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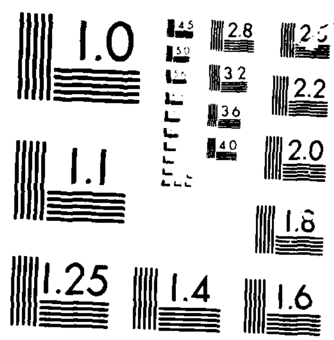
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STATISTICAL MECHANICS OF CHARGED OBJECTS: GENERAL METHOD AND APPLICATIONS TO SIMPLE SYSTEMS

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Statistical Mechanics of Charged Objects: General Method and Applications to Simple Systems

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ABSTRACT

A general variational approach to study systems composed of complex charged molecules is discussed. In this approach the variational trial functions for the free energy functionals are constructed from the asymptotic limiting (AL) forms of the direct correlation functions. A number of examples are discussed, and in each case the variational form of the direct correlation is given explicitely. The relation to Onsager's procedure of immersing the system in an infinite conducting fluid for obtaining an energy bound is discussed in detail.

Introduction

Real fluids are composed of molecules that are objects of complex geometries and charge distributions. In a previous note[(1)] we have shown that, by studying the asymptotic high density limit (AHDL) and the asymptotic strong coupling limit (ASCL) one is able to reduce the problem of computing the thermodynamics and correlation functions of the system to a geometrical calculation involving overlap integrals between the objects.

In previous work[2,3] a simple geometrical, physically intuitive meaning of the direct correlation functions (dcf) for point charges in a background[3,4] (as interactions between smeared charges) and hard spheres (as overlap volumes) within the mean spherical approximation (MSA) was given, thus also revealing its analytic structure. As a result, the above program can be carried out completely for relatively simple systems (as e.g. the general ionic mixture of the multicomponent plasmas[4,5]) using the MSA free energy functional which interpolates between the exact weak-(Debye-Huckel) and strong-("Onsager-type") coupling bounds for the potential energy. Though featuring fewer "idealistic" features, in view of the higher complexity of the problem, this approach was succesfuly used to analyze the "isotropic"-"nematic" transition of line-charges[2,6] and the coupling of the growth of micelles to their degree of alignment[6]. In the present communication we extend these methods to a much larger class of objects.

The proposed approach is to write down an approximate free energy functional which has to be variational with respect to the pair functions. These would be either the indirect[7] ($h_{ij}(r_{12})$) or direct[8,9] ($c_{ij}(r_{12})$) correlation functions. In order to get a convenient formalism, we have to use simple functions with physically motivated coefficients. Indeed, the direct correlation function in the asymptotic limits (AL = either AHDL, ASCL) provides such a simple instructive basis.

The approximate solutions also provide exact bounds for the free energy of system. In the present work we present a few results for simple system.

In section 2 we discuss the Mean Spherical Approximation (MSA) for hard core -Green function systems. The ASCL of the MSA and Hyphernetted Chain (HNC) are discussed in section 3. In section 4 we give the general "Onsager" solution for the charge smearing problem, which provides the basis - set functions for the MSA-HNC-ASCL problem. The variational solution by expansion in this set is discussed in section 5. Section 6 is devoted to the discussion of the PY theory for hard objects, in particular, the scaling of the direct correlation function. An interesting application to bonding and aggregation within the MSA is given in section 7. Section 8 contains a general discussion and conclusions.

2. Mean Spherical Approximation for hard-core Green's function systems

The general charged-hard-objects system to be considered (and termed hard-core-Green's-function (HCGF) system) consists of hard objects with imbedded charge distributions

$$\rho_i^*(\vec{r}) = \sum_{\ell,G} q_{i\ell G}\, \rho_{i\ell G}^*(\underset{\sim}{r}) \tag{2.1}$$

where $\rho^*_{i\ell G}$ is a normalized charge distribution of multipolarity ℓ, associated with the Green's function (GF) G, and $q_{i\ell G}$ is the corresponding coupling constant (="charge"). In this discrete representation for polydispersity, an object i of relative concentration X_i is considered distinct fron j if one of the characterizations in the tuple i = (shape, size, orientation, charge distribution) is different from that in j. In addition to the hard-core repulsion, the pair interaction between two objects i, j at a distance r is

$$\phi_{ij}(\underset{\sim}{r}) = \sum_{\ell\ell' G} \phi_{ij\,\ell G\,\ell' G}(\underset{\sim}{r}) \tag{2.2}$$

where

$$\phi_{ij\,\ell G \ell' G}(r) = q_{i\ell G}\, q_{j\ell' G} \int d\underset{\sim}{x}\, d\underset{\sim}{x}'\, \rho^*_{i\ell G}(x)\, \rho^*_{i\ell' G}(\underset{\sim}{x}')\, \phi_G(|\underset{\sim}{x}' - \underset{\sim}{x} - \underset{\sim}{r}|) \tag{2.3}$$

For example, a point monopole and a point dipole at the center of an object are represented by $\rho_{i0G} = q_{i0G}\,\delta(\underset{\sim}{x})$

and $\rho_{i1G}(\underset{\sim}{x}) = q_{i1G}(\underset{\sim}{\nabla}\cdot\delta(x)\cdot\hat{\underset{\sim}{p}})$, respectively. The Coulomb and screened-Coulomb potentials ($\phi(|x|) = 1/|x|$ and $\exp[-\lambda|x|]/|x|$ respectively in three dimensions) are the GF for the ∇^2 and $\nabla^2 - \lambda_G^2$ Liouville operators. We use the following notations: $n = (\Sigma N_i)/V$ = total number density; $\beta = 1/k_B T$ inverse temperature; overhead tildes denote Fourier transforms; "det" denotes the determinant;

D = dimensionality; $\overset{o}{\underset{\sim}{1}}$ = unit matrix δ_{ij} ; $\overset{o}{\underset{\sim}{C}}$ = matrix of dcf's with elements $n(x_i x_j)^{1/2}\tilde{C}_{ij}(k)$; $\rho_{TG} = n\sum_i x_i q_{i0G}$ total monopolar, G - type, charge density; δ_G = 0,1 according the whether $\tilde{\phi}_G(k=0)$ is finite (e.g. Yukawa) or infinite (e.g. Coulomb).

The MSA equations are obtained from the Ornstein-Zernike (OZ) relations between the direct correlation functions (dcf's) $c_{ij}(\underset{\sim}{r})$ and pair correlation functions (pcf's) $g_{ij}(\underset{\sim}{r}) = h_{ij}(\underset{\sim}{r}) + 1$,

$$h_{ij}(\underset{\sim}{r}) = c_{ij}(\underset{\sim}{r}) + n\sum_k x_k \int d\underset{\sim}{r}'\, h_{ik}(\underset{\sim}{r}-\underset{\sim}{r}')\, c_{kj}(\underset{\sim}{r}') \qquad (2.4)$$

and the closure relations:

$$g_{ij}(\underset{\sim}{r}) = 0\,, \quad \underset{\sim}{r} < \underset{\sim}{\sigma}_{ij} \qquad (2.5)$$

for the inner hard core excluded region, and

$$c_{ij}(\underset{\sim}{r}) = -\beta\,\phi_{ij}(\underset{\sim}{r}) \quad \underset{\sim}{r} > \underset{\sim}{\sigma}_{ij} \qquad (2.6)$$

in the outer hard core excluded regions. Eqs. (4) and (5) may be replaced by the variational equations:

$$\frac{\delta \mathcal{F}}{\delta c_{ij}(\underset{\sim}{r})} = 0 \qquad \underset{\sim}{r} < \sigma_{ij} \tag{2.7}$$

that ensure the vanishing of the pair correlation functions inside the exclusion region.

The MSA (or RPA) free energy functional, $\mathcal{F} = B+L$ is the sum of the MSA energy $(B + 1/2)$ and entropy $(L - 1/2)$ functionals.[10]

$$B = \frac{1}{2} n \sum_{i,j} x_i x_j \tilde{C}_{ij}(\underset{\sim}{k}=0) + \frac{1}{2} \sum_i x_i C_{ii}(\underset{\sim}{r}=0) \tag{2.8}$$

$$L = \frac{1}{2n} (2\pi)^{-D} \int d\underset{\sim}{k} \ \ln \det [\overset{\circ}{\underset{\sim}{1}} - \overset{\circ}{\underset{\sim}{C}}] \tag{2.9}$$

Let $\tilde{\mathcal{F}}_0$ denote the value of $\tilde{\mathcal{F}}$ for $\beta=0$, i.e. for the hard core system. Recall that $\tilde{\mathcal{F}}_0$ represents the compressibility factor,

$$Z = pV/NkT$$

as obtained from the PY (i.e. MSA) equation for the hard core system, via the relation [9,10]

$$\tilde{\mathcal{F}}_0 = (1/2)(Z_c - 1) \tag{2.10}$$

where Z_c denotes Z as obtained from the compressibility equation of state:

$$\left[\beta\left(\partial P/\partial n\right)_T\right]_0 = -\sum x_i c_{ii}(\underset{\sim}{r}=0) \tag{2.11}$$

If f represents the excess free energy per particle in units of kT and $f_0 = \lim_{\beta\to 0} f$, then the MSA approximation states that [10]

$$f - f_0 = \tilde{\mathcal{F}} - \tilde{\mathcal{F}}_0 \tag{2.12}$$

for the equation of state obtained from the expression for the energy of the system :

$$u = U/NkT = 1/2\ n \sum_{ij} x_i x_j \int d\underset{\sim}{r}\ g_{ij}(\underset{\sim}{r})\ \beta\ \phi_{ij}(\underset{\sim}{r}) \tag{2.13}$$

Central to our treatment below is the "Ewald" identity for any function (Ewald function) $\theta_{ij}(r)$ for which the Fourier transform $\tilde{\theta}_{ij}(\underset{\sim}{k})$ exists [4,10] :

$$1/2\ n \sum_{ij} x_i x_j \int d\underset{\sim}{r}\ g_{ij}(\underset{\sim}{r})\ \theta_{ij}(\underset{\sim}{r}) = 1/2\ n \sum_{ij} x_i x_j \int d\underset{\sim}{r}\ \theta_{ij}(\underset{\sim}{r})$$

$$- 1/2\ (2\pi)^{-D} \sum_i x_i \int d\underset{\sim}{k}\ \tilde{\theta}_{ii}(\underset{\sim}{k}) + 1/2\ (2\pi)^{-D} \sum_{ij} (x_i x_j)^{1/2} \int d\underset{\sim}{k}\ \tilde{\theta}_{ij}(\underset{\sim}{k})\ S_{ij}(\underset{\sim}{k}) \tag{2.14}$$

where the structure factors $S_{ij}(\underset{\sim}{k})$ defined by

$$n\,(x_i x_j)^{1/2}\,\tilde{h}_{ij}(\underset{\sim}{k}) = S_{ij}(\underset{\sim}{k}) - \delta_{ij} \tag{2.15}$$

are related by the OZ relations (2.4) to the the dcf's through the matrix relation

$$\hat{\underset{\sim}{S}} = (\hat{\underset{\sim}{1}} - \hat{\underset{\sim}{C}}) \tag{2.16}$$

Recalling the compressibility EOS obtained from

$$\beta\left(\partial P/\partial n\right)_T = 1 - n\sum_{ij} x_i\ x_j \int d\underset{\sim}{r}\ C_{ij}\,(\underset{\sim}{r}) \tag{2.17}$$

then, using (2.13) and (2.14) with $\Theta_{ij}(\underset{\sim}{r}) = C_{ij}(\underset{\sim}{r})$ we obtain

$$u = B[C] + 1/2 + 1/2\ n\sum_{ij} x_i x_j \int d\underset{\sim}{r}\ g_{ij}(\underset{\sim}{r})\,[C_{ij}(\underset{\sim}{r}) + \beta\phi_{ij}(\underset{\sim}{r})] \tag{2.18}$$

Therefore

$$u_{MSA} = B[C] + 1/2 \tag{2.19}$$

fom which (2.11) is obtained for systems of hard core objects upon setting $u_{MSA}=0$.

Finally note that when the total monopolar charge of the system is not zero we need , in the case when $\tilde{\phi}_G(\underset{\sim}{k}=0)=0$ (e.g.the Coulomb case), to introduce a compensating background charge density which is uniform in all space, i.e. it penetrates the hard objects. The background density is equal to $-\rho_{T,G}$. The potential energy of the system including the background is given by

$$U/NkT=1/2\; n \sum_{ij} x_i x_j \int d\underset{\sim}{r}\; h_{ij}(\underset{\sim}{r})\, \beta\, \phi_{ij}(\underset{\sim}{r}) \tag{2.20}$$

The general expression for $\beta(\partial P/\partial n)_T$ is thus given by

$$\beta(\partial P/\partial n)_T = 1 - n \sum_{ij} x_i x_j \int d\underset{\sim}{r}\; [C_{ij}(\underset{\sim}{r}) + \beta\phi_{ij}(\underset{\sim}{r})] \tag{2.21}$$

while the functional B is written as

$$B[C] = -1/2\, n \sum_{ij} x_i x_j \int d\underset{\sim}{r}\, [C_{ij}(\underset{\sim}{r}) - \beta\phi_{ij}(\underset{\sim}{r})] - 1/2 \sum_i x_i C_{ii}(\underset{\sim}{r}=0) \tag{2.22}$$

The sum over orientations, implicit in $\sum_{ij} x_i x_j$ ensures that for the HCGF systems

$$\sum_{ij} x_i x_j \int d\underset{\sim}{r}\, \phi_{ij}(\underset{\sim}{r}) = 0 \tag{2.23}$$

whenever total monopolar charge neutrality is preserved. In view of this (see 3.11) below), (2.20)-(2.22) contain (2.8), (2.13) and (2.17) as special cases.

a) Diagonalization of the variational free energy

A strong coupling (SC, superscript ∞) limit[3] for the MSA is reached when either the hard-core compressibility tends to zero, or when any of the coupling constants (the charges) tend to infinity so that the free energy is dominant by the energy term, $\mathcal{F}^{\infty} = B^{\infty}$. In either case the dcf's diverge , and in order to satisfy the non-negativity of the argument of the logarithm in L, the diverging dcf's satisfy[3,4]

$$\left[\tilde{C}^{\infty}_{ij}(\underset{\sim}{k})\right]^2 = \tilde{C}^{\infty}_{ii}(\underset{\sim}{k})\,\tilde{C}^{\infty}_{jj}(\underset{\sim}{k}) \tag{3.1}$$

$$\tilde{C}^{\infty}_{ii}(\underset{\sim}{k}) \leq 0 \tag{3.2}$$

In view of the closure (2.6) which servers as a boundary condition for the GF-potential (2.2; 2.3) these relations can be satisfied only by the following convolution type forms

$$\tilde{C}^{\infty}_{ij}(\underset{\sim}{k}) = \text{constant} \cdot \tilde{\rho}_{sm,i}(\underset{\sim}{k})\,\tilde{\rho}_{sm,j}(\underset{\sim}{k}) \quad \text{for hard core SC} \tag{3.3}$$

$$\tilde{C}^{\infty}_{ij}(\underset{\sim}{k}) = -\beta\,\tilde{\rho}_{sm,i}(\underset{\sim}{k})\,\tilde{\rho}_{sm,j}(\underset{\sim}{k})\,\tilde{\phi}_{ij}(\underset{\sim}{k}) \quad \text{for charge SC} \tag{3.4}$$

where SC denotes strong coupling.

The normalized "smearing" distributions, $\tilde{\rho}_{sm,i}(\underset{\sim}{k}=0) = 1$ are confined to the volume of the hard object i or its surface and must satisfy the MSA "boundary condition" (4). For (3.4) we specifically consider the new ("smeared" as opposed to smearing) coupling constant $q_{i\ell G}$, such that the corresponding smeared interaction between objects i and j,

$$\Psi_{ij,\ell G \ell' G'}(\underset{\sim}{r}) = q_{i\ell G}\, q_{j\ell' G'} \int_{v_i} d\underset{\sim}{x} \int_{v_j} d\underset{\sim}{x}'\; \rho_{i\ell G}(\underset{\sim}{x})\, \rho_{i\ell' G}(\underset{\sim}{x}')\, \phi_{GG'}(|\underset{\sim}{x}-\underset{\sim}{x}'-\underset{\sim}{r}|)$$

(3.5)

$$= \int_{v_i} d\underset{\sim}{x} \int_{v_j} d\underset{\sim}{x}'\; \rho_{sm,i\ell G}(\underset{\sim}{x})\, \rho_{sm,j\ell' G'}(\underset{\sim}{x}')\, \phi_{ij,\ell G,\ell' G'}(|\underset{\sim}{x}-\underset{\sim}{x}'-\underset{\sim}{r}|)$$

will satisfy the MSA boundary condition (2.6), namely

$$\Psi_{ij,\ell G,\ell' G'}(\underset{\sim}{r}) = \phi_{ij,\ell G,\ell' G'}(\underset{\sim}{r}), \quad \underset{\sim}{r} > \underset{\sim}{\sigma}_{ij} \tag{3.6}$$

Using (3.3) and (3.4) we now consider the strong coupling MSA problem, which may be posed separately for each diverging component- i.e. either hard core SC or the SC limit of any of the independent coupling constants $q_{i\ell G}$.

Inserting (3.3) into $B^{\infty}_{hc} = B_{hc}[C^{\infty}] = 0$ we find a direct generalization of the hard-spheres result[3], namely that the MSA hard-core EOS diverges when the total packing fraction,

η_T = (volume of objects/volume of system) = 1 with the dcf's satisfying

$$C^{\infty}_{ij}(\underset{\sim}{r}) \Big/ C^{\infty}_{ij}(\underset{\sim}{r}=0) = \omega_{ij}(\underset{\sim}{r}) \tag{3.7}$$

overlap volume of objects i and j with separation $\underline{r}$ divided by the overlap volume at zero separation.

In view of the additivity of the total interaction potential in terms of the independent "charges", we consider at once the most general case of strong coupling of <u>all</u> charges, although as stated above, each may be considered separately.

Inserting (3.4) into the SC-MSA functional $B[C^{\infty}]$ we obtain the Onsager-type[4,11] expression for the lower bound for the true potential energy of the system, given by (for reasons given below we prefer the "smeared" new charges $\rho_{i\ell G}$ over $\rho_{sm,i\ell G}$. This is choice of convenience and using either gives identical results).

$$\frac{1}{\beta} B\left[C^{\infty}\right] = \sum_{i\ell G} x_i \, B_{i\ell G}(\rho_{i\ell G}) \qquad (3.8)$$

$$B_{i\ell G}(\rho_{i\ell G}) = \frac{1}{2} \delta_{\ell 0} \left(\rho_{TG}/\rho^{T}_{i0G}\right) \int_{\substack{\text{all} \\ \text{space}}} d\underline{r} \left[\psi_{ii,\ell G,0G}(\underline{r}) - \phi_{ii,0G,0G}(\underline{r}) \, \delta_{G} \right]$$

$$- \frac{1}{2} \psi_{ii,\ell G,\ell G}(\underline{r}=0) \qquad (3.9)$$

The first (monopolar) term in (3.9), an Onsager background term, vanishes for globally neutral systems ($\rho_{T,G} = 0$). The second term is minus the self energy of the "smeared" charge distribution. Note the decoupling of all the components in (3.8), which is typical[2-6] to the Onsager best bound scheme and is analogous to the diagonalization of the Hamiltonian (sec Sec. V). The new "diagonal" MSA problem

$$\frac{\delta B_{i\ell G}(\rho_{i\ell G})}{\delta \rho_{i\ell G}(r)} = 0 \tag{3.10}$$

becomes an <u>electrostatics problem of finding the optimal Onsager "smeared" distributions</u>. The derivation of (3.8),(3.9) is made transparent in (b) below.

Even though a comprehensive analysis of the HNC theory for hard objects is the asymptotic strong coupling limit (ASCL) has not been performed yet, the charge strong coupling limit of the HNC can be shown to be identical to that of the MSA. Thus, the results (3.8) and (3.10) are equally valid for <u>both HNC and MSA</u>, and the corresponding "best bound" problem, which as we show in the next section has been solved already by Onsager, many years ago, provides the ASCL for charge strong coupling for both HNC and MSA.

(b) The Ewald identity and the Onsager Process

Considering the Ewald identity (2.14), notice that electrostatic interactions between charged particles, namely $\phi_{ij}(\underset{\sim}{r})$ or $\Psi_{ij}(\underset{\sim}{r})$ of (3.6), are legitimate Ewald functions $\Theta_{ij}(\underset{\sim}{r})$. The left hand side (l.h.s.) of (2.14) is correpondingly the total pair interaction potential energy per particle, of the objects carrying the original charge distributions $\rho_i^{\circ}(\underset{\sim}{x})$ and the smeared charge dstributions $\rho_i(\underset{\sim}{x})$. The first term on the right hand side (r.h.s.) of (2.14) vanishes for an electrically neutral system ($\sum x_i q_i = 0$), since

$$\sum_{ij} x_i x_j \int d\underset{\sim}{r}\, \phi_{ij}(\underset{\sim}{r}) = \lim_{k\to 0} \sum_{ij} x_i x_j q_i q_j \tilde{\rho}_i^{\circ}(\underset{\sim}{k})\, \tilde{\rho}_j^{\circ}(\underset{\sim}{k})\, \tilde{\phi}_G(\underset{\sim}{k}) =$$

$$= \lim_{k\to 0} \Big(\sum_i x_i q_i \tilde{\rho}_i^{\circ}(\underset{\sim}{k})\Big)^2 \tilde{\phi}_G(\underset{\sim}{k}) \qquad (3.11)$$

and similarly for $\sum x_i x_j \int d\underset{\sim}{r}\, \Psi_{ij}(\underset{\sim}{r})$. $\tilde{\phi}_G(\underset{\sim}{k})$ is the FT of the GF potential (e.g. Coulomb). The second term of the r.h.s. of (2.14) is easily recognized to be minus the self energy of the charge distributions, so that the last term of the r.h.s. of (2.14) represents the total electrostatic energy (per particle) of the system of charged objects:

$$1/2(2\pi)^{-D} \sum_{ij} (x_i x_j)^{1/2} \int d\underset{\sim}{k}\; S_{ij}(\underset{\sim}{k}) \begin{Bmatrix} \tilde{\phi}_{ij}(k) \\ \tilde{\Psi}_{ij}(k) \end{Bmatrix} = 1/(N\, 2\omega_D) \int dV \begin{Bmatrix} E_0^2 \\ E^2 \end{Bmatrix} > 0 \qquad (3.12)$$

where $\omega_D > 0$ is the surface of a D-dimensional unit sphere, $\underset{\sim}{E}_0$ and $\underset{\sim}{E}$ are respectively, and N is the number of particles in the volume V ($V \to \infty$, $N/V \to n$).

The Onsager process [11] is equivalent to adding and substracting the total electrostatic energy of the smeared charge distributions, and rearranging terms.Using (2.14), it is equivalent to the following Ewald identity (see Fig. 1):

$$U/N = (\, U/N - U^{\text{smeared}}/N) + U^{\text{smeared}}/N \tag{3.13a}$$

i.e.

$$\begin{aligned} 1/2 \; n \sum_{ij} x_i x_j \int d\underline{r}\; g_{ij}(\underline{r})\, \phi_{ij}(\underline{r}) = {} & 1/2 \; n \sum_{ij} x_i x_j \int d\underline{r}\; g_{ij}(\underline{r})\, [\phi_{ij}(\underline{r}) - \psi_{ij}(\underline{r})] \\ & + 1/2(2\pi)^{-D} \sum_{ij} (x_i x_j)^{1/2} \int d\underline{k}\; S_{ij}(\underline{k})\, \tilde{\psi}_{ij}(\underline{k}) - 1/2 \sum_i x_i \psi_{ii}(\underline{r}=0) \end{aligned} \tag{3.13b}$$

For hard core Green's function systems (HCGF) (2.5) is exact, so that due to (3.6) the first term on the r.h.s. of (3.13b) vanishes. By (3.12)the second term of the r.h.s. of (3.13b) is non-negative, so that the Onsager type bound is obtained:

$$U/N > -1/2 \sum_i x_i \psi_{ii}(r=0) = -\sum_i x_i u_i \tag{3.14}$$

where u_i is the self energy of the smeared charge distribution $q_i \rho_i(\underline{x})$

arbitrary N (number of objects) provided that the electroneutrality is preserved.

Returning to the SC-MSA problem, and denoting by "overbars" the optimized quantities obtained from the solutions of (3.10), we finally get:

i) The SC-MSA result is an exact lower bound to the potential energy of the system,

$$U/N > (U/N)^{\infty}_{MSA} = -\sum x_i \bar{u}_i = 1/\beta \, B[C^{\infty}] \qquad (3.15)$$

= Onsager Bound, despite the approximate nature of the MSA free energy

ii) The SC-MSA dcf's are given by $1/\beta \, C^{\infty}_{ij}(\underset{\sim}{r}) = \bar{\Psi}_{ij}(\underset{\sim}{r}) =$

= the interaction between the optimally smeared charges in objects i and j of separation $\underset{\sim}{r}$.

(3.16)

Note that as stated in "words", namely in terms of the basic characteristics of the interactions, our simple expressions (3.15) and (3.16), uncover the MSA meaning for arbitrary dimensionality.

When there is a background (3.14) takes the form

$$U/N = 1/2 \; n \sum_{ij} x_i x_j \int d\underset{\sim}{r} \, [\Psi_{ij}(\underset{\sim}{r}) - \phi_{ij}(\underset{\sim}{r})]$$
$$-1/2 \sum_i x_i \Psi_i (\underset{\sim}{r}=0) \qquad (3.17)$$

Note however that the second term of the r.h.s., which represents the difference of the interaction energies of the smeared charges and the original charges with the uniform background, is also diagonal.Indeed, we may write ((featuring, in full $i \leftrightarrow i, \ell, G$)

$$1/2 \quad n \sum_{ij} x_i x_j \int d\underset{\sim}{r} \; [\Psi_{ij}(\underset{\sim}{r}) - \phi_{ij}(\underset{\sim}{r})] = $$

$$= 1/2 \; n \sum_{i\ell, j\ell} x_i \; x_j \, q_{i\ell G} \, q_{j0G} \lim_{k \to 0} \; [\tilde{\rho}_{i0G}(\underset{\sim}{k}) \tilde{\rho}_{j0G}(\underset{\sim}{k}) - \tilde{\rho}^{\circ}_{i0G}(\underset{\sim}{k}) \; \tilde{\rho}_{j0G}(\underset{\sim}{k})] \tilde{\phi}_G(\underset{\sim}{k}) \quad \delta_{\ell 0} =$$

$$= \lim_{k \to 0} 1/2 \; n \; \left(\sum_{i\ell} x_i \, q_{i0G} [\tilde{\rho}_i \; (\underset{\sim}{k}) + \breve{\rho}^{\circ} \; (\underset{\sim}{k})]\right) \; \left(\sum_j x_j \, q_{j0G} [\tilde{\rho}_{j0G}(\underset{\sim}{k}) - \tilde{\rho}^{\circ}_{j0G}(\underset{\sim}{k})] \tilde{\phi}_G(k) \quad \delta_{\ell 0} =$$

$$= \rho_{TG} \sum_j x_j \, q_{j0G} \lim \; [\tilde{\rho}_{j0G}(\underset{\sim}{k}) - \tilde{\rho}^{\circ}_{j0G}(\underset{\sim}{k})] \tilde{\phi}_G(\underset{\sim}{k}) \quad =$$

$$= 1/2 \; \rho_{TG} \sum_{j\ell} x_j \, 1/q_{j0G} \int d\underset{\sim}{r} \; [\Psi_{jj}(\underset{\sim}{r}) - \phi_{jj}(\underset{\sim}{r})] \qquad (3.18)$$

and we recall that $\tilde{\rho}(k=0) = \breve{\rho}^{\circ}(k=0) = 1$.

Comparison with (3.9) shows that the MSA or HNC liquid theories, dictate that the smeared system, represented by $U^{smeared}/N$ in (3.13a) and discarded in obtaining U^{∞}_{MSA}/N , should be charge neutral also when $\tilde{\phi}_G(k=0) \neq 0$ .That is the reason for δ_G in (3.9) when $\tilde{\phi}_G$ (k=0)= 0 and we formally do not need to introduce the uniform background, since the

Onsager process, dictates that the "smeared system" should contain the Uniform Background and thus be totally charge neutral. Since $U^{smeared}$ is discarded in the MSA-Onsager estimate of the potential energy of the given system, it can be expected to be relativley small only for a totally charge neutral system.

4."Onsager Solution" of the MSA or HNC for Charge Strong Coupling

In his classic paper of 1939, Onsager [11] considered the problem of obtaining a lower bound to the potential energy of a system of charged hard objects. His method of solution is consistent with the MSA boundary condition (3.6) and, in fact, provides the solution of the ASCL for both the HNC and MSA (3.10).We consider in this section the Coulomb potential,to avoid the complications and specifics details of other GF potentials, to which the treatment also applies.This will allow us to use elementary electrostatics in 3 dimensions.We discuss electrically neutral systems, $\rho_{TG}=0$, in the first place, then systems that are not electrically neutral, and therefore require a neutralizing background for thermodynamic stability and at the end of this section we give examples for the special case of centrally charged hard spheres.

a) Total Charge Neutrality , $\rho_{TG}=0$

There are, in general, an infinfite number of ways to replace the charge distribution of an object,$\rho^{0}_{i\ell G}(\underset{\sim}{x})$ by a smeared distribution $\rho_{i\ell G}(\underset{\sim}{x})$ with the same potential outside of the object. The most obvious ones are those associated with the spherically symmetric distribution $\rho_{sm,i\ell G}(|x|)$ which by Gauss's theorem satisfy the required boundary condition (3.6).There is , however only one surface distribution $\rho_{i\ell G}(\underset{\sim}{x})$ which satisfies (3.6). This surface distribution is the one corresponding to minus the <u>induced charge</u> on the surface of the objects when the system is immersed in a uniform conducting fluid, as originally proposed by Onsager. As is discussed below in a special case, this

From this solution we compute the component of the electric field normal to the surface of the object, and just inside that surface

$$E^{<}_{i\hat{n}}(\underset{\sim}{s}) = -\nabla\phi^{<}_{i}(\underset{\sim}{x})\cdot\hat{n}\Big|_{\underset{\sim}{x}=\underset{\sim}{s}} \tag{4.7}$$

The induced charge on the surface of the object is given by

$$\sigma_i(\underset{\sim}{s}) = -E^{<}_{i,\hat{n}}(\underset{\sim}{s})/4\pi \tag{4.8}$$

The Onsager solution for the optimal smeared charge distribution $\bar{\rho}_i(\underset{\sim}{x})$ is

$$\bar{\rho}_i(\underset{\sim}{x}) = -\sigma_i(\underset{\sim}{s}) \tag{4.9}$$

Onsager's original bound to the potential energy of the system was given [11] in terms of the total potential energy of the "Onsager objects", namely the neutral objects consisting of the original charges $\rho^{o}_i(\underset{\sim}{x})$ plus the surface induced charges induced by them, $\sigma_i(\underset{\sim}{s})$. It is easy to show that this energy is equal to minus the self energy of the surface charge distributions:

$$u_i^{\text{Onsager}} = \int_S d\underset{\sim}{s}\ \phi_{i,0}(\underset{\sim}{s})\ \sigma(\underset{\sim}{s}) + 1/2\int_S d\underset{\sim}{s}\ \phi_{i,1}(s)\ \sigma(s) \tag{4.10}$$

from (4.4), however we obtain

$$u_i = -\frac{1}{2}\int ds\, \phi_{i,1}(\underset{\sim}{s})\, \sigma(\underset{\sim}{s}) = -(\text{self energy of the surface charge distribution } \sigma(\underset{\sim}{s})) \qquad (4.11)$$

In order to get some feeling for the optimization of $\rho_i(\underset{\sim}{x})$ obtained by the surface distribution, consider the special case $\phi_{i,0}(s)=c_o$=constant (e.g) a point monopole at the center of a sphere). The interior potential is given by $\phi_i(\underset{\sim}{x}) = \phi_{i,0}(x)-c_o$, i.e. $\phi_{i,1}(\underset{\sim}{x}) = -c_o$, the electric field inside the object due to the surface charge is zero, $\underset{\sim}{E}^{<}_{i,1}=0$. Outside the object we still have from (4.6) that $\underset{\sim}{E}^{>}_{i,1}=\underset{\sim}{E}^{>}_{i,0}$. The general conditionfor the validity of (3.6) is that the field outside the object due to the smeared charge is the same as that due to the original charge,

$$\left(\underset{\sim}{E}^{>}_{i}\right)_{smeared} = \underset{\sim}{E}^{>}_{i,0} \qquad (4.12)$$

The self energy of the smeared charge distribution i given by

$$u_i = 1/2\, \Phi_{ii}(r=0) = 1/8\pi \int_{\text{all space}} dV\, |(E_i)_{smeared}|^2$$

$$= 1/8\pi \int_{\substack{\text{inside}\\ \text{object}}} dV\, |(E^{<}_i)_{smeared}|^2 + 1/8\pi \int_{\substack{\text{outside}\\ \text{object}}} dV\, |(E_{o,i})|^2 \qquad (4.13)$$

The absolute minimum for this quantity is reached when $\left(\underset{\sim}{E}^{<}_i\right)_{smeared}=0$, which in the case considered above is obtained by the Onsager solution with $\underset{\sim}{E}^{<}_{i,1}=0$ for $\phi_{i,0}(\underset{\sim}{s})$= constant.

b) Systems in a Uniform Neutralizing Background

The Onsager procedure for the MSA-HNC best bound problem of immersing the system in a uniform conducting fluid, works well when there is a neutralizing background. The Onsager object now consists of the original charge distribution $\rho_i^o(\underset{\sim}{x})$, the uniform background density "trapped" inside the object, $\rho_b = -\rho_{T,b}$, and the induced charge on the surface due both to ρ_i^o and ρ_b . Eq. (4.1) now takes the form

$$\nabla^2 \phi_i^<(\underset{\sim}{x}) = -4\pi\rho_i^o(\underset{\sim}{x}) - 4\pi\rho_b \tag{4.14}$$

with the condition (4.2). Denoting by $\phi_{i,b}(\underset{\sim}{x})$ the solution of

$$\begin{aligned} \nabla^2 \phi_{i,b}(\underset{\sim}{x}) &= -4\pi\rho_b && \text{inside object} \\ \nabla^2 \phi_{i,b}(\underset{\sim}{x}) &= 0 && \text{outside object} \end{aligned} \tag{4.15}$$

with the condition that $\phi_{i,b}(x\to\infty)=0$, we use $\phi_{i,b}(\underset{\sim}{x})$ as defined prior to (4.3) to solve (4.3) with the boundary condition

$$\phi_{i,1}^<(\underset{\sim}{s}) = -\phi_{i,0}(\underset{\sim}{s}) - \phi_{i,b}(\underset{\sim}{s}) \tag{4.16}$$

to get

$$\phi_i^<(\underset{\sim}{x}) = \phi_{i,0}(\underset{\sim}{x}) + \phi_{i,b}(\underset{\sim}{x}) + \phi_{i,1}^<(\underset{\sim}{x}) \tag{4.17}$$

$$\phi'_{i,0}(\underset{\sim}{x}) = \phi_{i,0}(\underset{\sim}{x}) + \phi_{i,b}(\underset{\sim}{x}) + \phi'_{\varepsilon,c}(\underset{\sim}{x}) = 0 \qquad (4.18)$$

Thus $\phi_{i,0}(\underset{\sim}{x})$, $\phi_{i,b}(\underset{\sim}{x})$ and $\phi_{i,1}(\underset{\sim}{x})$ are, respectively, the electrostatic potentials due to $\rho_i^{(0)}$, ρ_b and $\sigma(\underset{\sim}{s})$ in the Onsager object. Let us denote by o the original fixed charge of the object, by b the background charge and by s the surface charge, and ob, os, bs, bb, ss, .. the electrostatic energies between those charge distributions .bb and ss are the self energies of the distributions ρ_b and $\sigma(\underset{\sim}{s})$. It is easy to see that (3.18) may be written , in the case of Onsager smearing as

$$1/2\ n\sum_{ij} x_i\ x_j \int d\underset{\sim}{r}\ [\psi_{ij}(\underset{\sim}{r}) - \phi_{ij}(\underset{\sim}{r})] = \sum_i x_i (bo+2bb+bs)_i \qquad (4.19)$$

while the first term in (3.17), the self energy term of the components in ψ_{ii}, is

$$-1/2 \sum_i x_i \quad \psi_{ii}(r=0) = -\sum_i x_i (ss+bb+bs)_i \qquad (4.20)$$

thus , (3.17) takes the form (see Appendix B)

$$U/N > (U/N)^{\infty}_{MSA} = -\sum_i x_i (ss-bb-bo)_i \qquad (4.21)$$

Consider, in turn the total energy of the Onsager object (relative, as usual to the self energy of ρ_i^o):

$$u_i^{Onsager} = (bs+bb+ss+bo+os)_i \tag{4.22}$$

It easy to see from (4.16) that

$$bs+os=-2ss \tag{4.23}$$

so that (4.21) becomes identical to

$$U/N \geq (U/N)^{\infty}_{MSA} = +\sum_i x_i u_i^{Onsager} \tag{4.24}$$

Thus, when there is a background, the Onsager solution for the optimal smeared charges is

$$\bar{\rho}_i(\underset{\sim}{x}) = -\sigma_i(\underset{\sim}{s}) - \rho_b \tag{4.25}$$

(c) Special Case: hard spherical centrally charged objects. The most general system for which a formal solution to the MSA has been found consist of hard spheres of arbitrary sizes with central point multipolar charges, for which the solution to the MSA-HNC-ASCL problem (3.10) can be summarized by the following simple statement (see Appendix C):

All multipolar charges, $\ell \geq 1$, should be uniformly smeared on the surface of the sphere. The monopolar charge, q_{i0G}, should be smeared uniformly on the surface and/or uniformly in the volume of the sphere according to whether $\rho_{T,G} = 0$ or $\rho_{T,G} \neq 0$ respectively.

All the analytic solutions of the MSA for HCGF systems, that are known to us, including hard spheres[12,13], hard spheres with centrally imbedded point monopolar charge (with[14] and without background[15]), hard spheres with centrally imbedded dipoles[16] and multipoles[17], mixtures of charged hard spheres with point ions[18], hard spheres with monopolar Yukawa charges[19], obey our relations (3.7), (3.11) and (3.12) with the analytic forms given by (3.11), (3.12) maintaining it at all densities and temperatures (couplings).

5. Variational Solutions of the MSA by Expansion in the Onsager "Basis Functions".

(a) Analogy with the Hamiltonian variational problem.

A typical liquid state calculation involves a (usually approximate) free energy functional which has to be variational with respect to the pair functions. In analogy to the Hamiltonian ($\longleftrightarrow$ free energy) ground state energy problem, the following "ideal" situation is desirable:

(i) To have a physically motivated, good choice, of a set of basis "wave" functions ($\longleftrightarrow$ pair functions) which obey all the symmetries of the "hamiltonian" ($\longleftrightarrow$ geometry of the object and the charge distributions); so that (ii) the pair functions could be expanded in terms of the basis set, with only the coefficients (which can be assigned intuitive physical meaning) to be determined by the variational free energy. A minimun set of coefficients must still involve the geometry of the objects and the values of the charges (iii). Eventually increasing the size of the basis set (the number of coefficients), more accurate solutions can be obtained.The exact solution is reached when the complete set of basis functions is involved.In general, however,a small number of coefficients will be required.

(iv)As in the Hamiltonian problem it is desirable to obtain from the approximate expansion and exact bound to the energy of the system.

The general idea of solving the variational MSA problem by using a trial dcf with coefficients to be determined by the variation equations in certainly not new. Never before we had, however, at our disposal the complete set of basis functions as we now have due to the mapping of the ASCL-MSA on the Onsager scheme, which provides the exact analytic form of the MSA dcf's. With trial dcf's having the exact analytic form of the full MSA solution it is only a method of employing the full set of required coefficients (i.e. expanding the solution in the complete set) in order to have, from the variational equations for the coefficients, the exact solution of the MSA. The Onsager basis set of functions, constructed by (3.12) using the Onsager smeared charges, (i) has a physicaly intuitive meaning, (ii) corresponds to an exact lower bound to the potential energy, and (iii) is constructed by using elementary electrostatics employing the basic geometrical-physical constraints that must be taken into account - the liquid state theory part of the problem does not make the problem more complex than it already is at the basic electrostatic level. Even if we "stick" to the full basis set, and attempt an exact solution, this procedure has the clear advantage of providing a direct physical description of the solution.

We may, however, with increasing experience, use only those elements of the basis set which are more important. The conceptual analogy with the widely used Hamiltonian variational solutions is complete.

(b) Practical Details: Examples and Comments.

The complete basis set of functions for the MSA consist of the overlap-volume functions (3.7) and the Onsager-smeared interactions (3.16). Recall that the MSA dcf's outside the cores are already specified by the closures (2.6), so that without further mention it is understood that only the region inside the core enters into the discussion.

Example(b1): restricted primitive model (RPM).

The RPM consists of a binary mixture of equal size and oppositely charged spheres. The overlaps volume function is of the form [3]

$$C_{hc}(x) = A_o + A_1 x + A_3 x^3, \quad x = \frac{r}{\sigma} < 1 \qquad (5.1)$$

The Onsager-smeared interactions between two uniformly surface charged spheres is of the form [15]

$$C_{ij,Onsager}(x) = Q_i Q_j (B_o + B_2 x), \quad x < 1 \qquad (5.2)$$

The exact trial solution is of the form:

$$C_{t,ij}(x) = (\alpha_o)_{ij} + (\alpha_1)_{ij}\, x + (\alpha_3)_{ij}\, x^3 \qquad x < 1 \qquad (5.3)$$

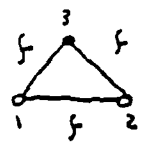
Symmetry considerations will reduce the initial number of independent coefficients.

Example(b2): charged hard spheres in uniform background.

The Onsager-smeared interactions are of the form: [3,14]

This happens in general <u>only</u> for hard spheres and for hard <u>alligned</u> ellipsoids. In these cases, the ASCL solution has the same analytic form as required of the PYHS theory at low densities. In the general case, however, the ASCL solution of the PYHS and the low density solution may have different forms, so that the overlap-volume basis set (3.7) will not be able to provide the exact solution at low packing fractions. As an ad-hoc tentative practical solution to this problem, we suggest to employ as a hard-core basis set the <u>union</u> of the set (3.7) and the overlap-volumes of shapes corresponding to the pair-excluded regions, i.e.

$$\{(3.7)\} + \{ \quad \} \qquad (5.6)$$



Comment(b5): A method due to Percus.

Once the exact analytic form of the dcf's is given, an alternative to the variational solution in provided by the simple and powerful method of Percus[20]. Use the OZ relations to <u>expand</u> the dcf's around the origin $\vec{r}=0$. With the known analytic form of the solution this will provide the set of Algebraic equations for the coefficients. i.e. a complete analytic solutions without resort to the factorization techniques

6. Approximations within the PY theory for hard-objects.

The formulation in secs. 1,2 holds also for uncharged hard objects in the PY approximation. The main points to note is that has a thermodynamic meaning (2.10)

The analogy, pointed out by Onsager, between a mixture of particles of different orientations and a mixture of hard spheres of diffrent sizes, is born out manisfestly in our formulation. In the asymptotic strong coupling limit we predict the following results for arbitrarily shaped convex hard objects: divergence at $\eta_T = 1$, (3.7), and (3.1), (3.2).

Consider now the following general approximation,

$$\left[\tilde{C}_{ij}(\underset{\sim}{k})\right]^2 = \tilde{C}_{ii}(\underset{\sim}{k})\,\tilde{C}_{jj}(\underset{\sim}{k}) \qquad (6.1)$$

by which the generating functional Z_c takes the following ("diagonalized") form:

$$Z_c^{diag} = 1 + \frac{1}{n}(2\pi)^{-D}\int d\underset{\sim}{k}\,\ln\left[1 - n\sum_i x_i\,\tilde{C}_{ii}(\underset{\sim}{k})\right] \qquad (6.2)$$

to be solved via

$$\frac{\delta Z_c^{diag}}{\delta C_{ii}(\underset{\sim}{r})} = 0 \qquad \underset{\sim}{r} < \underset{\sim}{\sigma}_{ii} \qquad (6.3)$$

In the limiting case when all objects are equal size spheres, eqs. (6.2), (6.3) reduce to the exact PY equation for hard spheres.

solution to the PY equation can be judged by (e.g. comparison with the available exact solution for hard sphere mixtures. For a binary mixture, (6.1) leads to the following relation among the partial structure factors:

$$S_{12}^{2}(k) = [S_{11}(k)-1][S_{22}(k)-1] \qquad (6.4)$$

This relation holds well only for mixtures of spheres with relatively small size differences. The Pynn-Lado 21,22 ansatz

namely

$$C_{ij}(\underset{\sim}{r}) = C_0\left(\eta_T, |\underset{\sim}{r}| / |\underset{\sim}{\sigma}_{ij}|\right) \qquad (6.5)$$

where C_0 (,r/R) is the solution of the PY approximation for equal size spheres,manifestly violates the overlap-volume analytic form for unequal size spheres (e.g. compare (5.1) with (5.5)), and so cannot be expected to be accurate for mixtures with large differences in particle' sizes. Lado's numerical results are encouraging to pursue this line of scaling type approximation. It would have been of interest to compare the results of (6.5) to those obtained from (6.1)

Note that (6.3) is an exact ASCL result, so that (6.5) and (2.11) give the exact results for the PY theory near the $\eta_T = 1$ limit:

$$\lim_{\eta_T \to 1} Z_c^{PY} = \frac{D}{(1-\eta_T)^D} \qquad (6.6)$$

It is interesting to observe that the most sucessful theories for the EOS of mixtures of hard spheres or non-spherical hard objects, like the y-expansion and the scaled particle theory, implicitly assume (6.6) or its corresponding "virial" PY-EOS:

$$\lim_{\eta_T \to 1} Z_T^{PY} = D\left(\frac{2}{1-\eta_T}\right)^{\frac{D-1}{2}} \qquad (6.7)$$

7. Bonding and Aggregation within the MSA and HNC Approximations.

One of the aims of Onsager's paper was to investigate simplified electrostatic metals of bonding and aggregation. The mapping of Onsager's procedure on the ASCL of integral equation theories of fluids, enables us to take a further step in the direction pointed out by Onsager.

Since the Onsager bounds correspond to the exact ASCL result of the HNC and MSA theories, it is possible to compare the Onsager bounds with the potential energy of different possible structures. To the extent that the Onsager energies correspond to a unique local structure, they may predict the bonding and aggregation effects within these integral equation theories in strong coupling, without the need for a detailed solution of those complex equations.

To illustrate this idea, consider a binary mixture of hard particles of, say, different sizes, with opposite charges situated inside the particles just off the surface. Specifically, let δ be the distance of each charge from its surface boundary, and let δ/σ_1 , $\delta/\sigma_2 \ll 1$, where σ_1 , σ_2 are typical dimensions of the particles. The Onsager self energy for each such object with charge Q (or-Q) the surface is

$$u^{\infty}_{MSA} = u^{\infty}_{HNC} = -u_{i\,\text{onsager}} = -Q^2/2\delta \qquad (7.1)$$

This is equal, however, to the potential energy of the two oppositely charged objects when they are forming a "molecule", with the equal and opposite charges are at distance 2δ from the other (Fig. 2a). Note that this is a unique local structure corresponding to (7.1), and thus we are able to predict that the HNC and MSA theories will feature this bonding effect when $\beta Q^2/2\delta \gg 1$.

This simple example ca be generalized to local structures of higher complexity (e.g. Fig. 2.b) and to include polarization and other intermal electrostatic effects that lead to aggregare formation. The treatment of polarization in Onsager's paper can be readily incorporated into the mapping on the integral equation theories. It may be thus possible to consider complex structures as rings, water etc. Although the possible aggregates that comply with Onsager's bounds do not always represent a unique local structure (e.g. charges near the centers of the objects)

they should be of help in the analysis along the lines set by Onsager's work, which -in view of our analysis- it is now possible to pursue.

8. Further Implications and Conclusions

The physically intuitive meaning of the dcf's and its role in a variational solution of the MSA -HNC type equations by expansion in the "Onsager basis set" , is not limited to uniform systems. It is a standard procedure [27], in the treatment of a system of hard particles near a neutral or charged wall (e.g. fluid near an electrode), to consider a mixture of different size particles and to let one radius go to infinity.This one particle represents the hard wall.In such a limiting process, done in the context of a specific approximation, such as the MSA or HNC preserves the fundamental form of the various dcf's (particle-particle,particle-wall) retains its intuitive meaning as overlap volumes or smeared interactions, and the procedures, as discussed in this paper, can be carried out in complete analogy to the uniform fluid case.Work along these lines is currently under way.

The Onsager procedure in conjugation with the Ewald identity serves as a guideline for the solution of the ASCL of th HNC or MSA equations for systems of concentrated charges without hard cores, e.g. plasmas , line charges, etc.(namely, the soft-MSA context,[2,3,6])

It provides the rationale for the emergence of the "ion-sphere" boundary conditions in the treatment of high density electrons+ions matter [3b].The insight we gain from te general HNC-MSA problem for HCGF systems may be used also in constructing analytic solutions for centrally charged spheres for non-uniform systems .Examples of such solutions are currently under investigation.

Our novel method applies to models of matter of a wide variety, approach will motivate more applications.

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Appendix A: Restricted Primitive Model (RPM) of electrolytes.

The RPM consist of a mixture of charged hard spheres of equal sizes, and obeys total charge neutrality $\sum x_i Q_i = 0$. The MSA for this model has been solved exactly to give the following dcf's:[15]

$$C_{ij}(r) = C_0(r) + 2\frac{\beta Q_i Q_j}{R} B\left[1 + \frac{1}{2} B \frac{r}{\sigma}\right] \qquad r < \sigma \tag{A.1}$$

where B has the property

$$\lim_{Q \to \infty} B = -1 \tag{A.2}$$

and $C_0(r)$ is the PYHS result for equal size spheres of diameter σ.

In the limit $Q_i \to \infty$ we have

$$-\frac{1}{\beta} C_{ij}(r) \xrightarrow[Q_i \to \infty]{} \frac{Q_i Q_j}{(\sigma/2)}\left[1 - \frac{1}{2}\frac{r}{\sigma}\right] \equiv \psi(r) \qquad r < \sigma \tag{A.3}$$

where $\psi(r)$ is the electrostatic interaction between two uniformly surface charged spheres.

Appendix B: Charged hard spheres in a uniform penetrating background

Defining $\beta Q^2/\sigma = \gamma$, $\eta = \frac{\pi}{6} n \sigma^3$, $x = r/\sigma$ and taking the limit $\gamma \to \infty$ for fixed $\eta < 1$, the solution of Palmer and Weeks[14] (PW)[3b] takes the form:

$$\lim_{\gamma \to \infty} C(x)/\gamma \equiv \psi(x) = 2 + \frac{2\eta^2}{5} - (1-\eta)^2 x - 4\eta x^2 + \eta(2+\eta) x^3 - \frac{2}{5}\eta^2 x^5 \qquad x \le 1 \tag{B.1}$$

Note that $\psi(x)$ can be written as

$$\psi(x) = \psi_{vv}(x) + \psi_{ss}(x) + \psi_{vs}(x) \tag{B.2}$$

where

$$\psi_{vv}(x) = \eta^2 \left(\frac{12}{5} - 4x^2 + 3x^3 - \frac{2}{5} x^5 \right) \tag{B.3}$$

$$\psi_{ss}(x) = (1-\eta)^2 (2 - x) \tag{B.4}$$

$$\psi_{vs}(x) = \eta(1-\eta)(4 - 4x^2 + 2x^3) \tag{B.5}$$

These functions are, respectively, the volume-volume, surface-surface, and volume-surface, electrostatic interactions between two spheres of unit diameters, each composed of charge

$(1-\eta)$ spread uniformly on the surface, and charge η spread uniformly in the volume.The Onsager object consists of the negative of these charges plus the original central unit point charge.Using $(\gamma=1)$ the definitions of sec. (4.b)

$$ss=(1-\eta)^2$$

$$bb=6/5\ \eta^2$$

$$bo=-3\eta$$

$$os=-2(1-\eta)^2$$

$$bs=2\eta(1-\eta) \qquad (B6)$$

we find that , in accordance with the results of section (4.b) the internal energy is

$$\beta(U/N)^{\infty}_{MSA}=-(1+\eta-\eta^2)\gamma=-ss+bb+bo \qquad (B7)$$

in agreement with the result obtained by direct integration of (3.17).

Appendix C : Onsager Solution for Hard Spheres with Centrally Imbedded Point Multipoles.

Appendix C : Onsager Solution for Hard Spheres with Centrally Imbedded Point Multipoles.

Consider a sphere of radius R with a centrally imbedded multipole of order l .The potential due to the central charges is

$$\phi_0(\underset{\sim}{r}) = \frac{4\pi}{2\ell+1}\sum_m q_{\ell m} Y_{\ell m}(\theta,\varphi)/r^{\ell+1} \tag{C1}$$

We solve the equation $\nabla^2 \phi_1 = 0$ inside the sphere with the boundary condition $\phi_1(\underset{\sim}{R}) = -\phi_0(\underset{\sim}{R})$ (see Sec.4).The solution for the interior is

$$\phi_1(\underset{\sim}{r}) = \frac{4\pi}{2\ell+1}\sum_m A_{\ell m} Y_{\ell m}(\theta,\varphi)\ r^{\ell} \tag{C2}$$

where

$$A_{\ell m} = -q_{\ell m} R^{-(2\ell+1)} \tag{C3}$$

The potential inside the sphere is

$$\phi^{<}(\underset{\sim}{r}) = \frac{4\pi}{2\ell+1}\sum_m q_{\ell m} Y_{\ell m}(\theta,\varphi)(r^{-(\ell+1)} - r^{\ell} R^{-(2\ell+1)}) \tag{C4}$$

The normal component of the electric field on the inside surface of the sphere is

$$E^{<}_{\hat{n}}(\underset{\sim}{R}) = 4\pi\sum_m q_{\ell m} Y_{\ell m}(\theta,\varphi)\ R^{-(\ell+2)} \tag{C5}$$

$$= (2\ell+1)/(\ell+1)\ E_{0\hat{n}}(\underset{\sim}{R})$$

(the one due to the original multipole). The induced surface charge density

$$\sigma(\underset{\sim}{R}) = -E^{<}_{\hat{n}}(R)/4\pi = -\bar{\rho}(\underset{\sim}{r}) \qquad \text{(C6)}$$

satisfies the charge neutrality condition

$$\int d^3r\, Y^{*}_{lm}(\theta,\varphi)\,\bar{\rho}(\underset{\sim}{r})\, r^{\ell} = q_{\ell m} \qquad \text{(C7)}$$

It is easy to see that the result (C5) is equivalent to a uniform spread of the multipole on the sphere.In the case of a sphere with a point dipole $\underset{\sim}{p}$ in the center (pointing in the direction of $\underset{\sim}{z}$), we have

$$\sigma(\underset{\sim}{R}) = -3p\cos\theta/4\pi R^{3} \qquad \text{(C8)}$$

The MSA for the ion-dipole mixture was solved some years ago[23,24]. Although the unequal size case was discussed a complete solution of this model is still not at hand.

Our present method, however, allows us to construct the DCF in the ASDL from purely electrostatic calculation consider first the most general case of two spheres of radii b_1 and b_2 and charge distributions $\rho_i(\underset{\sim}{b}_1)\ \rho_j(\underset{\sim}{b}_2)$. The center to center distance is $\vec{r}$. The interaction energy is

$$w_{ij} = \int d\underset{\sim}{b}_1\, d\underset{\sim}{b}_2\, \rho_i(\underset{\sim}{b}_1)\, \rho_j(\underset{\sim}{b}_2)\ 1/(|\underset{\sim}{r} - \underset{\sim}{b}_1 + \underset{\sim}{b}_2|) \tag{D.1}$$

Assume first that $b_1 > b_2$. Then we can write (D1) in the form

$$W_{ij} = \int d\underset{\sim}{b}_2 \; \rho_j(\underset{\sim}{b}_2)\, \phi_i(\underset{\sim}{b}_2, \underset{\sim}{r}) \qquad \text{(D.2)}$$

where $\phi_i(\underset{\sim}{b}_2, \underset{\sim}{r})$ is the potential due to the charge smeared on the surface of sphere 1.

$$\phi_i(\underset{\sim}{b}_2, \underset{\sim}{r}) = \int db_1 \; \rho_i(\underset{\sim}{b}_1) \frac{1}{|\underset{\sim}{r} + \underset{\sim}{b}_1 - \underset{\sim}{b}_2|} \qquad \text{(D.3)}$$

now for multipolar charge distributions on the surface of the sphere we have

$$\rho_i(\underset{\sim}{b}_1) = \frac{\delta(r - b_1)}{4\pi b_1^2} \sum_{m,\mu} a_\mu^m \; D_{0\mu}^m(\hat{b}_1) \qquad \text{(D.4)}$$

in a laboratory fixed reference frame. $\underset{\sim}{b}_1 = (b_1, \hat{b}_1)$ is a vector pointing to the direction $\hat{b}_1 = \varphi_1, \theta_1$ in a reference frame fixed to molecule i. a_μ^m is the value of the multipole moment of order m, polarization μ. We use Edmonds[25] notation for the Wigner spherical harmonics

$$D_{0\mu}^m(\hat{b}_1) = D_{0\mu}^m(0, \theta_1, \varphi_1) = \left[\frac{4\pi}{2m+1}\right]^{1/2} Y_\mu^m(\theta_1, \varphi_1) \qquad \text{(D.5)}$$

We adopt a reference frame in which the z-axis is the $\underset{\sim}{r}$ vector. Then

$$\rho_i(b_1) = \frac{\sigma(r \cdot b_1)}{4\pi b_1^2} \sum_{m \mu \mu'} a_\mu^n \, D_{0\mu'}^m(\hat{b}_1) \, D_{\mu'\mu}^m(\Omega_1) \tag{D.6}$$

where now $\hat{b}_1$, is the direction in a molecular reference frame and the Euler angles $\Omega_1 = \alpha_1 \beta_1 \gamma_1$, give the orientations of molecule 1 in this frame. Choosing the origin of the coordinates at the center of 1 we write (D.3) in the form

$$\varphi_i(x) = \int d\omega_1 \, \rho_i(\omega_1) \frac{1}{|b_1 - x_2|} \tag{D.7}$$

with

$$x_2 = r + b_2 \tag{D.8}$$

We expand now the last factor: Indeed we will have two cases

ϕ_i^e : $x_2 > b_1$ Region outside 1

ϕ_i^i : $x_2 < b_1$ Region inside 1

we get

$$\varphi_i = \phi_i^e + \phi_i^i \tag{D.9}$$

$$\phi_i^e = \sum_{m\mu\mu'} a_\mu^m D_{\mu'\mu}^m(\Omega_1)(-)^{\mu'} \frac{1}{2m+1} \frac{b_1^m}{x_2^{m+1}} D_{-\mu' 0}^m(\hat{x}_2) \quad (D.10)$$

$$\phi_i^i = \sum_{m\mu\mu'} a_\mu^m D_{\mu'\mu}^m(\Omega_1)(-)^{\mu'} \frac{1}{2m+1} \frac{x_2^m}{b_1^{m+1}} D_{-\mu' 0}^m(\hat{x}_2) \quad (D.11)$$

so that finally

$$W_{ij} = \sum_{m,n,\chi} W_\chi^{mn} \quad (D.12)$$

$$W_\chi^{mn} = \sum_{\mu,\nu} a_\mu^m a_\nu^n D_{\chi\mu}^m(\underset{\sim}{\Omega}_1) D_{-\chi\nu}^n(\underset{\sim}{\Omega}_2) I_\chi^{mn} \quad (D.13)$$

with

$$I_\chi^{mn} = I_\chi^{mn,e} + I_\chi^{mn,i} \quad (D.14)$$

where

$$I_\chi^{mn,e} = \frac{(-)^{\mu'}}{4\pi(2m+1)} \int_0^{2\pi} d\varphi_2 \int_{\theta_m}^{\pi} d\theta_2 \sin\theta_2 \frac{b_1^m}{x_2^{m+1}} D_{-\chi 0}^m(\hat{x}_2) D_{0\chi}^n(\hat{b}_2) \quad (D.15)$$

$$I_\chi^{mn,i} = \frac{(-)^{\mu'}}{4\pi(2m+1)} \int_0^{2\pi} d\varphi_2 \int_0^{\theta_m} d\theta_2 \sin\theta_2 \frac{x_2^m}{b_1^{n+1}} D_{-\chi 0}^m(\hat{x}_2) D_{0\chi}^n(\hat{b}_2) \quad (D.16)$$

$$\cos\theta_m = (b_1^2 - b_2^2 - r^2)/(2rb_2)$$

where the angle $\hat{x}_2 = \theta_x, \varphi_x$ is defined by

$$\varphi_2 = \varphi_x$$
$$\cos\theta_x = (r + b_2\cos\theta_2)/x_2 \qquad \text{(D.17)}$$
$$\sin\theta_x = b_2 \sin\theta_2 / x_2$$

The evaluation of the integrals (D.15) (D.16) is straight forward. We quote the results for m, n=0,1.

Ion-ion interaction

$$-C^{\infty}_{..}(r) \propto w^{00}_{0} = \frac{(a^0_0)^2}{4 b_1 b_2 r}\left[(b_1 - b_2)^2 + 2r(b_1 + b_2) - r^2\right] \qquad \text{(D.18)}$$

This form agrees exactly with the ASCL of that given by Hiroike[26].

When $b_1 = b_2 = b$, then we get

$$w^{00}_{0} = (a^0_0)^2 \frac{1}{b}\left[1 - \frac{r}{4b}\right] = \frac{2e^2}{\sigma}\left[1 - \frac{r}{2\sigma}\right] \qquad \text{(D.19)}$$

in agreement with known result (A3). For the ion-dipole case

$$-C^{\infty}_{p0}(12) = C^{\infty}_{01}(21) = w_{10}(12) = \frac{2\pi}{3\sqrt{3}} a^0_0 \sum_{\mu} a^1_{\mu} D^1_{0\mu}(\Omega_1) \frac{1}{8 r^2 b_1^2 b_1}$$

$$\left[-3r^4 + 8r^3 b_2 + 6r^2(b_1^2 - b_2^2) + (b_2 - b_1)^3(b_2 + 3b_1)\right] \qquad \text{(D.20)}$$

and finally the dipole-dipole

$\chi = 0$

$$w^{11}_{0} = \frac{\pi}{108}\sum_{\mu\nu} a_{\mu} a_{\nu} D^1_{0\mu}(\Omega_1) D^1_{0\nu}(\Omega_2) \frac{1}{r^3 b_1^2 b_1^2}$$

$$\left\{2r^6 - 9r^4(b_1^2 + b_2^2) + 8r^3(b_1^3 + b_2^3) - (b_1 - b_2)^4\left[(b_1 - b_2)^2 + 6b_1b_2\right]\right\} \qquad \text{(D.21)}$$

$\underline{\chi = 1}$

$$w^{11}_{1} = \left(\frac{1}{2}\right) \frac{\pi}{108} \sum_{\mu\nu} a^1_\mu a^1_\nu D^1_{1\mu}(\Omega_1) D^1_{-1\nu}(\Omega_2) \frac{1}{r^3 b_2^2 b_1^2}$$

$$\Big\{ r^6 - 9r^4(b_1^2 + b_2^2) + 16r^3(b_1^3 + b_2^3) - 9r^2(b_1^2 - b_2^2)^2$$

$$+ (b_1 - b_2)^4 \left[(b_1 - b_2)^2 + 6 b_1 b_2 \right] \Big\} \qquad (D.22)$$

References

1) Y. Rosenfeld and L. Blum, J. Phys. Chem, 89,5149 (1985)

2) Y. Rosenfeld and W.M. Gelbart, J. Chem. Phys. 81, 4574 (1984).

3) a) Y. Rosenfeld, Phys. Revs. A32,1834 (1985)
   b) submitted to Phys .Revs. A.

4) Y. Rosenfeld, Phys., Rev. A25, 1206 (1982).

5) Y. Rosenfeld, Phys., Rev. A26, 3622 (1982).

6) W.E. McMullen, W.M. Gelbart, and Y. Rosenfeld, to be published.

7) W. Olivares and D.A. McQuarrie, J. Chem. Phys. 65 3604 (1976).

8) H.C. Andersen and D. Chandler, J. Chem. Phys. 57, 1918 (1972).

9) R.J. Baxter, J. Chem. Phys. 52 4559 (1970).

10) Y. Rosenfeld, J. Stat. Phys. 37, 215 (1984).

11) L. Onsager, J. Phys. Chem. 63, 189 (1939).

12) M.S. Wertheim, Phys. Rev. Lett. 10, 321 (1963).

13) J.L. Lebowitz, Phys. Rev. 133, A895 (1964).

14) R.G. Palmer and J.D. Weeks, J. Chem. Phys. 58, 4171 (1973).

15) E. Waisman and J.L. Lebowitz, J. Chem. Phys. 56, 3086 and 3093 (1972). L. Blum, Mol. Phys. 30 1529 (1975).

16) M.S. Wertheim, J. Chem. Phys. 55, 4291 (1971).

17) L. Blum, J. Chem. Phys. 58, 3295 (1973).

18) M. Gillan, B. Larsen, M.P. Tosi, and N.H. March, J. Phys. C9, 889 (1976).

19) E. Waisman, Mol. Phys. 25, 45 (1973); L. Blum and J.S. Hoye, J. Stat., Phys. 19, 317 (1978); J.S. Hoye and G. Stell, Mol. Phys. 52, 1057 (1984).

20) J.K.Percus in "The Equilibrium Theory of Classical Fluids",H.L.Frisch and J.L.Lebowitz, Editors,W.A.Benjamin, New York 1964.

21) R. Pynn, J. Chem. Phys. 60 4579 (1974).

22) F. Lado, Mol. Phys. 54 407 (1985).

23) S.A. Adelman and J.M. Deutch J. Chem. Phys. 60 3935 (1974).

24) L. Blum, J. Chem. Phys. Letters 26 200 (1974).
J. Chem. Phsy. 61 2129 (1974).

25) A.R. Edmonds "Angular Momentum in Quantum Mechanics", Princeton University Press Princeton, N.J. 1960.

26) K. Hiroike, Mol. Phys. 33 1195 (1977).

27) H.Reiss , H.L.Frisch and J.L.Lebowitz,J.Chem. Phys. 31,369 (1959)
D.Henderson,F.Abraham and J.A.Barker,Mol. Phys.31,1291 (1976)
D.Henderson and L.Blum, J.Chem. Phys. 69,5441 (1978)

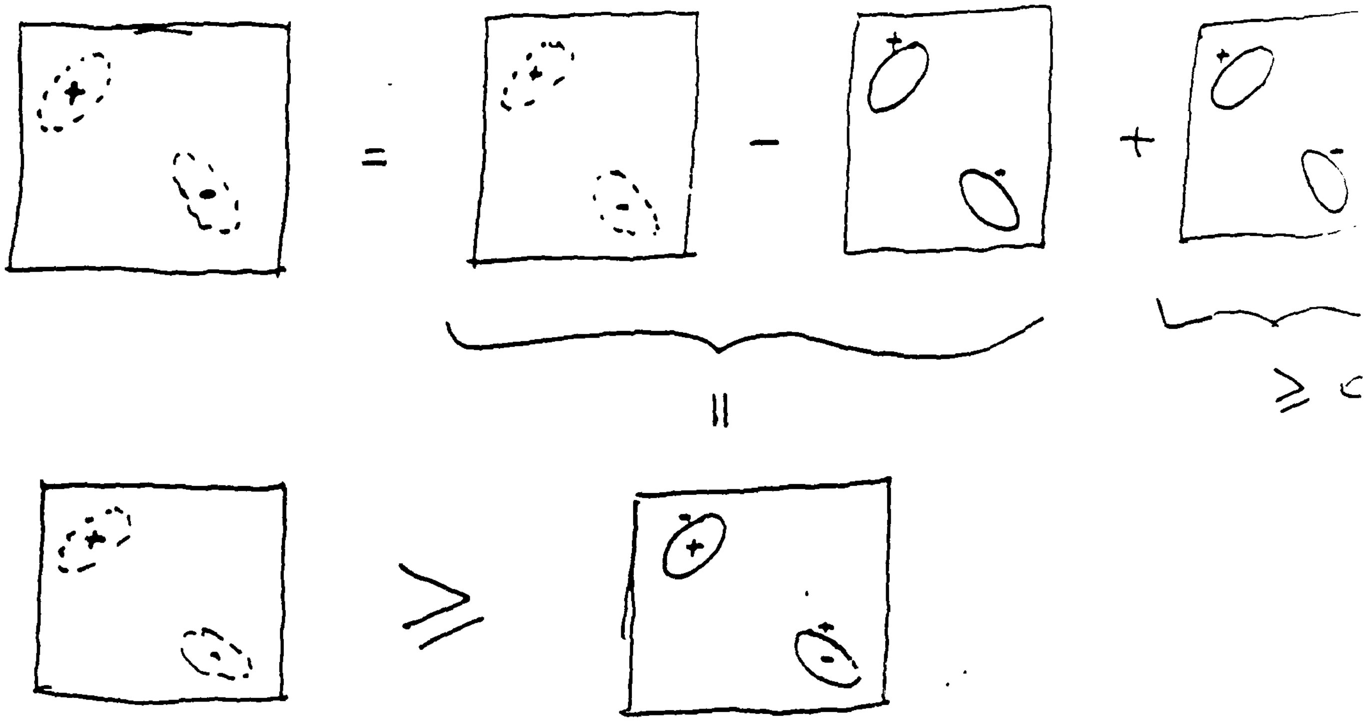

Fig 1: The Onsager process in pictures. The first "line is the Ewald identity i.e, we add and substract the energy of exactly the same system as the original but with the Onsager smeared charges replacing the original charges (see the text)

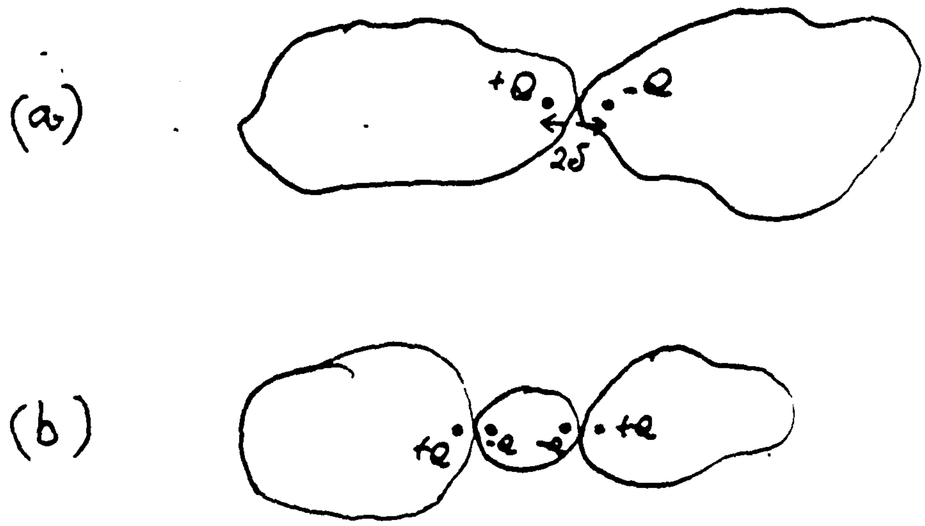

Fig 2: Bonding and Aggregation (see the text)

$$C_{onsager}(x) = A_0 + A_1 x + A_2 x^2 + A_3 x^3 + A_5 x^5 \qquad x < 1 \tag{5.4}$$

which is view of (5.1) is also the form of the exact trial function.

Example(b3): hard spheres will imbebbed monopoles and dipoles.

For unequal size spheres, the overlap value function has the form (with $x = r - \lambda$): [13] ..

$$C_{12,hc}(r) = A_0 \qquad r \leq \tfrac{1}{2}(\sigma_1 - \sigma_2) \equiv \lambda$$

$$= A_0 + \left(B_2 x^2 + B_3 x^3 + B_4 x^4\right)/r \tag{5.5}$$

$$\lambda \leq r \leq \tfrac{1}{2}(\sigma_1 + \sigma_2) \equiv \sigma_{12}$$

The Onsager smeared functions are given in Appendix D. when forming the trial dcf's we keep the angular dependence and attach coefficients to the radial part of each function. Compare with Wertheim's solution. [16]

Comment(b4): overlap-spheres and pair-excluded volumes for hard objects.

At low densities, at the 2nd virial level of approximation, the hard-core dcf is given by the overlap-volume of two objects having the shape of the pair excluded volume between the two relevant particles. As long as the pair excluded volume has the same shape as the two hard particles, then the two kinds of overlap volumes mentioned above have the same analytic form.

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