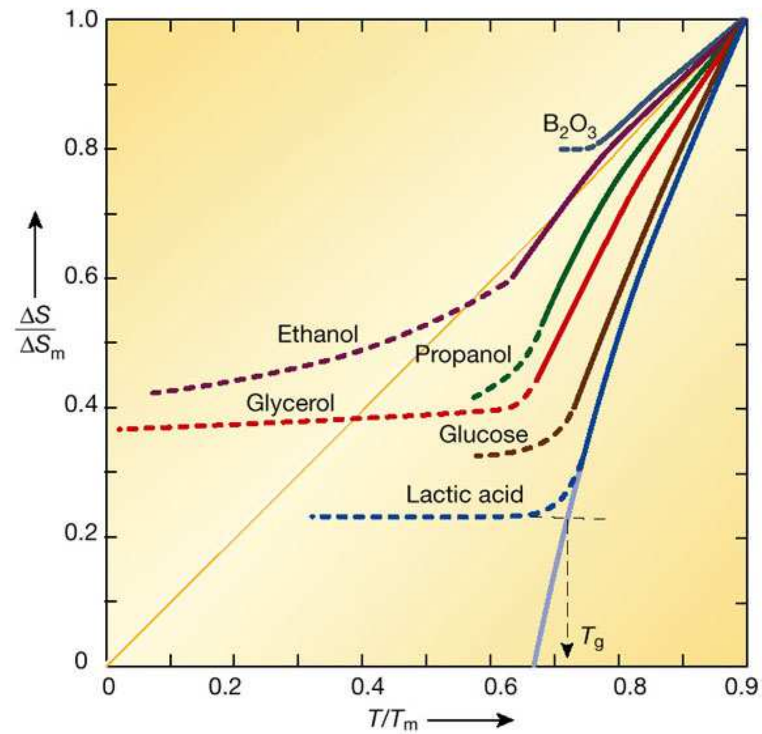


# Temperature crossovers

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




[G. Tarjus]

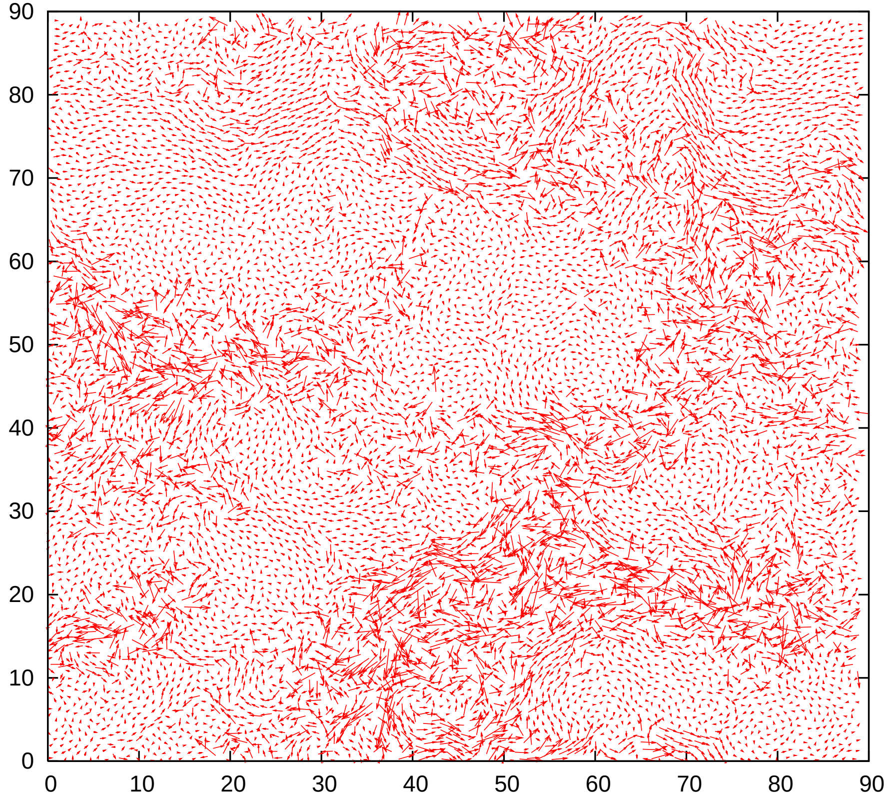



[Debenedetti & Stillinger]

• Extrapolated temperatures for dynamic and thermodynamic singularities: $T_0$, $T_K$. Existence and nature of "ideal glass transition" at Kauzmann temperature is controversial.

# 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 clearly established: point-to-set lengthscales, other structural indicators?

*Dynamical heterogeneities in glasses, colloids and granular materials*

Eds.: Berthier, Biroli, Bouchaud, Cipelletti, van Saarloos (Oxford Univ. Press, 2011).

# Dynamic heterogeneity

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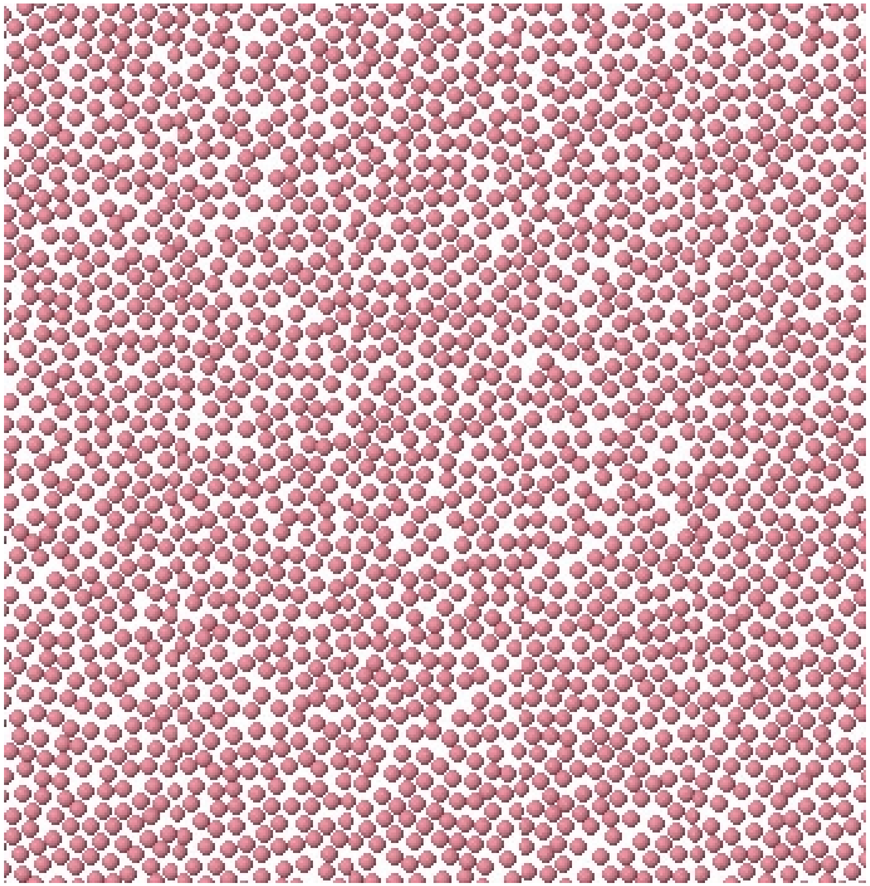


• Spatial fluctuations grow (modestly) near $T_g$.

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

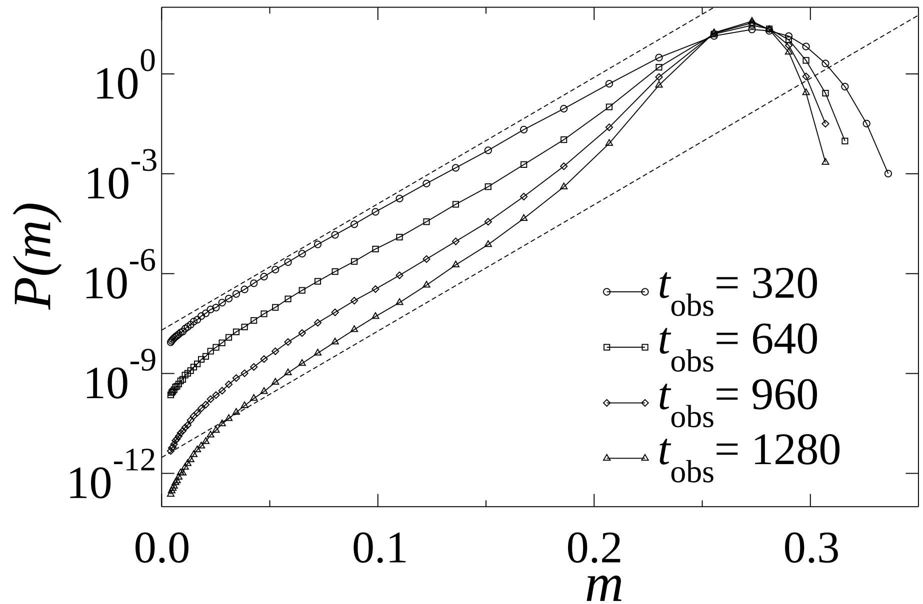
• Structural origin not clearly established: point-to-set lengthscales and other structural indicators?

• Do "convincing" thermodynamic fluctuations even exist?

# 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. Direct connection to dynamic heterogeneity.




[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" free energy landscape gives rise to same transition, but the transition exists without multiplicity of glassy states: KCM, plaquette models. [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: $H = -\sum_{i_1 \cdots i_p} J_{i_1 \ldots i_p} s_{i_1} \cdots s_{i_p}$.

• Recently demonstrated for hard spheres as $d \to \infty$ [Kurchan, Zamponi *et al.*]

• 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.

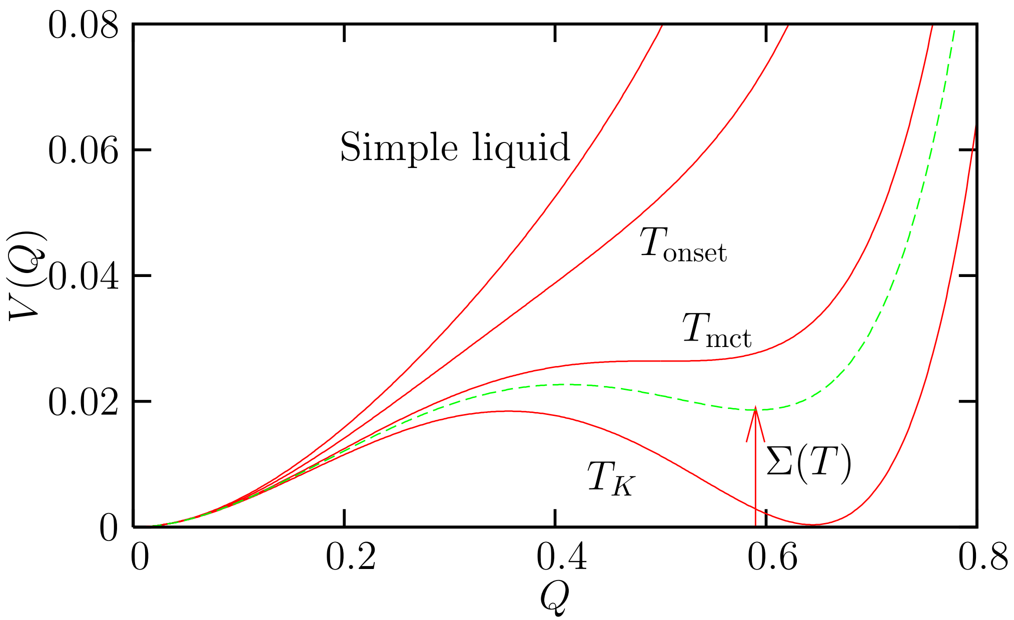
• Extension to finite dimensions ('mosaic picture') remains ambiguous.

# ‘Landau’ free energy

• Relevant thermodynamic fluctuations encoded in “effective potential” $V(Q)$. Free energy cost, i.e. configurational entropy, for 2 configurations to have overlap $Q$: [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: $Q_{12} = \frac{1}{N}\sum_{i,j=1}^{N} \theta(a - |\mathbf{r}_{1,i} - \mathbf{r}_{2,j}|)$.




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

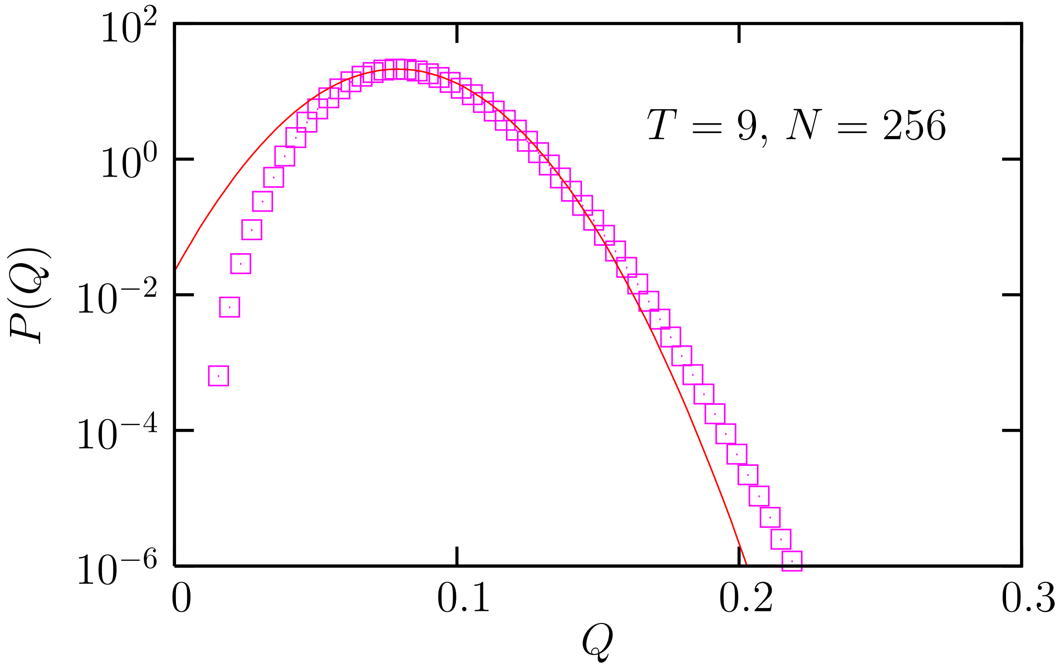
• $$P(Q) = \overline{\langle \delta(Q - Q_{12}) \rangle} \sim \exp[-\beta N V(Q)]$$

• 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 $Q_{12}$.

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




• Solution: Seek “large deviations” using umbrella sampling techniques.

[Berthier, PRE ’13]

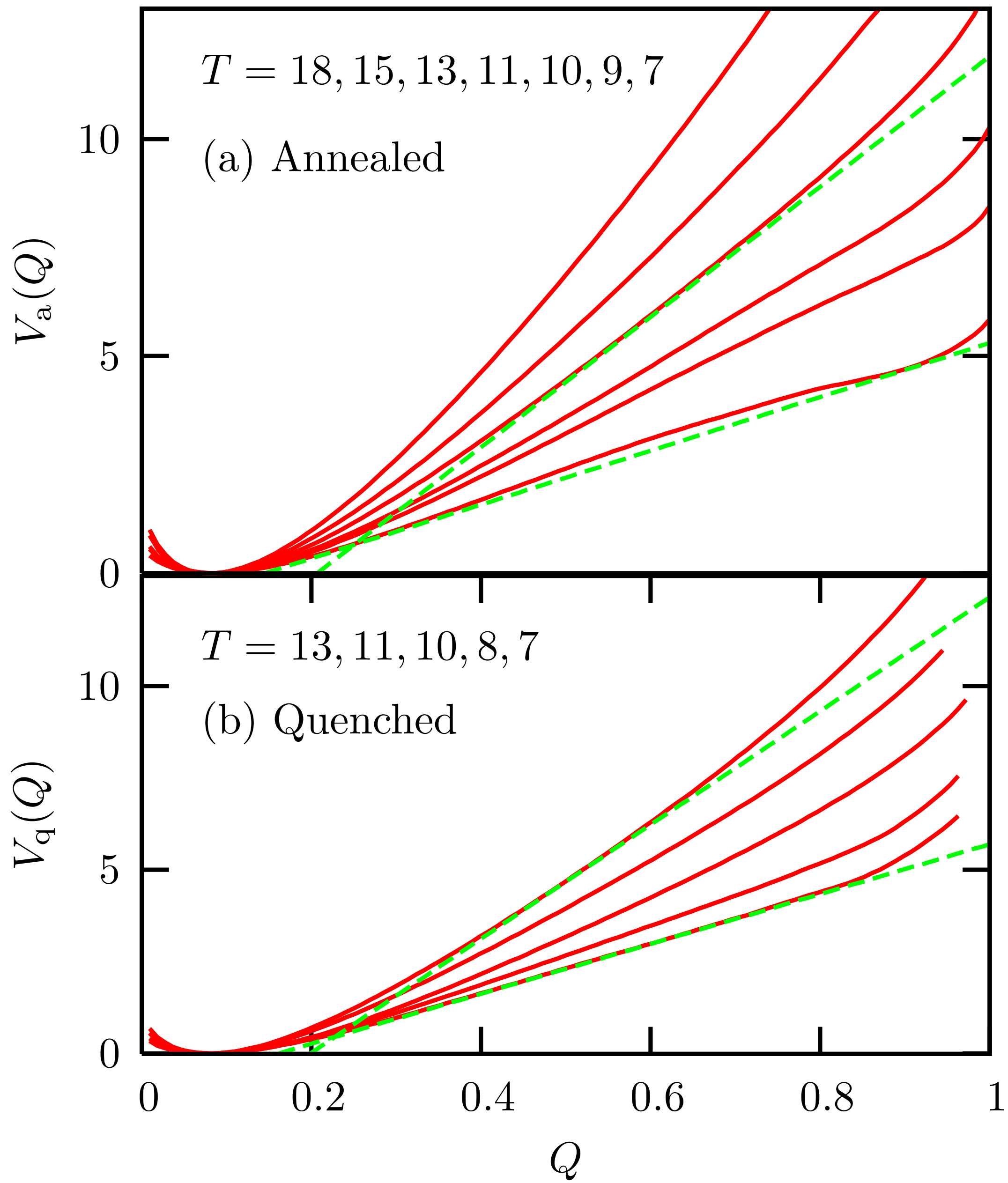
# Overlap fluctuations in $3d$ liquid

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

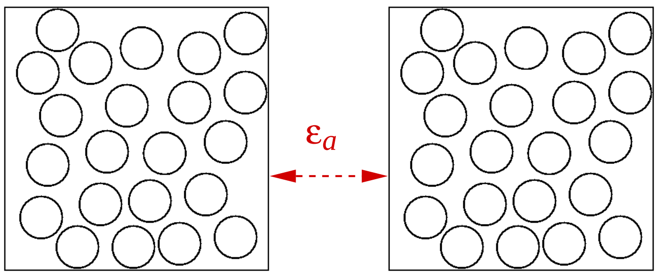
- Static fluctuations may control fluctuations and phase transitions in trajectory space.



# Equilibrium phase transitions

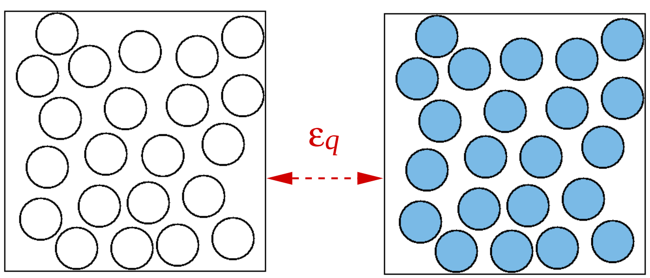
• Non-convex $V(Q)$ implies that an equilibrium phase transition can be induced by a field conjugated to $Q$. [Kurchan, Franz, Mézard, Cammarota, Biroli...]

• Annealed: 2 coupled copies.

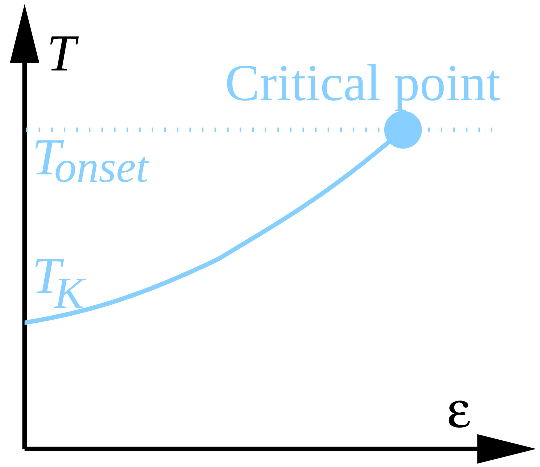



$$H = H_1 + H_2 - \epsilon_a Q_{12}$$

• Quenched: copy 2 is frozen.




$$H = H_1 - \epsilon_q Q_{12}$$




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

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

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

# Spin plaquette models

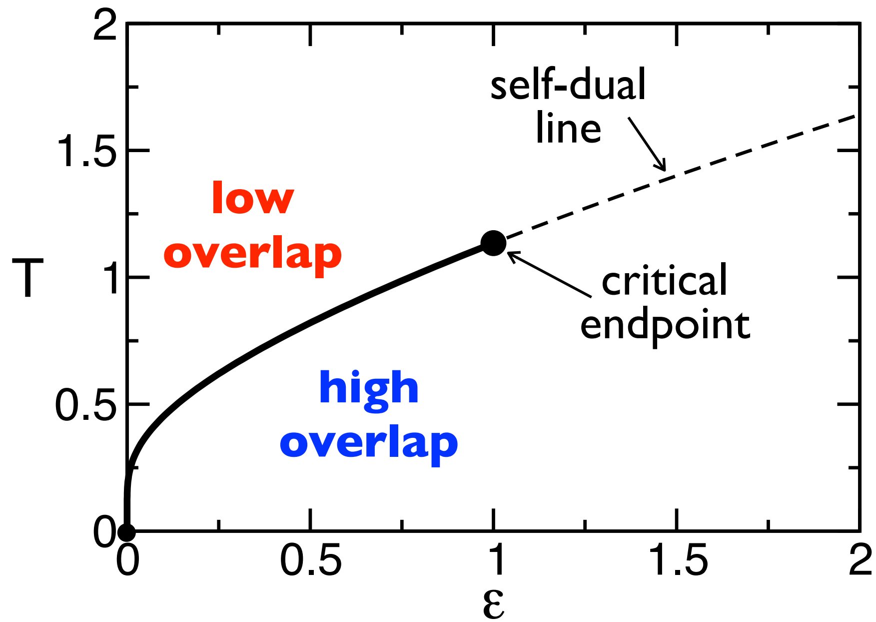
• Spin plaquette models are intermediate spin models between KCM and spin glass RFOT models: statics not fully trivial, localized defects and facilitated dynamics. E.g. in $d = 2$ on square lattice: $E = -\sum_{\square} s_1 s_2 s_3 s_4$.

• 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]

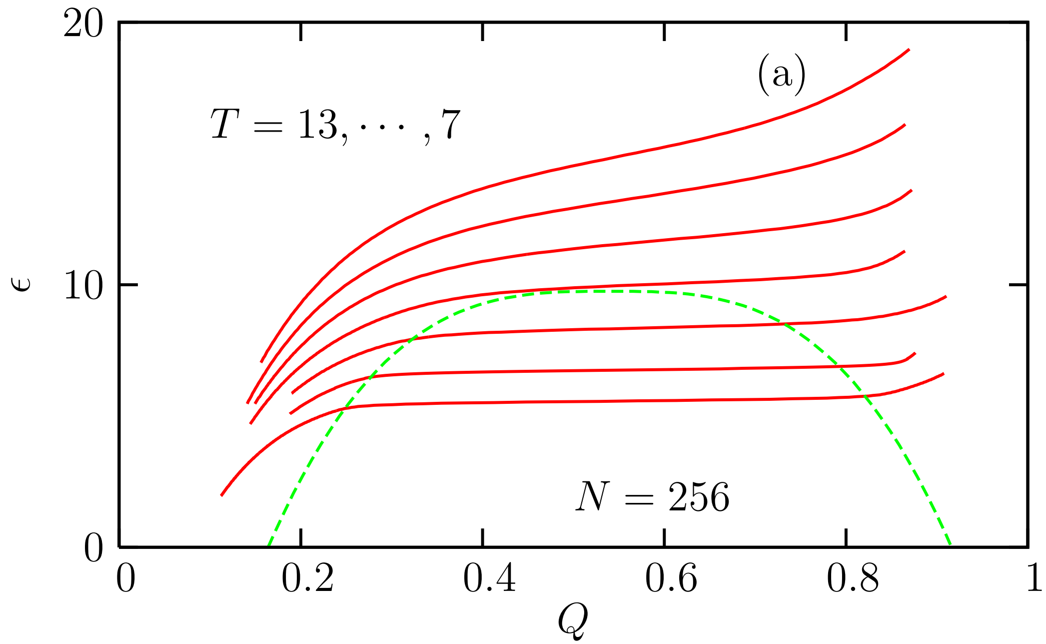
• "High-order" or "multi-point" static correlations develop without finite $T$ phase transitions.

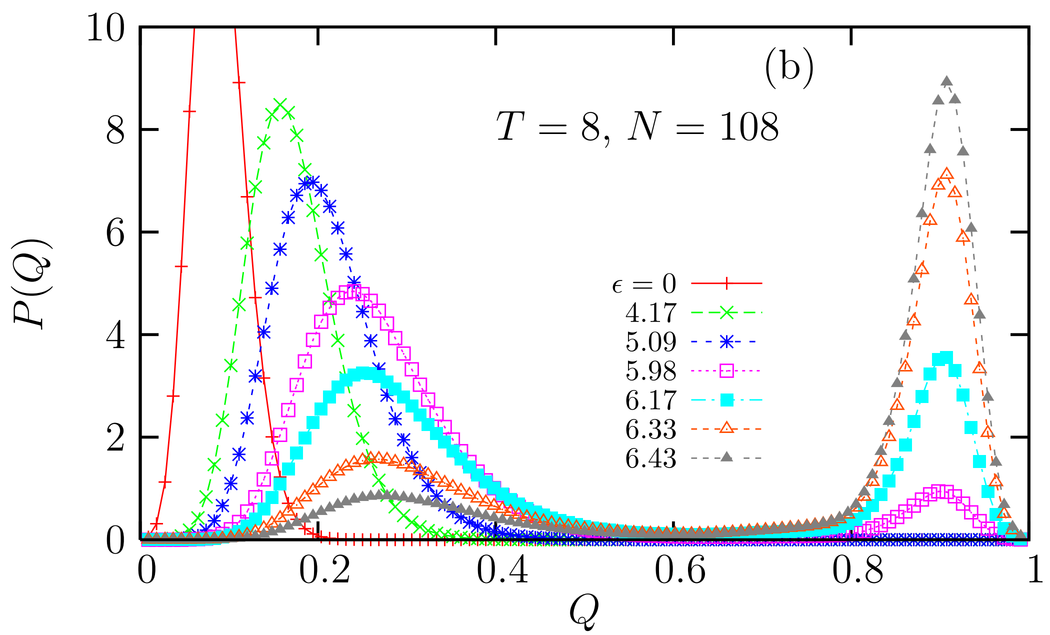
• For triangular plaquette model, annealed transition occurs [Garrahan, PRE '14]. Quenched? -> NO (Rob).



# Numerical evidence in $3d$ liquid

- Investigate $(T, \epsilon)$ 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 $T \lesssim T_c \approx 9.8$.

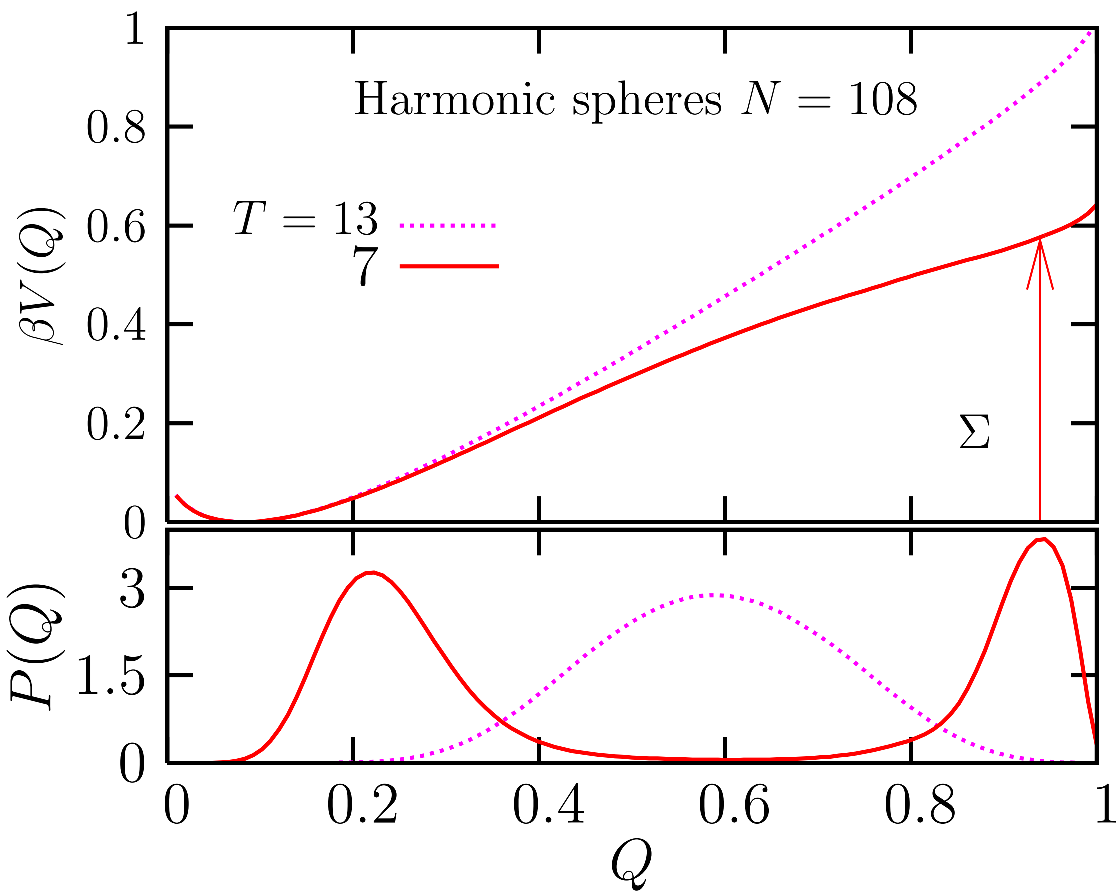
$\rightarrow$ Equilibrium first-order phase transition.

[see also Parisi & Seoane PRE ’14]

# Configurational entropy $\Sigma(T)$

- $\Sigma = k_B \log \mathcal{N}$ signals entropy crisis: $\Sigma(T \to T_K) = 0$. Problematic when $d < \infty$, because metastable states cannot be rigorously defined.

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




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

- Free energy cost to localize the system 'near' a given configuration: Well-defined even in finite $d$.

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

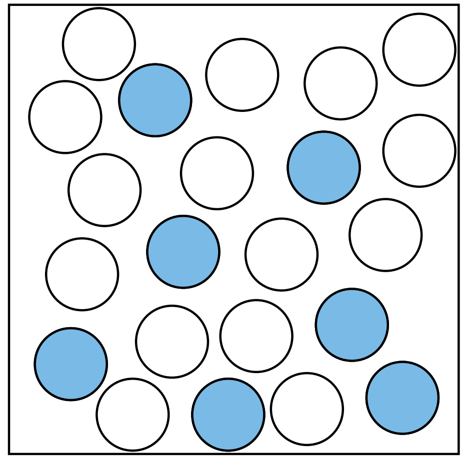
[Berthier and Coslovich, arXiv:1401.5260]

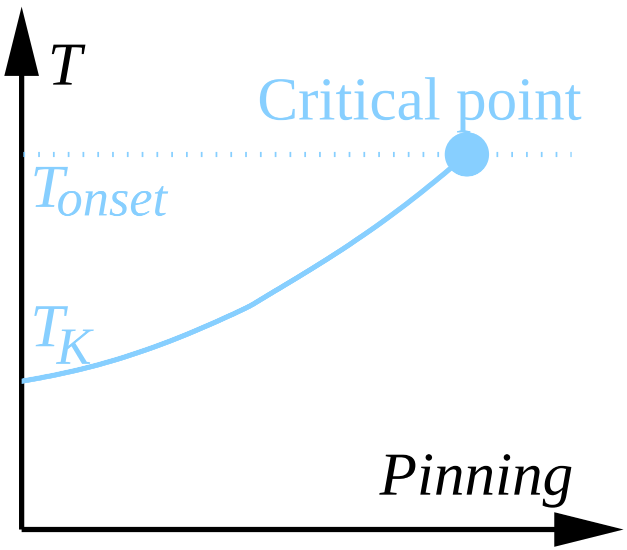
# Ideal glass transition?

• $\epsilon$ 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.

• Slowing down observed numerically.
[Kim, Scheidler...]





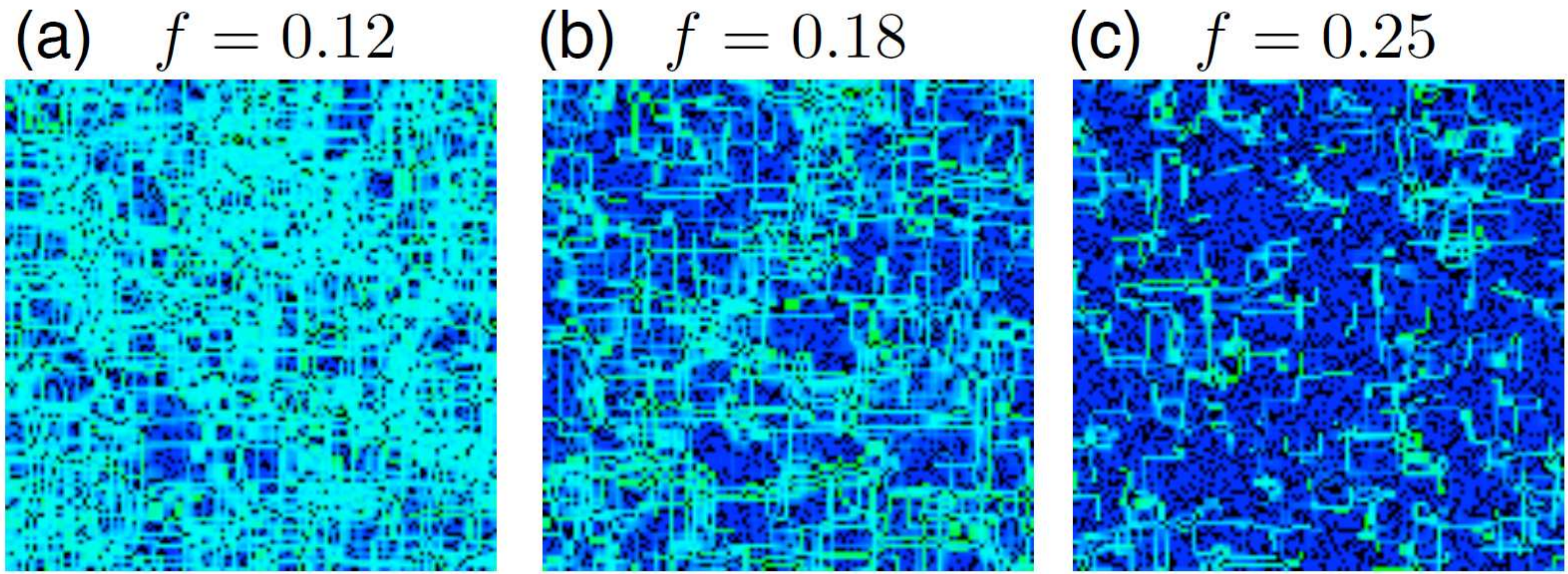

• Within RFOT, ideal glass transition line extends up to critical point.
[Cammarota & Biroli, PNAS '12]

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

# 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.



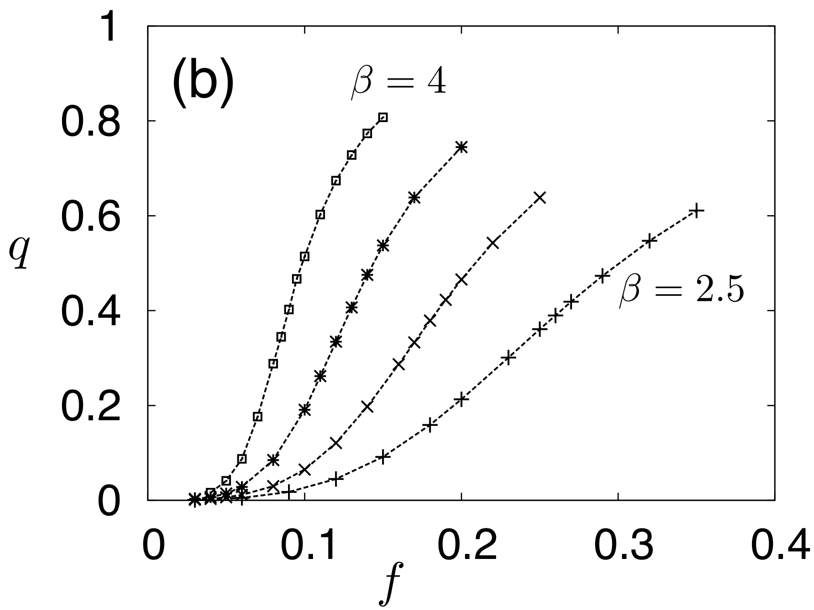

Light blue: mobile. Deep blue: frozen. Black: pinned.

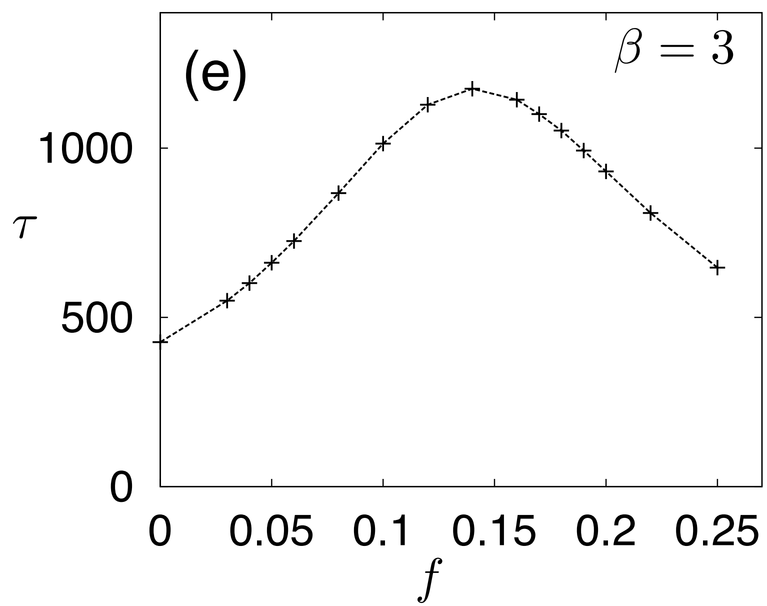
# Smooth crossover

• 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 $N \to \infty$.

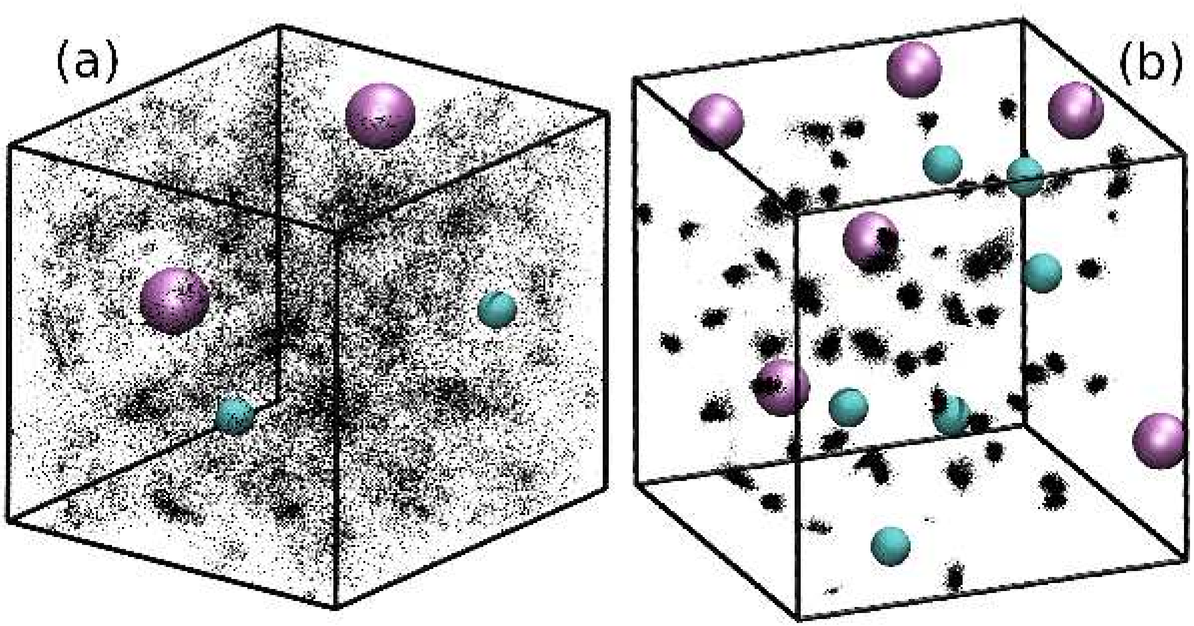
• Dynamics barely slows down with $f$, unlike atomistic models.



# 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]



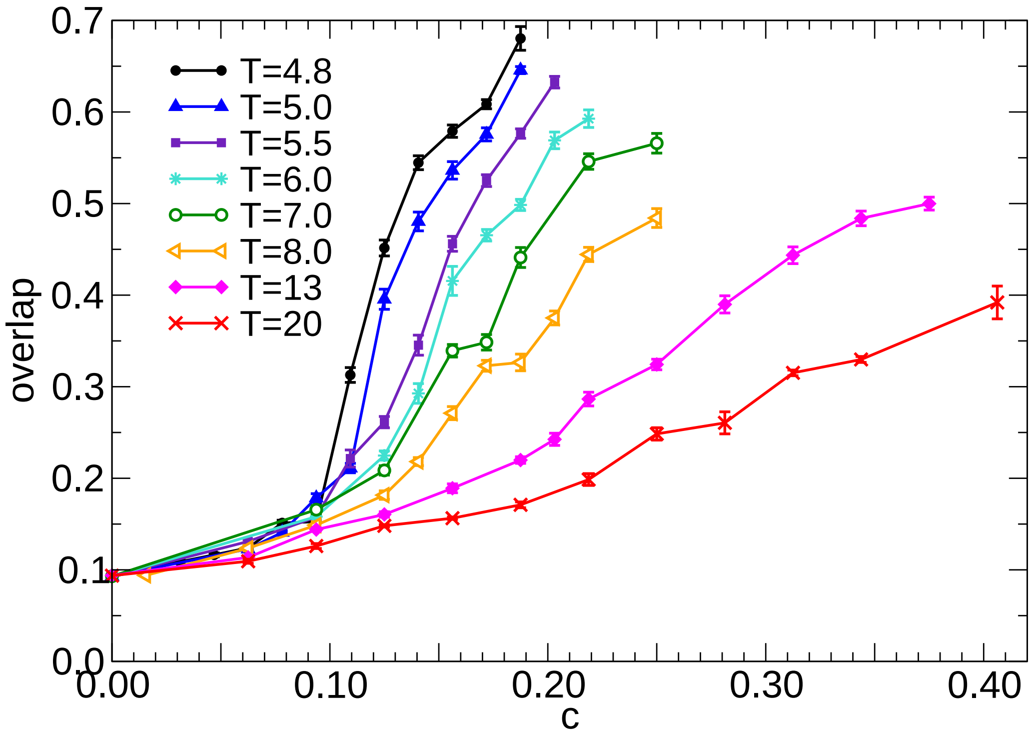

*Low-$c$ fluid* *High-$c$ glass*

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

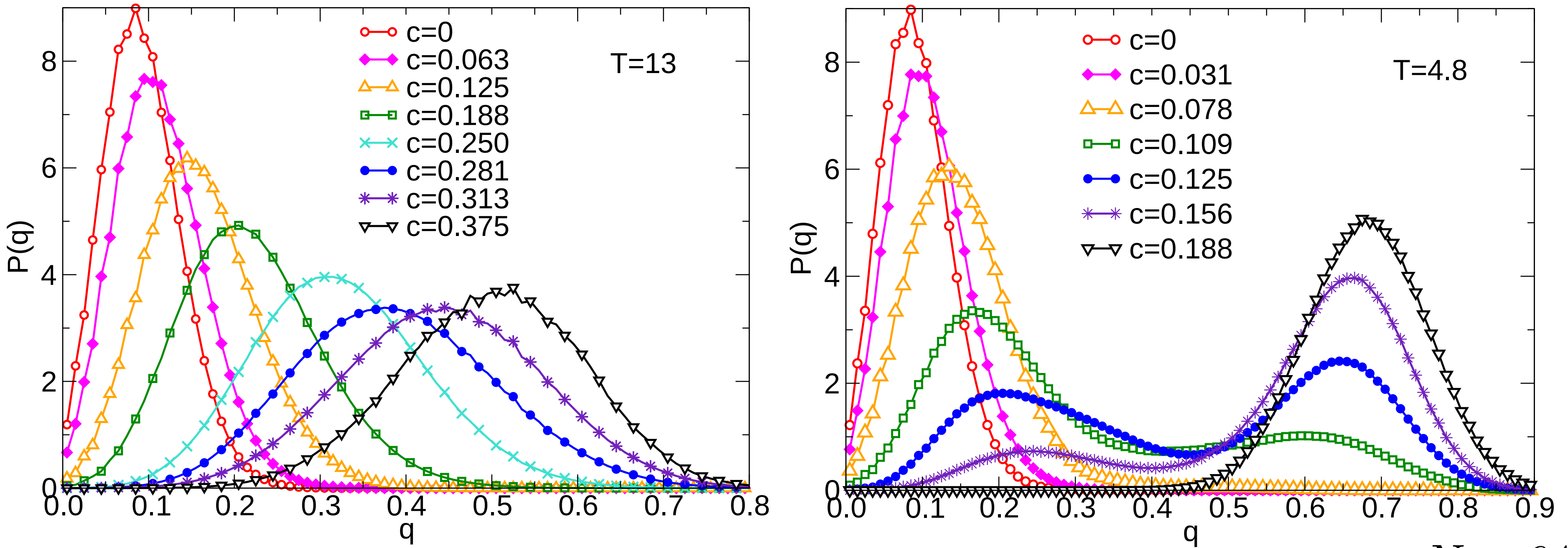



$N = 64$

• 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: $P(Q) = \langle \delta(Q - Q_{\alpha\beta}) \rangle$ .



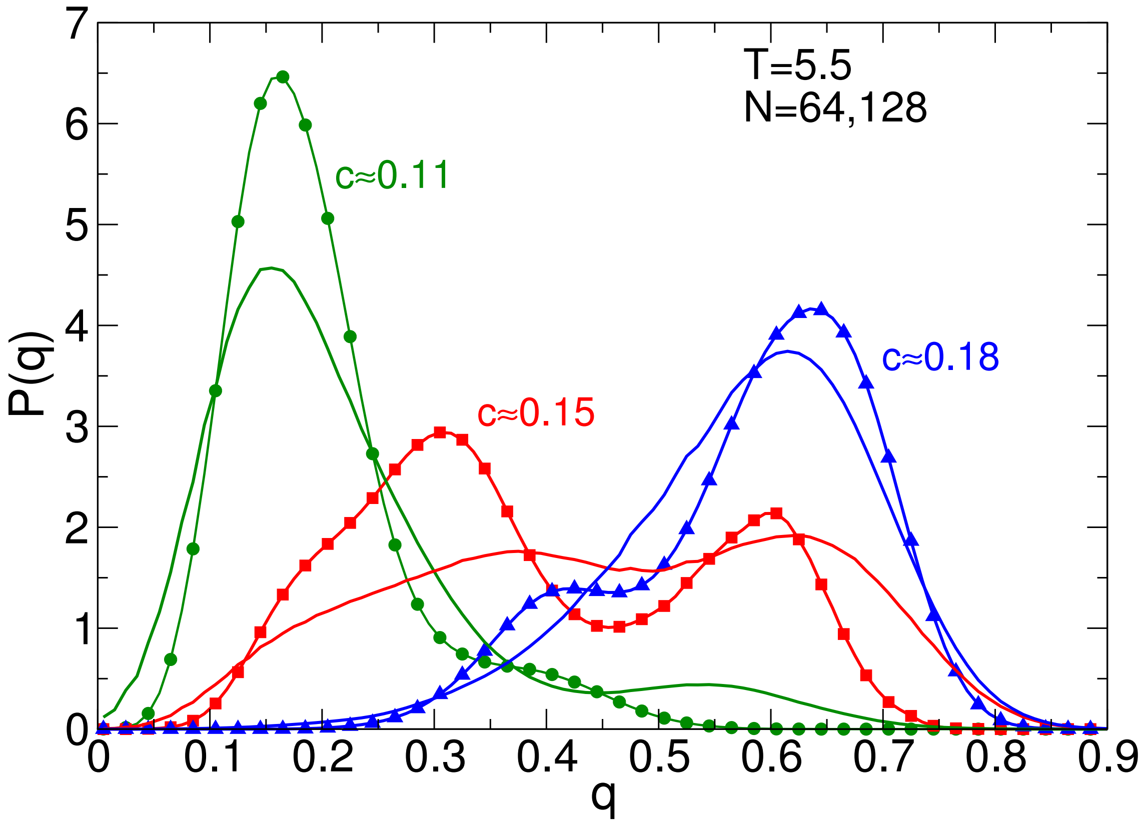

$N = 64$

- Distributions remain nearly Gaussian at high $T$.

- Bimodal distributions appear at low enough $T$, suggestive of phase coexistence at first-order transition, rounded by finite $N$ effects.

# Thermodynamic limit?

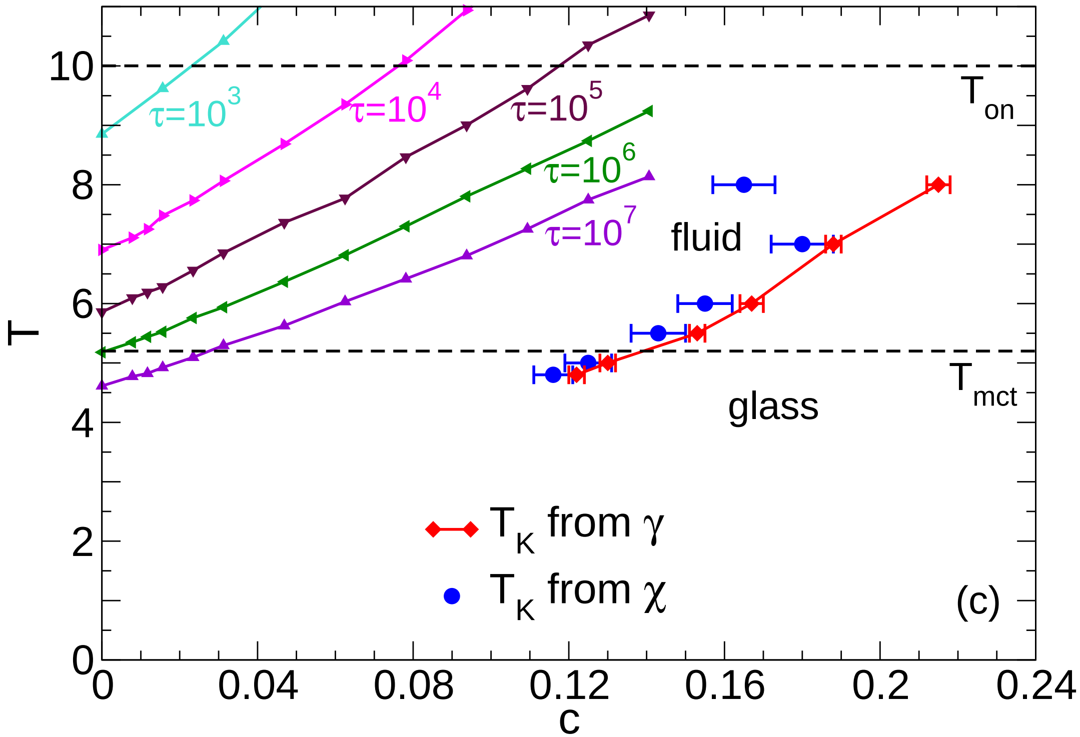
• Phase transition can only be proven using finite-size scaling techniques to extrapolate toward $N \to \infty$.




• 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.



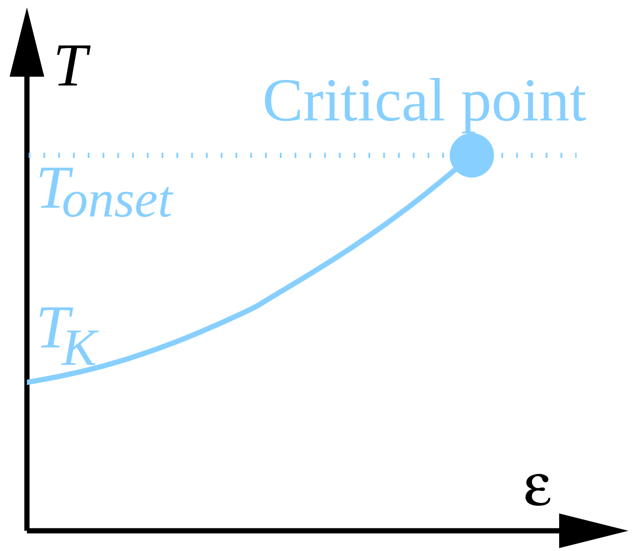

• Glass formation induced by random pinning has clear thermodynamic signatures which can be studied directly.

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

# Summary

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

• Adding a thermodynamic field can induce equilibrium phase transitions.




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

• Quenched coupling: first-order transition ending at random critical point. Specific to RFOT?

• Random pinning: random first order transition ending at random critical point. Specific to RFOT.

• Direct probes of peculiar thermodynamic underpinnings of RFOT theory.

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