Hydrodynamic Correlations slow down Crystallization of Soft Colloids

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Crystallization is often assumed to be a quasi-static process that is unaffected by details of particle transport other than the bulk diffusion coefficient. Therefore colloidal suspensions are frequently argued to be an ideal toy model for experimentally more difficult systems such as metal melts. In this letter, we want to challenge this assumption. To this aim, we have considered molecular dynamics simulations of the crystallization in a suspension of Yukawa-type colloids. In order to investigate the role of hydrodynamic interactions (HIs) mediated by the solvent, we modeled the solvent both implicitly and explicitly, using Langevin dynamics and the fluctuating Lattice Boltzmann method, respectively. Our simulations show a dramatic reduction of the crystal growth velocity due to HIs even at moderate hydrodynamic coupling. A detailed analysis shows that this slowdown is due to the wall-like properties of the crystal surface, which reduces the colloidal diffusion towards the crystal surface by hydrodynamic screening.

Crystallization in suspensions therefore differs strongly from pure melts, making them less useful as a toy model than previously thought.

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Crystallization and nucleation of undercooled melts are often studied using model systems of charged colloids in solution [10, 17, 18], such as polystyrene (PS) or polymethylmethacrylat (PMMA) spheres suspended in water [13, 20]. The solvent gives rise to hydrodynamic interactions (HI) between the colloidal particles that are not present in, e.g., metal melts. The influence of HIs on the dynamical properties of colloidal suspensions has been extensively studied in recent years [23, 24]. Löwen et al. [17, 19] showed that the ratio of the long-time to short-time self-diffusion coefficients has a universal value along the fluid freezing line. Recent studies by Pesche [25] and Nägele [21] of quasi-2D dispersions show that HIs have an impact on the self-diffusion function in these soft-sphere suspensions. However, since crystal growth happens on much larger time scales, it is commonly believed to be a quasi-static process that is unaffected by HIs. For example, in classical nucleation theory (CNT) [14], hydrodynamic interactions are assumed to enter only through the effective diffusion constant of the attaching colloids, which can be measured conveniently in the bulk liquid. Also in most computer simulation studies of nucleation, hydrodynamic interactions are neglected to avoid the high computational costs.

In the following, we will show with the help of computer simulations that HIs do have a remarkable influence on the dynamics of the crystallization in a colloidal suspension. Even at moderate coupling, we found the crystal growth velocity to be reduced by a factor of three. Similar findings have been reported by Schilling et al. using different simulations techniques [22].

To investigate the influence of hydrodynamic interactions on crystal growth, we studied the crystallization of Yukawa-type particles confined between two planar walls. The influence of hydrodynamic correlations on crystallization was evaluated by performing both simulations including and excluding HIs, by employing a fluctuating lattice Boltzmann method [6] and Langevin dynamics [12], respectively. We prepare our systems as an undercooled liquid and let the system crystallize. Due to the presence of the confining walls, the nucleation barrier is sufficiently small, so that we do not need special rare event sampling techniques. All simulations were performed using the MD simulation package ESPResSo [4, 5, 28].

As interparticle potential we used a screened Coulomb interaction potential

\[ U(r) = l_B k_B T \frac{Q_1 Q_2 \exp(-\lambda_D r)}{r}, \]

where \( l_B \) is the Bjerrum length, \( k_B \) is the Boltzmann constant, \( Q_1 \) and \( Q_2 \) give the charges on the interacting particles, \( r \) is distance between the particles. The range of the potential is determined by the Debye-Hückel screening length \( \lambda_D \). The static properties of a Yukawa system can be characterized by two dimensionless parameters [10]

\[ \kappa = \frac{w}{\lambda_D} \quad \text{and} \quad \Gamma = \frac{Q_1 Q_2}{4\pi \varepsilon_0 w k_B T} = \frac{Q_1 Q_2 l_B}{w}. \]

where \( w = (3/(4\pi \rho))^{1/3} \) is the Wigner-Seitz radius of the crystal phase and \( \rho \) the particle density. Phase diagrams of systems with Yukawa-type interactions have been calculated both by Monte Carlo simulations [21] and MD simulations [10, 11], which consistently found three regimes: a fluid phase and two different solid phases with FCC or BCC structure, respectively. For our simulations, we chose \( \kappa = 3.0 \) and \( \Gamma = 1260 \), which is slightly above the fluid-solid transition line in the BCC regime. The walls act on the particles via a Weeks-Chandler-Andersen (WCA) potential. When modeling the solvent by a Langevin thermostat [3], drag and random forces...
on the particles lead to the correct thermal distribution, 
but hydrodynamic interactions are suppressed. The only 
tunable parameter is the friction $\gamma$, which is inversely 
proportional to the single particle diffusion constant.

In order to introduce hydrodynamic interactions without 
simulating the solvent explicitly, we used the lattice 
Boltzmann method [3] on a three-dimensional (3D) lat-
tice with 19 velocity densities (D3Q19). In all reported 
simulations with HIs, we used a grid spacing of $g = 1.0$. 
The NVT ensemble was realized by the fluctuating LB algorithm [1, 29]. We treated the colloidal particles as 
point particles that are coupled to the LB fluid via a 
friction term with an adjustable friction constant $\gamma$. 
Note that this friction constant is equivalent to the fric-
tion coefficient $k_B T/6\pi \eta a$, and the lattice spacing of the 
fluid as well as the particle 

\[ r_H = \frac{k_B T}{6\pi \eta D_0}, \]  

where $r_H$ depends on the viscosity $\eta$ of the fluid as well as 
of the single particle diffusion coefficient $D_0$, which is inversely proportional to the friction constant $\gamma$. In 
contrast to other methods for including HIs, such as 
DPD [12], LB methods allow the friction $\gamma$ to be tuned 
independently from the viscosity $\eta$ of the fluid. The particle 
mobility is not simply the inverse of $\gamma$, but also depends on the viscosity $\eta$ and the lattice spacing of the 
LB grid due to feedback from the moving fluid [2, 31]. 
Also, the back flow of the solvent introduces finite-size effects in a system with periodic boundary conditions.

The equations of motion of the Yukawa particles were 
integrated by a Velocity-Verlet integrator [12]. If not 
otherwise stated, the simulations were performed with 
16,384 particles in a box of size $64 \times 16 \times 16$ confined 
by two planar walls located at $x = 0.5$ and $x = 65.5$. 
The time step of the Velocity Verlet integrator was set 
to $dt = 0.01$, the total simulation length 750,000 time 
steps. The same time step was also used for the LB fluid 
update, when applied. As basic length we use the mean 
particle distance in the crystal phase $a = 1.1$. The time 
step is $d\tau = 0.01\tau$, with $\tau = a\sqrt{k_B T/2m_p}$, where $m_p$ is the 
mass of the colloids. The viscosity is $\eta = 0.8$ and the 
density of the fluid is $\rho_H = 1.0$ as well as the particle 
density $\rho = 1.0$. The friction $\gamma$ varies between 0.5 and 
12.5.

The effective diffusion constant depends not only on 
the applied thermostat, but also on the interactions be-
tween the particles. In order to set up comparable sim-
ulations, we therefore matched the tracer diffusion coeffi-
cient in the bulk liquid. This was done by measuring 
the MSD of tracer particles in pure bulk systems, both 
with and without HIs. These measurements were done in 3D periodic systems consisting of 16,384 particles in a

\[ D_T^0 \propto \frac{1}{\gamma}. \]  

FIG. 1: The diffusion coefficient of the tracer particles in the 
bulk $D_T^0$ as a function of the single particle diffusion coeffi-
cients $D_0$. (in simulation units). Red squares show results for 
the system without HIs and the blue triangles for the systems 
with HI. The gray dashed lines are a guide to eye. The black 
lines illustrate the matching of the diffusion coefficient. Two 
different single particle diffusion $D_0$ in the Langevin dynamics 
and the LB coupling result in the same long-time diffusion coefficient $D_T^0$.

Using the matched tracer diffusion, we investigated the 
freezing of the undercooled fluid confined between 
two planar walls. In order to distinguish the liquid and 
the different solid phases, we used the Steinhardt or-
der parameter [30]. Investigations by Moroni et al. [22] 
showed that especially $q_6$ and $q_8$ are good choices to 
determine whether cubic or hexagonal structures are 
present in the system, respectively. In the following, 
we will focus on FCC and BCC crystal structures, for 
which the $q_6$ order parameter is well suited. Due to
the strong fluctuations in our system, we applied an enhanced averaging method for the Steinhardt order parameter $\overline{q}_6$, introduced by Lecher [16]. The literature values are $\overline{q}_6$(BCC) = 0.408018, $\overline{q}_6$(HCP) = 0.42181 and $\overline{q}_6$(LIQ) = 0.161962.

Figure 2 shows the measured $\overline{q}_6$ of three snapshots taken at different times during a typical simulation run. Note that the points only represent the peaks the distribution of $\overline{q}_6$, since in the crystal, there is a strong layering parallel to the wall. In between the peaks, the density drops nearly to zero in the crystal, and consequently so does the order parameter. As expected, the crystal starts with a HCP wall layer, followed by a BCC crystal front that grows with time. To evaluate the position of the crystal front, we fitted the $\overline{q}_6$ peaks to a function of shape $-h \cdot \arctan((x - s)/w)$, where $x$ is the $x$-position in the simulation box, $h$ is the height difference between $\overline{q}_6$ in the liquid and in the FCC phase, $w$ is the width of the liquid-crystal transition region and $s$ is the position of the crystal front. Note that $\overline{q}_6$ in the liquid bulk is larger than the literature value, since we report only the peaks, not the usual average value.

After some initial time, the crystal grew very uniformly, so that we could determine a constant growth velocity $u$ by a linear fitting of the front position. Figure 3 shows the measured velocities $u$ as a function of the hydrodynamic radius $r_H$, which we varied by changing the friction coefficient $\gamma$ and applying the matching procedure described above. Every measurement represents the mean growth velocity sampled from 24 independent runs. For hydrodynamic radii $r_H^*/a < 0.025$, where $a$ is the mean particle distance in the crystal phase, the influence of HI is almost negligible as one would expect. But already in case of moderate ratios $0.1 < r_H^*/a < 0.25$, hydrodynamic interactions reduce the crystal growth velocity by up to a factor of $3$ at $r_H^*/a = 0.25$. In case of no HIs the normalized growth velocity is virtually constant, with a decay for small frictions due to improper coupling to the thermostat.

In order to elucidate what causes this difference, we analyzed the particle diffusion in the system relative to the actual position of the crystal front. To accomplish this, we binned our system along the growth direction into bins of width $b = 2a$ and determined the long-time diffusion coefficient $D_{x}^{COM}$ of the center of mass in the direction of growth, which can be seen as a measure for the transport of particles towards the growing crystal front. In Fig. 3 $D_{x}^{COM}$ relative to the position of the crystal front $x^{rel}$, normalized by the center of mass diffusion in the bulk $D_{x}^{COM}$ of the Langevin simulation is shown. The front of the crystal is located at $x^{rel} = 0$, while the pure bulk fluid phase is located at $x^{rel} = 7$ and the crystal phase is present for $x^{rel} < 0$. As expected, the long-time diffusion coefficients for the center of mass in the crystalline region are almost zero, rise in the region of the crystal front, and settle off to the liquid bulk value far away of the crystal front. The left-hand side of Fig. 4 shows the values for low $r_H^*/a = 0.025$ ratio, which are virtually the same for both systems: with and
Our simulations show that hydrodynamic interactions have a strong influence on crystallization, even at moderate hydrodynamic radii. Similar finding has been reported by Schilling et al. [27] as well. The effects arise mainly on the particle transport towards the crystal front, which are in particular important for nucleation processes. This puts the common assumption into doubt that hydrodynamic interactions can be ignored when studying crystallization or nucleation in suspensions. At least in Yukawa suspensions, these processes do not seem to be quasi-static, and the often drawn analogy to true melts might not be true.

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