Computer Simulations of Glassy Systems with pinned Particles

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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!

- 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: $V(r) = \frac{1}{2} (r-\sigma_{ij})^2$ ; $\sigma_{11}=1.0$, $\sigma_{22}=1.4$
- $N=4320$ particles
- up to 830 million time steps
- between 10-30 samples
Overlap

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

- 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
• 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 $\alpha$-process of the $\text{Overlap}_{\text{self}}(z,t)$ can be fitted well by a KWW function $\Rightarrow$ obtain the relaxation time $\tau_{\text{self}}$ (via area under $\alpha$-process)

- System size is sufficiently large that $\tau_{\text{self}}(z)$ converges to bulk value

- Same behavior is observed for $\tau_{\text{coll}}(z)$
Relaxation times

- Empirically one finds that for \textit{intermediate and large} $z$

\[
\log\left[\frac{\tau_{\text{self}}(z,T)}{\tau_{\text{self}}(\text{bulk},T)}\right] = A(T) \exp\left(-\frac{z}{\xi_{\text{dyn}}(T)}\right)
\]

- This result allows to obtain a \textit{dynamic length scale} $\xi_{\text{dyn}}(T)$

- $\xi_{\text{dyn}}$ is non-monotonic in $T$!

- Same results are obtained for $\tau_{\text{coll}}(z,T)$
A closer look at $\tau_{\text{self}}(z,T)$

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

  ⇒ 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 $\tau_{\text{self}}(z,T)$ or $\tau_{\text{coll}}(z,T)$

Static length scale shows weak T-dependence for $g(r)$ and noticeable 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)
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 \( \tau(T,c) \)

\[
\Rightarrow \text{relaxation time } \tau(T,c) \text{ depends strongly on concentration } c \text{ of pinned particles}
\]
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
• $T_{\text{MCT}} (c=0) \approx 0.435$
• $T_{\text{K}} (c=0) \approx 0.30$

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 ($\alpha, \beta$) at temperature $T$ are the same or not

  - Reasonable definition of overlap: $q = q_{\alpha, \beta}(T) = N^{-1}\sum_{i,j} w(r_i(\alpha) - r_j(\beta))$

  - $q$ large/small: configurations $\alpha, \beta$ are similar/different
Distribution of overlap: $P(q)$

- Value of $q = q_{\alpha, \beta}(T) = N^{-1}\sum_{i,j} w(r_i^{(\alpha)} - r_j^{(\beta)})$ depends on $\alpha, \beta$
  $\Rightarrow q$ 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
• double peak structure at intermediate values of $c$
  ⇒ at low $T$ transition between delocalized states and localized states seems to be *discontinuous*
  ⇒ coexistence between two types of states: “similar” or “different”
  ⇒ Kauzmann point
The average of $P(q)$ increases monotonically with $c$.

At low temperatures $\langle q \rangle$ becomes very steep and seems to develop a singularity ($=\text{jump}$), i.e. compatible with the behavior expected for a system that undergoes a 1$^{\text{st}}$ 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

$$S_{\text{liq}} = S_{\text{vib}} + S_{\text{c}}$$

Configurational entropy $S_{\text{c}}$:

$S_{\text{c}}$ is related to the number of different liquid like configurations (without vibrations); $S_{\text{c}}$ seems to go to zero $\Rightarrow$ “ideal glass”
Entropy via thermodynamic integration

- Obtain $S_{\text{liq}}$ from thermodynamic integration (starting from very high $T$)
- Calculate $S_{\text{vib}}$ from the density of states of the inherent structures
- Define $S_c = S_{\text{liq}} - S_{\text{vib}}$
- At low intermediate and low $T$ $S_c$ does indeed go to zero

$\Rightarrow$ We have reached the Kauzmann point
• 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

- \( T_{\text{MCT}} \) is often obtained from fitting to T-dependence of relaxation times: 
  \[ \tau(T) \propto (T-T_{\text{MCT}})^{-\gamma} \]

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

- $T_{\text{MCT}}$ 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)