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On the Isothermal Density Derivative of $g(r)$ and a New Theory of the Pair Correlation Function of Hard Spheres

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A new representation is obtained for the isothermal density derivative of $g(r)$. It explicitly exhibits the contributions of potential energy terms that are not pairwise additive. Consideration of a previously known result shows that one has to be rather cautious when using it to obtain information on the triplet correlation function from the well-known relation between this function and $\partial g/\partial \rho$, due to large cancellations which take place at high density. By integrating with respect to density the new representation for $\partial g/\partial \rho$, after a suitable closure has been introduced, we obtain an augmented Percus–Yevick equation for hard spheres which has full thermodynamic consistency. The equation of state and the cavity function $y(r)$ are very accurate at low density and considerably improve PY at medium density, so that this appears to be a useful new approach to the theory of fluids, but it is necessary to improve the closure in order to treat a dense fluid.

KEY WORDS: Hard spheres; pair correlation function; triplet correlation function; Percus–Yevick.

1. INTRODUCTION

In this paper we first derive and examine a general identity relating the functional derivative of the pair distribution function of a molecular system with respect to local density $\delta g(12)/\delta \rho(3)$ and the triplet distribution function $g(123)$. We then use the identity to obtain an equation relating the density derivative $\partial g(12)/\partial \rho$ and an integral involving $g(123)$. The equation

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This paper is dedicated to Jerry Percus on the occasion of his 65th birthday.

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yields a representation for $\partial g(12)/\partial\rho$ that suggests a new integral equation for an approximate $g(12)$ which we investigate for a uniform system of hard spheres.

The identity relating $\delta g(12)/\delta\rho(3)$ and $g(123)$ has been used before by van Beijeren$^{(1)}$ in investigating the time-dependent properties of a hard-sphere system, but we have not found its derivation in the open literature. Since it is a useful and fundamental result in the functional calculus of statistical mechanics, we prove it, and then give it a graph-theoretic interpretation which helps illuminate its structure. Taking the volume integral of both sides of the identity yields a relation between the density derivative $\partial g(12)/\partial\rho$ and an integral involving $g(123)$. A form of this relation has been known for many years. It was derived by Buff and Brout and used by them as a test of the Kirkwood superposition approximation.$^{(2)}$ The relation was thereafter rediscovered by Schofield$^{(3)}$ (and restudied in connection with the superposition approximation by Hutchinson$^{(4)}$). It has been subsequently discussed and used by various workers; in particular, Raveché and Mountain have considered it in detail.$^{(5)}$

We focus on a representation of $\partial g(12)/\partial\rho$ different from that used by earlier workers, which our analysis suggests may be fruitful new starting point for approximation, and we explore its use for the case of a hard-sphere fluid.

In Section 2, we derive our identity. In Section 3, we rederive and analyze it using cluster expansions that include the contributions of intrinsic n-body potential energy terms for all n. In Section 4, we integrate over volume to get the Buff–Brout expression for $\partial g(12)/\partial\rho$ in terms of $g(123)$ as well as a variant of that expression. In Section 5, we use our results to motivate new integral equations to yield approximate radial distribution functions for a hard-sphere fluid. In Section 6, we consider some quantitative results of the closures. We summarize some conclusions in Section 7.

2. AN IDENTITY IN THE FUNCTIONAL CALCULUS

In the grand ensemble, the grand partition function Ξ is a fundamental generating functional. In particular, one generates the probability densities $\rho_n(\cdots n)$ by differentiating Ξ with respect to $z(i)$, where $z(i)=ze^{-\beta\varphi_1(i)}$, z is activity, and $\varphi_1(i)$ is external field,

$$\rho_n(1\cdots n)=\prod_{i=1}^{n} e(i)\,\delta^n\Xi\Big/\prod_{i=1}^{n}\delta\,z(i) \tag{2.1}$$

It is convenient to work with the distribution functions $g_n(1\cdots n)$, where

$$\prod_{i=1}^{n} \rho_1(i)\, g_n(1\cdots n) = \rho_n(1\cdots n) \tag{2.2}$$

We shall be principally interested here in $\rho_1(i)$, $\rho_2(12)$, $\rho_3(123)$, $u_2(12) = \rho_2(12) - \rho_1(1)\,\rho_1(2)$, $g_2(12)$, and $h_2(12) = g_2(12) - 1$. For convenience, we shall drop the subscripts on all these functions and write simply $\rho(1)$, $\rho(12)$, $\rho(123)$, $u(12)$, $g(12)$, and $h(12)$. We shall also use the delta function $\delta(12)$. For convenience we also introduce the symbol

$$H(12/3) = \delta g(12)/\delta\rho(3) \tag{2.3}$$

Our strategy will be to use the chain rule

$$z(3)\,\frac{\delta\rho(12)}{\delta z(3)} = z(3)\int d(4)\,\frac{\delta\rho(12)}{\delta\rho(4)}\,\frac{\delta\rho(4)}{\delta z(3)} \tag{2.4}$$

The left-hand side can be expressed in terms of $g(123)$, $g(12)$, and $\rho(i)$. The right-hand side can be expressed in terms of $H(12/3)$, $h(ij)$, and $\rho(i)$. We start with the left-hand side and use (2.1) to represent $\rho(12)$ and to identify $\rho(123)$. We find

$$\begin{aligned} z(3)\,\frac{\delta\rho(12)}{\delta z(3)} &= \rho(123) - \rho(12)\,\rho(3) + \rho(12)\,\delta(23) + \rho(12)\,\delta(13) \\ &= \rho(1)\,\rho(2)\,\rho(3)[g(123) - g(12)] + \rho(12)\,\delta(23) + \rho(12)\,\delta(13) \end{aligned} \tag{2.5}$$

In analyzing the right-hand side of (2.4), we use (2.1) to reexpress $z(3)[\delta\rho(4)/\delta z(3)]$:

$$z(3)\,\frac{\delta\rho(4)}{\delta z(3)} = u(34) + \rho(3)\,\delta(34) \tag{2.6}$$

We use (2.1) to reexpress $\delta\rho(12)/\delta\rho(3)$:

$$\frac{\delta\rho(12)}{\delta\rho(4)} = \rho(1)\,\rho(2)\,\frac{\delta g(12)}{\delta\rho(4)} + \frac{\rho(12)}{\rho(4)}\,[\delta(24) + \delta(14)] \tag{2.7}$$

Using (2.6) and (2.7) with (2.3), we have

$$\begin{aligned} z(3)\int d(4)\,&\frac{\delta\rho(12)}{\delta\rho(4)}\,\frac{\delta\rho(4)}{\delta z(3)} \\ &= \rho(1)\,\rho(2)\,\rho(3)\Bigg[H(12/3) + \int d(4)\,H(12/4)\,\rho(4)\,h(34) \\ &\quad + g(12)\,h(23) + g(12)\,h(13)\Bigg] + \rho(12)[\delta(23) + \delta(13)] \end{aligned} \tag{2.8}$$

Equating the right-hand sides of (2.5) and (2.8), we find

$$g(123)-g(12)[1+h(13)+h(23)]$$
$$=H(12/3)+\int d(4)\,H(12/4)\,\rho(4)\,h(34) \tag{2.9}$$

This is our sought identity. It is worth noting several several alternative ways of expressing it. First of all, the left-hand side can be reexpressed by using $g(ij)=h(ij)+1$:

$$g(123)-g(12)[1+h(13)+h(23)]$$
$$=g(123)-g(12)\,g(13)\,g(23)+g(12)\,h(13)\,h(23) \tag{2.10}$$

Thus, under the Kirkwood superposition approximation

$$g(123)=g(12)\,g(23)\,g(13) \tag{2.11}$$

the right-hand side becomes simply $g(12)\,h(13)\,h(23)$. Second, it is sometimes natural and convenient to consider (2.9) divided by $g(12)$. On the right-hand side, this is equivalent to replacing the $H(12/i)$, which is $\delta g(12)/\delta\rho(i)$, by $\delta \ln g(12)/\delta\rho(i)$, which we shall denote as $G^{Ii}(12/i)$:

$$G^{I3}(12/3)=\delta \ln g(12)/\delta\rho(3) \tag{2.12}$$

The superscript $I3$ refers to "irreducibility in the 3 direction" in a sense that is associated with a cluster-expansion representation of (2.12) considered in the next section. On the left-hand side of (2.9), division by $g(12)$ leaves us with a function we shall denote as $G(12/3)$,

$$G(12/3)=g(123)/g(12)-1-h(13)-h(23) \tag{2.13}$$

or, equivalently,

$$G(12/3)=g(123)/g(12)-g(13)\,g(23)+h(13)\,h(23) \tag{2.14}$$

In the superposition approximation

$$G(12/3)=h(13)\,h(23) \tag{2.15}$$

In the notation just introduced, our identity is

$$G(12/3)=G^{I3}(12/3)+\int d(4)\,G^{I4}(12/4)\,\rho(4)\,h(34) \tag{2.16}$$

3. CLUSTER-EXPANSION ANALYSIS

One gains additional insight into Eq. (2.16) by considering the ρ-vertex, h-bond cluster expansions of the functions that appear in it. By comparing the ρ-vertex, h-bond expansion of $G(12/3)$ with that of $\delta \ln g(12)/\delta\rho(3)$, we can in fact rederive (2.16) with $G^{I3}(12/3)$ given by (2.12). The derivation goes through whether we have intrinsic n-body potential terms, $\varphi_n(1 \cdots n)$, $n \geqslant 3$, or not. If we do, then the expansions we consider will have f_n-faces, $n \geqslant 3$, as well as ρ-vertices and h-bonds, where the f_n-faces represent the functions $\exp(-\beta\varphi_n) - 1$. The necessary expansions are given in Stell$^{(6)}$ and we follow the terminology and conventions of that reference, including its symmetry-number convention. From the expansion of $g(123)$ given there we have immediately

$G(12/3) = h(13)\,h(23) +$ the sum of all distinct connected graphs with three white 1-circles labeled 1, 2, and 3, respectively, at least one black ρ-circles, some or no h-bonds, and some or no f_s-faces, $s \geqslant 3$, such that the graphs are free of articulation circles and articulation pairs of circles and there is no bond between the circles labeled 1 and 2 (3.1)

Among these graphs, there will be those for which only a single h-bond and no $f_s - 1$ faces are incident upon the white circle labeled 3. Thus the representation of the sum of these graphs can be reduced to a convolution at a ρ-circle of a three-point function $A(12/4)$ and $h(43)$,

$$C^{R3}(12/3) = \int d(4)\, A(12/4)\, \rho(4)\, h(43) \tag{3.2}$$

Let us denote as $G^{I3}(12/3)$ the sum of all the rest of the graphs in $G(12/3)$ that cannot be so reduced. They can be characterized by an extra connectedness condition to give

$G^{I3}(12/3) = h(13)\,h(23) +$ the sum of graphs in (3.1) such that there are at least two paths along bonds or f_s-face edges from the circle labeled 3 to the circles labeled 1 and 2, respectively, that share no circles except the circle labeled 3 (3.3)

This is clearly the same sum that characterizes the $A(12/3)$ of Eq. (3.2), so we have

$$G(12/3) = G^{I3}(12/3) + G^{R3}(12/3) \tag{3.4a}$$

$$G^{R3}(12/3) = \int d(4)\, G^{I4}(12/4)\, \rho(4)\, h(43) \tag{3.4b}$$

We now show that $G^{I3}(12/3)$ is also just the sum of graphs in the ρ-vertex, h-bond, f_s-face, $s \geqslant 3$, expansion of $\delta \ln g(12)/\delta\rho(3)$, i.e., we shall demonstrate Eq. (2.12).

To do this, we first consider the ρ-vertex, f_s-face, $s \geqslant 2$, expansion of the 2-particle potential of mean force, or equivalently $\ln g(12)$. We have

> $\ln g(12) = -\beta\phi_2(12) +$ the sum of all distinct connected graphs with two white 1-circles labeled 1 and 2, respectively, at least one black ρ-circle, and f_s faces, $s \geqslant 2$, such that the graphs are free of articulation circles and free of a bond between the labeled circles, which are not an articulation pair of circles (3.5)

We note that the freedom from articulation circles implies that there are at least two paths along f_s-face edges from any black circle to the circles labeled 1 and 2, respectively, that share no circles except the terminal black circle. When each black circle becomes a while circle labeled 3, upon functional differentiation with respect to $\rho(3)$, this connectedness property persists. We have

> $\delta \ln g(12)/\delta\rho(3) =$ the sum of all distinct connected graphs with three white 1-circles labeled 1, 2, and 3, respectively, some or no black ρ-circles, and f_s-faces, $s \geqslant 2$, such that the graphs are free of articulation circles and free of a bond between the circles labeled 1 and 2, respectively, which are not an articulation pair of circles; moreover, there are at least two paths along f_s-face edges from the circle labeled 3 to the circles labeled 1 and 2, respectively, that share no circles except the circle labeled 3. (3.6)

Finally, we can reexpress this sum by eliminating f_2-faces (i.e., Mayer f-bonds) in favor of h-bonds by adding the stipulation that there are no articulation pairs of circles:

> $\delta \ln g(12)/\delta\rho(3) =$ the sum of (3.6) with h-bonds replacing f_2-faces and the added condition that there are no articulation pairs of circles (3.7)

Comparing (3.7) and (3.3), we arrive at (2.12).

The most important anticipated affect of intrinsic or excess n-body terms in the potential energy, $n \geqslant 3$, will be the direct effect of the 3-body term which represents a ρ-independent contribution to $g(123)$. One has[6]

$$g(123) = g(12)\, g(13)\, g(23)\, e_3(123) + O(\rho) \tag{3.8}$$

where $O(\rho)$ signifies a term of order ρ and

$$e_3(123) = \exp\{-\beta\varphi_3(123)\} = f_3(123) + 1 \tag{3.9}$$

Here $\varphi_3(123)$ is the contribution to the potential energy $\Phi_3(123)$ of three particles excess to the sum of pair potentials

$$\Phi_3(123) = \varphi(12) + \varphi(13) + \varphi(23) + \varphi_3(123) \tag{3.10}$$

From (3.8) and (2.13) it folows immediately that when $\varphi_3 \neq 0$, $h(13)\,h(23)$ is not the only term of zeroth order in ρ. Instead one has

$$G(12/3) = h(13)\,h(23) + g(13)\,g(23)\,f_3(123) + O(\rho) \qquad (3.11)$$

Equation (3.11) also immediately follows from Eq. (3.1).

4. EQUATION FOR $\partial \ln g(12)/\partial\rho$

For a uniform system [i.e., when $\rho(i) = \rho$] we can immediately obtain an equation involving $\partial \ln g(12)/\partial\rho$ by applying $\int d(3)\,\rho(3)$ to both sides of (2.16) and noting that, since $G^{I3}(12/3) = \delta \ln g(12)/\delta\rho(3)$,

$$\rho\,\frac{\partial \ln g(12)}{\partial\rho} = \int d(3)\,\rho(3)\,G^{I3}(12/3) \qquad (4.1)$$

We obtain from (2.16)

$$\int d(3)\,\rho(3)\,G(12/3) = \rho\,\frac{\partial \ln g(12)}{\partial\rho} + [S(0) - 1]\,\rho\,\frac{\partial \ln g(12)}{\partial\rho}$$

or

$$\int d(3)\,\rho(3)\,G(12/3) = S(0)\,\rho\,\frac{\partial \ln g(12)}{\partial\rho} \qquad (4.2)$$

Here $S(0)$, the structure factor $S(\mathbf{k})$ associated with $g(12)$ evaluated at $\mathbf{k} = 0$, is a dimensionless measure of isothermal compressibility that comes out of (2.16) upon the integration over $h(34)$:

$$S(0) = 1 + \int d(5)\,\rho(4)\,h(34) = (\partial\rho/\partial\mu)/\beta\rho \qquad (4.3)$$

When all potentials in the problem only depend upon the distances between particle centers, $\varphi(12)$, $g(12)$, and $h(12)$ are often written as $\varphi(r)$, $g(r)$, and $h(r)$, where $r_s = |\mathbf{r}_1 - \mathbf{r}_2|$, and we shall follow this practice where it is convenient to do so. It is also natural to separate the convolution between the two h-functions appearing in the integral over $G(12/3)$ in (4.2) from the rest of the expression and write

$$S(0)\rho\,\partial \ln g(r)/\partial\rho = \rho h \otimes h + F(r) \qquad (4.4)$$

where

$$h \otimes h = \int d(3)\,h(13)\,h(32) \qquad (4.5)$$

$$F(r) = \rho \int d(3)\,[g(123)/g(12) - g(13)\,g(23)] \qquad (4.6)$$

Equation (4.4) is the relation considered in refs. 2–5.

From our discussion at the end of the last section we see that in the absence of intrinsic n-body potential terms, $n \geqslant 3$, $F(r)$ is of order ρ^2. In the presence of such terms we have instead

$$F(r) = \rho \int d(3)\, g(13)\, g(23)\, f_3(123) + O(\rho^2) \tag{4.7}$$

For dense fluids, $S(0) \ll 1$ and a numerical comparison of the three terms in (4.4) shows that the first is small in magnitude compared to the two on the right-hand side, which are of opposite sign and similar magnitude. Thus, approximating $F(r)$ is not a felicitous procedure for obtaining an approximate $\partial \ln g(r)/\partial \rho$ via (4.4). It seems more promising to write

$$\rho \frac{\partial \ln g(r)}{\partial \rho} = \rho h \otimes h + F_{\mathrm{irr}}(r) \tag{4.8}$$

where $F_{\mathrm{irr}}(r)$ is defined directly in terms of G^{I3},

$$\int d(3)\, \rho(3)\, G^{I3}(12/3) = \rho h \otimes h + F_{\mathrm{irr}}(r) \tag{4.9}$$

Here $F_{\mathrm{irr}}(r)$ is thought of as being directly defined as a functional of h by the h-bond, f_s-face representation of $G^{I3}(12/3)$ given in Section 3. That is,

$$\begin{aligned} F_{\mathrm{irr}}(r) &= \rho \int d(3)\, g(13)\, g(23)\, f_3(123) \\ &\quad + \rho \int d(3) \left\{ \begin{array}{l} \text{the sum of all distinct connected graphs with three} \\ \text{white 1-cirles labeled 1, 2, 3, resp., at least one black} \\ \text{ρ-circle, some or no h-bonds and f_s-faces, $s \geqslant 3$,} \\ \text{such that the graphs are free of articulation circles} \\ \text{and articulation pairs of circles and have at least} \\ \text{two paths along bonds and/or f_s-face edges from the} \\ \text{circle labeled 3 to circles labeled 1 and 2, resp., that} \\ \text{share no circles except the circle labeled 3; there is} \\ \text{no h-bond between the circles labeled 1 and 2} \end{array} \right. \end{aligned} \tag{4.10}$$

We explore the use of (4.8) for a hard-sphere system in the remainder of this paper.

5. FROM THE ISOTHERMAL DENSITY DERIVATIVE OF $g(r)$ TO A THEORY FOR THE RADIAL DISTRIBUTION FUNCTION

The two relations (4.4) and (4.8) express the isothermal density derivative of $g(r)$ in term of the sum of the two terms; the first is the convolution of $h(r)$ with itself and the second is what we have called, respectively, $F(r)$ and $F_{\text{irr}}(r)$. Both $F(r)$ and $F_{\text{irr}}(r)$ are functionals just of $h(r)$, so that if these functions are approximated by an explicit functional of $h(r)$, one could integrate those equations with respect to density starting from the initial condition

$$g(r, \rho=0)=\exp[-\beta\phi(r)] \tag{5.1}$$

In this way we would obtain an approach to the theory of $g(r)$ with the remarkable property that the interatomic potential appears only in the initial condition. Actually, this would provide at the same time a theory of the cavity function

$$y(r)=g(r)\exp[\beta\phi(r)] \tag{5.2}$$

since $\partial \ln g(r)/\partial\rho = \partial \ln y(r)/\partial\rho$.

For instance, if the three-body correlation function $g^{(3)}(r_1, r_2, r_3)$ is approximated by the Kirkwood superposition approximation, the function $F(r)$ is identically zero and the resulting equation for $g(r)$ is

$$S(0)\,\partial \ln g(r)/\partial\rho = h\otimes h \tag{5.3}$$

If we attempt to integrate this equation, we find very poor results and we can easily understand the reason. We have already noted that at high density where $S(0) \ll 1$ there is an almost complete cancellation between $h\otimes h$ and some contributions to $F(r)$ due to triplet correlations in excess of superposition, so that only a very accurate approximation for $g^{(3)}$ can lead to a useful equation for $g(r)$. This compensation is built into the structure of the other relation (4.8) involving $F_{\text{irr}}(r)$, so that this appears to be a much better starting point.

This new correlation function $F_{\text{irr}}(r)$ has a well-defined cluster expansion as well as an expression in terms of functional differentiation, as shown in the previous section, but a clear physical interpretation of $F_{\text{irr}}(r)$ is still missing. However, if $g(r)$ is known at different densities for a given $\beta\phi$, the relation (4.8) can be used to actually compute $F_{\text{irr}}(r)$ and get some insight into this function.

We consider the case of hard spheres of diameter σ. The PY equation(7) is rather accurate for this interaction and we have computed $F_{\text{irr}}(r)$ within this approximation from the analytical solution(8) of the PY equation. For details of the computation see the Appendix. The Verlet–Weis(9) (VW) form for $g(r)$ gives an empirical rdf which is an accurate representation of the results of simulation computation at all densities. Also from the VW form, extended inside the core by Grundke and Henderson,(10) we have computed $F_{\text{irr}}(r)$ and this result should represent an essentially exact representation of $F_{\mathrm{irr}}(r)$ for hard spheres. The two $F_{\mathrm{irr}}(r)$ obtained from the VW and the PY $g(r)$ have a rather similar behavior at all densities and in Fig. 1 we show $F_{\mathrm{irr}}^{\mathrm{VW}}$ and the difference $F_{\mathrm{irr}}^{\mathrm{VW}} - F_{\mathrm{irr}}^{\mathrm{PY}}$ at the density $\rho\sigma^3 = 0.9$. The $F_{\mathrm{irr}}^{\mathrm{VW}}(r)$ is large and positive inside the core and then it oscillates around zero beyond the core; $F_{\mathrm{irr}}^{\mathrm{PY}}(r)$ outside the core is rather similar to $F_{\mathrm{irr}}^{\mathrm{VW}}$, but the oscillations have a slightly different amplitude. Around the core diameter the deviation between $F_{\mathrm{irr}}^{\mathrm{PY}}$ and $F_{\mathrm{irr}}^{\mathrm{VW}}$ becomes significantly larger until the two functions have a completely different behavior below a distance of order $\sigma/2$. The $F_{\mathrm{irr}}^{\mathrm{PY}}$ first has a maximum and then becomes negative as $r \to 0$, whereas $F_{\mathrm{irr}}^{\mathrm{VW}}$ becomes very large and positive at small r and has only a shallow maximum at short distance. This discrepancy is a consequence of the known inadequacy of the PY equation inside the core.

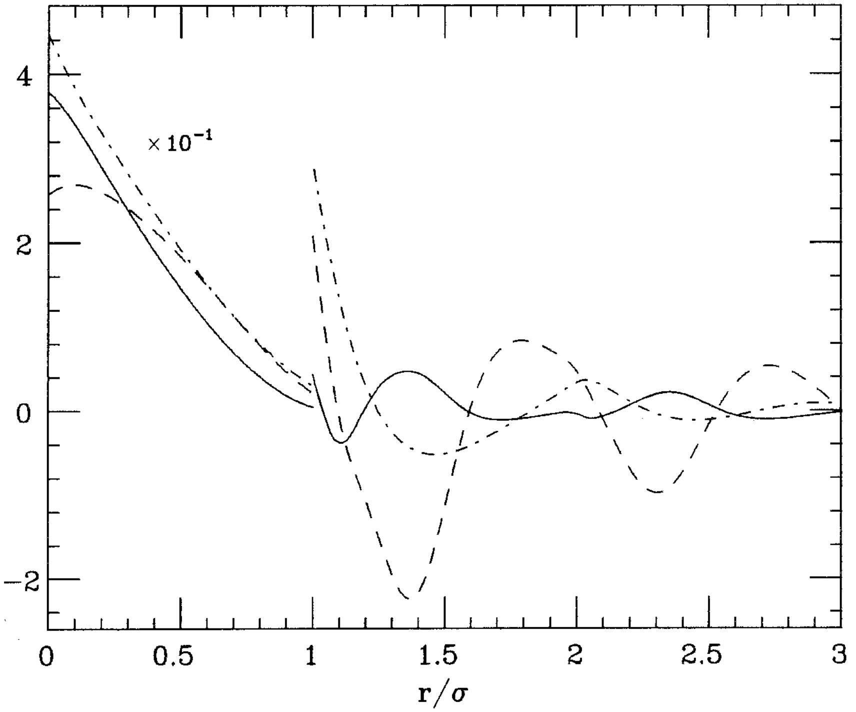

Fig. 1. Plot of $P_{\mathrm{irr}}^{\mathrm{VW}}$ corresponding to the Verlet–Weis form of g(- - -), of the difference $F_{\mathrm{irr}}^{\mathrm{VW}} - F_{\mathrm{irr}}^{\mathrm{PY}}$(—), and of $\theta = h - c$ corresponding to the Verlät–Weis g (-·-) at density $\rho\sigma^3 = 0.9$. For $r < \sigma$ the functions are reduced by a factor 10.

Our strategy to improve upon the PY equation is the following. We write the basic equation (4.8) in the form

$$\frac{\partial \ln y(r)}{\partial \rho} = h \otimes h + \frac{F_{\text{irr}}^{\text{PY}}(r)}{\rho} + \Delta(r) \tag{5.4}$$

where

$$F_{\text{irr}}^{\text{PY}} = \rho \frac{\partial \ln y^{\text{PY}}(r)}{\partial \rho} - \rho h^{\text{PY}} \otimes h^{\text{PY}} \tag{5.5}$$

is $F_{\text{irr}}(r)$ in the PY approximation at the same density (and temperature if the pair interaction is not the hard-sphere one) of the problem at hand. We model the correction term to PY:

$$\Delta(r) = \frac{F_{\text{irr}}(r)}{\rho} - \frac{F_{\text{irr}}^{\text{PY}}(r)}{\rho} \tag{5.6}$$

in terms of correlation functions of the system and here we can use thermodynamic consistency conditions as constraints on parameters introduced to represent $\Delta(r)$. It is clear that in (5.4)–(5.6) we could use in place of $F_{\text{irr}}^{\text{PY}}$ the approximate form corresponding to some other scheme like HNC if this is more accurate then PY.

In this paper we study only the hard-sphere system, so that the PY approximation appears to be the most appropriate starting point. It is clear that if we put $\Delta(r) = 0$ in Eq. (5.4), the integration of that equation gives back $y^{\text{PY}}(r)$. We consider three different closures for $\Delta(r)$.

Closure I. We have noticed that outside the core the "exact" $F_{\text{irr}}^{\text{VW}}$ differs from $F_{\text{irr}}^{\text{PY}}$ mainly for an amplitude factor and this suggests the following closure:

$$\Delta^{\text{I}}(t) = \gamma \frac{F_{\text{irr}}^{\text{PY}}(r)}{\rho} \tag{5.7}$$

This closure will give very poor results inside the core, but it is a property of Eq. (5.4) that $y(r)$ in the range $r > \sigma$ does not depend on the value taken by $y(r)$ for $r < \sigma$, so that this approximation might be of some value for $g(r)$. The parameter γ is implicitly fixed by the requirement that the equation of state obtained by the virial route be the same as that give by the compressibility route, i.e.,

$$S(0) = k_{\text{B}} T \Big/ \left(\frac{\partial p_v}{\partial \rho}\right), \qquad p_v = k_{\text{B}} T \rho \left[1 + \frac{2\pi}{3} \rho \sigma^3 y(\sigma)\right] \tag{5.8}$$

This condition is imposed at each density so that γ will be density dependent.

Closure II. For hard spheres additional constraints derive from zero-distance theorems for $y(r)$, but in order to use them, $\Delta(r)$ at short distance must correct the wrong behavior of $F_{\mathrm{irr}}^{\mathrm{PY}}$. As one can see from Fig. 1, the difference $F_{\mathrm{irr}}^{\mathrm{VW}} - F_{\mathrm{irr}}^{\mathrm{PY}}$ inside the core is rather similar to the function

$$\theta(r) = \rho h \otimes c = h(r) - c(r) \tag{5.9}$$

where $c(r)$ is the Ornstein–Zernike (OZ) direct correlation function and in (5.9) we have used the OZ relation in writing the last equality. This suggests that we write $\Delta(r)$ in terms of $\theta(r)$ and, in fact, one can give some support to this ansatz from an analysis of the diagrammatic expansion of $\Delta(r)$. However, this cannot be correct at large distance because the oscillations of F_{irr} and of θ around zero are not in phase. Therefore, we introduce a damping factor and our closure II reads

$$\Delta^{\mathrm{II}}(r) = A\theta(r)\exp[-(r/r_0)^2] \tag{5.10}$$

and the two parameters A and r_0 are determined by the consistency requirement (5.8) and by the constraint$^{(11)}$

$$y(0) = \exp(\beta\mu_{\mathrm{ex}}) = \exp\left\{\int_0^\rho \frac{d\rho}{\rho}\,[S^{-1}(0) - 1]\right\} \tag{5.11}$$

where μ_{ex} is the excess chemical potential. It is clear that with this ansatz we cannot expect to improve the PY equation at distances beyond the range r_0.

Closure III. In order to make use of the additional theorem$^{(12)}$

$$\left.\frac{d\ln y(r)}{dr}\right|_{r=0} = -\pi\rho\sigma^2 y(\sigma) \tag{5.12}$$

we have considered a three-parameter closure modeled on closures I and II, i.e., we write

$$\Delta^{\mathrm{III}}(r) = \left[\gamma\frac{F_{\mathrm{irr}}^{\mathrm{PY}}(r)}{\rho} + A\theta(r)\right]\exp\left[-\left(\frac{r}{r_0}\right)^8\right] \tag{5.13}$$

The choice of the power 8 in the damping factor is motivated by the low-density behavior of the equation as discussed in the next section. In Δ^{III} also the $F_{\mathrm{irr}}^{\mathrm{PY}}$ has a damping factor and the motivation is that is order to satisfy the two zero-distance constraints (5.11) and (5.12) the value of γ turns out to be substantially different from zero, so that the resulting large-distance behavior of $h(r)$ is unacceptable unless $F_{\text{irr}}^{\text{PY}}$ is also damped. The three parameters of this closure (γ, A, and r_0) are determined by conditions (5.8), (5.11), and (5.12).

Taking into account Eq. (5.4), we can write the consistency equations (5.8), (5.11), and (5.12) in the explicit form

$$S(0)=\left\{1+\frac{4\pi}{3}\rho\sigma^3 y(\sigma)+\frac{2\pi}{3}\sigma^3\rho^2 y(\sigma)\left[(h\otimes h)_\sigma+\frac{F_{\text{irr}}^{\text{PY}}(\sigma)}{\rho}+\Delta(\sigma)\right]\right\}^{-1} \tag{5.14}$$

$$(h\otimes h)_0+\frac{F_{\text{irr}}^{\text{PY}}(0)}{\rho}+\Delta(0)=\frac{1}{\rho}\left(\frac{1}{S(0)}-1\right) \tag{5.15}$$

$$(h\otimes h)'_0+\frac{F_{\text{irr}}^{\text{PY}'}(0)}{\rho}+\Delta'(0)=-\pi\sigma^2 y(\sigma)-\pi\rho\sigma^2 y(\sigma)\left[(h\otimes h)_\sigma+\frac{F_{\text{irr}}^{\text{PY}}(\sigma)}{\rho}+\Delta(\sigma)\right] \tag{5.16}$$

where a prime indicates d/dr and $(h\otimes h)_r$ indicates the convolution for external argument equal to r.

For closure I we just use (5.14) with the appropriate form for Δ, for closure II Eqs. (5.14), and (5.15) are used, and for closure III all three equations are used. Notice also that all correlation functions in (5.10)–(5.16), such as θ, y, and h, are *not* the PY functions, but are the ones corresponding to the unknown y for which we solve Eq. (5.4). $\theta(r)$ is related to $y(r)$ via the OZ relation in k space.

6. RESULTS FOR HARD SPHERES

First we study the low-density behavior of Eq. (5.4) wityh the closures introduced in the previous section. The low-order terms of the virial expansion of $y(r)$,

$$y(r)=y_0(r)+\rho\sigma^3 y_1(r)+\rho^2\sigma^6 y_2(r)+\cdots \tag{6.1}$$

can be obtained in a straightforward way by expanding both members of (5.4) and of (5.14)–(5.16) in power series of ρ. The F_{irr} is a quantity of order ρ^2, so that y_0 and y_1 given by (5.3) are exact for any approximation for $\Delta(r)$. Deviations appear in y_2 because $F_{\text{irr}}^{\text{PY}}$ is not exact already at lowest order, i.e., at order ρ^2 (see Fig. 2). Keeping in mind that $\theta(r)$ starts with a linear term in density, it turns out that the parameters contained in the closures (5.7), (5.10), and (5.13) have a nonzero limit at $\rho=0$. Correspondingly, the second and third viral coefficients of the equation of state are exact, but the fourth is not and the value depends on the closure,

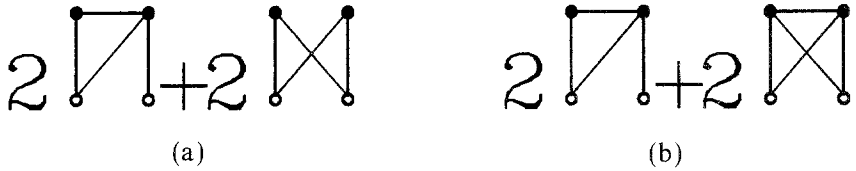

Fig. 2. Contributions of lowest order in density to (a) $F_{\mathrm{irr}}^{\mathrm{PY}}$ and (b) the exact F_{irr}, in terms of the f-bond, ρ-circle representation.

as one can see in Table I. For all three closures the virial and the compressibility route give the same value for B_4 due to the constraint (5.8). B_4 of closure I is about halfway between the virial and the compressibility PY values. The value of B_4 for closures II and III depends on the power contained in the damping factor in (5.10) and in (5.13), respectively, and the range of variations of the resulting B_4 brackets the exact value, so that for both closures there is a power which gives the exact B_4. The powers 2 and 8 used for closures II and III, respectively, are the integers which give the best result for B_4. Therefore the fact that closure II gives a slightly better value for B_4 than closure III is not significant.

With regard to the correlation function, closure I gives only a limited improvement for $y_2(r)$ outside the core compared to PY. On the other hand, closure II gives a significant improvement at all distances and inside the core the largest deviation is of order of 0.6 (see Fig. 3). For closure III there is a dramatic improvement; y_2 can be considered to be almost exact since the deviation from the exact y_2 is smaller than 0.001 at all distances and, moreover, $y_2(0)$ and $y_2'(0)$ are exact. We conclude that closure III is the best of the three at low density.

We have integrated numerically Eq. (5.4) and the details of the computation are given in the Appendix. We have performed various tests on the accuracy of the computation, such as reversing the direction of integra-

Table I. Fourth Virial Coefficient B_4 in Units of $B_2 = 2/3\,\pi\sigma^3$ [a]

	Exact	Δ^{I}	Δ^{II}	Δ^{III}	CS	PY_v	PY_c
B^4/B_2^3	0.28695	0.27456	0.28689	0.28681	0.28125	0.25000	0.29687
γ	—	0.059	—	−0.643	—	—	—
A	—	—	2.225	2.057	—	—	—
r_0/σ	—	—	0.675	1.371	—	—	—

[a] Exact results, present approximations labeled by the closure Δ^i, and Carnahan–Starling and PY (virial and compressibility route) results are given. The zero-density limit of the parameters γ, A, and r_0 for the three closures is also shown.

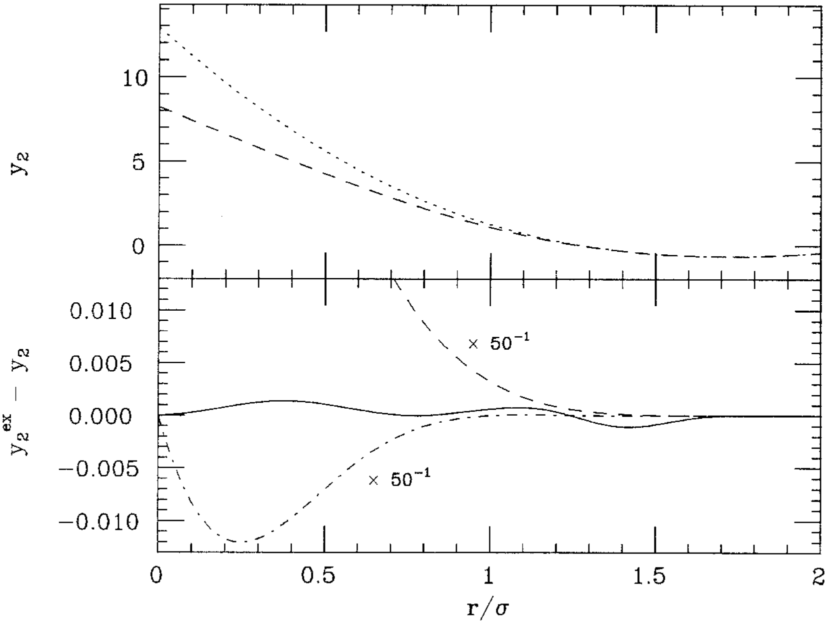

Fig. 3. $y_2(r)$ of hard spheres. Upper part: exact(12) (···) and PY (---). Lower part: difference between the exact y_z^{ex} and y^2 given by closure III (—), by closure II (---), and by PY (---). The two last differences are reduced by a factor of 50.

tion in ρ or recovering the PY $g(r)$ when $\Delta(r) = 0$. Due to the finite grid of integration in ρ, the consistency conditions (5.8), (5.11), and (5.12) are not exactly satisfied by the computed $y(r)$, but the deviations between the two members of these equations remain below the 0.2% level at all densities and we estimate that accuracy in the excess compressibility factor $Z_e = Z - 1 = \beta p/\rho - 1$ is better than 1%.

In Fig. 4 we show our results for the compressibility factor in the form $(Z_e^{EW} - Z_e)/Z_e^{EW}$, where Z_e^{EW} is the Padé approximant of Erpenbeck and Wood(13) obtained from a fit of simulation data. In the figure the PY virial results as well as the Carnahan–Starling(14) (CS) equation of state are shown. The equation of state for closure I is an improvement with respect to PY_v, but this improvement becomes marginal at a density of order 0.5–0.6. Closures II and III give improved results for Z; both of them are better than CS at low density since B_4 is closer to the exact result and closure III is better than CS up to a density of order of 0.25. At higher density the result is significantly better than PY_v but much less than CS. We find that the consistency equations (5.14)–(5.16) do not have a solution for both closures II and III above a certain density; this is of order of 0.55

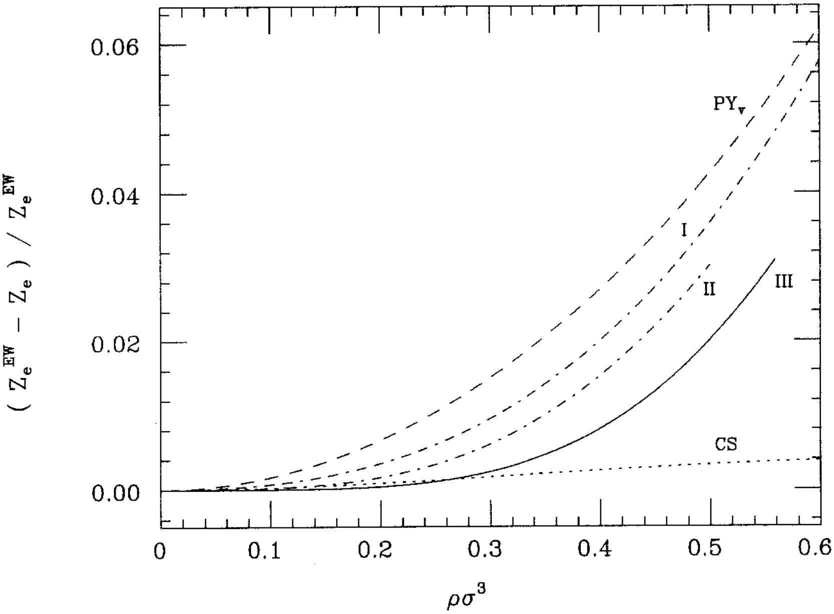

Fig. 4. Excess compressibility factor of hard spheres represented as a deviation from the Erpenbeck and Wood Padé approximant[13] for Percus–Yevick virial (PY_v), Carnahan–Starling (CS), and for closures I, II, and III.

for closure III. We believe that this is because the closures we have considered are not flexible enough to model F_{irr} at high density.

Next we consider the results for $y(r)$; the comparison with the VW $y(r)$ is shown in Fig. 5 at $\rho\sigma^3 = 0.5$. Inside the core both closures II and III give a large improvement with respect to the PY result. Improved results are obtained also in the region immediately outside the core, but a larger distances the results become very close to PY. This is a consequence of the presence of the damping factor in these closures. It is interesting to consider the behavior of the direct correlation function given by the present theory; the result at $\rho\sigma^3 = 0.5$ is shown in Fig. 6. Contrary to PY, $c(r)$ corresponding to our closures has a tail outside the core and this tail is significantly large than the VW one.

From these results we conclude that the closures we have considered for F_{irr} are appropriate at low density and in particular closure III gives excellent results. However, these closures fail to capture some essential feature of F_{irr} starting from an intermediate density and the quality of the results deteriorates at higher density.

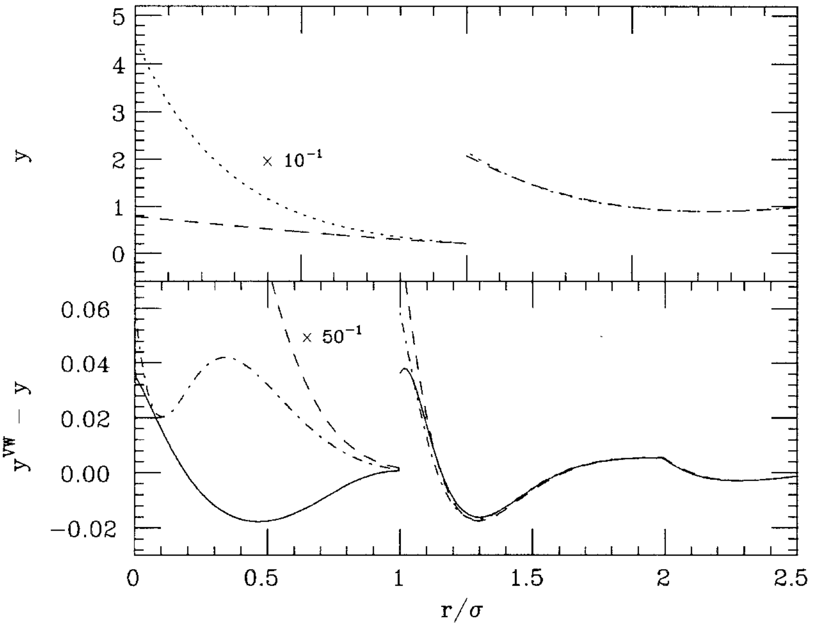

Fig. 5. $y(r)$ of hard spheres at density $\rho\sigma^3 = 0.5$. Upper part: VW (···) and PY (---). Lower part: difference $y^{\mathrm{VW}}(r) - y(r)$ for PY (---), closure II (-·-), and closure III (—). Notice the reduction factors applied for $r/\sigma < 1$.

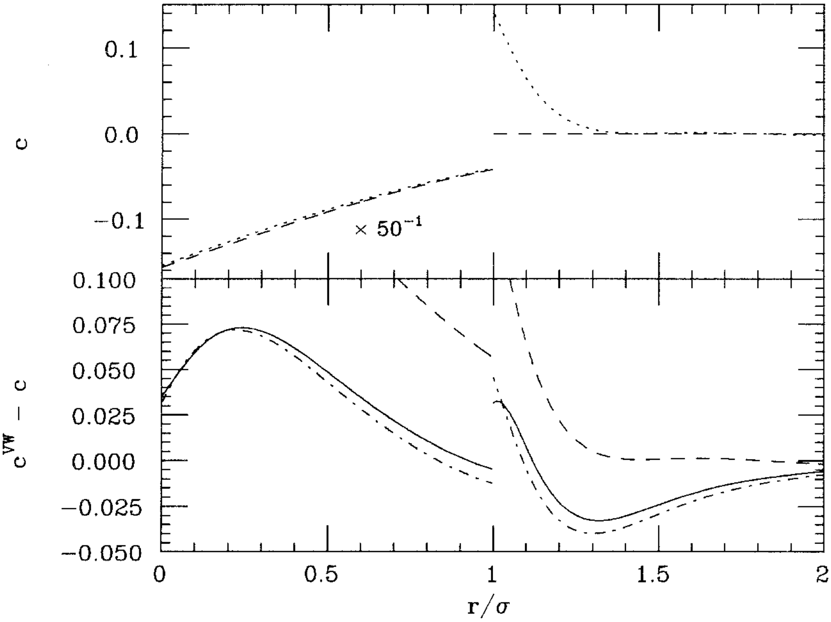

Fig. 6. Same key as in Fig. 5, but for $c(r)$. Also here a reduction factor has been applied for $r/\sigma < 1$, but only in the upper part.

7. DISCUSSION

We have analyzed two relations for the isothermal density derivative of $g(r)$ of a fluid. The first is the well-known relation between $\partial g/\partial \rho$ and a functional $F(r_{12} | g_3)$ of the triplet correlation function. Our analysis shows that one has to be rather careful in extracting information on the triplet correlation function from $\partial g/\partial \rho$. At high density, exactly where one is most interested in this problem, $S(0)$ is very small and there is a very large cancellation between the convolution term and the term $F(r)$ [Eq. (4.4)] which contains the information on g_3. On the experimental side, this implies that when using$^{(5,15)}$ relation (4.4) to obtain evidence for triplet correlations in excess of superposition, the convolution term has to be evaluated very carefully and, on the other hand, most of the information on g_3 given by $F(r)$ is just that due to the lowest-order Abe–Stell contribution. On the theoretical side, our analysis suggests that it will be difficult to develop a useful theory for $g(r)$ starting from the equation (4.4) for $\partial g/\partial \rho$ coupled with a suitable closure for g_3 because it would be necessary to devise an exceedingly accurate representation of g_3 in terms of the rdf. All this is due to a remarkable cancellation between terms of neighboring order in the cluster expansion in h bonds of $F(r | g_3)$.

The new relation (4.8) we obtain for $\partial g/\partial \rho$ does not involve the isothermal compressibility and the proof on the basis of the diagrammatic expansion makes clear that the cancellations mentioned above are fully taken into account. Now in place of $F(r | g_3)$ a new correlation function, $F_{\text{irr}}(r)$, appears which unfortunately we have not been able to relate in closed form to known correlation functions. In any case this new relation for $\partial g/\partial \rho$ appears as a better starting point to obtain a theory of $g(r)$ by using a suitable approximation for F_{irr}.

In the second part of the paper we have shown that indeed it is possible to construct a theory of $g(r)$ starting from this new relation for $\partial g/\partial \rho$. We have studied hard spheres and F_{irr} has been written as the PY value plus a correction term based on a suitable closure. In this way we obtain an augmented PY theory in which full thermodynamic consistency is enforced. In the low-density limit this approach is very accurate and the result is essentially exact for the most elaborate closure we have considered. The equation of state up to density $\rho\sigma^3 = 0.25$ is superior to the celebrated Carnahan–Starling one. In the intermediate density range 0.25–0.50 our approach represents an improvement over PY and, in particular, the cavity function $y(r)$ inside the core is very accurate. At still higher density none of the closures we have considered is adequate.

In conclusion we have shown that it is possible to build a theory of $g(r)$ and of the cavity function $y(r)$ starting from a relation for its isothermal density derivative. This is just the beginning and we have to learn much more about the correlation function F_{irr} before we can obtain useful results at high density, but our excellent results at low to medium density suggest that this is a new useful approach to the theory of fluids.

APPENDIX

Equation (5.4) is reduced to a finite system of nonlinear inhomogeneous differential equations of first order for the unknown $y(r_i, \rho)$, having discretized r space. We have used the step size $\delta(r/\sigma) = 5 \times 10^{-3}$ with $r_{\max} = 82\sigma$. The fourth-order Runge-Kutta method$^{(16)}$ has been used to solve the system with a step size $\delta(\rho\sigma^3) = 10^{-3}$. We started the integration from a very low density (0.01) where the virial expansion can be used in order to obtain the initial condition.

The convolutions appearing in (5.4), (5.5), and (5.9) have been computed through the convolution theorem and using a fast Fourier transform routine. For an accurate evaluation of the Fourier coefficients of the discontinuous function $h(r)$ we have considered the function

$$l(r) = \begin{cases} -1 & r < \sigma \\ L \exp[-\alpha(r-\sigma)]/r & r > \sigma \end{cases}$$

of which we know analytically the Fourier transform $\tilde{l}(k)$, and the auxiliary function $H(r) = h(r) - l(r)$. The parameters α and L are such that $H(r)$ and its first derivative are continuous at $r = \sigma$. The final result for $\tilde{h}(k)$ is given adding $\tilde{l}(k)$ to the numerical Fourier transform of $H(r)$.

In order to construct $F_{\text{irr}}^{\text{PY}}$ we need g^{PY} and $\partial g^{\text{PY}}/\partial\rho$. Starting from the analytic solution$^{(8)}$ of PY, $g^{\text{PY}}(r)$ has been computed exactly up to $r = 10\sigma$ with the method of Smith and Henderson.$^{(17)}$ Beyond this distance g^{PY} has been represented by its asymptotic behavior obtained from the contribution of the pair of poles (t_i, t_i^*) of the Laplace representation of $rg^{\text{PY}}(r)$ which are closest to the imaginary axis. In the range 9σ to 10σ the two representations of g^{PY} match each other perfectly well in the range of density we have considered here. The density derivative of g^{PY} has been computed with a Newton three-step formula with increment 5×10^{-5}.

During the integration in ρ the values of γ, A, and r_0 have been calculated solving at each step the system (5.14)–(5.16) at the values of the density required by the Runge-Kutta method.

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REFERENCES

1. H. van Beijeren, *Phys. Lett.* **105A**:191 (1984); see also A. F. E. M. Haffmans, I. M. de Schepper, J. P. J. Michels, and H. van Beijeren, *Phys. Rev. A* **37**:2698 (1988).
2. F. P. Buff and R. Brout, *J. Chem. Phys.* **33**:1417 (1960).
3. P. Schofield, *Proc. Phys. Soc.* **88**:149 (1966).
4. P. Hutchinson, *Proc. Phys. Soc.* **91**:506 (1967).
5. H. J. Raveché and R. D. Mountain, *J. Chem. Phys.* **53**:3101 (1970); **57**:3987 (1972).
6. G. Stell, in *Phase Transitions and Critical Phenomena*, Vol. 5B, C. Domb and M. S. Green, eds. (Academic Press, London, 1976).
7. J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**:1 (1958).
8. E. Thiele, *J. Chem. Phys.* **39**:474 (1963); M. S. Wertheim, *Phys. Rev. Lett.* **10**:321 (1963).
9. L. Verlet and J. J. Weis, *Phys. Rev. A* **5**:939 (1972).
10. E. W. Grundke and D. Henderson, *Mol. Phys.* **24**:269 (1972).
11. W. G. Hoover and J. C. Poirier, *J. Chem. Phys.* **37**:1041 (1962).
11. E. Meeron and A. J. F. Siegert, *J. Chem. Phys.* **48**:3139 (1968).
12. B. R. A. Nijboer and L. Van Hoven, *Phys. Rev.* **85**:777 (1952); F. H. Ree, R. N. Keeler, and S. L. McCarthy, *J. Chem. Phys.* **44**:3407 (1966).
13. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **35**:321 (1984).
14. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).
15. P. A. Egelstaff, D. I. Page, and C. R. T. Heard, *J. Phys. C* **4**:1453 (1971).
16. L. W. Johnson and R. Dean Riess, *Numerical Analysis* (Addison-Wesley, Reading, Massachusetts, 1982).
17. W. R. Smith and D. Henderson, *Mol. Phys.* **19**:411 (1970).