A MEAN SPHERICAL MODEL FOR SOFT POTENTIALS: THE HARD CORE REVEALED AS A PERTURBATION

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Abstract

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 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.

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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

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

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

$$(\beta = 1/k_B T)$$

together with the Ornstein Zernike (OZ) relation, which for a system of average density ρ is written

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

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, where the MSA is equivalent to the Percus-Yevick (PY) approximation. Another exception is the dense Coulomb gas ($u(r) \sim r^{-1}$) where 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 providing they possess, in their interparticle potentials, the fundamental hard-core property as 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 in the theory of liquid structure than its quantitative numerical predictions. Though founded on a more general statement of the MSA, (to be given in the next section), its practical realization is very similar. In particular a version applicable to soft potentials (the "soft" mean spherical approximation) is introduced, and in section III is compared to the modified hypernetted chain approach[4]. Some thermodynamic results are considered in section IV, and a variational principle for the model is given in section V. Finally, applications and attendant procedures are given for the one-component plasma in section VI. Some conclusions are drawn in section VII.

II. THE GENERALIZED MEAN SPHERICAL APPROXIMATION

Analysis[4] of a large body of computer simulation data compiled for a variety of disparate but mainly soft interparticle potentials has led to a conclusion that from the standpoint of its thermodynamic consequences, a replacement of (1b) by

$$\int d\underset{\sim}{r}\, g(r)[c(r) + \beta u(r)] = 0 \tag{3}$$

constitutes a relatively accurate reformulation of the approximation, and one which in the dense fluid regime of low compressibility is valid for any potential. The meaning of (3) is most easily gauged by recalling the exact relation[5]

$$c(0) = -\beta(\partial p/\partial \rho)_T + 2(\beta U/N) - \rho \int d\underset{\sim}{r}\, g(r)[c(r) + \beta u(r)] \tag{4}$$

where p is the pressure, also satisfying

$$\beta(\partial p/\partial \rho)_T = 1 - \rho \int d\underset{\sim}{r}\, c(\underset{\sim}{r}) \quad , \tag{5}$$

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

$$(\beta U/N) = \tfrac{1}{2}\rho\int g(r)\, \beta u(r) d\underset{\sim}{r} \,. \tag{6}$$

(We observe at this point that (4) holds for the one component plasma. For this system, however, the presence of a compensating uniform background requires us to replace c(r) in (5) by c(r) + βu(r) and g(r) in (6) by h(r).) The generalized mean spherical approximation (GMSA) is therefore specified by the equations

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

$$\int d\underset{\sim}{r}\, g(r)(c(r) + \beta u(r) = 0, \tag{1c}$$

whose solution will determine approximations to c(r) and g(r). For potentials with a hard core σ is just the hard core diameter. For soft core potentials σ can be a parameter (see below). Clearly the model can only be considered useful if the exact functions c(r) and g(r) satisfy

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

However, as already noted, condition (7) appears to be well satisfied in many dense systems of interest.

The implication of (3) is that the structural property c(0) (and indeed, c(r) for a small range of r where g(r) is itself practically zero) is determined almost entirely by thermodynamic functions. The generalized mean spherical approximation is therefore a model which demands (1a) and (1c) and in consequence sets

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

It is then clear that the usual mean spherical approximation is but one possible realization of (3). Its range of applicability is normally constrained by the condition

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

which might be compared with (7), the condition governing the range of applicability of the generalized mean spherical approximation. Condition (9), in turn is compatible with those u(r)'s characterized beyond the hard core by either a weak long range tail, or by a stronger tail but with restricted range. For the former, the tail has only minor effects on the structure of the underlying hard core system and the application of the MSA is then very much in the spirit of thermodynamic perturbation theory[1]. But the exact g(r) reflects, of course, the entire potential and if the hard core portion is to play any physical role at all, it is necessary that $g(r = \sigma^+) \sim \delta$, where δ is significantly different from zero. In fact, of course, the MSA leads to jump discontinuities in the solutions for g(r) and c(r) across $r = \sigma$ whose magnitudes depend on σ, u(r), and ρ. We shall need to take this into account in what follows, and shall introduce an approximation one of whose purposes is to eliminate such discontinuities.

In proposing an extension to the MSA for non hard-sphere systems we cannot be guided by the usual arguments founded on (9). Instead any practical realizations that might emerge must be sought from the GMSA postulate as summarized by equation (3). Such an argument can be given as follows: consider a real physical potential possessing not a hard core but a soft short range repulsion (examples might be r^{-n}, $(ar^{-12} - br^{-6})$ and so forth).

As is well known, such systems behave at high densities as if their pair potentials actually possess an effective hard core of diameter σ_{eff}, defined operationally by $g(r = \sigma_{eff}) = \delta \ll 1$. But though hard-core like, g(r) for these real systems is certainly devoid of discontinuities, and the same is true for c(r).

The GMSA models this real physical problem by taking the u(r) of equation (1) to be just the portion of the real potential that lies beyond an assumed hard core of dimension σ (this σ often being close, on physical grounds, to σ_{eff}). The problem is then solved and as noted, the approximate g(r) and c(r) may exhibit jump discontinuities. Let us compare these solutions (which obviously depend on the choice of σ being made) with another approach: suppose we return to the original problem and augment the soft potential u(r) with a genuine interior hard core whose diameter σ is chosen so that $\sigma < \sigma_{eff}$. Physically (not analytically) such an addition can have little influence either on the structural properties (g(r) or c(r), for instance,) or on the high density thermodynamic functions. An example of this can be seen in figure 1 where the results of introducing a hard core into the Coulomb potential, at high density, are displayed. Note the small change in c(r), and remember that c(0) reflects the thermodynamics. (To appreciate the difference between this and when the tail serves as a perturbation see Fig. 29 of ref. 1.) Thus again from the physical viewpoint, we may even choose to regard the results of existing Monte Carlo calculations for soft-potentials as in fact equivalent to the results of similar calculations, were such calculations actually carried out with an interior hard core (diameter $\sigma < \sigma_{eff}$) present in the potentials. Even though σ may be quite close to σ_{eff} we are evidently approaching a picture where the addition of an interior-hard-core is manifested only as a rather mild perturbation, a view which is quite contrary to the usual notions governing the application of the MSA[6].

Clearly we can extend this argument and state that any solution of the MSA, (equation (1)) which satisfies

$$g(r) = 0, \qquad r < \sigma ,$$
$$g(r = \sigma^{+}) = 0 ,$$

(i.e. no discontinuity at $r = \sigma$) can therefore also represent a MSA result for a soft-potential u(r). Such a model can be termed 'a soft-mean spherical approximation' (SMSA) and simply takes the view that for a dense fluid $c(r) = -\beta u(r)$ (the simplest realization of (3)) whenever g departs from zero. As will become clear later, solutions for g having this character are not guaranteed, but if a solution of SMSA does exist and yields a physically acceptable σ, this solution should be very similar to the results flowing from the HNC approximation (see below). In fact there is an analytic solution of the SMSA for the one component plasma[7]. For the Yukawa potential an analytic solution can also be obtained, the starting point being the solution of the MSA as augmented with Yukawa closure[8].

In both of these cases the SMSA range is determined by expanding c(r) around r = 0 in powers of r, and establishing through the choice of σ where the coefficient of the linear term vanishes. This then guarantees that the discontinuity in the MSA solution for g(r) actually vanishes (i.e. $g(r = \sigma^{+}) = 0$). Since both Coulomb and Yukawa potentials possess Fourier transforms, it is possible to obtain solutions of the SMSA which can be extended to the limit of low densities, where $\sigma \to 0$. An important potential in the same general class[4] is $u(r) \sim \mathrm{erfc}(\alpha r)/r$ whose study by simulation techniques can be of some benefit in assessing Monte Carlo results for the OCP via the Ewald image method[9]. Analytic solutions of the SMSA for this potential will be particularly useful.

III. MEAN SPHERICAL AND HYPERNETTED CHAIN APPROACHES

If we take literally the view that we have a system with a hard core but 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 argument. To this end we consider the familiar expansion of the total correlation function h(r), given by the diagrammatic method[10], namely

$$g(r) = \exp\,[-\beta u(r) + \theta(r) - b(r)] \tag{10}$$

where

$$\theta(r) = h(r) - c(r) \tag{11}$$

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 (10), (11) and (2) (the OZ relation) provide together an integral equation that can be iteratively solved for a given potential u(r). To make comparison with the MSA, we observe that (10), (11), and (1) also imply a specific choice for the bridge function, namely[4]

$$\begin{aligned} b_{MSA}(r) &= \infty, && (r < \sigma) \\ b_{MSA}(r) &= h(r) - \ln g(r), && (r > \sigma). \end{aligned} \tag{12}$$

Now in the SMSA limiting form,

$$\begin{aligned} g(r) &= 0, && (r < \sigma) \\ g(r) &= 0, && (r = \sigma^{+}) \end{aligned}$$

which can still be satisfied by a choice of b(r) of the form (12). For later use however, we shall find it convenient to replace (12) by the single statement

$$b_{SMSA} = h(r) - \ln g(r) \tag{13}$$

which formally continues the definition of b into the region where g(r) vanishes. As noted however, this region, by definition of the model, plays no physical role. The utility of (13) lies rather 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 potentials possessing Fourier transforms (the OCP provides a clear example) this integral equation has the interesting feature that it can display <u>two</u> classes of solutions that branch from the low density limit. One is the "Debye-Hückel" class characterized by $c(r) = -\beta u(r)$ <u>for all</u> 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). A numerical method for finding the desired solution will be based on a variational principle for the SMSA (see section V).

For numerical treatment the SMSA(eq. (13))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. (12). Observe also that the Percus-Yevick equation is characterized within the modified HNC scheme by the choice

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

and as is well known can be cast into a well defined diagrammatic expansion. The non-Debye-Hückel branch of the SMSA (eq. (13)) cannot however be cast into a diagrammatic expansion.

As with all integral equations so far introduced, 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 likewise exist.

IV. THERMODYNAMIC FUNCTIONS IN THE 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, the excess chemical potential for the system can be written[11]

$$\beta\mu^{ex} = \rho \int_0^1 d\lambda \int_0^\infty d\underset{\sim}{r}\, g(r,\lambda)\beta u(r) \ . \tag{14}$$

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

$$g(r,\lambda) = \exp[-\beta\lambda u(r) + \gamma(r,\lambda)] \tag{15}$$

and according to the diagrammatic expansion[10]

$$\gamma(r;\lambda) = h(r,\lambda) - c(r,\lambda) - b(r,\lambda) \tag{16}$$

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 (15) with respect to λ and obtain

$$\beta u(r)\, g(r,\lambda) = -\frac{\partial}{\partial\lambda} g(r,\lambda) + g(r,\lambda)\frac{\partial}{\partial\lambda}\gamma(r,\lambda) \tag{17}$$

which we insert into (14). With the aid of (16) we then find that

$$\begin{aligned}\beta\mu^{ex} = -\rho\int c(r)d\underset{\sim}{r} + \rho\int_0^1 d\lambda\int d\underset{\sim}{r}\, h(r,\lambda)\frac{\partial}{\partial\lambda}[h(r,\lambda) - c(r,\lambda)] \\ - \rho\int_0^1 d\lambda\int d\underset{\sim}{r}\, g(r,\lambda)\frac{\partial}{\partial\lambda} b(r,\lambda)\end{aligned} \tag{18}$$

which is a simple generalization of

$$\beta\mu^{ex} \doteq -\rho\int c(r)d\underset{\sim}{r} + \rho\int_0^1 d\lambda\int d\underset{\sim}{r}\, h(r,\lambda)\frac{\partial}{\partial\lambda}[h(r,\lambda) - c(r,\lambda)]$$

which in turn is a well known[12,13] expression for the excess chemical potential in HNC. We can therefore repeat the standard manipulations[12,13] on the first three terms of (18) to arrive at

$$\beta\mu^{ex} = -\rho\int c(r)d\underset{\sim}{r} + \tfrac{1}{2}\rho\int d\underset{\sim}{r}\, h(r)[h(r)-c(r)] - \rho\int_0^1 d\lambda\int d\underset{\sim}{r}\, g(r)\frac{\partial}{\partial\lambda} b(r,\lambda). \tag{19}$$

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 (19) will be equivalent to the energy equation of state.

We now write (19) in a form that is slightly more general and will later

permit us to make an application to the OCP. We use (5) and (6) (or their equivalents for the OCP) and find after a little manipulation that

$$\beta\mu^{ex} = \tfrac{1}{2}\left[\beta\left(\frac{\partial p}{\partial \rho}\right)_T - 1\right] + \frac{\beta U}{N} - \frac{\rho}{2}\int g(r)[c(r) + \beta u(r)]d\underset{\sim}{r}$$

$$+ \frac{\rho}{2}\int h^2(r)d\underset{\sim}{r} - \rho\int_0^1 d\lambda \int d\underset{\sim}{r}\, g(r,\lambda)\frac{\partial}{\partial\lambda} b(r,\lambda) \qquad (20)$$

which so far remains exact. We next consider the consequences in (20) of the approximations flowing from the statement (13) of the SMSA. (It must be noted that in any approximate theory, $\beta(\partial p/\partial\rho)_T$ and $(\beta U/N)$ in (20) should be taken from the compressibility and energy equations of state, respectively.)

For the SMSA we take (13) in its scaled form

$$b_{SMSA}(r,\lambda) = h(r,\lambda) - \ln g(r,\lambda) \qquad (21)$$

which is compatible with (3), and insert this into (20). Then using (3) we obtain

$$\beta\mu^{ex}_{SMSA} = \tfrac{1}{2}\left[\beta\left(\frac{\partial p}{\partial \rho}\right)_T - 1\right] + \frac{\beta U}{N} \qquad (22)$$

a relation which holds however only for potentials that possess Fourier transforms[14]. One such is the Coulomb interaction ($u(r) \sim r^{-1}$) for which, as is well known

$$\beta\frac{p}{\rho} - 1 = \frac{1}{3}\beta\frac{U}{N} \quad . \qquad (23)$$

Thus for the OCP (22) can be rewritten in terms of the Helmholtz free energy

$$\left(\beta\frac{F^{ex}}{N}\right)_{SMSA} = \tfrac{1}{2}\left[\beta\left(\frac{\partial p}{\partial \rho}\right)_T - 1\right] + \frac{2}{3}\left(\frac{\beta U}{N}\right). \tag{24}$$

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

$$a = (3/4\pi\rho)^{1/3} \tag{25}$$

is the Wigner-Seitz radius for the plasma, and

$$\Gamma = (Ze)^2\beta/a \tag{26}$$

is the standard plasma parameter, then in terms of Γ

$$\frac{\beta U}{N} = \Gamma\frac{d}{d\Gamma}(\beta F^{ex}/N). \tag{27}$$

Equations (7), (24) and (27) 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. A VARIATIONAL APPROACH TO THE SMSA

We start with the usual coupling constant expression for the excess free energy[15]

$$\beta F^{ex}/N = \tfrac{1}{2}\rho\int d\underset{\sim}{r}\; g(r,\lambda)\beta u(r) \tag{28}$$

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[10], and using equation (13) (the SMSA statement on the bridge function) we obtain

$$(\beta F^{ex}/N)_{SMSA} = -\tfrac{1}{2}\rho\int c(r)d\underset{\sim}{r} + \frac{1}{2\rho}\frac{1}{(2\pi)^3}\int d\underset{\sim}{k}[\rho c(k) + \ell n(1-\rho c(k))] \tag{29}$$

an approximate form for the free energy equivalent to that obtained from integrating the energy equation of state. In (29) c(k) is the Fourier transform of the direct correlation function c(r). From (28) we can determine the excess entropy

$$(S^{ex}/Nk_B) = -(\beta F^{ex}/N) + \frac{\rho}{2}\int d\underset{\sim}{r}\, g(r)\beta u(r)d\underset{\sim}{r} \quad . \tag{30}$$

But notice that the basic assumption of the generalized mean spherical approximation (equation (3)) allows us to write an approximate form for the excess entropy

$$\begin{aligned}(S^{ex}/Nk_B)_{SMSA} &= -\tfrac{1}{2}\rho\int d\underset{\sim}{r}\, h(r)c(r) - \frac{1}{2\rho}\frac{1}{(2\pi)^3}\int d\underset{\sim}{k}[\rho c(k) + \ell n(1-\rho c(k))], \\ &= -\frac{1}{2\rho}\frac{1}{(2\pi)^3}\left\{\int d\underset{\sim}{k}(\rho h(k))\rho c(k) + \int d\underset{\sim}{k}[\rho c(k) + \ell n(1-\rho c(k))]\right\}.\end{aligned} \tag{31}$$

We now observe that a functional derivative

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

of the right hand side of (31) will vanish, <u>provided</u> h and c are connected by

$$\rho h(k) = \rho c(k)/(1 - \rho c(k)) \quad . \tag{32}$$

But (32) is precisely the Fourier transform of the Ornstein-Zernike relation (equation (2)). It therefore follows that though intrinsically approximate the entropy functional (31) 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:

The functional given by the right hand side of (31) is already known[16] to possess the property that at the extremum, the Ornstein-Zernike relation will be satisfied. This suggests, in turn, a numerical procedure for obtaining a solution to the SMSA which is expected to be valid for any potential. This procedure is: (i) choose a value for σ and start with an assumed form for c(r), for example

$$c(r) = c_{>}(r) = -\beta u(r) \qquad (r > \sigma)$$

$$c(r) = c_{<}(r) = a + b(1 - r/\sigma) + (1 - r/\sigma) \sum_{n=0}^{\infty} a_n P_n(2r/\sigma - 1) , \qquad (r < \sigma), \qquad (35)$$

where the $\{a_n\}$ are all variational parameters, and the P_n are Legendre polynomials. The quantities a and b are fixed by the requirements of continuity on c(r) (and its first derivative) at $r = \sigma$.

(ii) Solve (for a_n) the set of equations resulting from the variational conditions

$$\frac{\partial}{\partial a_n}\left(\frac{S_{ex}}{Nk_B}\right) = 0 \qquad (n = 0, 1, \ldots)$$

(iii) alter the value of σ and repeat these steps until

$$g(r) \equiv 0 \qquad (r \leq \sigma)$$

to the desired numerical accuracy, and $g(r > \sigma) > 0$.

Observe that since the function $c_<(r)$ is expected to be a smooth function (and one that is not far from linear) we can expect that in a practical case a modest set of $\{a_n\}$ (say 5) 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 this numerical procedure and its utility.

VI. APPLICATION TO THE ONE COMPONENT PLASMA

The analytic solution of the SMSA for the OCP is given parametrically[17]. Let σ be the relevant inner hard core diameter, and $\eta = \frac{\pi}{6}\rho\sigma^3$ the associated packing fraction. Then we define

$$K = \frac{(1+2\eta)^2}{2(1-\eta)^3}\left\{\left(\left[\frac{(1+\frac{1}{2}\eta)24\eta}{(1+2\eta)^2}\right]^{\frac{1}{2}} + 1\right)^2 - 1\right\} , \tag{38}$$

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

and

$$\alpha = K^2/24\eta . \tag{40}$$

In terms of these we have the solution for the corresponding equivalent plasma parameter

$$\Gamma = 2\alpha\eta^{1/3} . \tag{41}$$

Further

$$\frac{\beta U}{N} = -[(1 + \eta - \tfrac{1}{5}\eta^2)\alpha - (1 + \tfrac{1}{2}\eta)^{\frac{1}{2}}\alpha^{\frac{1}{2}}] , \tag{42}$$

and

$$c(0) = -\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{Q^2}{4(1-\eta)^2} - \frac{(1+\eta)QK}{12\eta} - \frac{(5+\eta^2)K^2}{60(\eta)} . \tag{43}$$

Finally,

$$\beta(\partial p/\partial\rho)_T = 2(\beta U/N) - c(0) . \tag{44}$$

The energies given by (42) can be represented exceedingly well by the interpolation[18]

$$\frac{\beta U}{N} = -0.9005\Gamma + 0.2997\Gamma^{\frac{1}{2}} + 0.0007 \tag{45}$$

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

$$\frac{\beta U}{N} = -0.9\Gamma + \frac{\sqrt{3}}{6}\Gamma^{\frac{1}{2}} - \ldots \tag{46}$$

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

$$\frac{\beta U}{N} = a\Gamma + b\Gamma^{\frac{1}{2}} + c \tag{47}$$

then the solutions of (7) (24) and (27) are readily obtained:

$$\beta F^{ex}/N = a\Gamma + 2b\Gamma^{\frac{1}{2}} + c\,\ell n\,\Gamma + d\ ,$$

$$c(0) = \frac{4}{3}a\Gamma - \frac{2}{3}b\Gamma^{\frac{1}{2}} - 2c\,\ell n\,\Gamma + \left(\frac{10}{3}c - 2d - \tfrac{1}{2}\right) \tag{48}$$

and

$$\beta\left(\frac{\partial p}{\partial \rho}\right)_T = \frac{2}{3}a\Gamma + \frac{8}{3}b\Gamma^{\frac{1}{2}} + 2c\,\ell n\,\Gamma + \left(-\frac{4}{3}c + 2d + \tfrac{1}{2}\right)\ . \tag{49}$$

The values of a, and b corresponding to (46), then give, in particular

$$c(0) = -1.2\Gamma - \frac{\sqrt{3}}{9}\Gamma^{\frac{1}{2}} + \ldots \tag{50}$$

and

$$\beta(\partial p/\partial \rho)_T = -0.6\Gamma + \frac{4\sqrt{3}}{9}\Gamma^{\frac{1}{2}} - \ldots \quad . \tag{51}$$

In general the OCP energies given by the SMSA are in good agreement with the Monte Carlo results. But from (24) 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[19] for the OCP, particularly at $\Gamma \geq 1$. 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 $c(o)$. In comparison with HNC, however, the SMSA results are slightly shifted towards 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 one from the other only in a statement governing the long range nature of $b(r)$, the consequent differences in 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 in just this region do 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 direction, 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 possessed 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 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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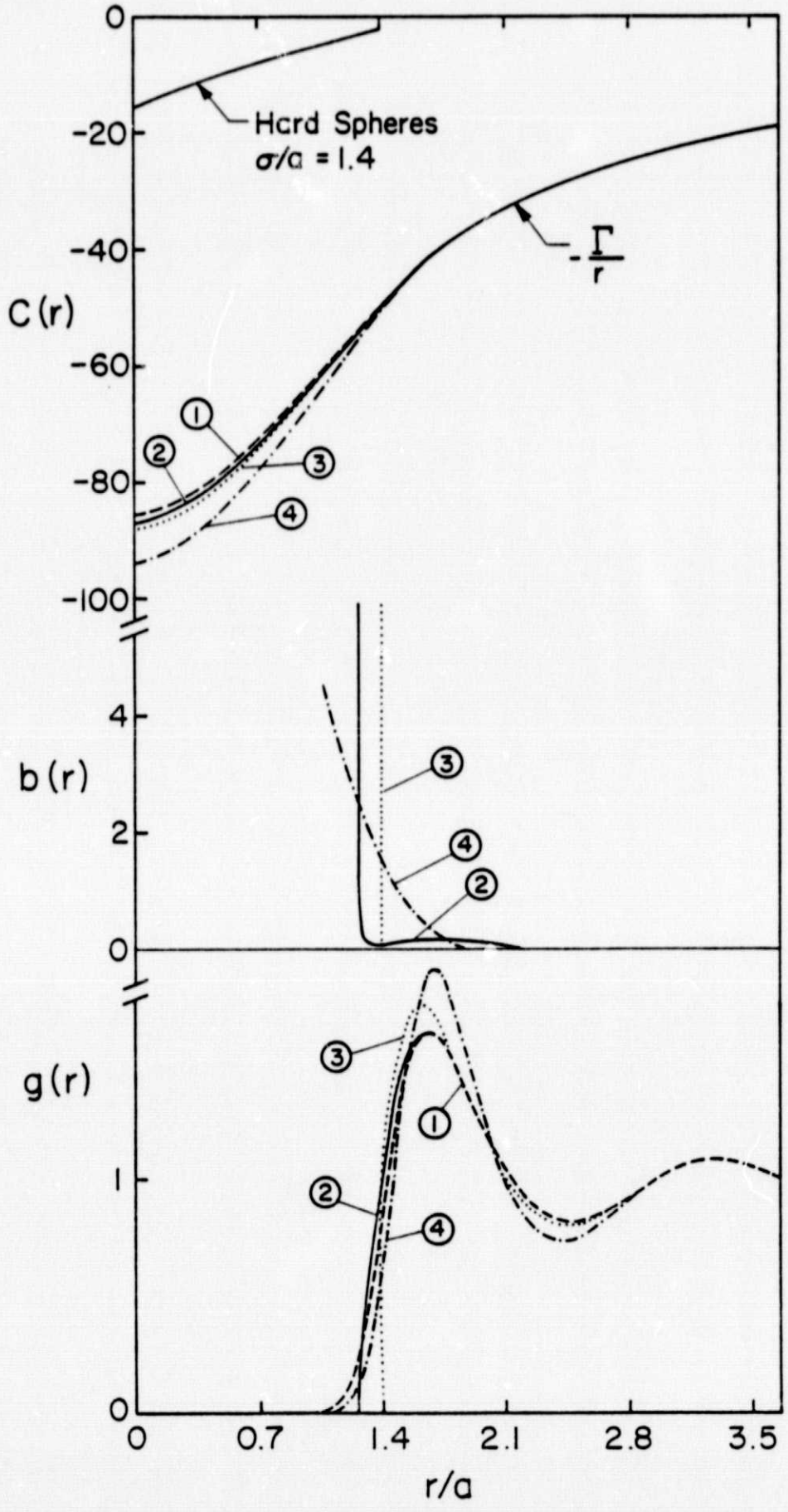
Figure Caption

Fig. 1 The pair distribution function, $g(r)$, and the 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. 1 - dashed line, corresponds to $b(r) = 0$ (i.e. pure HNC). 2 - full line corresponds to the SMSA. 3 - dotted line, corresponds to: $b(r < 1.4) = \infty$, $b(r > 1.4) = 0$. 4 - dot-dashed line, corresponds to $b(r) = b_{HS}(r; \eta = 0.4)$, 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 $c(r)$.


0
-20
-40
-60
-80
-100
C(r)
Hcrd Spheres
σ/a = 1.4
-Γ/r
①
②
③
④
4
2
0
b(r)
③
④
②
3
1
0
g(r)
③
①
②
④
0
0.7
1.4
2.1
2.8
3.5
r/a