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The Hard-Sphere Fluid: New Exact Results with Applications

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A theorem for convolution integrals is proved and then applied to extend the "second zero-separation theorem" to the bridge function $b(r)$ and direct-correlation tail functions $d(r)$. This theorem allows us to exactly relate $\partial b(r)/\partial r$ and $\partial d(r)/\partial r$ at $r=0$ for the hard-sphere fluid to the "contact value" of the radial distribution function $g(r)$ at $r=\sigma^+$. From this we obtain immediately the exact values of $\partial b(r)/\partial r$ and $\partial d(r)/\partial r$ at $r=0$ through second order in number density ρ. Using our results to compare the exact and Percus–Yevick (PY) bridge function, we find that they differ significantly. After obtaining the bridge function and tail function and their derivatives at $r=0$ and $r=\sigma$ through, we suggest new approximations for $b(0)$ and $d(0)$ as well as an analytical integral-equation theory to improve the PY approximation in the pure hard-sphere fluid. The major deficiency of that approximation has been its poor assessment of the cavity function inside the hard-core region. Our theory remedies this defect in a way that yields a $y(r)$ that is self-consistent with respct to the virial and compressibility relations and also the two zero-separation relations involving $y(r)$ and its spatial derivative at $r=0$.

KEY WORDS: Bridge function; tail function; cavity functions; hard-sphere fluids; second zero-separation theorem; self-consistent theory; equation of state.

1. INTRODUCTION

The fundamental contributions of Howard Reiss to the scaled-particle theory of fluids have had a major impact on modern liquid-state chemistry and physics. In particular, the conceptual insights that the scaled-particle picture affords as well as the accurate and simple approximations that can

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be derived from it have helped maintain the central role that the hard-sphere fluid continues to play in current liquid-state theory. Here we make some new observations concerning hard spheres that are very much in the scaled-particle tradition.

The contributions to the pair correlation function $h(r)$ and direct pair correlation function $c(r)$ that have come to be known as the bridge function(1-3) $b(r)$ and tail function(4,5) $d(r)$ play an essential role in improving the hypernetted chain (HNC) and Percus–Yevick (PY) approximations. However, not much is known about their exact analytic structure, due to their complexity. Even for a simple system such as the pure hard-sphere fluid, only the lowest-order contribution to $b(r)$ in the number density ρ, which is of order ρ^2, is known analytically.(6) For any pair potential with a hard core, the behavior of bridge functions and tail functions inside the core will not affect the structure factor and its transform $h(r)$, but they do affect the cavity function $y(r)$, which is defined as $e^{\beta u}[h(r)+1]$ (u is pair potential). The value of $y(0)$ for an important class of potentials (hard-sphere potentials for pure fluid and mixtures,(7) hard-core potentials with finite-range tails,(8) the charged hard-sphere potential(9)) is related to thermodynamic quantities according to "zero separation theorems."(7-9) It turns out(1) that the value of $y(0)$ is a very severe test for integral-equation theories. Therefore, the values of bridge functions and tail functions inside the core are very important.

By parametrizing $\ln y(r)$ inside the core for a hard-sphere fluid, Rosenfeld and Ashcroft(1) found an analytic approximation for the bridge function of a pure hard-sphere fluid from computer simulation results. They also concluded that the bridge functions for an important class of pair potentials [e.g., the Lennard-Jones potential and potentials of the form $(\sigma/r)^{-n}$] are remarkably similar to each other and to the hard-sphere bridge function $b^{\mathrm{HS}}(r, \rho)$ in the sense that there exists a λ_1 and a λ_2 such that to a good approximation

$$b(r; \rho, T) = b^{\mathrm{HS}}(\lambda_1 r; \lambda_2 \rho) \tag{1.1}$$

They refer to this as the "universality of bridge functions." They further concluded that the PY hard-sphere bridge function is for many purposes an adequate approximation to the exact hard-sphere $b(r)$ [and hence to this whole family of $b(r)$'s]. Their work has enhanced the role of the hard-sphere $b(r)$ in the statistical theory of fluid and has in addition given added importance to the question of how well $b^{\mathrm{PY}}(r)$ approximates $b(r)$ in a hard-sphere system.

In this paper we extend the second zero-separation theorem for y functions(7-9) to bridge functions and tail functions (Section 2). This extended theorem applies to systems of any pair potential with a hard core. We apply it here to the pure hard-sphere fluid in Section 3 as an example. One of our main purposes in this regard is to probe in detail the precise extent to which $b^{PY}(r)$ can be used to approximate the exact $b(r)$ in a hard-sphere system. The comparison between the exact results for $b'(0)$ and the PY results for $b'(0)$ indicates that b^{exact} is significantly different from b^{PY} (here and throughout the rest of the paper, a prime is used to denote a derivative with respect to r). A new approximate expression for $b(0)$ is found (the CS/PY expression) and compared with $b^{PY}(0)$ and another approximation suggested by Henderson and Grundke.(4) Exact values of $b(\sigma)$ and $d(\sigma)$ in the low-concentration limit are also given. In Section 4, we use a self-consistent method for pure hard spheres, which remedies the major deficiency of the PY equation, which is its poor assessment of the cavity function inside the hard-core region. To be more precise, there are two versions of the PY equation, as discussed in detail by Stell.(10) In the first of these, referred to simply as the PY equation throughout this paper, y_{ij} is given by (2.10b) below, with $d_{ij}=0$. In the second of these (referred to by Stell(10) as the "series-union" approximation) y inside the core remains undetermined and closure for the Ornstein–Zernike equation is given in terms that only involve h_{ij} and c_{ij} through Eq. (2.21) below. Our work extends earlier work by Waisman(11),[3] and by Giunta *et al.*(5) Our method yields a new integral equation for $y(r)$ that is self-consistent with respect to the virial and compressibility relations as well as the two zero-separation relations involving $y(r)$ and its spatial derivative at $r=0$. Our results are purely analytic, unlike those of ref. 5, and somewhat better results are obtained for $y(r)$ inside the core than those of that reference.

2. AN EXTENSION OF THE SECOND ZERO-SEPARATION THEOREM TO THE BRIDGE AND TAIL FUNCTIONS

2.1. A Zero-Separation Theorem for Convolution Integrals

Given any functions $f_1(r)$ and $f_2(r)$ with $f_1(0)$, $f_2(0)$, $\tilde{f}_1(0)$, and $\tilde{f}_2(0)$ all finite (the tilde denotes a 3D Fourier transform), the three-dimensional convolution integral of $f_1(r)$ with $f_2(r)$ can be written as

$$f_1 * f_2 \equiv \frac{2\pi}{r} G(r) \tag{2.1}$$

where

$$G(r) \equiv \int_0^\infty t\,dt \int_{|r-t|}^{r+t} s\,ds\, f_1(s)\, f_2(t) \tag{2.2}$$

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[3] A misprint in ref. 11 has been pointed out by Henderson *et al.*(12)

Then

$$G'(r) \equiv \frac{dG(r)}{dr} = \int_r^\infty t\,dt\,[(r+t)f_1(r+t) + (t-r)f_1(t-r)]\,f_2(t)$$
$$+ \int_0^r t\,dt\,[(r+t)f_1(r+t) - (r-t)f_1(r-t)]\,f_2(t) \tag{2.3}$$

Therefore,

$$\frac{d[f_1 * f_2]}{dr} = 2\pi \frac{d}{dr}\left(\frac{G(r)}{r}\right) = \frac{-f_1 * f_2 + 2\pi G'(r)}{r} \tag{2.4}$$

It is easy to see that, as $r \to 0$,

$$2\pi G'(r) - f_1 * f_2 \to 0 \tag{2.5}$$

Therefore, we can apply L'Hôpital's rule to obtain

$$\lim_{r \to 0} \frac{d[f_1 * f_2]}{dr} = -\left.\frac{d[f_1 * f_2]}{dr}\right|_{r \to 0} + 2\pi G''(r)|_{r \to 0}$$

or

$$\lim_{r \to 0} \frac{d[f_1 * f_2]}{dr} = \pi G''(0) \tag{2.6}$$

Now assume $f_1(r)$ and $f_2(r)$ each have one discontinuity at σ_1 and σ_2, respectively, but are otherwise continuous. Then, one can obtain (Appendix A)

$$\left.\frac{d[f_1 * f_2]}{dr}\right|_{r \to 0}$$
$$= \begin{cases} 0, & \sigma_1 \neq \sigma_2, \quad \text{(2.7a)} \\ -\pi\sigma^2[f_1(\sigma^+) - f_1(\sigma^-)][f_2(\sigma^+) - f_2(\sigma^-)], & \sigma_1 = \sigma_2 = \sigma \quad \text{(2.7b)} \end{cases}$$

where $\sigma^\pm$ means $\sigma \pm \delta$ in the limit $\delta \to 0$, $\delta > 0$.

2.2. A Zero-Separation Theorem for Bridge and Tail Functions

We apply this purely mathematical result to the Ornstein–Zernike (OZ) equation:

$$h_{ij} - c_{ij} = \sum_l \rho_l h_{il} * c_{lj} \tag{2.8}$$

where ρ_l is density of particles of species l and h_{ij} and c_{ij} are the indirect and direct pair correlation functions, respectively. Differentiating Eq. (2.8) respect to r, taking the $r \to 0$ limit, and using Eq. (2.7), we find

$$\left.\frac{\partial(h_{ij}-c_{ij})}{\partial r}\right|_{r\to 0} = \begin{cases} -\pi\delta_{ij}\sum\limits_l \rho_l \sigma_{il}^2 g_{il}^2(\sigma_{il}^+), & \sigma_i \neq \sigma_j \text{ if } i \neq j \qquad (2.9\text{a}) \\ -\pi\sigma^2 \sum\limits_l \rho_l g_{il}(\sigma^+)\, g_{lj}(\sigma^+), & \sigma_i = \sigma_j = \sigma \text{ for all } i, j \qquad (2.9\text{b}) \end{cases}$$

where we have used the relation $g_{ij}(r) = h_{ij}(r) + 1$, the fact that $h_{ij}(r)$ is -1 inside the hard core, and the continuity of $(h * c)_{ij}$ at $r = \sigma_{ij}$. Also, σ_{ij} is defined as $(\sigma_i + \sigma_j)/2$, σ_i is the hard-core diameter of the particle of species i, and δ_{ij} is Kronecker delta. The two cases in Eq. (2.9) are not exclusive. The equations for other cases (e.g., nonadditive diameters) can be obtained easily from Eq. (2.7), but we will not pursue them here. Equation (2.9) is satisfied by analytical solutions of the PY hard-sphere equation,(13) the MSA (mean sphere approximation) charged hard-sphere equation,(14) and the MSA Yukawa-sphere equation.(11)

The exact closure for the OZ equation can be written as

$$h_{ij} - c_{ij} = \ln(1 + h_{ij}) + \beta u_{ij} + b_{ij} = \ln y_{ij} + b_{ij} \qquad (2.10\text{a})$$

or

$$h_{ij} - c_{ij} = y_{ij} - d_{ij} - 1 \qquad (2.10\text{b})$$

where b_{ij} is the bridge function, the negative sum of elementary graphs,

$$b_{ij}(r) \equiv -E_{ij}(r)$$

and

$$y_{ij} \equiv [\exp(\beta u_{ij})]\, g_{ij}$$

u_{ij} is the pair potential, $\beta = 1/k_B T$, T is temperature, k_B is the Boltzmann constant, and d_{ij} is the tail function, which is neglected in the PY approximation. If b_{ij} and d_{ij} are zero, then Eqs. (2.10a) and (2.10b) reduce to HNC and PY closures, respectively. The relationship between b_{ij} and d_{ij} can be obtained from Eqs. (2.10a) and (2.10b) as

$$b_{ij} + d_{ij} = y_{ij} - \ln y_{ij} - 1 \qquad (2.11)$$

By using Eqs. (2.9), (2.10a), and (2.10b), we can easily obtain

$$b'_{ij}(0)=\begin{cases} -\dfrac{y'_{ij}(0)}{y_{ij}(0)}-\pi\delta_{ij}\sum\limits_{l}\rho_l\sigma_{il}^2 g_{il}^2(\sigma_{il}^+), & \sigma_i\neq\sigma_j \text{ if } i\neq j \qquad (2.12\text{a})\\ -\dfrac{y'_{ij}(0)}{y_{ij}(0)}-\pi\sigma^2\sum\limits_{l}\rho_l g_{il}(\sigma^+)g_{lj}(\sigma^+), & \sigma_i=\sigma_j=\sigma \text{ for all } i,j \qquad (2.12\text{b})\end{cases}$$

and

$$d'_{ij}(0)=\begin{cases} y'_{ij}(0)+\pi\delta_{ij}\sum\limits_{l}\rho_l\sigma_{il}^2 g_{il}^2(\sigma_{il}^+), & \sigma_i\neq\sigma_j \text{ if } i\neq j \qquad (2.13\text{a})\\ y'_{ij}(0)+\pi\sigma^2\sum\limits_{l}\rho_l g_{il}(\sigma^+)\,g_{lj}(\sigma^+), & \sigma_i=\sigma_j=\sigma \text{ for all } i,j \qquad (2.13\text{b})\end{cases}$$

Equations (2.12a), (2.12b), (2.13a), and (2.13b) are used for the system in which the potential has a hard core with any continuous tail.

We shall call Eqs. (2.12) and (2.13) the second zero-separation theorem for bridge functions and tail functions, respectively. For completeness, we recall the first and second zero-separation theorems for y_{ij} functions. For hard-sphere mixtures, the first zero-separation theorem is$^{(7)}$

$$y_{ij}(r\leqslant a_{ij})=(\exp v_i)/(\rho_i\lambda_i^3), \qquad \sigma_i\leqslant\sigma_j \tag{2.14}$$

where $v_i=\beta\mu_i$ and μ_i is the chemical potential, λ_i is the thermal wavelength, and a_{ij} is $|\sigma_j-\sigma_i|/2$. The second theorem is$^{(7)}$

$$\frac{d}{dr}\ln y_{ij}(a_{ij})=-\pi\delta_{ij}\sum_{l}\sigma_{lj}^2\rho_l y_{lj}(\sigma_{lj}) \tag{2.15}$$

The zero-separation theorem for y_{ij} functions in other systems can be found in refs. 8 and 9.

2.3. The Second Zero-Separation Theorem for y_{ij} in PY and HNC Approximations

For the PY approximation, we have

$$d_{ij}^{\mathrm{PY}}\equiv 0 \tag{2.16}$$

From Eq. (2.13) we immediately obtain

$$[y'_{ij}(0)]^{\mathrm{PY}}=\begin{cases} -\pi\delta_{ij}\sum\limits_{l}\rho_l\sigma_{il}^2[g_{il}^{\mathrm{PY}}(\sigma_{il}^+)]^2, & \sigma_i\neq\sigma_j \text{ if } i\neq j \qquad (2.17\text{a})\\ -\pi\sigma^2\sum\limits_{l}\rho_l g_{il}^{\mathrm{PY}}(\sigma^+)\,g_{lj}^{\mathrm{PY}}(\sigma^+), & \sigma_i=\sigma_j=\sigma \text{ for all } i,j \qquad (2.17\text{b})\end{cases}$$

Equation (2.17a) in the hard-sphere mixture case has been obtained by Lebowitz.(15)

For the HNC approximation, we have

$$b_{ij}^{\mathrm{HNC}} \equiv 0 \tag{2.18}$$

Then, from Eq. (2.12), we have an equation similar to (2.17),

$$\left[\frac{y'_{ij}(0)}{y_{ij}(0)}\right]^{\mathrm{HNC}}$$

$$= \begin{cases} -\pi\delta_{ij} \sum\limits_l \rho_l \sigma_{il}^2 [g_{il}^{\mathrm{HNC}}(\sigma_{il}^+)]^2, & \sigma_i \neq \sigma_j \text{ if } i \neq j \qquad (2.19\mathrm{a}) \\ -\pi\sigma^2 \sum\limits_l \rho_l g_{il}^{\mathrm{HNC}}(\sigma^+)\, g_{lj}^{\mathrm{HNC}}(\sigma^+), & \sigma_i = \sigma_j = \sigma \text{ for all } i, j \qquad (2.19\mathrm{b}) \end{cases}$$

The resemblance of Eq. (2.19) or (2.17) to the exact results for the hard-sphere fluid [Eq. (2.15)] is striking.

Our results have extended the second zero-separation theorem(7–9) to the bridge functions and tail functions. From the second zero-separation theorem, the exact result for $y'_{ij}(0)$ is known. Therefore, for the system in which the second zero-separation theorem for the $y_{ij}(r)$ functions is satisfied, we can obtain $b'_{ij}(0)$ and $d'_{ij}(0)$ easily. In the next section, we apply these exact equations to the one-component hard-sphere case.

For completeness we note that an exact closure for the OZ equation alternative to (2.10b) that does not involve y_{ij} is given by

$$c_{ij} = f_{ij}(g_{ij} - c_{ij}) + (f_{ij} + 1) d_{ij} \tag{2.20}$$

The series-union approximation,(10) weaker than the original PY approximation, is given by

$$(f_{ij} + 1) d_{ij} = 0 \tag{2.21}$$

where $f_{ij} = \exp(-\beta u_{ij}) - 1$.

3. LIMITING RESULTS OF THE BRIDGE AND TAIL FUNCTIONS FOR A PURE HARD-SPHERE FLUID

3.1. Exact Results for *b*′(0) and *d*′(0)

Next, we consider the simplest model among those described by our theories: the one-component hard-sphere model. For this system, a relation between $y'(0)$ and $y(\sigma)$ is well known(7):

$$\left.\frac{\partial \ln y(r)}{\partial r}\right|_{r \to 0} = \frac{y'(0)}{y(0)} = -6\eta \frac{y(\sigma)}{\sigma} \tag{3.1}$$

where η is the packing fraction ($\eta \equiv \frac{1}{6}\pi\rho\sigma^3$) and σ is the hard-sphere diameter.

Substituting Eq. (3.1) into (2.12), we obtain the exact result

$$b'(0) = -\frac{6\eta}{\sigma}\, y(\sigma)[y(\sigma)-1] \tag{3.2}$$

For the PY approximation, we have,(1) from Eq. (2.11),

$$b^{\mathrm{PY}}(r) = y^{\mathrm{PY}}(r) - 1 - \ln y^{\mathrm{PY}}(r) \tag{3.3}$$

Therefore,using Eq. (2.17), we have

$$[b'(0)]^{\mathrm{PY}} = -\frac{6\eta}{\sigma}\,[y^{\mathrm{PY}}(\sigma)]^2\left(1 - \frac{1}{y^{\mathrm{PY}}(0)}\right) \tag{3.4}$$

Very accurate results for $y(\sigma)$ can be found either from simulation results(16) or from the Carnahan–Starling (CS) equation of state,(17)

$$y^{\mathrm{CS}}(\sigma) = \frac{1}{2}\frac{(2-\eta)}{(1-\eta)^3} \tag{3.5}$$

as well as from the virial expansion(18):

$$\begin{aligned} y^{\mathrm{V}}(\sigma) &= 1 + \sum_{n=3}^{\infty} \frac{B_n}{4}\eta^{n-2} \\ &= 1 + \frac{10}{4}\eta + \frac{18.36}{4}\eta^2 + \frac{28.24}{4}\eta^3 + \frac{39.5}{4}\eta^4 + \frac{56.5}{4}\eta^5 + \cdots \end{aligned} \tag{3.6}$$

where B_n are reduced virial coefficients. The $y^{\mathrm{PY}}(0)$ and $y^{\mathrm{PY}}(\sigma)$ are well known,(13)

$$y^{\mathrm{PY}}(0) = \frac{(1+2\eta)^2}{(1-\eta)^4} \tag{3.7}$$

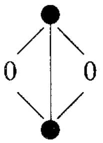
$$y^{\mathrm{PY}}(\sigma) = \frac{1}{2}\frac{(2+\eta)}{(1-\eta)^2} \tag{3.8}$$

Substituting Eqs. (3.5) and (3.6) into (3.2), respectively, we have

$$\begin{aligned} \sigma[b'(0)]^{\mathrm{CS}} &= -3\eta\frac{2-\eta}{(1-\eta)^3}\left(\frac{2-\eta}{2(1-\eta)^3} - 1\right) \\ &= -(15\eta^2 + 64.5\eta^3 + 177\eta^4 + 391.5\eta^5 + 759\eta^6 \\ &\quad + 1344\eta^7 + \cdots) \end{aligned} \tag{3.9}$$

$$\begin{aligned} \sigma[b'(0)]^{\mathrm{V}} &= -(15\eta^2 + 65.04\eta^3 + 180.06\eta^4 + 397.4586\eta^5 \\ &\quad + 769.8648\eta^6 + \cdots) \end{aligned} \tag{3.10}$$

Comparing Eq. (3.9) with (3.10), we find that, while the density expansion of the results obtained from the CS equation is exact only in the first term, the higher-order terms are seen to be quite accurate. It turns out that the first term in Eqs. (3.9) and (3.10) is exactly the contribution of the first bridge graph(6)



However, if we estimate the second term in the exact expression for $\sigma b'(0)$ from a Monte Carlo evaluation of the $O(\rho^3)$ term of $b(r)$, we find that it is about 52 instead of 65 in Eq. (3.10) (Appendix B). This is probably due to numerical error in the Monte Carlo estimates of integrals and the large

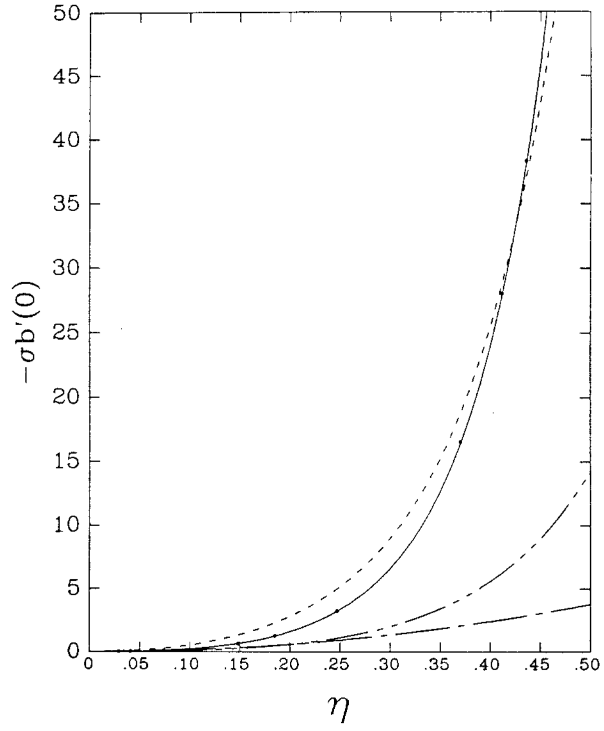


Fig. 1. The derivative of the bridge function at $r = 0$, $-\sigma b'(0)$, as a function of packing fraction η. (——) CS result; (– –) PY result; (●) simulation(16); (----) results from ref. 3; (---) $\sigma b_2'(0)\eta^2 = 15\eta^2$.

interval between two sample points (0.05 Å). Substituting Eqs. (3.7) and (3.8) into Eq. (3.4), we have

$$\sigma[b'(0)]^{\mathrm{PY}} = -\frac{3}{2}\eta\frac{(2+\eta)^2}{(1-\eta)^4}\left(1-\frac{(1-\eta)^4}{(1+2\eta)^2}\right)$$
$$= -(48\eta^2+36\eta^3+\cdots) \tag{3.11}$$

Therefore $[b'(0)]^{\mathrm{PY}}$ does not have the right low-concentration limit. In Fig. 1, $[b'(0)]^{\mathrm{CS}}$, $[b'(0)]^{\mathrm{PY}}$, $[b'(0)]^{\mathrm{MS}}$ (Monte Carlo and molecular dynamic simulation results(16)), $[b'(0)]^{\mathrm{ML}}$ (results obtained by a parametrization method(3)), and $\sigma b_2'(0)\eta^2 = -15\eta^2$ are plotted.[4] The plot shows that the two curves $[b'(0)]^{\mathrm{CS}}$ {which is almost indistinguishable in this figure from $[b'(0)]^{\mathrm{MS}}$} and $[b'(0)]^{\mathrm{PY}}$ cross at $\eta \sim 0.42$, which would not be the case if b^{PY} and b^{exact} are in the same universality class of curves in the sense of Rosenfeld and Ashcroft.(1) At high density, $[b'(0)]^{\mathrm{PY}}$ is remarkably close to the exact result. Since the crossing happens at very high concentration, using b^{PY} to approximate b^{exact} is still a reasonable approximation for low concentrations. However, later we will find out that even at low density the universality of the PY bridge function in the sense of ref. 1 is still only a rough approximation.

From Eq. (2.13), we can obtain the exact result for $d'(0)$,

$$d'(0) = -\frac{6\eta}{\sigma}\,y(\sigma)[y(0)-y(\sigma)] \tag{3.12}$$

The exact results for $y(0)$ in Eq. (3.12) can be obtained by using the first zero-separation theorem(7) in the one-component hard-sphere system,

$$\rho\frac{\partial}{\partial\rho}\ln y(0) = \beta\frac{\partial p}{\partial\rho} - 1 \tag{3.13}$$

The result obtained from the CS equation of state is(4)

$$\ln y^{\mathrm{CS}}(0) = \frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3}$$
$$= 8\eta+15\eta^2+24\eta^3+35\eta^4+48\eta^5+63\eta^6+\cdots \tag{3.14}$$

and the result from the virial expansion of pressure(18) is

$$\ln y^{\mathrm{V}}(0) = \sum_{n=1}^{\infty}\frac{n+1}{n}B_{n+1}\eta^n$$
$$= 8\eta+15\eta^2+24.48\eta^3+35.3\eta^4+47.4\eta^5+\frac{395.5}{6}\eta^6+\cdots \tag{3.15}$$

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[4] The definition of b_2 can be found in Eq. (3.20); $b_2\eta^2$ is the contribution of the first bridge graph.

Substituting Eqs. (3.5) and (3.14), or (3.6) and (3.15), respectively, into (3.12) yields

$$\begin{aligned}\sigma[d'(0)]^{\mathrm{CS}} &= -3\eta\frac{2-\eta}{(1-\eta)^3}\left\{\exp\left[\frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3}\right]-\frac{1}{2}\frac{2-\eta}{(1-\eta)^3}\right\}\\ &= -(33\eta^2+337.5\eta^3+2120\eta^4+10594.5\eta^5+\cdots) \qquad (3.16)\\ \sigma[d'(0)]^{\mathrm{V}} &= -(33\eta^2+336.96\eta^3+2124.14\eta^4\\ &\quad +10648.84\eta^5+46539.2744\eta^6+\cdots) \qquad (3.17)\end{aligned}$$

For comparison, the approximate expression suggested by Henderson and Grundke is⁽⁴⁾

$$\begin{aligned}\sigma[d'(0)]^{\mathrm{HG}} &= -33\eta^2-3\eta\frac{2-\eta}{(1-\eta)^3}\,d^{\mathrm{HG}}(0)\\ &= -(33\eta^2+102\eta^3+1199\eta^4+\cdots) \qquad (3.18)\end{aligned}$$

where the approximate $d^{\mathrm{HG}}(0)$ is given by⁽⁴⁾

$$d^{\mathrm{HG}}(0)=\exp\left[\frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3}\right]-\frac{1+4\eta+4\eta^2-4\eta^3+\eta^4}{(1-\eta)^4} \qquad (3.19)$$

Therefore, the $[d'(0)]^{\mathrm{HG}}$ is only good in the low-concentration limit.

3.2. Approximate Results for *b*(0), *d*(0), *b*(σ), *d*(σ)

We introduce the density expansions of the bridge function and the direct pair correlation function as follows:

$$b(r)=\sum_{n=2}[b_n(r)]\eta^n \qquad (3.20)$$

$$c(r)=-1+\sum_{n=1}[c_n(r)]\eta^n \qquad (3.21)$$

Substituting Eqs. (3.21), (3.20), and (3.15) into (2.10a), we have, at $r=0$,

$$\begin{aligned}b^{\mathrm{V}}(0) &= -1-c(0)-\ln y^{\mathrm{V}}(0)\\ &= \sum_{n=2}^{\infty}\left[-c_n(0)-\frac{n+1}{n}B_{n+1}\right]\eta^n \qquad (3.22)\end{aligned}$$

For the PY approximation, we have⁽¹³⁾

$$c^{\mathrm{PY}}(0)=-y^{\mathrm{PY}}(0)=-(1+8\eta+30\eta^2+76\eta^3+155\eta^4+\cdots) \qquad (3.23)$$

which is an approximation that is exact through the η^3 term.(6) Therefore, substituting $c^{\mathrm{PY}}(0)$ into Eq. (3.22), we can obtain an approximate form of $b(0)$ in which the first two terms are exact:

$$b^{\mathrm{V}}(0) = 15\eta^2 + 51.52\eta^3 + \cdots \tag{3.24}$$

where the first term is $b_2(0)\eta^2$, the contribution of the first bridge graph.(6) The MC value of $b_3(0)$ is 51.516, in good agreement with the exact result (Appendix B). If we substitute $\ln y^{\mathrm{CS}}(0)$ [Eq. (3.14)] and $c^{\mathrm{PY}}(0)$ into (2.10a) at $r = 0$, we obtain another approximation for $b(0)$, which we shall call the CS/PY approximation,

$$\begin{aligned} b(0) &= \frac{\eta^2(2\eta^2 - 8\eta + 15)}{(\eta - 1)^4} \\ &= 15\eta^2 + 52\eta^3 + 120\eta^4 + \cdots \end{aligned} \tag{3.25}$$

This is a more accurate expression than that suggested by Henderson and Grundke,(4)

$$\begin{aligned} b^{\mathrm{HG}}(0) &= y^{\mathrm{CS}}(0) - d^{\mathrm{HG}}(0) - \ln y^{\mathrm{CS}}(0) - 1 \\ &= \frac{3\eta^2(\eta^2 - 4\eta + 5)}{(\eta - 1)^4} \\ &= 15\eta^2 + 48\eta^3 + 105\eta^4 + \cdots \end{aligned} \tag{3.26}$$

where we have used Eqs. (2.11) and (3.19). The superscript HG denotes the Henderson and Grundke results. For comparison, $b^{\mathrm{PY}}(0)$ is [Eqs. (3.3) and (3.7)]

$$\begin{aligned} b^{\mathrm{PY}}(0) &= \frac{(1 + 2\eta)^2}{(1 - \eta)^4} - 1 - \ln \frac{(1 + 2\eta)^2}{(1 - \eta)^4} \\ &= 32\eta^2 + \frac{208}{3}\eta^3 + \cdots \end{aligned} \tag{3.27}$$

Here, we can see again that the PY results do not have an accurate low-concentration limit. In Fig. 2, the approximate $b(0)$ is shown as a function of η. It can be seen that $b^{\mathrm{PY}}(0)$ as a function of η is quite similar to the other approximations shown there. However, it is hard to say what $b^{\mathrm{exact}}(0)$ looks like. According to the calculation by Henderson and Grundke,(4) $c^{\mathrm{exact}}(0)$ is a little bit larger than $c^{\mathrm{PY}}(0)$; therefore, $b^{\mathrm{exact}}(0)$ should be slightly smaller than the result we obtained. The near-exact result obtained in Section 4 is also shown in Fig. 2 and is seen to be close

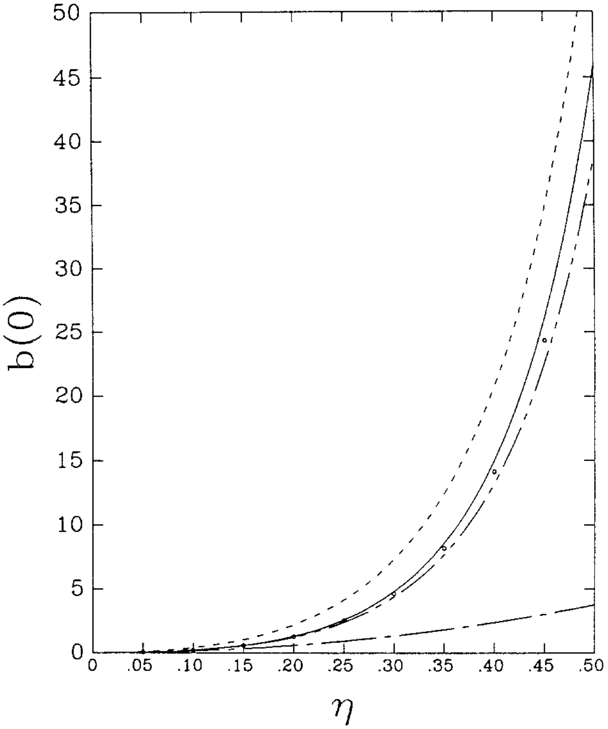

Fig. 2. The bridge function at $r=0$, $b(0)$, as a function of packing fraction η. (——) Results from Eq. (3.25); (– –) PY results; (----) results from Henderson and Grundke, Eq. (3.26); (○) results from the method in the Section 4.2 by using the CS equation of state; (—–) $b_2(0)\eta^2 = 15\eta^2$.

to our approximate $b(0)$ at low concentrations and to stay between our $b(0)$ and $b^{\mathrm{HG}}(0)$ at high concentrations. However, by changing the density of b^{PY} only, it is impossible to fit $b^{\mathrm{exact}}(0)$ and $b'(0)$ at the same time. This can easily be seen by looking at the low-density limit of the bridge function at $r=0$.

By using Eq. (2.10b), we can obtain an approximate expression for $d(0)$,

$$\begin{aligned} d(0) &= y^{\mathrm{CS}}(0) + c^{\mathrm{PY}}(0) \\ &= \exp\left[\frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3}\right] - \frac{(2\eta+1)^2}{(\eta-1)^4} \\ &= 17\eta^2 + \frac{460}{3}\eta^3 + \cdots, \qquad \frac{460}{3} = 153.3333 \end{aligned} \tag{3.28}$$

The exact first two terms of $d(0)$ obtained from virial coefficient are

$$d^{\mathrm{V}}(0) = 17\eta^2 + 153.81333\eta^3 + \cdots \tag{3.29}$$

where we see that the second term in the CS/PY approximation for $d(0)$ is equal to the exact term to within 0.3%.

By using the same procedure we have described above, we can obtain the exact low-concentration limit of $b(\sigma)$ and $d(\sigma)$:

$$b(\sigma) = 2.53\eta^2 + 3.6\eta^3 + \cdots \tag{3.30}$$

$$d(\sigma) = 0.59\eta^2 + 2.65\eta^3 + \cdots \tag{3.31}$$

where we have used the numerical value of $c_3(\sigma)$.(6) The two terms in Eq. (3.30) agree with the analytical result(6) and the numerical result (Appendix B). The first term in Eq. (3.31) was already found by Henderson and Grundke.(4)

For completeness, we give the low-concentration limit of the derivative of bridge function and tail function at $r = \sigma$. They are(6)

$$\sigma b'(\sigma) = -7.9\eta^2 + \cdots \tag{3.32}$$

$$\sigma d'(\sigma) = -3.35\eta^2 + \cdots \tag{3.33}$$

4. AN ANALYTICAL SELF-CONSISTENT EQUATION FOR CAVITY FUNCTION OF A PURE HARD-SPHERE SYSTEM

4.1. General Formulas

Now we set up an analytical approximation for the cavity function $y(r)$ of a pure hard-sphere system. We use a tail function of the form(5)

$$d(r) = \begin{cases} \exp\left[\sum\limits_{n=0}^{m} \alpha_n \left(\dfrac{r}{\sigma} - 1\right)^n\right], & r \leqslant \sigma \\ \dfrac{K}{r/\sigma} \exp\left[-z\left(\dfrac{r}{\sigma} - 1\right)\right], & r > \sigma \end{cases} \tag{4.1}$$

where $m = 3$ in this paper. With such a tail function, the OZ equation relating $h(r)$ and $c(r)$ is analytically solvable.(11) Thus, outside of the core, $y(r)$ is known through the exact relation $y(r) = h(r) + 1$, $r \geqslant \sigma$, while inside the core, we have $y(r)$ from the exact relation $y(r) = d(r) - c(r)$, $r < \sigma$. The direct correlation function inside the core is

$$-c(r) = a + \frac{\bar{b}r}{\sigma} + \frac{1}{2}\eta a \left(\frac{r}{\sigma}\right)^3 + v\,\frac{1 - \exp(-zr/\sigma)}{zr/\sigma} + v^2\,\frac{\cosh(zr/\sigma) - 1}{2r/\sigma K z^2 \exp(z)} \tag{4.2}$$

where a, $\bar{b}$,[5] and v are constants that satisfy complicated nonlinear equations,(11) and a has immediate thermodynamic significance:

$$a = \beta\, \partial p / \partial \rho \tag{4.3}$$

This set of equations is greatly simplified(19) if $y(\sigma)$ and a are known. Adopting the notation in ref. 19, we denote $y(\sigma)$ as y_0. Then we have(19)

$$z = \frac{2}{C - A} \{(U_0 + A - C)\sqrt{A} + [(U_0 + A - C)\, U_0 C]^{1/2}\} \tag{4.4}$$

$$K = \frac{z^2}{6\eta(z+2)^2} \left[\frac{\gamma - \tau x}{(\gamma - \tau)x}\right]^2 U_0 \tag{4.5}$$

$$v = K \frac{1 - x}{\gamma - \tau x} \tag{4.6}$$

$$\bar{b} = \frac{1}{4}\left[2vz - \frac{v^2}{K \exp(z)} - 24\eta y_0^2\right] \tag{4.7}$$

where

$$A = (1 - \eta)^2 a \tag{4.8}$$

$$C = \frac{(1 + 2\eta)^2}{(1 - \eta)^2} \tag{4.9}$$

$$U_0 = 6\eta y_0 - A + 1 \tag{4.10}$$

$$x = \frac{4 + 2z - z^2}{2(2 + z)} \frac{U_0}{U_1} \tag{4.11}$$

$$U_1 = (2 - \sqrt{C})\, U_0 - \Gamma \tag{4.12}$$

$$\Gamma = \frac{1}{2\sqrt{C}}\left[(U_0 + A - C)(U_0 + A) + \frac{1}{4} z^2 (C - A)\right] \tag{4.13}$$

$$\gamma = \frac{1}{2z}\left[\frac{z - 2}{z + 2} + \exp(-z)\right] \tag{4.14}$$

$$\tau = \frac{1}{2z}\left[\frac{z^2 + 2z - 4}{4 + 2z - z^2} + \exp(-z)\right] \tag{4.15}$$

(note that C is not the direct correlation function, which we denote as c).

---

[5] b has been used to denote a bridge function, so we use $\bar{b}$ here.

The only coefficients left to be determined are the α_n. By demanding $d(r)$ to be continuous at $r=\sigma$ up through its first derivative, we have[5]

$$\alpha_0 = \ln K \tag{4.16a}$$

$$\alpha_1 = -(z+1) \tag{4.16b}$$

Using constraints on $d(0)$ and $d'(0)$, we can obtain α_2 and α_3,

$$\alpha_2 = 3\ln\frac{d(0)}{K} + \sigma\frac{d'(0)}{d(0)} - 2z - 2 \tag{4.16d}$$

$$\alpha_3 = 2\ln\frac{d(0)}{K} + \sigma\frac{d'(0)}{d(0)} - z - 1 \tag{4.16e}$$

Once we know the equation of state, the procedure for calculating coefficients in the above equation is as follows:

1. The contact value of y can be obtained from the virial equation

$$y_0 = y(\sigma) = \frac{\beta p/\rho - 1}{4\eta} \tag{4.17}$$

   and the coefficient a obtained by using Eq. (4.3).
2. Then the coefficients z, K, v, and $\bar{b}$ can be calculated by using Eqs. (4.4)–(4.7) with Eqs. (4.8)–(4.15).
3. The tail function at $r=0$ can be obtained from Eqs. (2.10b) and (4.2):

$$d(0) = y(0) + c(0) = y(0) - a - v \tag{4.18}$$

   where $y(0)$ can be obtained from the equation of state by using Eq. (3.13). The derivative of the tail function $d'(0)$ can be obtained by using Eq. (3.12).
4. Finally, α_n is evaluated using Eq. (4.16).

Thus, all the coefficients have simple analytical expressions.

We assume that the equation of state of a pure hard-sphere system has the form

$$p = (1-\theta)\, p_c^{\mathrm{PY}} + \theta p_v^{\mathrm{PY}} \tag{4.19}$$

where p_c^{PY} and p_v^{PY} are the pressures obtained from the compressibility equation and the virial equation in the PY approximation, respectively. If $\theta = 1/3$, then Eq. (4.19) becomes the CS equation. However, using the CS equation of state, we cannot obtain a correct $d'(\sigma)$, as we shall see in Section 4.2. Therefore, we shall use a somewhat different approximate equation of state ($\theta = 1/4 + \eta/2$), which can give us a better result for $d(r)$ inside the core region, although it is a bit less accurate thermodynamicaly than the CS equation of state (it is more accurate than the PY compressibility equation of state, $\theta = 0$, however; see Fig. 3).

4.2. Results for the $\Theta = 1/3$ Approximation

We use the CS equation as the equation of state in this section and we have, by following the procedure we have described,

$$a = \frac{\eta^4 - 4\eta^3 + 4\eta^2 + 4\eta + 1}{(\eta - 1)^4} \tag{4.20}$$

The contact value y_0 is given by Eq. (3.5).

We first check the low-density limit of various coefficients,

$$z = 3.791 + 15.29\eta + 27.43\eta^2 + 37.546\eta^3 + \cdots \tag{4.21}$$

$$d(\sigma) \equiv K = 0.5\eta^2 + 2.8862\eta^3 + 5.88\eta^4 + \cdots \tag{4.22}$$

$$\sigma d'(\sigma) = -K(z+1) = -(1.8955\eta^2 + 18.58658\eta^3 + 80.136\eta^4 + \cdots) \tag{4.23}$$

When compared with the exact equation (3.31), Eq. (4.22) is seen to be remarkably close to the exact result considering such a rough approximation of $d(r)$ outside the core. It is worth noting that the wrong low-density limit ($0.5\eta^2$ instead of $0.59\eta^2$) is due to the error in the fourth virial coefficients in the CS equation.$^{(4)}$ Comparing it with Eq. (3.33), we see that Eq. (4.23) does not give us the correct low-concentration limit of $d'(\sigma)$.

The low-concentration limit for the direct pair correlation functions at $r = 0$ is

$$c(0) = -(a + v) = -(1 + 8\eta + 30\eta^2 + 76\eta^3 + 149.37\eta^4 + \cdots) \tag{4.24}$$

The first four terms are exact,$^{(6)}$ while the fifth is larger than the PY result (Eq. (3.23)], as expected.[6] Using Eqs. (2.10b) and (3.14), we will reproduce the first two terms in Eq. (3.28),

$$d(0) = 17\eta^2 + \frac{460}{3}\eta^3 + 840.8\eta^4 \cdots \tag{4.25}$$

---

[6] The arguments can be found in Section 3.

For the median densities, it has already been shown that the Yukawa form [Eq. (4.2)] of direct pair correlation functions after fitting K and z to generate "exact" pressure and compressibility is able to reproduce the computer simulation results for a pure hard-sphere fluid$^{(11)}$ and to reproduce very good direct correlation functions inside the core.$^{(5)}$

In Fig. 2, the bridge function at $r=0$, $b(0)$, which is calculated from $d(0)$ by using Eq. (2.11), is plotted. The figure is discussed in Section 3.

The tail-function approximations are plotted in Figs. 4 and 5. Discussions of these figures can be found below.

4.3. Results for the $\theta = \frac{1}{4} + \frac{1}{2}\eta$ Approximation

If we use the approximation $\theta = \frac{1}{4} + \frac{1}{2}\eta$, then we find that the equation of state is

$$\begin{aligned}\frac{\beta p}{\rho} &= \frac{-6\eta^4 - 3\eta^3 + 4\eta^2 + 4\eta + 4}{4(1-\eta)^3} \\ &= 1 + 4\eta + 10\eta^2 + 18.25\eta^3 + 27.25\eta^4 + 37\eta^5 + 47.5\eta^6 + \cdots \qquad (4.26)\end{aligned}$$

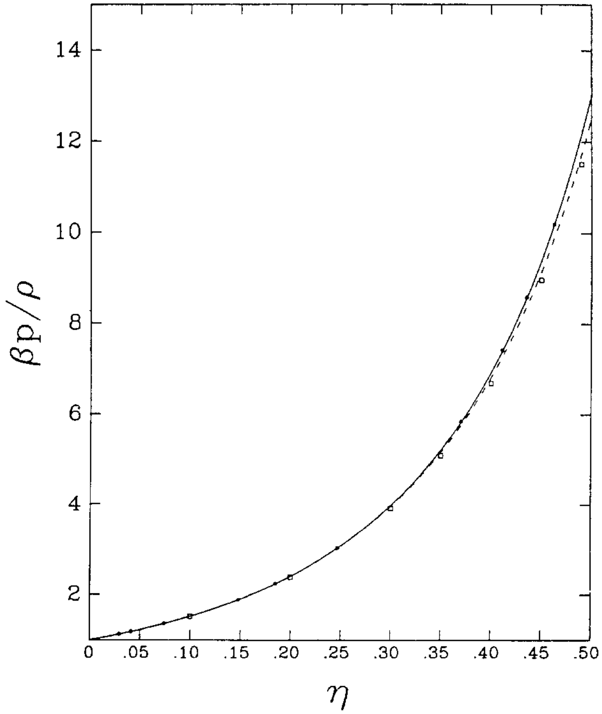

Fig. 3. Equation of state of the one-component hard-sphere fluid. (——) CS equation; (– –) Eq. (4.26) ($\theta = \frac{1}{4} + \frac{1}{2}\eta$); (●) simulation$^{(14)}$; (□) equation of state obtain in ref. 5.

The individual virial coefficients predicted by Eq. (4.26) are not of high accuracy beyond fourth order. However, as shown in Fig. 3, compared with the CS equation the overall results are still very accurate, except near the hard-sphere freezing point. It also turns out that this equation of state is more accurate than that obtained in ref. 5.

Following the procedures in Section 4.1, we have

$$a=\frac{12\eta^5-27\eta^4-12\eta^3+16\eta^2+16\eta+4}{4(1-\eta)^4} \tag{4.27}$$

$$\ln y(0)=\frac{17}{4}\ln(1-\eta)-\frac{\eta(24\eta^3-89\eta^2+157\eta-98)}{8(1-\eta)^3} \tag{4.28}$$

Now, using Eqs. (4.4)–(4.7) with Eqs. (4.8)–(4.15), we examine the low-concentration limit,

$$z=5.3423+7.1821\eta+15.231823\eta^2+\cdots \tag{4.29}$$

$$d(\sigma)=K=0.5625\eta^2+2.49\eta^3+5.87179\eta^4+\cdots \tag{4.30}$$

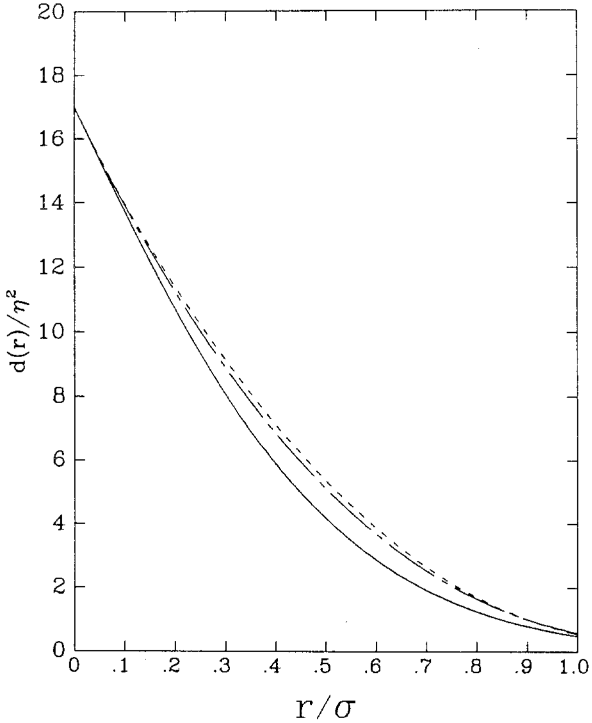

Fig. 4. Plot of $d(r)/\eta^2$ when $\eta \to 0$ as a function of distance. (---) Exact result[6]; (– –) results obtained by using Eq. (4.26); (——) results obtained by using CS equation of state.

$$\sigma d'(\sigma) = -K(z+1) = -(3\eta^2 + 17.34\eta^3 + 57.82\eta^4 + \cdots) \qquad (4.31)$$

$$c(0) = -(1 + 8\eta + 30\eta^2 + 76\eta^3 + 149.73\eta^4 + \cdots) \qquad (4.32)$$

$$d(0) = 17\eta^2 + \frac{461}{3}\eta^3 + 842.5\eta^4 \cdots \qquad (4.33)$$

For comparison, the low-concentration limiting values obtained by ref. 5 (denoted as GGM) are

$$K^{\text{GGM}} = 0.463\eta^2 + \cdots \qquad (4.34)$$

$$z^{\text{GGM}} = 3.184 + \cdots \qquad (4.35)$$

$$\sigma[d'(\sigma)]^{\text{GGM}} = -1.9\eta^2 \qquad (4.36)$$

Therefore, all the low-concentration limiting values predicted by Eq. (4.26) are better than those obtained from the CS equation of state [Eqs. (4.21)–(4.25)] and from ref. 5 [Eqs. (4.34)–(4.36)] compared with the

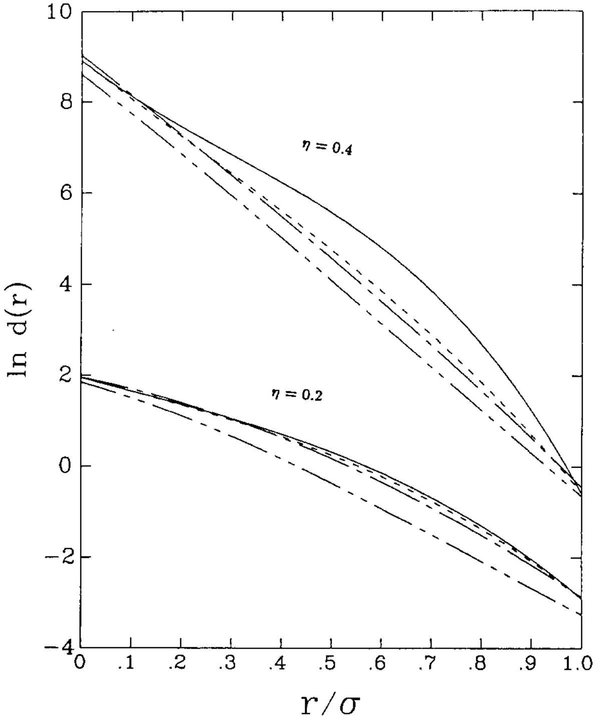

Fig. 5. Plot of ln $d(r)$ inside the core at different packing fractions. (---) Results obtained from ref. 4; (– –) from Eq. (4.26); (—) from CS equation; (----) from ref. 5.

exact results [Eqs. (3.29), (3.31), and (3.33)]. The coefficient α_n can be obtained from Eqs. (4.16a)–(4.16d). Figure 4 shows that the low-concentration limit of the tail function inside the core region is very close to the exact result obtained by ref. 6 and is better than that obtained from the CS equation of state. In Fig. 5, the tail function obtained from Eq. (4.26) is compared with that obtained from the CS equation of state, from ref. 5, and from the parametrization method of ref. 4.

Our conclusion concerning the improvement in the results for $d(r)$ inside the core region when one goes from use of the CS equation to a slightly less accurate equation of state is as follows. The one-Yukawa fit for $c(r)$, $r > \sigma$, is not accurate enough to support self-consistently an extremely accurate equation of state. If one used a two-Yukawa fit for $c(r)$, $r > \sigma$, this would no longer be the case. As yet, the algebra associated with the OZ equation with $c(r)$ of two-Yukawa form is a bit too formidable for it to provide a convenient analytic approach to $y(r)$, but further simplification appears possible.(20)

APPENDIX A

From Eq. (2.3), we have, for $\sigma_2 > \sigma_1$,

$$\begin{aligned}\frac{dG(r)}{dr} &= \left(\int_{\sigma_2+r}^{\infty} + \int_{\sigma_2-r}^{\sigma_2+r} + \int_{\sigma_1+r}^{\sigma_2-r} + \int_{\sigma_1-r}^{\sigma_1+r} + \int_{r}^{\sigma_1-r}\right) F_1(t, r)\, dt \\ &\quad + \int_0^r dt\, F_2(t, r) \\ &= \mathrm{I} + \mathrm{II} + \mathrm{III} + \mathrm{IV} + \mathrm{V} + \mathrm{VI} \qquad \text{(A.1)}\end{aligned}$$

where

$$\mathrm{I} \equiv \int_{\sigma_2+r}^{\infty} F_1(t, r)\, dt, \qquad \mathrm{II} \equiv \int_{\sigma_2-r}^{\sigma_2+r} F_1(t, r)\, dt$$

$$\mathrm{III} \equiv \int_{\sigma_1+r}^{\sigma_2-r} F_1(t, r)\, dt, \qquad \mathrm{IV} = \int_{\sigma_1-r}^{\sigma_1+r} F_1(t, r)\, dt$$

$$\mathrm{V} \equiv \int_{r}^{\sigma_1-r} F_1(t, r)\, dt, \qquad \mathrm{VI} \equiv \int_0^r F_2(t, r)\, dt$$

$$F_1(t, r) \equiv t[(r+t) f_1(r+t) + (t-r) f_1(t-r)]\, f_2(t)$$

$$F_2(t, r) \equiv t[(r+t) f_1(r+t) - (r-t) f_1(r-t)]\, f_2(t)$$

and we have used the condition $r < (\sigma_2 - \sigma_1)/2$, $\sigma_1/2$. Then it is easy to prove [notice that $f_1(\sigma_2) = f_1(\sigma_2^+) = f_1(\sigma_2^-)$, $f_2(\sigma_1) = f_2(\sigma_1^+) = f_2(\sigma_1^-)$]

$$\left.\frac{d}{dr}\,\mathrm{I}\right|_{r \to 0} = -2\sigma_2^2 f_1(\sigma_2)\, f_2(\sigma_2^+)$$

$$\left.\frac{d}{dr}\,\mathrm{II}\right|_{r \to 0} = 2\sigma_2^2 f_1(\sigma_2)\, f_2(\sigma_2^-) + 2\sigma_2^2 f_1(\sigma_2)\, f_2(\sigma_2^+)$$

$$\left.\frac{d}{dr}\,\mathrm{III}\right|_{r \to 0} = -2\sigma_2^2 f_1(\sigma_2)\, f_2(\sigma_2^-) - 2\sigma_1^2 f_1(\sigma_1^+)\, f_2(\sigma_1)$$

$$\left.\frac{d}{dr}\,\mathrm{IV}\right|_{r \to 0} = 2\sigma_1^2 f_1(\sigma_1^+)\, f_2(\sigma_1) + 2\sigma_1^2 f_1(\sigma_1^-)\, f_2(\sigma_1)$$

$$\left.\frac{d}{dr}\,\mathrm{V}\right|_{r \to 0} = -2\sigma_1^2 f_1(\sigma_1^-)\, f_2(\sigma_1)$$

$$\left.\frac{d}{dr}\,\mathrm{VI}\right|_{r \to 0} = 0$$

Therefore,

$$G''(0) = 0 \tag{A.3}$$

For $\sigma_1 = \sigma_2$, the procedure is the same. We only give the result,

$$G''(0) = -\sigma^2[f_1(\sigma^+) - f_1(\sigma^-)][f_2(\sigma^+) - f_2(\sigma^-)] \tag{A.4}$$

APPENDIX B

Expanding Eq. (2.10a) in terms of density, we have

$$b_3(r) = \begin{cases} -c_3(r) - y_3(r) + y_1(r)\, y_2(r) - [y_1(r)]^3/3, & r \leqslant \sigma \\ -c_3(r) + y_1(r)\, y_2(r) - [y_1(r)]^3/3, & r > \sigma \end{cases} \tag{B.1}$$

where

$$b(r) \equiv \sum_{n=2}^{\infty} b_n(r)\eta^n \tag{B.2}$$

$$y(r) \equiv \sum_{n=0}^{\infty} y_n(r)\eta^n \tag{B.3}$$

$$c(r) \equiv \sum_{n=0}^{\infty} c_n(r)\eta^n \tag{B.4}$$

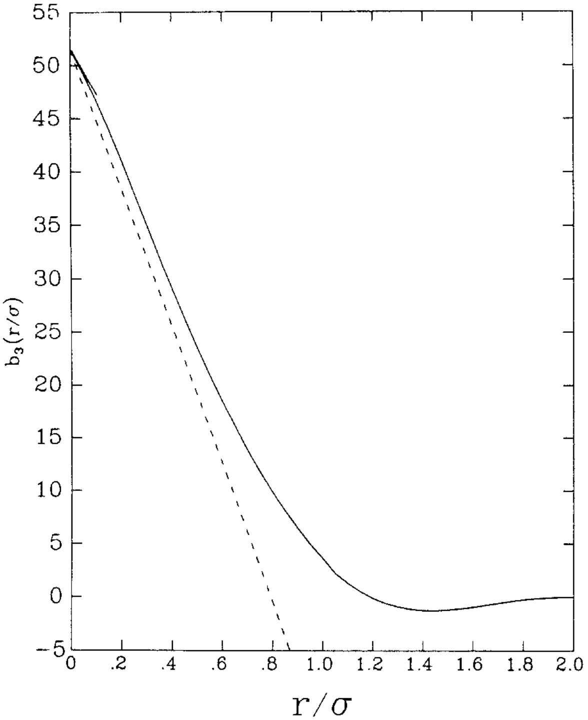

Fig. 6. Numerical $b_3(r/\sigma)$ [Eq. (B.1)] as a function of distance (r/σ). The straight dashed line is obtained from the exact value of $b_3(0)$ and the exact slope of $b_3(r)$ at $r=0$ [Eqs. (3.24) and (3.10)].

Since all functions on the right-hand side of Eq. (B.1) are known either analytically or numerically,(6) we can obtain a numerical assessment of $b_3(r)$ easily. As seen in Fig. 6, the resulting $b_3(0)=51.516$ is in good agreement with the exact analytical result 51.52. The derivative of the bridge function at $r=0$, $b'(0)$, obtained by the least-squares polynomial fit of the numerical $b_3(r)$ is about 52, however, which is in poor agreement with the exact result, 65.04, of Section 3. This must be due to numerical error in the available numerical assessment of $c_3(r)$ and $y_3(r)$. In Fig. 6 the numerical $b_3(r)$ is plotted and its slope is compared with the exact result of the slope at $r=0$ (straight line).

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