Thermodynamic fluctuations in model glasses

Ludovic Berthier

Laboratoire Charles Coulomb
Université Montpellier 2 & CNRS

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

- With:

  D. Coslovich (Montpellier)
  R. Jack (Bath)
  W. Kob (Montpellier)
Temperature crossovers

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

![Graph showing temperature crossovers](image)

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
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 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.

- Equivalently, a field coupled to local dynamics induces a nonequilibrium first-order phase transition in the “s-ensemble”.

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

• 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 $Q$:

$$V_q(Q) = -\left(\frac{T}{N}\right) \int dr_2 e^{-\beta H(r_2)} \log \int dr_1 e^{-\beta H(r_1)} \delta(Q - Q_{12})$$

where: $Q_{12} = \frac{1}{N} \sum_{i,j=1}^{N} \theta(a - |r_{1,i} - r_{2,j}|)$.

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

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

- 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 $Q \approx Q_i$.

- Reconstruct $P(Q)$ using reweighting techniques.

- Exponential tail below $T_{\text{onset}}$ → 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 $T_{\text{onset}}$.

- **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: $E = - \sum s_1 s_2 s_3 s_4$.

- 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 $T_{\text{onset}} \approx 10$.
- Suggests coexistence region ending at a critical point.

![Graph (a)]

- $P(Q)$ 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 $\Sigma(T)$

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

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

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

- 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 $T \to T_K$. 

\[ T \]

\[ T_{\text{onset}} \]

\[ T_K \]

Pinning

Critical point
Pinning in plaquette models

- Random pinning studies in spin plaquette models offer an alternative scenario to RFOT. [Jack & Berthier, PRE ’12]
- Crossover $f^*(T)$ from competition between bulk correlations and random pinning: directly reveals growing static correlation lengthscale.

(a) $f = 0.12$  (b) $f = 0.18$  (c) $f = 0.25$

Smooth crossover

- Static overlap $q$ increases rapidly with fraction $f$ of pinned spins, crossover $f^* = f^*(T)$, 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.

![Graphs showing smooth crossover behavior](image)
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]

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

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?

$N = 64$
Fluctuations: Phase coexistence

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

- 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.
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 $\approx T_{\text{onset}}$.

- 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.