

DLVO AND NON-DLVO SURFACE FORCES AND INTERACTIONS IN  
COLLOIDAL DISPERSIONS

D. N. Petsev, N. D. Denkov and P. A. Kralchevsky  
Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

ABSTRACT

Some aspects of DLVO and non-DLVO forces in colloidal systems are overviewed. The influence of long range interactions on some kinetic properties of dispersions, as Brownian diffusion, is discussed. It is shown, both theoretically and experimentally, that the electrostatic repulsion increases the collective diffusivity. The film stratification and oscillatory structure forces in colloidal suspensions are considered within the framework of a uniform approach. The presence of small colloidal species (e. g. micelles or polymer molecules) may lead to several maxima and minima in the disjoining pressure isotherm. The particular case of interacting emulsion droplets is examined accounting for the interfacial deformability. The droplet deformation acts as a soft repulsion but affects also the remaining contributions to the interaction energy due to changes of the droplet shape. A general procedure for calculating the inter-droplet interaction energy, as well as the equilibrium film radius and thickness in a doublet of droplets, is suggested. The energy of interaction between charged colloidal particles, due to correlations of the density fluctuations in the electric double layer is also studied. It is found that this effect may lead to attraction greater than the van der Waals contribution, especially when multivalent counter ions are present.

1. INTRODUCTION

Colloidal dispersions present a great interest from fundamental viewpoint by suggesting challenging theoretical and experimental research problems, most of them related to the stability with respect to flocculation or coalescence. The first successful attempt for quantitative treatment of the colloidal stability is Derjaguin-Landau-

Verwey-Overbeek (DLVO) theory<sup>1-3</sup>. According to this theory the dispersion stability is determined by a counter balance of electrostatic repulsion and van der Waals attraction between the particles. However, during the last decades it was shown (mostly by surface force balance experiments) that other types of surface forces could be present: steric, depletion, oscillatory structural forces, hydrophobic, hydration and ionic-correlation forces. The interparticle forces are important not only for the stability of colloidal systems but also for their rheological and diffusion properties. This allows to probe the interactions between particles by means of recently developed techniques as dynamic light scattering<sup>5</sup>.

In this paper we present a review of our recent studies on particle interactions and their impact on the properties of colloidal systems. The next Section deals with the influence of the long range DLVO forces, as electrostatic and van der Waals, on the diffusion coefficient of colloidal particles. Section 3 is devoted to the oscillatory structural forces which appear when smaller colloidal solutes, as micelles or polymer molecules, are present along with the larger colloidal particles. It is shown that the latter forces manifest themselves in a phenomenon called "stratification" (layer by layer thinning) of thin liquid films. Section 4 examines the effect of the interfacial deformability of emulsion and microemulsion droplets on the interdroplet interactions. Section 5 summarizes some results on ionic-correlation surface forces. The effect is mostly pronounced when multivalent counterions are present.

## 2. ELECTROSTATIC INTERACTIONS AND DIFFUSION OF CHARGED COLLOIDAL PARTICLES

The general theoretical approach for the treatment of the diffusion in suspensions of interacting particles at low volume fraction was developed by Batchelor<sup>6</sup> and Felderhof<sup>7</sup>. According to this approach the diffusion coefficient,  $D$ , in suspension of interacting particles, is presented as a power expansion for small values of the volume fraction,  $\phi$ ,

$$D = D_0(1 + \lambda \phi + \dots). \quad (1.1)$$

The first order coefficient  $\lambda$  contains several contributions which account for different kinds of particle interactions: hydrodynamic and surface forces. They are given by integrals over simple expressions, containing the radial distribution function<sup>7</sup>.  $D_0$  is the diffusion coefficient at infinite dilution. The motion of a given particle is characterized by the self diffusion coefficient,  $D_S$ , while that of an ensemble of particles by the col-

lective diffusion coefficient,  $D_C$ . Both coefficients,  $D_S$  and  $D_C$ , can be calculated but hereafter we will discuss mainly the collective diffusivity. Batchelor and Felderhof<sup>6,7</sup> presented numerical results for hard spheres which were in good agreement with each other. However, very often the colloidal particles are charged and a long ranged electrostatic repulsion is present. Recently we proposed a simple model for describing the diffusion in suspension of charged particles<sup>8,9</sup>. It suggests expressions for the coefficient  $\lambda$  as a function of the parameters of the particles and the surrounding medium: surface charge (or potential), particle radius, electrolyte concentration, etc. The case of *weakly charged* colloidal particles (the energy of electrostatic interaction over  $kT$  is less than 1) is very simple<sup>8</sup> and gives

$$\lambda = 1.45 + \frac{\Psi_0^2 \epsilon a}{kT} (1 + \kappa a) \frac{3}{(\kappa a)^2}. \quad (1.2)$$

The first term in the right hand side of eq. (1.2) accounts for the hard sphere contribution, while the second one originates from the electrostatic repulsion.  $\Psi_0$  is the particle surface potential,  $\epsilon$  is the dielectric constant of the solvent,  $a$  is the particle radius,  $\kappa$  is the Debye screening parameter which depends on the electrolyte concentration and  $kT$  is the thermal energy. The collective diffusion coefficient is liable to experimental determination by dynamic light scattering experiments. Such measurements were performed<sup>8</sup> at different particle volume fractions and electrolyte concentrations. Using eq. (1.1) one can obtain the coefficient  $\lambda$  at different electrolyte concentrations (different values for  $\kappa a$ ). The result is plotted in Figure 1 together with the theoretical prediction, eq. (1.2). The particle surface potential,  $\Psi_0$ , is regarded as a fitting parameter. It is seen that the agreement between the model and the experimental results is very good. The contribution of ion binding or release due to the particles could be neglected in the electrolyte concentration range we used. The increase in the collective diffusion coefficient at low electrolyte concentration is due to the stronger electrostatic repulsion. The self diffusion coefficient, however, exhibits the opposite behavior and decreases with the electrolyte concentration<sup>8</sup> (the same is true for the sedimentation velocity).

The diffusion of *strongly* charged particles (interaction energy over  $kT$  is greater than 1) is more complex from theoretical viewpoint. The coefficient  $\lambda$  can not be calculated by means of eq. (1.2) since it is strictly valid for particles with relatively low surface potential. This case could be treated by applying a perturbation procedure in combination with numerical solution of the Poisson-Boltzmann equation for determination of the electrostatic interaction energy<sup>9</sup>. In the case of thin electric double layers ( $\kappa a > 1$ ) the numerical calculations could be considerably simplified. The contribution

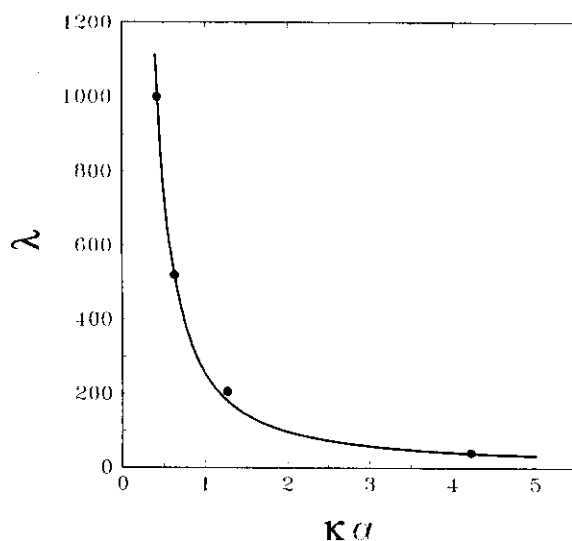


FIG. 1 Interaction parameter  $\lambda$  vs.  $\kappa a$  for latex spheres with radius  $a = 12.7$  nm. The curves (1) and (2) are calculated at constant surface potential  $\Psi_0 = 37.7$  mV.

of the van der Waals interactions was also analysed and it was established that they are not important for stable suspensions.

This approach allows either to predict the diffusion coefficient if the properties of the colloidal particles are known, or to quantitatively determine some of these properties (e. g. particle charge or potential) from dynamic light scattering experimental data.

### 3. OSCILLATORY FORCES AND FILM STRATIFICATION

Stratification (stepwise thinning) of foam films was observed in the beginning of the century by Johnnot and Perrin<sup>10</sup>. Later this phenomenon was investigated with foam<sup>11</sup> and emulsion<sup>12</sup> films formed from ionic micellar surfactant solutions. It was shown recently<sup>13</sup> that this phenomenon is more universal and can be observed also with non-ionic micelles, swollen micelles and even latex particles. In fact, stratification can be observed in films containing any submicron particles with narrow size distribution and repulsive interactions. Since stratification in micellar solutions occurs at sur-

factant concentrations much lower than those necessary for liquid crystal structure formation, and a similar stratification was observed with suspensions of submicron polystyrene latexes, one may conclude that the explanation of stratification with the presence of lamellar surfactant liquid crystal layers in the film is not relevant. Recently, we directly proved<sup>14</sup> by means of cryo-electron microscopy of frozen films from micellar solutions, that the stratification is caused by spherical surfactant micelles present in the film. We have shown that stratification is controlled by the particle volume fraction inside the film which increases during the thinning and depends on several factors (surfactant concentration, temperature, electrolyte concentration, etc.) affecting the volume fraction. A theoretical model was developed<sup>15</sup> for more quantitative treatment.

Below we outline a recent model<sup>16</sup> for quantifying the structural (oscillatory) component of the disjoining pressure in thin films. The following semiempirical formula is suggested,

$$\begin{aligned} \Pi_{\text{os}} &= P_0 \cos\left(\frac{2\pi h}{d_1}\right) \exp\left(\frac{d^3}{d_1^2 d_2} - \frac{h}{d_2}\right) \quad \text{for } h > d, \\ &= -P_0 \quad \text{for } 0 < h < d, \end{aligned} \quad (3.1)$$

where  $h$  is the film thickness and  $d$  is the particle diameter. The oscillatory period  $d_1$  and decay length  $d_2$  are given by

$$\frac{d_1}{d} = \sqrt{\frac{2}{3}} + a_1 \Delta\phi + a_2 (\Delta\phi)^2, \quad \frac{d_2}{d} = \frac{b_1}{\Delta\phi} - b_2. \quad (3.2)$$

The coefficients  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  are determined by comparison with the theory of Henderson<sup>17</sup>, while  $\Delta\phi = \phi_{\text{max}} - \phi$  is the difference between the close packing and the actual volume fraction of the particles. The particle osmotic pressure  $P_0$  in eq. (3.1) is calculated by means of the Carnahan-Starling formula<sup>18</sup>

$$P_0 = \frac{6\phi kT}{\pi d^3} \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}. \quad (3.3)$$

If long range interactions between the particles, as electrostatic, are present, an effective hard core diameter could be introduced

$$d(T) = \left[ \frac{3}{2\pi} B_2(T) \right]^{1/3}, \quad (3.4)$$

with  $B_2(T)$  being the second osmotic virial coefficient. One must bear in mind that all the free ions in the solution should be taken into account<sup>19</sup>.

The model described above was applied for calculation of the disjoining pressure isotherm of a stratifying foam film from a 0.06 M aqueous solution of sodium dodecyl sulfate -- Figure 2. The capillary pressure is plotted with dotted line indicating that several metastable states are possible.

The mechanism of stratification is important since it is related to the stability of many colloidal systems of practical interest as foams and emulsions. More details are available in a recently published review paper<sup>20</sup>.

#### 4. INTERACTION BETWEEN DEFORMABLE EMULSION DROPLETS

The main features, distinguishing emulsions from solid dispersions, are the deformability and fluidity of the droplet - continuous phase interface. It is known that when two droplets of millimeter or submillimeter size approach each other they deform and a planar film forms between them<sup>21</sup>. The stability of this film usually determines the overall emulsion stability. In a recent series of papers<sup>22,23,24</sup> we addressed the following questions:

- (1) Do the smaller emulsion droplets (of micron and submicron size) deform upon collision?
- (2) How the droplet deformation affects the direct (e. g. van der Waals, electrostatic, etc.) and hydrodynamic interactions?
- (3) How the interfacial extension and bending contribute to the total interdroplet interaction energy?
- (4) How to account properly for the Brownian force when dynamic processes like coalescence are considered?
- (5) How does the deformability affect collective properties like osmotic pressure, diffusion and viscosity?

In order to calculate the energy of interaction between two deformed droplets we assumed that they acquire the shape of truncated spheres<sup>22</sup> separated by a planar film. Such geometry allows the exact calculation<sup>22,25</sup> of van der Waals attraction following the method of Hamaker<sup>26</sup>. The result for the van der Waals energy  $W^{VW}$  is liable to considerable simplifications in some particular cases<sup>22</sup>. For small deformations and droplet separations the result reads

$$W^{VW}(h,r) = -\frac{A_H}{12} \left[ \frac{3}{4} + \frac{a}{h} + 2 \ln\left(\frac{h}{a}\right) + \frac{r^2}{h^2} - \frac{2r^2}{ah} \right]. \quad (4.1)$$

The last two terms are due to the interaction across the planar film, with radius  $r$ , and

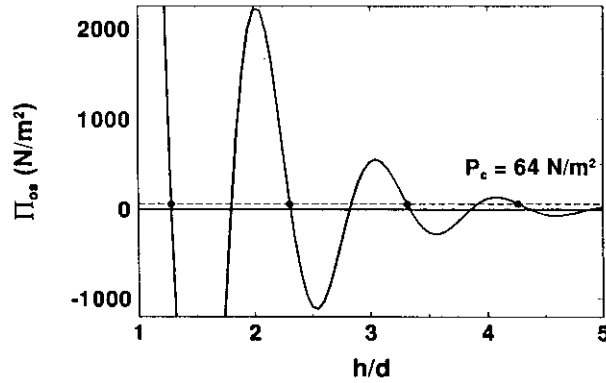


FIG. 2 Plot of the oscillatory disjoining pressure vs film thickness for stratifying foam film from 0.06 M aqueous solution of sodium dodecyl sulfate.  $P_c$  is the capillary pressure.

thickness  $h$ , formed between the droplets. The remaining terms correspond to interaction between spheres of radius  $a$ .  $A_H$  is the Hamaker constant<sup>26</sup>.

The electrostatic and other (as steric, depletion, oscillatory) contributions could be treated in the framework of a modified Derjaguin approach<sup>27</sup> which allows to present the energy as a sum of the interactions across the film and the adjacent spherical surfaces<sup>22,23</sup>.

The electrostatic repulsion is given by<sup>22</sup>

$$W^{El}(h, r) = \pi r^2 f^{El}(h) + \pi a \int_0^{\infty} f^{El}(H) dH, \quad (4.2)$$

where  $f^{El}(h)$  is the electrostatic free energy per unit area of an infinite planar film. The first term in the right hand side accounts for the repulsion across the film, while the second is due to interaction across the adjacent Plateau border. There are different expressions for this free energy, depending on the magnitude of the surface potentials and the electrolyte concentrations<sup>1-4</sup>. The simplest case is for high electrolyte concentration (thin electrical double layer) and arbitrary surface potentials

$$f^{El}(h) = 64 kT C_{El} \kappa^{-1} \tanh^2 \left( \frac{e \Psi_0}{4 kT} \right). \quad (4.3)$$

$C_{El}$  is the electrolyte concentration. Using appropriate expressions for the free energy

one may calculate the contribution of other types of interactions (e. g. steric, oscillatory, etc.) as well.<sup>23</sup>

The interfacial extension energy,  $W^S$ , and bending energy,  $W^B$ , which are a result of the droplet deformation, could be expressed as<sup>22,23</sup>

$$W^S(r) = \gamma \frac{\pi r^4}{2a^2} + E_G \frac{\pi r^8}{64a^6}, \quad (4.4)$$

and

$$W^B(r) = B_0 \frac{2\pi r^2}{a}. \quad (4.5)$$

$\gamma$  is the interfacial tension,  $E_G$  is the Gibbs elasticity and  $B_0$  is the interfacial bending moment. Often, the Gibbs elasticity term can be neglected in eq. (4.4). Eqs. (4.1)-(4.5) allow to calculate the total energy of interaction between two deformable droplets. This approach is convenient for analysing the formation of doublets of droplets and, hence, the flocculation in emulsions. In the special case of microemulsions, the bending contribution could be very important, leading to effective attractive energy of several tens of  $kT$ <sup>23,28</sup>.

As an illustration in Figure 3 we present a contour diagram of the interaction energy as a function of the film radius and thickness using eqs. (4.1)-(4.4). The Gibbs elasticity and the bending effects are not included and only the surface extension, electrostatic and van der Waals contributions are considered. The parameters, used for the calculation are:  $a = 1 \mu\text{m}$ ,  $\Psi_0 = 100 \text{ mV}$ ,  $\gamma = 1 \text{ mN/m}$ ,  $C_{E1} = 0.1 \text{ M}$  and  $A_H = 2 \times 10^{-20} \text{ J}$ . The depth of the minimum is  $W(h_e, r_e)/kT = -60.1$  at  $h_e/a = 0.0076$  and  $r_e/a = 0.076$ . The minimum corresponding to non-deformable spheres with the same set of parameters is  $W(h_e, r_e = 0)/kT = -51.1$  at  $h_e/a = 0.0062$ . Hence, the formation of a doublet of deformed droplets is energetically favorable.

The coalescence kinetics in emulsion requires an expression for the hydrodynamic resistance,  $\mu$ , acting between two approaching deformed droplets. Such expression was derived<sup>24</sup> and for tangentially immobile surfaces reads

$$\mu = \frac{3\pi\eta a^2}{2h} \left( 1 + \frac{r^2}{ah} + \frac{r^4}{a^2 h^2} \right). \quad (4.6)$$

$\eta$  denotes the dynamic viscosity of the solvent. Knowing the friction coefficient [eq. (4.6)] and the interaction energy [eqs. (4.1)-(4.5)] one may develop a Smoluchowski scheme, modified to account for the effects of the droplet deformability and flocculation followed by coalescence<sup>24</sup>.



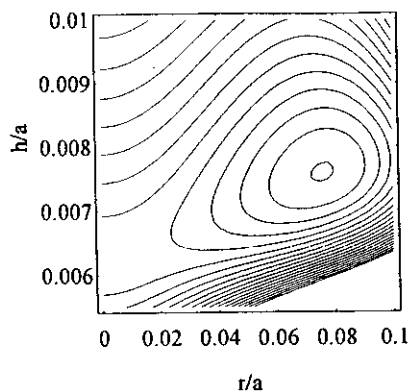


FIG. 3 Contour plot of the electrostatic and van der Waals interaction energy between two deformable droplets.  $A_{11} = 2 \times 10^{-20}$  J. The distance between two contours is  $2 kT$ .

Our approach is convenient for data interpretation, obtained with model monodisperse emulsions. A method for preparing such emulsions (based on depletion flocculation) was suggested by Bibette<sup>29</sup>.

### 5. IONIC CORRELATION SURFACE FORCES

In the case of two overlapping electric double layers, correlations in the ionic density fluctuations contribute to the free energy and disjoining pressure of the film. This effect was studied by Derjaguin and Muller<sup>2,3,30</sup> who considered such fluctuations only in the Stern layer. Further investigations took into account the ions inside the film by means of Monte Carlo method<sup>31</sup>, hypernetted chain integral equation<sup>32</sup> or by extending Poisson-Boltzmann theory<sup>33</sup>. These theories, however, present considerable mathematical difficulties and therefore are not often used in the interpretation of experimental results, though the ionic correlation effects are often significant and should be taken into account. For that reason we developed a conceptually and mathematically simpler approach by involving some model (stepwise ionic distribution) simplifications<sup>34</sup>. The actual smooth Poisson-Boltzmann ionic distribution is replaced by a model one in which different regions (with respect to ionic density) are defined. There are two regions of high (but uniform) density near the film surfaces (I) and a region of

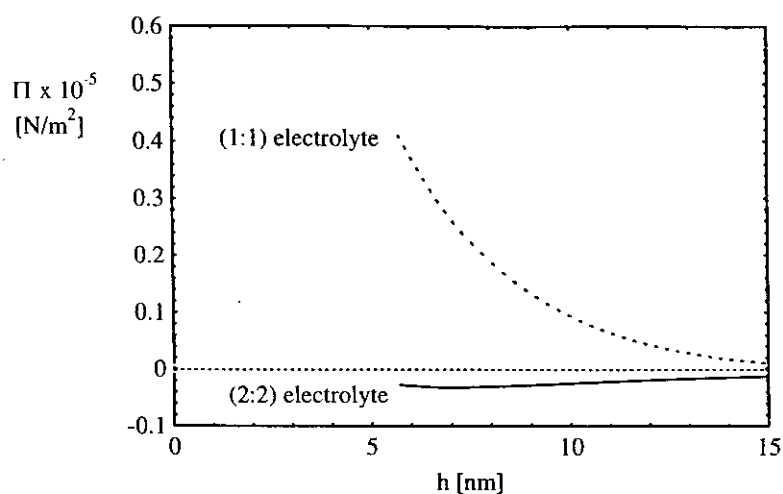


FIG. 4 Plot of the total disjoining pressure  $\Pi$  vs film thickness  $h$  at 0.04 M 1:1 (solid curve) and 2:2 (dashed curve) electrolyte concentration.

lower density in the middle (II). The sizes of these regions are determined within the framework of the model<sup>34</sup>. Such model allows the derivation of relatively simple (although still rather lengthy) analytical expressions for the correlation contribution to the free energy and disjoining pressure of the film. This approach gives not only simpler expressions but numerically correct results as well. The excess free energy, due to ionic correlations,  $\Delta f_{\text{corr}}$ , is given by

$$\Delta f_{\text{corr}} = 2 \frac{\hat{\kappa}_I^2}{8\pi} kT \left[ -\frac{2}{3} (\hat{\kappa}_I - \kappa_I) a + T \int_0^\infty \frac{dT}{T^2} \int_0^\infty dk k (H^I - H_\infty^I) \right] + \frac{\hat{\kappa}_{II}^2}{8\pi} kT \left[ -\frac{2}{3} (\hat{\kappa}_{II} - \kappa_{II}) s + T \int_0^\infty \frac{dT}{T^2} \int_0^\infty dk k (H^{II} - H_\infty^{II}) \right] \quad (5.1)$$

$\kappa$  and  $\hat{\kappa}$  are the local screening parameters in the actual and model ionic distributions respectively. The subscripts I and II denote different regions of the film. The functions  $H^I$  and  $H^{II}$  depend on the parameters of the system and their calculation is straightforward<sup>34</sup>. The disjoining pressure can be obtained directly from eq. (5.1) by using the relationship  $\Pi = -(\partial \Delta f_{\text{corr}} / \partial h)$ .

A calculation, based on the above approach, is illustrated in Figure 4. It shows the electrostatic and correlation contributions to the disjoining pressure for 0.04 M 1:1 and 2:2 electrolyte. The disjoining pressure is repulsive for 1:1 type of electrolyte and attractive for the 2:2 case. This means that the ionic correlation surface forces are more important when divalent ions are present. Negative values of the disjoining pressure have been also obtained by other authors<sup>31</sup>. The accuracy of the approximation, we used, was checked by comparison with the hypernetted chain results<sup>32</sup>. The agreement between the two approaches was shown to be very good<sup>34</sup>.

#### REFERENCES

1. E. J. W. Verwey and J. Th. G. Overbeek, "Theory and Stability of Lyophobic Colloids", Elsevier, Amsterdam, 1948.
2. B. V. Derjaguin, N. V. Churaev and V. M. Muller, "Surface Forces", Nauka, Moscow, 1985 (in Russian).
3. B. V. Derjaguin, "Theory of Stability of Colloids and Thin Films", Plenum, New York, 1989.
4. J. N. Israelachvili, "Intermolecular and Surface Forces", 2nd ed., Academic Press, London, 1991.
5. B. J. Berne and R. Pecora, "Dynamic Light Scattering", Wiley - Interscience, NY, 1984.
6. G. K. Batchelor, *J. Fluid Mech.*, 52, 245 (1972); *J. Fluid Mech.*, 74, 1 (1976).
7. B. U. Felderhof, *J. Phys. A* 11, 929 (1978); B. Cichocki and B. U. Felderhof, *J. Chem. Phys.*, 89, 1049 (1988); B. Cichocki, B. U. Felderhof and R. Schmitz, *Physico-Chem. Hydrodyn.*, 10, 383 (1988).
8. D. N. Petsev and N. D. Denkov, *J. Colloid Interface Sci.*, 149, 329 (1992).
9. N. D. Denkov and D. N. Petsev, *Physica A*, 183, 462 (1992); D. N. Petsev, N. D. Denkov and K. Nagayama, *Chem. Phys.*, 175, 265 (1993).
10. E. S. Johnnot, *Phil. Mag.*, 70, 1339 (1906); J. Perrin, *Ann. Phys. (Paris)*, 10, 160 (1918).
11. H. G. Bruil and J. Lyklema, *Nature (London)*, 233, 19 (1971); J. W. Kenskamp and J. Lyklema, *ACS Symp. Ser.*, 8, 191 (1975); S. Friberg, St. E. Linden and H. Saito, *Nature (London)*, 251, 494 (1974); E. Manev, J. E. Proust and L. Ter-Minassian-Saraga, *Colloid Polym. Sci.* 255, 1133 (1977).

12. E. Manev, S. V. Sazdanova and D. T. Wasan, *J. Dispersion Sci. Technol.*, 5, 111 (1984); P. M. Kruglyakov, *Kolloidn. Zh.*, 36, 160 (1974).
13. A. D. Nikolov, D. T. Wasan, P. A. Kralchevsky and I. B. Ivanov, in "Ordering and Organization in Ionic Solutions -- Proceedings of Yamada Conference XIX", World Scientific, Singapore, 1988; A. D. Nikolov and D. T. Wasan, *J. Colloid Interface Sci.*, 133, 1 (1989); A. D. Nikolov, D. T. Wasan, N. D. Denkov, P. A. Kralchevsky and I. B. Ivanov, *Prog. Colloid Polym. Sci.*, 82, 87 (1990).
14. N. D. Denkov, H. Yoshimura, K. Nagayama and T. Kouyama, *Phys. Rev. Lett.*, submitted for publication.
15. A. D. Nikolov, P. A. Kralchevsky, I. B. Ivanov and D. T. Wasan, *J. Colloid Interface Sci.*, 133, 13 (1989); P. A. Kralchevsky, A. D. Nikolov, D. T. Wasan and I. B. Ivanov, *Langmuir*, 6, 1180 (1990).
16. P. A. Kralchevsky and N. D. Denkov, *Chem. Phys. Lett.*, 240, 385 (1995); N. D. Denkov and P. A. Kralchevsky, *Progr. Colloid Polym. Sci.*, 98, 18 (1995).
17. D. Henderson, *J. Colloid Interface Sci.*, 121, 486 (1988).
18. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, 51, 635 (1969).
19. P. Richetti and P. Kekicheff, *Phys. Rev. Lett.*, 68, 1951 (1992).
20. D. T. Wasan, A. D. Nikolov, P. A. Kralchevsky and I. B. Ivanov, *Colloids Surfaces*, 67, 139 (1992).
21. I. B. Ivanov and D. S. Dimitrov, in "Thin Liquid Films", I. B. Ivanov, ed., Marcel Dekker, New York, 1988, chap. 2; I. B. Ivanov, *Pure Appl. Chem.*, 52, 1241 (1980).
22. N. D. Denkov, P. A. Kralchevsky, I. B. Ivanov and C. S. Vassilieff, *J. Colloid Interface Sci.*, 143, 157 (1991); K. D. Danov, D. N. Petsev, N. D. Denkov and R. Borwankar, *J. Chem. Phys.*, 99, 7179 (1993); K. D. Danov, D. N. Petsev, N. D. Denkov and R. Borwankar, *J. Chem. Phys.*, 100, 6164 (1994).
23. N. D. Denkov, D. N. Petsev and K. D. Danov, *Phys. Rev. Lett.*, 71, 3226 (1993); N. D. Denkov, D. N. Petsev and K. D. Danov, *J. Colloid Interface Sci.*, 176, 189 (1995); D. N. Petsev, N. D. Denkov and P. A. Kralchevsky, *J. Colloid Interface Sci.*, 176, 201 (1995).
24. K. D. Danov, N. D. Denkov, D. N. Petsev, I. B. Ivanov and R. Borwankar, *Langmuir*, 9, 1731 (1993); K. D. Danov, I. B. Ivanov, T. D. Gurkov and R. Borwankar, *J. Colloid Interface Sci.*, 167, 8 (1994).

25. J. K. Klahn, W. G. M. Agterof, van Voorst Vader, R. D. Groot and F. Graenweg, *Colloids Surfaces*, 65, 161 (1992).
26. H. C. Hamaker, *Physica*, 4, 1058 (1937).
27. B. V. Derjaguin, *Kolloid Z.*, 69, 155 (1934).
28. G. J. M. Koper, W. F. C. Sager, J. Smeets and D. Bedeaux, *J. Phys. Chem.*, 99, 13291 (1995); P. D. I. Fletcher and D. N. Petsev, *J. Chem. Soc., Faraday Trans.*, submitted
29. J. Bibette, *J. Colloid Interface Sci.*, 147, 474 (1990).
30. V. M. Muller and B. V. Derjaguin, *Colloids Surfaces*, 6, 205 (1983).
31. L. Gulbrand, B. Jonsson, H. Wennerstrom and P. Linse, *J. Chem. Phys.*, 80, 2221 (1984).
32. R. Kjellander and S. Marcelja, *J. Chem. Phys.*, 82, 2122 (1985); *Chem. Phys. Lett.*, 112, 49 (1984); *J. Chem. Phys.*, 90, 1230 (1986).
33. P. Attard, D. J. Mitchell and B. W. Ninham, *J. Chem. Phys.*, 88, 4987 (1988); *J. Chem. Phys.*, 89, 4358 (1988).
34. P. A. Kralchevsky and V. N. Paunov, *Colloids Surfaces*, 64, 245 (1992); V. N. Paunov and P. A. Kralchevsky, *Colloids Surfaces*, 64, 265 (1992).