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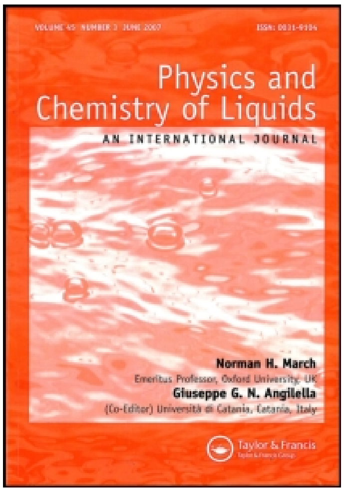

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Extended pressure—consistent equation for simple fluids

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Extended Pressure–Consistent Equation for Simple Fluids

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Abstract—A previous generalization of the Percus–Yevick (PY) and hypernetted chain (HNC) equations for simple fluids, involving a density- and temperature-dependent coefficient m, is extended by including a spatial dependence in m. The new approximation yields an exact fourth virial coefficient and, by further requirement, a consistent equation of state from both the virial and compressibility forms. Comparison of calculated results for the hard sphere potential shows an improvement over the PY, HNC, and previous pressure-consistent equations.

1. Introduction

As a consequence of the assumption that molecules of a fluid interact through two-body forces, the pair distribution function of a fluid plays a central role in the theoretical calculation of the fluid bulk properties. From a knowledge of the intermolecular potential $\varphi(r)$ and the resulting pair distribution function $g(r)$, for example, the internal energy, pressure, and isothermal compressibility of a sample in equilibrium can be immediately obtained by simple quadratures.⁽¹⁾

$$\frac{\beta E}{N} = \tfrac{3}{2} + \tfrac{1}{2}\rho\beta \int_0^\infty \varphi(r) g(r) 4\pi r^2 \, \mathrm{d}r, \tag{1}$$

$$\frac{\beta p}{\rho} = 1 - \tfrac{1}{6}\rho\beta \int_0^\infty r \frac{\mathrm{d}\varphi(r)}{\mathrm{d}r} g(r) 4\pi r^2 \, \mathrm{d}r, \tag{2}$$

$$\beta(\rho K_T)^{-1} = \beta\left(\frac{\partial p}{\partial \rho}\right)_T = 1 - \rho \int_0^\infty C(r) 4\pi r^2 \, \mathrm{d}r. \tag{3}$$

Here $C(r)$ is the direct correlation function, ρ is the number density N/V, and β is $(kT)^{-1}$. Furthermore, the liquid structure factor directly measured by X-ray and neutron scattering is obtainable as the Fourier transform of $g(r)$.

This quality of immediate usefulness has motivated an intensive and, at least for simple fluids, quite successful search for practical methods of determining $g(r)$, given the pair potential $\varphi(r)$; this paper is concerned with a simple extension of some of these equations. In the following paragraphs, we briefly outline the principle routes to approximate equations for $g(r)$ in use today.

An early approach was based on an exact hierarchy of equations relating the n-body distribution function g_n to the $(n+1)$-body function g_{n+1}.⁽¹⁾ In particular, $g \equiv g_2$ is connected to g_3 and if, in order to obtain an equation with a single unknown, g_3 is represented by the superposition approximation, the Yvon–Born–Green equation⁽¹,²⁾ for g results. This equation has fared poorly in numerical comparisons with others to be mentioned below. Some improvement has been made, however, by adding correction terms to the superposition approximation.⁽³⁾

A second avenue of approach is based on an expansion of $g(r)$ in powers of the density.⁽⁴⁾ A study of the coefficients of this expansion showed that many terms could be summed into compact forms, culminating, in a remarkable sequence of papers, in the hypernetted chain (HNC) equation, proposed independently by several authors.⁽⁵⁾ The Percus–Yevick (PY) equation, though originally obtained by an entirely different method,⁽⁶⁾ can best be understood in terms of the same series expansion.⁽⁷⁾ A significant limitation of this approach is that, having achieved these notable successes, it provides little practical guidance on how these approximate results may be systematically improved.

Partly in order to circumvent this difficulty, a third general approach⁽⁸⁾ has more recently been developed, based on functional Taylor expansions. These suffer from an inherent arbitrariness, in that the functional to be expanded and the function it is expanded in are essentially arbitrary choices. However, by taking the known equations as guides, systematic expansions yielding correction terms to these have been obtained.⁽⁸⁾ The difficulty with these corrections is that they again involve the three-particle function g_3, requiring additional approximations to reduce the set of equations to a single unknown. The practical task of determining $g(r)$ becomes quite involved.⁽⁹⁾

All of the above formulations lead to non-linear integral equations for g which must be solved numerically. There is a fourth, more direct approach to the calculation of g, based on mathematical simulation of the physical system, namely, the Monte Carlo$^{(10)}$ (MC) and molecular dynamics$^{(11)}$ (MD) techniques. These require a large-scale computing effort, but when the integral equations become excessively difficult to solve, they offer an attractive alternative, in that they are free of all uncontrolled approximations and are, in a certain sense, exact.

One of the advantages of the PY and HNC equations, then, is that they yield relatively good results with a comparatively modest amount of computational effort. In seeking to improve on these equations, it seems desirable to retain as much of this advantage as possible, since an excessively complicated equation will begin to compete, computationally, with the MC and MD "computer experiments" and hence may not, in practical terms, be worth solving.†

The approximate integral equation for g proposed in Sec. 2 is governed by this consideration. It is obtained in the context of the density expansion for g and extends an approach shown to be useful in previous publications.$^{(12-14)}$ Hard sphere results obtained from this equation are presented in Secs. 3 and 4.

2. Extended Pressure–Consistent Equation

A summary of some well-known results is helpful in motivating the desired approximation. In canonical ensemble formalism, the pair distribution function g is defined by

$$g(r_{12}) = \frac{N(N-1)}{\rho^2 Z}\int\cdots\int d\mathbf{r}_3\cdots d\mathbf{r}_N \exp\Big(-\beta\sum_{[i<j]}\varphi_{ij}\Big), \tag{4}$$

where

$$Z = \int\cdots\int d\mathbf{r}_1\cdots d\mathbf{r}_N \exp\Big(-\beta\sum_{i<j]}\varphi_{ij}\Big) \tag{5}$$

and where $\varphi_{ij} \equiv \varphi(r_{ij})$ is the interaction potential between molecules

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† There are, of course, other criteria to be considered in judging the integral equations. Besides their contributions to a general theory of fluids, they offer, e.g., the possibility of determining experimental intermolecular potentials from measured scattering factors.

i and *j*. Expansion of the integrand in (4) in products of Mayer *f*-functions

$$f(r) = \mathrm{e}^{-\beta\varphi(r)} - 1 \tag{6}$$

then leads to a power series in density for $g(r)$ which is the point of departure for all approximations to g based on diagram techniques. By classifying the coefficients of this expansion according to the properties of the associated diagrams, one writes(1)

$$g(r)\,\mathrm{e}^{\beta\varphi(r)} = 1 + S(r) + P(r) + B(r), \tag{7}$$

where S, P, and B are the sums of the series, parallel, and bridge diagrams, respectively. The expansions of these functions, through

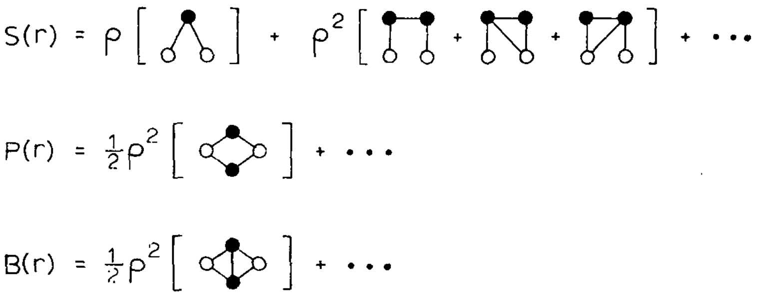


Figure 1. Density expansions of the series, parallel, and bridge sets of diagrams, through second order.

terms of second order in the density, are shown in Fig. 1 in the usual diagram notation. In addition, one defines a direct correlation function $C(r)$ by the relation

$$G(r) \equiv g(r) - 1 \tag{8}$$

$$= C(r) + S(r). \tag{9}$$

Because diagrams of the series type can be factored in Fourier transform space, while those of the parallel type can be factored in direct space, both the series S and P can be summed into simple functionals of g. These are(1)

$$S(r) = \rho \int C(r')G(|\mathbf{r} - \mathbf{r}'|)\,\mathrm{d}\mathbf{r}' \tag{10}$$

and

$$P(r) = g(r)\,\mathrm{e}^{\beta\varphi(r)} - 1 - \ln[g(r)\,\mathrm{e}^{\beta\varphi(r)}]. \tag{11}$$

Equations (9) and (10) constitute the Ornstein–Zernike equation

$$G(r) = C(r) + \rho \int C(r')G(|\mathbf{r} - \mathbf{r}'|)\,\mathrm{d}\mathbf{r}', \tag{12}$$

which yields G when C is known, while from (7) and (9) it follows that

$$C = f(1 + S + P + B) + P + B \tag{13}$$

$$= g\,\mathrm{e}^{\beta\varphi} f + P + B \tag{14}$$

$$= G - \ln g\,\mathrm{e}^{\beta\varphi} + B, \tag{15}$$

where the last equality is a consequence of (11). It is apparently not possible to express B as a simple functional of g, so that a closed set of equations is not achieved and approximations for B must be introduced. Among other things, this leads to inconsistent values of the equation of state as obtained from Eqs. (2) and (3).

The best known of these approximations are the PY and HNC equations, which are obtained by putting, respectively,

$$B(r) = -P(r) \quad \text{(PY)} \tag{16}$$

$$B(r) = 0. \quad \text{(HNC)} \tag{17}$$

The corresponding direct correlation functions are then

$$C = g\,\mathrm{e}^{\beta\varphi} f \quad \text{(PY)} \tag{18}$$

$$C = G - \ln g\,\mathrm{e}^{\beta\varphi}. \quad \text{(HNC)} \tag{19}$$

The fact that the PY equation, despite its neglect of an additional set of diagrams, leads to results that are generally superior to those of the HNC equation suggests that a partial cancellation occurs among the diagrams such that $P + B$ is more nearly negligible than B alone.

We now consider a generalization of these cases that may more accurately represent the small correction $P + B$ while still retaining the basic computational simplicity of the above equations. Define the ratio

$$m(r) = \frac{B(r)}{P(r)}, \tag{20}$$

so that the direct correlation function is now written

$$C = G + m(g\,\mathrm{e}^{\beta\varphi} - 1) - (1 + m)\ln g\,\mathrm{e}^{\beta\varphi}. \tag{21}$$

In this form, the PY and HNC equations result from the choice $m(r) = -1$ and $m(r) = 0$, respectively. Other possibilities may now be explored, however. For example, a choice of m with no functional dependence on r but designed to yield a consistent value for the pressure from both Eqs. (2) and (3) leads to a significant improvement over the PY and HNC equations for hard spheres.(13,15) This approximation, previously called pressure-consistent (PC), can in turn be easily extended to include a spatial dependence for $m(r)$, as will now be shown.

Write the density expansions of P and B in the form

$$P(r) = \sum_{k=2}^{\infty} \rho^k P_k(r), \tag{22}$$

$$B(r) = \sum_{k=2}^{\infty} \rho^k B_k(r), \tag{23}$$

so that the exact $m(r)$ is written

$$\begin{aligned} m(r) &= \{B_2(r) + \rho B_3(r) + \cdots\}/\{P_2(r) + \rho P_3(r) + \cdots\} \\ &= \frac{B_2(r)}{P_2(r)} \frac{1 + \rho B_3(r)/B_2(r) + \cdots}{1 + \rho P_3(r)/P_2(r) + \cdots} \\ &= \frac{B_2(r)}{P_2(r)} \left\{ 1 + \rho \left[\frac{B_3(r)}{B_2(r)} - \frac{P_3(r)}{P_2(r)} \right] + \cdots \right\}. \end{aligned} \tag{24}$$

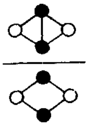
More generally, the expansion of $m(r)$ may be written

$$m(r) = m_0(r) \left\{ 1 + \sum_{k=1}^{\infty} \rho^k \alpha_k(r) \right\}, \tag{25}$$

where

$$m_0(r) = \frac{B_2(r)}{P_2(r)} \tag{26}$$

or, in diagram notation,

$m_0(r) =$  , (27)

and where

$$\alpha_k(r) = \frac{B_{k+2}(r)}{B_2(r)} - \frac{P_{k+2}(r)}{P_2(r)} - \sum_{j=1}^{k-1} \alpha_j(r) \frac{P_{k-j+2}(r)}{P_2(r)} \tag{28}$$

for $k > 1$. Clearly, the expansion (25), though formally exact, is of no direct utility since the coefficients $\alpha_k(r)$ are not readily obtainable. The approximation we propose consists in simply neglecting the r-dependence of these coefficients, thus letting $m_0(r)$ approximate the entire spatial dependence of $m(r)$, and determining the now-constant coefficients α_k by requiring consistency in the equation of state as calculated from (2) and (3). It is worthwhile noting that this approximation represents $B(r)$ as a particular infinite series and is not at all analogous to the straightforward extension of the HNC equation obtained by approximating $B(r)$ by $\rho^2 B_2(r)$, rather than zero.

There remains the problem of determining the integrals in $m_0(r)$. For hard spheres, analytic evaluations of these diagrams are already available in the literature.(16) In general, however, these integrals will need to be evaluated numerically, using Fourier transforms for $P_2(r)$ and Monte Carlo integration for $B_2(r)$, for example. It will, of course, be necessary to perform these calculations only once for each isotherm studied.

3. Virial Expansion for Hard Spheres

When the exact density expansions of g and C are used in (2) and (3), respectively, both equations yield the same virial expansion for the pressure of the fluid,

$$\frac{\beta p}{\rho} = 1 + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + \cdots, \tag{29}$$

a consistency that is lost when approximations are introduced. The PY and HNC equations, for example, become internally inconsistent in this sense at the fourth virial coefficient D.

With the approximation

$$m(r) = m_0(r)\left\{1 + \sum_{k=1}^{\infty} \rho^k \alpha_k\right\}, \tag{30}$$

the fourth virial coefficient is exact and the remaining coefficients can be made consistent, though approximate. The first few such coefficients can be readily calculated for the hard sphere model, where the diagrams needed for $m_0(r)$ have been analytically evaluated.(16) Many of the virial diagrams required for this calculation are also available in the literature.(17) Those not already available were computed, either analytically or numerically, and are listed in Table 1 with their numerical values.

TABLE 1 Additional Virial Diagrams Needed for the Calculation of the Fifth Virial Coefficient of Hard Spheres Using the Approximation of Eq. (30). Solid lines denote $f(r)$, dashed lines $rf'(r)$, and wavy lines $m_0(r)$. The first four diagrams were evaluated analytically, the last four sets numerically. b is $\frac{2}{3}\pi\sigma^3$.

 = 2.95370 b^4

 = -1.85692 b^4

 = 0.96303 b^4

 = -1.18772 b^4

 +  = 1.13068 b^4

 +  = -0.56613 b^4

 +  = 0.22122 b^4

 +  = 0.72605 b^4

The hard sphere $m_0(r)$ is pictured in Fig. 2, from which one sees that $m_0(r)$ takes on the PY value of -1 for $r/\sigma \geqq \surd 3$, where σ is the hard sphere diameter. (Actually, $m_0(r)$ for this potential becomes undefined for $r/\sigma > 2$, since both numerator and denominator of

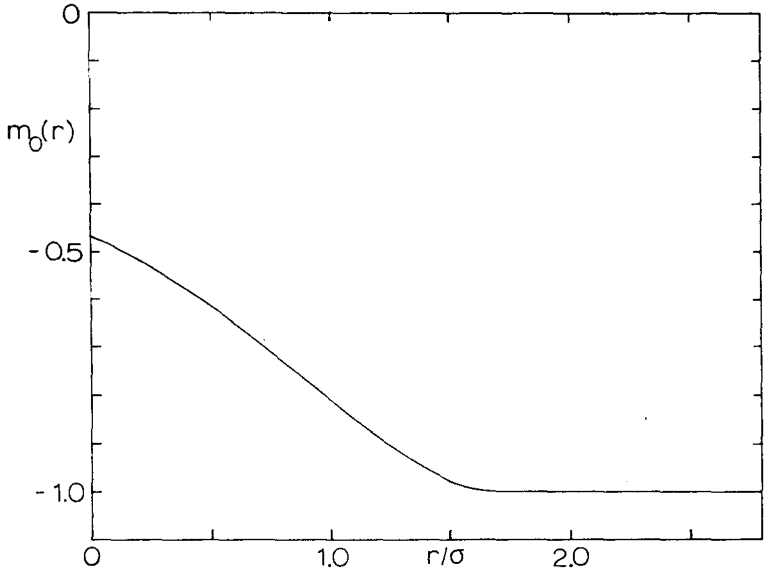


Figure 2. The function $m_0(r)$ for hard spheres of diameter σ.

(27) vanish. We have extrapolated the value -1 which holds between $r/\sigma = \sqrt{3}$ and $r/\sigma = 2$ to define $m_0(r)$ for values of r/σ greater than 2.) Given this property of $m_0(r)$, it is clear that in the present approximation, the sum

$$P(r) + B(r) = [1 + m(r)]P(r) \tag{31}$$

will be a relatively weak correction to the PY form of the direct correlation function, as expected. Note, however, that C will no longer vanish for values of r greater than a hard sphere diameter, as it does in the PY approximation.

With the numerical values of the required diagrams in hand, it is a straightforward, though increasingly tedious, task to determine the constant coefficients α_k required for pressure consistency. We have evaluated, under this condition, the first coefficient α_1, which gives

$$m(r) = m_0(r)\{1 - 0.1123b\rho + \cdots\} \tag{32}$$

for hard spheres, where $b \equiv \frac{2}{3}\pi\sigma^3$. This is sufficient to yield consistency through the fifth virial coefficient. The values of the fourth and fifth coefficients resulting from (32) are listed in Table 2, along with the corresponding results of the PY, HNC, and PC equations given by Rowlinson.(15) As mentioned earlier, the fourth virial coefficient is now exact, while the fifth is clearly an improvement over the other three equations.

TABLE 2 Fourth and Fifth Virial Coefficients for Hard Spheres.

		D/b^3	E/b^4
Exact		0.28695	0.1103
Eq. (30)		0.28695	0.1051
PC		0.2824	0.1041
PY	V	0.2500	0.0859
	C	0.2969	0.1211
HNC	V	0.4453	0.1447
	C	0.2092	0.0493

For a dependable comparison at higher densities, a complete numerical solution of the integral equation must be obtained. These results are presented in the next Section.

4. Numerical Solutions for Hard Spheres

The nonlinear integral equation for g which results from Eqs. (12), (21), and (30) may be solved iteratively using Fourier transforms. The details of the numerical procedure for this calculation have been described previously.(13,18) As before, the equation was solved for g in the form

$$H(r) = r[g(r)\, e^{\beta\varphi(r)} - 1], \tag{33}$$

evaluated at a finite number of discrete points r_j. Iteration was continued until the largest difference between two successive iterates of H was less than 10^{-4}. In addition, the pressures computed from the virial Eq. (2) and from a Simpson's rule integration of the inverse compressibility (3) were required to have a relative difference smaller than 5×10^{-4}. Calculations were performed in double precision on an IBM 360/75.

With these criteria, solutions were obtained for the hard-sphere model at reduced densities $\rho\sigma^3 = 0.1(0.1)0.8$. The computed equation of state is listed in Table 3, along with the values obtained from the Ree–Hoover $P(3, 3)$ approximant(19) (which we take as a reasonable

TABLE 3 Hard Sphere Equation of State Computed from the Extended Pressure-Consistent Equation (EPC), the Ree–Hoover $P(3, 3)$ Padé approximant (RH), and the earlier Pressure-Consistent Equation (PC).

		$\beta p/\rho$		
$\rho\sigma^3$	$m(r)/m_0(r)$	EPC	RH	PC
0.1	0.976	1.240	1.240	1.240
0.2	0.953	1.553	1.554	1.553
0.3	0.903	1.967	1.968	1.966
0.4	0.860	2.516	2.521	2.513
0.5	0.826	3.252	3.268	3.246
0.6	0.781	4.252	4.291	4.239
0.7	0.726	5.624	5.714	5.605
0.8	0.680	7.539	7.732	7.513

" standard solution ") and the earlier pressure-consistent (PC) equation.(13) It is clear from this table that the EPC equation gives a small but noticeable improvement over the earlier version. (These latter results in turn have been shown(13) to improve on the PY and HNC equation of state.) The values of the density-dependent part of $m(r)$ [see Eqs. (30) and (32)] needed to achieve a consistent equation of state are tabulated in the second column of Table 3.

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