

Experimental study of colloidal aggregation in two dimensions. III. Structural dynamics

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Time-dependent aspects of the structural self-similarity of colloidal aggregates formed in a two-dimensional system at a liquid-air interface are considered. The aggregation was induced by the addition of CaCl_2 to the aqueous phase, the electrolyte concentration governing the growth conditions. At all subphase molarities large clusters, necessarily formed late in the aggregation process, showed evidence of internal reorganization, the fractal dimension of the cores of the clusters being significantly larger than that for the global cluster structure. Early in the aggregation process, during a regime of slow cluster growth, the overall cluster morphology resembled that of reaction-limited cluster-cluster aggregation for all CaCl_2 concentrations. However, during the later, rapid growth phase the fractal dimensions of the clusters fell at high subphase molarities, becoming compatible with expectation for diffusion-limited aggregation. It is shown that all of these observations are in accord with the hypothesis that the intrinsic particle-particle reaction probability, while experimentally variable, was small under all conditions. A possible explanation for this hypothesis is discussed.

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I. INTRODUCTION

This is the third in a series of papers reporting the results of an extensive investigation of the aggregation of colloidal particles trapped at a liquid surface, where they form a quasi-two-dimensional system. The first paper of this series (hereafter referred to as paper I, [1]) considered structural aspects, and the second (paper II, [2]) kinetic aspects of these processes. This paper examines the evolution of the cluster structure with time as the aggregation proceeds, and shows how certain apparently conflicting aspects of the two separate studies can be reconciled.

It is appropriate to summarize certain relevant theoretical points briefly. Cluster-cluster aggregation has been widely used in computer simulations of random growth processes [3]. In diffusion-limited cluster-cluster aggregation (DLCA) particles and clusters diffuse, aggregating irreversibly on first contact (i.e., the probability of reaction approaches 1). Reaction-limited cluster-cluster aggregation (RLCA) only differs in that the reaction probability is much less than 1, allowing more contacts to be explored before irreversible aggregation occurs. Certain generalizations of the simple RLCA model [4–6], in which the cluster diffusivity or the reaction probability are allowed to vary with cluster size, predict scaling behavior in accord with the observed kinetics (paper II). The diffusion coefficient \mathcal{D}_s is assumed to scale as [4, 5]

$$\mathcal{D}_s = \mathcal{D}_0 s^\gamma, \quad (1)$$

where \mathcal{D}_0 is a constant and γ is the diffusivity exponent. Similarly, the probability that clusters of sizes i and j

react on contact to form a cluster of size $i + j$ is assumed to scale as [6]

$$P_{ij}(\sigma) = P_0 (ij)^\sigma, \quad (2)$$

where P_0 , the intrinsic or particle-particle reaction probability, is a constant and σ is the sticking probability exponent. The exponents γ or σ govern the aggregation kinetics. These may fall into two qualitatively different classes (corresponding to DLCA or RLCA), depending on whether the exponents lie above or below critical values [5, 6]. The critical value γ_c (or σ_c) at which crossover occurs depends upon the space dimensionality d and upon the magnitude of the other exponent, the effects of the two exponents being similar (and apparently additive) [5, 6].

The aggregates formed in our experiments were fractal in nature (paper I), the fractal dimension changing from a value characteristic of RLCA to one expected for DLCA as the electrolyte concentration in the fluid supporting the colloidal particles was increased above a critical value (about $0.45M$ CaCl_2). The average cluster anisotropy, while much more scattered, also appeared to change at this point. These morphological parameters were determined using data for the entire ensemble of clusters observed throughout the aggregation process. The structural studies thus suggest a rather clean and simple picture: at low substrate molarity electrostatic repulsion between the charged colloidal particles inhibited the close approach required for irreversible aggregation into the primary minimum of the interparticle potential, whereas at higher molarities the Debye screening length became so small that such reactions became the rule, and

DLCA would be expected.

However, the kinetics showed no clear signs of such a crossover from RLCA to DLCA behavior as the substrate molarity was increased (paper II). On the contrary, the cluster size distribution $n_s(t)$ never exhibited the well-defined peaks associated with DLCA, but generally decayed monotonically with cluster size s , as expected for RLCA. However, at all electrolyte concentrations a crossover from slow to rapid aggregation was evident in both the average cluster size and the number of clusters. Slow kinetics have usually been associated with RLCA, while rapid growth has been connected to DLCA. The observed dependence of the kinetic phenomena upon substrate molarity was restricted to a variation of the static and dynamic exponents describing the scaling behavior of the cluster size distribution. These variations could be understood as the consequences of an increase in the σ exponent as the electrolyte concentration was raised.

While cluster motion controlled by diffusion should involve $\gamma < 0$ (larger aggregates diffuse more slowly), the clusters observed in the present work tended to move more rapidly as they grew. While the underlying mechanism is not immediately apparent, and is not Brownian motion, this clearly implies an "effective" $\gamma > 0$ (paper II), the actual value probably being independent of subphase molarity. Thus the observed aggregation kinetics demanded that the sticking probability exponent σ , while negative, increased systematically with subphase molarity. Apparently this variation was not large enough to overcome the effects of the positive effective γ , so that the RLCA-like kinetics were not carried over to DLCA-like behavior under any circumstances.

There is thus some conflict between the results of papers I and II: distinct changes in structure do not seem to be accompanied by the expected corresponding changes in kinetics. Conversely, the crossovers seen in the time dependence of the kinetic behavior do not seem responsible for inducing those structural changes which are seen. The present paper considers the temporal evolution of the cluster structure as reflected by the self-similarity of the aggregates, and shows how these different results may be reconciled. A major conclusion is that a determination of either the fractal dimension of structures arising in a random aggregation process, or the growth kinetics alone, provides a rather limited amount of information on the physical processes involved.

II. EXPERIMENTAL CONSIDERATIONS

The experimental system comprised 1- μ m-diam polystyrene latex spheres dispersed as a monolayer on the surface of an aqueous subphase. Aggregation was initiated by adding a CaCl_2 solution to the subphase, thereby increasing the screening of the electric charge on the particles. Video-microscope images were recorded and analyzed to yield the structural characteristics of the clusters, as well as the cluster size distribution. Each pixel in the image was about the size of a colloidal particle, and so it is convenient to quote cluster masses and dimensions in units of pixels. The reader is referred to

papers I and II for all details of the experimental methods and data analysis.

In examining the self-similar structure of the clusters three methods were used (paper I); within errors they all gave the same value for the fractal dimension. In assessing changes in D with time we are therefore at liberty to use that method best suited to the particular situation in hand. The correlation method was the least precise, and is thus not used here. The radius of gyration method is based on the scaling of the global cluster structure:

$$M \propto R_g^D \quad (3)$$

and, with its effective r^2 weighting, is not well suited to study any internal restructuring. The nested-squares method, however, yields information on the internal self-similarity of the clusters. The number of particles in a self-similar cluster which fall within a box of side l centered on the cluster centroid should scale as

$$N_b(l) \propto l^D \quad (4)$$

(for details see paper I).

III. RESULTS AND DISCUSSION

We may select the size range of clusters to be included in the fractal analysis, or we may exercise a certain control over the age of the clusters, measured from the initiation of aggregation, by only including pictures taken at specific times. In this way we address two questions: the possible restructuring of the aggregates as they grow, and the interplay between the kinetics of the growth and the structure of the clusters.

A. Cluster restructuring

To investigate any internal reorganization which may have occurred we wish to study the structure, particularly the internal structure, of clusters formed in the later stages of the aggregation process. We consider a typical experiment, involving aggregation on a 0.73M CaCl_2 subphase. During this experiment 11 images were recorded at 15-min intervals following initiation of aggregation. Averaged over the ensemble of all aggregates observed in these images, the fractal structure was compatible with expectation for two-dimensional DLCA. We now consider how this structure evolves with time.

Figure 1 shows the evolution of the cluster size distribution as a function of time, enabling the growth of the clusters to be followed. Clusters of $s \geq 500$ were not observed in the images until $t > 75$ min; such clusters will be described, in terms of the experimental time scale, as "late" clusters. The structure of clusters formed late in the aggregation was selectively studied by including only such clusters in the analysis. Smaller clusters, however, were present at all times and thus cannot be separated: small and medium-sized clusters present in images recorded late in the aggregation may have been of recent formation or may have been relics of earlier stages of growth.

For considering restructuring effects the nested-squares

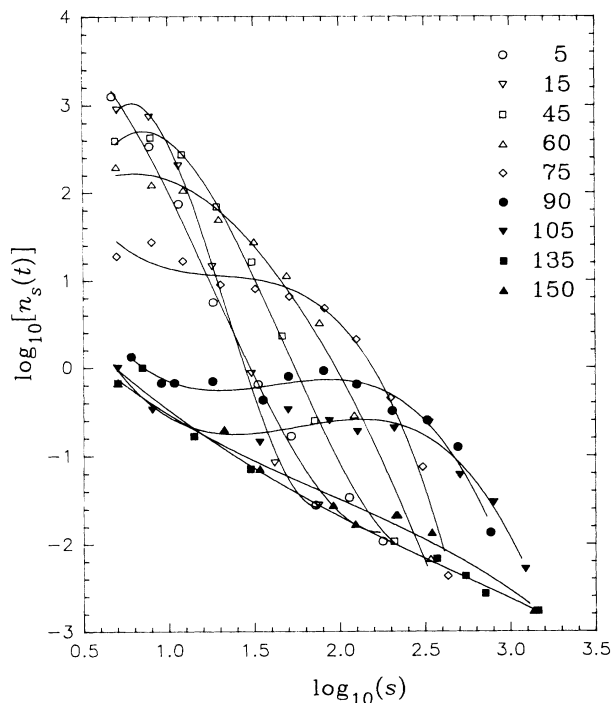


FIG. 1. Cluster size distributions measured at various times (in minutes, see legend) from initiation of aggregation for an experiment on a 0.73M CaCl_2 subphase. Data for 30 and 120 min are omitted for the sake of clarity. The lines are spline fits to the data and serve to guide the eye.

method was used. Figure 2(a) shows the scaling thus obtained when the ensemble of all clusters formed at any stage in the aggregation process was included. Fractal scaling is apparent over a large range in box sizes. As in paper I, data for $l < 10$ were neglected in determining the scaling, as they seem to depart somewhat from the overall trend. The fractal dimension D obtained from the remaining data was 1.434 ± 0.004 , in good accord with predictions for DLCA. Figure 2(b) shows the scaling behavior for clusters formed late in the aggregation process—i.e., those with $s > 500$. Clearly, these large or late clusters do not exhibit such simple self-similarity as all clusters: the data exhibit a prominent kink. The slopes obtained by a weighted least-squares fit to the data were 1.95 ± 0.01 for the first ten points on the graph (i.e., $l \leq 21$) and 1.45 ± 0.02 for data above the fourteenth point (i.e., $l \geq 29$). The central region of these large clusters, over a radius of approximately 20 pixels, thus appears to be more compact than the peripheral regions. However, the peripheral regions of the large clusters retain a DLCA-like fractal scaling. This behavior was not so apparent in the results of the radius of gyration method as it is less sensitive to such internal details of cluster morphology, the implicit weighting causing it to favor the scaling apparent at the extremities of the cluster.

Thus large clusters, formed during the later stages of the apparently DLCA aggregation process, are not as uniformly self-similar in structure as the smaller ones. The effects evident in Fig. 2(b) were not apparent when all clusters were included in a determination of the overall

statistical structure of the aggregates [Fig. 2(a)] because the much more numerous smaller aggregates dominated the scaling behavior at the smaller l .

While such restructuring effects would be expected, and are observed, at lower subphase molarities where the screening of the particle charge is incomplete, so that particle-particle reaction probability is much less than 1, its occurrence in the regime of apparent DLCA structure (associated with cluster-cluster reaction probability near unity) is unexpected. Similar results were, in fact, observed for experiments over the entire range of subphase molarities studied. In all cases D inferred from the central region of the large clusters lay in the range 1.9–2.0, while the self-similarity of the peripheral regions was in accord with the global values reported in paper I (i.e., RLCA or DLCA depending on subphase molarity).

This structural effect can be qualitatively understood on the basis of results from our study of the kinetic aspects of the growth (paper II). It was found that at all experimental molarities the particle-particle or particle-

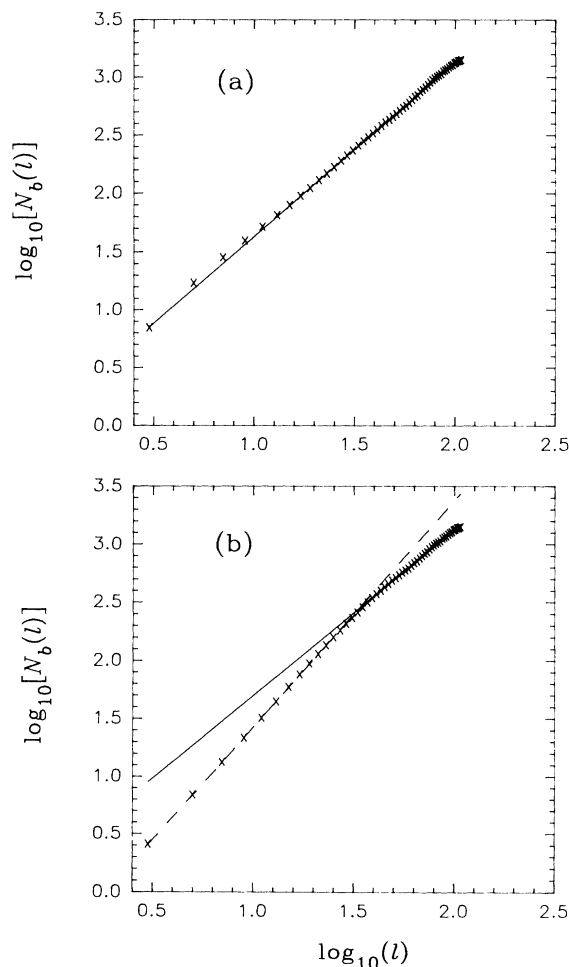


FIG. 2. Nested-squares scaling for the experiment of Fig. 1. (a) Including all clusters observed at all times in the experiment. The straight-line fit (of slope 1.434 ± 0.001) to data for $l > 10$ is shown. (b) For large clusters, $s > 500$. The lines are fits to the data at low ($l < 21$, slope 1.95 ± 0.01) and large ($l > 29$, slope 1.45 ± 0.02) box dimensions.

cluster sticking probability was small, suggesting that the particle charge was still incompletely screened even at the highest salt molarities. The high fractal dimension of the inner parts of late clusters could arise from any or all of the following effects:

(i) slow restructuring of individual particles within the cluster interior over a length scale of $\lesssim 20$ pixels, due to a shallow interaction potential [7];

(ii) mechanical instability of the clusters above a certain critical size, leading to a readjustment of the large “arms” of the cluster [8];

(iii) the larger clusters move faster than smaller ones, as described by the positive effective exponent γ : the observed quickening rate of aggregation mainly arises from the large clusters sweeping up small ones or individual particles as they move. Given the low intrinsic sticking probability deduced from the kinetics, small clusters or particles may be able to penetrate the tenuous structure of the larger clusters. The consequent attachment to inner sites would cause an increase in fractal dimension of the central region.

It is not clear which of these mechanisms actually leads to the observed results; indeed a combination may be involved. We have visually observed all the processes, but cannot assess their relative importance. However, all are based on the same premise: as postulated, the charge on the colloidal particles is incompletely screened, giving rise to remnant long-range electrostatic repulsive forces.

This report concerns observation of restructuring of colloidal aggregates in two dimensions. Aubert and Cannel [9] have reported restructuring of three-dimensional silica aggregates.

B. Interplay of structure and kinetics

If the particles in our interfacial system always had a small particle-particle sticking probability, irrespective of the molarity of the aqueous subphase, it would naively be expected that the structures and kinetics observed in our experiments should resemble those characteristic of RLCA. In experiments at all molarities there was a change in the aggregation kinetics from slow to rapid (Fig. 3) as the clusters grew larger (paper II). However, the measured fractal dimensions (paper I) did not reflect these observed changes in kinetics, being in accord with expectation for DLCA only at the higher molarities. This change in the kinetics is in fact entirely compatible with RLCA. Similar phenomena have been found in certain simulations [5, 6], and such a crossover has apparently been observed in other experiments [10]. The crossover to rapid growth occurs because of the many possible contact points between larger clusters, so that the cluster-cluster sticking probability tends to unity as the clusters grow, despite the small probability of irreversible reaction on first contact.

To investigate whether this pronounced change in aggregation kinetics also left its imprint on the cluster structure, we have analyzed images recorded before and after the crossover in the growth kinetics separately. To illustrate the range of results, data from two experiments

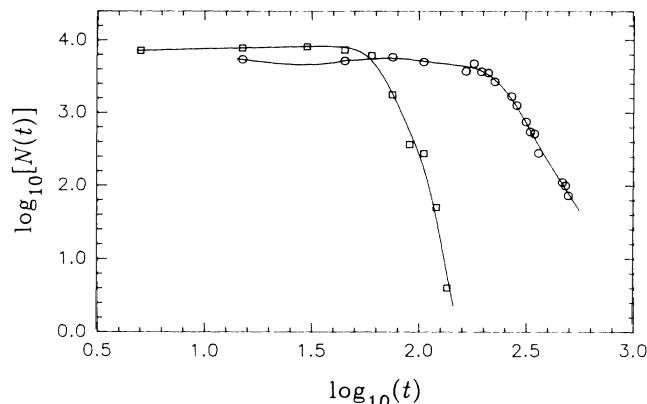


FIG. 3. The variations with time of the total number of clusters for two experiments, on a 0.25M subphase (○) and a 0.73M subphase (□). The lines are to guide the eye. Note the clear change in aggregation rate in both cases, indicated by the rapid decrease in $N(t)$. See text for discussion.

at opposite extremes of the range of subphase molarities used—0.25M and 0.73M—are considered (Fig. 3). The crossover, characterized by a rapid depletion of the number of clusters, occurred at different times in the two cases due to different experimental procedures used to poison the subphase with CaCl_2 . These differences affected neither the structural (paper I) nor kinetic (paper II) scaling behavior observed, and so are neglected. Here the overall cluster structure is of interest so that the radius of gyration method of determination of D is more appropriate, being less vulnerable to internal restructuring effects than the nested-squares method.

For a subphase molarity of 0.25M it was found that the fractal scaling was similar for all clusters (Fig. 4), whether observed before or after the change from slow to rapid aggregation. The fractal dimensions found were less precise than the value for all clusters together (1.58 ± 0.02), but were clearly identical: 1.60 ± 0.04 and 1.58 ± 0.03 before and after the crossover, respectively. D thus changed little with time and, within experimental error, was consistent with predictions for RLCA [3].

However, the experiment at 0.73M was quite different (Fig. 5): the scaling behaviors observed before and after the onset of rapid aggregation were distinctly different. Whereas over the entire ensemble of images for all experimental times the fractal dimension was found to be 1.443 ± 0.013 , the measured fractal dimensions for $t < 60$ min and $t > 60$ min were 1.58 ± 0.03 and 1.42 ± 0.02 , respectively. Thus at these high subphase molarities the crossover from slow to fast aggregation kinetics was associated with a change in the aggregate structure. During the slow aggregation phase the cluster morphology resembled that predicted for RLCA, whereas in the rapid phase DLCA-like structure appeared. Similar conclusions were drawn for all experiments involving subphase molarities above the critical value at which the apparent change in cluster structure from RLCA to DLCA occurred (paper I).

Why does such a change in structure only accompany the kinetic crossover at the higher subphase molarities?

Why does it not occur at the low molarities ($< 0.5M$)? The aggregation kinetics (paper II) confirmed that the sticking probability exponent (σ) varied with subphase molarity. The power-law divergence of the average cluster size, or the total number of clusters (Fig. 3), was more rapid for the higher subphase molarities, suggesting that the effective cluster-cluster sticking probability also increased. In particular, σ rose with CaCl_2 concentration from apparently rather small values at the lowest concentration used. If the exponents γ and σ do indeed affect the structure as well as the kinetics, as expected on the basis of the intimate relation between the two aspects of the aggregation process [11], then a rise in σ should be accompanied by changes in the morphological aspects of the clusters. At small subphase molarities σ was apparently so low that the cluster-cluster sticking probability [Eq. (2)] never became large enough to precipitate a crossover to DLCA-like structure, even in the later stages of aggregation where the growth became relatively rapid.

These conclusions are directly supported by the cluster size distributions observed in these experiments. These distributions can be written as

$$n_s(t) \propto s^{-2} F(s/t^z), \quad (5)$$

where z is a dynamic scaling exponent: the weight average cluster size $S(t)$ scales as t^z [4–6]. The cutoff function $F(x)$ can take one of two different universal forms, depending whether or not the combined diffusivity and sticking probability exponents exceed a critical value. Now γ appears to have been constant in the present experiments, so the universal form of $F(x)$ is determined solely by σ . If σ is above a critical value (affected by the, unknown, value of γ) then $F(x)$ falls algebraically with x for $x \ll 1$ and $F(x) \ll 1$ for $x \gg 1$ [6]. However, if σ is below this critical value, $F(x) \ll 1$ for both $x \ll 1$ and $x \gg 1$ [6]. See paper II for details.

Equation (5) suggests that if $s^2 n_s(t)$ is plotted against $s/S(t)$ the observed cluster size distributions should collapse onto a common form: $F(x)$. Rescaled cluster size distributions for two experiments at extremes of the range of electrolyte concentration are plotted in Fig. (6). The general shape of $F(x)$ is clearly similar in both cases, so we conclude that no great change in aggregation conditions occurs over this range. In particular the form of

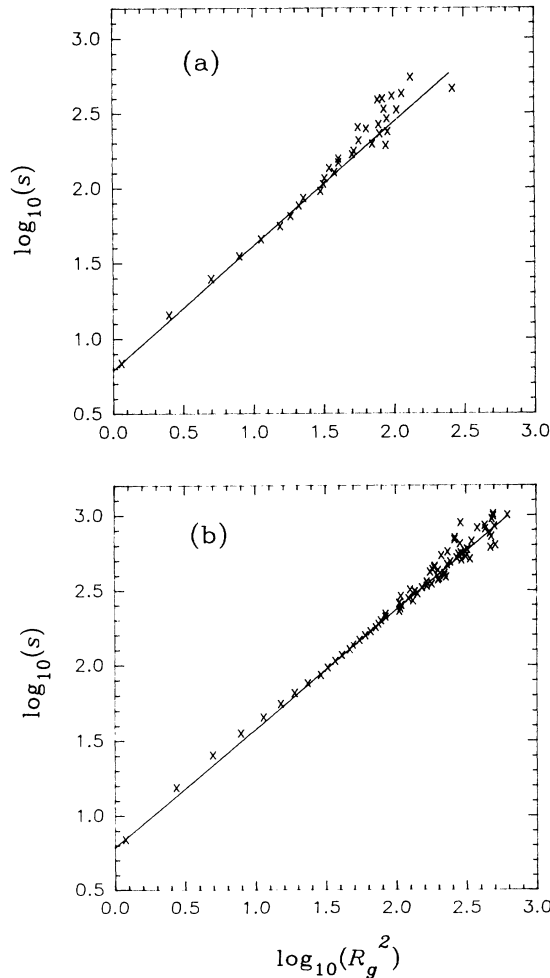


FIG. 4. The radius of gyration scaling for the 0.25M data of Fig. 3. (a) Data for the slow aggregation phase, i.e., for $t < 210$ min: $D = 1.60 \pm 0.04$. (b) Data for the rapid growth phase, after this time: $D = 1.58 \pm 0.03$.

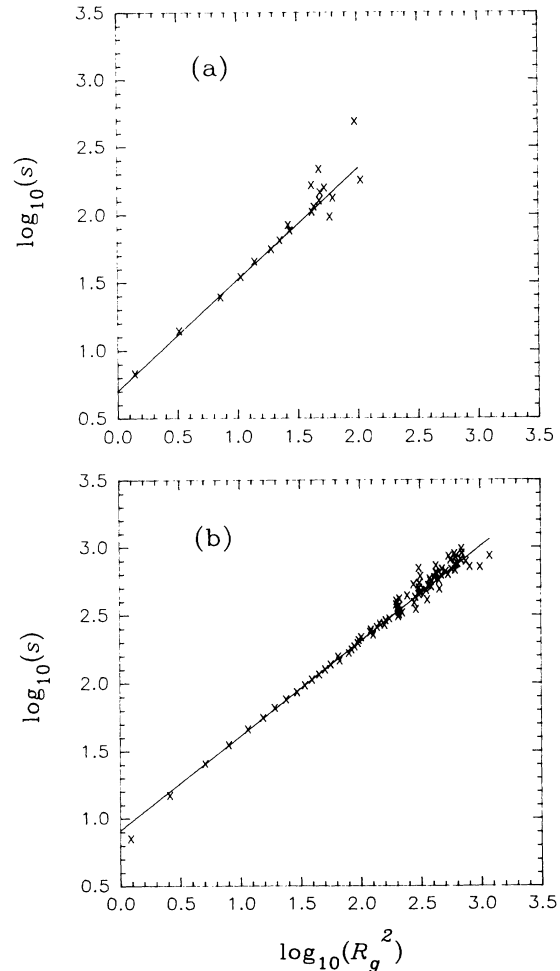


FIG. 5. The scaling for the 0.73M data of Fig. 3. (a) Data for the slow aggregation phase, i.e., for $t < 60$ min: $D = 1.58 \pm 0.03$. (b) Data for the rapid growth phase, after this time: $D = 1.42 \pm 0.02$.

$F(x)$ demands that the sticking probability exponent σ be below its critical value under all experimental conditions.

The basic growth process involved at all subphase molarities was thus chemically or reaction limited, and it now seems fortuitous that the fractal dimensions determined in paper I for the higher substrate molarities agreed so closely with the absolute values expected for DLCA. For these experiments all clusters, at all experimental times, were included in the analysis and values of $D \sim 1.44$ were obtained. The low values of D appear, in fact, to originate in a domination of the scaling over any extended region by the larger clusters. These only appear during the rapid growth regime, where the clusters seem to diverge algebraically in size, and usually have a low fractal dimension.

C. Interparticle interactions

Some features of the basic particle-particle interaction may now be deduced from these observations of the colloidal aggregation at a liquid surface. They may be applicable to similar systems.

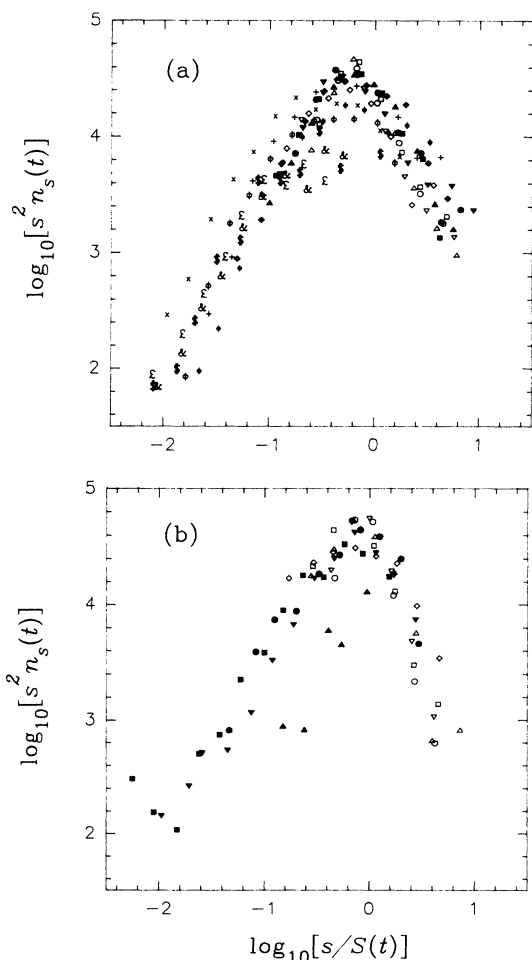


FIG. 6. Rescaled cluster size distributions for the experiments of Figs. 3–5: (a) 0.25M subphase, (b) 0.73M subphase. Note the similarity of the common form found in both cases.

The spatial distribution of the charge resulting from dissociation of the surface charge groups on the wetted area of the particle and the Debye-Hückel double layer in the fluid is asymmetric with respect to the plane of the interface, so that the electrostatic part of the interparticle force is a dipole-dipole repulsion [12]. The range of this repulsive force can be reduced by increasing the electrolyte concentration, until the van der Waals attraction would be expected to dominate.

However, the present data suggest that the particle-particle sticking probability never approaches unity, as would be expected from this simple picture. It was found (paper I) that the CaCl_2 concentration in the subphase required to induce aggregation in surface colloidal monolayers was far in excess of that required to cause aggregation in bulk colloidal suspensions. Hurd and Schaefer [13] have ascribed this to repulsive forces between counterions in the fluid and their image charges above the surface, which lead to a depletion in counterion density near the surface. While this may occur, another mechanism will provide an explanation for some of the apparent discrepancies between structure and kinetics in the present study.

We believe that these effects arise from a portion of the particle charge remaining unscreened by the counterions, even at high subphase molarities. The polystyrene latex spheres are not completely wetted by water: for typical tensions for the various interfaces [14] only about 70% of the surface of 1- μm spheres is wetted by the aqueous subphase. We believe that some surface charge on the particles may arise from dissociated surface groups which lie above the water-particle contact line. The particles are probably completely wetted during the rather turbulent spreading process, and defects on the molecularly rough particle surface would cause pinning of the contact line [15], and thus incomplete dewetting of the surface above the level of the fluid. Such remnant wetted areas may remain in contact with the subphase or might form isolated regions on the surface. Given the surface charge density on the particle ($4 \mu\text{C}/\text{cm}^2$, paper I), even a small fraction of dissociated surface charge groups above the fluid level would suffice to provide a significant remnant charge beyond the influence of the counterions in the subphase.

Thus raising the CaCl_2 concentration in the subphase increases the screening of only part of the particle charge, leaving part unscreened. This latter charge would be independent of the subphase molarity and would thus provide a constant particle-particle repulsion, leading to the rather low effective reaction probability evident in our experiments.

IV. CONCLUSIONS

A major conclusion of the present results is that, as an isolated parameter, the fractal dimension provides little evidence about the nature of the aggregation process; the overall picture is usually much more complex than that described by D alone. This clearly demonstrates the need to consider cluster structure and aggregation

kinetics in conjunction. While the absolute values of D found experimentally may have only limited significance, we have shown that the observed variations with sub-phase molarity of the fractal dimension and of the cluster size distribution are both consistent with a constant positive diffusion exponent and an experimentally variable sticking probability exponent.

The details of both the kinetics and the structure, particularly the dynamic aspects of the latter, were found to be consistent with these suggestions. However, the probability of a particle-particle encounter resulting in irreversible reaction was significantly less than unity, so the process was reaction limited under all conditions. This could occur if a fraction of the particle surface charge remained unscreened by the Debye cloud of counterions at all molarities. Using this hypothesis we have been able

to account for all the observed results in a self-consistent manner.

These results illustrate the crucial relationship between the dynamics and structure that is inherent in kinetic growth processes [11]. The fractal nature of the clusters directly affects the scaling of their mass with both time and size. Our results suggest that changes in the short-range interparticle interactions which can alter the dynamics of aggregation may also cause changes in the long-range structure of the resultant clusters.

ACKNOWLEDGMENTS

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