

Universality in film stratification due to colloid crystal formation

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Abstract

Experimental results with different colloidal systems (ionic and non-ionic micelles, swollen micelles, latex suspensions) are presented to demonstrate the universality of the phenomenon termed film stratification (stepwise thinning of liquid films). A general explanation of the phenomenon is proposed which assumes that the stratification is caused by the layer-by-layer expulsion of a colloid crystal-like structure formed by spherical particles (micelles, latex particles, etc.) inside the film. The effect of different factors on the stratification such as surfactant and electrolyte concentrations, temperature, etc. is explained from this viewpoint.

Keywords: Colloid crystal formation; liquid films; stratification.

Introduction

Johannott [1] and Perrin [2] long ago observed the phenomenon termed “stratification”, the stepwise thinning (through the formation and expansion of thinner spots) of foam films. Later on, stratification of both foam [3–6] and emulsion [7,8] films formed with ionic surfactants was observed and studied. Recently, we showed [9–11] that this phenomenon is much more universal and can also be observed with non-ionic micellar solutions, swollen micelles and even with suspensions of latex particles. We believe that stratification can be observed in films containing any submicron particles with a narrow size distribution and prevailing repulsive forces. We have shown that

(1) stratification in micellar solutions occurs at surfactant concentrations much lower than those at which liquid crystal structures are known to form, and (2) a similar stratification was observed with suspensions of submicron polystyrene latexes which are unable to form liquid crystal structures. We have proposed a new model for stratified films that assumes that stratification is caused by spherical micelles forming a colloid crystal-like structure. These and some other results, summarized below, suggest that stratification is a much more universal phenomenon than previously thought, and therefore must have a general explanation for all kinds of microparticles involved. We have shown that stratification (i) is controlled by the particle volume fraction inside the film which increases during the film thinning, thus causing the appearance of a colloid crystal structure, and (ii) depends on several factors (such as surfactant concentration, temperature, electrolyte concentration, etc.) affecting the volume fraction.

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Film stratification

We used two different methods to obtain stratifying films [9,10]. Microscopic films (less than 1 mm in diameter) were formed in a cylindrical capillary with hydrophilic inner walls (of radius $R = 1.5$ mm in our experiments). The films were created by sucking out the liquid from a biconcave drop inside the capillary through an orifice in the capillary wall. The resulting horizontal flat thin film is encircled by a biconcave liquid meniscus.

Using films from micellar solutions, we observed with a microscope (in reflected monochromatic light) the following phenomenon: after the film is formed, it immediately starts to decrease in thickness. When it becomes thinner than about 100 nm, the film thickness changes in several steps. The film first rests for a few seconds in a metastable state with uniform thickness, then one or several dark spots (of smaller thickness than the remaining part of the film) appear and gradually increase their area (see Fig. 1(a)). Soon, the spots cover the whole film, and it rests for several seconds in a new metastable state. Darker spots then appear again and, after their expansion, a subsequent metastable state is reached. This process continues until the film reaches a stable state and no more stepwise transitions occur. Films formed from latex

suspensions (Fig. 1(b)) stratify in a similar fashion to those formed from micellar solutions with one observable difference: the spots of smaller thickness may be not only darker, but also brighter than the remaining part of the film. This difference is due to the large diameter of the particles (in our case 91 nm), a diameter that exceeds the thickness corresponding to the last interferential maximum.

We used an interferometric technique to measure the film thickness during the stepwise thinning. In this technique, the light reflected from a small portion of the film is conducted to a photomultiplier by means of a fibre-optic probe. The recorded photocurrent (as a function of time) allows the calculation of the film thickness. A typical interferogram is presented in Fig. 2 (film formed from a micellar solution of a non-ionic surfactant). The metastable states of the film appear in the interferogram as steps whose width is proportional to the lifetime of the respective state. The calculated height of the steps is also shown in Fig. 2 and the magnitude is approximately constant for all steps (about 10.6 nm). For purposes of comparison, the diameter of a micelle is about 10 nm. In other words, the thickness of a spot is approximately one micellar diameter smaller than the thickness of the surrounding film. The same is true for films formed from latex suspensions.

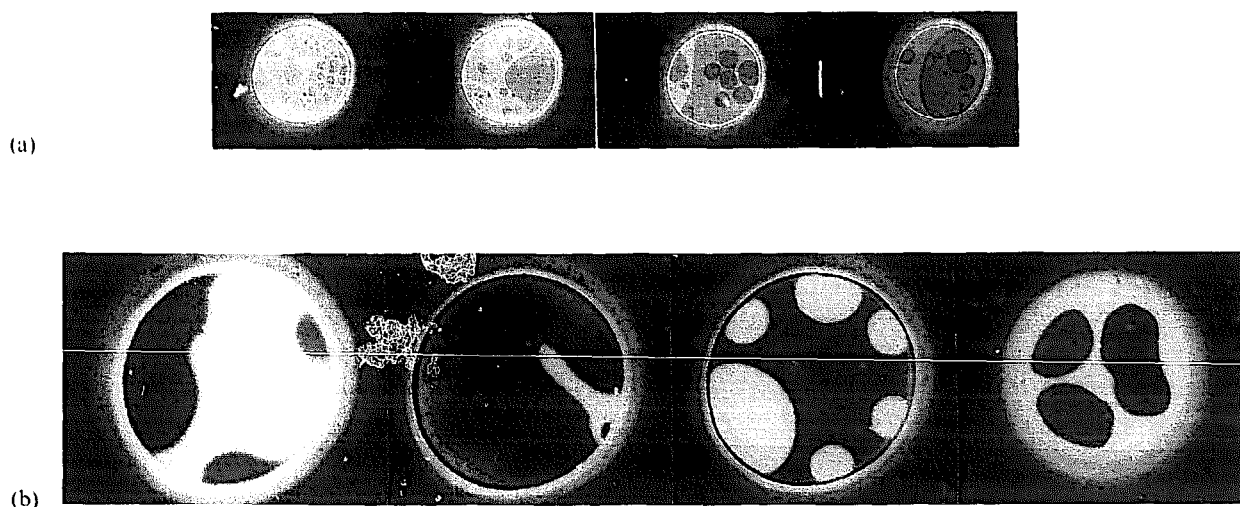


Fig. 1. Stratification of foam films: (a) 0.1 M sodium dodecyl sulfate; (b) formed from 30 wt.% latex suspension with particles 91 nm in diameter.

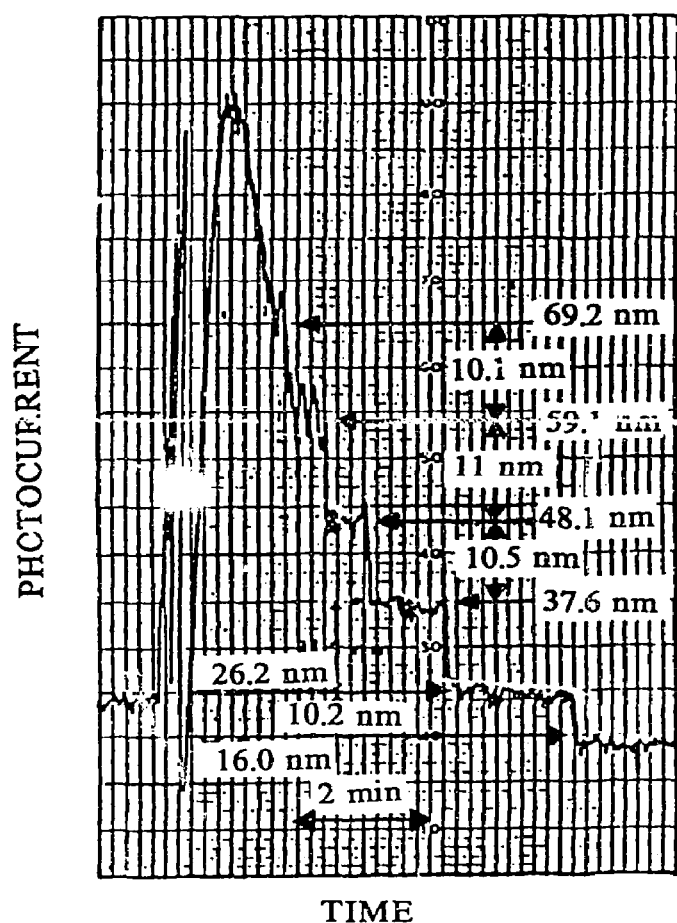


Fig. 2. Interferogram of a film formed from a solution of a non-ionic detergent (Enordet AE 1215-30, 0.052 *M*). As the film thins, less light is reflected. The formation of metastable states of uniform thickness is revealed by "steps". The height of a step (black arrow) corresponds to the thickness of film. The vertical distance between the steps corresponds to the micelle diameter, about 10 nm. The width of the steps is proportional to the lifetimes of the respective metastable states.

Macroscopic stratifying films were formed in a vertical frame. With films formed from latex solutions, one observes, in reflected white light, a series of stripes of uniform color at the upper part of the frame (see Fig. 3(a)). The boundaries between the stripes are very sharp, a consequence of the step-wise profile of the film surface in the region. We observed similar sharp stripes in films with non-ionic surfactant (micellar diameter about 10 nm (see Fig. 3(b)). All stripes, however, were gray in color, though of different intensities, because the diameter of the micelles is small.



Fig. 3. Interference patterns in white light reflected from a vertical foam film: (a) a vertical foam film formed from a 21 wt.% latex suspension with particles 38 nm in diameter; (b) a vertical foam film formed from $5.2 \cdot 10^{-2}$ *M* Enordet AE 1215-30 with a micellar diameter of about 10 nm.

Colloid crystal formation

If stratification is a universal phenomenon pertaining to films obtained from suspensions of sub-micron particles, it must have a general explanation valid for all these systems. The liquid crystal model obviously does not fit this requirement since it is not applicable to the polystyrene latex. Thus, we proposed [9,11] a new colloidal crystal model. Latex suspensions have been shown [12–15] to undergo a phase transition and to form ordered structures called colloidal crystals. It has also been shown [16–21] that the major factors governing the phase transition are the particle volume fraction and the Debye length $1/\kappa$ (in the case of charged particles). We now argue that when the solvent is squeezed out of a thinning film the particle volume

fraction inside the film is increased above its bulk value, causing the particles to come closer and to form, eventually, a crystal-like structure, as shown schematically in Fig. 4. (It is difficult to state exactly how this process occurs, but recent advances in theoretical [22] and experimental [23] studies of the kinetics of interaction between small particles have helped to shed some light on it.) This structure is probably loose (i.e. contains holes) and in most cases is metastable. Once the structure is formed, the subsequent (stepwise) thinning of the film consists in expelling one layer of particles after another. That is why the average height of a step, δ , in Fig. 2 approximately equals the particle diameter, $2R_p$. In the case of charged particles one can roughly assume that the effective particle radius R_κ is that of the Debye atmosphere surrounding the particle: $R_\kappa = R_p + 1/\kappa$.

Factors affecting the stratification

If this general picture is correct, one should expect that any factor decreasing the volume fraction ϕ of the particles will depress the particle ordering inside the film and hence the stratification. We have corroborated this statement by using other authors' data for micellar solutions for the same surfactants (or those similar to ours) to find the trend followed by ϕ when a given system parameter was changed. We defined the particle volume fraction ϕ as $\phi = C_p [4/3(\pi R^3)]$ where C_p is the particle (micellar) number density and R is R_p or R_κ depending on whether the particles are charged or not.

For solutions of SDS (sodium dodecyl sulfate) we found that increasing the surfactant concentration, C_s , resulted in a decrease in the height of

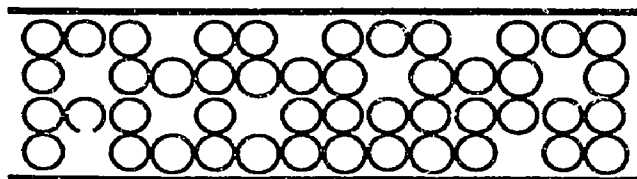


Fig. 4. Film structure containing uniform colloid particles.

the steps, δ , but enhanced the stratification process which was revealed by both the increased number of transitions and the lifetime of each metastable state. The available data [24] allowed us to show that the decrease in δ with increasing C_s is about the same as that of the Debye length $1/\kappa$ (SDS is a strong electrolyte), but the much stronger increase in the micellar (particle) concentration C_p was affecting the decrease in R_κ , to produce an overall increase in ϕ . This explains the enhanced stratification.

Quite different is the effect of a neutral strong electrolyte, NaCl, which was always found to decrease stratification. Indeed, the addition of NaCl in moderate concentrations to micellar solutions of SDS decreases $1/\kappa$ without an appreciable effect on the micellar aggregation number or the critical micelle concentration (CMC). This leads to a decrease in R_κ at (almost) constant C_p , which eventually leads to a decrease in ϕ . Above a given electrolyte concentration (specific for each surfactant concentration C_s), the stratification vanished altogether. These results are plotted in Fig. 5 as a phase diagram, the region on the left of the solid line corresponding to stratifying films and on the right of it to non-stratification. The broken line on the same figure shows the results of Hachisu et al. [12] and Ohtsuki et al. [25] for the order–disorder phase transition in latex suspensions (the ordered phase region is on the left of the broken line). Although the electrolyte concentration in our experiments was much higher, owing to the much smaller particle size, the close resemblance of the two plots bears out our explanation of the stratification as being a restricted-volume-induced phase transition.

Increasing the neutral electrolyte concentration is known to promote liquid crystal formation in surfactant systems [26]. Therefore, if stratification were due to the formation of a liquid crystal structure, it should be enhanced by adding electrolyte. However, both our results as well as those of Kersekemp and Lyklema [4] show the opposite trends.

We also found [27] similar parallel trends

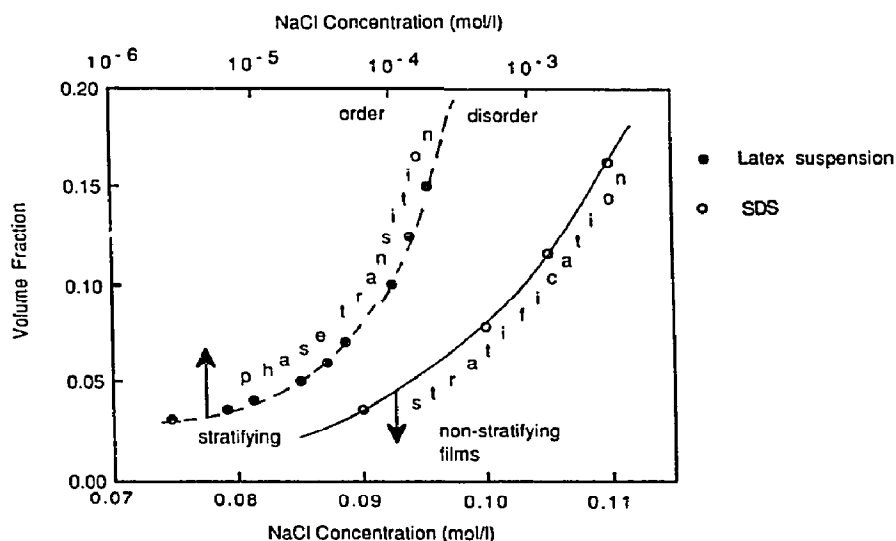


Fig. 5. Volume fraction vs concentration of added NaCl for latex suspension and micelles. The broken line is the experimental curve of Hachisu et al. [12] for the added electrolyte order–disorder phase diagram for latex dispersions. The results for stratifying–non-stratifying films are plotted also as a phase diagram. The region on the left of the solid line corresponds to stratified film and on the right to non-stratified film.

between micellization behavior and stratification with two non-ionic surfactants: Endoret AE 1215-9.4 and AE 1215-30 (both are products of Shell Co. and consist of a straight paraffinic chain with 12–15 carbon atoms ethoxylated with 9.4 or 30 ethylene oxide groups). We found out that increasing the surfactant concentration was enhancing the stratification. This is obviously a result of the increased particle concentration C_p . The step height δ slightly decreased with increasing C_s , but was always approximately equal to the micellar diameter $2R_p$ determined by dynamic light scattering: for example $\delta = 15.0 \pm 0.6$ nm vs $2R_p = 15.0 \pm 1.5$ nm for 0.008 M AE 1215-9.4 and $\delta = 11.2 \pm 0.6$ nm vs $2R_p = 10.6 \pm 2.1$ nm for 0.026 M AE 1215-30. The stratification with non-ionic surfactants is very sensitive to the temperature: whereas the stratification is pronounced at around 25°C, it decreases rapidly with the increase in temperature and above 35°C it completely disappears for all surfactant concentrations. The effect of the temperature on micellar structuring was studied by Nakagawa et al. [22] for the surfactant $C_{10}H_{21}O(C_2H_4O)_{12}CH_3$ which shows physico-chemical behavior close to that of Endoret

AE 1215-9.4. From their data we calculated C_p and R_p (for their solutions), the latter from the second virial coefficient, assuming that the micelles are hard spheres. We found out that while R_p did not change with the temperature, C_p decreased, thus leading to a decrease in ϕ which explains the depressed stratification in our experiments.

By pre-equilibrating a $5.2 \cdot 10^{-2}$ M solution of Endoret AE 1215-30 with *n*-decane we also established that the lifetimes of the metastable states became considerably shorter. The data of Nakagawa et al. [29] on the properties of solutions of swollen micelles of $C_{10}H_{21}O(C_2H_4O)_8CH_3$ allowed us to conclude that the solubilization of *n*-decane decreases both C_p and R_p . The ensuing decrease of ϕ explains why solubilization of oil weakens the stratification.

Model development

The hard-sphere model is quite satisfactory as far as non-ionic micelles are concerned. It might be questioned though when applied to ionic micelles, because depending on the force pushing the micelles against each other, the distance

between them could become considerably different from $2R_K$. That is why we attempted a more elaborate quantitative treatment [11,30] of stratifying films with ionic surfactants. The main points of the theoretical model developed in Refs [11] and [30] are briefly outlined below. We assumed that the micelles in a metastable microscopic film are under the combined action of the meniscus capillary pressure and the film disjoining pressure Π . We introduced a new component of the disjoining pressure Π^{ms} to account for the pair-wise micellar interaction (in a direction normal to the film surfaces) and thus for the micellar structure inside the film. Since the van der Waals attraction between the micelles turned out to be negligible, in the expression for Π^{ms} which we derived, we accounted only for the long-range screened electrostatic repulsion between the micelles [31]. However, since the van der Waals attraction between the film surfaces is important in the total disjoining pressure Π_n , for a film with n micellar layers in it, we included terms accounting for (i) the van der Waals attraction between the film surfaces, (ii) the electrostatic repulsion between them, and (iii) the intermicellar interaction Π^{ms} .

By integration of Π_n with respect to the film thickness h we derived an expression for the specific interaction energy Δf_n per unit area of the film. (For details of the calculation procedure the reader is referred to Refs [11] and [30].) The curves $\Delta f_n(h)$, $n=0, 1, 2, \dots$ (see Fig. 6) exhibit minima which correspond to the metastable states ($n=1, 2, 3, \dots$) and to the final stable state without micelles ($n=0$) of the film. A stepwise film-thickness transition can be interpreted as a transition from a given metastable state to the next. The experimental values of the film thickness are in good agreement with those calculated theoretically. The shape of the interaction energy curves, $\Delta f_n(h)$, also reflects properly the phenomenon of stratification, the energy of the metastable states decreasing with the decrease in the film thickness.

Since the derivative of the interaction energy $\Delta f_n(h)$ with respect to the thickness gives the interaction force between the film surfaces, the latter

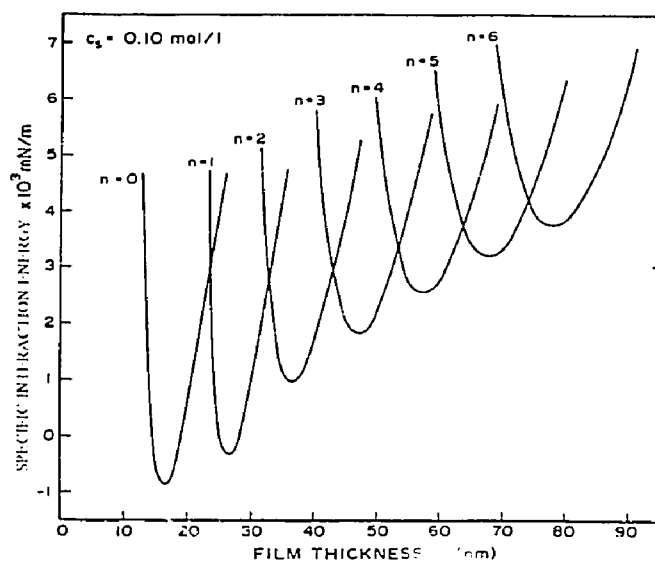


Fig. 6. Calculated isotherms of the specific interaction energy in the film $\Delta f_n(h)$ at a concentration of 0.1 M, and at different numbers of micellar layers in the film.

should be also oscillatory. This result is similar to the oscillatory forces reported by Israelachvili and Pashley [32] which are due to the short-range solvation forces of K^+ ions [33]; however, in our case the phenomenon of stratification is governed by long-range screened electrostatic repulsion between micelles. The oscillatory shape of the excess energy vs thickness curves (Fig. 6) was predicted on the ground of qualitative considerations by Kenskamp and Lyklema [4] for films with liquid-crystal-like structures [3].

Concluding remarks

It is important to understand the mechanism of stratification and the factors governing it, since foams or emulsions and particle suspensions are much more stable when the lamellae separating the bubbles or drops are stratifying. It is also possible that other systems, such as microemulsions, or solutions of globular proteins form stratifying films (for example in food emulsions). Besides controlling the stability of dispersions, it might be possible to create new materials such as biochips with prescribed microstructures.

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