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Radial Distribution Function of a Gas of Hard Spheres and the Superposition Approximation*

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The term $g_2(r)$ proportional to the square of the density in the expansion of the radial distribution function $g(r)$ of an imperfect gas in powers of the density is calculated exactly in the case of a gas consisting of hard spheres. The result is checked by means of Boltzmann's value of the 4th virial coefficient of such a gas. The integral equation for $g(r)$, obtained on applying the superposition approximation introduced by Kirkwood and by Born and Green, can also be solved by an expansion in powers of the density. For the case of hard spheres the approximate $g_2'(r)$ found in this way is compared with the exact $g_2(r)$. As a further application of our result on $g_2(r)$ a certain integral is discussed, which is of interest in the treatment of interference effects in neutron scattering problems.

I. INTRODUCTION

As has been shown by Yvon, Kirkwood, de Boer, and others,[1] the radial distribution function of a compressed gas may be expanded in powers of the density

$$g(r)=\exp\{-V(r)/kT\}\cdot\{1+\rho g_1(r)+\rho^2 g_2(r)+\cdots\}. \tag{I.1}$$

The distance between molecules has been denoted by r, the intermolecular potential by $V(r)$ and by ρ the number of molecules per unit volume. The function $g(r)$ is normalized to the value 1 for large distances. As is known, $g_1(r)$, $g_2(r)$, $\cdots$ can be expressed by cluster integrals in which the position of two particles is kept fixed. In classical statistical mechanics, and on the assumption of additivity of intermolecular forces, one has[2]

$$g_1(r_{12})=\int f(r_{13})f(r_{23})d\mathbf{r}_3, \tag{I.2}$$

$$g_2(r_{12})=\tfrac{1}{2}\{g_1(r_{12})\}^2+\varphi(r_{12})+2\psi(r_{12})+\tfrac{1}{2}\chi(r_{12}), \tag{I.3}$$

where r_{ik} is the distance $|\mathbf{r}_i-\mathbf{r}_k|$ between particles i and k, where the function $f(r)$ is related to the intermolecular potential by

$$f(r)=\exp\{-V(r)/kT\}-1 \tag{I.4}$$

and

$$\varphi(r_{12})=\int f(r_{13})f(r_{24})f(r_{34})d\mathbf{r}_3d\mathbf{r}_4, \tag{I.5}$$

$$\psi(r_{12})=\int f(r_{13})f(r_{23})f(r_{24})f(r_{34})d\mathbf{r}_3d\mathbf{r}_4, \tag{I.6}$$

$$\chi(r_{12})=\int f(r_{13})f(r_{23})f(r_{14})f(r_{24})f(r_{34})d\mathbf{r}_3d\mathbf{r}_4. \tag{I.7}$$

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[1] For a survey we refer to J. de Boer, "Reports on Progress in Physics," Phys. Soc. (London) 12, p. 305 (1949).

[2] J. de Boer and A. Michels, Physica 6, 97 (1939).

Kirkwood was the first to evaluate $g_1(r)$ in the simple case of hard spheres without attractive forces, for which, if the diameter of the spheres is taken as unit of length,

$$V(r)=\begin{cases}\infty & \text{for } 0\leqslant r<1\\ 0 & \text{for } r\geqslant 1\end{cases},\quad f(r)=\begin{cases}-1 & \text{for } 0\leqslant r<1\\ 0 & \text{for } r\geqslant 1\end{cases}. \tag{I.8}$$

He found[3]

$$g_1(r)=\begin{cases}\frac{2}{3}\pi(2-\frac{3}{2}r+\frac{1}{8}r^3) & \text{for } r\leqslant 2\\ 0 & \text{for } r\geqslant 2\end{cases}. \tag{I.9}$$

The function $g_1(r)$ was also calculated by numerical integration by de Boer and Michels[2] for the case of a Lennard-Jones potential.

For the simple case of hard spheres again we give in this work the calculation of the ρ^2-term $g_2(r)$, in the expansion (I.1). Our result enables us to test, at least for small densities, the validity of the so-called "superposition approximation" proposed by Kirkwood in the theory of liquids.[1] This test includes as a special case the recent work of Hart, Wallis, and Pode[4] as well as that of Rushbrooke and Scoins[5] who compared the exact value of the 4th virial coefficient in the case of hard spheres with the value obtained from the superposition assumption.

The superposition assumption, when applied as proposed by Born and Green,[6] leads for the $g(r)$-function to the approximate integral equation

$$kT\partial \ln g(r_{12})/\partial \mathbf{r}_1=-\partial V(r_{12})/\partial \mathbf{r}_1 -\rho\int[\partial V(r_{13})/\partial \mathbf{r}_1]g(r_{13})g(r_{23})d\mathbf{r}_3, \tag{I.10}$$

the solution of which from now on we will call $g'(r)$, in distinction from the exact $g(r)$. The function $g'(r)$ can also be expanded in powers of the density

$$g'(r)=\exp\{-V(r)/kT\}\cdot\{1+\rho g_1'(r)+\rho^2 g_2'(r)+\cdots\}. \tag{I.11}$$

As will be shown in Sec. IV, $g_1'(r)$ is identical with the corresponding $g_1(r)$-function of the exact expansion (I.1), whereas $g_2'(r)$ is different from $g_2(r)$. The calculation of $g_2'(r)$ and its comparison with the exact $g_2(r)$ will provide the test of the superposition approximation mentioned above. A short account of the results was published elsewhere.[7]

As a second application of the exact expression of $g_2(r)$, we use it to determine for small densities the value of the following integral

$$K=\int_0^\infty\{1-g(r)\}dr,$$

which is of interest in the discussion of interference effects in neutron scattering problems and has been discussed from quite a different standpoint in the region of large densities.[8]

II. CALCULATION OF $g_2(r)$

For the calculation of φ defined by (I.5) it turns out to be convenient first to calculate

$$\frac{d\varphi(r_{12})}{dr_{12}}=\int\frac{df(r_{13})}{dr_{13}}\frac{\mathbf{r}_{12}\cdot\mathbf{r}_{13}}{r_{12}r_{13}}f(r_{24})f(r_{34})d\mathbf{r}_3d\mathbf{r}_4 =\int\frac{df(r_{13})}{dr_{13}}\frac{\mathbf{r}_{12}\cdot\mathbf{r}_{13}}{r_{12}r_{13}}g_1(r_{23})d\mathbf{r}_3.$$

In the case of hard spheres, df/dr is the δ-function $\delta(r-1)$, and, when applying (I.9) and noting that φ vanishes for $r\geqslant 3$, we find

$$\varphi(r)=\begin{cases}\pi^2[-r^6/1260+r^4/20-r^3/6-r^2/4\\ \quad+(9/5)r-9/4+(27/70)(1/r)] \text{ for } 1\leqslant r\leqslant 3,\\ 0 \text{ for } r\geqslant 3.\end{cases} \tag{II.1}$$

The function $\psi(r)$ defined in (I.6) is calculated in the same simple way, with the result

$$\psi(r)=\begin{cases}\pi^2[r^6/1260-r^4/20+r^3/6+r^2/4-(97/60)r\\ \quad+16/9-(9/35)(1/r)] \text{ for } 1\leqslant r\leqslant 2,\\ 0 \text{ for } r\geqslant 2.\end{cases} \tag{II.2}$$

Now as to $\chi(r)$ given by (I.7), we may remark first that $\chi(r)=0$ for $r\geqslant 2$. Further, in the region $\sqrt{3}\leqslant r\leqslant 2$, the factor $f(r_{34})$ in (I.7) is -1 and hence in this region $\chi(r)$ reduces to $-\{g_1(r)\}^2$. The evaluation of $\chi(r)$ in the remaining region $1\leqslant r\leqslant\sqrt{3}$, proves to be much more complicated. We could perform it by applying the following somewhat indirect procedure, making use of the theory of Fourier transforms.

Let us introduce

$$F(h)=\int f(r)\exp(2\pi i\mathbf{h}\cdot\mathbf{r})d\mathbf{r}=-h^{-\frac{3}{2}}J_{\frac{3}{2}}(2\pi h), \tag{II.3}$$

where $J_{\frac{3}{2}}$ is the Bessel function of order $\frac{3}{2}$, and

$$G(\mathbf{h})=\int f(r_{13})f(r_{23})\exp\{2\pi i\mathbf{h}\cdot[\mathbf{r}_3-\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2)]\}d\mathbf{r}_3.$$

[3] J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).
[4] Hart, Wallis, and Pode, J. Chem. Phys. 19, 139 (1951).
[5] G. S. Rushbrooke and H. I. Scoins, Nature 167, 366 (1951); Phil. Mag. 42, 582 (1951).
[6] M. Born and H. S. Green, Proc. Roy. Soc. (London) A188, 10 (1946).
[7] B. R. A. Nijboer et L. Van Hove, Proc. Koninkl. Nederlandse Akad. Wetenschappen B54, 256 (1951). The relation for the compressibility integral [Eq. (III.3) in the present paper] was quoted incorrectly here.
[8] Placzek, Nijboer and Van Hove, Phys. Rev. 82, 392 (1951).

We make use of cylindrical coordinates z, ρ, φ with the axis passing through the points 1 and 2, and the origin midway between these points. We denote accordingly by h_z and h_ρ the components of $\mathbf{h}$ respectively parallel and perpendicular to the axis. The integration with respect to φ gives

$$\begin{aligned}G(\mathbf{h})&=4\pi\int_0^{1-\frac{1}{2}r_{12}}\cos(2\pi h_z z)dz\\&\quad\times\int_0^{\{1-(\frac{1}{2}r_{12}+z)^2\}^{\frac{1}{2}}}J_0(2\pi h_\rho\rho)\rho d\rho\\&=2h_\rho^{-1}\int_0^{1-\frac{1}{2}r_{12}}\cos(2\pi h_z z)\{1-(\tfrac{1}{2}r_{12}+z)^2\}^{\frac{1}{2}}\\&\quad\times J_1\{2\pi h_\rho[1-(\tfrac{1}{2}r_{12}+z)^2]^{\frac{1}{2}}\}dz.\end{aligned}\tag{II.4}$$

Known properties of the Fourier transformation give

$$\chi(r_{12})=\int F(h)\{G(\mathbf{h})\}^2 d\mathbf{h}.\tag{II.5}$$

Introducing (II.3) and (II.4) into (II.5) and noticing that

$$\begin{aligned}&2\cos(2\pi h_z z)\cos(2\pi h_z z')\\&\qquad=\cos\{2\pi h_z(z+z')\}+\cos\{2\pi h_z(z-z')\}\end{aligned}$$

and that[9] (for $|z\pm z'|\leqslant 1$)

$$\begin{aligned}&\int_{-\infty}^{+\infty}(h_\rho^2+h_z^2)^{-\frac{3}{4}}J_{\frac{3}{2}}\{2\pi(h_\rho^2+h_z^2)^{\frac{1}{2}}\}\cos\{2\pi h_z(z\pm z')\}dh_z\\&\qquad=h_\rho^{-1}\{1-(z\pm z')^2\}^{\frac{1}{2}}J_1\{2\pi h_\rho[1-(z\pm z')^2]^{\frac{1}{2}}\},\end{aligned}$$

we find ($r=r_{12}$)

$$\begin{aligned}\chi(r)&=-4\pi\int_0^{1-\frac{1}{2}r}dz\{1-(\tfrac{1}{2}r+z)^2\}^{\frac{1}{2}}\\&\quad\times\int_0^{1-\frac{1}{2}r}dz'\{1-(\tfrac{1}{2}r+z')^2\}^{\frac{1}{2}}\\&\quad\times\int_0^\infty J_1\{2\pi h_\rho[1-(\tfrac{1}{2}r+z)^2]^{\frac{1}{2}}\}\\&\quad\times J_1\{2\pi h_\rho[1-(\tfrac{1}{2}r+z')^2]^{\frac{1}{2}}\}\cdot[\{1-(z+z')^2\}^{\frac{1}{2}}\\&\quad\times J_1\{2\pi h_\rho[1-(z+z')^2]^{\frac{1}{2}}\}+\{1-(z-z')^2\}^{\frac{1}{2}}\\&\quad\times J_1\{2\pi h_\rho[1-(z-z')^2]^{\frac{1}{2}}\}]h_\rho^{-2}dh_\rho.\end{aligned}\tag{II.6}$$

Thus we are led to the calculation of an integral having the form

$$I=\int_0^\infty J_1(\alpha x)J_1(\beta x)J_1(\gamma x)x^{-2}dx.$$

Integrating by parts and using the relation

$$(d/dx)J_1(\alpha x)=x^{-1}J_1(\alpha x)-\alpha J_2(\alpha x),$$

we obtain

$$\begin{aligned}I&=\tfrac{1}{2}\alpha\int_0^\infty J_2(\alpha x)J_1(\beta x)J_1(\gamma x)x^{-1}dx\\&\quad+\tfrac{1}{2}\beta\int_0^\infty J_1(\alpha x)J_2(\beta x)J_1(\gamma x)x^{-1}dx\\&\quad+\tfrac{1}{2}\gamma\int_0^\infty J_1(\alpha x)J_1(\beta x)J_2(\gamma x)x^{-1}dx.\end{aligned}$$

This expression reduces to elementary functions when we apply the formula due to Sonine and Dougall (see reference 9, p. 37),

$$\int_0^\infty J_2(\alpha x)J_1(\beta x)J_1(\gamma x)x^{-1}dx=(4\pi\alpha^2)^{-1}\beta\gamma(2A-\sin 2A),$$

where

$$A=\begin{cases}0 & \text{for } \alpha^2<(\beta-\gamma)^2\\ \operatorname{arc\,cos}\{(2\beta\gamma)^{-1}(\beta^2+\gamma^2-\alpha^2)\} & \\ & \text{for } (\beta-\gamma)^2<\alpha^2<(\beta+\gamma)^2\\ \pi & \text{for } (\beta+\gamma)^2<\alpha^2.\end{cases}$$

Hence according to (II.6) the calculation of $\chi(r)$ is now reduced to the evaluation of a double integral. This turns out to be a straightforward though very lengthy process. The result is finally given by

$$\begin{aligned}\chi(r)=&-\{g_1(r)\}^2+\pi\{-(3/280)r^4+(41/420)r^2\}(3-r^2)^{\frac{1}{2}}\\&+\pi\{-(23/15)r+(36/35)(1/r)\}\\&\times\operatorname{arc\,cos}\{r[3(4-r^2)]^{-\frac{1}{2}}\}\\&+\pi\{(3/560)r^6-(1/15)r^4+\tfrac{1}{2}r^2+(2/15)r\\&-(9/35)(1/r)\}\operatorname{arc\,cos}\{(r^2+r-3)\\&\times[3(4-r^2)]^{-\frac{1}{2}}\}+\pi\{(3/560)r^6-(1/15)r^4\\&+\tfrac{1}{2}r^2-(2/15)r+(9/35)(1/r)\}\\&\times\operatorname{arc\,cos}\{(-r^2+r+3)[3(4-r^2)]^{-\frac{1}{2}}\}\\&\qquad\text{for } 1\leqslant r\leqslant\surd 3,\\ \chi(r)=&-\{g_1(r)\}^2\quad\text{for }\surd 3\leqslant r\leqslant 2,\\ \chi(r)=&\,0\qquad\text{for } r\geqslant 2.\end{aligned}\tag{II.7}$$

It is seen that $\chi(r)$ as well as $\varphi(r)$ and $\psi(r)$ can be expressed in terms of elementary functions.

III. NUMERICAL RESULTS AND CHECKS

The expressions occurring in (II.1), (II.2), and (II.7) have been computed numerically in the relevant interval $1\leqslant r\leqslant 3$ for the values of r indicated in the first column of Table I. Then from (I.3) the function $g_2(r)$ could be computed; the result is given in the second column of Table I. $g_2(r)$ is represented graphically in Fig. 1, a plot of $g_1(r)$ may be found in de Boer's article.[1]

[9] See W. Magnus und F. Oberhettinger, *Formeln und Sätze für die speziellen Funktionen der mathematischen Physik* (Julius Springer, Berlin, 1943), p. 119.

TABLE I. Numerical values of the term proportional to ρ^2 in the expansion of the radial distribution function of a gas of hard spheres in powers of the density ρ. $g_2(r)$ represents this term when calculated exactly, $g_2'(r)$ when the superposition approximation of Kirkwood and $g_2''(r)$ when another approximation mentioned in IV is used.

r	$g_2(r)$	$g_2'(r)$	$g_2''(r)$
1.00	1.258702	0.987940	1.096623
1.08	0.823710	0.575533	0.723392
1.16	0.453089	0.234207	0.394808
1.24	0.143406	−0.042523	0.112278
1.32	−0.108740	−0.260480	−0.123544
1.40	−0.307092	−0.425349	−0.313051
1.48	−0.455149	−0.542248	−0.456999
1.56	−0.556369	−0.615922	−0.556722
1.64	−0.613934	−0.650636	−0.613956
1.72	−0.630774	−0.650097	−0.630776
1.80	−0.608749	−0.617356	−0.608749
1.88	−0.552826	−0.554682	−0.552826
1.96	−0.463399	−0.463475	−0.463399
2.04	−0.350613	−0.350613	−0.350613
2.12	−0.254150	−0.254150	−0.254150
2.20	−0.178107	−0.178107	−0.178107
2.28	−0.119833	−0.119833	−0.119833
2.36	−0.076678	−0.076678	−0.076678
2.44	−0.046047	−0.046047	−0.046047
2.52	−0.025451	−0.025451	−0.025451
2.60	−0.012563	−0.012563	−0.012563
2.68	−0.005265	−0.005265	−0.005265
2.76	−0.001704	−0.001704	−0.001704
2.84	−0.000344	−0.000344	−0.000344
2.92	−0.000022	−0.000022	−0.000022
3.00	−0.000000	−0.000000	−0.000000

The result obtained for $g_2(r)$ may be checked in two ways by means of the known value of the fourth virial coefficient B_4 for a gas of hard spheres. First, as a consequence of the virial theorem we have generally (see e.g., reference 1, p. 327)

$$B_4=-2\pi(3kT)^{-1}\int_0^\infty \exp\{-V(r)/kT\} \times[dV(r)/dr]g_2(r)r^3dr.$$

In the case of hard spheres this becomes

$$B_4=\tfrac{2}{3}\pi\int_0^\infty \delta(r-1)g_2(r)r^3dr=\tfrac{2}{3}\pi g_2(1). \quad \text{(III.1)}$$

On substituting $r=1$ into our result for $g_2(r)$ we find an expression for B_4 which is analytically identical with the one obtained by Boltzmann.[10] Its numerical value is

$$B_4=0.2869b^3, \quad \text{(III.2)}$$

where according to the customary notation $\frac{1}{4}b$ is the volume of each particle.

An additional check which includes the values of $g_2(r)$ for all r can be based upon the well-known relation, due to Ornstein and Zernike, that connects the relative compressibility with the radial distribution function (see reference 1, p. 365)

$$kT(\partial\rho/\partial p)_T=1+4\pi\rho\int_0^\infty\{g(r)-1\}r^2dr. \quad \text{(III.3)}$$

Expanding both members of this relation into powers of ρ and equating the coefficients of equal powers, we are led to the following equality holding for hard spheres

$$B_4=-\tfrac{1}{8}b^3-\pi\int_1^\infty g_2(r)r^2dr. \quad \text{(III.4)}$$

Numerical integration of the function $g_2(r)$ gave again the result (III.2) for B_4.

IV. THE SUPERPOSITION APPROXIMATION

As has been mentioned in the introduction, the superposition assumption of Kirkwood when applied in the form as discussed by Born and Green leads to the integral Eq. (I.10) for the approximate radial distribution $g'(r)$. If we now substitute

$$g'(r)=v(r)\exp\{-V(r)/kT\},$$

then $v(r)$ obeys the integral equation

$$\frac{\partial v(r_{12})}{\partial \mathbf{r}_1}=-\frac{\rho v(r_{12})}{kT}\int v(r_{13})v(r_{23})\frac{\partial V(r_{13})}{\partial \mathbf{r}_1} \times\exp\left\{-\frac{V(r_{13})}{kT}-\frac{V(r_{23})}{kT}\right\}d\mathbf{r}_3. \quad \text{(IV.1)}$$

In accordance with the expansion (I.11) we try to solve this equation by the expansion

$$v(r)=1+\rho g_1'(r)+\rho^2 g_2'(r)+\ldots.$$

Introducing this expansion into (IV.1) and equating

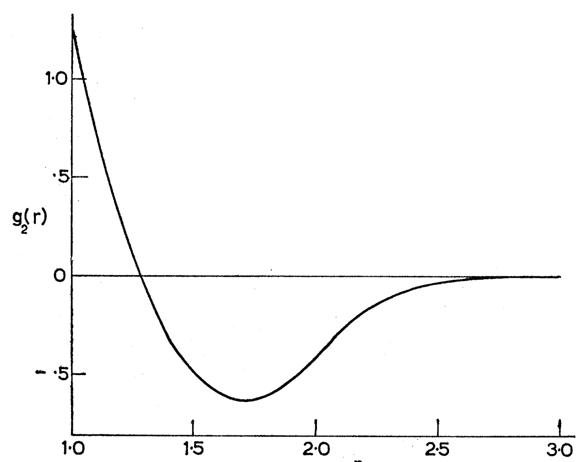

FIG. 1. The coefficient $g_2(r)$ of the term proportional to ρ^2 in the expansion of the radial distribution function for a gas of hard spheres into powers of the density ρ.

[10] L. Boltzmann, Verslag. Gewone Vergadering Afd. Natuurk. Nederlandse Akad. Wetensch. 7, 484 (1899), see also H. Happel, Ann. Physik **21**, 342 (1906); R. Majumdar, Bull. Calcutta Math. Soc. **21**, 107 (1929).

the coefficients of ρ on both sides we find, making use of the fact that $g_1'(r)\rightarrow 0$ as $r\rightarrow\infty$

$$g_1'(r)=\int f(r_{13})f(r_{23})d\mathbf{r}_3. \qquad \text{(IV.2)}$$

Comparison of (IV.2) with (I.2) shows that

$$g_1'(r)=g_1(r), \qquad \text{(IV.3)}$$

so that the approximate $g'(r)$ is exact to first order in ρ.

In a similar way it is found that

$$g_2'(r)=\tfrac{1}{2}\{g_1(r)\}^2+\varphi(r)+2\psi(r)+\tfrac{1}{2}\chi'(r), \qquad \text{(IV.4)}$$

so $g_2'(r)$ is identical with the exact $g_2(r)$ given by (I.3) except that $\chi(r)$ must be replaced by $\chi'(r)$ where

$$\partial\chi'(r_{12})/\partial\mathbf{r}_1=-2\int f(r_{13})f(r_{23})f(r_{34})[\partial f(r_{14})/\partial\mathbf{r}_1]d\mathbf{r}_3d\mathbf{r}_4,$$

or also

$$\frac{d\chi'(r_{12})}{dr_{12}}=-2\int f(r_{13})f(r_{23})\frac{\mathbf{r}_{12}\cdot\mathbf{r}_{13}}{r_{12}r_{13}}\frac{dg_1(r_{13})}{dr_{13}}d\mathbf{r}_3. \qquad \text{(IV.5)}$$

Thus it is seen that on the assumption of superposition $g_2(r)$ is given incorrectly. An analogous result was derived by Rushbrooke and Scoins for the 4th virial coefficient.[5] For the special case of hard spheres $\chi'(r)$ can be evaluated easily with the help of (I.9). One finds[11]

$$\chi'(r)=\begin{cases}\pi^2[-r^6/630+r^4/10-(19/72)r^3-r^2/2 \\ \quad +(12/5)r-22/9+(18/35)(1/r)] \\ \qquad\qquad \text{for } 1\leqslant r\leqslant 2, \\ 0 \text{ for } r\geqslant 2.\end{cases} \qquad \text{(IV.6)}$$

Numerical values for the approximate function $g_2'(r)$ in the case of hard spheres are given in the third column of Table I. The difference $g_2(r)-g_2'(r)$ is plotted as a function of r in Fig. 2 (full curve). It is seen that for $r=1$ the Kirkwood approximation $g_2'(r)$ deviates considerably (by more than 20 percent) from the exact $g_2(r)$; for larger values of r the deviation decreases quickly and for $r\geqslant 2$ $g_2'(r)$ is equal to $g_2(r)$.

It is now very easy to calculate an approximate value for the 4th virial coefficient B_4 on the assumption of superposition. Formula (III.1), derived from the virial theorem, gives

$$B_4'=0.2252b^3, \qquad \text{(IV.7)}$$

a value that was found recently in a different way by Hart, Wallis and Pode[4] as well as by Rushbrooke and Scoins.[5] However, B_4' may also be calculated from (III.4), that is from the relation of Ornstein and Zernike. Then one obtains

$$B_4'=0.3424b^3. \qquad \text{(IV.8)}$$

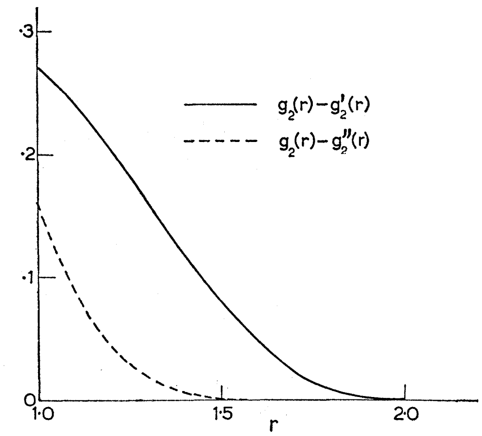

FIG. 2. Difference of the exact function $g_2(r)$ for hard spheres and the approximate functions $g_2'(r)$ (superposition approximation) and $g_2''(r)$.

We notice that the superposition approximation destroys the consistency between the equation of state as derived from $g(r)$ through the virial theorem and the equation of state resulting from the compressibility integral. This consistency requires some special analytical property of the exact $g(r)$, which is not compatible with the superposition assumption. In view of this fact one may think it questionable whether one is entitled to attach any physical meaning to analytical peculiarities exhibited by the approximate $g(r)$-function obtained under the superposition assumption. In particular conclusions drawn from Kirkwood's integral equation about a kind of condensation phenomenon for a fluid consisting of hard spheres should be accepted only with caution.[12,13]

It may be worth while to remark here that a better and simpler approximation for $g_2(r)$ is obtained in the case of hard spheres when in formula (I.7) for $\chi(r_{12})$ the factor $f(r_{34})$ in the integrand is replaced by -1, so that $\chi(r_{12})$ becomes $-\{g_1(r_{12})\}^2$. Then $g_2(r_{12})$ becomes simply [see Eq. (I.3)]

$$g_2''(r_{12})=\varphi(r_{12})+2\psi(r_{12}). \qquad \text{(IV.9)}$$

The numerical values of $g_2''(r)$ are given in the fourth column of Table I; the difference $g_2(r)-g_2''(r)$ is plotted as a dotted line in Fig. 2. The values for the 4th virial coefficient derived in this approximation from the virial theorem and from the relative compressibility integral are now respectively

$$B_4''=0.2500b^3 \quad\text{and}\quad B_4''=0.2969b^3.$$

This simple approximation is therefore much more satisfactory than that of Kirkwood, at least for the term $g_2(r)$ dealt with here. However, until now we have not

[11] This result can of course also be easily obtained directly from the integral equation (IV.1), after it has been reduced to the particularly simple form valid for hard spheres. Starting from that one could also easily calculate higher terms in the expansion of $g'(r)$ in powers of the density.

[12] Kirkwood, Maun, and Alder, J. Chem. Phys. **18**, 1040 (1950).

[13] See also R. J. Riddell, thesis (Ann Arbor, 1951).

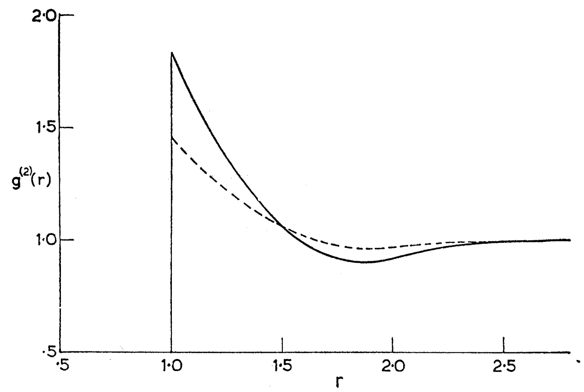

FIG. 3. Radial distribution function $g^{(2)}(r)$ (expansion into powers of the density ρ up to the term with ρ^2) for hard spheres as a function of r for values of $\rho=0.442$ (full line) and 0.275 (dotted line).

been able to extend it into a more general scheme superior to the superposition assumption.

Up to now we have discussed only the term $g_2(r)$ in the expansion (I.1) of the radial distribution function $g(r)$ into powers of the density. Evaluation of this term for hard spheres both exactly and on application of the superposition approximation made the deficiencies of the latter appear clearly. Let us consider now for a moment the radial distribution function $g(r)$ itself. Only for small densities does the part of the expansion up to the ρ^2-term, which we will call $g^{(2)}(r)$

$$g^{(2)}(r)=\exp\{-V(r)/kT\}\cdot\{1+\rho g_1(r)+\rho^2 g_2(r)\} \quad \text{(IV.10)}$$

give an adequate approximation for the function $g(r)$, because for larger densities the neglected terms would give an appreciable contribution. $g^{(2)}(r)$ has been plotted for the case of hard spheres in Fig. 3 for two values of the density: $\rho=0.442$ (full line) and $\rho=0.275$ (dotted line). It is for these densities and a few higher ones that Kirkwood, Maun, and Alder[12] recently calculated the total $g'(r)$-function for hard spheres by numerical integration of the integral Eq. (I.10). It is interesting to compare our graphs of $g^{(2)}(r)$ with the corresponding ones given by these authors for $g'(r)$; for these relatively low densities the deviations are only small. To obtain some insight in the behavior of the total $g'(r)$-function for the higher densities, one might reason as follows.[14]

From (IV.10) in combination with (I.9), (III.1), and (III.2) we have

$$g^{(2)}(1)=1+1.851\gamma+2.517\gamma^2, \quad \text{(IV.11)}$$

where $\gamma=2^{-\frac{1}{2}}\rho$ is the ratio of the density ρ to the density for close packing of the hard spheres. If in analogy with (IV.10) the function $g^{(2)\prime}(r)$ is defined by

$$g^{(2)\prime}(r)=\exp\{-V(r)/kT\}\cdot\{1+\rho g_1(r)+\rho^2 g_2'(r)\}, \quad \text{(IV.12)}$$

we find from (III.1) and (IV.7)

$$g^{(2)\prime}(1)=1+1.851\gamma+1.976\gamma^2. \quad \text{(IV.13)}$$

Table II compares, for various values of γ, the quantities $g^{(2)}(1)$ and $g^{(2)\prime}(1)$ with $g'(1)$ as obtained numerically by Kirkwood, Maun, and Alder.[12] We see that not only is

$$g'(1)<g^{(2)}(1), \quad \text{(IV.14)}$$

but also, for the higher densities

$$g'(1)<g^{(2)\prime}(1). \quad \text{(IV.15)}$$

From (IV.15) it follows that some of the virial coefficients obtained in the superposition approximation from the virial theorem are negative. It would seem extremely likely, however, that for hard spheres all virial coefficients are positive, though, as far as we are aware, this has not yet been proved in a rigorous way. Accepting this conjecture, one would conclude from (IV.14) that the pressure obtained in the superposition approximation from the virial theorem is too low, and for the higher densities, very much too low.

TABLE II. Values of the approximate radial distribution functions $g^{(2)}(r)$, $g^{(2)\prime}(r)$, and $g'(r)$ in the point $r=1$ for various densities in the case of hard spheres.

γ	$g^{(2)}(1)$	$g^{(2)\prime}(1)$	$g'(1)$
0.1942	1.455	1.434	1.45
0.3125	1.825	1.772	1.80
0.476	2.45	2.23	2.36
0.578	2.91	2.73	2.66
0.654	3.29	3.06	2.85
0.676	3.40	3.15	2.90

V. THE INTEGRAL $\int_0^\infty\{1-g(r)\}dr$

In a previous paper[8] it was shown that, when interference is taken into account, the total cross section for scattering of neutrons by a system of heavy nuclei is given asymptotically in the region of small wavelength by

$$(\sigma_{\mathrm{tot}})_{\mathrm{As}}=1-\rho\lambda^2/2\pi\int_0^\infty\{1-g(r)\}dr. \quad \text{(V.1)}$$

Here the total cross section of an isolated particle is taken as the unit of cross section and the radial distribution function $g(r)$ which has the same meaning as above, is obtained from the possibly angle dependent pair distribution function $g(\mathbf{r})$ by averaging over all directions. The value of the integral was investigated extensively for dense systems of particles in reference 8.

For the special case of hard spheres without attractive forces (we will take the diameter of the spheres as unit of length as we did in the foregoing) it was shown that in the region of high density the coefficient

$$K=\int_0^\infty\{1-g(r)\}dr \quad \text{(V.2)}$$

[14] The following argument was kindly pointed out to us by Dr. G. Placzek.

can approximately be represented by

$$K \approx 0.643\gamma^{-\frac{1}{3}}, \qquad \text{(V.3)}$$

where γ again is the ratio of the density ρ to the density for close packing of the spheres. Actually (V.3) does represent an upper bound, but the deviations of the true K from (V.3) may for high densities be expected to be small. On the other hand our calculation of the term $g_2(r)$ in the expansion (I.1) now enables us to

TABLE III. Values of the integrals $K=\int_0^\infty\{1-g(r)\}dr$ and $I=4.2^{1/6}\gamma^{1/3}K$ for various values of γ computed for the approximate radial distribution functions for hard spheres given by Kirkwood *et al.* (reference 12).

λ	K	γ(K.)	I(K.)	γ(B.G.)	I(B.G.)
5	0.89	0.211	2.38	0.194	2.31
10	0.84	0.353	2.67	0.313	2.56
20	0.78	0.562	2.91	0.476	2.75
33	0.72	0.775	2.98	0.654	2.81

evaluate K in the region of small densities. Indeed, the introduction of (I.1) into (V.2) gives

$$K=1-\sqrt{2}\gamma\int_1^\infty g_1(r)dr-2\gamma^2\int_1^\infty g_2(r)dr-\cdots. \qquad \text{(V.4)}$$

Computation of the integrals, the first from (I.9) and the second numerically from Table I, leads to

$$K=1-0.648\gamma+0.537\gamma^2-\cdots. \qquad \text{(V.5)}$$

It may be noted that, if we had replaced the exact $g_2(r)$ in (V.4) by $g_2'(r)$ (superposition approximation) or by $g_2''(r)$, the coefficient of γ^2 in (V.5) would have been 0.741 or 0.583, respectively.

It is rather remarkable that the integral K appears to be now pretty well known for all densities, because the two representations (V.3) and (V.5) valid for high and for small densities respectively join very nicely in the intermediate region. Both approximations namely yield for $\gamma=0.5$ the same value $K=0.810$ (which is of course accidental) and the slopes of the two $K(\gamma)$-curves are not too different at this junction. This fact is illustrated in Fig. 4, where the function $K(\gamma)$ is plotted using Eq. (V.5) for $0\leqslant\gamma\leqslant0.5$ and Eq. (V.3) for $0.5\leqslant\gamma\leqslant1$.

For comparison we have calculated values of K for the approximate functions $g'(r)$, mentioned already in IV, which were obtained by Kirkwood, Maun, and Alder by numerical integration of the integral equation (I.10).[12] Actually in their work to every solution $g'(r)$, characterized by the value of a certain parameter λ, belong

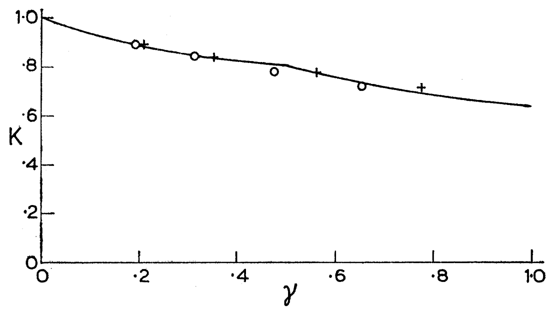

FIG. 4. The integral $K=\int_0^\infty\{1-g(r)\}dr$ for hard spheres as a function of the ratio γ of density to density for close packing. Values obtained from integration of the numerical solutions by Kirkwood *et al.* (reference 12) of the integral equation (I.10) are indicated by circles when the Born-Green, by crosses when the Kirkwood version of the theory is adopted.

two different values of the quantity γ, depending on whether the Born-Green or the slightly different Kirkwood version of the theory is used. By a rough numerical integration of their results for the $g'(r)$-functions we find the values of K, given in Table III.[15] In this table we have also given the respective values for $I=4\cdot2^{1/6}\gamma^{1/3}K$, because it was this quantity that, at least for high densities, was discussed extensively in an earlier paper.[8] The results for K are included in Fig. 4. The circles correspond to the γ-values according to Born and Green, the crosses to those according to Kirkwood. It is seen that in particular the circles (densities according to Born and Green) appear to lie rather closely on a curve joining smoothly the low and high density parts of our $K(\gamma)$-curve. In the opinion of the authors, however, the values of K do not readily lend themselves to a discussion of the validity of the superposition approximation; without a more precise investigation of accuracy the fact, that the K-values resulting from the superposition assumption lie in the neighborhood of our approximate $K(\gamma)$-curve, would hardly seem significant. As to the question of the validity (of the Born-Green form) of the superposition assumption we must rather refer to IV. In the light of the investigation in reference 8 one could only state that the values of I (and hence also of K) resulting from the Kirkwood form of the superposition assumption are definitely too high for the higher densities.

In conclusion the authors wish to thank Dr. G. Placzek of the Institute for Advanced Study, Princeton, New Jersey, who suggested the present investigation, for his stimulating interest.

[15] The values of K for the higher densities had also been computed by Kirkwood some time ago (private communication).