Ion-Pair Theory of Concentrated Electrolytes. III. Variational Principle

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Two major contributions are devised for that theory of concentrated electrolytes which by convention regards the ions as completely paired into uncharged dipolar "molecules." First, a more satisfactory expression is obtained for the wavelength-dependent static dielectric "constant" $\epsilon(k)$. Second, a variational principle for Helmholtz free energy F is displayed whose minimization with respect to the ion-pair size distribution $p^{(1)}$ serves to determine both F and $p^{(1)}$. In anticipation of future numerical applications, a binary collision approximation is specified for the short-range interaction aspect of the functional $F[p^{(1)}]$.

I. INTRODUCTION

Two earlier papers in this series[1,2] have developed a reformulation of equilibrium electrolyte theory, which promises to clarify the nature of concentrated solutions[3] and fused salts. This approach employs a rigorous extension of the Bjerrum ion-pair concept[4,5] to the point where *all* ions are paired (in a symmetrical electrolyte) to form dipolar "molecules" of variable size and orientation. Local structure in the fluid is then described by means of the static linear dielectric response function $\epsilon(k)$ for electrostatic field components of arbitrary spatial wave vector $\mathbf{k}$.

The present paper augments its predecessors in two major ways. First, an improved calculation for $\epsilon(k)$ has been devised. Second, the entire theory has been recast into a variational form wherein minimization of the Helmholtz free energy with respect to the ion-pair size distribution function $p^{(1)}(r)$ serves to determine this function uniquely; no such determination was previously possible.

Attention will be confined as before to the "primitive model" symmetrical electrolyte. This model involves uniformly charged rigid-sphere ions all with diameter a, suspended in a structureless solvent with dielectric constant ϵ_0. The anions and cations each number N, and, respectively, bear charges $-Ze$ and $+Ze$ so that the interaction potential can be written[6]

$$V_{N,N}(\mathbf{r}_1 \cdots \mathbf{r}_{2N}) = \left[\frac{(Ze)^2}{\epsilon_0}\right] \sum_{i<j=1}^{2N} \frac{(-1)^{i+j}}{r_{ij}}, \quad (1.1)$$

if all $r_{ij} > a$. Although generalization of our analysis to a far wider class of models (even including unsymmetrical electrolytes and mixtures) is certainly possible, this could only be done at the expense of reduced clarity. For those concepts which we wish to stress here, that expense would be entirely unwarranted.

In order to provide a suitable background for our improved $\epsilon(k)$ calculation, the probabilistic basis of the fundamental ion pairing process is reviewed in Sec. II for both the homogeneous electrolyte and for the inhomogeneous electrolyte subject to a weak sinusoidal external field which induces charge separation. Section III incorporates these results into a self-consistent torque calculation of $\epsilon(k)$.

The fact that $\epsilon(k)$ is a functional of the ion-pair size distribution $p^{(1)}(r)$ is suggestive since $\epsilon(k)$ leads directly to the electrostatic free energy for the electrolyte. Section IV therefore exhibits the *full* Helmholtz free energy F as a $p^{(1)}$ functional. Since the condition of thermal equilibrium requires that this free energy be at a minimum, one thus has a variational principle for simultaneous determination of free energy F and of $p^{(1)}$. This minimum principle is analogous to the familiar energy minimization in quantum mechanics, but now $p^{(1)}$ occurs in place of the wavefunction.

Section V contains a detailed analysis of the binary collision kernel which arises in the nonelectrostatic portion of the F variational principle. Its conclusions should be useful ultimately in numerical applications of the theory.

The following paper[7] applies some of the present results to examination of the charge distribution in ion atmospheres.

II. PAIRING PROCESS

A. Homogeneous Electrolyte

Let V denote the system volume. Except for zero-probability coincidences, any instantaneous configuration $\mathbf{r}_1 \cdots \mathbf{r}_{2N}$ of the ions leads to a unique pairing that assigns to each ion one (and only one) ion of the opposite species. First, the smallest anion–cation distance is identified, and the two ions producing it are regarded as paired. Within the remainder set of $N-1$ anions and $N-1$ cations, the new (now larger) minimum anion–cation distance is next identified and used to define a second ion pair. This remainder-set minimum anion–cation distance criterion is subsequently reapplied until all ions are paired.

It is obvious that the vector separations of the ion pairs[8] will vary depending on the initial ion configuration $\mathbf{r}_1 \cdots \mathbf{r}_{2N}$ chosen. Indeed $N!$ different pairings could arise, if the particles are treated as distinguishable. But in thermal equilibrium, with fixed temperature and density, a well-defined distribution of pair separations should exist. If N and V are macroscopic in size, furthermore, and the electrolyte is fluid, then this distribution involves only scalar distance r, and we shall denote it by $p^{(1)}(r)$. The normalization

$$c \equiv \frac{N}{V} = 4\pi \int_0^\infty r^2 p^{(1)}(r)\, dr \quad (2.1)$$

is convenient, for then $p^{(1)}(r_{ij})\, d\mathbf{r}_i d\mathbf{r}_j$ represents the prob-
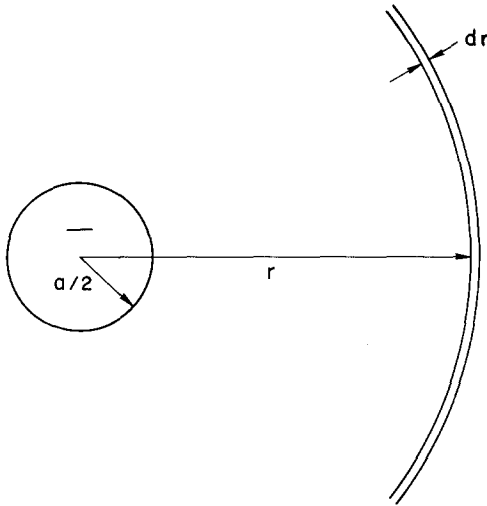
FIG. 1. Fixed hard-sphere anion with concentric spherical shell. One requires the probability that the cationic ($+$) partner center lies within the shell.

ability that differential volume elements $d\mathbf{r}_i$ and $d\mathbf{r}_j$ simultaneously and, respectively, contain the anion and cation of a single ion pair.

At that stage of the pairing process which involves forming ion pairs with size r, the density of as-yet-unpaired anions or cations is

$$\rho(r) = 4\pi \int_r^\infty s^2 p^{(1)}(s)\,ds, \qquad (2.2)$$

where of course

$$\rho(0) = c,$$
$$\lim_{r\to\infty} \rho(r) = 0. \qquad (2.3)$$

The rigid-sphere repulsions in the "primitive model" to be considered force $p^{(1)}(r)$ to vanish in the interval $0 \le r < a$, and so $\rho(r)$ remains equal to c in this interval.

We now inquire about the probability that a given anion ($-$) has its cationic partner ($+$) within a spherical shell of differential width dr, at radial distance r (see Fig. 1). By definition, this is

$$4\pi c^{-1} r^2 p^{(1)}(r)\,dr. \qquad (2.4)$$

The probability that the anion is *not* paired at a distance smaller than r is

$$1 - c^{-1}\int_0^r p^{(1)}(s)4\pi s^2 ds = c^{-1}\rho(r). \qquad (2.5)$$

The probability that it *is* paired in the requisite spherical shell must equal the expected number of available cations in that shell, i.e., cations which themselves have not been paired at distance less than r. The over-all density of such cations throughout the entire system is $\rho(r)$, and within a factor of unity order this is also correct for the spherical shell. Still, we must acknowledge the necessity of a local correlation factor $\Gamma(r)$ operative here, so that the expression

$$4\pi r^2 dr\rho(r)\,\Gamma(r) \qquad (2.6)$$

gives the expected number of cations.

By equating (2.4) to the product of (2.5) and (2.6), we find the relation

$$p^{(1)}(r) = \left[4\pi \int_r^\infty s^2\rho^{(1)}(s)\,ds\right]^2 \Gamma(r). \qquad (2.7)$$

Set

$$P^2(r) = \Gamma(r)/p^{(1)}(r), \qquad (2.8)$$

so that (2.7) transforms to

$$P^{-1}(r) = 4\pi \int_r^\infty s^2\Gamma(s)P^{-2}(s)\,ds. \qquad (2.9)$$

Application of an r differentiation next produces the elementary differential equation

$$P'(r) = 4\pi r^2\Gamma(r). \qquad (2.10)$$

This may easily be integrated with the help of normalization condition (2.1) to yield the result (for $r \ge a$)

$$p^{(1)}(r) = \left[\left[c^2\Gamma(r)\right]\middle/\left(1 + 4\pi c\int_a^r s^2\Gamma(s)\,ds\right)^2\right]. \qquad (2.11)$$

Equation (2.11) does not of course constitute a "solution" for $p^{(1)}(r)$ since $\Gamma(r)$ remains unspecified. Still, we know that $\Gamma(a)$ must be related to the density of contact pairs,[2] so that

$$\Gamma(a) = g_{+-}^{(2)}(a), \qquad (2.12)$$

where $g_{+-}^{(2)}(r)$ is the conventional anion–cation pair correlation function.[9] In addition, it is reasonable to expect $\Gamma(r)$ to be continuous and differentiable at least once.

Equation (2.11) may be inverted to give $\Gamma(r)$ in terms of $p^{(1)}(r)$

$$\Gamma(r) = \left[\left[c^{-2}p^{(1)}(r)\right]\middle/\left(1 - 4\pi c^{-1}\int_a^r s^2 p^{(1)}(s)\,ds\right)^2\right]. \qquad (2.13)$$

In the absence of the Coulomb interactions between ions (so that particles behave only as uncharged rigid spheres), arguments have been advanced[2] to indicate that for large r,

$$p^{(1)}(r) \sim \text{const} \times r^{-6}. \qquad (2.14)$$

Expression (2.13) subsequently implies that $\Gamma(r)$ approaches some positive constant as r increases to infinity, for discharged ions. For the moment we leave aside the question of how $\Gamma(r)$ behaves in the electrolyte, though it is clear that (2.13) will give this function provided an independent means for determining the electrolyte $p^{(1)}(r)$ is available.

B. Inhomogeneous Electrolyte

The next step requires that the initially homogeneous electrolyte be perturbed by the external potential

$$U_0 \sum_{i=1}^{2N} (-1)^i \sin(\mathbf{k}\cdot\mathbf{r}_i), \qquad (2.15)$$

in which U_0 is sufficiently small that the response is

linear. This potential produces charge separation in the form of sinusoidal concentration variations in space that are just out of phase with one another for anions ($-$) and for cations ($+$). One readily finds that these perturbed concentrations have the following forms:

$$c_-(\mathbf{r}) = c + \beta U_0 G(k) c \sin(\mathbf{k \cdot r}),$$

$$c_+(\mathbf{r}) = c - \beta U_0 G(k) c \sin(\mathbf{k \cdot r}), \qquad (2.16)$$

where

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

$$G(k) = 1 + c \int d\mathbf{r} \cos(\mathbf{k \cdot r}) [g_{++}^{(2)}(r) - g_{+-}^{(2)}(r)] \quad (2.17)$$

involves the Fourier transform of the standard ionic correlation functions.[9]

We seek to analyze the changes in the ion pairing process brought about by the inhomogeneity. The size distribution function may be written as the homogeneous fluid function plus a perturbation:

$$p^{(1)}(s) + \delta p^{(1)}(\mathbf{R, s}), \qquad (2.18)$$

where that perturbation will depend both on the position $\mathbf{R}$ of the center of the ion pair and on the vector separation $\mathbf{s}$ of that pair.

The remanent densities of anions or cations at stage s in the pairing were previously denoted by $\rho(s)$, but now at position $\mathbf{r}$ we must write

$$\rho_-(\mathbf{r} \mid s) = \rho(s)[1 + \beta U_0 G(k) f(k, s) \sin(\mathbf{k \cdot r})],$$

$$\rho_+(\mathbf{r} \mid s) = \rho(s)[1 - \beta U_0 G(k) f(k, s) \sin(\mathbf{k \cdot r})]. \quad (2.19)$$

These expressions manifest persistence of sinusoidal concentration variation during the pairing, and by inclusion of a factor $f(k, s)$ the possibility of relative amplitude change during the pairing process is admitted.

We shall tentatively assume that the same correlation factor $\Gamma(s)$ applies in the presence of weak inhomogeneity, that arises in the homogeneous fluid. As a result, the analog of previous Eq. (2.7) will be

$$p^{(1)}(s) + \delta p^{(1)}(\mathbf{R, s}) = \rho_+(\mathbf{R} + \tfrac{1}{2}\mathbf{s} \mid s) \rho_-(\mathbf{R} - \tfrac{1}{2}\mathbf{s} \mid s) \Gamma(s). \qquad (2.20)$$

Both this equation and (2.7) reflect the "second-order" character of the pairing, in that the product of concentrations at two spatially distinct points is involved. After expressions (2.19) are inserted into Eq. (2.20), it is possible to separate terms linear in U_0 to obtain

$$\delta p^{(1)}(\mathbf{R, s}) = \beta U_0 G(k) f(k, s) p^{(1)}(s)$$
$$\times \{ \sin[\mathbf{k} \cdot (\mathbf{R} - \tfrac{1}{2}\mathbf{s})] - \sin[\mathbf{k} \cdot (\mathbf{R} + \tfrac{1}{2}\mathbf{s})] \}. \quad (2.21)$$

As the pairing process proceeds by a small amount Δs, $\rho_+(\mathbf{r} \mid s)$ will change by the following:

$$\Delta \rho_+(\mathbf{r} \mid s) = -(\Delta s) \int d\Omega_s s^2 [p^{(1)}(s) + \delta p^{(1)}(\mathbf{r} - \tfrac{1}{2}\mathbf{s}, \mathbf{s})], \qquad (2.22)$$

where one integrates over the direction of $\mathbf{s}$ (but not

its length). Divide both sides by Δs, and then let this increment go to zero; if expression (2.21) is employed one obtains

$$\partial \rho_+(\mathbf{r} \mid s)/\partial s = -4\pi s^2 p^{(1)}(s)(1 + \beta U_0 G(k) f(k, s)$$
$$\times \{[\sin(ks)/ks] - 1\} \sin(\mathbf{k \cdot r})). \quad (2.23)$$

If we compare this relation with the s partial derivative of $\rho_+(\mathbf{r} \mid s)$ in Eq. (2.19), we conclude

$$(\partial/\partial s)[\rho(s) f(k, s)]$$
$$= 4\pi s^2 p^{(1)}(s) \{[\sin(ks)/ks] - 1\} f(k, s). \quad (2.24)$$

This may be integrated with the help of definition (2.2), and the requirement

$$f(k, 0) = 1, \qquad (2.25)$$

to produce finally an expression for $f(k, s)$:

$$f(k, s) = \exp\left\{ 4\pi k^{-1} \int_0^s t \sin(kt) p^{(1)}(t) [\rho(t)]^{-1} dt \right\}. \qquad (2.26)$$

The $p^{(1)}$ perturbation expression (2.21) could be regarded as the term linear in U_0 in the generating formula

$$p^{(1)}(s) \exp(-\beta U_0 G(k) f(k, s)$$
$$\times \{ \sin[\mathbf{k} \cdot (\mathbf{R} + \tfrac{1}{2}\mathbf{s})] - \sin[\mathbf{k} \cdot (\mathbf{R} - \tfrac{1}{2}\mathbf{s})] \}). \quad (2.27)$$

This, however, is precisely the form expected in the fluid for a dipole (ion pair) orientation distribution under the influence of an external potential of type (2.15). The coupling strength of that potential is $f(k, s) U_0$, rather than just U_0 alone. For this reason we shall refer to $f(k, s)$ as the "external field renormalization factor."

Owing to the fact that $p^{(1)}(t)$ vanishes for $t < a$, we have

$$f(k, s) = 1 \qquad (0 \leq s < a). \qquad (2.28)$$

Furthermore, one can readily verify that for s just exceeding a,

$$f(k, s) = 1 + (4\pi a/ck) p^{(1)}(a) \sin(ka)(s - a)$$
$$+ O[(s - a)^2]. \quad (2.29)$$

When s is held fixed, we also have

$$\lim_{k \to \infty} f(k, s) = 1. \qquad (2.30)$$

The opposite limit is also simple:

$$\lim_{k \to 0} f(k, s) = c/\rho(s). \qquad (2.31)$$

The most striking feature of $f(k, s)$ is that it depends on interactions between ions only through its functional dependence on $p^{(1)}$. In fact expression (2.26) depends in no way on the rigid-sphere character of the ions; any other core force common to all pairs of ions would produce the same result. This universality of $f(k, s)$ forms one of the essential ingredients in the dielectric response calculation to follow.
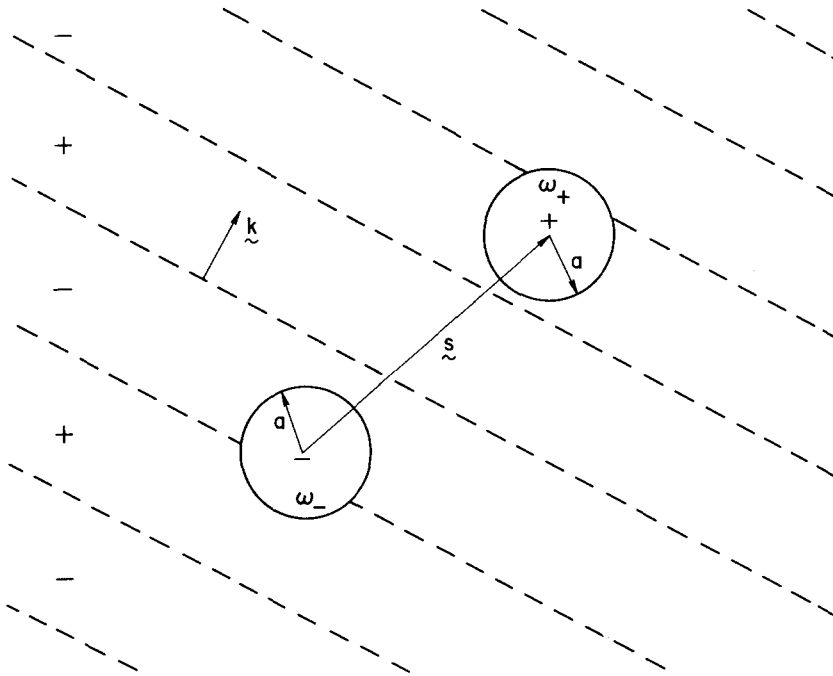
FIG. 2. Fixed ion pair in electrolyte polarized by ψ_{ap}. The surrounding ionic charge density is sinusoidal, with nodal planes explicitly shown. It is assumed that this density persists unaltered up to the exclusion spheres ω_+ and ω_-.

III. STATIC DIELECTRIC RESPONSE

The externally applied interaction (2.15) can be generated by using an applied electrostatic potential ψ_{ap} that has the form

$$\psi_{\text{ap}}(\mathbf{r}) = (\psi_0/\epsilon_0)\sin(\mathbf{k}\cdot\mathbf{r}), \qquad (3.1)$$

provided $\psi_0 = \epsilon_0 U_0/Ze$. The linear response of the conducting electrolyte tends to shield ψ_{ap} to an extent varying with k, but the resulting average electrostatic potential $\bar{\psi}$ may always be written

$$\bar{\psi}(\mathbf{r}) = [\psi_0/\epsilon(k)]\sin(\mathbf{k}\cdot\mathbf{r}). \qquad (3.2)$$

This constitutes the definition of the static wavelength-dependent dielectric function for the electrolyte, $\epsilon(k)$. By virtue of Poisson's equation, the corresponding induced ionic charge density resulting from ψ_{ap} must be

$$\rho_{\text{in}}(\mathbf{r}) = (\psi_0 k^2/4\pi)\{[\epsilon_0/\epsilon(k)] - 1\}\sin(\mathbf{k}\cdot\mathbf{r}). \quad (3.3)$$

The induced charge density may also be expressed as a Fourier transform of the homogeneous electrolyte pair correlation function difference $g_{+-}^{(2)} - g_{++}^{(2)}$. We therefore have a conjugate pair of relations linking this difference with $\epsilon(k)$[1]:

$$\frac{\epsilon_0}{\epsilon(k)} = 1 - \frac{\kappa^2}{k^2}\left\{1 - \frac{4\pi c}{k}\int_0^\infty r\sin(kr)\right.$$

$$\left. \times[g_{+-}^{(2)}(r) - g_{++}^{(2)}(r)]dr\right\}$$

$$\equiv 1 - [\kappa^2 G(k)/k^2]; \qquad (3.4)$$

$$g_{+-}^{(2)}(r) - g_{++}^{(2)}(r) = (2\pi^2 cr)^{-1}$$

$$\times \int_0^\infty k\sin(kr)\left\{\frac{k^2}{\kappa^2}\left[\frac{\epsilon_0}{\epsilon(k)} - 1\right] + 1\right\}dk, \quad (3.5)$$

where κ is the Debye parameter

$$\kappa^2 = 8\pi(Ze)^2 c/\epsilon_0 k_B T. \qquad (3.6)$$

The dielectric function $\epsilon(k)$ therefore contains all the information required to specify the ion atmosphere charge density in the primitive model.

We now proceed to calculate $\epsilon(k)$. Our approach will be patterned after the one used in Ref. 2 for a cruder estimate of this dielectric function. However, we shall now incorporate knowledge of the external field renormalization function $f(k, s)$ that was developed in the preceding section.

From the standpoint of equilibrium properties, it is possible and convenient to consider the ion pairs as stable diatomic molecules not subject to partner ex-
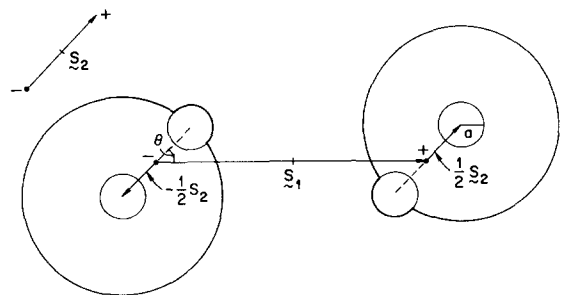

FIG. 3. Region $\Omega(s_1, s_2, \theta)$ inaccessible to the center of pair 2 due to presence of pair 1. In the example shown, with s_1 considerably greater than s_2, Ω consists of the two disconnected congruent portions with heavy outlines. The steric hindrance restriction accounts for the large radius-s_2 spheres, while ion–core repulsion produces the extra radius-a spherical caps (these caps are due to ions of the same type, since a spheres for unlike-ion repulsion are buried centrally in the s_2-spheres as shown).

changes. These pairs change size and orientation under the influence of thermal agitation, and a self-consistent torque calculation is required in the presence of ψ_{ap} to produce an expression for $\delta p^{(1)}$, and subsequently one for $\epsilon(k)$.

The requirement that a given pairing of ions be maintained implies that oppositely charged ends of two ion pairs, with sizes s_1 and s_2, can approach each other no more closely than the minimum of s_1 and s_2. If this were violated, it is clear that the fixed pairing would not be consistent with the sequential character of the pairing process as specified in Sec. III.A. Thus, the pairs are subject to a form of "steric hindrance" above and beyond their hard-sphere and Coulombic ion–ion interactions. These steric hindrance interactions encourage local parallel alignment of ion pairs, and the orientational response of these correlated pairs is cooperative. The steric hindrances are thus the primary source of the external field renormalization factor $f(k, s)$.

We shall employ $f(k, s)$ to provide the correct renormalization for the local average potential acting on an ion pair in the presence of ψ_{ap}. Figure 2 shows this chosen pair at a fixed position in the surrounding electrolytic medium. ψ_{ap} has induced this medium to exhibit the sinusoidal charge density ρ_{in} shown in Eq.

(3.3), and we shall assume that this density persists up to the spherical exclusion envelopes of radius a surrounding the ions of the fixed pair (ω_- and ω_+ in Fig. 2).

Let $\psi^*(\mathbf{r}, s)$ denote the electrostatic potential, both applied and due to surrounding induced charge, at the center of ω_- at $\mathbf{r}$, when ω_+ is centered at position $\mathbf{s}$ relative to ω_-. Then we may write the perturbed size distribution function as follows:

$$p^{(1)}(s) + \delta p^{(1)}(\mathbf{R}, \mathbf{s}) = p^{(1)}(s) \exp\{-\beta Z e f(k, s)$$
$$\times [\psi^*(\mathbf{R} + \tfrac{1}{2}\mathbf{s}, -\mathbf{s}) - \psi^*(\mathbf{R} - \tfrac{1}{2}\mathbf{s}, \mathbf{s})]\}. \quad (3.7)$$

One is obliged to linearize:

$$\delta p^{(1)}(\mathbf{R}, \mathbf{s}) = \beta Z e f(k, s) p^{(1)}(s)$$
$$\times [\psi^*(\mathbf{R} - \tfrac{1}{2}\mathbf{s}, \mathbf{s}) - \psi^*(\mathbf{R} + \tfrac{1}{2}\mathbf{s}, -\mathbf{s})]. \quad (3.8)$$

The induced charge density, whose phenomenological form is provided by Eq. (3.3), arises entirely from the perturbation $\delta p^{(1)}$:

$$\rho_{in}(\mathbf{r}) = Z e \int d\mathbf{s} [\delta p^{(1)}(\mathbf{r} - \tfrac{1}{2}\mathbf{s}, \mathbf{s}) - \delta p^{(1)}(\mathbf{r} + \tfrac{1}{2}\mathbf{s}, \mathbf{s})]$$
$$= 2\beta (Z e)^2 \int d\mathbf{s} f(k, s) p^{(1)}(s)$$
$$\times [\psi^*(\mathbf{r} + \mathbf{s}, -\mathbf{s}) - \psi^*(\mathbf{r}, \mathbf{s})]. \quad (3.9)$$

It is a straightforward matter[2] to show

$$\psi^*(\mathbf{r}, \mathbf{s}) = \frac{\psi_0}{\epsilon_0} \sin(\mathbf{k} \cdot \mathbf{r}) \left\{ \frac{\epsilon_0}{\epsilon(k)} + \left[1 - \frac{\epsilon_0}{\epsilon(k)}\right] [1 - \cos(ka)] - \int_{\omega^*(\mathbf{r}, \mathbf{s})} d\mathbf{r}' \frac{\rho_{in}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\}, \quad (3.10)$$

where $\omega^*(\mathbf{r}, \mathbf{s})$ is that portion of the exclusion cavity surrounding the point $\mathbf{r} + \mathbf{s}(\omega_+)$ which is external to the one surrounding $\mathbf{r}(\omega_-)$[10]:

$$\omega^*(\mathbf{r}, \mathbf{s}) = \omega_+(\mathbf{r} + \mathbf{s}) - \omega_+(\mathbf{r} + \mathbf{s}) \cap \omega_-(\mathbf{r}). \quad (3.11)$$

If expression (3.10) is employed in (3.9), the induced charge may be expressed as follows:

$$\rho_{in}(\mathbf{r}) = 2\beta (Z e)^2 c \frac{\psi_0}{\epsilon_0} \left\{ -\frac{\epsilon_0}{\epsilon(k)} + \left[\frac{\epsilon_0}{\epsilon(k)} - 1\right] [1 - \cos(ka)] \right\} \sin(\mathbf{k} \cdot \mathbf{r}) + 2\beta (Z e)^2 \int d\mathbf{s} f(k, s) p^{(1)}(s)$$
$$\times \left\{ \int_{\omega^*(\mathbf{r}, \mathbf{s})} d\mathbf{r}' \frac{\rho_{in}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int_{\omega^*(\mathbf{r} + \mathbf{s}, -\mathbf{s})} d\mathbf{r}' \frac{\rho_{in}(\mathbf{r}')}{|\mathbf{r} + \mathbf{s} - \mathbf{r}'|} \right\}; \quad (3.12)$$

in obtaining this form we have relied upon Eqs. (2.24) and (2.25) to effect simplifications.

The two integrals remaining in Eq. (3.12) may be carried out after (3.3) is used for $\rho_{in}(\mathbf{r}')$. Following this transformation, the result is required to equal the expression (3.3) itself. That requirement allows us to solve for $\epsilon(k)$, with the result

$$\epsilon_0/\epsilon(k) = 1 - \kappa^2/\{k^2 + \kappa^2 [\cos(ka) - k\mu(k)]\}, \quad (3.13)$$

where

$$\mu(k) = (4\pi c)^{-1} \int d\mathbf{s} p^{(1)}(s) f(k, s) [I_1(k, s) - I_2(k, s)], \quad (3.14)$$

and

$$I_1(k, s) = \frac{\pi}{s} \int_{\max(a, s-a)}^{s+a} dt [a^2 - (s-t)^2] \frac{\sin(kt)}{t},$$

$$I_2(k, s) = \frac{2\pi}{s} \int_0^a dt [s + t - \max(a, |s-t|)] \sin(kt). \quad (3.15)$$

Equation (3.13) constitutes the desired objective. $\epsilon(k)$ is indicated by that result to be a functional of $p^{(1)}$ through the latter's occurrence in the $\mu(k)$ integrand both explicitly and implicitly [through $f(k, s)$].

IV. VARIATIONAL PRINCIPLE

If the ionic Coulomb interactions (1.1) were reversibly switched on in an initially uncharged fluid of spheres, the size distribution function $p^{(1)}(s)$ would surely change its form. In particular, one would expect that attrac-

tion between oppositely charged ions would reduce the mean size of the ion pairs. Still, we may imagine that some external agency is present to prevent any change in $p^{(1)}(s)$ from its initially assigned form during the charging process. Under this artificial restraint, it is possible to derive an expression for the amount of electrical work expended in that charging.

Let $\pm \xi Ze$ be the fractional charges present in the course of the uniform charging procedure ($0 \leq \xi \leq 1$). The electrical work (i.e., electrical free energy F_{el}) exclusive of the self-energy of the ions may be exhibited as a ξ integral

$$\beta F_{el}[p^{(1)}] = 2N\beta Ze \int_0^1 d\xi \int d\mathbf{r} \frac{\xi Zec}{\epsilon_0 r} [g_{+\,+}^{(2)}(r, \xi) - g_{+\,-}^{(2)}(r, \xi)]. \tag{4.1}$$

Required here is the difference of pair correlation functions for the partially charged assembly of ions. In accord with Eq. (3.5), that difference may be expressed in terms of $\epsilon(k, \xi)$, the dielectric response function for fixed $p^{(1)}(r)$, but fractional charge

$$\beta F_{el}[p^{(1)}] = -\frac{4N(Ze)^2\beta}{\pi\epsilon_0} \int_0^1 d\xi \int_0^\infty dr \int_0^\infty dk \xi k \sin(kr) \left\{ \frac{k^2}{\kappa^2\xi^2} \left[\frac{\epsilon_0}{\epsilon(k, \xi)} - 1 \right] + 1 \right\}$$

$$= -\frac{4N(Ze)^2\beta}{\pi\epsilon_0} \int_0^1 d\xi \int_0^\infty dk \xi \left\{ \frac{k^2}{\kappa^2\xi^2} \left[\frac{\epsilon_0}{\epsilon(k, \xi)} - 1 \right] + 1 \right\}. \tag{4.2}$$

Here we have carried out the r integral according to the required prescription:

$$\lim_{\alpha \to 0} \int_0^\infty dr \exp(-\alpha r) \sin(kr) = k^{-1}. \tag{4.3}$$

The only way that $\epsilon(k, \xi)$ differs from the expression (3.13) derived for $\epsilon(k, 1) \equiv \epsilon(k)$ in the preceding section is by replacement of κ^2 by $\xi^2\kappa^2$:

$$[\epsilon_0/\epsilon(k, \xi)] - 1 = -\kappa^2\xi^2/\{k^2 + \kappa^2\xi^2[\cos(ka) - k\mu(k)]\}. \tag{4.4}$$

This simple ξ dependence permits one further integration (over ξ) to be carried out in Eq. (4.2):

$$\beta F_{el}[p^{(1)}] = -\frac{2N(Ze)^2\beta}{\pi\epsilon_0} \int_0^\infty dk\{1 - B^{-1}(k) \ln[1 + B(k)]\},$$

$$B(k) = \frac{\kappa^2}{k^2} [\cos(ka) - k\mu(k)]. \tag{4.5}$$

Since the equation of state for uncharged rigid spheres is accurately known at all densities below close packing,[11,12] we may consider the Helmholtz free energy F for our $2N$ spheres in volume V to be known when $\xi = 0$:

$$F(\xi = 0) \equiv F_0. \tag{4.6}$$

Even in concentrated solutions, it should suffice for most purposes to represent F_0 by the first few terms in its virial expansion.

We shall regard the actual electrolyte free energy $F(\xi = 1) \equiv F[p^{(1)}]$ as composed of three parts. The first is just F_0, the uncharged rigid-sphere part, for which the appropriate size distribution will be denoted by $p_0^{(1)}(r)$. The second part, $\Delta F[p^{(1)}]$ represents the amount of reversible work that must be expended in varying the size distribution for the uncharged spheres from $p_0^{(1)}(r)$ to $p^{(1)}(r)$. Finally, one has $F_{el}[p^{(1)}]$, Eq. (4.5), for the electrical charging work. Thus we write

$$F[p^{(1)}] = F_0 + \Delta F[p^{(1)}] + F_{el}[p^{(1)}]. \tag{4.7}$$

The condition of equilibrium requires that this combination be minimized with respect to variations in $p^{(1)}(r)$, where those variations are constrained to obey the basic normalization condition (2.1). Only the last two contributions to F in Eq. (4.7) are functionals of $p^{(1)}$, so our fundamental variational principle reads

$$\delta\{\Delta F[p^{(1)}] + F_{el}[p^{(1)}]\} = 0. \tag{4.8}$$

We still need to exhibit $\Delta F[p^{(1)}]$ in sufficiently explicit detail ultimately to permit the variational principle to be used in specific computations. Fortunately, the cluster theory generalized to molecules with internal degrees of freedom supplies a suitable expression for this quantity. In the present context, the "molecules" of course are the discharged ion pairs, and from Eq. (19) in Ref. 1 we immediately have

$$\beta\Delta F[p^{(1)}] = \int d\mathbf{x}_1 [p^{(1)}(s_1) \ln p^{(1)}(s_1) - p_0^{(1)}(s_1) \ln p_0^{(1)}(s_1)] - \sum_{n=1}^\infty [(n+1)!]^{-1} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_{n+1} S^{(n)}(\mathbf{x}_1 \cdots \mathbf{x}_{n+1})$$

$$\times [p^{(1)}(s_1) \cdots p^{(1)}(s_{n+1}) - p_0^{(1)}(s_1) \cdots p_0^{(1)}(s_{n+1})]. \tag{4.9}$$

Here the six-dimensional vector $\mathbf{x}_i$ comprises both center-of-mass position $\mathbf{R}_i$ and vector separation $\mathbf{s}_i$ for the ith pair:

$$\mathbf{x}_i = \mathbf{R}_i \oplus \mathbf{s}_i. \tag{4.10}$$

The quantity $S^{(n)}(\mathbf{x}_1 \cdots \mathbf{x}_{n+1})$ is the irreducible (i.e., at least doubly connected) cluster sum of Mayer f-function products for $n+1$ discharged ion pairs[13]; it is zero if neither rigid-sphere overlaps nor steric hindrance violations occur, and -1 otherwise

$$f(\mathbf{x}_i, \mathbf{x}_j) = -U[a - |\mathbf{R}_i - \tfrac{1}{2}\mathbf{s}_i - \mathbf{R}_j + \tfrac{1}{2}\mathbf{s}_j|] U[a - |\mathbf{R}_i - \tfrac{1}{2}\mathbf{s}_i - \mathbf{R}_j - \tfrac{1}{2}\mathbf{s}_j|]$$

$$\times U[a - |\mathbf{R}_i + \tfrac{1}{2}\mathbf{s}_i - \mathbf{R}_j + \tfrac{1}{2}\mathbf{s}_j|] U[a - |\mathbf{R}_i + \tfrac{1}{2}\mathbf{s}_i - \mathbf{R}_j - \tfrac{1}{2}\mathbf{s}_j|]$$

$$\times U[\min(s_i, s_j) - |\mathbf{R}_i - \tfrac{1}{2}\mathbf{s}_i - \mathbf{R}_j - \tfrac{1}{2}\mathbf{s}_j|] U[\min(s_i, s_j) - |\mathbf{R}_i + \tfrac{1}{2}\mathbf{s}_i - \mathbf{R}_j + \tfrac{1}{2}\mathbf{s}_j|]; \tag{4.11}$$

$$U(x) = 0 \qquad (x < 0)$$
$$= 1 \qquad (x \geq 0). \tag{4.12}$$

Since expression (4.9) refers only to uncharged particles, one need not be concerned with the necessity for infinite-order summations that apply in the presence of long-range electrostatic interactions.[14,15]

We are now in a position to write down the formal Euler equation that solves variational principle (4.8). By employing expressions (4.5) and (4.9), we find

$$p^{(1)}(s_1) = yU(s_1 - a) \exp\left\{ \sum_{n=1}^{\infty} (n!)^{-1} \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_{n+1} S^{(n)}(\mathbf{x}_1 \cdots \mathbf{x}_{n+1}) p^{(1)}(s_2) \cdots p^{(1)}(s_{n+1}) \right.$$

$$\left. - \frac{\kappa^4}{16\pi^3 s_1^2} \int_0^\infty \frac{dk}{k} \left(\frac{\ln[1 + B(k)]}{B^2(k)} - \{B(k)[1 + B(k)]\}^{-1} \right) \frac{\delta\mu(k)}{\delta p^{(1)}(s_1)} \right\}. \tag{4.13}$$

The constant y must be selected to enforce the normalization (2.1) required of $p^{(1)}$. The k integral appearing in Eq. (4.13) comprises the entire influence on $p^{(1)}(s_1)$ of electrostatic interactions, including both the direct attraction between the ions forming the pair, as well as the indirect effect of the surrounding polarizable medium of other ion pairs.

The remaining functional derivative $\delta\mu/\delta p^{(1)}$ in Eq. (4.13) can be evaluated by using Eq. (3.14). One ultimately finds

$$\frac{\delta\mu(k)}{\delta p^{(1)}(r)} = c^{-1} r^2 \left[f(k, r)[I_1(k, r) - I_2(k, r)] + \frac{4\pi \sin(kr)}{kr\rho(r)} \int_r^\infty ds\, s^2 p^{(1)}(s) f(k, s)[I_1(k, s) - I_2(k, s)] \right.$$

$$\left. - (4\pi)^2 \int_0^r dt \int_t^\infty ds\, s^2 t^2 \left(\frac{p^{(1)}(s) p^{(1)}(t)}{\rho^2(t)} \right) f(k, s)[I_1(k, s) - I_2(k, s)] \left(\frac{\sin(kt)}{(kt)} \right) \right].$$

V. BINARY COLLISION APPROXIMATION

The cluster integrals shown in Eq. (4.9) for $\Delta F[p^{(1)}]$ become successively more difficult to handle as their order n increases. The same is true for their analogs in the nonlinear $p^{(1)}$ integral equation (4.13). We shall therefore investigate in this section the approximation which disregards all cluster integrals beyond the first $(n=1)$, the binary collision integral.

A crude argument is available which indicates that this binary collision approximation is reasonable, at least if the rigid spheres are not densely packed. In the two-component ideal gas limit $(a=0, Ze=0)$, the binary collision approximation to Euler equation (4.13) has previously been worked out[2]:

$$p^{(1)}(s_1) = c^2 \exp\left[-\int_0^\infty H(s_1, s_2) p^{(1)}(s_2) ds_2 \right], \tag{5.1}$$

where the kernel H has the form

$$H(s_1, s_2) = (32\pi^2/3) s_1^3 s_2^2 h(s_2/s_1), \tag{5.2}$$

with

$$h(x) = x^3 \qquad (0 \leq x \leq \tfrac{1}{3}),$$
$$= (1/64)\{8x^2[4 - 3(1-x)^2] + 4x[8x^3 - (1-x)^3] + (1/5x)[(1-x)^5 - 32x^5]\} \qquad (\tfrac{1}{3} \leq x \leq 1),$$
$$= (1/64x)\{8[4x^2 - 3(x-1)^2] + 4[8 - (x-1)^3] + \tfrac{1}{5}[(x-1)^5 - 32]\} \qquad (1 \leq x \leq 3),$$
$$= 1 \qquad (3 \leq x). \tag{5.3}$$

The function $h(x)$ is numerically close to the simpler function[16]

$$h_0(x) = x^3 \qquad (0 \le x \le 1),$$
$$= 1 \qquad (1 \le x);$$

(5.4)

if h_0 is used in place of h in (5.2), the integral equation (5.1) may be solved exactly to yield

$$p^{(1)}(s_1) = \frac{c^2}{1 + (4\pi/3)cs_1{}^3}.$$

(5.5)

The logarithm of the configuration integral for $2N$ ideal gas particles is obviously

$$\ln\left\{ (N!)^{-2} \int_V d\mathbf{r}_1 \cdots \int_V d\mathbf{r}_{2N} \right\} = 2N[\ln(V/N) + 1 + o(1)].$$

(5.6)

This same quantity could alternatively be calculated as the configuration integral for a set of "diatomic molecules" whose bond lengths are distributed according to (5.5). If we account for the steric hindrances between these molecules just in the binary collision approximation, we find

$$\int d\mathbf{x}_1 p^{(1)}(s_1)[1 - \ln p^{(1)}(s_1)] + \tfrac{1}{2}\int d\mathbf{x}_1 \int d\mathbf{x}_2 S^{(1)}(\mathbf{x}_1, \mathbf{x}_2) p^{(1)}(s_1) p^{(1)}(s_2) = 2N[\ln(V/N) + \tfrac{3}{2}] + \tfrac{1}{2}V\int d\mathbf{s}_1 p^{(1)}(s_1) \ln p^{(1)}(s_1)$$
$$= 2N[\ln(V/N) + 1].$$

(5.7)

Here Eqs. (5.1) and (5.5) have been used to carry out the integrals. Thus we obtain the correct answer with the binary collision approximation, even though the steric hindrances play a nontrivial role in this simple test example.

We therefore proceed to examine the approximation for $a \neq 0$. The relevant integral in the $p^{(1)}$ Eq. (4.13) is as follows:

$$L(s_1) = \int d\mathbf{x}_2 f(\mathbf{x}_1, \mathbf{x}_2) p^{(1)}(s_2),$$

(5.8)

where the Mayer f function occurring here $[S^{(1)} \equiv f]$ has been previously displayed in Eq. (4.12). Since f is nonzero (and identically -1) only when the two pair configurations $\mathbf{x}_1$ and $\mathbf{x}_2$ lead to rigid-sphere or steric-hindrance overlap,

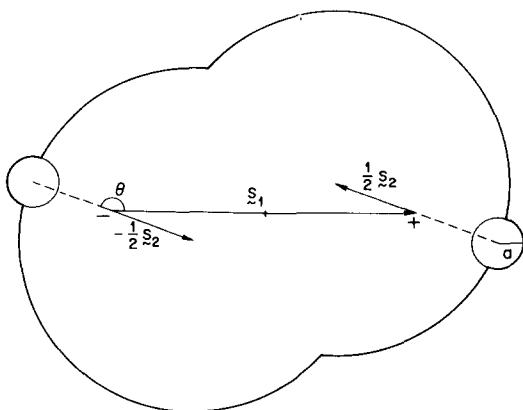$$L(s_1) = -2\pi \int_a^\infty ds_2 s_2{}^2 p^{(1)}(s_2) \int_0^\pi d\theta \sin\theta \, \Omega(s_1, s_2, \theta),$$

(5.9)

where θ is the angle between $\mathbf{s}_1$ and $\mathbf{s}_2$, and Ω is the total volume excluded to the center of pair 2 when $\mathbf{x}_1$ and s_2, θ are fixed.

Figure 3 shows Ω for a specific choice of s_1, s_2, and θ. The size s_1 of the fixed pair in this example is considerably larger than s_2, and Ω falls into two disconnected regions. These regions are identical in shape, and consist of spheres with radii s_2 that have "bumps" of radius a on their surfaces. It is easy to show for this class of configurations that Ω is θ independent and has the value

$$\Omega(s_1, s_2, \theta) = (8\pi/3)s_2{}^3 + \pi a^3[(4/3) + (a/2s_2)]. \quad (5.10)$$

The two terms here are, respectively, the volumes of the large radius-s_2 spheres, and the extra contribution of the radius-a spherical caps.
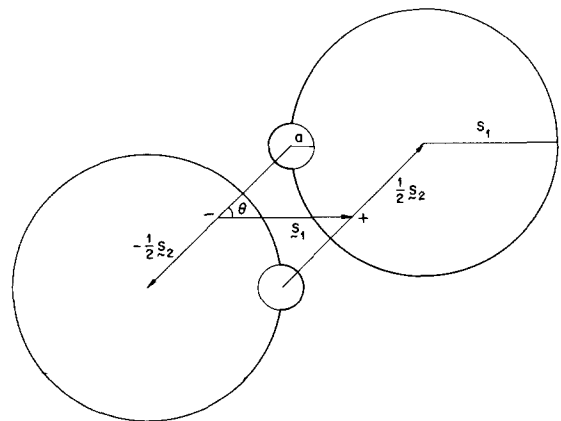
If $s_1 > 3s_2$ the two regions contributing to Ω remain

FIG. 4. Sphere overlap that can occur when $s_1 < 3s_2$, and appropriate θ.

FIG. 5. Region Ω for $s_2 > s_1$. The larger spheres maintain radii equal to s_1, and the radius-a spherical caps have transferred from one of these larger spheres (see Fig. 4) to the other.

distinct for all $0 \leq \theta \leq \pi$. However when s_2 begins to exceed $s_1/3$, the regions can overlap for some ranges of θ. Figure 4 illustrates one possibility, while s_1 still exceeds s_2, in which the larger spheres intersect. In this new set of configurations the small spherical caps are undisturbed, so we can still write

$$\Omega(s_1, s_2, \theta) = \Omega_0(s_1, s_2, \theta) + \pi a^3 [(4/3) + (a/2s_2)] \tag{5.11}$$

for this case, where Ω_0 is the volume of the intersecting larger spheres *without* caps:

$$\Omega_0 = \lim_{a \to 0} \Omega. \tag{5.12}$$

When s_2 begins to exceed s_1, the larger spheres determining Ω remain at radius s_1 on account of occurrence of $min(s_1, s_2)$ in the Mayer f function, Eq. (4.11). Unless $s_2 > 3s_1$, these large fixed-size spheres can still intersect one another for certain θ values. The radius-a caps continue to adhere to the surfaces of the larger spheres, but comparison of Fig. 5 with the preceding Fig. 4 shows that in effect these caps have transferred from one large sphere to the other. For those values of s_2 and θ such that only the larger spheres might overlap, Ω may be represented in a form directly analogous to (5.10) and (5.11):

$$\Omega(s_1, s_2, \theta) = \Omega_0(s_1, s_2, \theta) + \pi a^3 [(4/3) + (a/2s_1)]. \tag{5.13}$$

Finally, when $s_2 > 3s_1$, the two capped spheres remain distinct for all θ.

For each of the cases considered thus far,

$$\Omega(s_1, s_2, \theta) = \Omega_0(s_1, s_2, \theta)$$
$$+ \pi a^3 \{ (4/3) + [a/2 \min(s_1, s_2)] \}. \tag{5.14}$$

Exceptions to this Ω form will occur for those relatively restricted sets of values of s_1, s_2, and θ which permit the a caps to intersect one another or to intersect the large sphere upon which they do not formally reside. Figures 6 and 7 illustrate these two possibilities. It should be noted in this context that the centers of the a caps cannot enter these other large spheres. In view
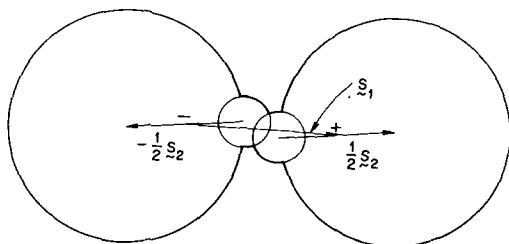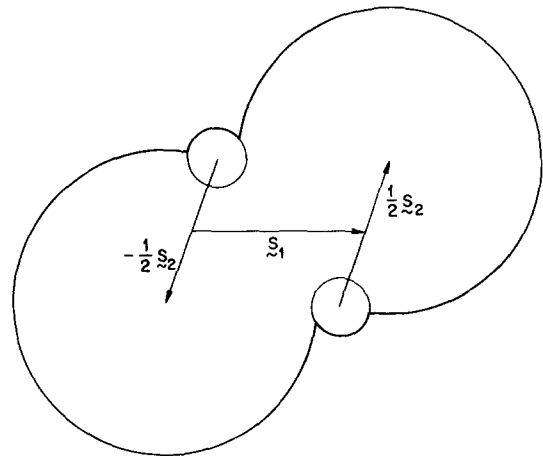

FIG. 7. Intersection of the a caps with the larger spheres on whose surfaces their centers are not located. These a-sphere centers are never interior to the larger spheres.

of the consequent improbability of these exceptions, it seems reasonable to adopt expression (5.14) as a valid approximation for all s_1, s_2, and θ.[17] As a result the integral $L(s_1)$, Eq. (5.9), adopts the following simple form

$$L(s_1) = - \int_a^\infty ds_2 \left\{ H(s_1, s_2) \right.$$
$$\left. + 2\pi a^3 s_2^2 \left[\frac{4}{3} + \frac{a}{2 \min(s_1, s_2)} \right] \right\} p^{(1)}(s_2), \tag{5.15}$$

where $H(s_1, s_2)$ has been previously defined in Eqs. (5.2) and (5.3). The corresponding binary collision integrals occurring in $\Delta F[p^{(1)}]$ subsequently may be obtained from $L(s_1)$ by a further integration.

VI. DISCUSSION

A variational form of the theory of electrolytes, such as we have advocated in this paper, presents obvious advantages. The free energy $F[p^{(1)}]$ may be computed from a trial family of model $p^{(1)}$ functions containing, say, a set of linear variational parameters. After F is minimized with respect to these parameters, one can be assured that error remaining in $p^{(1)}$ will only affect F in second and higher orders. Just as relatively crude wavefunctions in atomic and molecular quantum mechanics can yield relatively accurate energies in the usual energy variational minimization, one need not have determined $p^{(1)}$ with high precision to obtain F accurately for the electrolyte. In some applications, therefore, it may be considerably easier working directly with trial $p^{(1)}$'s in the variational principal (4.8), rather than trying to solve the complicated Euler equation (4.13).

Trial $p^{(1)}$ functions of course must be nonnegative,

FIG. 6. Intersection of a caps with each other to render the region Ω connected.

and must always satisfy the normalization condition (2.1). It is furthermore reasonable to expect that electrostatic attraction between oppositely charged ions will increase $p^{(1)}(r)$ near $r=a$ above the $p_0^{(1)}(r)$ values, perhaps even producing a very large maximum at contact $(r=a)$; sufficient flexibility should be present in the trial family to accommodate this possibility. The following paper[7] additionally argues that $p^{(1)}(r)$ maintains the same type of r^{-6} tail at large r exhibited by $p_0^{(1)}(r)$, albeit with diminished numerical magnitude.

One of the most interesting applications to which the present variational technique might be adapted is molten salts. These materials are clearly the most concentrated fluid electrolytes available, and would afford a stringent test of the theory. Potassium fluoride fits the primitive model assumptions rather well since it is charge symmetric and has monatomic ions of very nearly equal size $(a=2.69$ Å$)$. At its melting point $(1119°$K$)$ the reduced density of ion cores in liquid KF is

$$2Na^3/V = 0.772, \qquad (6.1)$$

somewhat over half the close-packed maximum $(\sqrt{2})$. Under this circumstance one must question the validity of the binary collision approximation outlined in the previous section, but still we wish to propose that this approximation preserves the qualitative sense of the fused salt behavior, and should provide a useful working tool.

The dielectric constant ϵ_0 that should be used in a fused salt calculation with the primitive model is the square of the refractive index $(\epsilon_0 \cong 1.62$ for molten KF at its melting point$)$. In elucidating fused salt structure it would eventually be useful to dispense with the primitive model's dielectric continuum assumption. The alternative would involve explicit consideration of individual ion polarizabilities, and our $\epsilon(k)$ calculation might then be reworked along the lines indicated by Onsager's theory of dielectric fluids.[18]

The tentative assumption used in Eq. (2.20) that the pairing correlation factor Γ may always be carried over from the homogeneous to the inhomogeneous regime, is not fully consistent with our $\epsilon(k)$ calculation. If it were true, comparison of expressions (2.21)

and (3.8) would require for fixed $\mathbf{k}$ that

$$\psi^*(\mathbf{R}-\tfrac{1}{2}\mathbf{s}, \mathbf{s}) - \psi^*(\mathbf{R}+\tfrac{1}{2}\mathbf{s}, -\mathbf{s})$$

$$\propto \sin[\mathbf{k}\cdot(\mathbf{R}-\tfrac{1}{2}\mathbf{s})] - \sin[\mathbf{k}\cdot(\mathbf{R}+\tfrac{1}{2}\mathbf{s})], \quad (6.2)$$

for all $\mathbf{R}$ and $\mathbf{s}$. The average potentials ψ^* acting on the ions, however, do not have this simple structure when $a>0$, so it is clear that long-range Coulomb interactions induce a shift in the factor Γ which violates the assumption. This does not mean that our $\epsilon(k)$ calculation is inconsistent, however, since the Γ invariance has only been used for short-range interactions (rigid sphere and steric hindrance) to obtain $f(k, s)$, and then the electrostatic interactions have been subsequently grafted onto the analysis in the self-consistent field calculation. Therefore, we needed initially only to have proposed the assumption in the narrower context of uncharged particles.

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[1] F. H. Stillinger, Jr. and R. Lovett, J. Chem. Phys. **48**, 3858 (1968).

[2] R. Lovett and F. H. Stillinger, Jr., J. Chem. Phys. **48**, 3869 (1968).

[3] F. H. Stillinger, Jr., Proc. Natl. Acad. Sci. U.S. **60**, 1138 (1968).

[4] N. Bjerrum, Kgl. Danske Videnskab. Selskab Mat. Fys. Medd. **7**, 1 (1926).

[5] R. M. Fuoss, Trans. Faraday Soc. **30**, 967 (1934).

[6] Anions have been numbered by the odd integers, and cations by the even integers.

[7] F. H. Stillinger and R. J. White, J. Chem. Phys. **54**, 3405 (1971), following paper, Paper IV.

[8] By convention, we always measure from anion center to cation center.

[9] The standard correlation functions $g_{\alpha\beta}^{(2)}(r)$ are normalized to unity at large r, and encompass all ions, whether paired by the present scheme or not.

[10] Cavities ω_+ and ω_- can overlap when $a \leq s < 2a$. But if $s \geq 2a$, $\omega^* = \omega_+$.

[11] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).

[12] B. J. Alder, W. G. Hoover, and D. A. Young, J. Chem. Phys. **49**, 3688 (1968).

[13] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940), Chap. 13.

[14] J. E. Mayer, J. Chem. Phys. **18**, 1426 (1950).

[15] D. W. Jepsen and H. L. Friedman, J. Chem. Phys. **38**, 846 (1963).

[16] See Fig. 2 in Ref. 2.

[17] It is of course an upper bound to the exact Ω.

[18] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).