Journal of Statistical Physics, Vol. 37, Nos. 1/2, 1984

Comments on the Mean Spherical Approximation for Hard-Core and Soft Potentials and an Application to the One-Component Plasma

Yaakov Rosenfeld[1]

Received March 28, 1984; revised April 24, 1984

The thermodynamic properties of the mean spherical (MSA), Percus–Yevick (PY), and hypernetted-chain (HNC) approximations are derived by a simple and unified approach by considering the RPA free-energy functional $\mathfrak{F}$ and employing an Ewald-type identity. It is demonstrated that with decreasing relative contribution of the hard-core insertion to the thermodynamic functions, the MSA changes its nature from PY-like to HNC-like, with $\mathfrak{F}$ changing its role from excess pressure to excess free energy, respectively. It is found that the condition of continuity of the MSA pair functions is equivalent to a stationarity condition for $\mathfrak{F}$ and leads to thermodynamic consistency between the "virial" and "energy" equations of state for the (thus defined) "soft"-MSA (SMSA), with $\mathfrak{F}$ playing the role of the excess free energy. It is shown that the PY-"compressibility" and "virial" equations of state for D-dimensional hard spheres may be simply obtained one from the other without knowing any details of the solution of the model. Using this relation we find an indication that the PY approximation for hard spheres becomes less accurate with increasing dimensionality. A general variational formulation is presented for the application of the MSA for soft potentials, and results for the one-component plasma are discussed and extended.

KEY WORDS: Mean-spherical approximations; equations of state; Coulomb systems; integral equations for fluids.

1. INTRODUCTION

The interest in the mean-spherical approximation (MSA)[1a] for simple fluids is partly due to the availability of analytic solutions[1b] of that model for certain special systems, of which those with the Coulomb and Yukawa pair

[1] Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024. On sabbatical leave from the Nuclear Research Center-Negev, P.O. Box 9001, Beer Sheva, Israel.

0022-4715/84/1000-0215$03.50/0

potentials supplementing the hard-core constraint have been the object of extensive analysis in recent years.[1c] An analytic study of the thermodynamic properties of the MSA for simple fluids and simple fluid mixtures has been made by Hoye and Stell,[2] and their method of derivation has been further simplified.[3] The MSA may serve as a model for soft potentials (without hard cores) when the hard-core diameters are considered as free parameters and are determined by appropriate physical constraints. The first application of this approach is due to Gillan.[4] He used the Palmer–Weeks[5] solution for charge hard spheres and imposed continuity of the pair function $g(r)$ to obtain rather accurate results for the Coulomb potential (i.e., the one-component plasma). Gillan's continuity condition has been subsequently applied for the Yukawa potential, as a model for the screened one-component plasma (OCP),[6] and for the description of dilute charged colloidal dispersions.[7]

Gillan's approach has been generalized and discussed in the light of the modified-HNC (MHNC) scheme,[8,9] and has been termed soft-MSA (SMSA). The physical motivation for the SMSA has been based on the idea of regarding the hard-core insertion in a potential as a perturbation.[9] The thermodynamic functions for the SMSA via the "energy" equation of state have been derived in two alternative ways, and the special role played by potentials that possess Fourier transforms has been emphasized.[3,9] It has been noted in practice,[10,11] from the numerical results, and derived on the basis of general arguments concerning the MSA,[12] that the continuity condition of Gillan is equivalent to an extremum condition for the potential energy when it is considered as a function of the hard-core diameters. This equivalence has played a key role in elucidating the physical nature of the SMSA for strongly coupled D-dimensional ν-component plasmas.[13] More recently MacGowan[14–16] considered alternative criteria for choosing the hard-core parameter of the MSA, leading to discontinuous pair functions but with apparently improved results for the thermodynamics (as demonstrated for the OCP).

Analytic solutions of the MSA may be useful also in the context of the variational perturbation theory (VPT) for simple classical fluids. Foiles and Ashcroft[17] have fitted the Lennard–Jones potential by a linear combination of Yukawa potentials for which the energy integrals using the Percus–Yevick (PY) pair functions for the hard spheres (namely, the MSA results for hard spheres) can be calculated analytically. Such modeling is especially fruitful when considering the VPT for mixtures. This approach can be further extended by employing the MSA pair functions for the Yukawa potential. The choice of the corresponding VPT entropy function has been recently discussed in light of the MHNC scheme.[18] An alternative approach but with a similar philosophy has been briefly sketched at the end of Ref. 2.

Another general possibility within the context of the MSA is to use the MSA result for one potential as a model for another hard-core potentials, by manipulating the MSA "tail" parameters. This idea originates from the work of Waisman[19] for hard spheres employing the MSA results for the Yukawa potential tail.

The aim of the present work is to extend the analysis of the MSA along directions mentioned above and in particular to demonstrate that with decreasing relative contribution of the hard-core insertion to the thermodynamic functions, the MSA free-energy functional changes its nature from Percus–Yevick-like to HNC-like. It it found that Gillan's continuity condition implies the requirement of "virial"-"energy" thermodynamic consistency for the MSA, and it is shown that the PY-"compressibility" and "virial" equations of state for D-dimensional spheres may be simply obtained one from the other without knowing any details of the solution.

This paper is organized as follows: In Section 2 the method of Ref. 3 is extended to provide a very simple derivation of all the general results for the MSA as obtained in Ref. 2, and is applied also to the PY and HNC theories for arbitrary potentials.[20] Hard-core potentials and derivatives with respect to the hard-core diameters are considered in Section 3, where it is also shown that the HNC free-energy functional as usually obtained via the energy equation of state by the "coupling constant" integration,[21] does represent the HNC "virial" excess free energy also for the hard-sphere potential. Hard-core and soft-core limits for the MSA are discussed in Section 4, and general results for the PY approximation for hard spheres on one hand, and for the SMSA, on the other hand, are displayed. Finally, an alternative motivation for a discontinuous MSA for soft potentials is offered in Section 5, a general variational formulation of the problem is given, and as an example of the utility of the results in Section 3, MacGowan's results for the OCP are discussed and extended.

2. THERMODYNAMIC FUNCTIONS

Consider a multicomponent system of particles of partial number concentrations x_i, total number density $\rho = N/V$, at temperature $T = (k_B\beta)^{-1}$, interacting through the pair potentials $\phi_{ij}(r)$. The pair functions $h_{ij}(r) \equiv g_{ij}(r) - 1$ are related to the direct correlation functions $c_{ij}(r)$ by the Ornstein–Zernike (OZ) equations

$$\tilde{h}_{ij}(k) = \tilde{c}_{ij}(k) + \rho \sum_l x_l \tilde{h}_{il}(k)\, \tilde{c}_{lj}(k) \tag{1}$$

where tilde signs denote Fourier transforms. The structure factors $S_{ij}(k)$ are defined by

$$\rho(x_i x_j)^{1/2} \tilde{h}_{ij}(k) = S_{ij}(k) - \delta_{ij} \tag{2}$$

From Eqs. (1) and (2) one obtains the matrix equation

$$\overset{\square}{S} = (\overset{\square}{1} - \overset{\square}{C})^{-1} \tag{3}$$

where $S_{ij}(k)$ are the elements of $\overset{\square}{S}$ and $(\overset{\square}{C})_{ij} = \rho(x_i x_j)^{1/2} \tilde{c}_{ij}(k)$ are the elements of $\overset{\square}{C}$, while $\overset{\square}{1}$ is the unit matrix with elements δ_{ij}.

The RPA free energy functional, $\mathfrak{F}$, is a key quantity in the integral equation approach to simple classical fluids. It is defined by

$$\mathfrak{F} = -\frac{1}{2}\rho \sum_{ij} x_i x_j \int c_{ij}(r)\, d\mathbf{r} + \frac{1}{2}(2\pi)^{-D} \sum_i x_i \int \tilde{c}_{ii}(k)\, d\mathbf{k} + \frac{1}{2\rho}(2\pi)^{-D} \int d\mathbf{k} \ln \det(\overset{\square}{1} - \overset{\square}{C}) \tag{4}$$

with "det" denoting the determinant and "D" the dimensionality. We shall first derive some general properties of $\mathfrak{F}$, valid for general pair functions and for arbitrary D, and then consider pair functions obeying various approximations, namely PY, HNC, and MSA.

2.1. General Results

$\mathfrak{F}$ is a functional of the $c_{ij}(r)$'s and a general variation in $\mathfrak{F}$ as a result of a variation in the c_{ij}'s is given by

$$\delta\mathfrak{F} = -\frac{1}{2}\rho \sum_{ij} x_i x_j \int \delta c_{ij}(r)\, d\mathbf{r} + \frac{1}{2}(2\pi)^{-D} \sum_i x_i \int \delta\tilde{c}_{ii}(k)\, d\mathbf{k} - \frac{1}{2}(2\pi)^{-D} \sum_{ij} (x_i x_j)^{1/2} \int S_{ij}(k)\, \delta\tilde{c}_{ij}(k)\, d\mathbf{k} \tag{5}$$

Using the Ewald-type identity that follows directly from (2), namely,

$$\rho \sum_{ij} x_i x_j \int g_{ij}(r)\, \theta_{ij}(r)\, d\mathbf{r} = \rho \sum_{ij} x_i x_j \int \theta_{ij}(r)\, d\mathbf{r} - (2\pi)^{-D} \sum_i x_i \int \tilde{\theta}_{ii}(k)\, d\mathbf{k} + (2\pi)^{-D} \sum_{ij} (x_i x_j)^{1/2} \int S_{ij}(k)\, \tilde{\theta}_{ij}(k)\, d\mathbf{k} \tag{6}$$

where $\theta_{ij}(r)$ are arbitrary functions that possess Fourier transforms $\tilde{\theta}_{ij}(k)$, it follows from (5) that

$$\delta\mathfrak{F} = -\frac{1}{2}\rho \sum_{ij} x_i x_j \int g_{ij}(r)\, \delta c_{ij}(r)\, d\mathbf{r} \tag{7}$$

or, in other words

$$\frac{\delta\mathfrak{F}}{\delta c_{ij}(r)} = -\frac{1}{2}\rho x_i x_j g_{ij}(r) \tag{8}$$

This relation, obtained previously[22] by graph theoretical methods, is derived here in a single step, showing the simplifying role played by (6) in this context.

Letting λ be a parameter of the pair functions other than ρ, we get from (7) that

$$\frac{\partial\mathfrak{F}}{\partial\lambda} = \frac{1}{2}\rho \sum_{ij} x_i x_j \int g_{ij}(r)\frac{\partial c_{ij}(r)}{\partial\lambda}\, d\mathbf{r} \tag{9}$$

To make use of the corresponding relation with $\lambda = \rho$ we first switch to the reduced variable $\xi = r\rho^{1/D}$. Using Eqs. (4)–(6) we get [instead of (7)]

$$\delta\mathfrak{F} = -\frac{1}{2}\sum_{ij} x_i x_j \int \bar{g}_{ij}(\xi)\, \delta\bar{c}_{ij}(\xi)\, d\boldsymbol{\xi} \tag{10}$$

where now $\delta\mathfrak{F}$ is a general variation on $\mathfrak{F}$ that may result also from varying the density. Here $\bar{g}_{ij}(\xi) = g_{ij}(\xi/\rho^{1/\mathrm{D}})$, $\bar{c}_{ij}(\xi) = c_{ij}(\xi/\rho^{1/\mathrm{D}})$. From (10) we get

$$\frac{\partial\mathfrak{F}}{\partial\rho} = -\frac{1}{2}\sum\nolimits_{ij} x_i x_j \int \bar{g}_{ij}(\xi)\frac{d\bar{c}_{ij}(\xi)}{d\rho}\, d\boldsymbol{\xi} \tag{11}$$

Defining

$$c'_{ij}(r) = \frac{\partial}{\partial r} c_{ij}(r)$$

we obtain

$$\frac{d}{d\rho}\bar{c}_{ij}(\xi,\rho,\beta) = c'_{ij}\left(\frac{\xi}{\rho^{1/\mathrm{D}}},\rho,\beta\right)\left(-\frac{1}{D}\right)\left(\frac{\xi}{\rho^{1/\mathrm{D}}}\right)\frac{1}{\rho} + \frac{\partial}{\partial\rho}c_{ij}(r,\rho,\beta) \tag{12}$$

where we display explicitly the ρ and β dependence of the c_{ij}'s.

Defining the virial-type integral J_V by (see Ref. 2)

$$J_V = \frac{\rho}{2D} \sum_{ij} x_i x_j \int g_{ij}(r)\, r \frac{\partial c_{ij}(r)}{\partial r}\, d\mathbf{r} \tag{13}$$

we use Eqs. (11), (12) to get

$$\rho \frac{\partial \mathfrak{F}}{\partial \rho} = J_V - \frac{\rho^2}{2} \sum_{ij} x_i x_j \int g_{ij}(r) \frac{\partial c_{ij}(r)}{\partial \rho}\, d\mathbf{r} \tag{14}$$

By direct differentiation of (4), on the other hand, using (6) we get

$$\rho \frac{\partial \mathfrak{F}}{\partial \rho} = -\left(\mathfrak{F} + \frac{1}{2}\right) + \frac{1}{2} \beta \frac{\partial P}{\partial \rho} - \frac{\rho}{2} \sum_{ij} x_i x_j \int g_{ij}(r) \left[c_{ij}(r) + \rho \frac{\partial c_{ij}(r)}{\partial \rho} \right] d\mathbf{r} \tag{15}$$

where the compressibility is given by

$$\beta \frac{\partial P}{\partial \rho} = 1 - \rho \sum_{ij} x_i x_j \int c_{ij}(r)\, d\mathbf{r} \tag{16}$$

Combining Eqs. (14) and (15) we finally get

$$J_V = \frac{1}{2} \left[\beta \frac{\partial P}{\partial \rho} - 1 \right] - \mathfrak{F} - \frac{\rho}{2} \sum_{ij} x_i x_j \int g_{ij}(r)\, c_{ij}(r)\, d\mathbf{r} \tag{17}$$

Let $Z_c = (\beta P/\rho)_c$ be the compressibility factor as obtained from Eq. (16) (i.e., the "compressibility" equation of state). We write

$$\mathfrak{F} = \tfrac{1}{2}(Z_c - 1) + \Delta \tag{18}$$

where, using Eq. (15),

$$\frac{\partial}{\partial \rho}(\rho \Delta) = -\frac{\rho}{2} \sum_{ij} x_i x_j \int g_{ij}(r) \left[c_{ij}(r) + \rho \frac{\partial c_{ij}(r)}{\partial \rho} \right] d\mathbf{r} \tag{19}$$

2.2. Application to the Approximate Theories

In the Percus–Yevick (PY) approximation

$$c_{ij}(r) = (1 - e^{\beta \phi_{ij}(r)})\, g_{ij}(r) \equiv \tau_{ij}(r)\, g_{ij}(r) \tag{20}$$

Eq. (19) takes the form

$$\frac{\partial}{\partial \rho}(\rho \Delta) = -\frac{\rho}{2}\sum_{ij} x_i x_j \int \tau_{ij}(r)\left[g_{ij}^2(r) + \rho \frac{\partial g_{ij}(r)}{\partial \rho} g_{ij}(r)\right] d\mathbf{r}$$
$$= -\frac{1}{2}\sum_{ij} x_i x_j \int \tau_{ij}(r) \frac{\partial}{\partial \rho}\left[\frac{\rho^2}{2} g_{ij}^2(r)\right] d\mathbf{r}$$

or

$$\Delta^{(\mathrm{PY})} = -\frac{\rho}{4}\sum_{ij} x_i x_j \int \tau_{ij}(r)\, g_{ij}^2(r)\, d\mathbf{r} = -\frac{\rho}{4}\sum_{ij} x_i x_j \int g_{ij}(r)\, c_{ij}(r)\, d\mathbf{r} \tag{21}$$

In view of Eq. (18) we finally obtain

$$Z_c^{(\mathrm{PY})} - 1 = 2\mathfrak{F} + \frac{\rho}{2}\sum_{ij} x_i x_j \int \tau_{ij}^{-1}(r)\, c_{ij}^2(r)\, d\mathbf{r} \tag{22}$$

which is the result obtained by Baxter[23,24] long ago: the functional $Z_c^{(\mathrm{PY})} - 1$ given by Eq. (22) is stationary with respect to small variations of the $c_{ij}(r)$'s provided that the PY approximation [Eq. (20)] is satisfied.

In the hypernetted chain (HNC) approximation

$$c_{ij}(r) = h_{ij}(r) - \ln[g_{ij}(r)\, e^{\beta\phi_{ij}(r)}] \tag{23}$$

The functional $f^{(\mathrm{HNC})}$ given by

$$f^{(\mathrm{HNC})} = \mathfrak{F} + \frac{\rho}{4}\sum_{ij} x_i x_j \int h_{ij}^2(r)\, d\mathbf{r} \tag{24}$$

is readily seen from Eq. (7) to be stationary with respect to small variations in the pair functions provided Eq. (23) holds. Using Eqs. (6) and (23) we get

$$\frac{\partial f^{(\mathrm{HNC})}}{\partial \lambda} = \frac{\rho}{2}\sum_{ij} x_i x_j \int g_{ij}(r) \frac{\partial}{\partial \lambda}[\beta\phi_{ij}(r)]\, d\mathbf{r} \tag{25}$$

and in particular, with $\lambda = \beta$

$$\beta \frac{\partial f^{(\mathrm{HNC})}}{\partial \beta} = u \tag{26}$$

where $u = \beta U/N$ is the potential energy

$$u = \frac{\rho}{2}\sum_{ij} x_i x_j \int g_{ij}(r)\, \beta\phi_{ij}(r)\, d\mathbf{r} \tag{27}$$

The pressure according to the virial theorem is given by

$$Z_V - 1 \equiv \left(\frac{\beta P}{\rho}\right)_V - 1 = -\frac{\rho}{2D}\sum_{ij} x_i x_j \int g_{ij}(r)\, r\beta \frac{\partial \phi_{ij}(r)}{\partial r}\, d\mathbf{r} \tag{28}$$

and using Eqs. (13) and (23) ones gets

$$J^{(\mathrm{HNC})} = Z_V - 1 - \frac{\rho}{4}\sum_{ij} x_i x_j \int h_{ij}^2(r)\, d\mathbf{r} \tag{29}$$

Using Eqs. (14), (23), and (24) one obtains for the HNC approximation

$$\rho \frac{\partial f^{(\mathrm{HNC})}}{\partial \rho} = J_V^{(\mathrm{HNC})} + \frac{\rho}{4}\sum_{ij} x_i x_j \int h_{ij}^2(r)\, d\mathbf{r}$$

so that

$$\rho \frac{\partial f^{(\mathrm{HNC})}}{\partial \rho} = Z_V^{(\mathrm{HNC})} - 1 \tag{30}$$

Using

$$\frac{\partial^2 f^{(\mathrm{HNC})}}{\partial \beta\, \partial \rho} = \frac{\partial^2 f^{(\mathrm{HNC})}}{\partial \rho\, \partial \beta}$$

Eqs. (26) and (30) show that the HNC approximation satisfies Hiroike's test[25]

$$\frac{\partial U}{\partial V} = T\left(\frac{\partial P}{\partial T}\right) - P \tag{31}$$

i.e., there is thermodynamic consistency between the "energy" and "virial" equations of state. The functional $f^{(\mathrm{HNC})}$ represents the excess free energy as obtained by either the "virial" or the "energy" equations within the HNC approximation.

In the mean spherical approximation (MSA) defined by

$$g_{ij}(r) = 0, \qquad r < R_{ij} \tag{32a}$$

$$c_{ij}(r) = -\beta\phi_{ij}(r), \qquad r > R_{ij} \tag{32b}$$

the solution is obtained by finding the functions $c_{ij}(r)$ for $r < R_{ij}$, such that the functions $g_{ij}(r)$ which satisfy the *OZ* relations (1) obey Eq. (32a). In view of Eq. (8), the MSA equations may be formulated variationally by requiring

$$\frac{\delta \mathfrak{F}}{\delta c_{ij}(r)} = 0, \qquad r < R_{ij} \tag{33}$$

Unlike the PY and HNC approximations for which the "generating" functionals $Z_c^{(\mathrm{PY})}$ and $f^{(\mathrm{HNC})}$ had a well-defined thermodynamic meaning, the interpretation of $\mathfrak{F}$ depends on the context of its application (see below).

3. HARD-CORE POTENTIALS

Consider the rather general "hard-core" pair functions of the form

$$g_{ij}(r) = g_{ij}^{<}(r)[H(r) - H(r - R_{ij})] + g_{ij}^{>}(r)\, H(r - R_{ij}) \tag{34a}$$

$$c_{ij}(r) = c_{ij}^{<}(r)[H(r) - H(r - R_{ij})] + c_{ij}^{>}(r)\, H(r - R_{ij}) \tag{34b}$$

with $g_{ij}^{<}(r) \equiv 0$, and the functions $g_{ij}^{>}(r)$, $c_{ij}^{<}(r)$, $c_{ij}^{>}(r)$ being smooth also across the (cores) R_{ij}. $H(x)$ denotes the unit step function: $H(x < 0) = 0$, $H(x \geqslant 0) = 1$. The continuity of the functions $[g_{ij}(r) - c_{ij}(r)]$ is ensured by the OZ relations and yields

$$c_{ij}^{<}(R_{ij}) - c_{ij}^{>}(R_{ij}) = -g_{ij}^{>}(R_{ij}) \tag{35}$$

Recall that the virial equation of state for such hard-core potentials is (with $\omega_D = 2\pi^{D/2}/\Gamma(D/2)$ the surface of a D-dimensional unit sphere)

$$Z_V = 1 + \frac{\rho \omega_D}{2D} \sum_{ij} x_i x_j R_{ij}^D g_{ij}(R_{ij})$$
$$- \frac{\rho}{2D} \sum_{ij} x_i x_j \int_{R_{ij}}^{\infty} g_{ij}(r)\, r \frac{\partial}{\partial r} [\beta \phi_{ij}(r)]\, d\mathbf{r} \tag{36}$$

As in the preceding section we shall derive at first general results and then consider specific approximate theories. The generalization of the present calculations to pair functions involving more jump discontinuities (e.g., those for square-well potentials) is straightforward.

3.1. General Results

In order to calculate $\partial \mathfrak{F}/\partial R_{lm}$ from Eq. (9) note that

$$\frac{\partial c_{ij}(r)}{\partial R_{lm}} = \frac{\partial c_{ij}^{<}(r)}{\partial R_{lm}} [H(r) - H(r - R_{ij})] + \frac{\partial c_{ij}^{>}(r)}{\partial R_{lm}} H(r - R_{ij})$$
$$+ [c_{ij}^{<}(r) - c_{ij}^{>}(r)] \frac{\partial R_{ij}}{\partial R_{lm}} \delta(r - R_{ij}) \tag{37}$$

$$\int [g_{ij}(r) - c_{ij}(r)] \frac{\partial c_{ij}(r)}{\partial R_{lm}} d\mathbf{r}$$

$$= \int_0^{R_{ij}} [g_{ij}^{<}(r) - c_{ij}^{<}(r)] \frac{\partial c_{ij}^{<}(r)}{\partial R_{lm}} d\mathbf{r} + \int_{R_{ij}}^{\infty} [g_{ij}^{>}(r) - c_{ij}^{>}(r)] \frac{\partial c_{ij}^{>}(r)}{\partial R_{lm}} d\mathbf{r}$$

$$+ [g_{ij}^{>}(R_{ij}) - c_{ij}^{>}(R_{ij})][c_{ij}^{<}(R_{ij}) - c_{ij}^{>}(R_{ij})] \frac{\partial R_{ij}}{\partial R_{lm}} \omega_{\mathrm{D}} R_{ij}^{D-1} \quad (38)$$

$$\int c_{ij}(r) \frac{\partial c_{ij}(r)}{\partial R_{lm}} d\mathbf{r} = \frac{1}{2} \int \frac{\partial}{\partial R_{lm}} c_{ij}^2(r)\, d\mathbf{r} = \int_0^{R_{ij}} c_{ij}^{<}(r) \frac{\partial c_{ij}^{<}(r)}{\partial R_{lm}} d\mathbf{r}$$

$$+ \int_{R_{ij}}^{\infty} c_{ij}^{>}(r) \frac{\partial c_{ij}^{>}(r)}{\partial R_{lm}} d\mathbf{r} + \frac{1}{2} \left\{ \left[c_{ij}^{<}(R_{ij}) \right]^2 - [c_{ij}^{>}(R_{ij})]^2 \right\} \frac{\partial R_{ij}}{\partial R_{lm}} \omega_{\mathrm{D}} R_{ij}^{D-1} \quad (39)$$

Combining Eqs. (38) and (39), we use Eq. (35) to get

$$\int g_{ij}(r) \frac{\partial x_{ij}(r)}{\partial R_{lm}} d\mathbf{r} = -\omega_{\mathrm{D}} R_{ij}^{D-1} \frac{1}{2} g_{ij}^2(R_{ij}) \frac{\partial R_{ij}}{\partial R_{lm}} + \int_{R_{ij}}^{\infty} g_{ij}^{>}(r) \frac{\partial c_{ij}^{>}(r)}{\partial R_{lm}} d\mathbf{r} \quad (40)$$

and finally,

$$\frac{\partial \mathfrak{F}}{\partial R_{lm}} = \frac{\rho}{4} \omega_{\mathrm{D}} \sum_{ij} x_i x_j R_{ij}^{D-1} g_{ij}^2(R_{ij}) \frac{\partial R_{ij}}{\partial R_{lm}} - \frac{\rho}{2} \sum_{ij} x_i x_j \int g_{ij}(r) \frac{\partial c_{ij}^{>}(r)}{\partial R_{lm}} d\mathbf{r} \quad (41)$$

By a procedure similar to that leading to Eq. (41) we find that

$$J_V = \rho \frac{\omega_{\mathrm{D}}}{4D} \sum_{ij} x_i x_j R_{ij}^D g_{ij}^2(R_{ij}) + \frac{\rho}{2D} \sum_{ij} x_i x_j \int_{R_{ij}}^{\infty} g_{ij}(r) r \frac{\partial c_{ij}(r)}{\partial r} d\mathbf{r} \quad (42)$$

3.2. PY Approximation

For the PY approximation the functions $y_{ij}(r) = g_{ij}(r) e^{\beta\phi_{ij}(r)}$ are continuous and from Eq. (22) using Eq. (9) and (20) we get

$$\frac{\partial Z_c^{(\mathrm{PY})}}{\partial \lambda} = -\frac{\rho}{2} \sum_{ij} x_i x_j \int y_{ij}^2(r) \frac{\partial}{\partial \lambda} (e^{-\beta\phi_{ij}(r)})\, d\mathbf{r} \quad (43)$$

and in particular

$$\frac{\partial Z_c^{(\mathrm{PY})}}{\partial R_{lm}} = \frac{\rho}{2} \omega_{\mathrm{D}} \sum_{ij} x_i x_j R_{ij}^{D-1} e^{\beta\phi_{ij}^{>}(R_{ij})} g_{ij}^2(R_{ij}) \frac{\partial R_{ij}}{\partial R_{lm}} \quad (44)$$

3.3. HNC Approximation

Similarly to the PY approximation, the continuity of the functions $y_{ij}(r)$ enables us to replace Eq. (25) by

$$\frac{\partial f^{(\mathrm{HNC})}}{\partial \lambda} = -\frac{\rho}{2} \sum_{ij} x_i x_j \int y_{ij}(r) \frac{\partial}{\partial \lambda} (e^{-\beta\phi_{ij}(r)})\, d\mathbf{r} \tag{45}$$

In particular

$$\frac{\partial f^{(\mathrm{HNC})}}{\partial R_{lm}} = \frac{\rho}{2} \omega_{\mathrm{D}} \sum_{ij} x_i x_j R_{ij}^{D-1} g_{ij}(R_{ij}) \frac{\partial R_{ij}}{\partial R_{lm}} \tag{46}$$

In the HNC approximation

$$\int_{R_{ij}}^{\infty} g_{ij}(r) r \frac{\partial c_{ij}(r)}{\partial r}\, d\mathbf{r}$$

$$= -\int_{R_{ij}}^{\infty} g_{ij}(r) r \frac{\partial}{\partial r} [\beta\phi_{ij}(r)]\, d\mathbf{r} + \int_{R_{ij}}^{\infty} h_{ij}(r) \frac{\partial h_{ij}(r)}{\partial r} r\, d\mathbf{r}$$

$$\int_{R_{ij}}^{\infty} h_{ij}(r) \frac{\partial h_{ij}(r)}{\partial r} r\, d\mathbf{r} = \frac{D\omega_{\mathrm{D}}}{2} \int_{R_{ij}}^{\infty} \frac{\partial}{\partial r} [h_{ij}^2(r)] \left(\frac{r^{\mathrm{D}}}{D}\right) dr$$

$$= -\frac{\omega_{\mathrm{D}}}{2} R_{ij}^D h_{ij}^2(R_{ij}) - \frac{D}{2} \int_{R_{ij}}^{\infty} h_{ij}^2(r)\, d\mathbf{r}$$

so that Eq. (42) takes the form

$$\begin{aligned} J_V^{(\mathrm{HNC})} = {} & \frac{\rho\omega_D}{2D} \sum_{ij} x_i x_j R_{ij}^D g_{ij}(R_{ij}) \\ & - \frac{\rho}{2D} \sum_{ij} x_i x_j \int_{R_{ij}}^{\infty} g_{ij}(r) r \frac{\partial}{\partial r} [\beta\phi_{ij}^{>}(r)]\, d\mathbf{r} \\ & - \frac{\rho}{4} \sum_{ij} x_i x_j \int_0^{\infty} h_{ij}^2(r)\, d\mathbf{r} \end{aligned} \tag{47}$$

Recalling the virial equation of state for hard-core potentials [Eq. 36)], we use Eqs. (47) and (29) to find that Eq. (30) holds also for hard-core potentials, and the functional $f^{(\mathrm{HNC})}$ represents the excess free energy via the "virial" equation of state even for the hard-sphere potential.

3.4. Mean-Spherical Approximation

For the mean-spherical approximation (MSA), with

$$c_{ij}^{>}(r) = -\beta\phi_{ij}(r) \tag{48}$$

being the usual "closure," we have $\partial c_{ij}^{>}(r)/\partial R_{lm}=0$, and Eq. (41) takes the form[26]

$$\left(\frac{\partial \mathfrak{F}}{\partial R_{lm}}\right)_{\mathrm{MSA}}=\frac{\rho}{4}\,\omega_{\mathrm{D}}\sum_{ij} x_i x_j R_{ij}^{D-1} g_{ij}^2(R_{ij})\,\frac{\partial R_{ij}}{\partial R_{lm}} \tag{49}$$

For hard spheres Eqs. (44) and (49) are identical and agree with the explicit solutions of Lebowitz[27] and of Lebowitz and Zomick[28] for additive hard spheres and nonadditive hard rods, respectively. From Eqs. (9) and (32) we get

$$\beta\frac{\partial \mathfrak{F}^{(\mathrm{MSA})}}{\partial \beta}=u \tag{50}$$

from Eqs. (14) and (32) we obtain

$$\rho\frac{\partial \mathfrak{F}^{(\mathrm{MSA})}}{\partial \rho}=J_V^{(\mathrm{MSA})} \tag{51}$$

while Eqs. (48), (42), and (36) yield

$$J_V^{(\mathrm{MSA})}=Z_V-1-\frac{\rho\omega_D}{2D}\sum_{ij} x_i x_j R_{ij}^D g_{ij}(R_{ij})$$
$$+\frac{\rho\omega_D}{4D}\sum_{ij} x_i x_j R_{ij}^D g_{ij}^2(R_{ij}) \tag{52}$$

The utility of these expressions will be obvious when considering (see below) the limit $g_{ij}(R_{ij})=0$.

3.5. Inequality for Hard-Core Systems and the Physical Role of $\mathfrak{F}$

From the Gibbs–Bogolinbov inequality it may be found that the free energy is a nondecreasing function of the hard-core diameters[14]:

$$\frac{\partial f}{\partial R_{lm}}\geqslant 0 \tag{53}$$

By Eqs. (44) and (46) we see that the excess free energies as obtained by the "compressibility" in PY theory,

$$f_c^{(\mathrm{PY})}=\int_0^{\rho}(Z_c-1)\,\frac{d\rho}{\rho}$$

or by the "energy" (="virial") in HNC theory, $f^{(\mathrm{HNC})}$, satisfy the exact inequality (53). The validity of (53) within the MSA depends, however, on our interpretation of the approximation. Let f_0 represent the excess free energy for the purely hard-core system, i.e., $f_0 = \lim_{\beta \to 0} f$; then the MSA "energy" equation of state, Eq. (50), provides an approximation for the difference

$$(f - f_0)_{\mathrm{MSA}} = (\mathfrak{F} - \mathfrak{F}_0)_{\mathrm{MSA}} \tag{54}$$

Recall that $\mathfrak{F}_0 = \lim_{\beta \to 0} \mathfrak{F}$ is related to the compressibility factor for the purely hard-core system as obtained in PY theory [$\Delta = 0$ in Eq. (18)],

$$\mathfrak{F}(\beta = 0, \rho, \{R_{ij}\}) = \tfrac{1}{2}[Z_c^{(\mathrm{PY})}(\rho, \{R_{ij}\}) - 1] \tag{55}$$

For a one-component system the condition (53) in the approximation (54) takes the form

$$g_{\mathrm{MSA}}^2(R) \geqslant [g_{\mathrm{HS}}^{(\mathrm{PY})}(R)]^2 - 2g_{\mathrm{HS}}(R) \tag{56}$$

The result (56) is obtained from (53) and (54) by using Eq. (49), i.e.,

$$\frac{\partial \mathfrak{F}_{\mathrm{MSA}}}{\partial R} = \frac{\rho}{4} \omega_{\mathrm{D}} R^{D-1} g_{\mathrm{MSA}}^2(R)$$

$$\frac{\partial \mathfrak{F}_0}{\partial R} = \frac{\rho}{4} \omega_{\mathrm{D}} R^{D-1} [g_{\mathrm{HS}}^{(\mathrm{PY})}(R)]^2$$

while the virial equation of state the hard spheres [see Eq. (36)] yields [with $\eta = (\rho\omega_{\mathrm{D}}/D)(R/2)^D$]

$$\frac{\partial f_0}{\partial R} = \frac{\partial f_0}{\partial \eta}\frac{\partial \eta}{\partial R} = \frac{Z_v - 1}{\eta}\frac{\partial \eta}{\partial R} = \frac{\dfrac{\rho\omega}{2D} R^D g_{\mathrm{HS}}(R)}{\dfrac{\rho\omega_{\mathrm{D}}}{2^D \cdot D} R^D} \cdot \frac{\rho\omega_{\mathrm{D}} R^{D-1}}{2^D}$$

$$= \frac{\rho}{4} \omega_{\mathrm{D}} R^{D-1} \cdot 2g_{\mathrm{HS}}(R)$$

If we use the PY-"virial" result for f_0 then (56) takes the form

$$g_{\mathrm{MSA}}^2(R) \geqslant [g_{\mathrm{HS}}^{(\mathrm{PY})}(R)]^2 - 2g_{\mathrm{HS}}^{(\mathrm{PY})}(R)$$

This inequality is always satisfies for

$$g_{\mathrm{HS}}^{(\mathrm{PY})}(R) \leqslant 2 \qquad [\text{i.e., } \eta = (\pi/6)\rho R^3 \leqslant 0.25 \text{ in 3D}]$$

but may be violated for larger values of the packing fraction η. Note, however, that if we choose $\mathfrak{F}$ to represent the excess free energy, as is suggested by the form of Eq. (54), i.e., $f_0 = \mathfrak{F}_0$ in Eq. (54), then by Eq. (49) we find that Eq. (53) will always be satisfied.

4. HARD-CORE AND SOFT-CORE LIMITS FOR THE MSA

The relative role played by the hard-core part of the interaction in determining the thermodynamic properties of the system is a parameter that tells us whether the MSA result is PY-like or HNC-like or of intermediate nature. In the "PY" limit, namely, for purely hard-core interactions, the MSA and PY results are identical and $\mathfrak{F} = \frac{1}{2}(Z_c - 1)$. On the other hand when the hard-core contribution is relatively small, $J_V^{(\mathrm{MSA})} \simeq Z_V - 1$, and in view of Eqs. (47) and (48) Hiroike's test will be satisfied with $\mathfrak{F}$ replacing $f^{(\mathrm{HNC})}$ as the excess free energy, i.e., we expect HNC-like results. It is interesting to note that in both limits the MSA has a remarkable property that the compressibility and virial equations of state may be inferred one from the other.

4.1. MSA for Purely Hard-Core Interactions: PY Limit

From Eqs. (22), (36), (51), and (52) we obtain for purely hard-core interactions

$$\frac{\partial Z_c^{(\mathrm{PY})}}{\partial \rho} = \frac{\omega_{\mathrm{D}}}{2D} \sum_{ij} x_i x_j R_{ij}^D g_{ij}^2(R_{ij}) \tag{57}$$

$$Z_V^{(\mathrm{PY})} - 1 = \rho \frac{\omega_{\mathrm{D}}}{2D} \sum_{ij} x_i x_j R_{ij}^D g_{ij}(R_{ij}) \tag{58}$$

For a one-component system of hard spheres with packing fraction $\eta = \rho(\omega_{\mathrm{D}}/D)(R/2)^D$ Eqs. (57) and (58) lead to a general relation between the PY-"virial" and PY-"compressibility" equations of state

$$\frac{dZ_c^{(\mathrm{PY})}(\eta)}{d\eta} = 2^{D-1} g^2(R, \eta) = \frac{(Z_V^{(\mathrm{PY})} - 1)^2}{2^{D-1}\eta^2} \tag{59}$$

Note that the *structure* of both Eqs. (57) and (58) is consistent with the van der Waals one-fluid picture of replacing the g_{ij}'s by a single "effective" $g_{\mathrm{eff}}(\bar{R})$ with $\bar{R}^D = \sum_{ij} x_i x_j R_{ij}^D$. Moreover, the assumption of thermodynamic consistency between Eqs. (57) and (58) is equivalent to the original van der

Waals equation of state: the relation $\partial Z_V/\partial\rho = \partial Z_c/\partial\rho$ yields [upon using Eqs. (57) and (58) for g_{eff}]

$$g^2_{\text{eff}}(\bar{R}) = g_{\text{eff}}(\bar{R}) + \rho \frac{\partial}{\partial\rho} g_{\text{eff}}(\bar{R}) \tag{60}$$

which with the proper boundary condition is equivalent to

$$g_{\text{eff}}(\bar{R}) = (1-\bar{\eta})^{-1} \tag{61}$$

$$\bar{\eta} = \rho \frac{\omega_{\text{D}}}{D}\left(\frac{\bar{R}}{2}\right)^D \tag{62}$$

i.e., the exact result for additive hard spheres in one dimension.

For the one-component hard-sphere system, the solution of the consistency equation *for any D*, with the boundary condition that $Z_V = Z_c$ diverges at $\eta = 1$, is the *one-dimensional* van der Waals result $g(R) = (1-\eta)^{-1}$. This finding provides an indication that the PY theory for hard spheres becomes less accurate as the dimensionality increases. In one, three, and five[29] dimensions the PY asymptotic ($\eta \to 1$ limit) behavior is found analytically to be $Z_c \sim (1-\eta)^{-D}$, $g(R) \sim Z_V \sim (1-\eta)^{-(D+1)/2}$, a result that seems to agree also with the numerical 2D results.[30]

First-order deviations from additivity in both PY and HNC theories follow the van der Waals picture. Consider a binary mixture of hard spheres with diameters $R_{11} = R_{22} = R$, $R_{12} = R_{21} = R(1+\alpha)$. Let $Z^{(0)}$ correspond to the additive case ($\alpha = 0$) which for the particular system considered corresponds to the single component system with diameter R, and let $Z^{(\alpha)}$ correspond to $\alpha \neq 0$. From Eq. (49), to first order in α, we have

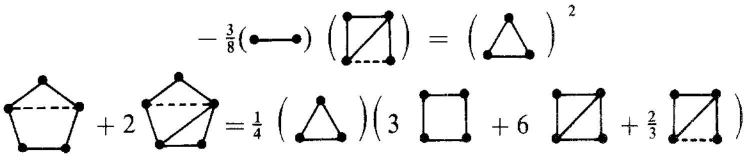
$$Z_c^{(\alpha)} = Z_c^{(0)} + x_1 x_2 \rho\omega_D R^D [g^{(0)}(R)]^2 \alpha \tag{63}$$

which in view of Eq. (59) takes the form

$$\begin{aligned} Z_c^{(\alpha)} &= Z_c^{(0)}(\eta) + x_1 x_2 2D\eta \frac{dZ_c^{(0)}(\eta)}{d\eta} \\ &\underset{\alpha \ll 1}{\cong} Z_c^{(0)}(\eta\{1 + 2x_1x_2[(1+\alpha)^\beta - 1]\}) \end{aligned} \tag{64}$$

Using Eq. (46) exactly the same result for $Z_V^{(\alpha)}$ is obtained for HNC.

Equation (59) provides relations between various hard-sphere cluster integrals, by considering the diagrammatic expressions for the virial coefficients in the expansion of Z_c and Z_V in powers of ρ. The simplest of these relations, obtained from the fourth and fifth virial coefficients for the PY theory, are


(65)
(66)

These "cluster" relations are valid for D-dimensional hard spheres, with the solid line representing an $f(r) = e^{-\beta\phi(r)} - 1$ bond, while a dotted line stands for an $rf'(r)$ bond.

4.2. MSA for Soft Potentials (SMSA): HNC-like Limit

From the physical point of view, an MSA result with $\phi_{ij}^{>}(r) = \phi_{ij}(r)$ will be considered as representing an approximation for the soft potentials $\phi_{ij}(r)$ in the limit when the contribution of the hard cores to the thermodynamics of the system vanishes, i.e., in the limit when the pair functions vanish at the cores:

$$g_{ij}(R_{ij}) = 0 \tag{67}$$

From Eq. (49) we see that this condition of continuity of the pair functions also automatically satisfies a stationarity condition for the functional $\mathfrak{F}$

$$\frac{\partial \mathfrak{F}}{\partial R_{ij}} = 0 \tag{68}$$

which in view of Eqs. (50)–(52) is now found to play the role of the excess free energy *satisfying Hiroike's test*

$$\rho \frac{\partial \mathfrak{F}}{\partial \rho} = Z_V - 1, \qquad \beta \frac{\partial \mathfrak{F}}{\partial \beta} = u \tag{69}$$

For general potentials $\phi_{ij}(r)$ we cannot assume *a priori* any relation between the core radii and should in principle treat an MSA model with all $R_{ij} = R_{ji}$ independent:

$$\frac{\partial \mathfrak{F}}{\partial R_{lm}} = \left\{ \begin{array}{ll} \dfrac{\rho}{4} \omega_D x_l^2 R_{ll}^{D-1} g_{ll}^2(R_{ll}), & l = m \\ \dfrac{\rho}{2} \omega_D x_l x_m R_{lm}^{D-1} g_{lm}^2(R_{lm}), & l \neq m \end{array} \right\} \geqslant 0 \tag{70}$$

In either case

$$\frac{\partial u}{\partial R_{lm}} = A g_{lm}(R_{lm}) \frac{\partial}{\partial \beta} g_{lm}(R_{lm}) \tag{71}$$

with $A \geqslant 0$. At $\beta = 0$ we have $g_{lm}^{(\mathrm{MSA})}(R_{lm}) = g_{lm}^{(\mathrm{PY})}(R_{lm}) > 0$ and as we increase β we expect to eventually cross $g_{lm}^{(\mathrm{MSA})}(R_{lm}) = 0$, so that if a solution of the type (67) is at all possible (and denoted R_{ij}^c) then in that vicinity $\partial g_{lm}^{(\mathrm{MSA})}(R_{lm})/\partial\beta < 0$. Assuming that $\partial g_{lm}^{(\mathrm{MSA})}(R_{lm})/R_{lm} \geqslant 0$ then for $R_{lm} > R_{lm}^c$ we have $\partial u/\partial R_{lm} < 0$ and for $R_{lm} < R_{lm}^c$ we have $\partial u/\partial R_{lm} > 0$, so that the points R_{ij}^c represent (at least) a local maximum for the potential energy.[26]

In addition, the "soft"-MSA (SMSA) satisfying Eq. (67) has the remarkable property [similar to Eq. (59) for the hard spheres] that the "compressibility" and "virial" ("energy") equations of state are related and may be inferred one from the other without the need to know details of the solution. For the MSA we find from Eqs. (19), (27), and (32) that

$$u = \frac{\partial}{\partial \rho}(\rho \Delta) \tag{72}$$

and by using Eqs. (15) and (69) we find

$$\frac{1}{2}\beta \frac{\partial^2 P_c}{\partial \rho^2} = 2\frac{\partial \mathfrak{F}}{\partial \rho} + \rho \frac{\partial^2 \mathfrak{F}}{\partial \rho^2} - \beta \frac{\partial^2 \mathfrak{F}}{\partial \beta\, \partial \rho} \tag{73}$$

For the repulsive inverse power potentials $\phi_{ij}(r) = \gamma_{ij} r^{-n}$, $\gamma_{ij} > 0$, in the strong coupling limit (high density and/or low temperatures) we have $\mathfrak{F} \simeq \mathscr{U}$ and Eq. (73) reduces to

$$\frac{\partial}{\partial \rho}\left[\frac{1}{2}\frac{\partial}{\partial \rho}(\rho Z_c) - Z_V\right] = 0 \tag{74}$$

Let $Z_V \sim a_V \rho^{n/D}$ and $Z_c \sim a_c \rho^{n/D}$ in the strong coupling limit; then from Eq. (74) we get

$$\frac{a_V}{a_c} = \lim_{\rho \to \infty} \frac{Z_V}{Z_c} = \frac{1}{2}\left(\frac{n}{D} + 1\right) \tag{75}$$

while $a_V/a_c = 1$ represents the "virial-compressibility" consistency. For the one-component plasma (OCP), $\phi(r) = r^{-1}$, it is thus expected that $a_V/a_c = 3/4, 2/3$ in two and three dimensions, respectively, which indeed agrees with the HNC results for the model.[31,32] The trend

$\lim_{h\to 3}(a_V/a_c)=1$ has been observed[33] in the numerical HNC results for the inverse power potentials in three dimensions.

The excess free energy difference between two states β, ρ and β_0, ρ_0 within the SMSA is [in view of Eqs. (68) and (69)]

$$(\Delta f)_{\text{SMSA}} = \mathfrak{F}(\beta, \rho, \{R_{ij}^c(\beta, \rho)\}) - \mathfrak{F}(\beta_0, \rho_0, \{R_{ij}^c(\beta_0, \rho_0)\}) \tag{6}$$

and in those special cases when Eq. (67) may be solved with $R_{ij}^c(\beta=0, \rho) = R_{ij}^c(\beta, \rho=0)=0$ [with is possible only for potentials $\phi_{ij}(r)$ possessing Fourier transform] then $\mathfrak{F}$ represents the excess free energy via the "virial" or "energy" equations of state. Of particular importance in this class of potentials is, of course, the D-dimensional Coulomb potential, $\tilde{\phi}(k) \sim k^{-2}$. The fact that $\mathfrak{F}$ represents a good model excess free energy for such systems, being at the same time a functional of the relatively structure less functions $c_{ij}(r)$ which may be, in turn, approximated well by interactions between smeared charge distributions,[13] is instrumental in the analysis of the thermodynamics of charged objects.[34,35]

5. VARIATIONAL MSA FO THE ONE-COMPONENT PLASMA

The finding that $u(\beta, \rho, \{R_{ij}^c(\beta, \rho)\})$ *maximizes* the expression for the poential energy $u(\beta, \rho, \{R_{ij}\})$ is of special significance in view of the expected similarity (see also Ref. 9) between the SMSA obeying Eq. (67) and the HNC results for the soft potentials. From the discussion of the nature of the bridge functions[8] it is expected that, in the general case, the HNC-"virial" equation of state overestimates the true pressures or energies for repulsive potentials (or for any potentials in the limit of very high densities). When modeling the structure and thermodynamics of the system with soft potentials $\phi_{ij}(r)$ one may wish to use the MSA results $u(\beta, \rho, \{R_{ij}\})$ with a judicious choice for $R_{ij}(\beta, \rho)$ with possibly $g_{ij}(R_{ij}) > 0$ (t.e., discontinuous pair functions) and thus improve upon the results obtained from Eq. (67). All such models, including Eq. (67), may be formulated variationally, as will be now demonstrated for the particular case of the one-component plasma (OCP), a system which has been the object of extensive study in recent years.[21]

The excess thermodynamic properties of the OCP (namely, point ions of charges Ze immersed in a uniform compensating background of electrons) depend on the single reduced variable $\Gamma = \beta(Ze)^2/a$ where a is the ion-sphere radius [$a=(3/4\pi\rho)^{1/3}$ in 3D]. The MSA for the related system that includes the hard-core insertion, namely, the charged hard spheres (CHS) has been solved analytically.[5] The CHS equation of state depends on Γ and the packing fraction $\eta = (\pi/6)\rho R^3$, i.e., $\mathfrak{F} = \mathfrak{F}(\Gamma, \eta)$, $u = u(\Gamma, \eta)$, $g(R) =$

$g(R, \Gamma, \eta)$. Note that $\mathfrak{F}(0, \eta)$ and $g(R, 0, \eta) = g_{\mathrm{PY}}(R, \eta)$ represent the results for the PY equation for hard spheres.

Consider the free-energy functional

$$f = f_0(\eta) + \mathfrak{F}(\Gamma, \eta) - \mathfrak{F}(0, \eta) \tag{77}$$

where $f_0(\eta)$ represents a fitting function such that the potential energy for the OCP is determined from

$$u_{\mathrm{OCP}}(\Gamma) = u_{\mathrm{CHS}}(\Gamma, \eta(\Gamma)) \tag{78}$$

If f is no represent the excess free energy for the OCP then

$$u_{\mathrm{OCP}} = \Gamma \frac{df}{d\Gamma} = \Gamma \frac{\partial f}{\partial \Gamma} + \Gamma \frac{\partial f}{\partial \eta} \frac{\partial \eta}{\partial \Gamma} \tag{79}$$

But since $u_{\mathrm{CHS}}(\Gamma, \eta) = \Gamma\, \partial \mathfrak{F}(\Gamma, \eta)/\partial \Gamma$ we obtain the variational condition

$$\frac{\partial f(\Gamma, \eta)}{\partial \eta} = 0 \tag{80}$$

as determining the function $\eta(\Gamma)$ in Eq. (78). It is through Eq. (80) that the choice of $f_0(\eta)$ affects the result $\eta(\Gamma)$. Note that the exact inequality (53), which for a one-component system will read $\partial f/\partial \eta \geqslant 0$, plays no role in obtaining Eq. (80). However, if Eq. (80) does not have a unique solution[14] then (53) may play a role in selecting the appropriate one.

In view of Eq. (49), we write Eq. (80) in the form

$$g^2_{\mathrm{CHS}}(R, \Gamma, \eta) = G^2(\eta) \tag{81}$$

where

$$G^2(\eta) = g^2_{\mathrm{PY}}(R, \eta) - 2g_0(\eta) \tag{82}$$

and we also define

$$g_0(\eta) = \frac{1}{4} \frac{\partial f_0(\eta)}{\partial \eta} \tag{83}$$

Equation (83) represents the obvious relation for a hard-sphere virial excess free energy $f_0(\eta)$ obtained from Eq. (36) when the contact value of the pair function $g_0(R, \eta)$ is given by $g_0(\eta)$. In particular, if we make the choice

$$f_0(\eta) = f_{\mathrm{PY},V}(\eta) = \frac{6\eta}{1 - \eta} + 2 \ln(1 - \eta)$$

i.e., the PY virial equation of state for the hard spheres, then

$$g_0(\eta) = g_{PY}(R, \eta) = \frac{1}{2} \frac{\eta + 2}{(1-\eta)^2}$$

This choice, termed[14] DMSA1, is immediately seen from Eqs. (81)–(83) to be limited to the range $g_{PY}(R, \eta) \geqslant 2$ or $\eta \geqslant 0.25$ THE SMSA model [Eq. (67)] is obtained by the choice $f_0(\eta) = \mathfrak{F}(0, \eta)$ as is easily seen directly from Eq. (77).

With the restriction that $g(R, \Gamma, \eta) \geqslant 0$, the OCP results as modeled by Eq. (77) may be cast in the following form, which is especially convenient for analyzing the strong coupling ($\Gamma \gg 1$) behavior for each choice of $f_0(\eta)$:

$$Q = \left\{ \frac{3\eta(\eta+2)}{(\eta+1/2)^2} \left[1 - \frac{G(\eta)}{g_{PY}(R, \eta)} \right] \right\}^{1/2} \geqslant 0 \tag{84}$$

$$\Gamma = \frac{1}{3} \left\{ \frac{(\eta+1/2)^2}{(1-\eta)^3 \eta^{1/3}} [(1+Q)^2 - 1] \right\}^2 \tag{85}$$

$$u = \frac{1}{6} \frac{(\eta+1/2)(3\Gamma)^{1/2}}{\eta^{2/3}} Q - \frac{(1+\eta-\frac{1}{5}\eta^2)\eta^{-1/3}}{2} \Gamma \tag{86}$$

The function $\eta(\Gamma)$ is obtained by eliminating Q from Eqs. (84) and (85). The function $Q(\Gamma, \eta)$ as obtained from Eq. (85) is zero for $\eta = 0$ and $\eta = 1$ and has a single maximum in between, with height that increases with Γ, being zero for $\Gamma = 0$. In order to obtain variational (fitting) results for all Γ, the function $Q(\eta)$ as defined in Eq. (84) should start on the $\eta = 1$ axis and terminate on the $Q = 0$ axis (see Fig. 2 in Ref. 14).

Let $\varepsilon = 1 - \eta$ and observe that the leading order in the expansion in powers of ε around $\varepsilon = 0$ is $Q \sim \varepsilon^2 g_0^{1/2}$, so that from Eq. (85) the leading order is $\Gamma \sim \varepsilon^{-2} g_0$, or

$$\Gamma \sim g_{PY}(R, \eta)\, g_0(\eta) \tag{87}$$

It is thus easy to see how the choice of $f_0(\eta)$ affects the asymptotic $\Gamma \gg 1$ expansion of $u_{OCP}(\Gamma)$. For $f_0(\eta) = f_{PY,V}(\eta)$, $g_0(\eta) \sim g_{PY,V}(R, \eta) \sim \varepsilon^{-2}$, and thus $\Gamma \sim \varepsilon^{-4}$ leading to $u_{OCP}(\Gamma) = -0.9\Gamma + b_1 \Gamma^{1/4} +$. For $f_0(\eta) = \mathfrak{F}(0, \eta)$, $g_0(\eta) \sim g_{PY}^2(R, \eta) \sim \varepsilon^{-4}$, so that $\Gamma \sim \varepsilon^{-6}$ and thus $u_{OCP} = -0.9\Gamma + b_2 \Gamma^{1/2} + \cdots$. Upon choosing $f_0(\eta) = f_{PY,c}(\eta)$ or $f_0(\eta) = f_{CS}(\eta)$, i.e., the PY-compressibility or the Carnahan–Starling (CS) expressions for the hard-sphere free energy,[14] we have $g_0 \sim \varepsilon^{-3}$ or $\Gamma \sim \varepsilon^{-5}$ with the form $u_{OCP} = -0.9\Gamma + b_3 \Gamma^{2/5} + \cdots$. It is interesting to note that the choice of $\eta(\Gamma)$ such that thermodynamic consistency is achieved between the "energy" and "compressibility" equations of state for the OCP via the MSA results for the

CHS, is governed[16] by an asymptotic behavior of the type $g_0(\eta) \sim_{\eta\to 1} g_{PY}(R, \eta)$. This result is probably valid for any D since the MSA result for the CHS should contain the term $\beta(\partial P/\partial\rho)_c^{(PY,HS)}$ in its expression for $\beta(\partial P/\partial\rho)_c$, as

$$\beta\left(\frac{\partial P}{\partial\rho}\right)_c^{(PY,HS)} = \lim_{\Gamma\to 0}\beta\left(\frac{\partial P}{\partial\rho}\right)_c$$

By Eq. (59) such a term should behave like $g_{PY}^2(R, \eta)$, and in turn should be of order Γ if thermodynamic consistency is required also for $\Gamma \to \infty$.

Finally observe that the choice $G(\eta) = g_{PY}(R, \eta) - 1$ corresponding to $f_0(\eta) = f_{PY,V}(\eta) - 2\eta$ in Eq. (77), leads by Eq. (84) to

$$Q = (6\eta)^{1/2}\,\frac{1-\eta}{\eta + 1/2} \tag{88}$$

This function, like that obtained from $f_0(\eta) = f_{PY,V}(\eta)$, starts from zero at $\eta = 1$, then rises (for smaller values of η) but instead of curving up and terminating at $\eta = 0.25$, it curves down and reaches zero for $\eta = 0$, like in the choice $f_0(\eta) = \mathfrak{F}(0, \eta)$. The resulting function $\eta(\Gamma)$ behaves asymptotically (in the limit $\Gamma \to \infty$) like that for DMSA1, leading to $u(\Gamma) = -0.9\Gamma + 2(\Gamma/18)^{1/4} - 1/2 + \cdots$, but in the region $10 \lesssim \Gamma \lesssim 200$ it follows rather closely the results of the "virial-compressibility" consistent model,[16] and finally for $\Gamma \lesssim 10$ it tends towards the SMSA results obeying Eq. (67). The simple analytic result obtained by Eqs. (88), (5), and (86) contains all the favorable features of the various MSA-based models for the OCP[14–16] and covers the full range $\Gamma \geqslant 0$.

ACKNOWLEDGMENTS

I thank Bill Gelbart and Joel Lebowitz for their encouragement, useful suggestions, and comments. I am indebted to David MacGowan for carefully reading the manuscript and for interesting discussions. Helpful remarks by Lesser Blum are gratefully acknowledged. This work was supported in part by NSF grant No. CHE80-24270.

REFERENCES

1. (a) J. K. Percus and G. Yevick, *Phys. Rev.* **136**:B290 (1964); J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **144**:251 (1966). (b) The pioneering methods for solving the MSA were established by M. S. Wertheim, *J. Math. Phys.* **5**:643 (1964); and R. J. Baxter, *Aust. J. Phys.* **21**:563 (1968). (c) References to earlier literature in the field are given by, e.g.,

L. Blum and J. S. Hoye, *J. Stat. Phys.* **19**:317 (1978); direction to more recent works may be found in, e.g., J. S. Hoye and G. Stell, *Mol. Phys.* **11**:1 (1984).
2. J. S. Hoye and G. Stell, *J. Chem. Phys.* **67**:439 (1977).
3. Y. Rosenfeld, *J. Chem. Phys.* **76**:1170 (1982).
4. M. J. Gillan, *J. Phys. C: Solid State Phys.* **7**:L1 (1974); a closely related approach employing a "marriage" between a short range PY behavior and long range MSA behavior for the direct correlation functions is described by A. H. Narten, L. Blum, and R. H. Fowler, *J. Chem. Phys.* **60**:3378 (1974), and see references therein.
5. R. G. Palmer and J. D. Weeks, *J. Chem. Phys.* **58**:4171 (1973).
6. G. Pastore, C. Napi, U. DeAngelis, and A. Forlani, *Phys. Lett.* **78A**:75 (1980).
7. J. P. Hansen and J. B. Hayter, *Mol. Phys.* **46**:651 (1982).
8. Y. Rosenfeld and N. W. Ashcroft, *Phys. Rev. A* **20**:1208 (1979).
9. Y. Rosenfeld and N. W. Ashcroft, *Phys. Rev. A* **20**:2162 (1979).
10. R. G. Palmer, *J. Chem. Phys.* **73**:2009 (1980).
11. U. DeAngelis, A. Forlani, and M. Giordano, *J. Phys. C.: Solid State Phys.* **13**:3649 (1980).
12. Y. Rosenfeld, *J. Phys. C.: Solid State Phys.* **15**:L125 (1982).
13. Y. Rosenfeld, *Phys. Rev. A* **25**:1206 (1982).
14. D. MacGowan, *J. Phys. C.: Solid State Phys.* **16**:59 (1983).
15. D. MacGowan, *J. Phys. C.: Solid State Phys.* **16**:L7 (1983).
16. D. MacGowan, *J. Stat. Phys.* **32**:123 (1983).
17. S. M. Foiles and N. W. Ashcroft, *J. Chem. Phys.* **75**:3594 (1981).
18. Y. Rosenfeld, *Phys. Rev. A* **29**:2877 (1984).
19. E. Waisman, *Mol. Phys.* **25**:45 (1973).
20. See, e.g., the review article by J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**:587 (1976).
21. M. Baus and J. P. Hansen, *Phys. Rep.* **59**:1 (1980).
22. H. C. Andersen and D. Chandler, *J. Chem. Phys.* **57**:1918 (1972).
23. R. J. Baxter, *J. Chem. Phys.* **47**:4855 (1967).
24. R. J. Baxter, *J. Chem. Phys.* **52**:4559 (1970).
25. R. E. Caligaris, A. E. Rodriguez, and M. Silbert, *J. Chem. Phys.* **51**:1016 (1969).
26. This result corrects an error in Ref. 12.
27. J. L. Lebowitz, *Phys. Rev.* **133**:A895 (1964).
28. J. L. Lebowitz and D. Zomick, *J. Chem. Phys.* **54**:3335 (1971).
29. B. C. Freasier and D. J. Isbister, *Mol. Phys.* **42**:927 (1981).
30. D. G. Chae, F. H. Ree, and T. Ree, *J. Chem. Phys.* **50**:1581 (1969).
31. K. C. Ng, *J. Chem. Phys.* **61**:2680 (1974).
32. F. Lado, *Phys. Rev. B* **17**:2827 (1978).
33. F. Rogers, private communication.
34. Y. Rosenfeld, *Phys. Rev.* **26**:3622 (1982).
35. Y. Rosenfeld and W. M. Gelbart, On the Statistical Thermodynamics of Charged Particles of Arbitrary Shape and Concentration, *J. Chem. Phys.*, in press.