Crystallization Close to the Glass Transition: Dynamic heterogeneities do not precede crystallization

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Mono disperse systems of hard spheres present a liquid to solid phase transition

Even at moderate overcompressions the early stages of the cluster formation are still studied and different mechanisms are discussed.

What happens if we overcompress the system even further?

Will there be modified pathway to the final equilibrium ground state (fcc lattice) because of the slowing down of the dynamics and caging effects?

I will choose a system of monodisperse hard ellipsoids instead of monodisperse hard spheres.
Monodisperse Hard Ellipsoids

NPT ensemble

\[ a/b = 1.25. \]

\[ P_{\text{coex}} = 14.34 \]
\[ \eta_f^{\text{coex}} = 0.515 \]
\[ \eta_c^{\text{coex}} = 0.544 \]

Preparation process

![Graph showing volume fraction as a function of MC steps for different values of \( P^* \).]
Dynamical Properties

\[ \langle \Delta s^2(t) \rangle = \langle (\vec{r}_i(t) - \vec{r}_i(0))^2 \rangle \]

\[ F_s(q,t) = \left\langle \frac{1}{N} \sum_{i} \exp[iq(\vec{r}_i(t) - \vec{r}_i(0))] \right\rangle \]

subdiffusive regime

previous work on the glass like dynamics in P. Pfleiderer et al 2008 EPL 84 16003
Crystallization process

\[ q_{lm}(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{lm}(\vec{r}_{ij}) \]

\[ q_6^1(i) \cdot q_6^*(j) > 0.7 \]

long induction time vs. immediate growth
Snapshots of the system

$P^* = 27$

$P^* = 40$
Structural and dynamical preconditions for crystallization

- Short time mobility
- Voronoi volume
- Orientational correlations
- Structure
Short time mobility

\[ \Delta r_i(t) = |\vec{r}_i(t) - \vec{r}_i(t - \Delta t)| \]

\[ \Delta t = 5 \cdot 10^5 \text{ MC steps} \]
Voronoi volume

\[ P(v) \]

\[ P^* = 27 \]

\[ P^* = 40 \]

\[ P^* = 50 \]

C.H. Roycroft, Chaos, 2009, 19, 041111
Orientational correlations

For hard spheres it has been reported that the mobility is enhanced at the surface of the crystalline cluster\cite{16, 18}. To test for this effect, we computed the mobility when 80% of the particles had crystallized, but we only took particles at the surface of the crystallite into account (i.e. with $n \leq 8$). In contrast to refs. \cite{16, 18}, for low pressures we find a shift to lower mobilities, and at higher pressures no shift at all. This observation is consistent with an analysis of the single particle free volume via Voronoi decomposition. FIG. 7 shows the distribution of the volume of the Voronoi cells of all particles in the surrounding liquid (circles) in comparison to those that are about to crystallize (squares) and those that are at the surface of the crystal, once it has formed (crosses). We observe no increase in the single particle free volume at the interface of the crystallite. There is no evidence of the modified crystallization process described in ref. \cite{16}.

As the absolute distance travelled by a particle is not related to its likelihood to crystallize, we now ask whether regions of orientationally correlated motion tend to crystallize faster than other regions. We define $\cos(\theta) := \frac{\Delta \vec{r}_i(t) \cdot \Delta \vec{r}_j(t)}{|\Delta \vec{r}_i(t)| \cdot |\Delta \vec{r}_j(t)|}$.

\begin{align*}
P^* = 27 \quad &\quad P^* = 40 \quad &\quad P^* = 50
\end{align*}
Brownian dynamics and produces the same behaviour on long time-scales [20–22]. The system consisted of \( N = 10^386 \) prolate hard ellipsoids with an aspect ratio of \( a/b = 1.25 \), where \( a \) is the length of the axis of symmetry and \( b \) is the length of any axis in the perpendicular plane. To simplify notation, we introduce the dimensionless pressure \( P^* = \frac{P}{8abk_B T} \) (where \( k_B \) is Boltzmann's constant). The coexistence pressure is \( P^* = 1.434 \) and the coexistence volume fractions of the fluid is \( \eta_{\text{coex}} = 0.515 \) resp. the crystal is \( \eta_{\text{coex}} = 0.544 \).

We studied suspensions at constant external pressures \( P^* = 27 \) \( P^* = 40 \) \( P^* = 50 \). The corresponding chemical potential differences between the supersaturated melt and the stable crystalline phase range from \( |\Delta \mu| = 0.57 k_B T \) particle to \( |\Delta \mu| = 1.08 k_B T \) particle.

In Fig. 1 we illustrate the state points studied here (diamonds) within simulation data at (a) the equation of state for our system as well as (b) the chemical potential difference between the overcompressed melt and the stable crystal. The diamonds indicate the overcompressions for which we studied the crystallization process.

During the simulation we monitored the volume fraction \( \eta \) and the local \( \bar{q}_{6} \) bond orientational order parameter [23, 24]. For an ellipsoid \( i \) with \( n(i) \) neighbours, the relative local bond orientation is characterized by

\[
\bar{q}_{lm}(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{lm}(\vec{r}_{ij})
\]
Conclusion

• crystallizing particles were studied backwards in time for their structural as well as dynamical properties

• no modification because of to the emerging glassy dynamics were found.

• the two mechanisms are acting on independent time scales.

• transition described by spinodal decomposition
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