Crystallization and dynamical arrest of attractive hard spheres

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Crystallization of hard spheres interacting with a square well potential was investigated by numerical simulations using so-called Brownian cluster dynamics. The phase diagram was determined over a broad range of volume fractions. The crystallization rate was studied as a function of the interaction strength expressed in terms of the second virial coefficient. For volume fractions below about 0.3 the rate was found to increase abruptly with increasing attraction at the binodal of the metastable liquid-liquid phase separation. The rate increased until a maximum was reached after which it decreased with a power law dependence on the second virial coefficient. Above a critical percolation concentration, a transient system spanning network of connected particles was formed. Crystals were formed initially as part of the network, but eventually crystallization led to the breakup of the network. The lifetime of the transient gels increased very rapidly over a small range of interaction energies. Weak attraction destabilized the so-called repulsive crystals formed in pure hard sphere systems and shifted the coexistence line to higher volume fractions. Stronger attraction led to the formation of a denser, so-called attractive, crystalline phase. Nucleation of attractive crystals in the repulsive crystalline phase was observed close to the transition. © 2009 American Institute of Physics. [DOI: 10.1063/1.3074310]

I. INTRODUCTION

Monodisperse attractive hard spheres have been intensively investigated because they serve as simple models for fluids in general.1 Depending on the strength and the range of the interaction these systems show a variety of equilibrium states, see Fig. 1. In the absence of attraction the hard core repulsion drives crystallization because that maximizes the entropy. The crystal phase has a volume fraction \( \phi = 0.545 \) and is in coexistence with a liquid at \( \phi = 0.494 \) in the two phase regime. The face centered cubic (fcc) phase has the lowest free energy,2 but the difference with the hexagonal close packed (hcp) phase is so small that in practice a mixture of both phases is often observed.3

Attractive interaction leads to the formation of denser crystals and broadens the coexistence gap. A fcc crystalline phase is formed if the interaction range is narrow, but for broader ranges other crystalline structures may also be stable.4 If the interaction range is larger than about 15% of the particle diameter, phase separation between a low and a high density liquid is observed at lower volume fractions, but this liquid-liquid phase separation becomes metastable when the interaction range is narrow. In any case, only phase separation between the low density liquid phase (gas) and the high density crystalline phase (solid) is observed if the attraction is sufficiently strong.

For very narrow interaction ranges, phase separation between a low and a high density fcc crystalline phase is predicted at high densities5,6 and found in computer simulations.7 The low density crystal is driven by hard core repulsion, while the high density crystal is driven by attraction and therefore its density at the binodal increases with decreasing interaction range. If the spheres are polydisperse, crystallization is inhibited and only liquid-liquid phase separation is observed.

Long lived nonequilibrium states are also found with extremely slow dynamics, see for a review Ref. 8. At high densities these states are called glasses, while at low densities they are usually called gels. In the absence of attraction the critical slowing down of the dynamics occurs at about \( \phi = 0.58 \). At that volume fraction crystallization becomes extremely slow although in the absence of gravity it has still been observed experimentally even for volume fractions as high as \( \phi = 0.62 \), i.e., very close to random close packing (0.64).9 With increasing attraction the glass transition shifts weakly to higher volume fractions because transient aggregation of the particles increases the accessible free volume. However, for strong attraction a different type of slowing down appears even at low densities caused by formation of bonds between the particles with a lifetime that increases with increasing attraction strength. Arrested states at high densities formed by increasing the attraction are sometimes called attractive glasses to distinguish them from repulsive glasses formed by crowding.

If bond formation is diffusion limited, long bond lifetimes require strong attraction. Numerical simulations showed that in this case the strong slowing down of the dynamics with increasing attraction is only found within the two phase regime.10 Percolating networks are formed for some duration during phase separation.11-14 The lifetime of these networks increases with increasing attraction14 until for very strong attraction the system appears arrested at least for the duration of the simulation. Experimentally, one finds in this situation long lived gels that resist mechanical stress.15 For reversible reaction limited aggregation long lived gels

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can also be found in the homogeneous regime because the bond lifetime can be arbitrarily long at any attraction strength. Of course, in this case it will also take a very long time to reach equilibrium.

An interesting question arises whether one can identify a critical interaction strength at which the rate of phase separation diverges\cite{16} or whether the rate of phase separation decreases exponentially with increasing interaction energy. In the latter case phase separation simply becomes too slow when the interaction is strong and the observed arrest is only apparent for the duration of the experiment. Dynamical arrest at a particular value of the attraction strength is predicted by mode coupling theory,\cite{3} but it is not evident that a mean field theory can be applied to the heterogeneous gels formed at lower volume fractions.

Another issue is whether fast nucleation of crystals at low volume fractions requires liquid-liquid phase separation as a first step as was suggested by numerical simulations\cite{14,17} and analytical calculation.\cite{18} The implication would be that the nucleation rate increases abruptly with increasing attraction at the binodal of the metastable liquid-liquid phase separation.

Here we report on computer simulations of the crystallization of hard spheres with a square well interaction with fixed well width \( \varepsilon = 0.1 \) in units of the sphere diameter. For short range interaction the equilibrium properties of the liquid are only weakly dependent on the shape of the potential if the latter is expressed in terms of the second virial coefficient \( B_2 \).\cite{19–21} \( B_2 \) is the sum of the hard sphere repulsion \( B_{hs} \) and the square well attraction \( B_{att} \): \( B_2 = B_{hs} + B_{att} \). Expressed in units of the particle volume, \( B_{hs} = 4 \) and

\[
B_{att} = 4[(1 + \varepsilon)^3 - 1][\exp(-u) - 1],
\]

where \( u \) is the well depth in units of the kinetic energy \((kT)\). We note that in the literature the interaction is sometimes expressed in terms of the so-called stickiness parameter, \( \tau = B_{att}^{\text{att}} \), of the so-called Baxter model.\cite{22} We have determined the liquid-crystal coexistence curve as a function of \( B_{att} \) and \( \phi \). The crystallization rate was investigated as a function of the interaction strength and the relationship with metastable liquid-liquid phase separation and percolation was explored. We will compare the results with earlier experiments and numerical simulations.

II. SIMULATION METHOD

The simulation method used here is called Brownian cluster dynamics (BCD). We will only briefly describe the method here, but see Ref. 23 for a more detailed description and a comparison with event driven Brownian dynamics simulations. Initially, \( N_0 \) nonoverlapping spheres with unit diameter are positioned randomly in a box with size \( L \) using periodic boundary conditions \([\phi = \pi N_0/(6L^3)]\). Different sizes between \( L=10 \) and \( L=100 \) were used, but the results shown here are not influenced significantly by finite size effects. During the so-called cluster construction step, spheres that are in contact, i.e., within each others interaction range, are bound with probability \( P \) leading to the formation of \( N_c \) clusters. \( P \) is related to the well depth \( u \) as follows:

\[
P = 1 - \exp(u).
\]

During the following so-called movement step the monomers are displaced randomly over a small distance. This leads to a small mean square displacement of the centers of mass of the clusters that is on average inversely proportional to the aggregation number of the clusters. If the movement of a particle leads to bond breaking or overlap with other spheres, it is refused. Next, each cluster is displaced an additional distance in the same direction so that the total displacement is proportional to the radius of the clusters and not their aggregation number. In this way hydrodynamic interactions within the clusters are simulated but not between clusters. Cluster reconstruction and movement steps are repeated consecutively. The step size has no influence on the results if it is chosen sufficiently small. The unit of time is the time needed for a free particle to diffuse over a distance equal to its diameter. This time is about one-half of a second for \( 1 \ \mu \text{m} \) particles in water at room temperature.

III. RESULTS

A. State diagram

The simulation led either to an equilibrium state consisting of transient randomly branched clusters that percolated at higher volume fractions or to phase separation into a phase with low density and a dense phase with crystalline order. The one phase equilibrium state has already been studied in\cite{23} and analytical calculation.\cite{24} The implication would be that

\[
P = 1 - \exp(u).
\]
course, whether the bonds are rigid or “slippery” does not matter for the equilibrium structure. However, crystallization was extremely slow when the bonds were rigid and in practice it was never observed in the simulations. Thus by imposing that the bonds are rigid the liquid-liquid phase separation can be studied.  

The liquid-crystal phase diagram is shown in Fig. 1. Close to the binodal, spontaneous crystallization became too slow, see below. Therefore the binodal was determined by decreasing $B_{att}$ until the crystal phase that was formed at higher $B_{att}$ melted. The difference in the $B_{att}$ values where we found slow growth of a crystal and slow melting of a crystal was small (smaller than 1). The binodal at high volume fractions was obtained by determining the density of the crystals at equilibrium from the pair correlation function, see below. The phase diagram is close to an experimental phase diagram obtained recently for spherical colloids with attraction in a range close to that used in the simulations.  

The binodal of the metastable liquid-liquid phase separation obtained for $\epsilon=0$ using Monte Carlo simulations is also shown. As mentioned above, if the interaction is expressed in terms of $B_{att}$ the liquid-liquid binodal depends only weakly on the interaction range when it is narrow. Results at a few volume fractions obtained from simulations using rigid bonds for $\epsilon=0.1$ (Ref. 21) are close to the binodal for $\epsilon=0$.

Theoretical phase diagrams for attractive spheres with short range interaction resemble the present simulation results. A quantitative comparison can be made for $\phi<0.4$ with the theoretical phase diagram presented by Dixit and Zukoski for hard spheres interacting with a square well potential with $\epsilon=0.1$. The theoretical binodals for liquid-crystal and metastable liquid-liquid phase separation are situated at somewhat lower values of $B_{att}$ than found in the simulations.

Weak attraction stabilizes the liquid at higher volume fractions and narrows the coexistence gap, see below. At stronger attraction a transition to a denser crystal structure occurs, which is discontinuous for very narrow interaction ranges. Stronger attraction destabilizes the liquid state at lower volume fractions and widens the coexistence gap. Over a broad range of volume fractions between 0.05 and 0.4 the phase boundary is situated at $B_{att} \approx 7$.

A transient percolating network is formed at higher volume fractions and stronger attraction, see Fig. 1. We need to distinguish between bond percolation of bound spheres and contact percolation of spheres that are within each others range but not necessarily bound. A network of spheres in contact can only resist mechanical stress due to jamming at high concentrations. At low concentrations only a network of bound spheres resists mechanical stress, at least for a time shorter than the bond lifetime. The percolation threshold was defined as the point where a cluster of bound spheres spans the simulation box. The exact position of the threshold was sensitive to the box size, but for the largest box size used here the error is relatively small. The bond percolation threshold is plotted in Fig. 1. Bond and contact percolation thresholds are almost the same for large $B_{att}$ where $P$ is close to unity, but contact percolation occurs even at $B_{att}=0$ for $\phi>0.30$, data not shown.

The combination of the bond percolation line and the binodal divides the phase diagram in four different domains. (I) At low $\phi$ and small $B_{att}$, the system contains a stable distribution of transient clusters; (II) at high $\phi$ and small $B_{att}$, the system contains a transient percolating network; (III) at low $\phi$ and large $B_{att}$, the system phase separates without percolating; (IV) at large $\phi$ and large $B_{att}$, the system percolates during the phase separation for a duration that increases with increasing $B_{att}$.

B. Crystallization at low volume fractions

The crystallization process was studied for different $\phi$ and $B_{att}$. Characteristic features of the process are illustrated in Fig. 2, which shows images of the crystalline phase at $\phi=0.08$ as a function of time for two different attraction strengths. The crystalline phase was defined as those particles that had 12 neighbors within the interaction range and their neighbors. At $B_{att}=12$ ($u=-2.3$), i.e., slightly below the metastable liquid-liquid binodal, only a few stable nuclei were formed after a relatively long lag time. Once formed, the nuclei grew rapidly into large more or less spherical crystals. At $B_{att}=100$ ($u=-4.3$), many nuclei were formed rapidly that grew more slowly and merged into branched crystal domains that percolated the space. Interestingly, for deep quenches initially many transient icosahedral agglomerates of 13 particles were formed.
There is a smooth transition between the formation of very few more or less spherical crystalline domains at weak attraction to the formation of a percolating network of crystal domains at strong attraction. Of course, the process always ends with a single crystal, but in practice this takes too long when the interaction is strong and cannot be observed in the simulations. Similar features also were reported for the metastable liquid-liquid transition. The two limiting phase separation pathways could be called nucleation and growth close to the binodal and spinodal decompositions for deep quenches, but it is clear that for all $B_{att}$ crystals nucleate and grow and that the difference is merely the amount of nuclei and the shape of the crystalline domains.

The fraction of the crystalline phase ($F_c$) at $\phi=0.08$ is plotted in Fig. 3(a) as a function of time for different $B_{att}$. The nucleation rate was very small close to the binodal of the metastable liquid-liquid phase separation ($B_{att}=9$) but once stable nuclei were formed the growth rate of the crystal phase was large. The nucleation rate increased rapidly with increasing $B_{att}$, but the growth rate of the nuclei decreased. The opposite effect of increasing nucleation rate and decreasing growth rate with increasing $B_{att}$ explains why the time dependencies of $F_c$ at different $B_{att}$ cross. We note that for irreversible aggregation ($B_{att}=\infty$) almost no particles with 12 neighbors were formed.

In Fig. 3(b) the average number of contacts per particle $\langle z \rangle$ is plotted as a function of time. $\langle z \rangle$ was averaged over all particles both in the liquid and the crystalline phase. It is related to the internal energy per particle as $u\langle z \rangle/2$. In all cases $\langle z \rangle$ increased initially because the particles aggregated. At $B_{att}=10$ ($u=-2.2$), the increase in $\langle z \rangle$ stopped when a steady state of transient clusters was reached. At this attraction strength crystallization was not observed until at least $t=10^3$. At $B_{att}=12$ ($u=-2.3$), $\langle z \rangle$ appeared to stagnate in a steady state of transient clusters but then increased again. This increase is due to liquid-liquid phase separation as was demonstrated using simulations of reversible aggregation with rigid bonds. At $t=700$ crystals nucleated in the metastable dense liquid domains leading to a sharp increase in $\langle z \rangle$, see also Fig. 2.

Initially, both the metastable liquid-liquid phase separation and the subsequent crystallization became faster with increasing $B_{att}$. However, when the attraction is very strong the lifetime of the bonds between the particles becomes long, which slows down the phase separation. For the largest interaction ($B_{att}=10^6$ or $u=-13.5$) investigated, $\langle z \rangle$ had the same evolution as for irreversible aggregation, while at $B_{att}=10^5$ ($u=-11.2$) only a weak deviation was found at long times.

We characterized the crystallization rate ($R$) as the inverse of the time needed to reach $F_c=0.1$. $R$ is plotted in Fig. 4 as a function of $B_{att}$ for two volume fractions: $\phi=0.08$ and $\phi=0.3$. Above the binodal of the metastable liquid-liquid phase separation the crystallization rate was immeasurably slow. With increasing $B_{att}$ the crystallization rate increased steeply to reach a maximum at $B_{att}=50$ ($u=-3.7$). Further increase in $B_{att}$ led to a gradual decrease in the crystallization rate due to increase in the bond lifetime.

The general features depend little on the precise definition of $R$, but the maximum shifts to smaller $B_{att}$ when it is taken at a larger $F_c$. Simulations at other volume fractions below $\phi<0.3$ showed that the crystallization rate always

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**FIG. 3.** Dependence on time (a) of the fraction of spheres with 12 neighbors including their neighbors and (b) of the average number of neighbors at different interaction strengths indicated in the figure.

**FIG. 4.** Dependence of the crystallization rate on the interaction strength at two volume fractions indicated in the figure. The solid line represents $R \propto B_{att}^{-0.4}$. 

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rapidly increased close to the metastable liquid-liquid binodal. The implication is that the formation of dense liquid domains is necessary for fast nucleation of crystals at lower volume fractions.

C. Structure

Elsewhere we have shown that irreversible aggregation with freely rotating bonds leads to the formation of a percolating network of branched strands that have a thickness of several particles. The local structure is tetrahedral since the spheres remain mobile until they are locked in by at least three bound neighbors. Local order extends to distances of a few particle diameters, but long range crystalline structure cannot be formed. On larger length scales the structure is self-similar with a fractal dimension $d_f=1.8$, i.e., equal to that found for diffusion limited cluster aggregation (DLCA) with rigid bonds. The self-similar structure extends to the correlation length beyond which the network is homogeneous. The correlation length decreases with increasing volume fraction and for $\phi>0.05$ it is less than ten particle diameters. During reversible aggregation the same structures were formed initially if the lifetime of the bonds was long, i.e., if $B_{att}$ was very large. At longer times crystallization occurred and more and more particles ordered into an fcc structure.

We will show here in more detail the evolution of the structure during crystallization for $\phi=0.08$ and $B_{att}=100$. This interaction strength is strong enough so that initially a percolating network is formed with a structure close to that obtained by irreversible DLCA. The evolution of $\langle z \rangle$ shown Fig. 3(b) is close to that of irreversible DLCA for $t<100$. However, this value of $B_{att}$ is weak enough so that significant crystallization can still be observed during the simulation. Images of the crystalline phase at different times are shown in Fig. 2. At $t=10$ most particles were already connected into a system spanning network, but only a few, mostly isolated, particles had 12 neighbors. At $t=100$ the crystalline phase had grown significantly and one observes thick strands of particles with 12 neighbors. With increasing time the crystalline phase grows and forms a system spanning network. We expect that after very long times the network will break up into large more or less spherical domains.

The evolution of the pair correlation function $g(r)$ is shown in Fig. 5(a). For comparison the results obtained for irreversible aggregation and the pure fcc crystal at equilibrium are shown in Fig. 5(b). At $t=100$, the network structure was almost completed and $g(r)$ resembled that of the irreversibly aggregated gel shown in Fig. 5(b). However, a significant fraction of crystals had also been formed, which caused the small peak at $r=1.5$ and the shoulder at $r=1.8$. With increasing time the fraction of the crystalline phase increased and as a consequence the fraction of spheres with tetrahedral order decreased. This explains the increase in the peak at $r=1.5$ and at $r=1.8$ at the detriment of the peak at $r=1.7$.

In the range $1.0<r<1.1$, $g(r)$ is determined by the number and the distribution of bond lengths (data not shown). We found that $g(r)$ was approximately constant in this range and increased progressively from 4 at $t=10$ to 7 at $t=7400$. After irreversible aggregation we found an excess of both stretched and compressed bonds. In the crystal, however, the bond length distribution was peaked at $r=1.05$.

The corresponding static structure factors are shown in Fig. 6. The oscillations at $q>7$ are caused by the bound nearest neighbors and are independent of the larger scale structure. The minimum at $q=4$, which reflects distances between next nearest neighbors, is initially close to that obtained after irreversible aggregation, but with increasing time it broadened due to crystallization. The upturn at the smallest $q$ values is caused by the increase in the size of dense crystal domains, which leads to an increase in the correlation length.

Similar features were also observed at other $\phi$ for relatively deep quenches. The larger is the value of $B_{att}$, the clearer one can distinguish the initial formation of the net-
work from the subsequent slow crystallization. Close to the metastable liquid-liquid binodal first dense liquid domains were formed in which subsequently the spheres crystallized.

D. Crystallization at high volume fractions

At higher volume fractions the smallest attraction where spontaneous crystallization could be observed during the simulation increased weakly with increasing $\phi$, e.g., for $\phi=0.49$ we found $R=5 \times 10^{-4}$ at $B_{att}=8$. Thus at large volume fractions liquid-liquid phase separation is no longer necessary for rapid crystallization. As mentioned in Sec. I, monodisperse hard spheres crystallize even in the absence of attraction for $\phi>0.49$. However, the crystallization rate was very small. Therefore the simulation at $B_{att}=0$ was started with a fcc crystal as the initial state. In this case equilibrium was reached relatively quickly. At $\phi=0.49$ the crystal melted completely. At larger $\phi$ a fraction of spheres in the crystalline state were stable in equilibrium with a liquid until for $\phi>0.54$ only crystal structure was observed. Systems with weak interaction were equilibrated either starting from the equilibrium state of noninteracting hard spheres or starting from the equilibrium state obtained with deep quenches.

Figure 7 compares the pair correlation functions of equilibrium states at $\phi=0.52$ and different interaction strengths. In the absence of attraction ($B_{att}=0$) or for very weak attraction ($B_{att}=0.5$, i.e., $u=-0.3$), the equilibrium crystal phase was characteristic of a mixture of hcp and fcc crystal phases. The position of the second peak at $r=1.57$ was consistent with a crystal density of 0.545. At $B_{att}=1$ the crystal melted and $g(r)$ of the equilibrium system was equal to that of a dense liquid showing the characteristic split of the second peak. At $B_{att}=1.5$ ($u=-0.8$) and lower, a purely fcc crystal phase was formed with a higher density $\phi=0.62$ in equilibrium with a low density liquid phase. The same equilibrium states were obtained when starting from the partially crystalline equilibrium states obtained without attraction ($B_{att}=0$) or with strong attraction ($B_{att}=10$, i.e., $u=-2.2$). This is illus-

FIG. 6. Static structure factors corresponding to the systems shown in Fig. 5(a) using the same symbols. The static structure factor of the DLCA gel is also shown for comparison (filled circles).

FIG. 8. Time dependence of $\langle z \rangle$ starting from equilibrium state at $B_{att}=0$ (square) or $B_{att}=10$ (circle) after quenching to $B_{att}=1$ at $\phi=0.52$.

FIG. 7. Pair correlation functions for $\phi=0.52$ at different $B_{att}$ as indicated in the figure. Curves are shifted along the $y$ axis for clarity.

FIG. 9. Pair correlation functions at $\phi=0.54$ at different $B_{att}$ as indicated in the figure. Curves are shifted along the $y$ axis for clarity.
treated in Fig. 8 where the average number of neighbors within the interaction range \(\langle z \rangle\) is plotted as a function of time.

At \(\phi=0.53\) and \(\phi=0.54\) coexistence between liquid and crystal was found at all \(B_{\text{att}}\). Figure 9 shows \(g(r)\) of equilibrated systems at \(\phi=0.54\) for different \(B_{\text{att}}\). The same equilibrium was reached starting from an equilibrium state at smaller or larger \(B_{\text{att}}\). The crystal phase in coexistence with the liquid was only very little influenced by attraction down to \(B_{\text{att}}=1.5\). However, the appearance of a shoulder at \(r=2.1\) indicated that somewhat more fcc compared to bcc structure was formed. A qualitative change occurred for \(B_{\text{att}}=2\) \((\mu=-0.9)\) where a purely fcc crystalline phase was obtained with a significantly higher density. The denser crystal is formed because internal energy is gained by forming a maximum of bonds. It has been called attractive crystal to distinguish it from the repulsive crystal formed with no or very weak attraction.\(^6\)

The evolution of \(\langle z \rangle\) with time at \(\phi=0.54\) is shown in Fig. 10 for different \(B_{\text{att}}\) starting from the equilibrium state without attraction that is almost fully crystalline. Up to \(B_{\text{att}}=1.5\), \(\langle z \rangle\) increased smoothly until it stabilized at a value that increased weakly with increasing \(B_{\text{att}}\). At \(B_{\text{att}}=2\), the evolution of \(\langle z \rangle\) was initially the same, but at a later time \(\langle z \rangle\) increased abruptly. At the same time a fraction of particles with 12 neighbors appeared that increased rapidly. It appears that the denser attractive crystal is formed by nucleation and growth in the less dense repulsive crystal. For larger \(B_{\text{att}}\), nucleation and growth of the dense crystal were faster. At \(\phi=0.55\) and \(\phi=0.60\) we found nucleation of the dense crystal even at \(B_{\text{att}}=1.5\) but not at \(B_{\text{att}}=1\) \((\mu=-0.6)\). It appears that \(B_{\text{att}}=1.5\) is very close to the critical value for attractive crystal formation when \(\epsilon=0.1\).

Figure 1 shows that the region where the crystal is completely melted by attraction covers only a relatively small range of densities \((0.49<\phi<0.53)\) and interaction strengths \((1.5>B_{\text{att}}>0)\). At \(B_{\text{att}}>1.5\) the density of the crystalline phase jumped to 0.62 as the attractive crystal was formed. Further increase in the attraction strength did not modify significantly the density of the crystals, but it led to a sharp decrease in the density of the liquid (gas) phase.

**IV. DISCUSSION**

A. Crystallization at high volume fractions

In the absence of attraction, spheres crystallize for \(\phi>0.495\). The rate of crystallization increases with increasing volume fraction until a maximum is reached at \(\phi=0.56\) beyond which it decreases.\(^{29–31}\) The decrease in the crystallization rate is caused by slowing down of the diffusion due to crowding. For colloidal particles the crystallization rate at higher volume fractions is even more slowed down by gravity.\(^{32}\)

We have found here that weak short range attraction stabilizes the liquid state at high densities so that the freezing line shifts to higher \(\phi\). The reason is that in the liquid more contacts are formed than in the repulsive crystal so that the internal energy decreases more by forming bonds in the liquid than in the crystal. This compensates for the lower entropy of the dense liquid compared to the crystal. The destabilizing effect extends down to \(B_{\text{att}}\approx 1.5\) for \(\epsilon=0.1\). In this range, the density of the liquid in the coexistence region increased to a value between 0.52 and 0.53, while the density of the crystal remained constant.

Stronger attraction induced the formation of denser attractive crystals in which each sphere formed 12 bonds which maximizes the internal energy. The density of the attractive crystal is thus determined by the interaction range and does not change when the well depth is further increased. For \(\epsilon=0.1\), the transition between the so-called repulsive and attractive crystals was sharp, but we did not observe coexistence of the two types of crystals which was predicted for even shorter interaction ranges.\(^{5,6}\) and found in simulations.\(^7\)

We may compare the BCD simulations at high volume fractions with Monte Carlo simulations by Bolhuis et al.\(^7\) These authors obtained the free energy of hard spheres with short range attraction assuming that the entropy was the same as that of noninteracting hard spheres and calculated the internal energy from the number of binary contacts obtained from their simulations. For the crystalline state they gave an analytical expression of \(\langle z \rangle\) as a function of \(\phi, \epsilon, \) and \(\mu\), which was in good agreement with results from our simulations. From the expressions of the free energy they calculated the liquid-crystal and the crystal-crystal coexistence curves. They showed that the critical point of the repulsive-attractive crystal phase separation was situated at the same well depth independent of the well width but shifted to lower densities with increasing well width. In terms of \(B_{\text{att}}\) the critical point decreased with increasing well width and would be situated at \(B_{\text{att}}\approx 3\) for \(\epsilon=0.1\). However, for \(\epsilon>0.06\) the repulsive-attractive crystal phase separation was found to be metastable with respect to the liquid-crystal phase separation.

The present simulations showed that the density of the crystals varied very little from that of noninteracting hard spheres down to about \(B_{\text{att}}=1.5\) but increased abruptly at larger \(B_{\text{att}}\). Thus we find that the coexistence density gap
narrors with increasing attraction up to $B_{att}=1.5$. Bolhuis et al.\textsuperscript{7} found that it broadened and the more so for larger interaction ranges. Only, for very narrow interaction ranges ($\varepsilon < 0.06$) did they find denser liquids for weak attraction. Since we find the same internal energy from the simulations as that used by Bolhuis et al. in their free energy calculations, the difference with the present simulation results has to be related to the effect of entropy. The origin of the discrepancy could be the approximation used in the free energy calculations that the entropy is not influenced by attraction.

### B. Crystallization at low volume fractions

The effect of short range attraction on crystallization of hard spheres at lower volume fractions has attracted much attention, in part for its relevance to protein crystallization where the aim is fast crystallization of large single crystals. In practice, useful crystallization was found only in a small domain of the $B_{att}$-$\phi$ phase diagram.\textsuperscript{33–35} In our simulations we found that the nucleation rate of crystals at low volume fractions sharply increased when metastable dense liquid domains were formed. This finding is in agreement with earlier computer simulations\textsuperscript{17} that showed that the formation of areas of high density liquid radically increased the crystal nucleation rate and that at lower concentrations liquid-liquid phase separation is a necessary precursor for crystallization. Lomakin et al.\textsuperscript{36} found in numerical simulations that the size of the liquid domains needs to exceed a critical value before crystallization occurred.

When the attraction was further increased, the nucleation rate kept increasing, but the rate of growth decreased due to increasing bond lifetime. The same effect had been noted earlier for liquid-liquid phase separation.\textsuperscript{21} Close to the liquid-liquid coexistence line, nucleation of dense liquid droplets was very slow, but their growth was rapid, while for strong attraction the nucleation rate was fast, but the growth was slow. The competition between the two effects leads to a maximum in the rate of both liquid-liquid and liquid-crystal phase separation as a function of $B_{att}$.

In experiments and in numerical simulations suspensions of attractive spheres appear arrested for the duration of the measurement if the attraction is strong. The arrested state is either a collection of clusters at low concentrations or a system spanning network at higher concentrations. In the former case one often observes a precipitate while in the latter case the system stops flowing. The transition to the apparently arrested state was found to occur over a relatively small range of the interaction strength.\textsuperscript{37–42} This can be understood from the fact that the bond lifetime increases exponentially with increasing attraction energy.

Two conditions are required to observe gelation: (1) the system needs to percolate and (2) the bond lifetime needs to be sufficiently long compared to the observation time. The first condition is met at the percolation threshold, i.e., at a critical value of $B_{att}$ for a given $\phi$ and at a critical $\phi$ for a given $B_{att}$. Whether the second condition is met at the percolation threshold depends on the lifetime of the bonds. The latter can be varied independently of $B_{att}$ by varying the rate of bond breaking and bond formation while keeping their ratio (and thus $B_{att}$) constant. If the bond lifetime is very long, gelation is observed at the percolation threshold. For reversible DLCA the bond lifetime is very short at the percolation threshold and gelation is observed only at significantly larger $B_{att}$.

The value of $B_{att}$ at the percolation threshold increases rapidly with decreasing $\phi$, see Fig. 1, and the percolation line crosses the liquid-crystal binodal at $\phi \approx 0.2$ for $\varepsilon = 0.1$. Therefore at lower volume fractions only temporary networks can be formed because coarsening leads to its breakup into two distinct phases. The rate of coarsening depends on the rate of bond breaking and formation. If the bond lifetime is long, initially the same network will be formed as during irreversible aggregation. The particles forming the network are locally ordered in tetrahedrons which gives rise to distinct peaks on $g(r)$.\textsuperscript{28}

Above the percolation threshold, crystallization necessarily starts on a percolating network. The crystals nucleate and grow on a preformed network of dense liquid, which explains why the crystal phase itself branches and even percolates, see Fig. 2. With increasing attraction the driving force to form a fcc phase increases. However, in order to form a fcc structure the tetrahedral structure needs to be broken, which becomes increasingly difficult as the bond lifetime increases. This explains the slowing down of crystal growth with increasing attraction.

We found that for large $B_{att}$, the crystallization rate decreased with increasing $B_{att}$ approximately following a power law. This is expected because the bond lifetime increases exponentially with increasing well depth: $B_{att} \approx \exp(-u)$ for $B_{att} \gg 1$. For the same reason the self-diffusion coefficient decreased in the homogeneous phase as a power law with increasing $B_{att}$.\textsuperscript{24} We expect that the rate of liquid-liquid phase separation if crystallization can be avoided (e.g., by polydispersity) also decreases as a power law with $B_{att}$.

The present simulation results may be compared with earlier Brownian dynamics simulations. Recently, Foffi et al.\textsuperscript{43} reported a detailed study of spheres with short range square well interaction using Brownian and Newtonian dynamics simulations. The spheres were polydisperse so that crystallization did not occur. They fixed $\varepsilon = 0.005$, but a comparison with the present simulations at $\varepsilon = 0.1$ can be made if we express the attraction in terms of the second virial coefficient. They studied the evolution of the system at different volume fractions for two very different interaction strengths: $B_{att} = 47$ ($u = -6.7$) and $B_{att} = 3 \times 10^7$ ($u = -20$). At $B_{att} = 47$ they observed phase separation while at $B_{att} = 3 \times 10^7$ they observed the formation of a percolating network of thick branched strands without further coarsening on the time scale of the simulation. The results obtained at $B_{att} = 3 \times 10^7$ were similar to those obtained for irreversible aggregation with freely rotating bonds.\textsuperscript{28} They and others\textsuperscript{6,34–47} suggested that there exists a well-defined finite critical attraction strength where dynamical arrest occurs due to glass formation of the dense liquid domains. However, it is clear from the present simulations that this is not the case. For strong attraction a well-defined percolating network is formed, but as long as $B_{att}$ is not infinite there is a finite possibility that particles break off and rearrange into the stable fcc phase.
With this remark we, of course, do not deny that the system may appear arrested for the duration of the experiment. All we are claiming is that the duration over which the system appears arrested increases continuously with increasing attraction.

Soga et al. simulated monodisperse spheres interacting with a short range depletion potential. This potential varies continuously with distance between the particles. The minimum of the interaction potential was at a distance less than 1.05 and the potential was cut off at 1.1 in order to have a well-defined bonds. The authors varied the strength at a fixed concentration $\phi=0.3$. The time dependence of $\langle z \rangle$ in these simulations was similar to that found in the present simulations. In particular, they also observed that the rapid increase in $\langle z \rangle$ caused by crystallization was preceded by a slow increase due to metastable liquid-liquid phase separation.

When the attraction was strong, Soga et al. also observed a rapid increase in $\langle z \rangle$ until it stagnated at a value of about 7 and the system appeared arrested. They noted that the slowing down of the crystallization rate with increasing attraction was gradual. The growth of the fraction of crystalline material defined in the same way as we did here was similar to that found with the present simulations. The pair correlation function of the arrested state was also similar to that shown here but contained a small peak at $r=1.4$ characteristic of the fcc structure. Contrary to the square well interaction studied here, the smooth depletion interaction potential used by Soga et al. allows for a small amount of crystallization even if the interaction is very strong, but these crystals did not grow.

Finally, we mention the theoretical analysis by Dixit and Zukoski of the competition between crystallization and amorphous aggregation for hard spheres interacting with a square well potential. The transition between the formation of large stable aggregates and large stable crystals derived by these authors for $\varepsilon=0.1$ is comparable to the percolation line found in the present simulations. However, in this work the authors did not consider that crystals may form slowly from large amorphous aggregates and gels as was observed by Kulkarni et al. Neither did they consider that metastable dense liquid domains can form from which the crystals can nucleate. Both phenomena were found to occur in the simulations presented here.

V. CONCLUSION

Nucleation of crystals at low volume fractions ($\phi<0.3$) speeds up dramatically by the formation of dense liquid domains below the binodal of the metastable liquid-liquid phase separation. Further increasing the attraction strength increases the nucleation rate but slows down the crystal growth. Therefore the rate with which a significant fraction of crystalline material is formed reaches a maximum. For large $B_m$, the crystallization rate decreases as a power law with increasing $B_m$ and thus exponentially with increasing interaction energy. There is no sign of critical dynamical arrest at a particular finite value of the interaction energy.

When the interaction is strong, crystallization occurs on a percolating network of bound particles leading to merging of the crystals into branched strands. Optimum crystallization requires fast growth of individual crystals. This can be best obtained in a small domain of the $\phi-B_m$ phase diagram situated between the metastable liquid-liquid coexistence curve and the percolation line.

At high volume fractions, weak attraction stabilizes the liquid phase and shifts the liquid-crystal coexistence line to slightly larger volume fractions. In the range $0.49<\phi<0.52$ crystals formed in hard sphere systems melt for weak attraction. At stronger attraction ($B_m>1.5$) a denser so-called attractive crystal is formed in equilibrium with a low density liquid.

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