

The interaction of ions in an ionic medium

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The energy of interaction, $W_{12}(R)$, of two ions at separation R in an ionic medium is considered using Debye–Hückel (DH) theory for spheres of diameter a_0 . The ions are treated as spheres of dielectric constant D' which may differ from that of the medium, say D ; they have radii b and carry equal or opposite point charges. The electrostatic potential $\varphi(\mathbf{r})$ in the ionic medium satisfies the DH equation $\nabla^2\varphi = \kappa^2\varphi$. An exact, closed-form expression is obtained for $W_{12}(R)$. In the limit of zero ionic strength ($\kappa \rightarrow 0$) previous asymptotic results for $R \rightarrow \infty$, indicating $\Phi_4/R^4 + \Phi_6/R^6 + \Phi_7/R^7 + \dots$ corrections to Coulomb's law, are reproduced; by contrast for $\kappa b > 0$ the leading interaction term when $R \rightarrow \infty$ varies, as expected, like $e^{-\kappa R}/DR$ but the first correction decays as $\kappa^2 e^{-2\kappa R}/DR^2$, i.e., with a squared screening factor, and can be stated for two ions differing in charge, radii, etc. The same calculations show that, within DH theory, modeling the ions with $D' \neq D$ has no effects on the predicted thermodynamics.

I. INTRODUCTION

In the study of electrolytes and ionic solutions the influence of the structure of an ion on the properties of the solution and on its interactions with other ions is a long-standing theme. Thus in 1934 Kirkwood¹ considered the thermodynamic influence of Zwitterions, i.e., hybrid ions with well localized charged centers but total zero charge. He modeled such compound ions as spheres of radius b and dielectric constant D' differing, in general, from that, D , describing the solvent; within each sphere were situated M discrete point charges, q_1, q_2, \dots , at fixed positions. Kirkwood used Debye–Hückel theory² to compute the contributions of such ions to the chemical potential of a dilute solution. More recently two of us^{3,4} have used the Kirkwood ion model (but with $D' = D$) to explicitly estimate the contribution of Bjerrum dipolar pairs to the low-temperature thermodynamics of ionic-driven phase separation in the restricted primitive model of an electrolyte solution.⁵ The approximation of a Bjerrum ion pair by two charges within a *single* sphere, rather than by charges residing in two distinct but closely associated spheres, is reasonable but not obviously satisfactory: one would like to do better.

At the next level of detail the interaction energy $W_{12}(R)$ of *two* ions in a solution separated by distance R was discussed in 1957–62 by Levine with Wrigley⁶ and with Bell.⁷ Each ion was modeled as a dielectric sphere (with D' distinct from D) and nontrivial terms proportional to $(D - D')$ and varying for large R as $1/R^4, 1/R^6, 1/R^7, 1/R^8, \dots$ were identified in $W_{12}(R)$. However, those authors considered only the case of *zero ionic strength* so that, essentially, they solved a problem in pure electrostatics. In this article we repair this deficiency in theory by computing $W_{12}(R)$ for an electrolyte solution of finite, nonzero ionic strength.⁸

Following Kirkwood¹ we suppose that the electrostatic potential $\varphi(\mathbf{r})$ within the ionic medium (external to the dielectric spheres representing the ions) satisfies the standard Debye–Hückel equation²

$$\nabla^2\varphi = \kappa^2\varphi. \quad (1.1)$$

This may be derived in the usual way^{2,5} by linearizing the Poisson–Boltzmann equation; however, if κ is chosen appropriately it is expected to have a significantly wider range of validity. The technical problems in handling Eq. (1.1) prove quite severe but we have succeeded in deriving an exact, closed-form expression for $W_{12}(R)$: see Eqs. (3.34), (3.44), and subsequent text. In the limit of zero ionic strength, which corresponds simply to $\kappa \rightarrow 0$, the results of Levine *et al.*^{6,7} can be recaptured. However, when $R \rightarrow \infty$ with *fixed* positive κ the behavior is quite different. If $b_1 = b_2 = b$ is the common radius of the two test ions and if b_0 is the radius of the ions constituting the ionic medium^{2,5} it is convenient to define $a = b_0 + b$. Then for test charges $q_1 = q, q_2 = \pm q$ we find

$$W_{12}(R) \approx \pm \vartheta^2 q^2 \frac{e^{-\kappa R}}{DR} + \vartheta^2 q^2 \kappa^2 a^3 \Delta \frac{e^{-2\kappa R}}{DR^2} \times \left[1 + O\left(\frac{a}{R}, \kappa^2 a^2\right) \right], \quad (1.2)$$

where the prefactors are

$$\vartheta = \frac{e^{\kappa a}}{1 + \kappa a}, \quad \Delta = \frac{1}{3} + \frac{D - D'}{2D + D'} \left(\frac{b}{a}\right)^3. \quad (1.3)$$

Apart from the solvation factors $\vartheta(\kappa a)$, the leading term in this result for $W_{12}(R)$ represents the expected, well-known screened Coulombic interaction. However, the leading *correction* term shows no sign of the Levine *et al.* $1/R^4$ variation! Rather, that term becomes *doubly* screened⁸ by a factor $e^{-2\kappa R}$ and the power of R changes to $1/R^2$. Note also that this $R \rightarrow \infty$ correction term does *not* reduce to the $1/R^4$ form when $\kappa \rightarrow 0$: in fact, a quite subtle crossover occurs which is elucidated below: see, in particular, Eqs. (4.2) and (4.10).^{8(b)}

As explained elsewhere,^{8(b)} the strong screening of the $1/R^4$ interaction at positive ionic strengths proves significant in connection with the theory of liquid–liquid criticality in electrolyte systems.⁹ Certain systems discovered by Pitzer and co-workers¹⁰ appear to display classical or van der Waals-like critical behavior ($\beta = \frac{1}{2}, \gamma = 1$, etc.) in place of the expected Ising-like exponents, $\beta \approx 0.33, \gamma \approx 1.24, \dots$. To ex-

plain this, Stell¹¹ suggests that effective long-range, $1/R^4$ ion-ion interactions, as found by Levine *et al.* when $D' \neq D$, might play a crucial role. However, since the observed critical points occur at ionic strengths corresponding to $\kappa a \approx 1$ where Eq. (1.2) indicates strong screening, this proposal seems unconvincing.^{8(b)} [It also encounters other difficulties in light of recent scattering experiments¹²: see Refs. 8(b) and 9(b).]

The solvation factor $\vartheta(\kappa a)$ which appears squared in the first term in the expression (1.2) for $W_{12}(R)$ has been noted previously.¹³ Indeed Thirumalai¹³ points out that this factor, which he calls a "geometric factor," plays a crucially important role in determining the equation of state of monodisperse charged colloidal particles: neglect of the finite diameter a leads to serious quantitative errors in estimating the liquid compressibility factor $pV/Nk_B T$ at quite moderate volume fractions.

The remainder of this article is set out as follows. In Sec. II the systems considered are specified precisely with definitions of the primary dimensionless variables and parameters; in addition the basic electrostatic equations and boundary conditions are stated. The solution of these equations, which entails an apparently novel, two-center expansion involving the spherical Bessel functions, is developed in Sec. III. The derivation of an essential set of expansion polynomials is presented in the Appendix. The asymptotic analysis of the exact results for large R requires some delicacy: this is presented in Sec. IV which contains our main conclusions. The solvation energy in the ionic medium of a pair of closely associated spherical ions, either $(+, -)q$ forming a neutral dipole, or $(+, +)q$, is addressed in Sec. V in order to improve on the Kirkwood effective-sphere model. The problem is solved formally; however, the sums in the requisite expressions may converge slowly and an efficient numerical method is not established. Section VI contains brief concluding remarks.

II. IONIC MODEL, BASIC EQUATIONS, AND PARAMETERS

We consider two ions, \mathcal{I}_1 and \mathcal{I}_2 , of radii b_i ($i=1,2$) and dielectric constants D_i , that carry centrally located point charges q_i and are immersed in an "ionic sea," i.e., an electrolyte solution, of dielectric constant D at separation R . For mathematical simplicity, we will focus on the two symmetric cases:

$$b_1 = b_2 = b, \quad D_1 = D_2 = D', \quad q_1 = q, \quad q_2 = \pm q; \quad (2.1)$$

see Fig. 1. However, when $R \rightarrow \infty$ the leading results can be stated for the general case: see Eq. (4.11) below.^{8(b)}

The electrostatic potential $\varphi(\mathbf{r})$ in the ($d=3$)-dimensional medium is, following Debye-Hückel (DH) theory,^{1,2,5} supposed to satisfy

$$\nabla^2 \varphi = \kappa^2 \varphi \quad \text{for } r_1, r_2 > a, \quad (2.2)$$

where the radial coordinates r_1 and r_2 are defined in Fig. 1 while $a \geq b$ represents the distance of closest approach of the centers of the ions \mathcal{I}_0^\pm constituting the ionic sea, to the cen-

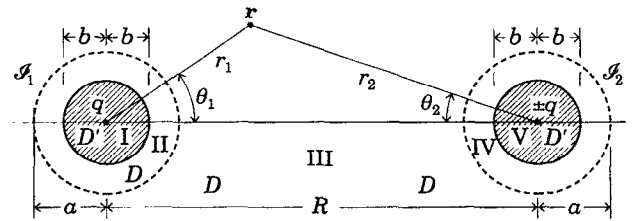


FIG. 1. Coordinates and dimensions for two test ions, \mathcal{I}_1 and \mathcal{I}_2 , of radii $b_1 = b_2 = b$, dielectric constant $D_1 = D_2 = D'$, and charges $q_1 = q$ and $q_2 = \pm q$, embedded in an ionic medium or sea of dielectric constant D . The radius $a = b + b_0$ represents the distance of closest approach to the test ions of ions of the sea which have radius b_0 . In the regions labeled I, ..., V, the electrostatic potential $\varphi(\mathbf{r})$ takes distinct analytic forms which match appropriately across the boundaries.

ters of the test ions \mathcal{I}_1 and \mathcal{I}_2 . We may suppose, again following DH, that the ions of the sea have a diameter $a_0 = 2b_0$: in those circumstances one has

$$a = b_0 + b. \quad (2.3)$$

If, as we may allow, the test ions are actually similar to those of the sea, one also has $a = 2b_0 = 2b$. Within DH theory the screening length $1/\kappa$ is given by^{2,5}

$$\kappa^2 = 4\pi\rho q_0^2 / Dk_B T, \quad (2.4)$$

where $\rho = \rho_+ + \rho_-$ is the overall number density of ions in the sea while their charges are $\pm q_0$. Clearly, however, this specific form for κ need play no role in our analysis.

The charges of the ionic sea cannot penetrate inside the spheres of radius a surrounding each test ion so we require

$$\nabla^2 \varphi = 0 \quad \text{for } r_1 \text{ or } r_2 < a. \quad (2.5)$$

In the notation of Fig. 1, this applies within regions I, II, IV, and V, while Eq. (2.2) applies in region III. If we denote the solutions in the various regions by $\varphi_I(\mathbf{r})$, $\varphi_{II}(\mathbf{r})$, etc., the appropriate boundary conditions are

$$\text{III: } \varphi_{III}(\mathbf{r}) \rightarrow 0 \quad \text{as } r_1, r_2 \rightarrow \infty, \quad (2.6)$$

$$\text{III-II: } \varphi_{III} = \varphi_{II}, \quad \frac{\partial \varphi_{III}}{\partial r_1} = \frac{\partial \varphi_{II}}{\partial r_1} \quad \text{on } r_1 = a, \quad (2.7)$$

$$\text{II-I: } \varphi_{II} = \varphi_I, \quad D \frac{\partial \varphi_{II}}{\partial r_1} = D' \frac{\partial \varphi_I}{\partial r_1} \quad \text{on } r_1 = b, \quad (2.8)$$

together with corresponding conditions at $r_2 = a$ and at $r_2 = b$.

If we choose $q = q_0$ and $2b = a = a_0$ and let $R \rightarrow \infty$ we are left with the original DH problem^{2,5} of one ion in a sea of similar ions. Now, however, the model is *extended* in that each ion is represented by a sphere of dielectric constant D' not necessarily equal to D , as is implicitly supposed in the usual theory. Our analysis will, therefore, provide the input for a theory of this *extended restrictive primitive model* at the DH level. [See also Footnote 15 in Ref. 8(b).]

It is convenient to introduce here, for later reference, scaled forms of the basic variables and various dimensionless parameters. Accordingly, we set

$$x \equiv \kappa a, \quad y \equiv R/a, \quad (2.9)$$

$$z \equiv xy = \kappa R, \quad w = e^{-z/y}, \quad (2.10)$$

and, for $n = 1, 2, 3, \dots$, define

$$\delta_n = \left(\frac{b}{a}\right)^{2n+1} \Omega_n, \quad \Omega_n = \frac{n(D-D')}{(n+1)D+nD'}. \quad (2.11)$$

Evidently Ω_n and δ_n vanish if $D=D'$. One may also measure the dielectric mismatch via

$$\Omega_n = \frac{2n\delta}{2n+1+\delta} \quad \text{with} \quad \delta = \frac{D-D'}{D+D'}. \quad (2.12)$$

Now within region I (i.e., $r_1 < b$: see Fig. 1) the electrostatic potential clearly has the form

$$\varphi_I(\mathbf{r}) = \frac{q}{D'r_1} + B_{\pm}(x, y; \delta, a/b) + O(r_1), \quad (2.13)$$

where, here and below, \pm refers to $q_2 = \pm q$. In the limit $R\alpha y \rightarrow \infty$ the constant term $B_{\pm}(x) \equiv B_{\pm}(x, \infty; \delta, a/b)$ represents the average electrostatic potential at the test ion \mathcal{I}_1 due to all the charges of the ionic sea. Following DH,^{2,5} the corresponding electrostatic energy is

$$W_1(x) = qB_{\pm}(x) \quad (2.14)$$

and by employing the usual charging process^{2,5} one computes the corresponding electrostatic free energy. When $\mathcal{I}_1 \equiv \mathcal{I}_0^+$, say, i.e., $q_1 = q_0$, $a = a_0$, this leads directly to the free energy of the full electrolyte (within DH theory).

On the other hand, for finite R the mutual interaction energy of \mathcal{I}_1 and \mathcal{I}_2 is given by^{1,7}

$$W_{12}^{\pm}(R) = qB_{\pm}(x, y; \delta, a/b) - qB_{\pm}(x, \infty; \delta, a/b). \quad (2.15)$$

Consequently, the aim of our calculation is to find an exact expression for B_{\pm} and then to study its behavior for large y .

III. ANALYSIS OF THE DEBYE-HÜCKEL EQUATIONS

A. Form of regional solutions

To solve Eqs. (2.2) and (2.5) subject to Eqs. (2.6)–(2.8) we suppose, as illustrated in Fig. 1, that $R > 2a$: the case $R < 2a$, when the exclusion spheres of radius a overlap, will be considered in Sec. V below. The linearity of Eqs. (2.2) and (2.5), the cylindrical symmetry about the line through the centers of \mathcal{I}_1 and \mathcal{I}_2 , and the reflection symmetry/antisymmetry (\pm) about the plane bisecting the line joining the charge centers, enables us to write the required solutions in the form

$$\varphi_I(\mathbf{r}) = \frac{q}{D'r_1} + B_0 + \sum_{m=1}^{\infty} B_m r_1^m P_m(\cos \theta_1), \quad (3.1)$$

$$\varphi_{II}(\mathbf{r}) = \sum_{m=0}^{\infty} \left(C_m r_1^m + \frac{D_m}{r_1^{m+1}} \right) P_m(\cos \theta_1), \quad (3.2)$$

$$\varphi_{III}(\mathbf{r}) = \sum_{m=0}^{\infty} A_m [k_m(\kappa r_1) P_m(\cos \theta_1) \pm k_m(\kappa r_2) P_m(\cos \theta_2)], \quad (3.3)$$

together with symmetrically related expressions for $\varphi_{IV}(\mathbf{r})$ and $\varphi_V(\mathbf{r})$, where θ_1 and θ_2 are defined in Fig. 1.

We employ the spherical Bessel functions $k_m(x)$ and, below, $i_m(x)$.¹⁴ These may be defined by

$$i_m(x) = \left(\frac{\pi}{2x}\right)^{1/2} I_{m+1/2}(x) = \sum_{j=0}^{\infty} \frac{x^{2j+m}}{2^j j! (2m+2j+1)!!}; \quad (3.4)$$

see E7.11 (16), (20), and E7.2 (12),¹⁴ and note

$$(2n-1)!! = (2n)!/2^n n!, \quad 0!! \equiv 1, \quad (-1)!! = 1; \quad (3.5)$$

and, using E7.2 (40) and (43),¹⁴

$$k_m(x) = \left(\frac{2}{\pi x}\right)^{1/2} K_{m+1/2}(x) = \frac{e^{-x}}{x} \sum_{l=0}^m q_{ml} x^l, \quad (3.6)$$

where the polynomial coefficients, important for us, are

$$q_{ml} = \frac{\Gamma(m+l+1)}{2^l l! \Gamma(m-l+1)} = (2l-1)!! \binom{m+l}{2l}. \quad (3.7)$$

For concreteness and convenience we record

$$k_0(x) = e^{-x}/x, \quad k_1(x) = (1+x)e^{-x}/x^2, \quad \dots, \quad (3.8)$$

$$i_0(x) = (\sinh x)/x,$$

$$i_1(x) = (\cosh x)/x - (\sinh x)/x^2, \quad \dots, \quad (3.9)$$

$$k_m(x) = (2m-1)!! x^{-m-1} [1 + O(x^2)], \quad (3.10)$$

for $m \geq 1$ as $x \rightarrow 0$, and note the recursion relations

$$k_{m-1}(x) - k_{m+1}(x) = -(2m+1)k_m(x)/x, \quad (3.11)$$

$$k'_m(x) = (m/x)k_m(x) - k_{m+1}(x), \quad (3.12)$$

$$i_m(x) = -\frac{1}{2l} [k_m(-x) + (-)^m k_m(x)]. \quad (3.13)$$

Now the expansion coefficients A_m , B_m , C_m , and D_m for $m \geq 0$ are to be determined by matching solutions on $r_1 = a$ and $r_1 = b$. Using Eq. (2.8) leads directly to

$$B_0 = \frac{q}{Db} - \frac{q}{D'b} + C_0, \quad D_0 = \frac{q}{D}, \quad (3.14)$$

and, recalling the definition (2.11), to

$$B_m = (1 + \Omega_m) C_m, \quad D_m = \Omega_m b^{2m+1} C_m \quad (3.15)$$

for $m \geq 1$. Evidently, the B_m and D_m for $m \geq 1$ can be eliminated in favor of the C_m .

B. Two-center expansion

To find the C_m one must match on $r_1 = a$ using Eq. (2.7): the difficulty in doing so arises from the second set of terms in Eq. (3.3) which entail the angle $\theta_2 = \sin^{-1}[(r_1/r_2)\sin \theta_1]$ and, with $s = \kappa r_1$, the scaled radial coordinate

$$\kappa r_2 = S(s, z) \equiv (z^2 - 2zs \cos \theta_1 + s^2)^{1/2}, \quad (3.16)$$

where $z = \kappa R$. To overcome this problem we advance the expansion

$$k_m(S) P_m(\cos \theta_2) = \sum_{n=0}^{\infty} (2n+1) i_n(s) P_n(\cos \theta_1)$$

$$\times e_{mn}(z)e^{-z}/z, \quad (3.17)$$

valid for $s < z$, i.e., $r_1 < R$. To justify this, first note that the left-hand side is a solution of the DH equation (2.2) which is regular at $s = r_1 = 0$. Hence it has an expansion in terms of the $i_n(s)$. Further, since $S(s, z)$ depends parametrically on z , the expansion coefficients must be functions of z . We choose to write them in the special form appearing in Eq. (3.17) because it transpires that the $e_{mn}(z)$ are simply *polynomials* of degree $m + n$ in z^{-1} satisfying

$$e_{mn}(z) = \sum_{r=0}^{m+n} e_{mnr}/z^r = e_{nm}(z); \quad (3.18)$$

compare with Eq. (3.6). The proof of this fact together with the evaluation of the coefficients e_{mnr} is presented in the Appendix. We note that Eq. (3.17) is similar to a well-known expansion for $P_m(\cos \theta_2)/r_2^{m+1}$ which was invoked by Levine and Bell⁷ to treat the case of zero ionic strength; that corresponds to $\kappa a \rightarrow 0$ and in this limit Eq. (3.17) will, of course, reduce to the simpler expansion. However, the more general ($\kappa > 0$) result we need seems not to be known.

From the explicit results for the e_{mnr} in the Appendix we find the particular values

$$e_{mn0} = 1, \quad e_{mn1} = \frac{1}{2}(m^2 + n^2 + m + n), \quad (3.19)$$

$$e_{mn2} = 3 \binom{m+2}{4} + 2 \binom{m+1}{2} \binom{n+1}{2} + 3 \binom{n+2}{4}, \quad (3.20)$$

valid for all $m, n \geq 0$ with the convention $\binom{i}{j} = 0$ if $i < j$, and, recalling Eq. (3.5),

$$e_{m,n,m+n} = e_{m,n,m+n-1} = (2m-1)!!(2n-1)!! \binom{m+n}{n}; \quad (3.21)$$

see Eq. (A11) and the recursion relations (A3) for $e_{mn}(z)$ in terms of $e_{m,n-2l}(z)$.

C. Matching equations

On using the expansion (3.17) in Eqs. (3.3) and (2.7) the matching at $r_1 = a$ can be performed straightforwardly eliminating the $\{C_m\}$ in favor of the set $\{A_m\}$. To express the resulting infinite set of equations in compact form some further notation is helpful. First we put

$$A_n \equiv A_0(x, y) x^n p_n(x, y) \quad \text{for } n \geq 0, \quad \text{with } p_0 \equiv 1. \quad (3.22)$$

Then we introduce alternate forms of the basic polynomials via

$$f_{mn}(z) \equiv z^{m+n} e_{mn}(z) \quad \text{and} \quad h_{mn}(x, y) = x^{m+n} e_{mn}(xy), \quad (3.23)$$

so that f_{mn} is polynomial in z of degree $m + n$ while h_{mn} is a homogeneous polynomial of degree $m + n$ in x and y^{-1} . The leading and trailing coefficients in these polynomials follow from Eqs. (3.19)–(3.21). The set of unknown coefficients $\{p_l\}_{l \geq 1}$ appear naturally in the generating functions

$$U_m(x, y) = f_{m0}(z) + \sum_{l=1}^{\infty} f_{ml}(z) p_l(x, y) / y^l, \quad (3.24)$$

$m \geq 0$. For brevity from here on we take

$$k_m \equiv k_m(x = \kappa a) \quad \text{and} \quad i_m \equiv i_m(x = \kappa a), \quad (3.25)$$

and for $m \geq 1$ introduce the coefficients

$$\omega_m(x; \delta, a/b) = \frac{2m+1}{x^{2m+1}} \frac{(1 + \delta_m) x i_{m+1} + (2m+1) \delta_m i_m}{(1 + \delta_m) x k_{m+1} - (2m+1) \delta_m k_m}, \quad (3.26)$$

which embody the basic parameters of the system: see Eq. (2.11). When $x = \kappa a \rightarrow 0$ one finds, for all $\delta \geq 0$,

$$\omega_m(x) = \frac{\delta_m + x^2/(2m+3)(2m+1)}{[(2m-1)!!]^2} [1 + O(x^2)]. \quad (3.27)$$

With these conventions matching yields

$$B_0 = \frac{q}{b} \left(\frac{1}{D} - \frac{1}{D'} \right) - \frac{q}{Da} + A_0 \left(k_0 \pm i_0 U_0 \frac{e^{-z}}{z} \right), \quad (3.28)$$

$$A_0 = \left(\frac{q}{Da} \right) / x \left(k_1 \mp i_1 U_0 \frac{e^{-z}}{z} \right), \quad (3.29)$$

which, since $B_0 \equiv B_{\pm}$ in Eq. (2.13), represents the desired answer, together with the infinite set of simultaneous linear equations

$$p_m(x, y) = \pm \omega_m(x) U_m(x, y) e^{-z/y^{m+1}}. \quad (3.30)$$

These must be solved to yield p_m ($m \geq 1$) which, via Eq. (3.24), can then be used to evaluate $U_0(x, y)$ and thence A_0 and $B_0(x, y)$. For completeness we also record

$$C_0 = A_0(k_0 \pm i_0 U_0 e^{-z}/z) - q/Da, \quad (3.31)$$

and, for $m \geq 1$,

$$a^m \delta_m C_m = A_0 [x^n k_n p_n \pm (2n+1) i_n U_n e^{-z}/z^{n+1}]. \quad (3.32)$$

D. Electrostatic energies

From Eqs. (3.28) and (3.29) we see that one may take the limit $R \rightarrow \infty$ upon which the terms involving U_0 drop out and yield a simple result for $B_0(x, \infty) \equiv B_{\infty}(x)$. By Eq. (2.14) the electrostatic energy of a single ion in the ionic sea follows as

$$W_1(x; \delta, a/b) = \frac{q^2}{b} \left(\frac{1}{D} - \frac{1}{D'} \right) - \frac{q^2 \kappa}{D(1 + \kappa a)}. \quad (3.33)$$

When a equals a_0 , the diameter of the sea ions, this has the standard DH form^{1,2,5} apart from the first term which depends on δ and b ($\leq a$). However, as one sees by following the usual procedure of charging the ionic sea,^{2,5} the first term here merely adds a fixed constant to the energy per ion. That has only a trivial effect on the predicted thermodynamics and, in particular, leaves the DH equation of state and coexistence curve^{3,4} unchanged from the $\delta = 0$ ($D' = D$) results.

An explicit result for the energy of interaction follows in a similar way from Eq. (2.15) as

$$W_{12}(R) = \pm \left(\frac{q^2}{Da} \right) \frac{\vartheta^2(x) U_0(x, y) w}{1 \mp v(x) U_0(x, y) w}, \quad (3.34)$$

where the solvation and coupling factors are

$$\vartheta(x) = e^x/(1+x), \quad (3.35)$$

TABLE I. Basic ionic polynomials $h_{mn}(x, y=1/y')=h_{nm}(x, y)$.

$h_{00}=1, \quad h_{10}=h_{01}=x+y',$
$h_{20}=h_{02}=x^2+3xy'+3y'^2, \quad h_{11}=x^2+2xy'+2y'^2$
$h_{30}=x^3+6x^2y'+15xy'^2+15y'^3, \quad h_{21}=x^3+4x^2y'+9xy'^2+9y'^3,$
$h_{22}=x^4+6x^3y'+24x^2y'^2+180xy'^3+180y'^4,$
$h_{m0}(x, y)=x^{m+1}y e^{xy}k_m(xy), \quad m=0, 1, 2, \dots$

$$v(x) = i_1(x)/xk_1(x) = \frac{1}{3}x^2[1 + O(x^2)]; \quad (3.36)$$

see Eqs. (3.8) and (3.9). Recall also that $w = e^{-z}/y = ae^{-\kappa R}/R$: this vanishes when $R \rightarrow \infty$ for any value of $\kappa \geq 0$ and thus constitutes a basic small expansion parameter.

E. Solution of matching equations

To solve the set of matching Eq. (3.30) with Eq. (3.24) for the set $\{p_m\}$ we aim to obtain a power series in w . To that end it is helpful to put

$$p_m(x, y) \equiv w \omega_m(x) u_m(x, y) \quad (3.37)$$

and to work with the coefficients $\{u_m\}_{m \geq 1}$. In terms of the polynomials $h_{mn}(x, y)$, defined in Eq. (3.23), the matching equations can then be rewritten as

$$u_n = \pm h_{n0} \pm w[h_{n1} \omega_1 u_1 + h_{n2} \omega_2 u_2 + \dots]. \quad (3.38)$$

For convenience, some of the low order polynomials h_{nm} are recorded in Table I: all remain well behaved when $y \rightarrow \infty$ and in that limit vary as x^{m+n} . They are therefore compatible with a solution in powers of w which we write

$$u_n(x, y) = \pm h_{n0}(x, y) + w G_{n1}(x, y) \pm w^2 G_{n2}(x, y) + \dots \quad (3.39)$$

The functions G_{nj} can now be found recursively by substituting in Eq. (3.38) and comparing powers of w . This successively yields

$$G_{n1} = \sum_{l=1}^{\infty} h_{nl} \omega_l h_{l0}, \quad (3.40)$$

$$G_{n2} = \sum_{l=1}^{\infty} h_{nl} \omega_l G_{l1} = \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} h_{nl} \omega_l h_{lm} \omega_m h_{m0}, \quad (3.41)$$

whence the general form is evident; but note that $G_{nk} \neq G_{kn}$.

Using these results in Eqs. (3.39) and (3.37) and then in Eqs. (3.24), (3.28), (3.29), (3.31), (3.32), (3.14) and (3.15) gives the general solution for the potential $\varphi(\mathbf{r})$ in all regions as a formal power series in w . One may alternatively write Eq. (3.38) as a matrix equation and solve in the form

$$\mathbf{u} \equiv [u_i] = \pm [\mathbf{I} \mp w \mathbf{G}]^{-1} \mathbf{h}_0, \quad (3.42)$$

where $\mathbf{h}_0 = [h_{0i}]$, while the infinite matrix \mathbf{G} has elements $g_{ij} = h_{ij} \omega_j$ ($i, j = 1, 2, 3, \dots$). Expanding the matrix inverse as a geometric progression reproduces the previous series. Then if the spectral norm of \mathbf{G} is λ_G (loosely, the modulus of the eigenvalue of largest magnitude) the radius of convergence of the power series expansions in w is $w_0 = 1/\lambda_G$. It is, of course, hard to estimate λ_G . However, inspection of Table I

suggests that the dominant elements of an $n \times n$ section of \mathbf{G} will lie on the diagonal and, very roughly, have a magnitude

$$\begin{aligned} |g_{nn}| &= (e_{nn0} x^{2n} + \dots + e_{n,n,2n} y^{-2n}) |\omega_n| \\ &\sim 2n \left\{ x^{2n} + [(2n-1)!!]^2 \binom{2n}{n} y^{-2n} \right\} \\ &\quad \times [(2n-1)!!]^{-2} |\delta_n + (x^2/4n^2)| \\ &\sim \left[\frac{x^{2n}}{(2n)!} + \frac{1}{\sqrt{n}} \left(\frac{2}{y} \right)^{2n} \right] \left| n \delta \left(\frac{b}{a} \right)^{2n+1} + \frac{x^2}{4n} \right|, \end{aligned} \quad (3.43)$$

where we have used Eqs. (3.19) and (3.21) for e_{nnr} , Eq. (3.27) for ω_n , and Eq. (2.11) for δ_n . For $x = O(1)$ this crude estimate suggests that the elements g_{ij} decrease faster than exponentially when $y > 2$ as $(i+j)$ increases which, in turn, suggests that λ_G is bounded and, indeed, of order unity. We conclude that the series in w may be expected to converge for small w provided $y \equiv R/a > 2$ and $x \equiv \kappa a$ is not too large. Certainly, our results should be asymptotically exact for $y \rightarrow \infty$ and $x = O(1)$.

Finally, to evaluate the ion-ion interaction energy $W_{12}(R)$ as given in Eqs. (3.34)–(3.36) we need Eqs. (3.24) and (3.37) which yield

$$U_0(x, y; \delta, a/b) = 1 + \sum_{j=1}^{\infty} G_{0j}(x, y) (\pm w)^j, \quad (3.44)$$

where we extend Eqs. (3.40) and (3.41) to $n=0$ in order to define $G_{0j}(x, y)$: these expressions entail (i) the $\omega_m(x)$ defined in Eq. (3.26) supplemented by Eq. (3.25) with Eqs. (3.4)–(3.7) and by Eq. (2.11) for δ_n , and (ii) the polynomials $h_{mn}(x, y)$ specified via Eqs. (3.23), (3.18), and (A11): see also Table I. In total, then, we have obtained an exact formal expansion for $W_{12}(R)$ in powers of $w \equiv ae^{-\kappa R}/R$ which is probably convergent for fixed $x \equiv \kappa a \geq 0$ as $y \equiv R/a \rightarrow \infty$. It remains to study the asymptotics in more detail for large y .

IV. ASYMPTOTIC BEHAVIOR OF THE INTERACTIONS

Let us now analyze the result (3.34) for the ion-ion interaction energy $W_{12}(R)$ for large R . When κ is positive the parameter $w = e^{-z}/y$ decays exponentially fast and is the natural expansion variable. In leading order we obtain just

$$\begin{aligned} W_{12}(R) &\approx W_{12}^0(R) = \pm \frac{q^2}{Da} \vartheta^2(x) w \\ &= \pm \left(\frac{q e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa R}}{DR}, \end{aligned} \quad (4.1)$$

as quoted in the Introduction. Note that this result is independent of $b/a \leq 1$ and D' . In the limit $\kappa \rightarrow 0$ it reduces uniformly to the pure Coulombic form $W_{12} = \pm q^2/DR$ as expected.

The more interesting *correction* to the leading screened Coulombic interaction may then be written

$$\Delta W_{12}(R) \equiv W_{12}(R) - W_{12}^0(R) = \left(\frac{\vartheta^2 q^2 w^2}{Da} \right) \Psi(x, y), \quad (4.2)$$

$$\Psi(x, y) = v + G_{01} \pm (v^2 + 2vG_{01} + G_{02})w + (v^3 + 3v^2G_{01} + 2vG_{02} + vG_{01}^2 + G_{03})w^2 \pm \dots, \quad (4.3)$$

where $v(x) \approx \frac{1}{3}x^2$ was defined in Eq. (3.36) while Eqs. (3.40) and (3.41) give $G_{01}(x, y)$, $G_{02}(x, y)$, The $G_{0j}(x, y)$ are clearly series in inverse powers of y : hence for $\kappa > 0$ the exponential factors $w^j \sim e^{-j\kappa R/R^j}$ dominate. Furthermore, using the character of the h_{nm} and ω_n [see Table I and Eq. (3.27)] the variation with δ as x and y^{-1} vanish in any way is given by

$$G_{0j}(x, y) = O[(x + y^{-1})^{2j}(\delta + x^2)^j]. \quad (4.4)$$

The general structure of $\Delta W_{12}(R)$ for large R when $\kappa > 0$ is thus clear.

On the other hand, when $\kappa = 0$ we have $v = 0$ and $w = y^{-1}$ so that

$$G_{0j}(x, y)w^{j+1} = O(\delta^j/y^{3j+1}). \quad (4.5)$$

One immediately sees that the first correction to $W_{12}^0(R)$ now varies as δ/R^4 , as found by Levine *et al.*^{6,7} Conversely, if one wishes to compute the coefficients of subsequent inverse powers out to, say, $1/R^p$, it is necessary to include the terms of order $w^{[p/2]-2}$ and lower in the expansion. By the same token, however, only the leading few terms in the expansions of G_{0j} in products of the polynomials h_{mn} are needed for fixed p .

From these remarks it is clear that a truncated formula that correctly gives the full asymptotic behavior of $\Delta W_{12}(R)$ for large R when $\kappa > 0$ will *not* uniformly reproduce the correct inverse power series in R when one allows $\kappa a \rightarrow 0$. With this proviso in mind we readily obtain from the leading terms in Eq. (4.3) a result valid for

(A) $y = R/a \rightarrow \infty$ at fixed $x = \kappa a > 0$, namely,

$$\Delta W_{12}(R) = q^2 \delta^2 a \frac{e^{-2\kappa R}}{DR^2} \left[v(\kappa a) + H(\kappa a) + J(\kappa a) \frac{a}{R} + O\left(\frac{a^2}{R^2}\right) \right] [1 + O(e^{-\kappa R}/R)]. \quad (4.6)$$

The auxiliary functions deriving from the expansion of $G_{01}(x, y)$ are

$$H(x) = \sum_{l=1}^{\infty} \omega_l(x) x^{2l} \approx \delta_1 x^2 + O(x^4), \quad (4.7)$$

$$J(x) = \sum_{l=1}^{\infty} l(l+1) \omega_l(x) x^{2l-1} \approx 2\delta_1 x + O(x^3). \quad (4.8)$$

Since the coefficients ω_l decrease as $\delta_l / [(2l-1)!!]^2$, at least for $x = O(1)$, these series should be rapidly convergent. On using Eqs. (3.36) and (2.11) the expression (4.6) yields the main result (1.2) quoted in the Introduction.

As anticipated, taking the limit $x = \kappa a \rightarrow 0$ in Eq. (4.6) does *not* reproduce the results of Levine *et al.*^{6,7} However, these can be recaptured and extended somewhat in the limit

(B) $x = \kappa a \rightarrow 0$ at fixed $z = \kappa R \leq 1$, $R/b \rightarrow \infty$.

Since this limit entails $x \rightarrow 0$ the terms in v vanish in Eq. (4.3) while the polynomials h_{mn} in the G_{0j} vary as y^{-m-n} times polynomials in z . Thence we obtain, recalling Eq. (2.11) for Ω_n ,

$$\Delta W_{12}(R) = q^2 \frac{e^{-2\kappa R}}{Db} \left(\frac{b}{R}\right)^4 (1 + \kappa R)^2 \times \left[\Omega_1 + \Omega_2 \frac{[1 + \kappa R + (1/3)\kappa^2 R^2]^2}{(1 + \kappa R)^2} \left(\frac{b}{R}\right)^2 \pm 2\Omega_1^2 e^{-\kappa R} \left(1 + \kappa R + \frac{1}{2}\kappa^2 R^2\right) \left(\frac{b}{R}\right)^3 + O\left(\frac{b^4}{R^4}\right) \right]. \quad (4.9)$$

On setting $\kappa R = 0$ this reproduces the terms Φ_4/R^4 , Φ_6/R^6 , and Φ_7/R^7 of Levine and Bell⁷ (who carried the expansion explicitly out to order $1/R^{11}$).

Note that Eq. (4.9) does not depend on the length a . This is rather artificial since even though we must have $a > b$ the limit specified in (B) is equivalent to taking $a \rightarrow 0$ at fixed κ . To obtain a *uniform* asymptotic expression one must analyze the leading term in Eq. (4.3) more delicately using Eq. (4.6): the cost is that some truncation in powers of x^2 is necessarily also entailed. We find the correction factor can be written

$$\Psi(x, y) = v(x) [1 \pm \frac{1}{3}(x^2/y) e^{-xy}] + \frac{1}{9}\delta_2(x^2 + 3xy^{-1} + 3y^{-2})^2 + (x + y^{-1})^2 \omega_1(x) \{1 \pm [\frac{2}{3}x^2 + \delta_1(x^2 + 2xy^{-1} + 2y^{-2})]/ye^{xy}\} \pm O[(x + y^{-1})^6], \quad (4.10)$$

which is correct for all $x \geq 0$ as $y \rightarrow \infty$ and includes terms in ΔW_{12} up to $e^{-2\kappa R/R^7}$ and $e^{-3\kappa R/R^5}$ when $x > 0$ while for $x = 0$ the terms Φ_n/R^n are given correctly for $n \leq 7$. Note, however, that in light of the error term in Eq. (4.10), the coefficients $v(x)$ and $\omega_1(x)$ are needed only up to orders x^4 and x^2 , respectively. It is evident from Eq. (4.10) and the previous discussions that a crossover from the extended Levine *et al.* results occurs for $y \geq 1/x$, i.e., $\kappa R \geq 1$ as might reasonably have been expected!

If errors of order $(x + y^{-1})^4$ are acceptable one may drop the factors $[\dots]$ and $\{\dots\}$ in Eq. (4.10), use $v(x) \approx \frac{1}{3}x^2$, $\omega_1(x) \approx \delta_1$, and set δ_2 to 0. This yields the result previously announced⁸: as explained, that, in turn, may be interpreted directly in physical terms as the sum of the interactions of the charge of each test ion (a) with the hole in the ionic atmosphere resulting from the exclusion of screening charge by the hard core of the other ion and (b) with the dipole induced in the dielectric sphere, constituting the other ion, by the screened electric field. This approach leads to an expression valid for *asymmetrical* test ions with distinct $a_i \equiv b_0 + b_i$, D_i , and q_i . Specifically, recalling Eq. (3.35) for $\vartheta(x)$, we conclude

$$W_{12}(R) = q_1 q_2 \vartheta(\kappa a_1) \vartheta(\kappa a_2) e^{-\kappa R} / DR + \frac{1}{2} \frac{e^{-2\kappa R}}{DR^2} \left\{ \vartheta^2(\kappa a_1) q_1^2 \left[\frac{1}{3} \kappa^2 a_2^3 + \frac{D-D_2}{2D+D_2} \left(\frac{1}{R} + \kappa \right)^2 b_2^3 \right] \right. \\ \left. + \vartheta^2(\kappa a_2) q_2^2 \left[\frac{1}{3} \kappa^2 a_1^3 + \frac{D-D_1}{2D+D_1} \left(\frac{1}{R} + \kappa \right)^2 b_1^3 \right] + O \left[\kappa^4 a_i^5, \left(\frac{1}{R} + \kappa \right)^4 b_i^5 \right] \right\}. \quad (4.11)$$

This result correctly reproduces the leading form of the decay of $W_{12}(R)$ as $R \rightarrow \infty$ for all $\kappa \geq 0$. However, it does not generate the Φ_6/R^6 correction when $\kappa \rightarrow 0$; nor does it contain contributions decaying as $e^{-3\kappa R}$, etc. These higher order terms, however, can be seen physically to represent the interaction of the hole charge of one ion with the hole charge of the other and with the induced dipole of the other, and of one induced dipole with the other induced dipole, and so on. Finally, the crossover occurring when $R \geq 1/\kappa$ is readily seen in Eq. (4.11).

V. BIPOLAR IONS

As mentioned in the Introduction, Fisher and Levin^{3,4} recently treated tightly bound, oppositely charged ions, forming neutral dipoles or Bjerrum pairs,³⁻⁵ by Kirkwood's compound-ion model.¹ Specifically, the pair of ions at relatively close separation $R \geq a$ was represented as two charges, $+q$ and $-q$, symmetrically embedded in a sphere of suitably chosen radius, b_{dip} . When R is less than $2a$ the regions of radius a , bounded by the dashed curves in Fig. 1, from which the ionic sea is to be excluded, merge to form a single, kidney-shaped domain. To approximate this domain formed of two overlapping spheres, the radius b_{dip} was chosen judiciously^{3,4} as a fixed average exclusion radius, $a_{\text{dip}} = b_0 + b_{\text{dip}}$, measured from the midpoint of the line joining the two ionic centers. At best, however, this choice is subject to some ambiguity and it would be clearly preferable to determine the solvation energy for a bipolar pair of nearby ions, say W_{bip} , by using the proper exclusion volume in solving the DH equations.

Accordingly, we discuss here the situation described by Fig. 1 but with $R < 2a$: then regions II and IV merge to form a connected domain, say, Π^+ ; likewise, if also $R < b$, regions I and V merge to form, say, I^+ . The dipolar pair, of most physical interest, corresponds to $q_2 = -q$; but, since it costs no more effort, we continue to treat a bipolar pair with $q_2 = \pm q$. Now the potential $\varphi(\mathbf{r})$ in I^+ must still obey Eq. (2.13) when $r_1 \rightarrow 0$; this defines $B_{\pm}(x, y; \delta, a/b)$. Then, as before, $qB_{\pm}(x, y)$ is the total energy of interaction of \mathcal{S}_1 with \mathcal{S}_2 and with all the sea ions while $W_1(x) = qB_{\pm}(x, \infty) \equiv qB_{\infty}(x)$ represents the energy of \mathcal{S}_1 alone in the ionic sea; the interaction energy $W_{12}^{\pm}(x, y)$ is still given by Eq. (2.15). In defining the bipolar solvation energy $W_{\text{bip}}(x, y)$ one must not include the formation energy of the isolated pair $\mathcal{S}_1, \mathcal{S}_2$ (removed from the ionic sea): if $D' = D$ this is simply $\pm q^2/DR$; more generally it is given by $W_{12}^{\pm}(0, y)$, i.e., by setting $x = \kappa a$ to zero. In total, therefore, we have

$$W_{\text{bip}}(x, y) = 2W_1(x) + W_{12}^{\pm}(x, y) - W_{12}^{\pm}(0, y)$$

$$= q[B_{\infty}(0) + B_{\infty}(x) + B(x, y) - B_{\pm}(0, y)], \quad (5.1)$$

where we may still use Eq. (3.33) for $W_1 = qB_{\infty}$. Integration of $W_{\text{bip}}(x, y)$ with respect to x corresponds to charging the ionic sea and yields the desired free energy of solvation for a bipolar pair.³⁻⁵

At first sight the calculations reported in Sec. III for $R > 2a$ lose validity when $R < 2a$. The boundary conditions (2.7) and (2.8) still apply but are needed only on restricted parts of the spheres $r_1 = a$ and $r_2 = a$ bounding region Π^+ (and similarly for region I^+); in addition one appears to need a further boundary condition on the plane $\theta_1 = \theta_2$ or, say, $z = 0$ which bisects the line joining the centers of \mathcal{S}_1 and \mathcal{S}_2 . Specifically in the $-$ or dipolar $(+, -)$ case one must have $\mathcal{B}^-: \varphi(\mathbf{r}) = 0$ on $z = 0$; but, for the $+$ or like-charge case, $\mathcal{B}^+: \varphi(\mathbf{r})$ and all derivatives across $z = 0$ must be continuous while all odd derivations must vanish. Consider, however, the forms of solution posited in Eqs. (3.1)–(3.3) for regions I, II, and III, respectively. The last of these, by its symmetric construction, automatically satisfies \mathcal{B}^{\pm} for all of space external to Π^+ and I^+ . If, however, Eq. (3.2) is extended to all of Π^+ and, when $R < 2b$, Eq. (3.1) to all of I^+ , it may not be a priori clear that \mathcal{B}^{\pm} is satisfied. Nevertheless, the symmetric/antisymmetric character of the boundary conditions and the analyticity of the solutions inside each of the (extended) regions will ensure the preservation of the symmetries and, hence, of the boundary conditions \mathcal{B}^{\pm} .

Somewhat more explicitly one may proceed as follows where, for simplicity, we consider only the case $D' = D$ when regions I^+ and Π^+ may be identified (or, by taking $b = a$, when one may neglect Π^+). Then the boundary conditions are clearly satisfied by

$$\varphi_{I^+}(\mathbf{r}) = \frac{q}{Dr_1} \pm \frac{q}{Dr_2} + \sum_{n=0}^{\infty} E_n [r_1^n P_n(\cos \theta_1) \pm r_2^n P_n(\cos \theta_2)] \quad (5.2)$$

for general $\{E_n\}$. One can expand $1/r_2$ in Legendre polynomials in $\cos \theta_1$ and similarly use

$$r_2^n P_n(\cos \theta_2) = \sum_{m=0}^n \binom{n}{m} R^{n-m} (-r_1)^m P_m(\cos \theta_1). \quad (5.3)$$

These substitutions lead to

$$\varphi_{I^+}(\mathbf{r}) = \frac{q}{Dr_1} + \sum_{n=0}^{\infty} \tilde{B}_n r_1^n P_n(\cos \theta_1), \quad (5.4)$$

where the expansion coefficients satisfy

$$\tilde{B}_n = \pm \frac{q}{DR^{n+1}} + E_n \pm (-)^n \sum_{m=0}^{\infty} \binom{n+m}{m} R^m E_{n+m}. \quad (5.5)$$

Now if one identifies \tilde{B}_n in Eq. (5.4) with B_n in Eq. (3.1) one sees that the expansions are identical! One may worry that the B_n were originally completely free while the \tilde{B}_n are constrained by Eq. (5.5). Nevertheless since the E_n are free these constraints serve only to embody the symmetry; but, as we have noted, this will be realized in any case when the I⁺–III boundary conditions are imposed because φ_{III} embodies the proper symmetry. Note that even though one does not need a boundary condition over the full sphere $r_1 = a$, one may still match the coefficients of the $P_m(\cos \theta_1)$ since doing so will ensure satisfaction of the boundary condition on the necessary surfaces. We conclude, as before, that the matching problem posed when $R < 2a$ is identical to that for $R > 2a$.

In summary, with the aid of Eqs. (3.33) and (3.34) we obtain from Eq. (5.1) the expression

$$W_{\text{bip}}(x, y) = \frac{q^2}{Da} \left[2 \frac{a}{b} \left(1 - \frac{D}{D'} \right) - \frac{2x}{1+x} \pm V_{\pm}(x, y) \right], \quad (5.6)$$

$$V_{\pm}(x, y) = \frac{\vartheta^2(x) U_0(x, y) e^{-xy}}{y \mp v(x) U_0(x, y) e^{-xy}} \frac{U_0(0, y)}{y}, \quad (5.7)$$

with, as previously, $U_0(x, y)$ defined formally via Eq. (3.44).

Since we are now interested in $(y-1)$ small the convergence of Eq. (3.44) is a serious issue. Certainly $y < 1$ will lie outside the domain of convergence since when $y=1$ the charge of \mathcal{S}_2 sits on the sphere $r_1 = a$ on which the matching is performed. When x is small, however, one may hope that correct asymptotic behavior will be generated by truncating the expansion for $U_0(x, y)$. To study that let us specialize to $D' = D$ so $\delta = 0$ (which case is of particular interest^{3,4}) and focus on small x . If we write

$$u_n(x, y) = \pm h_{n0}(x, y) t_n(x, y) \quad (5.8)$$

for $n \geq 1$, use Eqs. (3.21) and (3.23) to give

$$h_{mn} \approx (2m-1)!!(2n-1)!! \binom{m+n}{n} y^{-m-n} \times [1 + xy + O(x^2)], \quad (5.9)$$

and employ Eq. (3.27) for $\omega_m(x)$, the matching Eqs. (3.38) can be written

$$t_n \approx 1 \pm x^2 (y^{-1} + x) e^{-xy} \sum_{j=1}^{\infty} \binom{n+j}{j} \frac{y^{-2j} t_j}{(2j+3)(2j+1)}, \quad (5.10)$$

with $n \geq 1$, while Eq. (3.24) yields

$$U_0(x, y) \approx 1 \pm x^2 y^{-1} (1 + xy)^2 e^{-xy} \times \sum_{l=1}^{\infty} \frac{y^{-2l} t_l(x, y)}{(2l+3)(2l+1)}. \quad (5.11)$$

Note that a factor $[1 + O(x^2)]$ has been dropped from the second terms in both these expressions. Now when $x \rightarrow 0$ in

Eq. (5.10) one has $t_n = 1$ for all n with, formally, corrections of order x^2 . When this is inserted in Eq. (5.11) the sum converges to

$$S_0(y) = \frac{1}{4} y(y^2 - 1) \ln \left(\frac{y-1}{y+1} \right) + \frac{1}{2} y^2 - \frac{1}{3} \leq \frac{1}{6} \quad (5.12)$$

for $y > 1$, so yielding an explicit formula for $U_0(x, y)$ formally correct to $O(x^3)$. Via Eqs. (5.7) and (5.6) we thus obtain an expression for $W_{\text{bip}}(x, y)$ which is also formally correct to $O(x^3)$: we suspect this is truly asymptotic when $x \rightarrow 0$ at fixed $y > 1$.

On the other hand, the substitution $t_j = 1$ in Eq. (5.10) yields the sum

$$S_n(y) = \frac{1}{n!} \left(\frac{\partial}{\partial y^{-2}} \right)^n [y^{-2n} S_0(y)], \quad (5.13)$$

that for $n > 1$ and $y \rightarrow 1+$ diverges like $1/4n(n-1)(1-y^{-2})^{n-1} \sim \mu^n/n^2$ with $\mu \geq 1$. Consequently, for any x however small the leading corrections to t_n become of order 1 for large enough n and then diverge exponentially fast with n increasing! This is not inconsistent with an asymptotic character as $x \rightarrow 0$ but does raise the spectre of nonconvergence. A more general, heuristic diagnosis follows from the ansatz $t_n \sim \lambda^n$ for large n : Matching this to the behavior $S_n(\lambda/y) \sim [1 - (\lambda/y^2)]^{-n}$ in Eq. (5.10) yields the condition $\lambda(y^2 - \lambda) = y^2$. For $y \geq 2$ this equation has a real solution with $\lambda/y^2 \leq \frac{1}{2}$. For such a solution set $\{t_n\}$ the sums in Eqs. (5.10) and (5.11) converge rapidly. Beyond that when $y < 2$ one finds complex solutions but with modulus $|\lambda/y^2| = 1/y$. Thus provided one has $y > 1$ the sums still converge absolutely.

These considerations suggest that there are well behaved solutions $\{t_n\}$ of the set of equations (5.10) which do yield a convergent expression for $U_0(x, y)$ and then for $W_{\text{bip}}(x, y)$. However, direct iterative solution of Eq. (5.10) may not be successful when $y < 2$. Other numerical methods, such as truncating the set of equations at increasingly high order, might well prove adequate but we have not investigated the issue. It is also possible that a systematic expansion in powers of y at fixed x will yield convergent results, at least when $x^2(1+x)e^{-xy}$ is small. And, as already stated, we expect the truncated expansion in powers of x described above to be asymptotic. Nevertheless, without a more detailed investigation it is not clear that a practical improvement on the approximation of using an effective radius b_{dip} in the Kirkwood model^{3,4} can be gained for the range of principal interest, namely, $x \leq 1.5$.

VI. CONCLUSIONS

By solving the Debye–Hückel equations analytically for appropriate boundary conditions we have obtained expressions for the interaction energy $W_{12}(R)$ between two similar ions, represented as equally or oppositely charged dielectric spheres, at separation R in an ionic medium. The general result is contained in Eqs. (3.34)–(3.36) with Eq. (3.44). More explicit expressions valid when R becomes large are obtained in Sec. IV: the leading, screened Coulomb form $W_{12}^0(R)$ is stated in Eq. (4.1) with a correction, $\Delta W_{12}(R)$, in

Eqs. (4.2) and (4.3); explicit results for the correction in two distinct regimes, (A) positive ionic strength ($\kappa > 0$) and (B) asymptotically vanishing ionic strength ($\kappa \rightarrow 0$), are given in Eqs. (4.6) and (4.9). Results valid *uniformly* (for positive or zero ionic strength) follow from Eq. (4.10); finally, Eq. (4.11) presents the explicit leading order behavior of $\Delta W_{12}(R)$ for *dissimilar* ions with distinct charges, radii, and dielectric constants. The most fundamental conclusion is that the corrections $\Delta W_{12}(R)$ decay as the *square* of the leading, screened Coulomb coupling.⁸

The analytic results obtained rest on an apparently novel two-center expansion for spherical Bessel functions, which is established in the Appendix.

In Sec. V we have discussed the solvation energy of a closely associated (+,+) or (+,-) ion pair. The general analysis still yields formally exact results—see Eqs. (5.6) and (5.7)—which, in turn, lead to expressions asymptotic for small ionic strengths. However, as regards practical numerical computations for larger ionic strengths (corresponding to $\kappa a \geq 1$), further work is needed to test the efficacy of various methods that might be used to evaluate the general formulas.

Finally, it should, of course, be noted that the applicability of our results to real ionic solutions is subject to various caveats. In particular, the molecular details of the test ions and of the solute ions have been wholly subsumed into the dielectric sphere model; and no account of the molecular structure of the solvent has been given beyond assignment of an effective dielectric constant, D . Nonetheless, at a qualitative and semiquantitative level we expect our results to provide fairly reliable guides to the properties of real fluid systems.

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APPENDIX: PROOF OF THE TWO-CENTER EXPANSION

As explained in the text, the form of the expansion (3.17), in particular the appearance of the Legendre polynomials, follows from general principles. Here we explicitly evaluate the expansion coefficients $e_{mn}(z)$. It suffices to specialize to $\theta_1 = 0$ which implies $\theta_2 = 0$ so that $P_m(\cos \theta_2) = P_m(\cos \theta_1) = 1$ and, by Eq. (3.16), $S = z - s$ or $r_2 = R - r_1$. The expansion then reads

$$k_m(z-s) = \sum_{n=0}^{\infty} (2n+1) i_n(s) e_{mn}(z) e^{-z/z}. \quad (\text{A1})$$

Now on the left-hand side we may use Eq. (3.6) for $k_m(z-s)$ and the binomial expansion

$$(z-s)^{-l-1} = \frac{1}{z^{l+1}} \sum_{i=0}^{\infty} \binom{l+i}{l} \frac{s^i}{z^i}, \quad (\text{A2})$$

valid for $|s| < z$. On the right-hand side of Eq. (A1) we use Eq. (3.4) to expand $i_n(s)$ in powers of s . Comparing like powers yields the recursion relation

$$\frac{e_{mn}(z)}{(2n-1)!!} = \sum_{i=0}^m \sum_{j=0}^n q_{mi} \binom{i+j}{j} \frac{z^{-i-j}}{(n-j)!} - \sum_{l=1}^{[n/2]} \frac{2n-4l+1}{2^l l! (2n-2l+1)!!} e_{m,n-2l}(z), \quad (\text{A3})$$

where the q_{mi} are given in Eq. (3.7), while $[w]$ denotes the largest integer contained in w and an empty sum vanishes. This yields the polynomials

$$e_{m0}(z) = \sum_{i=0}^m q_{mi} z^i = z e^z k_m(z), \quad (\text{A4})$$

$$e_{m1}(z) = \sum_{i=0}^m q_{mi} (z+i+1) z^{i+1}, \quad (\text{A5})$$

of degrees m and $m+1$ in z^{-1} . Recursively one sees that $e_{mn}(z)$ is polynomial in z^{-1} of degree $m+n$ for all $m, n \geq 0$. Furthermore, the two terms of highest degree arise only from the double sum in Eq. (A3), namely for $i=m, j=n$, and $i+j=m+n-1$: the result (3.21) for $e_{m,n,m+n}$ and $e_{m,n,m+n-1}$ directly follows.

To obtain an explicit general expression for e_{mnr} note that the generalized Neumann transform¹⁴

$$\check{g}(s) \equiv \mathcal{N}_{n \rightarrow s} \{g_n\} = \sum_{n=0}^{\infty} (2n+1) i_n(s) g_n \quad (\text{A6})$$

has a unique inverse as follows from the orthonormality of $\{i_n(z)\}$ with weight $1/z$. Now E7.15 (1)¹⁴ states

$$z^\nu e^{\gamma z} = 2^\nu \Gamma(\nu) \sum_{n=0}^{\infty} (\nu+n) C_n^\nu(\gamma) I_{\nu+n}(z), \quad (\text{A7})$$

which on specializing to $\gamma=1$ and $\nu=p+\frac{1}{2}$ with $C_n^\nu(1)$ given by E10.9 (3), reduces to

$$\mathcal{N}_{s \rightarrow n}^{-1} \{s^p e^s\} = (2p-1)!! \binom{n+p}{n-p}, \quad n \geq p, \\ = 0, \quad n < p. \quad (\text{A8})$$

Applying this to Eq. (A1) and using Eqs. (3.6) and (A2) yields

$$e_{mn}(z) = \mathcal{N}_{s \rightarrow n}^{-1} \{z e^z k_m(z-s)\} \\ = \sum_{i=0}^{\infty} \sum_{l=0}^m \binom{l+i}{l} \frac{q_{mi}}{z^{l+i}} \mathcal{N}_{s \rightarrow n}^{-1} \{s^l e^s\}. \quad (\text{A9})$$

On rearranging terms and introducing

$$J^+(m,r) = \min(m,r) \quad \text{and} \quad J^-(n,r) = \max(0,r-n) \quad (\text{A10})$$

we obtain the final result

$$e_{mnr} = \frac{2^{-r}}{r!} \sum_{j=j^-}^{j^+} \binom{r}{j}^2 \frac{(m+j)! (n+r-j)!}{(m-j)! (n-r+j)!} = e_{nmr}, \quad (\text{A11})$$

where the symmetry under interchange of m and n is easily checked. Note that the sum on j may be left free if all terms with negative factorials are understood to vanish or to be deleted. The results quoted for $r=0, 1, 2$ in Eqs. (3.19) and (3.20) follow immediately from Eq. (A11). For small $r \leq m, n$ there are $r+1$ terms in the sum. However, for large $r \geq m, n$ there are $(m+n+1-r)$ terms; thus Eq. (3.21) for $r=m+n$ and $r=m+n-1$ may be crosschecked.

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⁸(a) A brief announcement of some of our results was made in September 1993 at the Second Liquid Matter Conference held in Florence, Italy. See also (b) X.-J. Li, Y. Levin, and M. E. Fisher, *Europhys. Lett.* (in press); (c) In this article it is noted that the reported double screening of the dielectric-mismatch contribution to the effective interaction between ions in an electrolyte arises also in the distinct problem of the screening of long-range, power-law dispersion (or van der Waals) forces between polarizable but uncharged dielectric bodies in an ionic medium at finite, positive temperatures. This effect is analyzed in J. Mahanty and B. W. Ninham, *Dispersion Forces* (Academic, New York, 1976), Chap. 7; see Eqs. (7.10) and (7.60)–(7.64).

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