Mean-spherical model for soft potentials: The hard core revealed as a perturbation

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The mean-spherical approximation for fluids is extended to treat the case of dense systems interacting via soft potentials. The extension takes the form of a generalized statement concerning the behavior of the direct-correlation function $c(r)$ and the radial-distribution function $g(r)$. From a detailed analysis that views the hard-core portion of a potential as a perturbation on the whole, a specific model is proposed which possesses analytic solutions for both Coulomb and Yukawa potentials, in addition to certain other remarkable properties. A variational principle for the model leads to a relatively simple method for obtaining numerical solutions.

I. INTRODUCTION

The mean-spherical approximation (MSA) has been applied[1] almost exclusively to dense liquids whose intermolecular potentials $u(r)$ possess a *hard core* of range σ. For such potentials the MSA is specified by the equations

$$g(r)=1+h(r)=0\,,\quad r<\sigma\,, \tag{1a}$$

$$c(r)+\beta u(r)=0\,,\quad r>\sigma\,, \tag{1b}$$

where $\beta=1/k_BT$, together with the Ornstein-Zernike (OZ) relation, which for a system of average density ρ is written

$$h(r)=c(r)+\rho\int d\vec{\mathbf{r}}'h(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|)c(\vec{\mathbf{r}}')\,. \tag{2}$$

Here $g(r)$ is the radial-distribution function and $c(r)$ the direct-correlation function for which (2) is the defining relation.

The mean-spherical approximation is not a satisfactory model for low-density fluids, since it normally fails to give the correct value for the second virial coefficient. An exception to this, however, is the system of hard spheres, in which the MSA is equivalent to the Percus-Yevick (PY) approximation. Another exception is the dense Coulomb gas $[u(r)\sim r^{-1}]$, in which the MSA gives the known Debye-Hückel limit[2] in a first-order "inverse range" expansion: it also leads to results that satisfy the Stillinger-Lovett conditions.[3] The major interest in the model, however, can be traced to the fact that it yields interesting analytic solutions for a fairly wide class of systems, provided they possess in their interparticle potentials the fundamental hard-core property represented in (1a). On the other hand, the evident disadvantage of the model has been an apparent lack of any systematic basis for its extension to non-hard-core potentials. The purpose of this paper is to provide such a basis, which is being proposed more for the qualitative insight it gives to the theory of liquid structure than for its quantitative numerical predictions. Though founded on a more general statement of the MSA (to be given in Sec. II), this basis has a practical realization that is very similar. In particular, a version applicable to soft potentials is introduced in Sec. II. It is simply a particular limiting form of the usual MSA. We refer to it here as the soft-mean-spherical approximation and in Sec. III compare it to the modified hypernetted-chain (HNC) approach.[4] Some thermodynamic results are considered in Sec. IV and a variational principle for the model is given in Sec. V. Finally, applications and attendant procedures are given in Sec. VI for the one-component plasma (OCP), and some conclusions are drawn in Sec. VII.

II. SOFT-MEAN-SPHERICAL APPROXIMATION

Analysis[4] of a large body of computer simulation data compiled for a variety of liquids with disparate but mainly *soft* interparticle potentials suggests that the quantity

$$\rho\int d\vec{\mathbf{r}}g(r)[c(r)+\beta u(r)]$$

is relatively small in the dense-fluid regime. More precisely, if p is the pressure satisfying

$$\beta\left(\frac{\partial p}{\partial\rho}\right)_T=1-\rho\int d\vec{\mathbf{r}}\,c(r) \tag{3}$$

and U/N is the internal energy per particle given by

$$\beta(U/N)=\tfrac{1}{2}\rho\int d\vec{\mathbf{r}}g(r)\beta u(r)\,, \tag{4}$$

then we have the exact relation[5]

$$c(0)=-\beta\left(\frac{\partial p}{\partial\rho}\right)_T+2\left(\frac{\beta U}{N}\right)-\rho\int d\vec{\mathbf{r}}g(r)[c(r)+\beta u(r)]\,. \tag{5}$$

The evidence[6] for dense fluids then suggests that

$$\rho \int d\vec{r}\, g(r)[c(r)+\beta u(r)] \ll c(0) \tag{6}$$

and that from the standpoint of its thermodynamic consequences it is plausible to assume

$$\rho \int d\vec{r}\, g(r)[c(r)+\beta u(r)] = 0 . \tag{7}$$

[Observe that for the one-component plasma, for which (5) remains true, the presence of the necessary compensating background requires us to replace $c(r)$ in (3) by $c(r)+\beta u(r)$ and $g(r)$ in (4) by $h(r)$.]

Given (7), it appears that a more *general* statement incorporating the spirit of the MSA can be summarized by

$$g(r) = 1 + h(r) = 0 , \quad (r < \sigma) ,$$

$$\int d\vec{r}\, g(r)[c(r)+\beta u(r)] = 0 ,$$

these being regarded, however, simply as constraints that might aid in establishing a wider class of models of the MSA type. By themselves 1(a) and 1(c) are, of course, insufficient to determine $c(r)$ and $g(r)$. For this purpose additional relationships are needed, one being, for example, statement 1(b), which clearly satisfies 1(c). More generally, however, it can be seen that within any class of models satisfying 1(a) and 1(c) the structural property $c(0)$ [and indeed $c(r)$ for that small range of r where $g(r)$ is practically zero] is determined almost entirely by thermodynamic functions. These models will fall within a generalized-mean-spherical approximation (GMSA) for which

$$c_{\mathrm{GMSA}}(0) = -\beta(\partial p/\partial \rho)_T + 2(\beta U/N) \tag{8}$$

must be reasonably well satisfied. We may compare (8) with the condition governing the range of applicability of the usual MSA, namely

$$\beta(\partial p/\partial \rho)_T \gg 2(\beta U/N) . \tag{9}$$

Condition (9) is known to be compatible with those $u(r)$'s characterized beyond a hard core by *either* a weak long-range potential *or* by a stronger potential but with restricted range. For the former the long-range part has only a minor effect on the structure of the underlying hard-core system. The application of the MSA is then very much along the lines of thermodynamic perturbation theory.[1]

What we are seeking, however, is an extension of the MSA approach for non-hard-sphere systems in which the potential is not weak and for which (9) is not satisfied. Towards this end we first note that at high densities such systems still behave *as if* their pair potentials actually possess an effective hard core of diameter σ_{eff}, defined approximately by the location of the leading edge of the principal peak of $g(r)$ [e.g., $g(\sigma_{\mathrm{eff}}) \sim \delta \ll 1$]. Evidently if $u(r)$ is now augmented by a genuine hard core whose diameter σ is *less* that σ_{eff}, then there can be little subsequent change either in the structure of the system or in its thermodynamics. An example of this can be seen in Fig. 1, where the result of introducing a hard core into a high-den-

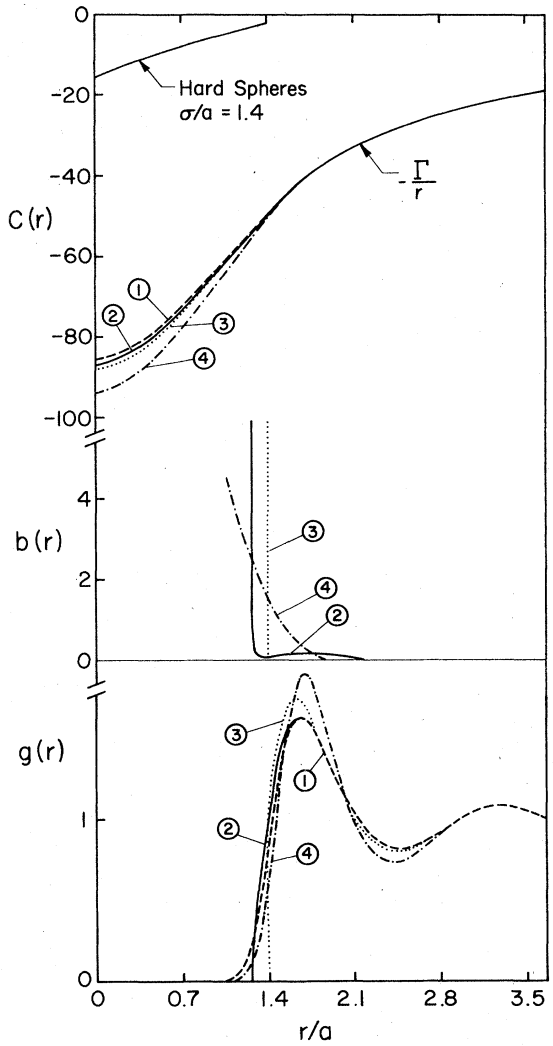

FIG. 1. Pair-distribution function $g(r)$ and direct-correlation function $c(r)$ for the OCP at $\Gamma = 70$ via various choices of the bridge function $b(r)$ as employed in the modified HNC equation. Case 1 (dashed line) corresponds to $b(r) = 0$ (i.e., pure HNC); Case 2 (solid line) corresponds to SMSA, Case 3 (dotted line) corresponds to $b(r<1.4) = \infty$, $b(r>1.4) = 0$, and Case 4 (dot-dashed line) corresponds to $b(r) = b_{\mathrm{HS}}(r;\ \eta = 0.4)$ and actually reproduces quite well the Monte Carlo results for the OCP at $\Gamma = 70$. On the scale of this plot, $c(r)$ for all cases considered above is indistinguishable from $-\Gamma/r$ for $r > 1.5$. Case 3 features a jump discontinuity of about 1 for $g(r)$ and $c(r)$, which is barely detectable on the scale of $c(r)$.

sity Coulomb system is displayed. Note in particular the small change in $c(r)$, an important point when we realize (as emphasized above) that $c(0)$ reflects the thermodynamics. (To appreciate the difference between this situation and the case in which the tail of the potential serves as a perturbation, see Fig. 29 of Ref. 1.) Thus even though σ may in practice be quite close to σ_{eff}, we are clearly approaching a physical picture in which the addition of an "interior" hard core reveals itself only as a rather mild perturbation. With this in mind we can now consider a possible extension of the MSA for *soft potentials* as follows:

The solutions to the MSA usually lead to jump discontinuities across $r=\sigma$ in both $g(r)$ and $c(r)$. These depend on σ, βu, and ρ, but through a careful choice of σ, $g(r)$ can in fact be forced to be continuous (though not in its first derivative); that is, there is a choice for which the solutions to the MSA give

$$g(r)=0\,,\quad (r<\sigma)\,,$$
$$g(r=\sigma^{+})=0\,. \tag{10}$$

If this choice is now regarded as the effective hard-sphere diameter discussed above, then by the argument just given, the addition of any further interior hard core produces only minor corrections to the g already obtained. Accordingly this g can then be considered an acceptable solution to the MSA for the soft potential. We therefore define the soft-mean-spherical approximation (SMSA) as a model in which $c(r)=-\beta u(r)$ and for which $g(r)$ is continuous. This is a limiting form of the usual MSA, and as such the general statement (7) is satisfied. To carry out the limiting process in practice we need only expand $c(r)$ around $r=0$ in powers of r and ensure that the coefficients of the term linear in r vanishes. For, as noted by Gillan *et al.*,[7] this coefficient is proportional to the square of the jump discontinuity in g across the hard core. As will become clear later, solutions for g having this character are *not* guaranteed, but if a solution for the SMSA does exist and yields a physically acceptable σ, then this solution should be very similar to results flowing from the HNC approximation. In fact there are analytic solutions of the one-component plasma[8] and also for the Yukawa potential,[9] both of which can be extended to the limit of low densities ($\sigma\to 0$). An interesting potential in the same general class[4] is $u(r)\sim \mathrm{erfc}\,(ar)/r$, the study of which by simulation techniques can be of some considerable benefit in assessing Monte Carlo results for the OCP via the Ewald image method.[10] Analytic solution of the SMSA for the same potential will also be particularly useful.

To complete this section we note that the line of argument being pursued here is not unlike that which led Percus and Yevick[11] to the MSA. Their Eq. (3.14) in Ref. 11 is a global statement similar to Eq. (7) above. On the other hand, their goal was to calculate the structure of a system (whose pair interaction contained a hard-core part) by an approximation method suitable for a *weak* long-ranged tail. In contrast to this, we are concerned with the problem of calculating the structure of soft-potential systems. As we shall see in Sec. III, the purpose in introducing the hard core at all is ultimately just a device for selecting the physically relevant solutions of the SMSA.

III. MEAN-SPHERICAL AND HYPERNETTED-CHAIN APPROACHES

If we take the view that we have a system with a hard core, but that the physical conditions are such that the hard core is not playing a major role, then we lack the important support of the random-phase argument so essential to the usual application of the MSA. It necessarily follows that any approximations of the mean-spherical character must be established by a rather different approach. To this end we consider the familiar expansion of the total correlation function $h(r)$, given by the diagrammatic method[12]:

$$g(r)=\exp[-\beta u(r)+\theta(r)-b(r)]\,, \tag{11}$$

where

$$\theta(r)=h(r)-c(r)\,, \tag{12}$$

and $b(r)$ (the bridge function) is the negative of the sum of all elementary diagrams. The hypernetted-chain approximation takes $b(r)\equiv 0$, so that (11), (12), and (2) (the OZ relation) together provide an integral equation that can be iteratively solved for a given potential $u(r)$. To make a comparison with the MSA, we observe that (11), (12), and (1) also imply a specific choice for the bridge function, namely[4]

$$b_{\mathrm{MSA}}(r)=\infty\,,\quad (r<\sigma)\,,$$
$$b_{\mathrm{MSA}}(r)=h(r)-\ln g(r)\,,\quad (r>\sigma)\,. \tag{13}$$

Now, in the SMSA limit Eqs. 1(a), 1(c), and (10) can still be satisfied by a choice of $b(r)$ of the form (13). For later use, however, we find it convenient to replace (13) by the single statement

$$b_{\mathrm{SMSA}}=h(r)-\ln g(r)\,, \tag{14}$$

which formally continues the definition of b into the region where $g(r)$ vanishes. (This extension is possible because solutions with the SMSA character possess a region where $\ln g(r)$ diverges negatively.) The utility of (14) lies in the following:

Any statement on the behavior of the bridge function is entirely equivalent to the specification of an effective interparticle potential for use in a hypernetted-chain approach. We may refer to this type of presentation of the problem as a modified HNC scheme.[4] It is apparent that the SMSA introduced above can therefore be cast into a well-defined integral equation method. For soft potentials possessing Fourier transforms (the OCP provides a clear example) this integral equation has the interesting feature that it can display *two* classes of solutions that branch from the low-density limit. One is the "Debye-Hückel" class characterized by $c(r)=-\beta u(r)$ *for all* r and $g(r)<0$ for small r. The other has the desired high-density behavior in $g(r)$, namely a range where $g(r)\equiv 0$ which is made self-consistently possible by virtue of the corresponding behavior in $b(r)$. For these solutions (14) is satisfied. A numerical method for finding the desired solution will be based on a variational principle of the SMSA (see Sec. V).

For numerical treatment the SMSA [Eq. (14)] should still be viewed in the context of the limit $g(r=\sigma^+)=0$ imposed on the modified HNC equation with the bridge function of Eq. (13). One purpose of introducing a hard core is that it will guarantee the selection of the correct branch. Otherwise the hard core is simply an intermediary and, once the branch is selected, can be dispensed with. Observe also that the Percus-Yevick equation is characterized within the modified HNC scheme by the choice

$$b_{\mathrm{PY}}(r)=g(r)-1-\ln g(r)-[c(r)+\beta u(r)]\,,$$

and as is known can be cast into a well-defined diagrammatic expansion. The non-Debye-Hückel branch of the SMSA [Eq. (14)] cannot however be cast into a diagrammatic expansion.

As with all the integral equations introduced so far, it is not possible to say *a priori* whether any physically acceptable solution will in fact emerge for an arbitrary potential. But in contrast to other methods, we *can* show that the SMSA solution (provided of course it exists) has very interesting physical features for the class of potentials $u(r)$ whose Fourier transforms also exist.

IV. THERMODYNAMIC FUNCTIONS IN SOFT-MEAN-SPHERICAL APPROXIMATION

We consider a system of particles interacting via a pair potential that is regular (i.e., lacks a hard core). If the potential for one additional particle is scaled by λ $(0\leq\lambda\leq 1)$ and $g(r,\lambda)=1+h(r,\lambda)$ is the pair-distribution function relative to this particular particle when the potential is thus scaled, then the excess chemical potential for the system can be written[13]

$$\beta\mu^{\mathrm{ex}}=\rho\int_0^1 d\lambda\int_0^\infty d\vec{\mathbf{r}}\,g(r,\lambda)\beta u(r)\,. \tag{15}$$

Let $\gamma(r,\lambda)$ be the difference between $\beta\lambda u(r)$ (the potential) and the potential of mean force for scaling λ. Then

$$g(r,\lambda)=\exp[-\beta\lambda u(r)+\gamma(r,\lambda)] \tag{16}$$

and according to the diagrammatic expansion[12]

$$\gamma(r,\lambda)=h(r,\lambda)-c(r,\lambda)-b(r,\lambda)\,, \tag{17}$$

where again $b(r,\lambda)$ is the negative of the sum of all elementary graphs. In these equations we have $g(r,\lambda=0)=1$, $h(r,\lambda=0)=0$, $c(r,\lambda=0)=0$, and $b(r,\lambda=0)=0$. It is also understood that $g(r,\lambda=1)=g(r)$, $h(r,\lambda=1)=h(r)$, and so on.

We now differentiate (16) with respect to λ and obtain

$$\beta u(r)g(r,\lambda)=-\frac{\partial}{\partial\lambda}g(r,\lambda)+g(r,\lambda)\frac{\partial}{\partial\lambda}\gamma(r,\lambda)\,, \tag{18}$$

which we insert into (15). With the aid of (17) we then find that

$$\begin{aligned}\beta\mu^{\mathrm{ex}}=&-\rho\int c(r)d\vec{\mathbf{r}}+\rho\int_0^1 d\lambda\int d\vec{\mathbf{r}}\,h(r,\lambda)\\&\times\frac{\partial}{\partial\lambda}[h(r,\lambda)-c(r,\lambda)]\\&-\rho\int_0^1 d\lambda\int d\vec{\mathbf{r}}\,g(r,\lambda)\frac{\partial}{\partial\lambda}b(r,\lambda)\,,\end{aligned} \tag{19}$$

which is a simple generalization of

$$\begin{aligned}\beta\mu^{\mathrm{ex}}\doteq&-\rho\int c(r)d\vec{\mathbf{r}}+\rho\int_0^1 d\lambda\int d\vec{\mathbf{r}}\,h(r,\lambda)\\&\times\frac{\partial}{\partial\lambda}[h(r,\lambda)-c(r,\lambda)]\,,\end{aligned}$$

which in turn is a well-known[14,15] expression for the excess chemical potential in HNC. We can therefore repeat the standard manipulations[14,15] on the first three terms of (19) to arrive at

$$\begin{aligned}\beta\mu^{\mathrm{ex}}=&-\rho\int c(r)d\vec{\mathbf{r}}+\tfrac{1}{2}\rho\int d\vec{\mathbf{r}}\,h(r)[h(r)-c(r)]\\&-\rho\int_0^1 d\lambda\int d\vec{\mathbf{r}}\,g(r)\frac{\partial}{\partial\lambda}b(r,\lambda)\,.\end{aligned} \tag{20}$$

In the HNC approximation ($b=0$) the chemical potential can be calculated directly; it is not necessary to integrate the energy equation of state. Notice that for any approximation expression (20) will be equivalent to the energy equation of state.

We now write (20) in a form that is slightly more general and will later permit us to make an application to the OCP. We use (3) and (4) (or their

equivalents for the OCP) and find after a little manipulation that

$$\beta\mu^{ex}=\frac{1}{2}\left[\beta\left(\frac{\partial p}{\partial\rho}\right)_T-1\right]+\frac{\beta U}{N}-\frac{\rho}{2}\int g(r)[c(r)+\beta u(r)]d\vec{r}$$
$$+\frac{\rho}{2}\int h^2(r)d\vec{r}-\rho\int_0^1 d\lambda\int d\vec{r}\,g(r,\lambda)\frac{\partial}{\partial\lambda}b(r,\lambda)\,, \tag{21}$$

which so far remains exact. We next consider the consequences in (21) of the approximations flowing from statement (14) of the SMSA. [It must be noted that in any approximate theroy $\beta(\partial p/\partial\rho)_T$ and $(\beta U/N)$ in (21) should be taken from the compressibility and energy equations of state, respectively.]

For the SMSA we take (14) (basically the Debye-Hückel statement, but applied to the *dense* branch). In a scaled form it reads

$$b_{\mathrm{SMSA}}(r,\lambda)=h(r,\lambda)-\ln g(r,\lambda)\,, \tag{22}$$

which is compatible with (7). We insert this into (21) and, using (7), we obtain

$$\beta\mu^{ex}_{\mathrm{SMSA}}=\frac{1}{2}\left[\beta\left(\frac{\partial p}{\partial\rho}\right)_T-1\right]+\frac{\beta U}{N}\,, \tag{23}$$

a relation which holds, however, only for potentials that possess Fourier transforms.[16] One such is the Coulomb interaction $[u(r)\sim r^{-1}]$, for which, as is well known,

$$\beta p/\rho-1=\tfrac{1}{3}\beta U/N\,. \tag{24}$$

Thus for the OCP, (23) can be rewritten in terms of the Helmholtz free energy:

$$\left(\frac{\beta F^{ex}}{N}\right)_{\mathrm{SMSA}}=\frac{1}{2}\left[\beta\left(\frac{\partial p}{\partial\rho}\right)_T-1\right]+\frac{2}{3}\frac{\beta U}{N}\,. \tag{25}$$

This last expression demonstrates a unique property of the model: The energy equation of state and the compressibility equation of state are each completely given in terms of the other. It is not necessary to know any structural details of the solution. Further, if

$$a=(3/4\pi\rho)^{1/3} \tag{26}$$

is the Wigner-Seitz radius for the plasma and

$$\Gamma=(Ze)^2\beta/a \tag{27}$$

is the standard plasma parameter, then in terms of Γ

$$\frac{\beta U}{N}=\Gamma\frac{d}{d\Gamma}(\beta F^{ex}/N)\,. \tag{28}$$

Equations (8), (25), and (28) then constitute a compact and relatively simple set of equations connecting the four quantities $(\beta U/N)$, $(\beta F^{ex}/N)$, $\beta(\partial p/\partial\rho)_T$, and $c(0)$, and are useful, notwithstanding the relative simplicity of the analytic expressions for the OCP.

V. VARIATIONAL APPROACH TO SMSA

We start with the usual coupling-constant expression for the excess free energy[17]:

$$\beta F^{ex}/N=\tfrac{1}{2}\rho\int d\vec{r}\,g(r,\lambda)\beta u(r)\,, \tag{29}$$

where $g(r,\lambda)$ is the radial-distribution function for isochoric systems of particles in which the pair potential is $\lambda u(r)$. Following the procedure of Morita and Hiroike[12] and using Eq. (14) (the SMSA statement on the bridge function), we obtain

$$(\beta F^{ex}/N)_{\mathrm{SMSA}}=-\tfrac{1}{2}\rho\int c(r)d\vec{r}+\frac{1}{2\rho}\frac{1}{(2\pi)^3}$$
$$\times\int d\vec{k}\{\rho c(k)+\ln[1-\rho c(k)]\}\,, \tag{30}$$

an approximate form for the free energy equivalent to that obtained by integrating the energy equation of state. In (30), $c(k)$ is the Fourier transform of the direct correlation function $c(r)$. From (29) we can determine the excess entropy:

$$(S^{ex}/Nk_B)=-\beta F^{ex}/N+\frac{\rho}{2}\int d\vec{r}\,g(r)\beta u(r)d\vec{r}\,. \tag{31}$$

But notice that the basic assumption of the generalized-mean-spherical approximation [Eq. (8)] allows us to write an approximate form for the excess entropy:

$$(S^{ex}/Nk_B)_{\mathrm{SMSA}}=-\tfrac{1}{2}\rho\int d\vec{r}\,h(r)c(r)-\frac{1}{2\rho}\frac{1}{(2\pi)^3}\int d\vec{k}\{\rho c(k)+\ln[1-\rho c(k)]\}$$
$$=-\frac{1}{2\rho}\frac{1}{(2\pi)^3}\left(\int d\vec{k}\,\rho h(k)\rho c(k)+\int d\vec{k}\{\rho c(k)+\ln[1-\rho c(k)]\}\right). \tag{32}$$

We now observe that a functional derivative,

$$\frac{\delta(S^{ex}/Nk_B)}{\delta c(k)}\,,$$

on the right-hand side of (32) will vanish, *provided* h and c are connected by

$$\rho h(k)=\rho c(k)/[1-\rho c(k)]\,. \tag{33}$$

But (33) is precisely the Fourier transform of the Ornstein-Zernike relation [Eq. (2)]. It therefore

follows that, though intrinsically approximate, the entropy functional (32) provides an expression for the excess entropy of the system (via the energy equation) that is exact for the SMSA model. The exact solution for the corresponding $c(r)$ is that direct-correlation function maximizing the entropy functional *under the restrictions of the model.*

There are two possibilities for utilizing a variational procedure in order to solve the SMSA. The first is based on the fact that S^{ex} given by Eq. (32) is variational with respect to c *at fixed* h, and the method of solution is valid for any choice of c for $r>\sigma$ (for example, c satisfying $dc(r)/dr = -\beta g(r)du(r)/dr$, as in Ref. 18). It proceeds as follows[18]: (i) Choose a value for σ and start with an assumed form for $c(r)$, for example

$$c(r)=c_>(r)=-\beta u(r)\,,\quad (r>\sigma)\,,$$
$$c(r)=c_<(r)=a+a_0(1-r/\sigma)+(1-r/\sigma)\sum_{n=1}^{\infty}a_nP_n(2r/\sigma-1)\,,\quad (r<\sigma)\,, \tag{34}$$

where the $\{a_n\}$ are all variational parameters and the P_n are Legendre polynomials. The parameter a is fixed by requiring $c(r)$ to be continuous at $r=\sigma$. (ii) Calculate the Fourier transform $c(k)$ of (34) and use the Ornstein-Zernike relation to calculate the corresponding $h(k)$. Substitute $c(k)$ and $h(k)$ into Eq. (32) and determine the new values of a_n from the condition

$$\frac{\partial S^{ex}}{\partial a_n}=0\,,\quad n=0,1,\ldots\,, \tag{35}$$

with $h(k)$ *held fixed*. With the new set of coefficients, a new $h(k)$ is determined and (35) is solved again. The procedure is iterated until self-consistency is attained. Experience gained with, for example, the HNC equation has shown that the iteration will require a "mixing" procedure in order to ensure convergence. Thus at the lth iteration

$$h_l^{in}(k)=\gamma h_{l-1}^{in}(k)+(1-\gamma)h_{l-1}^{out}(k)\,,\quad (0<\gamma<1)\,, \tag{36}$$

(iii) Now change the value of σ and repeat the steps above until

$$g(r)=0\,,\quad r\leq\sigma\,,$$
$$g(r)=0\,,\quad r=\sigma+0\,, \tag{37}$$
$$g(r)>0\,,\quad r>\sigma\,,$$

to the desired numerical accuracy.

The second method takes advantage of the fact that the SMSA is a limiting form of the MSA and thus F^{ex} of Eq. (30) is stationary with respect to small changes of $c(r)$ for r confined within the core.[19] Accordingly the coefficients a_n appearing in (30) can be determined by the condition

$$\frac{\partial F^{ex}}{\partial a_n}=0\,,\quad n=0,1,2,\ldots\,. \tag{38}$$

Observe that since the function $c_<(r)$ is expected to be a smooth function (and one that is not far from being linear), we can expect that in a practical case a modest set of $\{a_n\}$ (say five) will be quite sufficient. The existence of an analytic solution of the MSA for the Coulomb potential offers an opportunity to check both the validity of these numerical procedures and their utility.

VI. APPLICATION TO THE ONE-COMPONENT PLASMA

The analytic solution of the MSA for the Coulomb potential (i.e., a system of charged hard spheres in a neutralizing background) is given parametrically[20] in terms of the packing function $\eta=\frac{1}{6}\pi\rho\sigma^3$, where σ is the hard-core diameter. To obtain the SMSA limit it is only necessary to set to zero the coefficient of the term linear in r in the expansion of $c(r)$ for $r<\sigma$. Accordingly if we define

$$K=\frac{(1+2\eta)^2}{2(1-\eta)^3}\left\{\left[\left(\frac{(1+\frac{1}{2}\eta)24\eta}{(1+2\eta)^2}\right)^{1/2}+1\right]^2-1\right\}, \tag{39}$$

$$Q=-\left(\frac{(1+\frac{1}{2}\eta)}{(1-\eta)^2}24\eta\right)^{1/2}, \tag{40}$$

and

$$\alpha=K^2/24\eta\,, \tag{41}$$

then in terms of these we have the SMSA solution for the corresponding equivalent plasma parameter,

$$\Gamma=2\alpha\eta^{1/3}. \tag{42}$$

Further

$$\frac{\beta U}{N}=-\left[(1+\eta-\tfrac{1}{5}\eta^2)\alpha-(1+\tfrac{1}{2}\eta)^{1/2}\sqrt{\alpha}\,\right] \tag{43}$$

and

$$c(0)=-\frac{(1+2\eta)^2}{(1-\eta)^4}+\frac{Q^2}{4(1-\eta)^2}-\frac{(1+\eta)QK}{12\eta}-\frac{(5+\eta^2)K^2}{60\eta}\,. \tag{44}$$

Finally

$$\beta(\partial p/\partial\rho)_T=2(\beta U/N)-c(0)\,. \tag{45}$$

The energies given by (43) can be represented exceedingly well by the interpolation[21]

$$\beta U/N=-0.9005\Gamma+0.2997\Gamma^{1/2}+0.0007\,, \tag{46}$$

which for $\Gamma\gtrsim 1$ has an accuracy of better than 0.1%. For large Γ, on the other hand, the asymptotic form of the analytic solution gives

$$\beta U/N = -0.9\Gamma + \tfrac{1}{6}\sqrt{3}\Gamma^{1/2} - \cdots , \quad (47)$$

which, although only a two-term result, is actually in remarkable agreement with the results of the complete expansion for Γ values as low as $\Gamma \sim 1$. It follows that if we take the energy to have the form

$$\beta U/N = a\Gamma + b\Gamma^{1/2} + c , \quad (48)$$

then the solutions of (8), (25), and (28) are readily obtained:

$$\beta F^{ex}/N = a\Gamma + 2b\Gamma^{1/2} + c\ln\Gamma + d , \quad (49)$$

$$c(0) = \tfrac{4}{3}a\Gamma - \tfrac{2}{3}b\Gamma^{1/2} - 2c\ln\Gamma + (\tfrac{10}{3}c - 2d - \tfrac{1}{2}) , \quad (50)$$

and

$$\beta\left(\frac{\partial p}{\partial \rho}\right)_T = \tfrac{2}{3}a\Gamma + \tfrac{8}{3}b\Gamma^{1/2} + 2c\ln\Gamma + (-\tfrac{4}{3}c + 2d + \tfrac{1}{2}) . \quad (51)$$

The values of a and b corresponding to (47) then give in particular

$$c(0) = -1.2\Gamma - \tfrac{1}{9}\sqrt{3}\Gamma^{1/2} + \cdots \quad (52)$$

and

$$\beta(\partial p/\partial\rho)_T = -0.6\Gamma + \tfrac{4}{9}\sqrt{3}\,\Gamma^{1/2} - \cdots . \quad (53)$$

In general the OCP energies given by the SMSA are in good agreement with the Monte Carlo (MC) results. But from (25) we then see that the requirements of thermodynamic consistency must be badly violated [since we expect for large Γ that $\beta(\partial p/\partial\rho)_T \sim -0.4\Gamma$]. It is a unique property of the SMSA model that knowledge of its equation of state alone enables us to draw such a conclusion. It is not necessary to appeal to any details of the solution.

Finally it is instructive to compare the SMSA and HNC results[22] for the OCP, particularly at $\Gamma \gtrsim 1$. As a rule, the two solutions give nearly identical results for nearly all quantities of interest, but particularly for $(\beta U/N)$, $\beta(\partial p/\partial\rho)_T$, and $c(0)$. In comparison with HNC, however, the SMSA results are slightly shifted *toward* the MC data. This observation suggests an interesting possibility for constructing a crucial test of a general point made[4] in the context of the modified HNC scheme: It has been stated that since $b(r)$ enters this scheme as an effective potential, we then may expect that so long as two different theories diverge from each other only in a statement governing the *long range-nature of* $b(r)$, the consequent differences between their respective results must be quite small. It follows that the emphasis will focus rather naturally on the short-range nature of $b(r)$, especially its behavior in the region of r corresponding to the first peak of $g(r)$. But it is in just this region that we find in the SMSA a rather weak "potential" [i.e., $b(r)$, since the hard core is playing no role] that indeed shifts the HNC [$b(r) \equiv 0$] results in the right directions, as we expect (see Fig. 1).

VII. CONCLUSION

A common approach in the theory of classical fluids has been to apply perturbation theory from a *hard-sphere reference* system for all potentials that possess a hard-core part. It is clear from the discussion in the present paper that the physical role of the hard-core part of the potential has not always been interpreted correctly. It is true that the gross structure of dense fluids is determined by excluded volume effects and, for that matter, that all $g(r)$'s of dense fluids look very much the same. (The proper context of incorporating this first-order universality of $g(r)$ is, however, provided by the statement of universality of the *bridge functions*.[4]) But this need *not* imply that the hard-core part of the potential will always serve as a good reference system. To paraphrase the statement made at the end of Ref. 6, a successful perturbation theory in the presence of strong Coulomb interactions can be obtained only if the hard-core part will serve as a perturbation. We see here a systematic approach to this situation.

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