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Frequency dependence of aggregation in two-dimensional colloidal systems

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A systematic study has been carried out on the electric-field-induced aggregation in two-dimensional colloidal polystyrene systems. The kinetics of aggregation is investigated by means of an *in situ* observation technique. We found that our results can be explained by a theoretical model that takes into account the frequency-dependent interaction between colloidal spheres. This is demonstrated by Monte Carlo simulations of the model; the simulation results are in general agreement with the experimental results.

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Aggregation phenomena exist in many scientific fields [1]. The introduction of the concept of fractal and the general scaling theory of critical phenomena [2] has led to enormous progress in describing and understanding two fundamental aspects of aggregation: the static structure of the aggregates and their evolution. To date, there are mainly two types of colloidal systems that have been employed to study two-dimensional aggregation. One system is charge-stabilized colloidal particles dispersed at a liquid surface; in this system aggregation is induced by adding electrolyte to the liquid [3–10]. The other system is a two-dimensional suspension subjected to an external alternating electric field; in this case aggregation is induced by the ac field [11–13]. For both types of systems, the observed aggregates have traditionally been attributed to cluster-cluster aggregation (CCA). In fact, CCA is the model of cluster growth by diffusion-limited aggregation of clusters [14]. Theoretical studies addressing some observations have neglected the specificity of the interaction between colloidal particles [15,16]. In addition, a morphological difference between the aggregates induced by adding electrolyte to the liquid (electrolyte system) [8] and the aggregates induced by ac field (ac-field system) [13] is apparent to the naked eye. Fractal-like patterns have frequently been observed in electrolyte systems, but only compact clusters have been observed in two-dimensional ac-field systems. It is understood that electrolyte systems involve colloidal particles with like charges that repel each other through Coulomb interaction screened by ions in the background medium, and particles can be trapped at a liquid surface by surface tension and electrostatic forces. Adding electrolyte reduces the repulsive force, and allows the particles to approach sufficiently close so that the van der Waals attraction can cause adhesion. In such circumstances CCA would be expected. But for ac-field systems, the underlying physical reason for the aggregation and the aggregation dependence on the ac field have so far not been explored.

In this paper, the idea of a characteristic frequency dependence of fluctuating dipole-dipole interaction is proposed. The dependence of the aggregation on the field frequency and strength is studied. Furthermore, our results suggest that the aggregates are formed via a nucleation-growth process, i.e., nucleation-limited aggregation (NLA). Below we present first our experimental results, followed by a semiquantitative analysis and kinetic Monte Carlo simulations. Finally, a discussion is given on the experimental and simulation results.

The polystyrene latex spheres of ~ 1 μm diameter, which we used in our experiments, are synthesized by the emulsion polymerization method. The polydispersity is better than 4%. The latex spheres are confined between two parallel glass slides. The slides are coated with conducting material through which an external alternating electric field is applied. The field is perpendicular to the colloidal suspension film. The film thickness 50 μm is controlled by two mylar spacers placed between the two slides. The particle number density (the number per unit area) is measured to be 0.24. The aggregation process is observed *in situ* through an optical microscope equipped with a video system for image processing.

Direct observations in our experiments show that the spheres sink to the bottom surface of the cell under the gravity because the density of polystyrene is slightly higher than that of water. The colloidal suspension is generally stable and no clusters exist without external electric field due to the screened Coulomb repulsion between spheres. When the external ac field is turned on, the spheres are attracted swiftly to the bottom surface where they aggregate and can diffuse freely in the plane parallel to the cell surface. But the motion in the direction perpendicular to the surface is restricted. This indicates that our system is two dimensional in nature. The external ac field induces an interaction between the colloidal spheres, leading to movements and flocculation of spheres. In our experiments, the results depend strongly on the frequency of the ac field. It has been observed that a repulsive force is induced between spheres when the frequency ω is higher than 1 kHz. In case of $\omega > 1$ kHz, aggregation does not occur. If $\omega < 400$ Hz, we do not

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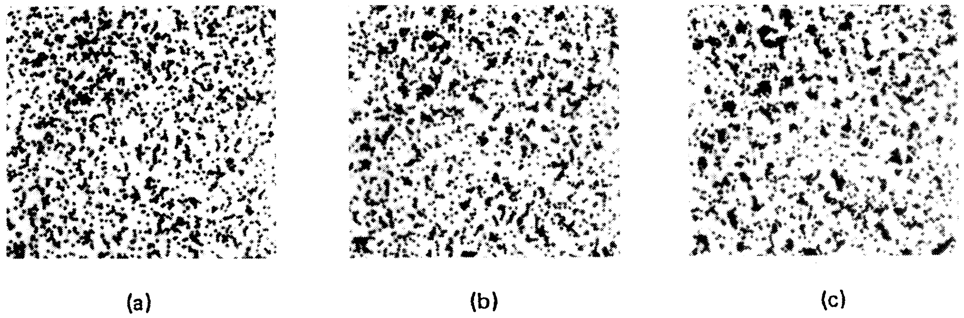


FIG. 1. Snapshots to show temporal evolution of clusters during the course of two-dimensional colloidal aggregation induced by the ac field. Experimental conditions: $\omega = 600$ Hz, $E = 2.0$ V/50 μm. (a) $t = 0$ sec, (b) $t = 20$ sec, (c) $t = 40$ sec.

observe any aggregation phenomenon. The aggregation process is apparent and proceeds rapidly when ω is about 600 Hz. So, in our experiments, the frequency is fixed at 600 Hz.

The typical temporal evolution of clusters during the course of the two-dimensional aggregation is shown in Figs. 1(a)–1(c). Initially, the colloidal spheres are randomly distributed above the surface [see Fig. 1(a)], and undergo Brownian motion. Once the external ac field is applied, the aggregation occurs. Many small clusters are formed as shown in Fig. 1(b). During the course of aggregation, some depletion regions are gradually developed around some clusters. The inner clusters are static afterwards and may be called *nuclei*. The nuclei grow by consuming monomers between them. Monomers within a nucleus may undergo significant local edge diffusion (rearrangement). Clusters are all finite and compact [see Fig. 1(c)].

We obtain the growth of weight-averaged cluster size $S(t)$ with time, defined as $S(t) = [\sum_s S^2 N_s(t)]/[\sum_s S N_s(t)]$, where $N_s(t)$ is the number of clusters of size S at time t. In Fig. 2(a), we show the plot of $S(t)$ for an ac-field strength $E = 2.0$ V/50 μm; its essential feature is the positive and increasing slope in the early stage of aggregation. In the late stage, it becomes a monotonic rising curve. In Fig. 2(b), the plot corresponds to $E = 2.5$ V/50 μm, in which case the slope of $S(t)$ versus t decreases with time. Cluster size distributions are shown in Figs. 3(a) and 3(b) corresponding to 2.0 V/50 μm and 2.5 V/50 μm, respectively.

A detailed understanding of cluster formation in colloidal aggregation, which allows predictions not only of the aggregation kinetics but also the nonequilibrium morphologies, requires the study of the interaction between colloidal spheres.

The electric double layer on the surface of the particle plays a primary role in many colloidal phenomena. The applied alternating electric field induces a dynamic polarization in the colloidal particle [17]. Due to the mismatch of the dielectric constants of the disperse (particles) and continuum (water) phases, the colloidal particles can be described as hard spheres having each a fluctuating dipole bound to its center, the Drude model. The dynamic dipolar moment of an isolated Drude sphere is given by

$$\vec{P} = \alpha(\omega)\vec{E}_{\text{loc}}, \qquad (1)$$

where $\vec{E}_{\text{loc}}$ is the local electric field of the particle induced by the external alternating electric field $\vec{E}$, $\vec{E}_{\text{loc}} = (\epsilon_{\text{H}_2\text{O}}/\epsilon_S)\vec{E}$, where $\epsilon_{\text{H}_2\text{O}}$ and ϵ_S are, respectively, the dielectric constants of pure water and the sphere [9], $\alpha(\omega)$ is the polarizability of the Drude sphere

$$\alpha(\omega) = \frac{\alpha_0}{1 - (\omega/\omega_0)^2}, \qquad (2)$$

and α_0 and ω_0 are the static polarizability and the characteristic frequency of the Drude sphere, respectively. The long-range dipole-dipole interaction between two dipolar hard spheres can be adequately treated to first

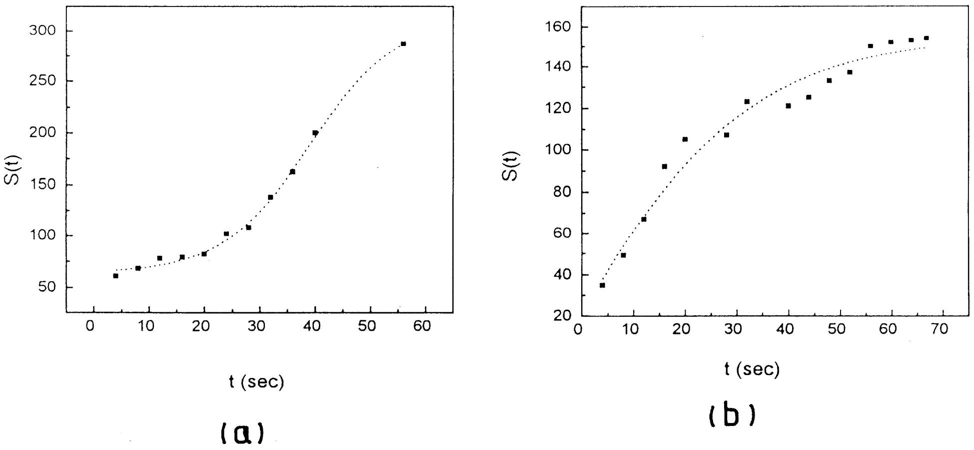


FIG. 2. Experimental data of weight-averaged cluster size as a function of time. (a) $\omega = 600$ Hz, $E = 2.0$ V/50 μm, (b) $\omega = 600$ Hz, $E = 2.5$ V/50 μm.

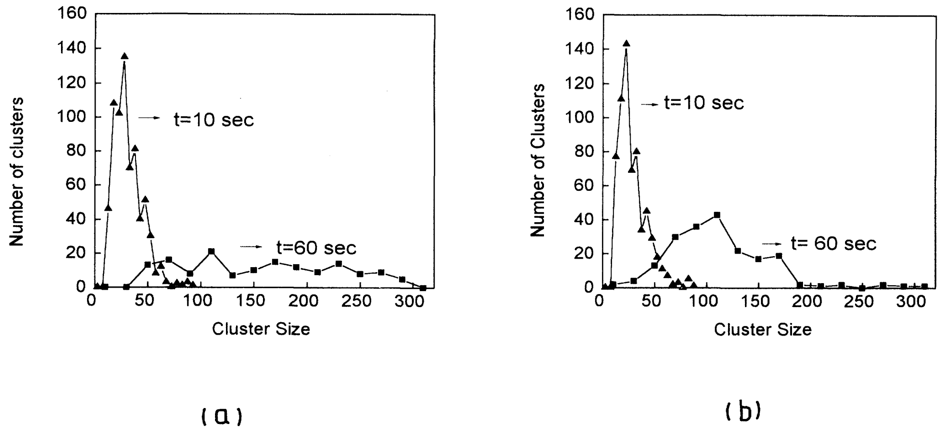


FIG. 3. The evolution of the cluster size distribution measured at different times. Typically 200–600 clusters were collected into 20 bins spanning the interval [size$_{\mathrm{min}}$, size$_{\mathrm{max}}$].

order by the dipolar interaction.

$$U_{ij} = \frac{\vec{P}_i \cdot \vec{P}_j}{a^3}. \tag{3}$$

For simplicity, the frequency ω and strength of the external alternating electric field E are fixed.

Because of the difference in surface chemistry among the colloidal particles, the characteristic frequencies of the colloidal particles have a distribution. We denote the characteristic frequencies of sphere i and sphere j by ω_{0i} and ω_{0j}, respectively. If both ω_{0i} and ω_{0j} are larger or smaller than ω, according to Eq. (2), $\vec{P}_i$ and $\vec{P}_j$ are parallel, $U_{ij} > 0$, and the interaction between sphere i and sphere j is therefore repulsive. If the values of ω_{0i} and ω_{0j} are separated by ω ($\omega_{0i} < \omega$, $\omega_{0j} \geq \omega$; or $\omega_{0i} \geq \omega$, $\omega_{0j} < \omega$), the interaction is attractive. This attractive force drives two-dimensional aggregation. The property of the interaction between two spheres is determined by their characteristic frequencies. From this point of view, we call it a characteristic frequency-dependent interaction. Clearly, there is an electric interaction between the sphere and its image due to the presence of the planar conductive slide. When the spheres are not too close to the slide, the interaction may be approximated by a dipole-dipole interaction $W = -2P^2/(2h)^3$, in which $\vec{P}$ is the dipolar moment and h is the distance from the center of the sphere to the conductive plane.

The interaction energy between two spheres may easily be compared with the thermal energy kT. When $\omega = 0$, U or $W \sim kT$ [9]. According to the theory [17], ω_0 is around several hundred Hz if the diameter of colloidal spheres is about 1 μm. According to our experimental observations, the characteristic frequencies have a distribution around 600 Hz. As we mentioned before, polarizability comes from the double layer around the particles, which is a volume phenomenon. Note that latex particles have a polydispersity of 4%. This would imply a nearly 10% fluctuation in their volume and consequently in their values of ω_0. We assume ω_0 is spread in the range from 500 Hz to 700 Hz randomly, if ω is fixed at 600 Hz, U or W is about $kT \sim 50kT$ depending on the ratio of ω/ω_0. There are disturbances caused by the particles as they move through the fluid. Based on the results of Thomson and Tait [18], one can estimate the order of this hydrodynamic interaction to be about 10^{-17} erg in a system like ours. This is much smaller than kT and is negligible.

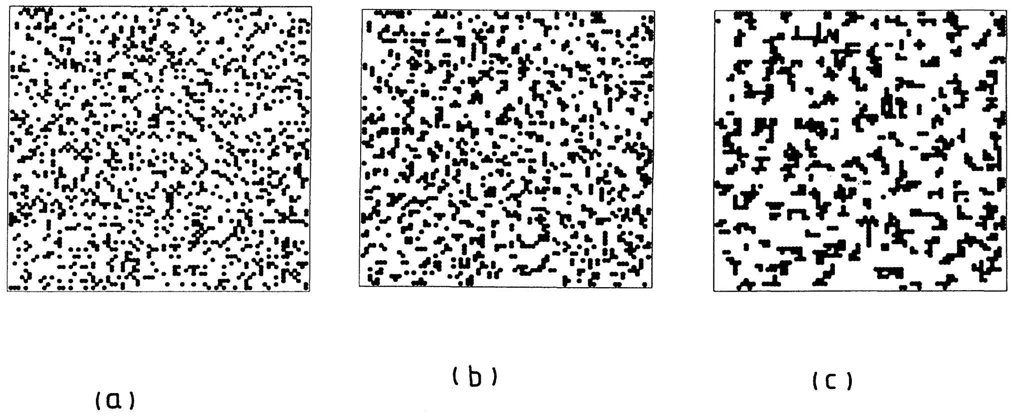
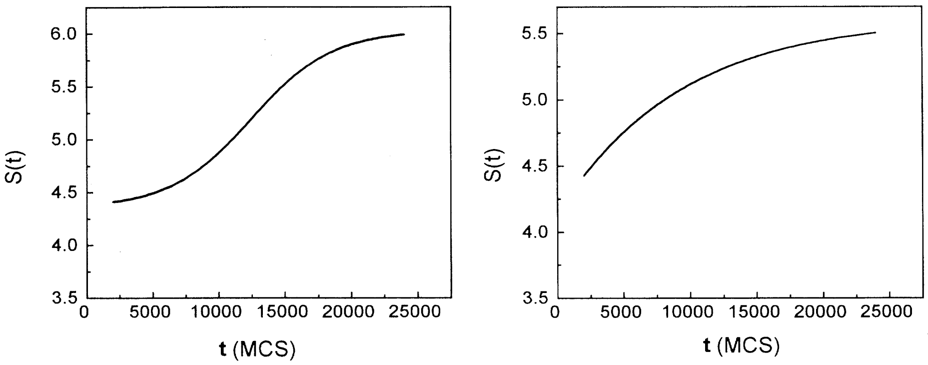


FIG. 4. Typical sequence of configurations of aggregation. This simulation is performed using 80×80 lattice size, particle concentration $P = 0.2$ (1303 particles), external ac-field strength $E = 300$ V/cm, field frequency is 600 Hz, and the characteristic frequencies of colloidal particles are dispersed from 500 Hz to 700 Hz randomly. (a) Initial configuration, (b) 2×10^4 Monte Carlo steps (MCS), (c) 1.6×10^5 MCS.



(a)

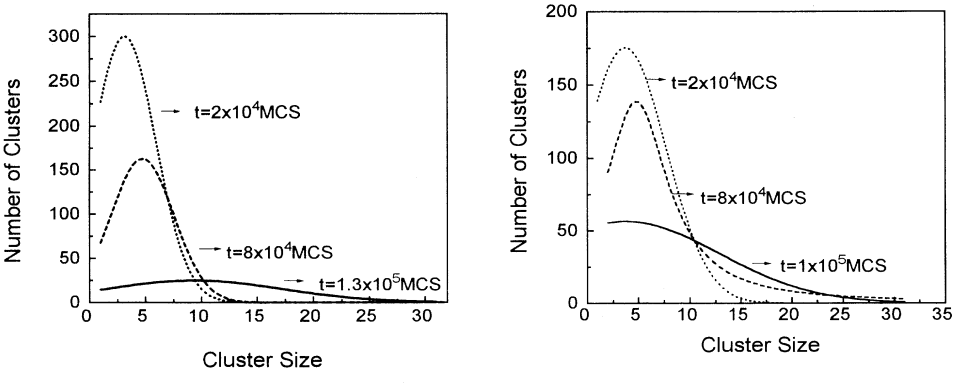
(b)

FIG. 5. Plots of weight-averaged clusters size as a function of time, for 80 × 80 lattice size, $P = 0.3$, $\omega = 600$ Hz, $\omega_0 = 500$–700 Hz randomly. (a) $S(t)$ vs t at $E = 300$ V/cm, (b) $S(t)$ vs t at $E = 400$ V/cm.

A theoretical investigation of the aggregation process requires essentially the complete ensemble distribution of the spheres. We therefore turn to Monte Carlo simulations. For simplicity, we assume that all colloidal particles have the same features except for their characteristic frequencies. Under an external alternating electric field, each sphere has a fluctuating dipole bound to its center. To carry out the simulation, we have taken a two-dimensional square lattice with periodic boundary conditions. It is worthwhile to point out that even though our simulations are restricted to the two-dimensional case, we consider the image interaction in the perpendicular direction; here two-dimensional aggregation means particles only move in the plane in which spheres are dispersed.

Figures 4–6 show the simulation results. Figure 4 presents the typical sequential configurations of the aggregation process. The dipole-dipole interaction initiates the aggregation. In Fig. 5, we show the curves of $S(t)$ vs t for $E = 300$ V/cm and $E = 400$ V/cm. Figure 6 depicts distributions at various times for two simulated external field strengths. Generally $N_s(t)$ broadens with time, the cluster number decreases, and the largest cluster mass increases with time. Initially, and for a period of time, the distributions tend to exhibit maximum at low $S(t)$. The simulation results are in general agreement with the data obtained in experiments.

From the interaction viewpoint, the aggregation kinetics depends on the field strength. When a field of lower strength is applied, a weaker interaction is induced, there are many monomers and very small clusters competing for particles, and the aggregation rate is slow. This situation corresponds to the early stage of aggregation [left part of lines in Figs. 2(a) and 5(a)]. However, as time goes by, fewer nuclei are formed, and aggregation becomes faster [the midpart of the lines in Figs. 2(a) and 5(a)]. As the nuclei grow, they consume monomers around them, the mean separation becomes larger, and fewer monomers exist between nuclei. So the growth rate is slowed down; this corresponds to the late stage of aggregation. In this case, there are fewer nuclei and they are not uniformly spaced on the square lattice. The nuclei where distances between neighboring nucleus are large may consume more monomers around them and grow into larger clusters. For the same reason, the nuclei where distances between nuclei are small will become smaller clusters. So, there are clusters of all sizes, and the size distribution is a rather broad curve [see Figs. 3(a) and 6(a)]. When a higher strength field is applied to the system, a stronger interaction is induced, and the rate of aggregation is fast. As the nuclei grow, more particles are attracted to the larger-sized clusters. The mean separation of nuclei increases and fewer monomers are left



(a)

(b)

FIG. 6. The evolution of cluster size distribution, the simulation conditions are the same as Fig. 4. (a) $E = 300$ V/cm, (b) $E = 400$ V/cm, the rather different form of $N_s(t)$ from that of (a) is evident.

between nuclei, thus slowing down their rate of growth [see Figs. 2(b) and 5(b)]. In this case there are more nuclei, and they are much more uniformly sized and spaced. Most of these nuclei will grow into small clusters. [This case corresponds to Figs. 3(b) and 6(b).] Obviously, the aggregation in this case is limited by the nucleation process, and for this reason we call it NLA.

The morphological difference between ac-field systems and electrolyte systems is attributed to the specificity of the interaction between colloidal spheres. In electrolyte systems, a particle is attracted to a cluster or another particle by surface tension and electrostatic force. If a bounded particle diffuses along the edge of a cluster, it overcomes the van der Waals attraction. So, if V_e and V_t correspond to the activation barrier for edge and terrace diffusion, the electrolyte system satisfies $V_e > V_t$ (i.e., edge diffusion is slower than terrace diffusion), and CCA would be expected; in ac-field systems, according to our model, the particle interaction is proportional to the inverse cube of the distance between particles, so $V_e < V_t$ (i.e., edge diffusion is faster than terrace diffusion). During the course of the aggregation, when depletion regions around some clusters have been developed, on one hand particles of an inner cluster will not leave and they may undergo significant local edge diffusion (rearrangement) because of $V_e < V_t$; on the other hand, the intercluster distance becomes larger, the interaction between clusters is weaker than the attraction between clusters and their images, and therefore the inner clusters are static, and the static nuclei grow by consuming monomers between them in the late stage of aggregation. The resulting aggregates are finite and compact. These may be the underlying physical reasons why the morphologies are different in the two types of systems.

In conclusion, we have proposed for the first time a model of frequency-dependent dipolar interaction in two-dimensional colloidal systems, which is subjected to an ac field. The simulation results of this model are in good agreement with those of the experiments. Colloids interact with each other in the two-dimensional plane and are attracted by their images. This is very similar to an epitaxy system. Adatoms interact with each other and with the substrate. In fact, recent studies of atomic deposition and epitaxy show clear information about the nucleation-growth-coalescence process (NLA) [19,20]. For an ac-field system like ours, if U and W can be adjusted precisely, it is a model system to study experimentally deposition, epitaxy processes, and related physical phenomena.

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