Clustering of Binary Colloidal Suspensions: Theory

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Recent experiments on binary colloidal suspensions have shown that particles of the first kind (e.g., alumina) can be induced to flocculate by the presence of particles of the second kind (e.g., polyacrylate), within a certain range of the density of the second species of particles. This is similar to the depletion flocculation and depletion stabilization of polymer–colloidal systems. We have thoroughly examined the binary-particle systems with numerical simulations (Monte Carlo) as well as with analytical equilibrium calculations [cluster variation method (CVM)]. The simulations show a peak in the flocculation rate as the number density of the second species particles is varied, in agreement with the experiments. The CVM calculations show a monotonic increase in cluster size as the particle 2 density is increased. Moreover, the simulations show an aging phenomenon at high particle 2 densities, i.e., the growth of the cluster size in the initially restabilized region, which has also been well observed in the experiment. We further show from free energy calculations that the flocculated state, including the seemingly restabilized state at high particle 2 densities, is metastable and the underlying thermodynamically stable state is phase separation. Therefore, the restabilization at high particle 2 densities is due to kinetics, namely the slowdown in particle movements, but not to thermodynamic reasons. Our calculations together with the experiments on binary colloids may shed some light on the understanding of polymer–colloidal systems. © 1991 Academic Press, Inc.

INTRODUCTION

The stability of binary suspensions of alumina particles and polyacrylate particles has recently been examined (1). Polyacrylate particles are made of organic polymeric units and can remain dispersed up to high densities. When polyacrylate particles were added to an initially dispersed alumina-particle suspension, the alumina particles started to flocculate as the number density of polyacrylate particles was above some value \( c^* \). The flocculation rate increased until it reached the peak and then gradually decreased as the density of the polyacrylate particles was further increased. Finally, when the density of the polyacrylate particles was above some value \( c^{**} \), the suspension became dispersed again.

The phenomenon that occurred in the binary-particle systems is very similar to what has long been observed in polymer–particle systems (2). The initially stable colloidal suspension started to undergo flocculation upon the addition of polymers to the solution when the polymeric density was above some value \( c^* \) (depletion flocculation) and the flocculation rate of the colloidal particles peaked at some higher polymeric density \( c^{***} > c^* \). Further increase in the polymeric density from that point only decreased the flocculation rate and the suspension appeared stabilized again when the polymeric density was higher than some other value \( c^{**} > c^{***} \) (depletion stabilization).

There is another puzzle in the polymer–colloidal system parallel to the depletion flocculation phenomenon: while certain systems show depletion flocculation, others undergo depletion phase separation. The two seemingly very different phenomena show exactly the same trend as when the flocculation (or when the phase separation) will occur while
the polymeric molecular weight or density is varied.

There have been theoretical studies concerning the phenomena occurring in the polymer–colloidal systems. The more sophisticated studies were done by Feigin and Napper (3) and Fleer et al. (4). The theories behind these studies are based on the calculations of effective interparticle interactions due to the presence of the polymers. Feigin and Napper (3) suggested that an effective particle–particle repulsive barrier develops upon the addition of polymers and that the height of the barrier increases with increase in the polymeric density, leading to the restabilization of the colloidal particles at higher polymeric densities. On the other hand, Fleer et al. (4) showed that the effective interparticle interaction is attractive at any polymeric density and that the restabilization at higher polymeric densities is a purely thermodynamic effect; i.e., Fleer et al. (4) obtained equilibrium homogeneous mixtures at high densities and phase separation at the intermediate densities. These theories have limitations in treating polymers, even without the controversy. These authors treat the polymers as a medium which can spontaneously equilibrate itself in response to any change in the particle configuration, which is true only when the dimensions of the polymers are much smaller than those of the particles and when the polymer density is low. The treatment becomes invalid when the polymeric molecular weight and/or the density of the polymers increase so that the polymers can no longer adjust their positions fast enough (5).

The purpose of this paper is to present a thorough theoretical study for the stability of a binary-particle system concerning flocculation as well as phase separation (i) through extensive numerical simulations in which kinetic effects are implicitly taken into account, and (ii) through analytical equilibrium calculations. By comparing the simulations with the equilibrium calculations, we will be able to address the kinetic effect correctly.

The fact that the stable–flocculation–restabilization type of transition can occur in a particle–particle system indicates that this phenomenon is not unique to the polymer–particle systems. Therefore, the study of a particle–particle system may shed some light on the polymer–colloidal system.

For simplicity, we use a lattice model and assume nearest-neighbor interactions. We also assume that the interactions are density independent. In the simulations, we allow particles as well as clusters to perform Brownian motion (random walk from one lattice point to another). When two particles collide they form a larger cluster and diffuse as a whole. Furthermore, a particle can unbind from a cluster, leading to the breakup of a cluster. A single particle can be thought of as the smallest cluster. Whether two clusters will collide to form a larger cluster and whether a particle will unbind to break a cluster are determined by the Boltzmann factor $e^{-\Delta E/T}$, where $\Delta E$ is the energy change associated with the processes, $T$ is the room temperature, and the units are chosen such that the Boltzmann constant $k_B$ is unity. This will be simulated by the Monte Carlo method (6). For the analytic equilibrium calculations we used the cluster variation method (CVM) (7), which has been very successfully applied to various systems.

Under conditions similar to those of the experiments, the result of the simulations shows a maximum in the flocculation rate of the first species particles when the density of the second species particles is increased, in contrast to that obtained by the CVM method, where the cluster size increases monotonically. The slowing down in the flocculation rate of the first species particles at higher particle 2 densities is due to the hindrance in particle movements. Detailed free energy calculations show that the flocculated state, i.e., a mixture with particle 1 flocs distributed in a particle 2 dispersion, is a metastable one. That is, if the system can fully relax to its equilibrium, one should have phase separation into a particle 1-rich phase and a particle 2-rich phase, rather than flocculation. Whether one observes phase separation or flocculation is again determined
by kinetics. Thus, our study may not only help explain the stable–floculation–restabilization transition but also the puzzle concerning depletion phase separation and depletion floculation.

MODEL

For convenience, we only perform calculations on a two-dimensional square lattice. Consider a *mixture* of $N_1$ particles 1 and $N_2$ particles 2 placed in a square lattice of area $A$. The number density of particles 1 is $c_1 = N_1 / A$ and that of particles 2 is $c_2 = N_2 / A$. The total particle number density is $c = c_1 + c_2$. We will take the area of a unit cell to be unity. Thus, $c = 1$ represents the case where the lattice is fully occupied. An unoccupied site represents the solvent. For the interactions, we assume that only nearest neighbors have non-zero interactions.

Simulations

Initially, we randomly distributed the $N_1$ particles 1 and the $N_2$ particles 2 in an $M \times M$ lattice with periodic boundary conditions. The random distribution is to mimic the initial mixing in the experiments. The particles are then performing Brownian motion (random walk). A particle of the $i$th species moves one lattice constant after every $\tau_{D,i}$. However, the Brownian motion of a particle may be modified when the particle is in the vicinity of other particles. Such modification is incorporated into the simulations by the use of a Boltzmann factor. When a particle is attempting motion, the motion is achieved according to the probability $e^{-\Delta E / T}$, where $\Delta E$ again is the energy change due to the motion. When two particles are adjacent to each other in the model, they can form a cluster and diffuse as a whole. The mobility of a cluster is roughly assumed to be inversely proportional to its mass. Except for this difference, a cluster is treated in the same way as a particle: the clusters are also performing Brownian motion and the motion is also modified by the Boltzmann factor. When two clusters collide, they form a larger cluster. A particle within a cluster can also unbind from its neighbors by thermal motion due to the finite attraction energy, leading to the fragmentation of the cluster. The unbinding of an $i$th species particle takes place according to the rate $(1 / \tau_{R,i}) e^{-<\Delta E / T>}$, where $\Delta E$ again is the energy change associated with the process and $\tau_{R,i}$ is the time constant associated with the unbinding of the $i$th species particles. For the modification of the Brownian motion and the unbinding process, we use the Monte Carlo method (the Metropolis algorithm) (6). A more detailed description of the aggregation model is given in Ref. (8).

There are seven parameters in general in a binary aggregation model such as this, namely, the interactions $E_{11}$, $E_{12}$, and $E_{22}$, and the time constants $\tau_{D,1}$, $\tau_{D,2}$, $\tau_{R,1}$, and $\tau_{R,2}$. The parameter $\tau_{D,i}$, where $i = 1$ or 2, is related to the mobility of the particles while the parameter $\tau_{R,i}$ is the inverse of the unbinding attempt frequencies and is more related to the surface properties of the particles. In general, $\tau_{D,i}$ is different from $\tau_{R,i}$. The mobility of particles 1 can also be different from that of particles 2. Unless mentioned, in most simulations we use $\tau_{R,i} = \tau_{D,i} = \tau$. The choice of a different set of $\tau_{R,i}$ and $\tau_{D,i}$ will mainly affect the aggregation rate but not the qualitative behavior (8) and our choice for $\tau_{D,i}$ and $\tau_{R,i}$ in this paper is arbitrary. However, it is worth noting that a smaller value of $\tau_{D,i}$ may be interpreted as a larger particle mobility and a smaller $\tau_{R,i}$ as a larger relaxation rate. In the simulations, we monitor the cluster size of particles 1 as well as the effective mobility of all particles. The reported results are the average over 10 different runs for each case.

CVM Calculations

For comparison, we also estimate the cluster sizes of the particles 1 from the cluster variation method (CVM), which is known to be a reliable approximation for calculating quantities at equilibrium and has been successfully applied to many systems. Assuming the suspension to be a mixture again, to mimic the initial mixing in the experiments for a given
partial density $c_1 = N_1/A$ of particles 1 and $c_2 = N_2/A$ of particles 2, we calculate the pair probability $y_{ij}$ with the pair approximation within CVM (7), where $y_{ij}$ denotes the probability of finding the $i$th species particles to be neighbored by the $j$th species particles. The CVM we used is equivalent to the quasi-chemical approximation, which may be better known. It is a method of equilibrium statistical mechanics for treating cooperative phenomena of interacting particles. The state of the system is described by a number of the basic probability variables, $y_{ij}$'s in the present case. The free energy is approximately written in terms of $y_{ij}$'s, and their values for the equilibrium state are derived by minimizing the free energy. The key point of the CVM lies in the way the entropy, and hence the free energy, is written in terms of the basic variables. Usually the CVM ends here. The simulation we have constructed, which may be called CVM + S (for simulation), is an additional feature. After the $y_{ij}$'s for the equilibrium state have been determined, we can construct a simulation of the system, as was first proposed in Ref. (9), in such a way that the probability of $i$–$j$ pairs in the system is given by $y_{ij}$. Knowing the densities $c_i$ and the pair probability $y_{ij}$, we then simulate the configurations on the $120 \times 120$ lattice. The procedure we use here was well documented in Ref. (9) except that we did it slightly differently from Ref. (9). That is, instead of sweeping the lattice row by row, we pick a lattice point each time at random and fill it with either a particle 1 or a particle 2 or nothing (representing the solvent) under the constraints that the probability for having a particle of the $i$th species to occupy one site is equal to $c_i$ and for having the solvent $1 - c$ where $c = c_1 + c_2$. The average cluster size of the particles 1 is then counted. The reported result is the average over 10 samples, for each case.

It is worth repeating here that the mode in which the CVM is used in obtaining the results to be shown later (in Fig. 5) is quite different from the way the CVM is usually used. It is probably appropriate to call the present usage the CVM + S (for simulation).

RESULTS

Flocculation and Restabilization

In the experiments the first species always flocculates before the second species, indicating that the interaction between particles 1 is more attractive than that between particles 2 or that between particles 1 and particles 2. Since we are interested only in the qualitative behaviors, for convenience we choose $E_{11}$ to be attractive and $E_{12} = E_{22}$ to be repulsive. In the following, the energies will be expressed in units of the room temperature $T$.

As an example of how the aggregation of the first species particles changes with the density of the second species particles, in Fig. 1 we show the pictures of the systems taken at $t = 100\tau$ for three different particle 2 densities $c_2 = 0, 0.122$, and 0.245 with $c_1 = 0.245$ fixed. With the periodic boundary conditions, it is clearly shown that the largest cluster (the darkened circles) in the system is larger in the midparticle 2 density than in the other two cases. Note that in the $c_2 = 0$ case, particles 1 have already flocculated. In general, we could choose the energy parameters such that we have a finite value of $c^*$ above which particles 1 flocculate as in many experimental conditions. In that case, we must go to higher densities to study the flocculation-restabilization transitions. For the computational ease, we choose the parameters such that we can focus on the flocculation-restabilization transitions at the manageable densities. To give more quantitative results, we plot the average excess cluster size $\Delta N$ of particles 1 as a function of particle 2 densities for three different particle 1 densities $c_1 = 0.122, 0.184$, and 0.245 in Fig. 2 where the excess cluster size $\Delta N$ denotes the difference in the cluster size $N$ for $c_2 \neq 0$ and for $c_2 = 0$. The calculations were performed for $E_{11} = -1$ and $E_{12} = E_{22} = 8$ on a $35 \times 35$ lattice. The cluster size was measured at $t = 300\tau$. In Fig. 2, it is clearly shown that there
is a peak in the $\Delta N$ versus $c_2$ plot for all cases. Note that the peak shifts to a lower value of $c_2$ when $c_1$ is increased. If one takes the value of $c_2$ at which the cluster size equals that at $c_2 = 0$ as the restabilization density $c^{**}$, one can also see that the value of $c^{**}$ decreases as $c_1$ is increased. These results agree with the experiments in a binary-particle system (1) and also with those in polymer-colloidal systems (2).

In Fig. 3, we plot the cluster size $N$ versus $c_2$ for different values of $E_{12} = E_{22}$ where $E_{11} = -1$ and $c_1 = 0.25$. The results were taken from calculations in a $20 \times 20$ lattice and at $t = 400r$. It is clearly shown that the peak shifts to lower values of $c_2$ when the value of $E_{12} = E_{22}$ is increased. To show the time dependence of the $N$ versus $c_2$ curve, we plot in Fig. 4a for $c_1 = 0.25$, $E_{11} = -1$, $E_{12} = E_{22} = 3$ at different times $t = 100r$, $400r$, and $1000r$. The calculations were done on a $20 \times 20$ lattice. For all cases, the curve shows a peak and the peak of the curve shifts to a higher value of $c_2$ at a later time. Note that at higher values of $c_2 > 0.2$, the initially small clusters grow with time. This kind of aging behavior has also been observed experimentally (1). Also shown in Fig. 4b is the effective particle mobility $\mu_{\text{eff}}$ versus $c_2$ for the same system as in Fig. 4a at

FIG. 1. Monte Carlo simulations at different densities of particle 2 (with periodic boundary conditions). $O$, a particle 1; $X$, a particle 2. The darkened circles denote the largest cluster in the system. (a) $c_2 = 0$, (b) $c_2 = 0.122$, and (c) $c_2 = 0.245$. In all three cases, $c_1 = 0.245$, $t = 100r$, $E_{11} = -1$, $E_{12} = E_{22} = 3$. Note that particles 2 remain dispersed while particles 1 are undergoing clustering and that the largest cluster size in (b) is larger than those in (a) and (c).

FIG. 2. Excess cluster size $\Delta N$ as a function of particle 2 density $c_2$, where $E_{11} = -1$, $E_{12} = E_{22} = 8$, and $t = 300r$. Note that there is a peak in $\Delta N$ for all cases. When $c_1$ is increased, the peak shifts to a low $c_2$ value.
FIG. 3. Average cluster size $N$ versus particle 2 density $c_2$ at different values of $E_{12}$ and $E_{22}$, where $E_{11} = -1$, $c_1 = 0.25$, and $t = 400\tau$. Note that the peak shifts to low values of $c_2$ as $E_{12} = E_{22}$ is increased.

$t = 100\tau$, where $\mu_{\text{eff}}$ is defined as the average number of movements made per particle within a time interval $\Delta t = 2\tau$. One can see that as $c_2$ increases, the movement of a particle becomes more and more hindered. As a result, the effective mobility decreases. Thus, Fig. 4 together indicates that the decrease in cluster size and the restabilization at high $c_2$ is a kinetic effect and hence cannot be predicted by equilibrium calculations. For instance, if one waits long enough, one should always see that the curve $N$ versus $c_2$ is going upward and should not bend over as it does at an earlier time. In Fig. 5, we plot the cluster size $N$ versus $c_2$ for $E_{11} = -1$, $E_{12} = E_{22} = 8$, and $c_1 = 0.245$. The solid lines represent the simulation results obtained in a $35 \times 35$ lattice at $t = 300\tau$. The symbol $\square$ represents $\tau_R/\tau_D = 0.5$ and $\bigcirc$ represents $\tau_R/\tau_D = 1$ where we assume $\tau_{R,1} = \tau_{R,2} = \tau_R$, $\tau_{D,1} = \tau_{D,2} = \tau_D$. The case $\tau_R/\tau_D = 0.5$ represents a slower aggregation rate and thus results in smaller cluster sizes than $\tau_R/\tau_D = 1$. Note that the peak of the curve shifts to a larger value of $c_2$ when the relaxation is more sufficient. Comparing the curve $\square$ with the CVM + S result, which represents the fully relaxed mixture state and is represented by the dashed line ($\bullet--\bullet$), one sees that at low $c_2$, the two curves overlap; at high $c_2$, the $\square$ curve bends over while the CVM + S does not and the discrepancy between the two curves widens. However, the fully relaxed mixture may not be the equilibrium state; phase separation may give a lower free energy. This will become clear in the following discussion.

Finally, since many of our results are obtained with simulations on a $20 \times 20$ lattice, which is a fairly small system, one might suspect the applicability of the numerical results to the real system, which typically contains $10^{15}$ particles/cm$^3$. To show the lattice size effect, we plot in Fig. 6 two curves of $N$ versus $c_2$ at different times where $c_1 = 0.25$, $E_{11} = -1$, and $E_{12} = E_{22} = 3$. Note that the cluster size increases with time and that the peak shifts to a higher value of $c_2$ at a later time. (b) Effective particle mobility $\mu_{\text{eff}}$ at $t = 100\tau$ is plotted versus $c_2$. Note that $\mu_{\text{eff}}$ decreases with increasing $c_2$. The smaller $\mu_{\text{eff}}$ at high $c_2$ is responsible for the decrease in flocculation rate.
What Is the True Stable State?

While we have successfully shown from our calculations that the slowdown of the flocculation rate at high values of \( c_2 \) is due to a kinetic effect, a more subtle question arises: What is the true equilibrium stable state of the system where this kind of flocculation-restabilization can occur? Should the stable state be phase separation into two regions, one of which is rich in particles 1 and the other rich in particles 2 separated by a distinct interface or a mixture with particle 1 clusters distributed in it as indicated by the CVM + S clustering results? To answer this question, we calculate the free energy of the system under the conditions we used for Fig. 5, namely, \( E_{11} = -1, E_{12} = E_{22} = 3 \). For each value of the total particle density \( c \), which is the sum of \( c_1 \) and \( c_2 \), we calculate the free energy of the system for all possible concentrations (from pure particle 1 solution to pure particle 2 solution at constant \( c \)). We find that for the density range used in Fig. 5, the underlying equilibrium state should always be phase separation. A typical example is shown in Fig. 7 where we plot the excess free energy \( \Delta F \) versus \( x \) for \( c = 0.25 \), where \( x \) is the concentration of particles 2 and \( \Delta F \) is defined as

\[
\Delta F = f(x) - (f(x_1) + f(x_2))\]

where \( f(x_1) \) and \( f(x_2) \) are the free energies of pure particle 1 and 2 solutions, respectively.
\[ \Delta F = F(x) - xF(x = 1) - (1 - x)F(x = 0), \]

where \( F \) denotes the Helmholtz free energy calculated from CVM with pair approximation. One can see from Fig. 7 that the excess free energy is always positive; therefore, the system should separate into two phases, one of which is rich in particles 1 and the other in particles 2, to lower the free energy. We should mention that the reason that \( \Delta F \) is always positive in Fig. 7 is that the parameters used in Fig. 7 correspond to a very low temperature case. Thus, we can conclude that the flocculated state (including the seemingly stable state at high densities) is really a result of a kinetic effect and is metastable. The underlying stable state is phase separation. This may help explain the puzzling similarity in the trends toward phase separation and toward depletion flocculation in the polymer-colloidal systems. Moreover, the aging phenomenon observed in the binary colloidal systems at high polyacrylate particle densities indicates that the restabilization at high densities is due to kinetics but not thermodynamics.

CONCLUDING REMARKS

We have studied the flocculation of a binary colloidal system thoroughly by extensive numerical simulations as well as by analytical equilibrium calculations. In particular, we have shown that even with density-independent interparticle interactions, we can still have a peak in the flocculation rate of particles 1 with respect to particle 2 densities, i.e., the seeming restabilization of particles 1 at high particle 2 densities. We have shown from detailed free energy calculations that the flocculated state (including the seemingly restabilized state at high densities) is actually metastable for the energy parameters we chose. The underlying stable state should be phase separation. The restabilization is attributed to kinetics, i.e., the slowing down in the particle movement at high densities, but not to thermodynamics. This turned out to be the case for binary-particle systems where the aging phenomenon, the growth of the cluster size with time in the initially restabilized region, as predicted by the simulations, has been well observed. It should be noted that we use the term kinetics differently than do Feigin and Napper (3). In the Feigin and Napper interpretation of the kinetic effect, there will be a repulsive barrier in the interparticle interaction due to the presence of the polymeric species and this barrier grows higher with increasing polymeric densities, which eventually will keep the particles from coming to the primary minimum at high enough polymeric densities. To check experimentally whether the polymer-particle system restabilization at high polymer concentrations is due to the slowing of particle movement as in the binary-particle system, one can either examine whether there is an aging effect at high polymer concentrations or directly look at the particle mobility at different polymer concentrations with ultracentrifuge experiments, as in Ref. (10). In Ref. (10), it has already been reported that the sedimentation rate of Ludox particles can be 20 times smaller in 1% polyethylene oxide solution than in water, while the overall viscosity of the 1% polyethylene oxide solution is only 2.4 times that of water. What happens is that the polymers in solution overlap at very low density and form a transient network which traps the particles. The other way of testing this concept is to look at the movements of the particles directly under an optical microscope when the particles are in the submicrometer range. If the restabilization at high polymeric densities is due to the repulsive barrier as Feigin and Napper showed or due to thermodynamics as shown by Fleer et al., one would see that a particle wanders around freely. On the other hand, if the restabilization is due to the slowing of particle movement, one would see that a particle moves as if it is enclosed in a cage. Within the cage, the particle may wander around freely. These invisible edges are formed by the polymers in solution. Finally, our results may also help explain the puzzling similarity in the trends toward phase separation.
and toward depletion flocculation in the polymer–colloidal systems since we have shown that the underlying equilibrium state of a flocculated system is phase separation.

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