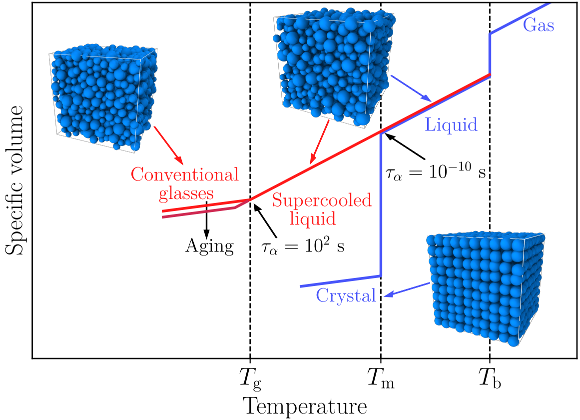
Demystifying the overlap order parameter in glass-forming liquids

Benjamin GUISELIN

The phenomenology of the glass transition

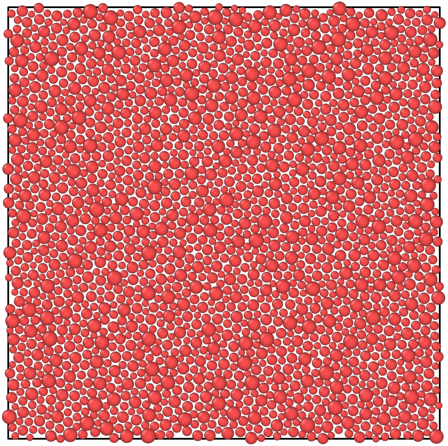
- Dramatic slowing down of the microscopic dynamics of a liquid upon cooling.
- The conventional glass is an out-of-equilibrium system.

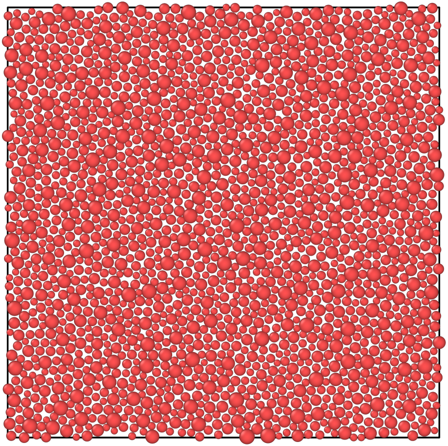


[Guiselin, Tarjus, Berthier (2022)]

Distinguish a glass from a liquid with naked eyes?

Try to guess which one is a glass sample.





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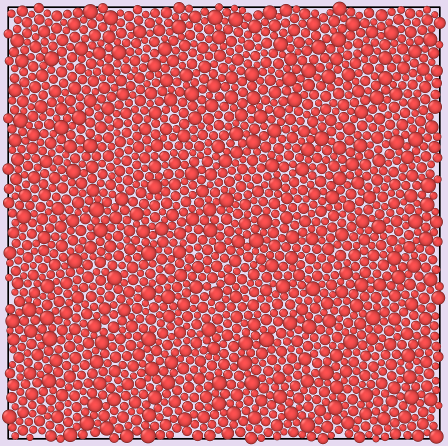
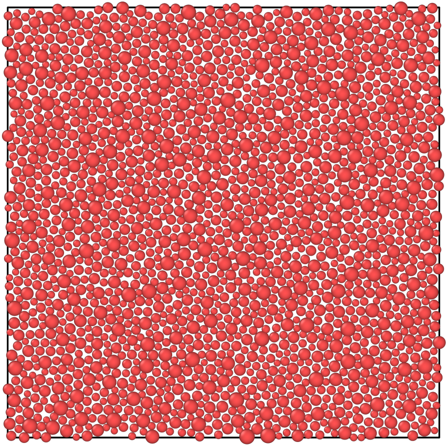
The answer is hard to tell with naked eyes.



$\tau_\alpha \simeq 3.10^{18}$ years $\gg$ Age of the Universe.



$\tau_\alpha \simeq 3$ μs.

Distinguish a glass from a liquid with naked eyes?

- Very weak structural changes while the dynamics varies a lot.

- The density field $\rho(\boldsymbol{x})$ and its fluctuations [*e.g.*, $g(r)$] are boring spectators of the glass transition.

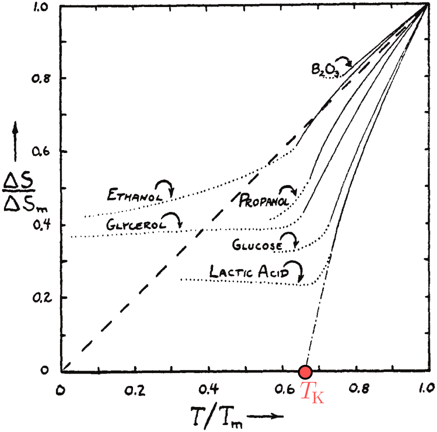
Is the glass transition a purely dynamic phenomenon or is it somehow related to structural/thermodynamic changes?

The Kauzmann entropy crisis (1948)

- Kauzmann measured the excess entropy in the supercooled regime:

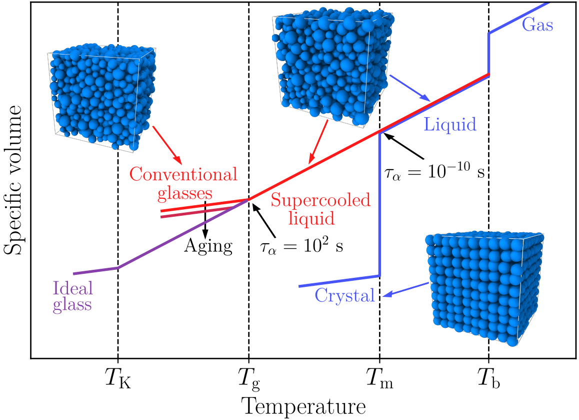
$$\Delta S(T) = S_{\mathrm{liq}}(T) - S_{\mathrm{xtal}}(T) \simeq S_{\mathrm{liq}}(T) - S_{\mathrm{vib}}(T) \simeq S_{\mathrm{conf}}(T).$$

- ΔS quantifies the number of independent density profiles in the liquid state.



[Kauzmann (1948)]

The ideal glass state



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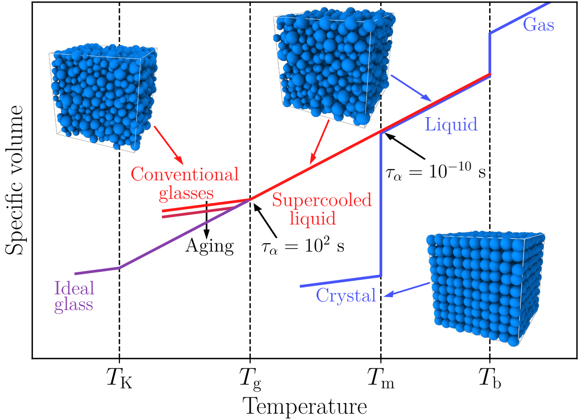

- Experimental data are consistent with an equilibrium phase transition between the liquid phase and the ideal glass phase at the Kauzmann temperature $T_K < T_g$.

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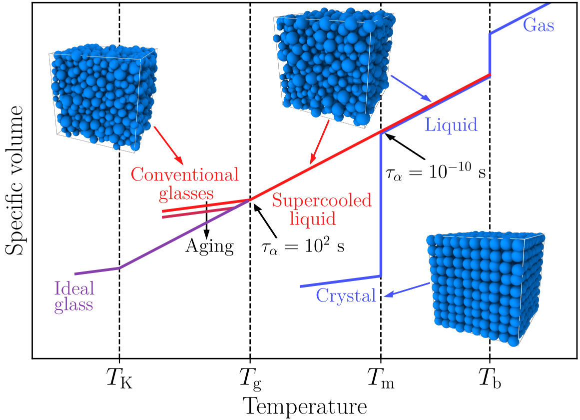

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What are the order parameter, the ordering field and the Landau free energy of this putative phase transition?

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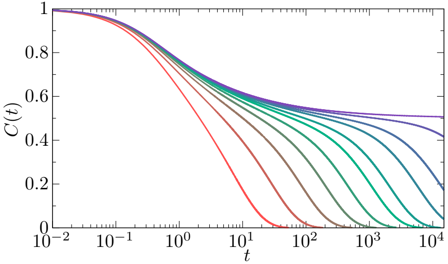
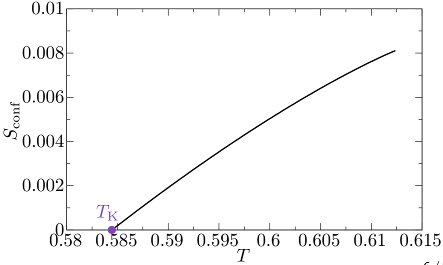
- Everything can be computed exactly: the statics [Crisanti, Sommers (1992)] and the dynamics [Crisanti, Horner, Sommers (1993)].





Reminders of phase transitions in mean-field: the Curie-Weiss model

- The Curie-Weiss model is the mean-field (long-range) formulation of the Ising model:

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- Landau free energy = large deviation rate function of the order parameter probability distribution $\mathcal{P}(M)$.

$$F(M) = -\frac{1}{N\beta} \ln \mathcal{P}(M) \quad \Longrightarrow \quad \mathcal{P}(M) \propto e^{-N\beta F(M)}.$$

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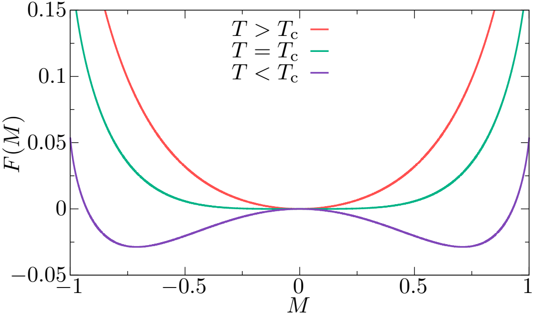
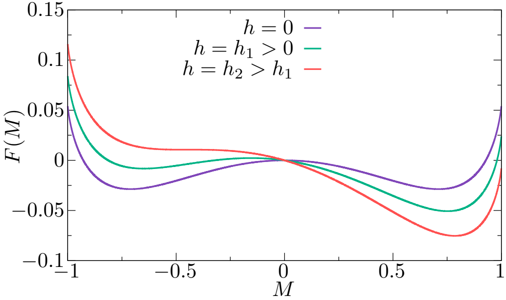


Reminders of phase transitions in mean-field: the Curie-Weiss model

- Couple the order parameter to an external field.

$$\begin{cases} \mathcal{H}(\mathcal{C}) \to \mathcal{H}(\mathcal{C}) - Nh\mathcal{M}(\mathcal{C}) \\ F(M) \to F(M) - hM \\ \mathcal{P}(M) \to \mathcal{P}(M)\, e^{N\beta h M} \end{cases} .$$



- Ordering field: external field h which breaks the spontaneous symmetry breaking below T_c.

The overlap order parameter

- $S_{\mathrm{conf}}(T) \underset{T \to T_{\mathrm{K}}}{\longrightarrow} 0$: the number of states the system can visit under equilibrium conditions decreases.
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$$\mathcal{Q}(\mathcal{C}, \mathcal{C}_0) = \frac{1}{N} \sum_{i=1}^{N} S_i S_i^{(0)}.$$

(spherical p-spin model)

- The overlap involves two copies/replicas of the same system.

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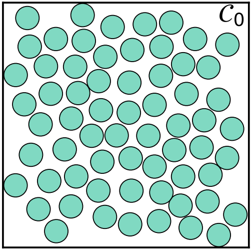

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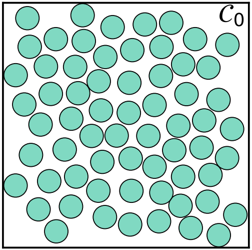

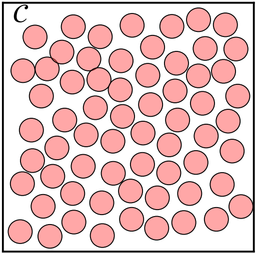

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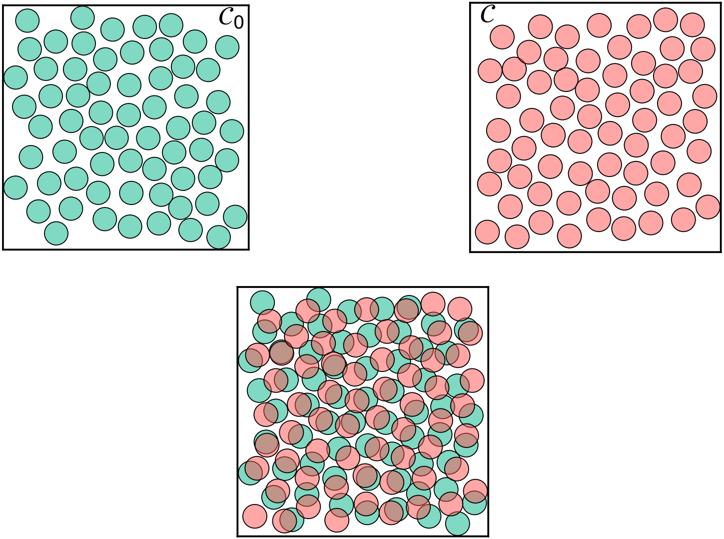
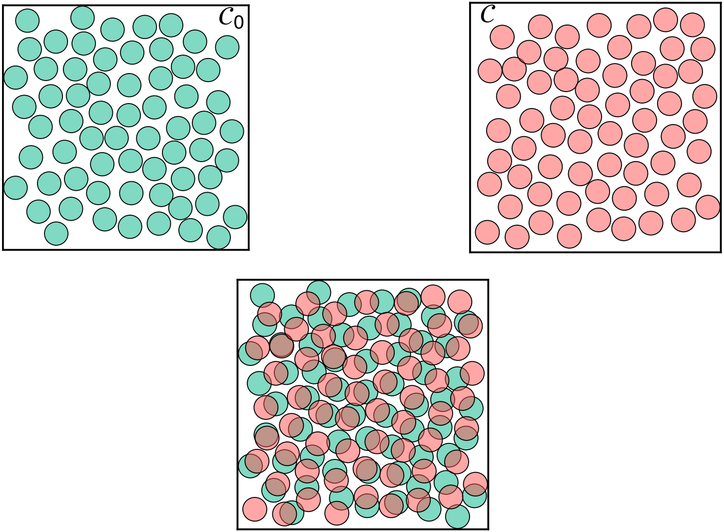


$\mathcal{Q}(\mathcal{C}, \mathcal{C}_0)$



- For $T > T_{\mathrm{K}}$, exponentially large number of density profiles (liquid phase): $\langle \mathcal{Q}(\mathcal{C}, \mathcal{C}_0) \rangle \simeq 0$.

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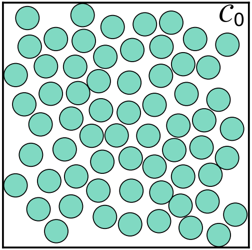

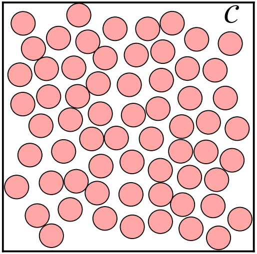

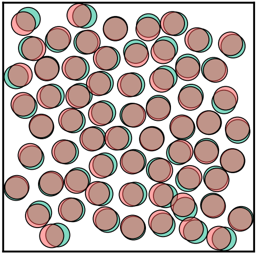

- For $T < T_{\mathrm{K}}$, small number of density profiles (ideal glass phase): finite probability to have $\mathcal{Q}(\mathcal{C}, \mathcal{C}_0) \simeq 1$.

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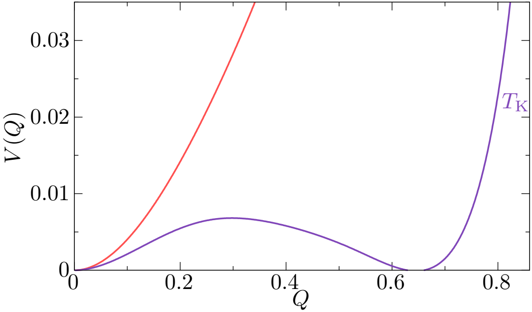

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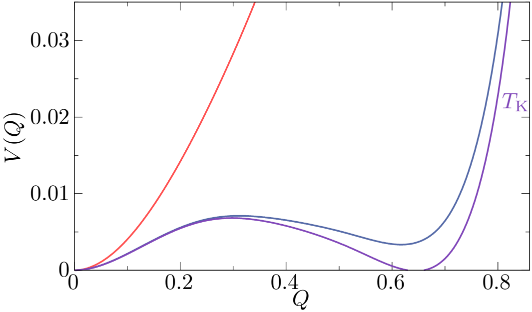

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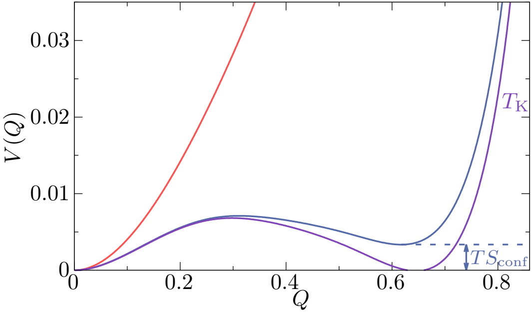

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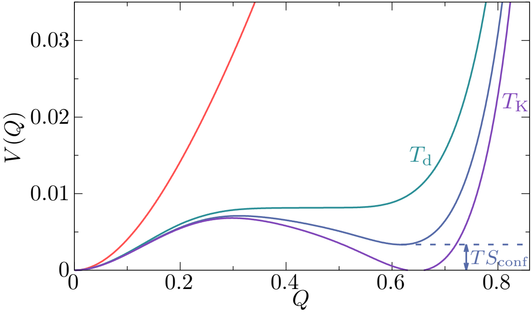

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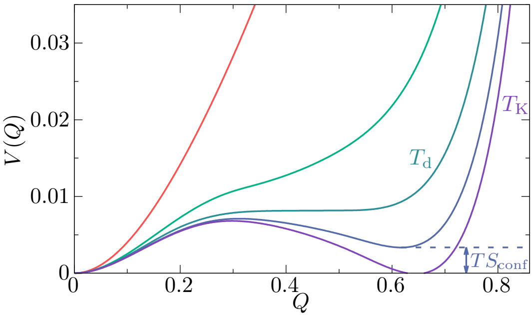

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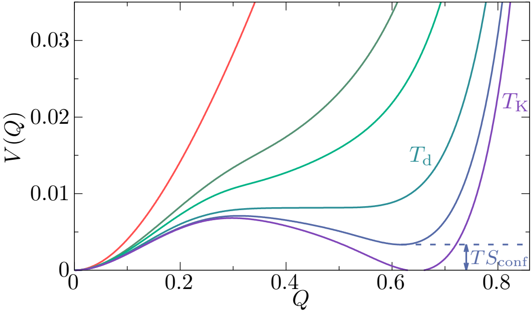

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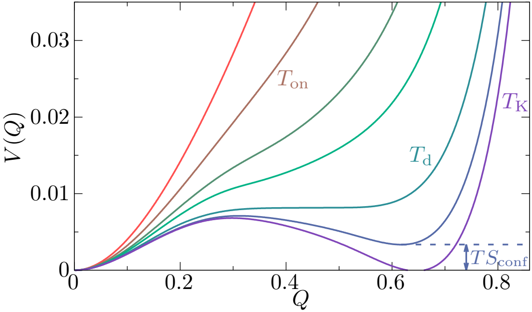

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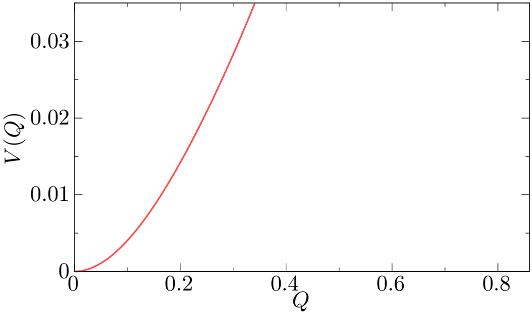

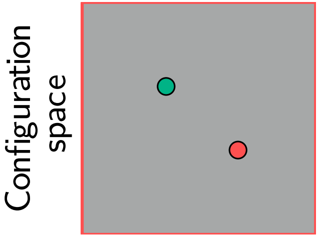

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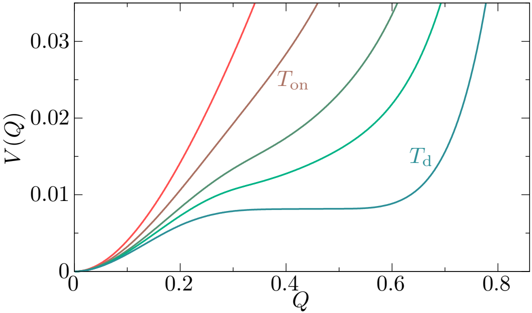

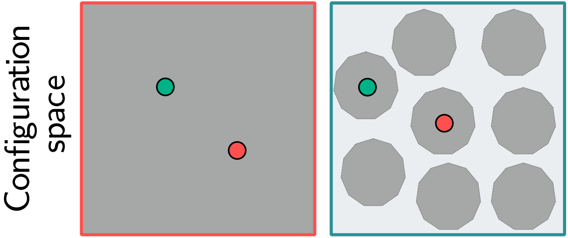

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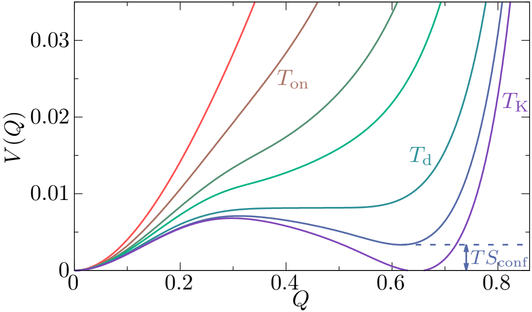

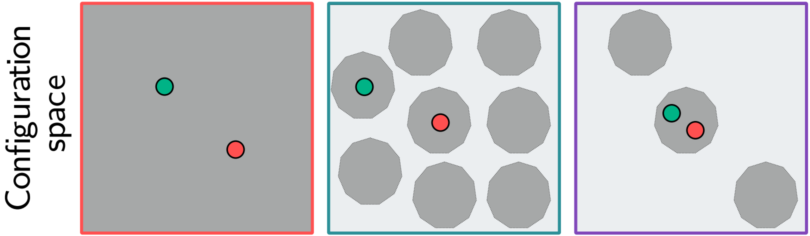

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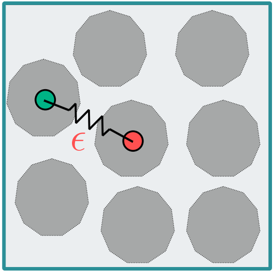

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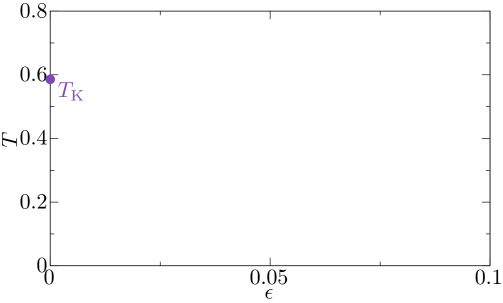

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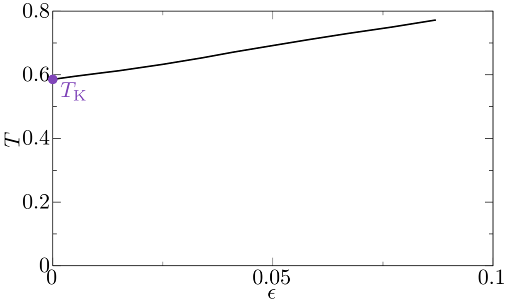

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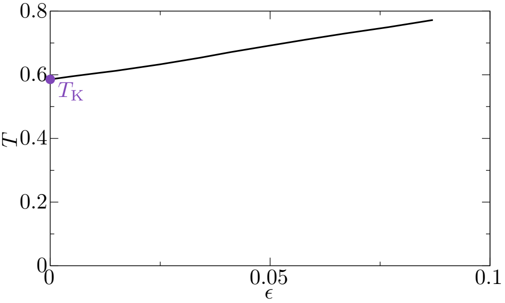

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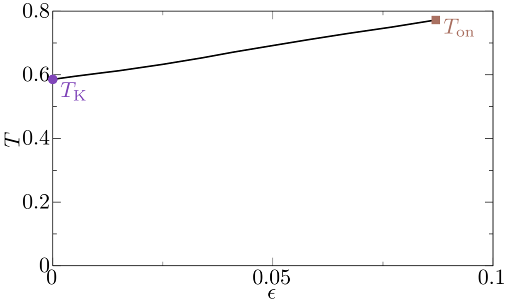

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The overlap for supercooled liquids in finite dimensions

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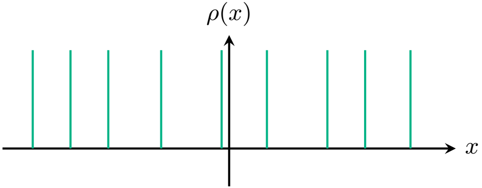
$$\rho(\boldsymbol{x}) = \sum_{i=1}^{N} \delta(\boldsymbol{x} - \boldsymbol{r}_i).$$



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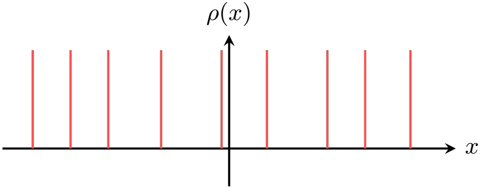

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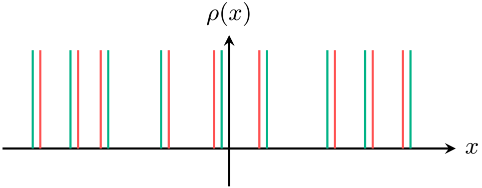

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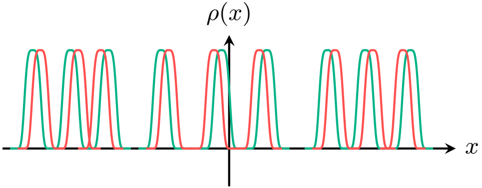

$$\mathcal{Q}(\mathcal{C}, \mathcal{C}_0) \simeq 1.$$

- The definition of the overlap requires coarse-graining on a typical length scale a:

$$\mathcal{Q}(\mathcal{C}, \mathcal{C}_0) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} w \left(\frac{|\boldsymbol{r}_i - \boldsymbol{r}_j^{(0)}|}{a} \right).$$

- Typically, a is a fraction of particle diameter to account for thermal vibrations (about 0.2-0.3) [Guiselin, Tarjus, Berthier (2020)].

- The function $w(x)$ decays on a typical scale of order 1 [*e.g.*, $w(x) = e^{-x^4 \ln(2)}$].

The Franz-Parisi potential for supercooled liquids in finite dimensions

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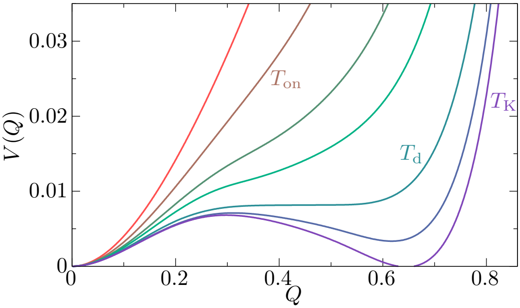

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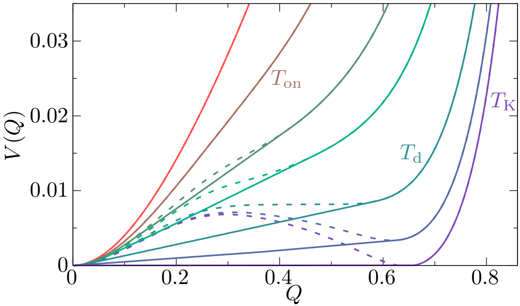

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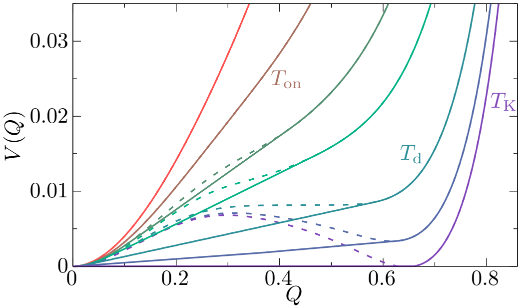

Putative results in finite dimensions.

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- One can still define a proxy for the configurational entropy $\epsilon^*(T) = TS_{\rm conf}(T)$.

Measuring the Franz-Parisi potential in computer simulations

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- Bias the simulation to visit very unlikely overlap fluctuations in a controlled way to recover the unbiased overlap probability distribution.

Measuring the Franz-Parisi potential via Umbrella Sampling

- Different ways of biasing the simulation: umbrella sampling [Berthier (2013), Parisi, Seoane (2014), Guiselin, Tarjus, Berthier (2022)], Wang-Landau [Nishikawa, Hukushima (2020)], etc.

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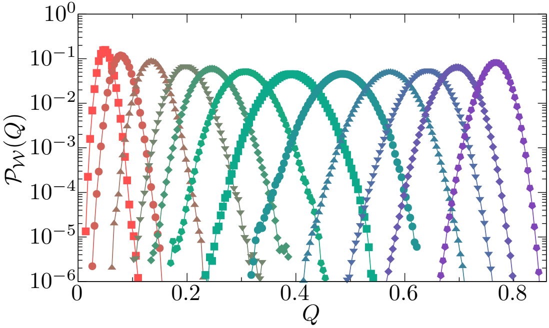

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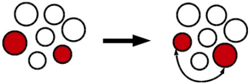

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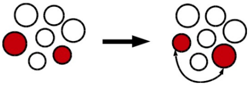

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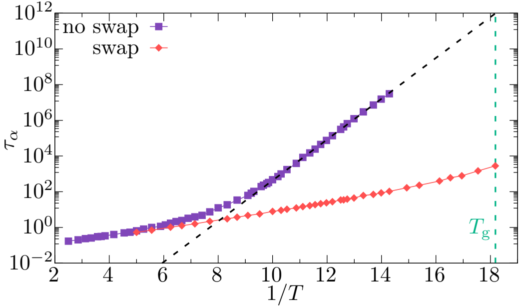

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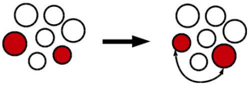

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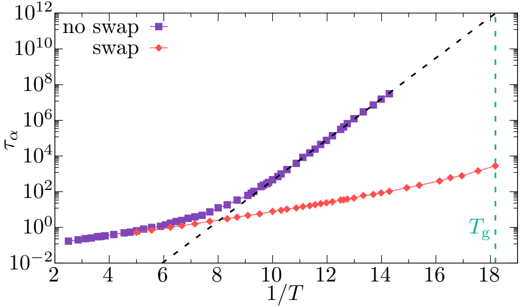

- Parallel tempering: running n simulations in parallel with different biases $\mathcal{W}_i$ (increasing values of Q_0) and exchanging the configurations of neighbouring $\mathcal{W}_i$ respecting detailed balance [Hukushima, Nemoto (1996)].

Combining the biased distributions

- How to reconstruct the unbiased distribution $\mathcal{P}(Q)$?
- Biased Hamiltonian + thermal equilibrium:

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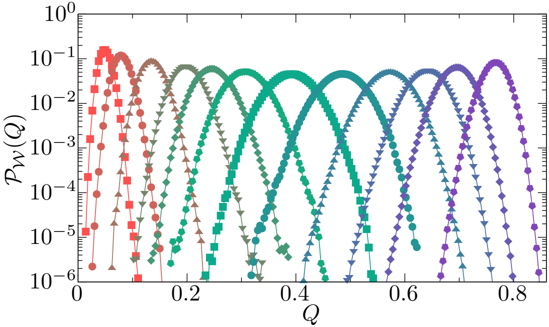

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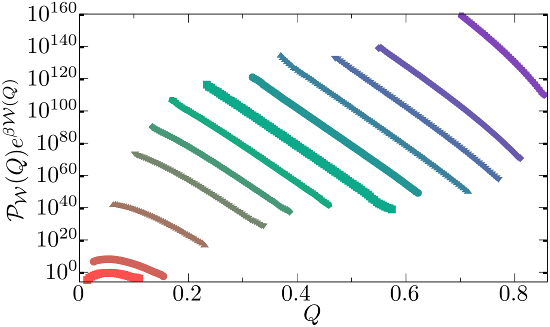

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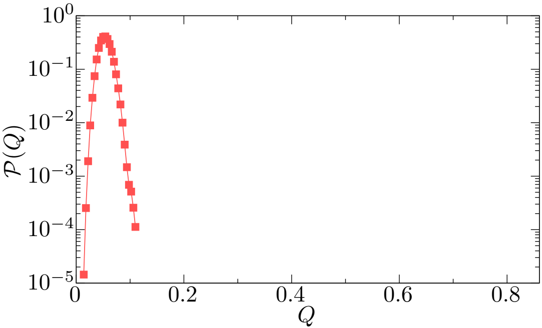

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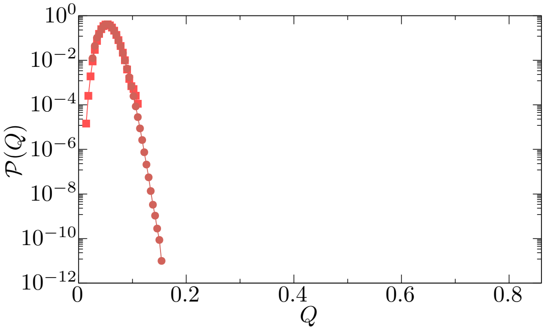

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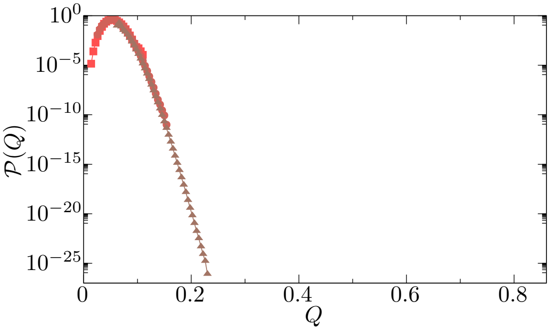

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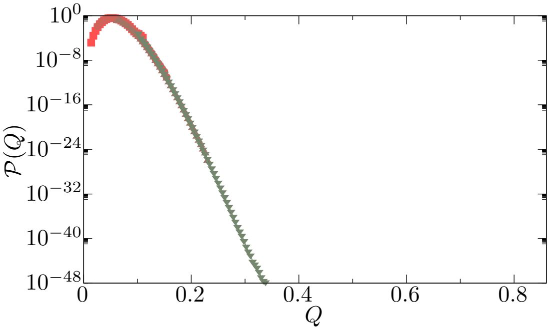

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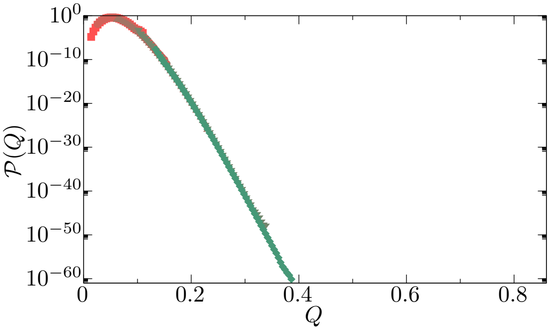

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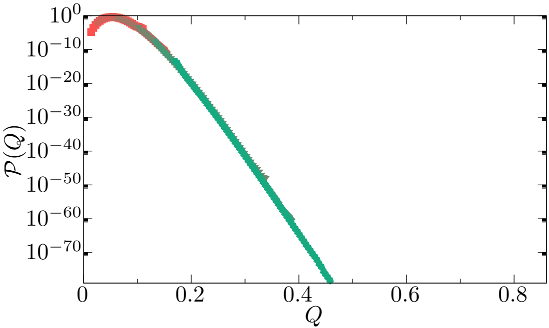

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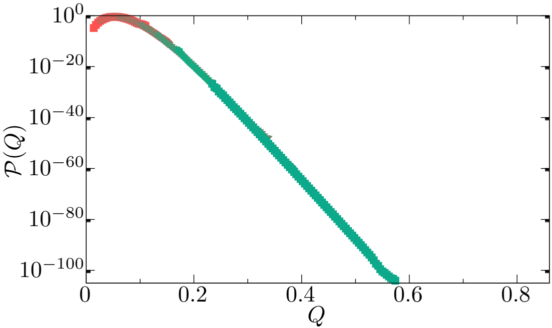

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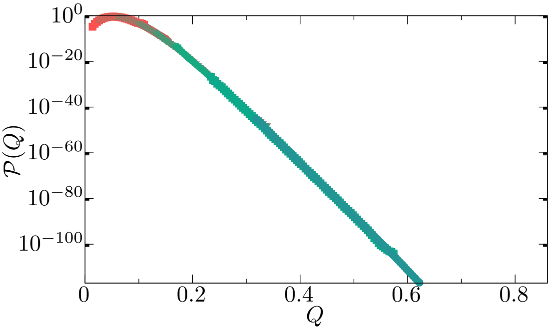

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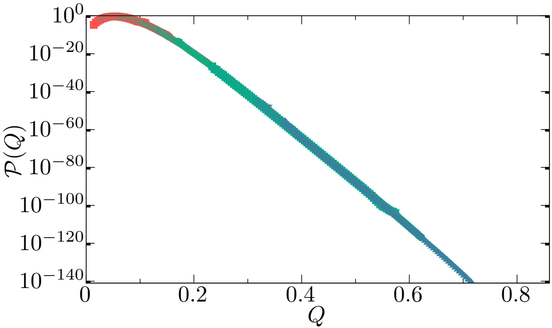

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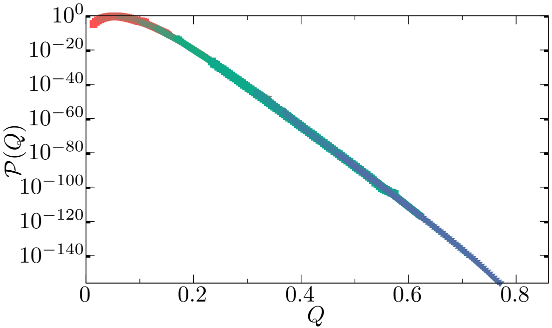

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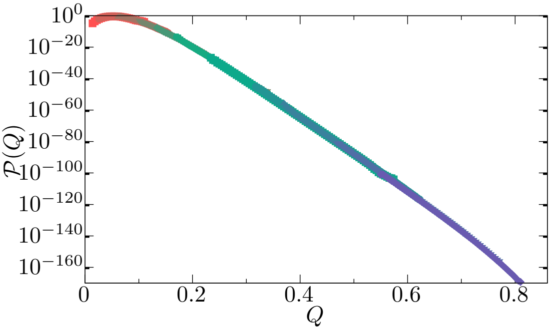

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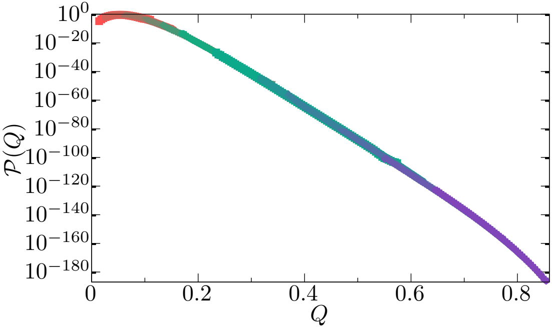

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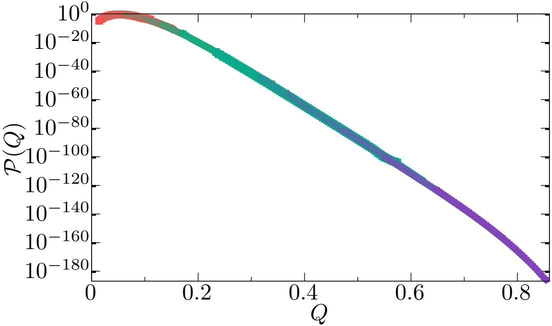
- Reconstruct the probability up to 10^{-180} $\to$ very rare events.



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- Second possibility: use the multiple histogram method [Ferrenberg, Swendsen (1989), Newman, Barkema (1999)].

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- Divide and Conquer strategy.

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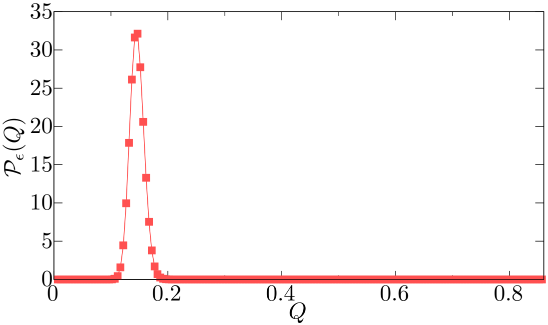

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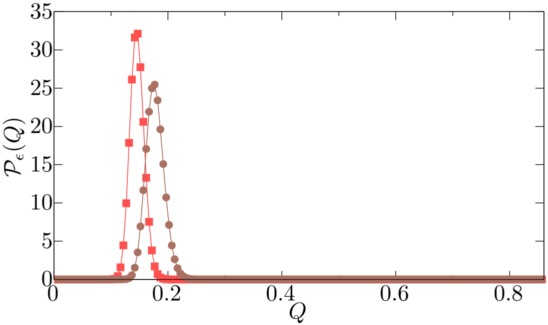

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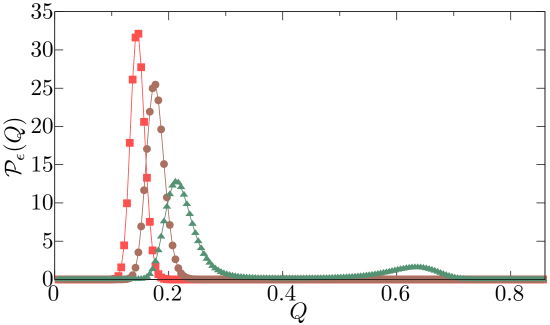

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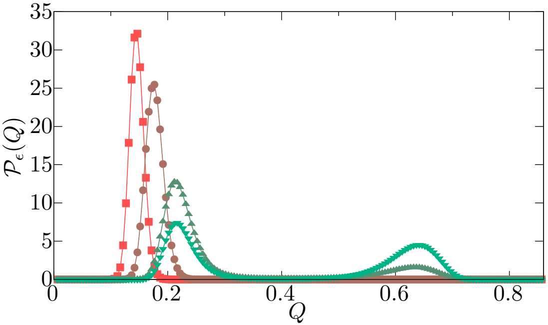

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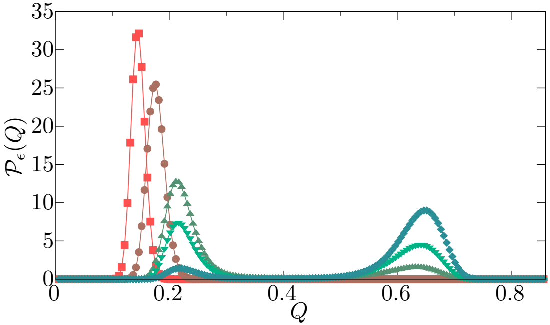

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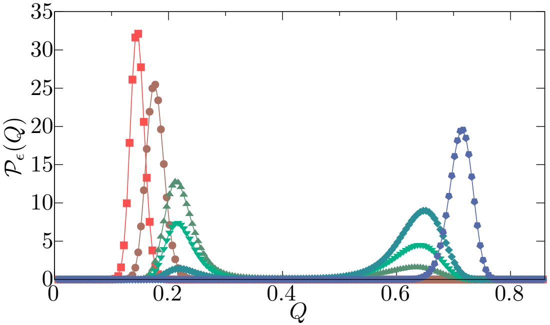

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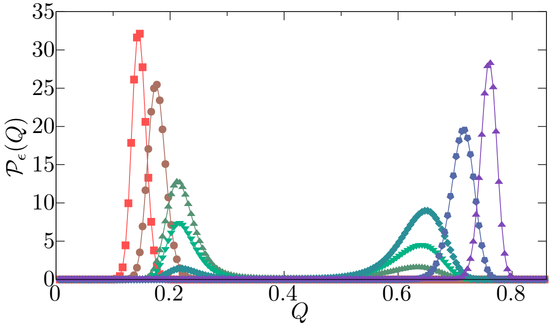
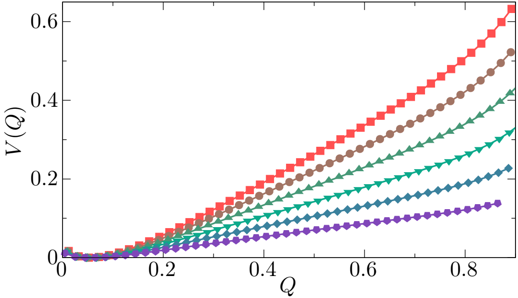


Temperature evolution of $V(Q)$ in finite-dimensional systems

- Eventually, one needs to repeat the entire procedure to average over several reference configurations, and at several temperatures.



[Guiselin, Berthier, Tarjus (2022)]

- Total CPU time:

30 simulations $\times$ 20 reference configurations $\times$ 6 temperatures $\times$ 4 system sizes $\simeq 276$ years for 1 CPU.

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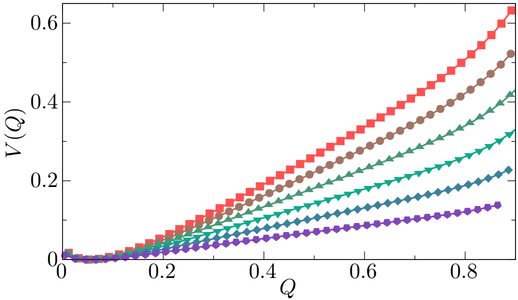

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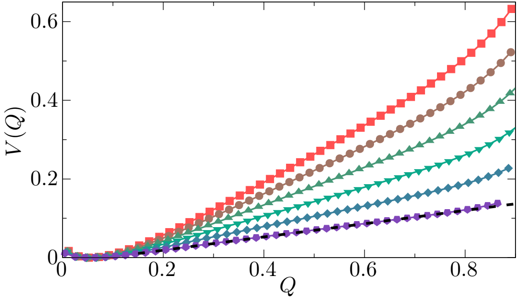

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Consistent with an underlying equilibrium phase transition.

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- In a finite-size system, the correlation length saturates to the linear size L of the system.

- In the vicinity of the critical point, all thermodynamic quantities now depend on L:

$$\chi = \frac{\partial \langle \mathcal{Q} \rangle}{\partial \epsilon} = N\beta \left[\langle \mathcal{Q}^2 \rangle - \langle \mathcal{Q} \rangle^2 \right] \sim L^{2-\eta}.$$

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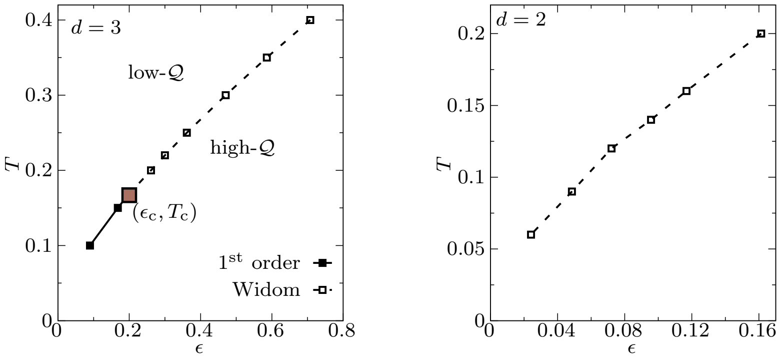
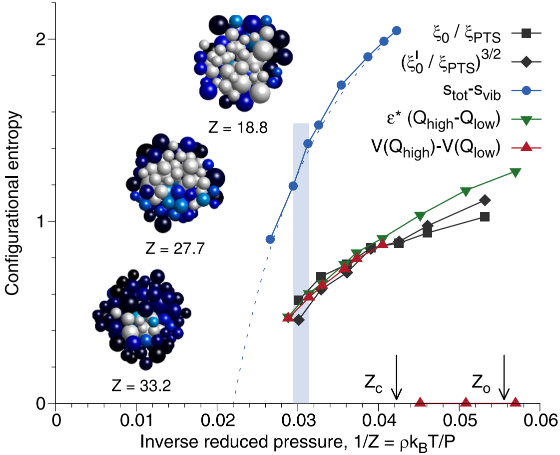


[Guiselin, Berthier, Tarjus (2020), Guiselin, Berthier, Tarjus (2022)]

- Random-Field Ising model criticality (lower critical dimension = 2).

The configurational entropy in finite-dimensional systems



Berthier, Charbonneau, Coslovich, Ninarello, Ozawa, Yaida (2017)

- Simulations data in $3d$ are consistent with a Kauzmann transition at $T_{\rm K} > 0$.

Overlap-related measurements in experiments

- Overlap measurements require to know the location of all microscopic constituants $\rightarrow$ restricted to colloidal glasses.

- One can imagine measuring the (ϕ, ϵ) phase diagram (ϕ: packing fraction) with optical tweezers.

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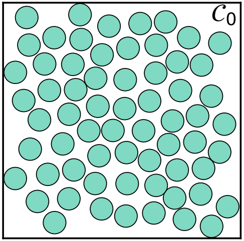

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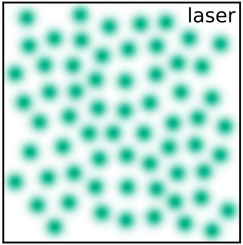

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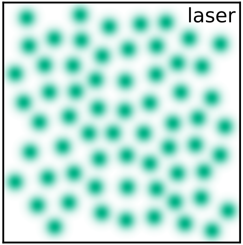

- But low degree of supercooling: the glassy slowing down in colloids is only about 6 orders of magnitude.

The point-to-set length

- Liquid-glass equilibrium phase transition: long-range order emerging at T_{K}.

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- Analogy with ferromagnetism:
  - Imhomogeneous magnetization profile $\mathcal{M}(\mathcal{C}, \boldsymbol{x})$.
  - The order parameter is correlated on a length scale $\xi \underset{T \to T_c^+}{\longrightarrow} +\infty$.
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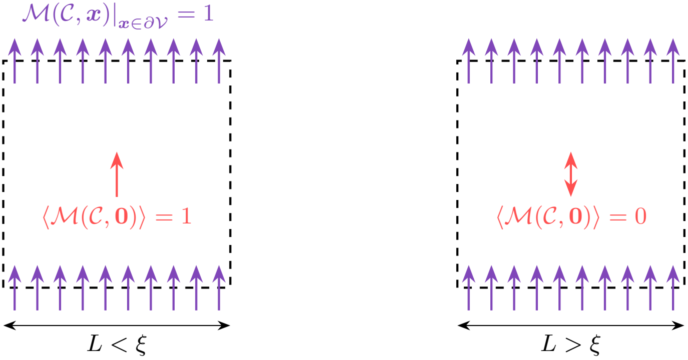

The point-to-set length

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- Definition of the point-to-set length $\xi_{\rm PTS}$:
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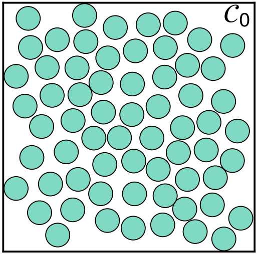

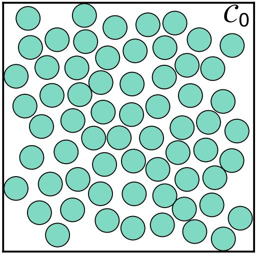

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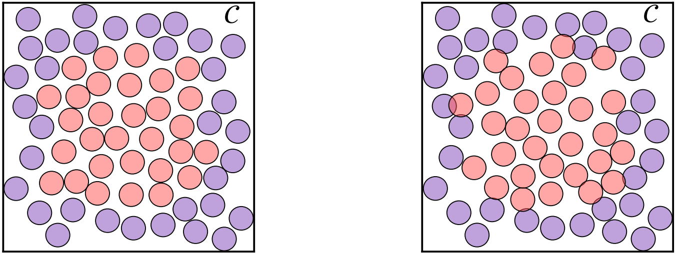

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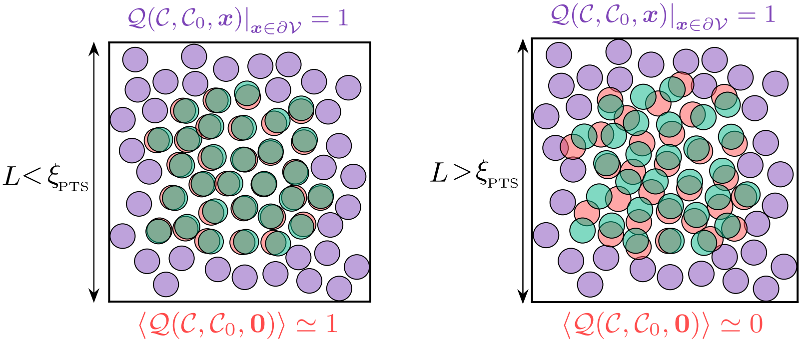

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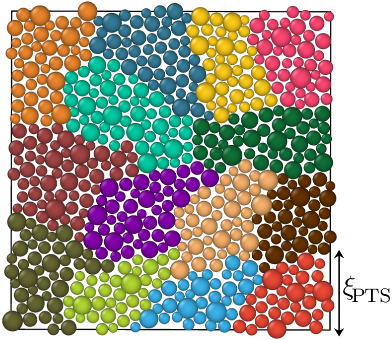
- But still impossible for atomic and molecular glasses.

The mosaic state

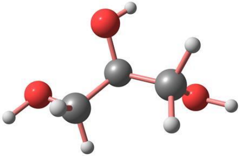
- For timescales $\lesssim \tau_\alpha$, particles are almost frozen $\rightarrow$ self-induced frozen boundaries.
- Supercooled liquids are mosaics of "glassites" of different density profiles of size ξ_{PTS} [Kirkpatrick, Thirumalai, Wolynes (1989)].
- Each glassite relaxes independently on a typical timescale τ_α.



(This is a cartoon!)

Probing the mosaic state in atomic and molecular glasses

- Liquid of anisotropic molecules in the presence of an oscillatory electric field E at an angular frequency $\omega \sim 1/\tau_\alpha$ [Bouchaud, Biroli (2005)].



Molecule of glycerol.

- Each glassite responds collectively with a typical induced dipolar moment $p_{\mathrm{g}} = \mu_{\mathrm{dip}} \left(\xi_{\mathrm{PTS}}/\ell\right)^{d/2}$ (random orientations):

$$\boldsymbol{p}_{\mathbf{g}} = \sum_{i \in \text{glassite}} \boldsymbol{p}_i \Longrightarrow \left\{ \vphantom{\begin{array}{c} a \\ b \\ c \\ d \end{array}} \right. .$$

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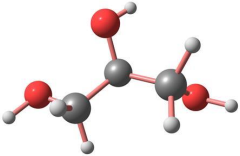

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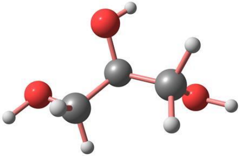

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Probing the mosaic state in atomic and molecular glasses

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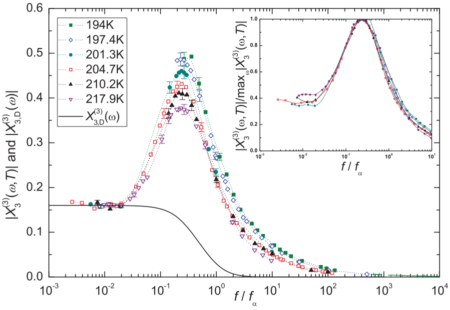
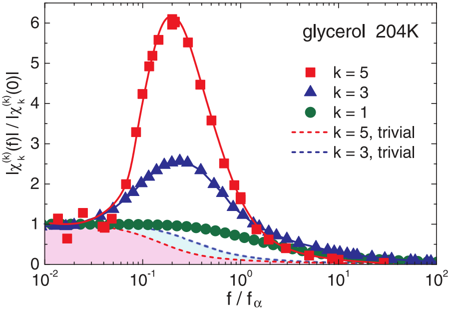
- The linear susceptibility remains finite at $T_{\rm K}$ (fluctuation-dissipation theorem), but non-linear susceptibilities should diverge.

Probing the mosaic state in atomic and molecular glasses



[Brun, Ladieu, L'Hote, Tarzia, Biroli, Bouchaud (2011)]



[Albert, Bauer, Michl, Biroli, Bouchaud, Loidl, Lunkenheimer, Tourbot, Wiertel-Gasquet, Ladieu (2016)]

- Experiments and simulations report a modest increase in ξ_{PTS} by a factor of 2.

Conclusions

- Static overlap fluctuations allow to probe the structure of the configuration space (free energy landscape).
- Well-defined (but not straightforward) strategies to study these fluctuations in simulations and experiments.
- Glass transition: overlap fluctuations reveal an underlying equilibrium phase transition towards an ideal glass phase at T_{K}.
- The overlap is a good static descriptor of the configuration space for disordered complex systems in general (not only glasses).

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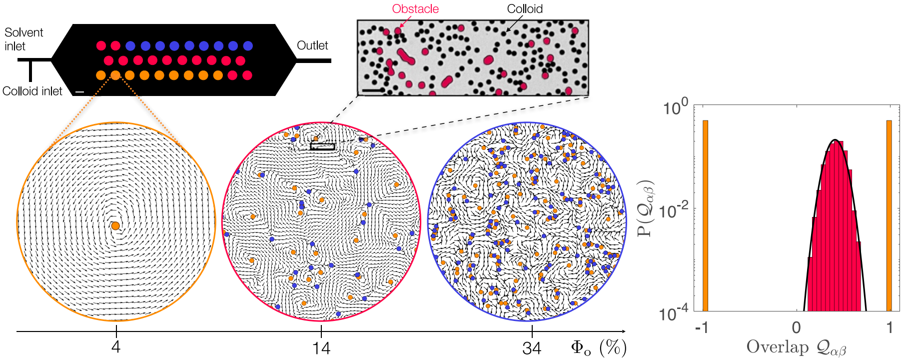

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