Formation of two-dimensional colloidal voids, soap froths, and clusters

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We report the observation of new pattern formation by spherical polystyrene particles trapped at the air-water interface; namely, the formation of two-dimensional void, soap-froth, and cluster structures. The formation of the soap-froth structure depends upon the initial surface concentration of particles. The void and soap-froth structures evolve with time. The clusters can be formed after deposition of the sample or as a result of the evolution of the soap-froth structure. The experimental observation can be explained in terms of a balance between electrostatic repulsive and attractive interactions. An optimum cluster size can be obtained from an energy analysis of the system. [S1063-651X(98)05605-0]

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During the past decade, colloidal systems have been used as model systems to try to understand phenomena that occur at the atomic level. For example, quasi-two-dimensional and two-dimensional studies have been performed and have given some light to our understanding of the two-dimensional (2D) melting transition [1]. Pieranski [2] was the first to show that charge-stabilized colloidal particles can be trapped at the air-water interface. Using 0.2 μm particles, he observed crystal-like ordering, which he attributed to a stabilization due to dipole-dipole repulsive interactions. Armstrong *et al.* [3] performed expansion-compression experiments in a Langmuir trough with latex particles, 1.01 and 2.88 μm in diameter, to study two-dimensional melting. They found evidence of the appearance of a hexatic phase. Onoda [4] used steric stabilized colloidal particles at the air-water interface, with particle diameters ranging from 1 to 15 μm. Depending on the size of the particle, he observed the formation of both reversible and irreversible clustering, which was attributed to the formation of a secondary minimum in the potential, due to a combination of short-range electrostatic repulsive and long-range van der Waals attractive interactions. Fractal clustering has also been observed with silica particles at the air-water interface [5], where bonding of the particles was also attributed to van der Waals interactions.

In this paper we report the formation of 2D void, soap-froth, and cluster structures by charge-stabilized spherical colloidal particles at the air-water interface. Similar structures appear in various systems in nature and have been of long standing interest, from experiments [6–8] to theory [9–11] and computer simulations [12]. We studied monodisperse fluorescent [13,14] particles with different diameters: 0.5, 1.01, 1.78, and 2.26 μm. The experiments were performed in a Teflon Langmuir trough and the particles were observed with a fluorescence microscope. Careful cleaning of the samples was found to be very important; we found reproducible results after 8–10 sonication-centrifugation cycles with methanol, which was used as solvent [2,3]. Recently, we have observed the same pattern formation with bioclean particles [14], which have the fluorescent dye chemically attached to the particle. We carefully deposited an aliquot of the colloidal solution, drop by drop, on a clean water surface (bioresearch grade, 18.3 MΩ cm of resistivity) with a 25 μl syringe.

After deposition of the samples, we observed that at high overall surface density the particles are arranged in a solidlike hexagonal (hexatic) structure [13], as shown in Fig. 1(a). However, at lower total surface density of particles, different structures were observed depending on the local density. Regions with relatively high local density developed "vacancies" that grew until they formed circular voids (bubble cells) of different sizes, as shown in Fig. 1(b). When bubbles became too large they deformed each other, forming the characteristic 2D soap-froth structure, as shown in Figs. 1(c) and 1(d). The soap-froth structure was formed only with particles of 1.01, 1.78, and 2.26 μm in diameter. The 0.5 μm particles did not form the soap-froth structure and only formed small short-lived and not well defined voids.

The soap-froth structure evolved with the well known [15] $T1$ or neighbor-switching and $T2$ or face-disappearing mechanisms. In addition, we observed that a large amount of single particle rearrangement is also responsible for the evolution of the structure. At the beginning, many cell walls have more than one row of particles. As the foam structure evolves, the particles move toward Plateau borders, thus most of the inner cell walls thin down to one row of particles (colloidal chain), as seen in Figs. 1(c) and 1(d). The formation and stabilization of a colloidal chain is remarkable, since the pair interactions between particles are isotropic. Formation of extended structures has been observed [6,7] and predicted [16] in dipolar systems of Langmuir monolayers, as a result of a balance between dipole-dipole interactions, which favor the formation of extended structures, and the line tension energy, which tries to minimize boundaries [17]. In the colloidal soap froth, the discreteness of the system may also allow the formation of metastable colloidal chains.

The evolution mechanisms and the particle rearrangements serve also to drain the particles toward the edge of the soap-froth structure: Plateau borders and walls at the edge get thicker. However, this thickening is not uniform, and some walls at the edge or parts of them remain formed by only a chain of particles. As the soap froth continues evolving, thin walls at the edge of the structure can break, allow-
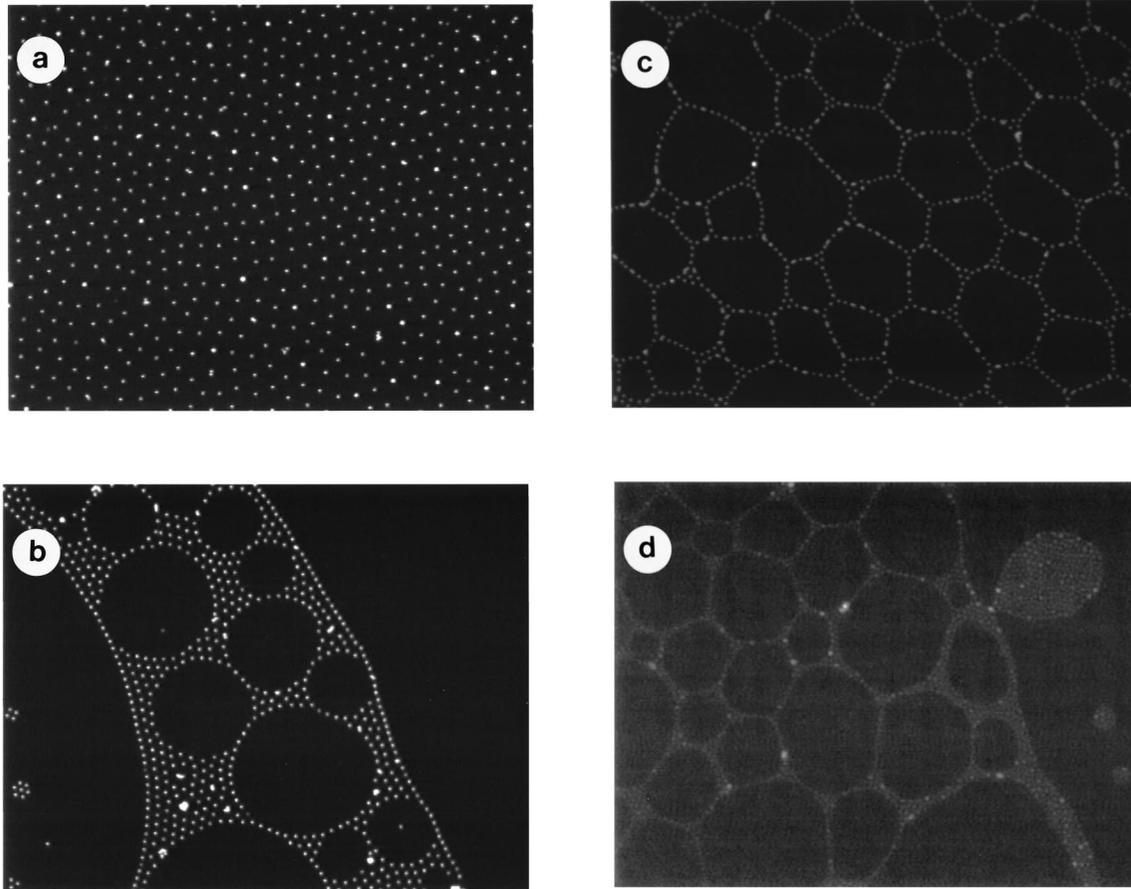
FIG. 1. Fluorescence images of colloidal particles at the air-water interface. (a) A hexagonal arrangement formed by 1.78 μm colloidal particles at high density. Note the presence of several small aggregates, doublets and triplets; these aggregates prevent long-range positional correlations. (b) A stripe formed by 1.78 μm colloidal particles develops circular voids when the local density is low. (c) A fully developed 2D colloidal soap-froth structure formed by 2.26 μm particles. (d) A cluster, developed after a wall at the edge broke, is about to detach from the soap-froth structure formed by 1.01 μm particles.

ing groups of particles to leave, leading to the formation of clusters. Figure 1(d) captures a colloidal cluster that is about to break apart from the edge of the soap-froth structure; it is observed that the density of colloidal clusters around the soap-froth structure increases with time.

A close examination of the images shows that the colloidal particles form two kinds of pseudoparticles: *aggregates* and *clusters*. Particles in aggregates are in direct contact whereas particles in clusters are separated by an average distance a_0, which depends on the diameter of the particles, but is typically between 1 and 4 particle diameters. This behavior can be interpreted as the formation of two minima in the total potential of the system: a deep *primary minimum* and a shallower *secondary minimum* separated by a *maximum*. Therefore, the aggregates can be attributed to particles that have fallen into the primary minimum, and represents the *thermodynamically* stable structure; after a few days the number of small aggregates increased. Clusters can be formed through the evolution of the soap-froth structure or directly after the deposition of the sample, being formed by particles that have fallen into the secondary minimum, and therefore form a *kinetically* stable structure.

The shape of the total potential assumed in our system is analogous to the classical Derjaguin-Landau-Verwey-Overbeck (DLVO) theory [18], developed to explain the sta-

bility of colloidal particle systems in three dimensions. This potential arises from the competition between repulsive and attractive interactions. In our system, it is clear that the repulsive interaction is electrostatic in nature and it is of longer range than its three-dimensional counterpart [2]. Medina-Noyola and Ivlev [19] have determined the exact form of the pairwise electrostatic interaction for colloidal particles at a vacuum-fluid interface; it has the form

$$V_0(r) = (Q^2/\varepsilon r) f(r/\lambda_D), \quad f(X) = 2/X^2[1-(1+X)e^{-X}], \tag{1}$$

where Q is the electronic surface charge of the colloidal particle, λ_D is the Debye screening length, and r is the interparticle separation. The potential can be interpreted as composed of an interaction through the vacuum plus a screened interaction through the fluid. The most interesting part of this repulsive interaction is at distances larger than λ_D, where most of the dynamical and structural properties of the system occur; at these distances the potential reduces to $V_0(r) = 2Q^2\lambda_D^2/\varepsilon r^3$, and the dipole-dipole electrostatic repulsion expression used by Pieranski [2] is recovered.

On the other hand, the origin of the attractive part of the potential, responsible for the formation of the secondary minimum, is not clear. One possible origin can be due to

capillary interactions. Chan *et al.* [20] have proposed a theoretical expression to calculate the capillary interaction energy for colloidal particles at the air-water interface as a function of size. They showed that capillary interactions for particles of the size used in our work are two to three orders of magnitude smaller than $k_B T$, and therefore should not be important. Onoda [4] has also estimated capillary interactions in explaining clustering in his colloidal system of equal size latex spheres sterically stabilized by sodium dodecyl sulfate (SDS). Using the Chan *et al.* equation and adding a range of contact angles from 0° to 180° to compensate for uncertainties introduced by the SDS, he estimated that capillary interactions for particle diameters from 0.1 to 5 μm were orders of magnitude smaller than $k_B T$ also. Clusters formed in our system differ from those observed by Onoda, however. For example, particles at clusters formed in the system studied by Onoda seem to be in contact, and clusters do not have a circular shape as the clusters we obtained. In regard to capillary forces, we can consider the clusters as big pseudoparticles compared with individual colloidal particles, and then capillary interactions between these pseudoparticles can become important. Another possible origin of the attractive part of the potential can be due to van der Waals interactions, but due to the large equilibrium distance between particles (>1 μm) we ruled out this possibility.

Recently, an interaction potential similar to the one assumed in this work has been observed in quasi-two-dimensional systems [21–23], with colloidal particles trapped between glass plates. Remarkably, the equilibrium distance between particles at the secondary minimum in these systems is found to be similar to those observed in our experiments: between 1 and 3 particle diameters with ≈ 0.5 μm latex particles. However, there are significant differences between both systems, especially regarding the repulsive potential, in our case the repulsive potential can be considered of arising from dipole-dipole repulsive interactions [2], while in the case of colloidal particles trapped between glass plates is of a Yukawa type. The origin of the attractive interaction is not clear in either system, thus careful theoretical considerations are still needed to explain it. In regard to the lack of structure formation in our system with the 0.5 μm particles, we believe it is due to particle interactions becoming much smaller than the thermal energy.

It is not necessary to know the origin of the attractive potential to draw some conclusions. Although there is a distribution of cluster sizes, as seen in Fig. 2(a), there seems to be an optimum cluster size, since it is observed that big clusters are unstable due to the fact that they develop circular voids that tend to break them apart to form smaller clusters, as seen in Fig. 2(b). We can define an optimal cluster size from an energy analysis of a system of clusters. We assume a system of N particles on an area $L \times L$, with clusters each containing n particles. N/n is the number of clusters in the system, and $I = L\sqrt{n/N}$ is the mean distance between clusters. The cluster size depends on a_0, and is of the order of $a_0\sqrt{n}$. The total energy of the system is given by $E_T(n) = E_0 + E_B + E_{ic}$, where E_0 is the electrostatic energy of the particles within one cluster multiplied by the number of clusters, E_B is the line tension energy of the cluster borders, and E_{ic} is the intercluster electrostatic energy. Using pairwise interactions, it can be shown [24] that
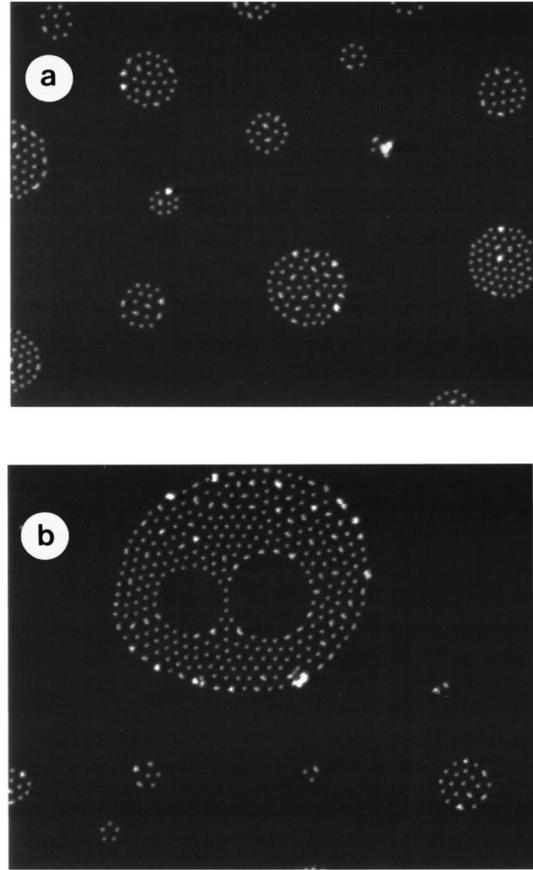

FIG. 2. Images of colloidal clusters. (a) Typical variations in sizes of clusters formed by 1.01 μm particles. Note that the intercluster separation is larger the bigger the clusters. (b) A big cluster formed by 1.01 μm particles has developed voids. The small aggregates also arrange within clusters and behave as if they were bigger particles. There exist small shape fluctuations of the clusters not captured by the images.

$$E_T(n) = (N/\sqrt{n})[U_0 + (Q\lambda_D)^2\rho^{3/2}]$$
$$+ N(Q/a_0)^2 \int_{a_0}^{a_0\sqrt{n}} dr \, f(r/\lambda_D). \tag{2}$$

The terms in the square brackets are the contributions of E_B and E_{ic}, respectively, and the second term is the contribution of E_0. U_0 is the potential at the secondary minimum for particles at the border of a cluster and $\rho = N/L^2$ is the average density of particles in the system. Minimization of $E_T(n)$ leads to an optimal number of particles, n_0, in a cluster

$$n_0 f(a_0\sqrt{n_0}/\lambda_D) = a_0 U_0/Q^2 + a_0\lambda_D^2\rho^{3/2}. \tag{3}$$

According to Eq. (3), if $U_0 a_0^3/Q^2\lambda_D^2$ is too large a big colloidal cluster will not disintegrate into separated smaller clusters [there is no solution of Eq. (3)]. Therefore, in order to reach clustering in the colloidal system, the condition $a_0 U_0/Q^2 \lesssim (\lambda_D/a_0)^2$ must be satisfied. This condition follows from Eqs. (1) and (3). Although the exact values of Q and U_0 are unknown, one can also draw some conclusions about n_0 since the parameter $a_0 U_0/Q^2$ is not small and can be estimated to be of the order of 1–10. This follows from

the experimental fact of the existence of a condensed colloidal system [Eq. (3)] and the clustering condition. Normally, the Debye screening length is not too different compared with a_0. So, one can estimate $n_0 \approx C(\lambda_D/a_0)^2$ where $C \approx 1-10$. These values correspond to the experimental observation of clusters being formed by a few tens of particles. Of course, according to Eq. (3), the increase on the concentration of colloidal particles results in the increase of cluster size, and at sufficiently big ρ there is no clustering, and the system can form a continuum (a cluster filling the whole surface) of colloidal particles separated by a distance corresponding to the secondary minimum; this also corresponds to experimental observation.

The observation of an optimum cluster size has important consequences for the formation of the soap-froth structure. Experimentally, it is observed that the initial stage of the soap-froth structure originates from a region with a high local density of particles. One can consider this region as a huge cluster, which is far out of the equilibrium size. The system will try to minimize its energy by breaking it apart, and out of the many ways it can be done, the system chooses the nucleation of voids and the further formation of the soap-froth structure that evolves to the formation of smaller clusters, which develop from the edge of the soap-froth structure, presumably closer to the equilibrium size.

We have shown an interesting phenomenon that occurs in colloidal systems: the formation of two-dimensional colloidal voids, soap-froth, and cluster structures, which resemble the dynamics and lead to static features observed in other systems. Two- and quasi-two-dimensional [21–23] colloidal systems have shown a richer behavior than thought before, but a satisfactory theoretical explanation of the particle interactions is still needed. On the other hand, the study of the coarsening of the colloidal soap froth can be very important, especially because it has predicted universal evolutive laws of soap-froth structures [6,15]. A detailed study of the evolution will be presented elsewhere [24].

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