

Free energy of electric double layers around finite particles

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Abstract. The classic problem of evaluating the free energy of an electric double layer around a planar electrode or polyion through an appropriate charging process is reconsidered, within the Poisson–Boltzmann framework. After a brief consideration of an infinite planar electrode, we examine finite-size effects. An application is made to swollen arrays of disc-shaped clay platelets.

1. Introduction

Polyelectrolytes are made up of highly charged mesoscopic polyions, oppositely charged microions and added salt, dissolved or suspended in a polar solvent, usually water. The polyion may be a line (charged polymer chain), a surface (e.g. a clay platelet or a membrane), or a three-dimensional object as in charge-stabilized colloidal suspensions or charged micellar solutions. Due to the high polyion charge, the microscopic counterions are strongly attracted while the coions (carrying a charge of the same sign as the polyions) are repelled, thus giving rise to electric double layers characterized by a strong inhomogeneity of the local densities of these ions in the vicinity of the polyion. The topology of the double layer is obviously determined by that of the polyions, and by their relative configurations. In the case of linear or rod-like polyions, we expect a sheath structure, while for charged platelets, the double layer is expected to be flat. A thermodynamic quantity of prime importance is the free energy of the double layer, which is a functional of the local densities of microscopic ions, depending parametrically on the instantaneous configuration of polyions.

Although the double layers of neighbouring polyions overlap and interfere, it is instructive to consider first the simpler problem of the free energy of an isolated polyion (infinite-dilution limit), or of a polyion in a Wigner–Seitz cell with appropriate boundary conditions, to mimic the effect of the neighbouring polyions which form a cage with some average topology, of volume equal to the volume per polyion. This problem, which has already been addressed by several authors [3, 4], is revisited in the present paper. Restriction will be made to rigid lamellar polyions, with special emphasis on finite-size effects, and an application to a suspension of disc-shaped clay platelets

2. Poisson–Boltzmann theory

We shall hereafter consider mesoscopic charged platelets \mathcal{P} immersed with their counterions in a symmetric 1:1 electrolyte within Poisson–Boltzmann (PB) theory. The platelets are modelled by infinitely thin rigid membranes of surface S . Without loss of generality,

the membranes are assumed to be negatively charged; they carry Z elementary structural charges $-e$ and their surface charge density is moreover taken as a constant, $\sigma = -Ze/S$. The solvent is replaced by a continuum of dielectric constant ε .

Different electrostatic situations can be distinguished. If the suspension is in equilibrium with a salt reservoir, the system must be considered as belonging to a grand canonical ensemble. The numbers of microions (+ and -) are determined by equating the chemical potential of the salt in the reservoir and in the solution. On the other hand, for a system with a given salt concentration (canonical situation), the number of coions N_- is known *a priori*, from which N_+ is deduced by means of the charge neutrality constraint: $N_+ - N_- = Z$. In both cases, the thermodynamic potential to be considered is straightforwardly obtained from the Helmholtz free energy F , the expression for which can be much simplified by choosing an adequate real or virtual charging process, as will be shown below.

In the framework of Poisson–Boltzmann mean-field theory, the microions are treated as an inhomogeneous ideal gas. The local density of microions is then related to the electrostatic potential $\varphi(\mathbf{r})$ by

$$\rho^\pm(\mathbf{r}) = \rho_0^\pm \exp[\mp\beta e\varphi(\mathbf{r})] \quad (1)$$

where $\beta = 1/kT$ is the inverse temperature. Equation (1) expresses the condition of chemical equilibrium: the electrochemical potential of the microions—i.e. the sum of the ideal chemical potential and the electrostatic energy—is constant throughout the solution:

$$\tilde{\mu}^\pm(\mathbf{r}) = \mu^\pm(\mathbf{r}) \pm e\varphi(\mathbf{r}) = kT \log(\Lambda^3 \rho^\pm(\mathbf{r})) \pm e\varphi(\mathbf{r}) = kT \log(\rho_0^\pm \Lambda^3) \quad (2)$$

where Λ is an arbitrary length. Equation (1) must be combined with the exact Poisson equation which reads, denoting the charge density of the platelets by $q_P(\mathbf{r})$,

$$\nabla^2\varphi(\mathbf{r}) = -\frac{4\pi}{\varepsilon} [q_P(\mathbf{r}) + e\rho^+(\mathbf{r}) - e\rho^-(\mathbf{r})]. \quad (3)$$

In the following two paragraphs, some simple geometries and boundary conditions allowing an analytic solution of equations (1) and (3) are briefly reviewed (i.e. Gouy–Chapman theory [1] for an infinite charged plane, where the electrostatic problem reduces to a one-dimensional one). General equivalent expressions for the free energy of the double layers will then be obtained before considering the simplifications introduced by the linearization of PB equations. Finite-size effects will be the subject of subsequent sections.

3. A single plane without added electrolyte

When no salt is added, the only microions present in the solution are the counterions: $\rho^- = 0$. The simplest problem to be solved is for an infinite platelet occupying the $z = 0$ plane. The platelet charge density is $q_P(\mathbf{r}) = \sigma \delta(z)$ where δ is the Dirac distribution and the counterions occupy the two half-spaces $z > 0$ and $z < 0$. The electric field vanishes at large z . For $z \neq 0$, one has to solve

$$\nabla^2\varphi = \frac{d^2\varphi}{dz^2} = -\frac{4\pi e}{\varepsilon} \rho_0^+ \exp(-\beta e\varphi). \quad (4)$$

The discontinuity of the electric field for $z = 0$ is related to the surface charge σ , so the boundary conditions are

$$\left. \frac{d\varphi}{dz} \right|_{z=0^+} = -\left. \frac{d\varphi}{dz} \right|_{z=0^-} = -\frac{2\pi\sigma}{\varepsilon}. \quad (5)$$

Two successive integrations yield [4]

$$\varphi(z) = \frac{2kT}{e} \log(|z| + b) + \varphi_0 \quad (6a)$$

$$\rho^+(z) = \rho_0^+ \frac{\exp(-\beta e \varphi_0)}{(|z| + b)^2} = \frac{1}{2\pi \ell_B} \frac{1}{(|z| + b)^2}. \quad (6b)$$

Two fundamental lengths have been introduced: $\ell_B = \beta e^2 / \varepsilon$ is the Bjerrum length which characterizes the strength of electrostatic interactions ($\ell_B \simeq 7.1 \text{ \AA}$ in water), and $b = e / (\pi \ell_B |\sigma|)$ is the Gouy length characterizing the thickness of the electric double layer.

The Helmholtz free energy per unit area reads $F = U - TS$ where

$$U = \frac{1}{2} \int_{-\infty}^{+\infty} (q_P + e\rho^+) \varphi \, dz \quad (7)$$

is the total electrostatic energy per unit area and the entropy S reduces to its ideal part consistent with PB theory:

$$S = -k \int_{-\infty}^{+\infty} \rho^+ [\log(\Lambda^3 \rho^+) - 1] \, dz. \quad (8)$$

Choosing $\rho_0^+ \Lambda^3 = 1$, and denoting by φ_P the surface potential one gets

$$F = \varphi_P \sigma - 2kT \frac{|\sigma|}{e} \quad (9)$$

with

$$\varphi_P = \varphi(z = 0). \quad (10)$$

Alternatively the free energy can be calculated from an isothermal charging process [2], where the surface charge of the membrane is varied from 0 to its final value:

$$F = \int_0^\sigma \varphi_P(\sigma') \, d\sigma'. \quad (11)$$

The reason for this ‘coincidence’ will be discussed below.

4. A periodic succession of parallel planes without added salt

The effects of finite polyion concentration can be analysed by considering a regular succession of infinite parallel planes located at $z = nh$ ($n \in \mathbb{Z}$). Each plane carries a uniform surface charge $\sigma < 0$. The density profiles around a given membrane, e.g. located at $z = 0$, can be obtained by restricting the solution of the PB equation to the Wigner–Seitz (WS) slab extending from $z = -h/2$ to $z = h/2$, with the boundary condition of vanishing electric field for $z = \pm h/2$. Choosing the edge of the slab as the reference potential ($\varphi(z = \pm h/2) = 0$), one obtains after two successive integrations [4]

$$\varphi(z) = \frac{kT}{e} \log \left[\cos^2 \left(\frac{|z| - h/2}{\lambda} \right) \right] < 0 \quad (12a)$$

$$\rho^+(z) = \frac{1}{2\pi \ell_B \lambda^2} \frac{1}{\cos^2((|z| - h/2)/\lambda)} \quad (12b)$$

where the screening length λ is related to the Gouy–Chapman length $b = e / (\pi \ell_B |\sigma|)$ by

$$\tan \left(\frac{h}{2\lambda} \right) = \frac{\lambda}{b}. \quad (13)$$

The free energy per unit area of membrane now reads

$$F = \varphi_P \sigma - \frac{kT|\sigma|}{e} \left[2 - \frac{hb}{2\lambda^2} \right] + kT \frac{|\sigma|}{e} \log(\rho_0^+ \Lambda^3). \quad (14)$$

This expression can be recovered by considering an isothermal charging process, but it does not coincide with the integral of the surface potential $\int_0^\sigma \varphi_P(\sigma') d\sigma'$. When an operator reversibly decreases the surface charge of the membrane from σ' to $\sigma' + \delta\sigma'$, the resulting variation of the free energy is related to the work done by the operator by

$$\delta F = \delta W_{\text{op}}(\sigma' \rightarrow \sigma' + \delta\sigma'). \quad (15)$$

The membrane can be considered as a reservoir of *grafted* cations (σ^+) and anions (σ^-) with the constraint $\sigma^- + \sigma^+ = \sigma$. In order to decrease σ' , the operator has to move $|\delta\sigma'|/e = -\delta\sigma'/e$ cations per unit surface from the membrane to the solution. The electrochemical potential of the grafted cations reduces to the electrostatic energy

$$\tilde{\mu}_P^+ = e \varphi_P \quad (16)$$

whereas in the solution the electrochemical potential is

$$\tilde{\mu}_{\text{sol}}^+ = kT \log(\rho_0^+ \Lambda^3). \quad (17)$$

The reversible work done by the operator in the operation is

$$\delta W_{\text{op}}(\sigma' \rightarrow \sigma' + \delta\sigma') = [\tilde{\mu}_{\text{sol}}^+ - \tilde{\mu}_P^+] \frac{|\delta\sigma'|}{e} \quad (18)$$

and therefore

$$F - F(\sigma = 0) = \int_0^\sigma \left[\varphi_P(\sigma') - \frac{kT}{e} \log(\rho_0^+ \Lambda^3) \right] d\sigma'. \quad (19)$$

Here, the prefactor $\rho_0^+ = 1/(2\pi \ell_B \lambda^2)$ defining the electrochemical potential of the microions in the solution (cf. equation (2)) depends on σ , which was not the case in the previous situation. From this correct expression of the free energy, the equation of state of the double layer can be derived. A little algebra yields

$$P \equiv - \left. \frac{\partial F}{\partial h} \right|_{\sigma, T} = \frac{kT}{2\pi \ell_B \lambda^2}. \quad (20)$$

Mechanical equilibrium in the solution requires

$$\nabla P_{\text{hydrostatic}} = e\rho^+(z) \mathbf{E} = \frac{\varepsilon}{4\pi} \mathbf{E} \operatorname{div} \mathbf{E} \quad (21)$$

and hence

$$P_{\text{hydrostatic}}(z) - \frac{1}{8\pi} \varepsilon E^2(z) = \text{constant} = P. \quad (22)$$

At each point in the solution, the osmotic pressure P has an ideal-gas contribution $P_{\text{hydrostatic}} = \rho^+(z) kT$ and an electrostatic contribution proportional to the square of the electric field. The latter vanishes at the edge of the WS cell ($z = \pm h/2$) where the osmotic pressure reduces to its ideal-gas contribution:

$$P = kT \rho^+(h/2) = \frac{kT}{2\pi \ell_B \lambda^2}. \quad (23)$$

Since $P > 0$, the platelets tend to repel each other: the ideal-gas repulsion exceeds the electrostatic attraction. This could no longer be true if the behaviour of the ions in the solution was nonideal.

5. General derivation of the free energy; finite-size effects

We henceforth consider charged platelets of finite size, e.g. mesoscopic clay particles. The reduction of the initial N -platelet problem to a one-platelet problem is based on the introduction of the WS cell. The difficulty lies in the choice of the boundary conditions to be imposed for the electrostatic potential [5]. For example, if the symmetries of the polyion, of its local environment and of the WS cell match, or if one is dealing with a crystal-like configuration of platelets, it is possible to impose a vanishing normal component of the electric field everywhere on the WS surface (Σ).

From a practical point of view, a direct evaluation of the free energy from $F = U - TS$ proves inconvenient. It is however possible to express the free energy in terms of a general charging process. The total electrostatic energy is

$$U \equiv \frac{1}{2} \int_V [q_P + e(\rho^+ - \rho^-)] \varphi \, d^3r = \int_V \frac{\varepsilon}{8\pi} E^2 \, d^3v - \oint_{\Sigma} \frac{\varepsilon}{8\pi} \varphi \, \nabla\varphi \cdot d\mathbf{S}. \quad (24)$$

On writing $\Phi = \beta e\varphi$, the free energy becomes

$$\begin{aligned} \beta F = & N_+ \log(\rho_0^+ \Lambda^3) + N_- \log(\rho_0^- \Lambda^3) - \frac{1}{8\pi\ell_B} \oint_{\Sigma} \Phi \, \nabla\Phi \cdot d\mathbf{S} \\ & + \int_V \left[(\rho^- - \rho^+) \Phi - (\rho^- + \rho^+) + \frac{1}{8\pi\ell_B} (\nabla\Phi)^2 \right] d^3v. \end{aligned} \quad (25)$$

The prefactors ρ_0^{\pm} are considered as free parameters, which will turn out to be useful for the linear (Debye–Hückel) approximation, but as long as a reference potential has not been specified, they individually have no significance. In a general variation $\Phi \rightarrow \Phi + \delta\Phi$, $\ell_B \rightarrow \ell_B + \delta\ell_B$, representing the elementary step of a generic charging process, one may write

$$\delta(\rho^+ + \rho^-) = \frac{\delta\rho_0^+}{\rho_0^+} \rho^+ + \frac{\delta\rho_0^-}{\rho_0^-} \rho^- + (\rho^- - \rho^+) \delta\Phi. \quad (26)$$

One of the terms appearing in the differential can be transformed into a surface integral over Σ since

$$\Phi \nabla^2(\delta\Phi) + \nabla\Phi \cdot \nabla(\delta\Phi) = \text{div} [\Phi \nabla(\delta\Phi)] \quad (27)$$

and finally, δF can be cast in the form

$$\begin{aligned} \delta(\beta F) = & \frac{1}{8\pi\ell_B} \oint_{\Sigma} [\Phi \nabla(\delta\Phi) - \delta\Phi \nabla\Phi] \cdot d\mathbf{S} + \beta U \frac{\delta\ell_B}{\ell_B} \\ & + \int_P \Phi \delta\left(\frac{\sigma}{e}\right) d^2r + [\log(\rho_0^+ \Lambda^3)] \delta N_+ + [\log(\rho_0^- \Lambda^3)] \delta N_- \end{aligned} \quad (28)$$

which can be interpreted in terms of various virtual or real charging processes. The surface integral represents the work necessary to maintain the boundary conditions (decoupled into ‘constant charge’ + ‘constant potential’ work). The term $U\delta\ell_B/\ell_B$ is associated with a variation of the strength of electrostatic interactions. In the situation where the electric field has no normal component on the WS surface, a charging process where the Bjerrum length varies yields

$$F(\ell_B) - F(\ell_B = 0) = kT \int_0^{\ell_B} \beta U(\ell') \frac{d\ell'}{\ell'} \quad (29)$$

because in this case, $\delta\sigma = 0$ and $\delta N_+ = \delta N_- = 0$. The above formula summarizes various expressions. For example, if the charging process is performed such that at any stage, all ions have a fraction λ of their final charge (cf. [2, 3]), $\delta\ell_B/\ell_B = \delta(e^2)/e^2 = 2\delta\lambda/\lambda$ and

$$F - F(\lambda = 0) = 2 \int_0^1 U(\lambda') \frac{d\lambda'}{\lambda'}. \quad (30)$$

Alternatively, if the integration is performed over the temperature (at constant dielectric permittivity and charges; see [3]),

$$F - F(\beta = 0) = T \int_\infty^T U(T') d\left(\frac{1}{T'}\right) \quad (31)$$

and the thermodynamic identity $\partial(\beta F)/\partial\beta = U$ is recovered.

Finally, the last contribution to $\delta(\beta F)$ can be re-expressed as

$$\begin{aligned} & \int_{\mathcal{P}} \Phi \frac{\delta\sigma}{e} d^2r + [\log(\rho_0^+ \Lambda^3)] \delta N_+ + [\log(\rho_0^- \Lambda^3)] \delta N_- \\ &= \int_{\mathcal{P}} \left\{ \underbrace{[\log(\rho_0^+ \Lambda^3) - \Phi]}_{\beta(\tilde{\mu}_{\text{sol}}^+ - \tilde{\mu}_{\mathcal{P}}^+)} \delta N_+ + \underbrace{[\log(\rho_0^- \Lambda^3) + \Phi]}_{\beta(\tilde{\mu}_{\text{sol}}^- - \tilde{\mu}_{\mathcal{P}}^-)} \delta N_- \right\} \frac{d^2r}{S} \\ &= \int_{\mathcal{P}} \left\{ \log[\rho^+(\mathbf{r}) \Lambda^3] \delta N_+ + \log[\rho^-(\mathbf{r}) \Lambda^3] \delta N_- \right\} \frac{d^2r}{S}. \end{aligned} \quad (32)$$

Indeed, the reversible work done by an operator varying isothermally N_+ by δN_+ and N_- by δN_- , by moving cations and anions from the platelet to the solution (or vice versa), is

$$\delta W_{\text{op}} = \int_{\mathcal{P}} \left\{ (\tilde{\mu}_{\text{sol}}^+ - \tilde{\mu}_{\mathcal{P}}^+) \frac{\delta N_+}{S} + (\tilde{\mu}_{\text{sol}}^- - \tilde{\mu}_{\mathcal{P}}^-) \frac{\delta N_-}{S} \right\} d^2r. \quad (33)$$

In the above operation, the charge migration is performed in such a way that the surface charge of the platelet remain constant.

The general expression (28) accounts for all possible charging processes. Depending on the physical situation under consideration, a given charging process may allow the free energy to be cast in a tractable form. In the next paragraph, we shall see which further simplifications the linearized version of PB theory brings about.

6. Free energy within linearized PB theory

The so-called Debye–Hückel approximation consists in linearizing the potential dependence of the ionic densities ρ^\pm . It is convenient to define the prefactors ρ_0^\pm such that

$$\rho^\pm(\mathbf{r}) = \rho_0^\pm \exp\{\mp\beta e[\varphi(\mathbf{r}) - \varphi^*]\} \quad (34)$$

where φ^* is a reference potential to be specified, and the approximate densities are

$$\rho^\pm(\mathbf{r}) = \rho_0^\pm [1 \mp \beta e(\varphi(\mathbf{r}) - \varphi^*)]. \quad (35)$$

The linearized PB equation now reads

$$\nabla^2\varphi(\mathbf{r}) = -\frac{4\pi}{\varepsilon} q_{\mathcal{P}}(\mathbf{r}) + \kappa_D^2 [\varphi(\mathbf{r}) - \gamma_0] \quad (36)$$

where $\kappa_D^2 = 4\pi\ell_B(\rho_0^+ + \rho_0^-) = 1/\lambda_D^2$ is the squared inverse Debye length, and $\gamma_0 = 4\pi e(\rho_0^+ - \rho_0^-)/(\varepsilon\kappa_D^2) + \varphi^*$. The numbers N_+ and $N_- = N_+ - Z = N_+ + S\sigma/e$ of counterions and coions in the WS cell of volume V are

$$\frac{N_\pm}{V} = \rho_0^\pm \{1 \pm \beta e(\varphi^* - \bar{\varphi})\} \quad (37)$$

where $\bar{\varphi}$ is the mean potential in the WS cell

$$\bar{\varphi} = \frac{1}{V} \int_V \varphi(\mathbf{r}). \quad (38)$$

The relation between the macroscopic quantities N_{\pm} and the Debye length is

$$4\pi\ell_B \frac{N_+ + N_-}{V} = \kappa_D^2 [1 - \beta^2 e^2 (\varphi^* - \bar{\varphi})^2] + 4\pi\ell_B \beta e (\varphi^* - \bar{\varphi}) \frac{Z}{V}. \quad (39)$$

A particularly simple choice is thus to linearize the densities around $\bar{\varphi}$, which implies taking $\bar{\varphi} = \varphi^*$. Under these circumstances

$$\rho_0^{\pm} = \frac{N_{\pm}}{V} \quad \text{and} \quad \kappa_D^2 = 4\pi\ell_B \frac{N_+ + N_-}{V}. \quad (40)$$

The difficulty in the calculation of the free energy (apart from the contribution of the boundary conditions) arises from the term $\int_{\mathcal{P}} \varphi_{\mathcal{P}} \delta\sigma \, d^2r$ in equation (28): the potential φ depends nonlinearly on the Debye length which generally varies with the surface charge σ . Indeed, the solution of equation (36) takes the form

$$\varphi(\mathbf{r}) = \gamma_0 + \frac{4\pi\sigma}{\varepsilon} \int_{\mathcal{P}} G(\mathbf{x} - \mathbf{r}, \kappa_D) \, d^2x \quad (41)$$

where G is the Green's function satisfying

$$(-\nabla^2 + \kappa_D^2)G(\mathbf{r}, \kappa_D) = \delta(\mathbf{r}) \quad (42)$$

with the required boundary conditions on the WS surface. It is however possible to construct an isothermal charging process where κ_D is held constant. The electroneutrality constraint reads $N_+ - N_- = Z$. The constancy of κ_D and hence of $N_+ + N_-$ is then achieved provided

$$\delta N_+ = -\delta N_- = \frac{\delta Z}{2} \quad (43)$$

at each elementary step of the charging process starting at $Z = 0$, $N_+^0 = N_-^0 = N_-^{\text{final}} + Z/2$. The integration along this path gives

$$\int_0^{\sigma} \int_{\mathcal{P}} \varphi_{\mathcal{P}} \, d^2r \, d\sigma = -Ze\gamma_0 + \frac{\sigma}{2} \int_{\mathcal{P}} \varphi_{\mathcal{P}} \, d^2r. \quad (44)$$

7. Application to clay colloid suspensions

The clay particle is modelled by an infinitely thin, rigid disc of radius r_0 carrying Z elementary charges $-e$ assumed to be uniformly distributed over the surface. This is a reasonable representation of the synthetic laponite clay particles [6] which have a typical diameter of 250 Å and a thickness of 10 Å. The positive counterions and negative coions are assumed to be monovalent point ions. The disc is placed at the centre of a Wigner-Seitz cell; the macroscopic concentration $n = N/V$ of clay particles determines the volume $v = 1/n$ of the cell. For a spherical cage, the radius is then unequivocally determined. For a cylindrical cell of radius R and height $2h$, only the product $2\pi R^2 h = v$ is fixed. The aspect ratio R/h is determined by minimizing the free energy as discussed later. A spherical cage corresponds, physically, to the limit of low platelet concentrations where the latter may rotate almost freely, while a cylindrical cage is better adapted to concentrated stacked configurations.

Due to the lack of spherical symmetry of the polyion, the question of the adequate boundary conditions to be imposed at the surface of the WS cell is a delicate one. In the simpler case of a spherical polyion in a WS sphere, the symmetry naturally imposes

that the electric field vanish at the surface of the sphere, on the assumption that the mean distribution of neighbouring polyions is essentially isotropic. In the case of a cylindrical WS cell, the symmetry of which is compatible with a circular polyion, we impose that the normal component of the electric field vanish everywhere on the surface of the cylinder.

For a cylindrical WS cell, one naturally uses cylindrical coordinates. The charge density of the platelet reads

$$q_{\mathcal{P}}(\mathbf{r}) = q_{\mathcal{P}}(r, z) = \sigma \delta(z) \Theta(r_0 - r) \quad (45)$$

where δ and Θ are the Dirac and Heaviside distributions respectively. The potential is expanded in a Bessel–Dini series which is well adapted to the boundary conditions specified below:

$$\varphi(r, z) = \sum_{n=1}^{\infty} A_n(z) J_0\left(y_n \frac{r}{R}\right) \quad (46)$$

where y_n is the n th root of $J_1(y) = -dJ_0(y)/dy = 0$, J_0 and J_1 are the Bessel functions of 0th and 1st order, and R is the radius of the cylinder. If $2h$ is its height, the boundary conditions which we have imposed are

$$\left. \frac{\partial \varphi(r, z)}{\partial r} \right|_{r=R} = 0$$

$$\left. \frac{\partial \varphi(r, z)}{\partial z} \right|_{z=\pm h} = 0.$$

With these conditions, one may assume $\bar{\varphi} = 0$, without loss of generality ($\varphi - \bar{\varphi}$ is independent of $\bar{\varphi}$).

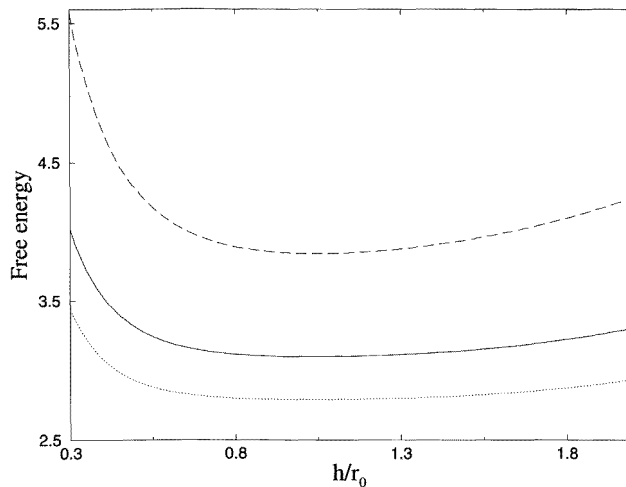


Figure 1. Determination of the ‘optimum’ cylindrical cell. The upper (dashed) and lower (dotted) curve correspond to charging processes where either coion or counterion concentrations are kept constant respectively. The solid line is obtained from the analytic expression (44) (constant- κ_D charging process). The three curves give the same minimum $h/r_0 \simeq 1.01$. The clay concentration is $n = 5 \times 10^{-5}$ M and the salt concentration is 10^{-4} M. The platelets carry $Z = 200$ elementary charges, $\epsilon_{CGS} = 78$ corresponding to water, and $T = 300$ K.

An analytical solution of equation (36) can be obtained [5]. The resulting density profiles are sensitive to the aspect ratio h/R for a given cell volume $2\pi R^2 h$. The ‘optimum’ aspect

ratio is determined by minimizing the free energy with respect to this ratio. In any charging process, the only aspect-ratio-dependent contribution to the free energy is

$$\int_0^\sigma d\sigma' \int_{\text{disc}} \varphi_{\sigma'}(r, z = 0) d^2r$$

which can be calculated analytically using the constant κ_D charging process described in section 6, or by numerical integration along simple paths. Examples are shown in figure 1: the three curves correspond to charging processes where coion concentration, counterion concentration or Debye screening length (analytical calculation) are kept constant. They all give the same minimum $h/r_0 \simeq 1.01$, which satisfies the physical requirement $R/r_0 > 1$. We may conclude that for finite clay platelets the swelling process leads to a well-defined value of the inter-lamellar spacing $2h$, under the action of electrostatic forces alone.

8. Perspectives

The expressions for the free energy given throughout this paper are valid within the mean-field (or Poisson–Boltzmann) approximation. The derivation of explicit, analytical expressions in the case of finite-size platelets requires moreover a linearization of PB theory, while estimates for the nonlinear theory require some numerical work. Correlation effects between microscopic ions, due to their hard core and Coulomb interactions, may be accounted for by including appropriate terms in the initial free-energy functional (for a recent application to charge-stabilized colloidal suspensions, see e.g. [7]).

Another crucial extension, which is currently being considered, is to include a more realistic description of the solvent than is afforded by the ‘primitive’ model. This may be achieved within the density functional formalism by modelling the solvent, e.g., by dipolar hard spheres, as is routinely done for bulk ionic solutions (see e.g. [8]), and by including the corresponding electrostatic and correlation terms in the free-energy functional. The latter must now be minimized with respect to the local densities of the ions, taken to be charged hard spheres, and of the dipolar hard-sphere solvent. Work along these lines is in progress.

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