**THE DIRECT CORRELATION FUNCTION OF A MIXTURE OF HARD IONS
IN THE MEAN SPHERICAL APPROXIMATION**

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1 Abstract

It is shown that the direct correlation function of a mixture of hard ions in the mean spherical approximation of Hiroike [1],(MSA) can be expressed in terms of overlap functions of charged spherical spherical shells. In particular, if the system has 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 $\frac{1}{2\Gamma}$. As in the theory of Rosenfeld [2] this direct correlation function can be derived from a free energy functional, and a simple extension to non-uniform systems is given.

2 Introduction

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 . This view was recently introduced by one of us [2, 3, 4], for systems of hard objects in general, and hard spheres in particular . In that work the relation between the grand potential, the direct correlation function and the scaled particle theory was clearly shown. We extend now this analysis to the case of charged hard spheres in general, and to 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 [5, 6]: In this limit the free energy and the internal diverge to the same order in the the coupling parameter while the entropy diverges at a slower rate and therefore the free energy and the energy coincide. 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 (and numerous test cases) point of view 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 different components in the system which may differ in size, shape, charge distribution an 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. This novel approach is based on the finding that both the weak and strong coupling solutions of the HNC equation are bounded from below by these limits. This is an exact new result. 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 an uniform neutralizing background of opposite sign), and for uncharged hard particle systems both in the uniform an non uniform cases. These two cases provide the basis for the treatment of the more general cae of the charged hard particle system. As it has been shown in the case of the non-uniform hard particles, this new approach provides an excellent starting point for the quantitative discussion of inhomogeneous uncharged hard sphere systems. We show that the MSA free energy is the appropiate functional from which the charge part of the direct correlation function is obtained by functional differentiation. This also suggests a simple extension of the pair MSA to inhomogeneous charged systems.

3   Direct Correlation Functions in Terms of Geometry and Electroststics

Consider an arbitrary mixture of charged hard spheres of radius $R_i = \sigma_i/2$, charge z_i and number density $\rho_i = N_i/V$. The temperature is T and Boltzmann's constant is k_B. We use the notation $\beta = \frac{1}{k_B T}$. We can imagine that the charges in our system can be turned on gradually: Then, the Helmholtz free energy F is the sum of two contributions, a term due to the excuded volume effects of the hard spheres F^{hs} and a term due to the charges F^{ch}, which usually will include cross terms of charge and excluded volume

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(cavity effects).

$$F = F^{hs} + F^{MSA} \tag{1}$$

The hard sphere term was discussed in detail in the original work of Rosenfeld [2, 3, 4], and can be written, for the general inhomogeneous system

$$F^{MSA} = \int d\mathbf{r}_1 \Phi^{ch}(\mathbf{r}) \tag{2}$$

where $\Phi^{ch}(\mathbf{r})$ is the local Helmholtz free energy per unit volume. In this note we use the mean spherical approximation (MSA) to compute this magnitude: In the homogeneous bulk phase [1, 8]

$$\Phi^{ch} \simeq \Phi^{MSA} = E^{charge} + \Gamma^3/3\pi \tag{3}$$

where the local internal energy per unit volume is

$$\beta E^{charge} = \gamma_0 \sum_i \rho_i z_i N_i \tag{4}$$

with

$$\gamma_0 = \frac{e^2}{\epsilon_0 k_B T} = \frac{\beta e^2}{\epsilon_0} \tag{5}$$

In this equation the parameter N_i represents on half of the potential of a spherical shell of radius $b_i = R_i + 1/2\Gamma$. This energy is the sum of the energy of a collection of uncorrelated spherical capacitors of radius b_i. We could use the Onsager picture of spherical shells in liquid metal to represent this system.

$$N_i = -\frac{\Gamma z_i^*}{1 + \Gamma \sigma_i} \tag{6}$$

where the effective charge is

$$z_i^* = z_i + \eta \sigma_i \tag{7}$$

and η is defined by

$$\eta = \frac{\sum_i \frac{\rho_i \sigma_i z_i}{1 + \Gamma \sigma_i}}{(2/\pi)(1 - \xi_3) + \sum_i \frac{\rho_i \sigma_i^3}{1 + \Gamma \sigma_i}} \tag{8}$$

with

$$\xi_3 = (\pi/6) \sum_i \rho_i R_i^3 \tag{9}$$

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The parameter η 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 paramenter Γ is obtained from the optimization condition

$$\frac{\partial \Phi^{ch}}{\partial \Gamma} = 0 \qquad (10)$$

which turns out to be exactly equivalent to the equation obtained directly from the boundary conditions of the MSA [7, 8]. The energy in the MSA can be considered as the sum of the energies of spherical capacitors of capacitance $C_i = b_i$[9]. The extension of 4 to non uniform systems is quite straightforward. Consider the total internal energy U

$$U^{MSA} = \int d\mathbf{r}_1 E^{MSA}(\mathbf{r}_1) \qquad (11)$$

where the local internal energy is

$$\beta E^{MSA}(\mathbf{r}) = \gamma_0 \sum_i \rho_i(\mathbf{r}) z_i N_i \qquad (12)$$

We rewrite this equation using the charge neutrality sum rule [10, 11, 12] for the inhomogeneous system

$$- z_i = \int d\mathbf{r}_1 \sum_j \rho_j(\mathbf{r}_1) z_j h_{ij}(\mathbf{r}_1, \mathbf{r}_2) \qquad (13)$$

Here the function h_{ij} prevents the overlap of ions. In the Onsagerian picture of the MSA, the plausible form of this function corresponds to completely uncorrelated distribution function for non overlapping pairs. Therefore this function is -1 when the distance $r < \sigma_{ij}$, and zero otherwise. Substituting 13 into 11 yields

$$\beta U^{MSA} = -\gamma_0 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{i,j} z_i N_j \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2) h_{ij}(\mathbf{r}_1, \mathbf{r}_2) \qquad (14)$$

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

$$\Psi_{i,j}(b_i, b_j; \mathbf{r}_{12}) = (1/2) \int d\mathbf{r}_3 q_i(\mathbf{r}_1 - \mathbf{r}_3) \phi_j(\mathbf{r}_3 - \mathbf{r}_2) \qquad \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 \quad (15)$$

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where the electrostatic potential ϕ is defined by

$$\phi_j(\mathbf{r}_{32}) = \int d\mathbf{r}_4 \frac{q_j(\mathbf{r}_4)}{|\mathbf{r}_{32} - \mathbf{r}_4|} \tag{16}$$

The charge density of the shells is

$$q_i(\mathbf{r}) = \frac{z_i}{4\pi b_i^2} \delta(|\mathbf{r}| - b_i) \tag{17}$$

The total energy is given by 14

$$\beta U^{MSA} = -(1/2)\gamma_0 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{i,j} \rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_2)\Psi_{i,j}(b_i, b_j; \mathbf{r}_{12}) \tag{18}$$

where we have made use of the extension of the electroneutrality relation 13 to the case of smeared charge distributions. Consider again the interaction of the spherical shells 15: When they overlap we get

$$\Psi_{i,j}(b_i, b_j; \mathbf{r}) = \frac{z_i z_j}{b_i b_j r}[(b_i - b_j)^2 - 2r(b_i + b_j) + r^2] \tag{19}$$

If we rearrange this expression, we obtain

$$\beta U^{MSA} = -(1/2)\gamma_0 \int d\mathbf{r}_3 \sum_{i,j} Q_i(\mathbf{r}_3)\Phi_j(\mathbf{r}_3) \tag{20}$$

where

$$Q_i(\mathbf{r}_3) = \int d\mathbf{r}_1 \rho_i(\mathbf{r}_1)q_i(\mathbf{r}_1 - \mathbf{r}_3) \tag{21}$$

and

$$\Phi_j(\mathbf{r}_3) = \int d\mathbf{r}_2 \rho_j(\mathbf{r}_2)\phi_j(\mathbf{r}_3 - \mathbf{r}_2) \tag{22}$$

For non-overlapping configurations and spatially uniform systems 20 is just equal to the starting equation 4. In fact, simple integration of 21 and 22 with 17 yields

$$Q_i(\mathbf{r}_3) = z_i \tag{23}$$

and

$$\Phi_j(\mathbf{r}_3) = -2N_j \tag{24}$$

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

$$c_{i,j}^{MSA}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\delta^2 \beta F^{MSA}}{\delta \rho_i(\mathbf{r}_1)\delta \rho_j(\mathbf{r}_2)} \tag{25}$$

Let us now restrict to the case in which $\eta = 0$. Functional differentiation will yield

$$c_{i,j}^{MSA}(\mathbf{r}_1, \mathbf{r}_2) = (1/2)\gamma_0 \Psi_{i,j}(b_i, b_j; \mathbf{r}_{12}) \tag{26}$$

which is exactly identical to the direct correlation function first derived by Hiroike [1]

Equation 26 is the natural extension of the MSA direct correlation function to inhomogeneous sytems. 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 13. A more detailed discussion will be published in the near future.

4   Acknowledgements

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