Direct Observation of the Dynamics of Latex Particles Confined inside Thinning Water−Air Films

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The dynamics of micrometer-size polystyrene latex particles confined in thinning foam films was investigated by microscopic interferometric observation. The behavior of the entrapped particles depends on the mobility of the film surfaces, the particle concentration, hydrophobicity, and rate of film formation. When the films were stabilized by sodium dodecyl sulfate, no entrapment of particles between the surfaces was possible. When protein was used as a stabilizer, a limited number of particles were caught inside the film area due to the decreased mobility of the interfaces. In this case, extraordinary long-ranged (>100 μm) capillary attraction leads to two-dimensional (2D) particle aggregation. A major change occurs when the microspheres are partially hydrophobized by the presence of cationic surfactant. After the foam films are opened and closed a few times, a layer of particles simultaneously adsorbed to the two interfaces is formed, which sterically inhibits any further film opening and thinning. The particles within this layer show an excellent 2D hexagonal ordering. The experimental data are relevant to the dynamics of defects in coating films, Pickering emulsions, and particle assembly into 2D arrays.

Introduction

Thin liquid films are a typical colloid system that can be encountered in a great number of practical materials and processes: foams and emulsions, coatings, lubricants, and others. Quite often these thin films contain solid particles, either as a result of the original composition or as outside bodies polluting the system. Examples of the first kind of system containing solid particles are the so-called Pickering emulsions,[1,2] some food emulsions containing protein aggregates,[3] ice creams, as well as latex and metallic dyes and coatings. The second kind of system is encountered when dust particles pollute foams, emulsions, and coating layers.

The behavior and the stability of the films in the presence of particles have been a subject of theoretical and experimental investigations.[1,4,5] A particular phenomenon caused by micelles and other small colloid particles inside foam films is the stratification.[6−9] To date however we are not aware of any study where direct

observation on the dynamics of the colloid particles in a foam film has been carried out. The dynamics may be of interest not only in relation to the above-mentioned problems but also in connection with obtaining of principally new materials such as two-dimensional (2D) arrays from particles of nanometer or micrometer size.[10]

The present study is aimed to explore the dynamics of latex particles confined between the surfaces of thinning foam film. We investigated the role of surface mobility, the surfactant type and concentration, the particle hydrophobicity, and the rate of film formation.

Experimental Section

Materials. The latex suspension contained 10 vol % of polystyrene microspheres (Dynospheres from IDC). The diameter of the latex particles was 7 μm. According to the producer specifications, the polystyrene latex particles are negatively charged due to the presence of sulfate groups on the surface and have a zeta-potential ≈−70 mV. For stabilization of the aqueous films against rupture, three ionic surface-active substances were alternatively added to the aqueous phase: sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB), or hexadecyltrimethylammonium bromide (HTAB). These surfactants were obtained from Sigma. The protein used, bovine serum albumin (BSA), was a lyophilized product from Sigma (Catalog No. A-3803). The solutions for the experiments were prepared with deionized water from a Millipore Milli-Q reverse osmosis system (Organex grade).

Methods. The experiments were carried out by the Scheludko-Exerowa cell for microinterferometric observation.[11,12] The films were formed by sucking liquid out of a biconcave meniscus held in a capillary of inner radius 3.20 ± 0.05 mm (Figure 1). Their diameters were controlled in the range of 50−500 μm by changing the pressure inside the liquid meniscus. The thickness and pattern of the thinning films are obtained from the interference microscopic picture obtained in reflected monochromatic illumination (for a detailed description of the method and

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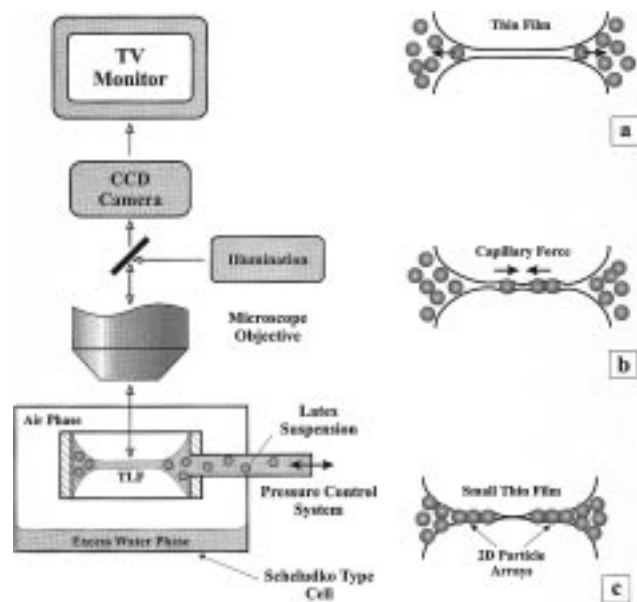
Figure 1. Schematic description of the used experimental setup and three of the most distinctive cases observed with different surfactants: (a) with anionic surfactant all of the particles are expelled out of the film area, (b) in the case of protein some particles are entrapped between the surfaces and exhibit long-ranged attraction and (c) ordered arrays of particles are formed between the surfaces in the presence of cationic surfactants.

experimental setup, see refs 11–14). During the experiments the films were kept in a closed environment saturated with water vapor, so that no evaporation from their surfaces takes place. The film evolution and the particle dynamics were observed by microscope in reflected monochromatic illumination and were recorded with the use of a video camera (Panasonic WV–BP50/G) and VHS recorder (Panasonic AG-7355). Selected frames from the record were processed on a PC computer equipped with a TARGA 16/32+ video digitizer board to reconstruct the film thickness profile.[12]

Results

The experiments were aimed to distinguish the effect of the used surface-active film stabilizer. Therefore the results will be presented following the type of used stabilizer. The initial concentrations of the surfactants were slightly above the critical micelle concentration, cmc, where the adsorption layers are complete, but no complex interference from the micelles due to depletion or stratification can be expected. The concentration of the BSA was also chosen to ensure a complete saturation of the monolayer,[15] at a pH that is not very close to the isoelectric point to avoid protein aggregation in solution. Studies at different concentrations were performed with DTAB, as in this case the effect of the concentration was found to be significant. A schematic graphical illustration of the different film/particle configurations described hereafter is presented in Figure 1.

Anionic Surfactant, SDS. The experiments were performed with solutions containing 0.016 M of SDS. The surfactant readily adsorbs on the liquid surface, and its interfacial viscosity is reported to be low ($2-4 \times 10^{-3}$ cP for a bulk concentration of $0.35-1.73$ M[16]). Thanks to its

negatively ionized head, it should repel the negatively charged particles away from the surface. Both of the above factors favor the expulsion of the particles out of the film area into the surrounding meniscus. In the experiments, all of the latex microspheres were immediately pushed out of the film area during the first few seconds of film thinning and before finishing the thinning stage of film evolution (Figure 2). This could not be changed by varying the rate of film formation and the local particle concentration.

Protein, BSA. The BSA concentration in the solutions was 0.1 wt %. The pH of the obtained solutions was found to be ≈6.4,[17] and no additional buffer was added. The isoelectric point of BSA is ≈4.7,[18] and the net charge of the molecules is negative. In contrast to SDS, the adsorbed layer of bovine serum albumin exhibits high interfacial viscosity (up to 2000 cP[19]). Therefore we expect that thanks to the protein adsorption the film surfaces become immobilized and the rate of film thinning and motion of the liquid inside are strongly impaired.[20] This should favor the entrapping of the microspheres within the film and their compression between the surfaces which was indeed observed experimentally. A number of different cases could be distinguished, depending on the quantity of the particles that were allowed to sediment on the lower meniscus before the film is formed (that is, the number of particles between the surfaces of the film at the moment of its opening).

When the number of particles between the surfaces was small (very incomplete coverage with a sedimented layer), only a few particles could be entrapped inside the film to follow their dynamics on the video record. The entrapment of the particles was achieved by quick film opening (for less than a second). In comparison with SDS, it was easy to notice that the mobility of the film and the particles was reduced, so the particles remained inside the thinning film for 4–12 s depending on their position and the preceding film dynamics. These entrapped particles were typically situated inside the dimple (dense, lenslike thicker formation[20]) in the film center. They tended to aggregate in small 2D groups between the surfaces, attracting each other from distances that could reach up to 100 μm (Figure 3). This aggregation is obviously governed by the so-called lateral capillary forces.[21–23] These small ordered 2D aggregates survived for a short time and were "spit" out at a later stage of the dimple evolution. On many occasions this stage was not reached, as the entrapped latexes caused rupture of the otherwise stable film. The above behavior is pertinent to the dynamics of "defects" in coating thin films and will be discussed from this viewpoint below.

At intermediate latex concentrations, more and more particles were caught between the surfaces. At a certain degree of coverage (∼50% by area) the appearance of the particle aggregates changed from single clusters to "bridges" and 2D foamlike formations, Figure 4a. Sometimes the film was spontaneously separated in two or three smaller films of asymmetric shape (Figure 4b). These 2D clusters appear similar to the ones observed and reported

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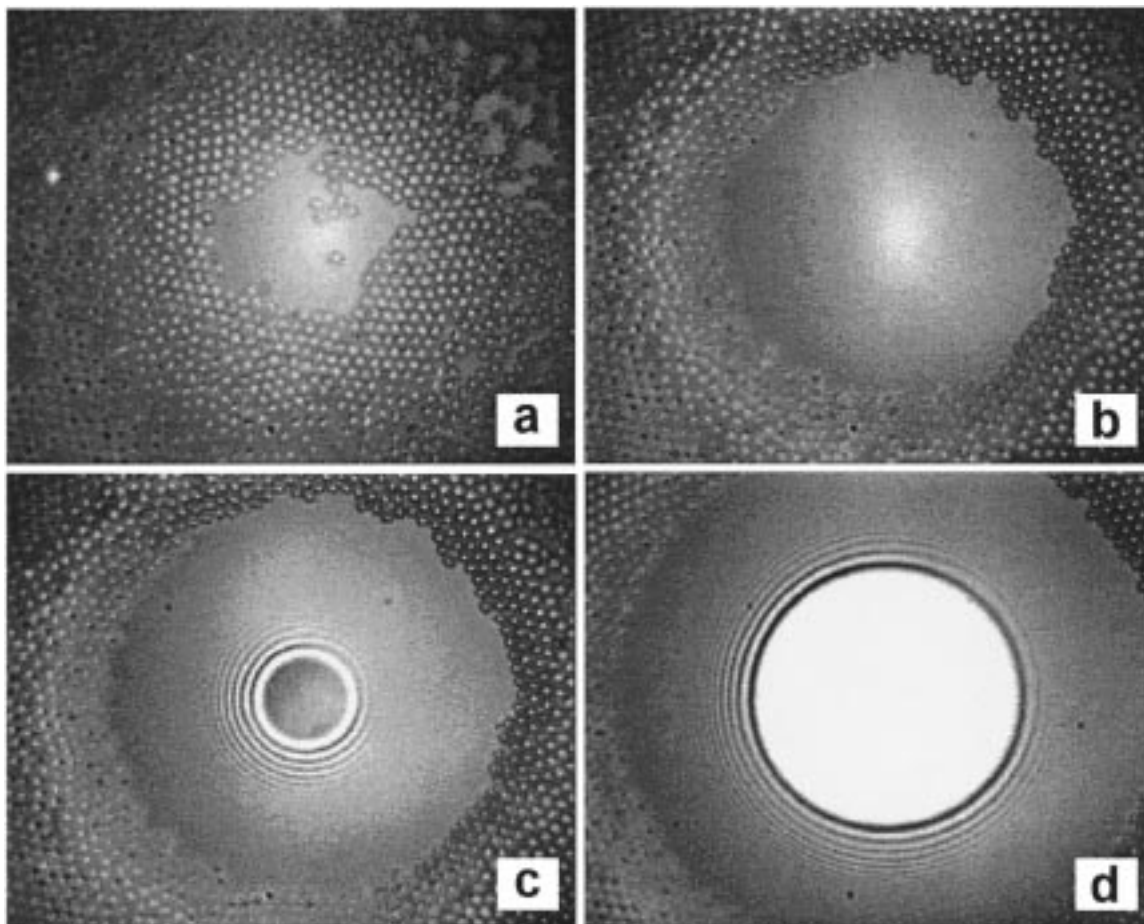(23) Kralchevsky, P. A.; Nagayama, K. *Langmuir* **1994**, *10*, 23.

Figure 2. Four consecutive (a–d) stages of the formation of a foam film stabilized by anionic surfactant (SDS) in the presence of latex particles. When the distance between the foam film surfaces approaches the particle diameter, the mobile latex microspheres are expelled out of the film area in ≈1 s.

earlier for particle dynamics in a film above the surface of fluorinated oil.[24] The formation of the latter is also a result of the capillary forces. In almost all cases the bridges and the 2D "foam" of particles were eventually broken and pushed out of the film. This process nevertheless strongly slows down the film evolution, and unlike the case of SDS, the particle islands and threads show a clearly visible rigidity, sometimes strongly changing the shape of the otherwise circular film meniscus. At higher initial coverage of the lower surface with latex particles the thinning of the film is more retarded and its shape deviates further from equilibrium.

Cationic Surfactants, DTAB and HTAB. While being excellent stabilizers of foam films, these surfactants are low molecular weight and are not expected to possess interfacial viscosity significantly higher than, e.g., SDS. Thus, we do not rely on the interfacial viscoelasticity as a factor to keep the particles between the surfaces. One very significant factor is however the hydrophobization of the polystyrene microspheres by the cationic surfactants. This phenomenon, utilized by us earlier[25,26] results from the coupling of the negative charges on the surface of the beads with the positively charged surfactant molecules. The hydrophobized microspheres tend to adsorb on the water/air interfaces due to the increased hydrophobic

attraction. The used surfactant concentrations were 0.0012, 0.006, and 0.03 M for DTAB and 0.001 M for HTAB (compare with the literature values for cmc_{DTAB} = 0.016 M,[27] cmc_{HTAB} = 0.00092 M.[27] The effect of the cationic surfactant on the film/particle dynamics was most conveniently observed at the intermediate concentration of DTAB, 0.006 M, when the partially hydrophobized microspheres stuck to the film interfaces, but no aggregation in the bulk suspension occurred. A panel that summarizes the basic stages of film evolution is presented in Figure 5. The beads initially adhered to the lower film interface due to sedimentation. When the film was formed for the first time, the particles were pushed out into the surrounding meniscus and this film was free of particles. During this process however, the particles in the ring closest to the film periphery got in contact with the upper surface and stuck to it, linking the lower and the upper surfaces together (Figure 5a). When the surfaces were withdrawn to close the film, these particles were sucked in the middle (Figure 5b,c). If the applied reverse pressure was not high enough to detach the upper surface from the layer of particles, the beads that have bound the surfaces together remained within the area of the next film, when it is opened (Figure 5d). During the next closure of the film these latexes were joined by a new group of particles that had adhered to the surfaces. In this way each opening and closing of the film added new particles to the ones already stuck between the interfaces.

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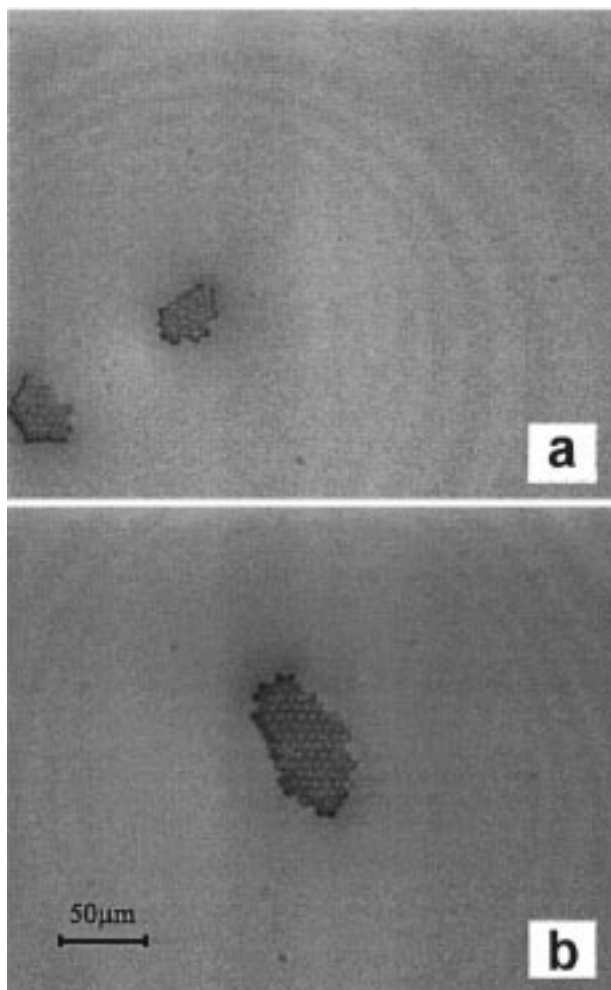
Figure 3. Example of an extraordinary long-ranged attraction (lateral capillary forces) inside a foam film with particles entrapped between the film surfaces. The two separate 2D latex aggregates (a) spontaneously approach and merge to form a bigger one (b). Note the ordering of the particles within the aggregates. Time elapsed between the two frames shown =1 s.

Two important features noticed in the observations of the "zipping" of the two film interfaces with a layer of particles need to be mentioned. The first one is that after a few cycles of opening and closing of the film, each adding new particles to the ones already present between the surfaces, the film area became covered with a complete layer of microspheres, Figure 5e. Once this occurred, it was impossible to open a new film within this area by applying the ordinary pressure. This reveals the possibility of effective sterical stabilization of emulsion systems and is commented on further below. The second important point is the excellent 2D ordering of the microspheres attached between the two surfaces (Figure 5f). This results from two reasons: (i) the compression of the adsorbed layer when reverse pressure is applied and (ii) the mobility of the particles within the 2D layer, which allows their rearrangement to obtain a good hexagonal lattice.

At low and intermediate DTAB concentration and high concentration of sedimented particles, adsorption of particles on both meniscus interfaces took place before the film was formed. In this case, one can observe the dynamics of transition from an ordered bilayer to an ordered monolayer of microspheres. The film was excessively well stabilized in this case, which has also a model
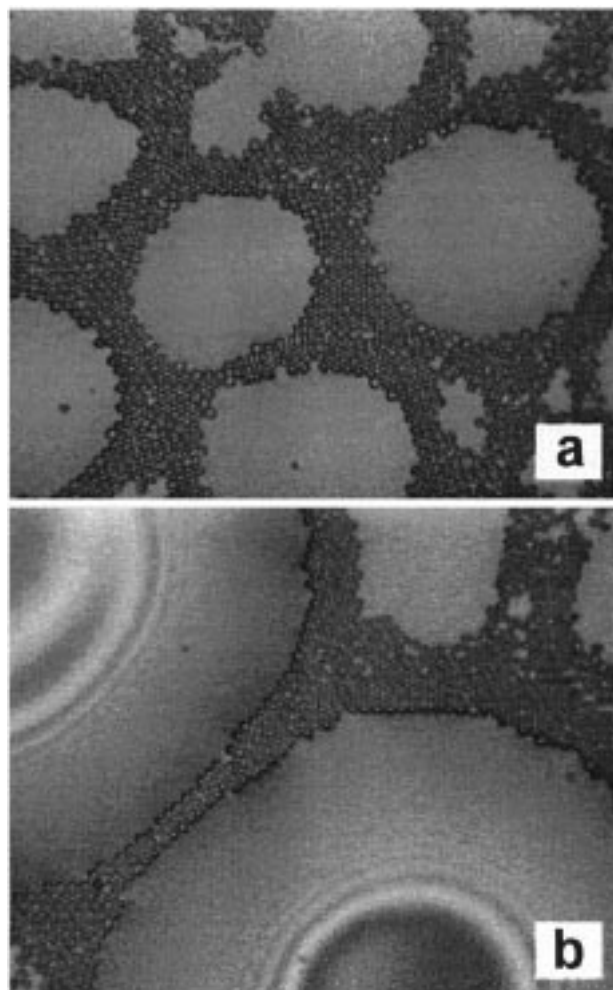

Figure 4. Particle structures formed during the evolution of a film stabilized by protein (BSA): (a) 2D foamlike formation from latex microspheres; (b) spontaneous formation of two foam films separated by a "bridge" from particles.

importance to the phenomenon of stratification.[6−9] At the highest DTAB concentration studied − 0.03 M, the layering, zipping, and stabilization phenomena were also present, but the quality of the particle arrays inside the film was lower, due to some degree of lateral coagulation of the latex beads, Figure 6. In this case the formed 2D arrays (Figure 6d) did not possess the excellent ordering present in the lower surfactant concentrations.

Similar particle dynamics was observed in the case with films stabilized by HTAB. On the basis of the DTAB data, we worked at a concentration of $\approx 1 \times$ cmc. High-quality 2D arrays with almost no lattice defects were obtained by carefully repeating the multistep procedures described above, Figure 7. The size of the single crystalline domains obtained could reach up to 3×10^4 μm^2. Thus, it was demonstrated that the method allows formation of large 2D crystals from latex particles modified with different types of cationic surfactant.

Discussion

The observed dynamics of the particles in the films and the obtained structures could provide new insight in the following three cases of theoretical and practical importance.

Dynamics of "Defects" in Liquid Films. When coating layers of dyes are applied, via "falling curtain" or other method involving film formation, particles are
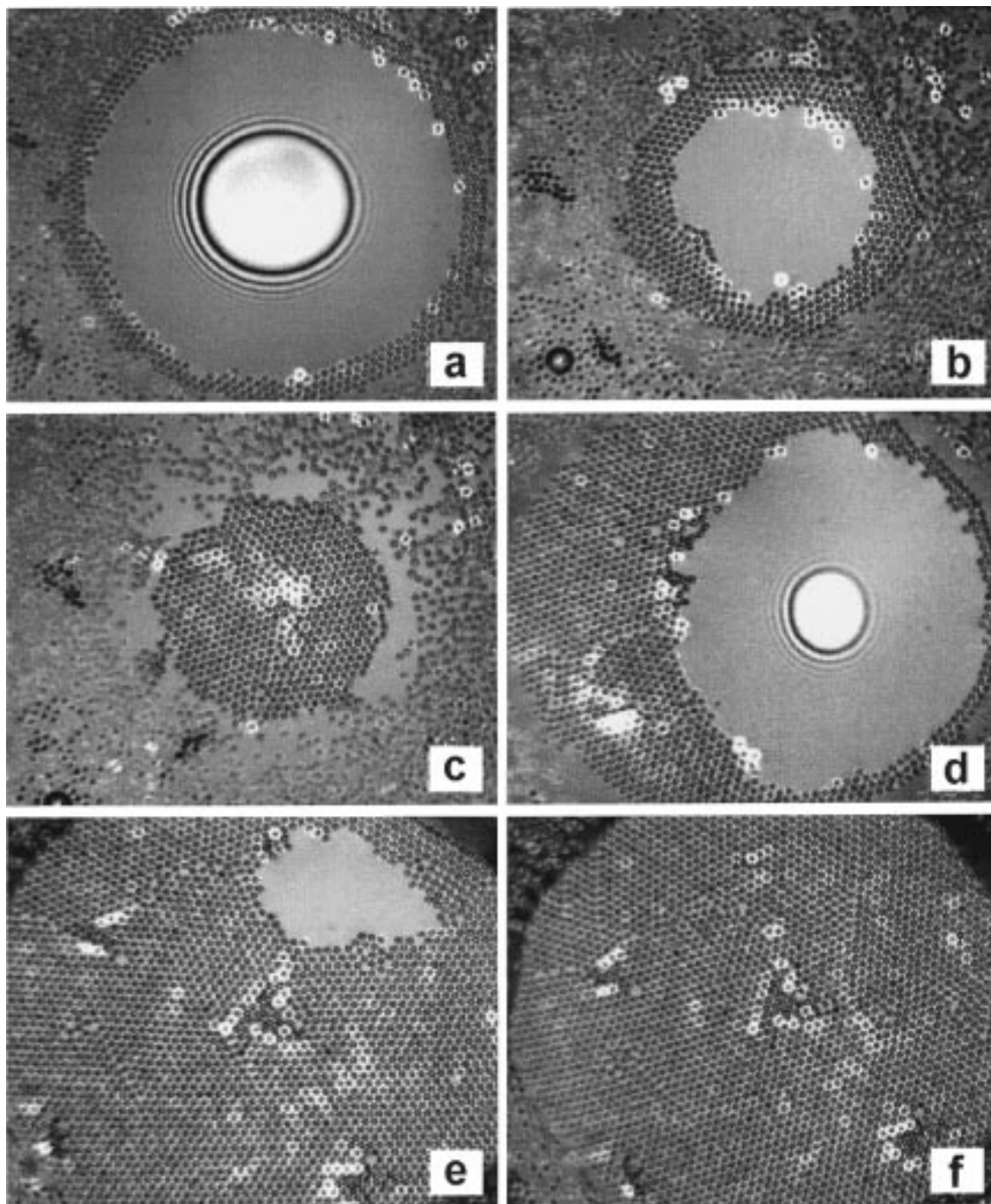
Figure 5. Stages of the formation of 2D ordered array from latex particles inside a thin foam film stabilized by 0.006 M DTAB: (a) the initial film is formed, the particles are pushed out into the surrounding meniscus and some stick to both surfaces; (b) closing of initial film, the particles in the vicinity of the film periphery are dragged toward the center; (c) reorganization of the "zipped" particles at higher reverse pressure and formation of 2D crystalline area; (d) opening of a second film of asymmetric shape close to the initially formed 2D array; (e) closing of the fourth film in a row; (f) big 2D crystalline array from latex particles is formed.

always present in the process environment. These either may be outside dust and impurities ("defects") or may be specifically present in some types of dyes. Two major factors, enhancing the entrapment of the particles are demonstrated by our experiments—the interfacial viscoelasticity and the surface hydrophobization. We also reveal by direct observation some of the phenomena that can be encountered once particles are entrapped in the coating processes: long-ranged attraction and 2D aggregation due to capillary forces, and film rupture due to the presence of a few particles compressed by the surfaces.

In view of the above, it is interesting to estimate the energy of capillary attraction between spherical latex particles confined inside a free foam film. We used the theory for capillary interactions between two equal spheres immersed in thin film on solid substrate developed by Kralchevsky et al.[21-23] To apply this theory for free foam films, we assume that total capillary interaction energy in foam films is two times the corresponding energy between particles on solid substrate with one liquid interface. This assumption fails only in the presence of significant disjoining pressure inside the film and should hold well in our case where the films are thicker than few micrometers. The formulas and the description of the numerical procedure are available in refs 21−23. The parameters used were interfacial tension, $\sigma = 54$ mN/m
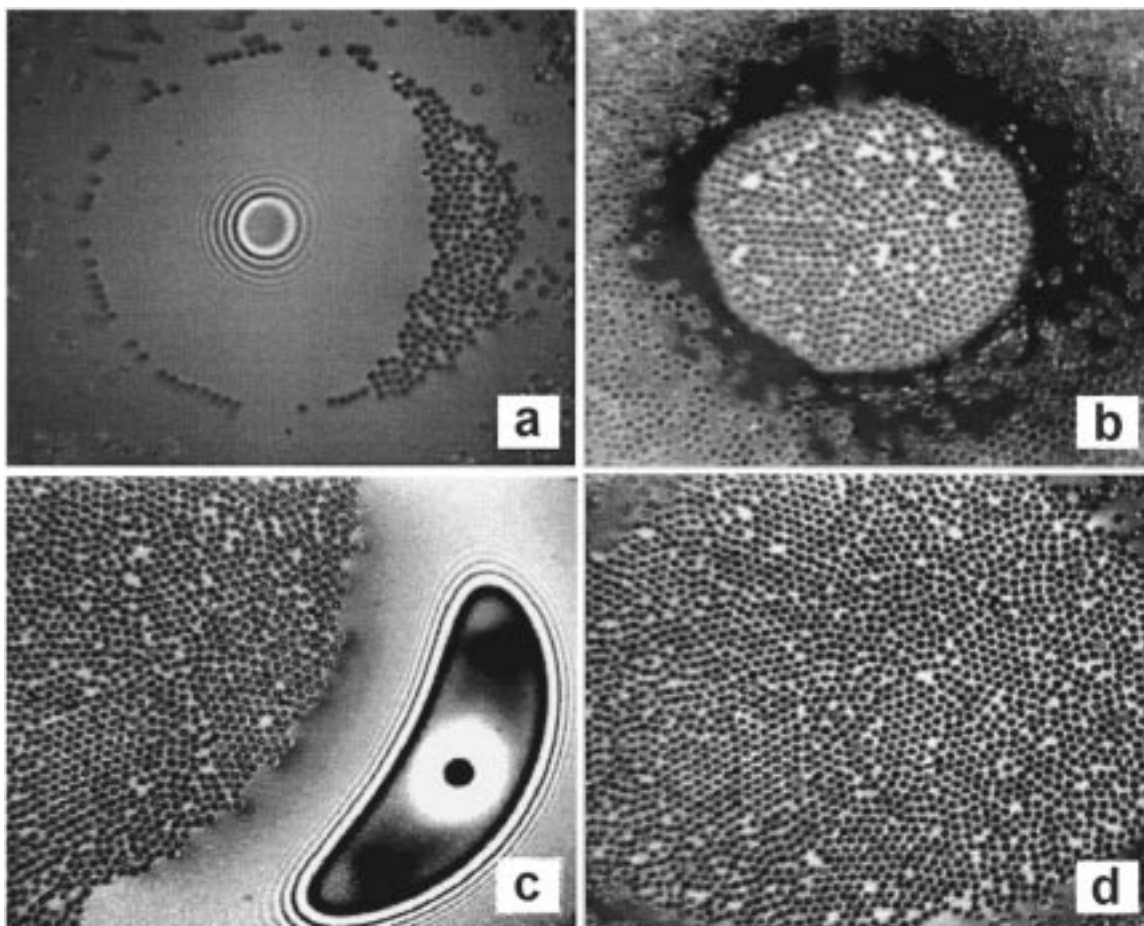
Figure 6. Stages of formation of 2D ordered layers from latex particles inside a thin foam film stabilized by 0.03 M DTAB. The consecutive pictures correspond to frames a, c, d, and f in Figure 5. Due to the increased surfactant concentration the 2D structures are more coagulated, with increased rigidity but lower degree of ordering.

(determined independently by tensiometry), and three-phase contact angle, $\psi = 41°$, as measured by others.[28] The results for films of different thickness are shown in Figure 8. The energy data plotted is normalized by the thermal energy $k_b T$. In the films studied, the surfaces will meet the latex particles without formation of a curved meniscus at a thickness of $\approx 5\ \mu$m, and no interactions will be present at this thickness. Capillary interaction could occur both above and below this thickness, but the menisci around the particles will have different curvatures (see the top and bottom inset in Figure 8). Notably, both of these interactions are attractive and it is seen from the figure that the interaction energy can increase to many orders of magnitude above $k_b T$ at distances as big as 100 times the particle diameters. Such high attractive interactions should cause quick approach and sticking together of the spheres. This is in complete agreements with our data and explains the strong long-ranged attraction and aggregation observed in the films with BSA and with cationic surfactants.

Another important point to be considered is the capillary interaction between the particles and the curved meniscus surrounding the film. The theory suggests[21] that the particles will be attracted to the film periphery when they protrude out of a thin film as shown in the bottom inset in Figure 8. This explains why the particles are expelled out in the cases of thinning protein-stabilized film. Adversely, the interaction will be repulsive and the particles will be pushed toward the film center in the case of thick films with concave menisci around the particles (as the ones shown in the top inset). This was observed with the thickening DTAB or HTAB films, where the particles stuck between the surfaces were repelled from the film periphery and compressed in the center, which leads to ordering. The capillary interactions thus play a major role in the 2D crystallization observed, and are possibly even more important than in the systems studied earlier,[24,25] where the assembly is executed mainly by the convective flux caused by water evaporation.

Pickering Emulsions. The new data may contribute to the understanding of emulsion and foam stabilization by solid particles. The experiment in the presence of SDS relates to practical films with nonadsorbing, media-loving particles. Such particles are always expelled out of the film area. These data confirm by direct observation the well-known fact that hydrophilic particles do not invoke any stabilization. From the viewpoint of Pickering emulsions, this suggests lack of any stabilization of the film between the droplets, which is a well-known experimental fact for strongly hydrophilic particles.[1,2]

More interestingly, the data for partially hydrophobized particles reveals an unexpected phenomenon not known by us to be reported earlier. This is the sticking of a layer of particles between the interfaces, which irreversibly "zips" the film surfaces at a certain distance apart. The assembly of such a layer in emulsions could take place due to, e.g., Brownian motion of the droplets. These observations confirm the applicability of recent theoretical

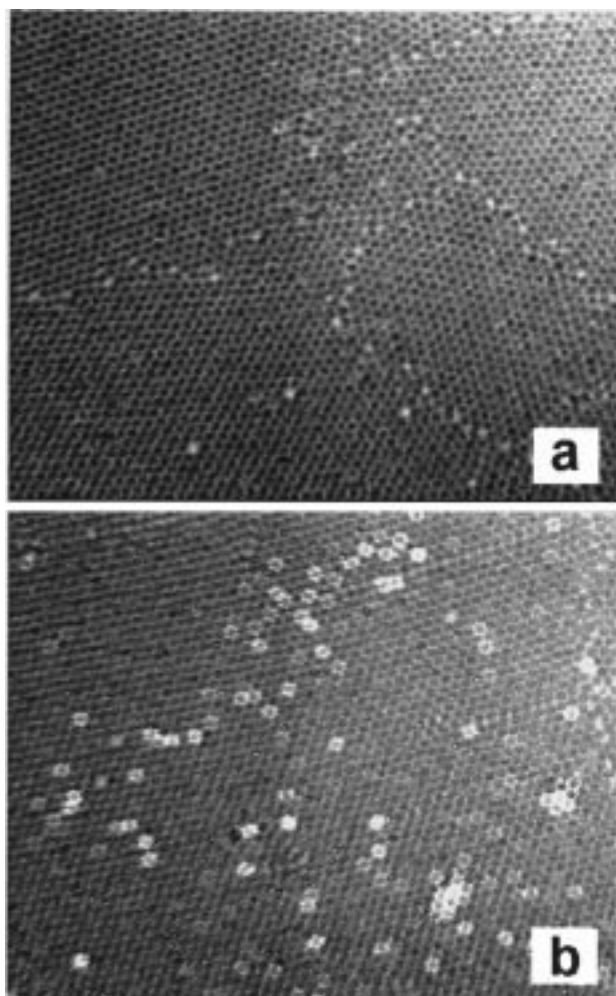(28) Hadjiiski, A.; Dimova, R.; Denkov, N. D.; Ivanov, I. B.; Borwankar, R. *Langmuir* **1996**, *12*, 6665.

Figure 7. Large 2D ordered arrays from latex microspheres in foam films with (a) DTAB or (b) HTAB.
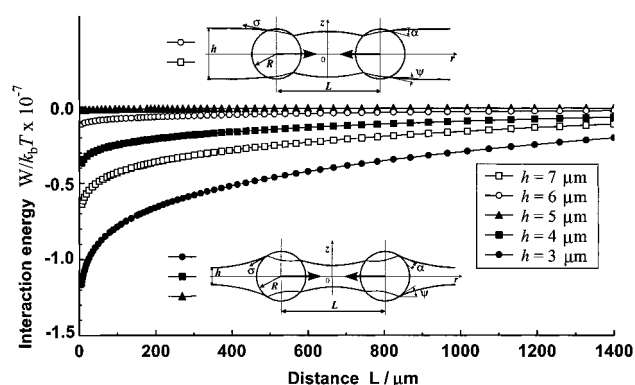

Figure 8. Dependence of the capillary meniscus interaction energy W on the distance between two similar spheres of radius 3.5 μm for different values of the film thickness h. The data calculated include both thick films with concave menisci (top inset) and thin films where the particles protrude out (bottom inset). Note that the interactions are always attractive.

developments on particle-stabilized emulsions,[4] as until now no direct experimental evidence has been available that the particles are able to reside between the surfaces without being pushed out.

New Materials. Recently, a great interest in ordered 2D structures of colloid particles has arisen due to their possible application in high technologies such as data storage and microelectronics. Schemes for the 2D crystallization of latexes on a solid substrate and on fluorinated

oil have been proposed.[10,24,25,29,30] Our data for the DTAB/ HTAB systems suggest another way for controlled growth of stable 2D crystals inside thin foam films by stepwise compression with the three-phase contact line. Notably, the quality of the obtained crystals and the number of involved particles (up to 1000 particles per single crystalline domain) (Figure 7) rank among the best ones obtained earlier on glass[10,25] or fluorinated oil[24] substrate. The main prerequisites for the obtaining of the large, high-quality arrays are, first, the choice of the appropriate surfactant concentration—enough to hydrophobize the microspheres, but not so high as to induce bulk aggregation—and, second, the controllable variations in the film diameter.

This method is technologically more complicated than the ones for 2D assembly reported earlier,[25,30] but it has the potential advantage to create single crystalline arrays of bigger size, whose structure will be determined by the interactions with the fluid surfaces only, rather than with a solid substrate. Its practical application for the fabrication of 2D arrays requires the exploration and development of procedures that allow the extraction of the assembled layers as separate solid-state materials. The development of such methods is beyond the goals of the present study. One procedure that can be used to achieve this is the ultrafast freezing of the foam films by, e.g., quick plunging in liquefied gases. A similar method has been reported recently[31] in the field of the cryoelectron[32] microscopy. Once the film with the ordered particles inside is frozen, it can be detached from the cell and placed upon an appropriate substrate and the water can be removed by melting or sublimation.

Conclusions

We directly observed the dynamics of micrometer-sized negatively charged latex particles, confined in thinning foam films of diameters 50−500 μm. The three different typical surface active agents used outlined different patterns of particle behavior. In films with anionic surfactant (SDS), no entrapment of particles between the surfaces was possible and all of the microspheres were expelled out of the film area. In the films stabilized with protein (BSA) a limited quantity of particles was caught inside the film area, due to the decreased mobility of the interfaces. In accordance with the theoretical calculations, extraordinary long-ranged attraction between the particles due to capillary forces was observed in this case. A drastic change in the film and particle behavior occurred when the microspheres (initially hydrophilic) were partially hydrophobized by a cationic surfactant (DTAB or HTAB). After the films were opened and closed a few times, a layer of particles simultaneously adsorbed to the two interfaces was formed. The particles inside this layer showed an excellent 2D hexagonal ordering and sterically inhibited any further opening and thinning of free foam film.

The experimental data point out the importance of the interfacial viscoelasticity, the capillary forces, and the particle−surface interactions for the type of obtained structures. The major way to control the process is to modify the surfactant type and concentration.

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