

Contribution of ionic correlations to excess free energy and disjoining pressure of thin liquid films

2. Electric double layers outside the film

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Abstract

A dielectric thin film of charged surfaces intervening between two electrolyte solutions is considered as a model of the non-electrolyte films in water-in-oil emulsions, lipid bilayers or biomembranes. The fluctuations of the ion-charge density in the two electrolyte phases interact through the oil film thus giving rise to an effective attraction between the film surfaces, which is due to the ion correlations. The respective ionic correlation free energy of the film is calculated and its dependence on various factors is investigated. It is found that when the dielectric permittivity of the film substance is relatively high, the effect of ion correlations is comparable with the effect of van der Waals forces and can influence the thin film contact angle and emulsion stability.

Keywords: Disjoining pressure; excess free energy; ionic correlations; thin liquid films.

1. Introduction

In Part 1 of this study, Ref. [1], we investigated quantitatively the forces due to ionic correlations in electrolyte-containing thin liquid films. The overlapping of the two electric double layers inside the film gives rise not only to electrostatic repulsion (described by the DLVO theory [2,3]) but also to attraction, which is due to the effects of ionic correlations and image forces; see Refs [1,4] and the literature quoted therein. In Part 1 we derived analytical expressions allowing calculation of the film correlation free energy and disjoining pressure.

In the present paper we consider the complementary case of electric double layers situated outside the thin film. Such a configuration can be observed

with oil films between aqueous emulsion droplets, with lipid bilayers, vesicles or biomembranes. In this case there is no overlapping of the two electric double layers. The ionic-charge density fluctuations in the two double layers interact through the thin oil film. Hence one can expect that the attraction due to ionic correlations will be smaller than in the case of inner double layers. However, in the latter case, the ionic-correlation attraction which appears on the film surfaces is missing when the double layers are outside the film. Therefore, even a smaller effect of the ionic correlations, in combination with the van der Waals and steric interactions, can be important for interpreting the equilibrium and the stability of emulsion-type oil films of charged surfaces.

In some aspects the system with two outer electric double layers is simpler than the system studied in Part 1, because both the surface charge and potential do not depend on the film thickness.

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The same is true for the ionic distribution in the electric double layers. The theoretical approach developed in Part 1 can be applied to the present case without any limitations.

Our aim below is to derive analytical expressions allowing calculation of the film excess correlation free energy and the respective component of the disjoining pressure. Then we investigate the dependence of the ionic-correlation attraction on different factors like concentration and valency of the ions, surface charge density and thickness of the Stern layer, temperature, film dielectric permittivity, etc. For the reader's convenience the algorithm of the numerical calculations is given in the Appendix.

2. Model of the ion distribution

The system under consideration consists of a plane-parallel thin dielectric film situated between two aqueous phases. The film surfaces are charged and electric double layers are formed in the two adjacent aqueous phases, whereas ions are not present in the film interior.

The film has thickness h and dielectric permittivity ϵ_1 (Fig. 1). Each electric double layer consists of a Stern layer of thickness w and of a diffuse double layer characterized by an ion-charge density

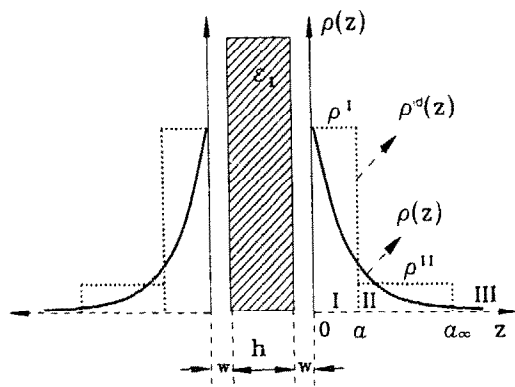


Fig. 1. Sketch of the ionic-charge distribution in two electric double layers situated outside a thin dielectric film of permittivity ϵ_1 and thickness h . The smooth and the stepwise profiles represent the real and the model charge distributions, $\rho(z)$ and $\rho^{\text{id}}(z)$, respectively; w is the width of the Stern layers.

distribution $\rho(z)$. The z -axis is directed normally to the film surfaces. The function $\rho(z)$ can be easily calculated by means of the Poisson–Boltzmann equation; see Eqns (A4) and (A8) in Part 1 [1].

In this paper we follow the notation used in Part 1. In particular, σ is the surface charge density; $q_1 = Ze$ and $q_2 = -Ze$ ($Z = \pm 1, \pm 2, \dots$) are the charges of a counterion and a co-ion, respectively. The numerical densities of both ion species are equal to n_0 far from the interface.

As mentioned in Part 1, for calculating the ionic-correlation energy it is convenient to replace the continuous real charge density distribution $\rho(z)$ with an idealized (model) one:

$$\rho^{\text{id}} \equiv \begin{cases} \rho^{\text{I}} & \text{for } 0 < z < a \\ \rho^{\text{II}} & \text{for } a < z < a_{\infty} \\ 0 & \text{for } z > a_{\infty} \end{cases} \quad (2.1)$$

see Fig. 1. Here ρ^{I} , ρ^{II} , a and a_{∞} are parameters of the model. They can be calculated from Eqns (3.5) and (3.7) in Part 1, which stem from some conditions for equivalence between the idealized stepwise distribution $\rho^{\text{id}}(z)$ and the continuous distribution $\rho(z)$.

In the case of electric double layers inside the film, considered in Part 1, the stepwise model can be used for a film of thickness h satisfying the condition $2a < h < 2a_{\infty}$. It is worthwhile noting that there are no such restrictions in the present case, when the double layers are situated outside the film.

The Debye screening parameters κ_{I} , κ_{II} and κ_0 corresponding to the three regions I, II and III (see Fig. 1) can be calculated as explained in Appendix B of Part 1.

The Brownian motion of the ions gives rise to fluctuations in the ion charge density. The fluctuation charges in the two adjacent electric double layers can interact across the intervening thin dielectric film. The resulting correlations between the fluctuation charges lead to the appearance of additional correlation free energy with a bulk density $f_{\text{cor}}^{(b)}(z, h)$. Since $f_{\text{cor}}^{(b)}$ depends on the film

thickness h , one can define an excess correlation free energy density

$$\Delta f_{\text{cor}}^{(b)}(z, h) = f_{\text{cor}}^{(b)}(z, h) - f_{\text{cor}}^{(b)}(z, \infty) \quad (2.2)$$

which accounts for the interactions across the thin film. Our aim is to calculate the excess correlation free energy per unit area of the film

$$\Delta f_{\text{cor}}(h) = 2 \int_0^\infty \Delta f_{\text{cor}}^{(b)}(z, h) dz \quad (2.3)$$

where the factor 2 accounts for the two symmetrical electric double layers. In accordance with the thermodynamics of thin liquid films [5-7] the derivative

$$\Pi_{\text{cor}} = - \left[\frac{\partial(\Delta f_{\text{cor}})}{\partial h} \right]_T \quad (2.4)$$

represents the ion-correlation component of the thin film disjoining pressure.

In the framework of our model the excess correlation free energy can be represented in the form

$$\Delta f_{\text{cor}} = 2(\Delta f_{\text{cor}}^{\text{I}} + \Delta f_{\text{cor}}^{\text{II}} + \Delta f_{\text{cor}}^{\text{III}}) \quad (2.5)$$

where

$$\begin{aligned} \Delta f_{\text{cor}}^{\text{I}} &= \int_0^a \Delta f_{\text{cor}}^{(b)} dz, & \Delta f_{\text{cor}}^{\text{II}} &= \int_a^{a_\infty} \Delta f_{\text{cor}}^{(b)} dz, \\ \Delta f_{\text{cor}}^{\text{III}} &= \int_{a_\infty}^\infty \Delta f_{\text{cor}}^{(b)} dz \end{aligned} \quad (2.6)$$

are the contributions of regions I, II, and III depicted in Fig. 1. Below we calculate consecutively $\Delta f_{\text{cor}}^{\text{Y}}$, (Y = I, II, III) by making use of the method developed in Part 1.

3. Correlation energy of region I

For an electrical charge q located at the point $r = r_0$, which belongs to region I, Eqn (4.5) of Part 1

reads

$$\frac{\partial^2 \phi}{\partial z^2} - \lambda^2 \phi = - \frac{q}{\pi \epsilon} \delta(z - \zeta) \quad (3.1)$$

where

$$\lambda^2 = k^2 + \kappa_1^2 \quad (3.2)$$

where $\phi(\mathbf{k}, z)$ is the Fourier transform of the fluctuation polarization electrical potential, $\mathbf{k} = (k_x, k_y, 0)$ is a two-dimensional wave vector of magnitude $k = |\mathbf{k}|$, ϵ is the dielectric permittivity of water, κ_1 is the Debye screening parameter in region I; compare with Eqns (3.12) and (4.3)-(4.4) of Part 1. By using the variables

$$u = \lambda z, \quad \xi = \lambda \zeta, \quad E_1 = \frac{q}{2\pi \epsilon \lambda} \quad (3.3)$$

one transforms Eqn (3.1) to read

$$\frac{\partial^2 \phi}{\partial u^2} - \phi = - 2E_1 \delta(u - \xi), \quad 0 < \xi < b_1 \quad (3.4)$$

The parameters

$$b_1 = \lambda a \quad \text{and} \quad b_2 = \lambda(a_\infty - a) \quad (3.5)$$

are the dimensionless widths of regions I and II; see Fig. 2. Similarly, the dimensionless thicknesses

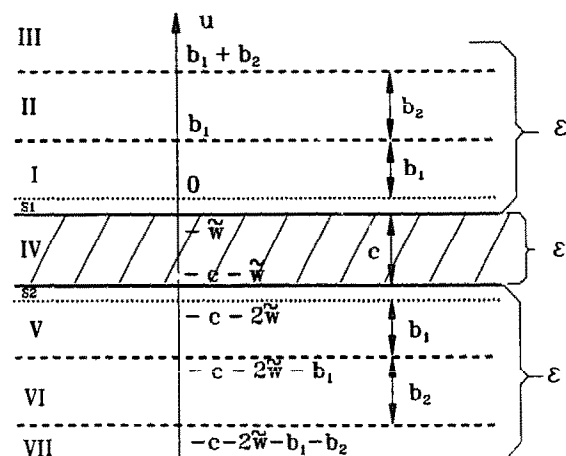


Fig. 2. Sketch of the regions of uniform ion-charge density in our model. Regions I, II and III are the same as in Fig. 1; region IV is the dielectric film; regions V, VI and VII are similar to regions I, II, and III, respectively; regions S1 and S2 represent the two Stern layers.

of the dielectric film and of the two adjacent Stern layers, S1 and S2, are denoted by

$$c = \lambda h \quad \text{and} \quad \tilde{w} = \lambda w \tag{3.6}$$

see Fig. 2. Besides, for the sake of convenience the film is denoted as region IV in Fig. 2. The remaining regions V, VI and VII are symmetrical to regions I, II and III respectively.

The solution of Eqn (3.4) for region I reads [8]

$$\begin{aligned} \phi^I(k, u) = & B_1 \exp(-u) + B_2 \exp u \\ & - E_1 \operatorname{sgn}(u - \xi) \sinh(u - \xi), \\ 0 < u < b_1 \end{aligned} \tag{3.7}$$

where B_1 and B_2 are integration constants and

$$\operatorname{sgn} x \equiv \begin{cases} -1 & \text{for } x < 0 \\ 0 & \text{for } x = 0 \\ 1 & \text{for } x > 0 \end{cases} \tag{3.8}$$

Since r_0 belongs to region I ($0 < \xi < b_1$), the counterparts of Eqn (3.4) for regions II and III are homogeneous equations:

$$\frac{\partial^2 \phi^{II}}{\partial u^2} - \alpha^2 \phi^{II} = 0, \quad b_1 < u < b_1 + b_2 \tag{3.9}$$

$$\frac{\partial^2 \phi^{III}}{\partial u^2} - \beta^2 \phi^{III} = 0, \quad b_1 + b_2 < u < \infty \tag{3.10}$$

where

$$\alpha = \frac{\sqrt{\kappa_{II}^2 + k^2}}{\lambda}, \quad \beta = \frac{\sqrt{\kappa_0^2 + k^2}}{\lambda} \tag{3.11}$$

The solutions of Eqns (3.9)–(3.10) read

$$\begin{aligned} \phi^{II}(k, u) = & A_1 \exp(-\alpha u) + A_2 \exp(\alpha u), \\ b_1 < u < b_1 + b_2 \end{aligned} \tag{3.12}$$

$$\begin{aligned} \phi^{III}(k, u) = & F_1 \exp(-\beta u), \quad b_1 + b_2 < u < \infty \\ \end{aligned} \tag{3.13}$$

where A_1 , A_2 and F_1 are constants. Similarly one calculates the fluctuation potentials in the

remaining regions:

$$\begin{aligned} \phi^V(k, u) = & C_1 \exp(-u) + C_2 \exp u, \\ -c - 2\tilde{w} - b_1 < u < -c - 2\tilde{w} \end{aligned} \tag{3.14}$$

$$\begin{aligned} \phi^{VI}(k, u) = & G_1 \exp(-\alpha u) + G_2 \exp(\alpha u), \\ -c - 2\tilde{w} - b_1 - b_2 < u < -c - 2\tilde{w} - b_1 \end{aligned} \tag{3.15}$$

$$\begin{aligned} \phi^{VII}(k, u) = & F_2 \exp(\beta u), \\ -\infty < u < -c - 2\tilde{w} - b_1 - b_2 \end{aligned} \tag{3.16}$$

$$\begin{aligned} \phi^{S1}(k, u) = & D_1 \exp(-\tau u) + D_2 \exp(\tau u), \\ -\tilde{w} < u < 0 \end{aligned} \tag{3.17}$$

$$\begin{aligned} \phi^{S2}(k, u) = & L_1 \exp(-\tau u) + L_2 \exp(\tau u), \\ -c - 2\tilde{w} < u < -c - \tilde{w} \end{aligned} \tag{3.18}$$

$$\begin{aligned} \phi^{IV}(k, u) = & M_1 \exp(-\tau u) + M_2 \exp(\tau u), \\ -c - \tilde{w} < u < -\tilde{w} \end{aligned} \tag{3.19}$$

where

$$\tau = k/\lambda \tag{3.20}$$

and A_i , B_i , C_i , D_i , F_i , G_i , L_i and M_i ($i = 1, 2$) are constants. The integration constants are to be determined from the standard boundary conditions

$$\phi^{Y1} = \phi^{Y2} \quad \text{and} \quad \epsilon^{Y1} \frac{\partial \phi^{Y1}}{\partial u} = \epsilon^{Y2} \frac{\partial \phi^{Y2}}{\partial u} \tag{3.21}$$

imposed at each boundary between two regions Y1 and Y2. The calculation of all integration constants is simple but tedious and finally yields

$$\int_0^a \phi^I(k, \xi) d\xi = \lambda E_1 [b_1/\lambda^2 + G^I(v, \omega, b_1)] \tag{3.22}$$

where

$$\begin{aligned} G^I(v, \omega, b_1) = & \frac{a^2}{b_1^2 Q_1} \\ & \times \{v - \omega + [2b_1(1-v)(\omega - 1) + \omega - v] \\ & \times \exp(-2b_1)\} \end{aligned} \tag{3.23}$$

$$Q_1 = (\nu + 1)(\omega + 1) + (\nu - 1)(\omega - 1) \exp(-2b_1) \tag{3.24}$$

$$\nu = \frac{1}{\tau} \frac{1 + \mu}{1 - \mu}, \quad \mu = \frac{\eta - 1}{\eta + 1} \exp(-2kw),$$

$$\eta = \frac{c}{\epsilon_1} \frac{1 + \delta}{1 - \delta} \tag{3.25}$$

$$\delta = \frac{\chi - 1}{\chi + 1} \exp(-2kh), \quad \chi = \frac{\epsilon_1}{\epsilon} \frac{1 + A}{1 - A},$$

$$A = \frac{\Gamma - 1}{\Gamma + 1} \exp(-2kw) \tag{3.26}$$

$$\Gamma = \tau \frac{1 + \gamma}{1 - \gamma}, \quad \gamma = \frac{1 - \omega}{1 + \omega} \exp(-2b_1),$$

$$\omega = \alpha \frac{1 - \Omega}{1 + \Omega} \tag{3.27}$$

$$\Omega = \frac{\alpha - \beta}{\alpha + \beta} \exp(-2\alpha b_2) \tag{3.28}$$

The variables $\lambda, b_1, b_2, c, \alpha, \beta,$ and τ are defined by Eqns (3.2), (3.5)–(3.6), (3.11) and (3.20) as functions of k .

The inverse Fourier transformation of Eqn (3.22) in view of Eqn (3.3) yields

$$\int_0^a \varphi^I(r_2, \zeta) d\zeta = \frac{q}{\epsilon} \left[\frac{a}{r_2} \exp(-\kappa_1 r_2) + \int_0^\infty k J_0(r_2 k) G^I(\nu, \omega, b_1) dk \right] \tag{3.29}$$

where $\varphi^I(r_2, \zeta)$ is the Fourier transform of $\phi^I(k, \zeta)$,

$$r_2 = (x, y, 0), \quad r_2 = |r_2| \tag{3.30}$$

is a position vector in the plane xy and J_0 is a Bessel function.

In the limit $h \rightarrow \infty$ (large film thickness) the fluctuation potential $\varphi^I(r_2, \zeta)$ tends to a function $\varphi_\infty^I(r_2, \zeta)$. In the same limit Eqn (3.29) transforms

into

$$\int_0^a \varphi_\infty^I(r_2, \zeta) d\zeta = \frac{q}{\epsilon} \left[\frac{a}{r_2} \exp(-\kappa_1 r_2) + \int_0^\infty k J_0(r_2 k) G^I(\nu_\infty, \omega, b_1) dk \right] \tag{3.31}$$

where

$$\nu_\infty = \frac{1}{\tau} \frac{1 + \mu_\infty}{1 - \mu_\infty}, \quad \mu_\infty = \frac{\epsilon - \epsilon_1}{\epsilon + \epsilon_1} \exp(-2kw) \tag{3.32}$$

are the limiting values of the parameters ν and μ for $h \rightarrow \infty$; the parameters b_1 and ω do not depend on h . (Note that in contrast to the case considered in Part I, in the present case the Debye parameters κ_1 and κ_{II} do not depend on h .)

Equations (3.29) and (3.31) are counterparts of Eqns (4.28) and (4.29) in Part I, respectively. Then following the procedure for derivation of Eqns (4.34) and (4.35) in Part I one obtains the sought-for expressions for the excess correlation internal and free energies per unit area of region I:

$$\Delta u_{\text{cor}}^I = \frac{\kappa_1^2 k_B T}{8\pi} \int_0^\infty dk \times k [G^I(\nu, \omega, b_1) - G^I(\nu_\infty, \omega, b_1)] \tag{3.33}$$

$$\Delta f_{\text{cor}}^I = \frac{\kappa_1^2 k_B T}{8\pi} \int_T^\infty \frac{dT}{T^2} \int_0^\infty dk \times k [G^I(\nu, \omega, b_1) - G^I(\nu_\infty, \omega, b_1)] \tag{3.34}$$

where T is temperature and k_B is the Boltzmann constant.

4. Correlation energy of region II

In this case $b_1 < \xi < b_1 + b_2$ (Fig. 2). Instead of Eqns (3.7) and (3.12) one has

$$\phi^I(k, u) = B_1 \exp(-u) + B_2 \exp u, \quad 0 < u < b_1 \tag{4.1}$$

$$\begin{aligned} \phi''(k, u) &= A_1 \exp(-\alpha u) + A_2 \exp(\alpha u) \\ &\quad - E_2 \operatorname{sgn}(u - \xi) \sinh \alpha(u - \xi), \\ b_1 < u < b_1 + b_2 \end{aligned} \tag{4.2}$$

where

$$E_2 = E_1/\alpha \tag{4.3}$$

Equations (3.13)–(3.19) hold also in the present case. The integration constants $A_i, B_i, C_i, D_i, F_i, G_i, L_i$ and M_i ($i = 1, 2$) can be determined from the boundary conditions (3.21). As a result of these simple but tedious calculations one obtains

$$\begin{aligned} \int_a^{a_\infty} \phi''(r_2, \zeta) d\zeta &= \frac{q}{\epsilon} \left[\frac{a_\infty - a}{r_2} \exp(-\kappa_{II} r_2) \right. \\ &\quad \left. + \int_0^\infty dk k J_0(r_2 k) G''(\theta, b_2, \alpha, \beta) \right] \end{aligned} \tag{4.4}$$

where

$$\begin{aligned} G''(\theta, b_2, \alpha, \beta) &= \frac{(a_\infty - a)^2}{b_2^2 Q_2} \\ &\quad \times \{ \beta - \theta\alpha + [2\alpha b_2(1 - \theta)(\alpha - \beta) \\ &\quad + \theta\alpha - \beta] \exp(-2\alpha b_2) \} \end{aligned} \tag{4.5}$$

$$\begin{aligned} Q_2 &= \alpha^2 [(\theta - 1)(\alpha - \beta) \exp(-2\alpha b_2) \\ &\quad - (\theta + 1)(\alpha + \beta)] \end{aligned} \tag{4.6}$$

$$\theta = \alpha \left[1 + \frac{v-1}{v+1} \exp(-2b_1) \right] / \left[1 - \frac{v-1}{v+1} \exp(-2b_1) \right] \tag{4.7}$$

The variables $b_1, b_2, \alpha, \beta,$ and v are defined by Eqns (3.5), (3.11) and (3.25)–(3.28) as functions of k . As usual r_2 is a two-dimensional position vector; cf. Eqn (3.30).

In the limit $h \rightarrow \infty$ the fluctuation potential $\phi''(r_2, \zeta)$ tends to a function $\phi''_\infty(r_2, \zeta)$, representing the fluctuation potential in region II of a single electric double layer (infinitely thick film). In the

same limit Eqn (4.4) reduces to

$$\begin{aligned} \int_a^{a_\infty} \phi''_\infty(r_2, \zeta) d\zeta &= \frac{q}{\epsilon} \left[\frac{a_\infty - a}{r_2} \exp(-\kappa_{II} r_2) \right. \\ &\quad \left. + \int_0^\infty dk k J_0(r_2 k) G''(\theta_\infty, b_2, \alpha, \beta) \right] \end{aligned} \tag{4.8}$$

where

$$\begin{aligned} \theta_\infty &= \alpha \left[1 + \frac{v_\infty - 1}{v_\infty + 1} \exp(-2b_1) \right] / \\ &\quad \left[1 - \frac{v_\infty - 1}{v_\infty + 1} \exp(-2b_1) \right] \end{aligned} \tag{4.9}$$

and v_∞ is given by Eqn (3.32).

Equations (4.4) and (4.8) are counterparts of Eqns (4.41) and (4.42) in Part I. Then following the procedure of derivation of Eqns (4.46) and (4.47) in Part I one obtains the sought-for expressions for the excess correlation internal and free energies per unit area of region II:

$$\begin{aligned} \Delta u_{\text{cor}}'' &= \frac{\kappa_{II}^2 k_B T}{8\pi} \int_0^\infty dk k [G''(\theta, b_2, \alpha, \beta) \\ &\quad - G''(\theta_\infty, b_2, \alpha, \beta)] \end{aligned} \tag{4.10}$$

$$\begin{aligned} \Delta f_{\text{cor}}'' &= \frac{\kappa_{II}^2 k_B T}{8\pi} \int_T^\infty \frac{dT}{T^2} \int_0^\infty dk k [G''(\theta, b_2, \alpha, \beta) \\ &\quad - G''(\theta_\infty, b_2, \alpha, \beta)] \end{aligned} \tag{4.11}$$

5. Correlation energy of region III

In this case $b_1 + b_2 < \xi < \infty$ (Fig. 2). Instead of Eqn (3.2) Eqn (4.1) holds and Eqn (3.13) must be replaced by

$$\begin{aligned} \phi'''(k, u) &= F_1 \exp(-\beta u) + F_3 \exp(\beta u) \\ &\quad - E_3 \operatorname{sgn}(u - \xi) \sinh \beta(u - \xi) \end{aligned} \tag{5.1}$$

where

$$E_3 \approx E_1/\beta \tag{5.2}$$

Equations (3.12) and (3.14)–(3.19) hold also in the present case. From the boundary condition ϕ^{III} for $(u - \xi) \rightarrow \infty$ one obtains

$$F_3 \approx \frac{1}{2} E_3 \exp(-\beta \xi) \tag{5.3}$$

The remaining integration constants $A_i, B_i, C_i, D_i, F_i, G_i, L_i,$ and M_i ($i = 1, 2$) are to be determined from the boundary conditions (3.21). After some calculations one obtains

$$\phi^{III}(k, u = \xi) = E_3 \left\{ \frac{g-1}{g+1} \exp[2\beta(b_1 + b_2 - \xi)] + 1 \right\} \tag{5.4}$$

where

$$g = \frac{\beta}{\alpha} \left[1 + \frac{\theta-1}{\theta+1} \exp(-2\alpha b_2) \right] / \left[1 - \frac{\theta-1}{\theta+1} \exp(-2\alpha b_2) \right] \tag{5.5}$$

and the variables b_2, α, β and θ are given by Eqns (3.5), (3.11) and (4.7) as functions of k . Then one can define

$$\begin{aligned} \Delta\phi^{III}(k, \xi) &= \phi^{III}(k, \xi) - \phi_{\infty}^{III}(k, \xi) \\ &= E_3 \left(\frac{g-1}{g+1} - \frac{g_{\infty}-1}{g_{\infty}+1} \right) \\ &\quad \times \exp[-2\beta(b_1 + b_2 - \xi)] \end{aligned} \tag{5.6}$$

where g_{∞} is the limiting value of g for $h \rightarrow \infty$:

$$g_{\infty} = \frac{\beta}{\alpha} \left[1 + \frac{\theta_{\infty}-1}{\theta_{\infty}+1} \exp(-2\alpha b_2) \right] / \left[1 - \frac{\theta_{\infty}-1}{\theta_{\infty}+1} \exp(-2\alpha b_2) \right] \tag{5.7}$$

see also Eqns (4.9) and (5.5). Analogously to Eqn (4.31) in Part I we define the excess fluctuation

potential at the point $r_0 = (0, 0, \zeta)$:

$$\Delta\phi^{III}(\zeta) = \lim_{r_2 \rightarrow 0} \int dk \exp(ik \cdot r_2) \Delta\phi^{III}(k, \xi) \tag{5.8}$$

Following the method developed in Part I from Eqns (3.3), (3.11), (5.2), (5.6) and (5.8) one easily derives the sought-for expressions for the excess internal and free energies per unit area of the region III:

$$\Delta u_{cor}^{III} = \frac{\kappa_0^2 k_B T}{16\pi} \int_0^{\infty} \left(\frac{g-1}{g+1} - \frac{g_{\infty}-1}{g_{\infty}+1} \right) \frac{kdk}{\kappa_0^2 + k^2} \tag{5.9}$$

$$\Delta f_{cor}^{III} = \frac{\kappa_0^2 k_B T}{16\pi} \int_T^{\infty} \frac{dT}{T^2} \int_0^{\infty} \left(\frac{g-1}{g+1} - \frac{g_{\infty}-1}{g_{\infty}+1} \right) \frac{kdk}{\kappa_0^2 + k^2} \tag{5.10}$$

6. Numerical data and discussion

The excess correlation free energy per unit area of the film, Δf_{cor} , can be calculated by substituting from Eqns (3.34), (4.11) and (5.10) into Eqn (2.5). The algorithm of calculations is described in the Appendix. The ion-correlation component of the disjoining pressure Π_{cor} can be calculated by numerical differentiation in accordance with Eqn (2.4).

Figure 3 illustrates the effect of the surface charge density and Stern layer on Δf_{cor} . Let us denote by

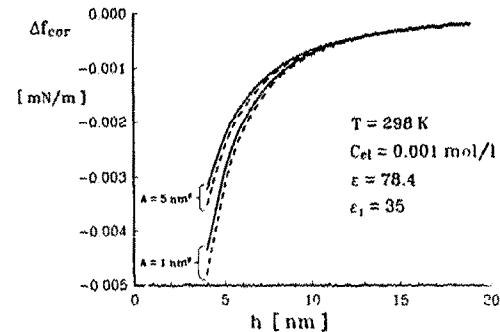


Fig. 3. Film excess correlation free energy Δf_{cor} vs film thickness h at two different values of the area per unit surface charge A . The full and dashed lines correspond to $w = 2 \text{ \AA}$ and $w = 0$, respectively.

A the area per unit surface charge at one of the film surfaces and let w be the width of the Stern layer. Each pair of one full and one dashed line in Fig. 3 represents the dependence of Δf_{cor} on film thickness h for a given value of A : ($A = 1 \text{ nm}^2$ and $A = 5 \text{ nm}^2$) and for two different values of w ($w = 0$ for the dashed line and $w = 2 \text{ \AA}$ for the full one). One sees that the increase of the surface charge density (the decrease of A) leads to an increase of the magnitude of the correlation free energy Δf_{cor} . As could be expected, Δf_{cor} is negative and corresponds to attraction between the two film surfaces (negative disjoining pressure). The small difference between the dashed lines in Fig. 3 and the respective full lines implies that the effect of the Stern layer is small and can be neglected. All curves in Fig. 3 are calculated for an electrolyte concentration $C_{\text{el}} = 0.001 \text{ mol l}^{-1}$ in the aqueous phase, temperature $T = 298 \text{ K}$, dielectric permittivities $\epsilon = 78.4$ for water and $\epsilon_1 = 35$ for the film substance.

The variation of the film dielectric permittivity ϵ_1 affects strongly the value of the ion-correlation energy Δf_{cor} . This effect is illustrated in Fig. 4 for four different values of ϵ_1 . The greater ϵ_1 , the greater the magnitude of Δf_{cor} . Hence the contribution of the ion correlations into the film free energy is more pronounced for emulsion films with a film phase of greater dielectric permittivity, like nitrobenzene.

In contrast to the effect of ϵ_1 , the effect of the electrolyte dissolved in the aqueous phases turns

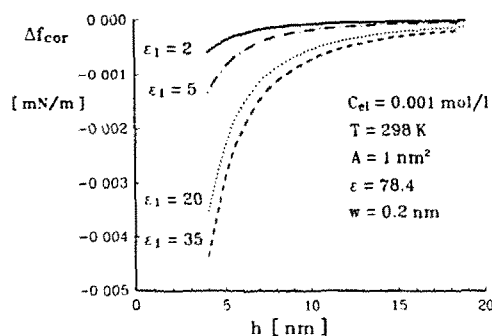


Fig. 4. Film excess correlation free energy Δf_{cor} vs film thickness h at several different values of the film dielectric permittivity ϵ_1 .

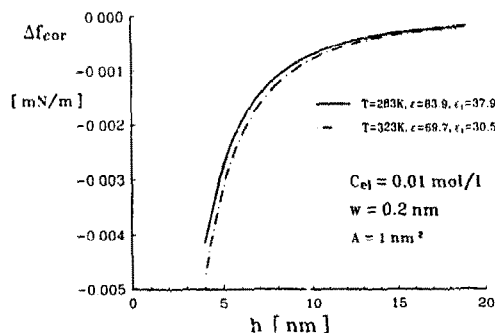


Fig. 5. Plot of Δf_{cor} vs h for different temperatures T .

out to be negligible. We varied C_{el} between 10^{-4} and $10^{-2} \text{ mol l}^{-1}$ without any pronounced effect on the Δf_{cor} vs h curves. A symmetrical 2:2 electrolyte provides a slightly greater magnitude of Δf_{cor} compared with a 1:1 electrolyte at the same concentration.

Figure 5 illustrates the effect of temperature on the dependence of Δf_{cor} vs h . To determine the system, the film substance was assumed to be nitrobenzene and the temperature dependence of the dielectric permittivities ϵ and ϵ_1 was taken into account. One can see that increasing the temperature affects slightly the effect of ionic correlations and leads to an increase in the magnitude of Δf_{cor} .

In Fig. 6, Δf_{cor} is compared with the van der Waals excess free energy per unit area of an emulsion film, Δf_{vw} . To calculate Δf_{vw} we used the well-known equation (see for example Ref. [9]).

$$\Delta f_{\text{vw}} = -\frac{A_H}{12\pi h^2} \quad (6.1)$$

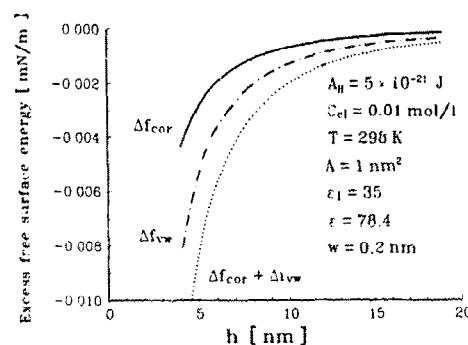


Fig. 6. Correlation and van der Waals excess free energies, Δf_{cor} and Δf_{vw} , and their sum, $\Delta f_{\text{cor}} + \Delta f_{\text{vw}}$, plotted against the film thickness h .

with Hamaker constant $A_H = 5 \cdot 10^{-21}$ J, which is a typical value for emulsion films. One sees in Fig. 6 that for the specified values of the parameters used, Δf_{cor} is about 50% of Δf_{vw} . Hence in some cases Δf_{cor} can contribute considerably to the energy of attraction in thin liquid films.

Concluding remarks

This paper considers a dielectric thin film of charged surfaces, which intervenes between two electrolyte solutions. A typical example is an oil film formed between two aqueous droplets in a water-in-oil emulsion. The fluctuations of the ionic-charge density in the two aqueous phases interact through the thin oil film. The correlations between these fluctuations give rise to an additional attraction between the thin film surfaces, which can be characterized by the excess free energy of ion correlations per unit area of the film, Δf_{cor} (Eqn (2.3)).

We derived analytical expressions for calculating Δf_{cor} by using the theoretical method developed in Part 1 [1]; see Eqns (2.5), (3.34), (4.11) and (5.10). The algorithm of the numerical calculations is described in detail in the Appendix. We studied numerically the role of various factors on the magnitude $|\Delta f_{\text{cor}}|$ of the correlation free energy.

It turns out that $|\Delta f_{\text{cor}}|$ depends strongly on the dielectric permittivity ϵ_1 of the film as well as on its surface charge density; see Figs 3 and 4. However, Δf_{cor} is insensitive to the width of the Stern layer and to the concentration and valency of the ions in the two aqueous phases. Besides, $|\Delta f_{\text{cor}}|$ slightly increases when increasing the temperature (Fig. 5).

In the case of an emulsion oil thin film of relatively high dielectric permittivity ($\epsilon_1 = 35$) Δf_{cor} can be about 50% of the excess free energy Δf_{vw} due to the van der Waals forces (Fig. 6). Hence the ionic correlations can provide a significant contribution to the attraction between the two film surfaces and to influence the value of the emulsion thin film contact angle, cf. Eqn (5.2) in Part 1.

In conclusion, it is instructive to compare the

effects of the ion correlations in the case of inner (Part 1) and outer (present paper) electric double layers, corresponding to oil-in-water and water-in-oil emulsions, respectively.

(i) In both cases the ion correlations lead to attraction between the film surfaces. However, $|\Delta f_{\text{cor}}|$ is much larger in the case when the electric double layers are inside the film.

(ii) In both cases Δf_{cor} is sensitive to the surface charge density; compare Fig. 13(a) in Part 1 with Fig. 3 in the present paper.

(iii) For inner double layers Δf_{cor} depends strongly on the ion concentration and valency, whereas such effects are not observed with outer double layers.

(iv) For outer double layers Δf_{cor} depends markedly on the dielectric permittivity ϵ_1 of the oil phase, whereas there is no such effect with inner double layers; compare Fig. 6 in Part 1 and Fig. 4 above.

(v) In both cases Δf_{cor} can be comparable with Δf_{vw} and can affect the magnitude of the thin film contact angle.

We believe the present study of the ionic correlation forces in thin liquid films will contribute to a better quantitative description and explanation of the thin film contact angles and emulsion stability.

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References

- 1 P.A. Kralchevsky and V.N. Paunov, Colloids Surfaces, 64 (1992) 245.
- 2 B.V. Derjaguin and L.D. Landau, Acta Physicochim. USSR, 14 (1941) 633.
- 3 E.J.W. Verwey and J.Th.G. Overbeek, The Theory of Stability of Lyophobic Colloids, Elsevier, Amsterdam, 1948.
- 4 P. Attard, D.J. Mitchel and B.W. Ninham, J. Chem. Phys., 89 (1988) 4358.
- 5 I.B. Ivanov and B.V. Toshev, Colloid Polym. Sci., 253 (1975) 593.
- 6 J.A. de Fejter, in I.B. Ivanov (Ed.), Thin Liquid Films, Marcel Dekker, New York, 1988, p. 1.

- 7 B.V. Derjaguin, Theory of Stability of Colloids and Thin Films, Moscow, 1986 (in Russian); Plenum Press, New York, 1989.
- 8 E. Kamke, Differentialgleichungen, Vol. 1, Nauka, Moscow, 1976 (in Russian).
- 9 S. Nir and C.S. Vassilief, in I.B. Ivanov (Ed.), Thin Liquid Films, Marcel Dekker, New York, 1988, p. 207.

Appendix: Algorithm for calculating the film excess free energy and the disjoining pressure

1. The input parameters are: area per unit surface charge, A (cm^2); bulk electrolyte concentration, n_0 (cm^{-3}); number of charges per ion, Z ; temperature, T (K); dielectric permittivities of the aqueous and oil phases ϵ and ϵ_1 ; width of the Stern layer, w (cm); electron charge, $e = 4.803 \cdot 10^{-10}$ CGSE units.

2. The parameters a , a_x , κ_0 , κ_1 and κ_{II} are calculated by using steps 2–5 of the algorithm in Appendix B of Ref. [1].

3. For a given value of the film thickness h one carries out numerically the integration with respect to k and T in Eqns (3.34), (4.11) and (5.10). For that purpose, for each given couple (k, T) one calculates λ from Eqn (3.11); b_1 and b_2 from Eqn (3.5); α and β from Eqn (3.2); τ from Eqn (3.20); v , v_x and ω from Eqns (3.25)–(3.28) and (3.32); $G^I(v, \omega, b_1)$ and $G^I(v_x, \omega, b_1)$ from Eqn (3.23); $G^{II}(\theta, b_2, \alpha, \beta)$ and $G^{II}(\theta_x, b_2, \alpha, \beta)$ from Eqns (4.5)–(4.7) and (4.9); g and g_x from Eqns (5.5) and (5.7).

4. After carrying out the integration in Eqns (3.34), (4.11) and (5.10) one obtains Δf_{cor} from Eqn (2.5). By varying the film thickness h one calculates the plot of Δf_{cor} vs h .

5. In accordance with Eqn (2.4) one calculates the ionic correlation component of disjoining pressure, Π_{cor} , by differentiating numerically Δf_{cor} with respect to h .

The integrals in Eqns (3.34), (4.11) and (5.10) are of the type

$$I = \int_{T_0}^{\infty} \frac{dT}{T^2} \int_0^{\infty} dk k F(k, T) \quad (\text{A1})$$

where the integrand F depends on T through the Debye screening parameters $\kappa_0(T)$, $\kappa_1(T)$ and $\kappa_{II}(T)$. To calculate numerically the integrals we used the following dimensionless variables:

$$u = \frac{1}{1 + (k/\kappa_{00})^2}, \quad v = \frac{T_0}{T} \quad (\text{A2})$$

where

$$\kappa_{00} = \kappa_0(T_0) \quad (\text{A3})$$

is a constant. Then Eqn (A1) transforms to read

$$I = \frac{\kappa_{00}^2}{2T_0} \int_0^1 dv \int_0^1 \frac{du}{u^2} F\left(\kappa_{00} \sqrt{\frac{1}{u} - 1}, T_0 v\right) \quad (\text{A4})$$

One can check, that

$$\lim_{u \rightarrow 0} \frac{1}{u^2} F\left(\kappa_{00} \sqrt{\frac{1}{u} - 1}, T_0 v\right) = \text{const.} \quad (\text{A5})$$

Hence there are no problems about the convergence of the integrals in Eqn (A4).