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# On the effect of discrete charges adsorbed at the interface on nonionic liquid film stability: charges in the film

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## Abstract

The effect of discrete charges embedded inside a dielectric film on the surface of an ionic substrate is examined. The analytical solution for the potential distribution is presented in the cases of diluted and concentrated electrolyte solutions. The image-charge contribution to the film stability is derived for charges randomly distributed at one of the film boundaries. It is shown that the image-charge component of the disjoining pressure can dominate over the other types of surface forces either for very thick films or for film thicknesses less than or comparable to the average charge separation.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

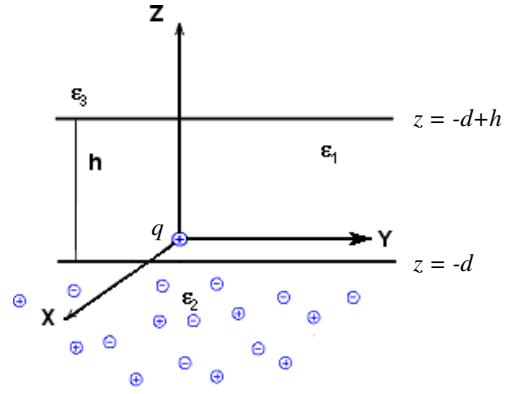
Understanding of the polarization effects and the electrostatic forces arising due to the presence of ionized and polar molecules or charged nanoparticles in the vicinity of interfaces is of considerable interest both in science and technology. During the last decades the theoretical analysis of this problem was given in numerous papers (see for example [1–12]), taking into account uniform and nonuniform smeared charge distribution as well as discrete charges. The main attention was attracted by the systems containing the charges embedded into an aqueous electrolyte half-space or thin film as the most relevant to colloid science, biophysics and biochemistry. For such systems the real charges are dressed by a cloud of counterions and coions, that is, the polarization effects and the electrostatic forces are significantly screened. At the same time the case of charges located inside a liquid insulator film on the top of a conducting, semiconducting, ionic liquid or aqueous electrolyte substrate may be of great interest on one hand for the studying the stability of such films. On the other hand, the interface charging can be effectively used in nanotechnological applications, for example in the controlling of thickness of nonpolar and nonionic coatings. Note that for charges located

in apolar or weakly polar dielectric media in the vicinity of a substrate with finite Debye length the screening of electrostatic effects will also take place, but to an essentially lower extent than for charges in electrolytes. In this paper we consider the surface forces arising in thin nonsymmetric nonpolar liquid interlayers due to discrete charges embedded inside the interlayer in the vicinity of one film boundary. So we will omit here the analysis of electrostatic interaction of film boundaries, related to trivial Coulomb interaction between charges on opposite sides of an interlayer across nonpolar media. The asymmetry of the free charge arrangement inside the films is characteristic for nonpolar wetting films grown on top of semiconductor substrates that have undergone mechano-chemical treatment (for example triboelectrization). Another way to produce such charging is to introduce into the system charged nanoparticles with different affinities to film interfaces. For thick hydrocarbon films on aqueous solution substrates, hydrophobic charged nanoparticles will adsorb on the oil–solution interface or the oil–air interface depending on the total potential of interaction (including van der Waals and image-charge contributions) between the particle and film boundaries.

In our paper for clarity we will restrict ourselves by consideration of a thin film confined by ionic liquid or an electrolyte aqueous solution substrate and another fluid

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(that might be air or another immiscible nonpolar liquid). The polarization of contacting media by the discrete charges embedded inside thin film will be treated by the method of images. It will be shown that the arising polarization effects lead to the appearance of an additional contribution to the disjoining pressure in the film associated with image-charge forces. To evaluate quantitatively the role of this contribution to the film stability in section 2 we solve the Poisson equations and derive the distribution of electrostatic potential induced by the single charge in the film. The analytical solution will be presented for the cases of diluted and concentrated solutions. In section 3 the net potential and image-charge force contribution will be calculated for a disordered ensemble of charges at one of the film boundaries. Finally we discuss our results.



**Figure 1.** The point charge  $q$  in the vicinity of an interface between an insulator film and electrolyte solution.

## 2. Electrostatic potential induced in the dielectric film by a single point charge

Our model system contains a film of a dielectric with thickness  $h$  and dielectric permittivity  $\epsilon_1$ , confined between two semi-infinite media with dielectric permittivities  $\epsilon_2$  and  $\epsilon_3$ , as shown in figure 1. Medium 2 represents an electrolyte solution or ionic liquid, while the two others are apolar or weakly polar media. A point charge  $q$  is located in the film at distance  $d$  above the 1–2 interface, and we choose the Cartesian coordinate system with the origin coinciding with the charge location and the  $z$  axis normal to the interface. The electrostatic field induced by point charge is screened in the electrolyte solution due to a cloud of solvated salt ions, and is affected by the polarization of phase boundaries. The distribution of ion charges in the solution is considered here as a continuous one. Within the Debye–Huckel approximation, valid for moderate charges, the ion density is proportional to the screened electrostatic potential inside the solution. Thus the electrostatic potential in all contacting media is described by the following set of Poisson equations:

$$\begin{aligned} \Delta\varphi^{(1)} &= -\frac{4\pi}{\epsilon_1}q\delta(x, y, z) & -d < z < -d+h \\ \Delta\varphi^{(2)} - \kappa^2\varphi^{(2)} &= 0 & z < -d \\ \Delta\varphi^{(3)} &= 0 & z > -d+h \end{aligned} \quad (1)$$

where  $\delta(x, y, z)$  is the Dirac’s delta-function and  $\kappa$  is the inverse Debye length for the electrolyte solution.

By virtue of the cylindrical symmetry of the problem, it is expedient to use a 2D Fourier transform for  $x$  and  $y$  axes, which leads to the system of ordinary differential equations

$$\begin{aligned} \frac{d^2 f^{(1)}(z)}{dz^2} - \lambda^2 f^{(1)}(z) &= -\frac{2q}{\epsilon_1}\delta(z) & -d < z < -d+h \\ \frac{d^2 f^{(2)}(z)}{dz^2} - (\kappa^2 + \lambda^2)f^{(2)}(z) &= 0 & z < -d \\ \frac{d^2 f^{(3)}(z)}{dz^2} - \lambda^2 f^{(3)}(z) &= 0 & z > -d+h \end{aligned} \quad (2)$$

with boundary conditions

$$\begin{aligned} z \rightarrow \infty & f^{(3)} \rightarrow 0 \\ z \rightarrow -\infty & f^{(2)} \rightarrow 0 \\ z = h-d & f^{(1)} = f^{(3)} \\ z = h-d & \frac{\epsilon_1 \partial f^{(1)}}{\partial z} = \frac{\epsilon_3 \partial f^{(3)}}{\partial z} \\ z = -d & f^{(1)} = f^{(2)} \\ z = -d & \frac{\epsilon_1 \partial f^{(1)}}{\partial z} = \frac{\epsilon_2 \partial f^{(2)}}{\partial z}. \end{aligned} \quad (3)$$

Solving the above boundary problem we find the Fourier transform of the potential in the film

$$\begin{aligned} f^{(1)}(z) &= \frac{q}{\lambda\epsilon_1} \{ \exp(-\lambda|z|) + \beta_{13} \exp[\lambda(z-2(h-d))] \\ &+ \beta'_{12} \exp[-\lambda(z+2d)] \\ &+ \beta'_{12}\beta_{13} \exp[-\lambda(2h-|z|)] \} \{ 1 - \beta'_{12}\beta_{13} \exp(-2\lambda h) \}^{-1} \end{aligned} \quad (4)$$

where  $\beta_{13} = (\epsilon_1 - \epsilon_3)/(\epsilon_1 + \epsilon_3)$ ;

$$\beta'_{12} = \left( \epsilon_1 - \epsilon_2 \sqrt{1 + \kappa^2/\lambda^2} \right) / \left( \epsilon_1 + \epsilon_2 \sqrt{1 + \kappa^2/\lambda^2} \right). \quad (5)$$

By using the identity

$$\frac{1}{1 - \beta'_{12}\beta_{13} \exp(-2\lambda h)} = \sum_{k=0}^{\infty} (\beta'_{12}\beta_{13})^k \exp(-2k\lambda h), \quad (6)$$

we can represent (4) as a sum of contributions from the charge itself and its sequential images in confining phases:

$$\begin{aligned} f^{(1)}(z) &= \frac{q}{\lambda\epsilon_1} \sum_{k=0}^{\infty} \{ (\beta'_{12}\beta_{13})^k \exp[-\lambda(|z| + 2kh)] \\ &+ \beta'_{12}(\beta'_{12}\beta_{13})^k \exp[-\lambda(z + 2d + 2kh)] \\ &+ \beta_{13}(\beta'_{12}\beta_{13})^k \exp[-\lambda(-z - 2d + 2(k+1)h)] \\ &+ (\beta'_{12}\beta_{13})^{k+1} \exp[-\lambda(2(k+1)h - |z|)] \}. \end{aligned} \quad (7)$$

To compute the potential distribution across the film, one needs to perform the inverse 2D Fourier transform of

equation (7). Due to the cylindrical symmetry it reduces to the Hankel transform:

$$\begin{aligned} \varphi^{(1)}(\rho, z) &= \int_0^\infty f^{(1)}(\lambda, z) J_0(\rho\lambda) \lambda d\lambda \\ &= \frac{q}{\varepsilon_1} \int_0^\infty J_0(\rho\lambda) d\lambda \sum_{k=0}^\infty \{(\beta'_{12}\beta_{13})^k \exp[-\lambda(|z| + 2kh)] \\ &\quad + \beta'_{12}(\beta'_{12}\beta_{13})^k \exp[-\lambda(z + 2d + 2kh)] \\ &\quad + \beta_{13}(\beta'_{12}\beta_{13})^k \exp[-\lambda(-z - 2d + 2(k+1)h)] \\ &\quad + (\beta'_{12}\beta_{13})^{k+1} \exp[-\lambda(2(k+1)h - |z|)]\} \end{aligned} \quad (8)$$

where  $\rho = (x^2 + y^2)^{1/2}$  and  $J_0(\rho\lambda)$  is the zero-order Bessel function of the first kind.

In the general case, due to the dependence of  $\beta'_{12}$  on  $\lambda$  (cf equation (5)), the integral in equation (8) cannot be expressed in analytical functions and has to be evaluated numerically. However, taking into account the fact that this integral is determined mainly by those values of wavevector  $\lambda$  for which the exponential terms in the integrand are close to unity, the further simplification of equation (8) might be based on the peculiarities of function  $\beta'_{12}(\lambda)$  (figure 2).

Note that we are dealing with the case of a low dielectric film on an electrolyte substrate, so that  $\varepsilon_2 > \varepsilon_1$ . For this case  $\beta'_{12}(\lambda)$  monotonically varies between  $-1$  for  $\lambda \ll \kappa$  and  $\beta_{12} = (\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + \varepsilon_2)$  for  $\lambda \gg \kappa$ , with a rather marked switch between the two asymptotic regimes at  $\kappa \approx \lambda$ .

Having this in mind, the simple analytical asymptotics can be derived from equation (8) for the potential of the electrostatic field induced in the dielectric film by single point charge, located near the interface with the electrolyte solution:

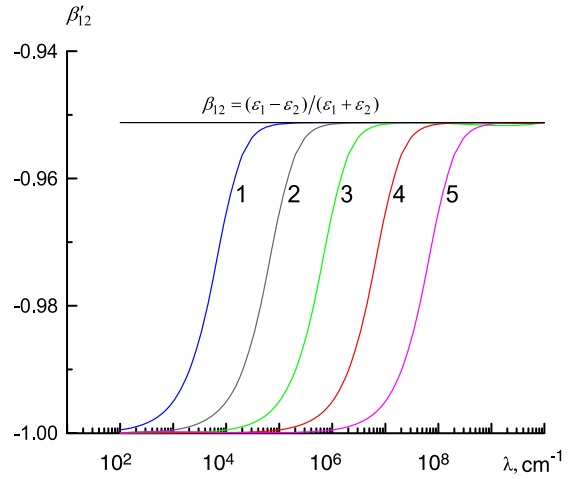
$$\begin{aligned} \varphi^{(1)}(\rho, z) &= \frac{q}{\varepsilon_1} \sum_{k=0}^\infty (\tilde{\beta}_{12}\beta_{13})^k \left\{ \frac{1}{\sqrt{\rho^2 + (|z| + 2kh)^2}} \right. \\ &\quad + \frac{\tilde{\beta}_{12}}{\sqrt{\rho^2 + (z + 2d + 2kh)^2}} \\ &\quad + \frac{\beta_{13}}{\sqrt{\rho^2 + [-z - 2d + 2(k+1)h]^2}} \\ &\quad \left. + \frac{\tilde{\beta}_{12}\beta_{13}}{\sqrt{\rho^2 + [2(k+1)h - |z|]^2}} \right\} \end{aligned} \quad (9)$$

where the  $\tilde{\beta}_{12}$  value depends on the approximation conditions. In the simplest case, for the analysis when  $\varepsilon_2 \gg \varepsilon_1$ , it is possible to put  $\tilde{\beta}_{12} = -1$ .

The same result is valid when the inequality

$$2(h-d)\kappa \geq 1 \quad (10)$$

holds. Condition (10) is the consequence of the simultaneous requirements for smallness of arguments of exponential functions in (8) and for holding of the inequality  $\sqrt{1 + \kappa^2/\lambda^2} \gg 1$  in (5). Evidently, the condition (10) for highly concentrated solutions is satisfied already at small film thicknesses and thus might be applied for the analysis of electrostatic potentials and interaction forces in the case of polymolecular wetting films. At the same time, the lowering of electrolyte concentration reduces the range of film thicknesses for which the approximation  $\tilde{\beta}_{12} = -1$  might be considered as sufficiently close.



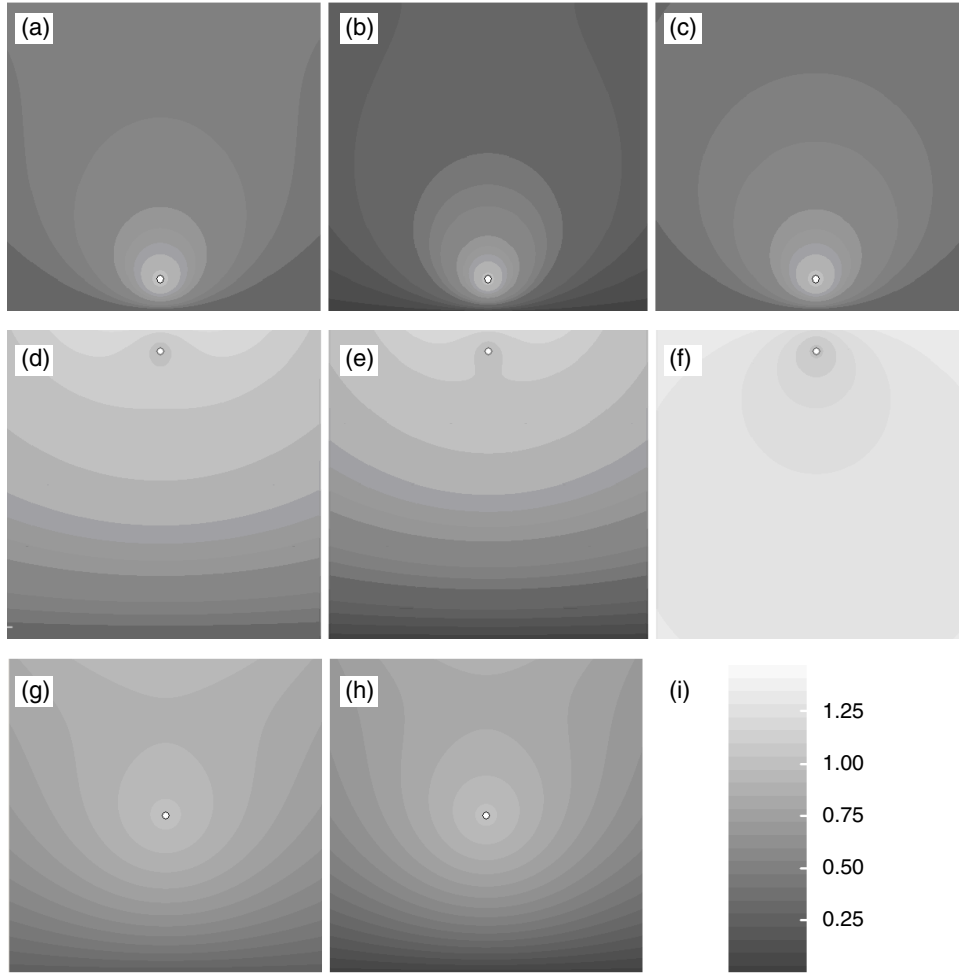
**Figure 2.** Parameter  $\beta'_{12}$  as a function of  $\lambda$  for different values of inverse Debye length  $\kappa$ :  $10^4$  (1),  $10^5$  (2),  $10^6$  (3),  $10^7$  (4) and  $10^8$   $\text{cm}^{-1}$  (5). Calculations were performed using equation (5) for  $\varepsilon_1 = 2$ ;  $\varepsilon_2 = 80$ .

The case of thin films on the surface of diluted electrolytes with  $2\kappa(h-d) \ll 1$ , when simultaneously for the entire range of  $\lambda$  values, essential for integral (8), the relation  $\lambda \gg \kappa$  holds, represents another asymptotic limit. One may then put

$$\tilde{\beta}_{12} \approx (\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + \varepsilon_2) = \beta_{12}. \quad (11)$$

Note by the way that the film thickness in (9) tending to infinity leads to the well known equation for the electrostatic field created by a point charge located near the interface between two semi-infinite dielectrics.

The analysis of equation (9) shows that the distribution of the electrostatic potential around the point charge inside the film ceases to be spherically symmetric. In the vicinity of the interface between two media, characterized by  $\beta_{1i} < 0$ , the electric field in the film is screened by the polarization (image) charges at the interface and the ion charges in the medium  $i$  (if present). The higher the dielectric permittivity or/and the inverse Debye length of medium  $i$ , the more pronounced the effect of potential decreasing. In contrast, for  $\beta_{1i} > 0$ , the field of polarization charges increases the potential in the film. The effect of potential alteration is long ranged, although it is more pronounced in the vicinity of the interface. For illustration, in figure 3 we have presented the results of the calculation of the distribution of the normalized potential, obtained as the ratio of the potential calculated from equation (9) to the potential created by the equivalent point charge in the bulk dielectric medium, for different charge positions inside the film. The calculations were performed for three positions of charge inside a film of hydrocarbon liquid ( $\varepsilon_1 = 2$ ), confined by air ( $\varepsilon_3 = 1$ ) from one side and ionic liquid ( $\varepsilon_2 = 16$ , however  $\tilde{\beta}_{12} = -1$  due to large  $\kappa$ ) or dielectric medium with dielectric permittivity  $\varepsilon_2 = 16$  and  $\kappa = 0$  from the other side. For comparison, the distribution of potential is also given for the charge placed near the interface between two semi-infinite media. The alteration from unity of the ratio of the potential inside the film to those in the bulk liquid is characterized by grey levels.



**Figure 3.** The distribution of normalized potential, obtained as the ratio of the potential described by equation (9) to the potential created by the equivalent point charge in the bulk dielectric medium, for different charge positions,  $d$ , inside the 1 nm thick film of dielectric with  $\epsilon_1 = 2$  confined by air ( $\epsilon_3 = 1$ ) and ionic liquid ( $\epsilon_2 = 16$ ). Panels (a) and (b) correspond to  $d = 0.1$  nm, (d) and (e) to  $d = 0.9$  nm, (g) and (h) to  $d = 0.5$  nm. For comparison, the cases of charge in the semi-infinite dielectric at distance  $d = 0.1$  nm from the interface with ionic liquid (c) and with air (f) are also presented. Distributions (a), (c), (d) and (g) were calculated for  $\tilde{\beta}_{12} = \beta_{12}$  while (b), (e) and (h) for  $\tilde{\beta}_{12} = -1$ . The magnitude of the normalized potential is represented by the grey level, as indicated by the scale in panel (i).

An important point which should be discussed here is related to the validity of equation (9) in view of the applicability of the linearized equation (1) for medium 2. Indeed, the Poisson equation  $\Delta\varphi^{(2)} - \kappa^2\varphi^{(2)} = 0$  for electrolyte media is the result of linearization of the Poisson–Boltzmann equation under the assumption  $q\varphi^{(2)}/kT \ll 1$ . Definitely for arbitrary position of charge inside the dielectric film with low dielectric permittivity the linearization of the Poisson–Boltzmann equation in electrolyte media is not generally valid. At the same time, for two limiting cases considered here the linearized form remains valid either owing to  $\kappa \rightarrow 0$  for diluted solutions or owing to  $\varphi^{(2)} \rightarrow 0$  as  $\tilde{\beta}_{12} \rightarrow -1$  for concentrated ones.

### 3. Electrostatic potential and forces induced in the dielectric film by the ensemble of point charges

Let us now consider the case of the set of disordered charges attached to (adsorbed at) one of the interfaces, in the plane

$z = 0$  at distance  $d$  from the 1–2 interface, with an average charge density  $\sigma = q/\pi\rho_0^2$ . This corresponds to the situation when one takes into account the influence of the thermal motion resulting in the smoothing of discontinuous charge density distribution. Then the total potential of the electrostatic field at the location of a given charge might be calculated using the cut-out disk model [12–14]. Since in the following analysis we will be interested in the electrostatic field inside the film only, for the sake of brevity and clarity we will omit the superscript (1).

In the model, the charge density around the chosen point charge is approximated by a step function

$$\sigma(\rho) = \begin{cases} 0 & 0 < \rho < \rho_0 \\ \sigma = q/\pi\rho_0^2 & \rho_0 < \rho < \infty \end{cases} \quad (12)$$

where  $\pi\rho_0^2$  is the average area per charge in the adsorption layer. Consequently, the potential,  $\varphi_\Sigma$ , of the electric field induced by all the real charges but the charge under

consideration, and by all the image charges, at the location of the given charge, is expressed as

$$\varphi_{\Sigma}(0, 0) = \varphi_0(0, 0) + \frac{2}{\rho_0^2} \int_{\rho_0}^{\infty} \varphi(\rho, 0) \rho \, d\rho \quad (13)$$

where  $\varphi_0$  is the potential of the field induced by all the images of the given charge, and  $\varphi(\rho, 0)$  is the potential induced by a point charge located at a distance  $\rho$  from the given charge and by all its images. The latter potential is determined by equation (9) with  $z = 0$ .

The energy of a given charge in the field induced by the image charges and by the other real charges adsorbed at the plane  $z = 0$  might be computed as  $U_1 = q\varphi_{\Sigma}(0, 0)$ . Then the total electrostatic energy associated with the interaction of adsorbed charges with the other real charges in the film (superscript ch–ch) and with the image charges (ch–im) will be given by

$$U = \frac{1}{2} \Gamma U_1^{\text{ch–ch}} + \Gamma U_1^{\text{ch–im}} = \Gamma U_1' \quad (14)$$

where the prime indicates the half-weighting of the potential energy of interaction between the real charges in order to avoid double counting of the contribution from each pair of charges;  $\Gamma = \sigma/q = 1/\pi\rho_0^2$  is the number of charges adsorbed per unit of interfacial area.

The contribution,  $\Pi_{\text{el}}$ , of the energy of electrostatic interactions to the disjoining pressure of the film (hereinafter referred to as the image-charge component of the disjoining pressure) is expressed as the thickness derivative of the total potential electric energy of the system containing the thin film [12]:

$$\begin{aligned} \Pi_{\text{el}} &= -\frac{1}{\Lambda} \frac{d}{dh} \int \int \int_V u \, dV \\ &= -\frac{1}{\Lambda} \frac{d}{dh} \left( \int \int \int_{V_0} u \, dV + \int \int \int_{V_f} u \, dV \right) \end{aligned} \quad (15)$$

where  $u$  is the density of potential electric energy,  $V$ ,  $V_0$ , and  $V_f$  are the total volume of the system and volumes of its bulk and film parts, respectively, and  $\Lambda$  is the film area. The energy,  $U$ , described by equation (14) is associated with the second integral in (15). As for the thickness derivative of the first integral, in the general case it will also be nonzero and is related to the redistribution of ions in phase 2 in the image-charge field due to its variation with film thickness changing. However, in this paper we are interesting in quantitative analysis of the image-charge component of disjoining pressure for two limiting cases, namely, diluted solutions with  $\kappa \rightarrow 0$  and concentrated ones with  $\tilde{\beta}_{12} \rightarrow -1$ . For both cases the first integral will vanish either due to negligible number of ions or due to zero potential of image charges inside the concentrated solution resulting from strong screening. Thus finally for the image-charge component of the disjoining pressure in the dielectric wetting film on the top of diluted or concentrated electrolyte solution we will get

$$\Pi_{\text{im}} = -\frac{d}{dh} (\Gamma U_1') = -\Gamma q \frac{d\varphi_{\Sigma}'}{dh} \quad (16)$$

where again the prime at  $\varphi_{\Sigma}$  indicates halving of the contribution of the real charges to the potential induced at the location of the given charge; however, since the real charge/real charge energy contribution does not depend on film thickness, it vanishes anyway upon differentiation. The second equality in equation (16) accounts for the fact that in the systems analysed in this paper the surface charge density (in other words, the adsorbed amount  $\Gamma$ ) is determined by the external conditions and does not depend on the film thickness. Otherwise one should consider in equation (16) the term proportional to  $d\Gamma/dh$  as well.

Combining the equations (9), (13), and (16), and changing the order of integration over  $\rho$  and differentiation with respect to  $h$ , we get

$$\begin{aligned} \Pi_{\text{im}} &= -\Gamma \left\{ q \frac{d\varphi_0}{dh} + 2\pi\sigma \int_{\rho_0}^{\infty} \frac{d\varphi'(\rho, 0)}{dh} \rho \, d\rho \right\} \\ &= \frac{q\sigma}{\varepsilon_1} \sum_{k=0}^{\infty} \sum_{l=1}^3 \frac{2b_{lk}}{z_{lk}^2} + \frac{4\pi\sigma^2}{\varepsilon_1} \sum_{k=0}^{\infty} \sum_{l=1}^3 \frac{b_{lk} z_{lk}}{(\rho_0^2 + z_{lk}^2)^{1/2}} \end{aligned} \quad (17)$$

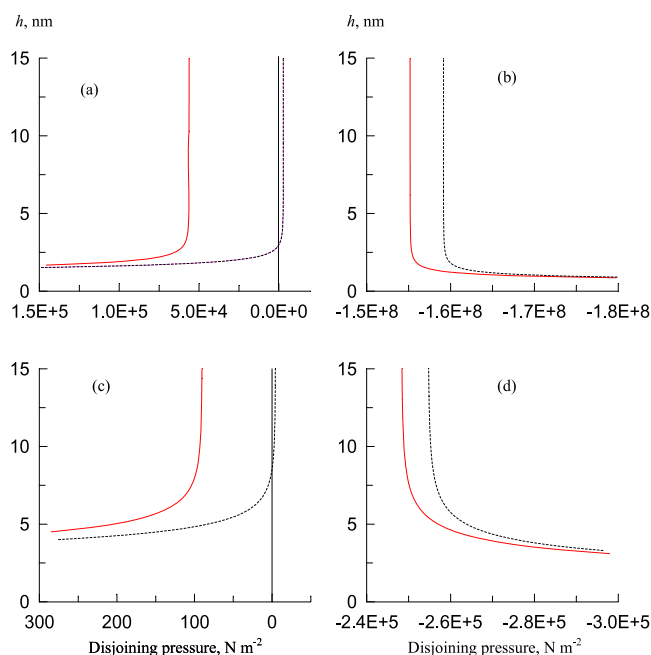
where

$$\begin{aligned} b_{1k} &= 2(k+1)(\tilde{\beta}_{12}\beta_{13})^{k+1} \\ b_{2k} &= k\tilde{\beta}_{12}(\tilde{\beta}_{12}\beta_{13})^k \\ b_{3k} &= \beta_{13}(k+1)(\tilde{\beta}_{12}\beta_{13})^k \\ Z_{1k} &= 2(k+1)h \\ Z_{2k} &= (2kh + 2d) \\ Z_{3k} &= (2kh + 2h - 2d). \end{aligned} \quad (18)$$

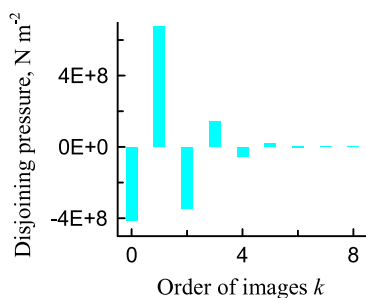
The image-charge component of the disjoining pressure in equation (17) is represented as a sum of two contributions, associated with the interaction of the real charges with their proper images of different order  $k$  in confining media (the first term) and with images of all the other charges (the second term).

#### 4. Discussion and summary

The analysis of equation (17) shows that the significant interactions arising between boundaries of the dielectric film are associated with polarization effects, caused by the charges embedded inside the film. The corresponding image-charge component of the disjoining pressure for small film thicknesses can amount to high values, comparable to or even greater than the van der Waals component of the disjoining pressure. For film thicknesses less than or comparable to the average charge separation  $\rho_0\sqrt{\pi}$  the main contribution to  $\Pi_{\text{im}}$  comes from the summation of the first series which arises due to the discreteness of charge distribution. At fixed value of each charge this contribution is proportional to the number charge density (figure 4) and strongly affected by charge position with respect to the interfaces. Note that although each term in this summation decays with the film thickness approximately as  $h^{-2}$ , the alternation of signs of contributions from images of different orders (see figure 5) provides much faster decaying of the disjoining pressure. Accurate calculations for small film thicknesses on the basis of equation (17) need to account for



**Figure 4.** The isotherms of the image-charge component of the disjoining pressure for pentane wetting films on a surface of aqueous solutions calculated with equation (17) for surface charge density  $\sigma = 5 \text{ mC cm}^{-2}$  (a), (b) and  $\sigma = 0.2 \text{ mC cm}^{-2}$  (c), (d). Solid lines correspond to neat water ( $\beta_{12} = \beta_{12} = -0.96$ ) and dashed lines to concentrated brine ( $\beta_{12} = -1$ ). Calculations were performed for charges adsorbed at the interface with the substrate (a), (c) and with the air (b), (d) at distance  $d = 0.3 \text{ nm}$  from the interface.



**Figure 5.** Contributions of images of different orders to the image-charge component of the disjoining pressure.

at least images up to five to eight orders. It is also seen from figure 5 that the greatest contributions might be associated with the interaction of real charge with images of nonzero order.

For films essentially thicker than the average charge separation the influence of charge discreteness vanishes and the interface with adsorbed real charges as well as the surfaces with image charges create the electric field characteristic for the surfaces with smeared charge. So for such film thicknesses the contribution of the first summation in equation (17) reduces to zero, whereas the second term tends to a constant value, making the disjoining pressure nearly independent of  $h$ . This term is quadratic in average density of charges. Importantly, although for physically reasonable values of charge densities

this second term is relatively small for thin films, its near independence from film thickness provides the dominance of the image-charge component of the disjoining pressure over the other types of surface forces for thick films.

Summarizing this part of the discussion, it is necessary to underline that the interface charging can be considered as a powerful instrument for controlling the thickness of nonpolar and nonionic coatings by variation of charge magnitude and density both inside the coating and the substrate. This opens new prospects for nanotechnological applications.

To conclude, we would like to discuss the possibility of using thin wetting films of nonpolar liquids to check the validity of theories of van der Waals forces. Traditionally such films are supposed to be a good model for systems ruled by dispersion (van der Waals) interactions only. At the same time, numerous experiments reveal the strong deviation of isotherms of disjoining pressure at small film thicknesses in the above films from those predicted by the theory of van der Waals forces. Such inconsistency is usually rationalized by the roughness of the substrate (for review and discussion see [1]). At the same time, the results of this study as well as [11, 12] indicate that image-charge forces related either to the presence at the interface of free charges or of the tiny amounts of polar molecules also might be the cause of such deviations.

## Acknowledgments

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