

Theory of the Diffuse Double Layer*

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The charge moment expansion for potentials of mean force acting between the ions of an electrolyte is reviewed in a form applicable to surface phases. An integral equation is in this manner derived for approximate determination of the average charge distribution near a planar electrode. The solution of the linearized equation is constructed for an electrolyte consisting of charged hard spheres suspended in a dielectric continuum. For very dilute solutions, the predictions of the linearized Poisson-Boltzmann equation are verified; at higher concentrations, the average space charge in the neighborhood of the electrode tends to alternate in sign as a result of local latticelike ion arrangement imposed effectively by short range ion repulsions. Predicted values of the ζ potential relative to those of the linear Poisson-Boltzmann theory are reported.

I. INTRODUCTION

THE understanding of the molecular basis of the diffuse, or Gouy, double layer provides insight into a number of phenomena of interest to electrochemists. In particular, it is possible to analyze the several electrokinetic phenomena (e.g., electrophoretic migration velocities and streaming potentials) to predict the stability of lyophobic colloids toward added salt, and to interpret the capacitance of metal electrodes in contact with electrolytic solutions. Theoretical determination of average ion distributions in diffuse double layers typically has employed, in the past, the Poisson-Boltzmann equation as adapted to the surface region. Recent developments for the planar interface are concerned either with solution of the Poisson-Boltzmann equation retaining nonlinear terms,¹⁻³ or, assuming this equation as a basis, with introduction of complicating *ad hoc* physical models to account for such electrolyte parameters as ion size and degree of hydration.⁴⁻⁶

Although such extensions are interesting and perhaps intuitively appealing, it is nevertheless true that the Poisson-Boltzmann equation can give at best only an approximate description of the molecular situation. The linear terms in the average electrostatic potential (with the Poisson-Boltzmann equation in expanded form) are alone consistent with a rigorous integrability condition satisfied by the excess electrostatic free energy.⁷

The viewpoint adopted in the following analysis involves determination of local ion densities in the double layer region from the well-developed fundamental theory of molecular distribution functions.

Specifically, a moment expansion in increasing orders of charge for a particular ion is derived for the potential of mean force acting in a set of particles (including the chosen ion). This is the diffuse double layer version of a similar treatment of bulk electrolytes which has been carried to some length by Kirkwood and Poirier.⁸ An alternative approach to our present problem would introduce a conditionally convergent Mayer cluster expansion appropriate to the interfacial region; in order to obtain finite results for the ionic distribution functions, it would be necessary, as is well known, to select certain sets of clusters for partial summation.⁹

By way of illustrating the profound effect that finite ion size can have upon the average charge distribution in the double layer, our distribution function technique is formulated in approximate fashion to deal extensively with an idealized electrolyte. The electrolyte is regarded as consisting of charged rigid spheres suspended in a dielectric continuum, and a planar, uniformly charged electrode produces the double layer in this model fluid. It is in fact then possible to establish that both the ion-exclusion volumes and the electrostatic charges are instrumental in determining even the qualitative features of the distributions of ions. For sufficiently large dilutions, the usual linear Poisson-Boltzmann result is obtained, but as the electrolyte concentration is allowed to increase, the short-range ion-ion repulsions tend to set up a local latticelike structure with alternating layers of positive and negative charge. Numerical computations for the reduced ζ potential clearly reflect the ionic ordering at distances further from the electrode than would be predicted by the linear Poisson-Boltzmann theory.

II. MOMENT EXPANSION

The molecular system to be discussed consists of a large set of N particles of species $1 \cdots \eta$, some of which are electrostatically charged (ions). These particles will be enclosed within a volume v . The surface of this

⁸ J. G. Kirkwood and J. C. Poirier, *J. Phys. Chem.* **58**, 591 (1954).

⁹ In this connection, see F. P. Buff and F. H. Stillinger, Jr., *J. Chem. Phys.* **25**, 312 (1956).

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¹ D. C. Grahame, *Chem. Rev.* **41**, 441 (1947).

² B. Breyer and F. Gutmann, *J. Chem. Phys.* **21**, 1323 (1953).

³ J. R. Macdonald and M. K. Brachman, *J. Chem. Phys.* **22**, 1314 (1954).

⁴ Freise, *Z. Elektrochem.* **56**, 822 (1952).

⁵ R. Schlögl, *Z. Physik* **202**, 379 (1954).

⁶ J. J. Bikerman, *Phil. Mag.* **33**, 384 (1942).

⁷ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The MacMillan Company, New York, 1956), p. 387.

volume may be regarded as a mathematical surface of discontinuity in the sense that it may be crossed by none of the particles. It might, for example, be represented by an infinitely steep and high potential barrier. It is necessary to have a certain portion of the containing surface (such as one face of a rectangular solid volume v) correspond to a charged electrode, which induces the Gouy double layer by creating an appropriate external force field.

Each of the N particles comprising our electrolyte is therefore subject to forces arising either from the charged electrode or from the other fluid particles. The total potential of interaction accordingly is split into single-particle, and particle-pair contributions, attributable to these two sources, respectively,

$$V_N(1 \cdots N) = \sum_{i=1}^N V_{\alpha_i}^{(1)}(i) + \sum_{i < j=1}^N V_{\alpha_i \alpha_j}^{(2)}(ij),$$

$$\alpha_i, \alpha_j = 1 \cdots \eta. \tag{1}$$

Here, α_i and α_j denote the species of particles i and j . Each of the singlet and pair potentials, furthermore, may be separated into parts of electrostatic (e), and short-range (s) character.

$$V_{\alpha_i}^{(1)}(i) = V_{\alpha_i}^{(1,e)}(i) + \xi_i V_{\alpha_i}^{(1,s)}(i),$$

$$V_{\alpha_i \alpha_j}^{(2)}(ij) = V_{\alpha_i \alpha_j}^{(2,e)}(ij) + \xi_i \xi_j V_{\alpha_i \alpha_j}^{(2,s)}(ij). \tag{2}$$

We have, for the sake of convenience, introduced charging parameters ξ_i for each of the particles in the ionic fluid, such that the charge on i will be $\xi_i e$ ($-e$ is the electronic charge). For neutral solvent species, ξ_i will of course vanish.

Specifically, the electrostatic interactions $V^{(1,e)}$ and $V^{(2,e)}$ will be written (including a dielectric constant appropriate to the fluid medium)

$$V_{\alpha_i}^{(1,e)}(i) = V^{(1,e)}(x_i) = -(2\pi\sigma e/D)x_i + A, \tag{3}$$

$$V_{\alpha_i \alpha_j}^{(2,e)}(ij) = V^{(2,e)}(r_{ij}) = e^2/D r_{ij}. \tag{4}$$

The singlet and pair electrostatic interactions therefore are species independent. The potential $V^{(1,e)}$ has been chosen as that for a uniformly charged (σ esu/cm²) planar electrode, with distance x_i measured normal to its surface and directed inward toward the solution. The value of the additive constant A depends upon the choice of a zero of potential energy; its magnitude can in no way affect the ionic distributions.

The probability of observing a set of n particles such as $1 \cdots n$ (the first particle is species α , \cdots , the n th particle is species ν) in a given set of positions $\mathbf{r}_1 \cdots \mathbf{r}_n$ in the system, is conveniently expressed in terms of a molecular correlation function $g_{\alpha \cdots \nu}^{(n)}(1 \cdots n)$. $g^{(n)}$ is normalized to unity when each member of the set $1 \cdots n$ is far both from other members of the set, and from the double layer region. $g^{(n)}$ may be written as a phase space integral of the normalized canonical distribution, over the configurations of the remaining

$N-n$ particles, correct to terms of order N^{-1} ,

$$g_{\alpha \cdots \nu}^{(n)}(1 \cdots n) = \exp[-\beta W_{\alpha \cdots \nu}^{(n)}(1 \cdots n)]$$

$$= \frac{v^n \int \cdots \int_v \exp[-\beta V_N(1 \cdots N)] dv_{n+1} \cdots dv_N}{\int \cdots \int_v \exp[-\beta V_N(1 \cdots N)] dv_1 \cdots dv_N},$$

$$\beta = (kT)^{-1}, \tag{5}$$

where $W^{(n)}$ is the potential of mean force for the n particle set.

When each of $1 \cdots n$ is microscopically far from the double layer region, $g^{(n)}$ assumes a value $g^{(n,b)}$ typical only of the bulk structure of the electrolytic fluid, and hence completely independent of the nature (shape, charge distribution) of the surface of the system. In particular, the pair correlation function $g^{(2,b)}$ depends only on the radial distance r separating a pair of particles.

The quantities of dominant interest for the double layer development are the singlet distributions, $g_{\alpha}^{(1)}(\mathbf{r})$. In the interior of the fluid they are unity, but deviations occur near the electrode on account of non-vanishing average force acting on a single particle there. For a position \mathbf{r} within the Gouy double layer, the mean electrostatic charge density ρ_{e1} may be expressed trivially in terms of the several $g_{\alpha}^{(1)}$,

$$\rho_{e1}(\mathbf{r}) = \sum_{\alpha=1}^{\eta} c_{\alpha} \xi_{\alpha} e g_{\alpha}^{(1)}(\mathbf{r}). \tag{6}$$

c_{α} is the bulk concentration of the α th species, and does not differ significantly from the reciprocal volume per α particle computed for the entire system volume v . This charge density ρ_{e1} vanishes when \mathbf{r} is within the bulk fluid; here, then, one has a bulk electroneutrality condition

$$\sum_{\alpha=1}^{\eta} c_{\alpha} \xi_{\alpha} = 0. \tag{7}$$

If our system includes the uniformly charged planar electrode giving rise to the potential (3), a second electroneutrality condition may be formulated. The average charge residing in the double layer must precisely neutralize the charge density σ

$$-\sigma = \int_i^u \rho_{e1}(x) dx. \tag{8}$$

The limits of integration on x , the normal distance to the electrode, must span the region over which excess space charge attributable to the ionic fluid is sensibly different from zero. These limits will be, respectively, just within the electrode (l), and well inside the electrolyte bulk (u).

The distribution of charge both on the electrode and induced within the electrolyte as the diffuse double

layer produces an average electric field. On account of the complete and exact shielding of the electrode charge, as illustrated by condition (8), this mean field will be nonzero only within the Gouy layer. By integration, the field defines an average potential $\psi(\mathbf{r})$ at a point \mathbf{r} in the double layer relative to the bulk liquid. The value of $\psi(\mathbf{r})$ for the present situation (planar, uniformly charged electrode) will depend only on the coordinate x . Simple electrostatics suffices to provide the result

$$\psi(x) = (4\pi/D) \int_x^u (x-y)\rho_{el}(y)dy. \tag{9}$$

Once again the upper integration limit u on y must be sufficiently large that ρ_{el} is substantially zero. The value of ψ at the electrode surface defines the ζ potential.

The correlation function definitions (5) may be manipulated to yield finally a power series expansion of each $W^{(n)}$ in the charging parameter ξ_j for one of the set $1 \dots n$ (we shall choose ξ_1). In order to do so, first rewrite the total potential V_N in the form,

$$\begin{aligned} V_N(1 \dots N; \xi_1) &= \xi_1[V^{(1,e)}(1) + \sum_{j=2}^n \xi_j V^{(2,e)}(1j) + V_{1,N-n}^{(2,e)}] \\ &\quad + V_N(1 \dots N; \xi_1=0), \\ V_{1,N-n}^{(2,e)} &= \sum_{k=n+1}^N \xi_k V^{(2,e)}(1k), \end{aligned} \tag{10}$$

which specifically emphasizes the dependence of this quantity on the charge of particle 1. If (10) is inserted in (5), the correlation functions may be transformed to $g_{\alpha \dots \nu}^{(n)}(1 \dots n; \xi_1) = \exp\{-\beta W_{\alpha \dots \nu}^{(n)}(1 \dots n; \xi_1=0)$

$$\begin{aligned} &-\beta \xi_1[V^{(1,e)}(1) + \sum_{j=2}^n \xi_j V^{(2,e)}(1j)] \rangle_{\xi_1=0^{(n)}} \\ &\times \frac{\langle \exp\{-\beta \xi_1 V_{1,N-n}^{(2,e)}\} \rangle_{\xi_1=0^{(n)}}}{\langle \exp\{-\beta \xi_1[V^{(1,e)}(1) + V_{1,N-n}^{(2,e)}]\} \rangle_{\xi_1=0^{(0)}}}. \end{aligned} \tag{11}$$

The angular brackets denote averages in a canonical ensemble in which particle 1 has been discharged (i.e., $\xi_1=0$),

$$\begin{aligned} \langle f \rangle_{\xi_1=0^{(i)}} &= \frac{\int \dots \int f \exp[-\beta V_N(\xi_1=0)] dv_{j+1} \dots dv_N}{\int \dots \int \exp[-\beta V_N(\xi_1=0)] dv_{j+1} \dots dv_N}. \end{aligned} \tag{12}$$

The process of removing, as in Eq. (12), the electrostatic charge from a single ion in an electrolyte has no physically operational meaning. From the standpoint of the correlation functions $g^{(n)}$, it is often con-

venient to regard a discharged ion as corresponding qualitatively to a noble gas atom (isoelectronic with the original ion) dissolved in the electrolyte. Since a discharged ion can interact with the electrode and other ions only through the short-range functions $V^{(1,e)}(\mathbf{r}_1)$ and $V^{(2,e)}(r_{12})$, the correlation functions $g_{\alpha}^{(1)}(\mathbf{r}_1; \xi_1=0)$ and $g_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \xi_1=0)$ can differ significantly from unity only when x_1 and r_{12} are small enough to bring these potentials into play. This behavior contrasts sharply with the correlations acting between fully charged ions, which extend over many molecular diameters on account of the long-range nature of electrostatic forces.

By taking logarithms in (11), and expanding the averaged exponential functions, the n th order potential of mean force becomes expressed as a contribution remaining when ion 1 is discharged, plus correction terms, which may be exhibited as the desired power series,

$$\begin{aligned} W_{\alpha \dots \nu}^{(n)}(1 \dots n; \xi_1) &= W_{\alpha \dots \nu}^{(n)}(1 \dots n; \xi_1=0) + \xi_1[V^{(1,e)}(1) + \sum_{j=2}^n \xi_j V^{(2,e)}(1j)] \\ &\quad - \beta^{-1} \log \left[\sum_{s=0}^{\infty} \frac{(-\beta \xi_1)^s}{s!} M_s \right] + \beta^{-1} \log \left[\sum_{s=1}^{\infty} \frac{(-\beta \xi_1)^s}{s!} \bar{M}_s \right] \\ &= W_{\alpha \dots \nu}^{(n)}(1 \dots n; \xi_1=0) + \xi_1[V^{(1,e)}(1) + \sum_{j=2}^n \xi_j V^{(2,e)}(1j)] \\ &\quad + \sum_{s=1}^{\infty} \frac{(-\beta)^{s-1}}{s!} [\Lambda_s(1 \dots n) - \bar{\Lambda}_s] \xi_1^s. \end{aligned} \tag{13}$$

M_s and \bar{M}_s are moments of the electrostatic interactions involving particle 1

$$\begin{aligned} M_s &= \langle [V_{1,N-n}^{(2,e)}]^s \rangle_{\xi_1=0^{(n)}}, \\ \bar{M}_s &= \langle [V_{1,N-n}^{(2,e)} + V^{(1,e)}(1)]^s \rangle_{\xi_1=0^{(0)}}, \end{aligned} \tag{14}$$

and are related to the cumulants $\Lambda_s, \bar{\Lambda}_s$ by the relations¹⁰

$$\begin{aligned} M_s &= \sum_{r=1}^s \binom{s-1}{r-1} \Lambda_r M_{s-r}, \\ \bar{M}_s &= \sum_{r=1}^s \binom{s-1}{r-1} \bar{\Lambda}_r \bar{M}_{s-r}, \\ M_0 &= \bar{M}_0 = 1. \end{aligned} \tag{15}$$

On solving for the cumulants, one easily finds:

$$\begin{aligned} \Lambda_1 &= M_1, \\ \Lambda_2 &= M_2 - (M_1)^2, \\ \Lambda_3 &= M_3 - 3M_2M_1 + 2(M_1)^3, \\ \Lambda_4 &= M_4 - 4M_3M_1 - 3(M_2)^2 + 12M_2(M_1)^2 - 6(M_1)^4; \end{aligned} \tag{16}$$

¹⁰ H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, New Jersey, 1946), p. 185.

precisely the same relations (16) hold for the barred quantities.

The power series (13) allows one, at least in principle, to compute each n th order potential of mean force in ascending orders of ionic charge. In practice, the integral equations arising in this task require knowledge of higher order W 's, and so in this sense are coupled to each other in complicated fashion. The following section proposes a scheme for circumventing some of these difficulties.

III. APPROXIMATE DOUBLE-LAYER IONIC DISTRIBUTIONS

Having outlined the general moment method for ionic correlations, we now proceed to apply these ideas specifically to the diffuse double layer region. The terms of increasing ξ_1 order in the complete expansion (13) rapidly become more and more complicated to evaluate, even for the single-particle distributions. We shall adopt the viewpoint, for the present, that retention of only those terms linear in ξ_1 will yield a sufficiently accurate description of the double layer.¹¹ In the interests of concreteness, furthermore, the electrolyte (chosen to be a single component salt solution) will be described as consisting of uniformly charged, spherically symmetric particles which are suspended in a dielectric continuum. The ions (anions and cations may have different short-range forces) can penetrate neither one another extensively on account of strong core repulsions, nor can they penetrate the planar electrode appreciably. The latter will act essentially as a rigid charged "wall," and for convenience the coordinate system may be chosen to locate it near $x=0$.¹²

It is a fairly simple matter to include the molecular nature of the solvent medium in the following development if these latter particles interact with central forces. However, the results of this generalization differ only slightly from those to be obtained with the dielectric continuum, and hence do not seem to merit the extra notational complication. Attention, then, will be focused only on particles of ionic nature, and since we wish to consider only a single electrolyte, the relevant charge parameters ξ_1 can assume only two values, ξ_+ (cations) and ξ_- (anions).

In the linear ξ_1 approximation, the singlet potentials of mean force are written

$$W_\alpha^{(1)}(\mathbf{r}_1; \xi_1) = W_\alpha^{(1)}(\mathbf{r}_1; \xi_1 = 0) + \xi_1 [V^{(1,e)}(x_1) + \langle V_{1,N-1}^{(2,e)} \rangle_{\xi_1=0}^{(1)} - \langle V_{1,N-1}^{(2,e)} + V^{(1,e)}(1) \rangle_{\xi_1=0}^{(0)}], \quad \alpha = +, - \quad (17)$$

¹¹ Reference to Eqs. (13) shows immediately that this approximation is equivalent to replacing the moments M_s and \bar{M}_s by $(M_1)^s$ and $(\bar{M}_1)^s$.

¹² The exact position of the electrode is not critical; we wish only to imply here that for x decreasing through zero, the short-range electrode potential $V^{(1,e)}(x)$ becomes rapidly very large (strong repulsion).

As anticipated earlier, the additive constant A has no effect on these expressions for the $W_\alpha^{(1)}$; it cancels in the combination

$$V^{(1,e)}(x_1) - \langle V^{(1,e)}(1) \rangle_{\xi_1=0}^{(0)}. \quad (18)$$

One may immediately make certain simplifying observations concerning relations (17). Because of the symmetry of our problem about the electrode normal direction, the singlet mean-force potentials $W_\alpha^{(1)}$ will depend only on the x_1 coordinate, as do $V^{(1,e)}$ and $V^{(1,e)}$. In addition, the second of the two average value quantities in (17) is just a constant, independent of \mathbf{r}_1 . In view of the fact that the electrostatic potential $V^{(1,e)}$ is a simple linear function of x_1 , a considerable reduction in complexity is achieved by performing a twofold x_1 differentiation on both members of (17)

$$d^2\phi_\alpha(x_1)/dx_1^2 = (D/2\pi e\sigma) (d^2/dx_1^2) \langle V_{1,N-1}^{(2,e)} \rangle_{\xi_1=0}^{(1)}. \quad (19)$$

ϕ_α is a reduced electrostatic single-particle average potential for the species α ,

$$W_\alpha^{(1)}(x_1; \xi_1) - W_\alpha^{(1)}(x_1; 0) = (2\pi e\sigma \xi_\alpha / D) \phi_\alpha(x_1). \quad (20)$$

The quantities ϕ_α therefore carry the long-range electrostatic correlation of the diffuse double layer.

By utilizing the definitions (5), the averaged potential remaining in Eq. (19) may be expressed in terms of the singlet and pair correlation functions for the discharged particle 1

$$\frac{d^2\phi_\alpha(x_1)}{dx_1^2} = \frac{e}{2\pi\sigma} \frac{d^2}{dx_1^2} \int \frac{d\mathbf{r}_2}{r_{12}} \left[c_+ \xi_+ \frac{g_{\alpha+}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; 0)}{g_\alpha^{(1)}(x_1; 0)} + c_- \xi_- \frac{g_{\alpha-}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; 0)}{g_\alpha^{(1)}(x_1; 0)} \right]. \quad (21)$$

The integration in this last expression is over all configurations \mathbf{r}_2 of a second ion inside the containing volume v .

When x_1 is sufficiently large, the $g_\alpha^{(1)}(\mathbf{r}_1; 0)$ do not differ sensibly from unity, and the pair correlations $g_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; 0)$ may be replaced by the product of a bulk pair correlation, and the long-range singlet correlation for charged ion 2,

$$g_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2; 0) \rightarrow g_{\alpha\beta}^{(2,b)}(r_{12}; 0) g_\beta^{(1)}(x_2). \quad (22)$$

This replacement is the analog, for the double-layer theory, of the superposition approximation used extensively in the molecular theory of bulk liquids. For the present purposes, it should be noted we find it necessary to use (22) only for large x_1 , rather than over the entire range of values for this variable.

In view of the reduction (22), one is led to the integrodifferential equation, valid if x_1 is not too small,

$$d^2\phi_\alpha(x_1)/dx_1^2 = (e/2\pi\sigma)[d^2I(x_1)/dx_1^2],$$

$$I(x_1) = \int_V (d\mathbf{r}_2/r_{12}) [c_+\xi_+g_{\alpha+}^{(2,b)}(r_{12}; 0)g_+^{(1)}(x_2) + c_-\xi_-g_{\alpha-}^{(2,b)}(r_{12}; 0)g_-^{(1)}(x_2)]. \quad (23)$$

Three contributions to $I(x_1)$ may be distinguished:

$$I(x_1) = I_1(x_1) + I_2(x_1) + I_3(x_1),$$

$$I_1(x_1) = \int_V (d\mathbf{r}_2/r_{12}) \{c_+\xi_+g_{\alpha+}^{(2,b)}(r_{12}; 0) \times [g_+^{(1)}(x_2) - 1 + (2\pi\sigma e\xi_+/DkT)\phi_+(x_2)] + c_-\xi_-g_{\alpha-}^{(2,b)}(r_{12}; 0) \times [g_-^{(1)}(x_2) - 1 + (2\pi\sigma e\xi_-/DkT)\phi_-(x_2)]\},$$

$$I_2(x_1) = \int_V (d\mathbf{r}_2/r_{12}) [c_+\xi_+g_{\alpha+}^{(2,b)}(r_{12}; 0) + c_-\xi_-g_{\alpha-}^{(2,b)}(r_{12}; 0)],$$

$$I_3(x_1) = -(2\pi\sigma e/DkT) \int_V (d\mathbf{r}_2/r_{12}) \times [c_+\xi_+^2g_{\alpha+}^{(2,b)}(r_{12}; 0)\phi_+(x_2) + c_-\xi_-^2g_{\alpha-}^{(2,b)}(r_{12}; 0)\phi_-(x_2)]. \quad (24)$$

The square-bracketed quantities in I_1 represent the nonlinear (in the ϕ_α) portions of the singlet correlations in the double layer, as well as the nonelectrostatic ($\xi_2=0$) correlation; these differ significantly from zero only in the immediate vicinity of the electrode. When x_1 is large, therefore, the only contribution to the integral I_1 occurs when r_{12} is large, so that each $g_{\alpha\beta}^{(2,b)}(r_{12}; 0)$ is essentially just unity. As a result, then, $I_1(x_1)$ represents (for x_1 large) the potential energy of a uniform and somewhat diffuse sheet of charge density $\rho^*(\mathbf{r}_2)$,

$$\rho^*(\mathbf{r}_2) = c_+\xi_+[g_+^{(1)}(x_2) - 1 + (2\pi\sigma e\xi_+/DkT)\phi_+(x_2)] + c_-\xi_-[g_-^{(1)}(x_2) - 1 + (2\pi\sigma e\xi_-/DkT)\phi_-(x_2)]. \quad (25)$$

This amounts to concluding that $I_1(x_1)$ is asymptotically a linear function of x_1 similar to (3).

Since the pair correlations $g_{\alpha\beta}^{(2,b)}(r_{12}; 0)$ settle down rapidly to unity, the integrand of $I_2(x_1)$ differs from zero only when particle 2 is near 1. As a result, again valid for large x_1 , the \mathbf{r}_2 integration may be extended over all space. It is established therefore that $I_2(x_1)$ is asymptotically constant.

On account of the double x_1 differentiation in Eq. (23), only $I_3(x_1)$ will survive in the large x_1 limit. After performing the requisite differentiations, and carrying out integrations parallel to the electrode surface, the ϕ_α are found asymptotically to satisfy

linear homogeneous integrodifferential equations

$$d^2\phi_\alpha(x_1)/dx_1^2 = \frac{1}{2} \int_0^\infty [\kappa_+^2 k_{\alpha+}(x_1-x_2)\phi_+(x_2) + \kappa_-^2 k_{\alpha-}(x_1-x_2)\phi_-(x_2)] dx_2, \\ k_{\alpha\beta}(x_1-x_2) = (d/dx_1)g_{\alpha\beta}^{(2,b)}(x_1-x_2; 0), \\ \kappa_\alpha^2 = 4\pi c_\alpha(\xi_\alpha e)^2/DkT. \quad (26)$$

In the large x_1 region, (26) is entirely independent of the lower x_2 integration limit, since the $k_{\alpha\beta}$ decay rapidly to zero. The origin has been chosen as this lower limit, since it has been made roughly to coincide with the electrode surface. The pair correlation functions $g_{\alpha\beta}^{(2,b)}$ have been defined in (26) as odd functions of their distance variable, so that the kernels $k_{\alpha\beta}$ are even. The well-known Debye-Hückel parameter κ , appropriate to our electrolytic fluid, is related to κ_+ and κ_- by

$$\kappa^2 = \kappa_+^2 + \kappa_-^2. \quad (27)$$

Since Eqs. (26) were derived under the supposition that x_1 was not small, the ϕ_α can be given exactly over the entire range $0 \leq x_1 < \infty$ by adding suitable inhomogeneous functions h_α to (26),

$$d^2\phi_\alpha(x_1)/dx_1^2 = h_\alpha(x_1) + \frac{1}{2} \int_0^\infty [\kappa_+^2 k_{\alpha+}(x_1-x_2)\phi_+(x_2) + \kappa_-^2 k_{\alpha-}(x_1-x_2)\phi_-(x_2)] dx_2. \quad (28)$$

The h_α are essentially designed to correct for the fact that the local density of β ions, in the environment of a discharged α ion at \mathbf{r}_1 near the electrode, is not precisely given by the expression

$$c_\beta g_{\alpha\beta}^{(2,b)}(r_{12}; 0) [1 - (2\pi\sigma e\xi_\beta/DkT)\phi_\beta(x_2)]. \quad (29)$$

It is of course necessary only that each h_α differ from zero near $x_1=0$, since outside this small region (26) and (28) are identical. These inhomogeneous functions contain contributions arising through short-range force electrode interface correlations, through deviations from superposability of the actual pair function $g_{\alpha\beta}^{(2)}$ near the electrode [in terms of the approximation $g_{\alpha\beta}^{(2,b)}(r_{12})g_{\alpha}^{(1)}(x_1)g_{\beta}^{(1)}(x_2)$], and finally through the nonlinear ϕ_α terms neglected in the integral $I_1(x_1)$.

It is rather instructive to examine the form of Eqs. (28) under a simplifying assumption regarding the bulk correlations $g_{\alpha\beta}^{(2,b)}(r_{12}; 0)$. In particular, suppose that each pair of ions, one of which is discharged, will be correlated only to the extent of exhibiting a sphere of exclusion, or impenetrability, of radius a (the same for all pairs). Accordingly,

$$g_{\alpha\beta}^{(2,b)}(r_{12}; 0) = 0 \quad 0 \leq r_{12} \leq a, \\ = 1 \quad r_{12} > a. \quad (30)$$

Since the derivative of this unit step is a Dirac delta

function, the kernels all have the common form

$$k_{\alpha\beta}(x) = \delta(x+a) + \delta(x-a). \tag{31}$$

Now when $x_1 > a$, the integral in (28) is trivial, and leads to a differential-difference equation satisfied by ϕ_α ,

$$d^2\phi_\alpha(x_1)/dx_1^2 = h_\alpha(x_1) + \frac{1}{2}\{\kappa_+^2[\phi_+(x_1+a) + \phi_+(x_1-a)] + \kappa_-^2[\phi_-(x_1+a) + \phi_-(x_1-a)]\}. \tag{32}$$

If the ionic diameter a is allowed now to vanish, ϕ_+ and ϕ_- satisfy the same second-order differential equation for x_1 sufficiently large. Since the difference $\phi_+ - \phi_-$ tends to zero as x_1 increases, both ϕ_+ and ϕ_- must asymptotically be equal to $\exp(-\kappa x_1)$ times a common constant. These rather naive assumptions therefore lead to the exponential decay solutions characteristic of the Poisson-Boltzmann theory. It will become apparent in the following section that retention of a finite ion size, even by means of the rather crude postulate (30), gives rise to solutions ϕ_α , and hence singlet correlations, which are qualitatively different from this monotonic decay function.

The pair of linear coupled Eqs. (28) may be formally solved by standard integral transform methods. It is desirable for this purpose to extend the definition of $\phi_\alpha(x_1)$ to negative x_1 , as the solution of (28) for these values of the variable; we set $h_\alpha(x_1)$ identically equal to zero on the negative axis. The functions $\phi_\alpha(x_1)$ may now be separated into two parts, $\phi_\alpha^{(n)}(x_1)$ and $\phi_\alpha^{(p)}(x_1)$, which are the negative axis, and positive axis parts of ϕ_α , respectively,

$$\begin{aligned} \phi_\alpha(x_1) &= \phi_\alpha^{(n)}(x_1) + \phi_\alpha^{(p)}(x_1), \\ \phi_\alpha^{(p)}(x_1) &= 0 \quad x_1 < 0, \\ \phi_\alpha^{(n)}(x_1) &= 0 \quad x_1 > 0. \end{aligned} \tag{33}$$

As a consequence, (28) is equivalent to

$$\begin{aligned} (d^2/dx_1^2)[\phi_\alpha^{(n)}(x_1) + \phi_\alpha^{(p)}(x_1)] \\ = h_\alpha(x_1) + \frac{1}{2} \int_{-\infty}^{+\infty} [\kappa_+^2 k_{\alpha+}(x_1-x_2) \phi_+^{(p)}(x_2) \\ + \kappa_-^2 k_{\alpha-}(x_1-x_2) \phi_-^{(p)}(x_2)] dx_2. \end{aligned} \tag{34}$$

In Fourier transform space, the integral equations (34) become a pair of simultaneous linear algebraic equations whose solution is elementary:

$$\begin{aligned} \Phi_+^{(p)}(z) \\ = 1/D(z) \begin{vmatrix} -H_+(z) - z^2\Phi_+^{(n)}(z) & \frac{1}{2}\kappa_-^2 K_{+-}(z) \\ -H_-(z) - z^2\Phi_-^{(n)}(z) & z^2 + \frac{1}{2}\kappa_-^2 K_{--}(z) \end{vmatrix}, \\ \Phi_-^{(p)}(z) \\ = 1/D(z) \begin{vmatrix} z^2 + \frac{1}{2}\kappa_+^2 K_{++}(z) & -H_+(z) - z^2\Phi_+^{(n)}(z) \\ \frac{1}{2}\kappa_+^2 K_{-+}(z) & -H_-(z) - z^2\Phi_-^{(n)}(z) \end{vmatrix}; \end{aligned} \tag{35}$$

$$D(z) = \begin{vmatrix} z^2 + \frac{1}{2}\kappa_+^2 K_{++}(z) & \frac{1}{2}\kappa_-^2 K_{+-}(z) \\ \frac{1}{2}\kappa_+^2 K_{-+}(z) & z^2 + \frac{1}{2}\kappa_-^2 K_{--}(z) \end{vmatrix}; \tag{36}$$

$$[\Phi_\alpha^{(\mu)}(z), H_\alpha(z), K_{\alpha\beta}(z)]$$

$$= \int_{-\infty}^{+\infty} \exp(izx) [\phi_\alpha^{(\mu)}(x), h_\alpha(x), k_{\alpha\beta}(x)] dx,$$

$$\alpha, \beta = +, -, \quad \mu = n, p.$$

The inversion integrals are

$$\phi_\alpha^{(p)}(x_1) = (1/2\pi) \int_{-\infty}^{+\infty} \exp(-ix_1z) \Phi_\alpha^{(p)}(z) dz, \tag{37}$$

where the results (35) are to be inserted for $\Phi_\alpha^{(p)}(z)$. The contour of integration for (37), when x_1 is positive, may be closed along the infinite, lower half-plane semicircle; subsequently, $\phi_\alpha(x_1)$ may be evaluated in terms of the poles z_j of the transform $\Phi_\alpha^{(p)}(z)$, lying below the real axis

$$\phi_\alpha(x_1) = \sum_{j=1}^{\infty} A_{j,\alpha} \exp(-iz_j x_1). \tag{38}$$

The multiplicative constants $A_{j,\alpha}$ are related in the usual way to the residues at these poles

$$A_{j,\alpha} = i \lim_{z \rightarrow z_j} [(z - z_j) \Phi_\alpha^{(p)}(z)]. \tag{39}$$

These constants must naturally be such to make ϕ_+ and ϕ_- real functions of the real variable x_1 .

Computation of the $A_{j,\alpha}$ by (39) clearly requires knowledge of $\Phi_\alpha^{(n)}(z)$. This transform must have the property of making the inversion integral (37) vanish identically for every negative x_1 . In practical cases, this condition may be met in either of two ways. If only a finite number m of terms in the entire series (38) would suffice to provide an adequate description of the double layer structure, each of the two integrals (37) could be equated to zero for m distinct negative values of x_1 , to provide a sufficient number of conditions for unique determination of the coefficients. Alternatively, (37) may be cast in the role of a pair of coupled integral equations on the negative axis for complete determination of the $\phi_\alpha^{(n)}(x_1)$; these solutions in turn would provide the entire set of $A_{j,\alpha}$ through (35) and (39).¹³

It should be remarked that the poles z_j may in general arise either as roots of the denominator $D(z)$, or as poles of the $K_{\alpha\beta}(z)$ or $H_\alpha(z)$ occurring in the determinantal numerators of (35). Since $\phi_\alpha^{(n)}(x_1)$ decays rapidly to zero with decreasing x_1 on the negative axis, the transforms $\Phi_\alpha^{(n)}(z)$ cannot have poles in the lower-half z plane; therefore, these two functions are effective only in determining the exact values of the multiplicative constants $A_{j,\alpha}$, rather than in providing z_j 's

¹³ The use of these integral equations actually corresponds to allowing m to increase to infinity.

for the solution (38). Furthermore, it should be noted at this juncture that since the $h_\alpha(x_1)$ decay rapidly to zero on the positive axis, the set of z_j contributed as poles of the $H_\alpha(z)$ lie well below the real axis; the corresponding terms in $\phi_\alpha(x_1)$ therefore themselves decay very rapidly with increasing x_1 .

If all of the kernels $k_{\alpha\beta}(x_1)$ as well as the inhomogeneous functions $h_\alpha(x_1)$ were zero for all x_1 greater than some fixed positive constant, then the transforms $K_{\alpha\beta}$ and H_α would be analytic in the entire z plane. As a result, each z_j would necessarily be a root,

$$D(z_j) = 0. \tag{40}$$

The series expressions (38) for ϕ_+ and ϕ_- under these circumstances would differ only insofar as the exact numerical values of the coefficients $A_{j,\alpha}$ are concerned, since the same exponential functions must appear for both anions and cations.

IV. SIMPLIFIED RIGID-SPHERE MODEL

To clarify the way in which the formalism of the preceding sections leads to predictions concerning the detailed nature of the double layer, we are now in a position to deduce the properties of a simple, though informative, model. We choose to investigate that system of equal-sized rigid spherical ions which led to the differential-difference Eqs. (32). For the sake of simplicity also, we shall wish to disregard the effect of the inhomogeneous functions $h_\alpha(x_1)$; it has already been noted in this connection that such an assumption can have no effect on the asymptotic (large x_1) equations determining the ionic distributions. The non-electrostatic effect of the planar electrode may be taken as that of a completely impenetrable "wall." By locating the surface of this wall at $x_1 = -a/2$ (a distance from the origin equal to the ion radii), the single particle potentials $V_\alpha^{(1,s)}$ are just

$$V_\alpha^{(1,s)}(x_1) = +\infty \quad x_1 \leq 0, \\ = 0 \quad x_1 > 0. \tag{41}$$

On account of the pair correlations (30) being identical for any species pair, we have already emphasized that the kernels $k_{\alpha\beta}$ are identical, as indicated by Eq. (31). As a result of the foregoing idealizations, one has to deal with only a single homogeneous integro-differential equation,

$$d^2\phi(x_1)/dx_1^2 = \frac{1}{2}\kappa^2 \int_0^\infty k(x_1-x_2)\phi(x_2)dx_2, \\ \phi_+(x_1) = \phi_-(x_1) = \phi(x_1), \quad k_{\alpha\beta}(x) = k(x). \tag{42}$$

The unpretentious double-layer picture described by the solution of (42) is probably a reasonable approximation to the actual physical state of affairs if the density of ion spheres is not too near the close-packed density; i.e.,

$$c_+ + c_- \ll 2^{\frac{1}{2}} a^{-3}. \tag{43}$$

The inversion integral for the solution to (42) may now be written down with the help of Eqs. (35)–(37)

$$\phi(x_1) = - (1/2\pi) \int_{-\infty}^{+\infty} \frac{\exp(-ix_1z)\Phi^{(n)}(z)}{z^2 + \kappa^2 \cos(az)} dz \quad (x_1 > 0) \\ = \sum_{j=1}^{\infty} A_j \exp(-iz_jx). \tag{44}$$

In accordance with previous remarks, the z_j are precisely the roots of the transcendental equation

$$z^2 + \kappa^2 \cos(az) = 0. \tag{45}$$

Consequently, the constants A_j may be displayed as

$$A_j = - \frac{iz_j^2 \Phi^{(n)}(z_j)}{2z_j - \kappa^2 a \sin(az_j)}. \tag{46}$$

For small values of the dimensionless parameter κa , the transcendental Eq. (45) has two roots $\pm z_1$, which may be expanded about $\kappa a = 0$

$$y_j = ia z_j, \\ y_1 = \kappa a [1 + \frac{1}{4}(\kappa a)^2 + \frac{1}{96}(\kappa a)^4 + \frac{2}{15}(\kappa a)^6 + \dots]. \tag{47}$$

The leading term in the series (44) corresponding to the root $+z_1$ produces a $\phi(x_1)$ of the form

$$\phi(x_1) \sim \exp(-\kappa x_1) \tag{48}$$

in the limit of zero electrolyte concentration. It is in this manner that the predictions of the linear Poisson-Boltzmann equation of the Debye-Hückel electrolyte theory are verified, even for finite ion sizes. It is possible to show that this result is in no way dependent upon the special form of the short-range ion-ion forces chosen for our simple model.

There is a second pair of pure imaginary roots $\pm z_2$ which, again for κa sufficiently small, may be represented by an asymptotic series

$$y_2 = \log[2/(\kappa a)^2] + 2 \log \log[2/(\kappa a)^2] + \dots \tag{49}$$

It is evident that in dilute solutions, the z_2 contribution to $\phi(x_1)$ damps to zero extremely fast.

The remaining roots of (45) in the small κa region are all complex, and occur in quadruples

$$y_j = \pm \alpha_j \pm i\beta_j. \tag{50}$$

Numerical analysis shows that as κa increases from zero, the roots z_1 and z_2 move toward each other on the negative imaginary axis. They finally merge at $\kappa a = 1.03$, and thereupon move away from the imaginary axis as complex conjugates. The values of the roots nearest the origin $z=0$ are exhibited in Table I for selected values of κa .

Even if only the first two terms in the complete sum (44) corresponding to z_1 and z_2 are retained as an approximation to the actual statistical state, it is clear that the ion size, or excluded volume, is capable of exerting a profound influence upon the charge density

in the double layer. Although for small κa , in this two-term approximation, ϕ is a sum of damped exponentials,

$$\phi(x_1) = A_1 \exp[-\gamma_1(x_1/a)] + A_2 \exp[-\gamma_2(x_1/a)], \quad (51)$$

this sum becomes a damped sinusoid when $\kappa a > 1.03$, and γ_1 and γ_2 are complex conjugates. On account of the resultant sign changes in ϕ , the average double-layer charge density likewise alternates in sign. This behavior denotes, in an average sense, that planar layers of anions and cations are held against, and parallel to, the electrode surface. This local structure is somewhat similar to the situation in ionic crystals where also alternate planes of positive and negative ions are encountered.

A detailed study of even the two roots z_1 and z_2 alone therefore provides insight into the transition from very dilute solutions, where the distribution of ions may be deduced from consideration of electrostatic forces alone, to concentrated solutions in which short-range forces are important. These latter begin to cause interference between the ions at moderate density, and to relieve this situation, the ions must begin to settle into locally ordered arrangements, the extreme case of which would be the long-range regularity of the ionic crystal. Only for very low electrolyte concentrations, therefore, is it reasonable to neglect exclusion volumes in deducing double layer structures.

The special kernel (31) gives the functional Eq. (42) for $\phi(x_1)$ three distinct forms in three different intervals

$$\begin{aligned} d^2\phi(x_1)/dx_1^2 &= 0 & x_1 < -a, \\ &= \frac{1}{2}\kappa^2\phi(x_1+a) & -a < x_1 < a, \\ &= \frac{1}{2}\kappa^2[\phi(x_1-a) + \phi(x_1+a)] & x_1 > a. \end{aligned} \quad (52)$$

In the first of these intervals, ϕ obviously must be the linear function

$$\phi(x_1) = B_1x_1 + B_0 \quad x_1 < -a, \quad (53)$$

with the constants B_1 and B_0 having values to provide a smooth fit onto $\phi(x_1)$ for $x_1 > -a$. Repeated use of (52) shows that ϕ has simple discontinuities in its second derivative at $-a$ and $+a$, in its fourth derivative at 0 and $2a$, and in the $2n$ th derivative ($n > 2$) at na . This series of discontinuities propagated down the x_1 axis arises solely by use of singular short-range ion interactions, and has no fundamental physical basis. It is of course possible to eliminate them by using differentiable functions $V_a^{(1,\phi)}$ and $V_a^{(2,\phi)}$.

A single restriction to which the constants A_j must conform is provided by the double layer electroneutrality condition (8). One might attempt further to determine the A_j for the present model by substitution into the integrodifferential equation (42), or equivalently, into the relations (52). When $x_1 > a$, no information is provided since each member of the sum (44) separately satisfies the condition imposed. However, the set of admissible values A_j is restricted by insisting that (44) satisfy (42) or (52) in the interval

TABLE I. Roots of the transcendental equation $y^2 - (\kappa a)^2 \cosh y = 0$ near $y=0$ in the complex plane; $y_j = \alpha_j + i\beta_j$.

κa	α_1	β_1	α_2	β_2	α_3, α_4	$\beta_3, -\beta_4$
0.100	0.100	0	9.88	0	11.11	14.42
0.500	0.536	0	5.48	0	7.70	14.75
0.900	1.22	0	3.28	0	6.48	14.89
1.00	1.62	0	2.56	0	6.26	14.90
1.03	2.07	0	2.07	0	6.19	14.91
1.06	2.03	0.45	2.03	-0.45	6.14	14.93
1.15	1.92	0.89	1.92	-0.89	5.97	14.95
1.50	1.53	1.62	1.53	-1.62	5.43	15.02
2.00	1.06	2.08	1.06	-2.08	4.84	15.07

$-a < x_1 < a$. Demanding that $\phi(x_1)$ be a solution for this entire finite interval provides sufficient constraint to fix all the A_j . This finite interval procedure has a distinct advantage over the more general integral equation subsidiary problem of Sec. III, in which case the function $\phi_a^{(n)}$ would have to be determined over the entire negative axis, $x_1 < 0$.¹⁴

For the purposes of numerical computation, the two term representation (51) of $\phi(x_1)$ discussed previously, will suffice. Since the terms to be neglected correspond to z_j 's with large negative imaginary parts, the predicted ion distributions will be in error only very near the electrode.

If the electrode surface charge is not too large, the double-layer electroneutrality condition adapted to the present example may be linearized with respect to ϕ to yield

$$2/\kappa^2 = \int_0^\infty \phi(x_1) dx_1. \quad (54)$$

The corresponding linearized result for the ζ potential, as expressed in (9) for $x=0$, becomes

$$\zeta(\sigma) = (2\pi\kappa^2\sigma/D) \int_0^\infty x_1\phi(x_1) dx_1. \quad (55)$$

The second condition on A_1 and A_2 in (51) to be utilized simultaneously with condition (54) results from the demand that the second of Eqs. (52) be satisfied at $x_1=0$,

$$d^2\phi(x_1=0)/dx_1^2 = \frac{1}{2}\kappa^2\phi(x_1=a); \quad (56)$$

this is precisely the center of the interval over which the second form in (52) is valid.

When the two term approximation (51) is inserted in each of (54) and (56), there is obtained a pair of independent linear equations in A_1 and A_2 . One thus readily finds

$$\begin{aligned} A_1 &= [2a/(\kappa a)^2] y_1 y_2 \left[\frac{\exp y_2}{y_2 \exp y_2 - y_1 \exp y_1} \right], \\ A_2 &= [2a/(\kappa a)^2] y_1 y_2 \left[-\frac{\exp y_1}{y_2 \exp y_2 - y_1 \exp y_1} \right]. \end{aligned} \quad (57)$$

¹⁴ Such simplification was inherent in the rigid-sphere model by using step-function pair correlations.

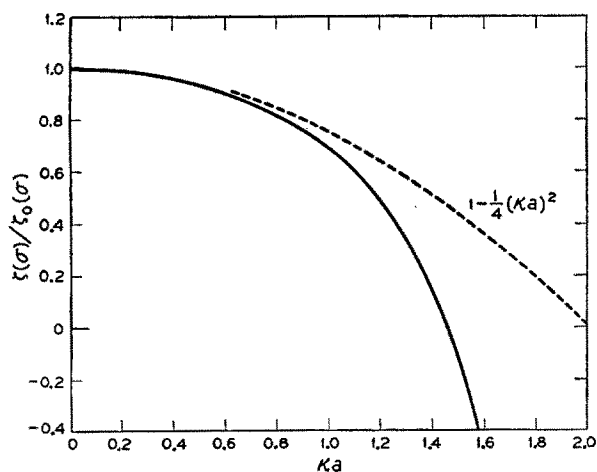


FIG. 1. Computed values of the ζ potential ratio (solid line), with the limiting parabolic behavior (dotted line) shown explicitly.

The results (57) reduce to

$$A_1 = 2/\kappa, \quad A_2 = 0, \quad (58)$$

as κa approaches zero, to yield the correct Debye-Hückel result anticipated earlier:

$$\phi_0(x_1) = (2/\kappa) \exp(-\kappa x_1). \quad (59)$$

The ζ potential predicted on the basis of (59) follows from (55)

$$\zeta_0(\sigma) = 4\pi\sigma/\kappa\hat{D}, \quad (60)$$

a well-known result.

The ζ potential for finite κa may be exhibited in the following reduced form:

$$\zeta(\sigma)/\zeta_0(\sigma) = (\kappa a/y_1) \left[\frac{1 - (y_1/y_2)^2 \exp(y_1 - y_2)}{1 - (y_1/y_2) \exp(y_1 - y_2)} \right]. \quad (61)$$

Reference to the asymptotes (47) and (49) for y_1 and y_2 show that the lowest order deviation (in κa) from ζ_0 is in the direction of decreasing ζ potential. In particular,

$$\zeta(\sigma)/\zeta_0(\sigma) = 1 - \frac{1}{4}(\kappa a)^2, \quad \kappa a \ll 1. \quad (62)$$

As noted earlier, y_1 and y_2 have a common value when $\kappa a = 1.03$. At this point, both A_1 and A_2 diverge, but ϕ in fact remains finite

$$\phi(x_1) = (c_1 x_1 + c_0) \exp[-y_1(x_1/a)], \quad \kappa a = 1.03. \quad (63)$$

Likewise, the ζ potential ratio as written in (61) is indeterminate, but may be properly evaluated as a limiting value as κa approaches 1.03 from either side.

When $\kappa a > 1.03$, the complex conjugates $y_1 = \alpha + i\beta$ and $y_2 = \alpha - i\beta$ yield the ratio,

$$\zeta(\sigma)/\zeta_0(\sigma) = \kappa a / (\alpha^2 + \beta^2) \left[\frac{(\alpha^2 - \beta^2) \sin\beta + 2\alpha\beta \cos\beta}{\alpha \sin\beta + \beta \cos\beta} \right]. \quad (64)$$

The ζ potential ratio has been computed on the basis of Eqs. (61) and (64) using the tabulated y_1 and y_2 values. The results are shown in Fig. 1. The low κa behavior is a parabolic decrease from unity in accord with (62). The ratio then decreases at an even more rapid rate, finally changing sign near $\kappa a = 1.46$.¹⁵ Since ζ_0 is always positive, therefore, we find that at a certain finite concentration, the ζ potential due to the diffuse Guoy layer (and, therefore, the Gouy layer reciprocal capacitance) becomes precisely zero. It is of interest to observe in addition that there is no break in the ζ potential curve at the singular value $\kappa a = 1.03$, although the nature of the mean charge density, ρ_{el} , changes rapidly there.

¹⁵ In water, at room temperature, this corresponds to about 0.8 moles/liter for a univalent electrolyte with a equal to 5×10^{-8} cm.