

# Equilibrium Properties of a System of Charged Particles\*

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Motivated by the formal identification that can be made between the electronic charge  $e$  and a range parameter  $\gamma$  that we have previously studied, we have developed high-temperature, high-density expansions of the Helmholtz free energy and potentials of average force for systems of ions with repulsive cores. It appears that the natural ordering parameter for our free energy expansion is  $\kappa R$ , where  $\kappa$  is the inverse Debye length and  $R$  an effective core diameter, and as a result the expansion is useful for *either* sufficiently high temperatures at any density *or* sufficiently low densities at any temperature. We find the terms in this expansion through order  $(\kappa R)^7$ . We have also found effects that will serve to modify the shielding length at high densities so that it is no longer just  $\kappa^{-1}$ . One such effect depends upon the disparity in the core sizes of the positive and negative ions, and it vanishes only when the disparity does. A higher-order modification of the shielding length that remains in this symmetric case is also discussed.

## I. INTRODUCTION

The first real understanding of fluids of charged particles was achieved by Debye and Hückel,<sup>1</sup> who started with Poisson's equations for the Coulomb potential  $v(r)$  between two ions and, after some approximations, arrived at an equation for the interionic potential of mean force  $\psi(r)$ . The central result of their work was that  $\psi(r)$  behaves like  $z_1 z_2 e^2 \exp(-\kappa r)/r$  as  $r \rightarrow \infty$  rather than like  $v(r) = z_1 z_2 e^2 / r$  itself, where  $z_1 e$  and  $z_2 e$  are the ionic charges and the Debye shielding length is  $\kappa^{-1} = (4\pi e^2 \beta \sum_i \rho_i z_i^2)^{-1/2}$ . Here  $\beta$  is the reciprocal temperature and  $\rho_i$  is the density of species  $i$ . Debye and Hückel applied this result to electrolytic solutions by further assuming that the only effect of the solvent is to modify the interionic potential so that it becomes  $z_1 z_2 e^2 / D r$ , where  $D$  is the dielectric constant of the solvent. Their expression for  $\psi(r)$  then remains unchanged except for the replacement of  $e^2$  by  $e^2 / D$ . From this they found that the excess osmotic free energy per unit volume is proportional to  $\kappa^3 \sim \rho^{3/2}$  where  $\rho$  is the average ionic density.

The results of Debye and Hückel are, however, valid only at very low density<sup>2,3</sup> and there are serious discrepancies between the theory and experimental results for real electrolytes. As a consequence work was subse-

quently done to improve their theory by embedding it in a perturbation scheme in which  $\rho$  is taken to be the ordering parameter.<sup>4</sup> Terms of higher order in  $\rho$  have been evaluated, and their use makes it possible to

<sup>4</sup>The first systematic study of this scheme was made by J. E. Mayer, *J. Chem. Phys.* **18**, 1426 (1950). Further work along these lines was continued by various workers; see, e.g., J. C. Poirier, *J. Chem. Phys.* **21**, 965 (1953); E. Haga, *J. Phys. Soc. Japan* **8**, 714 (1953); E. Meeron, *J. Chem. Phys.* **26**, 804 (1957); R. Abe, *Progr. Theoret. Phys. (Kyoto)* **22**, 213 (1959); and H. L. Friedman, *Mol. Phys.* **2**, 23, 190, 436 (1959). See Footnote 5 for a more complete bibliography. Numerous other approaches to the problem of systematically improving the Debye-Hückel theory have also been considered. [See e.g., Ref. 5 and the articles by J. Poirier and by G. Kelbg, in *Chemical Physics of Ionic Solutions*, B. E. Conway and R. G. Barradas, Eds. (John Wiley & Sons, Inc., New York, 1966).] None of those we have examined appear to be closely related to our work in any simple way (but see Ref. 6) although there are a few points of contact between such work and this work that we think are worth mentioning. We start by noting that the charging parameter technique of Kirkwood and Poirier [*J. Phys. Chem.* **58**, 591 (1954)] is a technique that can be much more directly associated with our ordering of terms in  $e^2 \beta$  than with ordering in  $\rho$ , and in this sense it is closer to our work than are the contents of the articles cited in the last paragraph, although the charging parameter was not used by Kirkwood and Poirier to systematically examine higher-order terms in  $e^2 \beta$ . In order to make such an examination in the case of ions with highly repulsive cores, it seems hard to avoid splitting up the potential into two parts as we do. S. Edwards [*Phil. Mag.* **4**, 1171 (1959)] and R. L. Guernsey [*Phys. Fluids* **7**, 792 (1964)] both consider such a decomposition of the potential, but Edwards makes a double expansion in  $e^2 \beta$  and  $\rho$  for charged hard spheres. (To make contact with his final results we would have to expand ours out in  $\rho$ .) Guernsey, on the other hand, never explicitly considers the case of a repulsive core and a Coulombic tail. He does examine the electron gas, treating the pure Coulombic potential for small  $r$  in one way and for large  $r$  another way. In our language, his decomposition consists of taking  $v(r) = e^2 / r$ , and letting  $q$  and  $w$  in our Eq. (2.1) be given by  $v(r) = q(r)$ ,  $w(r) = 0$  for  $r < a$  and  $v(r) = w(r)$ ,  $q(r) = 0$  for  $r > a$ , where  $a$  is the state dependent distance  $a = (\beta e^2 / \kappa)^{1/2}$ .

<sup>5</sup>H. L. Friedman, *Ionic Solution Theory* (Interscience Publishers, Inc., New York, 1962) offers a good summary of both the theoretical work done in obtaining expansions using  $\rho$  as an ordering parameter and the available experimental results that can be used in assessing these expansions.

<sup>6</sup>After completing this work we learned that L. Onsager has noted a related effect dependent upon a disparity in ionic charge strength rather than size. L. Onsager, *J. Am. Chem. Soc.* **86**, 3421 (1964).

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<sup>1</sup>P. Debye and E. Hückel, *Physik. Z.* **24**, 185, 305 (1923); *The Collected Papers of Peter J. W. Debye* (Interscience Publishers, Inc., New York, 1954), pp. 217, 264.

<sup>2</sup>The analyses of Onsager and of Fowler were instrumental in the recognition and clarification of the approximate character of the Debye-Hückel theory. L. Onsager, *Physik. Z.* **28**, 277 (1927); R. H. Fowler, *Trans. Faraday Soc.* **23**, 434 (1927). Further illuminating discussion of this point is found in L. Onsager, *Chem. Rev.* **13**, 73 (1933).

<sup>3</sup>A discussion of the Debye-Hückel theory in which its various limitations are examined in detail is given by R. H. Fowler and E. A. Guggenheim, in *Statistical Thermodynamics* (Cambridge University Press, London, 1939).

consider concentrations greater than those for which the Debye-Hückel limiting laws are useful. Nevertheless there is still a very wide range of concentrations over which the improvement gained by including these terms is not enough to yield adequate agreement with the observed properties of electrolytic solutions.<sup>5</sup>

It is not hard to see where at least one major difficulty lies. At higher densities one would expect that the effect of the highly repulsive cores of the ions is of major importance and cannot be handled sensibly as a perturbation of the effects of the Coulombic interaction. But this is essentially the way the expansion in the density handles it—the effects of the core show up a little bit at a time as one goes to higher and higher orders of  $\rho$ .

In this paper we investigate an expansion procedure<sup>7</sup> that is free from these difficulties, although it has its own drawbacks. In its simplest form it leads to the expansions in  $e^2\beta$  (or  $e^2\beta/D$  for ionic solutions) or in  $\kappa$  that are considered in this paper. In the case of classical point particles in a uniform background there is no difference between the use of  $e^2\beta$  and the use of  $\rho$  as ordering parameters, since the relevant dimensionless parameter is  $e^2\beta\rho^{1/3}$ . In the case of a system of ions with cores of effective diameter  $R$ , however, there is an additional parameter  $\rho R^3$  to be considered and it is the main feature of our analysis that we need not assume that this parameter is small. This generally makes the higher-order terms in  $e^2\beta$  (our formal ordering parameter) quite complex and they have not yet been evaluated explicitly (the relevant dimensionless parameter appears to be  $\kappa R$ ). Nevertheless, we believe that the dominant effects that the expansions reveal for large  $\rho R^3$  and small  $e^2\beta$  cast light on the general mechanisms at work in a fluid of charged particles whenever the effects of their cores cannot be neglected. One of the most interesting of these effects is revealed in the limiting form of the two-particle correlation function as  $e^2\beta \rightarrow 0$  when the positive and negative ions have different sizes. There is a characteristic shielding length, but it is not simply the Debye length. Rather it is the Debye length times a certain factor that can be expressed in terms of the thermodynamic properties of the system that would remain if the charged particles were to lose their charges but retain their cores. This factor is greater than unity for the model of equally charged hard spheres in a uniform background often used in the theoretical studies of electrolytes, and it reduces to unity in the symmetric case in which there is no disparity between the diameters of spheres of different charge.<sup>8</sup> This can be understood physically since the shielding which comes about in the first model by the depletion of like charged particles in the vicinity of a fixed particle is opposed by the short-range forces which try to keep the density uniform, an effect absent in the symmetric case. There is also a second effect described by a higher-order term in  $e^2\beta$

that causes a decrease in the shielding length regardless of whether or not there is a disparity in ionic sizes.

Extensive computations will be needed to determine the range of conditions over which the first few terms in the expansion we have obtained can adequately describe ionic systems. For the case of charged hard spheres, some of these computations can be made relatively easily through the use of the exact solution<sup>8-10</sup> of the Percus-Yevick equation for a hard-sphere fluid. The Percus-Yevick approximation is remarkably good over a wide range of fluid densities,<sup>11</sup> and the results of Wertheim<sup>8</sup> and Lebowitz<sup>10</sup> are of precisely the right form to be used in assessing the effect of the ionic cores in our expansion. Use can also be made of the molecular-dynamical study of Alder,<sup>12</sup> who concluded that the Kirkwood superposition approximation possesses a high degree of accuracy for a system of hard spheres. Using the superposition approximation to express the three-body correlations  $h_{ijk}^0$  of a hard-sphere system in terms of the two-body correlation  $h_{ij}^0$ , we are able to reduce the integrals in the first few terms of our expansions to a form that can be evaluated analytically with the aid of the Percus-Yevick approximation of  $h_{ij}^0$ .

## II. A SUMMARY AND DISCUSSION OF OUR RESULTS

### A. Preliminary Remarks

This article is the third<sup>13</sup> in a series devoted to the study of many-body systems in which the interaction potential  $v(\mathbf{r})$  presents itself as a sum of two terms,  $q(\mathbf{r})$  and  $w(\mathbf{r})$ , that are very different from one another and hence can profitably be handled by quite different methods. (We shall refer to the first paper of this series as I throughout this article.) In the case of simple un-ionized fluids there is a highly repulsive molecular core potential  $q(\mathbf{r})$  and a much weaker attractive tail  $w(\mathbf{r})$ . In the case of lattice systems such as the lattice gas, the impossibility of multiple occupancy (in spin language, the upness or downness of the spin) can be used to define  $q(\mathbf{r})$ , and the rest of the interaction—the exchange potential—then defines  $w(\mathbf{r})$ . In this paper  $w(\mathbf{r})$  is taken to be the Coulomb potential and  $q(\mathbf{r})$  is taken to define the short-range interactions.

We deal in general with a mixture of different species, and write the interparticle potential between particles of species  $i$  and  $j$  with charge numbers  $z_i, z_j$  as the sum of

<sup>8</sup> M. Wertheim, Phys. Rev. Letters **8**, 321 (1963).

<sup>9</sup> E. Thiele, J. Chem. Phys. **39**, 474 (1963).

<sup>10</sup> J. L. Lebowitz, Phys. Rev. **133**, A895 (1964); J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).

<sup>11</sup> See, e.g., S. A. Rice and P. G. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience Publishers, Inc., New York, 1965).

<sup>12</sup> B. J. Alder, Phys. Rev. Letters **12**, 317 (1964).

<sup>13</sup> J. L. Lebowitz, G. Stell, and S. Baer, J. Math. Phys. **6**, 1282 (1965); G. Stell, J. Lebowitz, S. Baer, and W. Theumann, *ibid.* **7**, (1966). We refer to the first of these papers as I throughout this article.

<sup>7</sup> J. L. Lebowitz and G. Stell, Bull. Am. Phys. Soc. **9**, 105 (1964).

two terms

$$v_{ij}(\mathbf{r}) = q_{ij}(\mathbf{r}) + w_{ij}(\mathbf{r}), \quad (2.1a)$$

where

$$w_{ij}(\mathbf{r}) = z_i z_j e^2 / r. \quad (2.1b)$$

For simplicity we shall further assume when ordering the terms in our expansions that  $q_{ij}$ , which we call the reference potential, is independent of  $e$ , but this additional assumption is unnecessary in deriving our expansions. The function  $q_{ij}$  is primarily an expression of the impenetrability of the particles but it can also include, for example, dipole-dipole terms or dipole-induced-dipole terms. In all cases a simple way to define the characteristic distances  $R_{ij}$  of the short-range potential  $q_{ij}$  is through the equation

$$4\pi R_{ij}^3 = 3 \int |\exp[-\beta q_{ij}(\mathbf{r})] - 1| d\mathbf{r} \quad (2.2a)$$

[the factor  $4\pi/3$  is included in (2.2a) so that  $R_{ij}$  reduces to an actual diameter in the case of hard-sphere ions].

In our previous articles we devoted considerable attention to the use of a range parameter  $\gamma$  for the long-range part of the potential  $w$  that, for a three-dimensional multispecies system, has the form

$$w_{ij}(\mathbf{r}) = \gamma^3 \phi_{ij}(\gamma r), \quad (2.2b)$$

where [see Eqs. (3.2)-(3.4) in I]

$$\int r^n |w_{ij}(\mathbf{r})| d\mathbf{r} < \infty, \quad n \geq 0 \quad (2.2c)$$

and

$$|w_{ij}(\mathbf{r})| < \infty \quad \text{for all } r \geq 0. \quad (2.2d)$$

The  $w_{ij}$  of (2.1) is precisely of the form indicated in (2.2b) if  $e$  and  $\gamma$  are identified, and it is for this reason that much of the formalism of our previous work<sup>13</sup>—and the still earlier work of Hemmer<sup>14</sup> as well as its extensions by Hauge<sup>15</sup> to a multispecies system—can be immediately taken over and applied to a charged system, leading in a very natural way to expansions in  $e^2\beta$ . However, many of our specific results relating to particular orders in  $\gamma$  cannot be taken over without modification because (2.2c) and (2.2d) are not satisfied by the  $w_{ij}$  of (2.1), and the satisfaction of (2.2c) and (2.2d) are necessary for certain aspects of the  $\gamma$  ordering to make sense. [In fact the integrals of (2.2c) and the  $w_{ij}(0)$  appear as factors in the coefficients of the  $\gamma$  expansions.]

In the case of an ionic solution, our formalism can be applied to the full system of solute ions and solvent molecules. Alternatively we can consider just the solute ions and deal not with the potential itself but with the potential of mean force  $\psi_{ij}^m$  between pairs of solute particles in the limit of infinite dilution. Starting with

this limiting  $\psi_{ij}^m$  one can compute osmotic pressures and other osmotic quantities using the McMillan-Mayer<sup>16</sup> or the Kirkwood-Buff<sup>17</sup> theories. We shall assume that the long-range part of the solute-solute potential of mean force at infinite dilution can be taken to be

$$w_{ij}^m = z_i z_j e^2 / D r, \quad (2.3)$$

where  $D$  is the dielectric constant of the solvent. [No specific assumption about the form of  $q_{ij}^m(\mathbf{r})$  is necessary for our formal results. The assumption that  $q_{ij}^m(\mathbf{r})$  is a pure hard-core potential corresponds to the "primitive model" of Mayer.] This  $w_{ij}^m(\mathbf{r})$  is just the effective interionic potential assumed by Debye and Hückel and corresponds to the neglect of the "granularity" of the solvent. The use of this  $w_{ij}^m(\mathbf{r})$  is consistent with the further approximation that the  $n$ -particle solute-solute potentials of mean force at infinite dilution are simply sums of the  $w_{ij}^m(\mathbf{r})$  over all pairs of the  $n$  particles. We shall include the  $D$  (but not the superscript  $m$ ) in writing our equations, so that they will be directly applicable to the computation of osmotic quantities. Whenever  $v_{ij}$  is taken to be the potential rather than the potential of mean force,  $D$  is simply equal to one. This is always implied when we speak of solute-solvent or solvent-solute interactions. [When using the approximation (2.3) the solvent enters into the theory *only* through  $D$  and does not appear as a species of particle in the same way that the solute does. Hence in this approximation solvent-solute and solvent-solvent interactions are never explicitly considered.]

## B. Results

Our results are contained in the following expansions, in which  $-kTS$  is the excess Helmholtz free energy per unit volume,  $h_{ij}(\mathbf{r}) = h_2(\mathbf{r}_1, \mathbf{r}_2; i, j) = -1 + g_{ij}$ , where  $g_{ij}$  is the "radial" distribution function such that

$$g_{ij}(\mathbf{r}_{12}) = g_2(\mathbf{r}_1, \mathbf{r}_2; i, j) \\ = n_2(\mathbf{r}_1, \mathbf{r}_2; i, j) / n_1(\mathbf{r}_1; i) n_1(\mathbf{r}_2; j), \quad (2.4)$$

and

$$n_i(\mathbf{r}_1, \dots, \mathbf{r}_i; i_1, \dots, i_i) = \text{the probability density for finding distinct particles of species } i_1, \dots, i_i \text{ at positions } \mathbf{r}_1, \dots, \mathbf{r}_i, \text{ respectively,} \quad (2.5)$$

$h_{ijk}$  = the three-particle cluster function, related to  $g_{ijk}(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{23}; i, j, k)$  and to  $F_3$ , the three-particle Ursell function by Eq. (3.1b).  $S^0$ ,  $h_{ij}^0$ , and  $h_{ijk}^0$  are quantities that refer to the system with potential  $v_{ij} = q_{ij}$ . We call this the reference system. Further

$$\kappa^2 = (4\pi e^2 \beta / D) \sum_i z_i^2 \rho_i \quad (2.6)$$

<sup>14</sup> P. C. Hemmer, J. Math. Phys. **5**, 75 (1964).

<sup>15</sup> E. H. Hauge, thesis, Trondheim, 1965, and J. Chem. Phys. **44**, 2249 (1966).

<sup>16</sup> W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).

<sup>17</sup> J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **14**, 164, (1946); **19**, 774 (1951).

is the square of the reciprocal Debye length;

$$K^2 = \frac{4\pi e^2 \beta}{D} \sum_j \left( z_j^2 \rho_j + \sum_i z_i z_j \rho_i \rho_j \int h_{ij}^0 d\mathbf{r} \right) = (4\pi e^2 \beta / D) \sum_i \rho_i \nu_i z_i, \tag{2.7}$$

where

$$\rho_i \nu_i = \sum_j z_j \left( \delta_{ij} \rho_i + \rho_i \rho_j \int h_{ij}^0 d\mathbf{r} \right) = \sum_j z_j \partial \rho_i / \partial \beta \mu_j^0, \tag{2.8}$$

and  $\mu_j^0$  is the chemical potential of species  $j$  in the reference system at the given densities  $\rho_i$ . The relationship between the integral of  $h_{ij}$  and the partial derivatives of the chemical potential is completely general. We also introduce the potential of mean or average force  $\psi_{ij}(r_{12}) = \psi(r_{12}; i, j) = -kT \ln g_{ij}$  as well as the quantity  $\theta = z^2 (\sum_i \rho_i)$  where  $z$  is used to denote the magnitude of  $z_i$  when it is the same for all charged species.

For an arbitrary system of charged particles, we find for a uniform fluid

$$S = S^0 - \frac{1}{2}(\beta e^2) \sum_{ij} \left( z_i z_j \rho_i \rho_j \int \frac{h_{ij}^0}{r} d\mathbf{r} \right) + \frac{K^3}{12\pi} + \dots \tag{2.9}$$

The terms that are unexhibited here and in the rest of this section appear to be of higher order in  $e^2\beta$  than the ones exhibited. (The missing ones here, for instance, are

of order  $e^4\beta^2$ .) In (2.9) the terms of next higher order involve four-particle correlations of the reference system and hence are of great analytic complexity even for the simple case of charged spheres.

The potential of mean force  $\psi_{ij}(r)$  behaves asymptotically for  $r \rightarrow \infty$ , and  $\beta e^2 \rightarrow 0$  as

$$\psi_{ij}(r) \sim \nu_i \nu_j (e^2 / Dr) \exp(-Kr). \tag{2.10}$$

The substitution of  $\nu_i$  for  $z_i$  and  $K$  for  $\kappa$  are the essential modifications of the Debye-Hückel results due to the short-range interaction between the ions.<sup>7</sup> It is interesting to note that in a solution the presence of charged particles induces long-range correlations between the uncharged particles. These are of higher order in the density, as might be expected. [Equation (2.10) can also be derived via the usual Debye-Hückel-type arguments (cf. the Appendix).]

A special but important case—the symmetric case—is defined by the conditions that  $|z_i|$  be  $z$  or  $0$  for all  $i$ , and  $\rho_i$  and  $q_{ij}$  be the same for all charged species. Important examples are the two-species case for which  $z_1 = -z_2$ , and the three-species case for which  $z_1 = -z_2$ ,  $z_3 = 0$ . A great deal of simplification occurs in this symmetric case as a result of the condition  $\sum_i \rho_i z_i^n = 0$  for odd  $n$ , and  $z_i z_j = \pm z^2$ . (In terms of our analysis by means of cluster diagrams, this simplification is very similar to that which occurs for the Ising model in the special case of zero field.) One finds that  $K = \kappa$  and the second term on the right-hand side of (2.9) becomes zero, but now the first few higher terms have a simple enough structure so that they can be evaluated with considerable precision for a hard-sphere reference system. We have

$$S = S^0 + (\kappa^3 / 12\pi) + \sum_{l \geq 4} (e^2 \beta / D)^{l/2} S_l, \tag{2.11a}$$

where

$$S_4 = \frac{1}{4} \theta^2 \int \frac{h_{12}^0}{r^2} d\mathbf{r}, \tag{2.11b}$$

$$S_6 = -\theta^{5/2} \pi^{1/2} \int \frac{h_{12}^0}{r} d\mathbf{r}, \tag{2.11c}$$

$$S_6 = -\frac{1}{6} \theta^3 \int \frac{h_{123}^0}{r_{12} r_{23} r_{31}} d\mathbf{r}_1 d\mathbf{r}_2 + 2\pi \theta^3 \int h_{12}^0 d\mathbf{r}, \tag{2.11d}$$

$$S_7 = \frac{\theta^{7/2}}{8\pi^{1/2}} \left\{ \lim_{\kappa \rightarrow 0} \int \frac{h_{12}^0 h_{34}^0 \kappa \exp[-\kappa(r_{12} + r_{23} + r_{34} + r_{41})]}{r_{12} r_{23} r_{34} r_{41}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \right\} + \theta^{7/2} \pi^{1/2} \int \frac{h_{113}^0}{r_{13} r_{23}} d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{3} (8\theta^{7/2} \pi^{3/2}) \int h_{12}^0 r d\mathbf{r}. \tag{2.11e}$$

The remaining terms appear to be of the order  $(e\beta^{1/2})^8$ . We note that  $R^3 (e^2 \beta / D)^{l/2} S_l$  is of order  $(\kappa R)^l$  so that  $\kappa R$  can be used as the single dimensionless ordering parameter in our expansion of  $R^3 S$  given by (2.11). This is very convenient since  $\kappa R$  is small if either  $\beta$  or  $\rho$  is sufficiently small. As a result (2.11) has a universality

lacking in previous expansions that use  $\rho R^3$  as an ordering parameter and are hence limited to small  $\rho R^3$ .

The extreme opposite of the symmetric case is the often-studied mathematical model of a single component charged fluid in a uniform background. We can treat this case as the limit of the two-species case in which

$z_2 \rightarrow 0$  in such a way that  $z_2 \rho_2 = -z_1 \rho_1$  and  $h_{12}^0 = h_{22}^0 = \psi_{12} = \psi_{22} = 0$ . We have, setting  $z_1 = z$ ,  $\rho_1 = \rho$ ,

$$\psi_{11} = \psi_{11}^0 + \left(\frac{\rho \chi^0}{\beta}\right)^2 \frac{z^2 e^2 \exp(-K\tau)}{D r} \text{ as } \beta e^2 \rightarrow 0, \quad (2.12)$$

$$K^2 = \kappa^2 \left(1 + \rho \int h^0 d\mathbf{r}\right) = \frac{\kappa^2}{d\beta P^0/d\rho} = \frac{\kappa^2 \rho \chi^0}{\beta}, \quad (2.13)$$

where  $P^0$  is the pressure and  $\chi^0$  the compressibility of the reference system. Since, for repulsive short-range interactions between the charged particles  $q_{11}(r)$ ,  $d\beta P^0/d\rho$  will generally be larger than unity (except when the reference system has a phase transition, which we shall not consider), the effect of the short-range interactions is to increase the shielding length. This can be understood physically since the shielding which comes about here by the depletion of like charged particles in the vicinity of a fixed particle is opposed by the short-range forces which try to keep the density uniform. This effect also reduces the magnitude of the correction term to  $\psi_{11}^0$ , and is completely lacking in the symmetric case (at least in lowest order).

### III. CLUSTER EXPANSIONS

In order to obtain the expressions given in Sec. II, we shall start out by setting down a few general cluster expansions, and then later consider  $\psi_{ij}$  and  $S$  in detail through the first few orders of  $e^2\beta$ . An appropriate set of functions for us to begin with is the set  $\{F_l\}$ , the  $l$ -particle Ursell functions associated with the  $n_l$  defined in (2.5):

$$F_1(\mathbf{r}_1; i) = n_1(\mathbf{r}_1; i),$$

$$F_2(\mathbf{r}_1, \mathbf{r}_2; i, j) = n_2(\mathbf{r}_1, \mathbf{r}_2; i, j) - n_1(\mathbf{r}_1; i) n_1(\mathbf{r}_2; j),$$

$$F_3(\mathbf{r}_1, \mathbf{r}_2; i, j, k) = n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; i, j, k)$$

$$- n_1(\mathbf{r}_1; i) n_2(\mathbf{r}_2, \mathbf{r}_3; j, k) - n_1(\mathbf{r}_2; j) n_2(\mathbf{r}_1, \mathbf{r}_3; i, k)$$

$$- n_1(\mathbf{r}_3; k) n_2(\mathbf{r}_1, \mathbf{r}_2; i, j)$$

$$+ 2n_1(\mathbf{r}_1; i) n_1(\mathbf{r}_2, j) n_1(\mathbf{r}_3, k). \quad (3.1a)$$

With respect to the  $h$ 's of Sec. II we have

$$\frac{F_2(\mathbf{r}_1, \mathbf{r}_2; i, j)}{n_1(\mathbf{r}_1; i) n_1(\mathbf{r}_2; j)} = h_2(\mathbf{r}_1, \mathbf{r}_2; i, j) = h_{ij}(\mathbf{r}_1, \mathbf{r}_2),$$

$$\frac{F_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; i, j, k)}{n_1(\mathbf{r}_1; i) n_1(\mathbf{r}_2; j) n_1(\mathbf{r}_3; k)} = h_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; i, j, k) = h_{ijk}(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{23}). \quad (3.1b)$$

The functions  $F_l$  have cluster expansions that can be represented in the usual way (see I) as a sum of linear graphs consisting of  $K$  bonds representing the function  $K(\mathbf{r}_1, \mathbf{r}_2; i, j) = \exp[-\beta q_{ij}(\mathbf{r}_1, \mathbf{r}_2)] - 1$ ,  $\Phi$  bonds representing the function  $\Phi(\mathbf{r}_1, \mathbf{r}_2; i, j) = -\beta w_{ij}(\mathbf{r}_{12})$ , and  $n_l$  vertices representing the function  $n_l(\mathbf{r}_1; i)$  (or  $\rho_i$  in a

uniform system). [Note that the  $K(\mathbf{r}_1, \mathbf{r}_2; i, j)$  is a quite different object than the  $K$  introduced in Eq. (2.7).] A vertex that is white and labeled by  $\mathbf{r}_i$  and  $i$  is associated with the coordinate  $\mathbf{r}_i$  and the species  $i$ ; a vertex that is black and unlabeled corresponds to a coordinate that has been integrated over the volume of the system and an index that has been summed over all possible species. Each graph then represents a sum of integrals—a sum over species and integrals over coordinates—divided by a symmetry factor that is the number of ways the bonds and black vertices can be relabeled (in one's imagination, that is; on the graphs, only the white vertices are actually labeled) without the relabeling leading to a graph that is distinguishable from the original graph. For  $F_l$  we have [cf. Eq. I (2.7)]

$$F_l(\mathbf{r}_1, \dots, \mathbf{r}_l; i_1, \dots, i_l) = \text{the sum of all irreducible graphs consisting of some } \Phi \text{ bonds and/or } K \text{ bonds, some or no black } n_1 \text{ vertices, and } l \text{ white vertices, labeled } \{\mathbf{r}_i, i_i\} \text{ through } \{\mathbf{r}_l, i_l\}; \text{ At most one } K \text{ bond, but an arbitrary number of } \Phi \text{ bonds (along or with the } K \text{ bond), can share a pair of vertices.} \quad (3.2)$$

Here, an irreducible graph is a graph free of articulation vertices, which are vertices whose removal separates the graphs into two or more parts, one of which is free of labeled vertices.

Letting  $-----$  represent  $K$ ,  $-----$  represent  $\Phi$ , and  $\circ$  or  $\bullet$  represent  $n_1$ , such a graphical prescription can be pictured as below:

$$F_2(\mathbf{r}_1, \mathbf{r}_2; i, j) = \circ-----\bullet + \text{---}\overset{\text{---}}{\text{---}}\text{---} + \dots + \text{---}\overset{\text{---}}{\text{---}}\text{---} + \dots, \quad (3.3)$$

where one white vertex on each graph is understood to carry the label  $\{\mathbf{r}_1; i\}$  and the other white vertex the label  $\{\mathbf{r}_2; j\}$ . (Often in picturing graphs we shall not bother to write in the labels. The fact that the labeled vertices are pictured as white circles already distinguishes them sufficiently for most of our purposes.) A typical graph in such a sum represents a sum of integrals; for example,

$$\text{---}\overset{\text{---}}{\text{---}}\text{---} = \sum_{j=1}^{\sigma} \int d\mathbf{r}_3 \Phi(\mathbf{r}_1, \mathbf{r}_3; i_1, j) \times K(\mathbf{r}_1, \mathbf{r}_3; i_1, j) \Phi(\mathbf{r}_3, \mathbf{r}_2; j, i_2),$$

where  $\sigma$  is the total number of species.

It is sometimes convenient to denote  $\{\mathbf{r}_i, i_i\}$  as a single vector  $\xi_i$ , and then we use the notation  $F_2(\xi_1, \xi_2) = F_2(\mathbf{r}_1, \mathbf{r}_2; i_1, i_2)$  and use the integral  $\int d\xi_i$  to mean the

generalized integral

$$\sum_{i=1}^n \int d\mathbf{r}_i.$$

We also use  $\int d\xi_{12}$  to mean

$$\sum_{i,j} \int d\mathbf{r}_{12},$$

Sometimes we shall lapse back into the use of  $\mathbf{r}_i$ 's and  $i_i$ 's when we think it will be a little clearer than the use of  $\xi_i$ 's.

The prescription for  $\psi_2(\xi_1, \xi_2) = \psi_{ij}(\mathbf{r}_{12})$  is very similar to that of  $F_2$  given by (3.2), but we add a constraint:

$$-\beta n_1(\xi_1) n_2(\xi_2) \psi_2(\xi_1, \xi_2) = -\beta n_1(\xi_1) n_1(\xi_2) v_{ij}(\mathbf{r}_{12}) + \text{the sum given in (3.2) when } l=2 \text{ such that (i) the white vertices are not a pair of vertices whose removal separates the graph into two or more pieces, and (ii) there is at least one black vertex.} \tag{3.4}$$

The prescription for  $\mathcal{S}$  is the simplest of all:

$$V\mathcal{S} = \text{the sum of (3.2) with } l=0, \text{ i.e., no white vertices.} \tag{3.5}$$

In order to carry out our program for obtaining results in which the properties of the reference systems are correctly taken into account to all orders in the density, we have to carry out a resummation of the above graphs. This has the effect of eliminating the  $K$  bonds and density vertices in favor of new entities more suitable for high-temperature (small  $\beta e^2$ ), high-density expansions. Following our procedure in I<sup>13</sup> we now introduce the modified Ursell functions  $\hat{F}_l$  which are related to the "modified distribution functions"  $\hat{n}_k$  in the same way that the  $F_l$  are related to the  $n_k$ . The  $\hat{n}_l$  have the same definition as the  $n_l$  given in (2.5) *except* that the  $l$  particles need not be distinct. Thus,

$$\hat{F}_2(\xi_i, \xi_j) = \rho_i \delta_{ij} \delta(\mathbf{r}_i - \mathbf{r}_j) + F_2(\xi_i, \xi_j).$$

The  $\hat{F}_l$  have the prescription

$$\hat{F}_l(\xi_1, \dots, \xi_l) = \text{the sum of all irreducible graphs consisting of some } \Phi \text{ bonds and/or } K \text{ bonds, some or no black } n_1 \text{ vertices, and } m \leq l \text{ white vertices that are each labeled by a subset of labels } \{\xi_1, \dots, \xi_l\}. \text{ For each graph the subsets are disjoint and exhaust the set } \{\xi_1, \dots, \xi_l\}. \text{ At most one } K \text{ bond but an arbitrary number of } \Phi \text{ bonds (alone or with a } K \text{ bond) can share a pair of vertices.} \tag{3.6}$$

We now define  $\hat{F}_l^s$ , the "short-range part" of  $\hat{F}_l$ , to be the function represented by the subset of all graphs in (3.6) such that all the white vertices in each graph would remain connected if the  $\Phi$  bonds were erased.

The  $\hat{F}_l^s$  will be represented by hypervertices (black circles with vertices attached in their perimeter)

$$\hat{F}_2^s = \text{---} \bullet \text{---}, \quad \hat{F}_3^s = \text{---} \bullet \text{---} \bullet \text{---}, \quad \text{etc., } \dots$$

The difference between  $\hat{F}_l$  and  $\hat{F}_l^s$  is denoted by  $\hat{F}_l^L$ , the "long range part" of  $F_l$ . It was shown in I that the  $\hat{F}_l$  can be expressed in terms of the  $\hat{F}_k^s$  and the  $\Phi$  bonds alone. It is also possible, and particularly useful for the Coulomb case we are considering, to eliminate also the  $\Phi$  bonds in favor of  $\mathcal{C}(\xi_1, \xi_2; \hat{F}_2^s)$ , the sum of chains of  $\Phi$  bonds that are connected together by  $\hat{F}_2^s$  hypervertices. We denote  $\mathcal{C}(\xi, \xi_2; \hat{F}_2^s)$  by a dot-dash line and refer to it as a  $\mathcal{C}(\hat{F}_2^s)$  bond:

$$\text{---} \text{---} \text{---} = \text{---} + \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} + \dots \tag{3.7}$$

Our prescription for  $\hat{F}_l$  in terms of  $\mathcal{C}(\hat{F}_2^s)$  and  $\hat{F}_l^s$  is given by

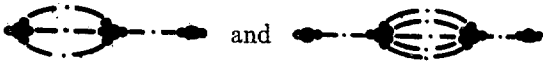
$$\hat{F}_l = \hat{F}_l^s + \text{the sum of all irreducible graphs consisting of some } \mathcal{C}(\hat{F}_2^s) \text{ bonds and } \hat{F}_k^s \text{ hypervertices, such that the graphs have } l \text{ white vertices labeled } \xi_1 \text{ through } \xi_l, \text{ respectively, and no } \hat{F}_2^s \text{ hypervertices containing two black vertices.} \tag{3.8}$$

Thus

$$\hat{F}_2 = \hat{F}_2^s + \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} + \text{---} \bullet \text{---} \bullet \text{---} \bullet \text{---} + \dots \tag{3.9}$$

The main distinction between the short-range parts and the long-range parts of the correlation functions, for example  $\hat{F}_2^s$  and  $\hat{F}_2^L$ , is in the dependence of their effective ranges on  $e$ , or on  $\kappa$  which is proportional to  $e$ , when this parameter becomes very small. As pointed out in I when considering expansions in  $\gamma$ , the inverse range of  $w(\mathbf{r}) = \gamma^2 \phi(\gamma \mathbf{r})$ , we expect that  $\hat{F}_2^s(\mathbf{r}, \gamma)$  and  $\hat{F}_2^L(\mathbf{r}, \gamma)$ ,  $\mathbf{y} \equiv \gamma \mathbf{r}$ , should have expansions in  $\gamma$  for fixed  $\mathbf{r}$  and  $\mathbf{y}$  with each order in the expansion approaching zero as  $\mathbf{r}$  or  $\mathbf{y}$  approach infinity. For  $w(\mathbf{r})$  satisfying (2.2c) and (2.2d) the formal expansion in  $\gamma$  is actually a power series (at least in the region away from a phase transition), with the order of a particular graph being equal to (or starting with)  $\gamma^{3(t-m)}$ , where  $t$  is the number of  $\Phi$  (or  $\mathcal{C}$  bonds and  $m$  the number of free integrations in the graph. The latter is equal to the number of "islands"

(pieces not containing root points), left when all the  $\Phi$  bonds are deleted. For graphs not containing root points (such as in  $VS$ ), the order in  $\gamma^3$  is one less than the number of  $\Phi$  bonds minus the number of islands. The reason for this is clear since each  $\Phi$  bond is of  $O(\gamma^3)$  while each "free" integration brings down a  $\gamma^3$ . In the Coulomb long-range case, where  $w(r) \sim e^2/er$ , the role of  $\gamma$  is formally assumed by  $e$ , but the situation is complicated by the violations of (2.2c) and (2.2d), and in fact it is clear that not all graphs with  $\mathcal{C}(\hat{F}_2^s)$  bonds and  $\hat{F}_n^s$  hypervertices in (3.8) will even be finite. For example, graphs like



are infinite as a result of there being more than two  $\mathcal{C}(\hat{F}_2^s)$  bonds between a pair of hypervertices. Such difficulties, however, can be overcome by suitable resummations and the introduction of new bond functions, such as

$$\mathcal{B} = \mathcal{C} + (1/2!) \mathcal{C}^2 + (1/3!) \mathcal{C}^3 + \dots$$

To help determine the order of the terms omitted from our final results, we have in fact used a  $\mathcal{C}(\hat{F}_2^0)$ -bond,  $\mathcal{B}(\hat{F}_2^0)$ -bond,  $h_0^0$ -bond,  $\rho$ -vertex representation of  $F_2$ , but since the systematic description of this representation is unnecessary for an understanding of the origin of the terms that are retained in (2.10) and (2.11), we do not give it here.

The complexities and associated modifications that must be considered in the case of a Coulomb potential are fortunately not present in the computation of the lowest-order term of  $F_2^L(y, e)$ ,  $y = er$ , the term corresponding to the one computed by Debye and Hückel for  $\rho R^3 \ll 1$ . This term is contained in the first graph—the chain graph—on the right side of (3.9). The Fourier transform of this graph with respect to the variable  $y$  denoted by  $\Gamma$ , has the easily verifiable form [cf. Eq. (4.3) in I]

$$\Gamma_{ij}(k, e) = \frac{e^3 \sum \bar{F}_{ii}^s(ek, e) z_{iZ_m} \bar{F}_{mj}^s(ek, e)}{D[k^2 - \sum z_{iZ_m} \bar{F}_{im}^s(ek, e)]}, \quad (3.10)$$

where  $\bar{F}_{ij}^s(k, e)$  is the Fourier transform with respect to the variable  $r$  of  $\hat{F}_2^s(r, e)$  for species  $i$  and  $j$  and we have exhibited its  $e$  dependence explicitly. To lowest order in  $e$ ,  $\bar{F}_2^s(r, e) = \hat{F}_2^0(r)$  from which follows (2.10) since to this order  $-\beta \rho_i \rho_j \psi^L \approx F_2^L \equiv \hat{F}_2^L$ . Alternatively, we could have done our analysis directly on  $\psi^L$ . It is clear that our result reduces to the Debye-Hückel result when, as is true at low densities,  $\hat{F}_2^s(\xi_1, \xi_2)$  is replaceable by  $n_1(\xi_1) \delta(\xi_1 - \xi_2)$ .

The lowest-order terms in  $\beta e^2$  of the free energy may now be computed by the method of Sec. 6 of I. We start by introducing a parameter  $\lambda$  into the definition of  $\Phi$  so

that

$$\Phi(\xi_1, \xi_2) = -\lambda e^2 \beta z_i z_j / r_{12}. \quad (3.11)$$

$\hat{F}_2$  now becomes a function of  $\lambda$  and we have [cf. Eq. (6.10) of I but note the difference in notation with respect to the inclusion of  $\lambda$  in  $\Phi$ ]

$$\mathcal{S} = \mathcal{S}^0 + (2V)^{-1} \int d\xi_1 d\xi_2 \Phi(\xi_1, \xi_2) n_1(\xi_1) n_1(\xi_2) + (2V)^{-1} \int_0^1 \frac{d\lambda}{\lambda} \int d\xi_1 d\xi_2 F_2(\xi_1, \xi_2) \Phi(\xi_1, \xi_2). \quad (3.12)$$

The second term on the right will vanish due to charge neutrality while to lowest order we replace  $F_2^L \equiv \hat{F}_2^L$  by the chain graph and  $F_2^s$  by  $F_2^0$  obtaining the result quoted in (2.9).

#### IV. ANALYSIS OF HIGHER-ORDER TERMS

In the preceding section we gave the general representation for the  $\hat{F}_n$  in terms of  $\mathcal{C}(\hat{F}_2^s)$  and the  $\hat{F}_i^s$ , and by taking only the lowest-order term in  $F_2^L$  and approximating  $\hat{F}_2^s$  by  $F_2^0$  we obtained (2.9) and (2.10). More generally the function  $F_i^s$  must be systematically given in terms of quantities that depend only on  $w_{ij}$  and the state of the reference system in order for us to obtain higher order terms. In this paper we need only be concerned with  $l=2$ .

From our results in I we can write

$$F_2^s = \text{---} + \text{---} + \dots, \quad (4.1)$$

where  $\text{---}$  in (4.1) and hereafter represents the function  $F_2^0$  and

$$\text{---} \text{ represents } \frac{1}{2} \int \frac{\delta F_2^0(\xi_1, \xi_2)}{\delta n_1(\xi_5) \delta n_1(\xi_6)} \times \hat{F}_2^0(\xi_3, \xi_5) \hat{F}_2^0(\xi_4, \xi_6) d\xi_5 d\xi_6. \quad (4.2)$$

Similarly, we have

$$\text{---} = \text{---} + \text{---} + \dots, \quad (4.3)$$

where  $\text{---}$  represents  $\hat{F}_2^0$ . The set of terms not shown in (4.1) and (4.2) can be represented by graphs with two or more  $\mathcal{C}(\hat{F}_2^s)$  bonds and hypervertices that represent various combinations of  $F_i^0$ 's and their functional derivations with respect to  $n_1(\xi_i)$ . For details of this representation we refer the reader to Appendix B of I,<sup>13</sup> where these hypervertices are called the  $H_{ij}$  hypervertices.

To complete our program of obtaining all functions in terms of  $\Phi$  and quantities relating to the reference system we must re-express  $\mathcal{C}(\hat{F}_2^0)$ . One way of doing this is by introducing a  $\mathcal{C}(\hat{F}_2^0)$  bond, which we denote by  $\text{---}\overset{\circ}{\bullet}\text{---}$ . The  $\circ$  is to remind us that we are looking at a  $\mathcal{C}(\hat{F}_2^0)$  bond instead of a  $\mathcal{C}(\hat{F}_2^s)$  bond.

$$\begin{aligned} \mathcal{C}(\xi_1, \xi_2; \hat{F}_2^0) &= \text{---}\overset{\circ}{\bullet}\text{---} \\ &= \text{---} + \text{---}\overset{\circ}{\bullet}\text{---} \\ &\quad + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \dots \end{aligned} \tag{4.4}$$

Putting the results of (3.7) and (4.3) together, we have

$$\mathcal{C}(\hat{F}_2^s) = \text{---}\overset{\circ}{\bullet}\text{---} + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \dots, \tag{4.5}$$

and this yields

$$\begin{aligned} \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} &= \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} \\ &\quad + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \dots, \end{aligned} \tag{4.6}$$

$$\text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} = \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \dots \tag{4.7}$$

We now have graphs in which the functional dependence on  $\Phi$  and on reference quantities is separated in a clear way. Nevertheless a function like



is still not a simple functional of  $\hat{F}_2^0$ , and consequently we must carry our manipulations one step further. We introduce the difference between  $\hat{F}_2^0(\mathbf{r}_1, \mathbf{r}_2; i, j)$  and the function  $M$ :

$$M(\mathbf{r}_1, \mathbf{r}_2; i, j) = \left[ \int d\mathbf{r}_2 \hat{F}_2^0(\mathbf{r}_1, \mathbf{r}_2; i, j) \right] \delta(\mathbf{r}_1 - \mathbf{r}_2) \tag{4.8}$$

and represent  $M$  by the symbol



We let the difference between  $\hat{F}_2^0$  and  $M$  be  $\Delta(\mathbf{r}_2, \mathbf{r}_2; i, j)$  which we represent by



$$\text{---}\overset{\circ}{\bullet}\text{---} = \text{---}\overset{\circ}{\bullet}\text{---} + \text{---}\overset{\circ}{\bullet}\text{---} \tag{4.9}$$

We introduce  $\mathcal{C}(M)$ :

$$\begin{aligned} \mathcal{C}(M) &= \text{---}\overset{\circ}{\bullet}\text{---} \\ &= \text{---} + \text{---}\overset{\circ}{\bullet}\text{---} \\ &\quad + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \dots, \end{aligned} \tag{4.10}$$

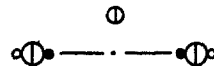
and we have then

$$\text{---}\overset{\circ}{\bullet}\text{---} = \text{---}\overset{\circ}{\bullet}\text{---} + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \dots, \tag{4.11}$$

$$\begin{aligned} \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} &= \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} \\ &\quad + \text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} + \dots \end{aligned} \tag{4.12}$$

Similar decomposition can be given for the higher  $\hat{F}_n^0$  but they are unnecessary for the purposes of this paper.

We find, finally, that



is a simple functional of  $\hat{F}_2^0$  for a uniform system:

$$\text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---}\overset{\circ}{\bullet}\text{---} = -\rho_i \rho_j \nu_i \nu_j (e^2 \beta / D) [\exp(-K\tau) / \tau], \tag{4.13}$$

where  $\nu_i$  and  $K$  are given in Eq. (2.7) and (2.8).

There is a remarkable simplification that takes place in these cluster expansions when we look at the uniform symmetric case in which for all charged species,  $|z_i| = z$ , and the  $\rho_i$  and  $q_{ij}$  are the same for all  $i$ . We have  $\sum z_i^l \rho_i = 0$  for all odd  $l$ , and this—along with the condition on  $q_{ij}$ —means that whenever there are an odd number of  $\Phi$  bonds [or  $\mathcal{C}(\hat{F}_0^s)$  bonds,  $\mathcal{C}(\hat{F}_2^0)$  bonds,  $\mathcal{C}(m_1)$  bonds—it does not make any difference] incident upon a black vertex, the graph is identically zero. We illustrate this state of affairs below by picturing the



expansions associated with a number of hypervertices in the symmetric case. Here



stands for  $F_3^0$ :

becomes , (4.14a)

so

= , (4.14b)

= zero, (4.14c)

and

= =  $\mathcal{C}(n_1)$  (4.14d)

(hereafter we represent  $\mathcal{C}(n_1)$  by ). We also find from symmetry

= zero (4.14e)

= + + + ... (4.14f)

= , (4.14g)

= zero, (4.14h)

= + ... (4.14i)

There is an alternative way of obtaining  $\mathcal{C}(\hat{F}_2^0)$  in terms of  $\Phi$  and quantities relating to the reference system that does not start with (4.5), and it seems to be especially useful in the symmetric case. The steps involved closely parallel the ones followed in Eq. (4.8)–(4.13).

We first introduce the difference between

$\hat{F}_2^s(\mathbf{r}_1, \mathbf{r}_2; i, j)$  and  $M^s$ ,

where  $M^s$  is the function

$M^s(\mathbf{r}_1, \mathbf{r}_2; i, j) = \left[ \int d\mathbf{r}_2 \hat{F}_2^s(\mathbf{r}_1, \mathbf{r}_2; i, j) \right] \delta(\mathbf{r}_1 - \mathbf{r}_2)$ . (4.15)

We represent  $M^s$  by



and let the difference between it and  $\hat{F}_2^s$  be denoted by



= + (4.16)

We denote the sum over chains of  $\Phi$  bonds connected by  $M^s$  vertices as  $\mathcal{C}(M^s)$  and represent it by :

$\mathcal{C}(M^s) =$  = + + ... (4.17)

and we have

$\mathcal{C}(\hat{F}_2^s) = \mathcal{C}(M^s) +$  + ... (4.18)

= + + ... (4.19)

and using (4.14i) and (4.16),

= + ... (4.20)

In the case of a uniform fluid

$\mathcal{C}(M^s) = -z_i z_j (e^{\beta/D}) [\exp(-K_s r) / r]$ , (4.21)

where

$K_s^2 = \frac{4\pi e^{\beta/D}}{D} \int d\xi_{12} z_i z_j \hat{F}_2^s(\xi_1, \xi_1)$ . (4.22)

If we expand  $\hat{F}_2^s$  out in terms of  $\mathcal{C}(\hat{F}_2^0)$  bonds and hypervertices that represent functions dependent only on the reference system, we get

$K_s^2 = \frac{4\pi e^{\beta/D}}{D} \int d\xi_{12} z_i z_j \left( \text{diagram 1} + \text{diagram 2} + \dots \right)$  (4.23)

This turns out to be  $K^2$  when we approximate it by retaining only the



in the brackets, and then we are back where we started

from with  $K_s^2 \approx K^2$ . However, in the symmetric case we have

$$K_s^2 = \frac{4\pi e^2 \beta}{D} \int d\xi_{12} z_i z_j$$

$$\times \left[ n_1(\xi_1) \delta(\xi_1 - \xi_2) + \text{---} \overset{\square}{\text{---}} \text{---} + \text{---} \overset{\triangle}{\text{---}} \text{---} + \dots \right], \quad (4.24)$$

which we can either use in some self-consistent scheme {--- $\overset{\square}{\text{---}}$ ---} is a function of  $K_s$ , [see (4.21)], or expand out in terms of  $\Phi$  and reference system quantities:

$$K_s^2 = \frac{4\pi e^2 \beta}{D} \int d\xi_{12} z_i z_j$$

$$\times \left[ n_1(\xi_1) \delta(\xi_1 - \xi_2) + \text{---} \overset{n}{\text{---}} \text{---} + \dots \right]. \quad (4.25)$$

We continue our discussion of  $K_s$  in Sec. V.

### V. HIGHER-ORDER TERMS IN THE POTENTIAL OF AVERAGE FORCE FOR THE SYMMETRIC CASE

Before deriving Eq. (2.11) we shall discuss briefly the leading contributions to  $F_2$  and  $\psi_2$  in the symmetric case. Our main purpose is to exhibit the terms that give rise to a shielding length at high density different from  $\kappa^{-1}$  even when there is no disparity in ionic diameters. We start with (3.9) where the graphs



and



are all identically zero because of symmetry [see (4.14h)].

From (4.19), we have

$$\text{---} \overset{\square}{\text{---}} \text{---} = \text{---} \overset{\square}{\text{---}} \text{---} + \dots \quad (5.1a)$$

In a uniform fluid in which  $\rho = \sum \rho_i$ , where the sum is over all charged species, we find

$$\text{---} \overset{\square}{\text{---}} \text{---} = [-z_i z_j \rho_i^2 e^2 \beta I^2 / D] [\exp(-K_s r) / r], \quad (5.1b)$$

where the  $I$  and  $K_s$  are related by the equation

$$K_s^2 = \kappa^2 I, \quad (5.1c)$$

and, from (4.24)

$$I = 1 - \frac{z^2 \rho e^2 \beta}{D} \int \frac{h_{12}^0}{r} d\mathbf{r} + \frac{z^4 \rho^2 e^4 \beta^2}{D^2} \int \frac{h_{123}^0}{r_{12} r_{23}} d\mathbf{r}_1 d\mathbf{r}_2 + \dots, \quad (5.1d)$$

while in a uniform system the first term in (4.20) can be evaluated to yield

$$\text{---} \overset{\square}{\text{---}} \text{---} = \left[ \frac{\rho_i z_i^2 e^2 \beta}{D} \right]^2$$

$$\times \left( 1 + \rho \int h_{12}^0 d\mathbf{r} + \dots \right)^2 \frac{\exp(-2K_s r)}{r^2}. \quad (5.2)$$

After taking into account the simplification of terms due to symmetry we find from (4.1) that

$$F_2^s = F_2^0 + \text{---} \overset{\square}{\text{---}} \text{---} + \dots \quad (5.3a)$$

In a uniform system this can be written as

$$F_2^s = F_2^0 - F_2^0(\mathbf{r}_1, \mathbf{r}_2; i, j)$$

$$\times \{ z_i z_j (e^2 \beta / D) [\exp(-K_s r_{12}) / r_{12}] \} + \dots \quad (5.3b)$$

The terms that are neglected in (5.1)–(5.3) contribute to  $F_2$  to higher order in  $e^2 \beta$  than the terms that are shown, but in order to obtain a final expression for  $F_2$  we are still faced with the task of comparing the terms in each one of these equations with the terms in each of the others. This brings up the general problem of ordering functions of  $r$  which we shall not pursue except to note that as  $r \rightarrow \infty$ ,  $\text{---} \overset{\square}{\text{---}} \text{---}$  is dominant over



as well as the next higher-order term in (5.3) (not shown), which contains two  $\text{---} \overset{\square}{\text{---}} \text{---}$  bonds. It is also clearly dominant over



Thus through order  $(e^2 \beta)^2$ ,  $\text{---} \overset{\square}{\text{---}} \text{---}$  appears to be the dominant term of  $F_2$  as  $r$  approaches infinity.

Although the analysis of this section thus far has been all in terms of  $F_2$  we have given our final results in Sec. II in terms of  $\psi_2$  in order to obtain an expansion that will provide, as it stands, reasonable and useful approximations to the exact state of affairs. There is a difficulty with our expansion for  $F_2$  that prevents it from providing such approximations. The problem is that we know  $F_2(\xi_1, \xi_2)$  must go to  $-n_1(\xi_1)n_1(\xi_2)$  [i.e., that  $g_2(\xi_1, \xi_2)$  must go to 0] when  $r_{12}$  goes to zero for any  $v_{ij}(r_{12})$  that goes to infinity when  $r_{12}$  goes to zero, but when we truncate our expansions for  $F_2$  after any finite number of terms, they will not, in general, satisfy this condition. (This problem of “small  $r$  boundary-condition breaking” is a functional and vexing one for any reasonable  $v = q + w$  and it is intimately connected with what goes wrong with  $\gamma$  expansions in the critical region for nonionic fluids.<sup>13</sup>) For a  $w(r)$  that goes to  $\infty$  as  $r$

goes to zero this difficulty is glaring even away from critical regions, but it can be very easily remedied by first obtaining an approximate  $\psi_2$  through the relation  $g_2 = \exp(-\beta\psi_2)$ . The  $F_2$  so obtained will of course no longer be represented by the first few terms in a simple ordering scheme involving  $e^2\beta$  the way  $\psi_2$  itself is, but there is nothing any more sacred about  $F_2$  than about  $\psi_2$  in this connection. Turning now to the problem of actually finding  $\psi_2(\xi_1, \xi_2)$ , when we carry along the results of the extra conditions given in (3.4) through the necessary resummation, we find that in the symmetric case, we have, instead of (3.9),

$$-\beta n_1(\xi_1) n_1(\xi_2) \psi_2(\xi_1, \xi_2) = -\beta n_1(\xi_1) n_1(\xi_2) \psi_2^s(\xi_1, \xi_2) + \text{diagram 1} + \text{diagram 2} - \text{diagram 3} + \dots, \quad (5.4)$$

and instead of (5.3) we have

$$n_1(\xi_1) n_1(\xi_2) \psi_2^s = n_1(\xi_1) n_1(\xi_2) \psi_2^0 + \dots \quad (5.5)$$

without



Otherwise the results for  $\psi_2$  are the same as those for  $F_2$  to the orders we consider here. In particular to  $O(e^2\beta)^2$ ,

$$-\beta n_1(\xi_1) n_1(\xi_2) \psi_2(\xi_1, \xi_2) = \text{diagram 4} \text{ for } r \rightarrow \infty. \quad (5.6)$$

We close this section by noting that Eqs. (5.6) and (5.1b) show that  $K_s^{-1}$  is the shielding length for sufficiently low  $\beta$ , and that (5.1c) and (5.1d) exhibit the dominant terms that give rise to the difference between  $\kappa$  and  $K_s$  when there is no disparity in ionic diameters.

VI. THE FREE ENERGY

To derive (2.11) we shall examine the free energy by means of Eq. (3.12). Letting  $\text{---}$  represent  $\Phi$  and  $\text{---}$  represent  $\mathcal{C}(\hat{F}_2^s)$  as before, we have from (3.9)

$$F_2(\xi_1, \xi_2) \Phi_2(\xi_1, \xi_2) = F_2^s(\xi_1, \xi_2) \Phi_2(\xi_1, \xi_2) + \text{diagram 5} + \text{diagram 6} + \text{diagram 7} + \text{diagram 8} + \dots \quad (6.1)$$

Thus we can write  $S$  as the following sum:

$$S = S^0 + (2V)^{-1} \int n(\xi_1) \Phi(\xi_1, \xi_2) n(\xi_2) d\xi_1 d\xi_2 + R + \sum, \quad (6.2a)$$

where

$$R = V^{-1} \int_0^1 \frac{d\lambda}{\lambda} \int d\xi_1 d\xi_2 \times \left( F_2^s(\xi_1, \xi_2) \Phi_2(\xi_1, \xi_2) + \text{diagram 9} \right) \quad (6.2b)$$

$$= V^{-1} \int_0^1 \frac{d\lambda}{\lambda} \int d\xi_1 d\xi_2 \left[ F_2^s(\xi_1, \xi_2) \Phi_2(\xi_1, \xi_2) + \text{diagram 10} + \text{diagram 11} + \text{diagram 12} + \dots \right] \quad (6.2c)$$

and

$$\sum = (2V)^{-1} \int_0^1 \frac{d\lambda}{\lambda} \int d\xi_1 d\xi_2 \times \left( \text{diagram 13} + \text{diagram 14} + \dots \right) \quad (6.2d)$$

Since  $F_2^s$  differs from  $F_2^0$  by an order of  $e^2\beta$  [Eq. (4.1)] we anticipate that the function  $R^0$  obtained from the replacement of  $F_2^s$  by  $\hat{F}_2^0$  and  $F_2^s$  by  $F_2^0$  in (6.2c), will differ from  $R$  by a function that contributes to a higher order in  $e^2\beta$  than  $R^0$  itself. We denote this function,  $R - R^0$ , as  $R'$ .

Because  $F_2^0$  is independent of  $\lambda$ , the integration of  $R^0$  with respect to  $\lambda$  is trivial and letting  $\text{---}$  represent  $F_2^0(\xi_1, \xi_2)$ ,  $\text{O}$  represent  $n_1(\xi_1)$ , and  $\text{diagram 15}$  represent  $\hat{F}_2^0(\xi_1, \xi_2)$  as before we have

$$R = V^{-1} \left( \text{diagram 16} + \text{diagram 17} + \text{diagram 18} + \text{diagram 19} + \dots \right) + R'. \quad (6.3)$$

To obtain Eq. (2.11) we use (4.8)-(4.12). This gives us

$$V(R - R^0) = \text{diagram 20} + \left( \text{diagram 21} + \text{diagram 22} + \text{diagram 23} + \dots \right) + \text{diagram 24} + \text{diagram 25} + \text{diagram 26} + \dots + \text{diagram 27} + \text{diagram 28} + \dots \quad (6.4)$$

In a uniform fluid, the sum of the terms in brackets is the simple function  $K^3/12\pi$ .

The subsequent terms can be written in terms of  $\mathcal{C}(M)$  instead of  $\Phi$  [Eq. (4.10)]. Denoting  $\mathcal{C}(M)$  by  $\bullet$  as in Sec. IV we have

$$R = (K^2/12\pi) + V^{-1} \left( \text{---} \bullet \text{---} + \text{---} \bullet \text{---} - \text{---} \bullet \text{---} \right) + R'. \quad (6.5)$$

The terms in  $R$  after the first graph can be shown to be of order  $(e^2\beta)^2$ . The lowest-order contribution from  $R'$  is also of order  $(e^2\beta)^2$  while  $\sum$  must be added to  $R'$  to give finite results; the lowest order in  $e^2\beta$  to which it contributes is  $(e^2\beta)^2 \log(e^2\beta)$ . Furthermore, because of neutrality the term before  $R$  in (6.2a) vanishes. This then leaves us with

$$s = s^0 + V^{-1} \left( \text{---} \bullet \text{---} \right) + (K^2/12\pi) + O(e^2\beta)^2. \quad (6.6)$$

In the case of a symmetric system, we can use the equations (4.14) to simplify (6.2)–(6.4), and as a result  $K^2/12\pi$  becomes  $\kappa^2/12\pi$  and (6.2) becomes

$$s = s^0 + (\kappa^2/12\pi) + \sum + R'. \quad (6.7)$$

The function  $R'$  has also simplified considerably now. We have

$$VR' = \text{---} \bullet \text{---} + \text{---} \bullet \text{---} + \text{---} \bullet \text{---} + \dots \quad (6.8)$$

When added to  $R'$ ,  $\sum$  still appears to contribute to higher order in  $e^2\beta$  than we shall consider here.

Since

$$\mathcal{C}(n_1) = (-z_i z_j e^2\beta / D) \exp(-\kappa r) \\ = (-z_i z_j e^2\beta / D) [r^{-1} - \kappa + \frac{1}{2}(\kappa^2 r) - \frac{1}{6}(\kappa^3 r^2) + \dots],$$

the terms in  $R'$  can be easily expanded to get a series in  $e\beta^{1/2}$ . The result, when inserted into (6.8), yields (2.11). All the terms given in (2.11b) through (2.11e) arise from the expansion of the three graphs shown in (6.8).

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APPENDIX: ALTERNATIVE DERIVATION OF CHANGE IN DEBYE LENGTH: EQ. (2.10)

Let  $\phi_j(r)$  be the "average" potential produced at  $r$  by the presence of a particle of species  $j$  at the origin; we have

$$\nabla^2 \phi_j(r) = 4\pi e \sum_i z_i \rho_i g_{ij}(r) = 4\pi e \sum_i z_i \rho_i h_{ij}(r) \quad (A1)$$

while for the constant chemical potential  $\mu_i$ , assumed to depend only on the local densities and average potential,

$$\mu_i = \mu_i^0(\{\rho_i[1+h_{ij}(r)]\}) + ez_i \phi_j(r) \\ = \mu_i^0(\{\rho_i\}) + \sum_i (\partial \mu_i^0 / \partial \rho_i) \rho_i h_{ij} + ez_i \phi_j \\ = \mu_i^0(\{\rho_i\}). \quad (A2)$$

Hence

$$\rho_i h_{ij}(r) = -e \sum_i z_i (\partial \rho_i / \partial \mu_i^0) \phi_j(r) \\ = -e\beta \rho_i \nu_i \phi_j(r). \quad (A3)$$

Substituting this (A3) into (A1) yields

$$\nabla^2 \phi_j(r) = -K^2 \phi_j(r)$$

whose solution is

$$\phi_j(r) = C_j \exp(-Kr) / r \\ = -(e\beta \nu_i)^{-1} h_{ij}(r).$$

By symmetry now

$$\nu_i C_j = \nu_j C_i$$

so  $\nu_j^{-1} C_j$  is a constant  $C$  independent of  $j$ . If we argue further that  $C$  should be independent also of the short-range interactions and that  $\phi_j(r)$  should go to  $ez_j/r$  as  $r \rightarrow 0$  when there are no short-range interactions, then we find  $C = e/D$ , which agrees with (2.10).