Biophysical Chemistry 12 (1980) 317–322

A THEORY OF THE INTERACTION BETWEEN ELECTRICAL DOUBLE LAYERS

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Received 1 April 1980

A generalization of the Poisson-Boltzmann approach to the repulsive electrostatic force between similar electrical double layers is presented. It is based on the integral equation formalism of the statistical mechanical theories of fluids and it is shown that the Poisson-Boltzmann result follows from a well-defined and improvable set of approximations.

The nature of the repulsive electrostatic force between similar electrical double layers is of great importance not only in the stability of colloidal systems but in biophysical systems as well. The classical theoretical treatment of this problem is based on the Poisson-Boltzmann equation and enjoys the same degree of success and validity as the Gouy-Chapman theory of the electrical double layer [1]. For dilute solutions of 1-1 electrolytes, the predictions of the theory are in satisfactory agreement with experiment [2–6], but just as in the corresponding Debye-Huckel theory of bulk electrolyte solutions, we expect to find discrepancies as the concentration and charge of the ions increases. In recent years the statistical mechanical theory of electrolyte solutions has reached the point where it has become possible to handle the short-range volume exclusion potential, which represents the finite size of the ions, and the long-range coulombic potential in one self-consistent formalism [7]. It turns out that the short-range contribution plays a significant role in the structural and thermodynamic properties even of 1-1 electrolyte solutions at 0.1 M. Most of these theories of bulk electrolyte solutions are based on extensions of the liquid theory integral equations for the n-body correlation functions [8]. These not only have been well developed for bulk solutions but recently several of these have been applied to electrical double layers as well [9–11]. Thus a next step in developing a theory of the electrical double layer and the interaction between double layers is to develop an integral equation formalism which allows one to include the effect of finite ionic size and which reduces to the Gouy-Chapman theory when the ionic size is set equal to zero and which is general enough that other extensions can be included also. Recently Croxton and McQuarrie [12] have solved the Born-Green-Yvon equation numerically for the restricted primitive model, in which the ions are modelled as rigid spheres of equal diameters with the charge located at the center and the solvent is treated as a continuum with a uniform dielectric constant ϵ. As its name implies, the model is indeed primitive but it does serve as a next logical step beyond the classical Debye-Hückel, Poisson-Boltzmann and Gouy-Chapman theories. Recent work in the theory of bulk solutions is attempting to extend the number of components in the system by one and to represent the solvent as a fluid of hard spheres with imbedded dipoles and to use a more realistic form for the short-range potential [13]. The formalism that we present does admit these extensions but their implementation lies in the future.

Based upon our success with the BGY equation for bulk solutions, we shall use an extension of this equation for inhomogeneous fluids. In addition, we introduce a new integral equation for this system, based on recent work by Lovett, Mou and Buff [14], which allows one to treat this problem through the direct correlation function rather than the n-body distribution functions. These two approaches are formally equivalent but one may be preferable to the other in a specific application.

Let the potential energy of the system be

$$U=\sum_{\alpha=1}^{\nu}\sum_{i=1}^{N_\alpha}u_\alpha(\mathbf{r}_{\alpha i})+\sum_{\alpha,\beta=1}^{\nu}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}u_{\alpha\beta}(\mathbf{r}_{\alpha i},\mathbf{r}_{\beta j}),\tag{1}$$

where ν is the number of ionic species, N_α is the number of ions of species α and $\mathbf{r}_{\alpha i}$ is the position of the ith ion of species α. The quantities $u_\alpha(\mathbf{r}_{i\alpha})$ and $u_{\alpha\beta}(\mathbf{r}_{i\alpha},\mathbf{r}_{j\beta})$ represent the interaction of a particle at $\mathbf{r}_{i\alpha}$ with an external field and the pair interaction between a particle located at $\mathbf{r}_{i\alpha}$ and one located at $\mathbf{r}_{j\beta}$, respectively. By a simple extension of the derivation of the Born-Green-Yvon hierarchy for a homogeneous fluid [8], one can derive

$$\nabla_1\rho_\sigma^{(1)}(\mathbf{r}_1)+\beta\rho_\sigma^{(1)}(\mathbf{r}_1)\nabla_1u_\sigma(\mathbf{r}_1)=-\beta\sum_{\alpha=1}^{\nu}\int\mathrm{d}\mathbf{r}_2\,\rho_{\alpha\sigma}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\nabla_1u_{\alpha\sigma}(\mathbf{r}_1,\mathbf{r}_2),\tag{2}$$

where ∇_1 denotes the gradient with respect to the position $\mathbf{r}_1$ and $\rho_\sigma^{(1)}(\mathbf{r}_1)$ and $\rho_{\alpha\sigma}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ are the one-particle and two-particle distribution functions, defined by

$$\rho^{(n)}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)=\frac{\int\ldots\int\mathrm{e}^{-\beta U}\,\mathrm{d}\mathbf{r}_{n+1}\ldots\mathrm{d}\mathbf{r}_n}{\int\ldots\int\mathrm{e}^{-\beta U}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\mathrm{d}\mathbf{r}_n}.\tag{3}$$

Eq. (2) is the first member of a hierarchy of integral equations, each involving $\rho^{(n)}$ in terms of $\rho^{(n+1)}$, and is exact. It can be shown that it is equivalent to the condition of mechanical equilibrium. Harasima [15] has shown that

$$\nabla_1\cdot\mathbf{p}(\mathbf{r}_1)=kT\nabla_1\rho^{(1)}(\mathbf{r}_1)+\sum_{\alpha,\sigma=1}^{\nu}\int\mathrm{d}\mathbf{r}_2\,\rho_{\alpha\sigma}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\nabla_1u_{\alpha\sigma}(\mathbf{r}_1,\mathbf{r}_2)\tag{4}$$

where $\mathbf{p}(\mathbf{r}_1)$ is the local pressure tensor and $\rho^{(1)}(\mathbf{r}_1)=\Sigma_{\alpha=1}^{\nu}\rho_\alpha^{(1)}(\mathbf{r}_1)$, so that eq. (2) is equivalent to

$$\nabla_1\cdot\mathbf{p}(\mathbf{r}_1)+\sum_{\alpha=1}^{\nu}\rho_\alpha^{(1)}(\mathbf{r}_1)\nabla_1u_\alpha(\mathbf{r}_1)=0,\tag{5}$$

which is a standard condition of mechanical or hydrodynamic equilibrium [16]. The statistical mechanical theory of transport in dense fluids gives a molecular definition of $\mathbf{p}(\mathbf{r}_1)$, viz. [17]

$$\mathbf{p}(\mathbf{r}_1)=kT\rho^{(1)}(\mathbf{r}_1)\mathbf{I}-\tfrac{1}{2}\sum_{\alpha,\sigma=1}^{\nu}\int\frac{\mathbf{r}\mathbf{r}}{r}\rho_{\alpha\sigma}^{(2)}(\mathbf{r}_1,\mathbf{r})\nabla u_{\alpha\sigma}\,\mathrm{d}\mathbf{r},\tag{6}$$

where $\mathbf{I}$ is the unit tensor. For the case in which $\mathbf{r}_1$ is in a region between two parallel uniform planar walls, eq. (5) becomes simply

$$\mathrm{d}p(x)/\mathrm{d}x+\beta\sum_{\alpha=1}^{\nu}\rho_\alpha^{(1)}(x)\,\mathrm{d}u_\alpha/\mathrm{d}x=0.\tag{7}$$

Note that u_α in this equation is the *external* potential. In the case of an electrical potential, $u_\alpha(x)$ is the unscreened potential due to the wall. The precise functional form of $u_\alpha(x)$ depends upon how the wall is modelled, but generally it is of the form $u_\alpha(x)=z_\alpha eu(x)$ and so eq. (7) becomes

$$\mathrm{d}p/\mathrm{d}x+\beta\rho_\mathrm{c}(x)\,\mathrm{d}u/\mathrm{d}x=0,\tag{8}$$

where $\rho_\mathrm{c}(x)=\Sigma\,z_\alpha e\rho_\alpha^{(1)}(x)$ is the charge density. This is to be compared to the equation of mechanical equilibrium that appears in Verwey and Overbeek and used extensively in the colloid literature, viz.

$$\mathrm{d}p/\mathrm{d}x+\rho_\mathrm{c}\,\mathrm{d}\psi/\mathrm{d}x=0,\tag{9}$$

where ψ is interpreted to be the screened potential, as given by the Poisson-Boltzmann equation. If $\rho_\mathrm{c}(x)$ is replaced by $-(\epsilon/4\pi)\,\mathrm{d}^2\psi/\mathrm{d}x^2$ then an integration gives that

$$p - (\epsilon/8\pi)\,(\mathrm{d}\psi/\mathrm{d}x)^2 = \text{constant}. \tag{10}$$

In the Gouy-Chapman theory of the interaction between planar double layers, p is replaced by $kT\rho$ and the well-known expression due to Langmuir results, viz. that the repulsive force R is given by

$$R = kT\rho_{\mathrm{d}} - kT\rho_{\mathrm{bulk}} = kT\rho\,\{\cosh(ze\psi_{\mathrm{d}}/kT) - 1\}, \tag{11}$$

where d is the point between the walls at which $\mathrm{d}\psi/\mathrm{d}x = 0$, i.e. the midpoint if the walls carry the same uniform charge density.

Eq. (11) has found great success in the colloid literature, and yet the nature of the potentials to be used in eqs. (8) and (9) are contradictory. In eq. (8) $u(x)$ is the unscreened potential (per unit charge) whereas in eq. (9) it is the screened potential. To resolve this discrepancy, we introduce the statistical mechanical concept of a potential of mean force $w_\alpha^{(1)}(\mathbf{r}_1)$ by

$$\rho_\alpha^{(1)}(\mathbf{r}_1) = \rho_\alpha \exp\,[-w^{(1)}(\mathbf{r}_1)/kT], \tag{12}$$

where ρ_α is the bulk number density of species α. Eq. (12) defines $w_\alpha^{(1)}(\mathbf{r}_1)$. If we take the gradient of both sides of this equation, we get

$$\nabla_1 \rho_\alpha^{(1)}(\mathbf{r}_1) + \beta\rho_\alpha^{(1)}(\mathbf{r}_1)\,\nabla_1 w_\alpha^{(1)}(\mathbf{r}_1) = 0. \tag{13}$$

By comparing this to the first member of the BGY hierarchy, viz. eq. (2), we see that

$$\rho_\alpha^{(1)}(\mathbf{r}_1)\,\nabla_1 w_\alpha^{(1)}(\mathbf{r}_1) = \rho_\alpha^{(1)}(\mathbf{r}_1)\,\nabla_1 u_\alpha(\mathbf{r}_1) - \sum_{\sigma=1}^{\nu} \int \mathrm{d}\mathbf{r}_2\, \rho_{\alpha\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\,\nabla_1 u_{\alpha\sigma}(\mathbf{r}_1, \mathbf{r}_2). \tag{14}$$

This equation nicely shows how the unscreened external potential term combines with the intermolecular potential term to produce the potential of mean force, i.e. the screened potential. Physically, the second term on the right-hand side of eq. (14) represents the adjustment of the ions to screen the external potential. Thus eq. (13), like eq. (5), is also a condition of mechanical equilibrium and if we sum eq. (13) over α we get

$$\nabla_1 \rho^{(1)}(\mathbf{r}_1) + \beta \sum_{\alpha=1}^{\nu} \rho_\alpha^{(1)}(\mathbf{r}_1)\,\nabla_1 w_\alpha^{(1)}(\mathbf{r}_1) = 0. \tag{15}$$

In the Poisson-Boltzmann or Gouy-Chapman theory, $w_\alpha^{(1)}(\mathbf{r}_1)$ is approximated by $z_\alpha e\psi(\mathbf{r}_1)$ where $\psi(\mathbf{r}_1)$ is the electrostatic potential (per unit charge) and so eq. (15) becomes

$$kT\,\mathrm{d}\rho^{(1)}/\mathrm{d}x + \rho_{\mathrm{c}}\,\mathrm{d}\psi/\mathrm{d}x = 0. \tag{16}$$

If we replace ρ_{c} by $-(\epsilon/4\pi)\,\mathrm{d}^2\psi/\mathrm{d}x^2$ and integrate once, we obtain

$$kT\rho^{(1)}(x) - (\epsilon/8\pi)\,(\mathrm{d}\psi/\mathrm{d}x)^2 = \text{constant} \tag{17}$$

as the condition of mechanical equilibrium. Notice that this yields Langmuir's result *without* approximating p by $kT\rho^{(1)}$. Thus it would be incorrect to try to use a better approximation for p in order to correct Langmuir's result for finite-size ions, and ion–ion correlations, etc.

We can formulate a rigorous theory of the repulsion between double layers by using eq. (6) to calculate the pressure at any point in the double layer region. In order to do this we must know $\rho^{(1)}(x)$ and $\rho^{(2)}(x, \mathbf{r}_{12})$. Perhaps the most satisfactory approach to this problem would be to use the first two members of the BGY hierarchy and to use some sort of a superposition approximation on the second one to approximate $\rho^{(3)}$ in terms of $\rho^{(2)}$. This leads to two simultaneous integral equations for $\rho^{(1)}$ and $\rho^{(2)}$. Such an approach has been used quite successfully by Buff and Stillinger [18] in a treatment of the surface tension of ionic solutions. Incidentally this paper also affords a direct, analytic example of how the interionic distribution term in eq. (14) cancels the unscreened potential term and produces a screened potential of mean force. In their case the external potential is the unscreened potential due to images.

A much simpler and yet possibly satisfactory approach would be to use only the first BGY equation and to introduce an intuitive approximation for $\rho^{(2)}$. As an example of this procedure, we shall now show how to derive the Gouy-Chapman approximation for this system directly from eq. (2). This gives good insight into the nature of the Gouy-Chapman theory and suggests other approximations that extend it. We shall consider a system of two uniformly-charged parallel planar walls of infinite extent. If the two walls carry an equal surface charge density, then the total external force between the two walls is zero. This rather anomalous result is peculiar to this geometry and results from the unrealistic limiting process, but, nevertheless, it can still be treated by eq. (2). If we write $\rho_\sigma^{(1)}(\mathbf{r}_1) = \rho_\sigma \exp[-w_\sigma^{(1)}(\mathbf{r}_1)/kT]$ and introduce the radial distribution function $g_{\alpha\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ through $\rho_{\alpha\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_\sigma^{(1)}(\mathbf{r}_1)\, \rho_\alpha^{(1)}(\mathbf{r}_2)\, g_{\alpha\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, eq. (2) can be written in the form

$$\beta \mathrm{d}w_\sigma^{(1)}/\mathrm{d}x = \sum_{\alpha=1}^{\nu} \int \mathrm{d}\mathbf{r}_2\, \rho_\alpha^{(1)}(x_2)\, g_{\alpha\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, \mathrm{d}u_{\alpha\sigma}/\mathrm{d}x_2 \equiv \mathrm{d}S_\sigma/\mathrm{d}x. \tag{18}$$

If we ignore any short-range interaction between the ions and write $u_{\alpha\sigma}$ as simply a coulombic potential $z_\alpha z_\sigma e^2/\epsilon r_{12}$, then

$$kT \frac{\mathrm{d}S_\sigma}{\mathrm{d}x} = \frac{z_\sigma E}{\epsilon} \sum_{\alpha=1}^{\nu} z_\alpha e \int_0^{2d} \mathrm{d}x_2 (x - x_2)\, \rho_\alpha^{(1)}(x_2) \int_{|x-x_2|}^{\infty} \frac{g_{\alpha\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}^3}\, 2\pi r_{12}\, \mathrm{d}r_{12}, \tag{19}$$

where $2d$ is the separation of the walls and where we have written the volume element $\mathrm{d}\mathbf{r}_2$ as $2\pi r_{12}\, \mathrm{d}r_{12}\, \mathrm{d}x_2$. We now ignore the ion–ion correlations and set $g_{\alpha\sigma}^{(2)} = 1$ and so eq. (19) becomes

$$\begin{aligned} kT \frac{\mathrm{d}S_\sigma}{\mathrm{d}x} &= \frac{z_\sigma e}{\epsilon} \int_0^{2d} \mathrm{d}x_2 (x - x_2)\, \rho_\mathrm{c}(x_2) \int_{|x_2-x|}^{\infty} 2\pi r_{12}^{-2}\, \mathrm{d}r_{12} \\ &= -\frac{2\pi z_\sigma e}{\epsilon} \int_0^{2d} \rho_\mathrm{c}(x_2) \frac{(x-x_2)}{|x-x_2|}\, \mathrm{d}x_2 = -\frac{2\pi z_\sigma e}{\epsilon} \left(\int_0^{x} \rho_\mathrm{c}(x_2)\, \mathrm{d}x_2 - \int_x^{2d} \rho_\mathrm{c}(x_2)\, \mathrm{d}x_2 \right). \end{aligned} \tag{20}$$

If we differentiate this once we obtain

$$kT \mathrm{d}^2 S_\sigma/\mathrm{d}x^2 = -(4\pi z_\sigma e/\epsilon)\, \rho_\mathrm{c}(x). \tag{21}$$

Eq. (18) shows that $kT \mathrm{d}^2 S_\alpha/\mathrm{d}x^2 = \mathrm{d}^2 w_\alpha^{(1)}/\mathrm{d}x^2$ and if we approximation $w_\alpha^{(1)}$ by $z_\alpha e\psi$ we obtain

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{4\pi}{\epsilon} \rho_\mathrm{c}(x) = -\frac{4\pi}{\epsilon} \sum_{\alpha=1}^{\nu} z_\alpha e \rho_\alpha \exp(-z_\alpha e\psi/kT). \tag{22}$$

Thus we see that by making a number of simplifying approximations in eq. (2) we recover the Poisson-Boltzmann equation. We propose here that a less severe approximation for $g_{\alpha\sigma}^{(2)}$ will result in a more general theory for the interaction between double layers. For example, a interionic radial distribution function that has found good success in the theory of bulk electrolyte solutions is [19] $g_{\alpha\sigma}^{(2)}(r) = g_{\alpha\sigma}^{\mathrm{HS}}(r) \exp(-\psi^{\mathrm{DH}}/kT)$ where $g_{\alpha\sigma}^{\mathrm{HS}}(r)$ is the hard sphere radial distribution function and ψ^{DH} is the Debye-Hückel screened coulomb potential. Using this form for $g_{\alpha\sigma}^{(2)}(r)$ eq. (2) can be solved for $\rho_\sigma^{(1)}$ which in turn can be used to calculate the pressure tensor and the resulting force. It appears, however, that this must be done numerically and will be the subject of later work.

Before concluding we will present an alternative route based on an exact integral equation recently presented by Lovett, Mou and Buff [14] in a discussion of the liquid-vapor interface in a pure fluid. Unlike the BGY equation, this equation involves the direct correlation function rather than the two-body distribution function. For pure fluids that interact only through a short-range potential, the direct correlation function appears to be a much simpler function than the radial distribution function and so lends itself to approximation more easily than does the radial distribution function. Consequently it may prove useful to explore this route. The multi-component generalization of the Lovett-Mou-Buff equation is

$$\nabla_1 [\ln \rho_\alpha^{(1)}(r_1) + \beta u_\alpha(r_1)] = \sum_{\sigma=1}^{\nu} \int \mathrm{d}r_2\, c_{\alpha\sigma}(r_1, r_2)\, \nabla_2 \rho_\sigma^{(1)}(r_2), \tag{23}$$

where $c_{\alpha\sigma}(r_1, r_2)$ is the direct correlation function and $u_\alpha(r_1)$, as before, is the external potential. Lovett et al. show that this equation may be manipulated into the form of eq. (5), once again proving that the condition of mechanical or hydrodynamic equilibrium involves the pressure and the external potential.

In order to illustrate the use of this equation, we shall show under what approximations it reduces to the Gouy-Chapman theory. For the planar geometry involved here, eq. (23) is

$$\frac{\mathrm{d} \ln \rho_\alpha^{(1)}(x)}{\mathrm{d}x} = \sum_{\sigma=1}^{\nu} \int \mathrm{d}r_2\, c_{\alpha\sigma}(r_1, r_2)\, \frac{\mathrm{d}\rho_\alpha^{(1)}(x_2)}{\mathrm{d}x_2} \equiv S_\alpha(x). \tag{24}$$

Using the same coordinate system that was used previously

$$S_\alpha(x) = 2\pi \sum_{\sigma=1}^{\nu} \int_0^{2d} \mathrm{d}x_2\, \frac{\mathrm{d}\rho_\sigma^{(1)}}{\mathrm{d}x_2} \int_{|x-x_2|}^{\infty} r_{12}\, c_{\alpha\sigma}(r_{12}, x_2)\, \mathrm{d}r_{12}. \tag{25}$$

As suggested by the Debye-Hückel theory of bulk solutions, we approximate $c_{\alpha\sigma}(r_1, r_2)$ by $-\beta u_{\alpha\sigma}(r_{12})$ where $u_{\alpha\sigma}(r_{12})$ is simply the coulomb potential $z_\alpha z_\sigma e^2/\epsilon r_{12}$ and so eq. (25) becomes

$$\begin{aligned} S_\alpha(x) &= -\lim_{L\to\infty} \sum_{\sigma=1}^{\nu} \frac{2\pi z_\alpha z_\sigma e^2}{\epsilon kT} \int_0^{2d} \frac{\mathrm{d}\rho_\sigma^{(1)}}{\mathrm{d}x_2}\, \mathrm{d}x_2 \int_{|x-x_2|}^{L} \mathrm{d}r \\ &= -\lim_{L\to\infty} \sum_{\sigma=1}^{\nu} \frac{2\pi z_\alpha z_\sigma e^2}{\epsilon kT} \left\{ -\int_0^{2d} |x-x_2|\, \frac{\mathrm{d}\rho_\sigma^{(1)}}{\mathrm{d}x_2}\, \mathrm{d}x_2 + L(\rho_\sigma^{(1)}(2d) - \rho_\sigma^{(1)}(0)) \right\}. \end{aligned} \tag{26}$$

Since the walls cary equal charge densities, $\rho_\sigma^{(1)}(0) = \rho_\sigma^{(1)}(2d)$ and so the awkward upper limit in the r_{12} integration vanishes. By integrating the integral over x_2 by parts, one gets

$$S_\alpha(x) = (4\pi z_\alpha e/\epsilon kT) \int_0^x \rho_c(x')\, \mathrm{d}x' - (2\pi z_\alpha e/\epsilon kT) \int_0^{2d} \rho_c(x)\, \mathrm{d}x. \tag{27}$$

The second integral here is equal to -2σ by electroneutrality and so

$$S_\alpha(x) = (4\pi z_\alpha e/\epsilon kT) \int_0^x \rho_c(x')\, \mathrm{d}x' + 4\pi\sigma z_\alpha e/\epsilon kT. \tag{28}$$

If we substitute this into eq. (24), differentiate once and write $\rho_\alpha^{(1)}(x) = \rho_\alpha \exp[-w_\alpha^{(1)}(x)/kT]$ with $w_\alpha^{(1)}(x)$ approximated by $z_\alpha e\psi(x)$, we once again get the Poisson-Boltzmann equation, eq. (22).

This work was supported by a grant from the National Institutes of Health, GM 26864-01 and by the Consejo de Desarrollo of the Universidad de los Andes, CDCH-C83.

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