Monte Carlo simulations for systems with glassy dynamics

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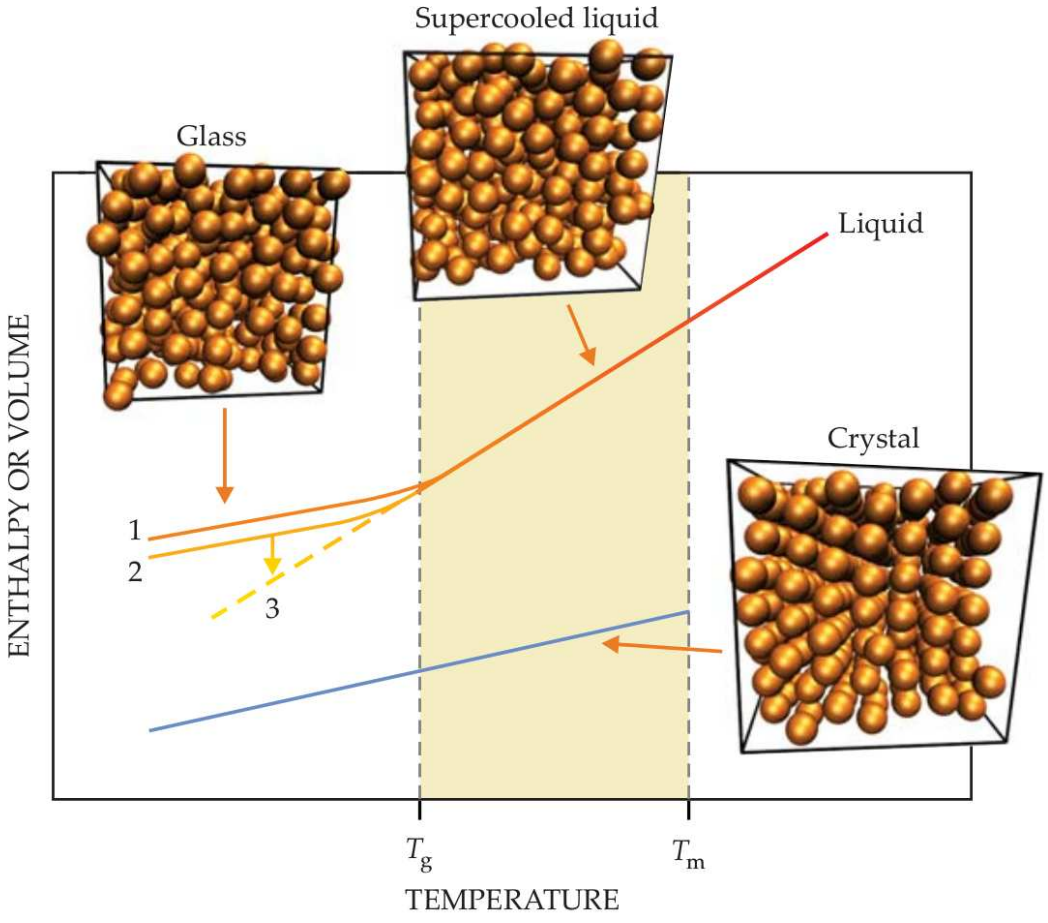
Physical problem

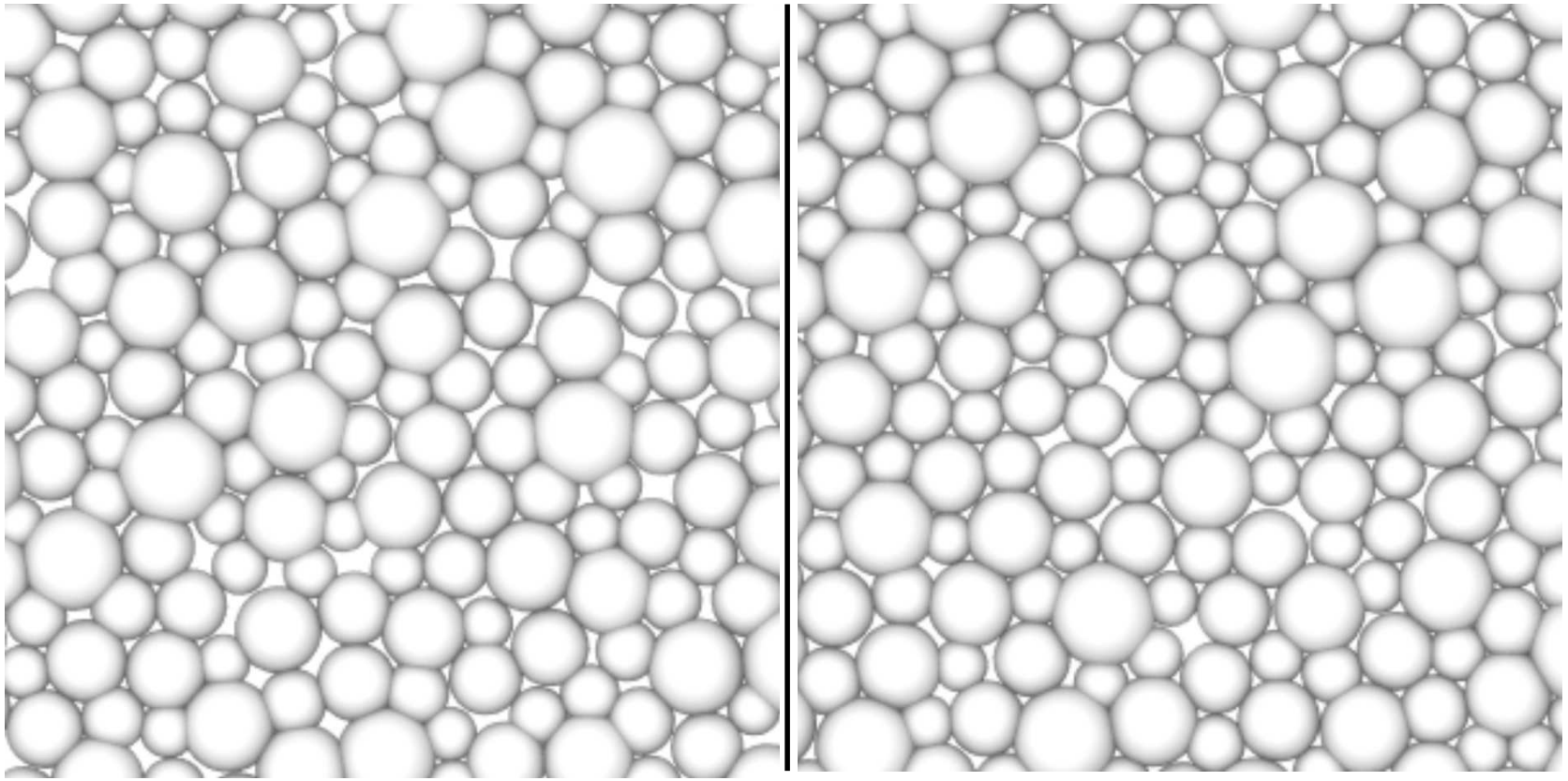
Glass “transition”



[Berthier & Ediger, Phys. Today ’16]

- Glasses are formed by cooling a liquid.
- T_g is set by competition between cooling rate dT/dt and relaxation time $\tau(T)$.
- Glass retains the structure frozen at T_g.

- Many open questions: crystallisation, dynamics, structure and properties of the glass, aging dynamics, low-T properties, phase transitions, etc.

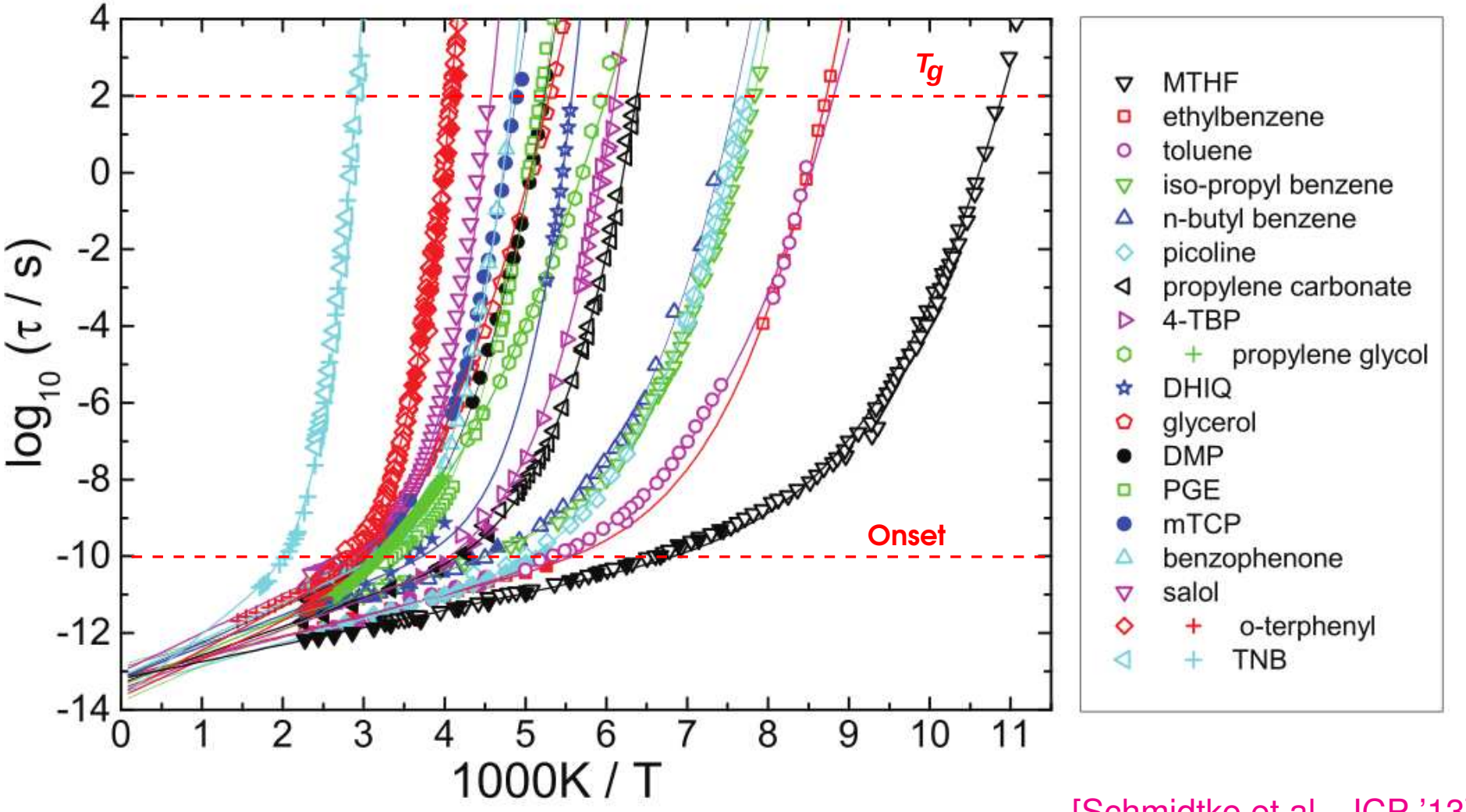


[Misaki Ozawa]

• Glasses: disordered structure of liquids, but rigidity of crystals without crossing any apparent phase transition.

• A glass prepared 10^{10} times slower looks identical: glassy order?

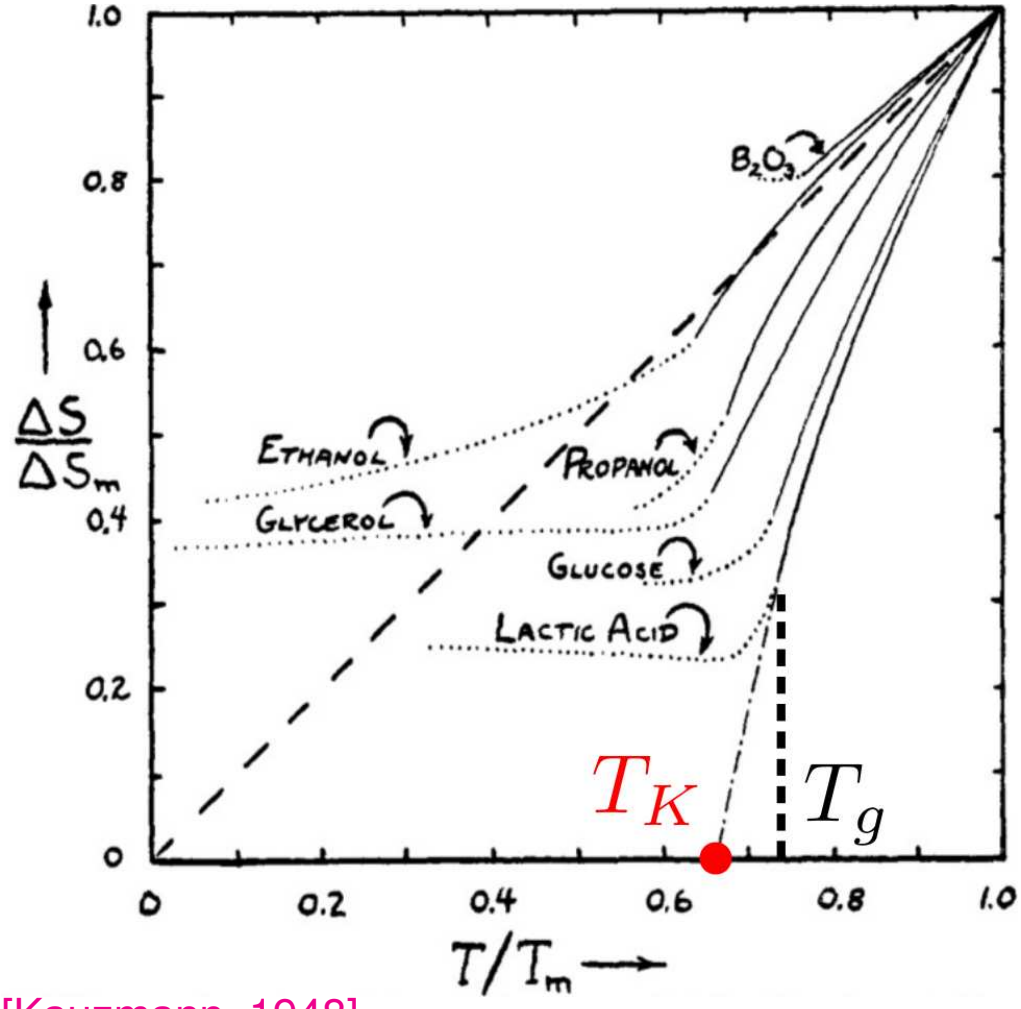
Dynamics



[Schmidtke et al., JCP '13]

- For $\tau \sim 100$ sec, $\tau/\tau_{\text{onset}} \sim 10^{12}$ for molecular glasses.

Thermodynamics



[Kauzmann, 1948]

- Configurational entropy, $S_{\rm conf} \approx S_{\rm tot} - S_{\rm xtal}$, decreases steeply as T decreases.

- Hint of inaccessible thermodynamic phase transition at $T_K > 0$ with "ideal" glass as "ordered" as crystal.

- Since 1948: experimental picture mostly unchanged except $S_{\rm conf} \approx S_{\rm tot} - S_{\rm glass}$.

- Recent work adds strong support and physical insight to this idea.

Statistical mechanics

Mean-field theory of glasses

- Random First Order Transition theory: theoretical construction based on exact mean-field results. [Kirkpatrick-Thirumalai-Wolynes '85 $\cdots$, $d \to \infty$ results '13-...]

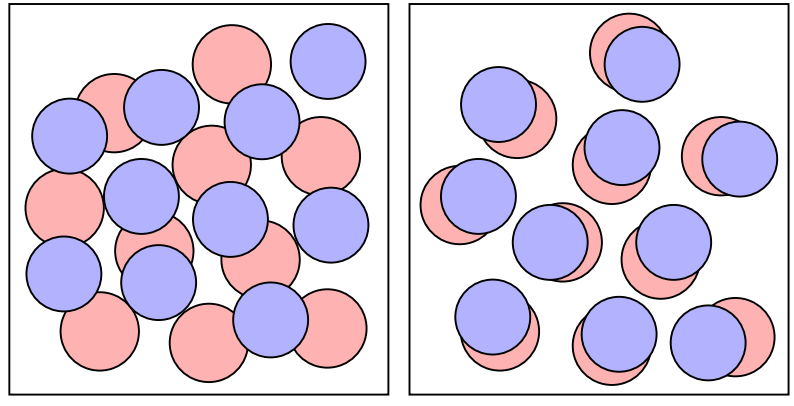
- Presented in: [Theory of simple glasses, Urbani, Parisi, Zamponi, Cambridge, 2020]

- Within mean-field, a thermodynamic glass transition is exactly realised. First-order transition with a discontinuous order parameter: the overlap Q.

- Overlap quantifies similarities between coarse-grained density profiles:

$$Q_{12} = \frac{1}{N} \sum_{i,j} \exp(-|\mathbf{r}_{1,i} - \mathbf{r}_{2,j}|^2/a^2)$$

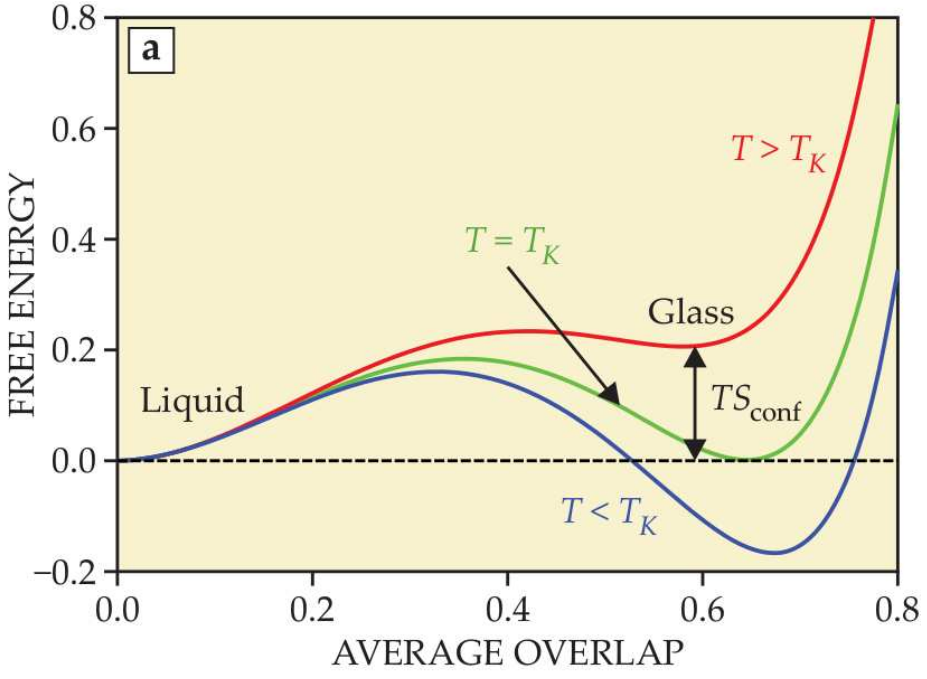
with $a \sim 0.2\sigma$.

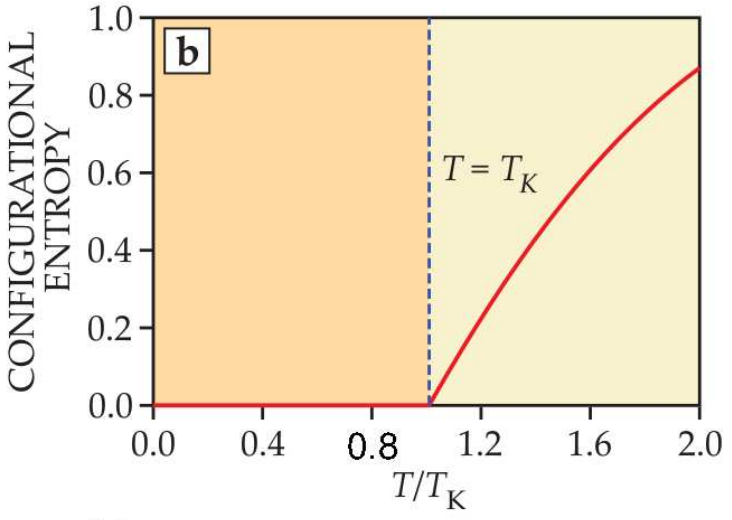


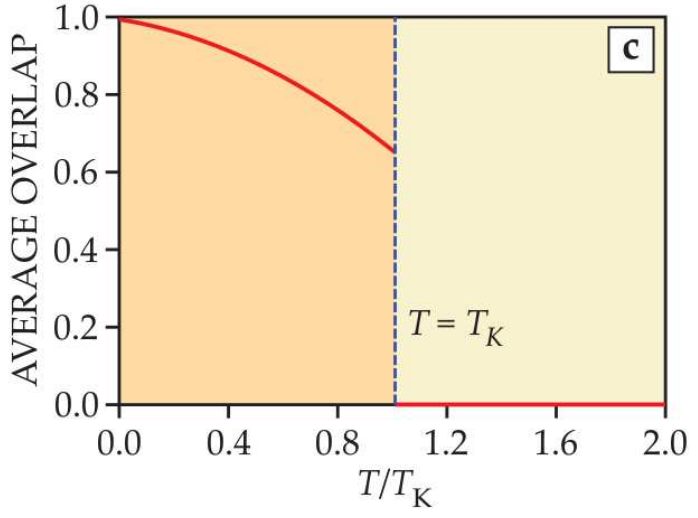
$Q \approx 0$ $Q \approx 1$

Landau free energy, $d = \infty$

• RFOT theory fully encoded in Franz-Parisi potential $V(Q)$ [PRL '97] related to overlap fluctuations, as in Landau description of phase transitions.







[Berthier & Ediger, Phys. Today '16]

Theoretical situation

- A first-order Kauzmann phase transition at $T_K > 0$ to ideal glass phase exists in $d \to \infty$, with known properties. The situation is clear for $d = \infty$.

- The (big) challenge is to identify and treat analytically relevant finite-d fluctuations, which may modify, or even destroy this picture.

- Alternative models and ideas have been put forward to complete (or replace) this physical picture in finite dimensions.

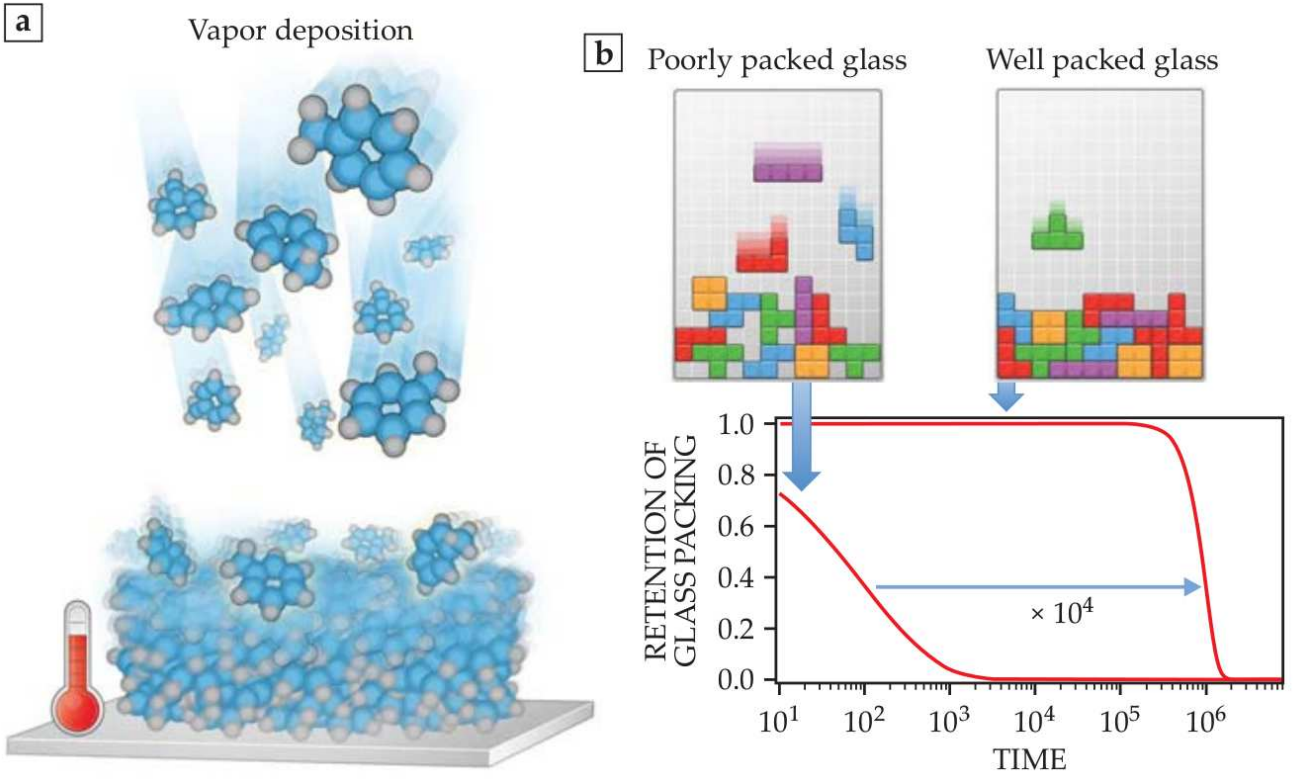
- Direct studies in $d = 2, 3$ are thus crucial: simulations and experiments with novel approaches are needed.

Efficient Monte Carlo simulations

Brute force equilibration (MD?)

Smarter equilibration (MC?)

- Direct production layer-by-layer. Vapor deposited glasses produces non-conventional ultrastable glasses. [Swallen *et al.*, Science '07]



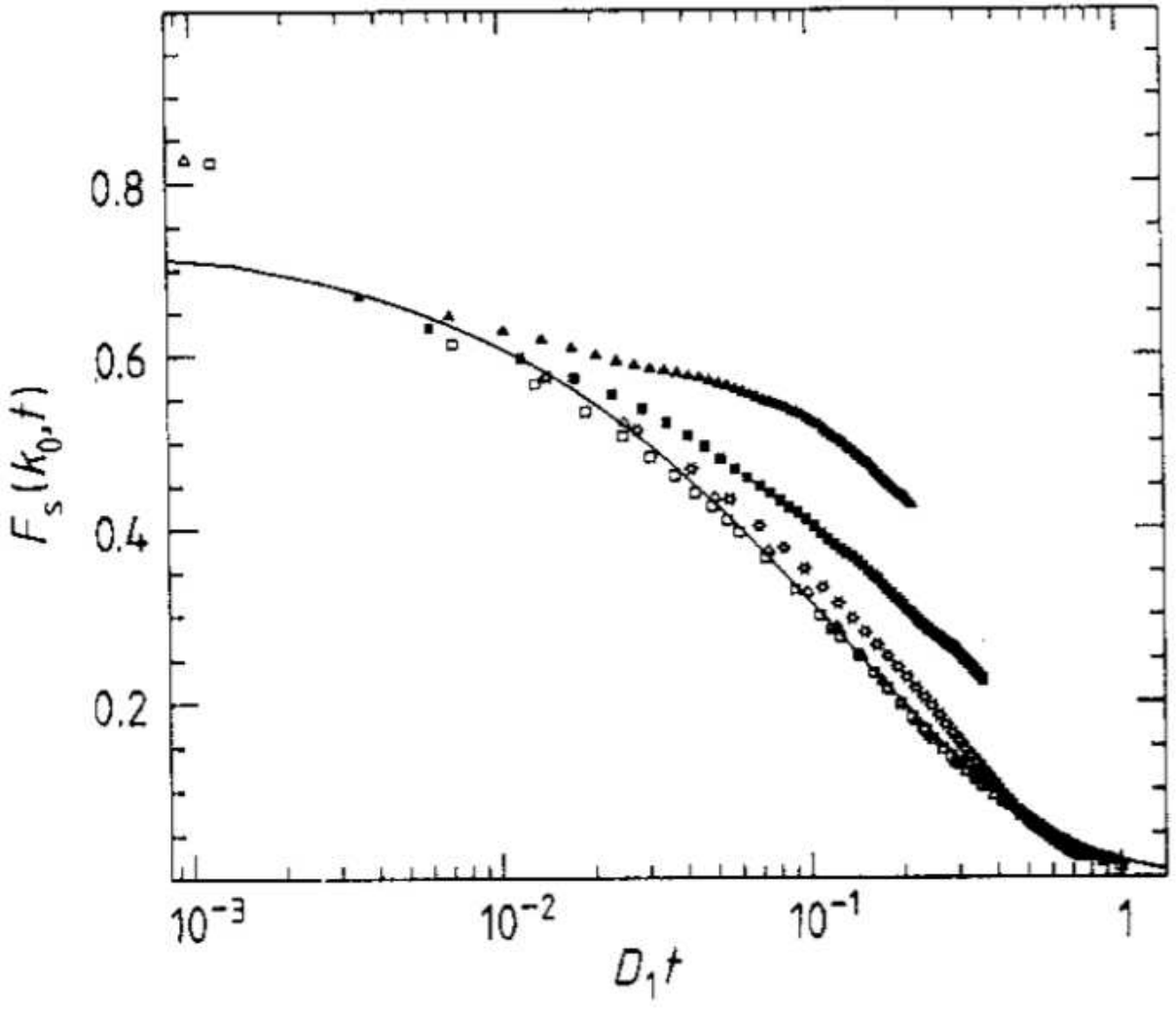
- These new materials behave as million-year old glasses. They make better materials for applications (pharmaceuticals, electronics).

Brute force computer simulations

• Classical pair potentials for simple polydisperse fluids composed of off-lattice point particles, simulated using Molecular Dynamics (molecules) and Brownian dynamics (colloids): discretise and integrate.

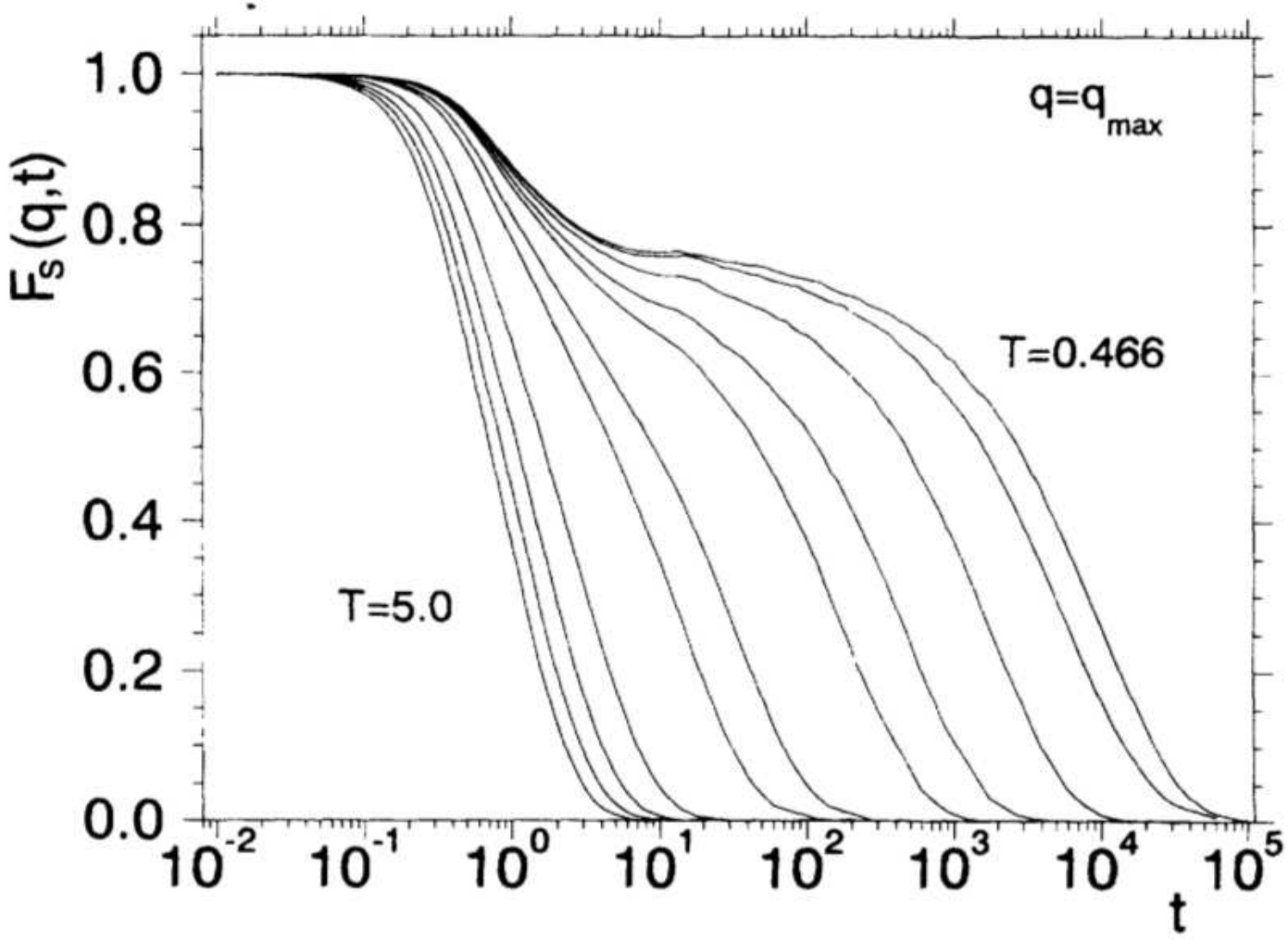
• From 2 decades of dynamic slowing down in mid-80's to 5 decades in 2019 (stuck near T_{mct}). Eight-decade gap with conventional experiment, 14 with ultrastable glasses—hopeless.

1989 - Soft spheres



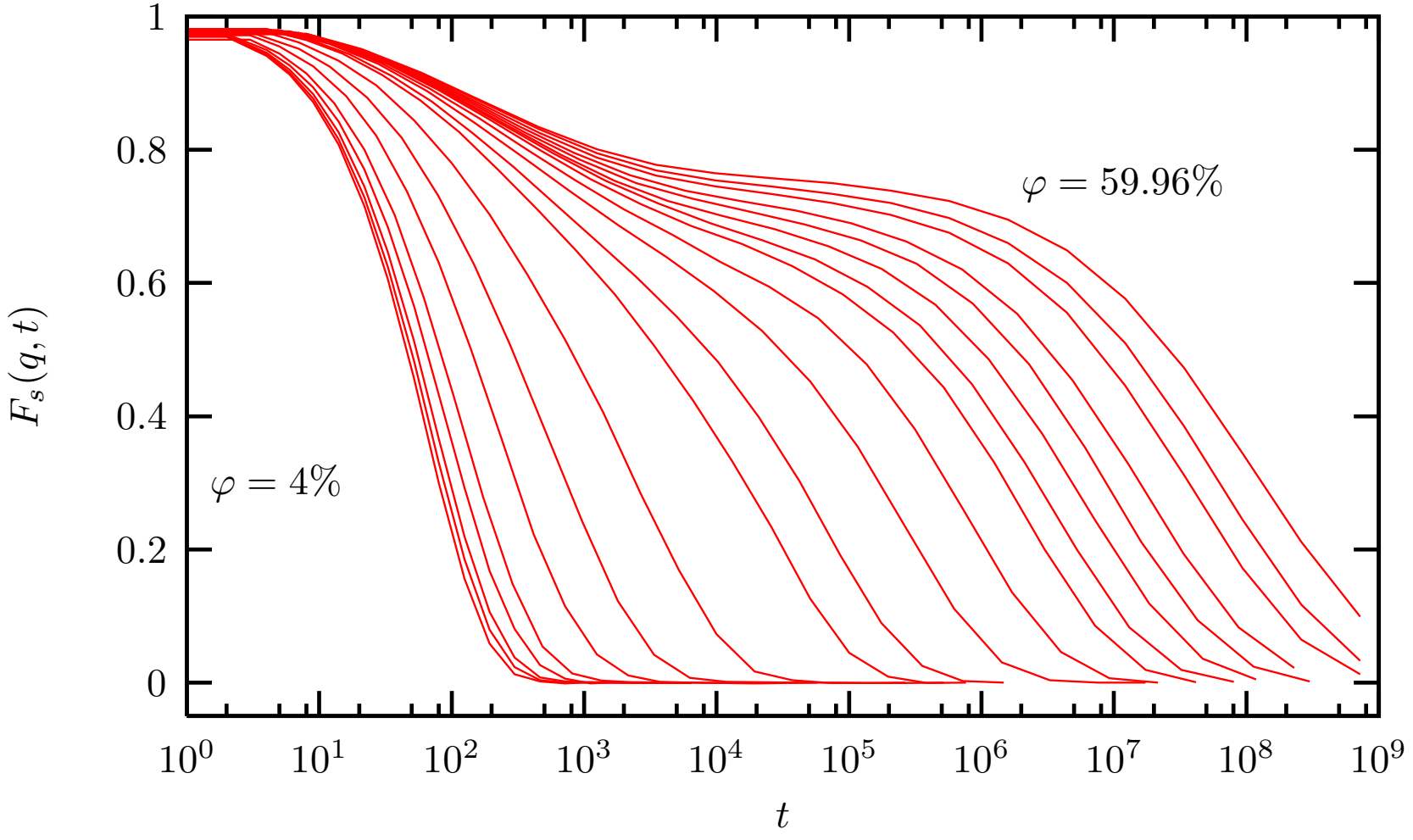
[Roux, Barrat, Hansen, J. Phys.: Condens. Matter 1, 7171 (1989)]

1995 - Binary Lennard-Jones



[Kob & Andersen, Phys Rev. Lett. 73, 1376 (1994)]

2009 - Hard spheres

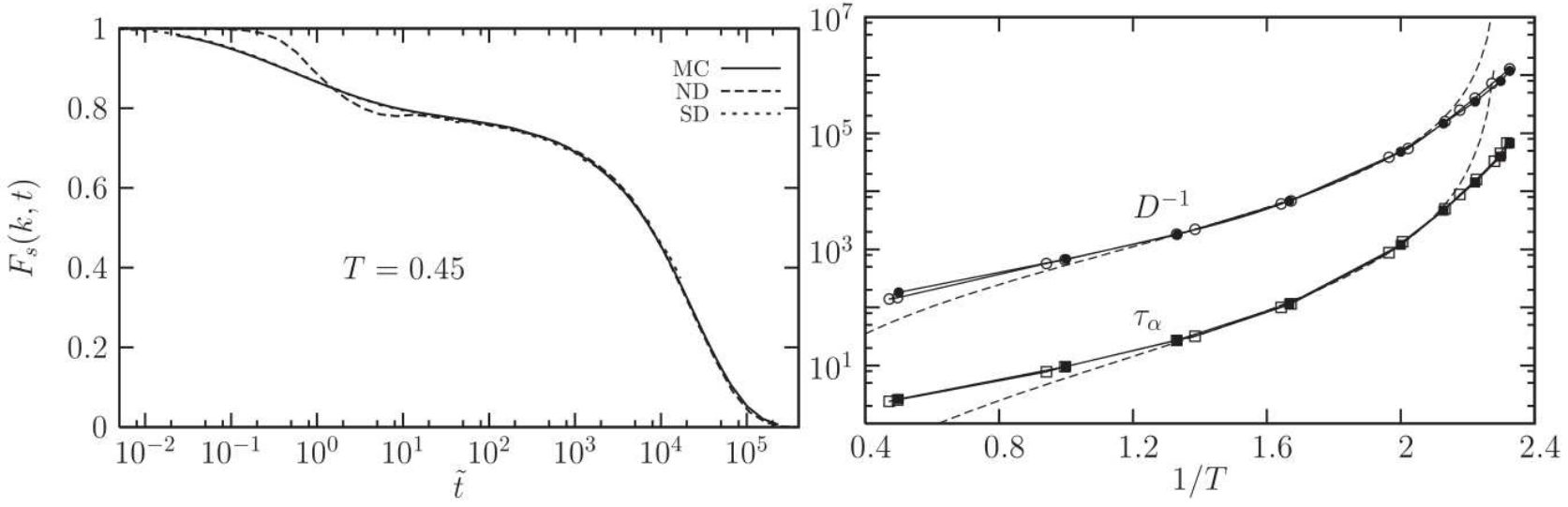


[Brambilla *et al.*, Phys Rev. Lett. 102, 085703 (2009)]

Simple Monte Carlo for fluids

- Pick one particle at random, small random displacement, Metropolis filter, repeat. Optimisation is very easy.

J. Phys.: Condens. Matter **19** (2007) 205130 L Berthier and W Kob



- Long time dynamics is identical to Molecular Dynamics apart from simple rescaling of time: non-trivial physical result.

- However, the gain in efficiency is almost null since global dynamics is unchanged (physical but not smart).

Smart Monte Carlo

- Parallel tempering: a chain of replica at different temperatures with exchange. This works well for spin glasses, but gain is modest ($\approx 10^2$?) in glassy fluids.

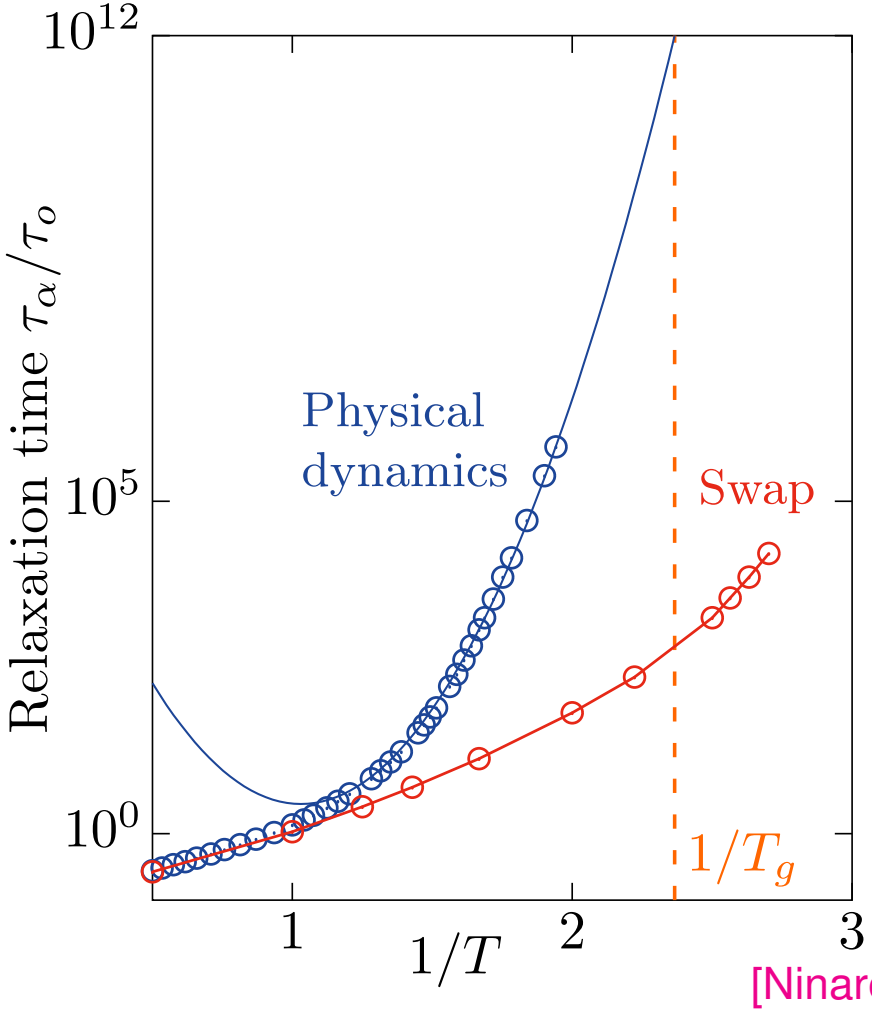
- Population annealing (next talk) is being used. Gain? [Machta]

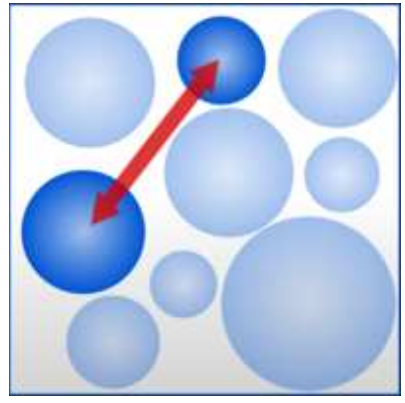
- Wang-Landau to explore phase space flatly has not really been tested. [De Pablo]

- Event-chain Monte Carlo (previous talk) has been used a little bit: gain by a factor ≈ 40? [Krauth, Isobe]

- Swap Monte Carlo: with proba p, ordinary translational move. With proba $(1-p)$, pick up two particles and attempt to swap their identities. [Grigera & Parisi, PRE '02] A factor ≈ 180 [Verrocchio] and crystallisation [Reichman].

Swap MC provides giant speedup





[Ninarello, Berthier, Coslovich, PRX '17]

- Swap Monte Carlo algorithm speeds up equilibration: at least $\times 10^{10}$ in $d = 3$, $\times 10^{40}$ in $d = 2$ (i.e., older than the age of the Universe).

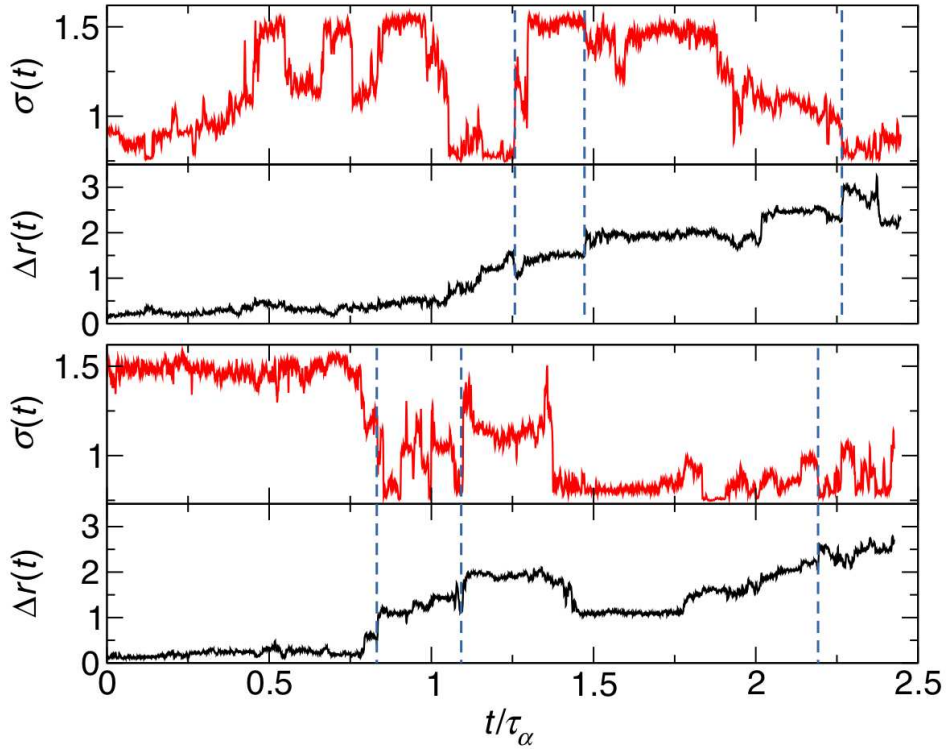
Why does it work?

- If dynamics is highly cooperative, a local algorithm should not work (think of Ising model and cluster algorithms).

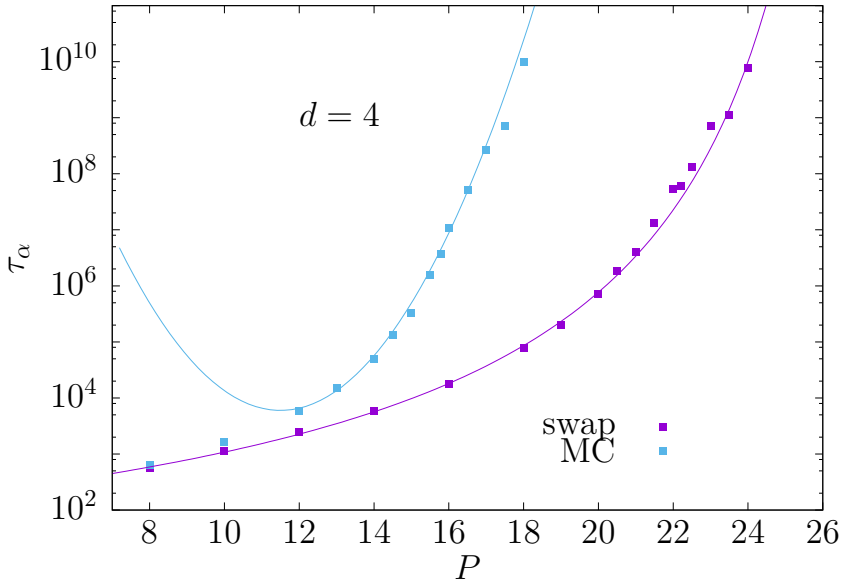
- Efficiency of swap algorithm is theoretically unreasonable, thus, unexpected. This has led to interesting debates about nature of glassy dynamics.

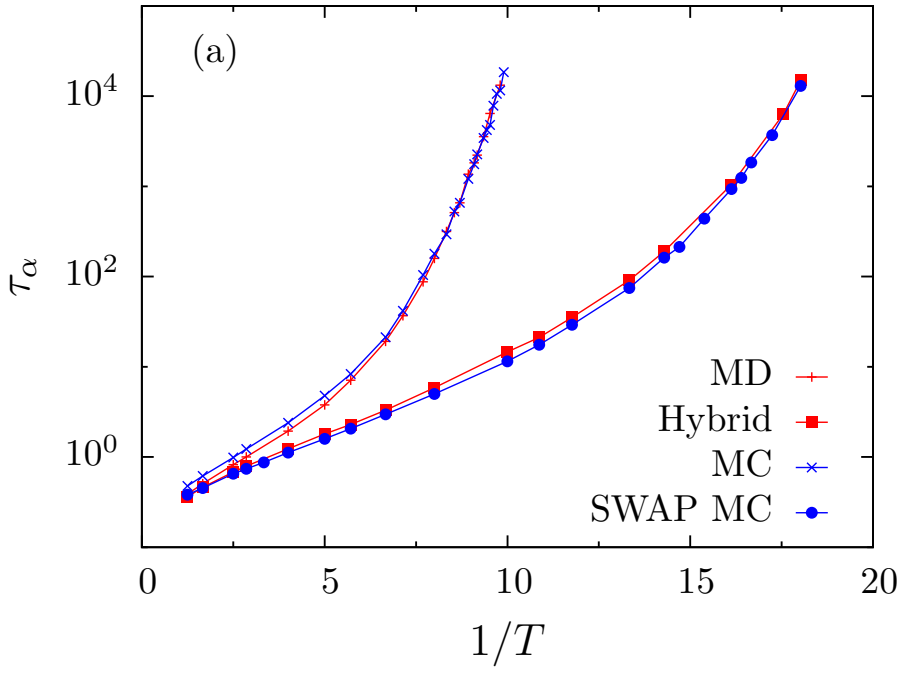
- Physics: diffusion in diameter space couples to particle diffusion in position space. Particles have “one more degree of freedom”.

- Can one improve the swap moves further?



Further developments



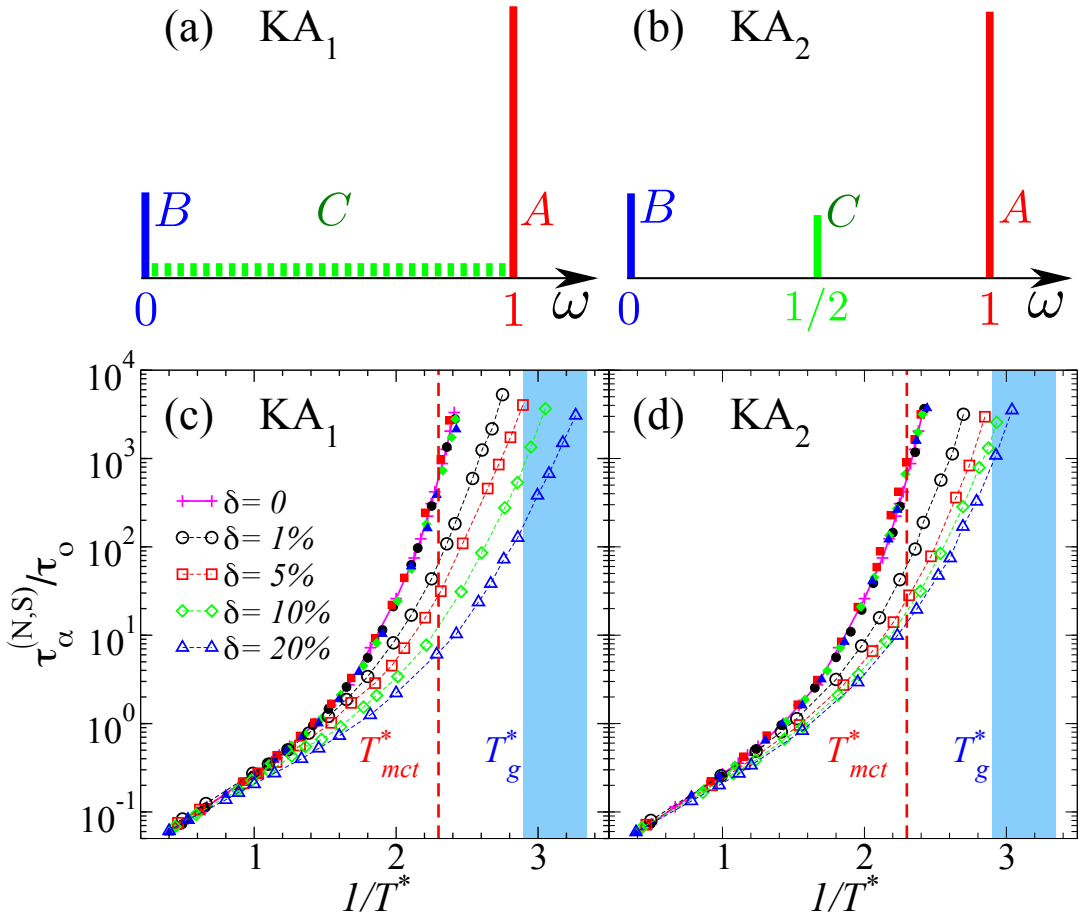


- Swap Monte Carlo is efficient in other dimensions, $d = 2 \cdots 8$.
[Kundu *et al.*, PRE'19]

- Hybrid MD/MC simulations as efficient as swap MC dynamics, now implemented in LAMMPS. [Berthier *et al.*, JSTAT'19]

- We developed a fully continuous time coupled dynamics for positions and diameters: MD and MC agree.

More complicated glasses



[Parmar, Ozawa, Berthier, PRL '20]

- Binary Kob-Andersen model for metallic glasses: unswappable.
- Idea: add a small amount of an intermediate specie to 'tunnel' between species.
- Speed up of 10^2 (1%) to 10^7 (20%). A 4-component model with 10^9.

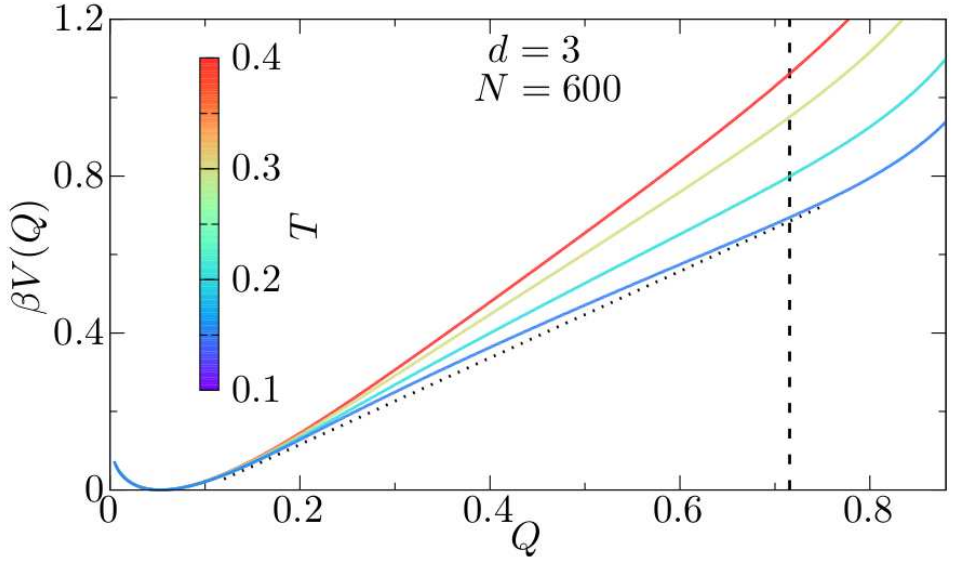
- These are good numerical representations of metallic glasses, which are novel materials. Can one do swap for polymer glasses? Molecules?

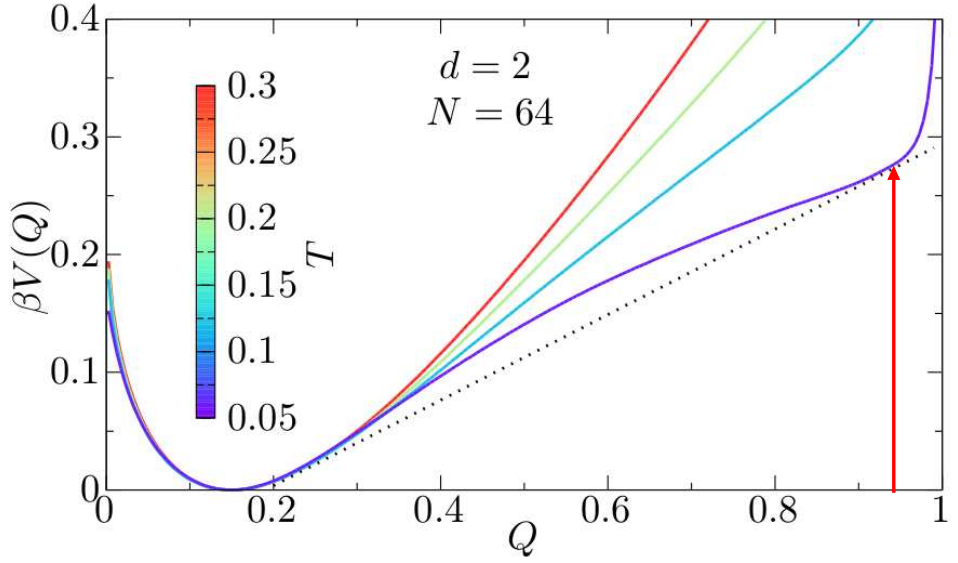
Monte Carlo simulations of the thermodynamics of glasses

Landau free energy, $d < \infty$

• Measurement of $V(Q) = -\frac{k_B T}{N} \overline{\log P(Q[\mathbf{r}, \mathbf{r}_{\rm ref}])}$ requires arsenal of computational tools. [Berthier, PRE '13]

• Biased simulations to access unlikely fluctuations of the overlap Q (umbrella sampling). Equilibration difficult (replica exchange, swap), disorder average required. These are heavy, but doable, simulations.

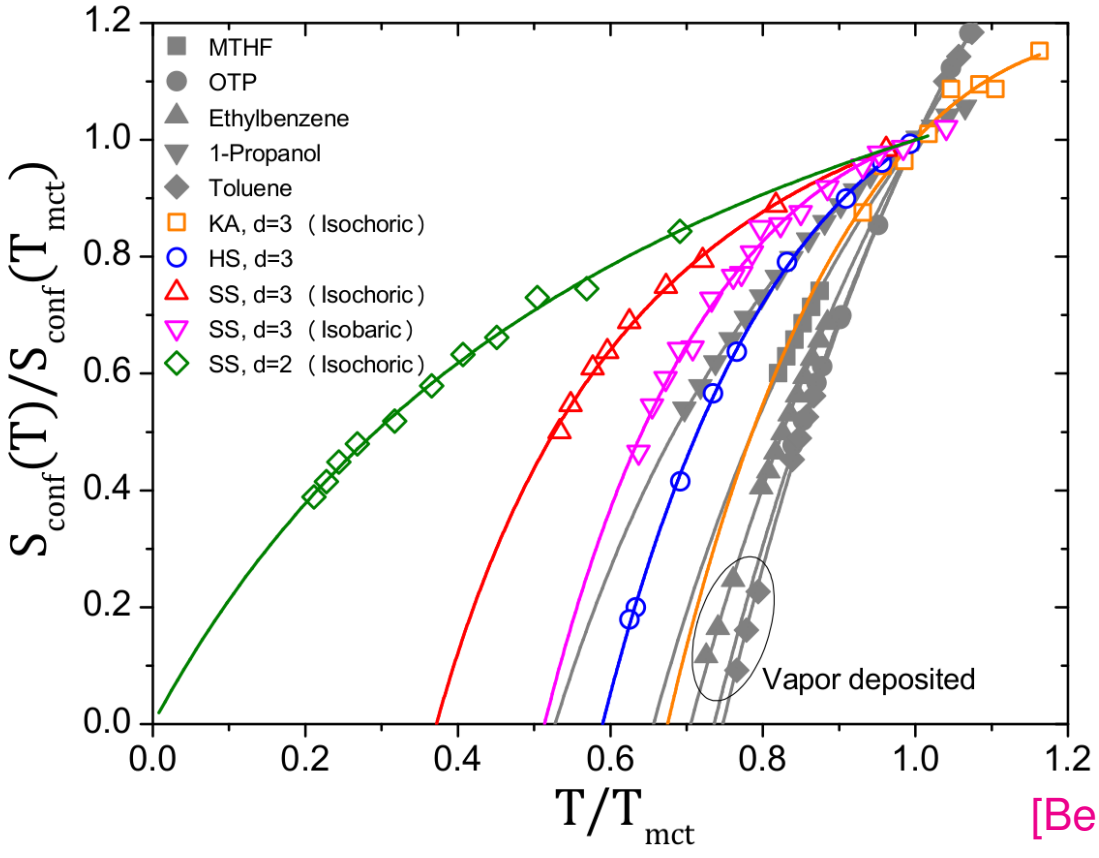




• Direct signature of incipient first-order phase transition directly observed in equilibrium conditions.

Kauzmann revisited: $S_{\rm conf}$

- $S_{\rm conf}$ as equilibrium free energy difference between liquid and glass.



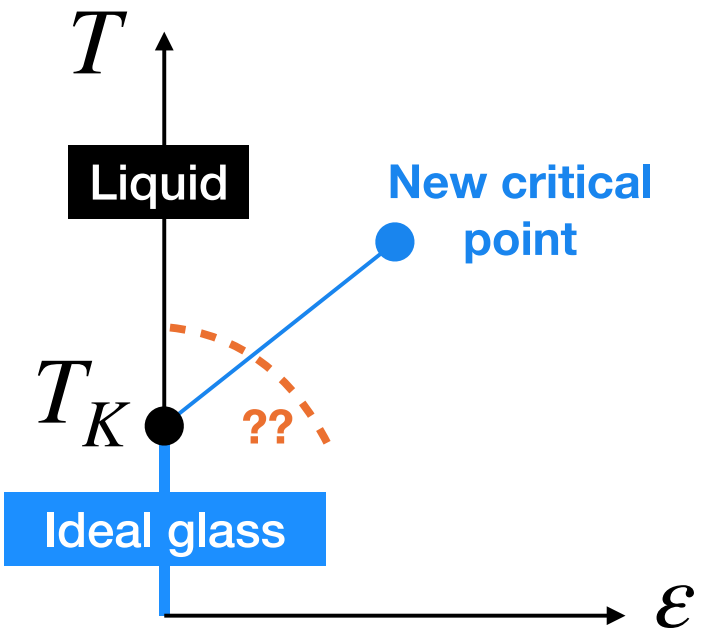
[Berthier *et al.*, JCP '19]

- Simulations outperform conventional experiments and confirm the approach to a phase transition at $T_K > 0$; $d = 2$ seems different with $T_K \simeq 0$.

More first-order transitions

- Change variable from Q to conjugate field ϵ: $F(\epsilon) = V(Q) - \epsilon Q$.

- Physically, ϵ is an attractive random field coupling the liquid to a quenched reference configuration favoring large Q. (Difficult to think of an experimental epsilon-meter.)

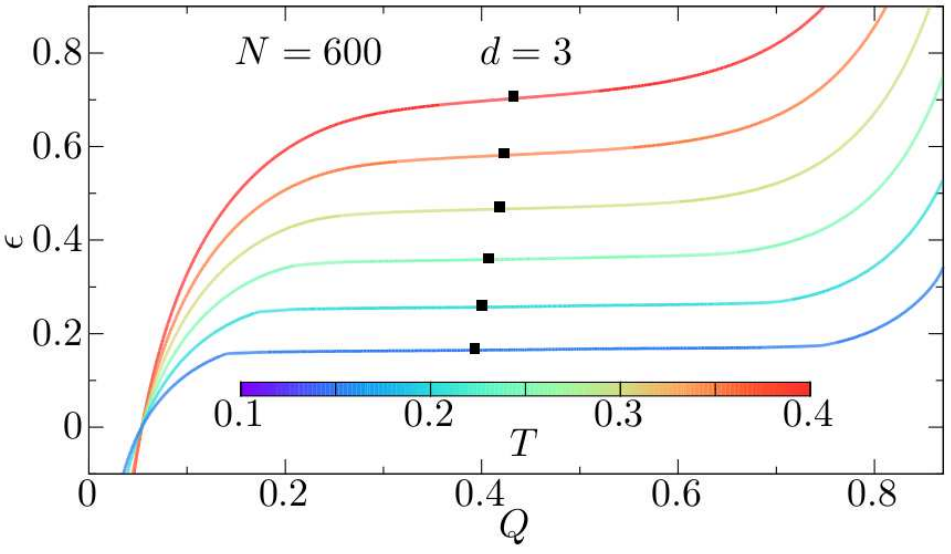


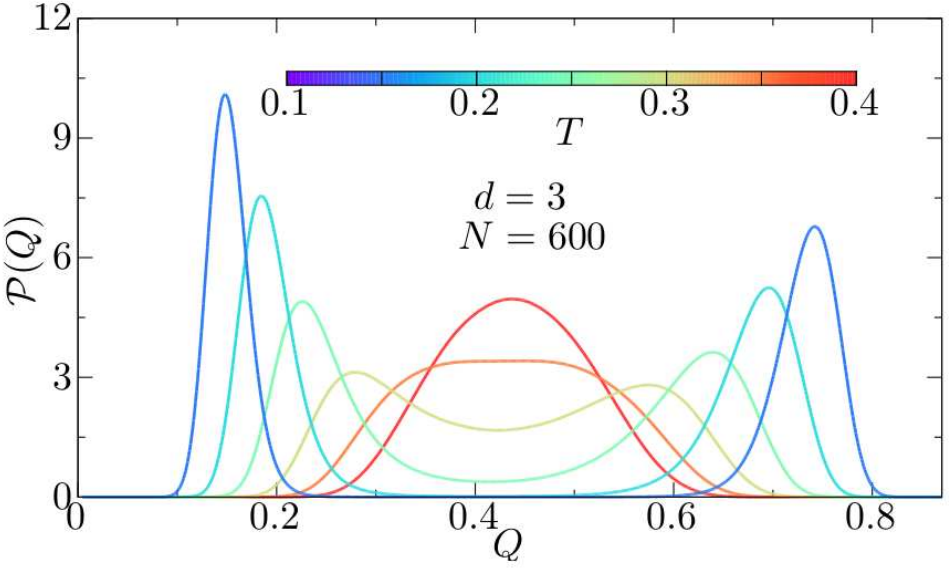
- Competition between entropy (exploring configuration space) and energy (staying close to reference) yields a first-order phase transition at $\epsilon^* \simeq V_{\rm liq} - V_{\rm glass} \simeq TS_{\rm conf}$.

- Field theoretical treatments predict RFIM universality class ($d_l = 2$) for critical end point (T_K more difficult).

[Franz & Parisi '13, Biroli *et al.* '14]

Isotherms and overlap fluctuations



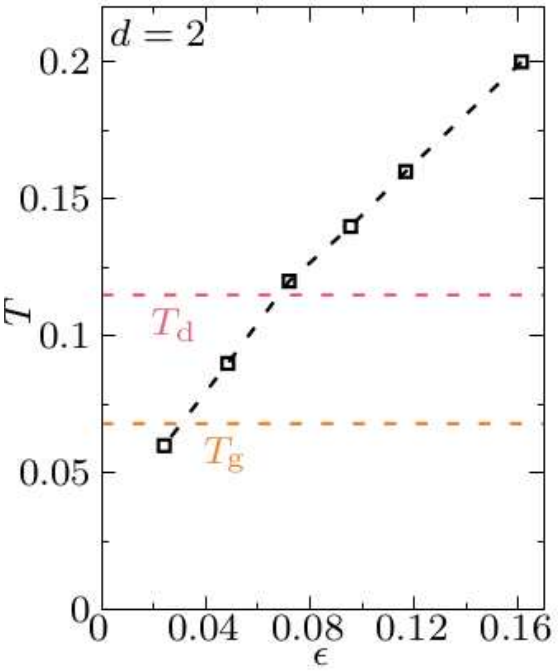


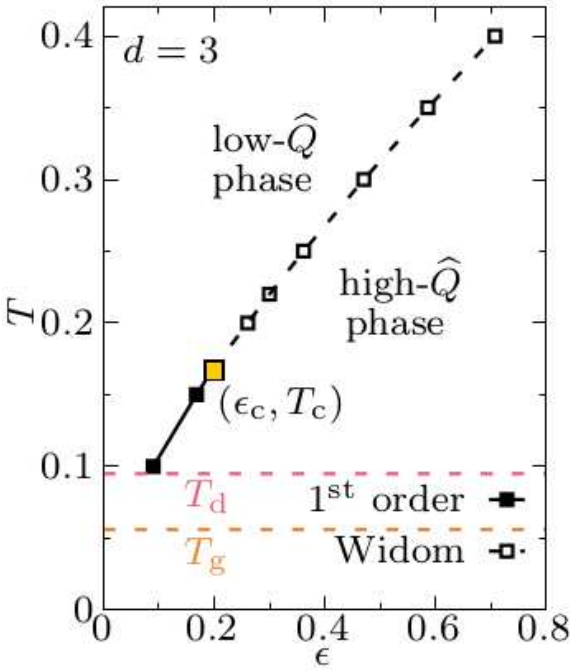
- Isotherms develop an inflection point becoming flat at low T.

- Overlap fluctuations at coexistence become bimodal, and reveal a line of maximal fluctuations (Widom line).

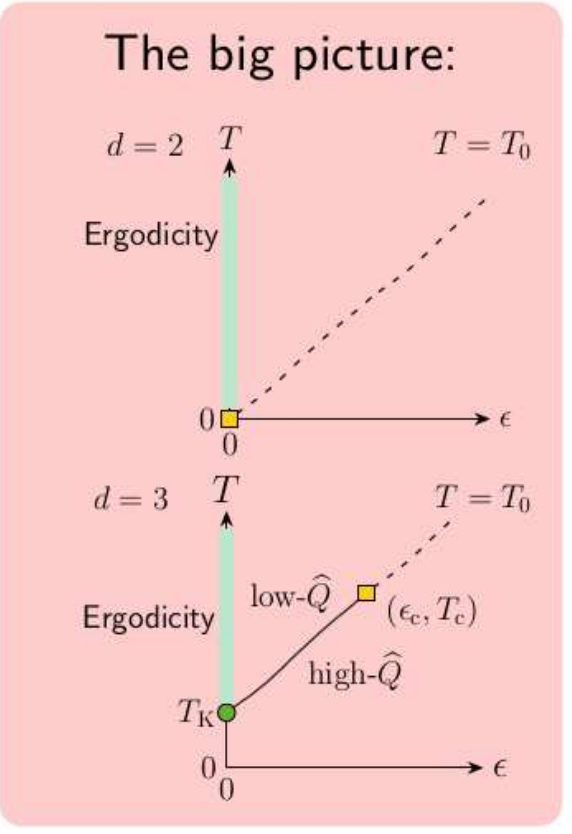
- Compatible with predicted macroscopic phase coexistence and phase transition. Thermodynamic limit studied using FSS analysis.

The big picture





[Guiselin *et al.*, '19-'21]



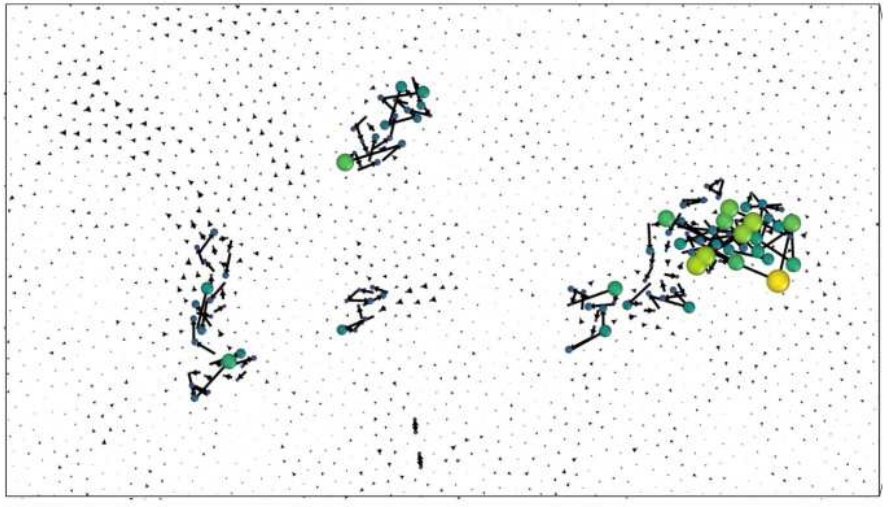
- Measured phase diagram in $d = 2$ reveals Widom line, (with $T_K = 0$?).

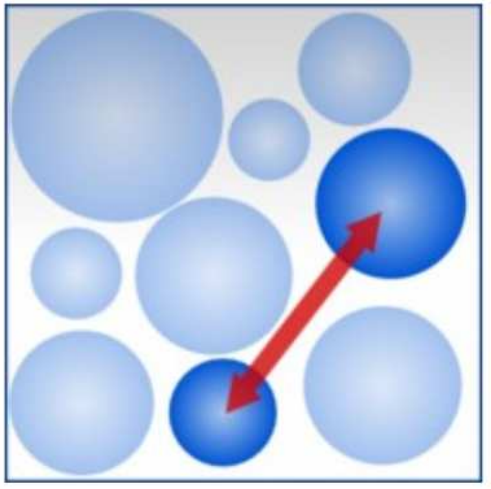
- Measured phase diagram in $d = 3$ reveals RFIM critical point (with $T_K > 0$?).

Perspective: Dynamics near T_g

- Swap Monte Carlo algorithm rapidly equilibrates configurations at any T: Useful to study equilibrium (thermodynamic) properties of glassy liquids.

- "Long" multi-CPU simulations can run up to 10^{10} steps, i.e. about 50 ms.





- Can we learn from the system itself the correct collective moves to be implemented in a Monte Carlo algorithm?