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# Calculating Total Electrostatic Energies with the Nonlinear Poisson-Boltzmann Equation

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The Poisson-Boltzmann (PB) equation is enjoying a resurgence in popularity and usefulness in biophysics and biochemistry due to numerical advances which allow the equation to be rapidly solved for arbitrary geometries and nonuniform dielectrics. The great simplification of PB models is to use the mean electrostatic potential to give an estimate of the potential of mean force (PMF) governing the distribution of the mobile ions in the solvent. This approximation enables both the mean potential and mean ion distribution to be obtained directly from solutions to the PB equation without performing complex statistical mechanical integrations. The nonlinear form of the PB equation has greater accuracy and range of validity than the linear form, but the approximation of the PMF by the mean potential creates theoretical difficulties in defining the total electrostatic energy for the former. In this paper we use the calculus of variations to provide a unique definition of the total energy and to obtain expressions for the total electrostatic free energy for various forms of the PB equation. These expressions involve energy density integrals over the volume of the system. Various equivalent expressions for the total energy are given and the physical meaning of the different terms that appear is discussed. Numerical calculations are carried out to demonstrate the feasibility of our approach and to assess the magnitude of the various terms that arise in the theory. Both the more familiar charging integral and the energy density integral methods can be applied to the PB equation with equal accuracy, but the latter is much more efficient computationally. The energy density integral involves the integral of the excess osmotic pressure of the ion atmosphere. The various forms of the PB equation which have been most widely discussed to date because of the availability of analytical solutions are shown to be special cases where the osmotic term is absent.

## Introduction

The Poisson-Boltzmann (PB) equation has long been used for modeling the electrostatic properties of membranes, colloids, polyelectrolytes and macromolecules. Analytical and series solutions to this equation are only possible for highly symmetric cases. Thus early studies used spherically symmetric solutions to model globular proteins and ions, cylindrical symmetries for polyelectrolytes and rodlike molecules, and planar symmetry for membranes and large colloid particles. Although more detailed and computationally more expensive models based on explicit atom treatments using Monte Carlo, molecular dynamics, and integral equation methods are now available, models based on the PB equation continue to be useful due to their simplicity and relatively modest computational requirements. In fact, these models are enjoying a resurgence in popularity and usefulness in biophysics and biochemistry, as testified in several recent reviews.<sup>1-3</sup> This is due to numerical advances which allow the Poisson-Boltzmann equation to be solved for arbitrary geometries and nonuniform dielectrics<sup>4-7</sup> enabling the calculations to include the detailed structural information available from X-ray diffraction studies on macromolecules. Poisson-Boltzmann methods have proven to be an efficient and accurate way to model the effects of water and ion screening on the potentials in and around soluble proteins, nucleic acids, membranes, and even small polar molecules and ions.

The PB equation is most commonly applied in its linearized form, as in the familiar Debye-Hückel theory. However, there are many cases where the linear approximation is not valid and the nonlinear form must be used. Unfortunately, there are difficulties in defining the total electrostatic energy for the nonlinear PB equation. Indeed in some cases it has been argued that there is no unique way of defining the energy. If correct, this would pose severe problems in any attempt to use the nonlinear PB equation. In this paper we use the calculus of variations to demonstrate that there is a unique definition of the total energy when the nonlinear PB equation is applied to macromolecules or colloids. Various expressions for the total energy are derived and the physical meaning of the different terms that appear is discussed. Due to the increasing use of numerical and series solutions of the nonlinear PB equation in studying protein and nucleic acid electrostatics, numerical as well as theoretical issues arise when calculating energies. In the second part of this paper numerical

calculations are carried out to demonstrate the feasibility of our approach and to assess the magnitude of the various terms that arise in the theory. In the remainder of the Introduction, previous work on the nonlinear PB equation, and the difficulties associated with its use, are summarized.

Debye and Hückel<sup>8</sup> first used the linearized PB equation, which is valid when the potentials are small compared to thermal energy (in this case for low charge densities, or dilute solutions), in developing a theory of ion activities. They took a single ion as a reference point and treated the other ions in an average way as forming the ion atmosphere around this central ion. Attempts to extend the range of validity of the theory by using the nonlinear PB (NLBP) equation were criticized by Fowler<sup>9</sup> and Onsager<sup>10</sup> who pointed out an inconsistency in the use of the equation. The difficulty is in determining the mean distribution of charge around the central ion. From statistical mechanics, the relative probability,  $g_{ij}(r)$ , of finding an ion  $j$  at a distance  $r$  from a second (reference) ion  $i$ , is given by  $g_{ij}(r) = \exp(-\beta\zeta_{ij}(r))$ , where  $\zeta_{ij}$  is the potential of mean force (PMF) between the two ions; i.e., the mobile ions are described by a Boltzmann distribution. In a full statistical mechanical treatment,  $\zeta_{ij}$  would be obtained from the mean energy of interaction between the two ions averaged over all the other degrees of freedom (i.e., other ion positions) of the system.<sup>11</sup> Such a system has three general properties.<sup>10,12</sup> (i) Reciprocity.  $\zeta_{ij}$  is the same whether ion  $i$  or  $j$  is taken as the reference point. (ii) Superposition. The PMF acting on an ion in the presence of a pair of ions is the sum of those arising from each of the ions alone. (iii) Nonadditivity. The mean distribution of charge in the neighborhood of two ions is not the sum of the distributions induced by each ion alone. The first two conditions ensure that

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the free energy of the system is a complete differential, or integrable, and is thus well defined. The third property means that, in general, the PMF is not a linear function of the mean ion distributions.

The great simplification of Debye-Huckel theory, and of models based on the PB equation as a whole, is to use the mean electrostatic potential to give an estimate of the PMF. The advantage of this approximation is that the mean potential is obtained directly from the mean ion distribution via Poisson's equation, obviating the complex statistical mechanical integration. The mean potential and ion distributions are thus obtained from a simultaneous solution to both the Boltzmann and Poisson equations. However, the mean electrostatic potential is inherently a linear function of the mean ion distributions because of the linear form of the Poisson equation, in contrast to point (iii) above. Thus the model can never be exact unless applied to a case where additivity holds, as in the linearized Debye-Huckel theory for dilute electrolytes.

A further consequence of using the mean electrostatic potential to estimate the PMF is that reciprocity and integrability is not satisfied. A different value for the free energy of the system will be obtained if all ion species are charged up simultaneously (the Debye process), or one at a time (the Guntelberg process). The inconsistency in the application of the NLBP equation to ionic solutions has been widely discussed,<sup>9,11-13</sup> although actual values for the discrepancy between energies provided by the Guntelberg and Debye charging process appear to be unavailable in the literature. There has consequently been some tendency to avoid the use of the nonlinear PB equation, and even to assume that the linear form is inherently preferable, even when the linearization approximation is not valid. The use of the nonuniform PB equation thus raises two questions. Firstly, how good is the approximation of the PMF by the mean electrostatic potential? Secondly, if the equation is to be used, can the electrostatic free energy of the system be defined uniquely and its value accurately determined? In the remainder of the introduction we consider evidence indicating that the answer to the first question is that the approximation is surprisingly good. The answer to the second question forms the subject of this paper.

In discussing the application of the nonlinear PB equation to ionic solution theory Kirkwood<sup>14</sup> and Onsager<sup>10</sup> themselves, using statistical mechanical arguments, came to the conclusion that for small symmetric electrolytes the lack of reciprocity in the PB equation is not large and that the discrepancy in the Debye and Guntelberg charging energies should be small. However, most applications of the equation have been to biophysical and colloid chemistry, rather than in ionic solution theory. (The term colloid will be used here rather generally to refer to any charged membrane, vesicle, polyelectrolyte, protein, nucleic acid, or more traditional colloid particle.) In this case there is less of a problem with the PMF approximation, due to the strong central field of the colloid,<sup>15</sup> and since the element of reciprocity between colloid and ions is lacking.<sup>16</sup> In applications to ionic solutions, each ion can be considered as part of the ion atmosphere of every other ion, and hence the choice of a particular ion as the fixed central reference ion introduces an artificial asymmetry. In contrast, a colloid, as the larger body, naturally forms a point of reference, and it would not usually be considered to form part of the ionic atmosphere of say a sodium ion. Thus only the Debye-Huckel interaction between the mobile ions is neglected, which generally will be a small correction.<sup>17</sup> The difference between the ionic solution and colloid applications of the PB equation is further emphasized in the different conditions under which the linearization approximation is valid: for the former it is at low ionic strength, while for the latter it is for weakly charged colloids, and/or at high ionic strengths.

Further evidence of the reliability of the nonlinear equation for certain cases comes from two areas. The first is from direct comparisons with statistical mechanical integrations using Monte Carlo or integral equation methods.<sup>18-21</sup> These studies show that for small 1:1 electrolytes the PB equation provides a remarkably good approximation to the mean ion distribution around a charged cylinder, underestimating the ion concentrations close to the cylinder by about 10-15%. However, the error in the PB equation for multivalent ions, and for calculating other quantities such as osmotic pressures, can be quite large,<sup>20,21</sup> while it is to be expected that the linear form of the equation would be even worse. The second is from the agreement between theoretical calculations of surface potentials for erythrocytes and vesicles with experimental measurements.<sup>2,22</sup>

Thus work to date shows firstly that the error due to the inconsistency of the nonlinear equation for 1-1 salt is likely to be small, and more importantly that it fits the data much better than the linear form, indicating that the greater accuracy and range of applicability of the former is generally preferable to the mere consistency of the latter.

Solutions to the PB equation have been studied for three forms of the equation: (i) the linearized form including added salt (LPB); (ii) the nonlinear form including added salt (NLPB); (iii) the nonlinear form in the absence of added salt. In the latter the solution contains only the counterions sufficient to balance the molecular charges. Electroneutrality is assumed to hold over some volume of solution containing the colloid and its counterions, and this model is referred to here as the cell model (CPB). Cases for which analytical solutions are available, even for the LPB equation, are extremely limited. The planar form of the NLBP equation (the Gouy-Chapman model), which is the only geometry admitting of an analytical solution, was applied early in surface chemistry.<sup>23,24</sup> The CPB equation which can only be solved analytically for cylindrical symmetry<sup>25</sup> has been applied primarily to polyelectrolytes, particularly DNA. More recently, series solutions to the NLPB equation for cylindrical symmetries have been applied to DNA.<sup>26-28</sup> In recent years a variety of numerical methods have also been developed.<sup>5,29</sup> The focus of these and related studies<sup>26,30-32</sup> has primarily been on the potential distribution at the colloid surface and on the counterion distribution, which are obtained directly from the solution to the PB equation. The electrostatic free energy of the system has to be obtained from the potential and ion distribution by a further calculation. Analysis of this problem is more difficult when using the nonlinear equation, even leaving aside the issue of consistency mentioned above, since there are no analytical solutions for the energy. The single exception is for the planar NLPB case.<sup>16</sup>

Verwey and Overbeek<sup>16</sup> discussed two ways of calculating the total free energy of the system: (i) the colloid is charged up in an isothermal process, the ionic atmosphere being in equilibrium at all stages; (ii) the energetic cost of assembling the ionic atmosphere around the already charged colloid is computed. An expression for the second process for the NLBP equation was first derived by Levine.<sup>33</sup> The equivalence of the two charging pro-

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cesses was shown by Casimir<sup>17</sup> and Verwey and Overbeek<sup>16</sup> (and more recently by Oosawa for the CPB model<sup>34</sup>). With few exceptions<sup>32</sup> studies with the nonlinear PB equation have used the first method for calculating energies. The second method is not widely used, probably because the thermodynamic arguments used to derive expressions for the energy of assembling the ionic atmosphere are rather complex, and most of the work in this area appears in the earlier colloid literature and does not seem to be generally known outside of this context. As will be shown in this paper, it is possible to derive equivalent expressions for any form of the PB equation in a simpler fashion by using the method of variational calculus.

### Theory

**Electrostatic Free Energy of the PB Equation.** The PB equation is based on the fundamental equation of electrostatics, the Poisson equation

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \varphi(\mathbf{r}) + 4\pi \rho(\mathbf{r}) = 0 \quad (1)$$

where  $\varphi$  is the potential,  $\rho$  is the charge density,  $\epsilon$  is the dielectric constant, and  $\mathbf{r}$  is the position vector. This equation is also valid when the potential and charge density are mean values given by some statistical mechanical calculation<sup>11</sup>

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \langle \varphi(\mathbf{r}) \rangle = -4\pi \langle \rho(\mathbf{r}) \rangle \quad (2)$$

where the brackets  $\langle \rangle$  denote a mean value. When mobile ions are present, the charge density can be written as  $\rho = \rho^m + \rho^f$ , where the superscripts m and f refer to the mobile and fixed charge components. In this context what is meant by mobile is that the distribution of these charges is affected by thermal motion: i.e., they are subject to some kind of thermodynamic averaging, and their mean position is one of the variables to be determined, along with the potential. In contrast, the term fixed indicates that the charges are not subject to this averaging; i.e., their positions are assumed to be known exactly, or at least form one of the inputs to the calculation. In fact there is no hard and fast rule to determine which charges are to be treated as fixed and which as mobile, but this will depend on what system is being modeled. In biophysical applications the source of the fixed charges are usually proteins, nucleic acids, and other macromolecules, or membranes, vesicles, and other charged particles. In addition, it is assumed that the amount of fixed charge is constant; i.e., we consider the case of constant surface charge, as opposed to constant surface potential.<sup>16</sup> In general, this will apply to colloids at a pH far from the  $pK_a$  of any ionizable surface groups. The reference state of zero energy is taken to be the totally discharged colloid, i.e., with all fixed charge dispersed to infinity, and the energy required is the charging energy, or the total electrostatic free energy.

To determine the distribution of mobile ions we require at equilibrium that the chemical potential of each ion specie  $\mu_i$  is uniform throughout the solution

$$\mu_i(\mathbf{r}) = \mu_i^\circ + kT \ln a_i(\mathbf{r}) + z_i e \varphi(\mathbf{r}) = \mu_i^\circ + kT \ln a_i^b \quad (3)$$

where  $\mu_i^\circ$  is the standard-state chemical potential,  $e$  is the proton charge,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $z_i$  is the valence of the ion,  $a_i$  is the activity, and  $a_i^b$  is the activity of the ion in the bulk solution, i.e., far from the colloid where the potential is zero. It is usually assumed that the activity coefficient is unity and independent of potential and concentration; thus  $a_i = c_i$ , the concentration. This assumption is equivalent to the neglect of the mutual Debye-Hückel interaction between the ionic atmosphere ions alluded to above.<sup>16,17</sup> Equation 3 is more familiarly written in the form of the Boltzmann expression (using mean quantities) as

$$\langle c_i(\mathbf{r}) \rangle / c_i^b = \exp(-z_i e \langle \varphi(\mathbf{r}) \rangle / kT) \quad (4)$$

where the exponent is an estimate of the potential of mean force between the ion and the colloid. We consider here only a 1-1 salt,

for which the PB equation is most applicable. For this case this leads to the NLPB equation (in terms of the dimensionless potential  $\phi = e\varphi/kT$ , where  $k$  is the Boltzmann's constant,  $T$  is the absolute temperature, and  $e$  is the proton charge) of the form

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) + f(\phi) = 0 \quad (5)$$

where

$$f(\phi) = -\epsilon \kappa^2 \sinh(\phi(\mathbf{r})) + 4\pi e \rho^f(\mathbf{r}) / kT \quad (6)$$

and  $\kappa^2 = 1/\lambda^2 = 8\pi e^2 I / \epsilon kT$ , where  $\lambda$  is the Debye length, and  $I$  is the ionic strength of the bulk solution. Analytical or numerical solutions of this equation yield the potential distribution throughout space. From this we require the total electrostatic energy of the system. Consider now some as yet undetermined function of the position, the potential and the partial differentials of potential with respect to the three spatial variables,  $\phi, \phi_x, \phi_y, \phi_z$ , designated  $F(x, y, z, \phi, \phi_x, \phi_y, \phi_z)$ . Equation 5 can be written in terms of  $F$  as

$$\partial F / \partial \phi - (\partial(\partial F / \partial \phi_x) / \partial x + \partial(\partial F / \partial \phi_y) / \partial y + \partial(\partial F / \partial \phi_z) / \partial z) = 0 \quad (7)$$

where

$$f(\phi) = \partial F / \partial \phi \quad (8)$$

and

$$-\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) = \partial(\partial F / \partial \phi_x) / \partial x + \partial(\partial F / \partial \phi_y) / \partial y + \partial(\partial F / \partial \phi_z) / \partial z \quad (9)$$

Equation 7 is a form of the Euler-Lagrange equation. A theorem from the calculus of variations<sup>35</sup> states that, for any differential equation that can be put in this form,  $F$  is the unique function whose integral over the independent variables  $x, y$ , and  $z$  is minimized by the solution to the differential equation. Since the condition for equilibrium is that the free energy of the system be at a minimum, we identify the integral

$$\Delta G^{\text{el}} = \int F(x, y, z, \phi, \phi_x, \phi_y, \phi_z) dv \quad (10)$$

as the total electrostatic free energy for the system described by the PB equation. For the NLPB equation it is straightforward to show that

$$F = 4\pi \rho^f \phi - \epsilon \kappa^2 \cosh(\phi) - \epsilon (\nabla \phi)^2 / 2 \quad (11)$$

Inspection of eq 7 shows that, in fact, any function  $C_1 F + C_0$  is also a solution, where the choice of constants  $C_1$  and  $C_0$  determines the units and zero point of the energy scale, respectively. To conform to the usual electrostatic convention we put  $C_1 = 1/4\pi$ . The constant  $C_0$  is determined from the requirement that  $\Delta G^{\text{el}} = 0$  when  $\phi$  is everywhere zero. For eq 5 this occurs when  $\rho^f = 0$ , and hence  $C_0 = \epsilon \kappa^2 / 4\pi$ . Substituting back for  $\kappa$  this yields

$$\Delta G^{\text{el}} = \int (\rho^f \phi - kT c^b [2 \cosh(\phi) - 2] - \mathbf{E} \cdot \mathbf{D} / 2) dv \quad (12)$$

where the integral is over all space,  $\Delta G$  is in units of  $kT$ ,  $\mathbf{D} = \epsilon \mathbf{E} / 4\pi$  is the electric displacement, and  $c^b$  is the bulk salt concentration. From eq 4 the term  $c^b(2 \cosh(\phi) - 2)$  is the excess concentration of ions at any point in solution compared to bulk, and hence we may write eq 12 as

$$\Delta G^{\text{el}} = \int (\rho^f \phi - \Delta \Pi - \mathbf{E} \cdot \mathbf{D} / 2) dv \quad (13)$$

where  $\Delta \Pi$  is the excess osmotic pressure of the mobile ion cloud and  $\mathbf{E} \cdot \mathbf{D} / 2$  is the electrostatic stress. The term  $\int \rho^f \phi dv$  is more familiarly written as either a surface integral, or a summation,  $\sum q_j \phi_j$ , depending on whether the fixed charge is represented as a smeared surface charge or as a collection of point charges  $q_j$ .

**The Linear PB Equation.** When  $\phi \ll 1$ , the exponential term in eq 4 may be expanded and truncated at the linear term giving for the LPB equation

$$f(\phi) = -\epsilon \kappa^2 \phi(\mathbf{r}) + 4\pi e \rho^f(\mathbf{r}) / kT \quad (14)$$

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$$F = 4\pi\rho^f\phi - \epsilon\kappa^2\phi^2/2 - \epsilon(\nabla\phi)^2/2 \quad (15)$$

Since for the linear case  $\rho^m = -\epsilon\kappa^2\phi/4\pi$ , this gives

$$\Delta G_2^{\text{el}} = \int (\rho^f\phi + \rho^m\phi/2 - \mathbf{E}\cdot\mathbf{D}/2) dv \quad (16)$$

**The Cell Model.** When there is no added salt in the solution, the only mobile ions present are those counterions necessary to neutralize the fixed charges. In this model, the system is not in equilibrium with a bulk solution of a given ionic strength. Instead it is assumed that all charges are confined to some volume,  $V$ , or cell of space which overall is electrically neutral. This model may represent some concentration  $1/V$  of polyelectrolyte in water for example. The equivalent of this model is frequently assumed in molecular simulations on biopolymers where enough mobile ions are included in the simulation system to just balance the net charge of the polyelectrolyte. For the cell model (choosing a positive colloid for concreteness)

$$f(\phi) = -4\pi e^2 c^r \exp(\phi(r))/kT + 4\pi e \rho^f(r)/kT \quad (17)$$

$$F = 4\pi\rho^f\phi - 4\pi e c^r \exp(\phi(r)) - \epsilon(\nabla\phi)^2/2 \quad (18)$$

where  $c^r$  is some reference counterion concentration, defined at the point where  $\phi = 0$ . The second term of eq 18 is the mobile ion charge density, and  $\int \rho^m dv = -q$ , the total counterion charge, which is independent of  $\phi$  or  $V$ . In the limiting case of  $V \rightarrow 0$ , the fixed and neutral charges coalesce, yielding  $\phi(r) = 0$ , so for  $\Delta G^{\text{el}} = 0$  we must have  $C_0 = q$ , giving

$$\Delta G_3^{\text{el}} = \int (\rho^f\phi - \mathbf{E}\cdot\mathbf{D}/2) dv \quad (19)$$

for the CPB equation, where now the integral is over the volume  $V$ .

Equations 12, 16, and 19, referred to here as energy density integrals, express the electrostatic free energy for each of the three forms of the PB equation. In each case the function  $F$  provides a unique expression for the energy. This formulation says nothing about the order of charging or assembling the components of the system; however, any such process is valid only to the extent that it provides the same energy as given by the appropriate energy density integral expression.

**Alternate Forms for the Energy.** We now consider various equivalent expressions for the energy density integrals, with the aid of two electrostatic identities. The first is

$$\int \mathbf{E}\cdot\mathbf{D}/2 dv = \int \rho\phi/2 dv \quad (20)$$

which is an expression of Gauss's law. Second, from the expression for the chemical potential of an ion (i.e., eq 3) we can express the entropy change of the ion atmosphere, with respect to the bulk solution, due to the counterions ( $-$ ) and co-ions ( $+$ ) as

$$T \int \Delta S dv = kT \int (c_+ \ln(c_+/c_+^b) + c_- \ln(c_-/c_-^b)) dv \quad (21)$$

which from eq 4 gives

$$T \int \Delta S dv = - \int \rho^m\phi dv \quad (22)$$

This identity is to be expected since in the type of charging process where the work is done charging the colloid, the ion atmosphere remains in thermal equilibrium. No net work is done in assembling the ion atmosphere in this process, so the gain in electrostatic energy of the mobile ions,  $\rho^m\phi$ , is balanced by the decrease in entropy of organizing them.

Taking the expression for the NLPB equation first, we may write eq 13, using eqs 20 and 22, as

$$\Delta G_1^{\text{el}} = \int (\mathbf{E}\cdot\mathbf{D}/2 - \rho^m\phi - \Delta\Pi) dv = \int (\mathbf{E}\cdot\mathbf{D}/2 + T\Delta S - \Delta\Pi) dv \quad (23)$$

which involves only integrals over the volume of the ion atmosphere. Alternatively the terms involving the field may be eliminated to give

$$\Delta G_1^{\text{el}} = \int (\rho^f\phi/2 + \rho^m\phi/2 + T\Delta S - \Delta\Pi) dv = \int (\rho^f\phi/2 - \rho^m\phi/2 - \Delta\Pi) dv \quad (24)$$

We may also split the potential up into contributions from the fixed charges,  $\phi^f$ , and the mobile charges,  $\phi^m$ , to give

$$\Delta G_1^{\text{el}} = \int (\rho^f\phi^f/2 + \rho^f\phi^m + \rho^m\phi^m/2 + T\Delta S - \Delta\Pi) dv \quad (25)$$

The only form of the NLPB equation that can be solved analytically is the planar case. The potential as a function of the distance normal to the plane,  $z$ , is given by<sup>16</sup>

$$\partial\phi/\partial z = -\kappa(2 \cosh \phi - 2)^{1/2} \quad (26)$$

from which it follows that

$$\mathbf{E}\cdot\mathbf{D}/2 = \Delta\Pi \quad (27)$$

The planar case is unique in that the electrostatic stress and excess osmotic pressure terms are equal. This gives a particularly simple form for the energy (from eq 23) as the electrostatic work of assembling the mobile ions:

$$\Delta G_1^{\text{el}} = - \int \rho^m\phi dv \quad (28)$$

Turning now to the linear case, substituting identity 20 into eq 16 yields

$$\Delta G_2^{\text{el}} = \int (\rho^f\phi/2) dv = \sum q_j\phi_j/2 \quad (29)$$

The expressions for the energy given above all involve integrals over space. It is also possible to obtain the energy from the usual charging integral

$$\Delta G^{\text{el}} = \int \phi_f \delta\rho^f \quad (30)$$

where  $\phi_f$  is the potential at the fixed charge, and eq 30 implicitly involves a summation or integration over all the fixed charges. This equation applies to all three forms of the PB equation.

## Numerical Methods

Since in most cases analytical or even series expressions for the integral of  $F$  will not be available, the best expression to use when calculating the energy will be governed by numerical criteria. Tests were carried out using the finite difference method. The three-dimensional version of this method is now widely used since it provides the simplest and most effective way of solving the NLPB equation for an arbitrarily shaped charged molecule, particle, etc. and for accounting for the different polarizabilities of the solvent and the molecule. The DELPHI program which implements a general three-dimensional finite-difference (TFD) solution to the NLPB equation, as described by Gilson et al.<sup>7</sup> and Jayaram et al.,<sup>29</sup> was used to obtain the potentials for a charged sphere or infinite cylinder of 3 Å radius at the Debye length of 4 Å. A  $65 \times 65 \times 65$  cubic lattice was used, of which the sphere filled approximately 35% of the linear dimension. Potentials on the edge of the lattice were approximated by using the Debye-Huckel expressions.<sup>6</sup> The cylinder was represented at the same scale, with periodic boundary conditions being applied on the lattice edges perpendicular to the axis to generate an infinite length cylinder.

The largest source of error in the finite difference method arises from the limited resolution of the lattice and the consequent error in representing the boundary of the object.<sup>7</sup> To determine this error, a one-dimensional finite difference procedure (OFD) was implemented in either spherical or cylindrical space as appropriate. In this case the sphere and cylinder boundaries are represented with no error, and the potential solutions should be essentially exact. For the spherical case the NLPB equation is

$$1/r^2 d(r^2\phi')/dr = \kappa^2 \sinh(\phi) \quad (31)$$

where the prime indicates differentiation with respect to distance. It is convenient to work in reciprocal dimensionless space,  $z = 1/(r\kappa)$ , giving

$$\phi'' = \sinh(\phi)/z^4 \quad (32)$$

similarly for the cylindrical case the NLPB equation

$$1/r \, d(r\phi')/dr = \kappa^2 \sinh(\phi) \quad (33)$$

becomes

$$\phi' + z\phi'' = \sinh(\phi)/z^3 \quad (34)$$

where now the differentiation is with respect to  $z$ . The  $\sinh$  function is first expanded in a power series. Then applying the central and symmetric finite difference operators to  $\phi''$  and  $\phi'$ , respectively, the iterative finite difference equations are

$$\phi_0^* = \frac{(\phi_+ + \phi_-)}{\left(2 + \frac{h^2}{z_0^4} \left\{1 + \frac{\phi_0^2}{3!} + \frac{\phi_0^4}{5!} + \dots\right\}\right)} \quad (35)$$

for the sphere, and

$$\phi_0^* = \frac{(\phi_+ \left(2 + \frac{h}{z_0}\right) + \phi_- \left(2 - \frac{h}{z_0}\right))}{\left(4 + \frac{2h^2}{z_0^4} \left\{1 + \frac{\phi_0^2}{3!} + \frac{\phi_0^4}{5!} + \dots\right\}\right)} \quad (36)$$

for the cylinder, where  $h$  is the mesh spacing in reciprocal space, and  $\phi_0$ ,  $\phi_-$ , and  $\phi_+$  are the previous iteration's estimate of potential at the mesh point and its two neighbors, respectively,  $\phi_0^*$  is the new estimate of the potential, and  $z_0$  is the reciprocal dimensionless radius at the mesh point. The boundary conditions are  $\phi = 0$  at  $z = 0$ , and  $\phi' = 4\pi\sigma/\epsilon$  at  $z = 1/\kappa a$ , where  $\epsilon = 78.6$ ,  $\sigma$  is the surface charge density, and  $a$  is the radius. Enough terms are kept in the denominator power series to keep the truncation error below 0.1%. Using 2000 mesh points, the potentials are initially set to zero and then iterated until the maximum change in potential in any mesh point is less than  $10^{-4} kT/e$ . As an additional check, several calculations were compared with published tables of potentials obtained from an iterative predictor corrector method for spheres<sup>36</sup> and Runge-Kutta solutions for cylinders.<sup>27</sup> Results in all cases agreed to within numerical error (<0.5%).

Energies for the charging process using OFD and TFD solutions are calculated using eq 30 by increasing the fixed charge in increments of 1% from zero to the full value, obtaining the potential on the surface of the sphere or cylinder,  $\phi(a)$ , and integrating using Simpson's rule. The energy density integrals of eq 23 are obtained by summing the appropriate quantities over all the finite difference mesh points after multiplying by the volume element associated with each mesh point.

Potentials for the cylindrical form of the CPB equation, with a cylinder radius,  $a = 3 \text{ \AA}$ , a cell radius,  $R = 40 \text{ \AA}$ , and a linear charge density,  $s$ , were calculated from the analytical solution of Fuoss et al.<sup>25</sup>

$$\phi = -\ln \{\kappa^2 r^2 \sinh^2(\beta \ln \{Ar\})/2\beta^2\} \quad (37)$$

where

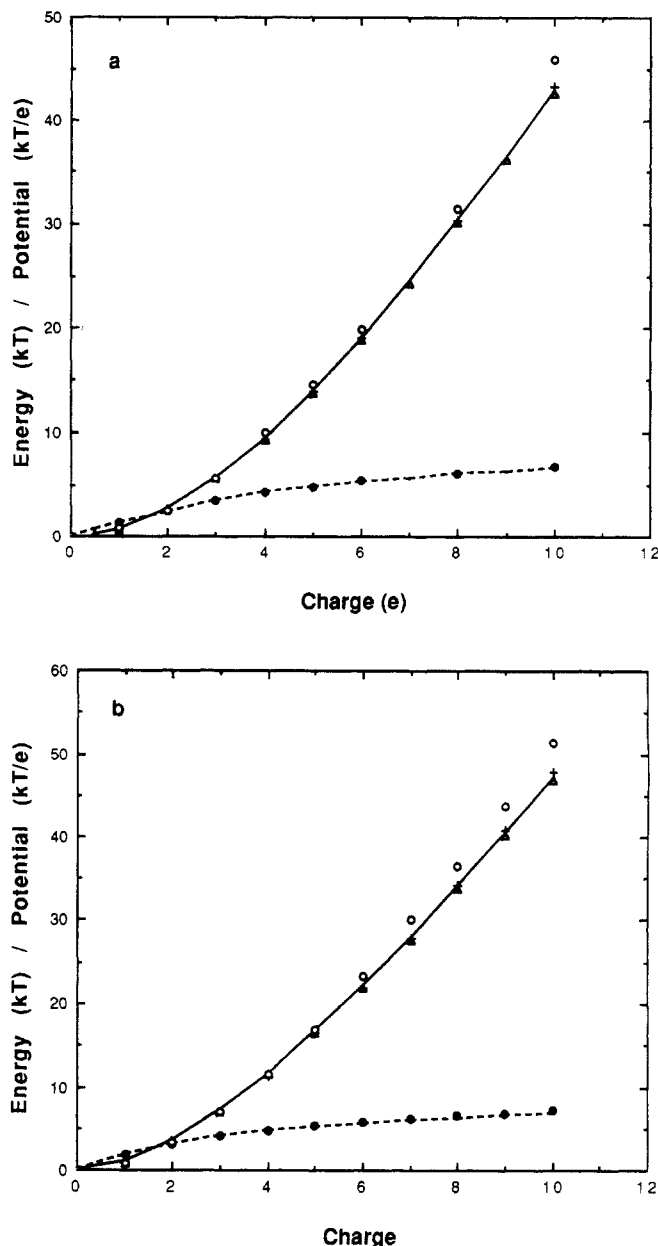
$$s = (1 - \beta^2)/(1 + \beta \coth \{\beta \ln(R/a)\}) \quad (38)$$

$$\ln(Ar) = \ln \{(1 - \beta)/(1 + \beta)\}/2\beta \quad (39)$$

The expression  $\kappa^2 = 2(1 - \beta^2)/R^2$  defines the "Debye", or decay length, for this case. Charging integrals were performed on  $\phi(a)$  obtained from eq 37, and energy density integrals on eq 16 by using Simpson's rule as above.

## Results

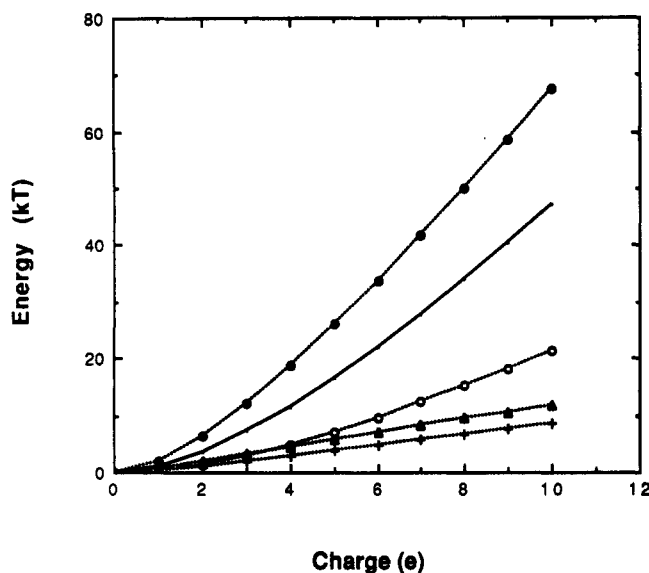
A comparison of the accuracies of the three volume integrations,  $E \cdot D/2$ ,  $\rho^m \phi$ , and  $\Delta \Pi$  for the sphere using the TFD method shows that it consistently overestimates the values compared to the OFD



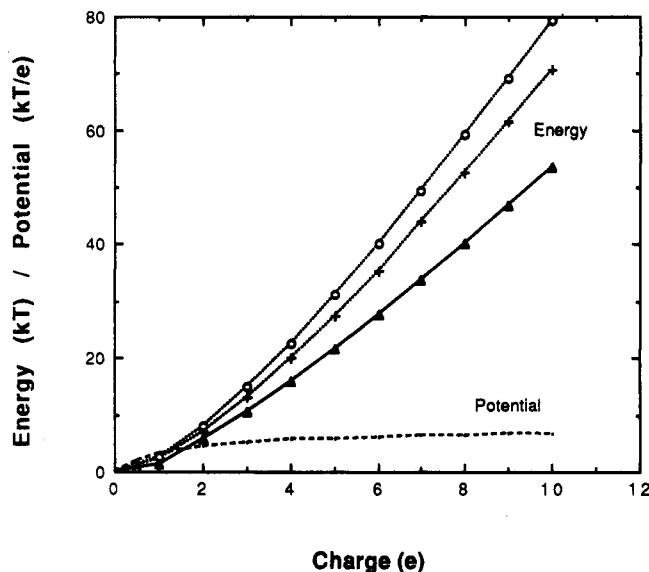
**Figure 1.** Total electrostatic free energy for the NLPB equation applied to a charged sphere (a) or cylinder (b) of radius 3 Å and with a Debye length of 4 Å. For the cylinder, the charge and energy are given per 6 Å length. "Exact" surface potential calculated by using the one-dimensional finite difference (OFD) method (---). Potential calculated from the three-dimensional finite difference (TFD) method (●). Energy density integral from OFD method (—), and TFD method (○). Charging energy integral from OFD method (Δ), and TFD method (+).

procedure by about 4%, 6%, and 3%, respectively, due no doubt to the uncertainty in defining the exact surface of the sphere on the cubic lattice. Figure 1a shows the surface potential and energies obtained from the one- and three-dimensional finite difference procedures applied to the NLPB equation for the sphere. Surface potentials are also slightly overestimated but generally agree well. Energies obtained from both the charging integral, eq 30, and the energy density integral, eq 23, are also shown. The energy density integral from the TFD method has a somewhat larger error than the corresponding charging integral, ranging from 3% to 5%, reflecting the larger error associated with the volume integrals, but overall the methods agree well. Similar results are obtained for the cylinder (Figure 1b). When an averaging procedure is used whereby the sphere or cylinder is moved around slightly on the grid and the potentials are recalculated, the errors in the density integrals drop to around 2% (results not shown). Such an averaging procedure decreases the errors incurred when

(36) Loeb, A. L.; Overbeek, J. T.; Wiersema, P. H. *Electrical Double Layer around a Spherical Colloid Particle*; MIT Press: Cambridge, MA, 1961.



**Figure 2.** Contributions to the energy density integral for a charged cylinder of radius 3 Å at a Debye length of 4 Å calculated by using the one-dimensional finite difference method. The charge and energy are given per 6 Å length. Total energy: solid line,  $\int \rho^2 \phi dv$  (●),  $\int -\rho^m \phi / 2 dv$  (○),  $\int \mathbf{E} \cdot \mathbf{D} / 2 dv$  (▲),  $\int \Delta \Pi dv$  (+).



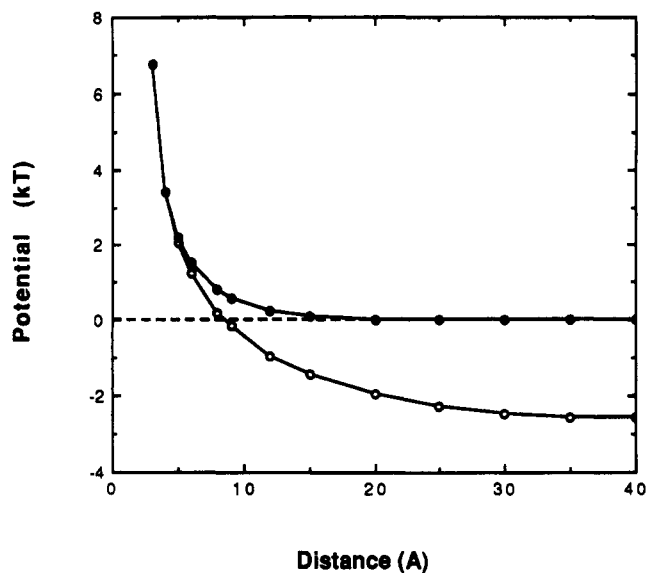
**Figure 3.** Total electrostatic free energy for the CPB equation applied to a 3-Å-radius cylinder contained in a cylindrical cell of 40 Å radius. The linear charge density is  $10e/6$  Å giving a decay length of 4 Å. The energy is given per 6-Å length of cylinder. Energy density integral (○) and charging integral (+) using the original expression from Fuoss et al.<sup>25</sup> (i.e., eq 36). Surface potential (---), energy density integral (—), and charging energy integral (Δ) using potentials from eq 40.

the object is mapped onto the lattice.<sup>7</sup>

The relative contributions of the different terms to the energy density integral is shown in Figure 2 for the cylindrical case. Of the integrals over the ion atmosphere volume, the osmotic pressure and electrostatic stress terms each represent about 20% of the total energy, and the electrostatic ion assembly work term is about 40%.

Figure 3 shows the surface potential and energy density integral for the CPB equation applied to a cylinder. The potential levels off more rapidly as the charge is increased for this equation compared to the NLBP equation. This is because in the CPB model, as the cylinder charge increases, so does the counterion concentration in the cell, and hence the Debye screening length decreases, whereas in the NLBP model, the screening length is fixed by the bulk ionic strength.

It is immediately obvious that the charging and energy density integral values for the energy do not agree for the CPB model



**Figure 4.** Comparison of potential profiles around a 3-Å-diameter cylinder with a linear charge density of  $10e/6$  Å for the NLBP equation, Debye length 4 Å (●), and the CPB equation, cell radius 40 Å, decay length 4 Å (○). The point at which the CPB curves crosses zero is where the local counterion concentration equals the mean concentration.

(dashed curves, Figure 3). This is because, in the original derivation of eq 36, the boundary condition on the edge of the cell was taken to be  $\phi = 0$ .<sup>25</sup> This then defines the reference concentration,  $c^*$  of eq 18. Since the original aim of the earlier work was to determine the counterion distribution, it was immaterial what reference potential was defined. However, for calculating energies, a consistent definition of reference potential is needed. This can be obtained as follows: The mean concentration of counterions in the cylindrical volume lying between  $r = a$  and  $r = R$  is  $c^{av} = s / \pi(R^2 - a^2)$ . Now if the electric field from the cylinder were switched off, these ions would be uniformly distributed in the cell volume. The effect of the field is to attract the ions toward the cylinder, increasing the concentration close in, and decreasing it further out. At some value of  $r$  the concentration will be unchanged at  $c^{av}$  and the potential at this point should be taken as zero. The concentration of counterions at  $r = R$  is given by<sup>25</sup>

$$c(R) = (1 - \beta^2) \epsilon kT / (2\pi R^2 e^2) \quad (40)$$

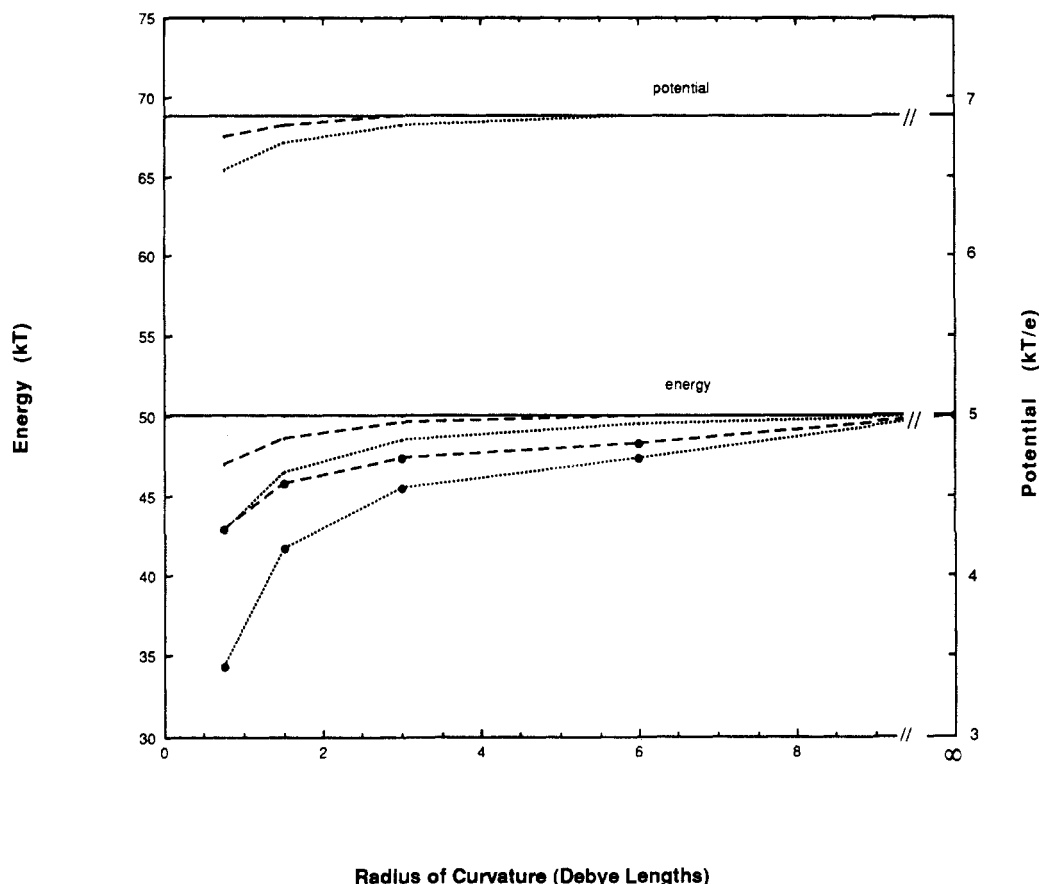
so the correction to the potential is given by  $\ln(c(R)/c^{av})$ , and now

$$\phi = -\ln[\kappa^2 r^2 \sinh^2(\beta \ln\{Ar\}) / 2\beta^2] + \ln(c(R)/c^{av}) \quad (41)$$

is the proper expression for the potential when calculating the energy. The results of the charging and energy density integrals now agree (solid curve, Figure 3).

The difference in reference potential definitions is illustrated in Figure 4, where the potential as a function of distance from the cylinder is shown for the NLBP and CPB equations. The bulk salt solution of the former and the cell radius of the latter were chosen to give the same effective decay length of 4 Å. Close to the cylinder the two models are indistinguishable, since the co-ions present in the NLBP model have a vanishingly small concentration where the potential is high, and do not affect the potential. Further from the cylinder the potential decays to zero in the NLBP model, but in the CPB model the potential changes sign, in accordance with a depletion of counterions.

Figure 5 illustrates the effect of curvature on the value of the surface potential and energy density integral for the spherical and cylindrical forms of the NLBP equation, with the planar form as the limiting case of infinite radius of curvature. The effect of curvature is greater for a sphere, which has curvature in two directions, than for a cylinder which has curvature in only one direction. The total energy calculated from the electrostatic ion assembly work, eq 28, which is strictly valid only for the planar



**Figure 5.** Effect of curvature on the electrostatic energy using the NLBP equation: A comparison of spherical (---), cylindrical (---), and planar (—) (infinite radius of curvature) geometries. Upper curves show the surface potentials, lower curves show the energy (normalized to the area of a 3-Å-radius sphere) calculated from the energy density integral, eq 13, or from the electrostatic work of ion assembly (●).

case, is also plotted. The planar approximation for the potential rapidly improves with radius, being better than 5% already at a curvature of  $1\lambda$ , even for the sphere, and better than 2% at  $2\lambda$ . The energy is more sensitive to curvature though, with about 3 times the error. Equation 28 is a relatively poor approximation to the energy, with an error twice as large still. This expression also shows a much slower asymptotic approach to the limiting planar value.

### Discussion

The calculus of variations provides a unified way to obtain an expression for the total energy for any form of the PB equation. The difference between the three forms discussed here is in the function  $f(\phi)$ , given by eqs 6, 14, and 17. The first term of  $f(\phi)$  should be thought of as a prescription for obtaining the mobile ion concentration which involves an approximation of the potential of mean force in terms of the mean electrostatic potential. Such an approximation may not satisfy all the statistical mechanical properties of a true potential of mean force, but the emphasis should be on how good the approximation is, not on how consistent it is, since within the PB model it is always possible to define a unique electrostatic energy for the system.

The variational approach is quite general in that it can be applied to any functional form for  $f(\phi)$  provided it can be integrated with respect to  $\phi$ . For example, it is possible to add nonelectrostatic terms to eq 4 to account for the finite ion size.<sup>37,38</sup> The variational approach can also be applied to the PB equation to develop approximate analytical solutions for the potential by constructing trial functions which minimize the energy integral.<sup>39,40</sup> One advantage of this method of solution is that the total electrostatic energy of the system is necessarily obtained along with

the potential functions. However, the difficulty of selecting sufficiently accurate trial functions even for simple cylindrical geometries,<sup>40</sup> and the availability of numerical methods, limit its use as a method for solving the PB equation.

For the LPB equation we obtain the familiar result<sup>41</sup> that  $\Delta G_2^{\text{el}} = \sum q_i \phi_i / 2$ . The integration factor of 1/2 is characteristic of any system where the potentials depend linearly on the fixed charge. In this case the total energy will depend quadratically on the charge. For the CPB equation we have eq 19, or using identity 22 we may also write

$$\Delta G_3^{\text{el}} = \int (\rho^f \phi / 2 - \rho^m \phi / 2) dv = \int (\rho^f \phi / 2 + \rho^m \phi / 2 + T \Delta S) dv \quad (42)$$

The first form of (42) is to be contrasted with the expression for the LPB equation, which lacks the  $\rho^m \phi$  term describing the electrostatic ion assembly energy. Since this term is always negative, for a given surface potential the CPB equation gives larger energies. It also means that the energy will depend less than quadratically on the fixed charges. The second form of (42) is identical with that derived by Oosawa from thermodynamic considerations<sup>34</sup> and can be thought of as the work of first charging the polyelectrolyte and then assembling the counterion atmosphere. This is equivalent to the process of isothermally charging up the polyelectrolyte in the presence of the ion atmosphere, as was shown by Oosawa. This is confirmed by the results in Figure 3, providing, however, that a consistent choice of reference potential is used. The original choice of  $\phi = 0$  on the cell boundary<sup>25</sup> is shown to be incorrect. Instead, the potential should be set to zero at the point where the local counterion concentration is equal to the mean counterion concentration in the cell. This correction is substantial, giving surface potentials about 30% smaller, and energies that

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(39) Dresner, L. *J. Phys. Chem.* **1963**, *67*, 2333.

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(41) Gilson, M.; Rashin, A.; Fine, R.; Honig, B. *J. Mol. Biol.* **1985**, *183*, 503.





adsorption energy, so equating expressions 43 and 44 and subtracting the chemical term  $-\sigma_0\phi_0$  from the latter yields

$$\Delta G_1^{\text{el}} = \sigma_0\phi_0 - \int (\mathbf{E} \cdot \mathbf{D}/2 + \Delta\Pi) dv \quad (45)$$

and recognizing  $\sigma_0\phi_0$  as the equivalent of the term  $\int (\rho^f\phi) dv$ , we again have eq 13 for the electrical energy. In the case where the surface charge arises from an acid/base dissociation process, rather than from adsorption, one again has a constant potential process for which eq 44 is applicable, where the "chemical" term,  $-\sigma_0\phi_0$ , is now a function of the bulk hydrogen ion concentration (pH), and the chemical dissociation work ( $pK_a$ ), and  $\sigma_0$  is the fraction of ionized groups at equilibrium.<sup>42</sup>

The energy density integral for the NLBP equation has been written in a number of equivalent forms in eqs 13 and 23-25. Which of these should be used in a particular application will be determined by numerical considerations. For the finite difference results reported here, the form given in eq 23 is convenient since it involves only integrals over the volume of the ion atmosphere. This expression does not require the potential at the fixed charges to be evaluated, which in the TFD method requires the subtraction of a grid potential, or renormalization procedure.<sup>3,43</sup> In addition to numerical considerations, the various forms represent different ways of assembling or charging up the system to its final state. The physical interpretations of eqs 13 and 24 have already been discussed. In eq 25 the potentials have been split up into their various contributions. The first term involves only the potentials arising from the colloid and the solvent (water) and thus gives the solvation energy of the colloid at zero ionic strength (see, for example, refs 3 and 43). The second term is the electrostatic work of placing the charged colloid in the already organized ion atmosphere, the third term is the electrostatic self-energy of ion atmosphere assembly, the fourth term is the entropy of ion organization, and the last term is the water chemical potential term.

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The second through fifth terms can also be thought of as the change in solvation energy of the colloid upon transferring it from pure water to a salt solution. The various interpretations of the energy density integral reiterate the point that there is a unique, unambiguous energy for any system modeled by the nonlinear PB equation, irrespective of the order or method of assembly of the components. The nonlinear PB equation may, however, be applied inconsistently, as in ionic solution theory, where one of the mobile ions is treated as fixed, i.e., not subject to thermal averaging. On the other hand, in the applications of most interest to biophysics, surface chemistry, etc., it is not inconsistent to treat colloids, surfaces, membranes, polyelectrolytes, or macromolecules as fixed charged bodies with respect to the much smaller mobile ions.

## Conclusions

The method of variational calculus provides a simple way to obtain an expression for the total electrostatic free energy for any form of the PB equation. The expression involves what is termed here an energy density integral. Both the more familiar charging integral and the energy density integral can be applied to numerical solutions of the PB equation with equal accuracy, but, for the latter, the equation need only be solved once, resulting in a much greater computational efficiency. A consistent definition of the potential is given for the cell model, without which the charging and energy density integrals do not agree. The energy density integral involves the integral of the excess osmotic pressure of the ion atmosphere. The various forms of the PB equation which have been most widely discussed because of the availability of analytical solutions are shown to be special cases in which, which for a number of reasons, the osmotic term is not necessary. In general, however, this term cannot be neglected when calculating total energies for the nonlinear PB equation, and its importance is reemphasized here.

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## Naphthalene/Triethylamine Exciplex and Pyrene Excimer Formation in Supercritical Fluid Solutions

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Supercritical fluids (SCFs), especially mixed solvents or those with entrainers, exhibit specific interactions that make them a very powerful media for separations. It is important to understand microscopic interactions between solutes and entrainers, as well as between two solute molecules, to develop predictive thermodynamic models of supercritical solutions. We present new fluorescence spectroscopy results of exciplex and excimer formation in SCF solutions and describe special considerations required in the analysis. The results indicate a significant solvent effect on the photophysical kinetics and the presence of solute/solute interactions in very dilute SCF solutions.

## Introduction

Supercritical fluids (SCFs) exhibit a variety of properties that make them particularly attractive for separation processes and yet especially challenging to characterize. Specifically, SCFs offer

the advantages of both distillation and extraction, in that they separate compounds not only by differences in vapor pressure but also by specific interactions with well-chosen solvent components. Two of these specific interactions, entrainer effects and solute-solute synergism, have been the object of macroscopic experimental investigation with little corresponding success in model development. Entrainment effects, where a small amount (0.1-5%) of an additional component with some functionality increases the sol-

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