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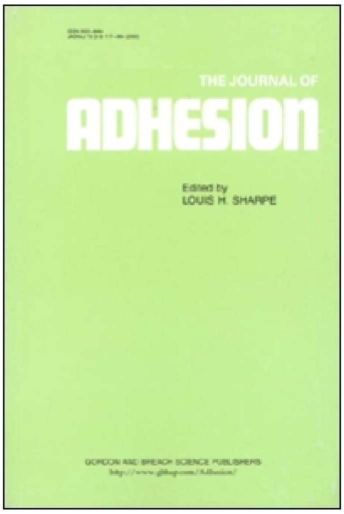

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Effect of Adhesion on Aggregation in Nanoparticle Dispersions

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Effect of Adhesion on Aggregation in Nanoparticle Dispersions

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The detailed structure of a dispersed nanoparticle suspension has been studied by transmission electron microscopy and dynamic light scattering for comparison with an off-lattice gas computer model. For low adhesion between particles, the structure of the suspension is shown to be a "gas with clusters" phase of particles comprising aggregates ranging from singlets, doublets, triplets, etc. to 16-plets in a continuous distribution. Further increasing the adhesion between the particles reduces the number of singlets and causes larger aggregates to form, without precipitation, as some condensed phase appears in the gas. This phase appears as metastable clumps, which do not grow rapidly until adhesion is raised. Then, at high adhesion, flocculation occurs with aggregates growing with time and a large reduction in the number of singlets. Experiments on monosize 62-nm-diameter hematite particles in water confirm this behaviour. An off-lattice computational model based on a square well adhesion potential qualitatively described the dynamic light scattering and transmission electron microscopy results.

Keywords: Aggregation; Computer model; Metastable aggregates; Nanoparticles; Off lattice; Particle adhesion

INTRODUCTION

There is a significant problem in understanding the structure of dispersions containing adherent nanoparticles. Some authors suggest

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that such a dispersion can be represented by submicrometre-sized particles fully separated in a medium [1], whereas others suggest that the particles cannot be fully separate and must generally display aggregation [2–5]. The situation is sketched in Figure 1, which shows equal spheres, either all separated as in 1a or in partly aggregated form as singlets, doublets, triplets, *etc.* in 1b. Of course, the true picture is dynamic, because the particles are moving under Brownian impacts and the aggregates are continually breaking up and reforming, a process neatly shown in computer models [6].

The problem is exacerbated by the fact that particle-size measuring instruments, such as the dynamic light-scattering apparatus (3 in 1 system, Brookhaven Instruments Corp., Holtsville, NY, USA) tend to show a single sharp peak for well-dispersed monosize spheres in suspension and cannot resolve the doublet and triplet aggregates, which are very close together. Only when the large primary particle peak is suppressed can the doublets be resolved as demonstrated using a Coulter blood-cell counter [2,7].

Theoretically, the problem is heightened by the old idea that aggregation, when it becomes visible to the naked eye, is irreversible, as defined by the fast coagulation process first described by Smoluchowski's theory [8]. That theory demonstrated that when the adhesion of the particles is increased by altering pH, particles make immediate adhesive contact and coagulate, with aggregates then growing with time until they sediment to the bottom of the container. Thus, it has been widely accepted that only two states of the nanoparticle dispersion exist: the dispersed state in which the particles remain separate and the coagulated state where the particles stick together and sediment into a dense phase.

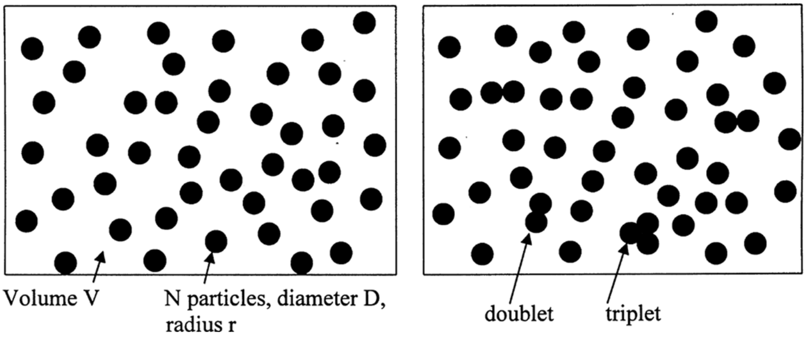

FIGURE 1 Nanoparticles depicted in two ways: a) fully separated and b) as a distribution of aggregates (*e.g.*, singlets plus doublets, triplets, etc.) in a gas phase.

The purpose of this article is to show, both by experiments in electron microscopy with dynamic light scattering and by theory with computer modeling, that the real state of nanoparticles in fluids is more complex. First, aggregates must generally be present even in the best-dispersed stable equilibrium systems. Indeed, the number of aggregates in a dispersion is a measure of the adhesive interaction potential between the particles [2]. Then, it is demonstrated that increasing the attraction between particles to a critical value leads to a phase separation that does not immediately give sedimentation but instead produces larger aggregates, which remain suspended in a nonequilibrium metastable state. Eventually, at larger adhesion values, the system coagulates irreversibly, and large flocs grow continuously with time to give a sedimenting condensed phase.

THEORY

Consider an ensemble of uniform spheres in a kinetic model (Figure 1). The spheres move with a Boltzmann distribution of velocities and interact through a square well potential as shown in Figure 2a such that reversible adhesion is observed. The square well model is the simplest description of the interaction between one attractive and one repulsive potential, whatever the source of those potentials [2].

The square well model has been used frequently to describe adhering particle systems [9,10]. In a particular study of red blood cells, a molecular dynamics model showed how doublets, triplets, etc. were formed by collisions of the particles, but the equilibration of the system required long times and only limited numbers of particles were considered [2–5]. Figure 2b shows a typical distribution of aggregates obtained by a molecular dynamics computer model for adhesion energy $\varepsilon = -2\text{kT}$ and volume fraction $\phi = 0.03$ [3]. In a more recent study, Babu *et al.* [11] carried out three-dimensional computations of particle aggregation using an off-lattice gas model with various adhesion energies and volume fractions from $\phi = 0.02$ to $\phi = 0.2$.

The computational results shown in Figure 2b indicate that for low adhesion, there should be a distribution of aggregate sizes in this dispersed system, with a steadily decreasing number of larger aggregates followed by a cutoff. It is known that in a cubic lattice gas model, the particles with low adhesion form a single "gas with clusters" phase, whose aggregated structure can be varied by changing the concentration, ϕ, or the adhesion, ε, as illustrated in the phase diagram of Figure 3 [12]. The particles in the lattice model never come into full contact but approach each other by moving randomly in discrete lattice steps using the rules of Brownian motion and square well

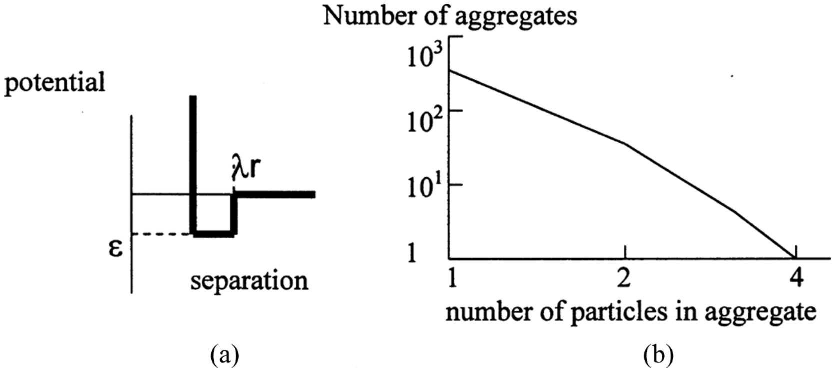

FIGURE 2 a) Square well potential defined by the adhesion energy, ε, and the range, λ. Adhesion energy ε in this model is the energy gained by a particle as it falls into the potential well, thus converting additional kinetic energy to thermal energy, which is on average 3kT/2. The adhesion energy is subsequently lost to the particle as it rebounds off the repulsive wall and jumps out of the well. b) Computed distribution of aggregates for $\varepsilon = -2$kT, $\lambda = 1.001$, and $\phi = 0.03$ [3].

adhesive interaction. In particular, as the adhesion is increased from zero at constant volume fraction, more clusters appear until a point is reached where a phase change from "gas with clusters" to

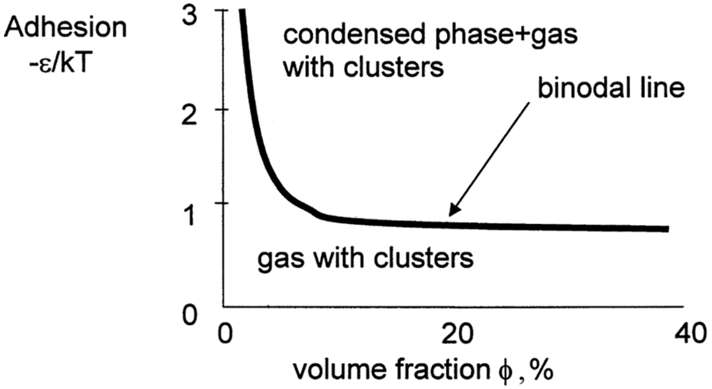

FIGURE 3 Phase diagram for the square well model showing the gas with clusters phase at low adhesion, then condensed phase plus gas with clusters at high adhesion [12]. The binodal line is the line in the lattice gas-phase diagram, which separates the gas-like phase from the dense phase.

"condensed plus gas with clusters" occurs. At different concentrations, this point traces out a binodal curve.

It is evident from this picture that the small aggregates *e.g.*, the doublets, triplets, *etc.* should exist on both sides of the phase boundary and so be somewhere intermediate between the true gas and the true condensed phase.

The effect of increasing particle adhesion is shown by the lattice gas calculations of Figure 4 which is adapted from Ref. [11].

This graph shows the off-lattice computed number of contacts per particle with time as aggregation proceeds from a perfect dispersion. The bottom line shows low adhesion of -2kT and reveals at long times that the number of contacts is very small, about 0.1 per particle, reflecting the small numbers of aggregates in the gas with clusters phase. Just above the binodal (thick line) at $\varepsilon = -3\text{kT}$, where phase change should occur, increased adhesion should give a condensed phase in addition to gas with clusters. However, this condensed phase does not nucleate in the time of the calculation, showing that the

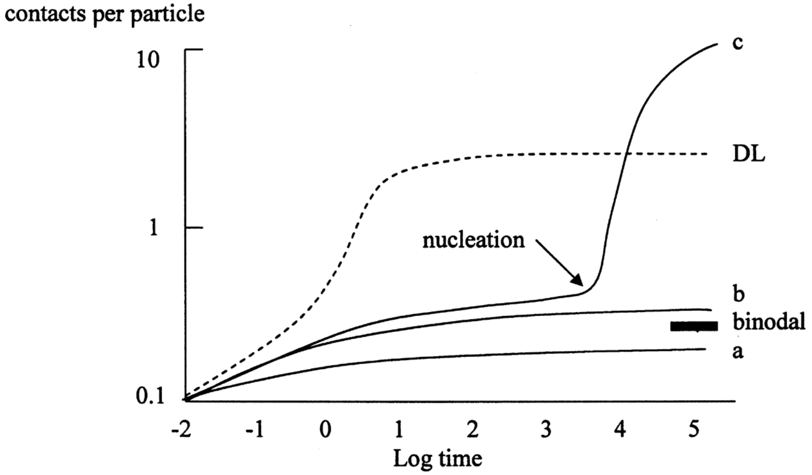

FIGURE 4 Schematic plot of computational results for the off-lattice model showing the number of contacts per particle as time t extends for several adhesion values; $\varepsilon = -2\text{kT}$, $\varepsilon = -3\text{kT}$, and $\varepsilon = -4\text{kT}$. The graph shows three types of behaviour: a) gas with cluster phase below the binodal line, b) metastable gas with clusters just above the binodal, and c)flocculation to condensed phase at larger adhesion. The binodal energy is shown as a short thick line, and the infinite adhesion case is shown as a dotted curve, corresponding to diffusion limited (DL) Smoluchowski irreversible coagulation. Reprinted with permission from Ref. [11]. Copyright 2006, American Institute of Physics.

process is sluggish at this point. Increasing the adhesion further to –4kT illustrates the nucleation process clearly. Condensed phase forms substantially at time 10^4, and the curve then rises rapidly toward 12 contacts per particle at long times, reflecting dense hexagonal packing which is the maximum achievable for uniform rigid spheres. The dashed line shows diffusion limited (DL) aggregation, leading to fractal aggregates with two contacts per particle for infinite adhesion where the particles stick once and for all and there is no reversible adhesion.

It is clear from these computations that there are two problems of attaining equilibrium in this model. The first is for high irreversible adhesion, where two contacts per particle limit the structure to fractal types of solid aggregates [13]. The second is for adhesion just above the binodal line, where metastable gas with clusters exists for long periods. This is the condition explored in depth here.

EXPERIMENTAL

Hematite particles were synthesized by the forced hydrolysis of homogeneous $FeCl_3$ solutions under controlled conditions [13,14]. $FeCl_3.6H_2O$ (2.43 g) was diluted in 12.5 ml of 3.75×10^{-3} M HCl and mixed with 487.5 ml of 3.75×10^{-3} M HCl preheated to 100°C. Vigorous stirring was applied during addition to ensure a homogeneous mixture, and nuclei were seen in the suspension. Growth of the monosize hematite particles was achieved by incubating the mixture for 24 h at 100°C, then cooling to room temperature before carrying out the washing step. Centrifugation was used to separate the particles after adding KCl to flocculate the particles. The supernatant liquid was discarded, and the sediment was redispersed in 10^{-3} M HCl by ultrasonication. This washing procedure was repeated five more times. The suspension was stored at pH 3 and diluted with $HClO_4$ solutions to give various concentrations around 100 ppm by volume and various pH values to vary the adhesion between particles. The particle-size distributions were measured directly on the samples by dynamic light scattering (Brookhaven 3-in-1 system, Brookhaven Instruments Corporation, Holtsville, NY, USA) and by transmission electron microscopy (TEM) (Hitachi H7000, Tokyo, Japan) after evaporating a droplet of suspension on a carbon-coated grid.

At pH 2, the dispersions appeared to be completely stable and gave a single peak in the dynamic light-scattering measurements shown in Figure 5, suggesting that the particles were all in the gas phase and all separate. This cannot be correct (see Figure 7).

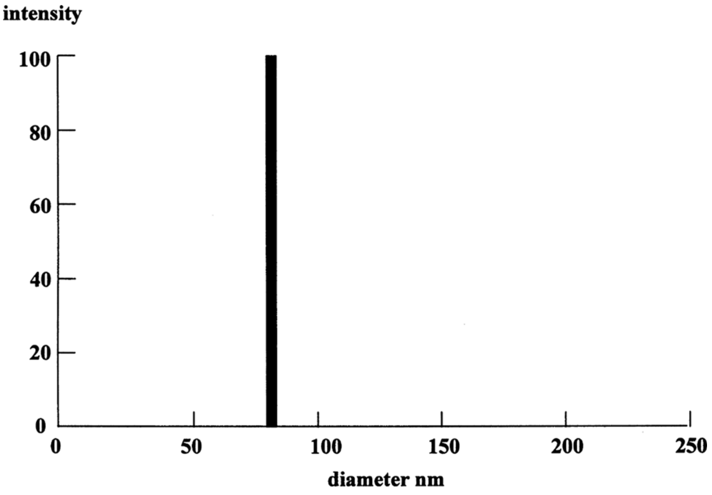

FIGURE 5 Single peak of particles by dynamic light-scattering measurement of stable, monosize hematite dispersion at pH 2, showing a narrow peak at 77 nm.

This peak was at 77 nm rather than the 62 nm found from TEM. The reason for this discrepancy was thought to be the poor resolution of the dynamic light-scattering instrument, which is not capable of detecting doublets, triplets, etc. in the dispersion. Hence, it tends to produce an average result larger than the true particle size. Another

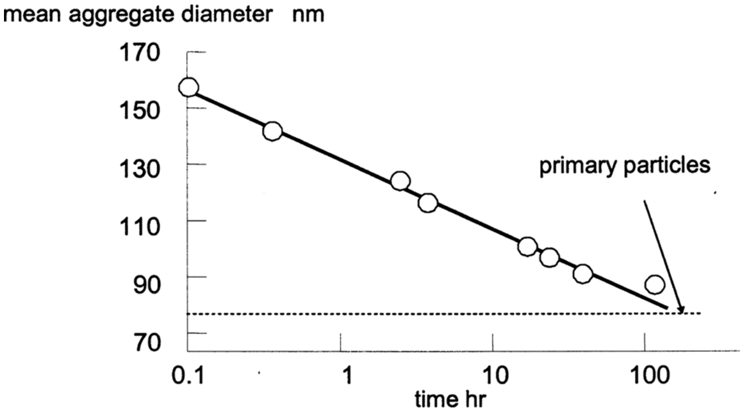

FIGURE 6 Change in mean aggregate diameter with time measured by dynamic light scattering.

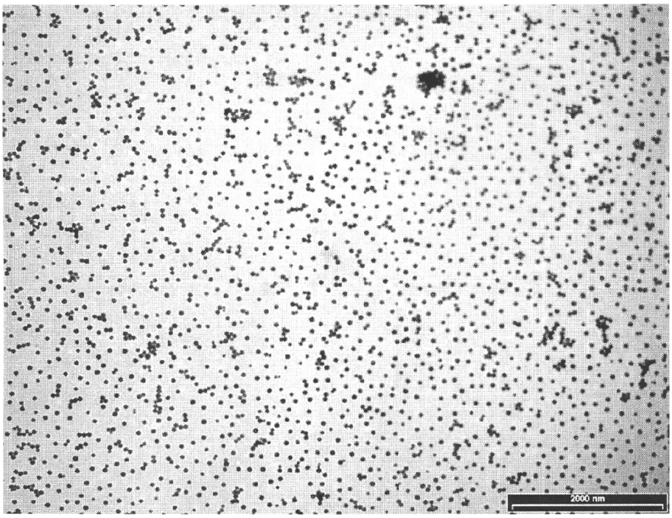

FIGURE 7 Transmission electron micrograph (TEM) of hematite particles from dried dispersion at pH 2 showing the distribution of aggregate sizes.

possibility is that the hydrodynamic diameter of the particles is larger than the true size [13].

Previous work on blood cells and polymer latex has suggested that aggregation can be reversible under certain circumstances [2,7], proving that Brownian impacts can break apart the aggregates. To test this reversibility for the hematite nanoparticles, a stable dispersion of volume fraction 0.0001 at pH 3 was raised to pH 7 by adding NaOH solution and measured by light scattering to obtain a mean particle size of 160 nm, due to aggregation (Figure 6). The pH was then reduced to 3 again by adding $HClO_4$, and the change in the mean particle size was observed by light scattering over time. The mean size of the particles gradually decreased as the aggregates broke down until, after 100 h, there was only a single peak at 85 nm. The conclusions were that aggregation was a reversible process under these conditions and that the system was in dynamic equilibrium as required by the lattice gas theory.

Because the equilibriation time for this experiment was about 100 h, much longer than the drying time of 10 min for electron microscopy samples, it was believed that the TEM sample preparation method would not change the suspension structure too much and that TEM pictures would truly represent the dispersion state of the hematite nanoparticles.

Figure 7 shows a typical TEM picture for the hematite nanoparticles, showing that the particles were always at low concentration during drying and demonstrating that the hematite was in the form of almost equal spheres, 62 nm diameter, with a range of doublets, triplets, and higher aggregates, up to a limit of around 16 particles. This confirmed the concept that nanoparticle suspensions are not fully separated in general but display a range of aggregate sizes. The numbers of singlets, doublets, and triplets were counted from several such pictures, and the statistics are plotted in Figure 8.

This curve fitting to the experiments suggested that the hematite dispersion was in the gas with clusters phase just below the binodal point. The off-lattice model [11] did not quite fit the experimental results but gave qualitatively similar behaviour, following almost a power law curve with a cutoff around aggregate size 16.

The pH of the suspension was then raised to 6 by adding dilute sodium hydroxide solution, with the intention of increasing the adhesion between the particles by approaching the isoelectric point of pH 9 for this system. The dispersion appeared to be stable, and no sedimentation was observed as the particles equilibriated at pH 6 for 2 days. However, the light-scattering measurements of Figure 9 showed that a significant peak of aggregates had appeared at 230 μm

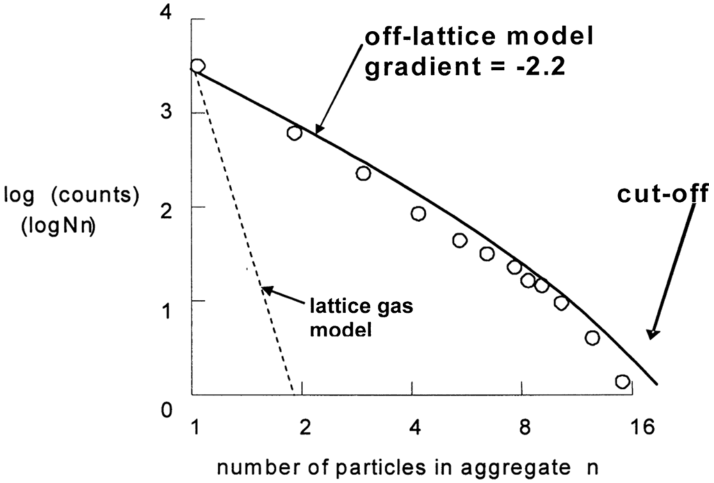

FIGURE 8 Plot of aggregate counts at pH 2 *versus* aggregate size on log–log scales for comparison with off-lattice computer model theoretical prediction [11]. The lattice gas model is shown for comparison.

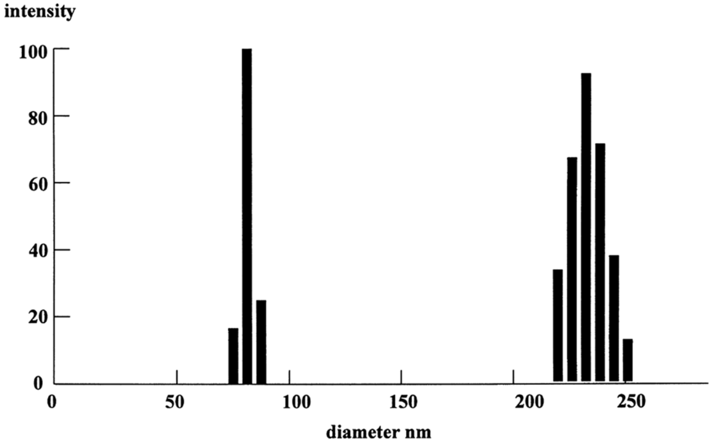

FIGURE 9 Dynamic light-scattering results for the hematite dispersion at pH 6 showing the large aggregates at 230 nm.

diameter, nearly four times as large as the primary particles, suggesting that about 35 particles would be contained in such aggregates.

Transmission electron micrographs at pH 6 (Figure 10), showed that there were singlets, doublets, and triplets in this TEM as before, but now there were several larger aggregates containing about 35 particles.

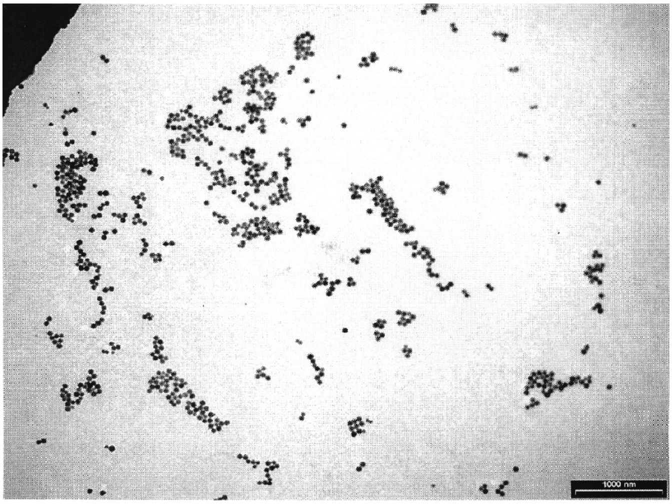

FIGURE 10 TEM picture of aggregates at pH 6, showing structures containing about 35 particles.

Counting these aggregates over a number of TEM fields allowed the distribution to be plotted on log–log scales, as shown in Figure 11. The shape of the distribution was now modified in two ways from Figure 8 by this increased adhesion at pH 6. First, there were relatively fewer singlets and doublets so that the gradient of the curve was flatter than Figure 8 for the small aggregates, thus reducing the gradient predicted in Ref. [11]. Second, there were more large aggregates in the distribution with several aggregates containing around 30 particles. However, the dispersion did not sediment or change its optical appearance. The conclusion was that some condensed phase had appeared in the dispersion, but this was not growing rapidly with time, probably because the aggregates were smaller than the critical nucleation size for rapid growth. This was similar to the lattice gas model prediction just above the binodal in Figure 4. In a previous article [15], such metastable aggregates were called *nucleags* to distinguish them from *flocs*, which grow and sediment with time.

When adhesion between the hematite particles was further increased by raising the pH of the suspension to 8, flocculation occurred, as demonstrated by laser diffraction tests [15], and the condensed material sedimented to the bottom of the container, leaving a clear supernatant fluid containing very few nanoparticles. This is the DL behaviour shown in the off-lattice gas model in Figure 4, well above the binodal line.

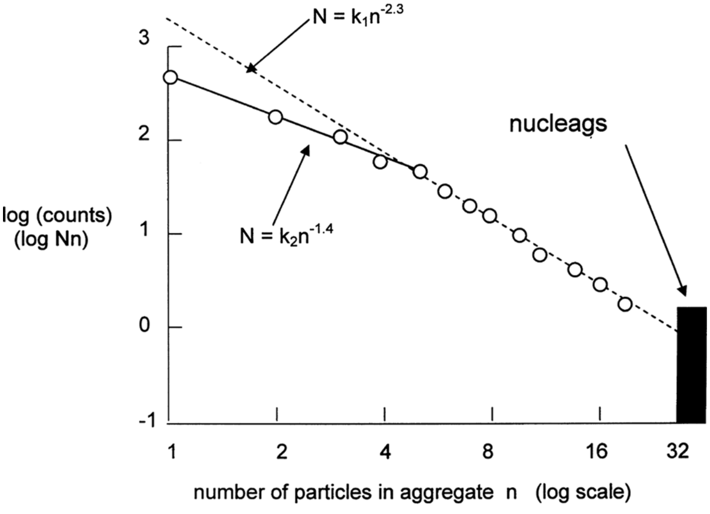

FIGURE 11 Log–log plot of the experimental aggregate-size distribution from TEM at pH 6.

CONCLUSIONS

A model for aggregation in a dilute dispersion of equal spheres interacting with a square well attractive potential suggests that aggregates should always be present for nonzero adhesion and that the distribution of aggregate sizes should change to show three regimes of behaviour as adhesion $-\varepsilon/kT$ is increased.

For low adhesion, below the binodal line, the dispersion is in a gas with clusters phase such that the distribution of aggregates should be continuous with singlets, doublets, *etc.* having a cutoff above a certain size of aggregate.

At higher adhesion, well above the binodal line but still reversible, the particles should be in a condensed phase such that most particles are attached to other particles, causing sedimentation of flocculated material, which phase separates.

Just above the binodal adhesion, where a phase change from gas to condensed occurs, larger aggregates can form, but these do not grow rapidly with time to cause solidification. Therefore, the suspension appears to be colloidally stable but actually contains surprisingly large numbers of big aggregates, many times larger than the primary particles.

Experimental observations using dynamic light scattering and TEM observations on hematite colloids with 62-nm-diameter spheres confirm this behaviour. At pH 2, the adhesion between particles was small and a continuous distribution of aggregates was measured, with few aggregates containing more than 16 particles. Raising the adhesion by increasing pH to 6 gave a metastable state where large aggregates containing about 35 particles were seen by TEM. Dynamic light scattering also revealed a metastable peak three times the diameter of the primary particles, indicating aggregates of 38 particles for hexagonally packed spheres. Raising the pH further, *e.g.*, to pH 8, to give higher adhesion, produced flocculation and aggregates that grew continuously with time, giving a sludge on the bottom of the container. Laser diffraction measurements confirmed these coagulation predictions.

Thus, there are three states that can be detected in the model and also in the experimental system: a gas with clusters phase at low adhesion, displaying aggregation to a limited extent; a condensed phase formed by flocculation at high adhesion to produce large aggregates; and a metastable state at intermediate adhesion where aggregates containing around 30 particles can exist for a long time in nonequilibrium with the gas phase.

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