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Theory of simple classical fluids: Universality in the short-range structure

Yaakov Rosenfeld* and N. W. Ashcroft
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

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It is shown to within the accuracy of present-day computer-simulation studies that the bridge functions (i.e., the sum of elementary graphs, assumed zero in the hypernetted-chain approximation) constitute the same universal family of curves, irrespective of the assumed pair potential. In view of the known parametrized results for hard spheres, this observation introduces a new method in the theory of fluids, one that is applicable to any potential. The method requires the solution of a modified hypernetted-chain equation with inclusion of a one-parameter bridge-function family appropriate to hard spheres, and the single free parameter (the hard-sphere packing fraction) can be determined by appealing to the requirements of thermodynamic consistency. The assertion of universality is actually demonstrated via the application of this new method to a wide class of different potentials: e.g., hard spheres, Lennard-Jones, an inverse fifth power (r^{-5}) applicable to the helium problem, the Coulomb potential (i.e., the one-component plasma), charged hard spheres, an oscillatory potential proposed for certain liquid metals, and the Yukawa potential.

I. INTRODUCTION

Central to the theory of fluids is the radial distribution function (RDF) $g(r)$, defined for classical systems by

$$g(r_{12}) = \lim_{N\to\infty,\, V\to\infty,\, N/V\to\rho} \frac{V^2 \int\cdots\int e^{(-\beta\Phi)}\, d\vec{r}_3 \cdots d\vec{r}_N}{\int\cdots\int e^{(-\beta\Phi)}\, d\vec{r}_1 \cdots d\vec{r}_N},$$

where $\beta = 1/k_B T$ and $\Phi = \Phi(\vec{r}_1, \ldots, \vec{r}_N)$ is the total interaction potential for the system. The long-range behavior of g satisfies

$$\lim_{r\to\infty} g(r) = 1, \quad (r = r_{12} = |\vec{r}_1 - \vec{r}_2|) .$$

In particular, the RDF for a system of identical particles interacting with central pairwise forces, i.e.,

$$\Phi = \sum_{i<j} u(r_{ij}) ,$$

has been the object of many investigations. The quantity that is determined from scattering experiments is, however, the structure factor $S(k)$ related to $g(r)$ by

$$S(k) = 1 + \rho \int_V [g(r) - 1] e^{i\vec{k}\cdot\vec{r}}\, d\vec{r} .$$

There are many approximate methods[1] for calculating $g(r)$, the most accurate of which, and sometimes referred to as "exact," is the method of computer simulations. Indeed, Monte-Carlo (MC) or molecular-dynamics (MD) methods with sufficiently long runs and with proper regard to the N (number) dependence, yield both the RDF and the equation of state (EOS) to an accuracy of better than 1%. In addition to providing valuable information for particular physical problems, the MC or MD results serve as reference points, to which all other semianalytic methods can be compared and tested. These simulation methods have, however, two main shortcomings: (i) $g(r)$ is only given in the range $0 < r < \frac{1}{2}L$, where L^3 is the volume of the "basic cell." For a dense liquid, with $N \sim 10^3$, this range only covers about the first three peaks of $g(r)$. (ii) In the region of very strong repulsion close to $r = 0$, where, say, $g(r) \lesssim 10^{-3}$, there is generally no means of calculating the behavior of $\ln g(r)$, which as we shall see is an important quantity in the theory of fluids.

The first of these difficulties prohibits an unambiguous determination of $S(k)$, since this quantity depends on the way one extends the RDF beyond the simulation range of $\frac{1}{2}L$. Despite the fact that more or less satisfactory solutions for this problem can be achieved by joining the RDF "tails" to the solution for $g(r)$ from approximate integral equations,[2,3] there is, apparently, not a single case in the literature where the results of such a scheme are actually tested for thermodynamic consistency with the original simulation results. The second difficulty exposes a far more severe problem, as will become clearer later on.

Semianalytic approximate methods are divided into two classes[1]: (i) those based on integral equations, and (ii) those based on perturbation calculations. The integral equations, generally being approximate, cannot give thermodynamically consistent results. In most cases the "energy equation" seems to be the closest to the MC or MD equation of state. Integral-equation methods fail to yield satisfactory results for systems described by Lennard-Jones (12-6) potentials, but on the other hand constitute (by the hyperchain equation) the best semianalytic method to treat plasmas.

Different integral equations appear to work better for different systems, but because none of them has the ability to reproduce the MC or MD $g(r)$ data for rather steep potentials in the very important region of the first peak, they have given way to perturbation methods.

These perturbation methods treat the equation of state and $g(r)$ on very different footings. They prove successful for calculating the equation of state of systems with harsh short-range repulsion, and either a short-ranged attraction [like Lennard-Jones (12-6)] *or* a weak long-range tail, but they fail to treat correctly systems whose potentials exhibit *strong* long-range tails,[4] to say nothing about soft repulsive potentials (like r^{-5} or r^{-1}). Even in the more successful cases, the resulting $g(r)$ will fail to give the same level of accuracy as the corresponding perturbation expression for the free energy.

There are two important problems in the literature, for which all existing semianalytical treatments fail, namely plasmas (e.g., the one-component plasma model), and variational calculations of ground-state energies via a Jastrow-type wave functions where the quantum problem is mapped on a related classical problem.[5] This latter problem provides a very severe test for any theory since it demands agreement with the MC $g(r)$ not merely on a rough basis, but also indirectly through stringent moment tests.

The overall picture that emerges therefore is one of many approximate treatments, each devised to tackle a different kind of problem, with some of them being moderately (even very) successful in particular cases. This by itself could constitute just a healthy state of a field in which theoretical methods are compared with experiment (i.e., MC, MD) in order to improve the understanding, except however for the fact that in most cases the link to experiment is summarized in a statement of the form: thus we find that method "*X*" agrees to "*Y*" extent (e.g., *Y* percent) to the MC (or MD) results. The hard-sphere system being the most extensively studied system in the literature, is perhaps the only case where critical comparison to "experimental" data yields some useful information. DeWitt has performed an exhaustive analysis of the Monte-Carlo results for the one-component plasma. His as-yet-unpublished results, (kindly made available to us) have proven extremely helpful, particularly when viewed in conjunction with the published results for the hard spheres.

The basic motivation for the present work starts from premise that there is already sufficient computer-simulation data for various systems, and that provided a proper method can be found for its analysis it can be used to extract information to improve our understanding of just *why* method "*X*" compares "so and so" with experiment. Further, it ought to be possible to use this information to improve on existing methods, particularly for the cases where *none* of those methods prove sufficiently accurate.

The two most important integral-equation methods lead to the Percus-Yevick (PY) and hypernetted-chain (HNC) equations.[6] Both equations can be derived via the diagramatic analysis of $g(r)$ provided one ignores a certain class of diagrams. Clearly, if one *knew* the function represented by the sum of diagrams ignored (the "*E*" set for HNC, or the "*D*" set for PY) then one could write the appropriately modified integral equation and thus get the exact $g(r)$. Percus-Yevick and hypernetted-chain theories lead to integral equations corresponding to well-defined diagrammatic statements. In addition there are hybrid or mixed integral-equation methods[7,8] whose diagrammatic basis is less clear. As we shall see, however, one of these (a recent formulation by Lado[8] for the charged hard-sphere problem) turns out to have a practical similarity to the method we propose, a similarity that is best exposed when viewed in terms of the interesting properties of the E set. It will become evident however, that the observations we make concerning E are of a general nature and not confined to the charged hard-sphere system.

One should keep in mind that since the radius of convergence of the diagrammatic power series in the density is not generally known, a thermodynamically consistent solution of, say, the *modified* HNC equation that we shall introduce, that completely agrees with the Monte Carlo data (assuming that it is exact), actually *defines* the function $E(r)$ required in the theory. It should also be kept in mind though that the integral equations (like PY, HNC, and the mixed type) can be derived by functional differentiation, *without* resort to the diagrammatic expansion.[9] It is certainly conceivable that the exact results (the Monte Carlo results in the present state of the art) contain features not explicable by the diagrammatic approach. It is the usual and often reasonable practice in the theory of liquids, however, to extend diagrammatic ideas and their results to the treatment of dense matter. Thus $E(r)$ can be defined in terms of diagrams at low densities, while the thermodynamically consistent solution of the modified HNC equation (an equation derived by the diagrammatic analysis) that is compatible with the Monte Carlo results at high densities, defines a function $E(r)$ that merely represents a practical parametrization of these Monte Carlo results. This particular parametrization in terms of (an) $E(r)$, as it stands, will enable us to compare this function with assumptions implied about it in various theories, thus satisfying the basic motivation mentioned before. It is possible, however, that *this particular form* of the "experimental data" (the Monte Carlo results) will enable us to make general statements of a predictive character, i.e., to formulate a new approximation scheme in the theory of fluids. It is worth noting that the hard spheres constitute the *only* system for which the quantity $H(r) = \ln y(r) = \ln[g(r)e^{\beta u(r)}]$, at small separations ($r \approx 0$) can be related directly to the equation of state, thus enabling the parametrization to also include the interior of the core.[10] Generally speaking, the unknown function is practically undefined (by this way of parametrization) in the region where $g(r)$ is essentially zero.

Suppose we indeed try to parametrize all simulation data for all systems considered in the literature. We should demand from the resulting fit that it will agree with MC or MD data to within the noise inherent in these methods, and that the resulting $g(r)$ must satisfy any rigorous moment conditions known to exist. We expect the fitting function [for the unknown $D(r)$ or $E(r)$] to be *sensitive* to the requirements of thermodynamic consistency, otherwise our fit is indeed ill defined.

In the spirit of perturbation theory we could expect that the unknown functions will look similar to those of the hard spheres if the potential is strongly repulsive. Moreover, recall that in the variational calculations it is possible to determine a *single* variational parameter (i.e., the hard-sphere diameter) that yields good results, even for the one-component plasma.[11] Since at relatively high densities many structural features can be regarded as universal for all simple fluids, it cannot be ruled out *a priori* that a single one-parameter family of functions like those for the hard spheres will also yield, by this approach, reasonable results for all such systems. Indeed it is worth noting that $E(r)$ can be written entirely in terms of diagrams containing $h(r)$ bonds, and since to the extent the $g(r)$ is universal we may expect, from the nature of the diagrams, the $E(r)$ to be more so. There are certain features of the results of the HNC equation that seem to prevail for any system for which this equation has been solved and its results compared with computer-simulation data. This, together with other features of the HNC method leads us to place strong emphasis on this equation, and to choose $E(r)$ (assumed zero in HNC) as the function to seek.[10] Now, suppose the task has been completed, and we have parametrized all the data available, i.e., found for each potential a family of functions $E(r)$ such that the solution of the modified HNC equation [an equation that takes into account these $E(r)$] is thermodynamically consistent and agrees with the MC or MD results to *within the accuracy of the latter*. Then it would be reasonable to ask whether there are certain universal features of the fitted functions, that if taken alone, (ignoring a residuum that is peculiar to each potential) could still yield *both* thermodynamic consistency, and good agreement (but of course more restricted) with the simulation results.

Our work started, in fact from this proposition and resulted in the following anzatz of universality: *To within the accuracy of present-day computer-simulation studies [usually about 2% for $g(r)$] the bridge functions [i.e., the sum of the elementary graphs = $E(r)$, assumed zero in HNC] constitute the same family of curves, irrespective of the assumed pair potential.*

In view of the known parametrized results for hard spheres the above assertion, if correct, defines a *new method* in the theory of fluids and one that is applicable to *any* potential. It proceeds as follows: Solve the modified HNC equation (with inclusion of the one-parameter bridge functions appropriate to *hard spheres*), and determine the only free parameter η (related to the hard-sphere diameter) by requiring thermodynamic consistency. (See Sec. III.)

The most important physical result of the present work is that our starting ansatz is demonstrably correct, to surprisingly high accuracy, and for a variety of potentials: hard spheres, Lennard-Jones, an inverse fifth power (r^{-5}) applicable to the helium problem, Coulomb potential [the one-component plasma (OCP)], Yukawa potential, charged hard spheres, and finally an oscillatory potential proposed for liquid gallium and other metals with significantly large screened fluctuating-dipole interactions. Further, an observation about the relation between the solutions of the PY equation for hard spheres and the "exact" computer results, enables us to generalize the method to mixtures.

With these introductory remarks in mind the plan of the paper is now this: In Sec. II we briefly review the results of the diagrammatic expansion of $h(r)$ and record the HNC and PY integral equations and the corresponding *modified* equations. In Sec. III we comment on some possibilities of establishing the thermodynamic consistency of a given $g(r)$ (radial distribution function). Section IV is devoted to an analysis of the role of the elementary graphs and the relative importance of the information needed. Some useful inequalities are derived. In Sec. V we describe the hard-sphere bridge functions. Certain results in the literature that feature universal characteristics of the bridge functions are discussed in Sec. VI. Finally, the new method proposed in this work is tested for various potentials in Secs. VII (the one-component plasma), VIII (Yukawa), IX (ground state energy of liquid ^{4}He via the r^{-5} potential in the Jastrow wavefunction), and X (Lennard-Jones) and XI (an oscillatory potential for certain liquid metals). The combined results lead to a re-examination of the mean spherical approximation which is given in Sec. XII. Some concluding remarks are given in Sec. XIII. Finally, Appendix A deals with possibilities of checking the "Ewald-method" Monte Carlo results for plasmas. In Appendix B we present a diagrammatic analysis of the HNC equation for the Coulomb potential and discuss the asymptotic behavior in the low-density regime.

II. DIAGRAMMATIC EXPANSIONS AND INTEGRAL EQUATIONS

We briefly review some standard[12] definitions required in the subsequent development. Define the total (or pair) correlation function

$$h(r) = g(r) - 1 . \tag{1}$$

It is possible to formally expand $h(r)$ in a power series in the density ρ (without guarantee of convergence at liquid densities) and resum in the form

$$1 + h(r) = e^{-\beta u(r) + \theta(r) - E(r)} , \tag{2}$$

where

$$\theta(r) = h(r) - C(r) \tag{3}$$

and $C(r)$ satisfies the Ornstein-Zernike (OZ) equation

$$h(r) = C(r) + \rho \int d\vec{r}\,' h(|\vec{r} - \vec{r}\,'|) C(r') . \tag{4}$$

The quantity $E(r)$ in (2) is the sum of the elementary diagrams that are not nodal. Note that $E(r)$ can be written entirely in terms of diagrams possessing $h(r)$ bonds.[6] The usual HNC equation is obtained via (2) and (4) from the assumption that $E(r) = 0$, i.e.,

$$g(r) = e^{-\beta u(r) + \theta(r)}, \quad C(r) = g(r) - 1 - \theta(r) , \tag{5}$$

with $\theta(r)$ given in terms of $h(r)$ and $C(r)$ by (4), i.e.,

$$\theta(r) = \frac{2\pi}{r} \rho \int_0^\infty h(x) x\, dx \int_{|x-r|}^{x+r} C(y) y\, dy . \tag{6}$$

Now with some given function $E(r)$ (not necessarily the *correct* sum of the elementary graphs) one can clearly solve a modified HNC equation, (5) but with $u(r)$ replaced by an effective potential $u(r) - (1/\beta)E(r)$. With the exact $E(r)$ this modified HNC equation would also be exact. Otherwise for an approximate $E(r)$ the *modified HNC* equation takes the form

$$\begin{aligned} g(r) &= e^{-[\beta u(r) - E(r)] + \theta(r)} , \\ C(r) &= g(r) - 1 - \theta(r) , \\ \theta(r) &= \frac{2\pi\rho}{r} \int_0^\infty dx\, x(g(x) - 1) \int_{|x-r|}^{x+r} C(y) y\, dy . \end{aligned} \tag{7}$$

We shall return to (7) and its consequences shortly, but before doing so we briefly examine the corresponding steps in the analysis leading to the Percus-Yevick equation. Let $D(r)$ be the set of connected diagrams free from bridge points and lacking direct bonds between the root points. This set contains the elementary diagrams $E(r)$ and in addition is related to $C(r)$ by

$$C(r) = (e^{-\beta u(r)} - 1) y(r) + D(r) , \tag{8}$$

where

$$y(r) = e^{\beta u(r)} g(r) . \tag{9}$$

As noted earlier we shall also need the quantity $H(r) = \ln y(r)$ [where $H(r) + \beta u(r)$ is the potential of mean force]. If we assume $D(r) = 0$ we get the PY equation:

$$C(r) = [1 - e^{\beta u(r)}] g(r), \quad C(r) = g(r) - 1 - \theta(r) . \tag{10}$$

Evidently we can define a modified PY equation by the inclusion of an assumed function $D(r)$ [not necessarily the exact $D(r)$]. With the exact $D(r)$ the modified PY equation is, of course, also exact.

Analysis in terms of $E(r)$ [rather than, say, $D(r)$] seems to us more attractive for two main reasons: (i) $E(r)$ enters the modified HNC equation as an effective potential which can be given physical meaning. (ii) $E(r)$ is a much better behaved function than $D(r)$. To illustrate this point let us consider the system of hard spheres. Near and outside the hard core $-E(r)$ and $D(r)$ behave similarly, i.e., are rapidly decaying functions that take on values $O(1)$ at the core. Inside the core, however, say at $r = 0$, $-E(r) = 1 - C(0) - H(0)$ and for a dense hard-sphere fluid takes values $O(10)$ (see below). But $D(r)$ under the same conditions takes values $D(0) = C(0) + e^{H(0)} \approx O(e^{10})$. Inside the core $E(r)$ behaves nearly linearly, while $D(r)$ behaves exponentially.

III. THERMODYNAMIC CONSISTENCY

There are simple formulae that express the thermodynamic functions of a system in terms of the structural functions C and g. The pressure, for example, can be given in terms of g and the virial, and the isothermal compressibility in terms of C. These are themselves related for the pressure once known can be differentiated with respect to density to give the compressibility: with the exact C and g the results from the two routes to the compressibility necessarily agree. If the theory giving g and C is approximate, the difference in the two results is a measure of thermodynamic inconsistency. If, on the other hand the theory is approximate but embodies a disposable parameter, thermodynamic consistency can be required in each state of the system, a constraint that can be imposed in order to determine the corresponding values of the parameter.[7]

Now consider this question of thermodynamic consistency from the standpoint of the *universality* of the bridge functions. If we accept that this universality has indeed been established, then we may choose the family for the hard-sphere system as the representatives of all bridge functions. But a hard-sphere bridge function is specified by one parameter, the packing fraction, and it now appears that we have an example of a theory framed in terms of a single disposable parameter. However, in this instance it is a necessary consequence of universality that for a chosen state there is a particular value of this parameter that will always lead to thermodynamically consistent values of energy, pressure, or compressibility. If necessary this value can be established by the procedure described above; alternatively when simulation data on a given system exist it is equivalent to demonstrate by direct comparison that for each state a specific choice of η can be identified that leads to corresponding and consistent values of energy, pressure, or compressibility.

There is however a further structural property that is connected to another thermodynamic function (though not very directly), namely,[13]

$$H(0)=\beta[F^E(0,N)-F^E(1,N-2)]\,, \tag{11}$$

where $F^E(n,m)$ is the excess free energy of a system with $n+m$ particles interacting with the given potential, of which m are assigned "charge" of 1 and n "charge" of 2, such that the interaction energy between particles i and j is

$$[\text{"charge" }(i)][\text{"charge" }(j)][u(r_{ij})]\,.$$

The hard-spheres constitute the only system for which $H(0)$ can be related directly to the equation of state. Since the "charging" process does not affect the hard-sphere potential, one has

$$H(0)_{\text{hard spheres}}=\beta[F^E(N)-F^E(N-1)]=\beta\frac{\partial F^E}{\partial N}=\beta\mu^E\,, \tag{12}$$

where μ^E is the excess chemical potential given by

$$\beta\mu^E=\beta F^E/N+\beta P/\rho-1\,. \tag{13}$$

The only other system where a good approximation for the value of $H(0)$ is given via simulation methods is the OCP. The MC results and the solutions of the HNC equation for the OCP and the two-component plasma (ions of two different charges in a compensating background), indicate that to good accuracy[14] (especially at high densities), one can assume that the excess free energy of mixing vanishes. This enables one to write $H(0)$ in terms of the equation of state of the OCP that was obtained also to high accuracy by computer simulations.[15]

The only way to calculate $H(0)$ directly [or in fact $H(r)$ in the region of very strong repulsion, where $g(r)\approx 0$], is by summing the defining diagrams. Computer simulation can only be used to obtain it indirectly, via (11), which in the two cases above can be well approximated by means of the computer-calculated equation of state.

The values of $H(r)$ in the inaccessible region therefore seem to provide a rather severe test for assessing the overall merit of approximate methods. Note that for the hard spheres both the PY and HNC equations yield the correct second and third virial coefficients via the "pressure" and "compressibility" equations,[1] but fail to do so for the third virial coefficient via the expression for $H(0)$. Note also that the PY equation for hard spheres in one dimension (hard rods) yields both the exact $g(r)$ and $C(r)$, thus producing a thermodynamically consistent (and exact) equation of state. It nevertheless fails to give the correct $H(r)$ inside the core, thus producing an incorrect equation of state via $H(0)$.[16] This merely demonstrates that the diagrammatic statement of the PY equation is incorrect, while the resulting equation [actually the mean-spherical approximation for $C(r)$] is, however, exact.

IV. ANALYSIS OF THE ROLE OF THE ELEMENTARY GRAPHS

The sum of elementary graphs enters the modified HNC equation [Eq. (7)] as part of an effective potential. Let us see what is required of an expression for $E(r)$ (in terms of the correlation functions) in order that the modified HNC equation will become identical in terms of the resulting $g(r)$ to various known integral equations for fluids.[1] In summary these are

(i) HNC:

$$E(r)=0\,; \tag{14}$$

(ii) PY:

$$E(r)=-[\,y(r)-1-\ln y(r)]$$

or (15)

$$E(r)=-[\,g(r)-1-\ln g(r)]+[C(r)+\beta u(r)]\,;$$

(iii) mean spherical approximation (MSA):

$$E(r)=\begin{cases}-\infty \;\;[\text{or undefined if } u(r)=\infty], & r<r_0\\ -[g(r)-1-\ln g(r)], & r>r_0,\end{cases} \tag{16}$$

where $g(r<r_0)=0$ and $g(r_0+0)=0$ for $u(r_0-0)\neq\infty$ (see Sec. X);

(iv) Rowlinson-Lado (RL)[7]:

$$E(r)=-\alpha[y(r)-1-\ln y(r)] \tag{17}$$

with α determined by imposing thermodynamic consistency;

(v) Mixed integral equations[8]: Begin by writing the interaction as $u(r)=u_1(r)+u_2(r)$, and solve the PY equation for $u_1(r)$ [usually the repulsive short-range part]. Then, assume that for $u(r)$,

$$E(r)=-[y_1(r)-1-\ln y_1(r)]\,.$$

More generally, we could suppose the exact $E_1(r)$ for the potential $u_1(r)$ is known; in that case we take $E(r)=E_1(r)$.

To proceed with the analysis let us define the bridge function $b(r)$, as

$$b(r)=-E(r)\,, \tag{18}$$

which as we shall see will turn out to be equivalent to a repulsive short ranged potential.

From the definition of the functions involved it is easy to establish the following asymptotic behavior:

$$B(r)+\beta u(r)\sim\tfrac{1}{2}h^2(r)\,, \tag{19}$$

$$C(r)+\beta u(r)\sim\tfrac{1}{2}h^2(r)+E(r)\,, \tag{20}$$

$$h(r)\sim[N(r)-\beta u(r)]+E(r)\,, \tag{21}$$

where $B(r)$ is the set of "bundle" diagrams and $N(r)$ the set of nodal diagrams.[10] If we draw an analogy from the Coulomb case (OCP) then we can assume the following hierarchy[17] for large r:

$$h(r)\sim[N(r)-\beta u(r)]>E(r)\,.$$

This assumed hierachy, however, is not essential to the subsequent arguments in view of the role of $E(r)$ as an effective potential. In fact, all the approximations (i)–(v) take the view that for values of r beyond the first peak of $g(r)$, $E(r)$ is of the order of $\frac{1}{2}h^2(r)$. To have some appreciation for the effect of the tail of $E(r)$ on the resulting $g(r)$ (via the modified HNC equation) consider the structural effect of a LJ (12-6) tail on a hard-sphere system under conditions where $\epsilon/kT\lesssim\frac{1}{50}$, or, say, the difference in structure between the LJ (12-6) system from that of the r^{-12} part of it, when $\epsilon/kT\lesssim\frac{1}{50}$. In both cases the difference is barely detectable by computer simulations. Thus in the context of solving the modified HNC equation[e.g., with (i)–(v)] the tail of $E(r)$ evidently plays a very minor role.

In the region close to the origin where the potential is very highly repulsive, and where the resulting $g(r)$ takes on very small values (practically zero in fact), $E(r)$ will be undefined in the sense that no matter what finite value it assumes, it will hardly effect $g(r)$. In the extreme case of hard spheres, $g(r)=0$ inside the core, irrespective of $E(r)$. This effect is connected to shortcoming (2) discussed in the introduction. Now according to a theorem due to Widom,[13] given any nonsingular potential, we can expand $H(r)$ near the origin in a power series in r, involving only even powers, and with the coefficients alternating in sign:

$$H(r)=H(0)-a_1r^2+a_2r^4-\cdots\quad(a_i>0)\,. \tag{22}$$

Indeed, the coefficient a_1 for the OCP was found by Jancovici[13] to be $\frac{1}{4}\Gamma$, where $\Gamma=\beta(Ze)^2/(3\rho/4\pi)^{1/3}$ is the plasma parameter and r is measured in units of $a=(3\rho/4\pi)^{1/3}$. For hard spheres this behavior breaks down and the function starts linearly near the origin,[8,19] i.e.,

$$H(r)=\beta\mu^E-\tfrac{3}{2}(\beta P/\rho-1)r+\cdots\,, \tag{23}$$

with r in units of d, the hard-sphere diameter.

Now recall the relation [Eqs. (2) and (4)]

$$h(r)=C(r)+H(r)-E(r)\,.$$

Since for a dense fluid $h(r)=-1$ over some region near $r=0$, it follows that $C(r)-E(r)$ behaves as $H(r)$ near the origin. It is then plausible that *both* $C(r)$ and $E(r)$ behave essentially as $H(r)$ near the origin.[18]

Thus the linear behavior of $E(r)$ for the hard spheres, near $r=0$, is a distinct feature. This however, is in no way an obstacle in searching for universal characteristics because the region where this feature *is* distinct is obviously the region where for computational purposes $E(r)$ is undefined. In turn observe that the shape of $H(r)$ for the OCP is nearly linear[19] over the region $[r\!: g(r)>10^{-3},\ r\!: g(r)=\max]$, a feature shared *also* by the system of hard spheres.[8]

We therefore arrive at the conclusion that the important region in which $E(r)$ must be specified, *in any theory*, is the region of the first peak of $g(r)$, defined roughly by $[r\!: g(r)>10^{-3},\ r\!: g(r)$ takes its first minimum nonzero value$]$. The main disagreements between the results of the various theories, say, (i)–(v), and their mutual disagreement with MC results, is a consequence of the respective assumptions made on $E(r)$ in this region.

We end this section by noting that the role of $E(r)$ as an effective potential enables us to derive certain useful inequalities. The Gibbs-Bogoliubov inequality[20] can be written

$$\tfrac{1}{2}\beta\rho \int g(r)\Delta\varphi(r)\,d\vec{\mathrm{r}} \leqslant \frac{\beta F_0}{N} - \frac{\beta F_0}{N}$$

$$\leqslant \tfrac{1}{2}\beta\rho \int g_0(r)\Delta\varphi(r)\,d\vec{\mathrm{r}}\,, \qquad (24)$$

(which is merely a statement that the function e^{-x} is convex). Here F, g, φ and F_0, g_0, $\varphi - \Delta\varphi$ are the free energy, the RDF and the pair potential of one system and another (the "zero") system, respectively.

Next, we note that the solution of the modified HNC equation for the potential $u(r) - (1/\beta)E_i(r)$, gives the exact RDF, $g(r)$, for the potential

$$\varphi(r) \approx u(r) + (1/\beta)[E(r) - E_i(r)]\,,$$

where $E(r)$ is the exact sum of elementary diagrams for $u(r)$, and $E_i(r)$ is some assumed form [say, one of (i)–(v), or the exact one]. With the bridge function of Eq. (18), we can immediately deduce that

$$\int [g_{b_i}(r) - g_{b_j}(r)][b_j(r) - b_i(r)]\,d\vec{\mathrm{r}} \geqslant \epsilon \sim 0\,. \qquad (25)$$

In particular

$$\int [g_{\mathrm{HNC}}(r) - g_{\mathrm{exact}}(r)]b_{\mathrm{exact}}(r)\,d\vec{\mathrm{r}} \geqslant \epsilon \sim 0 \qquad (26)$$

and

$$\int [g_{b_j}(r) - g_{\mathrm{exact}}(r)][b_{\mathrm{exact}}(r) - b_j(r)]\,d\vec{\mathrm{r}} \geqslant \epsilon \sim 0\,. \qquad (27)$$

Thus differences between the results of various theories among themselves, and between them and MC results can be analyzed, to some extent, via these inequalities. Their main power is, however, in the final stages of a parametrization of $b(r)$, when they lose their integral nature and become more local relations.

V. HARD-SPHERE POTENTIAL

As noted, the system of hard spheres is the most extensively studied system in the literature, both by simulations and by analytical methods.[1] Of the latter, the analytic solution of the PY equation[21] (identical to the MSA for hard spheres), and of the MSA with Yukawa closure,[22] has played a most significant role. The MC results for this system have been parametrized in a sufficiently accurate manner,[8] and this fact enables us to infer the corresponding bridge functions. To do this we need $g(x,\eta)$, $C(x,\eta)$, and $H(x,\eta)$, where $x = r/\sigma$ (σ being the hard sphere diameter) and $\eta = \frac{1}{6}\pi\rho\sigma^3$ is the packing fraction. Both g and C have been accurately parametrized[23] in a manner consistent with the semiempirical Carnahan-Starling[24] equation of state for hard spheres. Both are formulated as corrected versions of the corresponding Percus-Yevick results, analytic formulas for which are given in the literature.[25] The function, $H(r)$, is continuous across $r = \sigma$ (also in PY theory), and both its value and its first derivative at the origin are known. A convenient approximation for $H(r)$ *inside* the core is therefore given by

$$H(x) = \alpha_0 + \alpha_1 x + \alpha_2 x^2 + \alpha_3 x^3, \quad x \leqslant 1 \qquad (28)$$

where the coefficients α_i are straightforwardly determined from the excess thermodynamic functions for the hard-sphere system.[8] Given this information, we can now construct b from

$$b(r) = g(r) - 1 - C(r) - H(r)\,. \qquad (29)$$

For the sake of comparison we also construct the PY result (15) given by

$$b_{\mathrm{PY}}(r) = -C_{\mathrm{PY}}(r) - 1 - \ln[-C_{\mathrm{PY}}(r)], \quad r < \sigma$$

$$= g_{\mathrm{PY}}(r) - 1 - \ln g_{\mathrm{PY}}(r), \quad r > \sigma\,. \qquad (30)$$

Note that both (29) and (30) define continuous functions.

The one-parameter (η) bridge-function family of curves for the hard spheres, from (29) and (30), is plotted in Fig. 1. The bridge functions turn out to be very simple in shape, beginning linearly at the origin and then becoming convex and acquiring *very* small values starting at about $x \approx 1.2$. Thereafter they behave essentially as $\frac{1}{2}h^2(r)$. The validity of inequality (27) is demonstrated if one observes that near contact, $g_{\mathrm{PY}}(r) < g_{\mathrm{MC}}(r)$, while correspondingly, $b_{\mathrm{PY}}(r;\eta) > b_{\mathrm{MC}}(r;\eta)$, in that region. For HNC, $b(r) = 0$ and correspondingly, $g_{\mathrm{HNC}}(r) > g_{\mathrm{MC}}(r)$, near contact. Note the highly nonlinear behavior of the bridge functions as functions of the parameter η. Observe that to a high degree of accuracy, the two families of bridge functions (29) and (30), are identical, except for the relabeling of the parameter η. These last two points [given that assumption (v) substantially improves on the PY results for hard spheres[7]] strongly suggest that the solution of the modified HNC equation with the simple PY family of bridge functions, will yield very accurate results for hard spheres, provided thermodynamic consistency is imposed. We can expect good results also for $H(r)$ *inside* the core. At this stage there is however, little incentive for actually performing this calculation. The observation will be of more value however when considering mixtures for which no parametrization has ever been attempted except for the hard spheres. We shall elaborate on this point later.

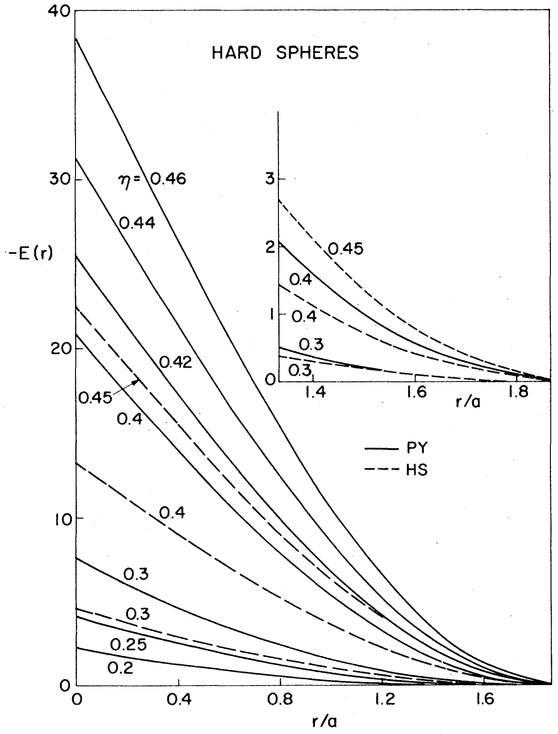

FIG. 1. Bridge functions ($b(r)=-E(r)$) for hard spheres. PY denotes the functions obtained from the solution of the Percus-Yevick equation [see Eq. (30)]. HS denotes the functions obtained from a parametrization of the Monte Carlo data [see Eq. (29)]. The distance r is given in units of a [the Wigner-Seitz radius, $a = (3/4\pi\rho)^{1/3}$] to facilitate comparison with the OCP results.

VI. UNIVERSAL CHARACTERISTICS OF THE BRIDGE FUNCTIONS

Keeping in mind the shape of the bridge functions for the hard spheres, let us investigate other published data for other systems to see whether they can tell us anything about the corresponding functions $b(r)$. Solutions of the HNC equation are of particular importance for comparison with MC results since all the differences between these results stem from the HNC assumption that $b(r) = 0$.

All of the results for quite a variety of potentials, namely, hard-spheres and square wells,[26] Coulomb,[27] Yukawa,[28] LJ,[29] r^{-5}, and other inverse powers[30] share the following common features:

(i) The HNC pressures are larger than the corresponding MC results, i.e.,

$$P_{\text{HNC}} > P_{\text{MC}} . \tag{31}$$

(ii) The HNC inverse compressibilities are smaller than the corresponding MC results, i.e.,

$$\beta\left(\frac{\partial P}{\partial \rho}\right)_{T,\text{HNC}} < \beta\left(\frac{\partial P}{\partial \rho}\right)_{T,\text{MC}} . \tag{32}$$

These results are of course just a reflection of the differences between the $g(r)$'s. As a rule the HNC $g(r)$ is shifted [in comparison with $g_{\text{MC}}(r)$] somewhat towards the origin, thus being larger than $g_{\text{MC}}(r)$ in the region of the first rising slope of the first peak [hence (31)], and somewhat smaller in the first declining slope. The corresponding features look noticeably different for hard spheres, but point to the same physical effect. Result (32) follows from the fact that $|C_{\text{HNC}}(r)|$ is smaller than $|C_{\text{MC}}(r)|$ in the region close to the origin.

In the language of the modified HNC equation, all these results point towards an essentially repulsive perturbing potential [i.e., $b(r)$] in conformity with the shape of the bridge function for the hard spheres. This observation is rewarding. There is, however, one particular result in the literature that enables us to see things on a much finer scale.

We focus attention on the system of charged hard spheres as treated by Lado[8] by the method of mixed integral equations. As we remarked earlier, Lado's treatment of this problem is similar in certain respects to the method being proposed here. It amounts to the use of the PY hard-sphere bridge functions in a HNC equation for the Coulomb problem, the results of which are very instructive. In particular let us select the case $\Gamma = 70$ and $\eta = 0.342$ [i.e., $\sigma = 1.4a$, $a = (3\rho/4\pi)^{1/3}$]. Physically the system of point charges (the OCP) behaves at $\Gamma = 70$ as if it has a core of $\sigma' \sim 1.3a$ [$g(r) = 0$ for $r < 1.3a$], and actually introducing a hard-core repulsion with $\sigma = 1.4a$ has only a minor effect on all the thermodynamic properties of the corresponding point charges. The solution of the mixed integral equations for structure of the *charged hard spheres*, in the state described above, is completely equivalent to the solution of the modified HNC equation for the structure of *point charges* above at $\Gamma = 70$, with the following bridge function:

$$\begin{aligned} b(r) &= \infty, \quad r < \sigma = 1.4a \\ &= b_{\text{PY}}(r;\eta = 0.343), \quad r > \sigma = 1.4a . \end{aligned} \tag{33}$$

Comparing the results of Lado for (33) (his Figs. 1–3) with the MC results for point charges[3,31,42] we find that (i) the structure factors agree very well, (ii) the $C(r)$'s agree very well except for the small jump discontinuity at $r = \sigma$, and (iii) the $g(r)$'s agree very well except for a jump discontinuity at $r = \sigma$. The overall agreement represents a vast improvement over the solution with $b(r) = 0$ (i.e., HNC), especially in terms of thermodynamic consistency. What is even more striking about these results is the fact that continuing $b_{\mathrm{PY}}(r; \eta = 0.343)$ *inside* the core will yield very reasonable values for $H(0)$. This observation, in view of the fact that the Coulomb potential is so much different from the hard spheres, is very suggestive. The family of bridge functions for the hard spheres is manifested as a set of repulsive potentials that change monotonically, i.e., become stronger with increasing η. Recall that the deviations of the HNC equation from the MC results [Eqs. (31) and (32)] are also monotonic with the density, the HNC equation being exact at low densities. Solving the modified HNC equation with this family of bridge functions, we expect that at a given density the solutions will start to float in the direction of the MC results. We terminate this by imposing thermodynamic consistency. The procedure just outlined would have given an exact result if our anzatz in the Introduction was exact. The actual accuracy of this procedure will be demonstrated for systems of interest in Secs. VII–X.

Before proceeding with this task, let us note the following: For a general potential the bridge functions represent a two-parameter (ρ, T) family of curves, and only for homogeneous inverse power potentials (r^{-n}) do they depend on one reduced temperature-density variable $(\rho T^{-3/n})$. Parametrization of the exact results for a given potential via the solution of the modified HNC equation with the hard-sphere family of bridge function, defines a mapping $\eta \longleftrightarrow (\rho, T)$ similar to, say, the effective hard-sphere diameter in the perturbation calculation with a hard-sphere reference system.[1] Employing the one-parameter family of bridge functions of the hard spheres in the scheme outlined above is (in a way) in the spirit of perturbation theory, but it does not rely on the given potential having too much resemblance to the hard-sphere potential. By the same token, in view of the anzatz of universality (Sec. I) we could employ a two-parameter family of bridge functions, or a one-parameter family of some inverse power potential. The reason for using the hard spheres is mainly because they represent a rather well-known, highly parametrized system.

VII. CLASSICAL ONE-COMPONENT PLASMA (OCP)

The OCP is an assembly of point ions immersed in a uniform background of opposite charge to make the potential energy extensive. This system with a uniform background of degenerate electrons actually gives a first-order description of some situations in astrophysics. Since it is very possibly the simplest system with long-range Coulomb interactions, it is an important testing ground for various theoretical methods. The OCP has been extensively studied by the MC and MD methods, which usually invoke the "Ewald image potential" technique.[31] An important check of the results with the Ewald method can be made via perturbation theory using the method of Lado.[8] Additional checks and properties of the OCP are provided in Appendix A.

The interaction potential, in dimensionless units $(\rho = 3/4\pi,\ \beta = 1)$, is $\beta u(r) = \Gamma/r$ and in terms of the plasma parameter Γ the potential energy of the system $\beta U/N$ is bounded below[33] by -0.9Γ (the ion-sphere result, or uniform-sphere approximation) and also[34] by $-\frac{1}{2}\sqrt{3}\,\Gamma^{3/2}$ [the Debye-Hückel (DH) result]. In addition the Debye-Hückel model gives the exact long-range correlations in the system for any Γ. Furthermore, Stillinger and Lovett[35] (SL) have shown that the small-k limit of the structure factor is also given by the Debye-Hückel model which imposes, as a consequence, two moment conditions (the SL conditions) on $g(r)$. For the range $\Gamma > 1$, the MC results for $\beta U/N$ can be very accurately represented by the simple empirical equation of state proposed by de Witt[36]:

$$\beta U/N = -0.89461\Gamma + 0.8165\Gamma^{1/4} - 0.5012\,. \tag{34}$$

The OCP is also found[37] to undergo a solid-fluid transition at $\Gamma = 155 \pm 10$.

In attempts to understand the facts just described, the HNC equation and its consequences has proven, so far, to be the best semianalytic approach.[38] It yields a very good equation of state, but nevertheless fails badly in terms of thermodynamic consistency since it gives far too high values for $|\beta(\partial P/\partial\rho)_T|$ (about 50% too high near crystallization). The HNC equation yields exactly the DH limit for $\Gamma \ll 1$, and its thermodynamic inconsistency rises monotonically with increasing Γ. (The low-Γ behavior of the HNC solutions is discussed in Appendix B.) Since the bridge functions for the OCP fall exponentially[39] at large r, the solutions of the pure HNC equation (and of any modified HNC equation with exponentially decaying bridge functions) satisfy the SL conditions.[32] The wrong HNC "compressibility" equation of state just reflects the rather poor results for $g(r)$, and the success of the energy equation is the result of the insensitivity of the corresponding integral to these discrepancies arising from the long range nature of the Coulomb potential. (For that matter even the hard sphere RDF will do.[40]) We shall discuss the MSA results (in a broader context) in Sec. X.

We have solved the modified HNC equation [Eq. (7)] for the OCP, for a large set of Γ's ranging between 1 and 170. For each Γ we solved the equation for a set of hard-sphere bridge functions by varying the parameter η. We used the method of Ng[27] and imposed similar criteria of accuracy. Our results for $b(r)=0$ (i.e., the pure HNC) are in complete agreement with Ng's results, thus providing a mutual numerical check. Most of our calculations were performed using both (29) and (30) with practically indistinguishable results[41] except for the relabeling of the parameter η. For heuristic purposes we prefer the simpler PY family of bridge functions and all the results presented in this paper are obtained with this choice.

Before presenting our results, it is worth noting that the MC $g(r)$ data of Hansen were joined with a DH $C(r)$ tail for $r>\frac{1}{2}L$, and the solution of the resulting MSA type of equation provides, via Fourier transformation, quite accurate curves for $C(r)$ and $S(k)$.[42]

From the bulk of our own numerical work we choose a representative set of cases to be presented here, and it should be emphasized that they are truly typical in the sense that all trends observed, in the figures and table presented here, apply with equal validity to all values of $\Gamma<160$.

The results are presented in Figs. 2–10 and Table I, and can be summarized by the following statement: For each value of Γ we can identify a single hard-sphere bridge function, characterized by some η, such that the solution of the modified HNC equation will yield $\beta U/N$, $\beta(\partial P/\partial\rho)_T$, $g(r)$, $C(r)$, $S(k)$ in excellent agreement with the corresponding MC (or MC-derived) results. Taking into account the MC noise, and the N dependence of the MC results (with indeed a higher peak for the larger system!), the agreement above is within the uncertainty of the MC results [about 1% for $g(r)$ and about 0.1% for $\beta U/N$].

Two points deserve specific comment:

(a) The MC-derived results give us the values of $C(r)$, and the values of $H(r)$ can be calculated directly from the MC $g(r)$'s via $H(r)=\ln g(r)+\Gamma/r$. When $g(r)$ is too small (it is practically zero near the origin), $\ln g(r)$ is then ill defined and we have used instead[19]

$$H(r)=\Gamma(1.25-0.39r). \tag{35}$$

which, as noted earlier is an excellent representation of the potential of mean force. In this region our results are perfectly compatible with the MC-derived results. For small values of r we use a linear bridge function, a form that is incorrect for the OCP [see (11), (22), (23), and the discussion thereafter]. Assuming that the excess free energy of mixing is negligible for a *two*- component plasma with $z_1=1$, $z_2=2$, one can derive[15] the relation

$$\beta F(M,N)=Nf_0\left[\Gamma\left(\frac{N+2M}{N+M}\right)^{1/3}\right]+Mf_0\left[\Gamma\left(\frac{N+2M}{N+M}\right)^{5/3}\right], \tag{36}$$

where $F(M,N)$ is the excess free energy of a system with M charges $z_2=2$, and N charges $z_1=1$, in a compensating background, and $f_0(\Gamma)$ is the reduced $(=\beta F^E/N)$ excess free energy of the OCP, given, for example, by (34). Thus we can write

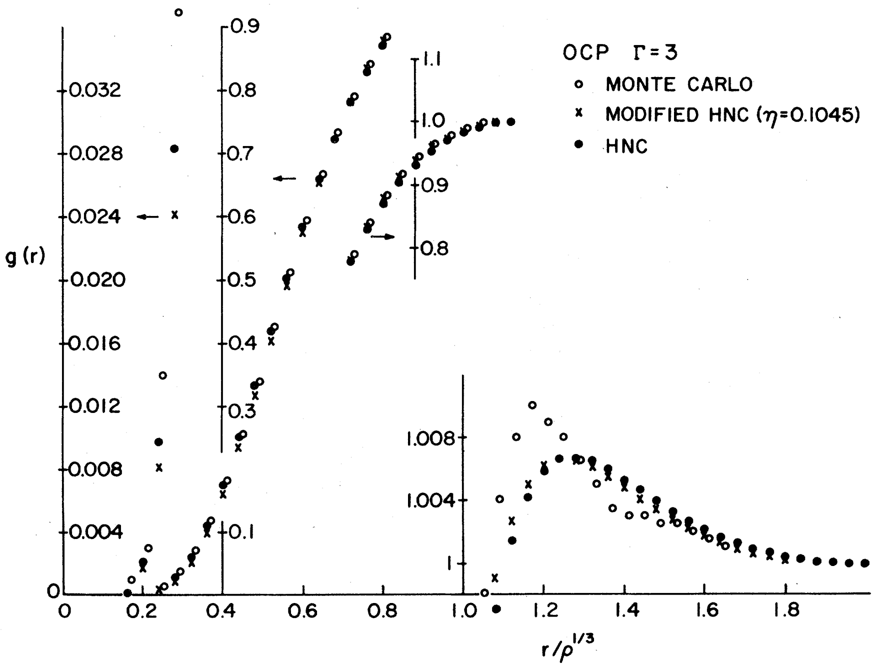

FIG. 2. OCP $g(r)$ at $\Gamma=3$. The Monte Carlo data is taken from Hansen (Ref. 31). The modified HNC equation incorporates the PY bridge function. Note the differences of scales and the MC noise near the first peak.

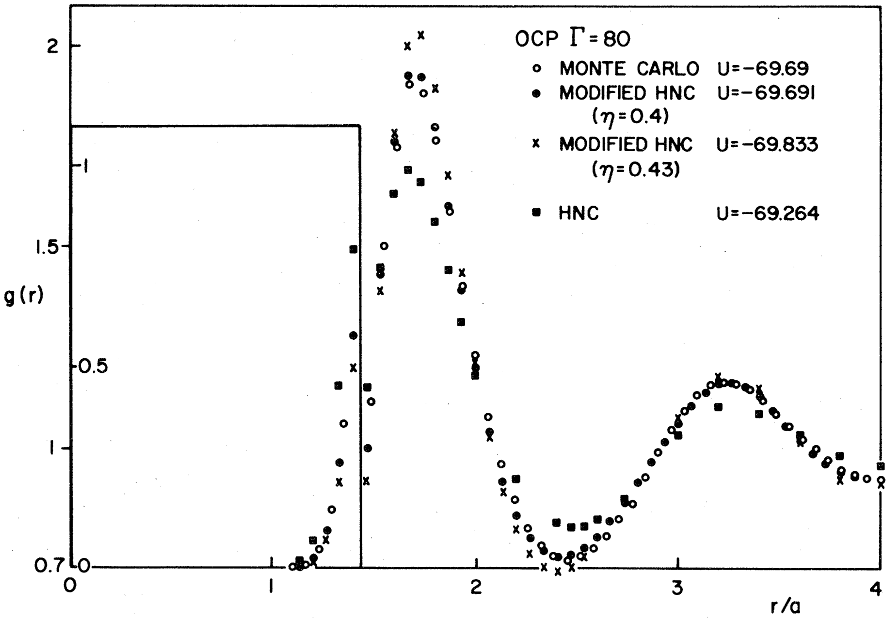

FIG. 3. OCP $g(r)$ at $\Gamma=80$. The Monte Carlo $g(r)$ has been provided by DeWitt (Ref. 42) and is based upon inversion of Hansen's (Ref. 3) $C(r)$ data. The modified HNC equations incorporate the PY bridge function. Note that with increasing η the points move monotonically in the same direction. Here U denotes the potential energy per particle in units of kT, $U=\beta E_{\rm pot}/N$.

$$H(0)=2f_0(\Gamma)-f_0(2^{5/3}\Gamma)=1.050\,99\Gamma+2.1724\Gamma^{1/4}-0.5012\ln\Gamma-2.237\quad(\Gamma>1)\,. \tag{37}$$

At large Γ this is in good agreement with the ion-sphere result[43]

$$H_{\rm ion\ sphere}(0)=(2^{5/3}-2)0.9\Gamma=1.0573\Gamma\,. \tag{38}$$

The interest in $H(0)$ for the OCP stems from its role in the calculation of the enhancement ϵ of the rate of nuclear reactions in dense ionized media via[44,45]

$$\epsilon=e^{[H(0)]}\,. \tag{39}$$

As seen in Fig. 10 our results for $H(0)$ are in good agreement with (37), indicating that the assumed linear (instead of quadratic) behavior of the bridge functions near the origin, is not as inappropriate as might be imagined. As a matter of fact, taken as a whole, our results for the OCP represent the only case where an integral equation has been solved for a dense fluid to yield not only

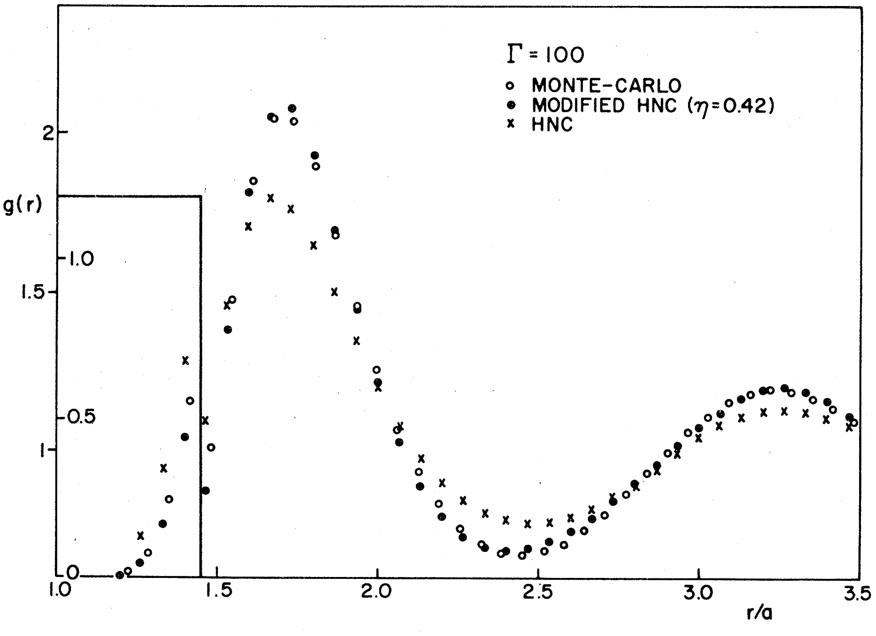

FIG. 4. OCP $g(r)$ at $\Gamma=100$. The Monte Carlo $g(r)$ has been provided by DeWitt (see caption to Fig. 3).

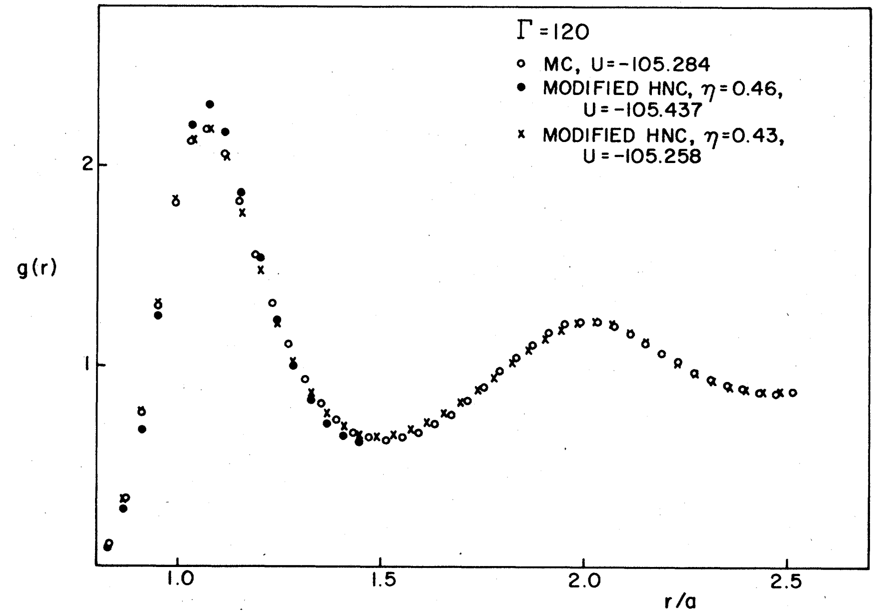

FIG. 5. OCP $g(r)$ at $\Gamma=120$. The Monte Carlo $g(r)$ is from Hansen (Ref. 31) (see caption to Fig. 3).

excellent agreement with machine calculations (or exact results) but also thermodynamic consistency with respect to $H(0)$.

(b) In the limit of small Γ pure HNC is exact. At large values of Γ, $H_{\mathrm{HNC}}(0) > H_{\mathrm{MC}}(0)$, and this situation seems to agree with (37) (or a more accurate expression appropriate for $\Gamma<40$) down to $\Gamma\sim 5$. A similar situation exists for the hard spheres, but there one has a strong indication of the validity of the inequality, $H_{\mathrm{HNC}}(0) \geq H_{\mathrm{exact}}(0)$, given that the third virial coefficient derived from the HNC $H(0)$ is twice as large as the exact one.[1] Inspecting the trends for the OCP from our results, we anticipate that the inequality $H_{\mathrm{HNC}}(0) \geq H_{\mathrm{exact}}(0)$ is generally correct for the OCP. (see Appendix B). It is, however, in slight disagreement with current predictions in the intermediate-coupling region $1<\Gamma<5$, based on the assumption that the excess free energy of mixing is negligible. The validity of the proposed inequality can be checked

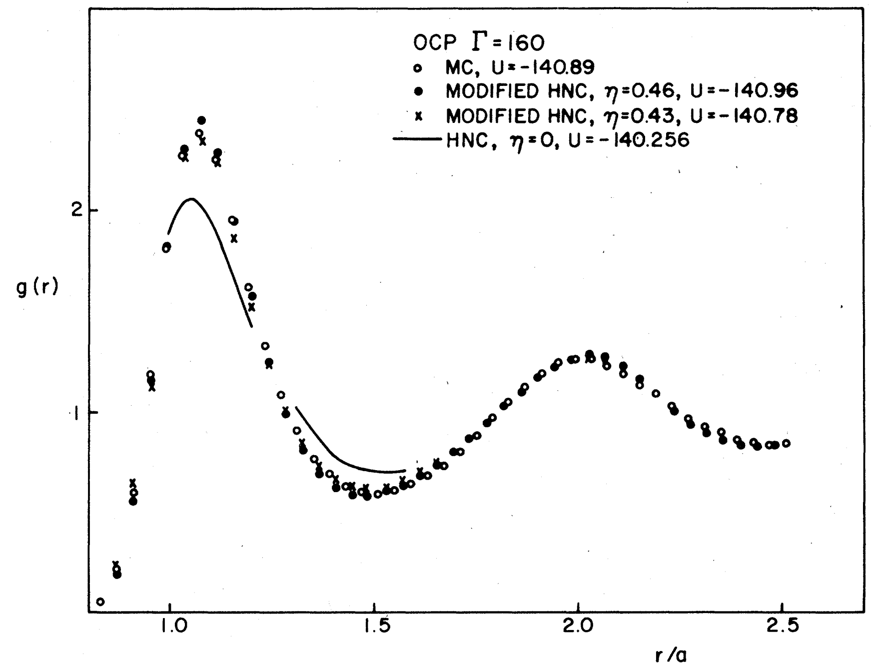

FIG. 6. OCP $g(r)$ at $\Gamma=160$ (near crystallization). The Monte Carlo $g(r)$ is from Hansen (Ref. 31) (see caption to Fig. 3).

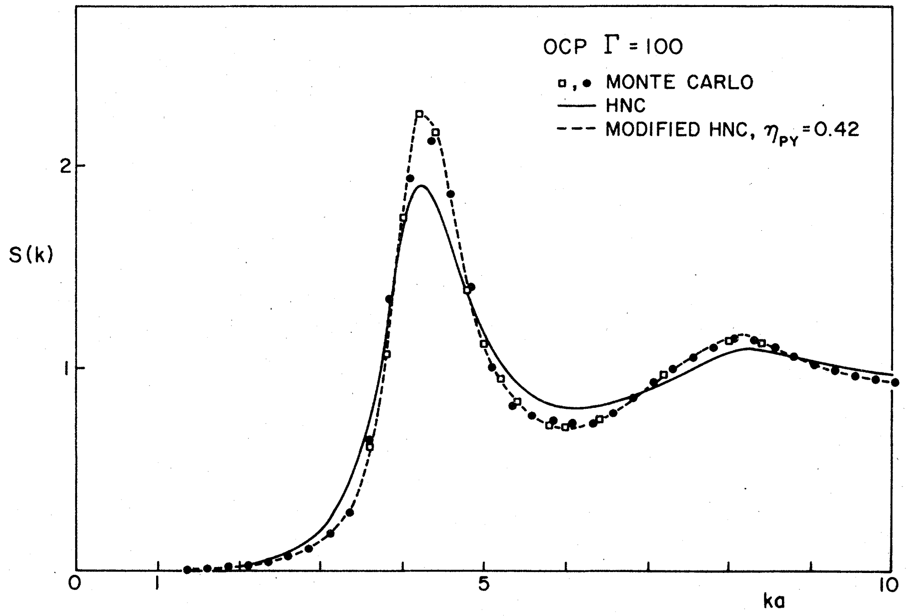

FIG. 7. OCP structure factor $S(k)$ for $\Gamma = 100$. The black dots represent the direct MC data of Hansen (Ref. 31). The squares represent the "smoothed" data, obtained by inversion of $C(r)$ (Ref. 3). The modified HNC results follow the "smooth" data.

by evaluating the small-r behavior of the bridge diagrams, or by solving the eigenvalue problem for the matrix that relates the "response" of $C(r)$ to small changes in the effective potential $u(r) - 1/\beta\, E(r)$, via the linearized operator of the modified HNC equation. This procedure is similar to the one used by Ballantine and Jones[46] for analyzing pair potentials in liquid metals from the experimental $S(k)$ data.

VIII. YUKAWA POTENTIAL

Consideration of the Yukawa potential arises for example in connection with electron screening corrections to the thermodynamic properties of the OCP, in the Thomas-Fermi high-density limit and the Debye-Hückel low-density limit. In the reduced units introduced before, the Hamiltonian for the screening problem can be cast in the form:

$$\beta H = \beta H^{(0)} - \frac{N\Gamma}{2}\alpha + \sum_{i<j}\frac{\Gamma}{r_{ij}}\left(e^{-\alpha r_{ij}} - 1\right), \qquad (40)$$

where $\beta H^{(0)}$ is the Hamiltonian for the OCP. For example, in some astro-physical problems $\Gamma \sim 50$ and $\alpha \sim 1$ correspond to the situation in Jupiter, and $\Gamma \sim 6$ and $\alpha \sim 0.25$ to white dwarf stars.

In the limit $\alpha \to 0$, we expect that the structure

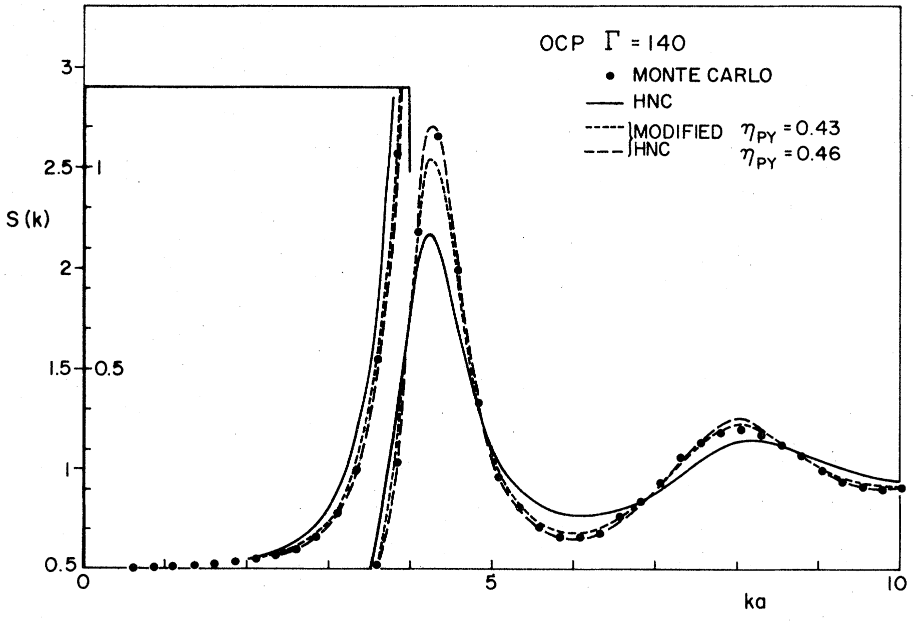

FIG. 8. OCP structure factor $S(k)$ for $\Gamma = 140$. The Monte Carlo dots are from the data of Hansen (Ref. 31).

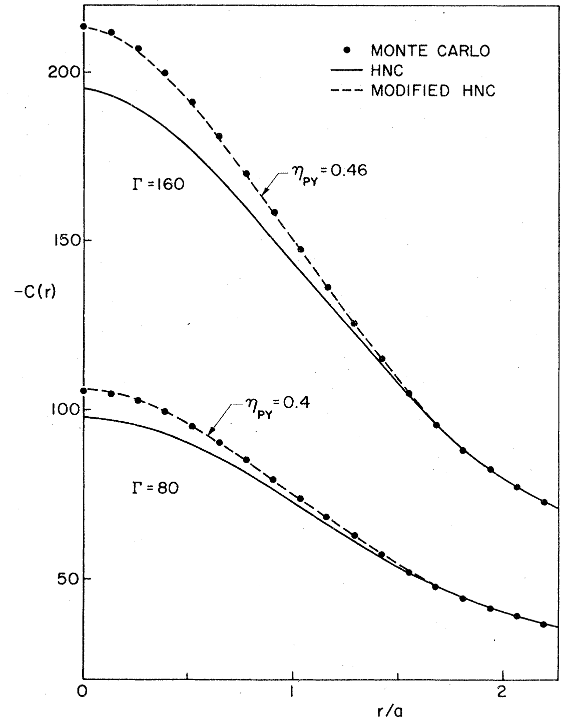

FIG. 9. OCP direct correlation function for $\Gamma = 80, 160$. The Monte Carlo $C(r)$ (see Ref. 42) has been provided by DeWitt.

and the thermodynamics of the system described by (40) to go over to those for the OCP. Consider, in turn, the Hamiltonian

$$\beta\mathcal{H} = \sum_{i<j} \frac{\Gamma}{r_{ij}} e^{-\alpha r_{ij}} - \frac{N}{2}\frac{3\Gamma}{\alpha^2}, \tag{41}$$

that approaches the OCP case in the limit $\alpha \to 0$, with the structure-independent term then cancelling the dominant (infinite in the limit $\alpha \to 0$) term in the structure-dependent part. Then the thermodynamic properties of the system governed by (41) can be expressed in terms of the correlation functions, in forms similar to those for the OCP; i.e.,

$$\frac{\beta U}{N} = \frac{3}{2}\Gamma \int_0^\infty r e^{-\alpha r}[g(r) - 1]dr, \tag{42}$$

$$\beta\left(\frac{\partial P}{\partial \rho}\right) = 1 - \frac{3}{4\pi}\int_0^\infty \left(C(r) + \frac{\Gamma}{r}e^{-\alpha r}\right) d^3r, \tag{43}$$

and

$$\beta\frac{P}{\rho} = 1 + \frac{\Gamma}{2}\int_0^\infty r e^{-\alpha r}(1 + \Gamma 2 r^2)[g(r) - 1]dr. \tag{44}$$

These expressions will yield, for small α, values close to the corresponding OCP values. If the dominant structure-independent term is not subtracted every approximate theory for the pure

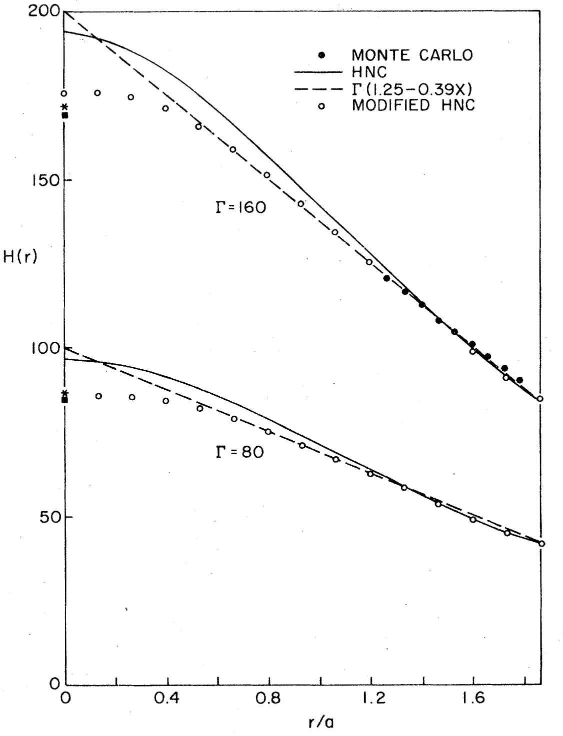

FIG. 10. OCP potential of mean force, $H(r) - \beta u(r) = \ln g(r)$, at small distances, for $\Gamma = 80, 160$. The Monte Carlo dots are taken directly from Hansen's $g(r)$ (Ref. 31). The broken line is the fit given by Eq. (35). The bridge functions used in the modified HNC equation are the same as in Fig. 9. The symbols ■ and * stand for $H(0)$ given by Eqs. (38) and (37), respectively.

Yukawa problem will yield excellent (but possibly meaningless!) agreement with the MC results via the "energy" equation.

The results of the modified HNC equation and their comparison with the MC data,[47] are summarized in Table II and Figs. 11 and 12, essentially confirming our findings for the OCP.

IX. GROUND-STATE ENERGY OF A BOSON SYSTEM

We consider the ground-state energy of a system of bosons by the variational method using a Jastrow wave function. Various integral-equation methods have been used to study the ground-state properties of boson fluids.[48] In these methods the analogy between the many-particle Jastrow wave function and the Gibbs statistical probability factor is exploited to carry over the whole machinery of classical theories to the quantum case, via a standard variational procedure.

If the variational many-particle wave function is taken to have the form

TABLE I. Results for the OCP from the modified HNC equation as function of the parameter η_{PY} and compared with the MC data.[a]

Γ	η_{PY}	$\beta U/N$	$\beta\left(\frac{\partial P}{\partial \rho}\right)_T$
3	0	−2.1026	−0.08758
	0.07	−2.1053	−0.07446
	0.08	−2.1068	−0.06591
	0.09	−2.1086	−0.05393
	0.095	−2.1097	−0.04643
	0.1	−2.1110	−0.03780
	0.1045	−2.1122	−0.02896
	0.105	−2.1124	−0.02791
	MC	−2.111 ± 0.001	−0.029 ± 0.002
20	0	−16.5377	−8.6258
	0.10	−16.5408	−8.6043
	0.15	−16.5528	−8.4917
	0.20	−16.5810	−8.1570
	0.25	−16.6341	−7.3848
	0.275	−16.6728	−6.7303
	0.30	−16.7208	−5.8149
	MC	−16.667 ± 0.01	−6.498 ± 0.007
80	0	−69.2639	−42.1949
	0.3	−69.3956	−39.8761
	0.4	−69.6908	−31.9432
	0.43	−69.8334	−26.8764
	0.46	−70.0048	−19.5534
	MC	−69.69 ± 0.03	−30.12 ± 0.02
100	0	−86.9734	−53.6
	0.3	−87.0971	−51.4
	0.4	−87.3865	−43.6
	0.42	−87.4790	−40.4899
	0.43	−87.5303	−38.6
	0.44	−87.5852	−36.4672
	0.45	−87.6438	−34.0522
	MC	−87.48 ± 0.04	−38.04 ± 0.02
120	0	−104.7131	−65.4
	0.3	−104.8304	−62.0
	0.4	−105.1142	−55.4
	0.43	−105.2580	−50.4
	0.46	−105.4366	−43.2
	MC	−105.28 ± 0.07	−45.95 ± 0.04
140	0	−122.4755	−77.1
	0.3	−122.5875	−75.1
	0.4	−122.8659	−67.3
	0.43	−123.0092	−62.2
	0.46	−123.1893	−55.0
	MC	−123.1 ± 0.1	−53.9 ± 0.05
160	0	−140.2556	−89
	0.3	−140.3631	−87
	0.4	−140.6364	−79
	0.43	−140.7789	−74
	0.46	−140.9597	−67
	0.48	−151.0	−62
	MC	−140.89 ± 0.1	−61.8 ± 0.05

[a] The MC data for the energies is taken from Hansen (Ref. 31) and the error bars are determined from remarks in that paper. The results for the inverse compressibility are obtained by writing $\beta(\partial P/\partial\rho)_T = 1 + \frac{4}{9}(\beta U/N) + \delta$, where δ, via Eq. (34), is given by a form $a - b\Gamma^{1/4}$. We compared various proposals for a and b (see Ref. 36) and took the "central" value. The error in $\beta(\partial P/\partial\rho)_T$ is smaller than in $\beta U/N$ in view of the factor $\frac{4}{9}$ and the fact that the difference between various predictions for δ is small.

$$\psi = \prod_{i<j} f(r_{ij}) = \exp\left(-\frac{1}{2}\sum_{i<j} \bar{u}(r_{ij})\right)$$

then the ground-state energy per atom is bounded above by

$$\frac{U}{N} = \frac{1}{2}\rho \int d\vec{r}\, g(r)\left(\frac{\hbar^2}{2m}\nabla^2 \bar{u}(r) + v(r)\right) \tag{45}$$

where $g(r)$ can be regarded as the classical radial distribution function for a system of particles in which $\beta = 1$, the number density is ρ, and the pair potential is $\bar{u}(r)$. Here $v(r)$ is now the assumed two-body interaction.

For the variational calculation one can parametrize either $g(r)$ [or $\bar{u}(r)$] and calculate the corresponding $\bar{u}(r)$ [or $g(r)$]. Since this normally involves a formidable many-body integral, the most accurate method that one can usually exploit is the MC or MD methods of classical statistical mechanics, i.e., parametrize $\bar{u}(r)$ and simulate the corresponding $g(r)$'s. The practical methods for handling this problem make use of the approximate integral equations for classical fluids (e.g., HNC, PY, etc.), with the additional freedom to choose the appropriate kinetic-energy functional that will be least sensitive to errors in the classical correspondence (via an approximate integral equation) between $g(r)$ and $\bar{u}(r)$. An additional advantage is provided by the fact that the classical system, with potential $\bar{u}(r)$, is usually taken to be at relatively low densities, i.e., about $\frac{1}{8}$ of the expected fluid-solid transition for that system. This is a region where in the classical problem the integral equations yield quite accurate RDF's and equations of state. Despite these advantages, however, even the best-known method (the HNC) gives a U/N that deviates (near equilibrium) by about 20% from the corresponding MC or MD results in liquid ^{4}He. As an example of the present

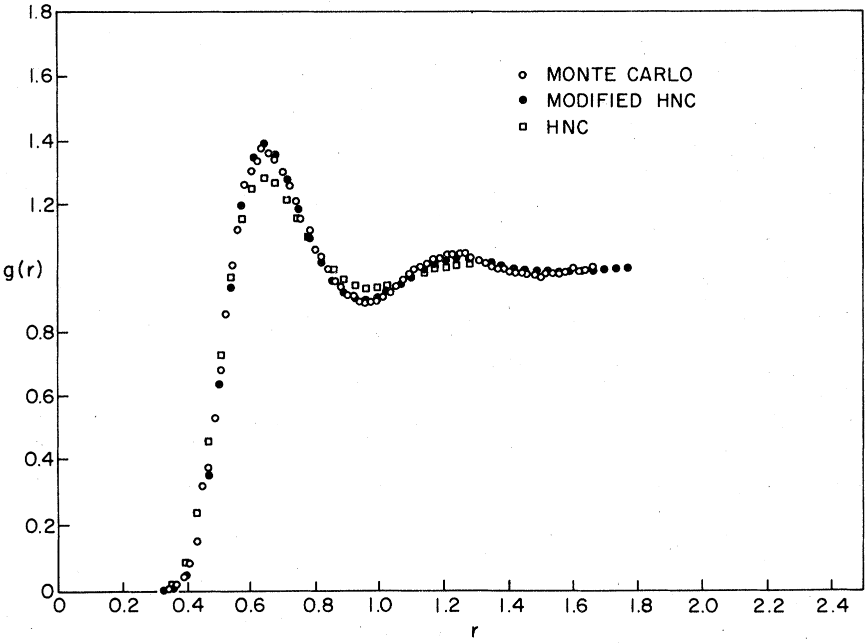

FIG. 11. Radial distribution function $g(r)$, for the Yukawa potential, at $\Gamma = 25.5885$ and $\alpha = 0.3908$ (see text). The distance r is measured in units of a/α, with a being the Wigner-Seitz radius. The Monte Carlo data is due to Gann (Ref. 47). The modified HNC equation is with the PY bridge function ($\eta_{\text{PY}} = 0.3$). From Appendix B, this case is also to be regarded as representative of the situation for the OCP at $\Gamma \sim 25$.

method consider the calculation of the ground-state energy of liquid ^{4}He. The interatomic potential is taken to be the *LJ* (12-6) form:

$$v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

with $\epsilon = 10.22$ °K, $\sigma = 2.556$Å, and the quantum parameter is thus $\hbar^2/m\epsilon\sigma^2 = 0.1815$. The Jastrow pair function can be inferred, to a certain extent, from the quantum-mechanical solution of the ^{4}He-^{4}He problem in, say, the WKB approximation, i.e.,

$$\bar{u}(r) = b^5(\sigma/r)^5, \tag{46}$$

with b being the variational parameter.

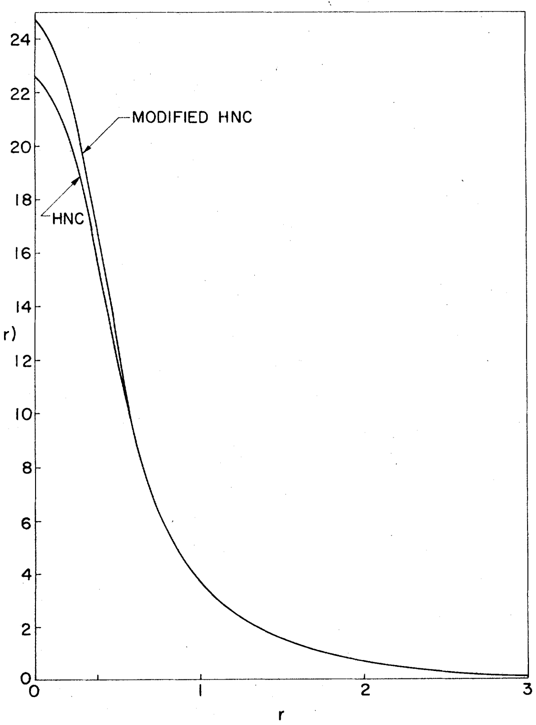

FIG. 12. Direct correlation function $C(r)$ for the Yukawa potential at $\Gamma = 25.5885$, $\alpha = 0.3908$ (see caption to Fig. 11).

Taking $b\sigma$ as the unit length, and defining a reduced density by $D = \rho(b\sigma)^3 = \rho^* b^3$, the ground-state energy per particle in °K that should be minimized with respect to b at each ρ, is given by

$$\mathcal{E} = V + T, \tag{47}$$

where the potential energy per particle, is

$$V = 40.88[b^{-12}\langle x^{-12}\rangle_{\rho,b} - b^{-6}\langle x^{-6}\rangle_{\rho,b}], \tag{48}$$

and the kinetic energy per particle, is

$$T = 9.27465 b^{-2}\langle x^{-7}\rangle_{\rho,b}. \tag{49}$$

The averages are defined by

$$\langle x^{-m}\rangle_{\rho,b} = \frac{D}{2}\int g(x;D)x^{-m}\,d\vec{x} = \langle x^{-m}\rangle_D, \tag{50}$$

where $g(x;D)$ is the RDF of the *classical system* with the pair potential given by (46). The "D" dependence in (50) implies certain scaling relations that reduce the amount of computation required in the search of the minimum energy, and is a direct consequence of the homogeneity of the form (46).

The ^{4}He equilibrium density is $\rho_0 = 0.3648/\sigma^3$ Å^{-3}. The MD results of Schiff and Verlet[49] find the minimum at $\rho = 0.9\rho_0$ with $b = 1.16$, i.e., $D = 0.5125$, and with $\mathcal{E} = -5.96$ °K/atom. This may be compared with $\mathcal{E} = -7.14$ °K/atom, the experimental

TABLE II. Results[a] for the Yukawa potential, $\Gamma = 25.5885$, $\alpha = 0.3908$.

	Monte Carlo	Modified HNC ($\eta_{\mathrm{PY}} = 0.3$)	HNC
$\beta U/N$	−17.019	−17.002	−16.828
$\beta P/\rho$	−8.037	−8.019	−7.954
$\beta\left(\frac{\partial P}{\partial \rho}\right)_T$		−10.622	−13.555

[a] Provided by Gann, Ref. 47.

result. The HNC results are extensively compared with the MD data by Miller.[50] In the course of solving the modified HNC equation for the potential given by (46) we checked the values quoted by Miller for the various $\langle x^{-m}\rangle_D$ averages, and the agreement serves again as a mutual numerical corroboration. In Table III we compare the results of the pure HNC equation with the MC results at the MD equilibrium density parameters ($D = 0.5125$, $b = 1.16$). We can see that in the near cancellation of the large numbers (V, T) an inaccuracy of about 20% builds up in the remainder. On the other hand, the same HNC procedure employed for the thermodynamics of the classical $\bar{u}(r)$ system will yield at this density an equation of state *nearly* thermodynamically consistent, and an error of less than 2% in the energy and less than 5% in the compressibility. The situation for the quantum problem can thus be summarized by the following statement: given $\bar{u}(r)$, the HNC procedure yields $g(r)$ with satisfactory overall agreement with the corresponding MD $g(r)$, but fails however in calculating the energy of the quantum system because of the need for extreme accuracy in the calculation of high moments (such as x^{-12}). The results of the *modified HNC* equation for $D = 0.5125$, $b = 1.16$ are now presented in Fig. 13 as a float diagram showing the values of the averages as functions of the hard-sphere parameter η used in the *PY bridge functions*. The value $\eta = 0$ represents the results of the pure HNC equation, and the MC results (with the appropriate error bars) are also indicated. We find that a single bridge function of the hard spheres [in this case $b_{\mathrm{PY}}(r; \eta \approx 0.2)$] will accurately yield the MD results for various quite high moments of $g(r)$. This provides a severe test on the anzatz of universality. We expect that the application of the modified HNC procedure to the ^{4}He problem should therefore yield results close to the simulation values. In fact, taking $\eta = 0.2$ the results for the energy is (in °K/atom) −5.94 (vs. −5.96 from MD). The corresponding results for the equation of state of the classical system with the $\bar{u}(r)$ potential are summarized in Table IV. In view of these results

TABLE III. Results of the HNC equation compared with MD data (Ref. 49) (see text).

	$\langle x^{-6}\rangle$	$\langle x^{-7}\rangle$	$\langle x^{-12}\rangle$	V	T	E
MD	1.874	1.677	2.002	−17.55	11.59	−5.96
HNC	1.926	1.746	2.227	−16.95	12.05	−4.90
Deviation	2.9%	4.3%	11.5%	3.4%	4.3%	17%

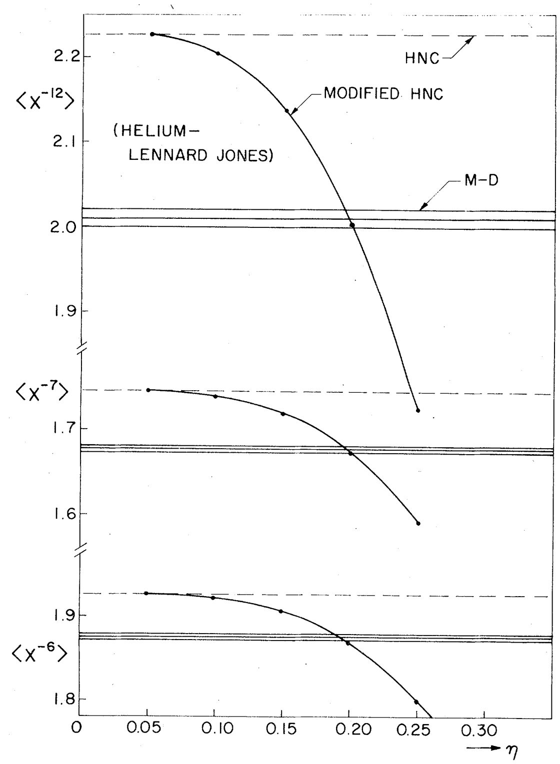

FIG. 13. Moments of the radial distribution function used in the calculation of the ground state energy of liquid ^{4}He (see text). The molecular-dynamics data (Ref. 49) is represented by a central line and two additional lines representing the error bars quoted in Ref. 49. The HNC results denoted by broken horizontal line correspond to $\eta_{\mathrm{PY}} = 0$ in the scheme of the modified HNC equation.

TABLE IV. Thermodynamics of the classical r^{-5} potential system via the HNC ($\eta = 0$) and a modified HNC ($\eta = 0.2$) equations (see text).

D	η	$\beta P/\rho$	$\beta\left(\frac{\partial P}{\partial \rho}\right)_T$
0.5	0	4.7603	9.1116
0.525	0	5.0199	9.6668
0.5125	0	4.8895	9.3877
	0.2	4.8135	9.8485

for high moments of $g(r)$ we are sure that both $\langle x^{-5}\rangle_D$ and $\beta(\partial P/\partial\rho)_T$ will be given accurately by $\eta \approx 0.2$. Further, given that the underlying classical system is one of relatively low density, there has been an effort (see Zabolitsky[48]) to actually calculate the lowest-order elementary graphs, with the hope that the HNC procedure will construct from these *all* parallel connections (as described by Van Leeuwen *et al.*[6]) to then yield improved results. We wish to emphasize that the relative merit of such a scheme should first be judged in the context of the classical problem (e.g., by thermodynamic consistency). The outcome of the HNC procedure is demonstrated by our results above, and the outcome of using the sum of a limited number of elementary graphs can be estimated readily by comparing the resulting function with the hard-sphere bridge functions, especially in the region of the first peak of the $g(r)$ considered.

X. CLASSICAL LENNARD-JONES SYSTEM

The problem of classical particles interacting via the pair potential

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$$

[the well known Lennard-Jones (LJ) 12-6 potential], is so ubiquitous that it deserves little commentary. However to demonstrate the general point made before, we present our results for the modified HNC equation for this system near the triple point ($\rho\sigma^3 = 0.85$, $kT/\epsilon = 0.72$), together with the MC and MD data.[51,52] These are given in Figs. 14 and 15. For comparison we also give the results for PY, HNC, and MSA integral-equations solutions.[1] Again we see that a *single* hard-sphere bridge function is able to reproduce *all* the equation-of-state data and $g(r)$ data to an accuracy within the simulation noise and N dependence.

XI. OSCILLATORY POTENTIALS FOR LIQUID METALS

A rather limited study of a numerically given pair potential proposed for liquid Ga (Fig. 16) shows a dramatic (and correct) effect of the inclusion of the bridge functions. In Fig. 17 we present $g(r)$ from MC[53] together with the results of the pure HNC and the modified HNC equations. With a hard-sphere bridge function the MC $g(r)$ is reproduced to high accuracy. Note the large effect on the first small peak. From a structural point of view this kind of a potential offers the opportunity of studying the possibility of the appearance of a shoulder (or perhaps another small peak) in the region of the main peak of $S(k)$. It would be interesting to see whether the inclusion of the hard-sphere bridge functions will affect the occurrence of this phenomena, thus in a way either confirming or casting doubt (depending on the case) on the predictions of approximate methods.

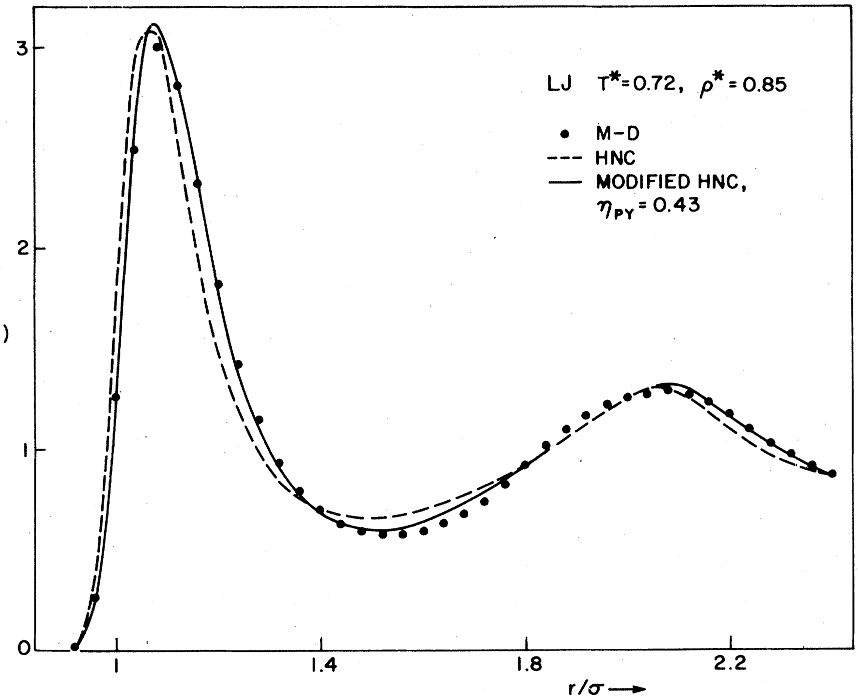

FIG. 14. Radial distribution function for the Lennard-Jones system near the triple point. The molecular dynamics dots are from Verlet (Ref. 51).

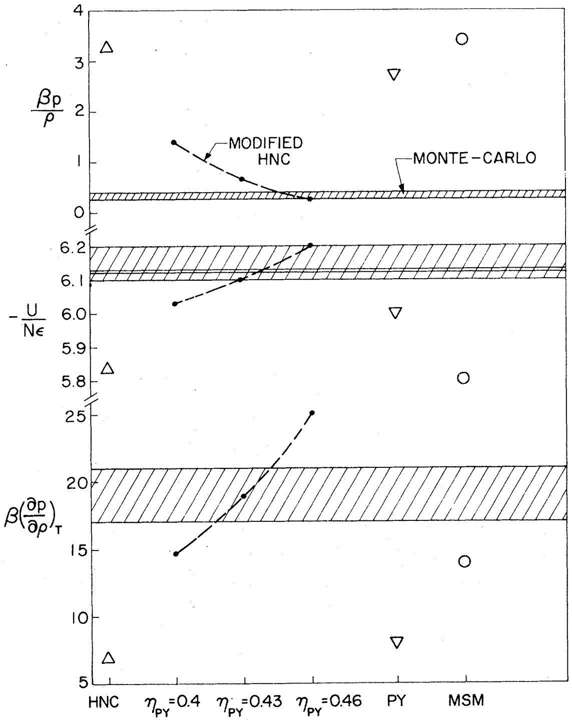

FIG. 15. Thermodynamic properties of the Lennard-Jones system near the triple point [corresponding to the $g(r)$ in Fig. 14]. By Monte Carlo we mean here both the Monte Carlo and molecular-dynamics data (Ref. 51), again giving a central value and the spread in the results or an error bar quoted. The HNC results (△) correspond to $\eta_{PY}=0$ in the modified HNC (●) scheme. Also given are the Percus-Yevick (▽) and the mean spherical (○) results.

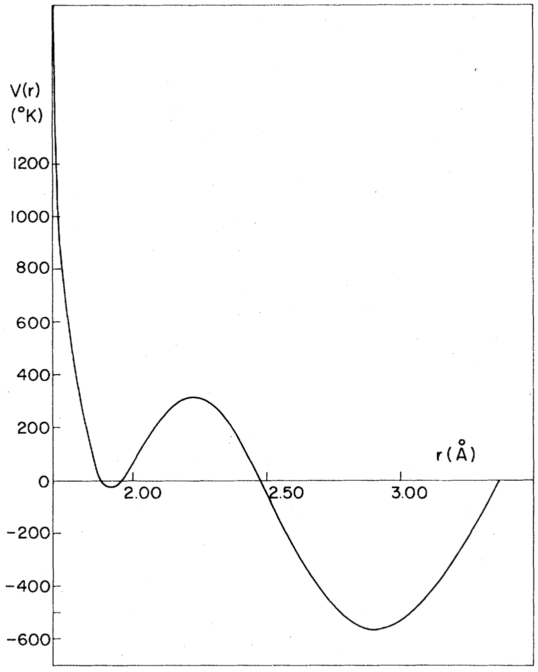

FIG. 16. Proposed effective pair potential for liquid gallium (Ref. 53) at a number density 0.0528/Å^3.

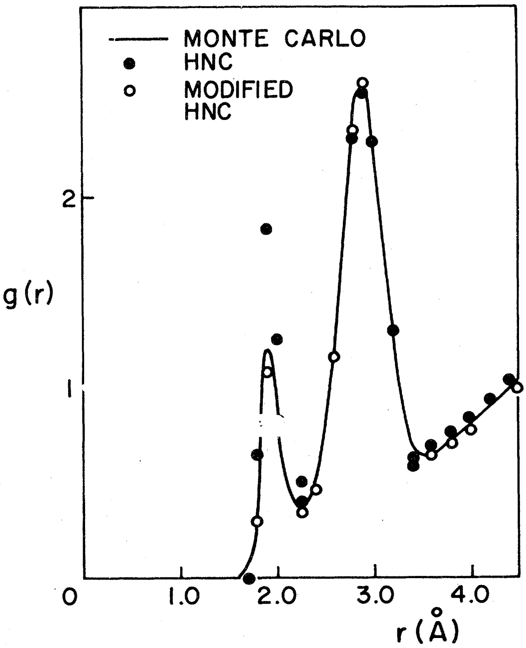

FIG. 17. Radial distribution function $g(r)$ for the potential in Fig. 16, at a temperature $T=373$ °K. The Monte Carlo data is due to Mon (Ref. 53). The modified HNC equation is with the PY hard-sphere bridge function $\eta_{PY}=0.3$.

XII. THE MEAN-SPHERICAL APPROXIMATION AND RELATED MODELS

The mean-spherical approximation (MSA), has been applied[1] almost exclusively to potentials with a hard core of diameter σ. For such potentials, the MSA is specified by

$$\begin{aligned} &g(r)=0, \quad r<\sigma \\ &C(r)+\beta u(r)=0, \quad r>\sigma . \end{aligned} \tag{51}$$

together with the OZ relation. The coefficients in the MSA density expansion cannot normally be expressed in terms of integrals involving the Mayer f function, and the MSA is not generally exact in the limit of low densities. The exception to this is the hard-sphere potential ($C(r)=0$, $r>\sigma$) for which the MSA equation *is* identical to the PY equation. Analytic solutions of (51) have been found for the following $C(r)$ tails: $C(r)=0$ (the PY equation for hard spheres[21]), $C(r)=-1/r$ (charged hard spheres[54]), and $C(r)=Ae^{-\alpha r}/r$ (Yukawa[22]). From a structural point of view, any solution of the

MSA can be viewed also as a particular parametrization of the structure of some given related system, and if there are free parameters they can be used in demanding thermodynamic consistency. Thus, the solution of the MSA with Yukawa closure serves in the parametrization of the hard-sphere potential. Considered in this way, the success or failure of the MSA to reproduce the "exact" results is an immediate outcome of the suitability (or unsuitability) of the chosen form for $C(r)$ in representing the actual situation. For potentials lacking a hard core one can still solve (51) and, provided it is remains structurally valid [i.e., $g(r)$ does not become negative], one can treat σ simply as a parameter to be determined by letting $g(r)$ go smoothly to zero.[55] However, given parametrized computer-simulation results, it is possible to apply a direct quantitative test to the MSA, via the following relation.

Start first with the OZ equation

$$h(r_{12}) = C(r_{12}) + \rho \int h(r_{13}) C(r_{23}) d\vec{r}_3 ,$$

and take the limit $r_{12} \to 0$ to obtain

$$h(0) = C(0) + \rho \int h(r) C(r) d\vec{r} .$$

With $h(0) = -1$ this takes the form

$$C(0) + \left(1 - \rho \int C(r) d\vec{r}\right) = -\rho \int C(r) g(r) d\vec{r} . \qquad (52)$$

Using the standard relations for internal energy and compressibility, we obtain

$$\frac{\beta U}{N} = \frac{1}{2}\left[C(0) + \beta\left(\frac{\partial P}{\partial \rho}\right)_T\right] + \frac{1}{2}\rho \int [C(r) + \beta u(r)] g(r) d\vec{r} \qquad (53)$$

which is exact.

Now define a generalized MSA (GMSA) [compare with (51)] by the requirement

$$\int [C(r) + \beta u(r)] g(r) d\vec{r} = 0 , \qquad (54)$$

i.e.,

$$C_{\mathrm{GMSA}}(0) = 2\left(\frac{\beta U}{N}\right) - \beta\left(\frac{\partial P}{\partial \rho}\right)_T . \qquad (55)$$

The ordinary MSA (i.e., PY for hard spheres), the results for charged hard spheres, together with results of Gillan[55] for point charges, are all special cases of (54). The results for hard-spheres, point-charges, square well and LJ systems, when compared with the corresponding results for HNC and PY, seem to indicate that the MSA evidently combines the virtues of both PY and HNC theories.[1] In view of the rather accurate parametrization of the simulation data achieved with the inclusion of the hard-sphere bridge functions, we can check the validity of (55) by comparing it with (53). For the OCP, where HNC gives similar results to MSA we find that indeed both methods conform to (55) with high accuracy, comparable in fact to the parametrized results. In Table V we give the values of $C(0)$ as given from (53) and (55) for the "exact" and HNC results while the MSA results of Gillan obey (54) exactly. For the LJ system near the triple point (Sec. X), the HNC gives $C(0) = -28$ while (54) yields -23.3. The modified HNC yields $C(0) = -37$ and (54) gives -36. Thus imposing (54) in a judicious form significantly improves upon the HNC results for the LJ system. We expect (54) to be a rather good approximation for any potential. In view of the discussion presented in Sec. IV, the most important improvement of the usual MSA is effected on $C(r)$ for r in the region of the main peak of $g(r)$. Thus, it is not the PY approximation that underlines its success for the hard spheres, but rather the mean spherical assumption itself that embodies a rather accurate statement that is apparently valid for any potential.

TABLE V. $C(0)$ for the OCP from the HNC equation, and the modified HNC equation.

	Modified HNC			HNC	
Γ	Eq. (53)	Eq. (55)	η	Eq. (53)	Eq. (55)
2	−3.14	−3.04	0.10	−3.10	−2.96
100	−133.4	−134.47		−122	−120

XIII. CONCLUSION

We have demonstrated that a large body of computer-simulation data compiled for a variety of quite disparate interparticle potentials can be fitted rather accurately by a single one-parameter family of bridge functions. To within the accuracy of present-day simulation methods [currently about 2% for $g(r)$ and less than 1% for thermodynamics] we are led to the conclusion that the bridge-function families of all potentials can be well represented by the family appropriate to any one such potential. It is an interesting happenstance that the exact analytic solution of the PY equation for hard spheres provides the bridge function family that supplements, with such strikingly accurate results, the HNC equation to yield the most useful modified form. Though it will ultimately be rewarding to understand why this is so for pure systems, it is clear that from the practical standpoint the same approach can be used for mixtures by using the PY bridge functions for multicomponent hard-sphere system[56] in a correspondingly modified HNC equation.

It is important to emphasize once again that the bridge function enters the HNC schemes as an effective potential and this fact has a consequence which is not shared by other standard approximations. This is that any solution of the HNC equation for a given potential $\beta\mu_0(r)$ must yield the *exact* structure for the potential $\beta\mu_1(r)=\beta\mu_0(r)-b_1(r)$, albeit that the potential $u_1(r)$ might remain formally unknown. It follows that in terms of the iterative procedure normally performed on the class of integro-differential equations (of which hypernetted chain is an example), the HNC scheme possesses an inherent stability property which is not guaranteed, for instance, in PY since the latter by its very form does not admit of an identification of effective potentials. Experience with the HNC equation has indeed shown it to be numerically very stable. Accordingly, if one is in possession of a "pure" HNC solution for some physical potential, there is no subsequent difficulty in introducing the bridge function. For this reason we may conclude that the scheme introduced above provides a sound basis for the fitting of simulation data if for no other reason than the later determination of structure factors.[57]

By extending the analysis presented above we believe that it may be possible to place the simple parameterization scheme offered here on a rigorous footing to the extent that if applied on a routine basis in conjunction with every MC or MD simulation, correspondingly "rigorous" error statements can be made about the statement of universality. One might then hope that at least in a restricted sense the notion of universality will be useful in summarizing both the structure and the thermodynamics of classical fluids. Pending this analysis however, we may nevertheless conclude from the results given above that the modified HNC equation gives a new and rather powerful approach in the theory of fluids. Even in its simplest form (with the PY bridge functions and constrained by the requirement of thermodynamic consistency), it is apparently applicable to all physically interesting potentials.

ACKNOWLEDGMENTS

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APPENDIX A

(On using the Ewald method to check the Monte Carlo calculation for the Coulomb potential.)

The Hamiltonian for the one-component plasma is

$$\beta H^{(0)}=\sum_{i<j}\frac{\Gamma}{r_{ij}}-\tfrac{1}{2}\beta\rho\tilde{u}(0)\,, \tag{A1}$$

where

$$\beta u^{(0)}(r)=\Gamma/r \text{ and } \beta\rho\tilde{u}^{(0)}(k)=3\Gamma/k^2\,.$$

Consider the Hamiltonian $H^{(\alpha)}$ for a system with a potential that has the *same* short-range behavior as the Coulomb potential, but differs at longer range in the sense that the energy is demonstrably extensive. Thus

$$\beta H^{(\alpha)}=\sum_{i<j}\beta u^{(\alpha)}(r_{ij})\,, \tag{A2}$$

where α is an inverse length parameter so chosen that

$$\lim_{\alpha\to 0}\beta u^{(\alpha)}(r_{ij})\equiv\beta u^{(0)}(r_{ij})=\Gamma/r_{ij}\,. \tag{A3}$$

For specific examples we may take

(a) Yukawa:

$$\beta u^{(\alpha)}(r)=\frac{\Gamma}{r}\,e^{-\alpha r}\,,\quad \beta\rho\tilde{u}^{(\alpha)}(k)=\frac{3\Gamma}{k^2+\alpha^2}\,, \tag{A4}$$

where

$$\lim_{r\to 0}(\Gamma/r)(e^{-\alpha r}-1)=-\Gamma\alpha\,.$$

(b) The complementary error function (erfc) potential:

$$\beta u^{(\alpha)}(r)=(\Gamma/r)\,\mathrm{erfc}(\alpha r)\,,$$
$$\beta\rho\tilde{u}^{(\alpha)}(k)=(3\Gamma/k^2)(1-e^{-k^2/4\alpha^2})\,, \tag{A5}$$

where

$$\lim_{r\to 0}-(\Gamma/r)[1-\mathrm{erfc}(\alpha r)]=-2\Gamma\alpha/\sqrt{\pi}\,.$$

We recall that

$$\mathrm{erf}(z)=1-\mathrm{erfc}(z)=\frac{2}{\sqrt{\pi}_0}\int_0^z e^{-f^2}\,df$$
$$=\frac{2}{\sqrt{\pi}}(z-\tfrac{1}{3}z^3+\cdots)\,,\quad (z\ll 1)\,.$$

Now the free energies of the systems described by interactions (A1) and (A2) are related by the following *exact* relation[58]:

$$\begin{aligned}\frac{\beta F^{(\alpha)}}{N}-\frac{\beta F^{(0)}}{N}&=\tfrac{1}{2}\beta\rho\tilde{u}^{(0)}(0)+\tfrac{1}{2}\rho\int_0^1 d\lambda\int[\beta u^{(\alpha)}(r)-\beta u^{(0)}(r)]g_\lambda(r)d^3r\\&=\tfrac{1}{2}\beta\rho\tilde{u}^{(\alpha)}(0)+\tfrac{1}{2}\rho\int_0^1 d\lambda\int[\beta u^{(\alpha)}(r)-\beta u^{(0)}(r)][g_\lambda(r)-1]d^3r\\&=\tfrac{1}{2}\beta\rho\tilde{u}^{(\alpha)}(0)+\frac{1}{2(2\pi)^3}\int_0^1 d\lambda[\beta\tilde{u}^{(\alpha)}(k)-\beta\tilde{u}^{(0)}(k)][S_\lambda(k)-1]d^3k\,.\end{aligned}$$

In other words

$$\frac{\beta F^{(0)}}{N}=\frac{\beta F^{(\alpha)}}{N}-\tfrac{1}{2}\beta\rho\tilde{u}^{(\alpha)}(0)+\tfrac{1}{2}\lim_{r\to0}[\beta u^{(\alpha)}(r)-\beta u^{(0)}(r)]-\frac{1}{2(2\pi)^3}\int d\lambda\int[\rho u^{(\alpha)}(k)-\beta u^{(0)}(k)]S_\lambda(k)d^3k\,, \tag{A6}$$

where $g_\lambda(r)$ and $S_\lambda(k)$ are, respectively, the RDF and structure factor for the system described by the potential

$$u^{(0)}(r)+\lambda[u^{(\alpha)}(r)-u^{(0)}(r)]\,.$$

For the two specific cases considered above,

$$\frac{\beta F^{(0)}}{N}=\frac{\beta F^{(\alpha)}}{N}-\frac{3\Gamma}{2\alpha^2}-\frac{\Gamma}{2}\alpha+\frac{\Gamma}{\pi}\int_0^1 d\lambda\int S_\lambda(k)\frac{\alpha^2}{\alpha^2+k^2}dk\ \text{(Yukawa)}, \tag{A7}$$

$$\frac{\beta F^{(0)}}{N}=\frac{\beta F^{(\alpha)}}{N}-\frac{3\Gamma}{2(2\alpha)^2}-\frac{\Gamma}{2\sqrt{\pi}}(2\alpha)+\frac{\Gamma}{\pi}\int_0^1 d\lambda\int S_\lambda(k)e^{-(k/2\alpha)^2}dk\ \text{(erfc)}. \tag{A8}$$

As an example of the use of these results consider the static-lattice limit, at which

$$S_\lambda(\vec{k})=\rho\sum_{\vec{g}\neq0}\delta(\vec{k}-\vec{g})\,,\quad \lim_{V\to\infty}\frac{1}{V}\sum_{\vec{k}}=\frac{1}{(2\pi)^3}\int d\vec{k}\,,$$

where $\vec{g}$ is a reciprocal-lattice vector. Then the two expressions take very familiar forms, namely,

$$\frac{\beta U^{(0)}}{N}=\frac{\beta U^{(\alpha)}}{N}-\frac{3\Gamma}{2\alpha^2}-\frac{\Gamma}{2}\alpha+\frac{3\Gamma}{2}\sum_{\vec{g}\neq0}\frac{\alpha^2}{g^2(\alpha^2+g^2)}\ \text{(Yukawa)} \tag{A9}$$

and

$$\frac{\beta U^{(0)}}{N}=\frac{\beta U^{(\alpha)}}{N}-\frac{3\Gamma}{2(2\alpha)^2}-\frac{\Gamma}{2\sqrt{\pi}}(2\alpha)+\frac{3\Gamma}{2}\sum_{\vec{g}\neq0}\frac{e^{-(g/2\alpha)^2}}{g^2}\ \text{(erfc)}, \tag{A10}$$

where $\vec{g}$ is given in units $(\gamma 6\pi^2)^{1/3}$ ($\gamma=\sqrt{2}$ for a fcc reciprocal lattice). The first order in α value of the integral in (A7) was calculated by Hansen[59] to give (via $\beta U/N=\Gamma(\partial/\partial\Gamma)(\beta F/N)$) the relations

$$\frac{\beta U^{(0)}}{N}=\frac{\beta U^{(\alpha)}}{N}-\frac{3\Gamma}{2\alpha^2}-\frac{\Gamma}{2}\alpha+\frac{\Gamma^{1/2}}{4\sqrt{3}}\alpha^2 \tag{A11}$$

in the *Debye-Hückel limit,*

$$\frac{\beta U^{(0)}}{N}=\frac{\beta U^{(\alpha)}}{N}-\frac{3\Gamma}{2\alpha^2}-\frac{\Gamma}{2}\alpha+\frac{0.326}{\pi}\Gamma\alpha^2 \tag{A12}$$

in the static-lattice limit, and an interpolation formula for the α^2 term based on the OCP results for $S(k)$ has also been derived[59] via

$$\left[\frac{\Gamma}{\pi}I_1(\Gamma)+\frac{\Gamma^2}{\pi}I_1'(\Gamma)\right]\alpha^2 \tag{A13}$$

where

$$I_1(\Gamma)=\Gamma^{-1/2}[0.326\,0702(4.592\,037+\Gamma)^{1/2}+2.413\,892(134.471\,01+\Gamma)^{-1/2}]\,.$$

In the particular case considered in Sec. VIII ($\Gamma=25.5885$, $\alpha=0.3908$), we get via the very accurate deWitt formula for the OCP, $\beta U^{(0)}/N=-21.557$ which is a result that should be very close to the MC data. From (A7) and (A13) we get the following expansion ($\beta U^{(\alpha)}/N$ is from MC calculations for the Yukawa[47]):

$$\begin{aligned}\beta U^{(0)}/N&=234.308-251.3100-5.0000+0.47\\&=-21.53\,.\end{aligned}$$

We see that for this small value of α, the series is rapidly convergent. Note however that the term quadratic in α is by no means *small* (2.5% of $\beta U^{(0)}/N$).

In the "erfc" case the α^2 behavior is replaced by a fast exponential decay, and in view of the success of the Ewald summation method for lattice sums (A10) we can anticipate similar behavior for the dense fluid. The integral in (A8) will yield a negligible contribution to the potential energy when its Γ dependence is very weak. For small k and small α,

$$S_0(k)=\frac{k^2}{3\Gamma+k^2[1-(3/4\pi)\int [C(r)+\Gamma/r]dr]} \tag{A14}$$

and

$$S_1(k)=\frac{(2\alpha)^2}{3\Gamma+(2\alpha)^2\{1-(3/4\pi)\int [C(r)+(\Gamma/r)\,\mathrm{erfc}(dr)]dr\}} \tag{A15}$$

and we can expect that the integrals will take similar values, i.e.,

$$1-\frac{3}{4\pi}\int [C(r)+\beta u^{(\alpha)}(r)]d\vec{r}\approx\beta\left(\frac{\partial P^{(0)}}{\partial\rho}\right)_T\approx\frac{4}{10}\Gamma$$

for the dense fluid ($\Gamma\gg 1$).

Thus the integral

$$\frac{\Gamma}{\pi}\int S_\lambda(k)e^{-(k/2\alpha)^2}dk$$

will have negligible Γ dependence when

$$(2\alpha)^2\ll 3\Gamma/\beta\left(\frac{\partial P^{(0)}}{\partial\rho}\right)\approx\frac{3\Gamma}{\frac{4}{10}\Gamma}$$

or $\alpha\ll\sqrt{2}$. In the dense fluid region the first $S(k)$ peak is around $k\sim 5$. We can now calculate the Γ dependence by expanding (see A14)

$$\frac{\Gamma}{\pi}\int S_\lambda(k)e^{-(k/2\alpha)^2}dk$$
$$\approx\frac{\Gamma}{\pi}2\alpha\,\mathrm{erfc}\left(\frac{k_1}{2\alpha}\right)+\frac{1}{3\pi}\int_0^{k_1}k^2e^{-(k/2\alpha)^2}dk$$
$$-\frac{\Gamma}{\pi}\frac{\beta(\partial P^{(0)}/\partial\rho)}{(3\Gamma)^2}\int_0^{k_1}k^4e^{-(k/2\alpha)^2}dk\,,\quad k_1\approx 3\,.$$

The first term, for $\alpha\approx\frac{1}{2}$ is negligible (well within the MC noise for the energy for instance), the second is Γ independent, and the third has a slight Γ dependence arising from $\beta(\partial P^{(0)}/\partial\rho)_T$. Gathering the terms together, we obtain (for the Γ-dependent term)

$$\frac{\Gamma}{\pi}\int S_\lambda(k)e^{-(2/2\alpha)^2}dk$$
$$\approx\frac{\Gamma}{\pi}2\alpha\,\mathrm{erfc}\left(\frac{k_1}{2\alpha}\right)-\frac{\beta(\partial P^{(0)})}{3\pi\Gamma}\frac{d^2}{d^2[1/(2\alpha)^2]}$$
$$\times\left[\mathrm{erf}\left(\frac{k_1}{2\alpha}\right)2\alpha\right],\quad k_1\approx 3\,.$$

Thus it can be easily established that in the dense fluid region, roughly defined by

$$(\beta U^{(0)}/N)/(\beta U^{(0)}/N)_{\text{static lattice}}\approx 1\,,$$

or, say, $\Gamma>10$, the following is an overestimate (much closer than a factor of 2) for the integral:

$$\frac{\Gamma}{\pi}\int S_\lambda(k)e^{-(k^2/2\alpha)^2}dk\approx\frac{\Gamma}{\pi}(2\alpha)\,\mathrm{erfc}\left(\frac{k_1}{2\alpha}\right),\quad k_1\gtrsim 3$$
$$\approx\frac{\Gamma}{\pi\sqrt{\pi}}(2\alpha)^2e^{-(k_1/2\alpha)^2},\quad k_1\gtrsim 3\,. \tag{A16}$$

To state it simply, the dominant Γ dependence comes from the asymptotic behavior of the integral in (A8) (say, $k>k_0\approx 3-4$). In that region an estimate of the result to within a factor of 2 is given by $S(k)=1$. We emphasize that with $k_1=3$, (A16) represents a substantial overestimation of the true result as can be seen from a close inspection of the possible values that $S(k)$ can obtain in the small-k region. Even then, with the feasible choice α of $1/1.7$, the value of the remainder (integral term) is quite negligible, i.e., much smaller than the inherent MC noise for the energy. This can be demonstrated via the results for $\alpha=1/1.5$ (which were obtained by Ceperley and Chester for checking the MC results for the OCP via a different approach[32]) that are presented in Table VI. We see that even for this case the deviations are within the combined statistical error.

In view of the analysis above we expect that for $\alpha=1/1.7$ (for which with $N=256$ one can still treat the tail by conventional methods) both $g(r)$ and the energy via [(A8) *without* the integral term] constitute an excellent estimate of the situation for the OCP, thus providing a *direct* and rather severe test of the Ewald method employed for the latter.

TABLE VI. Direct check of the Monte Carlo results for the OCP (see text).

Γ	$\frac{\beta U^{(\alpha)}}{N}$ Ref. 32	$\frac{\beta U^{(\alpha)}}{N}-\frac{3\Gamma}{2(2\alpha)^2}-\frac{\Gamma}{2\sqrt{\pi}}(2\alpha)$	$\frac{\beta U^{(0)}}{N}$ Ref. 31	Deviation
50	17.853	−43.141	−43.093	0.048
75	26.17	−65.320	−65.255	0.065
120	41.01	−105.385	−105.284	0.101

APPENDIX B

[Diagrammatic analysis of the HNC equation for the OCP; we consider the low-density, high-temperature ($\lambda \ll 1$) limit.]

Because of the long-range nature of the Coulomb potential

$$\beta u(r) = \lambda / r$$

[where $\lambda = 3\Gamma^{3/2}$ is the ratio of the Landau length e^2/k_BT and the Debye length $(4\pi n e^2/kT)^{-1/2}$, and r in units of the Debye length] the expansion presented in Sec. II is not adequate. Many of the cluster integrals actually diverge at large r. The escape from this difficulty is to expand the Mayer f function in a power series in $\beta u(r)$, performing the summation over chains of "u" bonds first. This results in the following expansion for the potential of mean force[60]:

$H(r) - \beta u(r) = -\beta u^D(r)$

+ {the sum of all simple irreducible 1-2 graphs with
k field points in which (a) there can be k_{ij} lines between
the points (ij) represented by the bond $[-\beta u^D(r_{ij})]^{k_{ij}}/k_{ij}!$,
and (b) every field point is of degree greater than 2}. (B1)

Note that $\beta u^D(r) = (\lambda/r)e^{-r}$, and the "degree of a point" is equal to the number of lines terminating at this point.

Now, the sum of all graphs that are identical (except that $k_{ij} \geq 2$) is equivalent to a single "prototype" graph having $k_{ij} = 2$. This two-line bond is equal to

$$\sum_{k_{ij}=2}^{\infty} \frac{[-\beta u_{ij}^D]^{k_{ij}}}{k_{ij}!} = \exp[-\beta u_{ij}^D] - 1 + \beta u_{ij}^D$$

and the procedure eliminates the remaining short-range divergences in the graphs in (B1). This resummation leads to the following expansion in "Meeron" graphs[60]:

$H(r) - \beta u(r) = -\beta u^D(r)$

+ [the sum of all simple irreducible 1-2 graphs, in which the
bonds (lines) between the points are of two types: (a) a Debye
bond (line) representing the factor $-\beta u_{ij}^D$, and (b) a Meeron
bond (line) representing the factor $\exp(-\beta u_{ij}^D) - 1 + \beta u_{ij}^D$, such
that only one line may connect any two points, and there may be
no points where only two Debye lines join]. (B2)

All the terms in this "prototype" cluster expansion are well behaved. This expansion is not ordered in powers of λ. The *lowest order* in λ to which a given graph contributes is given, however, by twice the number of Meeron lines, plus the number of Debye lines, minus the number of field points. In the Debye-Hückel limit, i.e., fixed r and vanishing λ, the $-\beta u^D(r)$ is the leading term in (B2). Observe that the graphical expansion of the Debye line in terms of the βu line is just a special case of the Ornstein-Zernike relation, i.e.,

$\tilde{A}(k) = \dfrac{\rho(\tilde{B}(k))^2}{1 - \rho B(k)} \Rightarrow$ [$A(r)$ is the sum of all possible nodal diagrams
obtained from diagrams in $B(r)$ by connecting in series].

The diagrammatic expansion of the HNC approximation for $H(r)$ will contain all those Meeron graphs that do not contain *anywhere* the elementary graph topology, i.e., every graph will be a nodal graph built by connecting in series subgraphs that are themselves built by parallel connections of nodal graphs. No subgraph can then be an elementary graph. Clearly, all these diagrams can be built by an iterative procedure.

Let us now write the HNC equation for the Coulomb potential in the following form:

(i) $C_0(r) \equiv C(r) + \beta u(r)$

$$= e^{-[H(r) - \beta u(r)]} - [H(r) - \beta u(r)] - 1 .$$

This can be shown to be equal to[6,12]

[all possible parallel connections of graphs
in $H(r) - \beta u(r) \equiv H_0(r)$] (B3a)

(ii) $\tilde{H}(k) = \rho[\tilde{C}(k)]^2 / [1 - \rho\tilde{C}(k)]$.

Here $H(r)$ is

[the sum of all possible nodal diagrams obtained from diagrams in $C(r)$ by series connection].

(B3b)

It is not difficult to see how the iterative procedure implied by (B3) actually starts with a Coulomb line, builds both the Debye and Meeron lines in the first iteration, and then continues to construct all eligible (nonelementary) "prototype" graphs in the expansion (B2), *and no other graphs whatsoever.* Thus, if the diagrammatic expansion converges, this procedure actually *proves* that the HNC equation contains the Debye-Hückel limit (i.e., HNC obeys the Stillinger-Lovett conditions and $C(r) \to -\beta u(r)$ as $r \to \infty$). With this rigorous result we can repeat the analysis of Ng[27] and prove that $C_0(r)$, $H_0(r)$, and $h(r)$ fall of exponentially as $r \to \infty$, and their Fourier transforms can therefore be expanded in terms of even powers of k at $k = 0$.

Let us actually follow the first few iterations:

$$H^{(1)}(r) = \lambda/x, \quad H_0^{(1)}(r) = 0\,;$$

$$C^{(1)}(r) = -\lambda/x, \quad C_0^{(1)}(r) = 0\,;$$

$$H^{(2)}(r) = (\lambda/x) - (\lambda/x)e^{-x}, \quad H_0^{(2)}(r) = -(\lambda/x)e^{-x}\,;$$

$$C_0^{(2)}(r) = \exp[-(\lambda/x)e^{-x}] + (\lambda/x)e^{-x} - 1\,;$$

and so on. We then find

$$\tilde{H}^{(3)}(k) = \frac{\frac{1}{4\pi\lambda}\left(\tilde{C}_0^{(2)}(k) - \frac{4\pi\lambda}{k^2}\right)^2}{\left[1 - \frac{1}{4\pi\lambda}\left(\tilde{C}_0^{(2)}(k) - \frac{4\pi\lambda}{k^2}\right)\right]} = \frac{1}{4\pi\lambda}\left(\tilde{C}_0^{(2)}(k) - \frac{4\pi\lambda}{k^2}\right)S^{(2)}(k)\,. \tag{B4}$$

Recall the low-λ expansion of the internal energy as given by Abe[61] and extended by Cohen and Murphy[62]:

$$U/NkT = -\tfrac{1}{2}\lambda - \tfrac{1}{4}\lambda^2 \ln\lambda - \lambda^2(\tfrac{1}{2}\gamma + \tfrac{1}{4}\ln^3 - \tfrac{1}{3}) - \tfrac{3}{8}\lambda^2 \ln\lambda + (0.2528 \pm 0.0004)\lambda^3 + \cdots\,,$$

where $\gamma = 0.57722...$ is the Euler constant.

Recall[62] also that the first "non-HNC" graphs contribute only to the λ^3 term, but constitute only a small part of it. Moreover, the contribution of the lowest-order elementary graphs to $H(0)$ is negative, thus implying in a sense, similar behavior to the hard-sphere case where the HNC values of $H(0)$ bound from above the exact values.

The expression (B4) and in particular $\tilde{C}^{(2)}(k)$ has seen the object of extensive studies[17,63] in the effort to establish the asymptotic behavior of $H_0(r)$, via the behavior of the zero, k_1, closest to the real k axis of the denominator in (B4). It has been established[62,63] that in the $\lambda \ll 1$ limit

$$H_0(r) \xrightarrow[r\to\infty]{} -C_1\lambda_e - C_2 x/x\,,$$

where

$$C_1 = 1 + (\tfrac{3}{8}\ln 3 + \tfrac{1}{6})\lambda + \cdots$$

and

$$C_2 = 1 + (\tfrac{1}{8}\ln 3)\lambda + \cdots\,.$$

In particular, there has been an effort[17,63] to determine the value λ_c (or Γ_c) for which the real part of k_c the lowest zero of the denominator in (B4), just takes on a nonzero value, thus marking the onset of oscillations in the asymptotic regime (i.e., k_c is the value of k_1 at the onset of oscillation). It has been found[17,63] that $k_c \cong 1.5i$ and $\lambda_c = 4.25$ ($\Gamma_c \cong 1.8$). For these values $g(r)$ takes its maximum value of about 1.04 at $r \sim 1$, clearly in disagreement with the Monte-Carlo results. Recall, however, that the approximations (B5a) is a very good approximation for the MC $g(r)$ up to $\lambda \sim 1$, better, in fact, than the exact diagrammatic expansion to order $\lambda^4 \ln\lambda$ in $H(r)$.[62] This demonstrates both the validity of the HNC approximation at low λ *and* the importance of summation of diagrams to infinity.

We have used out low-λ solutions of the HNC equation to investigate the coefficients of the moment expansion of the denominator of $S(k)$,

$$\frac{k^2}{S(k)} = 3\Gamma + \left[\beta\left(\frac{\partial P}{\partial \rho}\right)_T\right]k^2 + a_1 k^4 + a_2 k^6 + \cdots\,, \tag{B5}$$

with

$$a_1 = \tfrac{1}{2}\int_0^\infty r^4 C_0(r)\,dr\,,$$

$$a_2 = -\frac{1}{40}\int_0^\infty r^6 C_0(r)\,dr\,,$$

etc. Now given the approximation (B4), i.e., with $S^{(2)}(k)$, one has

$$\beta\left(\frac{\partial P}{\partial \rho}\right)_T = 1 - \lambda A(\lambda) \tag{B6}$$

and

$$a_1 = \lambda B(\lambda)/3\Gamma,$$

where we use the notations of Ref. 17. Both $A(\lambda)$ and $B(\lambda)$ are given in terms of an infinite power series involving powers of λ and lnλ. For the solutions of the HNC equation we found that the series in (B5) is very rapidly convergent, even for relatively large k. For example, at $\Gamma = 1$ ($\lambda = \sqrt{3}$, $k_{\mathrm{Debye}} = \sqrt{3}$), the expansion up to k^4 gives $k^2/S(k)$ to within 1% even for $k = 2.5$ (i.e., twice the expected $|k_1|$). Keeping terms up to k^4 we obtain $|k_1|$

TABLE VII. Moments of $\tilde{C}_0(k)$ in the HNC approximation for the OCP, compared with the predictions of its second iteration, Eq. (B7) (see text).

	Monte Carlo		HNC			Eq. (B6)	
Γ	$\left(\frac{\beta U}{N}\right)$	$\beta\left(\frac{\partial P}{\partial \rho}\right)_T$	$\frac{\beta U}{N}$	$\beta\left(\frac{\partial P}{\partial \rho}\right)_T$	a_1	$\beta\left(\frac{\partial P}{\partial \rho}\right)_T$	a_1
0.2			−0.0685	0.9665	0.5712×10^{-2}	0.968	0.527×10^{-2}
1	−0.580	0.726	−0.5705	0.7176	0.01783	0.7428	0.015925
2	−1.318	0.384	−1.3153	0.3332	0.03532	0.670	0.0116
3	−2.111	−0.029	−2.1026	−0.088	0.055	0.5799	0.01203

$=1.25680$, $\mathrm{Re}k_1=0$, while with the addition of the k^6 term the result is $|k_1|=1.28517$, $\mathrm{Re}k_1=0$. At $\Gamma=1.2$ we get, respectively, $|k_1|=1.4282$, $\mathrm{Re}k_1=0$, and $|k_1|=1.62727$, $\mathrm{Re}k_1=0.1853$. The HNC equation predicts the onset of oscillations in $g(r)$ to take place at $\Gamma_c \sim 1$, in accordance with the result of Choquard and Sari[64] and probably a very good estimate (in view of the rather high accuracy of the HNC equation) of the true situation.[65] On the other hand, the Monte Carlo data shows oscillations in $g(r)$ when $\Gamma=3$ (see Fig. 2) but does not show oscillations in $g(r)$ when $\Gamma=2$. It predicts the onset of oscillations for $2<\Gamma<3$, in contradiction with HNC. This, however, is not a real contradiction if one observes the values of $g_{\max}(r)$ as predicted by HNC, i.e. (to seven figures), 1.000000 for $\Gamma=1.3$, 1.000004 for $\Gamma=1.4$, 1.000019 for $\Gamma=1.5$, 1.000709 for $\Gamma=2$. In view of the agreement of HNC and MC $g(r)$ (e.g., Fig. 2) it is conceivable that the peak for $\Gamma=2$ is just too small to be detected to the accuracy of the published MC calculations. The crudeness of the approximation (B4) in detecting the onset of oscillations needs no further comments other than those implied in Table VII (especially in view of our remarks above). Equation (B4) being just the second iteration in the HNC procedure is adequate at low Γ (say, $\Gamma=0.2$) but fails badly for $\Gamma \gtrsim 1$ and thus is completely unsuitable for examining the onset of the long-range oscillations.

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[*] On leave of absence from the Nuclear Research Center—Negev, P. O. Box 9001, Beer-Sheva, Israel.

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As a bonus, however, we get all the physical information contained in the bridge function. Indeed, even our "first-order" estimates utilizing the hard-sphere bridge function lead to excellent agreement with the MC data for $g(r)$.

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