

Relation Between the Free Energy and the Direct Correlation Function in the Mean Spherical Approximation

L. Blum¹ and Yaakov Rosenfeld²

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It is shown that the direct correlation function of a mixture of hard ions in the mean spherical approximation (MSA) can be expressed in terms of overlap functions of charged spherical shells. In particular, if the system is a mixture of pairs of ions of equal size and opposite charge, then the MSA direct correlation function is given by the electrostatic energy of a pair of charged shells, of radius equal to the radius of the hard ion plus $1/(2T)$. This direct correlation function can be derived from a free energy functional, and a simple extension to nonuniform systems is given.

KEY WORDS: Ionic fluids; mean spherical approximation; inhomogeneous fluids; scaled particle theory.

1. INTRODUCTION

It is with great pleasure that we contribute this paper to the issue in honor of Jerry Percus, truly one of the founding fathers of modern liquid theory. The research described below has originated from one of Jerry's seminal papers⁽¹⁾ and discusses an application to ionic fluids theory, also pioneered by him.^(2,3)

Liquid-state theories like the MSA and the HNC can be derived as variational problems of the free energy functional, which is written in terms of the Ornstein–Zernike direct correlation function and interpolates between the low-coupling Mayer and high-coupling Onsager limits. This view, as recently taken by one of us,^(4–6) for systems of hard objects in

¹ Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931-3343.

² Nuclear Research Center-Negev, Beer-Sheva, Israel.

general, and hard spheres in particular, uncovered interesting relations between the grand potential, the direct correlation function, and the scaled particle theory. In this work we begin to extend this analysis to the case of charged hard spheres in general, and the primitive model of electrolytes in particular.

The asymptotic limit of strong Coulomb interactions between the charged particles, that is, the limit in which either the charge goes to infinity or the temperature goes to zero, is the starting point of our present discussion⁽⁷⁻⁹⁾: The free energy and the internal energy diverge to the same order in the coupling parameter, while the entropy diverges at a slower rate. In this asymptotic limit, the free energy and the energy coincide, and furthermore, the mean spherical approximation (MSA) and the hypernetted chain approximation (HNC) coincide. This is a very gratifying feature, because the HNC, which from the diagram expansion point of view (and numerous test cases) is the more accurate theory, is in general difficult to solve numerically, while the MSA is analytical in most cases, and in the asymptotic limit, of a rather surprisingly simple form. In the asymptotic limit the excess electrostatic energy is identical to the exact *Onsager lower bound*, which is achieved by immersing the entire hard-core system in an infinite neutral and perfectly conducting (liquid metal) fluid. The Onsager process of introducing the infinite conductor naturally decouples all the components in the system which may differ in size, shape, charge distribution, and relative orientation in space. As a result, the variational free energy functional in the high-coupling limit diagonalizes, and the mathematical solution of the asymptotic problem is given in terms of geometrical properties of the individual particles in the system.

As an illustration, consider the charges induced on the surface of each particle when placed in an infinite conductor. Then the direct correlation function in the asymptotic strong-coupling limit (Onsager picture) is obtained directly from the electrostatic interaction of the charges of the particles smeared on the surface of those particles. The calculation of the bridge function (the part missing in the HNC approximation) involves the construct of *Onsager molecules* for the potential of mean force. Another asymptotic limit is the *high-density limit*, in which the compressibility tends to zero because of the tight packing of the particles. In this case the MSA solution is also obtained from a simple geometric argument by computing the overlap volume of the particles as a function of their distance and their relative orientation. These two distinct limits provide the set of basis functions for the representation of the direct correlation function, which can be shown to be sufficient to represent the dcf of the complete MSA solution. In other words, these two limits provide the full *functional basis set* for the exact solution of the MSA equations and also an asymptotic

approximation of the HNC solution for all densities and temperatures, for hard charged objects. This enables us to replace a functional variational problem by a variational problem in which the basis functional set is fixed, and known, and where we only need to find the weights of the basis functions. The asymptotic Onsager state of the system is essentially the analog of the diagonalizable reference Hamiltonian of quantum mechanics when the Schrödinger equation has to be solved. In our case the basis functions for the functional expansion of the direct correlation function are obtained from linear combinations of overlap functions, such as the volume, the surface, and the convex radius, and the electrostatic interaction between surface smeared charges. The full solution is obtained by associating free parameters with various parts of the basis functions. By proper manipulation of the free parameters, and by a judicious selection of the basis set of trial functions, one can obtain, as in quantum mechanics, different levels of approximations. The physically intuitive meaning of the basis functions in the representation of the dcf is particularly illuminating in the formulation of perturbation treatments. The use of the asymptotic basis set of functions ensures that at all levels of the perturbation approximation, the resulting free energy has the desired property of interpolating between two exact lower bounds, the Debye–Hückel result (which is effective at weak coupling) and the Onsager result (which is effective at high coupling). These two limits pin the free energy.

The Onsager approach to charged hard-particle systems, as outlined above, has been developed for plasmas of various kinds (charges of one sign, with no hard-core excluded-volume constraints, and in a uniform neutralizing background of opposite sign), and for uncharged hard-particle systems in both the uniform and nonuniform cases. These two cases provide the basis for the treatment of the more general case of the charged hard-particle system. As it has been shown in the case of the nonuniform hard particles, this new approach provides an excellent starting point for the quantitative discussion of inhomogeneous uncharged hard-sphere systems.^(5,6) The interpolation between the low- and high-density limits, which is inherent to this variational approach, leads in a very natural way to the scaled particle⁽¹⁰⁾ theory for the structure and thermodynamics of isotropic fluids of hard particles.

A free energy density functional for the inhomogeneous hard-sphere fluid was constructed, based on fundamental geometric measures of the particles. It provides the first *unified derivation* of the most comprehensive analytic description available of the hard-sphere thermodynamics and pair distribution functions as given by the Percus–Yevick and scaled particle theories, and yields simple explicit expressions for the higher direct correlation functions of the uniform fluid.

The present work makes the first step in extending this approach to charged hard spheres. Following the steps of the above theory for neutral hard spheres, we show that the seemingly complex dcf for the MSA of ionic mixtures obtained by Hiroike⁽¹¹⁾ can be written in terms of the basis functions mentioned above. We then provide more insight into the nature and physical meaning of the solution as represented in the resulting free energy. Finally we point out possible directions along which free energy models of the inhomogeneous fluid can be constructed.

2. DIRECT CORRELATION FUNCTIONS IN TERMS OF GEOMETRY AND ELECTROSTATICS

We consider an arbitrary mixture of charged hard spheres. The general solution of the MSA⁽¹²⁾ yields simple expressions for the thermodynamics and pair correlation functions. The dcf was obtained by Hiroike⁽¹¹⁾: For a system of hard spheres of radius $R_i = \sigma_i/2$, charges z_i , and number density $\rho_i = \mathcal{N}_i/V$, the dcf $c_{ij}(r)$ can be written

$$c_{ij}(r) = c_{ij}^{\text{HS}}(r) + \gamma_0 c_{ij}^{\text{charge}}(r) \quad (1)$$

where

$$\gamma_0 = \frac{e^2}{\epsilon_0 k_B T} \quad (2)$$

is the Landau length of the system, measuring the relative importance of the electrostatic contributions. When $\gamma_0 = 0$, that is, when either the dielectric constant ϵ_0 or the temperature T go to ∞ , or when the charges are shut off by formally letting the electron charge e to be zero, the system corresponds to a neutral uncharged hard-sphere mixture for which the dcf $c_{ij}^{\text{HS}}(r)$ is that of the Percus–Yevick theory. An important step in constructing a free energy model for the hard-sphere mixture begins by casting the known $c_{ij}^{\text{HS}}(r)$ in geometric form⁽⁴⁾

$$-c_{ij}^{\text{HS}}(r) = \chi^{(3)} \Delta V_{ij}(r) + \chi^{(2)} \Delta S_{ij}(r) + \chi^{(1)} \Delta R_{ij}(r) + \chi^{(0)} \Theta_{ij}(r) \quad (3)$$

obeying the MSA closure

$$c_{ij}^{\text{HS}}(r > R_i + R_j) = 0 \quad (4)$$

For two spheres of radii R_i and R_j at a distance r , $\Delta V_{ij}(r)$ is the overlap volume, $\Delta S_{ij}(r)$ is the overlap surface area,

$$\begin{aligned} \Delta R_{ij}(r) &= \theta[r - (R_i + R_j)][R_i + R_j - (\text{mean radius of convex} \\ &\quad \text{envelope of the union of two spheres})] \\ &= \frac{\Delta S_{ij}(r)}{4\pi(R_i + R_j)} + \theta[r - (R_i + R_j)] \frac{R_i R_j}{R_i + R_j}, \end{aligned} \tag{5}$$

and $\Theta_{ij}(r) = \theta[r - (R_i + R_j)]$.

with

$$\chi^q = \frac{\partial \Phi^{\text{HS}}[(\xi_m)]}{\partial \xi_3 \partial \xi_q} \tag{6}$$

where

$$\chi^{(0)} = \frac{1}{1 - \xi_3}, \tag{7}$$

$$\chi^{(1)} = \frac{\xi_2}{(1 - \xi_3)^2}, \tag{8}$$

$$\chi^{(2)} = \frac{\xi_1}{(1 - \xi_3)^2} + \frac{(1/4\pi)\xi_2^2}{(1 - \xi_3)^3}, \tag{9}$$

$$\chi^{(3)} = \frac{\xi_0}{(1 - \xi_3)^2} + \frac{2\xi_1\xi_2}{(1 - \xi_3)^3} + \left(\frac{1}{4}\pi\right)\xi_2^3 \frac{1}{(1 - \xi_3)^4}, \tag{10}$$

are the inverse compressibility coefficients in the expansion

$$\chi_i = \sum_q \chi^q[(\xi_m)] R_i^q = \frac{\partial(P/k_B T)}{\partial \rho_i} \tag{11}$$

and ξ_q are the fundamental measure variables

$$\xi_q = \sum_i \rho_i R_i^q \tag{12}$$

with $R_i^q = V_i, S_i, R_i, 1$ for $q = 3, 2, 1, 0$, respectively.

Our first step is to rewrite the dcf of the MSA as written by Hiroike in terms of the geometric and/or electrostatic forms, for the charge part $c_{ij}^{\text{charge}}(r)$. We shall present expressions for core overlap configurations $r \leq (R_i + R_j)$, recalling that the MSA closure is

$$c_{ij}^{\text{charge}}(r) = \frac{-Z_i Z_j}{r}, \quad r > R_i + R_j \tag{13}$$

After some manipulations, Hiroike's dcf can be cast in the form

$$c_{ij}^{\text{charge}}(r) = (4/\pi)\eta^2 \Delta V_{ij}(r) + 4R_i R_j [\eta(X_i + X_j) - N_i N_j] \Psi_{ij}(r) + 2(N_i X_j - \eta \sigma_i X_j) \Theta_{ij}(r) \quad (14)$$

where $\Psi_{ij}(r)$ is the electrostatic interaction of two charged hard spheres of unit charge smeared on the surface. The spheres are of radius R_i, R_j and they are separated by a distance r . The other parameters of the direct correlation functions are given in terms of a scaling parameter Γ ,⁽¹²⁾ the sizes and charges of the hard spheres, and their concentrations. A new system parameter η , is defined by

$$\eta = \sum_i \frac{\rho_i \sigma_i z_i}{1 + \Gamma \sigma_i} \left[\frac{1}{(2/\pi)(1 - \zeta_3) + \sum_j [\rho_j \sigma_j^3 / (1 + \Gamma \sigma_j)]} \right]. \quad (15)$$

This parameter is related to the symmetry of the solution: In the restricted case, in which all the diameters of the ions are equal, $\eta = 0$. A less restrictive case, in which pair of ions have the same diameter, which, however, may change from pair to pair, also yields η equal to zero. In terms of these parameters we get

$$X_i = \frac{z_i - \eta \sigma_i^2}{1 + \Gamma \sigma_i} \quad (16)$$

$$N_i = -\frac{\Gamma z_i + \eta \sigma_i}{1 + \Gamma \sigma_i} \quad (17)$$

The important single parameter of the solution is the capacitance length $(2\Gamma)^{-1} = \lambda_c$, whose role and name will become apparent when we will discuss the thermodynamics of the system in the next section. Before we proceed, however, note that the prefactor of Θ_{ij} in Eq. (14) is also symmetric,

$$-\sigma_i X_j \eta + N_j X_i = -(\eta \sigma_i X_j + \eta \sigma_j X_i + \Gamma X_j X_i) \quad (18)$$

Unlike the case of the neutral hard spheres, where there is a unique way of writing down the dcf, because of the fact that $\Psi_{ij}(r)$ can be written as a linear combination of the geometric overlap functions, there is no unique way to perform the factorization of the charge dcf. This is in part one of the technical problems that need to be overcome. Specifically, the following relations are true:

$$R_i R_j \Psi_{ij}(R_i, R_j; r) = (R_i + d_i)(R_j + d_j) \Psi_{ij}(R_i + d_i, R_j + d_j; r) \begin{cases} -d_i, & r < R_j - R_i \\ -(d_i + d_j)/2, & r > R_j - R_i \end{cases} \quad (19)$$

for any positive d_i, d_j ,

$$\Psi_{ij}(R_i; R_j) = \frac{\Delta R_{ij}}{R_i R_j} = \frac{\Delta S_{ij}}{4\pi R_i R_j (R_i + R_j)} + \frac{\Theta_{ij}}{R_i + R_j} \quad (20)$$

and

$$2(N_j X_i - \eta \sigma_i X_j) = \frac{-(2N_j)(2N_i)}{2\Gamma} + \frac{(2\eta \sigma_j)(2\eta \sigma_i)}{2\Gamma} \quad (21)$$

We can also write for core overlap configurations

$$c_{ij}^{\text{charge}}(r) = \frac{4}{\pi} \eta^2 \Delta V_{ij}(r) + \frac{4[\eta(X_i + X_j) - N_i N_j]}{4\pi(R_i + R_j)} \Delta S_{ij}(r) + \frac{X_i X_j}{R_i + R_j} \Theta_{ij}(r) \quad (22)$$

or, if we take into account the boundary condition of the MSA Eq. (13) and in view of the Onsager limit, we can write

$$c_{ij}^{\text{charge}}(r) = -z_i z_j \Psi_{ij}(r) + \frac{4}{\pi} \eta^2 \Delta V_{ij}(r) + \frac{4[\eta(X_i + X_j) - N_i N_j]}{4\pi R_i R_j (R_i + R_j)} \Delta S_{ij}(r) + \frac{z_i z_j}{R_i R_j} R_{ij}(r) + \frac{X_i X_j}{R_i + R_j} \Theta_{ij}(r) \quad (23)$$

Recalling the results for uncharged hard spheres, we see that independently of the particular decomposition in terms of geometric electrostatic basis “weighted densities” characterizing the geometry of individual particles play the same vital role in the present “charged” case. In the uncharged case we had the scaled particle theory as a guide, and we followed the MSA-compressibility route to the thermodynamics. For the “charge part” we must follow the energy route, so that the result is in a mixed representation, which is more cumbersome.

3. THERMODYNAMICS: INTERPOLATION BETWEEN THE ONSAGER AND DEBYE-HÜCKEL LOWER BOUNDS FOR THE FREE ENERGY WITH A VARIATIONAL CAPACITANCE LENGTH

We denote by

$$A^{\text{charge}} = A - A^{\text{HS}} \quad (24)$$

the contribution of the charge to the Helmholtz free energy of the system, in our case, the general mixture of hard spheres. The following relations hold for the MSA:

$$U^{\text{charge}}/N = (1/2) \left[\sum_i \rho_i c_{ii}^{\text{charge}}(0)/\rho + \chi^{\text{charge}} \right] \quad (25)$$

where U/N is the potential energy per particle, and χ is the inverse compressibility, $[\partial(P/k_B T)/\partial\rho]_T$, obtained from the direct correlations function, and

$$F^{\text{charge}}/N = U^{\text{charge}} + 1/2\chi^{\text{charge}} - \beta P_{\text{ex}}^{\text{charge}}/\rho \quad (26)$$

where F is the excess free energy obtained from the "energy" way, that is, integrating $U = \beta \partial F/\partial\beta$, and P_{ex} is the pressure obtained from the thermodynamic relation $\beta P_{\text{ex}}/\rho = \rho \partial(F_{\text{ex}}/N)/\partial\rho$. We also use the definition $\Phi = \rho f = F/V$, the excess free energy per unit volume. The following results were obtained:

$$\chi^{\text{charge}} = -(4/\pi)\eta^2\gamma_0 \quad (27)$$

$$E^{\text{charge}} \equiv \frac{U}{N} = -\gamma_0 \sum_i \rho_i \left(\frac{z_i^2 \Gamma}{1 + \Gamma\sigma_i} + \frac{z_i \sigma_i \eta}{1 + \Gamma\sigma_i} \right) \quad (28)$$

$$\beta P^{\text{charge}} = -(\Gamma^3/3\pi + 2\eta^2\gamma_0/\pi) \quad (29)$$

$$\Phi^{\text{charge}} = E^{\text{charge}} + k_B T \Gamma^3/3\pi \quad (30)$$

where the parameters Γ and η are determined from

$$\Gamma^2 = \pi\gamma_0 \sum_i \rho_i \left(\frac{z_i - \eta\sigma_i^2}{1 + \Gamma\sigma_i} \right)^2 \quad (31)$$

and η was defined previously, Eq. (15).

Consider first the case when $\eta = 0$. We make the following observations:

(a) The potential energy (28) is given by the sum of the self-energies of spherical capacitors, with an effective characteristic radius b_i . In fact,

$$E^{\text{charge}} \equiv \frac{U}{N} = \left(-\frac{\gamma_0}{V} \right) \sum_i N_i \frac{z_i^2}{2C_i} \quad (32)$$

where the capacitance is

$$C_i = b_i = R_i + \frac{1}{2\Gamma} \quad (33)$$

and N_i is the number of ions i .

(b) The capacitance length, the MSA analog of the Debye length, is $\lambda_c \equiv 1/(2\Gamma)$, and is found by *optimizing* the free energy

$$\frac{\partial \Phi^{\text{charge}}}{\partial \Gamma} = 0 \tag{34}$$

which turns out to be exactly equivalent to Eq. (31), also in the more general case in which $\eta \neq 0$.

These results reveal the physical meaning of the MSA solution as an interpolation between two exact lower bounds, the Debye lower bound, effective when $\gamma_0 \rightarrow 0$, and the Onsager bound, effective for $\gamma_0 \rightarrow \infty$. This interpolation is achieved by a variational free energy functional, which has the parameter $\lambda_c = 1/(2\Gamma)$, the capacitance length, as the variational parameter. With *hindsight* we can construct the MSA solution for $\eta = 0$ using only dimensional analysis, as follows: (a) Write the excess free energy density in the general form

$$\Phi^{\text{charge}} = \gamma_0 \mathcal{U}(\lambda_c) + S(\lambda_c) \tag{35}$$

where the expression for the energy density

$$\gamma_0 \mathcal{U} = -\frac{e^2}{2\epsilon_0 k_B T} \sum_i \rho_i \frac{z_i^2}{R_i + \lambda_c} \tag{36}$$

defines the role of this system averaged length scale λ_c , and where we have assumed that the entropy term $S(\lambda_c)$ depends only on λ_c . This is an important assumption, and as a result, and in order to have the correct dimensionality of $[\Phi]$, we write

$$S(\lambda_c) = A\lambda_c^{-3} \tag{37}$$

where A is a constant to be determined by adjusting the behavior at low concentrations to the Debye-Hückel picture. The variational equation (34), $\partial \Phi^{\text{charge}}/\partial \lambda_c = 0$, yields

$$\lambda_c^{-4} = -\frac{1}{6A} \frac{e^2}{\epsilon_0 k_B T} \sum_i \rho_i \frac{z_i^2}{(R_i + \lambda_c)^2} \tag{38}$$

In the limit γ_0 we expect the Debye-Hückel result to hold. This limit corresponds to $\lambda_c \rightarrow \infty$, which yields

$$\lambda_c^{-2} = -\frac{1}{6A} \frac{e^2}{\epsilon_0 k_B T} \sum_i \rho_i z_i^2 \tag{39}$$

from which we see that $A = 1/24\pi$.

For uncharged hard spheres we have already gained enough insight to enable us to derive the complete solution of the MSA (which is really the Percus–Yevick hard-sphere approximation) directly from the functional free energy model with a limited basis function set. It is very desirable to have a similar model for charged hard particles. This will have important consequences also for plasmas. Analysis of the uncharged case revealed the particular fine tuning which happens to occur only in three dimensions to be able to satisfy the core condition $g(r < R_i + R_j) = 0$ exactly. So, although it will be very nice if eventually we understand how to obtain it from a free energy model, we can also gain insight from the MSA solution in order to explore the free energy models for inhomogeneous systems.

4. FREE ENERGY MODELS FOR NONUNIFORM MIXTURES OF CHARGED HARD SPHERES

The Helmholtz free energy F is the sum of two contributions, a term due to the excluded-volume effects of the hard spheres F^{HS} and the charge term F^{charge} , which usually will include cross terms of charge and excluded volume (cavity effects),

$$F = F^{\text{HS}} + F^{\text{MSA}} \quad (40)$$

Similarly to the hard-sphere term that was discussed in detail in the original work of Rosenfeld,^(4,6) the “charge” term can be written, for the general inhomogeneous system,

$$F^{\text{MSA}} = \int d\mathbf{r}_1 \Phi^{\text{charge}}(\mathbf{r}_1) \quad (41)$$

where $\Phi^{\text{charge}}(\mathbf{r})$ is the local Helmholtz free energy per unit volume. The mean spherical approximation (MSA) yields in the homogeneous bulk phase^(11–13)

$$\Phi^{\text{charge}} \simeq \Phi^{\text{MSA}} = E^{\text{charge}} + k_B T \Gamma^3 / 3\pi \quad (42)$$

The parameter η , Eq. (15), is generally small for ionic solutions, and is zero for the restricted case of ions of only one diameter, and also when neutral pairs of ions are of the same size. The parameter Γ is obtained from the optimization condition

$$\frac{\partial \Phi^{\text{charge}}}{\partial \Gamma} = 0 \quad (43)$$

which, after some algebra, turns out to be exactly equivalent to the equation obtained directly from the boundary conditions of the MSA.^(12,13) The

energy in the MSA is the sum of the energies of spherical capacitors of capacitance⁽¹⁴⁾ $C_i = b_i$ also for nonprimitive models of electrolytes.

Consider the total internal energy

$$U^{\text{MSA}} = \int d\mathbf{r}_1 E^{\text{MSA}}(\mathbf{r}_1) \tag{44}$$

where $E^{\text{MSA}}(\mathbf{r}_1)$ is the local internal energy.

Consider now the interaction of two charged shells of radii b_i, b_j , with centers at positions $\mathbf{r}_1, \mathbf{r}_2$. From simple electrostatics we know that

$$\Psi_{i,j}(b_i, b_j; \mathbf{r}_{12}) = (1/2) \int d\mathbf{r}_3 q_i(\mathbf{r}_1 - \mathbf{r}_3) \phi_j(\mathbf{r}_3 - \mathbf{r}_2), \quad \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 \tag{45}$$

where the electrostatic potential ϕ is defined by

$$\phi_j(\mathbf{r}_{32}) = \int d\mathbf{r}_4 \frac{q_j(\mathbf{r}_4)}{|\mathbf{r}_{32} - \mathbf{r}_4|} \tag{46}$$

The charge density of the shells is

$$q_i(\mathbf{r}) = \frac{z_i}{4\pi b_i^2} \delta(|\mathbf{r}| - b_i) \tag{47}$$

The total energy is approximated by

$$\beta U^{\text{MSA}} = -(1/2)\gamma_0 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{i,j} \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2) \Psi_{i,j}(b_i, b_j; \mathbf{r}_{12}) \tag{48}$$

Consider again the interaction of the spherical shells, Eq. (45): When they overlap we get

$$\Psi_{i,j}(b_i, b_j; \mathbf{r}) = \frac{z_i z_j}{b_i b_j r} [(b_i - b_j)^2 - 2r(b_i + b_j) + r^2] \tag{49}$$

If we rearrange this expression, we obtain

$$\beta U^{\text{MSA}} = -(1/2)\gamma_0 \int d\mathbf{r}_3 \sum_{i,j} Q_i(\mathbf{r}_3) \Phi_j(\mathbf{r}_3) \tag{50}$$

where

$$Q_i(\mathbf{r}_3) = \int d\mathbf{r}_1 \rho_i(\mathbf{r}_1) q_i(\mathbf{r}_1 - \mathbf{r}_3) \tag{51}$$

and

$$\Phi_j(\mathbf{r}_3) = \int d\mathbf{r}_2 \rho_j(\mathbf{r}_2) \phi_j(\mathbf{r}_3 - \mathbf{r}_2) \quad (52)$$

For uniform systems, Eq. (50) is just equal to the starting equation (28). In fact, simple integration of Eqs. (51) and (52) with Eq. (48) yields

$$Q_i(\mathbf{r}_3) = z_i \rho_i \quad (53)$$

and

$$\Phi_j(\mathbf{r}_3) = -2N_j \quad (54)$$

(assuming $\eta = 0$).

We recall now the relation between the Helmholtz free energy and the direct correlation function

$$c_{i,j}^{\text{MSA}}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\delta^2 \beta F^{\text{MSA}}}{\delta \rho_i(\mathbf{r}_1) \delta \rho_j(\mathbf{r}_2)} \quad (55)$$

Functional differentiation will yield

$$c_{i,j}^{\text{MSA}}(\mathbf{r}_1, \mathbf{r}_2) = (1/2) \gamma_0 \Psi_{i,j}(b_i, b_j; \mathbf{r}_{12}) \quad (56)$$

which is equal to the direct correlation function first derived by Hiroike⁽¹¹⁾ for $\eta = 0$, but considerably simpler.

Equation (56) is a possible extension of the MSA direct correlation function to inhomogeneous systems. To a first approximation we may take the bulk value of Γ , although refinements are possible. The pair correlation functions which are computed from the Ornstein-Zernike equation can be shown to satisfy the local electroneutrality condition.⁽¹⁵⁾

Recall that the MSA direct correlation function can be written as convolutions, Eqs. (3) and (22), which suggest forms based on generalizations of the hard-sphere formalism,⁽⁵⁾

$$F^{\text{HS}}/Vk_B T = \int d\mathbf{r} \Phi[\{n_\alpha(\mathbf{r})\}] \quad (57)$$

where $n_\alpha(\mathbf{r})$ are the system-averaged fundamental measures of the particles. For example,

$$n_2(\mathbf{r}) = \sum_i \int d\mathbf{r}_1 \rho_i(\mathbf{r}_1) \delta(|\mathbf{r} - \mathbf{r}_1| - R_i) \quad (58)$$

represents the system-averaged density, i.e.,

$$\omega_i^{(2)}(\mathbf{r}) = \delta(|\mathbf{r}| - R_i) \tag{59}$$

represents the characteristic function for the surface of a sphere of radius R_i , centered at the origin.

We introduce now the characteristic functions for spheres of displaced radius b_i , Eq. (33),

$$\omega_{b_i}^{(2)}(\mathbf{r}) = \delta(|\mathbf{r}| - b_i) \tag{60}$$

and corresponding weighted charge densities

$$n_2^b(\mathbf{r}) = \sum_i \int d\mathbf{r}_1 \rho_i(\mathbf{r}_1) z_i \omega_{b_i}^{(2)}(\mathbf{r} - \mathbf{r}_1) \tag{61}$$

We remark that now the internal energy (44) can be written

$$\beta U^{\text{MSA}} = \int d\mathbf{r}_1 \int d\mathbf{r} \frac{n_2^b(\mathbf{r}) n_2^b(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} \tag{62}$$

and will also yield Eq. (56) upon functional differentiation. [Note that Eq. (62) still needs further adjustments to the uniform limit, for the case $\eta \neq 0$.]

The forms (48) and (62) represent two possible free energy functional forms which follow from the convolution geometric picture of the MSA solution for the pair direct correlation function (dcf). Other generic forms are possible in view of the different equivalent forms for c_{ij} , as given in Section 3. Having the uniform fluid dcf's in a geometric form enables us to build a "weighted density" approximate free energy functional for the nonuniform fluid which is either (i) tailored to the *detailed* analytic properties of the uniform limit, or (ii) derives the uniform limit from more general principles. Both these possibilities are advantageous with respect to the usual applications of the weighted density ideas. Stage (ii) was already achieved for the hard spheres, while the "charge part" of the problem is still in stage (i), as represented in the example above. From the results of Section 2 and the Rosenfeld derivation of the functional for nonuniform, hard spheres, it seems that many (if not all) details of the Hiroike dcf of the MSA can be obtained directly from Eq. (55), by imposing several constraints on a generic form for the free energy functional. For example, one may seek the extensions to nonuniform systems of the simple interpolation formulas of Section 3.

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