An Interpolation of the
HNC and PY Integral Equations
for Classical Fluids

Tohru Morita

Department of Applied Science
Faculty of Engineering
Tohoku University, Sendai

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A new integral equation for the pair distribution function of classical fluids is proposed. The integral equation is an interpolation of the HNC (hyper-netted chain) and PY (Percus-Yevick) equation. The one-parameter interpolation formula proposed has a structure as simple as the HNC integral equation and is considered to be convenient for practical purposes. The one-parameter interpolation formula is used to calculate the fourth and fifth virial coefficients for a hard-sphere gas. Excellent simultaneous agreements of the fourth and fifth virial coefficients with the exact ones are achieved by a choice of the parameter. Those coefficients are also calculated by assuming the parameter to depend on the density and determining it so as to secure the consistency of the pressures, obtained with the aid of the virial equation and the compressibility equation. The result is compared with the results obtained in the past for other approximations by a similar procedure.

§ 1. Introduction

For a low density gas, the expansions of physical quantities in powers of density are useful. The expansion coefficients are expressed in terms of multiple integrals which are called cluster integrals and whose structures are shown by diagrams. When density of gas is higher, we have to evaluate the more cluster integrals. Their calculations are not easy even for a hard-sphere system when five or more particle integrals are concerned. It was, however, noticed that the cluster integrals of some character can be calculated in principle, with the aid of the Fourier transform and the convolution theorem. The approximation in which all these cluster integrals are taken into account was proposed; that is the HNC (hyper-netted chain) approximation.1,2)

On the other hand, the PY (Percus-Yevick) approximation, first proposed by a different approach,3) was shown to be obtained by a sum of a subset of cluster integrals considered in the HNC approximation.4) When one attempts to get an approximation from a series expansion, one is tempted to believe that an approximation where the more terms are taken into account must be the better one. Then one may favours the HNC approximation compared with the PY approximation. However, the PY approximation is shown to be exact for one-dimensional
hard-sphere gas but the HNC approximation is not. Moreover most of the numerical calculations performed for three-dimensional fluids look to suggest that the PY approximation is better.

We recall here a work by Rushbrooke and Hutchinson where they gave an attempt of improving the HNC approximation. In that work, they showed that some of the diagrams (cluster integrals) neglected in the HNC approximation have a contribution of the same order of magnitude but with different sign as some diagrams considered in the same approximation. On the basis of this fact, they proposed such an approximation that those contributions are canceled out. As a result, the approximation may be considered as an approximation where both of these diagrams are ignored. Stell noticed that such a cancellation would lead the HNC approximation to the PY approximation.

In the present paper, we first confirm generally that, for each diagram \((T_1)\) taken into account in the HNC approximation but neglected in the PY approximation, we find some diagrams \((T_2)\) in the set of diagrams neglected in the HNC approximation, and these \((T_2)\) cancel the contribution of the original diagram \((T_1)\) partly. The numerical calculations suggest that it is better to neglect both of these diagrams \((T_1)\) and \((T_2)\) than to retain one \((T_1)\) of these, especially for the hard-sphere gas. But considering that the cancellation is not perfect even for the hard-sphere gas, the entire neglect would not be the best approximation.

The purpose of this paper is to propose an approximation in which these diagrams \((T_1)\) are taken into account with weights. When the weights are put equal to unity, the approximation reduces to the HNC approximation, and when they are set zero, it reduces to the PY approximation. By a suitable choice of the weights expressed in terms of one parameter, the structure of the equations becomes as simple as those for the HNC approximation. The one-parameter interpolation formula is considered to be useful for numerical calculations. In §5, the one-parameter interpolation formula is used to calculate the fourth and fifth virial coefficients of the hard-sphere gas, and comparison is made with the exact ones. In the last section, discussions of the value of the parameter in the one-parameter interpolation formula are given. Discussions are also given about the related works by Hurst, Rowlinson et al.

§2. Integral equations for the pair distribution functions

The exact integral equation for the pair distribution function for the classical fluids was obtained by many authors. That can be expressed in terms of diagrams in the most direct way. The one by Morita and Hiroike is given in the following, for it suits for our following argument. When the number density of particles is \(\rho\), the two-particle distribution function \(n^{(2)}(r)\) at distance \(r\) tends to \(\rho^2\) as \(r \to \infty\). The radial distribution function \(g(r)\) is defined by

\[
n^{(2)}(r) = \rho^2 g(r).
\]
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The $g(r)$ tends to unity at large $r$. The function $v(r)$ is defined by
\[ g(r) = 1 + v(r). \]  

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The exact set of equations for the pair distribution function is given in Fig. 1 in terms of diagrams. The explicit forms of these equations are written as
\[ v(r) = z(r) + z_s(r), \]
\[ z_s(r_{13}) = \rho \int dr_3 z(r_{13}) v(r_{32}) \quad \text{or} \quad Z_s(k) = \rho Z(k) V(k), \]
\[ z(r) = b(r) \left\{ 1 + w(r) + \frac{1}{2!} w(r)^2 + \frac{1}{3!} w(r)^3 + \cdots \right\} \]
\[ + x(r) + \left\{ \frac{1}{2!} w(r)^2 + \frac{1}{3!} w(r)^3 + \cdots \right\} \]
\[ = \{b(r) + 1\} e^{w(r)} - 1 - w(r) + x(r) \]  

and
\[ w(r) = z_s(r) + x(r) = v(r) - z(r) + x(r), \]

where $V(k)$, $Z(k)$ and $Z_s(k)$ are the Fourier transforms of $v(r)$, $z(r)$ and $z_s(r)$, respectively: e.g.
\[ V(k) = \int dr v(r) e^{ik \cdot r}. \]

The factor corresponding to the $b$-bond is
\[ b(r) = e^{-\phi(r)/kT} - 1, \]

where $\phi(r)$ is the interaction potential of two particles separated by distance $r$. 

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**Fig. 1.** Exact set of equations for the pair distribution function.
Table 1. Comparison of notations with other authors.

<table>
<thead>
<tr>
<th></th>
<th>$b(r)$</th>
<th>$v(r)$</th>
<th>$z_b(r)$</th>
<th>$w(r)$</th>
<th>$x(r)$</th>
<th>${b(r)+1}e^{\beta(r)}-1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>de Boer et al.'s</td>
<td>$f(r)$</td>
<td>$G(r)$</td>
<td>$X(r)$</td>
<td>$S(r)$</td>
<td>$E(r)$</td>
<td>$F(r)$</td>
</tr>
<tr>
<td>Stell's</td>
<td>$f(r)$</td>
<td>$h_2(r)$</td>
<td>$e(r)$</td>
<td>$t(r)$</td>
<td>$w_2(r)$</td>
<td>$b(r)$</td>
</tr>
</tbody>
</table>

$T$ is the temperature and $k$ is the Boltzmann constant. For convenience of comparison, the above notations are compared with those by Van Leeuwen et al.\(^3\) and those used by Stell\(^4\) in his review article. The term $x(r)$ on the right-hand side of diagrammatic equations (c) and (d) in Fig. 1 is expressed as a sum of diagrams which can in principle be calculated from the knowledge of $v(r)$ as given at the end of this section, but it is a difficult task to calculate them. The HNC approximation is the approximation in which that term is neglected. Hence the diagrammatical equation (c) and (d) in Fig. 1 are replaced by the one given in Fig. 2 in that approximation.

\[
\begin{align*}
Z_b &= b + \sum \left( Z_b Z_b \right) + \sum \left( Z_b \right) + \sum \left( Z_b Z_b \right) + \cdots \\
&= b + \left( Z_b Z_b \right)
\end{align*}
\]

Fig. 2. In the HNC approximation, (c) and (d) in Fig. 1 are replaced by this diagrammatical equation.

On the other hand, Stell\(^4\) showed that the PY approximation can be interpreted in a similar fashion. According to him, in that approximation, the diagrammatical equations (c) and (d) in Fig. 1 are replaced by the one given in Fig. 3.

These two approximations are different in the terms with two or more parallel $z_b$-bonds.

The $x$-bond is the sum of all the diagrams which are composed of two white (open) circles $o_1$ and $o_2$, two or more black (full) circles and $v$-bonds connecting them. When a direct bond is inserted between the two white circles, all the diagrams must become more than doubly connected. Here a diagram is called "more than doubly connected" if, by removing any one pair of two circles, the diagram is not divided into two or more parts in such a way that each of these parts contains one or more circles.
§ 3. Cancellation of the diagrams

As noticed above, the HNC and PY approximations are different by the diagrams with two or more parallel \( z_e \)-bonds; cf. Figs. 2 and 3. In the present section, it is shown that those diagrams have their counterparts on the right-hand side of (c) in Fig. 1 and that those contributions are canceled partly by each other.

\[
\begin{align*}
(A) & + (B) = (C) \\
\end{align*}
\]

Fig. 4. Contributions of two diagrams (A) and (B) cancel partly with each other. The \( e \)-bond in the sum (C) represents a factor \( \exp(-\phi(r)/kT) \).

Let us consider an example given in Fig. 4. Diagrams (A) and (B) are the ones considered by Rushbrooke and Hutchinson in their attempt of improving the HNC approximation. We shall consider their contributions in the case of a hard-sphere gas. Then \( b(r) \) is minus unity within the atomic diameter and zero outside. It is to be noticed that the \( b \)-bond forming a bridge in (B) is minus unity within most regions where none of the other \( b(r) \) are zero. Therefore, the contribution of (A) is almost cancelled by that of (B). A diagram of the type (B) but with \( v \)-bond is the leading term in the \( x \)-bond. Rushbrooke and Hutchinson proposed to consider that term in addition to those considered in the HNC approximation but to estimate the additional term by associating minus unity to the bond forming the bridge. It is to be noticed that (A) is included in the HNC approximation but (B) is neglected; while in the PY approximation, both are neglected.

In fact, in estimating the error of the PY approximation, Percus and Yevick considered a leading correction to \( 0(\rho^3) \). That is given by the sum of (A) and (B). They rewrote them as (C) where the \( e \)-bond represents a factor \( \exp(-\phi(r)/kT) \) and noticed that this factor in (C) is zero in most of the regions integration where all the \( b(r) \)'s in (C) are not zero.

Percus and Yevick and Stell suggested that a similar situation appears for all the diagrams neglected in the PY approximation. Here we confirm that to each of the diagrams \( (T_1) \) which are included in Fig. 2 but neglected in Fig. 3, there exist a set of diagrams \( (T_2) \) on the right-hand side of (c) in Fig. 1 and the contributions from those diagrams \( (T_1 \) and \( T_2 \) cancel partly with each other. Let us consider a diagram with \( n \) parallel \( z_e \)-bonds. The diagram can be written as Fig. 5 in terms of \( z \)-bonds and \( v \)-bonds (see (b) in Fig. 1). Corresponding to this diagram, we find, on the right-hand side of (c) in Fig. 1, a set of diagrams in which an arbitrary number of pairs of the black circles are connected by the \( v \)-bond.
Fig. 5. General diagram included in the HNC approximation but neglected in the PY approximation.

The sum of these diagrams and original one results in one diagram in which each pair of black circles are connected by the $g$-bond; cf. Fig. 4. When $z(r)$ (or $v(r)$) has a finite range $r_n$, the contribution appears only when $n$ coordinates for $n$ black circles are inside the range $r_0$ from the left (or right) white circle of Fig. 5, because of the $n$ $z$-bonds (or $n$ $v$-bonds) connecting them. If $n$ is large, at least one pair of black circles must be nearer than the atomic hard-core radius and the corresponding $g$-factor is zero. Hence the contribution vanishes for large $n$.

§ 4. Interpolation formula

In the HNC approximation, we take account of the diagrams like Fig. 5 but neglect those which appear when the $x$-bond is considered. The discussion in the preceding section shows that such an approximation is not fair. However, the complete neglect of the former diagrams (the PY approximation) will not be the best choice. It will be better to introduce some interpolation between those two limits. Namely, we introduce weight parameters $\gamma_1$, $\gamma_2$, ..., and $\gamma'_1$, $\gamma'_2$, ... and adopt Fig. 6 in place of Fig. 2 or Fig. 3.

![Fig. 6. Interpolation between Fig. 2 (HNC approximation) and Fig. 3 (PY approximation).](attachment:fig6.png)

As shown in the preceding section, $\gamma_n$ and $\gamma'_n$ must be smaller for larger $n$. Considering this requirement, the simplest trial form of $\gamma_n$ and $\gamma'_n$ would be

$$\gamma_n = \gamma'^{n-1}, \quad \gamma'_n = \gamma^{n-1}. \quad (6)$$

Then the equation given in Fig. 6 is written as

$$z(r) = b(r) + \frac{1}{\gamma} \left\{ e^{\alpha z_2(r)} - 1 \right\} b(r) + \frac{1}{\gamma'} \left\{ e^{\alpha' z_2(r)} - 1 - \alpha' z_2(r) \right\}.$$  \[ (7) \]

When $\gamma = \gamma' = \alpha$, the result is further simplified. That is

$$z(r) = b(r) - z_2(r) + \frac{1}{\alpha} \left\{ e^{\alpha z_2(r)} - 1 - \alpha z_2(r) \right\}.$$  \[ (8) \]
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or

\[ v(r) - b(r) = \frac{1}{\alpha} \left\{ e^{\alpha v(r)} - 1 \right\} e^{-v(r)/kT}. \]  

Equation (8) or (9) is a one-parameter interpolation formula. It reduces to the PY approximation (Fig. 3) when \( \alpha \to 0 \) and to the HNC approximation (Fig. 2) when \( \alpha = 1 \). The discussions in the following sections are devoted to this formula.

§ 5. The fourth and fifth virial coefficients of a hard-sphere gas

A check of the validity of various approximations for the pair distribution function has been made by the aid of the virial coefficients for the hard-sphere gas. In this section, such a check is made for the pair distribution function obtained by the one-parameter interpolation formula proposed in the preceding section. That is, the fourth and fifth virial coefficients of the hard-sphere gas are calculated by using that formula and compared with the exact values.

The equation of state is obtained by two different methods from an approximate pair distribution function; the “virial equation”:

\[ \frac{P}{kT} = \rho - \frac{1}{6} \rho^3 \int r g'(r) g(r) dr \]  

and the “compressibility equation”

\[ \frac{\partial}{\partial \rho} \frac{P}{kT} = 1 - \rho \int z(r) dr. \]  

The result is written as

\[ \frac{P}{kT} = \rho + B \rho^3 + C \rho^5 + D \rho^7 + E \rho^9 + \cdots. \]  

The fourth and fifth virial coefficients calculated by the virial equation (10) are denoted by \( D_\rho \) and \( E_\rho \). They are expressed in Fig. 7 in terms of diagram. The corresponding coefficients obtained by the compressibility equation (11) are

\[ D_\rho = -3 \left\{ \frac{1}{8} \bigcirc + \frac{1}{4} \bigcirc \right\} - \frac{1}{12} (1 - \alpha) \bigcirc \]

\[ E_\rho = -4 \left\{ \frac{1}{10} \bigcirc + \frac{1}{2} \bigcirc + \frac{1}{2} \bigcirc + \frac{a}{12} \bigcirc + \frac{a}{12} \bigcirc \right\} \]

\[ - \frac{1}{6} (1 - \alpha) \bigcirc - \frac{1}{3} (1 - \alpha) \bigcirc - \frac{1}{36} (a - a^2) \bigcirc \]

Fig. 7. Fourth and fifth virial coefficients calculated from the virial equation (10), when the one-parameter interpolation formula is adopted.\(^*\)

\(^*\) See the footnote on page 346.
\[ D_c = -\frac{1}{4}\left\{ \left(1 + \frac{a}{2} \right) \begin{array}{c} \hline \ \hline \end{array} + \left(2 + \frac{a}{2} \right) \begin{array}{c} \hline \ \hline \end{array} \right\} \]

\[ E_c = -\frac{1}{5}\left\{ \left(1 + a \right) \begin{array}{c} \hline \ \hline \end{array} + \left(5 + 3a \right) \begin{array}{c} \hline \ \hline \end{array} + \left(5 + 2a \right) \begin{array}{c} \hline \ \hline \end{array} \right\} \]

\[ \begin{array}{c} \hline \ \hline \end{array} + \left(\alpha + \frac{a^2}{6} \right) \begin{array}{c} \hline \ \hline \end{array} + \left(\alpha + \frac{a^2}{6} \right) \begin{array}{c} \hline \ \hline \end{array} \right\} \]

Fig. 8. Fourth and fifth virial coefficients calculated from the compressibility equation (11), when the one-parameter interpolation formula is used.\(^*\)

denoted by \( D_c \) and \( E_c \) and are given in Fig. 8.\(^*\) The numerical values corresponding to the diagrams given in Figs. 7 and 8 have been tabulated for a hard-sphere gas, by Rushbrooke and Hutchinson\(^6\) and Barker and Henderson.\(^1\) By using these values, \( D_p, D_e, E_p \) and \( E_e \) are calculated as

\[ \frac{D_p}{B^3} = 0.2500 + 0.1953\alpha, \]  
(13)

\[ \frac{D_e}{B^3} = 0.2969 - 0.0877\alpha, \]  
(14)

\[ \frac{E_p}{B^4} = 0.0859 + 0.0181\alpha + 0.0407\alpha^2, \]  
(15)

\[ \frac{E_e}{B^4} = 0.1211 - 0.0621\alpha - 0.0097\alpha^2, \]  
(16)

where the second virial coefficient \( B \) is equal to \( 2\pi a^3/3 \); \( a \) being the diameter of a hard sphere.

When \( \alpha \) is determined by the consistency of the value of \( D: D_p = D_e \), then \( \alpha \) is 0.1656. In Table II, the coefficients \( D_p = D_e, E_p \) and \( E_e \) for this value of \( \alpha \) are compared with the values for the HNC and PY approximations and the exact ones, given by Stell,\(^6\) Rushbrooke and Hutchinson\(^6,11\) and Ree and Hoover.\(^1\) The \( E_p \) and \( E_e \) are also listed for the values of \( \alpha \) which make the value \( D_p \) or \( D_e \) be identical to the exact value of \( D \).

Table II. Comparison of the fourth and fifth virial coefficients calculated by various approximations for the hard-sphere gas.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha )</th>
<th>( D_p/B^3 )</th>
<th>( D_e/B^3 )</th>
<th>( E_p/B^4 )</th>
<th>( E_e/B^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNC</td>
<td>1</td>
<td>0.4453</td>
<td>0.2092</td>
<td>0.1447</td>
<td>0.0493</td>
</tr>
<tr>
<td>PY</td>
<td>0</td>
<td>0.25</td>
<td>0.2969</td>
<td>0.0859</td>
<td>0.1211</td>
</tr>
<tr>
<td>( D_p=D_e )</td>
<td>0.1656</td>
<td>0.2824</td>
<td>0.2824</td>
<td>0.0900</td>
<td>0.1105</td>
</tr>
<tr>
<td>( D_p=D )</td>
<td>0.1889</td>
<td>0.2869</td>
<td>0.2869</td>
<td>0.0908</td>
<td>0.1139</td>
</tr>
<tr>
<td>( D_e=D )</td>
<td>0.1138</td>
<td>0.2869</td>
<td>0.2869</td>
<td>0.1103±0.0003</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) A diagram in Figs. 7 and 8 represents an integral of the products of factors for the solid and dashed lines, over all but one coordinates associated to the dots. The factors are \( b(r) \) and \( rdb(r)/dr \), respectively, for a solid line and a dashed line. (No symmetry number is necessary to consider.)
§ 6. Concluding remarks and comparison with related works

An argument has been given to suggest the use of an interpolation between the HNC and PY integral equation for the pair distribution function of classical fluids. One-parameter interpolation is considered to be of special convenience. That interpolation reduces to the PY approximation when the parameter \( \alpha = 0 \) and the HNC approximation when \( \alpha = 1 \). For a hard-sphere gas, the parameter \( \alpha \) is determined such that the fourth virial coefficient becomes the exact value. Then \( \alpha \) is found to be 0.11~0.18.

Considering our discussions about the cancellation of diagrams, we expect the value \( \alpha \) to be the smallest for hard-sphere gas. The value of \( \alpha \) would be larger especially when \( b(r) = \exp\{-\phi(r)/kT\} - 1 \) is positive at some \( r \), namely, the interaction potential has an attractive part. For such a case, \( \alpha \) would take the value for the hard-sphere gas at higher temperatures, where the attractive part is not important. At the lower temperature, the value of \( \alpha \) would become the larger.

As the density is higher the cluster integrals with longer chains in Fig. 5 would be important and then the cluster integrals with more chains would have contribution. This means that \( \alpha \) would be larger.

Up to this point, the parameter \( \alpha \) has been considered as a number. The calculation would not become complicated even if one replaces the parameter \( \alpha \) in Eqs. (8) and (9) by a function \( \alpha(r) \) of \( r \). Our argument of cancellation of diagrams suggests that \( \alpha(r) \) would be large for \( r \) smaller than the atomic diameter and takes a small value near the atomic diameter. The behavior at larger \( r \) would depend on the situation.

A simultaneous agreement of the fourth and fifth virial coefficients with the exact ones has been achieved for a hard-sphere gas by a choice of \( \alpha \). This result might be fortuitous but yet would be a support for our interpolation formula.

Before ending this paper, we compare our one-parameter approximation with the related works. First of all, our virial coefficients are compared with those for the generalized HNC approximation by Hurst.

\[
D_p = D_e = 0.2824, \quad E_p = 0.0915, \quad E_e = 0.1102.
\]

The agreement with the exact ones is almost the same (ours are slightly worse).

In the next place, we recall another interpolation of the HNC and PY approximation proposed by Carley and Lad0 and Rowlinson. Thier interpolation formula is obtained by introducing the approximation

\[
x(r) + [e^{\phi(r)} - 1 - w(r)] = \Phi[e^{\phi(r)} - 1 - w(r)]
\]

in (c) of Fig. 1 and retaining (d) in Fig. 1. Rowlinson assumed that \( \Phi \) is a parameter depending on the density \( \rho \) and the temperature \( T \) and could obtain
a fairly good agreement of the virial coefficients for the hard-sphere gas, by determining the \( \Phi \) as a function of \( \rho \) in such a way that the pressures calculated by the virial equation and the compressibility equation become the same.

A similar self-consistent treatment can be applied to our one-parameter formula by assuming that the parameter \( \alpha \) depends on the density \( \rho \). The series expansion of \( \alpha \) in powers of \( \rho \) is written as

\[
\alpha = \alpha_4 + \alpha_5 \rho + \alpha_6 \rho^2 + \cdots \tag{18}
\]

Then the fourth virial coefficients \( D_4 \) and \( D_5 \) for the hard-sphere gas are given by (13) and (14), respectively, where \( \alpha \) must be replaced by \( \alpha_4 \). The fifth virial coefficients, \( E_p \) and \( E_c \), are given in Fig. 9 or explicitly by the equations:

\[
E_p = \{ E_p \text{ given by (15)} \text{ where } \alpha = \alpha_4 \} + 0.1953 \alpha_5 B^3,
\]

\[
E_c = \{ E_c \text{ given by (16)} \text{ where } \alpha = \alpha_4 \} - 0.0701 \alpha_5 B^3.
\]

\[
E_p = \left\{ \begin{array}{l}
E_p \text{ given in Fig. 7 where } \alpha \text{ is replaced by } \alpha_4
\end{array} \right\} + \frac{1}{12} \alpha_5 + \ldots
\]

\[
E_c = \left\{ \begin{array}{l}
E_c \text{ given in Fig. 8 where } \alpha \text{ is replaced by } \alpha_4
\end{array} \right\} - \frac{1}{10} \alpha_5 \left\{ \begin{array}{l}
\ldots
\end{array} \right\}
\]

Fig. 9. The diagrammatical expressions of the fifth virial coefficients, \( E_p \) and \( E_c \), obtained from the one-parameter interpolation formula when the parameter \( \alpha \) is given by Eq. (18).

The parameter \( \alpha_4 \) is determined as 0.1656 by the self-consistency condition \( D_c = D_p \). The parameter \( \alpha_5 \) is found to be 0.0772 \( B \) by the consistency of the fifth virial coefficient, \( E_p = E_c \). Those consistent fourth and fifth virial coefficients are given in Table III, with the consistent values obtained by Rowlinson for Carly, Lado and Rowlinson’s approximation. The table also includes the values which Henderson obtained for the Hurst generalized HNC approximation mentioned above by a similar procedure. The parameters \( \alpha_4 \) and \( \alpha_5 \) and the corresponding values are also compared in the same table.

Table III. Self-consistent values of fourth and fifth virial coefficients of the hard-sphere gas for various approximations. The parameters \( \alpha_4 \) and \( \alpha_5 \) and their corresponding values are also listed.

<table>
<thead>
<tr>
<th>Approximation</th>
<th>4th virial coefficient/( B^3 )</th>
<th>5th virial coefficient/( B^4 )</th>
<th>( \alpha_4 )</th>
<th>( \alpha_5/\alpha_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carley-Lado, Rowlinson</td>
<td>0.2824</td>
<td>0.1041</td>
<td>( \phi_4 )</td>
<td>0.1656</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \phi_4/\alpha_4 )</td>
<td>0.1297</td>
</tr>
<tr>
<td>Hurst-Henderson</td>
<td>0.2824</td>
<td>0.1053</td>
<td>( 1-2m_4 )</td>
<td>0.1656</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( -2m_4/\alpha_4 )</td>
<td>0.0704</td>
</tr>
<tr>
<td>This paper</td>
<td>0.2824</td>
<td>0.1051</td>
<td>0.1656</td>
<td>0.0772</td>
</tr>
<tr>
<td>Exact</td>
<td>0.2869</td>
<td>0.1103±0.0003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
This table shows that the present approximation is almost equivalent to the Hurst-Henderson approximation (ours is slightly worse) but is superior to the Carley-Lado and Rowlinson approximation, in the respects of the values of the virial coefficients as well as of the convergence of the parameters. The superiority over this approximation is interpreted due to the following situation:

Our one-parameter approximation is considered to be obtained by introducing the approximation

\[ x(r) + [e^{w(r)} - 1 - w(r)] = \frac{1}{\alpha} [e^{azs(r)} - 1 - azs(r)] \]  (19)

in (c) of Fig. 1. The parameter \( \alpha \) in (19) has been introduced so as to make the coefficients of the higher power of \( z_s(r) \) the smaller, while such a care has not been taken in determining the \( \phi \)-dependence of (17).

For various approximate theories presented in the past, various examination methods have been applied. Application of similar examinations to the present approximation are left as future problems.

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**References**

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