

Calculation of the dielectric constant of polyatomic fluids with the interaction site formalism†

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The proper integral equation theory for interaction site models of polyatomic fluids is used to study the static dielectric constant, ϵ . It is shown that the well known failure of the RISM theory to improve upon the ideal gas result, $\epsilon - 1 = 3y$, is a consequence of the RISM approximation in which the hypervortex functions, Ω , are replaced by their low density limit, ω . By accounting for the differences between Ω and ω , non-trivial results for ϵ are obtained, and these results do not require the use of unusual long ranged direct correlation functions. An illustrative calculation is presented to show that the ϵ^{-1} renormalization of bare coulombic interactions leads in the interaction formalism to the Onsager saturation $\epsilon \propto y$ for large ϵ .

1. INTRODUCTION

The RISM equation and related approximations [1] have played an important role in our developing understanding of the local structures of polyatomic fluids. However, when applied to the calculation of long wavelength properties such as the dielectric constant of a molecular liquid, these theories yield trivial and incorrect results [2]. In a recent article [3], it was shown that the Ornstein-Zernike-like equation introduced as the basis of the RISM theories is not consistent with a topological reduction of the exact interaction site cluster series [4]. In this sense, the RISM equation and related approximations are not diagrammatically proper theories, and we show herein that the failure of the RISM equation when applied to the calculations of long wavelength properties is intimately linked to its improper footing in graph theory.

The Ornstein-Zernike-like equation used as the basis for the RISM theories is

$$\omega + \rho \mathbf{h} = (\mathbf{1} - \rho \omega \mathbf{c})^{-1} \omega, \quad (1.1)$$

where we employ the notation defined in [3], and for notational simplicity, confine ourselves to one component uniform fluids. (Generalizations to more complex systems are straightforward.) In [3] it was shown that a topological

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reduction of the interaction site cluster series [4] leads not to equation (1.1) but rather to a generalization which can be expressed as

$$\boldsymbol{\omega} + \rho \mathbf{h} = (\mathbf{1} - \rho \boldsymbol{\Omega} \mathbf{c}_0)^{-1} \boldsymbol{\Omega}, \quad (1.2)$$

where \mathbf{c}_0 is a matrix with elements given by a set of direct correlation functions, and

$$\boldsymbol{\Omega} = \boldsymbol{\omega} + \Delta \boldsymbol{\Omega}, \quad (1.3)$$

where $\Delta \boldsymbol{\Omega}$ is a functional of another set of topologically distinct direct correlation functions which form the elements of the matrices \mathbf{c}_r , \mathbf{c}_l and \mathbf{c}_b . (See (4.12) below or (3.4) of [3].) The RISM form of integral equation and related approximations can be obtained by neglecting $\Delta \boldsymbol{\Omega}$ and associating the RISM \mathbf{c} with \mathbf{c}_0 .

In this paper we show that when $\Delta \boldsymbol{\Omega}$ is not neglected, (1.2) will yield non-trivial results for the dielectric constant. We begin in § 2 with a review of some basic formulas required for the calculation of the dielectric constant from the interaction site formalism. The deficiency of the RISM equation and related approximations is illustrated in § 3. Then, in § 4 we construct a simple theory for $\Delta \boldsymbol{\Omega}$ to illustrate the use of (1.2) in deriving expressions for the dielectric constant.

A final introductory note: For the sake of brevity, this article has been written assuming that the reader is familiar with [3].

2. DIELECTRIC CONSTANT AND INTERACTION SITE CORRELATION FUNCTIONS

When treating polar fluids with the interaction site model, the interaction sites are assumed to possess charges, and at large distances the site-site interactions are asymptotic to the coulomb potential. This potential times $(-k_B T)^{-1} = -\beta$ is given by

$$\phi_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = -\beta z_\alpha z_\gamma / |\mathbf{r} - \mathbf{r}'|. \quad (2.1)$$

Here z_α is the charge on the α th site, and assuming the molecules are neutral,

$$\sum_{\alpha=1}^m z_\alpha = 0, \quad (2.2)$$

where m is the number of interaction sites per molecules.

An analysis of the interaction site cluster series has been carried out in which $\boldsymbol{\phi}$ is treated as a perturbation [5]. The analysis shows that

$$\boldsymbol{\chi} = \rho \boldsymbol{\omega} + \rho^2 \mathbf{h} \quad (2.3)$$

can be expressed as

$$\boldsymbol{\chi} = (\mathbf{1} - \boldsymbol{\Omega}_D \boldsymbol{\phi})^{-1} \boldsymbol{\Omega}_D, \quad (2.4)$$

where $\boldsymbol{\Omega}_D$ is characterized diagrammatically as the sum of all contributions to $\boldsymbol{\chi}$ which cannot be disconnected by removing one $\boldsymbol{\phi}$ bond. Provided all the interactions other than the coulombic potentials are short ranged, it has been shown that the elements of $\boldsymbol{\Omega}_D$ are short ranged [5]. That is, $\Omega_{\alpha\gamma, D}(\mathbf{r}, \mathbf{r}')$ decays at least as fast as $|\mathbf{r} - \mathbf{r}'|^{-6}$ for large $|\mathbf{r} - \mathbf{r}'|$. (In [5], this matrix of functions was labelled $\boldsymbol{\Omega}$; the subscript 'D' is added here to avoid confusion

with the functions Ω introduced in [3].) The dielectric constant, ϵ , can be obtained from the second moments of Ω_D . In particular [5],

$$\epsilon - 1 = -\text{Tr } \Phi \Omega_D^{(2)}, \quad (2.5)$$

where Φ is the matrix with elements

$$\Phi_{\alpha\gamma} = -\beta 4\pi z_\alpha z_\gamma \quad (2.6)$$

and $\Omega_D^{(2)}$ is defined by the expansion of the Fourier transform of Ω_D at small wavevectors,

$$\hat{\Omega}_D(k) = \hat{\Omega}_D(0) + k^2 \Omega_D^{(2)} + \dots \quad (2.7)$$

As discussed in [5], the function $\Omega_{\alpha\gamma, D}(r)$ is an integral over the Nienhuis-Deutch [6] hypervortex function $G_2^{(0)}(1, 2)$ when sites α and γ in molecules 1 and 2, respectively, are held a distance r apart. Indeed, (2.5) is equivalent to the Nienhuis-Deutch formula [6] for ϵ .

A comparison of the proper integral equation formula (1.2), with the perturbation formula, (2.4), shows that

$$\Omega_D = \rho \Omega (\mathbf{1} - \rho \Delta \mathbf{c} \Omega)^{-1}, \quad (2.8)$$

where

$$\Delta \mathbf{c} = \mathbf{c}_0 - \Phi. \quad (2.9)$$

Equation (2.8) and its inverse,

$$\rho \Omega = \Omega_D (\mathbf{1} + \Delta \mathbf{c} \Omega_D)^{-1}, \quad (2.8')$$

provides the connection between the dielectric hypervortex functions, Ω_D and the topologically distinct site-site direct correlation functions introduced in [3]. This connection is a central result of this paper. We will use it to analyse the dielectric constant predictions of certain classes of approximations for the direct correlation functions.

3. RISM THEORIES

This class of theories rests on two assumptions: (1) $\Delta \mathbf{c}$ is a matrix of short ranged functions; and (2) Ω can be approximated by its low density limit,

$$\Omega \approx \omega. \quad (3.1)$$

The class includes the RISM (or ISM) equations and Rossky's recent extensions of these equations [1]. Indeed, it would appear that any integral equation based upon (1.1) (i.e. $\Delta \Omega = 0$) will fall into this classification, provided the closure relations for the site-site direct correlation functions are chosen in analogy to simple atomic liquid theories. By neglecting $\Delta \Omega$, however, these integral equations will sum unallowed cluster diagrams, and in this sense, these theories are considered improper integral equations.

We believe that in a proper diagrammatic theory, $\Delta \mathbf{c}$ probably is a short ranged function. However, if the extreme limit embodied in (3.1) is used, a short ranged $\Delta \mathbf{c}$ will guarantee a trivial result for the dielectric constant. To see why, note that (3.1) and (2.8) yield

$$\Omega_D = \rho \omega (\mathbf{1} - \rho \Delta \mathbf{c} \omega)^{-1}. \quad (3.2)$$

The right-hand-side can be expanded for low wavevectors using $\hat{\omega}(k) = \hat{\omega}(0) + k^2 \omega^{(2)} + \dots$, and $\Delta \hat{c}(k) = \Delta \hat{c}(0) + k^2 \Delta c^{(2)} + \dots$. The expansion gives

$$\Phi \Omega_D = \rho k^2 \Phi \omega^{(2)} [1 - \rho \Delta \hat{c}(0) \hat{\omega}(0)]^{-1} + O(k^4), \quad (3.3)$$

where we have noted that neutrality, (2.2), implies

$$\Phi \hat{\omega}(0) = 0. \quad (3.4)$$

To obtain the prediction for ϵ from this theory, we take the trace of (3.3), and apply (3.4) once more. These manipulations together with (2.5) give

$$\epsilon - 1 = -\rho \text{Tr} \Phi \omega^{(2)} \quad (3.5)$$

which is the low density (ideal gas) formula for the dielectric constant.

Thus, no matter how sophisticated we make our choice of Δc , provided it is short ranged, we shall obtain an incorrect result for ϵ if we neglect the difference between Ω and its low density limit, ω .

4. PROPER INTEGRAL EQUATION THEORIES

Let us now continue to assume that the non-coulombic portions of the site-site direct correlation functions are short ranged, but consider $\Delta \Omega$ to be non-zero. From the small wavevector expansion of (2.8), we find

$$\Phi \Omega_D = \rho k^2 \Phi \Omega^{(2)} [1 - \rho \Delta \hat{c}(0) \hat{\Omega}(0)]^{-1} + O(k^4), \quad (4.1)$$

where we have noted that

$$\Phi \hat{\Omega}(0) = 0, \quad (4.2)$$

which follows from (2.8') and the local neutrality condition, $\Phi \hat{\Omega}_D(0) = 0$ (equation (5.9) of [5]), and we define $\Omega^{(2)}$ through the series $\hat{\Omega}(k) = \hat{\Omega}(0) + k^2 \Omega^{(2)} + \dots$. The dielectric constant can be determined from (2.5) and (4.1) by taking the trace of the right hand side of (4.1) and applying (4.2) once again. The result is

$$\epsilon - 1 = -\rho \text{Tr} \Phi \Omega^{(2)}, \quad (4.3)$$

which, of course, reduces to the ideal gas RISM result of the previous section when Ω is replaced by its low density limit, ω .

We have derived (4.3) as an approximation which relies on the assumption that Δc and the direct correlation functions contributing to Ω are short ranged. Approximate theories such as generalizations of the mean spherical and hypernetted chain approximations will agree with this assumption. The issue of whether

$$\epsilon - 1 = -\rho \lim_{k \rightarrow 0} [\Phi \hat{\Omega}(k)/k^2],$$

is actually an exact result is outside the scope of the present article. However, we conjecture that it is exact. The study of its general correctness will be left to future research.

To illustrate the use of (4.3), we could identify those graphs contributing to c_b , c_r , and c_b which when combined with (4.3) yield the Clausius-Mossotti-Debye (CMD) formula

$$\epsilon - 1 = 3y/(1 - y),$$

or

$$(\epsilon - 1)/(\epsilon + 2) = y,$$

where

$$y = \frac{4}{9}\pi\beta\rho\mu^2, \quad (4.4)$$

with μ denoting the dipole moment given by

$$\begin{aligned} \mu^2 &= \left\langle \left| \sum_{\alpha} z_{\alpha} \mathbf{r}_i^{(\alpha)} \right|^2 \right\rangle \\ &= -\frac{1}{2} \int d\mathbf{r} r^2 \text{Tr } \Phi \omega(\mathbf{r}). \end{aligned} \quad (4.5)$$

The CMD graphs can be found in [5]. In particular, one may identify the nodeless graphs in figure 4 *b* of [5] as contributions to \mathbf{c}_b , \mathbf{c}_r and \mathbf{c}_b in this theory.

The CMD formula for the dielectric constant contains an unphysical divergence as $y \rightarrow 1$. On the other hand Onsager's expression (7) for the dielectric constant

$$(\epsilon - 1) \left(\frac{2\epsilon + 1}{9\epsilon} \right) = y$$

exhibits the physically expected saturation, $\epsilon \propto y$ for large y . It seems appropriate to illustrate the theory with a calculation which exhibits the qualitative aspects of this saturation.

To this end, it is useful to note that one may topologically reduce the graphical series for the direct correlation functions \mathbf{c}_b , \mathbf{c}_r and \mathbf{c}_b (defined in [3]) in such a way that their functional dependence upon the site-site potentials is replaced with a dependence on \mathbf{h}_0 . Here, \mathbf{h}_0 (defined in [3]) is the sum of graphs contributing to \mathbf{h} for which the roots are not \mathbf{s} circles. From this graphical definition of \mathbf{h}_0 , we can make the physical identification,

$$h_{\alpha\gamma,0}(r) = \text{pair correlation function for two free sites (i.e. not attached to a molecule) dissolved at infinite dilution in the molecular fluid.} \quad (4.6)$$

Since we associate charges with these interaction sites, we know [5]

$$h_{\alpha\gamma,0}(r) \sim -\beta z_{\alpha} z_{\gamma} / \epsilon r, \quad (4.7)$$

for large r . To see how this result follows from the proper integral equation theory of [3], we note that ((3.9 *a*) of [3])

$$\mathbf{h}_0 = (\mathbf{1} + \mathbf{\Omega}_r) \mathbf{c}_0 (\mathbf{1} + \rho \mathbf{\Omega} \mathbf{c}_0)^{-1} (\mathbf{1} + \mathbf{\Omega}_l). \quad (4.8)$$

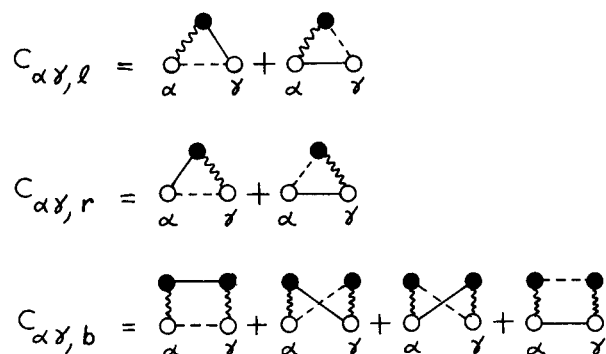
In Fourier transform space we find from this result and (4.2) and (4.3) that

$$\mathbf{h}_0(k) \sim [\mathbf{1} + \hat{\mathbf{\Omega}}_r(0)] (\Phi / \epsilon k^2) [\mathbf{1} + \hat{\mathbf{\Omega}}_l(0)], \quad (4.9)$$

for small k . Equation (4.7) follows immediately provided

$$\Phi \hat{\mathbf{\Omega}}_l(0) = \hat{\mathbf{\Omega}}_r(0) \Phi = 0. \quad (4.10)$$

Thus, to obtain acceptable dielectric theories from the proper integral equations of [3], the integral equations must be constructed to satisfy the local neutrality conditions expressed by (4.2) and (4.10).



Interaction site cluster diagrams for the elements of the direct correlation function matrices \mathbf{c}_l , \mathbf{c}_r and \mathbf{c}_b . See text for definition of bonds.

Since \mathbf{h}_0 is smaller than the bare coulombic interaction by a factor of ϵ^{-1} , the use of a cluster theory with \mathbf{h}_0 bonds would appear more profitable than that with Φ bonds, especially at large values of ϵ . Expansions designed for large ϵ can regard these renormalized coulombic bonds as small interactions. A simple theory linear in \mathbf{h}_0 , constructed with this idea in mind is illustrated in the figure. The solid lines represent $\epsilon^{-1} \Phi$ bonds (the asymptotic behaviour of \mathbf{h}_0), the wavy bonds depict $s_{\alpha\gamma}(r) = (1 - \delta_{\alpha\gamma})\omega_{\alpha\gamma}(r)$, and the dashed lines denote the short function

$$F_{\alpha\gamma}(r) = -A, \quad r < \sigma, \\ = 0, \quad r > \sigma, \quad (4.11)$$

used to embody the short ranged correlations in the molecular fluid. The constant A should be of the order of unity, and its precise value should depend upon the nature of these short ranged correlations.

By fixing \mathbf{c}_r , \mathbf{c}_l and \mathbf{c}_b , we determine Ω through (3.4) of [3];

$$\Omega = (\mathbf{1} - \rho \mathbf{c}_l)^{-1} (\omega + \rho \mathbf{c}_b) (\mathbf{1} - \rho \mathbf{c}_r)^{-1}. \quad (4.12)$$

One finds that the local neutrality conditions for $\hat{\Omega}(0)$ and for $\hat{\Omega}_l(0)$ and $\hat{\Omega}_r(0)$ where

$$\hat{\Omega}_l = \rho (\mathbf{1} - \rho \mathbf{c}_l)^{-1} \mathbf{c}_l = \hat{\Omega}_r^\dagger \quad (4.13)$$

are indeed satisfied when the graphs shown in the figure are used to describe the direct correlation functions. Further, after a straightforward though algebraically tedious calculation (the details are sketched in the Appendix) one finds from (4.3) that the graphs in the figure imply

$$\epsilon - 1 = 3y + 12Ay^2/\epsilon \quad (4.14 a)$$

or, assuming ϵ is large,

$$\epsilon \approx [\frac{3}{2} + (9 + 48A)^{1/2}/2]y. \quad (4.14 b)$$

This result can be compared with the formal result (6),

$$(\epsilon - 1)(2\epsilon + 1)/9\epsilon = yg, \quad (4.15 a)$$

where g is Kirkwood's pair correlation factor [8]. At large ϵ , this equation leads to

$$\epsilon \approx \left(\frac{9}{2}g\right)y, \quad (4.15 b)$$

which suggests the identification

$$A = 3[(3g - 1)^2 - 1]/16. \quad (4.16)$$

When $g = 1$, the identification would imply $A = 9/16$, and (4.14) would be in accord with Onsager's theory [7] for large ϵ , $\epsilon \approx (9/2)y$.

This calculation illustrates how reasonable dielectric theories can be obtained from the interaction site formalism of molecular fluids. In these theories, the direct correlation functions ($\mathbf{c}_0 - \boldsymbol{\phi}$), \mathbf{c}_b , \mathbf{c}_r and \mathbf{c}_t are short ranged. The ideal gas result, $\epsilon - 1 = 3y$, is obtained in the RISM approximations: $\boldsymbol{\Omega} \approx \boldsymbol{\omega}$, and the assumption that ($\mathbf{c}_0 - \boldsymbol{\phi}$) is short ranged. While this approximation can be quite useful in many applications, the dielectric constant of a molecular fluid cannot be correctly described without accounting for $\Delta\boldsymbol{\Omega} = \boldsymbol{\Omega} - \boldsymbol{\omega}$. Our illustrative calculation shows that such an accounting is not difficult to achieve.

Note added in proof.—In a recent publication, Cummings and Stell [9] remark that “one of the penalties in utilizing the interaction site formalism, as opposed to the full molecular formalism [by which Cummings and Stell mean (1.1)], is the inability to be predictive in a non-trivial way about such quantities as $\epsilon \dots$ while restricting oneself to closure relations of a relatively simple form [in (1.1)].” Cummings and Stell also conclude that even when intermolecular interactions are short ranged, the site-site direct correlation functions must be long ranged or diverge at large distances. For example, they predict that the site-site direct correlation functions for an asymmetric triatomic molecule will be proportional to r for large r . Cummings and Stell (and more recently, Cummings and Sullivan [10]) arrive at these ideas by employing (1.1) as a definition of \mathbf{c} and requiring this definition to be consistent with the correct long wavelength structure of molecular fluids as manifested by the dielectric constant and other orientational pair correlation factors. In contrast, the present paper emphasizes that the RISM approximation, which employs (1.1) (i.e. $\Delta\boldsymbol{\Omega} = 0$), is not appropriate in the long wavelength regime, and that by accounting for $\Delta\boldsymbol{\Omega}$, non-trivial predictions can be made for this regime without invoking unphysically long ranged site-site direct correlation functions.

APPENDIX

Derivation of equation (4.14 a)

We take as our starting point equation (4.3) of the text. Noting also (4.12), and introducing the notation

$$\left. \begin{aligned} \mathbf{M} &= (\mathbf{1} - \rho \mathbf{c}_t)^{-1}, \\ \mathbf{N} &= \boldsymbol{\omega} + \rho \mathbf{c}_b, \\ \mathbf{P} &= (\mathbf{1} - \rho \mathbf{c}_r)^{-1}, \end{aligned} \right\} \quad (\text{A } 1)$$

we obtain

$$\epsilon - 1 = -\rho \operatorname{Tr} \Phi (\mathbf{M}^{(2)} \mathbf{N}^{(0)} \mathbf{P}^{(0)} + \mathbf{M}^{(0)} \mathbf{N}^{(2)} \mathbf{P}^{(0)} + \mathbf{M}^{(0)} \mathbf{N}^{(0)} \mathbf{P}^{(2)}). \quad (\text{A } 2)$$

It is at once apparent that this result may be simplified considerably. For from the figure we can see that the matrix of $\mathbf{c}_l^{(0)}$ is the null matrix. Thus $\Phi \mathbf{M}^{(0)} = \Phi$, and similarly $\mathbf{P}^{(0)} \Phi = \Phi$. On the other hand,

$$\mathbf{N}^{(0)} \propto \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

so that $\Phi \mathbf{N}^{(0)} = \mathbf{N}^{(0)} \Phi = 0$.

$$\left[\Phi \text{ is proportional to } \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \right].$$

Therefore (A 2) reduces to

$$\epsilon - 1 = -\rho \operatorname{Tr} \Phi \mathbf{N}^{(2)}. \quad (\text{A } 3)$$

Only the graphs in \mathbf{c}_b contribute to the dielectric constant. These may be evaluated using the basic convolution [4]

$$\int dr' s_{12}(|\mathbf{r} - \mathbf{r}'|) F(r') = (2rd)^{-1} \int_{|r-d|}^{r+d} dx x F(x). \quad (\text{A } 4)$$

Here, $F(r)$ is any function of r , and d is the intramolecular site-site separation. We find, omitting in each case a factor of $-A\beta z_\alpha z_\gamma / \epsilon$, and assuming $\sigma > 2d$:

$$\left. \begin{aligned} A_{\alpha\gamma} &= \frac{1}{d} \left(1 - \frac{r}{4d} \right), & r < 2d, \\ &= \frac{1}{r}, & 2d < r < \sigma, \\ &= 0, & \sigma < r, \\ B_{\alpha\gamma} = C_{\alpha\gamma} &= -\frac{1}{d}, & r < d, \\ &= -\frac{1}{r}, & d < r < \sigma - d, \\ &= \frac{-1}{4dr^2} [\sigma^2 - (r-d)^2] & \sigma - d < r < \sigma + d, \\ &= 0, & \sigma + d < r, \\ D_{\alpha\gamma} &= 1/r, & r < \sigma - 2d, \\ &= \frac{1}{8d^2 r^2} \{ 2d[(\sigma-d)^2 - (r-d)^2] \\ &\quad + \sigma^2(r+2d-\sigma) - \frac{1}{3}r^3 + \frac{1}{3}(\sigma-2d)^3 \}, & \sigma - 2d < r < \sigma, \\ &= \frac{1}{8d^2 r^2} \{ \sigma^2(\sigma-r+2d) - \frac{1}{3}\sigma^3 + \frac{1}{3}(r-2d)^3 \}, & \sigma < r < \sigma + 2d, \\ &= 0, & \sigma + 2d < r, \end{aligned} \right\} \quad (\text{A } 5)$$

where **A**, **B**, **C** and **D** stand for the first, second, third and fourth \mathbf{c}_b graphs, respectively, in the figure. Note that

$$c_{\alpha\gamma,b}(\mathbf{r}) = A_{\alpha\gamma}(\mathbf{r}) + B_{\alpha\gamma}(\mathbf{r}) + C_{\alpha\gamma}(\mathbf{r}) + D_{\alpha\gamma}(\mathbf{r}). \quad (\text{A } 6)$$

Transforming to k -space using the relation

$$\hat{c}_{\alpha\gamma,b}(\mathbf{k}) = 4\pi \int_0^\infty j_0(kr) c_{\alpha\gamma,b}(\mathbf{r}) r^2 dr, \quad (\text{A } 7)$$

in which $j_0(x) = 1 - \frac{1}{6}x^2 + O(x^4)$ is the spherical Bessel function of order 0, we obtain

$$\hat{c}_{\alpha\gamma,b}(\mathbf{k}) = \hat{A}_{\alpha\gamma}(\mathbf{k}) + \hat{B}_{\alpha\gamma}(\mathbf{k}) + \hat{C}_{\alpha\gamma}(\mathbf{k}) + \hat{D}_{\alpha\gamma}(\mathbf{k}), \quad (\text{A } 8)$$

where

$$\left. \begin{aligned} \hat{A}_{\alpha\gamma}^{(2)}(\mathbf{k}) &= \left(\frac{1}{4}\sigma^4 - \frac{4}{15}d^4\right) \frac{4\pi \beta z_\alpha z_\gamma A}{6 \epsilon}, \\ \hat{B}_{\alpha\gamma}^{(2)}(\mathbf{k}) = \hat{C}_{\alpha\gamma}^{(2)}(\mathbf{k}) &= -\left(\frac{1}{4}\sigma^4 + \frac{1}{8}\sigma^2 d^2 - \frac{1}{15}d^4\right) \frac{4\pi \beta z_\alpha z_\gamma A}{6 \epsilon}, \\ \hat{D}_{\alpha\gamma}^{(2)}(\mathbf{k}) &= \left(\frac{1}{4}\sigma^4 + \frac{1}{3}\sigma^2 d^2 - \frac{4}{45}d^4\right) \frac{4\pi \beta z_\alpha z_\gamma A}{6 \epsilon}. \end{aligned} \right\} \quad (\text{A } 9)$$

Hence

$$\rho \mathbf{c}_b^{(2)} = -\frac{Ay d^2}{3\epsilon} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \quad (\text{A } 10)$$

Noting also that

$$\mathbf{s}^{(2)} = -\frac{1}{8}d^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (\text{A } 11)$$

and using (A 1), (A 10) and (A 11) in (A 3), and also (2.6), (4.4), we find

$$\epsilon - 1 = 3y + 12Ay^2/\epsilon \quad (\text{A } 12)$$

which is equation (4.14 *a*) of the text.

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