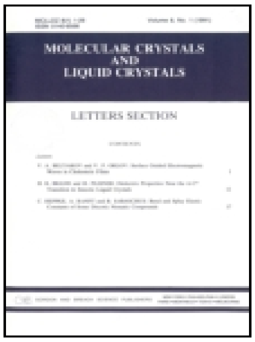

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Nanoparticle Aggregation and Fractal Growth in Fluid Smectic Membranes

K. MEIENBERG, T. MALININA, Z. NGUYEN, C. S. PARK, M. A. GLASER, N. A. CLARK, AND J. E. MACLENNAN

Department of Physics, and the Soft Materials Research Center, University of Colorado, Boulder, CO, USA

We observe directly the diffusion and aggregation of buckyball clusters dispersed in thin, freely-suspended films of smectic liquid crystal using reflected light microscopy. The buckyballs at early times are barely resolvable, nanoscale clusters, which diffuse stochastically in the film. Clusters eventually coalesce to form micron-scale, fractal aggregates whose effective radius increases approximately linearly with time, so that after several days, millimeter-size fractals extend across the entire film. The measured fractal dimension of these final networks suggests that the aggregation of the buckyball clusters in the film is a diffusion-limited process.

Keywords liquid crystal; smectic film; nanoparticle; aggregation; fractal pattern

Introduction

The aggregation of microscopic materials from atoms to microspheres into fractal patterns has been extensively studied in the decades since B.B. Mandelbrot first formalized his idea of the fractal dimension [1] and proposed using this measure as a way to understand how fractal clusters are formed. Models predict that diffusion-limited aggregation (DLA) and reaction-limited aggregation (RLA) in three dimensions (3D) yield objects with fractal dimensions of 1.8 and 2.1, respectively [2–4]. Experiments on the aggregation of aqueous gold colloids [5] and C60 fullerene [6] in 3D yield fractal dimensions of 1.75 and 1.8, corresponding to DLA. Measurements of the growth rate of the radius and fractal dimension of buckyball clusters in several solvents have also been performed [7]. Models of aggregation in 2D suggest that fractal structures form in direct response to the sticking probability of the particles [8–12], with a high sticking probability leading to DLA [13,14] and a fractal dimension of around 1.5, and a low sticking probability to RLA and a fractal dimension of around 1.8. Few measurements have, however, been performed in 2D. DLA has been observed in systems of polystyrene latex particles confined to two dimensions at an air-water interface [15,16], where structures with a fractal dimension of 1.43 and 1.48 form, in agreement with simulations. A simple displacement reaction of copper sulfate and aluminum in a cell [17] yields fractal aggregates with fractal dimension 1.66. Methyl Red,

*Address correspondence to C. S. Park, Department of Physics, and the Soft Materials Research Center, University of Colorado, Boulder, CO, 80309, USA. Email: cpark@colorado.edu

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Figure 1. Buckyball clusters in a smectic A film of 8CB at early time. Compact nano-clusters around 500 nm in diameter which are highly mobile and diffuse rapidly by Brownian motion are generally observed about an hour after the film is drawn. The scale bar is 50 microns.

a dye molecule that is weakly soluble in liquid crystal, was observed to precipitate out of a thin film over the course of several hours [18], forming aggregates with a fractal dimension of 1.61.

Liquid crystals, well known for their electrooptic properties and widespread application in displays, exhibit phases with varying degrees of orientational and positional order, making them attractive tools for controlling self-assembly at the nanoscale [19, 20]. In addition, the promise of using freely-suspended films as a platform for modeling biological membranes provides a unique motivation for studying hydrodynamics in these essentially two-dimensional fluids [21–23]. The ability of smectic A liquid crystals to form inherently stable, thin membranes with quantized thickness has led to several experimental studies of the diffusion of inclusions in films. Experimental measurements of tracer diffusion in thin freely-suspended films has shown that the diffusion coefficient depends significantly on the number of layers and on air coupling [24]. A theoretical model proposed by Saffman and Delbrück [25, 26] and later extended by Hughes, Pailthorpe, and White [27] describes the Brownian diffusion of inclusions in thin membranes embedded in another medium, such as air. Recent experiments have verified these model predictions for the hydrodynamic behavior of micron-size inclusions in fluid smectic films [21–23]. There have been several reports on the self-organization of droplets and islands in smectic films [28–30] but there are few studies of the diffusion and aggregation of nanoparticles in these systems. In this paper, we describe the slow, diffusion-limited aggregation of buckyball clusters dispersed in 2D smectic membranes into macroscopic fractal clusters.

Experimental Methods

Buckyballs (C60 Fullerene, Sigma-Aldrich) are mixed with 8CB liquid crystal (4-n-octyl-4′-cyanobiphenyl, Sigma-Aldrich), a room temperature Smectic A material, at a concentration of 0.5% by weight [31]. Toluene is then added as a solvent in order to disperse the particles [32]. After a few minutes of sonication, the toluene is evaporated quickly

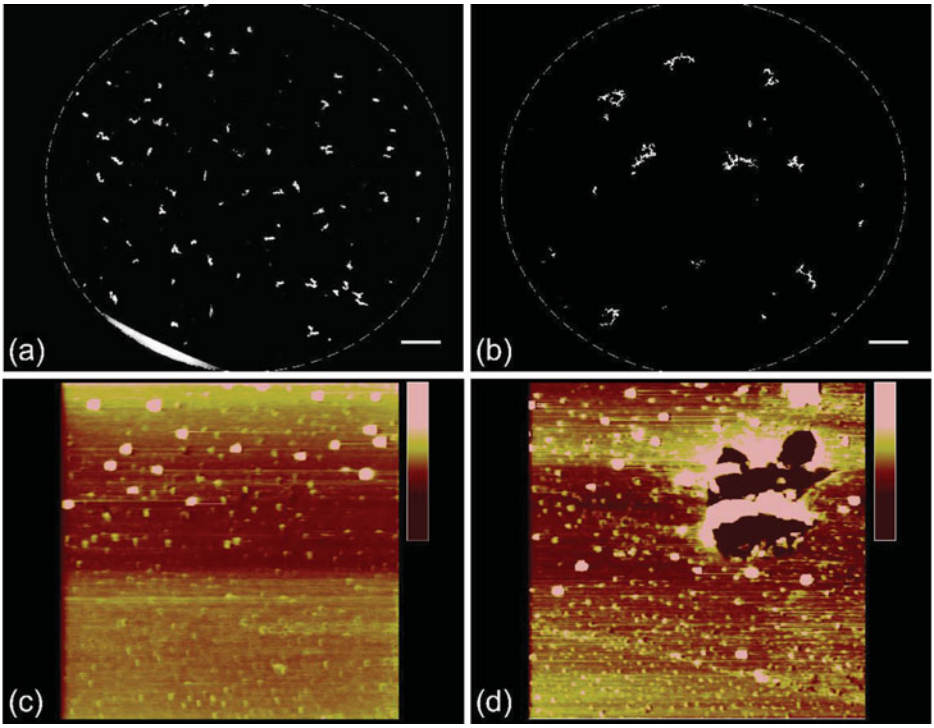

Figure 2. Morphology of buckyball clusters. (a) When initially compact clusters collide, they create long, worm-like chains of buckyballs, which continue to diffuse in the film. The bright meniscus of the film can be seen in the lower left of the image. The field of view is indicated by a dashed circle. (b) Larger fractal clusters form following collisions of the buckyball chains. The scale bars are 50 microns. (c) AFM image of sub-optical resolution buckyball clusters on a silicon substrate an hour after the film was made. (d) AFM image of late-stage aggregation, showing a micron-size chain in addition to smaller clusters. The AFM images are 5 microns wide. The height scale of 50 nm is shown at right.

using a rotary evaporator and left to sit overnight until any remaining solvent has been removed. Films made with this fresh mixture are typically unstable, presumably because the concentration of buckyballs is so high that it disturbs the layer structure of the film. Thin films can be drawn successfully, however, if the sample is left to sit and re-aggregate for a further two days before use. The films are created by spreading the material across a 5-mm diameter circular hole in a glass cover slip. The filmholder is kept in a closed chamber in order to limit the effects of air currents and is leveled in order to minimize gravitational drift. The films are viewed in a reflection microscope and the aggregates are recorded in grayscale using a high-speed video camera (GXlink GX-3 MEMRECAM, NAC) and a low-speed camera (WAC-902H Ultimate, Watec) programmed to capture images over the long time intervals needed to observe the aggregation process. In an effort to characterize the detailed morphology of the nano-clusters and micron-sized fractals, freely-suspended films were also transferred onto nano-polished silicon substrates [33] and probed using an AFM (NanoScope III Scanning Probe Microscope, Digital Instruments).

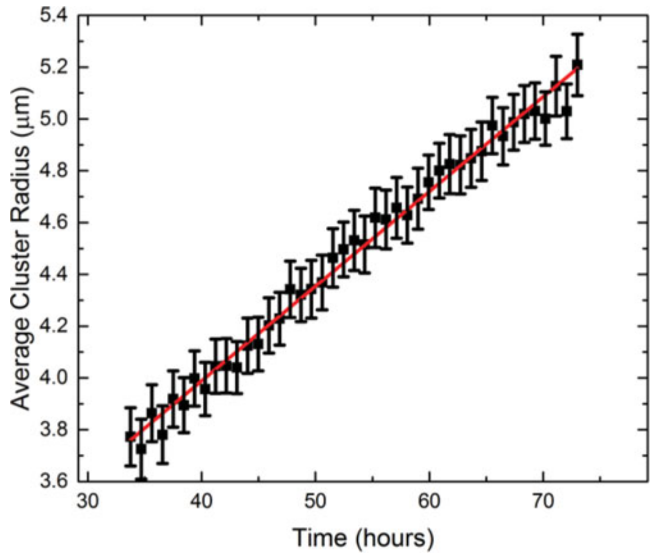

Figure 3. Buckyball cluster growth in the transition regime. The film was imaged once a minute and the "instantaneous" mean cluster radius was computed. To account for the non-uniform distribution of clusters in the film and the limited field of view, the cluster radius was further averaged over sets of 55 frames, an integration time corresponding to the period of the slow convection in the film.

Results and Discussion

When the film is drawn, any larger buckyball clusters remain in the meniscus, and only the smallest particles remain dispersed in the film. Initially, these particles are not big enough to see (the film appears uniformly dark) but after about 30 minutes the buckyballs have aggregated enough that small nano-clusters can be observed diffusing in the film, as shown in Figure 1. These clusters are generally circular when they first become visible in the film and proceed to grow, presumably from collisions with smaller, sub-resolution nanoclusters in a cluster-particle type aggregation process.

After several hours, small fractals form in the film in coexistence with the original compact clusters. During this "transition" stage of aggregation, buckyball clusters a few microns in diameter grow both from cluster-particle aggregation (as seen by the continuous appearance and growth of new, small nano-clusters in the film), and from collisions with other micron-size clusters in typical cluster-cluster aggregation. At this stage, we often observe long, worm-like chains (Figure 2a), which eventually collide to form recognizably fractal aggregates (Figure 2b). AFM images were taken of such films transferred to a smooth substrate in order to resolve the clusters' morphology. The AFM images confirm that early stage clusters are generally compact (Figure 2c), whereas during the transition stage more extended, worm-like clusters are also observed (Figure 2d).

To better understand the dynamics of cluster growth, we measured the effective cluster radius (corresponding to a circle with the same area as the cluster) as a function of time at intervals of one minute, averaging over all of the objects in the limited field of view of the 20X microscope objective to obtain a mean radius. The distribution of clusters in the film at this stage was non-uniform but slow convection caused by heat from the microscope illumination allowed us to sample over a more representative distribution of objects. The

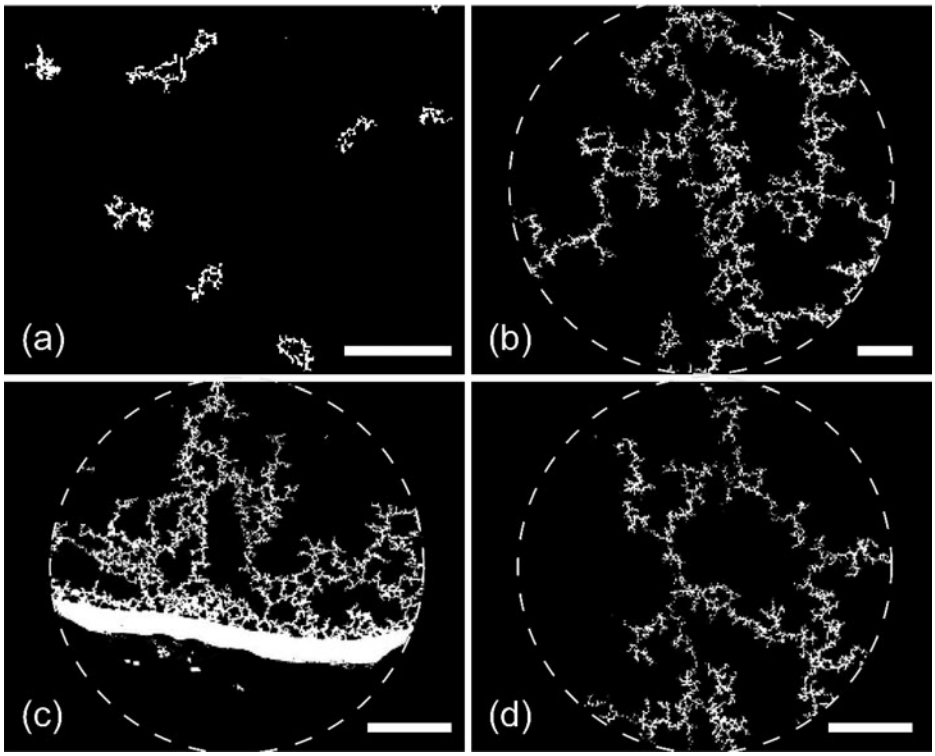

Figure 4. Large fractal clusters in the final stages of buckyball aggregation. (a) Large fractals continue to diffuse in the film, but repulsive interactions keep them from colliding with each other. After several more days, no further buckyball clusters form, which indicates that the aggregation of the fractal clusters comes to an end. (b-d) Large, millimeter-scale fractals near the edge of a slightly-tilted film. The fractal dimension varies slightly across the film, with areas near the meniscus having the largest values, but the measurements are all consistent with a diffusion-limited aggregation process. The field of view is indicated by a dashed circle. The bright meniscus of the film can be seen in the lower portion of (c). The scale bars correspond to 50 microns.

period of this convection (after which the original set of objects reappeared in the field of view) was around 55 minutes, allowing us to average the measurements of the radius over the many different ensembles seen during this period. This mean radius of the clusters increases approximately linearly in time, as shown in Figure 3, at a rate of 6.1 ± 0.1 Å per minute.

Many days after the film is drawn, the structure is dominated by fractals with few if any smaller clusters remaining in the film. Any remaining visible clusters continue to aggregate until no more remain, by which time the reservoir of buckyballs dispersed in the liquid has presumably been exhausted. In films that have been carefully leveled, we finally observe stable fractal aggregates tens of microns in diameter that are kept from each other by repulsive hydrodynamic interactions (Figure 4a). In films with even the slightest tilt, a "supercluster", typically more than a millimeter across, forms at the meniscus on the lower edge of the film, as seen in Figures 4b-d.

We measured the fractal dimension of the late stage aggregates using the box-counting method implemented in FracLac software [34], obtaining a mean value of 1.56 ± 0.08. This is consistent with the value predicted for diffusion-limited aggregation in 2D, indicating that the sticking probability in this system is relatively high.

Conclusion

Using smectic membranes to observe the aggregation of nanoparticles allows us to characterize diffusion and aggregation in a two-dimensional fluid. Analysis of the aggregation of clusters during the transition from small nano-clusters to larger micron-size fractals shows that the radial growth rate of the clusters is approximately constant over time. Cluster-particle aggregation at early times leads to the formation of compact clusters, while cluster-cluster aggregation at later times leads to the growth of fractal assemblies. The fractal dimension of these structures indicates that the aggregation of buckyballs in thin smectic membranes is 2D diffusion-limited.

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