"Onsager-molecule" approach to liquid structure: Derivation of the universal bridge functions

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The direct [$\phi(r)\rightarrow S(k)$] and inverse [$S(k)\rightarrow\phi(r)$] problems of liquid pair structure can be solved by a hypernetted-chain (HNC) integral equation provided the bridge functions $B(r)$ are known. The asymptotic high-density properties of the HNC equation are mapped on the Onsager lower bound to the potential energy, which features "atoms" and "molecules" as mathematical constructs (e.g., the confined-atom Thomas-Fermi model for dense bulk matter). This asymptotic HNC Onsager "state" provides a starting point for analyzing the structure of dense fluids—like the ideal-gas state for dilute fluids. Using only the asymptotic properties of the HNC equation and the single assumption that $B(r)$ is nonsingular, I present the first direct calculation of the bridge functions for a highly correlated fluid and derive their universal characteristics.

I. INTRODUCTION

It has been a long-standing problem in statistical mechanics to determine the structure and thermodynamics of a highly correlated system such as a classical fluid.[1] The classical direct [$\phi(r)\rightarrow S(k)$] and inverse [$S(k)\rightarrow\phi(r)$] problems for liquid pair structure, relating the structure factor $S(k)$ to the pair potential $\phi(r)$, can be reduced by exact diagrammatic analysis[2] to the solution of the hypernetted-chain (HNC) integral equation for an effective potential [$\beta=(k_BT)^{-1}$],

$$\phi_{\rm eff}(r)=\phi(r)+B(r)/\beta\ . \tag{1}$$

The "exact" HNC equation is composed of the Ornstein-Zernike (OZ) relation between the direct correlation function $c(r)$ and the radial distribution function $g(r)\equiv h(r)-1$, with the k-space form

$$\tilde{h}(k)=\tilde{c}(k)+\rho\tilde{h}(k)\tilde{c}(k)\equiv S(k)\tilde{c}(k)\ , \tag{2}$$

and the HNC closure for $\phi_{\rm eff}(r)$,

$$H(r)-\beta\phi(r)\equiv\ln g(r)=-\beta\phi_{\rm eff}(r)+h(r)-c(r)\ . \tag{3}$$

$\rho=N/V$ is the number density and tildes denote Fourier transforms. The heart of the problem is $B(r)$—the bridge function—which may be expanded in diagrams with the "dressed" $h(r)$ bond. The HNC approximation (HNCA) is defined by $B(r)=0$, i.e., $\phi_{\rm eff}(r)=\phi(r)$. The diagrammatic low-density expansion represents a very slowly convergent route for obtaining meaningful results for a highly correlated system like a dense fluid, while on the other hand, even the HNC approximation provides an excellent point of departure for describing liquid pair structure. Along this alternative route, a first-order improvement on the HNC approximation, the ansatz of the universality[3,4] of the repulsive short-range structure of $B(r)$, was found empirically[5] to be very accurate. It provides the key to the most-successful presently available solutions[6] of the direct and inverse "scattering problems." Heuristic arguments[3] were given in favor of "universality," but the computational intractability of the bridge diagrams prohibited its direct assessment.

Unlike the dilute gas and the solid, which have natural reference states (ideal gas and harmonic solid, respectively) for starting their description by expansion in a small parameter, the dense fluid (say, near freezing) does not offer a natural small parameter. In effect, the modified HNC approach[3,4] identifies the small parameter as the deviation from universality of the bridge functions. In turn, the confined-atom Thomas-Fermi theory, which provides the working hypothesis for treating very dense matter, corresponds to a limit of the HNC equation for classical plasmas.[7,8] Since this HNC limit features universal characteristics, independent of the pair potential, the confined-atom Thomas-Fermi picture can be used as a starting point for developing a theory for the structure of dense classical fluids.

Here I follow this new route. Making the single assumption that the bridge function is not singular, I investigate the high-density properties of the HNC *equation* for $\phi(r)$ and $\phi_{\rm eff}(r)$. The asymptotic high-density properties of the HNC equation are mapped on the Onsager lower bound to the potential energy, which features "atoms" and "molecules" as mathematical constructs. Using these and the single assumption that $B(r)$ is not singular, I *derive* for the first time the leading high-density form of $B(r)$, and determine its universal characteristics. The results taken at face value show that a high-density singularity, of the type found in the Percus-Yevick (PY) theory for hard spheres at packing fraction $\eta=1$, is a universal "ideal" state (dual to the ideal-gas $\eta=1$ state) for analyzing highly correlated fluids.

II. ASYMPTOTIC PROPERTIES OF THE HNC EQUATION

It was recently shown[7,8] that the variational solution of the HNC equation, in the asymptotic high-density limit (AHDL, superscript ∞), maps on the Onsager[9] lower bound for the potential energy of the system. Onsager's method replaces the customary (Gaussian) Ewald func-

tion by a function of short range R comparable to the Wigner-Seitz radius a_{WS},

$$f_E(x)=\exp(-x^2) \Longrightarrow f_{OE}(x), \quad f_{OE}(x \geq R)=0 . \quad (4)$$

As a result, the structure-independent term in the Ewald summation[10] provides a much tighter lower bound to the full lattice sum ($\leftrightarrow$ energy integral). For a one-component plasma (OCP), i.e., positive ions in a uniform background of electrons, the Onsager lower bound corresponds to the sum of the self-energies of the neutral Onsager-Thomas-Fermi atoms, each composed of a point ion at the center of a sphere of uniform negative charge density.[7] The asymptotic-high-density-limit HNC direct correlation functions $c^{\infty}_{HNCA}(r)$ are given by[7] the electrostatic interaction between the two uniform spheres as function of their separation r. The Onsager lower bound for charge-cluster plasmas[11] features Onsager molecules which are direct generalizations of the atoms. The short range of the Onsager-Ewald functions, f_{OE} [Eq. (4)], ensures that the description of the Onsager lower bound in terms of individual contributions of confined Onsager atoms (OA's) and Onsager molecules (OM's) remains valid even for nonelectrostatic interactions. These asymptotic properties of the HNC equation govern its behavior in the entire liquid (dense-fluid) domain.[7,12]

For any nonsingular potential $\Phi(r)$ with strong repulsion at short distances, the asymptotic high density limit solution of the HNC equation has the following *universal* features[7] (from now on I use a_{WS} [$=(3\rho/4\pi)^{1/3}$ in three dimensions (3D)] as the unit of length). (i) $g^{\infty}(r \leq 2)=0$, i.e., the limit $\rho \rightarrow \infty$ is associated with an effective packing fraction $\eta=1$. (ii) $c^{\infty}(r \geq 2)=-H^{\infty}(r \geq 2) =-\beta\Phi(r)$. (iii) $\tilde{c}^{\infty}(k) \leq 0$. (iv) Let $\Omega(r)$ denote the overlap volume of two D-dimensional unit spheres at separation r [$\Omega(0)=\Omega_D$ is the volume of unit D-dimensional sphere] and define $\omega(r)=\Omega(r)/\Omega(0)$. The zeros $\tilde{c}^{\infty}(k_i)=0$ are identical to the zeros $\tilde{\omega}(k_i)=0$, e.g., $k_i=\tan(k_i)$ in 3D. For the Coulomb potential, $\tilde{c}^{\infty}(k)=-\beta\tilde{\omega}(k)\Phi_{Coulomb}(k)$. (v) Define (the inverse compressibility) $\chi[c]=1-\rho\int c(r)dr$, then the asymptotic-high-density-limit configurational free energy is given by the Onsager lower bound to the potential-energy integral

$$\tfrac{1}{2}\rho\int g^{\infty}(r)\beta\Phi(r)d\mathbf{r}=\tfrac{1}{2}\{\chi[c^{\infty}]+c^{\infty}(0)\} =\tfrac{1}{2}\Omega_D^{-1}\int g_D(r)\beta\Phi(r)d\mathbf{r} \quad (5)$$

(in our units $\rho=\Omega_D^{-1}$). The *universal* functions $g_D(r)$ denote the limit $\eta \rightarrow 1$ of the solution of the PY equation for D-dimensional hard spheres.

Recall that $\phi_{eff}(r)$ is just a "device" to get from the HNC equation the structure of the physical $\phi(r)$. Due to the universal properties above, then as long as the bridge function is not singular the solution of the HNC equation for $\phi_{eff}(r)$ will yield the same asymptotic-high-density-limit thermodynamics for the physical $\phi(r)$: Using $\Phi(r)=\phi(r)$ in (5) I get (denoting $\chi^{\infty}=\chi[c^{\infty}]$)

$$(\beta U/N)^{\infty}=\beta u_{OA}=\beta u^{\infty}_{HNCA}(\rho)=\tfrac{1}{2}\Omega_D^{-1}\int g_D(r)\beta\phi(r)d\mathbf{r} =\tfrac{1}{2}[\chi^{\infty}_{HNCA}+c^{\infty}_{HNCA}(0)] . \quad (6)$$

Specifically for the one-component plasma, the solution of the HNC equation with *any* nonsingular bridge function will yield the *same* leading "Madelung" term -0.9Γ.

It is interesting that the universal length scale 2 (in a_{WS} units) reflects the thermodynamic inconsistency of the (energy-virial consistent) HNC approximation with respect to the compressibility; denoting $Z=\beta P/\rho$, the length scale is given by the ratio[7]

$$\chi^{\infty}_{HNCA}/Z^{\infty}_{HNCA}=2 . \quad (7)$$

III. ASYMPTOTIC HIGH-DENSITY PROPERTIES OF THE SELF-CONSISTENT MODIFIED-HNC SCHEME

The self-consistent modified-HNC scheme for classical fluids was motivated by the universality hypothesis for the bridge functions.[3,4] One makes a judicious choice for a parametrized trial bridge function, solves the HNC equation for $\phi_{eff}(r)$, and determines the free parameters by imposing thermodynamic consistency conditions. For example, using the one-parameter bridge functions from the Percus-Yevick theory for hard spheres, very good agreement with computer simulations, for a wide variety of potentials, was obtained for both structure and thermodynamics.[3-5] The solution of the HNC equation is insensitive to values of $B(r)$ in the region where $g_{HNCA}(r)$ is close to zero anyway. In order to obtain iformation on $B(r)$ in that region, then on top of the usual requirement of energy-virial-compressibility consistency, it is indispensable[3,4] to impose consistency with respect to the Widom relation[13]

$$\ln g(r)=-\beta[F_1(\bullet\!\!-\!\!\bullet,(N-2)\bullet)-F_0(N\bullet)] . \quad (8a)$$

F_0 is the configurational free energy of the given system of N particles. F_1 is the configurational free energy of an identical system except for one pair of particles, which is kept at fixed separation r to form an interaction-site molecule. Here F_1 does contain the intramolecular interaction, i.e., $\phi(r)$. I now seek an energy-virial-compressibility consistent solution of Eqs. (1)–(3) and (8a) in the asymptotic-high-density limit. In that limit, however, for any nonsingular bridge functions, both F_0 and F_1 are dominated by their (HNC) Onsager lower bound, so that (8a) is expressed[14] in terms of the "self-energies" of the (mathematical constructs featured as) Onsager atoms and Onsager molecule:

$$H^{\infty}(r)=\beta[2u_{OA}-u_{OM}(r)+\phi(r)] . \quad (8b)$$

$H^{\infty}(r)$ is a difference between two tight lower bounds for the corresponding energies U_0 and U_1.

The existence of a universal asymptotic-high-density-limit length scale (i.e., the "atomic" diameter a_{WS}) implies that the Onsager molecule "dissociates" whenever

there is no atomic overlap: $H^{\infty}(r\geq 2)=\beta\phi(r)$. This implies, in view of (ii) above, that the asymptotic-high-density-limit bridge functions, which are consistent with respect to (8a), must be short ranged: $B^{\infty}(r\geq 2)=0$. The "antibonding" property of the Onsager molecule, $H^{\infty}(r)-\beta\phi(r)=2u_{\rm OA}-u_{\rm OM}(r)\leq 0$, is well known in the context of the Thomas-Fermi theory.[15] Here, in view of (8b), it gives $g^{\infty}(r\leq 2)=0$, in agreement with (i) above. Using (5) with $\Phi(r)=\phi_{\rm eff}(r)$, property (iii) above, the short-range nature of $B^{\infty}(r)$, and Eq. (6), define $\Delta c(r)=c(r)-c_{\rm HNCA}(r)$ to obtain

$$\beta u_{\rm OA}=\tfrac{1}{2}[\chi^{\infty}+c^{\infty}(0)]=\tfrac{1}{2}[\chi^{\infty}_{\rm HNCA}+c^{\infty}_{\rm HNCA}(0)]\ , \tag{9a}$$

$$\Delta c^{\infty}(0)=\Omega_{\rm D}^{-1}\int \Delta c^{\infty}(r)d\mathbf{r}\ , \tag{9b}$$

$$\Delta\tilde{c}^{\infty}(k)\leq 0\ . \tag{9c}$$

Equations (9b) and (9c) were first encountered[7] when treating the asymptotic-high-density limit of the PY equation for D-dimensional hard spheres. Recalling (7), the only nontrivial solution of Eqs. (9) is given by

$$\Delta c^{\infty}(r)=-(\chi^{\infty}-2Z^{\infty})\omega(r)\ , \tag{10}$$

which is the key result of this section. It now remains to calculate $u_{\rm OM}(r)$, from which, using (8b), we shall finally obtain

$$B^{\infty}(r)=-c^{\infty}_{\rm HNCA}(r)-\Delta c^{\infty}(r)-H^{\infty}(r)\ . \tag{11}$$

The continuity of the function $u_{\rm OM}(r)$ at dissociation ($r=2$) implies that there is a region close to $r=2$ where we have $H^{\infty}(r\sim 2)=-c^{\infty}_{\rm HNCA}(r)=\beta\phi(r)$. A generic universal form for the bridge function is thus given by

$$B^{\infty}_{\rm univeral}(r\leq 2,\ r\sim 2)=-\Delta c^{\infty}(r)=q^{\infty}\omega(r)\ , \tag{12}$$

where $q\equiv\chi-2Z$. Recall at this stage that from the standpoint of the scattering problem it does not matter if $B(r)$ fails close to $r=0$ since the values of $B(r)$ do not play a role when $g_{\rm HNCA}(r)$ is zero anyway.[3]

IV. ONSAGER MOLECULE SELF-ENERGIES

Instead of solving numerically the variational Onsager lower bound problem in order to obtain $u_{\rm OM}(r)$, which is nontrivial even for the "simplest" OCP case, I use an analytic approximation[11,16] that provides the exact $H^{\infty}(r=0)$ for the D-dimensional Coulomb potential, has the "dissociation" property at $r=2$, and accurately interpolates between $r=0$ and 2. It amounts to using the optimal atomic Onsager-Ewald functions, in scaled form $f_{\rm OE}(r/b)$, for the two interaction-site centers, and optimizing the resulting expression for $u_{\rm OM}(r)$ only with respect to the scale b. With $b=1$ the exact $u_{\rm OA}$ and $u_{\rm OM}(r=2)=2u_{\rm OA}$ are obtained, while $b=2^{1/D}$ gives the exact $u_{\rm OM}$ ($r=0$) for the D-dimensional Coulomb potential.

For inverse-power potentials $\beta\phi(r)=\Gamma r^{-m}$, define $c^{\infty}_{\rm HNCA}(r)=-\Gamma\Psi(r)$, $f(t)=[\Psi(2t)+2t\Psi'(2t)/m]/\Psi(0)$, $u_{\rm OA}=\alpha\Gamma$. The Ewald function obeys $f(t\geq 1)=0$, and $\alpha=\alpha(m,D)$ is the HNCA Madelung constant. The analytic approximation has the following parametric form:[17]

$$H^{\infty}(r)/2\alpha\Gamma=1-\frac{[1+mf(t)/D-\Psi(2t)/2\alpha]}{[1+f(t)]^{m/D}}, \tag{13a}$$

$$t=r/2b,\quad b=[1+f(t)]^{1/D}\ . \tag{13b}$$

The exact analytic form for the Onsager lower bound Ewald functions is available at present only for the hard spheres (HS) and Coulomb (C) potentials;[7] e.g.,

$$\begin{aligned} &f_{\rm HS,1D}(t)=\omega_{\rm 1D}(r=2t)=1-t\ ,\\ &f_{\rm C,1D}(t)=1-3t^2+2t^3\ ,\\ &f_{\rm HS,3D}(t)=\omega_{\rm 3D}(r=2t)=1-3t^2/2+t^3/2\ ,\\ &f_{\rm C,3D}(t)=1-5t^2+5t^3-t^5\ . \end{aligned} \tag{14}$$

For any given D, the functions $f(t)=f_{m,D}(t)$ are monotonic in m, and their expansion coefficients are expressed by means of moments of $g_D(r)$. $\alpha(m,D=1)=\zeta(m)$, where ζ is the Riemann ζ function. Combining the known features of the HNCA Ewald functions[7] into

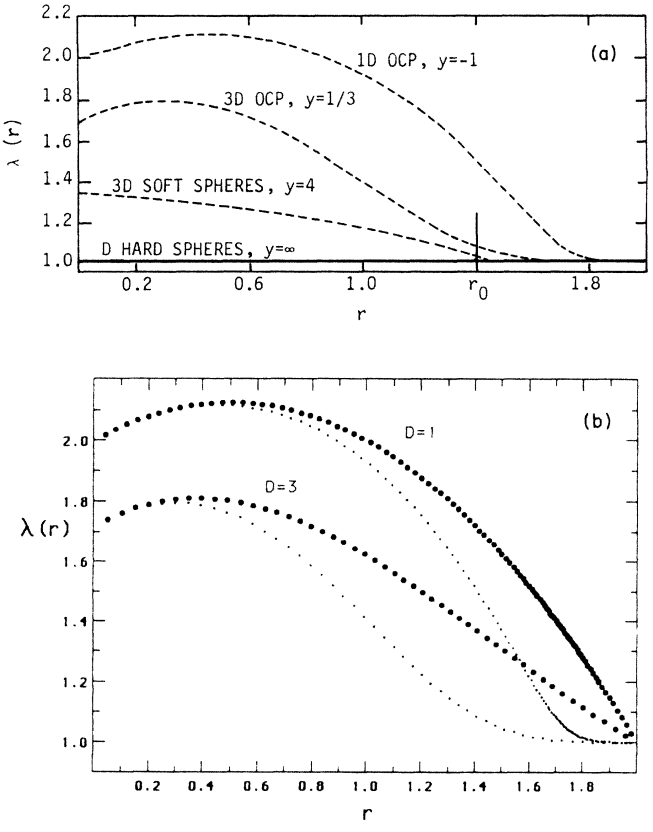

FIG. 1. (a) High-density ratio $\lambda(r)$ of the bridge function to its universal component, for inverse-power potentials $\beta\phi(r)=\Gamma r^{-m}$, as a function of the power m and dimensionality D. $y=m/D$ and r is in $a_{\rm WS}$ units [see the text, Eq. (13)]. (b) The ratio of the asymptotic strong coupling bridge function to its universal component for the $D=1$ and $D=3$ one-component plasma. The exact Onsager-molecule results $\lambda_{\rm OM}(r)$ (represented by large dots), are compared with the Onsager "smearing" approximation [from Eq. (13), represented by small dots]. See the text, and compare with (a).

(10)–(13), the ratio $\lambda(r)=B^{\infty}(r)/B^{\infty}_{\text{universal}}(r)$ is presented in Fig. 1(a). $\lambda(r=0)=\lambda_0(m/D)$ is a monotonically decreasing function of the ratio $y=m/D$,

$$\lambda_0(y)=[y(y+1)-4(1-2^{-y})]/[y(y-1)] . \quad (15)$$

It is 1 for hard spheres ($y=\infty$), 1.354... for soft spheres ($y=4$), 1.614... $=3-2\ln 2$ for the $D=\infty$ Coulomb plasma ($m=D-2$, $y=1$), 1.773... $=4\ln 2-1$ for $y=0$ (corresponding to the 2D Coulomb potential $\ln r$), and 2 for the 1D Coulomb potential ($y=-1$). The ratio $\lambda(r)$ is generally monotonic in m for fixed D, and in D for fixed m. Like $\lambda(0)$, $\lambda(r)$ depends mainly on the ratio m/D and approaches unity as m/D increases. There is a characteristic distance $r_0(m,D)$ beyond which λ is very close to unity. r_0 decreases with increasing m/D. Recalling the remark after (12) note that in three dimensions and $m\geq 1$, $r_0\approx 1.45$, corresponding to effective packing fraction $\eta_{\text{eff}}\approx(r_0/2)^3\approx 0.35$. On the basis of the Onsager ("smearing") bound estimates of $\lambda(r)$ as presented in Fig. 1(a), it may be concluded that from the standpoint of the scattering problem, the nonuniversal features of the leading contribution to the bridge function will not come into play for $\eta_{\text{eff}}\geq 0.35$ (freezing corresponds to $\eta\approx 0.45$).

The extremely high accuracy required for a meaningful analysis of the bridge functions can be appreciated from Fig. 1(b). The exact $u_{\text{OM}}(r)$ as obtained analytically for the $D=1$ Coulomb potential, and numerically[11(b)] for the $D=3$ Coulomb potential, improves the estimates [Eq. (13)] by less than 1%. The corresponding changes in $\lambda(r)$, as presented in Fig. 1(b), can reach 30%. On the basis of Fig. 1(b) we conclude that nonuniversal contributions to the bridge functions, although relatively small for dense fluids, cannot be ignored.

V. EXAMPLES

A. One-component plasma in three dimensions

Using Eqs. (10)–(14) for the three-dimensional one-component plasma, and recalling that $\alpha(D=3, m=1)=-0.9$, we obtain $q^{(\infty)}=0.2\Gamma$, so that

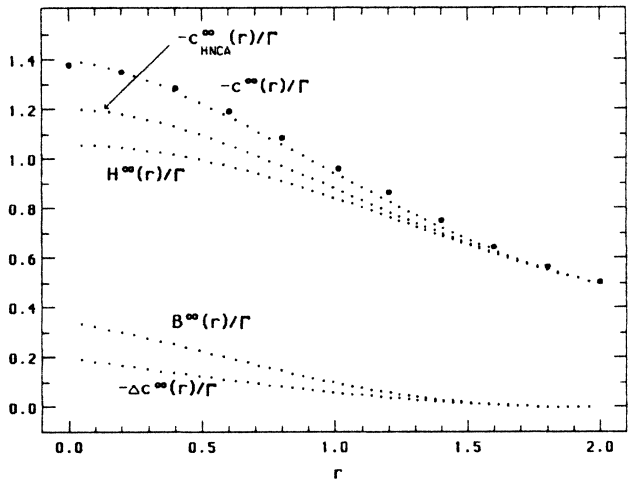

FIG. 2. Asymptotic ($\Gamma\to\infty$) correlation functions for the 3D one component plasma (see the text). The circles denote the $c(r)/\Gamma$ results of Poll *et al.* (Ref. 6) for $\Gamma=100$.

$$c^{(\infty)}(0)=-1.4\Gamma, c^{(\infty)}_{\text{HNCA}}(0)=-1.2\Gamma ,$$
$$H^{(\infty)}(0)=1.057...\Gamma, \quad B^{(\infty)}(0)=0.343...\Gamma , \quad (16)$$
$$B^{(\infty)}_{\text{universal}}(0)=0.2\Gamma .$$

The leading asymptotic ($\Gamma\to\infty$) functions are plotted in Fig. 2, along with recent very elaborate results for $c(r)$ at $\Gamma=100$ obtained by Poll *et al.*[6] by inverting Monte Carlo $g(r)$ data. In addition, we solved the modified HNC equation using

$$B(r,\Gamma=100)=0.2\Gamma\omega(r) = \begin{cases} 20[1-1.5(r/2)+0.5(r/2)^3], & r\leq 2 \\ 0, & r\geq 2 . \end{cases} \quad (17)$$

The results (see Table I) are in very good agreement with the simulation $g(r)$ data. To better appreciate the accu-

TABLE I. Direct correlation function for the 3D one-component plasma. $c^{\infty}(r)/\Gamma=0.2\omega(r)+c^{\infty}_{\text{HNCA}}(r)/\Gamma$ is the theoretical prediction [Eq. (10)]. $c_{\text{PAD}}(r)/\Gamma$ is the result of Poll, Ashcroft, and DeWitt (Ref. 6) for $\Gamma=100$. $c_{\text{GH}}(r)/\Gamma$ is the result of Galam and Hansen (Ref. 18) for $\Gamma=100$. $c_B(r)/\Gamma$ is the modified HNC result for $\Gamma=100$ using Eq. (17). $c^{\infty}_{\text{HNCA}}(r)/\Gamma$ and $B^{\infty}(r)/\Gamma=0.2\omega(r)$ are given for comparison.

r	B^{∞}/Γ	$c^{\infty}_{\text{HNCA}}/\Gamma$	c^{∞}/Γ	c_{PAD}/Γ	c_B/Γ	c_{GH}/Γ
0	0.2	1.2	1.4	1.376	1.346	1.325
0.2	0.1701	1.181	1.352	1.351	1.322	1.301
0.4	0.1408	1.132	1.273	1.285	1.259	1.237
0.6	0.1127	1.060	1.173	1.192	1.169	1.148
0.8	0.0864	0.974	1.060	1.085	1.065	1.044
1	0.0625	0.881	0.944	0.957	0.954	0.936
1.2	0.0416	0.788	0.830	0.859	0.844	0.828
1.4	0.0243	0.701	0.725	0.750	0.737	0.723
1.6	0.0112	0.622	0.634	0.644	0.634	0.623
1.8	0.0029	0.555	0.558	0.563	0.556	0.548
2	0	0.500	0.500	0.506	0.500	0.496

racy of our prediction for $c(r)/\Gamma$ we also present the results obtained by Galam and Hansen[18] using another inversion scheme. The discrepancies between the asymptotic functions and their values for $\Gamma=100$ are of the order of the entropic contributions to the free energies (6a) at $\Gamma=100$, which are not taken into account by the asymptotic results based on (8b).

The systematic extraction of the bridge function from the simulation $g(r)$ data should start with the representation

$$B(r,\Gamma)=0.2\Gamma\omega(r)+\Delta B(r,\Gamma)\ , \tag{18}$$

noting that from the standpoint of the scattering problem $\Delta B(r)$ is always relatively small compared with the leading term: $\Delta B(r)$ is substantial only where $g(r)$ is close to zero anyway. In that region $B(r)$ itself is not relevant to the scattering problem and it can be evaluated only via (8a) [or (8b), in the asymptotic limit]. Figure 3 illustrates both the validity of this approach and the difficulty of otherwise obtaining a unique $B(r)$ that will agree with the simulation $g(r)$ data: Long-range ($r\geq 2$) contributions appear only at the $\Delta B(r)$ level and have a relatively small (yet noticeable) effect on $g(r)$ in strong coupling.

In order to demonstrate the self-consistency of our approach we present in Fig. 4 the results for $\Gamma=100$, as obtained from the numerical solution of the modified-HNC equation that employs the exact asymptotic bridge function, namely, $B_{\rm OM}(r)=0.2\Gamma\omega(r)\lambda_{\rm OM}(r)$, where $\lambda_{\rm OM}(r)$ can be well fitted by [see Fig. 1(b)]

$$\lambda_{\rm OM}(r)=1.713+1.07(r/2)-3.24(r/2)^2 +1.457(r/2)^3,\quad r\leq 2\ .$$

These results are compared with the theoretical asymptotic functions [e.g., (8b) and (10)] from which $B_{\rm OM}(r)$ was derived [using (11)]. The agreement is striking, and the remaining gaps should be closed in the limit $\Gamma\to\infty$.

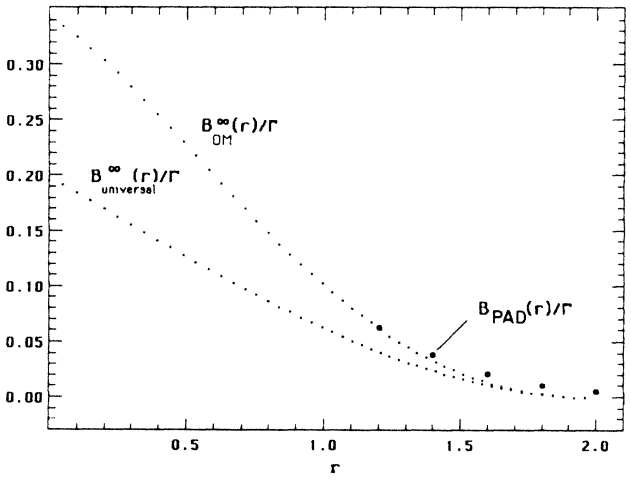

FIG. 3. Asymptotic bridge function $B_{\rm OM}(r)$ for the 3D one-component plasma compared with its universal component $0.2\omega(r)$ and the $\Gamma=100$ result of Poll *et al.* (Ref. 6). Note that for $r\lesssim 2$, $g_{\rm simulation}(r)=0$.

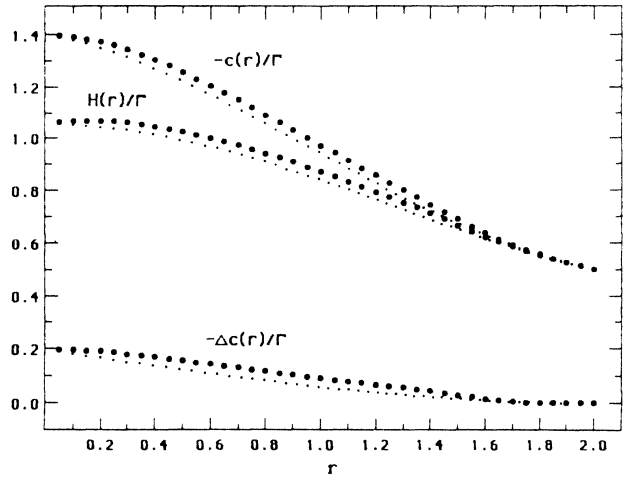

FIG. 4. Correlation functions $-c(r)/\Gamma$, $H(r)/\Gamma$, and $-\Delta c(r)/\Gamma$, as obtained from the solution of the modified-HNC equation for the $D=3$ one-component plasma using $B_{\rm OM}(r)$. The $\Gamma=100$ results, represented by large dots, are compared with the theoretical $\Gamma\to\infty$ values, represented by small dots (see the text).

The corresponding $g(r)$, which is not plotted, replicates the simulation data used by Poll *et al.*[6] to within the statistical noise.

This discussion applies as well to other dimensionalities and other inverse-power potentials, but it should be noticed that as the ratio m/D increases and the potential becomes of shorter range, the less dominant is the asymptotic leading term for densities in the region of the fluid-solid transition.

B. Mixtures

Straightforward extension of the asymptotic analysis to mixtures leads to the following result:

$$\Delta c_{ij}^{(\infty)}(r)=c_{ij}^{(\infty)}(r)-[c_{ij}^{(\infty)}(r)]_{\rm HNCA} =-[B_{ij}^{(\infty)}(r)]_{\rm universal}\ , \tag{19}$$

where

$$[B_{ij}^{(\infty)}(r)]_{\rm universal}=(\chi^{\infty}-2Z^{\infty})\left[R_i^D\Big/\sum x_i R_i^D\right]\omega_{ij}(r) \tag{20}$$

and $\omega_{ij}(r)=\Omega_{ij}(r)/\Omega_{ij}$ $(r=0)$, with $\Omega_{ij}(r)$ denoting the overlap volume of two D-dimensional spheres of radii R_i, and R_{ij} $(R_i<R_j)$. The R_i are the radii of the Onsager atoms. For a $D=3$ multicomponent plasma we have $R_i=(Q_i/\langle Q\rangle)^{1/3}$,

$$q^{\infty}=(\chi^{\infty}-2Z^{\infty})=0.2\Gamma\langle Q^{5/3}\rangle(\langle Q\rangle)^{1/3}\ ,$$

so that (with $Q_i<Q_j$)

$$[B_{ij}^{(\infty)}(r)]_{\rm universal} =0.2\Gamma\langle Q^{5/3}\rangle(\langle Q\rangle)^{1/3}(Q_i/\langle Q\rangle)\omega_{ij}(r)\ , \tag{21}$$

where $\langle Q^s \rangle = \sum x_i Q_i^s$. This result agrees well with the calculations[4] based on the Percus-Yevick hard-sphere bridge functions for the mixture near freezing.

C. Density profiles against a hard wall

The density profile of particles against a hard wall can be treated as a limit case of a mixture in which one hard particle-type grows in size and diminishes in concentration. For the special case of a one-component system against a hard wall, the particle-wall bridge function is expressed through the fraction of the particle's volume outside the wall when its center is at distance z from the wall,

$$\omega_{3D,\text{wall}}(z) = \begin{cases} 1-3[(z+1)/2]^2+2[(z+1)/2]^3, & z \le 1 \\ 0, & z \ge 1 \ . \end{cases} \tag{22}$$

Specifically, the asymptotic particle-wall bridge function is given by

$$[B_{ij}^{(\infty)}(z)]_{\text{wall}} = \begin{cases} q^\infty\{1-3[(z+1-\lambda)/2]^2 \\ \quad +2[(z+1-\lambda)/2]^3\}, & z \le 1+\lambda \\ 0, & z \ge 1+\lambda \end{cases} \tag{23}$$

where q^∞ *retains* its bulk value, and λ is a shift parameter.[19] The q dependence of the universal bridge functions first appeared in the analysis of density profiles.[19] The fact that it can be derived from two completely different approaches supports its validity.

VI. CONCLUSION

Starting from the HNC-Onsager asymptotic state, using only asymptotic properties of the HNC *equation* and assuming that the bridge functions are nonsingular, I derived various features of the dense-fluid structure (mainly the bridge functions), in full agreement with previous empirical and semiempirical approaches to the problem. The derived universal part of the leading term in the high-density expansion of $B(r)$, $B_{\text{universal}}(r) = q\omega(r) + \cdots$, should be the dominant contribution in the entire liquid (dense-fluid) region, and thus provide the starting point for the solution of the classical inverse scattering problem. The analysis of density profiles of particles against a hard wall predicted[19] that if $B(r)$ is universal then it should be of the form $B(r,q)$—in agreement with (12). Moreover, the present result is in complete accord with the highly successful modified-HNC theory based on the empirical PY bridge functions for hard spheres and thermodynamic consistency.[3] It can be checked numerically that this theory features $B_{\text{PYHS}}(r \ge 1.4, \eta \ge 0.35) \approx q\omega(r)$, it features analytically $B_{\text{PYHS}}(r)/B_{\text{PYHS}}(0) \to \omega(r)$ for $\eta \to 1$, and is actually expected to obey (12). The numerical extraction of the universal and nonuniversal terms in $B(r)$, from computer simulation data, does not lead to a unique solution.[6] The inclusion of the correct leading term derived above [e.g., via Eq. (18)] should lead to more physically meaningful results. Numerical solution[20] of the modified-HNC equation for the 2D bulk one-component plasma, and for the 3D one-component plasma density profiles against a hard wall, using (12) and (23), respectively, also confirms our analysis.

The present derivation of the asymptotic properties of the bridge functions is based only on the analysis of the HNC integral equation. The 1D HNC-Onsager lower bound corresponds to the linear lattice structure and (12) is exact for hard rods. If the HNC-Onsager lower bound, corresponding to the (unphysical for $D > 1$) packing fraction $\eta \to 1$, is a true singular point of the diagrammatic expansion, then $B^\infty(r)$ given by (11) and its universal component (12) become generally exact. The various features mentioned above support this interesting possibility. Recent analysis of the hard-sphere virial series finds that a singularity at $\eta = 1$ possibly exists.[21]

It may be argued, however, that the ansatz of universality of the short-range part of $B(r)$ makes good sense in general, but not at densities $\eta = 1$, which is well beyond close packing for hard disks or spheres. Indeed, even before close packing on a lattice is approached, one would expect a singularity at random close packing if radial symmetry is imposed, as it is in the Percus-Yevick or HNC equations. Since these singularities reflect geometrical packing constraints, it would seem that they must determine the physics at very high densities and not the behavior at still higher unphysical densities with $\eta = 1$. This argument casts strong doubts on the role of the $\eta = 1$ singularity as an *exact* singular point of the diagrammatic expansion, but not on its apparent utility for analyzing dense-fluid structure. As demonstrated above and as extensively analyzed for plasmas in particular,[22] the asymptotic expansion around the HNC-Onsager lower bound ($\eta = 1$) state fastly converges for highly correlated fluids, and then $\eta = 1$ singularity easily relaxes into the physical regime: Note that the Laplace transform of the HNC $rg(r)$, namely $G(s)$, features for $\eta = 1$ the set of purely imaginary poles given by $s_j = \pm ik_j$ [see property (iv) after Eq. (5)]. Only a relatively small change in the poles' positions is required in order to describe the physical dense-fluid structure (see, e.g., Ref. 7). Thus even if it is not a true singular point of the exact virial series, the $\eta = 1$ HNC state (like a "dual" to the ideal-gas $\eta = 0$ state) provides if not a natural then at least an efficient starting point for treating highly correlated fluids. This point of view is best understood when considering the classical Coulomb and screened Coulomb (Yukawa) potential systems: The HNC-Onsager singular state corresponds to the confined-atom Thomas-Fermi model for dense bulk matter, which although "unphysical" is manifestly useful.

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