

Ion-Pair Theory of Concentrated Electrolytes. I. Basic Concepts

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The statistical thermodynamics of symmetrical "primitive-model" electrolytes is formulated in such a way that all ions are uniquely paired. The behavior of the resulting fluid of "polar molecules" may conveniently be described by a wavelength-dependent dielectric constant $\epsilon(k)$. A rigorous formula of the Kirkwood type for $\epsilon(k)$ is derived. Since ion-atmosphere mean charge densities may be obtained from $\epsilon(k)$, this dielectric function is utilized in construction of an electrolyte free-energy expression [Eq. (50)], as well as to establish an exact second-moment condition on the ion atmospheres [Eq. (73)]. From the latter it is demonstrated that for rigid spherical ions of diameter a , the ion atmospheres necessarily each have nonuniform charge sign when $\kappa a > 6^{1/2}$ (κ^{-1} = Debye length).

I. INTRODUCTION

Shortly after the classic Debye-Hückel¹ theory of dilute electrolytes appeared, Bjerrum² suggested the intuitively appealing notion of ion pairing as a means of extending its applicability to higher concentration. The present paper, and the following one, represent implementation of the Bjerrum idea in an extreme form, since all ions are forced to pair by convention. Although the theoretical style and physical emphasis of this work differ from Bjerrum's, we feel that the approach serves to clarify the fundamental basis of

this work, as well as that of several other notable contributions to ion-pair theory.³⁻⁵

In the interests of expository simplicity, the material reported here is restricted in scope to the so-called "primitive-model" electrolyte; that is, the ions are all regarded as rigid spheres of identical size in a linear structureless dielectric solvent, and they bear charges $\pm Ze$. For this highly idealized electrolyte, there are two fundamental physical parameters characterizing the system. The first is a dimensionless density giving the extent of geometric packing of the rigid ion cores of diameter a :

$$\zeta_1 = 2Na^3/V. \quad (1)$$

Here it is presumed that N anions and N cations comprise the ionic solution in volume V . ζ_1 can in

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¹ P. Debye and E. Hückel, *Physik. Z.* **24**, 185, 305 (1923).

² N. Bjerrum, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.* **7**, 1 (1926). A more accessible reference for the Bjerrum analysis is R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, England, 1960), p. 409.

³ R. M. Fuoss, *Trans. Faraday Soc.* **30**, 967 (1934).

⁴ H. Reiss, *J. Chem. Phys.* **25**, 400, 408 (1956).

⁵ J. C. Poirier and J. H. DeLap, *J. Chem. Phys.* **35**, 213 (1961).

principle vary between 0 and the upper limit $2^{1/2}$ imposed by close packing of the spheres. The electrostatic interaction in the system may be measured in terms of a second parameter, the potential energy of two like ions in contact, divided by the thermal energy $k_B T$:

$$\zeta_2 = (Ze)^2 / \epsilon_0 a k_B T, \quad (2)$$

where ϵ_0 is the solvent dielectric constant. The possibility that ζ_2 might have any nonnegative real value must be considered.

The basic goal consists in finding the Helmholtz free energy per ion divided by $k_B T$ for the primitive model, $F(\zeta_1, \zeta_2) / 2N k_B T$. If this quantity is written with the noninteracting (ideal-ion-solution) portion separated,

$$F(\zeta_1, \zeta_2) / 2N k_B T = (F_{\text{ideal}} / 2N k_B T) + F_1(\zeta_1, \zeta_2), \quad (3)$$

then $F_1(\zeta_1, \zeta_2)$ embodies all interaction effects.

In order to establish a suitable context in which to view the present work, Fig. 1 provides a schematic phase diagram for the primitive model in the ζ_1, ζ_2 plane. Although the system should exhibit at least two crystalline phases, we shall be solely concerned with that portion of the diagram in which a single fluid phase obtains.

Along the ζ_1 axis ($\zeta_2 = 0$), the system consists essentially of uncharged rigid spheres, the statistical properties of which are sufficiently well known for present purposes.⁶ In particular we note the virial series for $F_1(\zeta_1, 0)$ in integral powers of ζ_1 :

$$F_1(\zeta_1, 0) = (2\pi/3)\zeta_1 + (5\pi^2/36)\zeta_1^2 + 0.87874\zeta_1^3 + \dots \quad (4)$$

In the reverse situation with finite $\zeta_2 > 0$ but $\zeta_1 = 0$,

$$F_1(0, \zeta_2) = 0, \quad (5)$$

since this case is equivalent to infinite dilution. The famous Debye-Hückel limiting law specifies the lowest ζ_2 -order contribution to F_1 at any value of ζ_1 , and in the present notation has the following form:

$$F_1(\zeta_1, \zeta_2) \sim F_1(\zeta_1, 0) - (2\pi^{1/2}/3)\zeta_1^{1/2}\zeta_2^{3/2}. \quad (6)$$

It is the task of concentrated-electrolyte theory to extend this development to higher ζ_2 order.

The process of formally pairing all ions serves two purposes. First the difficulty of the long-range nature of Coulomb forces is mitigated somewhat in that the resulting "dipolar molecules" have obviously zero net charge, and may be described by the well-understood techniques of the statistical mechanics of dielectrics. Second, it is likely that the complicated solvation and specific saturable chemical interactions operative in real electrolytes act mainly between the two members of ion pairs (on account of their closeness) rather than between ions unpaired with each other, so that any theory including these effects finds the ion-pair approach as its natural starting point.

The basic statistical-mechanical treatment of the

⁶ H. L. Frisch, *Advan. Chem. Phys.* **6**, 229 (1964).

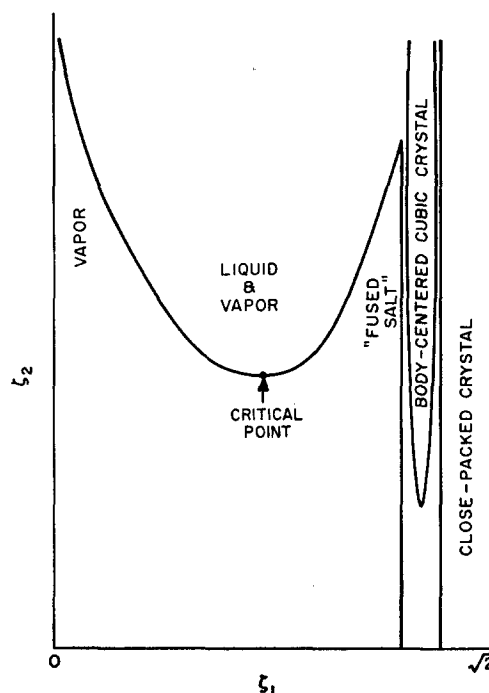


FIG. 1. Phase diagram for the primitive-model electrolyte. The Debye-Hückel regime corresponds to the immediate vicinity of the ζ_1 axis. For sufficiently large electrostatic coupling ζ_2 , a phase separation should occur into a fused-salt-like concentrated fluid and its coexistent dilute vapor, analogous to the situation with real fused salts. Although the body-centered cubic crystal minimizes the electrostatic Madelung energy, and thus should be stable at low temperature (large ζ_2), it would be destroyed by sufficient compression ($\zeta_1 \rightarrow 2^{1/2}$).

complete ion-pairing process is contained in the next section (II). This is followed in Sec. III by introduction of the electrolyte dielectric function $\epsilon(k)$, for which several properties are deduced, including a formula of the Kirkwood type and a free-energy expression in terms of $\epsilon(k)$. In Sec. IV it is shown that the connection between $\epsilon(k)$ and the ion-atmosphere charge distribution leads to a second spatial moment condition on the latter. This moment condition is finally shown to imply that ion atmospheres for the primitive model necessarily possess concentric regions of both charge signs when κa exceeds $6^{1/2} \cong 2.4495$ (κ^{-1} is the Debye length).

The following paper explores a direct approach to calculation of $\epsilon(k)$.

II. ION-PAIRING PROCESS

A. Configuration-Space Splitup

We begin with the canonical partition function for the N anions (numbered 1 to N) and N cations (numbered $N+1$ to $2N$) in volume V ,

$$Q_{N,N} = (\lambda_- \lambda_+)^{-3N} (N!)^{-2} \int_V d\mathbf{r}_1 \cdots \int_V d\mathbf{r}_{2N} \times \exp[-\beta V_{N,N}(\mathbf{r}_1 \cdots \mathbf{r}_{2N})], \quad (7)$$

$$\beta = (k_B T)^{-1},$$

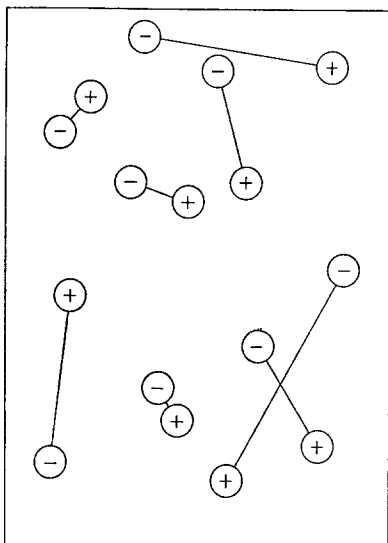


FIG. 2. Typical configuration of ions in the primitive electrolyte model. The unique pairing of all ions specified in the text is indicated by the straight lines.

where λ_- and λ_+ are the anion and cation thermal de Broglie wavelengths, respectively. For the primitive electrolyte model the potential energy consists of a sum of particle-pair terms each of which displays rigid sphere (v_a) and electrostatic parts,

$$\begin{aligned} v_a(r_{ij}) &\pm (Ze)^2/\epsilon_0 r_{ij}, \\ v_a(r_{ij}) &= +\infty \quad (r_{ij} \leq a) \\ &= 0 \quad (r_{ij} > a). \end{aligned} \quad (8)$$

A typical electrolyte ion configuration is diagrammed schematically in Fig. 2 for the primitive model. It is easy to see that aside from special configurations of zero weight, a unique pairing of ions of opposite sign may be executed: (a) out of the entire set of distances between unlike ion pairs, select the smallest and pair off the corresponding anion and cation; (b) after having removed this first ion pair from further consideration, select next the remaining smallest anion-cation distance that exists involving the remaining $2N-2$ ions only, and designate the choice as the second ion pair; (c) continue this process of smallest-distance selection within ion remainder sets until all ions have been paired. The net result (as indicated in Fig. 2) is that each ion serves as a partner for one and only one of opposite charge type.

Obviously the set of ion positions $\mathbf{r}_1 \cdots \mathbf{r}_{2N}$ alone determines which anions pair with which cations. Let \mathcal{R}_N denote that portion of the full $6N$ -dimensional configuration space for the electrolyte for which anion 1 is paired with cation $N+1$, \cdots , anion j with cation $N+j$, \cdots , anion N with cation $2N$. On account of the basic equivalence of all ions of the same charge, $Q_{N,N}$ in Eq. (7) may be written as an integral only over \mathcal{R}_N , if a factor $N!$ is introduced to account for the

fact that this number of possible pairings each contribute equally to $Q_{N,N}$:

$$Q_{N,N} = (\lambda_- \lambda_+)^{-3N} (N!)^{-1} \int_{\mathcal{R}_N} d\mathbf{r}_1 \cdots \int d\mathbf{r}_{2N} \times \exp[-\beta V_{N,N}(\mathbf{r}_1 \cdots \mathbf{r}_{2N})]. \quad (9)$$

The integral restriction in Eq. (9) to region \mathcal{R}_N may be given a very simple interpretation. In order that the given pairing obtain, one must prevent ions of opposite charge contained in *different* pairs from approaching one another more closely than the *shorter* of the distances internal to the two pairs involved. If such a close approach were allowed, say, between anion i and cation j , then the pairing procedure surely would have linked i to j , in contradiction to the postulated pairing. Figure 3 illustrates the configurational restriction for two selected ion pairs.

In the following it is especially convenient to consider this set of restrictions generating \mathcal{R}_N to have arisen from a potential energy function operative between pairs of the "dipolar molecules" (ion pairs). Let the six-component vector \mathbf{x}_i describe the configurational state of ion pair i ,⁷ where \mathbf{x}_i is the direct sum $\mathbf{R}_i \oplus \mathbf{s}_i$ of the pair's center position \mathbf{R}_i and anion-to-cation relative displacement \mathbf{s}_i . Then define $u(\mathbf{x}_i, \mathbf{x}_j)$ to be 0 for all $\mathbf{x}_i, \mathbf{x}_j$ compatible with the postulated ion pairing, and $+\infty$ otherwise, exactly as shown in Fig. 3. By introducing u 's into Eq. (9) Boltzmann-factor integrand for all pairs of ion pairs, the integrations may once again be extended over the entire vessel V :

$$Q_{N,N} = (\lambda_+ \lambda_-)^{-3N} (N!)^{-1} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \times \exp\{-\beta[\sum_{i=1}^N \phi_1(\mathbf{x}_i) + \sum_{i<j=1}^N \phi_2(\mathbf{x}_i, \mathbf{x}_j)]\}, \quad (10)$$

where

$$\begin{aligned} \phi_1(\mathbf{x}_i) &= v_a(r_{i,N+i}) - [(Ze)^2/\epsilon_0 r_{i,N+i}]; \\ \phi_2(\mathbf{x}_i, \mathbf{x}_j) &= u(\mathbf{x}_i, \mathbf{x}_j) + v_a(r_{ij}) + v_a(r_{N+i,j}) + v_a(r_{i,N+j}) \\ &\quad + v_a(r_{N+i,N+j}) + [(Ze)^2/\epsilon_0](r_{ij}^{-1} - r_{N+i,j}^{-1} \\ &\quad - r_{i,N+j}^{-1} + r_{N+i,N+j}^{-1}). \end{aligned} \quad (12)$$

The partition-function expression (10) represents the result of an important transformation. We have thus been able to show that from the standpoint of equilibrium properties the primitive electrolyte is equivalent to a system of dipolar molecules with internal potentials ϕ_1 interacting through pairwise additive (but noncentral) potentials $\phi_2(\mathbf{x}_i, \mathbf{x}_j)$. Although the original hard-sphere and Coulombic interactions comprise part of the potential ϕ_2 acting between two ion pairs, the "steric-hindrance" portion u plays an important role in the subsequent theory.

⁷ We shall use the same index for an ion pair as originally given its anionic member: pair i consists of anion i and cation $N+i$.

B. Ion-Pair Probability Functions

The traditional approach to the statistical thermodynamics of electrolytes examines the molecular distribution functions for sets of ions.⁸ In view of our restatement of the problem in terms of dipolar molecules, we shall now investigate an analogous set of distribution functions for these composite entities.

As is often the case, the theory is most conveniently developed in a grand ensemble context. We therefore utilize the $Q_{N,N}$ in Eq. (10) to construct a grand partition function for our assembly of dipolar molecules,

$$\begin{aligned} \exp(-\beta\Omega) &= 1 + \sum_{N=1}^{\infty} Q_{N,N} [\exp(\beta\mu_{\pm})]^N \\ &= 1 + \sum_{N=1}^{\infty} \frac{y^N}{N!} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \\ &\quad \times \exp\left\{-\beta\left[\sum_{i=1}^N \phi_1(\mathbf{x}_i) + \sum_{i < j=1}^N \phi_2(\mathbf{x}_i, \mathbf{x}_j)\right]\right\}, \quad (13) \end{aligned}$$

where μ_{\pm} is the dipolar-molecule chemical potential (i.e., the chemical potential of the electrolyte), and where we set

$$y = (\lambda_- \lambda_+)^{-3} \exp(\beta\mu_{\pm}). \quad (14)$$

Although unlike the usual binary-system grand partition function Eq. (13) permits only equal numbers of anions and cations in the system, the macroscopic electroneutrality condition renders this restriction irrelevant in the so-called "thermodynamic limit"; in particular the grand potential Ω may be identified as usual in this limit

$$\Omega \sim -pV, \quad (15)$$

where p is the osmotic pressure.⁹

Dipolar-molecule distribution functions are now defined by the statement that for $n=1, 2, \dots$,

$$p^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) d\mathbf{x}_1 \cdots d\mathbf{x}_n \quad (16)$$

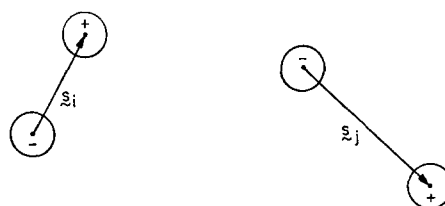
represents the probability that dipolar molecules (ion pairs) simultaneously occupy center-position and orientation-length space elements $d\mathbf{x}_1 \cdots d\mathbf{x}_n$, irrespective of the state of the remainder of the system. By invoking the standard probabilistic interpretation of the terms in Eq. (13), the $p^{(n)}$ are found to be¹⁰

$$\begin{aligned} p^{(n)}(\mathbf{x}_1 \cdots \mathbf{x}_n) &= \exp(\beta\Omega) \sum_{N=n}^{\infty} \frac{y^N}{(N-n)!} \int d\mathbf{x}_{n+1} \cdots \int d\mathbf{x}_N \\ &\quad \times \exp\left\{-\beta\left[\sum_{i=1}^N \phi_1(\mathbf{x}_i) + \sum_{i < j=1}^N \phi_2(\mathbf{x}_i, \mathbf{x}_j)\right]\right\}. \quad (17) \end{aligned}$$

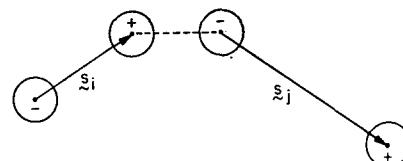
⁸ J. G. Kirkwood and J. C. Poirier, *J. Phys. Chem.* **58**, 591 (1954).

⁹ W. G. McMillan and J. E. Mayer, *J. Chem. Phys.* **13**, 276 (1945).

¹⁰ T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Co. New York, 1956), Sec. 37.



(a) ALLOWED CONFIGURATION, $u(\mathbf{x}_i, \mathbf{x}_j) = 0$



(b) UNALLOWED CONFIGURATION, $u(\mathbf{x}_i, \mathbf{x}_j) = +\infty$

FIG. 3. Configurational restrictions for a given ion pairing (vector connections \mathbf{s}_i and \mathbf{s}_j). In case (a) the oppositely charged ends of the different pairs are farther apart than the minimum of s_i and s_j , so the configuration is permissible and "steric hindrance" potential u vanishes. In case (b) the condition is violated, the dotted line should have been drawn in the pairing process, so u is taken to be $+\infty$.

In the special case $n=1$, the quantity $p^{(1)}$ will depend only on the ion-pair scalar separation s in the isotropic homogeneous electrolyte bulk, and its variation with s will give the distribution of ion-pair sizes. The more complicated ion-pair doublet probability $p^{(2)}$ likewise will display certain invariances stemming from isotropy, and could be used in connection with ϕ_1 and ϕ_2 to write out quadratures for the mean energy, the osmotic pressure in virial form, and the isothermal osmotic compressibility for the electrolyte.

It is important to recognize that the set of functions $p^{(n)}$ carry greater structural information about the microscopic state of the electrolyte than do the more orthodox ion-distribution functions. As an illustration we remark that no finite set of the ordinary ionic-distribution functions suffice to give any $p^{(n)}$, but from $p^{(1)}, \dots, p^{(n)}$ all of the ordinary ionic-distribution functions of orders 1 to n may be obtained.¹¹

C. Cluster Expansions

Although Ursell-Mayer cluster expansions¹² have been mainstays in the theory of fluids of interacting particles, they encounter special convergence difficulties in the case of long-range Coulomb interactions between ions.^{13,14} The transformation to ion pairs as the

¹¹ A concrete example for $n=2$ appears in the following paper [R. Lovett and F. H. Stillinger, Jr., *J. Chem. Phys.* **48**, 3869 (1968)], Appendix A.

¹² J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chap. 13.

¹³ J. E. Mayer, *J. Chem. Phys.* **18**, 1426 (1950).

¹⁴ H. L. Friedman, *Ionic Solution Theory* (Interscience Publishers, Inc., New York, 1962).

fundamental uncharged particles in the system very likely improves the convergence properties of the cluster expansions. But even if it is still necessary to perform partial graph summations to ensure finiteness, the formal cluster expansions still have heuristic value in revealing qualitative properties of the electrolyte. For this reason we now turn attention briefly to these cluster expansions.

Owing to the internal degrees of freedom of the ion pairs, as well as the noncentral forces between them, the cluster theory usually exhibited requires some notational generalization for present purposes. Thus the Mayer f function

$$f(\mathbf{x}_i, \mathbf{x}_j) = \exp[-\beta\phi_2(\mathbf{x}_i, \mathbf{x}_j)] - 1, \quad (18)$$

now clearly depends on the sizes and relative orientations of the two pairs, as well as their distance apart.

With this modification, and the observation that the ion-pair internal potential ϕ_1 has formally the character of an external potential acting on the dipolar molecules, we may immediately draw upon the results of the cluster theory of inhomogeneous fluids.^{15,16} The Helmholtz free energy accordingly adopts the following form:

$$\begin{aligned} \beta F[p^{(1)}] = & \int d\mathbf{x}_1 p^{(1)}(\mathbf{x}_1) \\ & \times \{ \beta\phi_1(\mathbf{x}_1) + \ln[(\lambda_{-}\lambda_{+})^3 p^{(1)}(\mathbf{x}_1)] - 1 \} - \sum_{n=1}^{\infty} [(n+1)!]^{-1} \\ & \times \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_{n+1} S^{(n)}(\mathbf{x}_1 \cdots \mathbf{x}_{n+1}) \\ & \times p^{(1)}(\mathbf{x}_1) \cdots p^{(1)}(\mathbf{x}_{n+1}), \quad (19) \end{aligned}$$

and may be regarded as a functional of $p^{(1)}$. Here, $S^{(n)}$ is the irreducible (at least doubly connected) cluster sum of f -function products for $n+1$ ion pairs.¹²

It is useful to think of ion pairs with different sizes $s_i = |\mathbf{s}_i|$ as being different chemical species. As a result of thermal motion in the electrolyte, pairs will of course change size, as well as change partners. The result is a dynamical equilibrium that is established between different sized species with concentrations corresponding to free-energy minimization. This, in the terminology of chemical equilibrium, is the basis of the known variational property of $\beta F[p^{(1)}]$ in Eq. (19)¹⁶; the correct ion-pair singlet size distribution $p^{(1)}$ is the function for which $\beta F[p^{(1)}]$ achieves its absolute minimum subject to the constraint

$$N = \int d\mathbf{x}_1 p^{(1)}(\mathbf{x}_1). \quad (20)$$

The explicit variational calculation is easy to carry out by the standard approach. One finds that the

¹⁵ F. H. Stillinger, Jr., and F. P. Buff, *J. Chem. Phys.* **37**, 1 (1962).

¹⁶ T. Morita and K. Hiroike, *Progr. Theoret. Phys. (Kyoto)* **25**, 537 (1961).

condition on $p^{(1)}$ that produces the absolute free-energy minimum is

$$\begin{aligned} p^{(1)}(\mathbf{x}_1) = & y \exp\left(-\beta\phi_1(\mathbf{x}_1) + \sum_{n=1}^{\infty} (n!)^{-1}\right. \\ & \times \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_{n+1} S^{(n)}(\mathbf{x}_1 \cdots \mathbf{x}_{n+1}) \\ & \left. \times p^{(1)}(\mathbf{x}_2) \cdots p^{(1)}(\mathbf{x}_{n+1})\right); \quad (21) \end{aligned}$$

that is, $p^{(1)}$ is required to satisfy a nonlinear integral equation. The electrolyte activity parameter y arises of course as a Lagrange multiplier for constraint (20).

The cluster sum appearing in the right-hand member of Eq. (21) is known to have a simple interpretation.¹⁷ It is the reversible isothermal work $W_c(\mathbf{x}_1)$ that must be performed on the medium in order to open up an empty cavity sufficiently large to contain, without geometrically unallowed overlaps, the ion pair at position \mathbf{x}_1 :

$$p^{(1)}(\mathbf{x}_1) = y \exp\{-\beta[\phi_1(\mathbf{x}_1) + W_c(\mathbf{x}_1)]\}. \quad (22)$$

In the case of large cluster size s_1 , the steric-hindrance potential u clearly can restrict quite severely the motion freedom for ion pairs neighboring the one of interest at \mathbf{x}_1 . Consequently W_c should be large and positive, and from Eq. (22) the corresponding large-ion-pair probability should be small. In the following paper we shall investigate in quantitative detail the implications for $p^{(1)}$ of this sterically produced cavity free energy W_c .

The ion-pair doublet probability has exactly the same generic representation as any other molecular-pair distribution function.¹⁸ It equals a product of $p^{(1)}$'s for each of the pairs times a correlation factor that reduces to unity when the two pairs are microscopically distant from each other:

$$p^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = p^{(1)}(\mathbf{x}_1) p^{(1)}(\mathbf{x}_2) \exp[-\beta w^{(2)}(\mathbf{x}_1, \mathbf{x}_2)]. \quad (23)$$

The quantity $w^{(2)}$ is the usual potential of mean force operative between the two pairs,¹⁸ and in the present circumstance depends obviously on the entire set of relative distances and angles. The cluster expansion for the mean force potential,

$$\begin{aligned} -\beta w^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = & -\beta\phi_2(\mathbf{x}_1, \mathbf{x}_2) + \sum_{n=1}^{\infty} (n!)^{-1} \\ & \times \int d\mathbf{x}_3 \cdots \int d\mathbf{x}_{n+2} S_2^{(n)}(\mathbf{x}_1, \mathbf{x}_2 | \mathbf{x}_3 \cdots \mathbf{x}_{n+2}) \\ & \times p^{(1)}(\mathbf{x}_3) \cdots p^{(1)}(\mathbf{x}_{n+2}), \quad (24) \end{aligned}$$

¹⁷ F. H. Stillinger, Jr., *J. Chem. Phys.* **38**, 1486 (1963); see especially Eq. (27). Although this reference is devoted to the general statistical-mechanical theory of physical clusters of all sizes, its results apply in particular to two-particle ion pairs.

¹⁸ Reference 10, Chap. 6.

involves in $S_2^{(n)}$ all products of f functions whose graphs are at least singly connected among the n field points (none of which are permitted to be articulation points), and are additionally doubly rooted at \mathbf{x}_1 and \mathbf{x}_2 .¹⁹

The density of ion pairs at \mathbf{x}_2 in the proximity of a fixed ion pair at \mathbf{x}_1 is of course given by the ratio

$$p^{(2)}(\mathbf{x}_1, \mathbf{x}_2) / p^{(1)}(\mathbf{x}_1) = p^{(1)}(\mathbf{x}_2) \exp[-\beta w^{(2)}(\mathbf{x}_1, \mathbf{x}_2)]. \quad (25)$$

Starting from this conditional probability, we may calculate, say, the density of cations, ρ_+ , in the vicinity of the fixed ion pair. Figure 4 shows a convenient choice of coordinates for this purpose: t measures displacement of the cationic end of pair 2 from the center of pair 1, with θ the angle between t and \mathbf{s}_1 . The ion density $\rho_+(t)$ may be obtained merely by integrating quantity (25) with respect to \mathbf{s}_2 ,

$$\rho_+(t) = \int d\mathbf{s}_2 p^{(1)}(s_2) \exp[-\beta w^{(2)}(\mathbf{s}_1, \mathbf{s}_2, t)], \quad (26)$$

where dependence on the new variables has been explicitly indicated.

In the $w^{(2)}$ cluster expansion shown in Eq. (24), we have the option of separating the contribution of $u(\mathbf{x}_1, \mathbf{x}_2)$, the direct steric-hindrance potential for pairs 1 and 2, from the remainder of $\phi_2(\mathbf{x}_1, \mathbf{x}_2)$ as well as the entire cluster sum. In other words we write

$$-\beta w^{(2)}(\mathbf{x}_1, \mathbf{x}_2) = -\beta u(\mathbf{x}_1, \mathbf{x}_2) - \beta \tilde{w}(\mathbf{x}_1, \mathbf{x}_2), \quad (27)$$

with \tilde{w} the requisite remainder. Now the Boltzmann factor $\exp[-\beta u(\mathbf{x}_1, \mathbf{x}_2)]$ is either 0 or 1 depending on the relative disposition of the two pairs. By taking account of the definition of u , Eq. (26) may be rearranged into the following form:

$$\rho_+(t) = \int d\mathbf{s}_2 p^{(1)}(s_2) \times \langle \exp[-\beta \tilde{w}(\mathbf{s}_1, \mathbf{s}_2, t)] \rangle_{\chi} \chi(s_1, s_2, t, \theta) \times U_0[d - \min(s_1, s_2)]; \quad (28)$$

$$U_0(x) = 0 \quad (x \leq 0) \\ = 1 \quad (x > 0); \quad (29)$$

$$d = [(s_1/2)^2 + t^2 + s_1 t \cos \theta]^{1/2}. \quad (30)$$

χ stands for that fraction of the total solid angle through which pair 2 may be rotated (at fixed s_2) without its negative end getting closer to the positive end of pair 1 than the minimum of distances s_1 and s_2 , $\min(s_1, s_2)$. The quantity $\langle \exp(-\beta \tilde{w}) \rangle_{\chi}$ then is the average value over this fractional solid angle of the indicated Boltzmann factor.

Each of the integrand factors $p^{(1)}$, $\langle \exp(-\beta \tilde{w}) \rangle_{\chi}$, and χ in Eq. (28) are continuous functions s_2 , t , and θ .

¹⁹ J. M. J. van Leeuwen, J. Groeneveld, and J. de Boer, *Physica* **25**, 792 (1959).

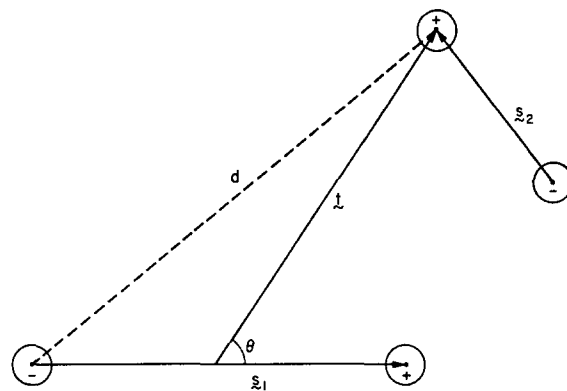


FIG. 4. Coordinate system used in evaluating local ion densities in the neighborhood of a fixed ion pair (the pair with separation s_1).

However the unit step-function factor produces two distinct forms for Expression (28) depending on whether d is less, or greater than s_1 :

$$\rho_+(t) = \int_{(s_2 < d)} d\mathbf{s}_2 p^{(1)}(s_2) \langle \exp(-\beta \tilde{w}) \rangle_{\chi} \chi \quad (d < s_1) \\ = \int_{(s_2 < \infty)} d\mathbf{s}_2 p^{(1)}(s_2) \langle \exp(-\beta \tilde{w}) \rangle_{\chi} \chi \quad (d > s_1). \quad (31)$$

This sudden change from integrating only over sizes $s_2 < d$ for pair 2, to all sizes as d increases beyond s_1 , implies a discontinuity in $\rho_+(t)$. From Fig. 4 it is easy to see that $\rho_+(t)$ is discontinuous across the entire spherical surface of radius s_1 centered at the anion of pair 1.

The local ion density $\rho_+(t)$ must possess cylindrical symmetry about the axis of ion pair 1. Furthermore the manifest charge symmetry of the primitive electrolyte model implies that the local anion density ρ_- may be obtained immediately from ρ_+ by an inversion operation,

$$\rho_-(t) = \rho_+(-t), \quad (32)$$

so that ρ_- must be discontinuous at the s_1 -sphere surface centered about the cation of pair 1. The local average electrostatic charge density around the fixed ion pair 1 is provided by the linear combination

$$Ze[\rho_+(t) - \rho_-(t)], \quad (33)$$

and since both s_1 spheres are its discontinuity surfaces, it generates three lens-shaped regions about the fixed ion pair, as shown in Fig. 5.

This type of elaborate statistical structure in the ionic medium surrounding any ion pair apparently has not been heretofore uncovered in ion-pair theory. We have seen it arise here however as a natural outgrowth of the use of steric-hindrance potentials to represent configurational constraints. It must however be kept in mind that these discontinuities result from the mathematical complexity of the ion-pair descriptive approach, and do not imply striking new observable phenomena in electrolytes.

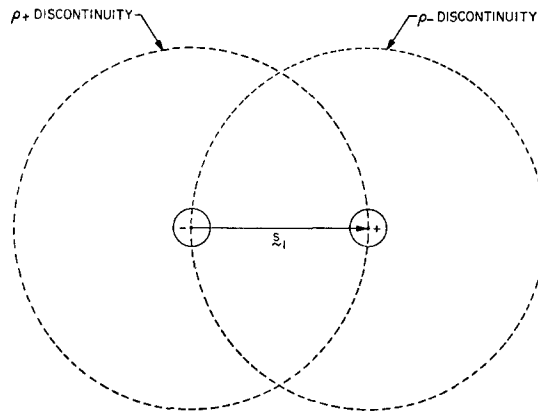


FIG. 5. Discontinuity surfaces for local charge density in the vicinity of a fixed ion pair.

III. DIELECTRIC FORMALISM

A. Phenomenological Basis

By using a language for electrolytes slanted toward the view of ion pairs as polar molecules, it becomes natural to inquire into dielectric behavior. It is now our task to analyze the linear response of the electrolyte to an applied sinusoidal electrostatic potential.

The requisite applied potential generally cannot be generated by a charge distribution external to the system. Instead, an applied potential

$$\psi_{\text{ap}}(\mathbf{r}) = (\psi_0/\epsilon_0) \sin(\mathbf{k} \cdot \mathbf{r}), \quad (34)$$

in pure solvent with dielectric constant ϵ_0 , can arise only from an applied charge distribution

$$\rho_{\text{ap}}(\mathbf{r}) = (\psi_0 k^2/4\pi) \sin(\mathbf{k} \cdot \mathbf{r}) \quad (35)$$

throughout the same region.²⁰ Since we wish also to examine the response of electrolyte to ψ_{ap} , the charge ρ_{ap} must be idealized to permit ions to move freely through it, except insofar as they interact with ψ_{ap} itself.

Because the electrolyte is a conducting medium, it will tend to rearrange under the influence of ψ_{ap} in such a way as to shield this applied potential. In the presence of electrolyte, then, the resulting mean sinusoidal potential $\bar{\psi}(\mathbf{r})$ for given (small) ψ_0 will not have the amplitude given in Eq. (34), but instead may be described phenomenologically by means of an electrolyte dielectric function $\epsilon(k)$:

$$\bar{\psi}(\mathbf{r}) = [\psi_0/\epsilon(k)] \sin(\mathbf{k} \cdot \mathbf{r}). \quad (36)$$

Exactly as Poisson's equation relates ψ_{ap} and ρ_{ap} for pure solvent, $\bar{\psi}$ corresponds to a total charge

$$\begin{aligned} \rho_t(\mathbf{r}) &= (\epsilon_0 k^2/4\pi) \bar{\psi}(\mathbf{r}) \\ &= [\psi_0 \epsilon_0 k^2/4\pi \epsilon(k)] \sin(\mathbf{k} \cdot \mathbf{r}). \end{aligned} \quad (37)$$

²⁰ We suppose from now on that periodic boundary conditions apply to the system, and that \mathbf{k} is selected from the appropriate reciprocal lattice.

This total charge comprises both the applied charge ρ_{ap} , as well as the charge ρ_{in} that is induced in the rearranging electrolyte. Therefore

$$\begin{aligned} \rho_{\text{in}}(\mathbf{r}) &= \rho_t(\mathbf{r}) - \rho_{\text{ap}}(\mathbf{r}) \\ &= (\psi_0 k^2/4\pi) \{[\epsilon_0/\epsilon(k)] - 1\} \sin(\mathbf{k} \cdot \mathbf{r}). \end{aligned} \quad (38)$$

The electrolyte can do a perfect job of shielding if it is given enough room in which to perform the task. Therefore, at any concentration $N/V > 0$,

$$\lim_{k \rightarrow 0} \epsilon(k) = +\infty. \quad (39)$$

On the other hand, with fixed $k > 0$, reduction of concentration to zero must result in pure solvent behavior, so

$$\lim_{(N/V) \rightarrow 0} \epsilon(k) = \epsilon_0 \quad (k > 0). \quad (40)$$

In addition, the fact that there is but a fixed number of ionic charges at fixed electrolyte concentration available to shield the many hills and valleys of ψ_{ap} for large k implies that

$$\lim_{k \rightarrow \infty} \epsilon(k) = \epsilon_0. \quad (41)$$

Finally we append the thermodynamic stability criterion,²¹

$$\epsilon_0/\epsilon(k) \leq 1. \quad (42)$$

B. Relation to Ion Atmospheres

There are two available routes in calculation of $\epsilon(k)$ in the fundamental statistical mechanical theory. One employs the direct and conventional description in terms of ions, the other employs our polar fluid representation. Both approaches need to be followed through independently, since the forms of the results are different, and at the same time useful.

In pursuit of the first of these, we convert grand partition function (13) into single-ion coordinate language, involving the initially introduced anion positions $\mathbf{r}_1 \cdots \mathbf{r}_N$ and cation position $\mathbf{r}_{N+1} \cdots \mathbf{r}_{2N}$:

$$\begin{aligned} \exp(-\beta\Omega) &= 1 + \sum_{N=1}^{\infty} \frac{y^N}{(N!)^2} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_{2N} \\ &\quad \times \exp[-\beta V_{N,N}(\mathbf{r}_1 \cdots \mathbf{r}_{2N})]. \end{aligned} \quad (43)$$

The two independent ionic-doublet correlation functions in the system, normalized to unity at large separation, may be denoted by $g_{++}^{(2)}(r)$ and $g_{+-}^{(2)}(r)$.

²¹ L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, Inc., New York, 1960), pp. 63-64.

In accord with Eq. (43), we have

$$\left(\frac{\bar{N}}{V}\right)^2 g_{+-}^{(2)}(\mathbf{r}_{1,N}) = \exp(\beta\Omega) \sum_{N=1}^{\infty} \frac{y^N}{[(N-1)!]^2} \times \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N \int d\mathbf{r}_{N+2} \cdots \int d\mathbf{r}_{2N} \times \exp[-\beta V_{N,N}(\mathbf{r}_1 \cdots \mathbf{r}_{2N})], \quad (44)$$

$$\left(\frac{\bar{N}}{V}\right)^2 g_{++}^{(2)}(\mathbf{r}_{N+1,N+2}) = \exp(\beta\Omega) \sum_{N=2}^{\infty} \frac{y^N}{N!(N-2)!} \times \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \int d\mathbf{r}_{N+3} \cdots \int d\mathbf{r}_{2N} \times \exp[-\beta V_{N,N}(\mathbf{r}_1 \cdots \mathbf{r}_{2N})],$$

to within terms of negligible order, where \bar{N} is the mean occupation number of the open system.

When the sinusoidal potential ψ_{ap} is turned on, it is necessary to introduce an extra potential energy,

$$Ze \left[- \sum_{i=1}^N \psi_{ap}(\mathbf{r}_i) + \sum_{i=N+1}^{2N} \psi_{ap}(\mathbf{r}_i) \right], \quad (45)$$

into the Boltzmann-factor integrands of Eqs. (43) and (44). At the same time it is a straightforward matter to compute the charge density induced in the electrolyte (in linear approximation). By using definitions (44), and comparing with phenomenological Eq. (38), one obtains an expression for $\epsilon(k)$ in terms of the ionic-doublet correlation functions,

$$\frac{\epsilon_0}{\epsilon(k)} = 1 - \frac{\kappa^2}{k^2} \left(1 + \frac{4\pi\bar{N}}{Vk} \int_0^{\infty} r \sin(kr) \times [g_{++}^{(2)}(r) - g_{+-}^{(2)}(r)] dr \right), \quad (46)$$

where $\kappa^2 = 8\pi(Ze)^2\bar{N}/\epsilon_0 V k_B T$.

This last expression contains a Fourier transform of the correlation function difference, and as such may immediately be inverted to give the ion-atmosphere charge density surrounding a cation,

$$Ze \frac{\bar{N}}{V} [g_{++}^{(2)}(r) - g_{+-}^{(2)}(r)] = - \frac{Ze}{2\pi^2 r} \int_0^{\infty} k \sin(kr) \times \left(\frac{k^2}{\kappa^2} \left[\frac{\epsilon_0}{\epsilon(k)} - 1 \right] + 1 \right) dk, \quad (47)$$

and of course the same result with a sign change applies to the ion atmosphere around an anion. It is especially interesting to notice that the ion atmosphere which surely represents a *nonlinear* response of the surrounding electrolyte to the presence of a fixed ion, can be exactly expressed in terms of the strictly *linear* dielectric response function. By way of contrast we note that the induced charge cloud surrounding a small point

test charge of magnitude δq has the form

$$\frac{\delta q}{2\pi^2 r} \int_0^{\infty} k \sin(kr) \left(\frac{\epsilon_0}{\epsilon(k)} - 1 \right) dk, \quad (48)$$

which follows directly from the definition of $\epsilon(k)$.

The interaction free energy $F_1(\xi_1, \xi_2)$ defined in Eq. (3) may be thought of as consisting of two parts,

$$F_1(\xi_1, \xi_2) = F_1(\xi_1, 0) + F^{(e1)}(\xi_1, \xi_2). \quad (49)$$

The first is just the reduced free energy of the discharged ion cores at the packing density of ultimate interest, and the second is β times the amount of electrical work that must be done per ion in simultaneously charging all ions to their final values, $\pm Ze$. Let the intermediate ion charge values be represented by $\pm Ze\xi$, with $0 \leq \xi \leq 1$, and let $\epsilon(k, \xi)$ stand for the corresponding dielectric response function. Equation (47) may then be taken as the basis for computation of the electrical work by the standard Debye¹ procedure. One finally obtains

$$F^{(e1)}(\xi_1, \xi_2) = - \frac{2(Ze)^2\beta}{\pi} \int_0^1 d\xi \int_0^{\infty} dr \int_0^{\infty} dk k \sin(kr) \times \left[\frac{k^2}{\kappa^2 \xi^2} \left(\frac{\epsilon_0}{\epsilon(k, \xi)} - 1 \right) + 1 \right]. \quad (50)$$

By way of illustration, we remark that Eq. (46) for partially coupled point ions in the Debye-Hückel approximation may be used to compute a "Debye-Hückel dielectric function":

$$\epsilon_0/\epsilon(k, \xi) \cong 1 - [\kappa^2 \xi^2 / (k^2 + \kappa^2 \xi^2)]. \quad (51)$$

Use of this approximation in the free-energy expression (50) generates elementary integrals whose evaluation leads ultimately to the limiting law, Eq. (6).

C. Generalized Kirkwood Formula

Some years ago, Kirkwood²² derived a formally exact expression for the static dielectric constant of a polar fluid. We outline now derivation of the same type of result for the wavelength-dependent dielectric function $\epsilon(k)$.

The action of ψ_{ap} on an ion pair in configuration $\mathbf{x}_i = \mathbf{R}_i \oplus \mathbf{s}_i$ amounts to a potential function

$$U(\mathbf{x}_i) = (Ze\psi_0/\epsilon_0) \{ \sin[\mathbf{k} \cdot (\mathbf{R}_i + \frac{1}{2}\mathbf{s}_i)] - \sin[\mathbf{k} \cdot (\mathbf{R}_i - \frac{1}{2}\mathbf{s}_i)] \} = (2Ze\psi_0/\epsilon_0) \cos(\mathbf{k} \cdot \mathbf{R}_i) \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_i). \quad (52)$$

By symmetry we know that the grand partition function (13) has no variation linear in the strength of the external potentials U acting on the dipolar molecules. However the ion-pair singlet probability $p^{(1)}(\mathbf{x})$ does have such a linear variation. Denote by $p^{(n,0)}(\mathbf{x})$ the value of the distribution functions in the absence of U .

²² J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

From Eq. (17) we find the linear variation to be

$$p^{(1)}(\mathbf{x}_1) = p^{(1,0)}(\mathbf{x}_1) - \beta \left(U(\mathbf{x}_1) p^{(1,0)}(\mathbf{x}_1) + \int d\mathbf{x}_2 U(\mathbf{x}_2) p^{(2,0)}(\mathbf{x}_1, \mathbf{x}_2) \right) \equiv p^{(1,0)}(\mathbf{x}_1) + p^{(1,1)}(\mathbf{x}_1). \quad (53)$$

Since the unperturbed $p^{(1,0)}(\mathbf{x}_1)$ refers to the isotropic fluid, it is spherically symmetric with respect to directions of \mathbf{s}_1 and independent of \mathbf{R}_1 , so it cannot contribute to $\rho_{in}(\mathbf{r})$. This induced ionic charge therefore arises solely from $p^{(1,1)}(\mathbf{x}_1) \equiv p^{(1,1)}(\mathbf{R}_1, \mathbf{s}_1)$; by counting both anionic and cationic ends of these "perturbed" dipolar molecules we may write

$$\rho_{in}(\mathbf{r}) = Ze \int d\mathbf{s}_1 [p^{(1,1)}(\mathbf{r} - \frac{1}{2}\mathbf{s}_1, \mathbf{s}_1) - p^{(1,1)}(\mathbf{r} + \frac{1}{2}\mathbf{s}_1, \mathbf{s}_1)]. \quad (54)$$

This may be transformed first by use of the explicit $p^{(1,1)}$ expression in Eq. (53), and then Eq. (52) for U . After some rather tedious and uninformative manipulation, one obtains

$$\rho_{in}(\mathbf{r}) = -4(Ze)^2 \beta \frac{\psi_0}{\epsilon_0} \sin(\mathbf{k} \cdot \mathbf{r}) \times \int d\mathbf{s}_1 \left(\sin^2(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_1) p^{(1,0)}(s_1) + \int d\mathbf{x}_2 \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_1) \times \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_2) \cos(\mathbf{k} \cdot \mathbf{R}_{12}) p^{(2,0)}(\mathbf{s}_1, \mathbf{R}_{12}, \mathbf{s}_2) \right), \quad (55)$$

$\mathbf{R}_{12} = \mathbf{R}_2 - \mathbf{R}_1$. By comparing this last formula for ρ_{in} with the phenomenological equation (38), the second microscopic $\epsilon(k)$ expression is deduced,

$$\frac{\epsilon_0}{\epsilon(k)} - 1 = - \frac{16\pi(Ze)^2 \beta}{\epsilon_0 k^2} \int d\mathbf{s}_1 \left(\sin^2(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_1) p^{(1,0)}(s_1) + \int d\mathbf{R}_{12} \int d\mathbf{s}_2 \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_1) \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_2) \cos(\mathbf{k} \cdot \mathbf{R}_{12}) \times p^{(2,0)}(\mathbf{s}_1, \mathbf{R}_{12}, \mathbf{s}_2) \right). \quad (56)$$

The standard Kirkwood dielectric formula refers to the infinite wavelength limit. We shall explicitly consider this limit in general formula (56) because mathematical details of passage to $k=0$ are nontrivial, and because the result provides important structural insights into our equivalent dipolar fluid.

First we rewrite Eq. (56) in a slightly modified form. The integrand factor

$$\sin^2(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_1) = \frac{1}{2}[1 - \cos(\mathbf{k} \cdot \mathbf{s}_1)] \quad (57)$$

will be replaced by its spherical average over directions of \mathbf{s}_1 , which is

$$\frac{1}{2}\{1 - [\sin(k s_1)/k s_1]\}. \quad (58)$$

Also, $p^{(1,0)}(s_1) p^{(1,0)}(s_2)$ may be subtracted from the $p^{(2,0)}$ factor without changing the value of the integral. Consequently,

$$\frac{\epsilon_0}{\epsilon(k)} - 1 = - \frac{16\pi(Ze)^2 \beta}{\epsilon_0 k^2} \times \int d\mathbf{s}_1 \left[\frac{1}{2} \left(1 - \frac{\sin(k s_1)}{k s_1} \right) p^{(1,0)}(s_1) + \int d\mathbf{R}_{12} \times \int d\mathbf{s}_2 \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_1) \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{s}_2) \cos(\mathbf{k} \cdot \mathbf{R}_{12}) \times [p^{(2,0)}(\mathbf{s}_1, \mathbf{R}_{12}, \mathbf{s}_2) - p^{(1,0)}(s_1) p^{(1,0)}(s_2)] \right]. \quad (59)$$

One of the results of the following paper is that the ion-pair singlet distribution function $p^{(1,0)}(s_1)$ goes to zero sufficiently rapidly with increasing s_1 that

$$\int_0^\infty ds_1 s_1^2 p^{(1,0)}(s_1) < \infty, \quad (60)$$

i.e., the integral converges. This being the case, it is then justified to replace $\sin(k s_1)/k s_1$ in Eq. (59) by the first two terms of its power series expansion, when k is small. Therefore, upon introducing the ion-pair dipole moment,

$$\mathbf{u}_1 = Ze \mathbf{s}_1, \quad (61)$$

the long-wavelength limit in (59) becomes²³

$$\frac{\epsilon_0}{\epsilon(0)} - 1 = - \frac{4\pi\beta\bar{N}}{3\epsilon_0 V} \langle \mathbf{u}_1 \cdot \mathbf{u}_1 \rangle - \frac{4\pi\beta}{\epsilon_0} \lim_{k \rightarrow 0} \int d\mathbf{s}_1 \int d\mathbf{R}_{12} \times \int d\mathbf{s}_2 (\mathbf{e} \cdot \mathbf{u}_1) (\mathbf{e} \cdot \mathbf{u}_2) \cos(\mathbf{k} \cdot \mathbf{R}_{12}) \times [p^{(2,0)}(\mathbf{s}_1, \mathbf{R}_{12}, \mathbf{s}_2) - p^{(1,0)}(s_1) p^{(1,0)}(s_2)]; \quad (62)$$

where

$$\mathbf{e} = \mathbf{k}/k, \quad \langle \mathbf{u}_1 \cdot \mathbf{u}_1 \rangle = \frac{V}{\bar{N}} \int d\mathbf{s}_1 \mathbf{u}_1 \cdot \mathbf{u}_1 p^{(1,0)}(s_1).$$

It is not immediately possible to utilize the leading series terms for $\cos(\mathbf{k} \cdot \mathbf{R}_{12})$ in the remaining integral, for we wish implicitly to carry out the computation in an infinitely large system, so that regardless of how small k might get (but still > 0), there will be large regions for which the truncated series is inadequate.

It has already been noted that ion pairs interfere with one another's free rotation largely on account of the hindrance potential $u(\mathbf{x}_1, \mathbf{x}_2)$. Following Kirkwood's argument,²² we therefore expect that the immediate neighborhood of a fixed ion pair with dipole moment \mathbf{u}_1 will itself possess an average moment parallel to \mathbf{u}_1 , which we shall denote by \mathbf{u}^+ . Let ω ,

²³ Of course for the electrolyte we have $\epsilon(0) = \infty$. However we shall proceed for the moment without making this specific identification so as to preserve the parallel with Kirkwood's work.

as shown in Fig. 6, be a spherical region centered about \mathbf{u}_1 , whose radius is very much larger than the mean ion-pair size, yet still of less than macroscopic extent.²⁴ We presume that \mathbf{u}^+ is entirely contained within ω .

The R_{12} integration is now split into two parts. The first, over the finite region ω , allows $\cos(\mathbf{k} \cdot \mathbf{R}_{12})$ to be replaced by unity, so the integral over both \mathbf{R}_{12} and \mathbf{s}_2 gives precisely \mathbf{u}^+ , a function of \mathbf{u}_1 . Equation (62) then becomes the following:

$$\frac{\epsilon_0}{\epsilon(0)} - 1 = -\frac{4\pi\beta\bar{N}}{3\epsilon_0 V} \langle \mathbf{u}_1 \cdot \bar{\mathbf{u}}_1 \rangle - \frac{4\pi\beta}{\epsilon_0} \lim_{\mathbf{k} \rightarrow 0} \int d\mathbf{s}_1 \times \int_{V-\omega} d\mathbf{R}_{12} \int d\mathbf{s}_2 (\mathbf{e} \cdot \mathbf{u}_1) (\mathbf{e} \cdot \mathbf{u}_2) \cos(\mathbf{k} \cdot \mathbf{R}_{12}) \times [\rho^{(2,0)}(\mathbf{s}_1, \mathbf{R}_{12}, \mathbf{s}_2) - \rho^{(1,0)}(s_1) \rho^{(1,0)}(s_2)], \quad (63)$$

where we have set

$$\bar{\mathbf{u}}_1 = \mathbf{u}_1 + \mathbf{u}^+(\mathbf{u}_1). \quad (64)$$

Due to the fact that ω is large on the ion-pair size scale, the deviation of $\rho^{(2,0)}(\mathbf{s}_1, \mathbf{R}_{12}, \mathbf{s}_2)$ from the product of singlet functions when \mathbf{R}_{12} is in $V-\omega$ arise from long-range electrostatic effects. The material in $V-\omega$ is sufficiently far from the center of ω that it will be polarized as a macroscopic dielectric medium under the influence of \mathbf{u}_1 as a point source. With \mathbf{s}_1 and \mathbf{R}_{12} fixed, the integral

$$\int d\mathbf{s}_2 \mathbf{u}_2 [\rho^{(2,0)}(\mathbf{s}_1, \mathbf{R}_{12}, \mathbf{s}_2) - \rho^{(1,0)}(s_1) \rho^{(1,0)}(s_2)] \quad (65)$$

will equal \mathbf{P} , the polarization vector outside ω , and this quantity is related to the mean electric field $\mathbf{E}(\bar{\mathbf{u}}_1)$ by

$$4\pi\mathbf{P} = [\epsilon(0) - \epsilon_0] \mathbf{E}. \quad (66)$$

The point dipole form for \mathbf{E} is

$$\mathbf{E} = \{3\epsilon(0)/[2\epsilon(0) + \epsilon_0]\} \{-\nabla_2[\bar{\mathbf{u}}_1 \cdot \mathbf{R}_{12}/\epsilon(0) R_{12}^3]\}, \quad (67)$$

where the first factor, as Kirkwood has remarked,²² is necessary to transform from $\bar{\mathbf{u}}_1$ to the so-called "external moment."

If Relations (65)–(67) are utilized in Eq. (63), the passage to $\mathbf{k} \rightarrow 0$ may be accomplished in relatively straightforward manner, using the properties of spherical harmonics. We omit details. The result has the following simple form:

$$\frac{\epsilon_0}{\epsilon(0)} - 1 = \frac{4\pi\beta\bar{N}}{3\epsilon_0 V} \langle \mathbf{u}_1 \cdot \bar{\mathbf{u}}_1 \rangle \left\{ \frac{2\epsilon(0)}{2\epsilon(0) + \epsilon_0} \left[\frac{\epsilon_0}{1 - \epsilon(0)} \right] - 1 \right\}. \quad (68)$$

The solution for $\epsilon(0)/\epsilon_0$ may be readily obtained,

$$\epsilon(0)/\epsilon_0 = \frac{1}{4} \{3C + 1 + [(3C + 1)^2 + 8]^{1/2}\}, \quad (69)$$

$$C = (4\pi\beta\bar{N}/3\epsilon_0 V) \langle \mathbf{u}_1 \cdot \bar{\mathbf{u}}_1 \rangle.$$

²⁴ In accord with Footnote 23, ω will be regarded as fixed in size, while the system size passes to infinity.

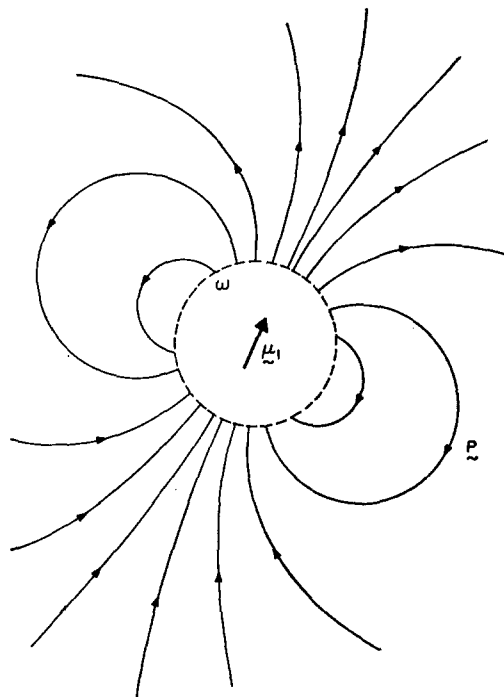


FIG. 6. Spherical cavity ω , surrounding a fixed ion-pair dipole \mathbf{u}_1 , used in derivation of the general Kirkwood-type dielectric formula. The immediate surroundings of \mathbf{u}_1 , contained entirely within ω , display an average moment \mathbf{u}^+ parallel to \mathbf{u}_1 . Polarization field \mathbf{P} is due to the total moment $\mathbf{u}_1 + \mathbf{u}^+$.

This is in fact Kirkwood's formula for the infinite-wavelength static dielectric constant, though our derivation has differed from his in several important ways.

The only way that the electrolyte $\epsilon(0)$ can be infinite, as we know it must, is for the quantity C in Eq. (69) to be infinite, and this in turn implies that $\langle \mathbf{u}_1 \cdot \bar{\mathbf{u}}_1 \rangle$ also must be infinite. The microscopic structural implication is that the average moment \mathbf{u}^+ created by steric hindrances between the fixed finite moment \mathbf{u}_1 and its surroundings must be likewise infinite as a result of outward propagation of orientational correlation. It is therefore appropriate to consider the electrolyte, in the dipolar fluid convention, to exist at a ferroelectric Curie point, for which long-range orientational correlations and infinite dielectric response at $\mathbf{k}=0$ are characteristic. It is thus very clear that the steric hindrance potentials $u(\mathbf{x}_i, \mathbf{x}_j)$ acting between ion pairs exert a very profound influence.

IV. ION-ATMOSPHERE MOMENT CONDITIONS

In this final section we return to consideration of Eq. (46), with particular attention to the manner in which the $k=0$ limit is attained. The left member of this equation, $\epsilon_0/\epsilon(k)$, we expect should pass smoothly to zero as $k \rightarrow 0$, indicative of the electrical conductivity of the medium. That the right-hand member should do the same is not at all obvious.

It is required that

$$\lim_{k \rightarrow 0} \frac{\kappa^2}{k^2} \left\{ 1 + \frac{4\pi\bar{N}}{Vk} \int_0^\infty r \sin(kr) \times [g_{+}^{(2)}(r) - g_{+}^{-(2)}(r)] dr \right\} = 1. \quad (70)$$

Expand the sine function:

$$1 = \lim_{k \rightarrow 0} \frac{\kappa^2}{k^2} \left\{ 1 + \frac{4\pi\bar{N}}{V} \int_0^\infty r^2 [g_{+}^{(2)}(r) - g_{+}^{-(2)}(r)] dr - \frac{2\pi\bar{N}k^2}{3V} \int_0^\infty r^4 [g_{+}^{(2)}(r) - g_{+}^{-(2)}(r)] dr + O(k^4) \right\}. \quad (71)$$

The $O(k^4)$ terms of course do not contribute to the requisite limit, but we see that the term in braces in Eq. (71) that is independent of k must vanish, and the one proportional to k^2 must equal precisely k^2/κ^2 ;

$$-1 = \frac{4\pi\bar{N}}{V} \int_0^\infty r^2 [g_{+}^{(2)}(r) - g_{+}^{-(2)}(r)] dr; \quad (72)$$

$$-\frac{6}{\kappa^2} = \frac{4\pi\bar{N}}{V} \int_0^\infty r^4 [g_{+}^{(2)}(r) - g_{+}^{-(2)}(r)] dr. \quad (73)$$

The first of these integral conditions is the well-known local electroneutrality condition; it states merely that the total amount of average charge in the ion atmosphere of a given ion exactly counterbalances that ion's own charge. The second condition (73) however is new, and precisely specifies the second radial moment of the primitive-model ion-atmosphere densities.

An electroneutrality condition (72) is the consequence of a nonintegrable large- r "tail" for interionic potentials. Such a condition would obtain even if the Coulomb potential between ions were to fall off as rapidly as r^{-3} . The existence of a second moment condition (73) however appears to arise because the Coulomb interactions fall to zero much less rapidly than r^{-3} .

The second-moment condition leads to an interesting and important conclusion concerning primitive-model

ion atmospheres at high concentration. Note first that the rigid-sphere ion cores in the model permit Eq. (73) to be re-expressed thus,

$$-\frac{6}{\kappa^2} = \frac{4\pi\bar{N}}{V} \int_a^\infty r^4 [g_{+}^{(2)}(r) - g_{+}^{-(2)}(r)] dr. \quad (74)$$

The Debye-Hückel theory¹ (appropriate at low concentration ζ_1 or low charge ζ_2) and its nonlinear extensions²⁵ agree that the ion atmospheres have the same charge sign at all radial distances; that is

$$g_{+}^{(2)}(r) - g_{+}^{-(2)}(r) \leq 0 \quad (a \leq r < \infty). \quad (75)$$

Without specifically invoking these theories, we now ask under what conditions inequality (75) is consistent with Eq. (74).

Over the integration range $a \leq r < \infty$,

$$r^4 \geq a^2 r^2. \quad (76)$$

Therefore if inequality (75) is satisfied, moment condition (74) implies

$$-\frac{6}{\kappa^2} \leq \frac{4\pi\bar{N}}{V} \int_a^\infty a^2 r^2 [g_{+}^{(2)}(r) - g_{+}^{-(2)}(r)] dr. \quad (77)$$

The remaining integral may be eliminated by electro-neutrality condition (72), so

$$-(6/\kappa^2) \leq -a^2, \quad \kappa^2 a^2 \leq 6. \quad (78)$$

The important consequence is that if $\kappa a = (4\pi\zeta_1\zeta_2)^{1/2}$ exceeds $6^{1/2}$, inequality (75) *cannot* be correct. For the primitive model, ion atmospheres then must exhibit *at least* one change in charge sign as r increases. This conclusion lends considerable credence to the detailed statistical-mechanical electrolyte theories that have predicted oscillatory ion-atmosphere charge densities^{8,26} at high concentration. Indeed, the value $6^{1/2}$ probably represents a considerable overestimate of the κa value for which the model actually would first possess ion-atmosphere charge alteration; more likely $\kappa a \cong 1.0-1.5$ is the relevant lower-limit range.

²⁵ H. Müller, *Physik. Z.* **28**, 324 (1927).

²⁶ J. G. Kirkwood, *Chem. Rev.* **19**, 275 (1936).