Phase separation and percolation of reversibly aggregating spheres with a square-well attraction potential

Sujin Babu, Jean Christophe Gimel, and Taco Nicolai

Polymeres Colloides Interfaces, CNRS UMR 6120, Université du Maine, F-72085 Le Mans Cedex 9, France

(Received 30 June 2006; accepted 6 October 2006; published online 14 November 2006)

Reversible aggregation of spheres is simulated using a novel method in which clusters of bound spheres diffuse collectively with a diffusion coefficient proportional to their radius. It is shown that the equilibrium state is the same as with other simulation techniques, but with the present method more realistic kinetics are obtained. The behavior as a function of volume fraction and interaction strength was tested for two different attraction ranges. The binodal and the percolation threshold were determined. The cluster structure and size distribution close to the percolation threshold were found to be consistent with the percolation model. Close to the binodal phase separation occurred through the growth of spherical dense domains, while for deep quenches a system spanning network is formed that coarsens with a rate that decreases with increasing attraction. We found no indication for arrest of the coarsening.


I. INTRODUCTION

The structure of a wide range of complex liquids is determined by the aggregation of small particles such as colloids,1–4 protein,5–7 micelles,8,9 or oil droplets.10 Depending on the concentration, the range and strength of the attraction, stable cluster dispersions, transient gels, or phase separated systems can be formed. In order to better understand these processes computer simulations have been done of model systems.

When the attraction is infinitely strong, irreversible aggregation occurs, which in theory always leads to percolation in the thermodynamic limit; however small is the concentration. Of course, in practice gravity may cause precipitation in the thermodynamic limit; however small is the concentration. Of course, in practice gravity may cause precipitation before a space filling network is formed. Irreversible aggregation has been studied in detail using lattice and off-lattice numerical simulations.11–32 In the case of diffusion limited cluster aggregation (DLCA) particles form a bond with probability \( \alpha = 1 \) at each collision, while in the case of reaction limited cluster aggregation (RLCA) \( \alpha \rightarrow 0 \). Reversible aggregation has also been simulated by introducing a probability \( (\beta) \) that the bond breaks.32–45 In this way, systems in equilibrium are formed that are either a collection of transient clusters or a transient gel. The average probability that particles in contact are bound is \( P = \frac{\alpha}{\alpha + \beta} \).

Here, we present off-lattice numerical simulations of reversible aggregation of hard spheres with a finite interaction range. Rigid bonds are formed and broken with probabilities \( \alpha \) and \( \beta \) if the spheres are situated at a distance between 1 and \( 1 + \epsilon \) in units of the diameter of the spheres. The interaction is thus equivalent to that of hard spheres with a square-well potential with depth \( u \) in units of \( kT \) and width \( \epsilon \). Particles that are within the interaction range are able to move independently only when their bonds are broken, which occurs with probability

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

For square-well interactions it is straightforward to define bound particles as those that are at distances smaller than \( 1 + \epsilon \) from each other. In this way clusters can be defined as ensembles of bound particles. With increasing volume fraction or interaction energy the average cluster size increases. The percolation threshold is defined as the point where a cluster spans the whole volume and has been determined for a limited number of cases.46,47

For the case of reversible aggregation, particles are bound only with probability \( P \) if they are within each other’s interaction range. As a consequence there are two different ways to define clusters: either as collections of particles that are within the interaction range or as collections of bound particles. We will call percolation in the first case contact percolation and in the second case bond percolation. The situation is analogous to that of site-bond percolation on lattices. Obviously, contact percolation occurs at lower volume fractions and weaker interactions than bond percolation as was shown in Ref. 43 for lattice simulations.

The equilibrium properties of spheres with square-well interaction have been obtained using various simulation techniques for a range of widths.46–74 Phase separation is found if the attraction exceeds a critical value depending on the volume fraction \( (\phi) \) and \( \epsilon \). Coexistence curves have been determined for a number of well widths including the case \( \epsilon = 0 \) but with constant second virial coefficient \( (B_2) \),75,76 i.e., the Baxter model.75–83 The results are strongly dependent on \( \epsilon \), if expressed in terms of the interaction energy. However, they are close if expressed in terms of \( B_2 \). In fact, it turns out that the coexistence curves of any short range interaction potential are similar if expressed in terms of \( B_2 \).84,85

In this paper we will show that the simulation of reversible aggregation leads to the same equilibrium properties as obtained from Monte Carlo simulations, although not as efficiently. However, the method presented here allows one to...
study the development of the system. This is especially important for the detection of temporary gel formation during phase separation. The dynamics of spheres with a square-well interaction have been extensively investigated using molecular dynamics, but with this method the nondraining Brownian motion of the clusters is not correctly simulated. In addition, no distinction was made between contact and bond percolation.

The method employed here ensures that the diffusion coefficient of the clusters is inversely proportional to their radius. We have shown that this method leads to the correct aggregation kinetics for DLCA. As mentioned above we simulate the situation that the bonds are rigid so that bound particles cannot move relative to each other. We are currently working on a modification of the method in which the particles within the clusters are free to move as long as no bonds are broken, which is the case in most molecular dynamics simulations.

We have done a systematic study for systems with ε = 0.5 and 0.1. We will present the results in terms of the second virial coefficient normalized by the particle volume (B2), because, as mentioned above, the properties for different interaction ranges are close if the interaction is expressed in terms of B2. B2 is the sum of the excluded volume repulsion and the square-well attraction: 

\[ B_2 = B_{\text{rep}} - B_{\text{att}} \]

and \( B_{\text{att}} \) can be expressed in terms of \( P \) and \( \varepsilon \):

\[ B_{\text{att}} = \frac{4P}{1 - P} [(1 + \varepsilon)^3 - 1], \]

where we have used Eq. (1) to relate \( u \) and \( P \). We will discuss first the phase behavior and compare the binodal with Monte Carlo simulations reported in the literature. Then we will discuss contact and bond percolations. By an analysis of the structure and the size distribution of clusters we will show that they have the well-known properties of percolating clusters. As far as we know, an analysis of the cluster structure during reversible aggregation using off-lattice simulation has not been reported earlier. Elsewhere, we will discuss the pair correlation function, the static structure factor, and the dynamical properties. We have checked that the initial concentration dependence of the pressure and the susceptibility was consistent with the virial development using the analytical expressions for the second and third virial coefficients.

Recently, we reported a detailed study of the structure and size distribution of clusters formed by off-lattice reversible aggregation with zero interaction range. The differences with results obtained here for nonzero interaction range will be discussed.

II. SIMULATION METHOD

The simulations were done in a cubic box of size \( L \) with or without periodic boundary conditions. The unit of length is given by the diameter of the spheres. The starting configuration consists of \( N \) randomly positioned nonoverlapping spheres in a box with size \( L \) so that the volume fraction is \( \phi = (\pi/6)N/L^3 \). The starting configuration is obtained either by a random insertion procedure or by equilibrating an initially nonrandom distribution by repeatedly moving the spheres a distance \( s \) in a random direction. If the displacement of a particle leads to overlap it is truncated at contact. The average distance between centers of mass of nearest neighbors is defined as \( (1 + \Delta) \). In the initial state it is equal to the theoretical values obtained by Torquato as long as \( s \) is significantly smaller than \( \Delta \).

After the random starting configuration is reached, clusters are formed in a cluster formation procedure by creating bonds with probability \( P \) between spheres that are at a distance between 1 and \( 1 + \varepsilon \). Then, in a displacement procedure, clusters (including monomers) are chosen randomly and attempted to be moved with step size \( s \) in a random direction. It is important to choose small step sizes, because the kinetics of the aggregation process is influenced if \( s \) is larger than about \( \Delta/3 \). In addition, the pair correlation function of the systems is influenced by the use of a finite step size for distances between 1 and \( 1 + \varepsilon \). The displacement occurs with a probability inversely proportional to the radius of gyration of the cluster, which simulates Brownian motion for nondraining clusters. If the displacement of a cluster leads to overlap between two spheres (or the wall for fixed boundary conditions) it is truncated at contact. During a single displacement procedure each cluster is on average chosen once. Thus the monomers have on average moved a distance \( s \) and the clusters a distance \( s \) divided by their radius. After the displacement procedure the simulation time \( (t_{\text{sim}}) \) is incremented.

The physical time is defined as the time needed for an individual sphere to diffuse a distance equal to its diameter: \( t = s^2 t_{\text{sim}} \). For example, the time unit would be 0.4 s for spheres with a diameter of 1 \( \mu \text{m} \) in water at 20 °C. After the displacement procedure has been repeated \( n \) times the cluster formation procedure is run. Bonds are thus formed and broken with attempt frequency \( f = 1/(ns^2) \) in physical time units. Instead of forming bonds with probability \( P \) irrespective of history one can break existing bonds with probability \( \beta \) and make new bonds with probability \( \alpha \) during the cluster formation procedure. We have verified that this method gives the same equilibrium results if \( P/(1 - P) = \alpha/\beta \). Reducing the attempt frequency is equivalent to reducing both the bond formation and bond breaking probability by the same factor.

Figure 1 shows an example of the evolution of the average bond coordination number \( (z_b) \) of the particles for \( \phi = 2\% \), \( \varepsilon = 0.5 \), and \( B_{\text{att}} = 15 \) using different attempt frequencies. As expected, the same equilibrium state is reached independent of the attempt frequency, but the time to reach equilibrium increases if \( n \) is large. \( n = 1 \) corresponds to diffusion limited aggregation, while \( n \rightarrow \infty \) corresponds to reaction limited aggregation. Since the CPU time of the cluster formation procedure is longer than the displacement procedure it is favorable to increase \( n \). The kinetics in terms of the physical time will be influenced up to at least \( ns^2 \). In practice the gain of increasing \( n \) becomes negligible for \( n > 10 \) and we have used \( n = 10 \) in most of the simulations presented here.

For reversible aggregation with \( \varepsilon = 0 \) and finite step size it was shown that the equilibrium properties are not determined by the average lifetime of a bond, but by the average
The lifetime of an encounter between two spheres. The latter is longer than the former, because two spheres can have many correlated collisions. It was shown\(^\text{45}\) that the number of correlated collisions is inversely proportional to \(s\). The (physical) lifetime of an encounter is proportional to the number of correlated collisions and thus for a given attempt frequency it increases linearly with the step size.

For finite interaction ranges with \(s < \varepsilon\) the encounter lifetime is longer, because the spheres have to diffuse out of each other’s interaction range. Since the particles can only move if they are not bound the average diffusion coefficient within the well is multiplied by \((1 - P)\) compared to diffusion outside the well. The lifetime of an encounter is determined by the physical time it takes to diffuse out of the well, which becomes independent of the step size for \(s < \varepsilon\). We verified that the influence of the step size on the equilibrium results is negligible for \(s < \varepsilon/5\). In our simulations we have used step sizes that were smaller than \(\min(\Delta/3, \varepsilon/5)\). It is clear that very small step sizes need to be used at high concentrations or small interactions ranges, which limits the physical time that can be explored.

The effect of finite box size was studied and is negligible as long as the largest cluster in the box is smaller than \(L\). The results shown in this paper are not influenced by finite size effects unless specified explicitly. Both fixed and periodic boundary conditions have been used with the same results.

### III. RESULTS AND DISCUSSION

#### A. Phase behavior

Figure 2 shows the evolution of the average bond coordination number \(z_b\) for different values of \(B_{\text{att}}\) at \(\phi=2\%\) and \(\varepsilon=0.5\). For \(B_{\text{att}}\) smaller than about 16, \(z_b\) increases monotonically and then stabilizes when equilibrium is reached. For \(B_{\text{att}}\) larger than 16, however, \(z_b\) continues to increase and shows no sign of stabilizing within the duration of the simulation. The reason is that for \(B_{\text{att}}\) larger than 16 the system phase separates into a phase with low density (gas phase) and one with high density (dense phase). For \(B_{\text{att}} > 10^3\) the initial increase is close to that of irreversible aggregation \((B_{\text{att}}=\infty)\), but it deviates after a time that increases with increasing \(B_{\text{att}}\). A second metastable state is observed very close to the binodal, because a certain time is needed to create large enough nuclei to initiate growth of the dense phase.

Figure 3 shows images of the system during phase separation for two values of \(B_{\text{att}}\). Very close to the binodal \((B_{\text{att}}=17)\), phase separation occurs by the formation of a dense domain that grows with time. In order to observe the formation of the dense cluster more clearly in the sea of small clusters, we show only clusters containing more than 20 particles. It can be seen that most large clusters have an open ramified structure. Only when by chance one of these clusters obtains a denser structure does it serve as a seed for further growth. Clearly, for nucleating a dense liquid it is not enough that the cluster reaches a critical size, but in addition it needs to have a dense structure.

With increasing attraction the fractal clusters grow larger and the concentration of nuclei increases. The critical size of the nuclei is much smaller than the radius of the larger clusters. Therefore phase separation occurs as densification of fractal clusters, which is in competition with the growth of the clusters. The strands of the clusters thicken progressively and the clusters become progressively more spherical. Above a critical value of \(B_{\text{att}}\) a space filling ramified structure is formed that coarsens. The dense phase is initially a percolating structure of increasingly thicker strands in equilibrium with a gas phase of small clusters that retain their fractal structure. In the long run, coarsening leads to breakup of the system spanning structure. With increasing \(B_{\text{att}}\) the coarsening process slows down until in the limit of irreversible aggregation only the initial process of the formation of the percolating structure is observed.

Similar features have been shown and discussed earlier for lattice simulations.\(^{43}\) These characteristic features are generally called nucleation and growth, and spinodal decomposition, respectively. We stress, however, that there is no unambiguous signature to distinguish nucleation and growth from spinodal decomposition. We have not seen crystallization during the duration of the simulations, even though in
It was suggested that the absence of ripening for large $B_{\text{att}}$ was caused by glass formation of the dense phase.\textsuperscript{73,90} Clearly, glass formation will impede further densification so that the dense phase may not reach its equilibrium density. However, bulk vitrification does not stop coarsening through a process of evaporation and condensation, since the particles at the surface are not in the glassy state. In our view the coarsening is simply too slow at very large $B_{\text{att}}$ to be observed due to the very small probability to break bonds.

Just below the phase boundary $z_b$ levels off for some duration. The reason is that just below the phase boundary the system is metastable until a dense nucleus of sufficient size and density is formed by random fluctuations. The duration of the metastable state increases with decreasing $B_{\text{att}}$ and diverges at the binodal. As mentioned before, a second metastable state is observed for very large values of $B_{\text{att}}$ during which the coarsening of the network is not yet significant. The properties of this metastable state are the same as those obtained by irreversible aggregation. Only for these cases can cluster growth be distinguished in time from phase separation. At intermediate values of $B_{\text{att}}$ the two occur simultaneously.

One way to determine the binodal is to increase $B_{\text{att}}$ progressively until an upturn is observed for $z_b$ as a function of time. Obviously, the value of $B_{\text{att}}$ at the binodal will be overestimated in this way to an extent that depends on the total duration of the simulation. Alternatively, one can determine the value of $B_2$ at the binodal by decreasing $B_{\text{att}}$ starting from a phase separated system until the dense phase melts completely. Combining the two methods it can be verified that a system is in true equilibrium. In this way we found that the system at $B_{\text{att}}=15.8$ is, in fact, metastable, while the system at $B_{\text{att}}=15$ is stable, see Fig. 4. At $B_{\text{att}}=15.8$ the dense phase forms at larger $B_{\text{att}}$ initially evaporates partially, but some of it remains to serve as a nucleus for further long time growth. At $B_{\text{att}}=15$ the dense phase evaporates completely.

For a given value of $B_{\text{att}}$ in the two phase regime, one can estimate the densities of the two phases by measuring the local density distribution. This was done by placing randomly a sphere with diameter $D$ and counting the number of particles in this sphere. $D$ has to be chosen large enough so that the fluctuations within each phase are not too big, but significantly smaller than the domain size of the dense phase. We have found that $D$ between 5 and 6 constitutes a good compromise.

Figure 5 shows an example of the evolution of the density distribution during phase separation at $B_{\text{att}}=16$, $\phi=5\%$, and $e=0.5$. Initially, one observes broadening of the distribution and a shift of the peak position to smaller densities. After some time the position stabilizes and a separated peak representing the dense phase develops as the dense domains grow. The broad range of intermediate values between the two peaks is caused by the surface of the dense domains. The high density peak will continue to grow and become better separated from the low density peak as the coarsening process continues. After completion of the coarsening process the relative amplitudes of the peaks depend on the concentration, but their positions are the same for a given $B_{\text{att}}$. Unfortunately, since the simulation took already several weeks

![FIG. 3. Images of attractive spheres (\(\phi=2\%\), \(L=100\), and \(e=0.5\)) taken at different times indicated in the figure. For \(B_{\text{att}}=17\) (left panel) the phase separation occurs through nucleation and growth, while for \(B_{\text{att}}=40\) (right panel) a network structure is formed that coarsens. For clarity, only clusters containing more than 20 particles are shown for \(B_{\text{att}}=17\).](image-url)

some situations the crystal phase is most stable. The reason is that the pathway to create crystals is highly improbable when only rigid bonds are formed.

Very recently, molecular dynamics simulations of spheres with a very narrow square-well interaction ($e=0.005$) were reported.\textsuperscript{73} For a quench at $B_{\text{att}}=48$ they observed slow coarsening of the percolated structure similar to the results obtained here and the earlier lattice simulations. However, for a very deep quench of $B_{\text{att}}=2.9 \times 10^7$ they found no sign of ripening of the network within the duration of the simulations. This situation corresponds to the metastable state that is reached when the bond breaking probability is very low. The percolated structure obtained by molecular dynamics at very large $B_{\text{att}}$ shows thicker strands than obtained by the present simulation method and $z_b$ is larger. The reason is that with the former method particles can move freely within the interaction range without breaking bonds. With the present method the bonds are rigid so that even for relative movements within the interaction range bonds need to be broken.
it is not possible to extend it to much longer time with the current generation of computers. The peak position of the low density peak stabilizes relatively quickly, but for the high density peak long simulation times are needed to approach its equilibrium value.

Examples of density distributions at long times are shown in Fig. 6 at different values of $B_{att}$ for $/H9278=5\%$ and $/H9255=0.5$. In Fig. 6 the peak positions, but not their shapes, are close to equilibrium. In the one phase regime a single peak is observed that broadens with increasing $B_{att}$. For phase separated systems one observes two peaks representing the densities of the two phases.

Using a combination of methods we have estimated the binodal for $/H9255=0.5$ and $/H9255=0.1$, see Fig. 7. The results for $/H9255=0.5$ are compared with Monte Carlo simulations reported in the literature. The results obtained by the present simulation method are consistent with earlier results albeit not as accurate especially concerning the dense phase. However, the objective of the simulation method presented here was not to obtain an accurate description of the binodal, but to obtain realistic kinetics of the evolution of the system.
The average bond energy per particle, $E_B$, at different values of $\phi$ indicated in the figure for $\varepsilon=0.1$ (filled symbols) and $\varepsilon=0.5$ (open symbols). The solid lines represent $z_b = 2B_{att}$.  

Interestingly, the equilibrium values of $z_b$ in the one phase regime increase linearly with $B_{att}$ until the binodal is approached for $\phi<10\%$ or the percolation threshold for $\phi > 10\%$, see Fig. 8. The slope is proportional to the concentration and we find $z_b = 2B_{att}$ both for $\varepsilon=0.1$ and $\varepsilon=0.5$. $z_b$ is equal to the average contact coordination number ($z_c$) multiplied with the probability that a bond is formed: $z_b = Pz_c$. The average bond energy per particle ($E_B$) is $\nu$ times the number of contacts per particle, i.e., $E_B = 1/2z_c\nu$. Since $\nu = \ln(1-P)$ it follows that $E_B = 1/2z_b\ln(1-P)/P$. In the mean field approximation the decrease of the free energy per particle caused by bond formation may be written as $E_B = -B_{att}\phi$ if we consider only binary contacts. It follows that in this approximation $z_b = -2B_{att}\phi P/\ln(1-P)$, which is equal to $z_b = 2B_{att}\phi$ for small value of $P$ and thus small values of $B_{att}$. However, the latter relation is observed also for larger values of $P$. Apparently, the effect of finite $P$ is compensated by the loss of configurational entropy, which is ignored in the mean field approximation.

### B. Percolation

The percolation threshold was defined as the point where a system spanning cluster is first observed. It was reported earlier that the percolation threshold was not very sensitive to finite size effects for $L > 10$. Figure 9 shows an example of the probability to percolate as a function of $\phi$ for $B_{att}=10$ and $\varepsilon=0.5$. There is a small, but significant finite size effect even for $L > 10$. Finite size effects are perhaps not very important when determining the percolation threshold, but it is clear that for a proper analysis of the structure and the size distribution of the clusters, shown below, large box sizes are necessary. We have used $L=100$ for $\phi=10\%$ and $L=50$ for higher volume fractions.

In the two phase regime only the dense phase percolates at equilibrium, with the exception of a very small regime close to the critical point where both phases percolate, because the percolation line crosses the binodal below the critical concentration. However, as the system evolves starting from a random distribution, the whole system may percolate temporarily. An example of percolation during phase separation is shown in Fig. 3 for $B_{att}=40$. Breakup of the percolation due to coarsening was not yet observed during the simulation, but it has been shown to occur in lattice simulations of reversible aggregation.

Figure 10 shows that the percolation thresholds expressed in terms of $B_2 = 4 - B_{att}$ are close for $\varepsilon=0.5$ and 0.1. For $\phi<10\%$ the percolation is temporary since the system phase separates. Simulations of the Baxter model, i.e., $\varepsilon=0$ and $\nu=-\infty$, gave a percolation threshold at a slightly higher concentration for a given value of $B_2$. These results were,
however, obtained for very small box sizes ($L < 10$). Note that the adhesiveness parameter used in the Baxter model (written as $\tau$) is equal to $B_{att}^{-1}$. The results may also be compared with the percolation threshold of randomly distributed spheres, i.e., the system at the start of the simulation. This process is called static percolation in distinction with the present case where the particles diffuse that we call dynamic percolation. In Ref. 91 results were reported for static percolation of randomly distributed hard spheres with different interaction ranges. The percolation thresholds could be described analytically in terms of the free volume. The results are reproduced in Fig. 10 for $\varepsilon=0.5$ and 0.1 in terms of $B_2$. At high volume fractions the static percolation thresholds are very close to the ones for dynamic percolation implying that Brownian motion does not lead to strong modification of the relative positions of the particles and that the percolation process is essentially random distribution of bonds. The reason is that for high concentrations $\Delta < \varepsilon$ and the interaction range of the particles is already strongly overlapping at $t=0$. As a consequence, the percolation threshold becomes independent of $\varepsilon$ and depends only on $P$. Thus for large $\phi$ when $\Delta < \varepsilon$ the percolation threshold is not independent of $\varepsilon$ when expressed in terms of $B_2$ even for small $\varepsilon$. At low volume fractions the randomly distributed system cannot percolate even for $P=1$ ($B_2 \to -\infty$) and Brownian motion is necessary for percolation to occur.

So far we have considered bond percolation, but the same can be done for contact percolation. As mentioned above, for $\varepsilon \to 0$ contact and bond percolations are the same ($P \to 1$). The contact percolation thresholds for $\varepsilon=0.1$ and 0.5 are close to those obtained from Monte Carlo simulations. Contact percolation is obtained for smaller $B_{att}$ than bond percolation, see Fig. 10, but they become close at low concentrations for which $P$ approaches unity at the percolation threshold. For contact percolation attraction is not a necessary condition. Static contact percolation occurs even for randomly distributed hard spheres without attraction ($P=0$) for $\phi > 10\%$ at $\varepsilon=0.5$ and for $\phi > 28\%$ at $\varepsilon=0.1$.91

C. Cluster structure and size distribution

Figure 11 shows the dependence of the aggregation number $m$ on the radius of gyration $R_g$ for clusters formed at different concentrations indicated in the figure with $\varepsilon=0.1$ (top) or $\varepsilon=0.5$ (bottom). The solid lines in each figure have slopes of 2.5 and 2.6.

We have determined the number of clusters with aggregation number $m[N(m)]$ at equilibrium. $N(m)$ decreases with $m$ following a power law with a cutoff at a characteristic size $m^*$:

$$N(m) \propto m^{-\gamma}f(m/m^*) .$$

The cutoff function has the properties of becoming a constant for $m \ll m^*$ and decreases more rapidly than a power law for $m > m^*$. Figure 12 shows examples of $N(m)$ for different values of $B_{att}$ at $\phi=10\%$ and $\varepsilon=0.5$. Similar results are obtained for other volume fractions and for $\varepsilon=0.1$. $N(m)$ broadens with increasing $B_{att}$ until the system percolates and a space filling network is formed. If $B_{att}$ is further increased the cluster size distribution splits up between a gel and sol fraction. In the thermodynamic limit ($L \to \infty$) the molar mass of the percolating cluster diverges, but for finite box sizes it cannot exceed the total number of particles used in the simulation.

At the percolation threshold $N(m)$ is expected to follow a power law decay for large $m$: $N(m) \propto m^{-\tau}$. We find for all concentrations and both interaction ranges $\tau=2.15 \pm 0.05$, which is compatible with the percolation model.92

We have calculated the weight average aggregation number of the clusters as $m_w = \sum m^3 N(m)/N$. The dependence of $m_w$ on $B_{att}$ at equilibrium is shown in Fig. 13. In this representation the results for $\varepsilon=0.1$ and 0.5 are close. With in-
Increasing $B_{\text{att}}$, the size of equilibrium clusters grows and $m_w$ diverges at the percolation threshold. For volume fractions below approximately 10% the binodal is reached before the system percolates and the value of $m_w$ at the binodal decreases strongly with further decrease of the concentration. Beyond the percolation threshold the gel fraction increases and $m_w$ of the sol fraction decreases with increasing $B_{\text{att}}$.

Figure 14 shows that $m_w$ plotted as a function of $z_b$ is independent of $\phi$ and $\varepsilon$ for small $z_b$. We found the same initial dependence of $m_w$ on $z_b$ also for on-lattice simulations and off-lattice simulations with $\varepsilon=0$. The average number of bonds per particle at the percolation threshold is close to 2 at lower concentrations and decreases weakly with increasing $\phi$. If the aggregates contain no loops then $z_b=2(1-1/m_n)$, where $m_n$ is the number average aggregation number: $m_n=N/\Sigma N(m)$. The fraction of loops is calculated as $1-2(1-1/m_n)/z_b$. In the homogeneous regime it is less than 0.2 up to the percolation threshold. For the same $\phi$ and $B_{\text{att}}$ the fraction of loops is somewhat smaller when $\varepsilon=0.5$ than when $\varepsilon=0.1$.

D. Comparison with reversible aggregation with zero interaction range

Recently, we reported a detailed study of the structure and size distribution of clusters formed by off-lattice reversible aggregation with zero interaction range. These simulations are different from the Baxter model for which the interaction range also approaches zero, because the aggregation is kinetically driven and the bonds are rigid. The equilibrium properties of the system depend on the lifetime of an encounter between particles, which is a function both of $P$ and the attempt frequency to form and break bonds. Since the bonds are rigid the average coordination number $z_c$ is at most 2 so that there is no densification and phase separation. This means that, contrary to the present simulations, homogeneous systems containing large aggregates or a percolating network could be formed at equilibrium even at low volume fractions.

During the aggregation process up to the gel point, two regimes could be distinguished: the so-called flocculation regime when the clusters were on average well separated and the percolation regime close to the gel point when the clusters were highly interpenetrated. In both regimes large clusters had a self-similar structure and a power size distribution. In the percolation regime we found $d_f=2.7$ and $\tau=2.1$, while in the flocculation regime we found $d_f=2.0$ and $\tau=1.5$. The crossover between the two regimes occurs at characteristic aggregation number ($m_c$) that decreases with increasing volume fraction. The two different regimes were also observed for irreversible aggregation. For reversible aggregation with a finite interaction range, one cannot create stable systems with large clusters at small $\phi$. A percolated system is formed at equilibrium only for volume fractions above about 10% for which $m_c$ is small. Therefore the two regimes cannot be distinguished and essentially only the percolating clusters are observed.

IV. SUMMARY

Reversible aggregation with finite interaction range leads to four different situations depending on $B_2$ and $\phi$, see Fig. 15: (I) a homogeneous system containing transient clusters;
(II) a homogeneous system containing a transient percolating network together with clusters; (III) a phase separating system without formation of a temporarily percolating network; (IV) a phase separating system with formation of a temporarily percolating network. In addition to these domains the system may show transient contact percolation without bond percolation.

For given values of $B_2$ and $\phi$ the size of the equilibrium clusters is little dependent on the interaction range as long as the latter is smaller than the average distance between the random distributed spheres.

Close to the binodal, phase separation occurs through nucleation and growth of spherical dense domains. Systems that are quenched deeper in the two phase regime phase separate through coarsening of large fractal clusters or the percolated network. This ripening process leads finally to the breakup of the temporary network and the formation of spherical dense domains.

**ACKNOWLEDGMENTS**

We thank Dominique Durand for stimulating discussions. This work has been supported in part by a grant from the Marie Curie Program of the European Union numbered MRTN-CT-2003-504712.
86 T. Kihara, Rev. Mod. Phys. 25, 831 (1953).