

MULTI-STEPWISE DRAINAGE AND VISCOSITY OF MACROSCOPIC FILMS FORMED FROM LATEX SUSPENSIONS

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Vertical, macroscopic thinning films formed from micellar solutions or latex suspensions exhibit a series of parallel, colored horizontal stripes of different thickness and, with time, of gradually increasing width. Such a step-wise profile can be explained by the existence of an ordered structure of spherical colloidal particles inside the film. It was established experimentally that, at a given temperature, the boundaries between the stripes are moving downwards with constant velocities. In addition, it was observed that colored circular spots, of lesser thickness than the surrounding film, are moving upwards in the lower stripes and, eventually, fuse with the corresponding colored stripe. The motion of the circular spots in a vertical stratifying film was used to determine the viscous properties of the ordered structure inside the film. It was found that the effective dynamic viscosity of the colloid crystal-like structure inside the film was about 100 times larger than the viscosity of the pure solvent.

INTRODUCTION

Step-wise thinning of liquid foam films was observed long ago by Johnnott¹ and Perrin². This phenomenon, called stratification, was later observed and investigated by many authors, with both foam films³⁻⁷ and emulsion films^{8,9}. A possible explanation of the step-wise decrease of the film thickness, suggested in some works^{7,9}, is that a lamellar liquid crystal structure is formed inside the stratifying film. However, some recent experiments with both latexes and micellar solutions of ionic and nonionic surfactants¹⁰⁻¹² revealed that stratification is observed with films formed from solutions containing monodisperse spherical colloid

particles. These results lead us to the conclusion that surfactant micelles or latex particles inside the film form a colloid crystal structure which resembles the structures observed by Hachisu et al.¹³ for latex particles in bulk aqueous solutions. A theoretical model based on this idea provided a quantitative explanation of the metastable states of the film¹⁴ and of the mechanism of stratification.¹⁵

The stratification of horizontal, microscopic liquid films represents a process of consecutive formation and expansion of spots having lesser thickness than the remaining part of the film^{11,12,15}. The appearance of stratification is quite different with macroscopic vertical or inclined films, which can be formed in a frame or in a test tube - Figure 1a. With films formed from latex suspensions, one observes a series of horizontal stripes of different, uniform colors at the upper part of the film¹⁰. The different colors are due to interference of the common (polychromatic) light reflected by stripes of different, uniform thicknesses. The boundaries between the stripes are very sharp, a consequence of the step-wise profile of the film surface in this region (Figure 1b) and the liquid meniscus below the film appears as a region with gradually changing colors. Similar pictures with horizontal stripes can be observed with micellar solutions of nonionic surfactants¹⁰. However, in the latter case, all stripes are gray in color, though with different intensity because the diameter of the micelles is smaller (about 10 nm in Ref.10) than that of the latex particles.

According to the colloid crystal model, the stripes of different thicknesses contain different numbers of micellar layers inside the film (Figure 1b). In the case of charged particles (ionic surfactant micelles or latex particles) the height of a step is approximately equal to the effective particle diameter, i.e. the sum of the diameter of the particle itself and the thickness of its Debye atmosphere^{11,14}.

Similar detailed experimental studies of vertical stratifying films are still missing and the present paper is a first step in this direction. We measured both the velocity of the boundaries between the colored stripes of different thicknesses and the speed of rising circular spots. These data provide information about the viscosity and other properties of the colloid crystal structure inside the film. As a model system, we chose an aqueous solution of submicron latex particles and the results of these experiments are presented and discussed below.

EXPERIMENTAL SET-UP AND OBSERVATIONS

In our experiments we used a monodisperse, latex suspension of particles with a diameter of 156 nm (Dow Chemical) and were in a 44 wt% concentration. The concentration was determined by measuring the weight of a sample of the suspension before and after dehydration.

The suspension was placed in a cylindrical test-tube with an optical glass wall and the inner tube diameter was 2.5 cm. By shaking the test-tube one forms a flat, circular liquid film. The tube is then laid horizontally (Figure 1a) in a thermostated cell with a metal bottom and transparent walls made of optical glass. After being placed in a vertical position, the film was observed by means of a horizontal microscope and a set of horizontal stripes of different colors appear in the upper part of the film. The upper stripe is black when observed in reflected light and the next lower stripes have the following colors: white, yellow, blue and red. Following this, a sequence of alternating green and red stripes of different nuances were observed. Because the boundaries of the stripes are moving downwards with different velocities, the area of the stripes

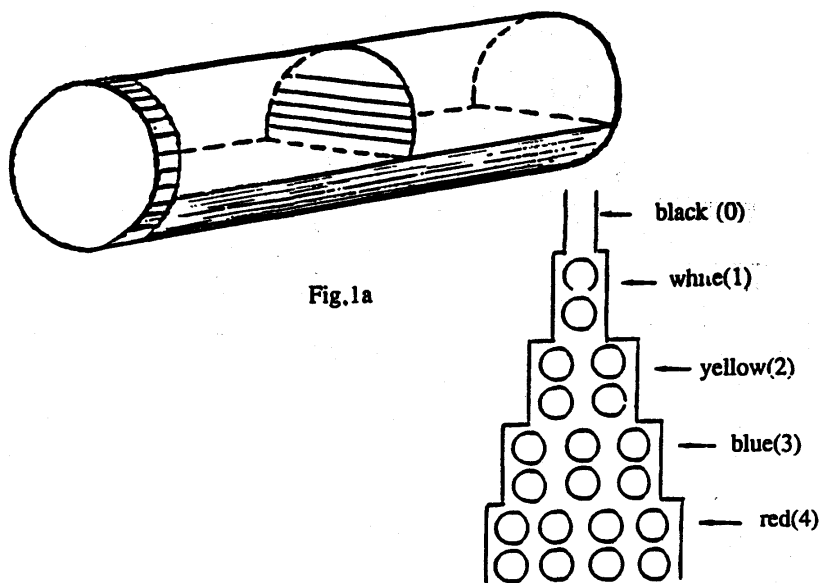


Fig. 1a

Fig. 1b

Figure 1. A vertical stratifying film formed from a latex suspension in a test tube (a). The multi-stepwise profile of the film can be explained by the formation of a colloid crystal structure (b).

increases and the lower stripes disappear one after another after reaching the meniscus of the bulk suspension situated below the film.

According to the colloid crystal model, the stripes of different color (thickness) contain different numbers of particle layers. More specifically, the black stripe (very thin film) does not contain particles; the white stripe contains 1 layer, the yellow one - 2 layers, the blue one - 3 layers, the red one - 4 layers, etc. To check this hypothesis we carried out the following experiment.

We illuminated the film with a beam of monochromatic light and observed the light reflected by the film. The angle of incidence was chosen to be 45° and the light wavelength λ could be gradually varied by means of a monochromator. The different thicknesses of the stripes are identifiable due to the difference in reflectivity. When varying λ , the reflectivity of a given stripe except the black one exhibits maxima and minima because of the light interference. In particular, we found that the "yellow" and the "blue" stripes had minimum reflectivity at $\lambda=445$ nm and 670 nm, respectively. (We name the stripes after their colors in reflected, polychromatic light.)

The thickness h of a given stripe can be estimated from the condition for interference minimum¹⁶

$$(k - \frac{1}{2})\lambda = 2nh \cos r, \quad k = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \dots, \quad (1)$$

where k is the order of interference, n is the refractive index of the film, and r is the refraction angle. For n we used the value 1.4 of the refractive

index of the bulk suspension. Since $\sin r = (\sin 45^\circ)/n$, we calculated $r=30.3^\circ$.

The colloid crystal model is consistent with a value $k=5/2$ for the order of the observed interference minima in the "yellow" and the "blue" stripes. Indeed, with $k=5/2$, $\lambda_y=445$ nm and $\lambda_b=670$ nm, Eq.(1) yields $h_y=368$ nm and $h_b=554$ nm (the subscripts "y" and "b" stand for "yellow" and "blue", respectively). Since these two stripes are neighboring, the difference $\delta=h_b-h_y=186$ nm is the height of the step-wise thickness change - see Figure 1b. Moreover, in agreement with the colloid crystal model the thickness of the white stripe is $h_w=h_y/2=184$ nm, i.e., $h_w \approx \delta$ where $\delta=185$ nm is the mean value of the height of a step. The latter value is 29 nm greater than the particle diameter (156 nm). Hence, the effective thickness of the Debye counterion atmosphere around a latex particle is 14.5 nm, which corresponds to 2×10^{-3} mol/l ionic strength of the solution.

MOTION OF THE BOUNDARIES BETWEEN THE STRIPES

The positions of the boundaries were measured in the following way. By means of the horizontal microscope, an arbitrarily chosen area of the vertical film was observed. The measurement scale, located in the microscope eye-piece, was also vertically oriented. The boundaries between the stripes of different colors were observed through the microscope. The position, L , of each boundary with respect to the zeroth division of the eye-piece scale, was recorded as a function of time, t . The results are presented in Figure 2 and the experiment showed that these results do not depend on the choice of the observation area.

The zero on the time axis in Figure 2 corresponds to the moment when a boundary reaches the zero on the eye-piece scale. One sees that each of the boundaries between the stripes is moving with constant velocity during the observation period.

The question of what the driving force is behind the stripes motion is still open and several possibilities are discussed below.

(i) In principle, the *weight of the thicker film* below each stripe can force it to expand with time. The direction of the stripes motion confirms the role of gravity as a driving force. However, the weight of the film decreases with time, whereas the stripes velocities do not depend on time - see Figure 2. Hence, the role of gravity, despite its undoubted importance, is not directly manifested through the weight of the film.

(ii) If γ_1 and γ_2 are the film tensions of two neighboring stripes of the film, then the difference $\Delta\gamma = \gamma_2 - \gamma_1$ can also be the driving force acting on the contact line. An argument in favor of such an assumption is the experiment of Yamanaka¹⁷, who established that the velocity of the boundary between two vertical films of different thicknesses is proportional to $\Delta\gamma$. The role of $\Delta\gamma$ can be confirmed or rejected in experiments with horizontal stratifying films (like those in Refs. 10 - 12) which allows direct measurement of $\Delta\gamma$ for the different color stripes.

(iii) Another possible explanation is provided by the *vacancy diffusion mechanism*, originally proposed in Ref.15 to explain the formation and expansion of dark spots in horizontal stratifying films. According to this mechanism, vacancies exist in the colloid crystal structure inside the film. A vacancy is formed when a colloidal particle leaves the film and enters the Plateau border. Upon formation, the vacancies move throughout the film, due to selfdiffusion, and "condense" after reaching the boundary of the film with lesser thickness¹⁵. Thus,

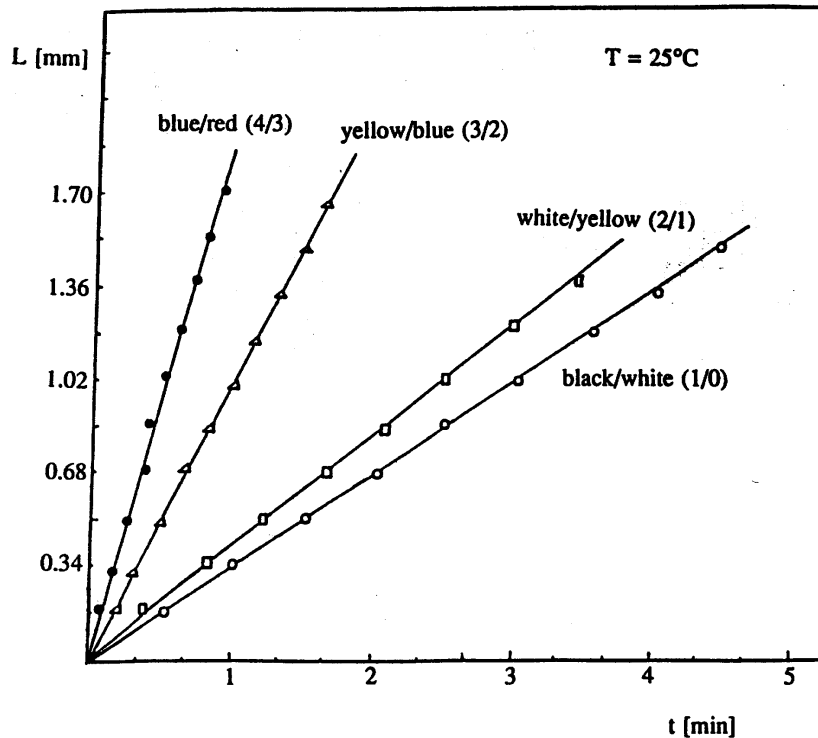


Figure 2. Experimental data for the vertical coordinate, L , of the boundary between two stripes of different colors as a function of time, t . $T = 25^\circ\text{C}$.

new area is added to the thinner film and the contact line moves toward the thicker film. The experiments with horizontal films¹⁵ showed that the thicker the film, the faster the contact line motion. Similar behavior is observed with the vertical films - see Figure 2. Most probably the source of the vacancies is located at the boundary of each stripe with the narrow circular Plateau border between the film and the framing glass wall. Indeed, one observes continuous disturbances of the interference fringes in this marginal Plateau border which can be attributed to the outflux of particles and solvent due to the incessant formation and condensation of vacancies. As observed by Hudales and Stein¹⁸, the main outflux of the excess solution from a thinning vertical film is realized through the marginal Plateau border.

MOTION OF SPOTS IN THE STRIPES AND VISCOSITY OF THE COLLOID PARTICLE STRUCTURE

The vacancy diffusion mechanism is also supported by the following observation. As mentioned above, the lower stripe contacts with the meniscus of the bulk solution - see Figure 1a. At the contact line between the lower stripe and the meniscus, circular spots appear. They have the color of the next upper stripe and they move upwards until reaching and joining it - Figure 3. In accordance with Ref.15 such spots can be formed by condensation of vacancies when the concentration of the latter exceeds some threshold value. Such spots are observed only in the lower stripe, where the formation of vacancies is enhanced due to the contact with both the marginal Plateau border and with the bulk solution meniscus beneath.

The spots move upwards with a constant velocity, just like bubbles rising in a viscous fluid. Near the upper boundary of the stripe, the velocity of the spot decreases due to hydrodynamic interactions with the boundary. The shape of the spots is almost circular, which is an indication of the action of positive line tension (a one-dimensional counterpart of the surface tension). The larger spots rise faster. If

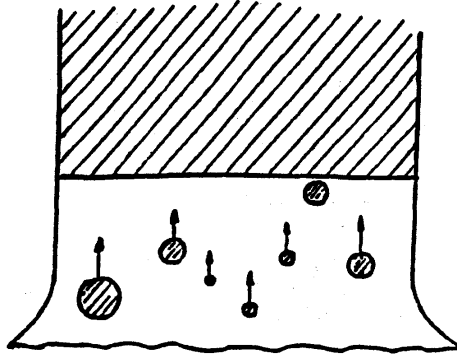


Figure 3. Circular spots of different sizes in the lower stripe. The arrows denote the direction of the spot motion.

two spots come close enough to one another, disturbances in their velocities are observed. This is an obvious manifestation of two-dimensional hydrodynamic interactions.

The analogy between rising spots and bubbles led us to try and determine the effective viscosity of the colloid crystal structure inside the film by using a two-dimensional analogue of the known Stokes formula. With this end in view we measured the radius a and the velocity v of a number of spots satisfying the following conditions:

- (i) the spot is far enough from the stripe boundaries so that it moves with constant velocity;
- (ii) the velocity of the spot is not perturbed by the proximity of other spots.

The cross section of a spot is presented schematically in Figure 4 where h_n is the thickness of a film containing n layers of particles inside. In reality the spot diameter is much larger than its thickness: $2a \gg h_{n-1}$ (for example, for a typical spot $2a = 4 \times 10^{-2}$ cm, whereas $h_{n-1} = 5 \times 10^{-5}$ cm). To estimate the effective viscosity η of the substance inside the film, we will assume that during the motion of the spot, in the cylinder with cross-section ABCD (Figure 4), it is streamlined by the surrounding substance. The total friction force can be estimated by using the equation¹⁹

$$F = 2 \frac{4\pi\eta v(\delta/2)}{\ln \frac{C}{Re}} \quad (2)$$

which describes the force F acting on two portions, each of length $\delta/2$ ($\delta = h_n - h_{n-1}$ is the height of a step), of an infinitely long cylinder which is streamlined by a fluid of velocity v and viscosity η . Here

$$Re = \frac{2apV}{\eta} \quad (3)$$

is the Reynolds number, ρ is the density of the film substance and a is the radius of the cylinder; C is a dimensionless constant equal to 7.406 for an infinite cylinder¹⁹.

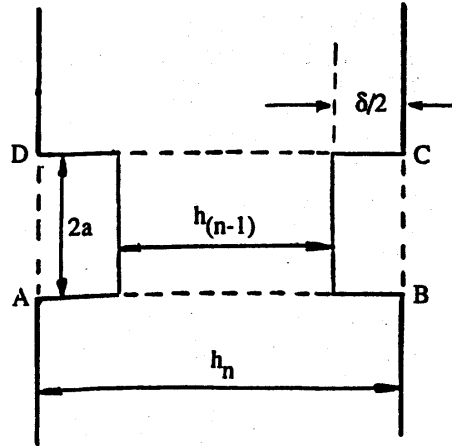


Figure 4. Section of a vertical film of thickness h_n containing spot of thickness h_{n-1} and diameter $2a$. In reality $a \gg h_{n-1}$.

When applying Eq.(2) to rising spots we have neglected the following effects:

- 1) "edge" effects due to the fact that the spot (the cylinder ABCD in Figure 4) is not a part of an infinitely long cylinder;
- 2) surface viscous effects in the film surfaces;
- 3) the observed slight deformation of the spot (deviation from circular shape) due to the streamlining.

Since the rising velocity of a spot is constant, the friction force counterbalances the buoyancy force, i.e.

$$F = 2\rho g \pi a^2 \left(\frac{\delta}{2}\right) \quad (4)$$

where g is the gravity acceleration. By eliminating F and Re between Eqs.(2), (3) and (4) one derives

$$-\ln \tilde{Re} = -\ln \frac{C\eta}{\eta_0} + \frac{4\eta v}{\rho g a^2} \quad (5)$$

where

$$\tilde{Re} = \frac{2\rho a v}{\eta_0} \quad (6)$$

and $\eta_0 = 0.01 \text{ g.cm}^{-1}.\text{s}^{-1}$ by definition. Our data for v and a are presented in Figure 5 in coordinates, allowing the determination from Eq. (5) of the viscosity η .

The data shown in Figure 5 are taken at a temperature of 25°C . The upper line corresponds to blue spots in the red stripe ($h_n = 740 \text{ nm}$), whereas the lower line corresponds to yellow spots in the blue stripe ($h_n = 555 \text{ nm}$). From the slopes of both lines one calculates $\eta \approx 1.6 \text{ p}$ ($1 \text{ p} = 1 \text{ g.cm}^{-1}.\text{s}^{-1}$). In view of the approximate character of the calculated values of η one can only conclude that the value of η is of the order of $1 \text{ g.cm}^{-1}.\text{s}^{-1}$. If one calculates the constant C from the intercepts of the lines in Figure 5 by using η as determined from the slopes, values of C different from 7.406 are obtained. This is not surprising in view of the limitations on the applicability of Eq.(2) to our case. (As mentioned above, $C=7.406$ for an infinite cylinder, whereas in our case the "cylinder" is, in fact, a very thin disk; as a result, edge effects can be important.)

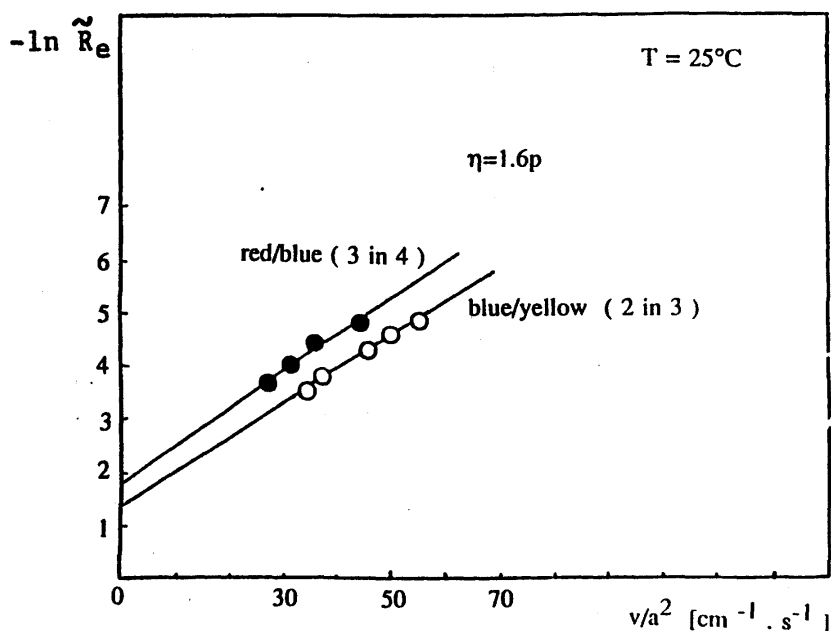


Figure 5. Plot of $-\ln \tilde{R}_e$ vs v/a^2 for blue spots in the red stripe \bullet and for yellow spots in the blue stripe \circ at 25°C .

DISCUSSION

Benzing and Russel²⁰ measured the dynamic viscosity η of latex suspensions by using an oscillatory viscosimeter. For particle volume fractions $0 < \phi < 0.3$, they determined values of η that are all of the order of $10^{-2} \text{ g.cm}^{-1}.\text{s}^{-1}$ - see Fig.9 in Ref.20. The particle radius in their experiment was $b = 52.5 \text{ nm}$, i.e. of the same order as in our experiment ($b = 78 \text{ nm}$). However, the values of η determined in the previous section from the motion of the spots are two orders of magnitude larger than the values measured in Ref.20. This difference deserves a special discussion. One reason for it might be the possible disruption of the colloid crystal structure caused by oscillations in the method used by Benzing and Russel²⁰. If this is the case, the discrepancy between the experimental

values of the suspension viscosity may be due to the fact that, in our experiments, we measured the dynamic viscosity of an ordered suspension, whereas the values of η determined in Ref.20 correspond to disordered suspensions. Indeed, the plot of η vs ϕ in Ref.20 agrees well with the equation²¹

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi + 6.2\phi^2 \quad (7)$$

which holds for a disordered suspension (η_0 is the viscosity of the pure solvent).

Below, we will try to demonstrate that a value of the viscosity $\eta \approx 1 \text{ g.cm}^{-1} \text{ s}^{-1}$ is reasonable for an *ordered* suspension. For that purpose we will use the known Frenkel equation²²

$$\eta = \frac{2kT}{\omega b \delta^2} \exp\left(\frac{U_m}{kT}\right), \quad (8)$$

where $\omega = 2\pi\nu$ is the angular frequency of the particle oscillations around the equilibrium position in the colloid crystal lattice, δ is the distance between the sites in the lattice, b is the radius of a particle, U_m is the energetic barrier between two neighboring sites, T is absolute temperature and k is Boltzmann's constant. The distance δ can be calculated from the particle volume fraction, ϕ , which is usually a known parameter of the experiment. With simple cubic packing one obtains:

$$\delta = b \left(\frac{4\pi}{3\phi} \right)^{\frac{1}{3}}. \quad (9)$$

The other two parameters in Eq.(8), ω and U_m , can be determined from the experimental values of the elastic shear modulus G' . The latter is defined as the coefficient of proportionality between stress and strain²³:

$$\tau = G' [\nabla u + (\nabla u)^T]. \quad (10)$$

Here u is the vector of the elementary displacement and τ is the resulting stress tensor. For a shearing parallel to the x-axis ($\Delta u_x = u$, $\Delta u_y = \Delta u_z = 0$) Eq.(10) reduces to

$$\tau_{xz} = G' \left(\frac{\Delta u_x}{\Delta z} + \frac{\Delta u_z}{\Delta x} \right) = G' \frac{\Delta u_x}{\Delta z} = G' \frac{u}{\delta}, \quad (11)$$

where we have substituted $\Delta z = \delta$ for the distance between two neighboring particle layers. The area per particle is δ^2 , and the force exerted on a particle is

$$f = \tau_{xz} \delta^2 = G' u \delta \quad (12)$$

On the other hand, the potential energy of a particle in the crystal lattice can be written in the form

$$U = \frac{1}{2} m \omega^2 u^2, \quad (13)$$

where m is the mass of the particle. The magnitude of the force is

$$f = \frac{dU}{du} = m \omega^2 u \quad (14)$$

Comparison of Eqs.(12) and (14) yields

$$\omega = \left(\frac{G' \delta}{m} \right)^{\frac{1}{2}} \quad (15)$$

In accordance with Figure 6 and Eq.(13) one calculates

$$U_m = U \left(\frac{\delta}{2} \right) = \frac{m \omega^2 \delta^2}{8} \quad (16)$$

One sees, that Eq.(8), along with Eqs.(9), (15) and (16), allows the calculation of the dynamic viscosity η of ordered suspensions if experimental values of φ and G' are available. G' was measured in Refs.20 and 24 and was found to vary between 0 and 700 N/m² for volume fractions $0 < \varphi < 0.3$. For our estimates we took values of G' from Figure 4b of Ref.20 for electrolyte concentration 10^{-5} mol/l - Table 1. The values of the other parameters are $b=52.5$ nm, $kT=4.1 \times 10^{-21}$ J. Assuming that the particle density is 1 g/cm³, we calculated $m=6.06 \times 10^{-19}$ g.

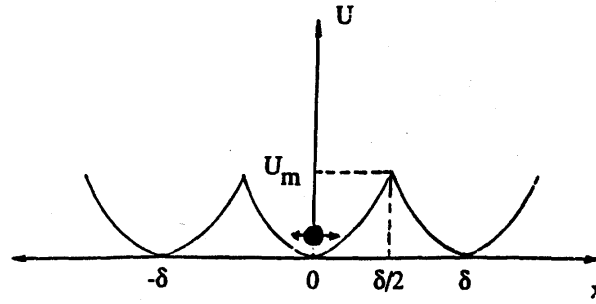


Figure 6. Potential energy U of a latex particle in a colloid crystal lattice of lattice constant δ .

The calculated viscosity η (Table 1) turns out to be strongly dependent on the volume fraction ϕ . The value of η for $\phi=0.30$ is of the same order as the values obtained by us from the motion of the spots at $\phi=0.44$. In other words, in ordered latexes, and at sufficiently large particle volume fractions ($\phi=0.3-0.5$), the effective dynamic viscosity can be 100 times larger than the viscosity of the solvent. Of course, this conclusion is valid only when Eqs.(2) and (8) can be applied.

Table 1. The calculated model parameters.

ϕ	0.25	0.30
G' (dyn/cm ²)	3530	5320
δ (nm), (Eq.9)	134	126
ω (s ⁻¹), (Eq.15)	2.8×10^8	3.3×10^8
U_m/kT (Eq.16)	13.0	16.3
η (g.cm ⁻¹ s ⁻¹) (Eq.8)	0.1	2.5

CONCLUDING REMARKS

In this work we focused our attention on the multi-stepwise thinning (stratification) of vertical films. This phenomenon is observed with films formed from solutions containing spherical particles: e.g. latexes or micelles of ionic and nonionic surfactants. The observed stepwise profile can be explained by the existence of a colloid-crystal structure inside the stratifying film.

In our experiments, as a model system, we used a suspension of monodisperse latex particles of diameter 156 nm. It was established that the boundaries between the stripes of different thicknesses (and colors) are moving with constant velocity. Different mechanisms for the motion of the stripes can be proposed and additional experiments are needed to discriminate between them.

Motion of small, almost circular spots was observed in the lower stripe. Since the spots have a lesser thickness than the surrounding film, their motion upwards is caused by the buoyancy force. By measuring the velocities and the radii of the spots we estimated the effective dynamic viscosity, η , of the colloid crystal structure inside the film. η turned out to be about 100 times larger than the viscosity of the pure solvent. Values of η of the same order are calculated from the experimentally measured elastic shearing modulus of ordered latex suspensions.

ACKNOWLEDGEMENT

This work was supported by the Bulgarian Ministry of Science and Higher Education and National Science Foundation.

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