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Abstract
We consider the electrostatic potential arising from charge-modulated planes. By partitioning the potential, we treat the system partially within full non-linear Poisson–Boltzmann (PB) theory, and partially within linearized PB theory. Using this partial linearization, we generate closed-form expressions for the electrostatic potential arising from a single plate, in both salt-free and added-salt environments, and for two parallel plates, in the salt-free case only. We show that these potentials are a much better approximation to the exact PB potential than those generated by full linearization. We then show how one may use the potential between two such charge-modulated plates to generate expressions for the disjoining pressure and transverse stress induced by the charge modulation. We show that the disjoining pressure thus calculated can be significantly (20–30%) different to that calculated from uniformly charged plates of the same average charge.

1. Introduction

Forces between charged surfaces and electric double layers have received considerable experimental investigation and theoretical attention ever since the pioneering papers of Gouy [1] and Chapman [2], almost a century ago. The reasons for this prolonged interest lies in the crucial importance of electric double layers in electrochemistry, in colloid science, and in biophysics. The earlier theoretical work was essentially based on the Poisson–Boltzmann (PB) equation, a mean-field version of classical density functional theory (DFT), while some more recent simulations and theoretical approaches incorporate correlations between microscopic co-ions and counter-ions [3]. While PB theory invariably leads to repulsion between electric double layers, the inclusion of correlations, which are of growing importance for divalent and higher-valence counter-ions, may lead to effective short-range attractions between equally charged surfaces [3].

However, almost all investigations so far have neglected two potentially important aspects of double-layer interactions, namely the discrete, molecular, nature of the solvent, and the

discrete nature of the charge density on the surfaces. As regards the former approximation, most theories and simulations adopt the 'primitive model' picture, whereby the solvent is replaced by a dielectric continuum, although there have been some recent attempts to include a molecular description of the solvent near charged surfaces either within DFT [4] or in simulations [5]. As for the surface charge density, it is almost invariably assumed to be uniformly distributed, a model which in most instances leads to considerable simplifications. This is consistent with the continuum assumption for the solvent, and clearly justified when considering, e.g., colloidal particles with typical diameters of hundreds of nanometres, which is much larger than the spacing between charged radicals on the colloidal surfaces. However, this may no longer be true for nanoparticles or biomolecules such as proteins, which carry only a few charged residues on their surface. In fact it was recently realized that the effective interactions between two globular proteins in an aqueous solution differ significantly when uniform ('smeared-out') or discrete charge patterns are considered [6]. But even for larger charged surfaces, the effects of charge modulation on the effective force between two surfaces may be expected to become important when the distance between surfaces becomes of the order of the characteristic scale of the modulation, which should reflect the mean distance between charged surface sites. Such situations are common, e.g. when studying the swelling of clays [7].

This paper addresses the problem of the electrostatic potential in the vicinity of charge-modulated planar surfaces in the presence of co-ions and counter-ions, and of the force between two such planes within the framework of PB theory. A single, infinite planar surface will be considered first (section 2), and a distinction will be made between two geometries: an infinite thin plate immersed in an electrolyte, and a charged plane separating an electrolyte on one side from a dielectric medium on the other. The two situations obviously differ in the electrostatic boundary conditions (bc); the former is a model for an isolated clay platelet in an ionic solution, while the latter pertains to a large spherical colloidal particle suspended in an aqueous solution, in the limit where the diameter is much larger than all other relevant length scales.

Sections 3 and 4 deal with the case of two parallel charged planes immersed in an ionic solution, or backed by a dielectric substrate and confining an ionic solution. Expressions are given for the normal and tangential forces acting between the two planes. As an application, these forces are explicitly evaluated for the simple case of striped charge densities (one-dimensional charge modulation).

A 'primitive model' description will be used throughout, i.e. the solvent is treated as a dielectric continuum of permittivity ϵ. We shall restrict ourselves to fully closed-form solutions, which may only be achieved by partial or complete linearization of the PB equation. Some of the equations obtained in the present work are similar to equations derived for a physically different situation, namely the electric double layer near a geometrically rough surface carrying a uniformly distributed charge [8]. While in the process of writing the present paper, the authors' attention was drawn to a preprint by Lukatsky *et al* since published [9], which addresses the problem of the counter-ion distribution near a single charge-modulated plane; this analysis is restricted to counter-ions only (no added electrolyte) and finds a significant enhancement of counter-ion localization due to the surface charge modulation, in qualitative agreement with the findings of [6].

2. Electrostatic potential near a single charge-modulated plate

Consider an infinite planar surface placed at $z = 0$, carrying a modulated charge density $-e\sigma(x, y)$, separating two dielectric media, with dielectric permittivities ϵ_I (region I, $z < 0$), and ϵ_{II} (region II, $z > 0$). If $\rho_I(\mathbf{r})$ and $\rho_{II}(\mathbf{r})$ are the local charge densities of free charges in

each region, the electrostatic potential $\phi(r)$ satisfies Poisson's equation in both regions:

$$\nabla^2 \phi(r) = -\frac{\rho_\alpha(r)}{\epsilon_0 \epsilon_\alpha}; \qquad \alpha = \text{I, II}. \tag{1}$$

The usual bc are that, at $z = 0$, $\phi(r)$ be continuous, and the electric field, $E(r) = -\nabla\phi(r)$, undergo the discontinuity

$$\epsilon_0(\epsilon_{\text{II}} E_z^{(\text{II})}(x, y, z = 0^-) - \epsilon_{\text{I}} E_z^{(\text{I})}(x, y, z = 0^+)) = -e\sigma(x, y). \tag{2}$$

Two physically different situations will be considered in this paper.

(i) Situation A corresponds to an infinitely thin plate immersed in an ionic solution containing monovalent co-ions and counter-ions of bulk densities $n_i^{(0)}$ ($i = -, +$). In this case, regions I and II have identical properties, and in particular, $\epsilon_{\text{I}} = \epsilon_{\text{II}} = \epsilon$. To close the above equations, a mean-field, PB, approximation is made, whereby

$$\rho(r) = e(n_+(r) - n_-(r)) = e(n_+^{(0)}e^{-\psi(r)} - n_-^{(0)}e^{\psi(r)}) \tag{3}$$

and the dimensionless potential $\psi(r) = e\phi(r)/k_B T$ is introduced. In the presence of a finite concentration of added salt, $n_+^{(0)} = n_-^{(0)} = n_0$. Introducing the Bjerrum length, $l_b = e^2/(4\pi\epsilon_{\text{II}}\epsilon_0 k_B T)$, and the inverse Debye screening length, $\kappa = \sqrt{8\pi l_b n_0}$, the PB equation, obtained by substituting (3) into (1), reduces to the well-known form

$$\nabla^2 \psi(r) = \kappa^2 \sinh[\psi(r)] \tag{4}$$

while the bc (2) reduces to

$$\left(\left.\frac{\mathrm{d}\psi}{\mathrm{d}z}\right|_{z=0^-} - \left.\frac{\mathrm{d}\psi}{\mathrm{d}z}\right|_{z=0^+}\right) = 4\pi l_b \sigma \tag{5}$$

which determines the opposite slopes of $\psi(r)$ on either side of the plane at $z = 0$.
In the somewhat academic case of vanishing salt concentration, when only counter-ions are present, equation (4) must be replaced by

$$\nabla^2 \psi(r) = -4\pi l_b n_0 e^{-\psi(r)} \tag{6}$$

where the counter-ion 'density' prefactor is undetermined, as is the average surface potential per unit area.

(ii) Case B corresponds to a charged planar surface separating a charge-free dielectric substrate in region I from an ionic solution in region II. The PB equations (4) or (6) must now be solved in region II, while in region I the potential satisfies the Laplace equation

$$\nabla^2 \psi^{(\text{I})}(r) = 0; \qquad z < 0, \tag{7}$$

and the bc are

$$\psi^{(\text{I})}(x, y, z = 0^-) = \psi^{(\text{II})}(x, y, z = 0^+) \tag{8a}$$

$$\epsilon_{\text{I}} \left.\frac{\partial \psi^{(\text{I})}(x, y, z)}{\partial z}\right|_{z=0^-} - \epsilon_{\text{II}} \left.\frac{\partial \psi(z, y, z)}{\partial z}\right|_{z=0^+} = 4\pi l_b \epsilon_{\text{II}} \sigma(x, y). \tag{8b}$$

In the case of a uniformly charged plane, i.e. $\sigma(x, y) = \sigma_0$, the PB equation is easily solved in all cases considered above [1, 2, 10]. This paper examines the case where the charge density varies along x and y. The modulation is assumed to be periodic over a rectangular array of unit cells $[-l \leqslant x \leqslant l; -h \leqslant y \leqslant h]$. The most general real Fourier representation of the charge density is then

$$\sigma(x, y) = \sum_{m,n=0}^{\infty} \lambda_{mn} f_{mn}(x, y) \tag{9a}$$

where

$$f_{mn}(x, y) = a_{mn} \cos\left[\frac{m\pi x}{l}\right] \cos\left[\frac{n\pi y}{h}\right] + b_{mn} \sin\left[\frac{m\pi x}{l}\right] \cos\left[\frac{n\pi y}{h}\right]$$
$$+ c_{mn} \cos\left[\frac{m\pi x}{l}\right] \sin\left[\frac{n\pi y}{h}\right] + d_{mn} \sin\left[\frac{m\pi x}{l}\right] \sin\left[\frac{n\pi y}{h}\right], \tag{9b}$$

and a_{mn} etc are four independent coefficients, determined by the usual rules of Fourier series, while the λ_{mn} are merely weights for the special cases where one ($\lambda = 1/2$) or both ($\lambda = 1/4$) of the indices are zero.

In the presence of such modulated surface charge densities, the non-linear PB equation cannot be solved analytically, contrary to the case of a uniform charge density, corresponding to the $m = n = 0$ Fourier component of (9a). In view of the three-dimensional nature of the problem, the numerical solution of the PB equation would be computationally very demanding. Consequently, additional simplifications are required. In this paper, fully and partially linearized versions of the PB equation are considered.

2.1. Linearized theory

The linearized Poisson–Boltzmann (LPB) version of the PB equation (4), including the source term, reads

$$(\nabla^2 - \kappa^2)\psi(x, y, z) = 4\pi l_b \sigma(x, y)\delta(z). \tag{10}$$

In view of the linearity, this LPB is trivially solved for each Fourier component[1], and the resulting potential for an infinitely thin plate (case A) is simply

$$\psi = -2\pi l_b \sum_{m,n=0}^{\infty} \lambda_{mn} f_{mn} \frac{e^{-q_{mn}|z|}}{q_{mn}} \tag{11}$$

where $q_{mn} = \sqrt{\kappa^2 + (m\pi/l)^2 + (n\pi/h)^2}$.

In case B (surface backed by dielectric), the solution has different forms in the two regions;

$$\psi^{(I)} = -4\pi l_b \sum_{m,n=0}^{\infty} \lambda_{mn} f_{mn} \frac{e^{-p_{mn}z}}{\frac{\epsilon_I}{\epsilon_{II}} p_{mn} + q_{mn}}, \tag{12a}$$

$$\psi^{(II)} = -4\pi l_b \sum_{m,n=0}^{\infty} \lambda_{mn} f_{mn} \frac{e^{-q_{mn}z}}{\frac{\epsilon_I}{\epsilon_{II}} p_{mn} + q_{mn}}, \tag{12b}$$

where $p_{mn} = \sqrt{(m\pi/l)^2 + (n\pi/h)^2}$.

2.2. Partially linearized theory

The above solutions of LPB theory are valid only for sufficiently low surface charge or surface potential (for a uniformly charged plane, the requirement would be that $\psi_0 \leqslant 1$ or $\phi_0 \leqslant 25$ mV). On the other hand, non-linear PB solutions are available for uniform surface charge. It is hence natural to seek a solution of the partially linearized Poisson–Boltzmann (PLPB) equation by separating the modulated surface charge into its mean value σ_0 (i.e. $\sigma(x, y)$ averaged over one periodically repeated rectangular cell), and the x- and y-dependent remainder; i.e. $\sigma(x, y) = \sigma_0 + \sigma_1(x, y)$. The reduced electrostatic potential $\psi(r)$ may likewise be separated as $\psi(r) = \psi_0(r) + \psi_1(r)$. The Gouy–Chapman solution for $\psi_0(z)$ is, for $z > 0$,

$$\psi_0(z) = -4\frac{\sigma_0}{|\sigma_0|} \text{arctanh}[e^{-\kappa(z+z_0)}] \tag{13}$$

[1] Using the Green function $\mathcal{G}(r - r') = \exp(-\kappa|r - r'|)/4\pi|r - r'|$ of the Helmholtz operator.

where z_0 is determined by the gradient of the potential at contact, i.e. $\kappa z_0 = \text{arcsinh}[\kappa/(\pi l_b|\sigma_0|)]$ for case A (infinitely thin plane) and $\kappa z_0 = \text{arcsinh}[\kappa/(2\pi l_b\sigma_0)]$ for case B.

The remaining part of the potential, $\psi_1(r)$, satisfies the following non-linear equation:

$$\nabla^2\psi_1(r) = \kappa^2(\sinh[\psi_0(z)](\cosh[\psi_1(r)] - 1) + \cosh[\psi_0(z)]\sinh[\psi_1(r)]). \tag{14}$$

Equation (14) is exact within non-linear PB theory. A closed-form expression may only be obtained upon expanding the rhs to first order in ψ_1, yielding the linear partial differential equation

$$\nabla^2\psi_1(r) = \kappa^2\cosh[\psi_0(z)]\psi_1(r) \tag{15}$$

where $\psi_0(z)$ is given by equation (13). The x- and y-coordinates are now transformed into Fourier space, leaving a set of simple differential equations:

$$\left(\frac{d^2}{dz^2} - q^2 - 2\kappa^2\text{cosech}^2[\kappa(z + z_0)]\right)\hat{\psi}_1(k, z) = 0, \tag{16}$$

where $q^2 = k^2 + \kappa^2$, and $k^2 = k_x^2 + k_y^2$, with k_x, k_y the Fourier variables conjugate to x and y. These linearized equations are identical in form to those derived in [8] in the different context of rough interfaces. The solution may hence be directly taken from that paper, namely

$$\hat{\psi}_1(k, z) = A(k)e^{-q(z+z_0)}(\kappa\coth[\kappa(z + z_0)] + q). \tag{17}$$

The prefactor A is determined by the bc (2) in the case of an infinitely thin plane, with $\sigma(x, y)$ now replaced by $\sigma_1(x, y)$, with the result

$$A = \frac{-2\pi l_b\hat{\sigma}_1(k_x, k_y)e^{qz_0}}{q^2 + \kappa q\coth(\kappa z_0) + \kappa^2\text{cosech}^2(\kappa z_0)}, \tag{18}$$

where $\hat{\sigma}_1(k_x, k_y)$ is the Fourier transform of $\sigma_1(x, y)$. Upon Fourier transforming the solution (17), (18) back into (x, y) space, one arrives at the required result

$$\psi_1(x, y, z) = -2\pi l_b\sum_{m,n=0}^{\infty}\lambda_{mn}f_{mn}(x, y)e^{-q_{mn}z}\frac{\kappa\coth[\kappa(z + z_0)] + q_{mn}}{q_{mn}^2 + \kappa q_{mn}\coth[\kappa z_0] + \kappa^2\text{cosech}^2[\kappa z_0]} \tag{19}$$

from which the co-ion and counter-ion densities are immediately determined, using the partially linearized (with respect to ψ_1) version of equation (3).

In order to test the accuracy of the solution of the PLPB, one would ideally like to compare it to the corresponding solution of the fully non-linear PB equation. However, since no closed-form solution of the latter is available for a modulated surface charge, the test will be carried out on the case of a uniform charge density, which will be arbitrarily split into two constant parts σ_0 and σ_1. In this case, the only non-zero Fourier component in equation (9b) is $a_{00} = 4\sigma_1$. The fully linearized, partially linearized and fully non-linear solutions to be compared are

$$\psi_{lin} = -2\pi l_b(\sigma_0 + \sigma_1)\frac{e^{-\kappa z}}{\kappa}, \tag{20a}$$

$$\psi_{pl} = -4\,\text{arctanh}[e^{-\kappa(z+z_0)}] - 2\pi l_b\sigma_1\frac{e^{-\kappa z}}{\kappa}\frac{\coth[\kappa(z + z_0)] + 1}{1 + \coth[\kappa z_0] + \text{cosech}^2[\kappa z_0]}, \qquad z_0 = z_0(\sigma_0), \tag{20b}$$

$$\psi = -4\,\text{arctanh}[e^{-\kappa(z+z_0)}], \qquad z_0 = z_0(\sigma_0 + \sigma_1). \tag{20c}$$

z_0, as given after equation (13), has different values in equations (20b) and (20c).

Figure 1 shows the ratios of contact values of the partially linearized potential over the exact PB potential, as functions of σ, for two salt concentrations. Contours of constant deviation
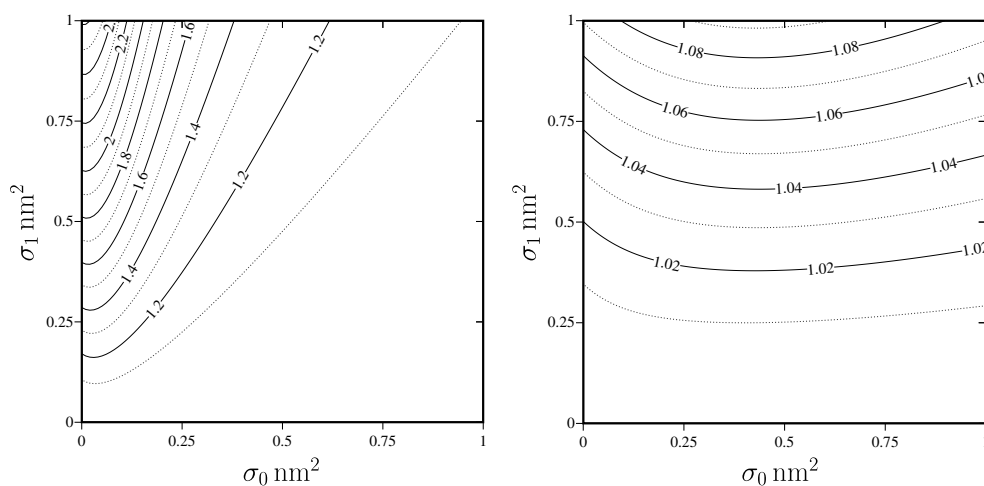
Figure 1. The ratio of contact values for $\psi_{pl}(z = 0)/\psi(z = 0)$, over a range of surface charge densities. In the left-hand figure, $n_s = 0.01$ M, and the contours represent differences of 10% from unity, while on the right, $n_s = 1$ M, and the contours represent differences of 1% from unity.
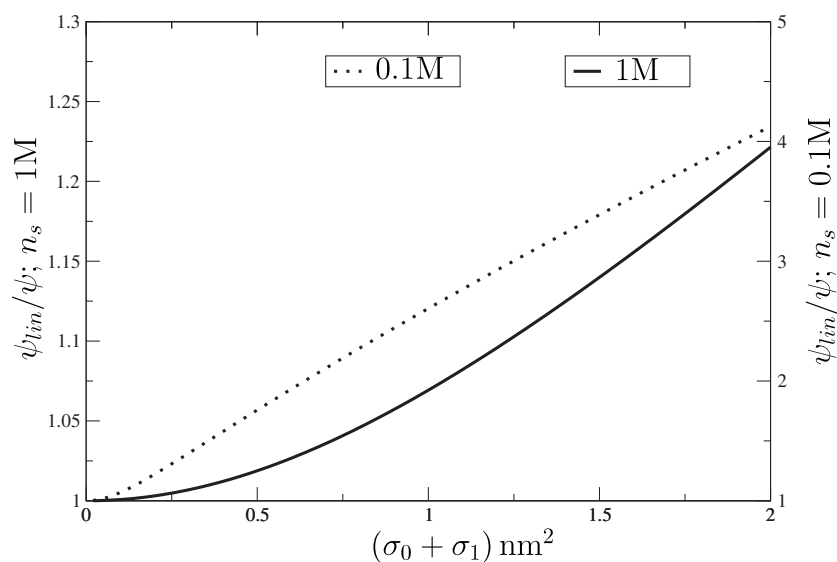

Figure 2. The ratio of contact values for ψ_{lin}/ψ, over a range of surface charge densities. The dotted curve is for $n_s = 1$ M, and its scale is on the left of the graph, while the solid curve is for $n_s = 0.1$ M, and its scale is on the right.

from unity are shown. This may be compared to figure 2, which shows the ratio of contact values of the linearized potential over the exact PB potential, for the same range of σ. While the linearized theory becomes rapidly inadequate with increasing σ at lower concentrations, the partially linearized theory yields surprisingly accurate results. Even at higher salt concentration where the surface charge is more efficiently shielded, and the fully linearized approximation is more useful, the partially linearized potential is still significantly better. The decay behaviour of the partially linearized potential is shown in figure 3. It can be seen that as z increases, the
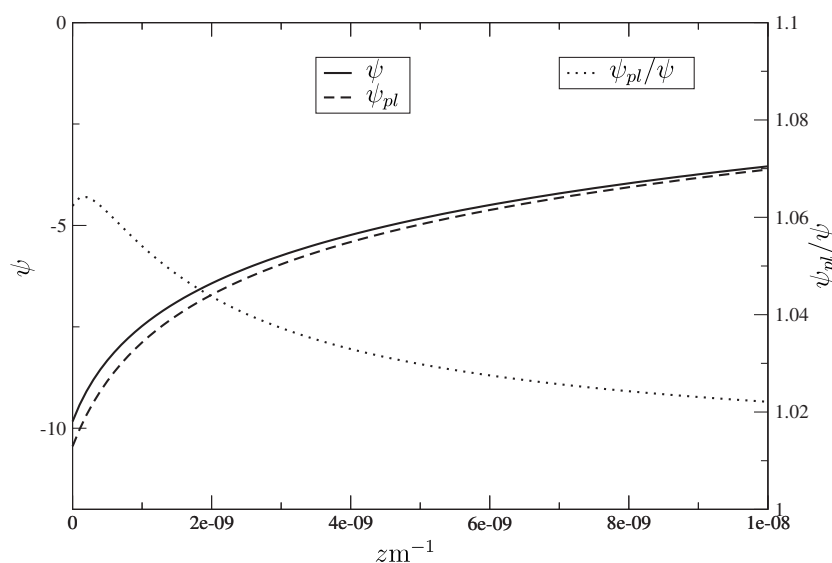
Figure 3. The decay behaviour of partially linearized and fully non-linear potentials as z increases. $n_s = 0.01$ M; $\sigma_0 = \sigma_1 = 0.5$ nm^{-2}. This corresponds to the point in the middle of the left-hand graph in figure 1. The overestimation of the potential by the partially linearized theory decreases as z increases.

partially linearized potential becomes a better approximation to the fully non-linear potential, as one would expect.

Finally, consider the salt-free case where only counter-ions are present. The solution of the non-linear PB equation (6), for a uniform surface charge density σ_0, is then

$$\psi_0(z) = \ln[2\pi l_b n_0 (b + z)^2] \tag{21}$$

where the Gouy length $b = (2\pi l_b \sigma_0)^{-1}$ is determined by the bc (2). n_0 is undetermined, and its choice merely sets the zero of the potential scale.

Performing the same partitioning and expansion as before, one arrives at the salt-free equivalent of equation (16), namely

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}z^2} - k^2 - \frac{2}{(b+z)^2}\right)\hat{\psi}_1(\boldsymbol{k}, z) = 0. \tag{22}$$

The solution which vanishes as $z \to \infty$ is (region II)

$$\hat{\psi}_1^{(\mathrm{II})}(z) = A^{(\mathrm{II})}(\boldsymbol{k})\mathrm{e}^{-k(b+z)}\left(k + \frac{1}{b+z}\right). \tag{23}$$

The same solution holds in region I, with z replaced by $-z$.

In considering a plate surrounded by counter-ions, it must be noted that while the number of counter-ions is mandated by the requirement of charge neutrality, their allocation between regions I and II is entirely a matter of choice. The physically most reasonable choice is to divide them equally between the two regions, and it may be shown that this arrangement in fact minimizes the total free energy of the system.

Imposing the bc (2) then leads to the required solution

$$\psi_1(\boldsymbol{r}) = -\frac{2\pi l_b b^2}{b + |z|} \sum_{m,n} \frac{(1 + p_{mn}(b + |z|))\mathrm{e}^{-p_{mn}|z|}}{1 + bp_{mn}(1 + bp_{mn})} \lambda_{mn} f_{mn}(x, y). \tag{24}$$

As in the case with added salt, the partially linearized potential yields a surprisingly accurate approximation to the fully non-linear potential over most of the parameter space.

3. Potential between two charge-modulated plates

Since the ultimate goal of this study is the calculation of the force (or disjoining pressure) acting between two charge-modulated plates, the next step is to determine the electrostatic potential between two such plates, placed at $z = 0$ and D. As in the previous section, two situations are possible. Situation A corresponds to two infinitely thin plates immersed in an ionic solution. Regions I–III have identical properties, and in particular, identical dielectric constants $\epsilon_I = \epsilon_{II} = \epsilon_{III} = \epsilon$. In situation B, a solution of dielectric constant ϵ_{II} is confined between two semi-infinite dielectric slabs, or substrates, $z < 0$ and $z > D$, of dielectric constant $\epsilon_I = \epsilon_{III}$.

In this paper, we shall only treat case A, infinitely thin plates. Case B is dealt with in more detail in [11].

The surface charge densities (divided by $-e$) are of the form

$$\sigma_1(x, y) = \sum_{m,n=0} \lambda_{mn} f_{mn}^{(1)}(x, y); \qquad z = 0, \tag{25a}$$

$$\sigma_2(x, y) = \sum_{m,n=0} \lambda_{mn} f_{mn}^{(2)}(x, y); \qquad z = D \tag{25b}$$

where the functions $f_{mn}^{(i)}$ are again given by equation (9b), with different coefficients a_{mn}, b_{mn}, c_{mn}, and d_{mn} for the two plates, which will in general carry different modulated surface charge densities.

In the special case of uniformly charged planes, an explicit solution of PB theory for two plates exists only in the salt-free (counter-ion-only) limit [10]. Since an explicit solution is needed for a fully analytic treatment of the partially linearized PB theory introduced in the previous section, the following discussion is restricted to fully LPB theory in the presence of added salt, while the salt-free case will be treated within the PLPB theory, which is expected to have a much broader range of validity.

3.1. Linearized theory

In situation A, the linear solution for the reduced potential may be easily calculated from the Green function representation

$$\psi(\mathbf{r}) = -l_b \int \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} (\sigma_1(x', y')\delta(z') + \sigma_2(x', y')\delta(z' - D)) \, d\mathbf{r}'. \tag{26}$$

Substitution of the surface charge densities (25a) then leads immediately to the result

$$\psi(\mathbf{r}) = -2\pi l_b \sum_{m,n=0}^{\infty} \frac{\lambda_{mn}}{q_{mn}} (f_{mn}^{(1)}(x, y)e^{-q_{mn}|z|} + f_{mn}^{(2)}(x, y)e^{-q_{mn}|D-z|}) \tag{27}$$

where the q_{mn} are defined after equation (11). Equation (27) is valid in all three regions.

Case B is slightly more complicated due to the dielectric bc which must now be imposed at the interfaces between regions I and II ($z = 0$), and between II and III ($z = D$). The resulting reduced electrostatic potentials in regions I, II, and III are available in TOW's PhD thesis [11].

3.2. Partially linearized theory

For the reasons explained earlier, restriction is made here to the salt-free case. The dimensionless potential in region II satisfies the PB equation

$$\nabla^2 \psi^{(II)}(\boldsymbol{r}) = -2C^2 e^{-\psi^{(II)}(\boldsymbol{r})} \tag{28}$$

where $C^2 = 2\pi l_b n_+^{(m)}$, and $n_+^{(m)}$ is a reference mean mid-plane counter-ion density, which is fixed by the constraint of charge neutrality. Within PLPB theory, ψ is split into ψ_0 and ψ_1, where ψ_0 is the dimensionless electrostatic potential due to two equally and uniformly charged plates at $z = 0$ and D; the solution of the non-linear PB equation for ψ_0 is [10]

$$\psi_0(z) = \ln\left[\cos^2\left[C\left(z - \frac{D}{2}\right)\right]\right]. \tag{29}$$

C is determined by the bc on the gradient of the potential at either plate (which is equivalent to imposing charge neutrality); the corresponding equation for C is

$$C \tan\left[\frac{CD}{2}\right] = 2\pi l_b \sigma_0. \tag{30}$$

Upon linearization of the PB equation (28) with respect to ψ_1, the latter is found to satisfy the following equation in region II:

$$\nabla^2 \psi^{(II)}(\boldsymbol{r}) = 2C^2 \sec^2\left[C\left(z - \frac{D}{2}\right)\right]\psi_1^{(II)}(\boldsymbol{r}). \tag{31}$$

Taking the Fourier transform with respect to the coordinates x and y, one arrives at the following differential equation for $\psi_1^{(II)}(k, z)$:

$$\left(\frac{d^2}{dz^2} - k^2 - 2C^2 \sec^2\left[C\left(z - \frac{D}{2}\right)\right]\right)\hat{\psi}_1^{(II)}(\boldsymbol{k}, z) = 0, \tag{32}$$

the general solution to which is

$$\hat{\psi}_1^{(II)}(\boldsymbol{k}, z) = A^{(II-)}(\boldsymbol{k})e^{-k(z-\frac{D}{2})}\left(C \tan\left[C\left(z - \frac{D}{2}\right)\right] - k\right)$$

$$+ A^{(II+)}(\boldsymbol{k})e^{k(z-\frac{D}{2})}\frac{C \tan\left[C\left(z - \frac{D}{2}\right)\right] + k}{2k(C^2 + k^2)}. \tag{33}$$

This solution does not apply when $\boldsymbol{k} = 0$, but this is not required if σ_1 is not chosen such that its mean is zero.

Considering case A, that of infinitely thin plates, it is clear that the potential outside the plates, in regions I and III, will have the same form as seen in equation (23). In this case we must also consider the distribution of counter-ions between the three regions. Analysis shows that the minimum-free-energy configuration actually occurs when all counter-ions are outside the plates, due to the entropy thus gained. However, this is not physically reasonable. We shall therefore again let the counter-ions from each plate be divided half and half each side of that plate.

Taking these forms for the potentials, and applying the necessary boundary conditions, we can find an expression for the potential in each region. These expressions are shown in the appendix.

Case B, of dielectric-backed plates, will not be considered here, but is examined in [11].

We may note that both forms for potentials shown here (and all of those shown in [11]) have the form

$$\psi_1^{(i)} = \sum_{mn} \lambda_{mn}(\alpha_i^{(1)}(z; m, n) f_{mn}^{(1)}(x, y) + \alpha_i^{(2)}(z; m, n) f_{mn}^{(2)}(x, y)). \tag{34}$$

That is, $\alpha_{II}^{(1)}(z; m, n)$ represents the influence, in region II, of the m, nth Fourier component of the charge modulation on plate 1.

4. Normal and tangential forces between charge-modulated plates

Having explicit expressions for the reduced electrostatic potential in the system of two plates, we may now calculate the pressure in the system.

In a system of charged particles with no short-range interactions, the stress tensor is

$$T_{\alpha\beta} = \left(\Pi - \frac{\epsilon\epsilon_0}{2}E^2\right)\delta_{\alpha\beta} + \epsilon\epsilon_0 EE \tag{35}$$

where $\Pi = k_B T \sum_i n_i(x, y, z)$ is the osmotic pressure. Within one-dimensional fully non-linear PB theory, the stress tensor is constant between two plates, which renders the calculation of the disjoining pressure very simple. This is no longer true for a system involving charge modulation in the (x, y) plane; nor when the PB equation is approximated from full non-linearity.

To calculate the stress on the plates, we therefore integrate the stress tensor around both plates, and sum the forces. The force on one repeating area of the first plate is

$$\boldsymbol{F}^{(1)} = \oint \underline{\underline{T}} \cdot \mathrm{d}\boldsymbol{n} = \int\int_{-l,-h}^{l,h} (\underline{\underline{T}}(z = 0^+) - \underline{\underline{T}}(z = 0^-)) \cdot \hat{z}\,\mathrm{d}x\,\mathrm{d}y \tag{36}$$

and similarly on the second plate. The total stress between the plates is then

$$S = \frac{\boldsymbol{F}_2 - \boldsymbol{F}_1}{8lh}. \tag{37}$$

The disjoining pressure is given by the z-component of equation (37), and the transverse stress by the x- and y-components. Inserting equation (35) into (36), and making various simplifications due to Gauss's law, it can be seen that the force at any point on the first plate is given by

$$\boldsymbol{F}^{(1)}(x, y) = \frac{1}{\beta}\begin{pmatrix} \sigma_1\frac{\partial\psi_1}{\partial x} \\ \sigma_1\frac{\partial\psi_1}{\partial y} \\ \mathcal{B}[\psi]\sum_i(n_{0,i}^{(\mathrm{II})} - n_{0,i}^{(\mathrm{I})}) + \frac{1}{2}\sigma_1\left(\frac{\partial\psi^{(\mathrm{II})}}{\partial z} + \frac{\partial\psi^{(\mathrm{I})}}{\partial z}\right) \end{pmatrix}_{z=0}, \tag{38}$$

where $\mathcal{B}[\psi]$ denotes the appropriate Boltzmann distribution, whether fully non-linear, partially linear, or fully linear.

4.1. Disjoining pressure

Considering the components of the stress tensor separately, we will look first at the z-component, corresponding to the normal stress. Its calculation is simplified by the fact that the $f_{mn}^{(i)}$ integrate to zero over one repeated area. Separating out those parts without dependence on x, y, we may write the force on one repeated area as

$$F_z^{(1)} = \frac{4lh}{\beta}\left[\mathcal{B}_0[\psi_0]\sum_i(n_{i,\mathrm{II}}^{(0)} - n_{i,\mathrm{I}}^{(0)}) + \frac{1}{2}\sigma_0^{(1)}\left(\frac{\partial\psi_0^{(\mathrm{II})}}{\partial z} + \frac{\partial\psi_0^{(\mathrm{I})}}{\partial z}\right)\right]$$
$$+ \frac{1}{2\beta}\int\int_{-l,-h}^{l,h}\mathrm{d}x\,\mathrm{d}y\,\sigma_1^{(1)}\left(\frac{\partial\psi_1^{(\mathrm{II})}}{\partial z} + \frac{\partial\psi_1^{(\mathrm{I})}}{\partial z}\right), \tag{39}$$

where $\mathcal{B}_0[\psi_0]$ is the Boltzmann distribution applicable to ψ_0. The first two terms of equation (39) give the force due to uniform charge, from which we can see that in this formulation, the pressure due to uniform charge is

$$P_0 = \frac{1}{\beta}\left[\mathcal{B}_0[\psi_0]\sum_i(n_{i,\mathrm{II}}^{(0)} - n_{i,\mathrm{I}}^{(0)}) + \frac{1}{2}\sigma_0^{(1)}\left(\frac{\partial\psi_0^{(\mathrm{II})}}{\partial z} + \frac{\partial\psi_0^{(\mathrm{I})}}{\partial z}\right)\right]. \tag{40}$$

Noting again that all the expressions for the potentials $\psi_1^{(i)}$ (for region i) in the two plate systems may be written in the form $\sum_{mn} \lambda_{mn}(\alpha_i^{(1)} f_{mn}^{(1)} + \alpha_i^{(2)} f_{mn}^{(2)})$, we may write the additional force as

$$
F_{1,z}^{(1)} = \frac{1}{2\beta} \sum_{m,n} \sum_{m',n'} \lambda_{mn} \lambda_{m'n'} \int \int_{-l,-h}^{l,h} \mathrm{d}x \, \mathrm{d}y \, f_{mn}^{(1)}
$$

$$
\times \left(\frac{\partial}{\partial z}(\alpha_{\mathrm{I}}^{(1)} + \alpha_{\mathrm{II}}^{(1)}) f_{m'n'}^{(1)} + \frac{\partial}{\partial z}(\alpha_{\mathrm{I}}^{(2)} + \alpha_{\mathrm{II}}^{(2)}) f_{m'n'}^{(2)} \right). \tag{41}
$$

The Fourier series form of f_{mn} allows the relatively simple evaluation of the double integral:

$$
\sum_{m,n} \sum_{m',n'} \lambda_{mn} \lambda_{m'n'} \int \int_{-l,-h}^{l,h} \mathrm{d}x \, \mathrm{d}y \, f_{mn}^{(1)} f_{m'n'}^{(2)}
$$

$$
= lh \sum_{mn} \lambda_{mn} (a_{mn}^{(1)} a_{mn}^{(2)} + b_{mn}^{(1)} b_{mn}^{(2)} + c_{mn}^{(1)} c_{mn}^{(2)} + d_{mn}^{(1)} d_{mn}^{(2)}). \tag{42}
$$

The underlying symmetry of the uniformly charged system allows us to simplify the expression resulting from the insertion of equation (42) into (41), and the additional pressure may be written as

$$
P_1 = -\frac{1}{16\beta} \sum_{m,n} \lambda_{mn} \left(2\frac{\partial}{\partial z}(\alpha_{\mathrm{I}}^{(2)} + \alpha_{\mathrm{II}}^{(2)})_{z=0} (a_{mn}^{(1)} a_{mn}^{(2)} + b_{mn}^{(1)} b_{mn}^{(2)} + c_{mn}^{(1)} c_{mn}^{(2)} + d_{mn}^{(1)} d_{mn}^{(2)}) \right.
$$

$$
+ \frac{\partial}{\partial z}(\alpha_{\mathrm{I}}^{(1)} + \alpha_{\mathrm{II}}^{(1)})_{z=0} (a_{mn}^{(1)2} + a_{mn}^{(2)2} + b_{mn}^{(1)2} + b_{mn}^{(2)2}
$$

$$
\left. + c_{mn}^{(1)2} + c_{mn}^{(2)2} + d_{mn}^{(1)2} + d_{mn}^{(2)2}) \right). \tag{43}
$$

4.2. Transverse stress

Clearly there is no contribution from the uniform surface charge to the transverse stress.

Considering only the x-component, the force on one repeated area of the first plate is

$$
F_{1,x} = \frac{1}{\beta} \sum_{mn} \sum_{m',n'} \lambda_{mn} \lambda_{m'n'} \int \int_{-l,-h}^{l,h} \mathrm{d}x \, \mathrm{d}y \, f_{mn}^{(1)} \left(\alpha_{\mathrm{I}}^{(1)} \frac{\partial f_{m'n'}^{(1)}}{\partial x} + \alpha_{\mathrm{I}}^{(2)} \frac{\partial f_{m'n'}^{(2)}}{\partial x} \right). \tag{44}
$$

The integral to be summed is

$$
\sum_{m,n} \sum_{m',n'} \lambda_{mn} \lambda_{m'n'} \int \int_{-l,-h}^{l,h} \mathrm{d}x \, \mathrm{d}y \, f_{mn}^{(1)} \frac{\partial f_{m'n'}^{(2)}}{\partial x}
$$

$$
= hm\pi \sum_{mn} \lambda_{mn} (a_{mn}^{(2)} b_{mn}^{(1)} - a_{mn}^{(1)} b_{mn}^{(2)} + c_{mn}^{(2)} d_{mn}^{(1)} - c_{mn}^{(1)} d_{mn}^{(2)}). \tag{45}
$$

Remembering again the symmetry of the uniformly charged system, the transverse stress may be written as the two-dimensional vector

$$
S_t = \frac{\pi}{4\beta} \sum_{mn} \lambda_{mn} \begin{pmatrix} \frac{m}{l} \alpha_{\mathrm{I}}^{(2)}(z=0; m, n)(a_{mn}^{(1)} b_{mn}^{(2)} - a_{mn}^{(2)} b_{mn}^{(1)} + c_{mn}^{(1)} d_{mn}^{(2)} - c_{mn}^{(2)} d_{mn}^{(1)}) \\ \frac{n}{h} \alpha_{\mathrm{I}}^{(2)}(z=0; m, n)(a_{mn}^{(1)} c_{mn}^{(2)} - a_{mn}^{(2)} c_{mn}^{(1)} + b_{mn}^{(1)} d_{mn}^{(2)} - b_{mn}^{(2)} d_{mn}^{(1)}) \end{pmatrix}. \tag{46}
$$

5. An application to 'striped' charge densities

We shall now use the expressions above to study one particular type of modulated charge density: specifically, 'stripes' of charge. That is, on each plate the charge density is modulated by a one-dimensional sinusoidal wave, with a phase offset of θ between the two plates. Thus

$$f^{(1)}(x, y) = \tau \cos\left[\frac{\pi x}{l}\right], \qquad f^{(2)}(x, y) = \tau \cos\left[\frac{\pi x}{l} + \theta\right], \tag{47}$$

where τ is the magnitude of the modulation. The only non-zero Fourier components are

$$a_{10}^{(1)} = 2\tau, \qquad a_{10}^{(2)} = 2\tau \cos[\theta], \qquad b_{10}^{(2)} = 2\tau \sin[\theta]. \tag{48}$$

Under these conditions, the additional disjoining pressure is

$$P_1 = -\frac{\tau^2}{4\beta}\left\{\frac{\partial}{\partial z}\left(\alpha_{\mathrm{I}}^{(1)}\begin{pmatrix} m = 1 \\ n = 0 \end{pmatrix} + \alpha_{\mathrm{II}}^{(1)}\begin{pmatrix} m = 1 \\ n = 0 \end{pmatrix}_{z=0}\right)\right.$$
$$\left. + \frac{\partial}{\partial z}\left(\alpha_{\mathrm{I}}^{(2)}\begin{pmatrix} m = 1 \\ n = 0 \end{pmatrix} + \alpha_{\mathrm{II}}^{(2)}\begin{pmatrix} m = 1 \\ n = 0 \end{pmatrix}_{z=0}\right)\cos[\theta]\right\}, \tag{49}$$

which has two parts: a constant part and an angularly dependent part. Given the shape of the $\alpha_i^{(2)}$ (which are both decreasing at $z = 0$), the coefficient of the angular part is positive, and thus the pressure will be greater at $\theta = 0$ than π. This is expected since when the two modulations are in phase, areas of high charge will be closer together than when they are out of phase.

The presence of the constant term is rather more surprising. If it is non-zero, this means that the pressure due to charge-modulated plates, averaged over all phase offsets, is not equal to the pressure due to uniformly charged plates of the same average charge; i.e., that averaging out the charge modulation is not equivalent to averaging over the phase offsets, which is what one might naively expect.

This term arises from the self-interaction of the potential due to each plate. Given that the additional potential is linear, and therefore additive, we have separated out that portion of the additional potential due to each plate. While this would be symmetrical about the plate if there were only one plate, it is not when there are two; and for each plate the gradients of this partial potential on either side of the plate are opposite in sign, but not necessarily equal in magnitude, and this constant term is proportional to the sum of these gradients; i.e. the difference in their magnitude. In principle, this difference may be positive or negative; it may augment or reduce the pressure; in practice we have found that it increases the pressure under all reasonable conditions.

It should be noted that the effect of this term is not related to the counter-ion density enhancement found in [9], since their analysis relied upon expanding the distribution to quadratic order. The present term appears at linear order, and is due to the fact that the pressure involves the square of the electric field, allowing linear terms to contribute to the integral over the repeated area.

The transverse stress under these conditions is trivially seen to be

$$S_x = \frac{\tau^2 \pi}{2\beta l}\alpha_{\mathrm{I}}^{(2)}(z = 0)\sin[\theta]. \tag{50}$$

Clearly, at $\theta = 0$ and π, the stress will be zero, since these represent the maximum and minimum, respectively, of energy. Again, the sign of α shows that the stress elsewhere pushes the plates towards a configuration of $\theta = \pi$, i.e. the configuration of minimum energy, and has a maximum at $\theta = \pi/2$.

5.1. Linearized, added-salt case

The potential from the fully linearized system containing added salt is of limited applicability, due to the limitations of the linear approximation, but does have a particularly simple form, which is useful for illustrative purposes.

The disjoining pressure due to uniform charge in this case, from equation (40), is due entirely to the interaction of each plate with the potential from the other, and has a magnitude of $2\pi l_b \sigma_0^2 e^{-\kappa D}/\beta$. For the additional potential, we can immediately see that the first, self-interaction, term in equation (49) is always 0. That is, there is no effect on the average pressure when charge modulation is introduced. The variable part, however, has an amplitude of $2\pi l_b \tau^2 e^{-q_{10}D}/\beta$. The ratio of this amplitude to the uniform pressure is $\frac{1}{2}\left(\frac{\tau}{\sigma_0}\right)^2 e^{(\kappa - q_{10})D}$. Thus the importance of this excess pressure is proportional to τ^2/σ_0^2, and decays exponentially as the plate separation increases.

The stress, from equation (50), on the other hand, is

$$S_x = -\frac{\tau^2 \pi^2 l_b}{\beta q_{10} l} e^{-q_{10}D} \sin[\theta]. \tag{51}$$

5.2. Partially linearized, salt-free case

The potentials for two plates surrounded by counter-ions are shown in the appendix. In this case, the pressure between the uniformly charged plates is given by the first term of equation (40):

$$P_0 = \frac{1}{2\beta} e^{-\psi_0}(2n_0^{(II)} - n_0^{(I)} - n_0^{(III)}) \tag{52}$$

where $n_0^{(i)}$ is the 'bulk' density in each region; namely $n_+^{(m)}$ between the plates, in region II, and the undetermined constant n_{0+} outside, in regions I and III. However, in this case, the 'undetermined' constant may be determined by the constraint of the continuity of the potential across the plates. Given this, we may say that $n_0^{(I)} = n_0^{(III)} = n_0^{(II)} \sin^2[\frac{CD}{2}]$, and thus $P_0 = n_+^{(m)}/\beta$, where, as before, $C^2 = \pi l_b n_+^{(m)}$ and $C\tan[\frac{CD}{2}] = \pi l_b \sigma_0$. This value for the uniform pressure accords with the standard result [10].

The amplitude of the θ-dependent part of the partially linearized pressure is

$$\frac{\tau^2}{\beta} \frac{4\pi l_b}{\mathcal{D}} b p_{10} e^{p_{10}D}(1 + b p_{10})(C^2 + p_{10}^2)(1 + b p_{10}(1 + b p_{10})). \tag{53}$$

The ratio of this amplitude to the uniform pressure is shown on the left in figure 4, for a range of values of D and σ_0. τ is kept constant at a value corresponding to stripes of $\pm 1e$ nm^{-2}. The region of particularly high value on the left-hand side is unlikely to be an accurate reflection of the actual pressure, since it corresponds to a very strong modulation on a very weakly charged surface, which is precisely the region where our approximation is least correct.

The constant term in the additional pressure results from inserting equations (A.2)–(A.4) into equation (49). The ratio of this constant, self-interaction, term, to the uniform pressure (that is, the pressure in the absence of modulations, but with the same average charge) is shown in the right of figure 4, for the same striped charges as before. It can be seen that the difference that this extra term makes is fairly small compared to that due to the phase-dependent term. Only at very close separations does it make more than a 1% difference. In nearly all cases it increases the pressure, but it should be noted that there is a small region in the bottom right-hand corner (which represents a very small separation, and a very small amount of the charge being treated by modulation—the very small separation rendering this area uninteresting), where the sign of this extra term is negative. This is the only area in which the magnitude of the potential
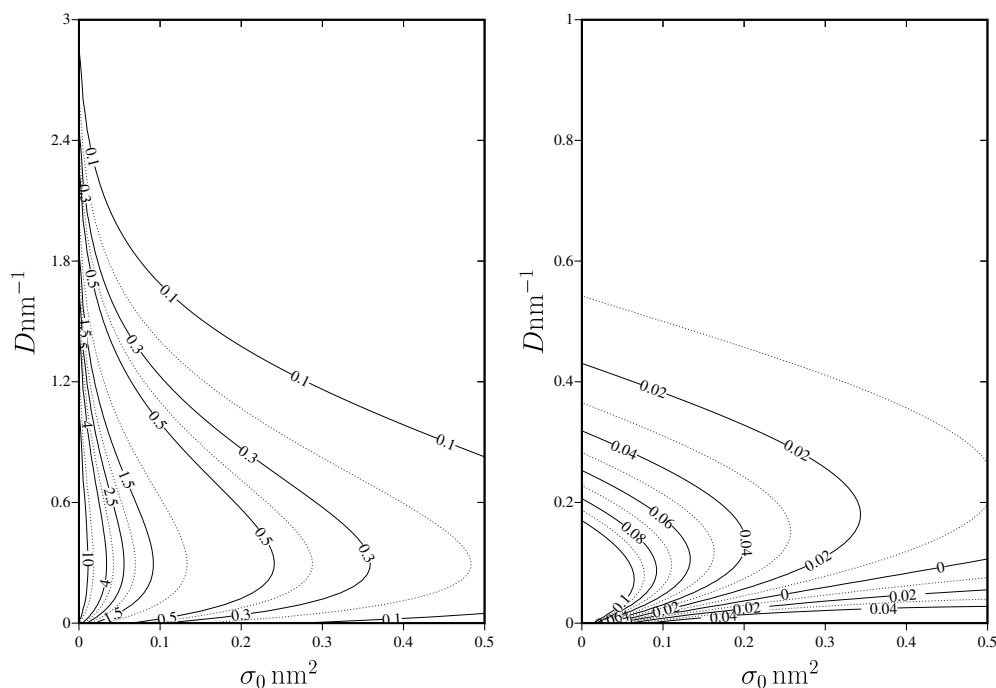
Figure 4. The additional pressure due to charge modulations in a salt-free system. The left-hand graph is the ratio of the amplitude of the angularly dependent part of the additional pressure to the pressure from uniformly charged plates. The right-hand graph shows the ratio of the constant (angularly independent) term to the pressure due to uniformly charged plates. The contour lines are not equally spaced; solid curves are marked with values, and dotted curves have values halfway between their neighbouring solid curves. Note the difference in scale between the graphs.

gradient on the right-hand side of the first plane is greater than that on the left, which is caused largely by the proximity of the planes.

The transverse stress in the system is given by the formula

$$S_x = -\frac{\tau^2 \pi}{\beta l} \frac{8\pi l_b}{\mathcal{D}} b^2 e^{-p_{10}D} p_{10}(1 + bp_{10})^2 (C^2 + p_{10}^2) \sin[\theta]. \tag{54}$$

Figure 5 plots the ratio of the peak value of the stress to the uniform pressure, over the same range of σ_0 and D, and with the same value for τ as before. It can be seen that the magnitude of this effect decays very quickly; the exponent is proportional to $1/l$, where l is the wavelength of the modulation, which is 2 nm in this case. Should the modulation have a greater wavelength, the stress would be correspondingly more important.

6. Conclusions

We have examined the electrostatic potentials in the vicinity of isolated or pairs of parallel, infinite plates, carrying a spatially modulated surface charge density, within PB theory. The potentials were calculated within fully or partially linearized versions of the theory, for which fully closed-form solutions were obtained. The PLPB theory can be tested against results for the full non-linear equation in the case of a uniform surface charge, and was shown to be surprisingly accurate.
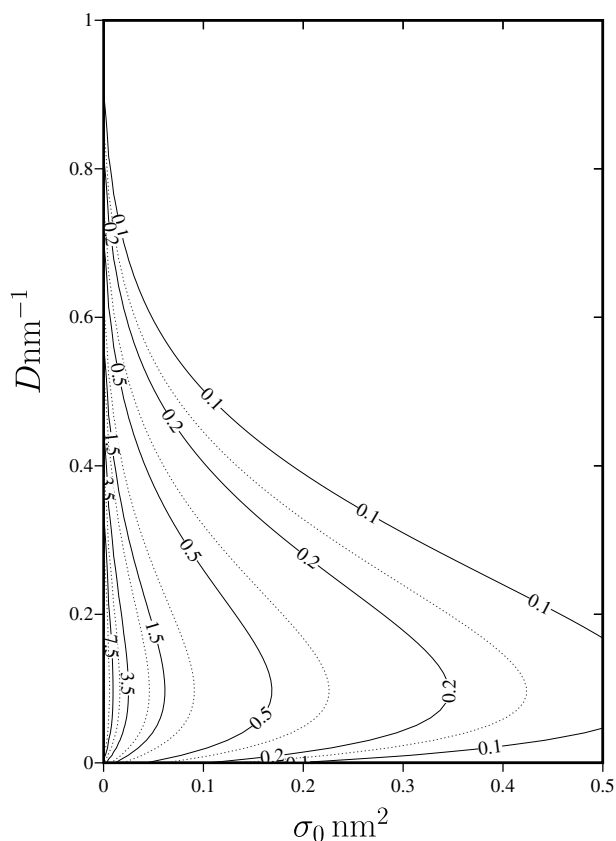
Figure 5. The peak value of the transverse stress in a salt-free system. The contour lines are not equally spaced; solid curves are marked with values, and dotted curves have values halfway between their neighbouring solid curves.

The main application of the potentials is the calculation of the stress tensor associated with ionic solutions in the field due to two charge-modulated plates. We have obtained closed-form expressions for the normal and transverse components of the stress, averaged over a unit planar cell of the periodically repeated charge pattern. These expressions were explicitly evaluated in the case of a one-dimensional striped charge pattern on the plates. The normal component of the stress, the disjoining pressure, is found to be significantly enhanced compared to the case of uniformly charged plates. The maximum enhancement occurs when the striped patterns are in phase, while the disjoining pressure is lowered when the patterns are out of phase. For an interplate separation, D, comparable to the periodicity of the striped pattern, the enhancement can be as large as 30%.

The present results are limited to cases where full or partial linearization of PB theory leads to fully closed-form expressions. In the case of the forces between two plates, this means that the accurate PLPB theory could only be worked out for the salt-free case. It will clearly be of interest to extend the present calculations to two-dimensional charge patterns on the plates, for which the expressions derived in this paper are directly applicable; and for the case of added salt, which will require numerical work, except in the case of fully linearized PB theory.

Acknowledgment

Appendix. Partially linearized potential between two plates surrounded by counter-ions

Taking the general solution for the potential given in equation (33), and applying the appropriate boundary conditions; i.e.,

$$
\begin{aligned}
&\hat{\psi}_1^{(\mathrm{I})}(\boldsymbol{k}, z=0) = \hat{\psi}_1^{(\mathrm{II})}(\boldsymbol{k}, z=0); \\
&\left.\frac{\partial \hat{\psi}_1^{(\mathrm{I})}(\boldsymbol{k}, z)}{\partial z}\right|_{z=0} - \left.\frac{\partial \hat{\psi}_1^{(\mathrm{II})}(\boldsymbol{k}, z)}{\partial z}\right|_{z=0} = 4\pi l_b \hat{\sigma}_1(k_x, k_y); \\
&\hat{\psi}_1^{(\mathrm{II})}(\boldsymbol{k}, z=D) = \hat{\psi}_1^{(\mathrm{III})}(\boldsymbol{k}, z=D); \\
&\left.\frac{\partial \hat{\psi}_1^{(\mathrm{II})}(\boldsymbol{k}, z)}{\partial z}\right|_{z=D} - \left.\frac{\partial \hat{\psi}_1^{(\mathrm{III})}(\boldsymbol{k}, z)}{\partial z}\right|_{z=D} = 4\pi l_b \hat{\sigma}_2(k_x, k_y);
\end{aligned}
\tag{A.1}
$$

we may solve the resultant linear equations to determine that the potentials in the three regions are

$$
\begin{aligned}
\psi_1^{(\mathrm{I})}(x, y, z) = -\frac{4\pi l_b b^2}{b-z} \sum_{m,n=0} \frac{\lambda_{mn}}{\mathcal{D}}(1 + p_{mn}(b-z)) \Bigg\{ & f_{mn}^{(1)} \mathrm{e}^{p_{mn}z} \left[-\left(p_{mn} - C\tan\left[\frac{CD}{2}\right] \right)^2 \right. \\
& + \mathrm{e}^{2p_{mn}D}(1 + 2bp_{mn}(1 + bp_{mn}))\left(p_{mn} + C\tan\left[\frac{CD}{2}\right] \right)^2 \\
& + 2bC^2(1 + bp_{mn})\mathrm{e}^{-p_{mn}D}\sec^2\left[\frac{CD}{2}\right]\left(p_{mn}\cosh[p_{mn}D] \right. \\
& \left. + C\sinh[p_{mn}D]\tan\left[\frac{CD}{2}\right] \right) \Bigg] + f_{mn}^{(2)} 2b\mathrm{e}^{p_{mn}(D+z)} p_{mn}(1 + bp_{mn})(C^2 + p_{mn}^2) \Bigg\},
\end{aligned}
\tag{A.2}
$$

$$
\begin{aligned}
\psi_1^{(\mathrm{II})}(x, y, z) = -4\pi l_b b \sum_{m,n=0} & \frac{\lambda_{mn}}{\mathcal{D}}(1 + bp_{mn}) \\
\times \Bigg\{ & \mathrm{e}^{-p_{mn}z} f_{mn}^{(1)} \left[\frac{\mathrm{e}^{2p_{mn}z}}{1 + \cos[CD]}\left(p_{mn} + C\tan\left[C\left(z - \frac{D}{2}\right)\right] \right)(2bC^2(1 + bp_{mn}) \right. \\
& - p_{mn} - p_{mn}\cos[CD] + C\sin[CD]) \\
& + \mathrm{e}^{2p_{mn}D}\left(p_{mn} - C\tan\left[C\left(z - \frac{D}{2}\right)\right] \right)\left(bC^2(1 + bp_{mn})\sec^2\left[\frac{CD}{2}\right] \right. \\
& \left. + (1 + 2bp_{mn}(1 + bp_{mn}))\left(p_{mn} + C\tan\left[\frac{CD}{2}\right] \right) \right) \Bigg] \\
& + \mathrm{e}^{-p_{mn}(D-z)} f_{mn}^{(2)} \left[\frac{\mathrm{e}^{2p_{mn}(D-z)}}{1 + \cos[CD]}\left(p_{mn} - C\tan\left[C\left(z - \frac{D}{2}\right)\right] \right)(2bC^2(1 + bp_{mn}) \right. \\
& - p_{mn} - p_{mn}\cos[CD] + C\sin[CD]) \\
& + \mathrm{e}^{2p_{mn}D}\left(p_{mn} + C\tan\left[C\left(z - \frac{D}{2}\right)\right] \right)\left(bC^2(1 + bp_{mn})\sec^2\left[\frac{CD}{2}\right] \right. \\
& \left. \left. + (1 + 2bp_{mn}(1 + bp_{mn}))\left(p_{mn} + C\tan\left[\frac{CD}{2}\right] \right) \right) \right] \Bigg\},
\end{aligned}
\tag{A.3}
$$

$$\psi_1^{(\mathrm{III})}(x, y, z) = -\frac{4\pi l_b b^2}{b - D + z} \sum_{m,n=0} \frac{\lambda_{mn}}{\mathcal{D}} (1 + p_{mn}(b - D + z))$$

$$\times \left\{ f_{mn}^{(1)} 2b \mathrm{e}^{p_{mn}(2D-z)} p_{mn}(1 + bp_{mn})(C^2 + p_{mn}^2) \right.$$

$$+ f_{mn}^{(2)} \mathrm{e}^{p_{mn}(D-z)} \left[(1 + 2bp_{mn}(1 + bp_{mn})) \mathrm{e}^{2p_{mn}D} \left(p_{mn} + C \tan\left[\frac{CD}{2}\right] \right)^2 \right.$$

$$- \left(p_{mn} - C \tan\left[\frac{CD}{2}\right] \right)^2$$

$$+ 2bC^2(1 + bp_{mn}) \mathrm{e}^{-p_{mn}D} \sec^2\left[\frac{CD}{2}\right] \left(p_{mn} \cosh[p_{mn}D] \right.$$

$$\left. \left. \left. + C \sinh[p_{mn}D]\left[\frac{CD}{2}\right] \right) \right] \right\}. \tag{A.4}$$

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