Computer Simulations of Glassy Systems with pinned Particles

Walter Kob

Université Montpellier
France

In collaboration with: Misaki Ozawa, Sandalo Roldan-Vargas, Ludovic Berthier, Kunimasa Miyazaki, and Atsushi Ikeda

Cargese
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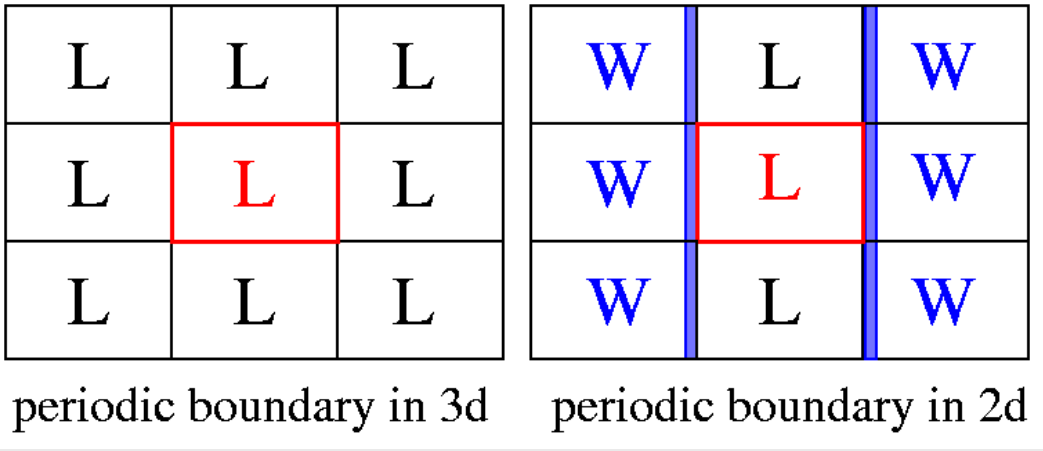
Using Walls to determine Length Scales

Generation of liquid confined by two walls:

- Equilibrate a system of size $L_x=L_y=13.7$ and $L_z=34.2=D$ using periodic boundary conditions
- At t=0 we freeze the particles with $z < 0$ and $z > D$ permanently $\Rightarrow$ wall
- Add a hard core potential at $z = 0$ and $z = D$

$\Rightarrow$ confined liquid of thickness D and dimensions $L_x=L_y$

N.B. liquid is in equilibrium!
Scheidler, W. K., Binder (2004)



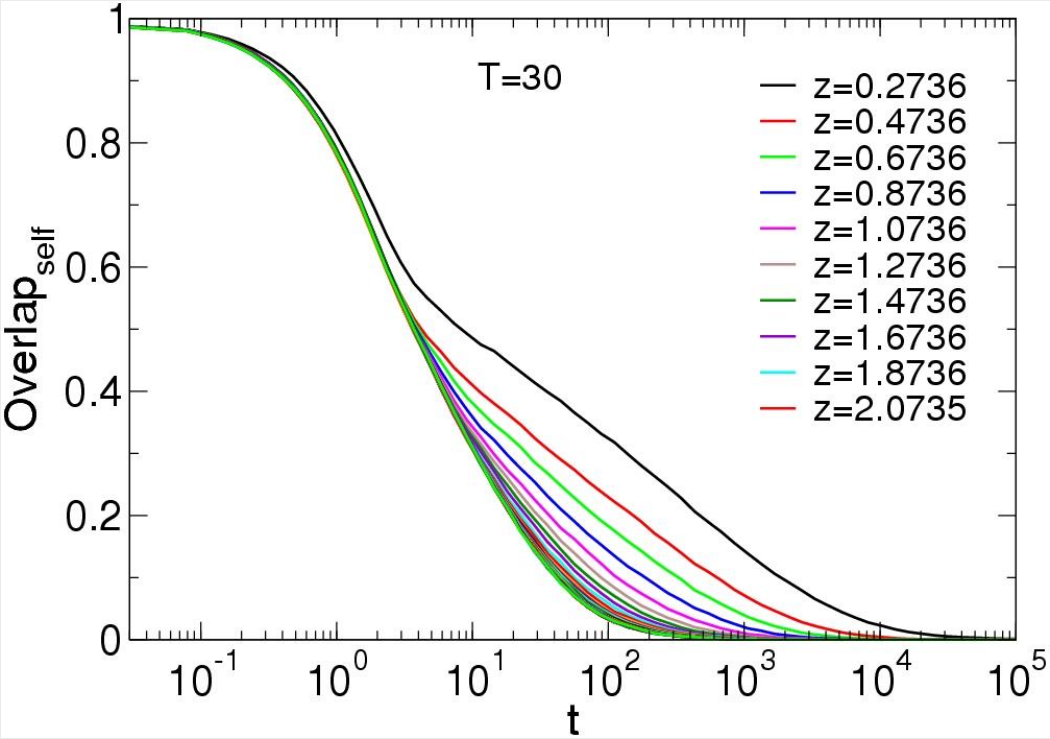
- One simulation at temperature T allows to determine the static and dynamic properties of the liquid for all values of z (=distance from the wall)
- Access to multi-point correlation functions (point to set correlations)

System studied:

- binary mixture of additive elastic spheres: $V(r) = ½ (r-\sigma_{ij})^2$; $\sigma_{11}=1.0$, $\sigma_{22}=1.4$
- N=4320 particles
- up to 830 million time steps
- between 10-30 samples

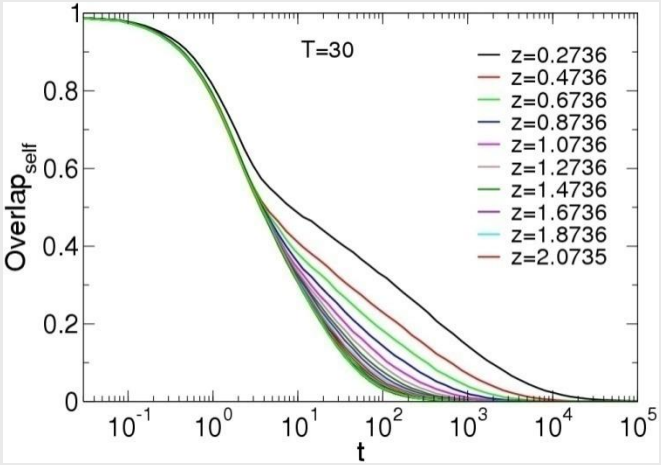
Overlap

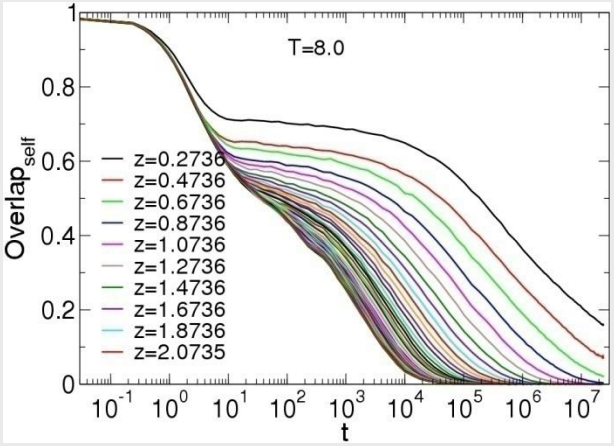
- Divide sample in small cells (0.55σ) and introduce occupation number n_i
- Define $Overlap_{self}(z,t) = m^{-1}\sum_i \langle n_i(t)\, n_i(0)\rangle$ (sum only over cells that have distance z from the wall)

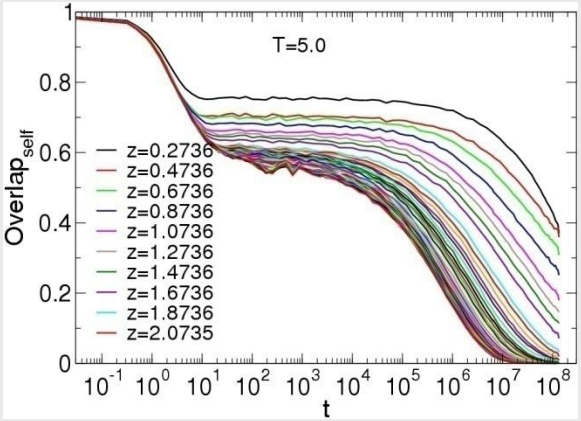


- Overlap has better statistics than intermediate scattering function, but contains (basically) the same information
- Slowing down of the relaxation dynamics with decreasing z
- For large z the function does not depend anymore on z
  $\Rightarrow$ bulk behavior

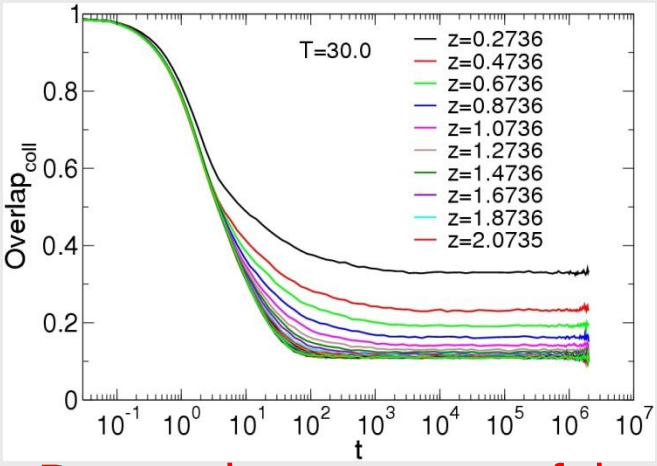
Self and Collective Overlap

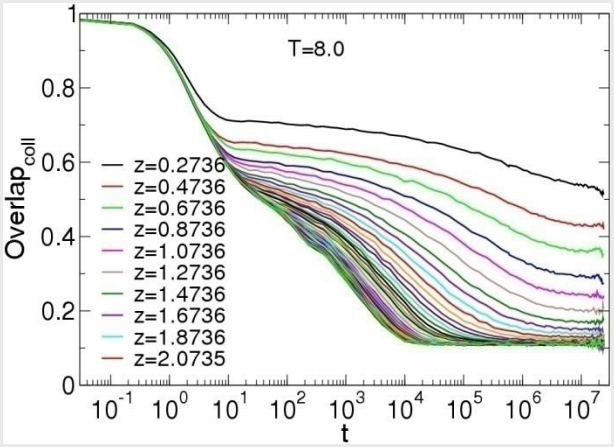


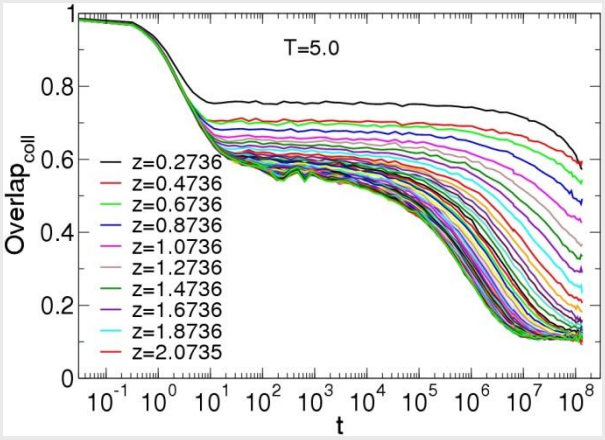




- Region in which the wall influences the dynamics increases with decreasing T
- Similarly to the self overlap, one can define a collective overlap





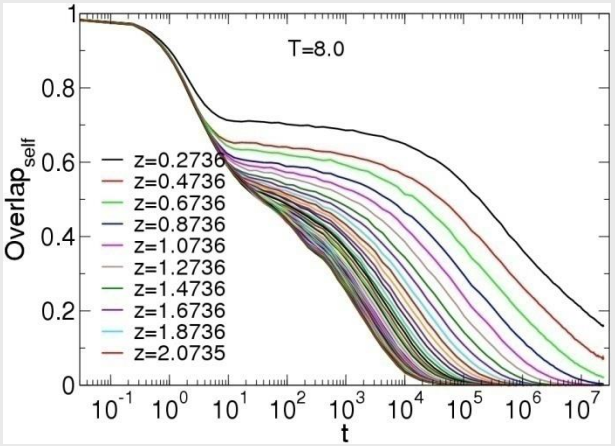


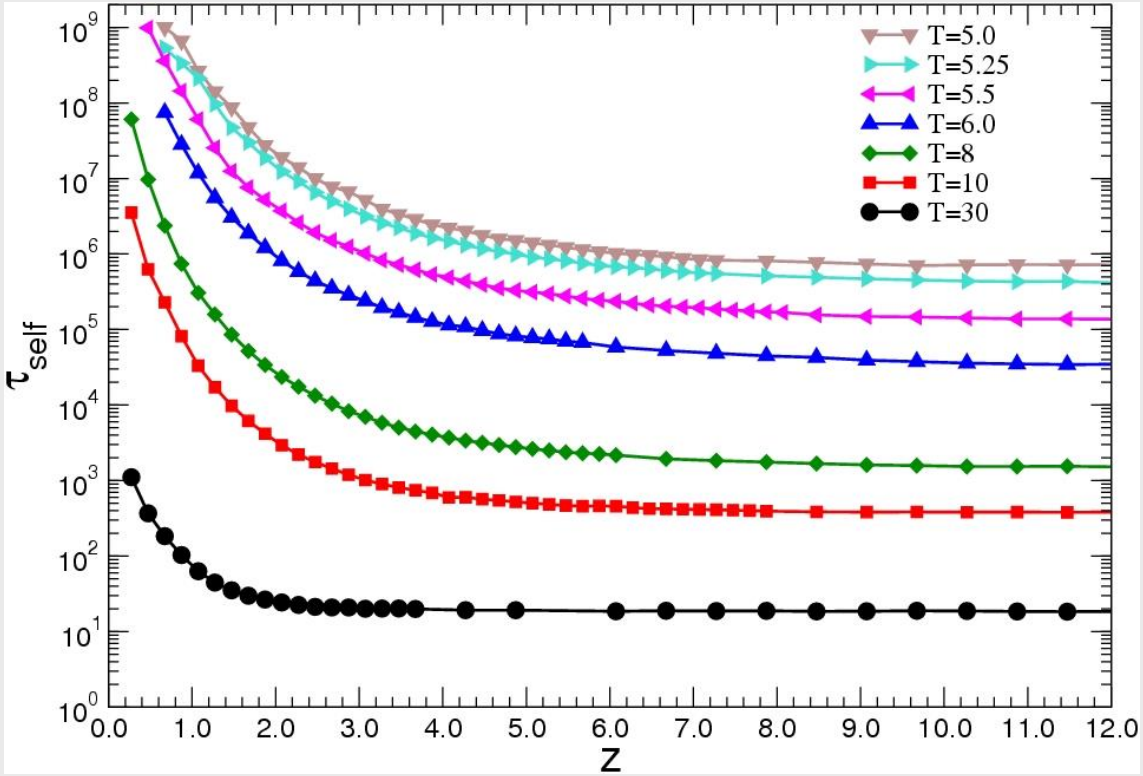
- Due to the structure of the wall the collective overlap does not go to zero for finite z even if $t \to \infty$

  $\Rightarrow$ measure the value of the overlap at $t \to \infty$ for different z (static observable!)

Relaxation Times

- The α-process of the $Overlap_{self}(z,t)$ can be fitted well by a KWW function $\Rightarrow$ obtain the relaxation time τ_{self} (via area under α-process)



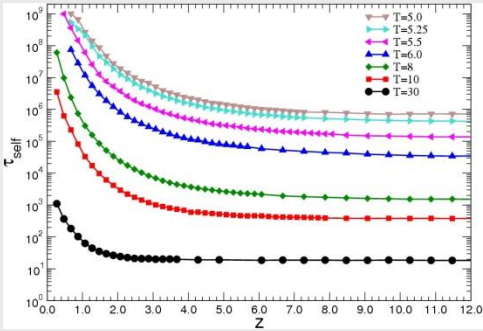


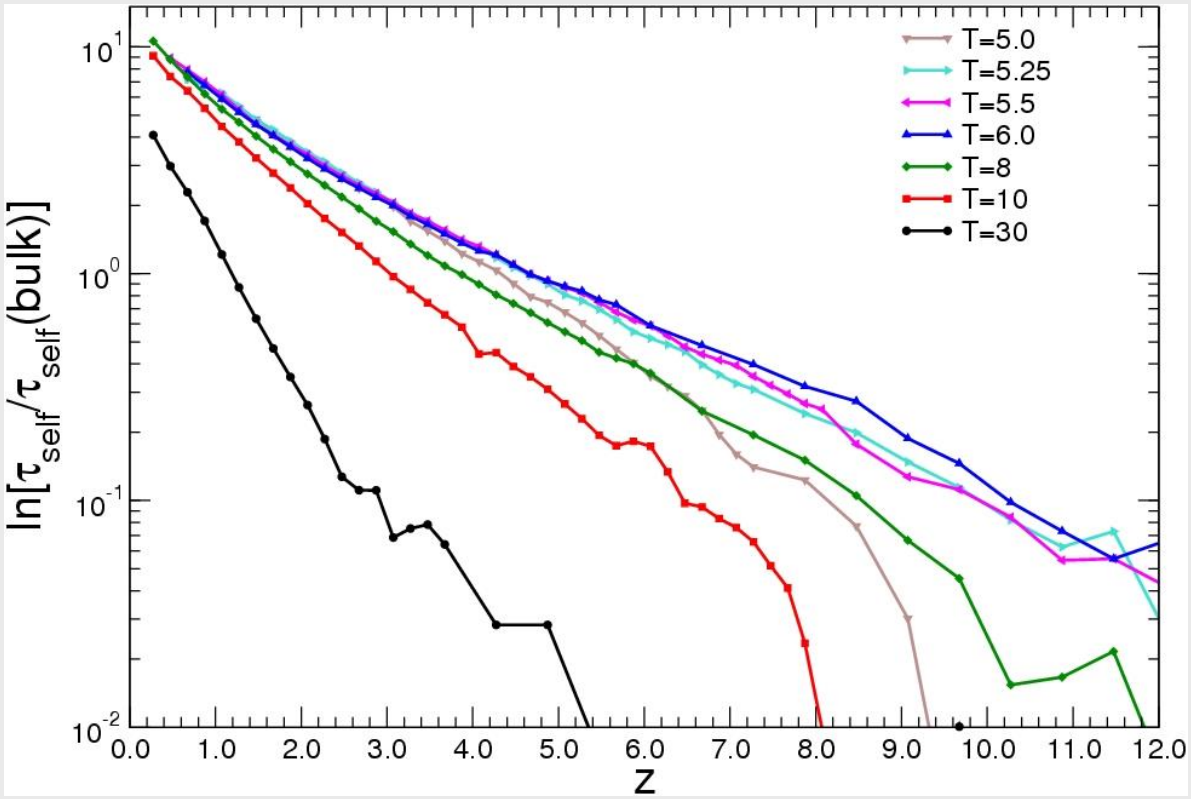
- System size is sufficiently large that $\tau_{self}(z)$ converges to bulk value
- Same behavior is observed for $\tau_{coll}(z)$

Relaxation times

- Empirically one finds that for *intermediate and large z*

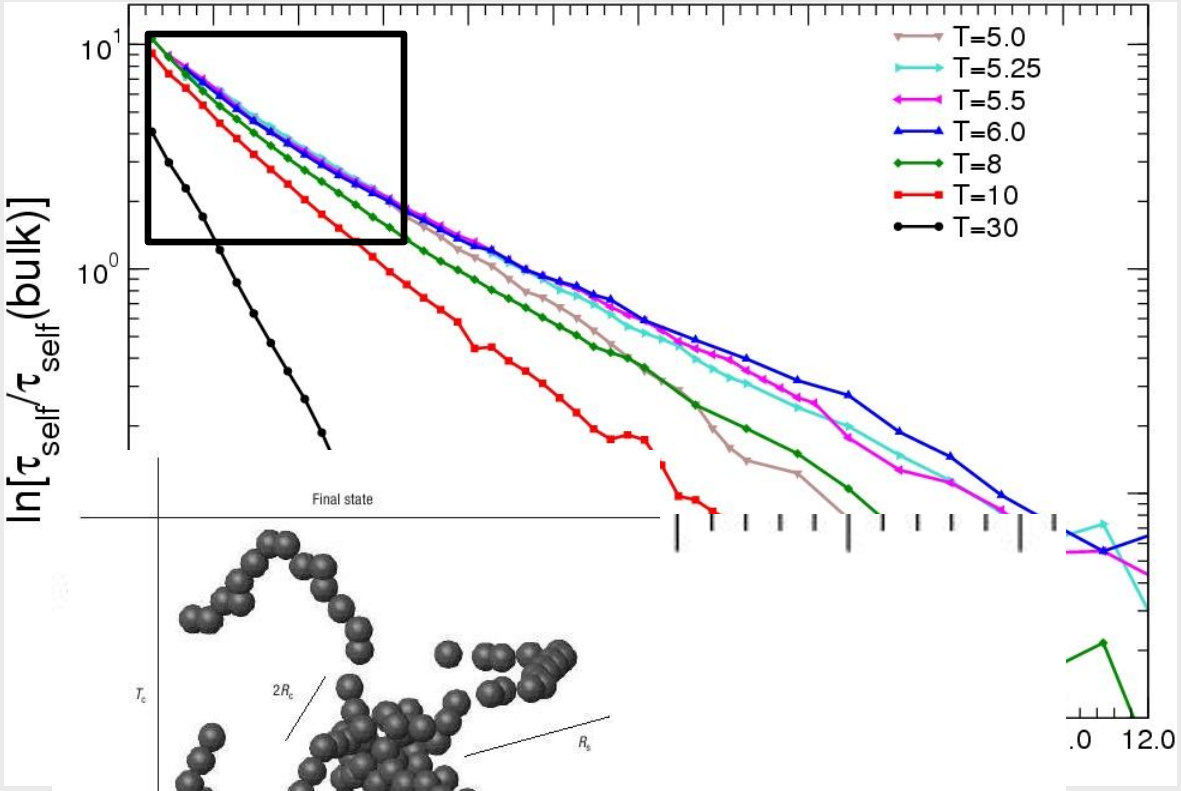
$$\log[\tau_{self}(z,T) / \tau_{self}(bulk,T)] = A(T) \exp(-z/\xi_{dyn}(T))$$

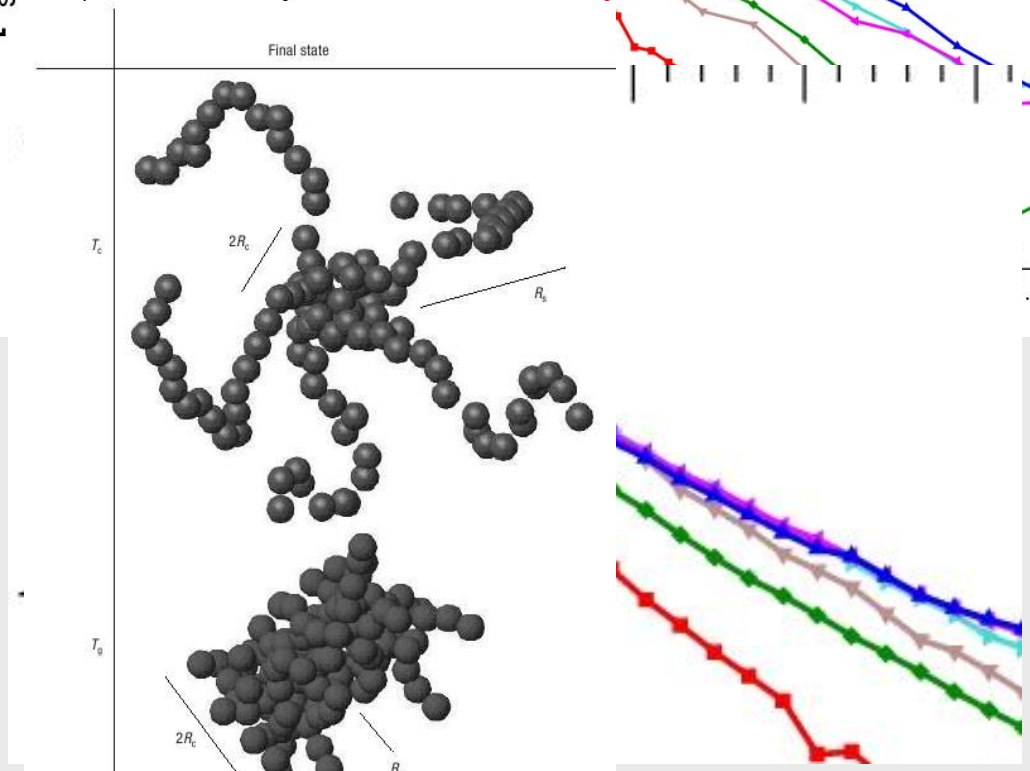




- This result allows to obtain a *dynamic* length scale $\xi_{dyn}(T)$
- ξ_{dyn} is non-monotonic in T!
- Same results are obtained for $\tau_{coll}(z,T)$

A closer look at $\tau_{self}(z,T)$





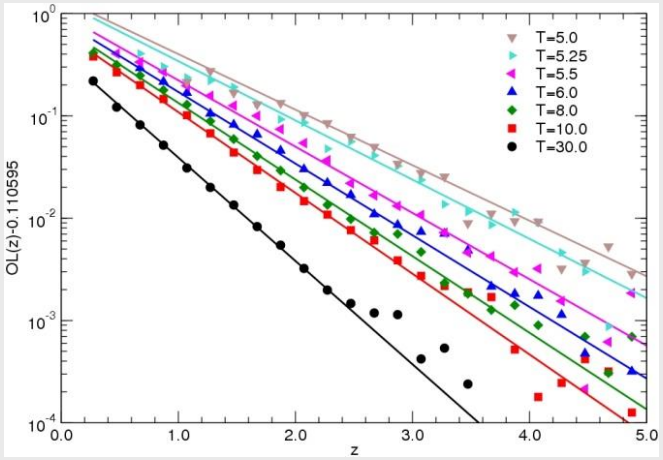
- At low T, the normalized $\tau_{self}(z,T)$ becomes independent of T for *small and intermediate z*, i.e. T-dependence is seen only at large z

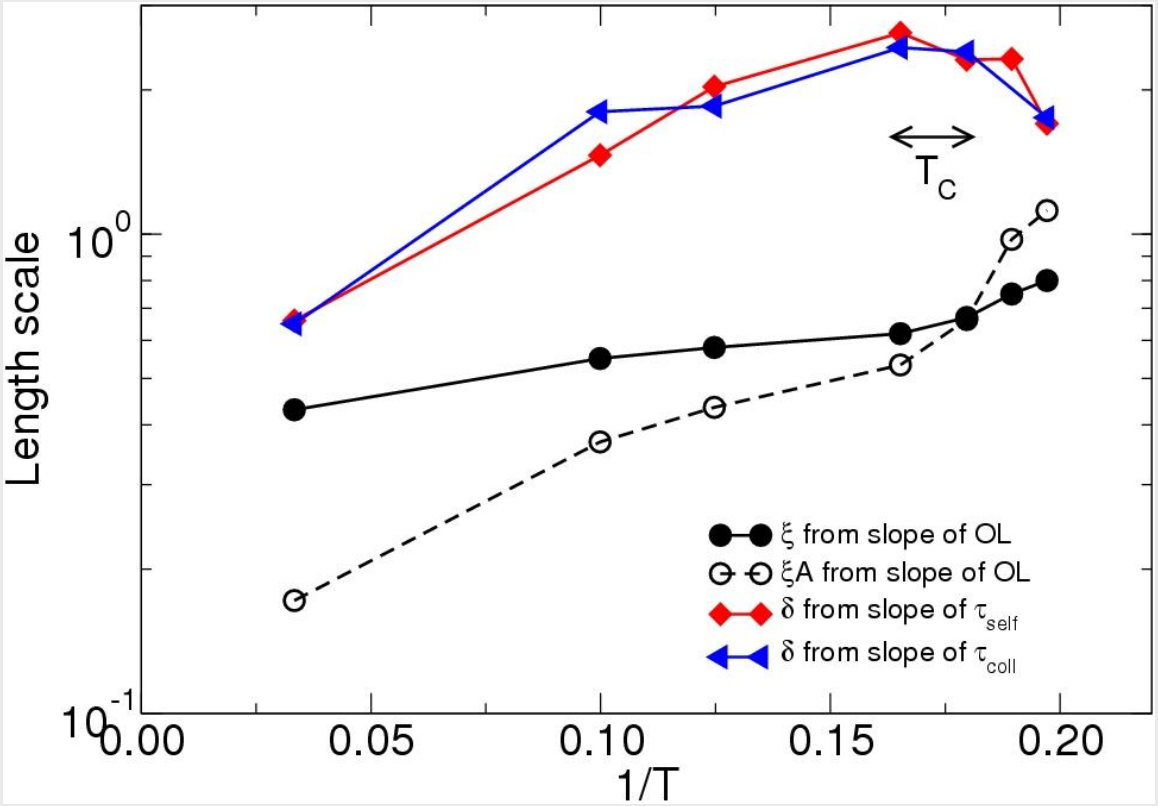
  $\Rightarrow$ evidence that there are *two length scales* for the relaxation process; with decreasing T the relaxing entity becomes more compact

- Result seems (!) to be compatible with RFOT view of Stevenson, Schmalian and Wolynes (Nat. Phys. 2006)

Length Scales

- static length scale from g(r)
- static length scale from *collective* overlap: two choices
  - 1/slope
  - prefactor/slope
- dynamic length scale from $\tau_{self}(z,T)$ or $\tau_{coll}(z,T)$





- Static length scale shows weak T-dependence for g(r) and noticable T-dependence for point-to-set correlator
- dynamic length scale shows maximum around T_c
- dynamic scale is larger than static one

Summary (part 1)

- Influence of wall on collective overlap decreases exponentially with distance from the wall for all T (even below T_c)
- Length scale associated with higher order static correlation functions does show a significant T-dependence; the length scale for dynamic correlations has an even stronger one
- Evidence that relaxation process changes nature around T_c . Relaxing entities have *two* length scales and one of them is non-monotonic in T

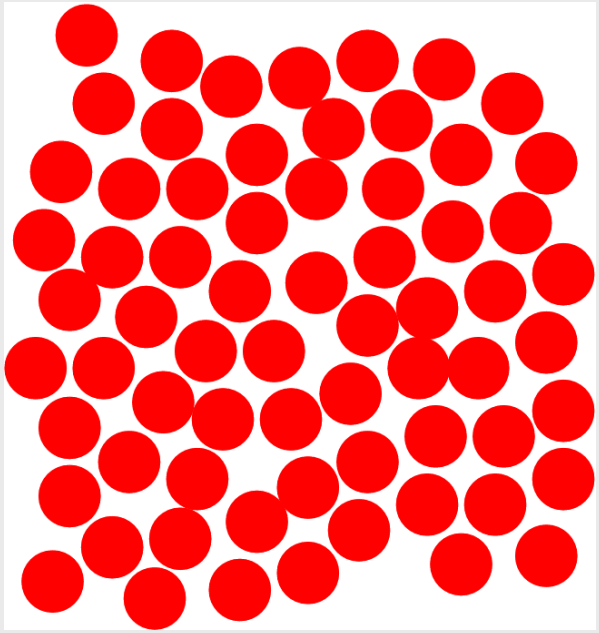
Reference:

L. Berthier and W. Kob, PRE **85**, 011102 (2012)

W. Kob, S. Roldan-Vargas, and L. Berthier, Nature Phys. **8**, 164 (2012)

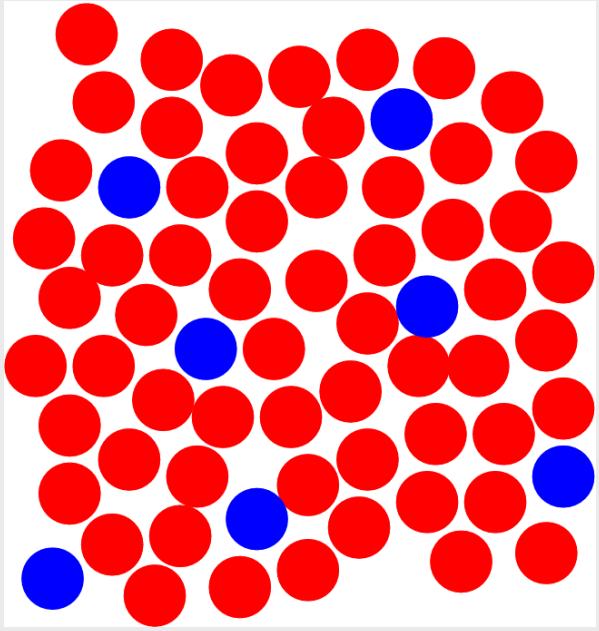
G. Hocky, L. Berthier, W. Kob, and D.R. Reichman, PRE **89**, 052311 (2014)

Probing a liquid by pinning particles



1) Equilibrate the liquid at the state point of interest (temperature+ density)

2) Pin some of the particles (=fix their position permanently) $\Rightarrow$ “pinned particles” (concentration c) and “fluid particles”

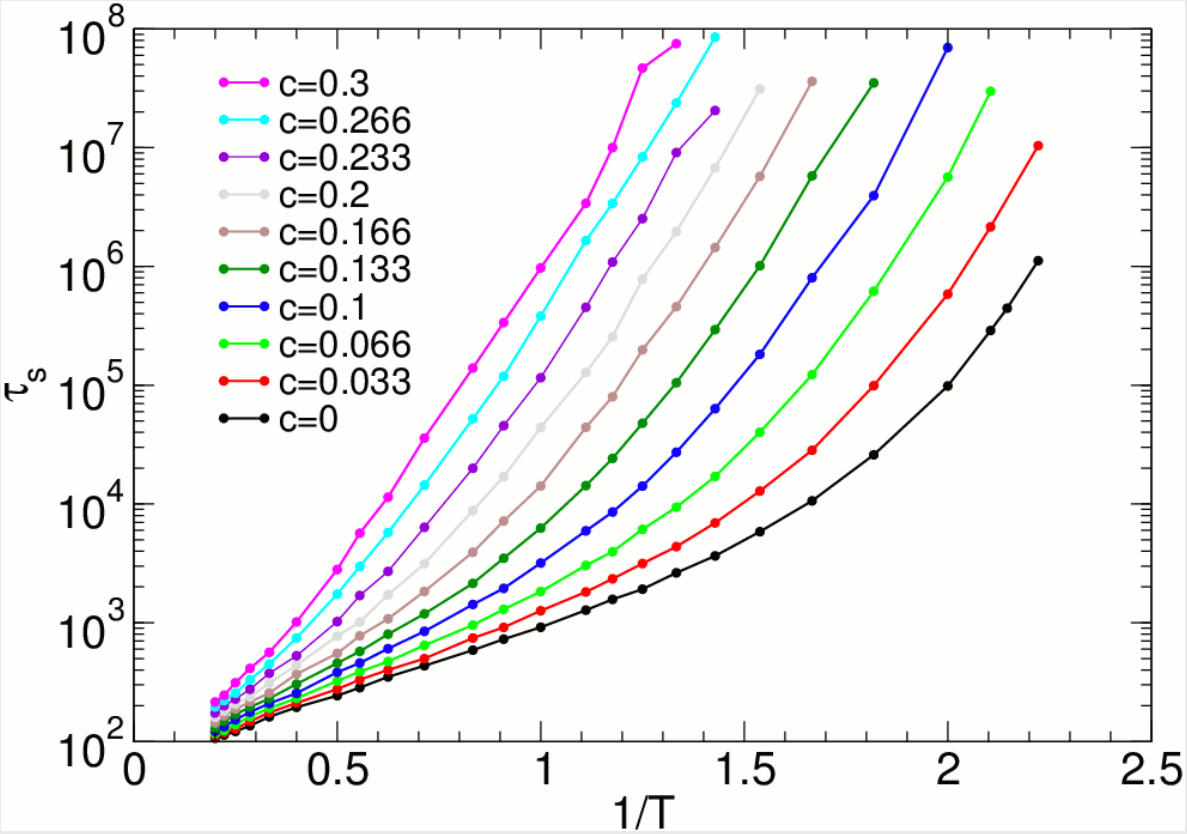


It can be shown that the *structural* properties of the fluid are not changed by the pinning *if* one takes the average over many disorder configurations and if the system is large

Scheidler, Kob, Binder (2004); Krakoviack (2005, 2010)

Dynamics of pinned system

- Structural properties are not changed but the dynamics is strongly affected by the pinning: Consider the intermediate scattering function (=density-density correlation function) $\Rightarrow$ relaxation time $\tau(T,c)$

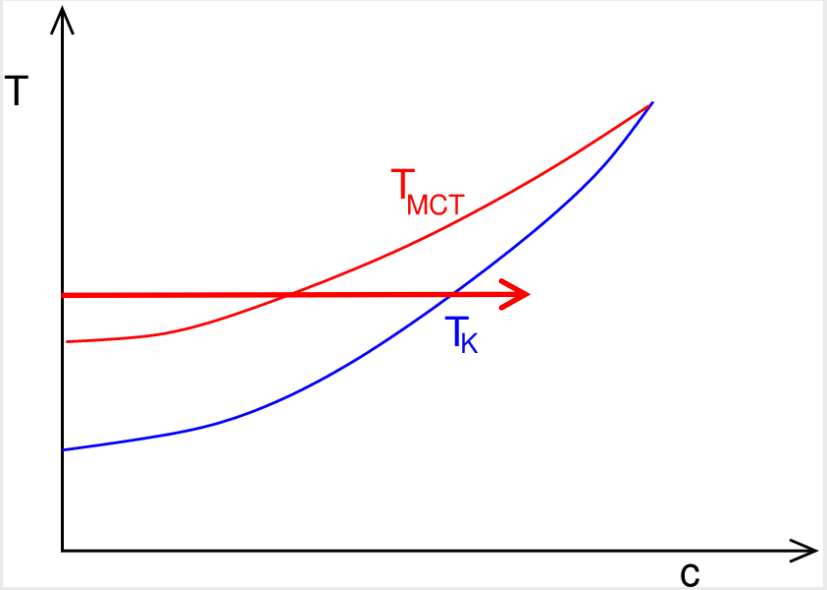


$\Rightarrow$ relaxation time $\tau(T,c)$ depends strongly on concentration c of pinned particles

Model and Simulations

System studied:

- binary mixture of Lennard-Jones particles:
- N = 300 particles
- Use parallel tempering algorithm to probe the thermodynamic properties of the system as a function of c (use 24 replicas)
- up to $2 \cdot 10^{10}$ time steps
- between 5-20 samples
- T_{MCT} (c=0) ≈ 0.435
- T_K (c=0) ≈ 0.30



Cammarota, Biroli
PNAS (2012)

Overlap q

- Kauzmann temperature: For $T>T_K$ the system has access to exponentially many configurations/states (neglect vibrations)
$\Rightarrow$ configurational entropy is positive

for $T < T_K$ there are only "few" states left $\Rightarrow$ configurational entropy is zero

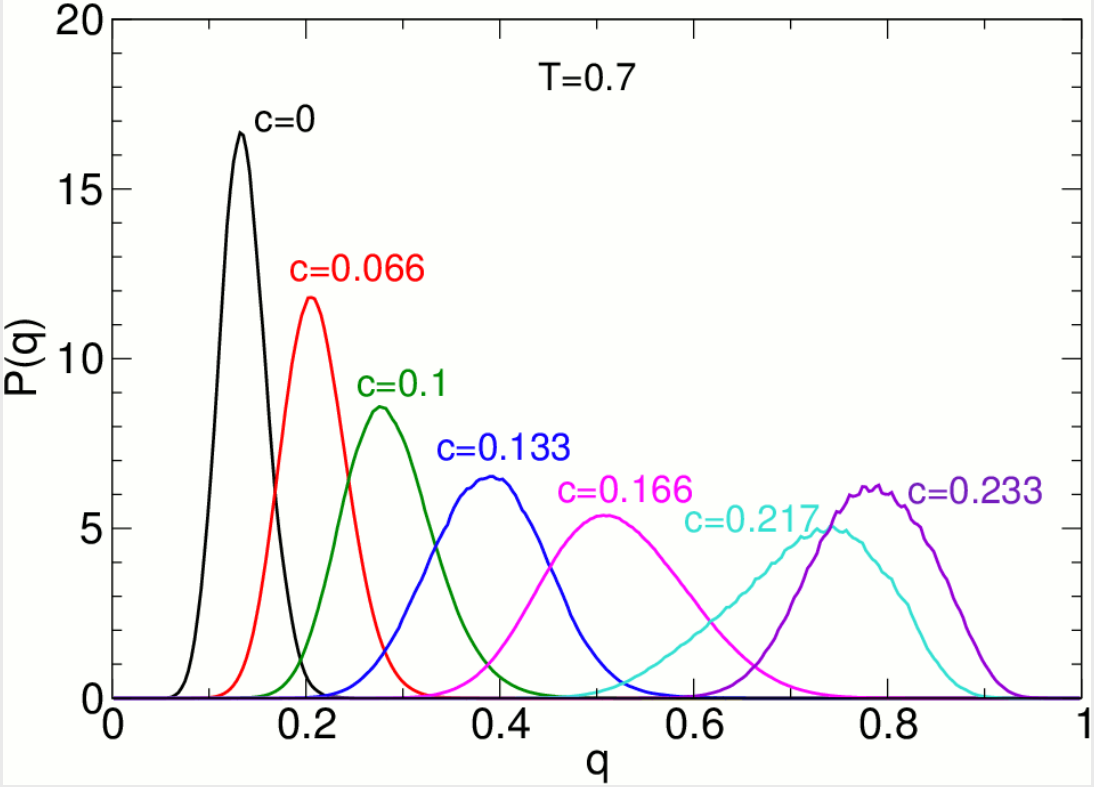
$\Rightarrow$ need a quantity to measure the number of states

- Idea from spin glasses: Look at overlap q
- q measures whether two arbitrary equilibrium configurations (α, β) at temperature T are the same or not
- Reasonable definition of overlap: $q = q_{\alpha,\beta}(T) = N^{-1}\Sigma_{i,j}\, w(r_i^{(\alpha)} - r_j^{(\beta)})$
- q large/small: configurations α, β are similar/different

Distribution of overlap: P(q)

- Value of $q = q_{\alpha,\beta}(T) = N^{-1}\Sigma_{i,j}\, w(r_i^{(\alpha)} - r_j^{(\beta)})$ depends on α, β

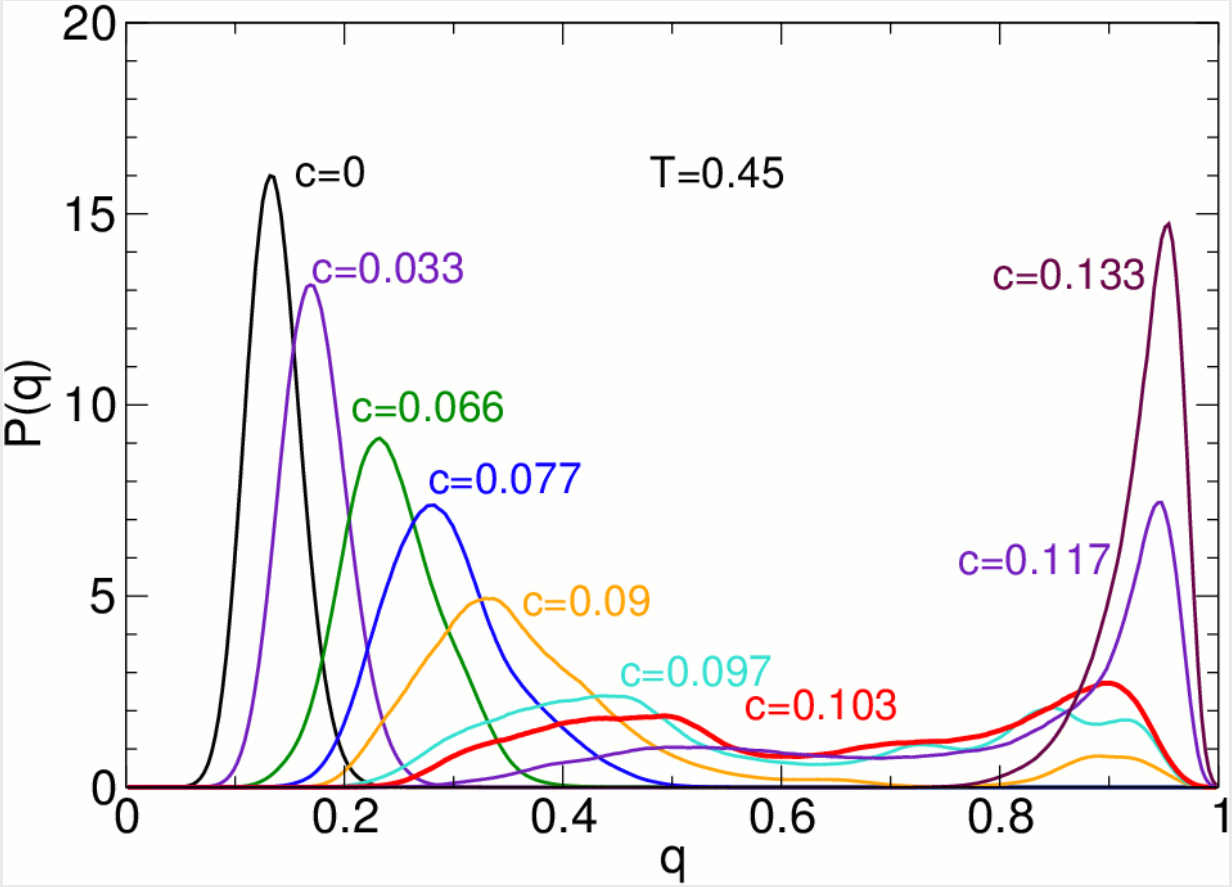
  $\Rightarrow$ q is distributed $\Rightarrow$ distribution function P(q)



$\Rightarrow$continuous localization transition similar to a Lorentz gas

$\Rightarrow$relevant length scale is just the distance between pinned particles

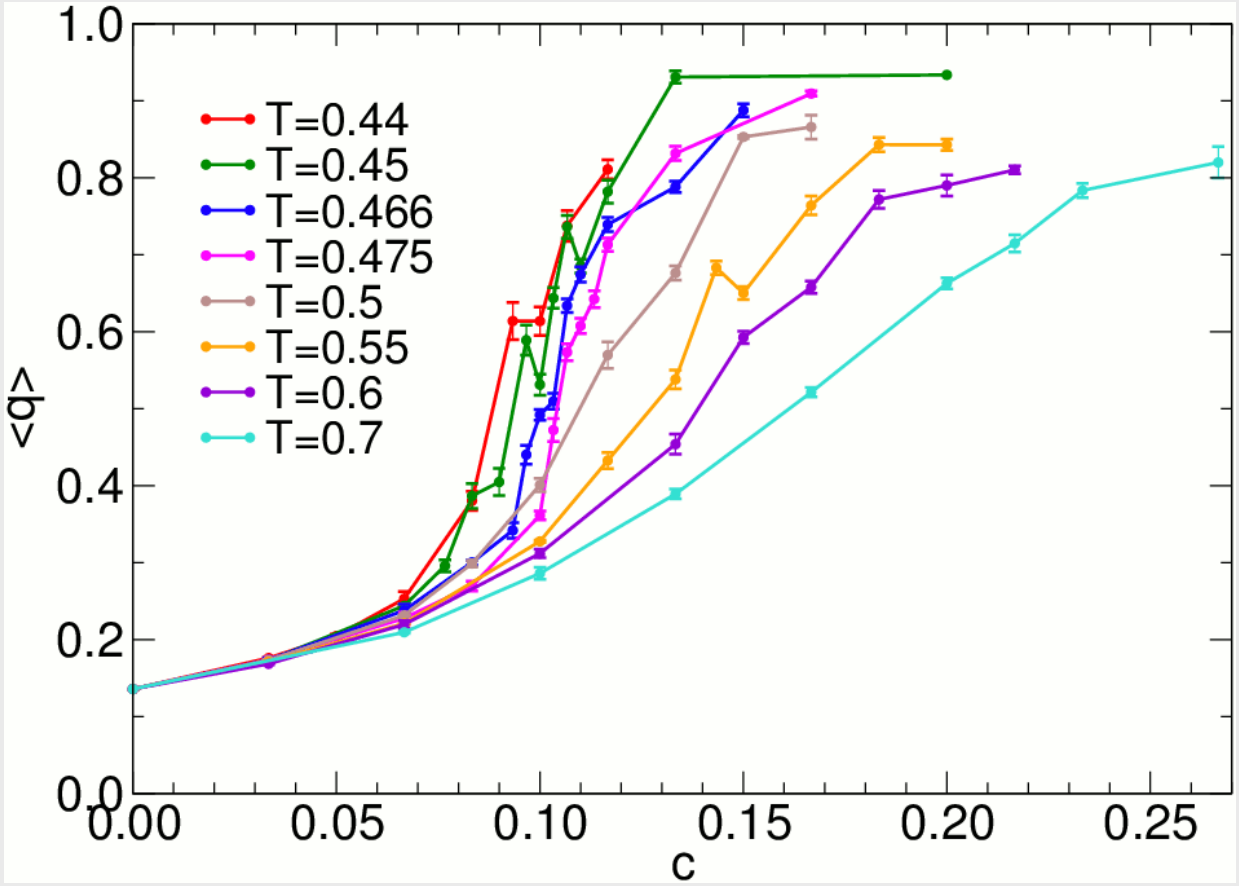
Distribution of overlap: Low T



- double peak structure at intermediate values of c
  $\Rightarrow$ at low T transition between delocalized states and localized states seems to be *discontinuous*
  $\Rightarrow$ coexistence between two types of states: “similar” or “different”
  $\Rightarrow$ Kauzmann point

Mean overlap ⟨q⟩

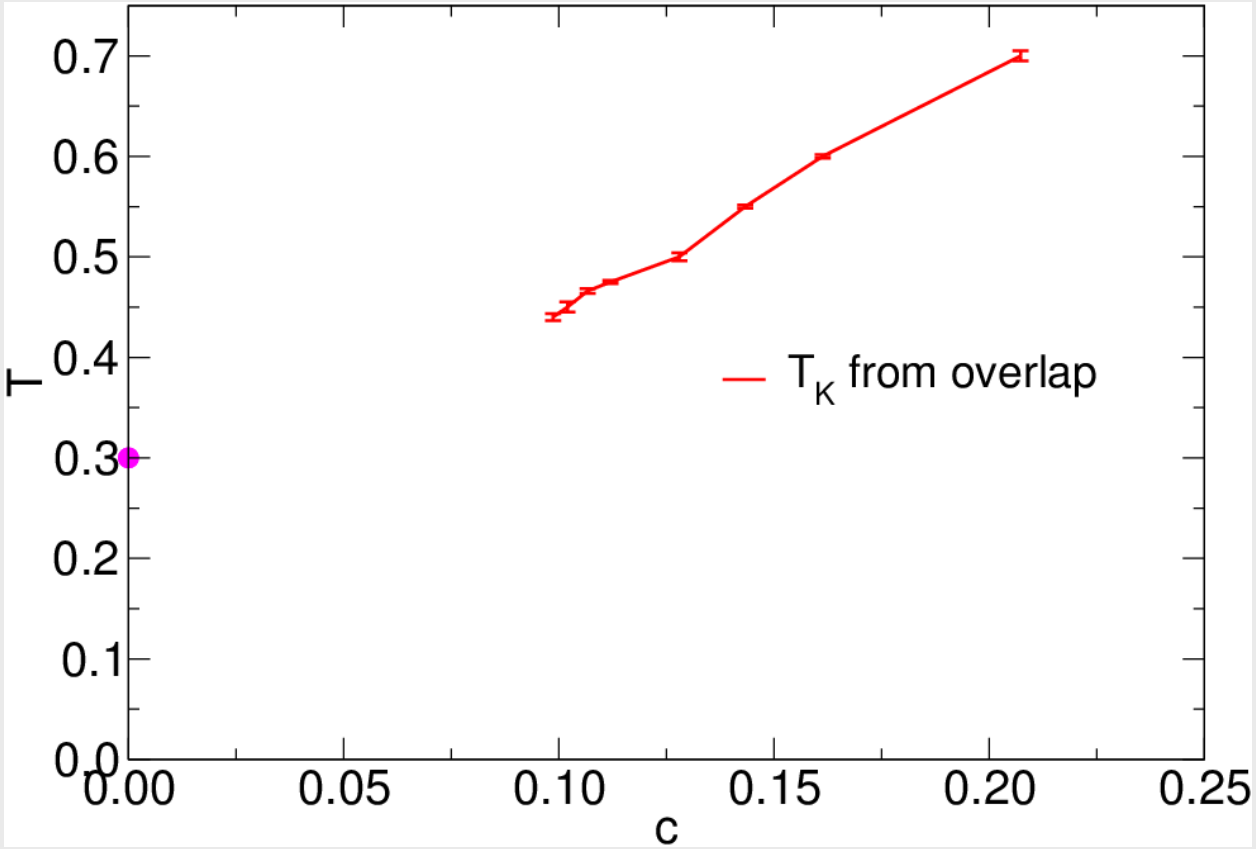
$$\langle q \rangle = \int P(q)\, q\, dq$$



- The average of P(q) increases monotonically with c
- At low temperatures ⟨q⟩ becomes very steep and seems to develop a singularity (=jump), i.e. compatible with the behavior expected for a system that undergoes a 1st order transition

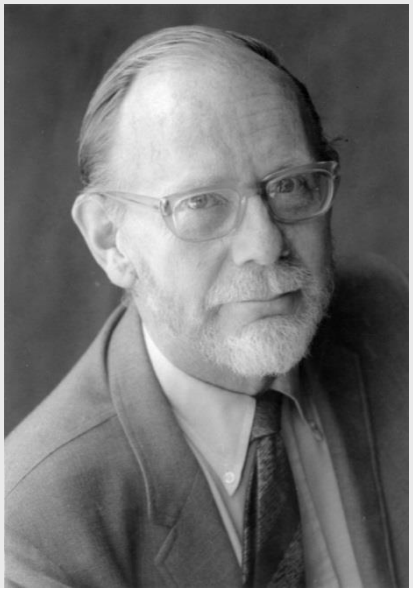
The Kauzmann line

- Estimate of $T_K(c)$: skewness $\gamma(T,c)$ (=third moment of P(q) =0)



- Obtain a Kauzmann line in the T-c plane.
- extrapolation to c=0 gives a $T_K(c=0) > 0$
- extrapolation is compatible with previous estimates for T_K in the bulk (from thermodynamic integration (Sciortino, Kob, Tartaglia, (2000))

The Kauzmann Temperature (Bulk)

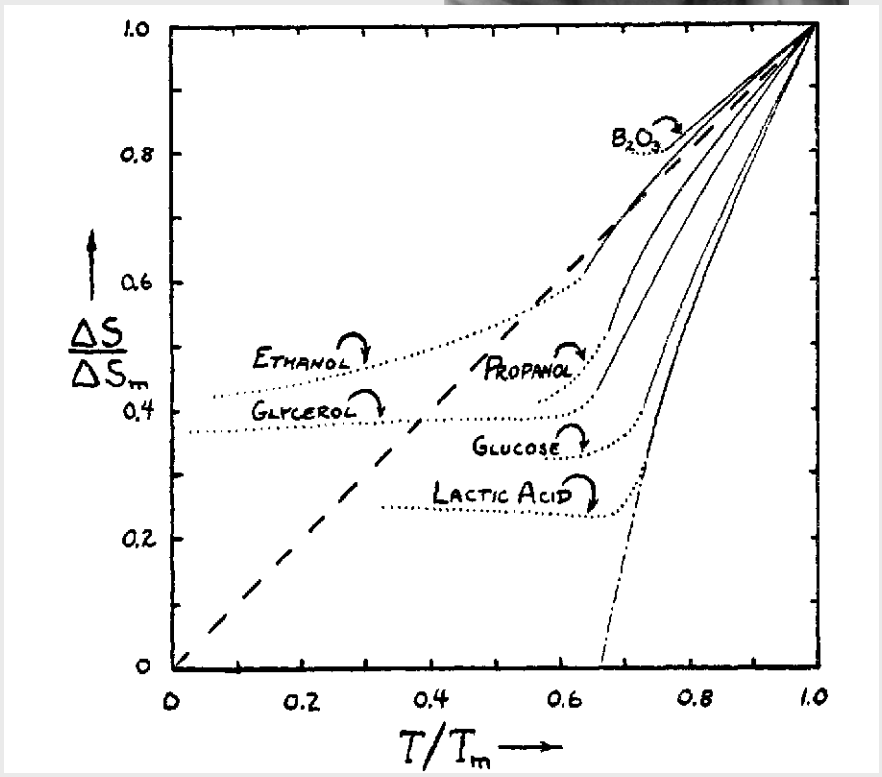


Kauzmann temperature T_K
(W. Kauzmann 1948):

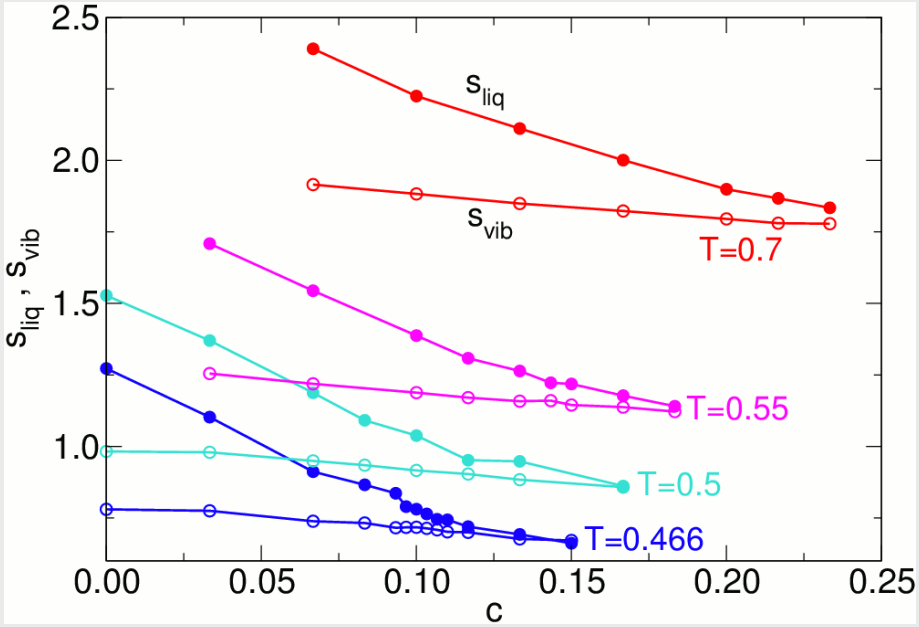
Entropy of glassy liquid can be decomposed into vibrational part + rest

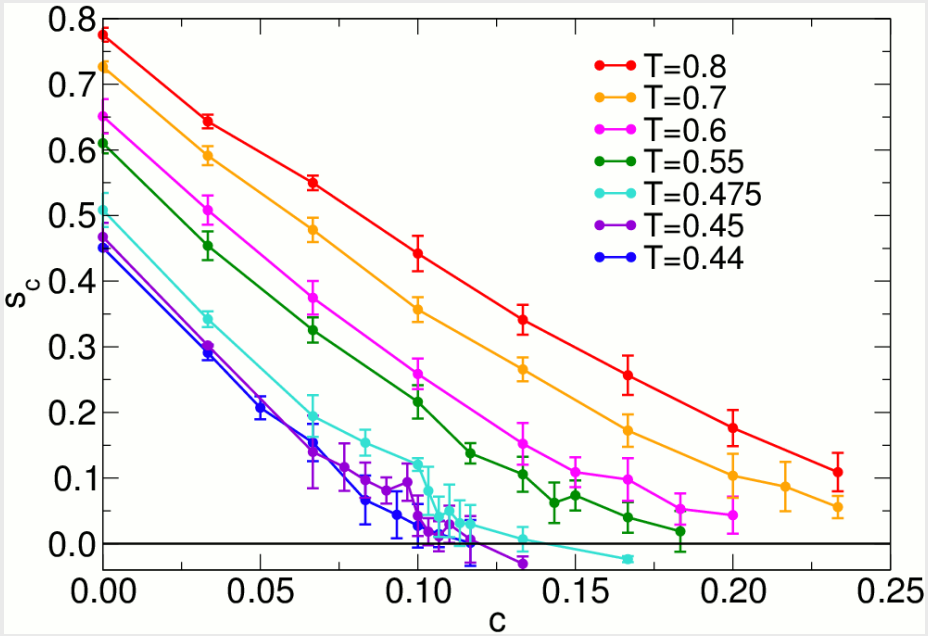
$$S_{liq} = S_{vib} + S_c$$

Configurational entropy S_c :
S_c is related to the number of different liquid like configurations (without vibrations); S_c seems to go to zero $\Rightarrow$ "ideal glass"



Entropy via thermodynamic integration





- Obtain S_{liq} from thermodynamic integration (starting from very high T)
- Calculate S_{vib} from the density of states of the inherent structures
- Define

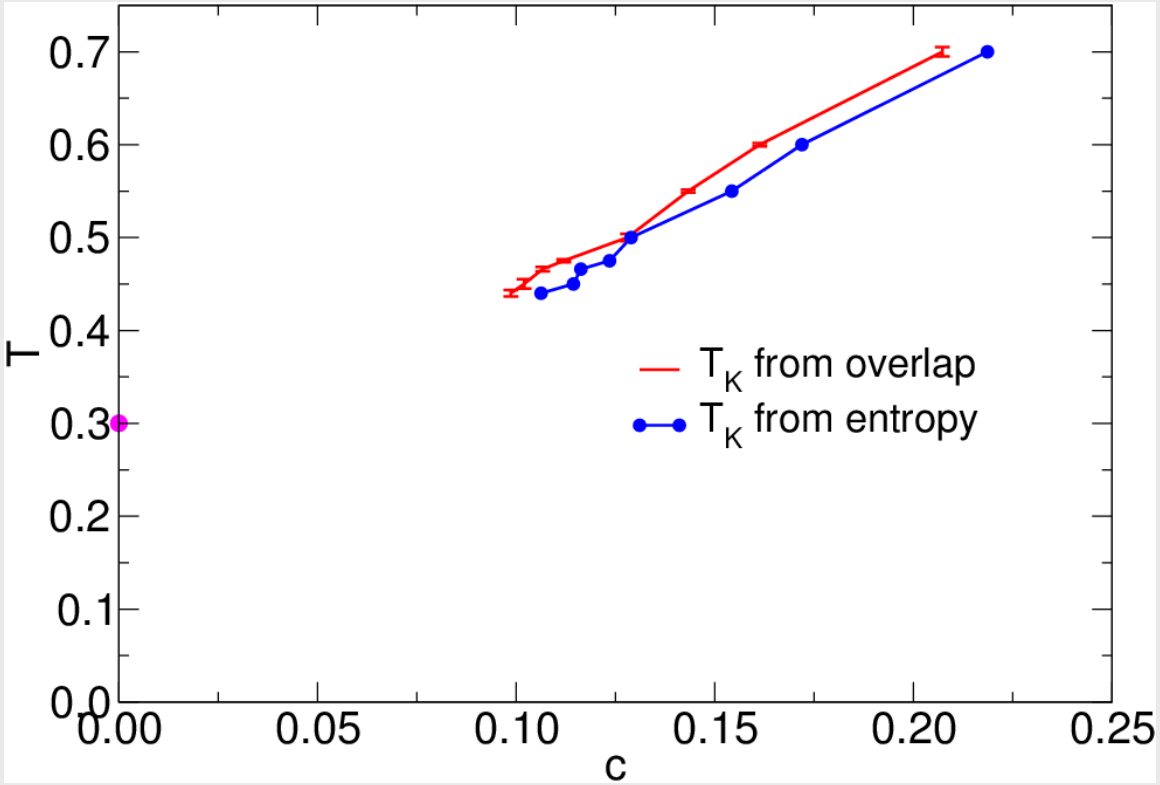
$$S_c = S_{liq} - S_{vib}$$

- At low intermediate and low T S_c does indeed go to zero

$\Rightarrow$ We have reached the Kauzmann point

Kauzmann line: 2

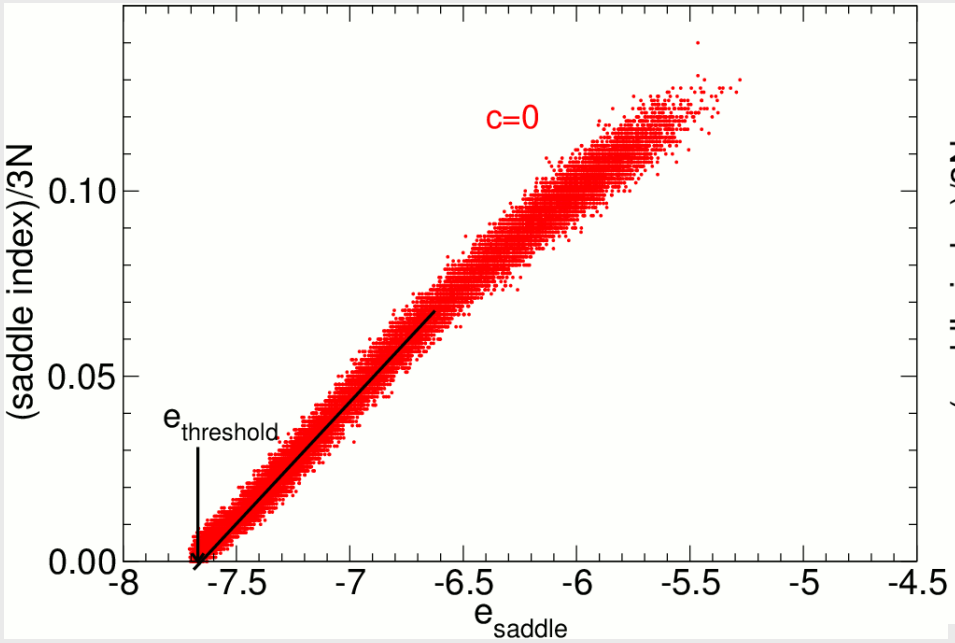
- Compare the c-dependence of the Kauzmann points as obtained from the two approaches

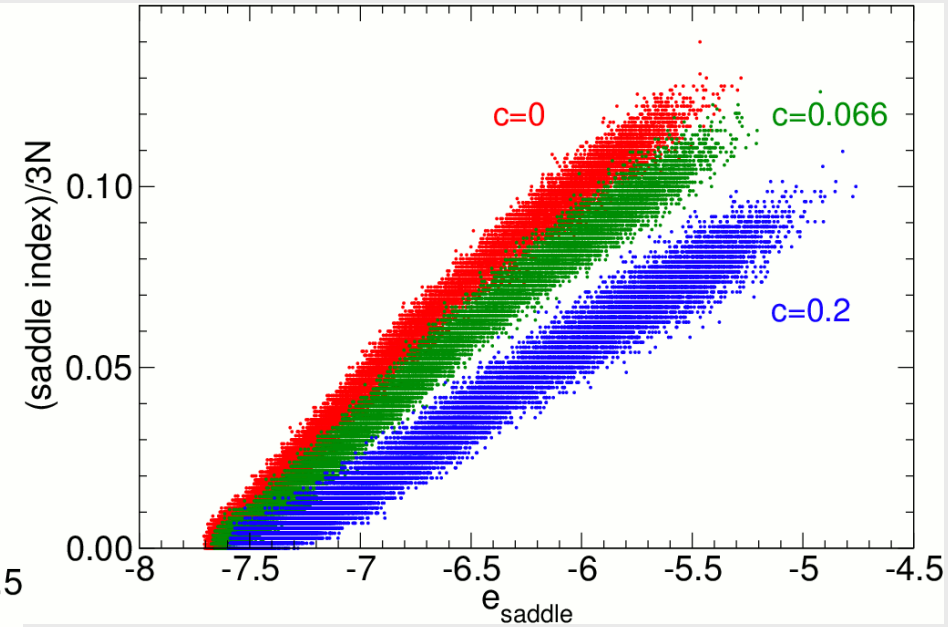


- Estimate of T_K (c) from distribution function P(q) and from thermodynamic integration gives compatible results

Critical temperature of MCT

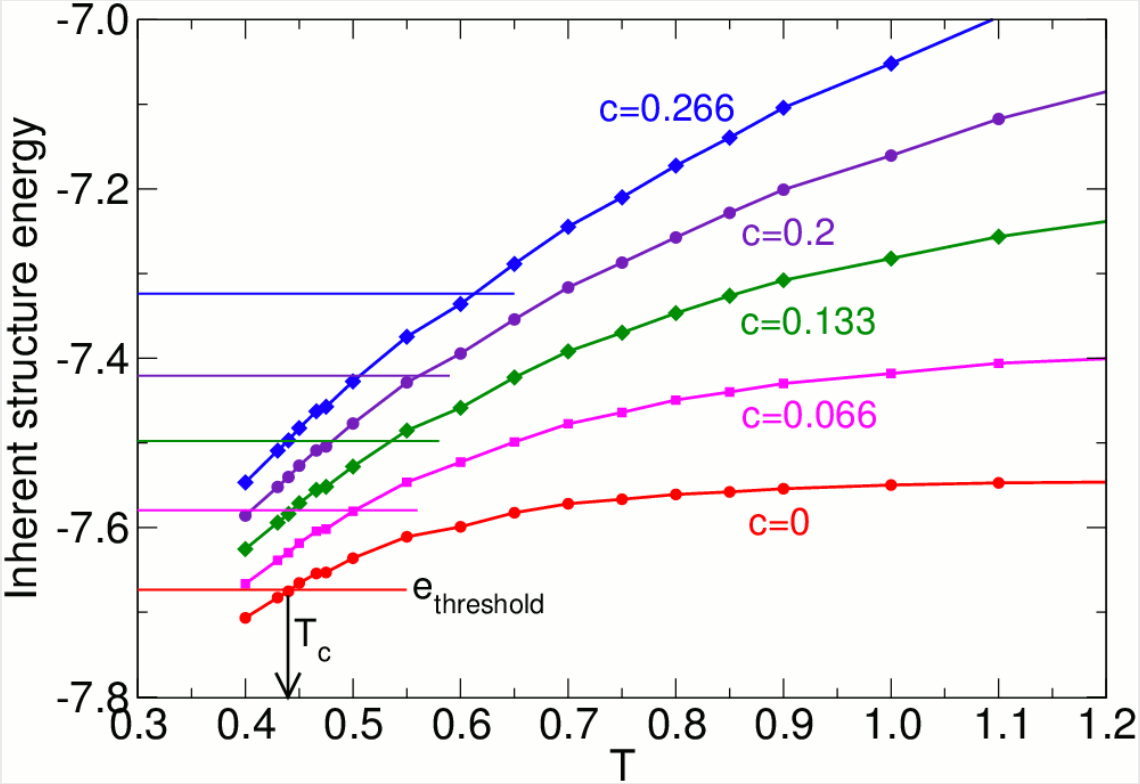
- T_{MCT} is often obtained from fitting to T-dependence of relaxation times: $\tau(T) \propto (T-T_{MCT})^{-\gamma}$
- Problem: 3 fit parameters
- Alternative: Use properties of potential energy landscape (Broderix et al 2000, Angelani et al 2000); measure the number of negative eigenvalues of the saddles





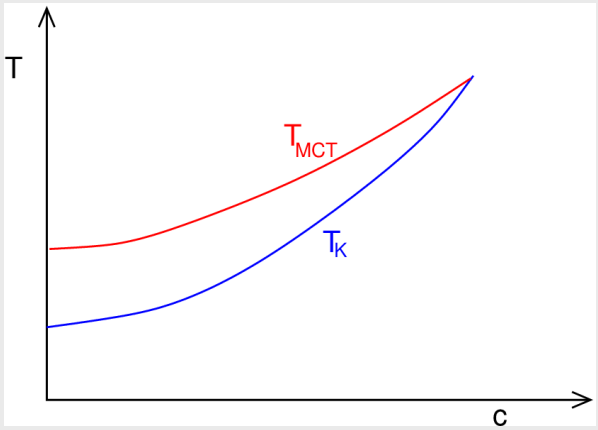
Critical temperature of MCT: 2

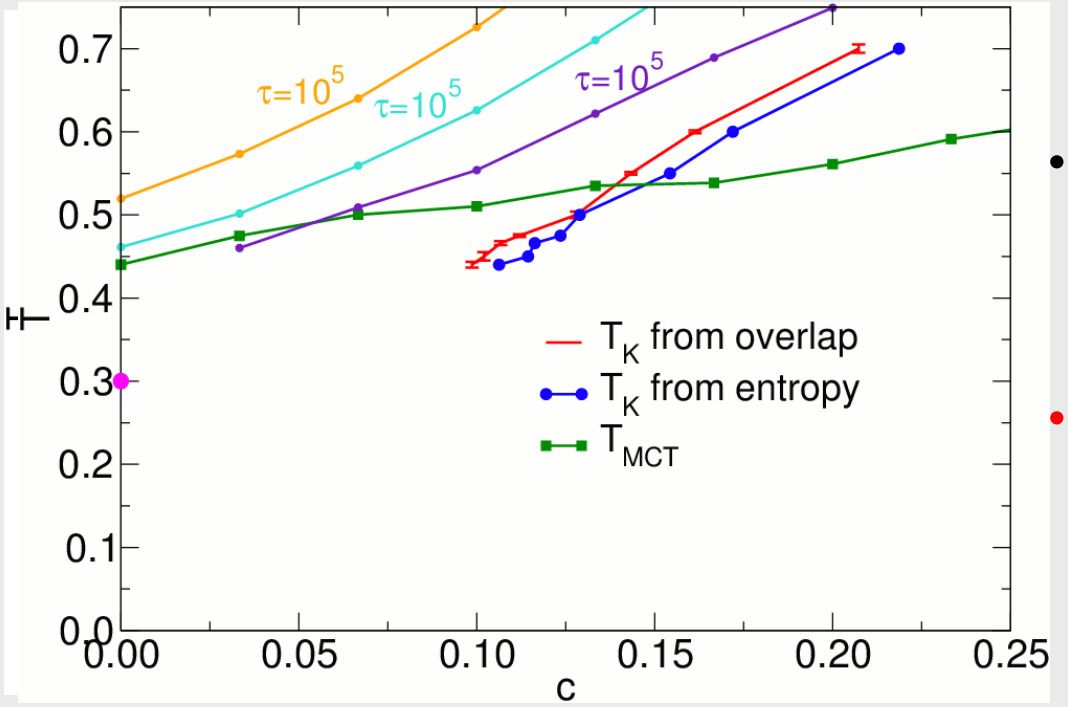
- At T_{MCT} the system sees mainly local minima
  $\Rightarrow$ Its inherent structure energy is equal to $e_{threshold}$



- T_{MCT} can be obtained with good precision and “without” fitting

Phase diagram





- Phase diagram looks qualitatively very similar to the one predicted by Cammarota and Biroli
- NB: For large c the T_K line from the simulation is an artifact! No double peak structure in P(q), no convincing S_c=0

- Dynamics slows down very quickly upon approach of the T_K line

Summary (part 2)

- Simulations of a simple glass former with “randomly”pinned particles
- Relevant temperatures of the glassy liquid depend on concentration of pinned particles
- Parallel tempering allows to cross the Kauzmann line $T_K(c)$
- At $T_K(c)$ the order parameter (overlap) seems to make a jump like in a first order transition; jump height increases with decreasing T
- For decreasing T_K c seems to go to zero $\Rightarrow$ diverging length scale $\Rightarrow$ evidence that there is indeed *only one glass state* even in the bulk
- Phase diagram in qualitative agreement with RFOT predictions

Reference:

- W. Kob and L. Berthier PRL **110**, 245702 (2013)
- M. Ozawa, W. Kob, A. Ikeda, K. Miyazaki (in preparation)