Statistical Mechanical Theory of Double-Layer Structure and Properties*

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The general cluster theory of inhomogeneous fluids is applied to the determination of ion and mean potential distributions in the interfacial region between electrolytic solutions and metallic electrodes (specifically mercury), as well as in colloidal suspensions. The relevant electrostatic problem involving distinct inner and outer Helmholtz regions is solved in closed form. Summation of the linearized cyclic clusters appropriate to dilute solutions demonstrates for the first time the limitations of local Debye–Hückel activity corrections in the method called "local thermodynamic balance." An explicit adsorption isotherm formalism results from proper treatment of cluster vertices confined to the inner Helmholtz plane; this permits proper deduction of the "discreteness-of-charge" effect, as well as nonelectrostatic ion size effects in this plane. It is furthermore shown that accounting for ion size to lowest order in the diffuse layer necessarily contradicts the local thermodynamic balance approach. The systematic cluster theory formulation of the colloid stability problem also suggests hitherto unused corrections to the relevant double-layer free energies.

I. INTRODUCTION

THE primary purpose of this paper is to show how the general cluster theory of fluids in external force fields may be applied to the molecular formulation of the electrical double-layer structure, and colloid stability problems. On the basis of the best currently available physical model, the unaveraged potential energy is calculated precisely, and in conjunction with the statistical mechanical formalism, it is utilized first in description of the outer Helmholtz region under dilute concentration conditions, and then to specification of the inner layer adsorption isotherm. These applications yield corrections to the intuitive classical equations, and provide criteria for the breakdown of local thermodynamic formulations.

The working equations derived below specify the diffuse charge layer structure at low electrolyte concentration, which is the only circumstance under which this region contributes substantially to measured differ-

ential capacitance, or to the relevant free energy of uncoagulated hydrophobic colloids. On the other hand, the description of the adsorbed layer in the inner Helmholtz region extends to high ambient electrolyte concentration, due to complete treatment of ion size effects, and the resulting adsorption isotherm should apply over a wide range of experimental conditions.

In view of the fact that substrate surfaces are regarded as smooth (i.e., no specific adsorption sites), and that definite inner and outer regions are distinguished, this work applies primarily to the water–mercury interface. One must of course bear in mind that this is experimentally the most intensively investigated case, but in principle our method can be extended to include models with specific adsorption sites.

The first object in the following text (Sec. II) involves examination of the electrostatic problem. We reiterate the basic notions of the "inner" and "outer" Helmholtz regions at the substrate–aqueous solution interface, and exhibit in closed Bessel integral form the electrostatic potentials of mean force (in pure solvent) induced by ions. We thereby avoid the necessity of working with multiple image sums.

In Sec. III, the two principal results of the inhomoge-

neous fluid cluster theory are recalled, which give the local singlet densities and osmotic pressure in terms of suitably defined generalizations of the Mayer irreducible cluster integrals of imperfect gas theory. In view of the now well-established fact that only cyclic diagrams linearized in the Coulomb interaction contribute to the dilute solution (Debye–Hückel) limit of both bulk[1] and interfacial[2] properties, the necessary reductions are performed on the singlet density expressions. It is then established that in the diffuse outer Helmholtz layer, the local Debye–Hückel activity corrections apply in this limit (to within negligible screened image potential terms) in spite of the fact that they fundamentally involve pair correlations over distances comparable to the diffuse layer thickness.

The phenomenon of inner-layer ion adsorption provides the subject of analysis in Sec. IV. A theory of the adsorption isotherm is developed from the same starting point as for the diffuse layer, but the spatial separation of inner and outer regions allows statistical decoupling of these two regions in all but a very simple way. Furthermore, the proximity of adsorbed ions to their own images allows once again electrostatic contributions to be treated as small perturbations, although the adsorbed assembly might even be near the close-packed condition. Using these reductions, the adsorption equations involve only knowledge of the equation of state and pair distribution functions for the two-dimensional system of completely discharged ions. The result exhibits the so-called "discreteness-of-charge" effect, often attributed ultimately to Frumkin.[3-6]

After having postulated in Sec. IV that short-range (nonelectrostatic) interactions may reasonably be disregarded between pairs of ions, one each in the inner and outer layers, we return in V to an examination of the role that these short-range forces have in determining the structure of the diffuse charge layer. It is shown that even in lowest order (beyond the limiting Debye–Hückel regime) that ion size destroys the locality property of activity corrections in the Prigogine method of local thermodynamic balance.[7] The necessary revision in this order is obtained explicitly.

The last section, VI, is devoted to the free-energy properties of double layers, which are especially important in questions of colloidal stability. The development hinges on use of the standard dilute solution version of the local osmotic pressure series. We reestablish the Verwey and Overbeek expression.[8] But

in addition it is demonstrated that local Debye–Hückel nonideality and screened image corrections may rigorously be applied (analogous to the activity and image corrections encountered in Sec. III), and the contribution of the adsorbed ions are related to the corresponding uncharged two-dimensional assembly spreading pressure and pair distribution.

II. ELECTROSTATICS

In order to explain features of differential capacitance curves for the mercury–aqueous solution interface, it has been suggested[9] that a layer of water molecules, with low effective dielectric constant, and a thickness comparable to molecular dimensions, is interposed between the surface of the metallic phase, and the bulk of the aqueous solution. The possibility that the permanent dipole orientation for these interfacial molecules may not be free to contribute to the dielectric response to an applied field is strongly suggested by large measured adsorption heats of water onto mercury.[10] Mott, Parsons, and Watts-Tobin[9] have pointed out that observed insensitivity of differential capacitance (for cathodic polarizations) to the nature of cations present may be understood by postulating that the solution-side boundary of this region, at which the dielectric constant suddenly rises to approximately the bulk water value, lies no farther from the mercury than the plane of closest approach of unadsorbed (hence fully hydrated) ions.

For the present calculations, we here adopt such a model of local dielectric behavior. Figure 1 shows, for the planar interface, that we consider there to be two planes of discontinuity in dielectric constant. The first, from which normal distances to the interface are measured, corresponds to the change from infinite dielectric constant in the mercury phase to a value K_0 within the inner region (numbered I) of water anomalously oriented next to the mercury. Subsequently, the dielectric constant is assumed to rise abruptly at $z=h_d$ to a larger value K equal to that appropriate to the interior of the solution phase.

Two other planes are shown in Fig. 1. In cases where specific adsorption of some ion (such as iodide) is known to occur, it is convenient to suppose that the strong bonds, whose existence is thus implied, between these ions and the mercury have very definite length, and thereby constrain the adsorbed ions to lie essentially with coplanar centers at z_a (often called the inner Helmholtz plane). Ions which either do not adsorb or are not adsorbed, on the other hand, strongly bind at least a single shell of water molecules. To retain an intact hydration sheath, these latter freely mobile ions could not possibly be as close to the mercury as z_a, but

[1] J. E. Mayer, J. Chem. Phys. **18**, 1426 (1950).
[2] F. P. Buff and F. H. Stillinger, J. Chem. Phys. **25**, 312 (1956).
[3] A. N. Frumkin, Usp. Khim. **4**, 938 (1935).
[4] O. A. Esin and B. F. Markov, Acta Physicochim. U.R.S.S. **10**, 353 (1939).
[5] O. A. Esin and V. Shikov, Zh. Fiz. Khim. **17**, 236 (1943).
[6] D. C. Grahame, Z. Elektrochem. **62**, 264 (1958).
[7] I. Prigogine, P. Mazur, and R. Defay, J. Chim. Phys. **50**, 146 (1953).
[8] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier Publishing Company, Inc., New York, 1948).

[9] N. F. Mott, R. Parsons, and R. J. Watts-Tobin, Phil. Mag. **7**, 483 (1962).
[10] C. Kemball, Proc. Roy. Soc. (London) **A190**, 117 (1947).

the closest available distance h_0 must amount roughly to the sum of the ion radius and water molecule diameter. Thus, the average charge density in the aqueous phase ($z>0$) can be nonvanishing only at $z=z_a$, and for z greater than h_0 (the outer Helmholtz plane).

As drawn in Fig. 1, $h_0>h_d$, and $h_d \cong 2z_a$, though the precise relations between these lengths are not subjects of investigation in this article. Proper answers to such detailed structural questions, as well as possible replacement of our dielectric discontinuity model, must await development of a reasonably convincing statistical mechanical theory of interfacial dielectric properties, possibly along the lines introduced by Kirkwood.[11] In any event, it is doubtful that even the most careful measurements of differential capacitance can distinguish any but the grossest of features of interfacial dielectric behavior, and for the present, our model should entirely suffice. We might remark here, however, that explicit electrostatic potential solutions analogous to those given below, can also be found for certain other dielectric constant distributions in the interfacial region.

The statistical mechanical theory in the next, and following, sections requires the electrostatic interactions of ions, regarded as point charges, when they are placed at arbitrary available positions: at z_a, or $z>h_0$. Kirkwood[12] recognized long ago that finite ion size gives rise to deviations from point-ion interactions, in a dielectric medium, but these deviations are significant only for relatively small separations between the ions. We simply absorb these contributions in the "short-range interactions."

The electrostatic potential $\psi(\mathbf{r})$ in the aqueous phase, for a fixed set of ion positions, arises from three sources. The first two are, respectively, the ions on the adsorption plane $z=z_a$ in Region I of low dielectric constant, and ions in Region II with high dielectric constant. The third is equivalent to specifying the boundary condition for the electrostatic problem to be solved, at $z=0$ and $z=\infty$. We suppose that

$$\psi(z=0)=A, \qquad (1)$$

where A is some constant (whose precise value has no bearing on double-layer structure), and that

$$\mathbf{N} \cdot \nabla \psi(\mathbf{r}) \sim -4\pi\sigma/K \qquad (2)$$

asymptotically as $z \to \infty$. Here, $\mathbf{N}$ is the unit vector in the z direction, and the constant σ is equal to the amount of charge that would have to be transferred (per unit area) between two initially shorted, identical planar electrodes, parallel to one another, to set up this second boundary condition in the intervening space.

The linearity of our electrostatic problem implies

that $\psi(\mathbf{r})$ may be expressed

$$\psi(\mathbf{r})=\psi^{(e)}(\mathbf{r})+\sum_{j=1}^{N_a}\psi^{(a)}(\mathbf{r},\mathbf{r}_j)+\sum_{j=1}^{N_d}\psi^{(d)}(\mathbf{r},\mathbf{r}_j). \qquad (3)$$

The first term is just the solution to Laplace's equation in Regions I and II, corresponding to the boundary conditions (1) and (2)

$$\psi_{\mathrm{I}}^{(e)}(\mathbf{r})=A-(4\pi\sigma/K_0)z \qquad (0 \leq z \leq h_d)$$

$$\psi_{\mathrm{II}}^{(e)}(\mathbf{r})=A-4\pi\sigma[(h_d/K_0)+(z-h_d)/K] \qquad (z>h_d).$$

$$(4)$$

(Here, and in the following, the subscripts I and II on ψ's denote functional forms when $\mathbf{r}$ is restricted to the corresponding regions.) The quantities $\psi^{(a)}(\mathbf{r},\mathbf{r}_j)$ and $\psi^{(d)}(\mathbf{r},\mathbf{r}_j)$ represent the potentials due to ions with charges ϵ_j at $\mathbf{r}_j$, respectively, on the adsorption plane and in the solution ($z>h_0$). $\psi^{(a)}$ and $\psi^{(d)}$ are solutions to the corresponding Poisson equations subject to the boundary conditions (1) and (2), but where these latter are modified by setting $A=0$, $\sigma=0$.

First consider a charge adsorbed at z_a. We obtain $\psi^{(a)}$ by the standard method of Fourier–Bessel integrals.[13] Assume, for Regions I and II, the integral expansions

$$\psi_{\mathrm{I}}^{(a)}(\mathbf{r},\mathbf{r}_j)=\frac{\epsilon_j}{K_0}\int_0^\infty \{\exp(-k\,|\,z-z_j\,|)$$
$$+A^{(a)}(k)\,\exp(-kz)+B^{(a)}(k)\,\exp(kz)\}\,J_0(ks_j)dk,$$

$$\psi_{\mathrm{II}}^{(a)}(\mathbf{r},\mathbf{r}_j)=\frac{\epsilon_j}{K}\int_0^\infty C^{(a)}(k)\,\exp(-kz)\,J_0(ks_j)dk, \qquad (5)$$

where, of course, $z_j=z_a$, and

$$s_j=[(x-x_j)^2+(y-y_j)^2]^{\frac{1}{2}}$$

is the length of the projection of $\mathbf{r}-\mathbf{r}_j$ onto the interface.

The functions $A^{(a)}$, $B^{(a)}$, and $C^{(a)}$ may be evaluated as usual by observing the customary electrostatic boundary conditions at the planes $z=0$ and $z=h_d$. One finds:

$$A^{(a)}(k)=-\frac{1-\delta \exp[-2(h_d-z_a)k]}{1-\delta \exp(-2h_dk)}\exp(-z_ak),$$

$$B^{(a)}(k)=-\delta\frac{\exp(z_ak)-\exp(-z_ak)}{\exp(2h_dk)-\delta},$$

$$C^{(a)}(k)=(1+\delta)\frac{\exp(z_ak)-\exp(-z_ak)}{1-\delta \exp(-2h_dk)}, \qquad (6)$$

where we have set

$$\delta=(K-K_0)/(K+K_0).$$

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[11] J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).
[12] J. G. Kirkwood, Chem. Revs. **19**, 275 (1936).

[13] W. R. Smythe, *Static and Dynamic Electricity* (McGraw-Hill Book Company, Inc., New York, 1950), p. 182.

Substitution of these results back into (5) yields:

$$\psi_I^{(a)}(\mathbf{r}, \mathbf{r}_j) = \frac{\epsilon_j}{K_0} \int_0^\infty J_0(ks_j) \left\{ \exp(-k\,|\,z-z_a\,|) \right.$$

$$-\frac{1-\delta\,\exp[-2(h_d-z_a)k]}{1-\delta\,\exp(-2h_dk)}$$

$$\times \exp[-(z+z_a)k]$$

$$\left. -\delta\frac{\exp(z_ak)-\exp(-z_ak)}{\exp(2h_dk)-\delta}\,\exp(kz) \right\} dk,$$

$$\psi_{II}^{(a)}(\mathbf{r}, \mathbf{r}_j) = [2\epsilon_j/(K+K_0)]$$

$$\times \int_0^\infty J_0(ks_j)\frac{\exp(z_ak)-\exp(-z_ak)}{1-\delta\,\exp(-2h_dk)}\,\exp(-kz)dk. \quad (7)$$

In the case of an ion in Region II, one assumes the potential to have the form:

$$\psi_{II}^{(d)}(\mathbf{r}, \mathbf{r}_j) = \frac{\epsilon_j}{K} \int_0^\infty J_0(ks_j)\{\exp(-\,|\,z-z_j\,|\,k)$$

$$+A^{(d)}(k)\,\exp(-zk)\}dk,$$

$$\psi_I^{(d)}(\mathbf{r}, \mathbf{r}_j) = \frac{\epsilon_j}{K_0} \int_0^\infty J_0(ks_j)\{B^{(d)}(k)\,\exp(zk)$$

$$+C^{(d)}(k)\,\exp(-zk)\}dk. \quad (8)$$

Application of the boundary conditions at $z=0$ and $z=h_d$, as before, leads to

$$A^{(d)}(k) = -\frac{1-\delta\,\exp(2h_dk)}{1-\delta\,\exp(-2h_dk)}\,\exp(-z_jk),$$

$$B^{(d)}(k) = (1-\delta)\frac{\exp(-z_jk)}{1-\delta\,\exp(-2h_dk)},$$

$$C^{(d)}(k) = (\delta-1)\frac{\exp(-z_jk)}{1-\delta\,\exp(-2h_dk)}. \quad (9)$$

Substituting into Eqs. (8), one has:

$$\psi_I^{(d)}(\mathbf{r}, \mathbf{r}_j) = [2\epsilon_j/(K+K_0)]$$

$$\times \int_0^\infty J_0(ks_j)\frac{\exp[k(z-z_j)]-\exp[-k(z+z_j)]}{1-\delta\,\exp(-2h_dk)}dk,$$

$$\psi_{II}^{(d)}(\mathbf{r}, \mathbf{r}_j) = \frac{\epsilon_j}{K} \int_0^\infty J_0(ks_j)\left\{ \exp(-k\,|\,z-z_j\,|) \right.$$

$$\left. -\frac{1-\delta\,\exp(2h_dk)}{1-\delta\,\exp(-2h_dk)}\,\exp[-k(z+z_j)] \right\} dk. \quad (10)$$

Equations (8) and (10) constitute the exact closed form solution to the relevant electrostatic problems. These inner and outer region potentials have often been examined from the point of view of images.[5,14] It is interesting to note that these multiple image solutions can be recovered from the present results by means of expanding the integrand denominators in infinite series.

[14] B. V. Ershler, Zh. Fiz. Khim. **20**, 679 (1946).

Our closed solutions therefore constitute a convenient way of summing images of all orders.

In considering $\psi^{(d)}$, an ion far from the interface has z_j large, and the only portion of $A^{(d)}(k)$ which can contribute significantly to the first of Eqs. (8) is that portion near $k=0$. But in this region (at least through linear terms in k), the first of Eqs. (9) may be replaced by:

$$A^{(d)}(k) \cong -\exp\{-2[z_j+(K-K_0)h_d/K_0]k\}, \quad (11)$$

leading to an elementary integral:

$$\psi_{II}^{(d)}(\mathbf{r}, \mathbf{r}_j) \cong (\epsilon_j/K)$$

$$\times \{|\,\mathbf{r}-\mathbf{r}_j\,|^{-1} - |\,\mathbf{r}-\mathbf{r}_j+2[z_j+(K-K_0)h_d/K_0]\mathbf{N}\,|^{-1}\}. \quad (12)$$

This is precisely the form of the single-image solution to a point charge and single dielectric discontinuity problem. Thus, to an ion sufficiently far from the mercury surface, the variation in dielectric constant near the surface has the apparent effect only of shifting the metal–water surface from $z=0$ to[15]

$$z = -(K-K_0)h_d/K_0.$$

This type of asymptotic result is not restricted to our model, exhibited in Fig. 1, but with an arbitrary $K(z)$ which approaches the bulk solution dielectric constant $K(\infty)$ as z increases, the apparent position of the mercury–water surface to a far removed ion is z_0, the unique solution to

$$0 = \int_{-\infty}^{z_0}\frac{dz}{K(z)} + \int_{z_0}^\infty\left[\frac{1}{K(z)}-\frac{1}{K(\infty)}\right]dz. \quad (13)$$

For dilute electrolytes, most diffuse layer ions will be sufficiently far from the interface $z=0$ that the asymptotic expressions should apply.

III. DILUTE SOLUTIONS

There are two principal results that may be derived in the equilibrium cluster theory of inhomogeneous fluids.[16] They are, respectively, series expansions of the singlet densities $\rho_\alpha(\mathbf{r})$ for the various species $\alpha=1\cdots\nu$ in the system, and of a local pressure quantity whose spatial integral yields the grand partition function. In the case of electrolytes, we may adopt an approach from general solution theory,[17] and by interpreting the "interactions" between sets of ions as potentials of mean force (at infinite dilution), the local pressure becomes a local osmotic pressure $\prod(\mathbf{r})$.

In the customary boldface multicomponent cluster

[15] This phenomenon is entirely analogous to that of observing a table top through a plate of glass: the illusion is that the table top has been shifted upward, but it appears undistorted.

[16] F. H. Stillinger and F. P. Buff, J. Chem. Phys. **37**, 1 (1962).

[17] W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945); J. G. Kirkwood and F. P. Buff, *ibid.* **19**, 774 (1951).

theory notation,[18] the general expressions are:

$$\rho_\alpha(\mathbf{r}_1) = y_\alpha \exp\left\{-\frac{W_\alpha^{(1)}(\mathbf{r}_1)}{kT} + \sum_n (\mathbf{n}!)^{-1} \int S_{\alpha n}(1\cdots n+1)\right.$$

$$\left. \times \rho_{\theta(2)}(\mathbf{r}_2)\cdots\rho_{\theta(n+1)}(\mathbf{r}_{n+1})d\mathbf{r}_2\cdots d\mathbf{r}_{n+1}\right\}; \quad (14)$$

$$\prod(\mathbf{r}_1)$$

$$= kT\sum_{\alpha=1}^{\nu}\left\{\rho_\alpha(\mathbf{r}_1)\left[1 - \sum_n \frac{n}{(n+1)\mathbf{n}!}\int S_{\alpha n}(1\cdots n+1)\right.\right.$$

$$\left.\left. \times \rho_{\theta(2)}(\mathbf{r}_2)\cdots\rho_{\theta(n+1)}(\mathbf{r}_{n+1})d\mathbf{r}_2\cdots d\mathbf{r}_{n+1}\right]\right\}, \quad (15)$$

$$n = \sum_{\alpha=1}^{\nu} n_\alpha.$$

y_α is the absolute activity of species α, which is related to the chemical potential μ_α by

$$y_\alpha = h^3 \exp(\mu_\alpha/kT)/(2\pi m_\alpha kT)^{3/2},$$

in standard notation. $W_\alpha^{(1)}(\mathbf{r}_1)$ in Eq. (14) stands for the singlet potential of mean force acting on an ion of type α, at position $\mathbf{r}_1$, in pure solvent, and includes both electrostatic and nonelectrostatic contributions. $S_{\alpha n}(1\cdots n+1)$ is the irreducible cluster sum for $n+1$ particles at positions $\mathbf{r}_1\cdots\mathbf{r}_{n+1}$, which are species α, $\theta(2)$, $\theta(3)$, $\cdots$, $\theta(n+1)$, respectively. If the potentials of mean force (excepting the external field parts) for such sets of ions may be decomposed into pair contributions $W_{\alpha\beta}^{(2)}$ only, then it is known that the contributing terms in $S_{\alpha n}$ consist of sums of products of Mayer f bonds:

$$f_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \exp[-W_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)/kT] - 1, \quad (16)$$

which correspond uniquely to irreducible (at least doubly connected) graphs.

In the homogeneous fluid limit, Eqs. (14) and (15) pass over into a relation between density and chemical potential, and the virial expansion for solution osmotic pressure. One sees that the necessary generalization for regions of static inhomogeneity (the double-layer region in the present investigation) amounts to insertion of position-dependent densities $\rho_\theta(\mathbf{r})$ under the integrals. In the case of both (14) and (15), one clearly sees that particle interactions, which manifest themselves through nonvanishing of the $S_{\alpha n}$, demand that the point functions $\rho_\alpha(\mathbf{r})$ and $\prod(\mathbf{r})$ depend generally not only on the local densities at the point $\mathbf{r}$ of observation, but on the densities at neighboring positions as well. Because both (14) and (15) are rigorous expansions (at least within the convergence limits of cluster theory), they may be taken as the starting point for consistent and complete (no unevaluated phenomenological param-

eters) gradient expansions of the Cahn–Hilliard–Hart type.[16,19,20]

The local osmotic pressure $\prod(\mathbf{r})$ has a free-energy property. Its integral over the double-layer region, with the bulk value of $\prod$ subtracted for convergence, gives the free energy of the double layer. We return to application of (15) only in the last section, under the heading of colloid stability.

In order to make explicit use of Eqs. (14) and (15) it is of course necessary to have the various ion pair mean potentials at infinite dilution, $W_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. In the previous section, we obtained the solution to the electrostatic problem involved in arbitrary placing of a set of ions; an elementary electrostatic theorem[21] subsequently provides the corresponding electrostatic free energy for fixed ions suspended in pure solvent as one-half the spatial integral of the product of charge density and electrostatic potential. Because the ions are treated as point charges in that calculation, we must be careful to include corrections $\varphi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$ (they are short-range) due to ion size and solvent molecular structure. We finally obtain a total potential of mean force in pure solvent, $W^{(N)}$, for $N = N_a + N_d$ ions distributed between inner $(z=z_a)$ and outer $(z\geq h_0)$ regions, of the form

$$W^{(N)}(N_a, N_d) = \sum_{i=1}^{N_a}\{U_{\theta(i)}(z_i) + \epsilon_i[w^{(1)}(z_i) + \psi_\mathrm{I}^{(e)}(z_i)]\}$$

$$+ \sum_{j=1}^{N_d}\epsilon_j[w^{(1)}(z_j) + \psi_\mathrm{II}^{(e)}(z_j)]$$

$$+ \sum_{i<i'=1}^{N_a}[\varphi_{\theta(i)\theta(i')}(\mathbf{r}_i, \mathbf{r}_{i'}) + \epsilon_i\epsilon_{i'}w^{(2)}(\mathbf{r}_i, \mathbf{r}_{i'})]$$

$$+ \sum_{i=1}^{N_a}\sum_{j=1}^{N_d}\epsilon_i\epsilon_j w^{(2)}(\mathbf{r}_i, \mathbf{r}_j)$$

$$+ \sum_{j<j'=1}^{N_d}[\varphi_{\theta(j)\theta(j')}(\mathbf{r}_j, \mathbf{r}_{j'}) + \epsilon_j\epsilon_{j'}w^{(2)}(\mathbf{r}_j, \mathbf{r}_{j'})]. \quad (17)$$

In this expression we have the singlet $(w^{(1)})$ and pair $(w^{(2)})$ unit charge interaction energies, defined by

$$w^{(1)}(z_i) = (\epsilon_i)^{-1}\lim_{\mathbf{r}\to\mathbf{r}_i}\{[\psi_\mathrm{I}^{(a)}(\mathbf{r}, \mathbf{r}_i), \psi_\mathrm{II}^{(d)}(\mathbf{r}, \mathbf{r}_i)]$$

$$- [(K_0 |\mathbf{r}-\mathbf{r}_i|)^{-1}, (K |\mathbf{r}-\mathbf{r}_i|)^{-1}]\},$$

$$w^{(2)}(\mathbf{r}_i, \mathbf{r}_j)$$

$$= (\epsilon_j)^{-1}[\psi_\mathrm{I}^{(a)}(\mathbf{r}_i, \mathbf{r}_j), \psi_\mathrm{II}^{(a)}(\mathbf{r}_i, \mathbf{r}_j), \psi_\mathrm{II}^{(d)}(\mathbf{r}_i, \mathbf{r}_j)],$$

where the various choices indicated correspond to the different ways of placing ions in Regions I and II. In obtaining Eq. (17), we have used the fact that $J_0(0) = 1$. The functions $U_{\theta(i)}(z_i)$ are the nonelectrostatic part of the ions' singlet potentials of mean force. Consistent

[18] E. Meeron, J. Chem. Phys. 27, 1238 (1957).

[19] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. 28, 258 (1958).
[20] E. W. Hart, Phys. Rev. 113, 412 (1959).
[21] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company Inc., New York, 1941), p. 106.
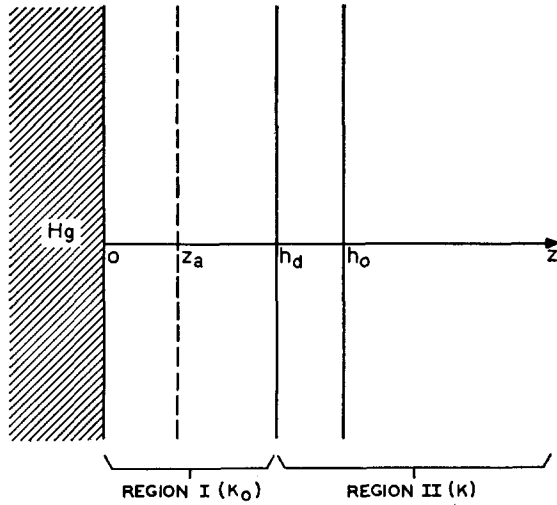
FIG. 1. Diagram of the relative positions of the planes of dielectric constant discontinuity ($z=0$ and $z=h_d$), of ion adsorption ($z=z_a$), and of closest approach of unadsorbed ions ($z=h_0$).

with the model of Fig. 1, U rises from zero to essentially infinity as z_i decreases below h_0; for ions which adsorb specifically on the mercury surface, U has additionally a narrow and deep minimum at z_a, leading to the inner layer (see Fig. 2). Of course no $U_\theta(z)$ is an infinitely high barrier for $z_a < a < h_0$, but it is assumed to be sufficiently large in this range to confine all ions in Region I essentially to the plane $z = z_a$.

In view of the marked spatial separation between the N_a adsorbed ions and those N_d ions in the Region II, Eq. (17) has been written without any short-range interaction between pairs of ions, one of which is in each region. Although our general formalism is fully capable of handling the more elaborate case with inclusion of such further short-range interactions, it seems worthwhile to investigate the simpler case, since it is fully consistent with the geometry of our model, and since very little is known about the form φ's should take for pair separations spanning the outer Helmholtz plane, h_0.

In the light of these preliminary observations, we pass now to reduction of the ion density equations (14) in the diffuse layer Region II, in the low concentration limit. In Region II, the several $U_\alpha(z)$ of course are assumed to vanish. The fundamental cluster summation basis of this Debye–Hückel limit was exhibited in a classical paper on bulk electrolyte properties by Mayer,[1] and the relevance of the linearized cyclic diagrams to electrolyte interfacial problems has also been established.[2] Therefore, we need include only ring clusters in each $S_{\alpha n}$, in which the Mayer f bonds, Eq. (16), are linearized with respect to the electrostatic part of $W_{\alpha\beta}^{(2)}$, and short-range contributions dropped:

$$f_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \cong -\epsilon_\alpha \epsilon_\beta w^{(2)}(\mathbf{r}_1, \mathbf{r}_2)/kT. \quad (18)$$

First, within the ring cluster approximation, we re-

write Eq. (14) for Region II ($z_1 > h_0$) as

$$\rho_\alpha(\mathbf{r}_1) = y_\alpha \exp\left\{-\frac{\epsilon_\alpha}{kT}[w^{(1)}(z_1) + \psi_{II}^{(e)}(z_1)]\right.$$

$$+ \sum_{\beta=1}^{\nu}\int [f_{\alpha\beta}(12) - \tfrac{1}{2}f_{\alpha\beta}^2(12)]\rho_\beta(2)d\mathbf{r}_2$$

$$+ \tfrac{1}{2}\sum_{n=1}^{\infty}\sum_{\theta(2)\ldots\theta(n+1)=1}^{\nu}\int\int f_{\alpha\theta(2)}(12)\rho_{\theta(2)}(2)\cdots\rho_{\theta(n+1)}(n+1)$$

$$\left. \times f_{\theta(n+1)\alpha}(n+1, 1)d\mathbf{r}_2\cdots d\mathbf{r}_{n+1}\right\}, \quad (19)$$

where by addition and subtraction of the square of an f bond, the ring sum is taken to begin with the "two-sided polygon." To within terms consistent with the linearization, this does not modify the value of the first integral in Eq. (19), and so the $f_{\alpha\beta}^2$ in its integrand may, in this approximation, be dropped.

We now use (18) and (19) to obtain

$$\rho_\alpha(z_1) = y_\alpha \exp\left\{-\frac{\epsilon_\alpha}{kT}[w^{(1)}(z_1) + \bar\psi(z_1)]\right.$$

$$\left. + \frac{\epsilon_\alpha^2}{2KkT}\int_{II} d\mathbf{r}_2[Kw^{(2)}(12)]\frac{\kappa^2(2)}{4\pi}\chi(2,1)\right\}, \quad (20)$$

where $\bar\psi(z_1)$ is the average electrostatic potential at position z_1, satisfying the Poisson equation

$$\nabla^2\bar\psi(z) = -\frac{4\pi}{K}\sum_{\alpha=1}^{\nu}\epsilon_\alpha\rho_\alpha(z); \quad (21)$$

we select the arbitrary zero for this mean potential so that

$$\lim_{z\to\infty}\bar\psi(z) = 0.$$

$\bar\psi(z)$ arises by combining the linearized first integral in

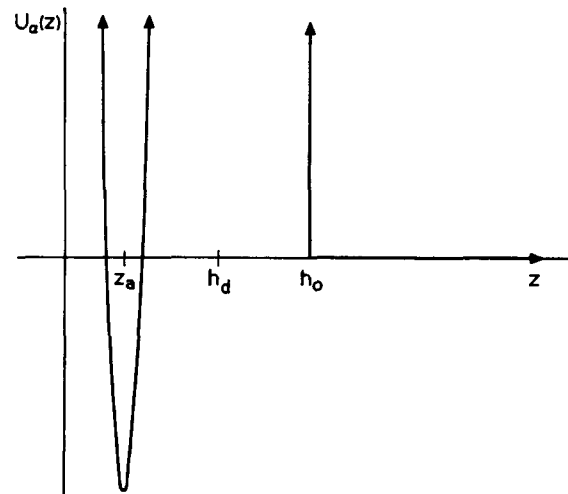FIG. 2. Plot of the nonelectrostatic part of the singlet potential of mean force for ions of type α, according to the model. The deep and narrow potential well is not present for unadsorbed species.

(19) with $\psi_{II}^{(e)}$. The function $\chi(2, 1)$ represents summation and integration over all but one link of the ring graphs; its multiple convolution character is evident by iterating its determining integral equation

$$\chi(2, 1) = Kw^{(2)}(2, 1)$$
$$- \int_{II} [Kw^{(2)}(2, 3)]\frac{\kappa^2(3)}{4\pi}\chi(3, 1)d\mathbf{r_3}. \quad (22)$$

$\kappa(z)$ is the local value of the Debye–Hückel parameter

$$\kappa^2(z) = 4\pi\sum_{\alpha=1}^{\nu}\epsilon_\alpha^2\rho_\alpha(z)/KkT. \quad (23)$$

By virtue of the fact that $w^{(2)}(2, 1)$ satisfies a Poisson equation with a single source term, Eq. (22) may be considerably simplified by application of the Laplace differential operator to both sides:

$$\nabla_2^2\chi(2, 1) = -4\pi\delta(\mathbf{r_2}-\mathbf{r_1}) - \kappa^2(2)\chi(2, 1), \quad (24)$$

where $\delta(\mathbf{r_2}-\mathbf{r_1})$ is the three-dimensional Dirac delta function. In the bulk of the electrolyte phase, the solution to Eq. (24) is the famous spherically symmetric shielded Coulomb potential, and of course $Kw^{(2)}(2, 3)$ is just $1/r_{23}$. When $\mathbf{r_1}$ is in the interfacial region, though, χ and $w^{(2)}$ are no longer functions just of pair distance, so the integral remaining in Eq. (20) is not so simple. It may however be reduced by using Eq. (24) to replace $\kappa^2(2)\chi(2, 1)$ by

$$\nabla_2^2\chi(2, 1) + 4\pi\delta(\mathbf{r_2}-\mathbf{r_1}) = \nabla_2^2[\chi(2, 1) - Kw^{(2)}(2, 1)].$$

After this is inserted in Eq. (20), a partial integration transformation (Green's second identity[22]) may be performed. One finds

$$\rho_\alpha(z_1) = y_\alpha \exp\{-\epsilon_\alpha[w^{(1)}(z_1) + \bar{\psi}(z_1)]/kT + I_0(z_1)$$
$$- (\epsilon_\alpha^2/2KkT) \lim_{\mathbf{r_2}\to\mathbf{r_1}} [\chi(\mathbf{r_2}, \mathbf{r_1}) - Kw^{(2)}(\mathbf{r_2}, \mathbf{r_1})]\}. \quad (25)$$

In this expression, I_0 is the surface integral over the outer Helmholtz plane (OHP) that arises[23]

$$I_0(z_1) = (\epsilon_\alpha^2/8\pi KkT)$$
$$\int_{OHP} d\mathbf{s}\cdot\{[Kw^{(2)}(2, 1)]\nabla_2[\chi(2, 1) - Kw^{(2)}(2, 1)]$$
$$- [\nabla_2 Kw^{(2)}(2, 1)][\chi(2, 1) - Kw^{(2)}(2, 1)]\}. \quad (26)$$

Generally, one would require numerical solution for $w^{(2)}$ and χ before the local density expression (25) could be evaluated. In the dilute solution limit, however, to which the ring cluster approximation only strictly applies, matters are especially simple. We have already noted that under this circumstance Region I has only the effect of shifting the metal surface ($z=0$), so far as most ions in the wide diffuse charge region are

concerned. Therefore, to the extent that it is required to obtain charge distributions which lead to correct dilute solution observables such as differential capacitance, we may use this simplification for $w^{(1)}$ and $w^{(2)}$ without thereby affecting those dilute solution results at all. For convenience in writing in the remainder of this section, therefore, shift the origin $z=0$ to make z_0 in Eq. (13) vanish. Then

$$\epsilon_\alpha w^{(1)}(z_1) = -\epsilon_\alpha^2/4Kz_1,$$
$$Kw^{(2)}(\mathbf{r_1}, \mathbf{r_2}) = (r_{12})^{-1} - (r_{12}^*)^{-1},$$
$$r_{12}^* = |\mathbf{r_2} - \mathbf{r_1} + 2z_1\mathbf{N}|; \quad (27)$$

these are characteristic of the single effective image approximation.

For evaluation of the limit in Eq. (25), χ is required. Since the diffuse portion of the double layer is wide in dilute solutions, $\kappa(z)$ is a slowly varying function of position. This is precisely the condition under which a WKB solution to partial differential equation (24) is physically meaningful.[24] Consistent with the foregoing, we solve it subject to the boundary condition that χ is to vanish on the new $z=0$ plane. One readily finds

$$\chi(\mathbf{r_1}, \mathbf{r_2}) = \exp[-\bar{\kappa}(\mathbf{r_1}, \mathbf{r_2})r_{12}]/r_{12}$$
$$- \exp[-\bar{\kappa}(\mathbf{r_1}, \mathbf{r_2})r_{12}^*]/r_{12}^*,$$
$$\bar{\kappa}(\mathbf{r_1}, \mathbf{r_2}) = (z_2-z_1)^{-1}\int_{z_1}^{z_2}\kappa(z)dz. \quad (28)$$

Thus, the WKB solution is very simply a shielded version of $Kw^{(2)}(\mathbf{r_1}, \mathbf{r_2})$, albeit with a locally averaged κ as exponential decay "constant." Aside from a reversal of sign for the image term, this solution also arises in the theory of ionic solution surface tension, which is described in Ref. 2.

We may now use our WKB solution to evaluate the last term in Eq. (25). Also, this solution allows estimation of the magnitude of the surface integral $I_0(z_1)$, with the conclusion that it is of higher order in electrolyte concentration than the limit term; as a result, it is permissible to disregard I_0 in dilute solutions. We finally obtain from (25):

$$\rho_\alpha(z_1) = y_\alpha \exp\{\epsilon_\alpha[-\bar{\psi}(z_1) + (\epsilon_\alpha/4Kz_1) \exp[-2\kappa(z_1)z_1]$$
$$+ (\epsilon_\alpha/2K)\kappa(z_1)]/kT\}. \quad (29)$$

The terms on the right side are easily identifiable as the effects on an α ion of: (1) the mean electrostatic potential at position z_1, (2) the ion's own shielded image, (3) the local activity constant correction at position z_1.

Since Eq. (29) refers only to the outer Helmholtz region, $z \geq h_0$, and since in many applications the screened image term is small in this region by comparison with the $\bar{\psi}$ term, one may reasonably drop it. The

[22] O. D. Kellogg, *Foundations of Potential Theory* (Dover Publications, Inc., New York, 1953), p. 215.
[23] Here and in the following, $d\mathbf{s}$ indicates integration over some specified two-dimensional surface, to be distinguished from volume integrations $d\mathbf{r}$.
[24] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. II, p. 1105.

resulting expression is one encountered in the method of local thermodynamic balance,[7] whereby the relations between local densities, mean potentials, and activities are dictated by extension of thermodynamic reasoning to the microscopic domain. However, in the event that the electrode, including adsorbed ions, is uncharged (the "electrocapillary maximum"), it is the image terms which yield dominant local concentration variations in the outer Helmholtz region of dilute solutions. In this case these image terms produce the entire contribution to such properties as the surface tension,[2] whereas local thermodynamic balance yields nothing. This observation supplies one criterion for applicability of local thermodynamic balance; another arises in Sec. V in examination of ion size effects.

On the basis of Eq. (29), we conclude that in spite of the fact that the activity correction for an ion at z_1 is due to its average charge cloud extending over distances comparable with the entire diffuse layer thickness, in the dilute solution limit the pointwise use of bulk solution activity coefficients, as suggested by local thermodynamic balance, is rigorously valid.

The set of relations (29), in conjunction with the Poisson equation (21), constitute a nonlinear coupled set of equations which, with a suitable specification of boundary conditions, may be solved iteratively. In the case of a single symmetrical electrolyte (ion charges $\pm\epsilon$), the Poisson equation (21) may be somewhat more explicitly presented in which the y_α are eliminated [since one is only interested in the ratios $\rho_\alpha(z_1)/\rho_\alpha(\infty)$]

$$\nabla^2[\epsilon\bar{\psi}(z_1)/kT] = \kappa^2(\infty)\,\exp([\epsilon^2/2KkT]\{\kappa(z_1)-\kappa(\infty)$$

$$+\exp[-2\kappa(z_1)z_1]/2z_1\})\sinh[\epsilon\bar{\psi}(z_1)/kT]. \quad (30)$$

This way of writing clearly shows the manner in which shielded image and local activity corrections modify the standard nonlinear Poisson–Boltzmann equation [in which the second factor on the right-hand side of Eq. (30) is missing]. Because the interposition of the inner region prevents z_1 even from getting as small as h_0 (remembering the coordinate system origin shift), the shielded image term is seldom significant in determining $\bar{\psi}$, consistent with the preceding remarks.

The modified Poisson–Boltzmann equation (30) and the density expressions (29) are implicit in several existing calculations on double-layer structure.[25,26] For a number of applications it has in the past been felt desirable to include the possibility of dielectric saturation and electrostriction as modifying effects on the double layer.[27] It must be strongly emphasized at this point, however, that it is only under our assumed conditions of linear and composition-independent dielectric behavior that our rigorous demonstration of dilute solution local thermodynamic balance goes through. The manner in which saturation and electrostriction

must be handled within the context of cluster theory, since they generate many-body mean potentials of arbitrarily high order, has never been solved. Consequently, we can add nothing at this time in the way of rigorous microscopic justification of the *ad hoc* prescriptions that have been used to account for these phenomena, although this problem will be the object of future investigation. In passing, it is perhaps worthwhile exhibiting the resulting form of the Poisson–Boltzmann equation, after extension to include these generalizations by means of a complete and consistent local thermodynamics

$$K_T\nabla^2\bar{\psi}(\mathbf{r}) + (K_N-K_T)\frac{\partial^2\bar{\psi}(\mathbf{r})}{\partial z^2}$$

$$= -4\pi\sum_{\alpha=1}^{\nu}\epsilon_\alpha\left\{\rho_\alpha(\mathbf{r}) - \mathbf{E}\cdot\left(\frac{\partial\rho_\alpha(\mathbf{r})}{\partial\mathbf{E}}\right)_{T,\{\bar{\mu}\},\bar{\psi}}\right\}. \quad (31)$$

We have used the mean electric field $\mathbf{E} = -\nabla\bar{\psi}$ to define a differential dielectric tensor with generally different composition-, field-, and temperature-dependent normal (K_N) and tangential (K_T) components:

$$(\partial\mathbf{D}/\partial\mathbf{E})_{T\{\bar{\mu}\}\bar{\psi}} = K_N\mathbf{NN} + K_T(\mathbf{1}-\mathbf{NN}), \quad (32)$$

where $\mathbf{D}$ is the dielectric displacement vector, and where $\mathbf{1}$ is the unit dyadic tensor. In the event that K_N is a function of $|\mathbf{E}| = E$, and not of invariants constructed from higher-order spatial derivatives of $\bar{\psi}$, one can show that K_T is simply related to K_N:

$$K_T = (\partial EK_N/\partial E)_{T\{\bar{\mu}\}\bar{\psi}}.$$

The mean field derivatives in (31) and (32) are to be calculated under conditions of constant augmented electrochemical potential:

$$\bar{\mu}_\alpha = \mu_\alpha[\rho_1(\mathbf{r})\cdots\rho_\nu(\mathbf{r})] + \epsilon_\alpha\bar{\psi}(\mathbf{r})$$

$$-\frac{1}{4\pi}\int_0^{\mathbf{E}}\left(\frac{\partial\mathbf{D}}{\partial\rho_\alpha}\right)_{T,\mathbf{E}',\bar{\psi},\rho_\beta}\cdot d\mathbf{E}'.$$

Equation (31) refers to the more general spherical interface (z still the normal direction), rather than just the planar situation treated in the rest of this paper. The deduction of Eq. (31) from a general variational formulation of electrocapillarity will be reserved for later publication. The problem of how to generalize the image and activity terms in the set of density relations (29), so as to preserve consistency with the fundamental principles of statistical mechanics, is entirely unknown at present.

IV. ADSORPTION ISOTHERM

Thus far, the ion densities in the diffuse portion of the double layer have been assumed sufficiently small, that the ion sizes (i.e., the short-range mean potentials $\varphi_{\alpha\beta}$) would have negligible effect on the mean electrostatic potential and density distributions in this region. But in the case that one or more species of ion have a strong tendency to adsorb on the mercury surface,

[25] A. L. Loeb, J. Colloid Sci. **6**, 75 (1951).
[26] S. Levine and G. M. Bell, J. Phys. Chem. **64**, 1188 (1960).
[27] M. J. Sparnaay, Rec. Trav. Chim. Pays-Bas **77**, 872 (1958).

these ions may be quite crowded on the inner Helmholtz plane, and still be in equilibrium with a dilute diffuse region. For this reason, it is desirable to develop the application of the fundamental relation (14) to the set of adsorbed ions, in such a way that the mutual exclusion effect of these particles becomes fully clarified.

The key element in manipulation of the density equations to yield adsorption isotherms is that electrostatic interactions for ion pairs, at least one member of which is at z_a, are weak, on account of the proximity of such ions to the conducting surface $z=0$. Consequently, we account for interactions between one ion in Region I and another in Region II only through the linearized leading particle-pair cluster integral in Eq. (14), and within Region I we take

$$f_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \cong \{\exp[-\varphi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)/kT]-1\}$$
$$-\epsilon_\alpha\epsilon_\beta \exp[-\varphi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)/kT]w^{(2)}(\mathbf{r}_1, \mathbf{r}_2)/kT, \quad (33)$$

where the terms correspond to the f bond for just the short-range part of the ion–ion interaction, and to an electrostatic perturbation, respectively.

In view of the large occupation of the adsorption plane, with a consequent primary role given to size effects, it is mandatory to retain all short-range bond contributions in each $S_{\alpha n}$, but since the $w^{(2)}$'s are being regarded as weak perturbations, we need to account only for linear correction terms in $w^{(2)}$ in each $S_{\alpha n}$.

The fact that the potential wells giving rise to adsorption, when they exist for a given species α, are very deep and narrow, implies that virtually all adsorbed ions are confined to a small neighborhood $z_a-\epsilon<z< z_a+\epsilon$, of the adsorption plane z_a, where ϵ is some small positive number which we may suppose satisfies the conditions

$$0<z_a-\epsilon, \qquad h_d>z_a+\epsilon. \quad (34)$$

This inherent narrowness of the adsorption zone leads to a very useful reduction of Eq. (14). Thus, the number of ions of type α per unit area that are adsorbed may be denoted by

$$\rho_\alpha^{\text{ads}} = \int_{z_a-\epsilon}^{z_a+\epsilon} \rho_\alpha(z)\,dz, \quad (35)$$

which is independent of lateral position.

Consistent with previous remarks, we consider all vertices of the $S_{\alpha n}$ to be confined to the adsorption region, with the single exception of the two-ion electrostatically linearized clusters. For such constrained cluster integrals, variation of vertex positions normal to the interface, within the narrow zone, causes no significant variation of $S_{\alpha n}$, so the various $\rho_\theta(r)$ may be replaced by the constant ρ_θ^{ads} (which then may be taken outside the integrals), and subsequently the position integrations are confined to just the $z=z_a$ plane.

The ion-pair cluster integrals may be split into two parts, corresponding to interaction with the diffuse

layer in Region II, and with other ions in Region I. We may again make the appropriate $\rho_\theta(\mathbf{r})\rightarrow\rho_\theta^{\text{ads}}$ replacememts. When combined with $\psi_\text{I}^{(e)}$ and an integral of the form

$$-\frac{\epsilon_\alpha}{kT}\sum_{\beta=1}^{\nu}\epsilon_\beta\rho_\beta^{\text{ads}}\int_{\text{I.H.P.}} w^{(2)}(\mathbf{s})\,d\mathbf{s}, \quad (36)$$

the diffuse layer interaction part gives precisely $-\epsilon_\alpha\bar{\psi}(z_a)/kT$. If furthermore we define a length parameter,

$$l_\alpha = \int_{z_a-\epsilon}^{z_a+\epsilon} \exp\left\{\frac{-U_\alpha(z)+\epsilon_\alpha w^{(1)}(z)}{kT}\right\}dz, \quad (37)$$

then the fundamental Eq. (14) transforms into an adsorption equation:

$$\rho_\alpha^{\text{ads}} = (y_\alpha l_\alpha)\exp\left\{-\frac{\epsilon_\alpha\bar{\psi}(z_a)}{kT}+\frac{\epsilon_\alpha}{kT}\sum_{\beta=1}^{\nu}\epsilon_\beta\rho_\beta^{\text{ads}}\int w^{(2)}(\mathbf{s})\,d\mathbf{s}\right.$$
$$\left.+\sum_n[(\varrho^{\text{ads}})^n/\mathbf{n}!]\int S_{\alpha n}(1\cdots n+1)\,d\mathbf{s}_2\cdots d\mathbf{s}_{n+1}\right\}. \quad (38)$$

We must now compute the remaining set of planar cluster integrals through first order in $w^{(2)}(\mathbf{s})$. For simplicity, we assume that only one species (α) can adsorb. The unperturbed cluster sum may be denoted by $H(\rho_\alpha^{\text{ads}})$. In any cluster sum $S_{\alpha n}$ (for $n+1$ α ions at z_a), the electrostatic perturbation could act between any of the

$$(n+1)!/2!(n-1)!$$

distinct pairs of vertices. On account of translational invariance in the adsorption plane, it is in each case possible to renumber vertices so that the perturbation acts between Particles 1 and 2. Consequently, the total perturbation may be written as

$$\sum_{n=1}^{\infty}\left[\frac{(n+1)(\rho_\alpha^{\text{ads}})^n}{2(n-1)!}\right]$$
$$\times\int\left[\frac{-\epsilon_\alpha^2 w^{(2)}(\mathbf{s})}{kT}\right]\exp\left[\frac{-\varphi_{\alpha\alpha}(\mathbf{s})}{kT}\right]T_{n-1}(\mathbf{s})\,d\mathbf{s}.$$

Because of the original irreducible character of the $S_{\alpha n}$, the quantities $T_{n-1}(\mathbf{s})$ consist of products of unperturbed f bonds, which have associated graphs of $n-1$ free vertices that are rooted at both 1 and 2 (separated by $\mathbf{s}$), and which are at least singly connected in the free vertices, and are without articulation points.[28] For convenience, we also set

$$T_0(\mathbf{s})=1. \quad (40)$$

The T diagrams are precisely those that are generated by the pair distribution function $\rho_{\alpha\alpha}^{(2,0)}(\mathbf{s})$ for the

[28] Explanation of the terminology and techniques of cluster theory appear in: G. E. Uhlenbeck and G. W. Ford, "The Theory of Linear Graphs with Applications to the Theory of the Virial Development of the Properties of Gases," in *Studies in Statistical Mechanics*, edited by J. deBoer and G. E. Uhlenbeck (Interscience Publishers, Inc., New York, 1962), Vol. I.

two-dimensional fluid whose particles interact with just the short-range (superscript "0") mean potential for pairs of adsorbed α ions.[28] The numerical factors preceding each integral in Eq. (39) are not quite correct, though, unless first a density derivative is applied. Finally, therefore, Eq. (38) in the case of single-ion adsorption takes the form:

$$\rho_\alpha{}^{ads} = (y_\alpha l_\alpha) \exp\left\{ H(\rho_\alpha{}^{ads}) - \epsilon_\alpha \bar{\psi}(z_a)/kT \right.$$

$$\left. - \frac{\epsilon_\alpha{}^2}{kT} \int d\mathbf{s} w^{(2)}(\mathbf{s}) \left[\frac{1}{2}\left(\frac{\partial \rho_{\alpha\alpha}{}^{(2,0)}(|\mathbf{s}|)}{\partial \rho_\alpha{}^{ads}} \right) - \rho_\alpha{}^{ads} \right] \right\}. \quad (41)$$

For many applications, the pre-exponential factor $y_\alpha l_\alpha$ may effectively be eliminated, since the primary interest is in the variation of $\rho_\alpha{}^{ads}$ with applied potential, or ambient electrolyte concentration in the dilute bulk solution range. The simplest and most traditional way of introducing ion–ion short-range forces into the theory is to suppose that $\varphi_{\alpha\alpha}(\mathbf{s})$ is the rigid-sphere potential (with a sphere diameter a, however, not necessarily equal to the hydrated ion size in solution, due to the anomalous nature of water in Region I). For this model, the ions in the adsorption plane form a two-dimensional rigid-sphere gas, and for such a system, a very accurate evaluation of H is available from the work of Helfand, Frisch, and Lebowitz[29]:

$$H(\rho) = \log(1-y) + y(2y-3)/(1-y)^2,$$
$$y = \pi \rho a^2/4. \quad (42)$$

For single-ion adsorption this should provide a much better account of H than, say, the rather crude Flory–Huggins volume fraction statistics employed by Levine, Bell, and Calvert.[30] The electrostatic perturbation $w^{(2)}(\mathbf{s})$ is available from numerical integration of the first of Eqs. (7) for pairs of positions on the inner Helmholtz plane separated by $\mathbf{s}$. The pair distributions $\rho_{\alpha\alpha}{}^{(2,0)}(s)$ for the "uncharged" adsorbed ions are thus the only unevaluated quantities in the adsorption equation (41). There exist a number of standard techniques for computing these functions,[31] and undoubtedly tabulated values will eventually become generally available. In the interim period, it is probably sufficient to use the step-function approximation:

$$\rho_{\alpha\alpha}{}^{(2,0)}(s) = 0 \qquad s < a,$$
$$= (\rho_\alpha{}^{ads})^2 \quad s \geq a \quad (43)$$

in which case the integral in Eq. (41) reduces to an expression used by Levine, Bell, and Calvert.[30]

The more exact expression (41) in its unapproximated form constitutes an adsorption isotherm taking

full account of the so-called "discreteness-of-charge effect."[6,80] The manner in which two-dimensional distribution functions naturally arise in this application of cluster theory to the double layer shows that one can in principle account for the effect of finite ion size on adsorption without introducing artificial lattice structures on the adsorption plane for making elaborate (but in the case of mercury, rather spurious) discrete-charge potential calculations.[14]

By a slight elaboration of our combinatorial arguments, it is easily possible to derive a generalization of Eq. (41) to the case of several ionic species simultaneously adsorbing on the same plane. One finds

$$\rho_\alpha{}^{ads} = (y_\alpha l_\alpha) \exp\left(H(\rho_1{}^{ads}, \cdots, \rho_\nu{}^{ads}) \right.$$

$$- \epsilon_\alpha \bar{\psi}(z_a)/kT - (kT)^{-1} \sum_{\beta,\gamma=1}^{\nu} \int d\mathbf{s} w^{(2)}(s)$$

$$\left. \times \left\{ \frac{\epsilon_\beta \epsilon_\gamma}{2}\left[\frac{\partial \rho_{\beta\gamma}{}^{(2,0)}(s)}{\partial \rho_\alpha{}^{ads}} \right] - \epsilon_\alpha \epsilon_\beta \delta_{\beta\gamma} \rho_\beta{}^{ads} \right\} \right), \quad (44)$$

where $\delta_{\beta\gamma}$ is the Kronecker delta. In the event that all adsorbed species may be regarded as spheres of the same size, the H in (44) reduces to the same function as before, but evaluated at the total adsorbed ion density.

V. SIZE EFFECTS IN THE DIFFUSE REGION

The adsorption equations adduced in the previous section are affected by the charge distribution in the diffuse region of the double layer only by the value of the mean potential at the adsorption plane, $\bar{\psi}(z_a)$, a quantity which must be self-consistently determined by the charge distribution in both inner and outer regions. As stated earlier, the adsorbed ions might well be closely crowded together, while at the same time those in the diffuse region are at sufficiently low concentration that their short-range forces seldom come into play. We wish now, however, to indicate briefly the way in which the considerations of Sec. III would have to be extended in order to account for the lowest-order effects of ion size (i.e., their short-range forces) as electrolyte concentration in the Region II is increased.

One recognizes that there are basically two dimensionless parameters that may be used to classify the range of applicability of electrolyte calculations. If we let b stand for a typical length characteristic of the ion sizes, then these two parameters may be taken as

$$\lambda_1 = \epsilon^2/DkTb,$$
$$\lambda_2 = \kappa(\infty)b.$$

The calculations of Sec. III were predicated upon the assumption that terms of lowest nonvanishing order in both λ_1 and λ_2 were sufficient to describe the diffuse region. The extension presently under consideration

[29] E. Helfand, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **34**, 1037 (1961).
[30] S. Levine, G. M. Bell, and D. Calvert, Can. J. Chem. **40**, 518 (1962).
[31] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

still works to lowest order in λ_1, but retains *two* leading orders in λ_2.

It has already been recognized that the ring clusters yield the proper local activity corrections without ion size. In the same spirit as for the adsorption isotherm calculation, we regard these clusters as the "unperturbed" quantity, and then add in the effect of the $\varphi_{\alpha\beta}$ to the lowest order. Now, though, the roles of long- and short-range interactions are reversed.

We therefore require two modifications of the previous calculation:

(1) in each link of the cyclic cluster integrals in the last term of Eq. (19), the size-independent approximate f function shown in Eq. (18) must be replaced by the second term in Eq. (33), which has the effect of removing the singularity at $r_{12}=0$;

(2) both terms in Eq. (33) must be considered in the pair integrals in Eq. (19). The resulting theory should thereupon be correct through the requisite orders.[32]

As before, we assume for convenience that the short-range forces between all pairs of ions have hard-sphere character, with the same repulsive diameter

$$\varphi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \varphi(r_{12}) = \infty \quad r_{12} < b$$
$$= 0 \quad r_{12} \geq b; \quad (45)$$

in view of hydration difference between Regions I and II, b should probably be chosen larger than its corresponding value a on the adsorption plane.

The final result is found to be

$$\rho_\alpha(\mathbf{r}_1) = y_\alpha \exp\Bigg(-(\epsilon_\alpha/kT)[w^{(1)}(z_1) + \bar{\psi}_{\text{cav}}(\mathbf{r}_1)] + B(z_1)$$

$$+ \frac{\epsilon_\alpha^2}{2KkT} \int_{\text{II}} d\mathbf{r}_2 \Big\{ Kw^{(2)}(12) \exp\Big[-\frac{\varphi(12)}{kT}\Big] \Big\}$$

$$\times \Big[\frac{\kappa^2(2)}{4\pi}\Big]\chi(2, 1) \Bigg), \quad (46)$$

which is closely analogous to (and reduces to) the previous Eq. (20). Now, $\chi(2, 1)$ is the solution to a size-modified version of Eq. (21)

$$\chi(2, 1) = K \exp[-\phi(21)/kT]w^{(2)}(21)$$

$$- \int_{\text{II}} \Big\{ K \exp\Big[-\frac{\varphi(23)}{kT}\Big]w^{(2)}(23) \Big\}$$

$$\times \Big[\frac{\kappa^2(3)}{4\pi}\Big]\chi(3, 1)d\mathbf{r}_3. \quad (47)$$

The mean electrostatic potential denoted now by $\bar{\psi}_{\text{cav}}(\mathbf{r}_1)$ differs from that used previously, $\bar{\psi}(z_1)$, in that the associated charge distribution producing it is

the mean double-layer charge *minus* the charge that would lie, on the average, within the spherical cavity of radius b surrounding the point $\mathbf{r}_1$; of course

$$\bar{\psi}_{\text{cav}}(\mathbf{r}_1) = \bar{\psi}_{\text{cav}}(z_1)$$

due to the symmetry of our problem. Finally, $B(z_1)$ represents an activitylike correction due just to the rigid spherical ion cores:

$$B(z_1) = \int_{h0}^\infty L(z_1, z_2)\rho(z_2)dz_2;$$

$$\rho(z_2) = \sum_{\alpha=1}^\nu \rho_\alpha(z_2);$$

$$L(z_1, z_2) = \tfrac{1}{2}\pi[(z_1 - z_2)^2 - b^2] \quad |z_1 - z_2| \leq b$$
$$= 0 \quad |z_1 - z_2| \geq b. \quad (48)$$

Because the product

$$\exp[-\varphi(r_{12})/kT]w^{(2)}(\mathbf{r}_1, \mathbf{r}_2),$$

unlike $w^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ itself, is not a Green's function for the Laplace differential operator, it is no longer possible to perform the partial integrations which allowed Eq. (20) ultimately to be transformed into the Eq. (29), involving true local activity corrections. Thus the inclusion of ion size, even to lowest contributing order in λ_2, invalidates the method of local thermodynamic balance even if image terms are negligible. On the basis of our extended density distribution results, Eq. (46), we see that all three terms: $\bar{\psi}_{\text{cav}}(\mathbf{r}_1)$, $B(z_1)$, and the $\chi(2, 1)$ integral, depend not on just the mean potential and mean densities at $\mathbf{r}_1$, but instead involve these distributions over at least a finite spatial extension about $\mathbf{r}_1$. This more complicated functional dependence extends into every succeeding order. Diffuse layer theories which properly account for ion size are therefore necessarily nonlocal in nature. Of course, the Poisson equation (21) for the physically important mean potential $\bar{\psi}$ always remains valid.

Unfortunately it is not possible to make many general statements about the effect that ion size has upon potential and ion distributions in the diffuse layer. It is known that if the $\bar{\psi}_{\text{cav}}$ term is retained in place of $\bar{\psi}$ as the only important modification of Eq. (29), that the resulting charge and potential distributions change even their qualitative nature as the dimensionless quantity λ_2 becomes of order 1.[33,34] Because an infinity of potential and charge distributions in the diffuse layer would yield the same values for typically measured macroscopic quantities (such as differential capacitance) there is at present no logical justification for supposing that the monotonically decaying (as z_1 increases) solutions for $\bar{\psi}(z_1)$ and $\rho_\alpha(z_1)$ of the local

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[32] It may be shown that more complicated clusters than the rings, such as a ring with a single short-range bond cross link, are all of higher order in one or both of λ_1 and λ_2 than it is necessary to retain.

[33] F. H. Stillinger and J. G. Kirkwood, J. Chem. Phys. **33**, 1282 (1960).

[34] V. S. Krylov and V. G. Levich, Zh. Fiz. Khim. **37**, 106 (1963).

balance theory bear any recognizable relation to the true state of affairs above, say, 1 mole/liter in uni-univalent aqueous electrolytes.

VI. COLLOID STABILITY

Finally, we apply the inhomogeneous fluid cluster theory to the colloid stability problem. Here, it is required to calculate the free energy of the total (and often interfering) set of electrical double layers surrounding colloid particles suspended in the aqueous electrolyte medium.[8] We shall be interested in a dilute solution theory corresponding to the calculation of Secs. III and IV.

Figure 3 displays schematically a set of colloid particles, for which we assume that it is adsorption of ions, on the total surface S_a, which imparts charge to prevent coagulation. The ions in the diffuse layer lie outside another surface S_0; thus S_a and S_0 are the respective analogs of the inner and outer Helmholtz planes used previously.

As before, even if ions outside S_0 are dilute, the ions at S_a may be quite crowded, so although ion size will be neglected between pairs in the diffuse layers, it must again be taken into account for adsorbed ions. We continue to suppose that no short-range forces are operative across S_0.

Although our Fig. 3 perhaps realistically shows the particles as somewhat irregular in shape, electrostatic calculations such as performed in Sec. II, and which underlie any subsequent detailed statistical mechanical calculations, are necessarily restricted to very simple geometries. We initially assume, though, that for any problem of interest, the $w^{(1)}$'s and $w^{(2)}$'s are available. Furthermore, we suppose that colloid charge is due *only* to adsorbed ions, so that in calculation of $w^{(1)}$ and $w^{(2)}$, the dielectric displacement will be continuous across the water–colloid surface.[35]

From the thermodynamic identification procedure in the theory of the grand partition function,[16] we find that the extra interfacial free-energy F of the electrolyte (beyond what it would exhibit if it were not invaded by colloid particles), may be obtained by computing the integral

$$F = \int [\Pi(\mathbf{r}_1) - \Delta_s(\mathbf{r}_1)\Pi(\infty)]d\mathbf{r}_1, \qquad (49)$$

where $\Pi(\mathbf{r}_1)$ is the local osmotic pressure given in Eq. (15) as an inhomogeneous fluid cluster sum, and $\Pi(\infty)$ is the osmotic pressure of the homogeneous electrolyte at a position far away from colloid particles. $\Delta_s(\mathbf{r}_1)$ is a unit step function which discontinuously jumps from 0 to 1 in crossing an arbitrary dividing surface S, parallel to the colloid surface, when going from the colloid to the solution phase; since it is pri-

marily colloid particle position dependence of F which is significant for the stability problem, and since variations in position of S can only add constants to F, we may for convenience identify S with S_0.

The calculation of $\Pi(\mathbf{r}_1)$ follows closely the procedure given in Secs. III and IV, so that all details need not be reiterated. It is however worth noting that in F, electrostatic contributions to the set of pair clusters (in which the Coulomb part of the f bonds are treated in linear fashion as before), may be first identified as

$$\tfrac{1}{2}\int \rho_{el}(\mathbf{r}_1)w^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\rho_{el}(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \qquad (50)$$

where

$$\rho_{el}(\mathbf{r}) = \sum_{\alpha=1}^{\nu}\epsilon_\alpha\rho_\alpha(\mathbf{r}),$$

which is the total electrostatic charge interaction energy integral. Subsequently, the expression (50) may be transformed to

$$\frac{1}{8\pi}\int \mathbf{D}(\mathbf{r}_1)\cdot\mathbf{E}(\mathbf{r}_1)d\mathbf{r}_1 \qquad (51)$$

(where $\mathbf{D}$ and $\mathbf{E}$ are the local mean dielectric displacement, and electric field), by means of Poisson's equation and partial integration.

It is ultimately found that

$$F = \int \frac{\mathbf{D}\cdot\mathbf{E}}{8\pi}d\mathbf{r}_1$$
$$+ \int_{\Pi} d\mathbf{r}_1 \sum_{\alpha=1}^{\nu}\left(\rho_\alpha(\mathbf{r}_1)\left\{ kT - \frac{\epsilon_\alpha^2\kappa(\mathbf{r}_1)}{K}\left[\frac{1}{6} + J(\mathbf{r}_1)\right]\right\}\right.$$
$$\left. - \rho_\alpha(\infty)\left[kT - \frac{\epsilon_\alpha^2\kappa(\infty)}{6K}\right]\right) + \int_{S_a}\Pi_a(\mathbf{s})d\mathbf{s}. \qquad (52)$$
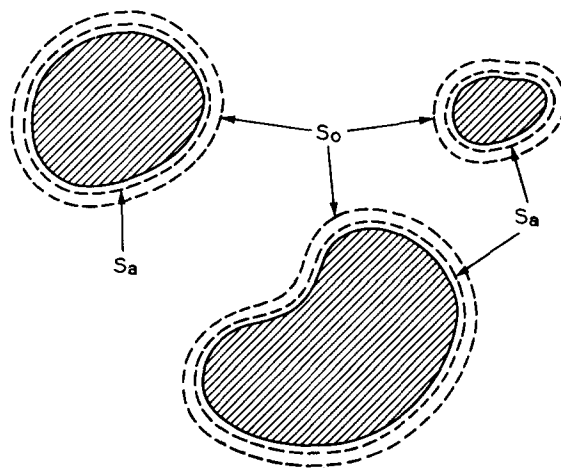

FIG. 3. Colloid particles suspended in aqueous electrolyte. S_a is the ion adsorption surface, and S_0 is the surface of closest approach for unadsorbed ions.

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[35] In Sec. II, this boundary condition would have been equivalent to setting $\sigma = 0$.

The first integral, over all space, is of course the double-layer field free energy (51). The second integral over the Region (II) accessible to unadsorbed ions, has as its integrand (aside from J) the local value of the osmotic pressure deviation, in the dilute solution Debye–Hückel form. The electrostatic images produced by ions in the large colloid particles yield a contribution to this integral also, denoted by $J(\mathbf{r}_1)$, which is unanticipated by the bulk osmotic pressure theory. Since these images have rapidly declining effects as one recedes into Region II from the surface S_0, it is perhaps adequate to adopt the form of J appropriate to a single platelike particle, which (if it is metallic) demands[2]

$$J(\mathbf{r}_1) = \frac{1}{u^3} - \left(\frac{1}{2u} + \frac{1}{u^2} + \frac{1}{u^3}\right) \exp(-u),$$

$$u = 2\kappa(\mathbf{r}_1) z_1. \qquad (53)$$

Finally, $\Pi_a(\mathbf{s})$ is a local two-dimensional spreading pressure on S_a for the adsorbed ions, for which it has been assumed there is but one type, α:

$$\Pi_a(\mathbf{s}_1) = \int_{z_a-\epsilon}^{z_a+\epsilon} dz_1 \bigg\{ \Pi(\mathbf{r}_1) - \tfrac{1}{2}\rho_{el}(\mathbf{r}_1)$$

$$\times \int w^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rho_{el}(\mathbf{r}_2) d\mathbf{r}_2 \bigg\}$$

$$\to \Pi_a^{(0)}(\rho_\alpha{}^{ads}) + \tfrac{1}{2}(\epsilon_\alpha \rho_\alpha{}^{ads})^2$$

$$\times \int d\mathbf{s}_{12} w^{(2)}(\mathbf{s}_{12}) \left\{ \frac{\partial}{\partial \rho_\alpha{}^{ads}} \left[\frac{\rho_{\alpha\alpha}{}^{(2,0)}(s_{12})}{\rho_\alpha{}^{ads}} \right] - 1 \right\}; \qquad (54)$$

analogous to our previous calculations, the distance z_1 is measured normal to the surface S_a at position $\mathbf{s}_1$. In deriving the result following the arrow in (54), it has been postulated that at least locally the adsorbed system may be regarded as flat and homogeneous. $\Pi_a^{(0)}$ is the hypothetical spreading pressure for the adsorbed set of ions, assuming they interact only through their short-range forces.

In the same manner as led previously to Eq. (42), $\Pi_a^{(0)}$ may be assigned an explicit form if it is proper to assume that the short-range forces acting on surface S_a are those for rigid spheres of diameter a. The Helfand–Frisch–Lebowitz theory[29] leads to:

$$\Pi_a^{(0)}(\rho_\alpha{}^{ads}) = kT\rho_\alpha{}^{ads}[1 - \pi\rho_\alpha{}^{ads}a^2/4]^{-2}. \qquad (55)$$

Equations (52)–(55) constitute a microscopically explicit prescription for finding double-layer free energy in colloidal suspensions. The field free-energy term in (52), as well as the ideal solution part of the osmotic pressure in Region II, have traditionally been employed since Verwey and Overbeek's original calculations.[8] Our consistent analysis suggests local activity and image corrections in the diffuse charge region as additional contributions. Furthermore, we have obtained explicit expressions for the adsorbed ion portion of the interfacial free energy. Having thus obtained F by means of our approach, the colloid stability question is then answerable by means of standard calculations.[8]

It has already been noted in Sec. II that dielectric saturation and electrostriction cannot at present be built into cluster theory in a completely natural and logical fashion. Again, though, it is possible to account approximately for these phenomena in the present double-layer free-energy calculation by a suggestion from the variational version of local thermodynamics. One finds that if the correct local densities are used in the remaining terms in Eq. (52), it is only necessary to replace the field free-energy term by:

$$\frac{1}{4\pi} \int d\mathbf{r}_1 \int_0^{\mathbf{E}(\mathbf{r}_1)} \bigg[\mathbf{D}(\mathbf{E}', \mathbf{r}_1) - \sum_{\alpha=1}^{\nu} \rho_\alpha(\mathbf{r}_1)$$

$$\times \left[\frac{\partial \mathbf{D}(\mathbf{E}', \mathbf{r}_1)}{\partial \rho_\alpha} \right]_{T, \mathbf{E}', \bar{\psi}, \rho_{\beta \neq \alpha}} \bigg] \cdot d\mathbf{E}', \qquad (56)$$

where the field integration is to be carried out at fixed local composition. In view of the fact that the extended macroscopic description embodied in Eq. (56) includes electrostrictive terms (the composition derivatives of $\mathbf{D}$), the resulting augmented theory accounts at least partially for mutual polarization effects between particles in the strong fields of the double layer region.

As before, one can show that retention of lowest order ion size effects in Region II invalidates the use of an osmotic pressure, as appears in Eq. (52), with the same functional dependence on local concentrations as exhibited by the bulk phase osmotic pressure.