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Scattering of Small Wavelength Neutrons by a Gas of Hard Spheres

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The modern theory of classical fluids, using the Born-Green-Yvon equation and a modified form of the Kirkwood superposition approximation involving powers of the particle number density n , is used to investigate the total neutron elastic scattering cross section for high energy neutrons and heavy nuclei regarded as hard sphere particles, in the low density limit where a number density expansion is valid. It is found by the present arguments that up to the fourth power of the density

$$\sigma_{\text{tot}} = 1 - (\lambda^2/2\pi)(n - 0.458n^2 + 0.273n^3 - 0.213n^4),$$

in this low density limit, where the symbols have their usual meaning.

1. INTRODUCTION

IT has been shown by Placzek, Nijboer, and Van Hove¹ that the total neutron scattering cross section (including the effects of interference) by heavy nuclei (hereafter called particles) has the asymptotic form for small wavelengths

$$\sigma_{\text{tot}} = 1 - (n\lambda^2/2\pi)K, \quad (1)$$

where

$$K = \int_0^\infty [1 - g(r)]dr. \quad (2)$$

Here, σ_{tot} is the total cross section with that of an isolated particle taken as the unit; $g(r)$ is the (if necessary angle-averaged) particle radial distribution function; n is the particle number density ($=N/V$, if N particles are contained in a volume V); and λ is the (small) wavelength. The representation of the particles as hard spheres, with no properties of attraction, has physical interest at high neutron energies. The integral K can be evaluated fairly readily in the two limits of high and low density; Placzek *et al.* have discussed the form of the integral K in some detail at these limits.

For very high densities, it appears that $K \sim 0.722n^{-1}$. For low densities, K can be expanded in powers of the density and evaluated using the arguments of classical fluid statistical mechanics.² The present paper is con-

cerned with the further discussion of the integral (2) defining K in the low-particle density region using improved and consistent arguments recently found successful by the present author in the theory of fluids.^{3,4}

2. EXPANSION IN POWERS OF THE DENSITY

For densities which are not too high, the radial distribution $g(r)$ appearing in Eq. (2) can be expanded in powers of n according to

$$g(r) = \exp\left\{-\frac{\psi(r)}{kT}\right\} \times [1 + a_1(r)n + a_2(r)n^2 + a_3(r)n^3 + \dots]. \quad (3)$$

In this expression k and T have their usual meanings; $\psi(r)$ is the potential of the interparticle force which is ultimately to be given the form appropriate to hard spheres (see Sec. 6), and the coefficients a_i are as yet unknown. The a_i will in fact be determined by making a direct appeal to the formulas of statistical mechanics; we use here the Born-Green-Yvon equation for this purpose, viz.,

$$\begin{aligned} \frac{\partial g(r)}{\partial r} + \frac{1}{kT} \frac{\partial \psi(r)}{\partial r} g(r) \\ = -\frac{n}{kT} \int_0^\infty \frac{\partial \psi(r_{13})}{\partial r_{13}} g^{(3)}(r, r_{13}, r_{23}) 4\pi r_{13}^2 dr_{13}, \end{aligned} \quad (4)$$

¹ G. Placzek, B. R. A. Nijboer, and L. Van Hove, *Phys. Rev.* **82**, 392 (1951).

² B. R. A. Nijboer and L. Van Hove, *Phys. Rev.* **85**, 777 (1952).

³ G. H. A. Cole, *J. Chem. Phys.* **34**, 2016 (1961).

⁴ G. H. A. Cole, *J. Chem. Phys.* **36**, 1680 (1962).

where $g^{(3)}$ is the triplet distribution and (r, r_{13}, r_{23}) are the three associated particle separation distances. The insertion of (3) into (4) provides an equation involving powers of the density from which the coefficients of the expansion (3) are determined from the consideration of equal powers of the density. With the coefficients a_i known, the insertion of (3) into (2) gives at once K explicitly as an expansion in powers of n .

This procedure is possible if $g^{(3)}$ is known in terms of $g(r)$. A widely used relation is the approximation due to Kirkwood

$$g^{(3)}(r, r_{13}, r_{23}) = g(r)g(r_{13})g(r_{23}), \quad (5)$$

which will be denoted by $g_K^{(3)}$ in what follows.

The virial expansion of the particle pressure in terms of the density can be derived by an appeal either to the virial theorem (pressure considerations) or to the fluctuation theory (relative compressibility arguments). The virial theorem leads to the formula for the pressure

$$p = nkT - \frac{n^2}{6} \int_0^\infty \frac{\partial \psi(r)}{\partial r} g(r) 4\pi r^3 dr, \quad (6a)$$

while the alternative compressibility formula is

$$kT \left. \frac{\partial n}{\partial p} \right|_T = 1 + 4\pi n \int_0^\infty [g(r) - 1] r^2 dr. \quad (6b)$$

It is required of any expansion (3) for $g(r)$ which is to be inserted into the Eq. (2) for K that it should not cause the two independent formulas (6) for the pressure to be mutually inconsistent. It is, however, known^{2,5} that the function calculated from (3) and (4) using the original Kirkwood approximation (5) does lead to inconsistent values in the fourth, fifth, and higher virial coefficients (conventionally written D , E , and so on) when calculated from (6a) and (6b), although the second and third virial coefficients (B and C) are fully consistent. The theory, then, needs further alteration before being applied to the calculation of the cross section by way of the integral (2).

The present author has recently reconsidered^{3,4} the virial expansion by modifying the expression (5) to include explicitly powers of the density. For this purpose write

$$g^{(3)}(r, r_{13}, r_{23}) = g_K^{(3)}(r, r_{13}, r_{23}) [1 + X_1 n + X_2 n^2 + \dots], \quad (7)$$

where $g_K^{(3)}$ denotes the simple approximation (5). The coefficients X_i are in general functions of r , r_{13} , r_{23} , and ψ/kT . Although the X_i can, at least in principle, be deduced from the consideration of cluster integrals,⁶ they can alternatively be selected so as to ensure simple internal consistency within the theory in connection with the Eqs. (6) and this is the point of view to be taken here.

⁵ G. S. Rushbrooke and H. I. Scoins, Phil. Mag. **42**, 582 (1951).

⁶ J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

3. RELATIONS INVOLVING THE X_i

For determining the coefficients X_i in the expansion (7) we shall appeal to the virial expansion of the pressure in powers of the density derived from each of the equations (6); in what follows the fourth and fifth coefficients will be invoked (respectively, D and E) leading to the coefficients X_1 and X_2 in (7). Further coefficients in (7) can be derived if required; the extension is straightforward although extremely tedious.

The insertion of the expansion (3) into each of the formulas (6) leads readily to the following expressions for D and E . If a subscript p refers to the pressure equation (6a) while a subscript c refers to the compressibility equation (6b);

$$D_p = \frac{2\pi}{3} \int_0^\infty a_2(r) \alpha'(r) r^3 dr, \\ D_c = 3BC - 2B^3 - \pi \int_0^\infty [\alpha(r) + 1] a_2(r) r^2 dr; \quad (8a)$$

and

$$E_p = \frac{2\pi}{3} \int_0^\infty a_3(r) \alpha'(r) r^3 dr, \\ E_c = \frac{16B}{5} \left[D_c + B^3 - \frac{9BC}{4} \right] \\ + \frac{9C}{5} - \frac{4\pi}{5} \int_0^\infty [\alpha(r) + 1] a_3(r) r^2 dr. \quad (8b)$$

Here,

$$\alpha(r) = \exp \left\{ -\frac{\psi(r)}{kT} \right\} - 1, \\ \alpha'(r) = -\frac{1}{kT} \frac{\partial \psi(r)}{\partial r} \exp \left\{ -\frac{\psi(r)}{kT} \right\}. \quad (8c)$$

These expressions can be evaluated if the functions $a_2(r)$ and $a_3(r)$ are known; we shall require that $D_p = D_c$ and $E_p = E_c$ simultaneously.

The insertion of the approximation (7) and the expansion (3) into Eq. (4) leads eventually to the following expressions^{3,4} for a_2 and a_3 ; a_2^K and a_3^K are those respective forms of the functions when $X_1 = X_2 = 0$, i.e., when (7) reduces to the original Kirkwood approximation (5). For $a_2(r)$;

$$a_2(r) = a_2^K(r) + \Xi_2(r), \quad (9a)$$

where

$$\Xi_2(r) = -\pi \int_0^\infty \int_{-s}^s X_1(r, s, t) \left(\frac{r+t}{r} \right) \\ \times (s^2 - t^2) \alpha(r+t) d\alpha'(s) ds; \quad (9b)$$

and for $a_3(r)$;

$$a_3(r) = a_3^K(r) + \Xi_3(r), \quad (10a)$$

where

$$\begin{aligned}\Xi_3(r) = & -\pi \int_0^\infty \int_{\lambda-s}^s X_1(r, s, t) \left(\frac{r+t}{r} \right) \\ & \times (s^2 - t^2) a_1(r+t) [\alpha(r+t) + 1] dt \alpha'(s) ds \\ & - \pi \int_0^\infty \int_{-s}^s X_1(r, s, t) \left(\frac{r+t}{r} \right) \\ & \times (s^2 - t^2) \alpha(r+t) dt a_1(s) \alpha'(s) ds \\ & - \pi \int_0^\infty \int_{-s}^s X_2(r, s, t) \left(\frac{r+t}{r} \right) \\ & \times (s^2 - t^2) \alpha(r+t) dt \alpha'(s) ds. \quad (10b)\end{aligned}$$

We have here reverted to the conventional notation by writing $s \equiv r_{13}$ and $t \equiv r_{23}$. The functions a_1 , a_2^K , and a_3^K will be written out explicitly later (Sec. 5) for hard spheres, and so can be taken as being known in what follows.

According to the formulas (8a) and (9), the condition $D_p = D_c$ holds if Ξ_2 satisfies the condition

$$\frac{2\pi}{3} \int_0^\infty \{r\alpha'(r) + \frac{3}{2}[\alpha(r) + 1]\} \Xi_2(r) r^2 dr = D_c^K - D_p^K. \quad (11)$$

According to the formulas (8b) and (10) the simultaneous condition $E_p = E_c$ is true if Ξ_3 satisfies the condition

$$\begin{aligned}\frac{2\pi}{3} \int_0^\infty \{r\alpha'(r) + (6/5)[\alpha(r) + 1]\} \Xi_3(r) r^2 dr \\ - \frac{16B}{5} (D^M - D_c^K) = E_c^K - E_p^K, \quad (12)\end{aligned}$$

where D^M is the single consistent modified value of D which is compatible with the condition (11). Reference to Eq. (9b) shows that the condition (11) involves X_1 , while reference to Eq. (10b) shows that the condition (12) involves both X_1 and X_2 . Further members of the series can be included into the scheme by including higher virial coefficients than E .

4. DETERMINATION OF THE X_i

The integral conditions (11) and (12) can be arranged into elementary expressions for the direct determination of X_1 and X_2 if an approximation is accepted. This approximation (the utility of which will be considered in Sec. 7) is that both X_1 and X_2 can be treated as being simple constants (e.g., some average values) in the expansion (7) for $g^{(3)}$. The function $g^{(3)}$ calculated in this way is then not a correct function in its own right but is instead merely a function which leads to significant information about the interesting function $g(r)$. If this approximation is accepted then the expres-

sions (9b) and (10b) simplify drastically. Thus we have

$$\Xi_2(r) = X_1 a_1(r), \quad (13a)$$

and

$$\Xi_3(r) = X_1 [a_2^K(r) - \frac{1}{2} a_1^2(r)] + X_2 a_1(r). \quad (13b)$$

Since we know a_1 and a_2^K , X_1 and X_2 are now the only unknowns on the right-hand side of these two expressions.

The insertion of (13a) and (9a) into (11) then leads immediately to an expression for X_1 :

$$(4B^2 + C)X_1 = D_c^K - D_p^K, \quad (14a)$$

where the virial coefficients B and C are defined as usual as in reference 3, Eqs. (8) and (9). The insertion of (13b) and (10a) into (12) leads alternatively to the expression for X_2 :

$$\begin{aligned}2(C + 2B^2)X_2 = & 5(E_c^K - E_p^K) \\ & - X_1(5D_p^K - 4D_c^K + 12BC - 8B^2 - f(r)), \quad (14b)\end{aligned}$$

where

$$3f(r) = \pi \int_0^\infty \{5\alpha'(r)r + 3[\alpha(r) + 1]\} a_1^2(r) r^2 dr. \quad (14c)$$

It will be found in Sec. 5 that for hard spheres the functions a_1 , a_2 , and a_3 become zero after a distance of only a few molecular diameters so that the requirement $X_i = \text{constant}$ means that the X_i are essentially independent of the particle separation up to such a moderate distance. Normalization requirements associated with $g^{(3)}$ can be fully met with, for hard spheres, because we are concerned with calculating an accurate $g(r)$ without first calculating a physically exact $g^{(3)}$.

5. FUNCTIONS a_1 , a_2 , AND a_3

The coefficients of the terms in the expansion (3) for $g(r)$ which follow from the modified superposition approximation (7) can be calculated if the analogous coefficients derived from the use of original Kirkwood form of the approximation (5) are known, provided also that the coefficients X_i in (7) are also known. Assuming that $X_i = \text{constant}$ is a significant approximation, then reference to Eqs. (9), (10), (13), and (14) shows that the values of the coefficients X_1 and X_2 then follow simply from a knowledge of a_1 , a_2^K , a_3^K , so that a detailed knowledge of the solutions of the various equations under the Kirkwood approximation (5) is necessary before any improvement on the present lines can be attempted.

The functions a_1 , a_2^K , a_3^K , and so on, are obtained by inserting (3) and (5) into (4) and equating the coefficients for equal powers of n in the ensuing equation. The coefficient of the linear term in n is $a_1(r)$; for hard spheres Kirkwood showed long ago that

$$\begin{aligned}a_1(r) = & \pi \left(\frac{4}{3} - r + \frac{1}{12} r^3 \right), \quad \text{for } r < 2, \\ & = 0, \quad \text{for } r > 2\end{aligned} \quad (15)$$

where the particle diameter is chosen as being the unit of distance. The coefficient of the quadratic term in n gives^{2,3,7} $a_2^K(r)$:

$$a_2^K(r) = \chi_2(r) + \omega_2(r), \quad (16a)$$

$$\chi_2(r) = \pi^2 \left\{ \frac{9}{70} \frac{1}{r} - \frac{35}{36} + \frac{47}{30} r - \frac{1}{2} r^2 + \frac{7}{48} r^3 - \frac{1}{12} r^4 + \frac{1}{288} r^6 \right\},$$

$$(1 \leq r \leq 2),$$

$$= 0 \quad \text{for } r > 2. \quad (16b)$$

$$\omega_2(r) = \pi^2 \left\{ \frac{27}{70} \frac{1}{r} - \frac{9}{4} + \frac{9}{5} r - \frac{1}{4} r^2 - \frac{1}{6} r^3 + \frac{1}{20} r^4 - \frac{1}{1260} r^6 \right\},$$

$$(2 \leq r \leq 3)$$

$$= 0, \quad \text{for } r < 2 \quad \text{and for } r > 3. \quad (16c)$$

The term proportional to n^3 gives⁴ for $a_3^K(r)$:

$$a_3^K(r) = a_1(r)a_2^K(r) - \frac{1}{3}a_1^3(r) + \chi_3(r) + \omega_3(r) + \vartheta_3(r), \quad (17a)$$

where

$$\chi_3(r) = \pi^3 \left\{ \frac{10829}{57600} \frac{1}{r} - \frac{26659}{45360} + \frac{9913}{16128} r - \frac{64}{315} r^2 - \frac{7951}{120960} r^3 \right. \\ \left. + \frac{14}{225} r^4 - \frac{1}{90} r^5 - \frac{1}{945} r^6 + \frac{1}{2520} r^7 - \frac{1}{453600} r^9 \right\},$$

$$(1 \leq r \leq 2),$$

$$= 0, \quad \text{for } r > 2, \quad (17b)$$

$$\omega_3(r) = \pi^3 \left\{ \frac{80539}{403200} \frac{1}{r} - \frac{20963}{9072} + \frac{30331}{11520} r - \frac{3793}{5040} r^2 - \frac{749}{3456} r^3 \right. \\ \left. + \frac{533}{3600} r^4 - \frac{31}{1920} r^5 - \frac{61}{15120} r^6 + \frac{5}{5376} r^7 - \frac{1}{103680} r^9 \right\},$$

$$(2 \leq r \leq 3)$$

$$= 0, \quad \text{for } r < 2 \quad \text{and for } r > 3; \quad (17c)$$

$$\vartheta_3(r) = \pi^3 \left\{ -\frac{2048}{1575} \frac{1}{r} + \frac{11264}{2835} - \frac{128}{45} r + \frac{128}{315} r^2 + \frac{8}{27} r^3 \right. \\ \left. - \frac{28}{225} r^4 + \frac{1}{90} r^5 + \frac{2}{945} r^6 - \frac{1}{2520} r^7 + \frac{1}{453600} r^9 \right\},$$

$$(3 \leq r \leq 4)$$

$$= 0, \quad \text{for } r < 3 \quad \text{and for } r > 4. \quad (17d)$$

With these functions known for hard spheres, the coefficients in the expansion (3) of g in powers of n can be determined.

⁷ A. E. Rodriguez, Proc. Roy. Soc. (London) A239, 373 (1957).

6. DENSITY EXPANSION FOR K

The expansion (3) for g in powers of n (being known) is next inserted into Eqs. (1) and (2) to yield the total neutron scattering cross section in powers of the density. We introduce the necessary restriction of hard spheres in the formulas, characterized by the potential form (with the particle diameter taken as the unit of distance)

$$\psi(r) = \infty, \quad \alpha(r) = -1, \quad \text{for } r < 1, \\ \psi(r) = 0, \quad \alpha(r) = 0, \quad \text{for } r > 1, \quad (18) \\ \alpha'(r) = \delta(r-1);$$

where δ is the Dirac delta function. The result is that K is expanded as:

$$K = 1 + I_1 n + I_2 n^2 + I_3 n^3 + \dots, \quad (19a)$$

where

$$I_1 = - \int_1^\infty a_1(r) dr, \quad I_2 = - \int_1^\infty a_2(r) dr, \\ I_3 = - \int_1^\infty a_3(r) dr, \quad \text{etc.}, \quad (19b)$$

$a_2(r)$ and $a_3(r)$ are given by Eqs. (9a) and (10a).

7. NUMERICAL RESULTS

We are now in the position of computing numerical values for the coefficients I_i . There is no difficulty over I_1 ; $a_1(r)$ given by (15) leads directly to the value $I_1 = -0.458$, and no inconsistency arises if this value of $a_1(r)$ is inserted into the formulas (6a) and (6b) for the derivation of the third virial coefficient. It is found that $C = (5/8)b^2$, where b is four times a particle volume, and $B = b$.

Inconsistency in the theory, when the approximation (5) is used, arises from this point on. As explained in Sec. 4, this inconsistency is now to be eliminated using the approximation (7) in place of (5). Using the original approximation (5) in (3) and (4) yields the Kirkwood value a_2^K , given by Eqs. (16) for hard spheres. Then, from Eq. (8a) it follows that $D_p^K = 0.2252b^3$ and $D_e^K = 0.3424b^3$. The value of X_1 follows immediately from (14a), explicitly,

$$X_1 = 0.1014b. \quad (20)$$

Inserting this value of X_1 into (13a) yields the modified function $a_2^M(r)$. This modified function is then used in (19b) to give for the coefficient of n^3 in the density expansion of K , viz:

$$I_3^M = +0.273. \quad (21)$$

A direct test of this value (which is compatible with a completely consistent theory and which leads to a fourth virial coefficient $D^M = D_p = D_e = 0.2885b^4$ in place of the known exact value $D = 0.2869b^4$) is possible, since Nijboer and Van Hove² have derived the exact $a_2(r)$ function for hard spheres. These authors give the exact

value $I_2 = +0.268$ so that our value, based on the modern theory of fluids and the modified superposition approximation (7) itself only in approximate form, is correct to 2%. Other approaches have given rather worse values. The original Kirkwood approximation (5) gives $I_2^K = +0.370$. It will be realized from (9a), (13a), and (19b) that $\delta I_2 \equiv I_2^M - I_2^K$ is in fact given (under the present approximation $X_1 = \text{constant}$) by the expression $\delta I_2 = X_1 I_1 = -0.097$.

Another approach, viz., the netted chain approximation (not discussed here), gives $I_2^N = +0.291$. The relative accuracy of these values is readily seen by calculating the difference $\Delta I = \text{calculated value} - \text{exact value}$:

$$\Delta I^K = +0.103 \quad [\text{Kirkwood approximation (5)}],$$

$$\Delta I^N = +0.023 \quad (\text{Netted chain approximation}),$$

$$\Delta I^M = +0.005 \quad [\text{Modified approximation (7)}].$$

These figures add confidence to the arguments developed so far in this paper.

The calculation of I_3 involves the calculation of X_2 as is seen by reference to (19b), (14b) and (14c). The Kirkwood values of E , derived⁴ using (5) and (3) in (4), are $E_p^K = 0.0475b^4$ and $E_e^K = 0.1335b^4$. Using (14b, c) and (20) we obtain for X_2 the value

$$X_2 = -0.0424b^2. \quad (22)$$

This value assures consistency between the expressions (6a) and (6b), and gives a modified fifth virial coefficient $E^M = 0.0240b^4$. The exact value of E for a hard sphere gas is not known so that no final test of the accuracy of this value for E^M is at present possible. It is, however, positive which is in agreement with current elementary expectations.

With $a_3^K(r)$ given by the Eqs. (17), and X_1 and X_2 given, respectively, by (20) and (22), the modified function $a_3^M(r)$ follows from (10a) and (13b). Numerical values of I_3 follow immediately from (19b). Thus for the original Kirkwood approximation (5), which leads to $a_3^K(r)$, it is readily found that $I_3^K = -0.416$. This value is now to be corrected; using (19b) it is easily seen that

$$\begin{aligned} \delta I_3^M &\equiv I_3^M - I_3^K = - \int_0^\infty [a_3^M(r) - a_3^K(r)] dr \\ &= X_1 \left\{ I_2^K + \frac{1}{2} \int_0^\infty a_1^2(r) dr \right\} + X_2 I_1. \end{aligned}$$

Substituting the various known values into this expression it is found that $\delta I_3^K = +0.203$. Consequently we obtain finally

$$I_3^M = -0.213, \quad (23)$$

for the modified value of I_3 appearing in the expansion (19a) for K .

8. CONCLUSION

The total elastic scattering cross section for high-energy neutrons and a low-density gas of heavy nuclei has been calculated using classical arguments in which the heavy nuclei are represented by rigid spheres. The theory is in addition made consistent internally in respect to the thermodynamic (virial) properties of the gas by employing a modified form of the usual Kirkwood form of the superposition approximation. The numerical results of these calculations are plotted in Fig. 1, which displays the integral $K(n)$ as function of n . The curve A is derived from the expression obtained in this paper, viz.,

$$K_A(n) = 1 - 0.458n + 0.273n^2 - 0.213n^3. \quad (24a)$$

The curve B for comparison represents the expansion only as far as the quadratic term but now, using the known exact coefficients of the expansion (see reference 2),

$$K_B(n) = 1 - 0.458n + 0.268n^2. \quad (24b)$$

The difference between (24b) and the corresponding first three terms of (24a) is very small (of the order 0.1% or less) for the low densities where these expressions are valid. The effect of the cubic term in (24a) is very apparent. For further comparison curve C indicates the numerical solution (using electronic computer techniques) of the Born-Green-Yvon equation (4) and is not based on a number density expansion; the data is that reported by Kirkwood, Maun, and Alder.⁸ Although the curve A agrees more closely with curve C

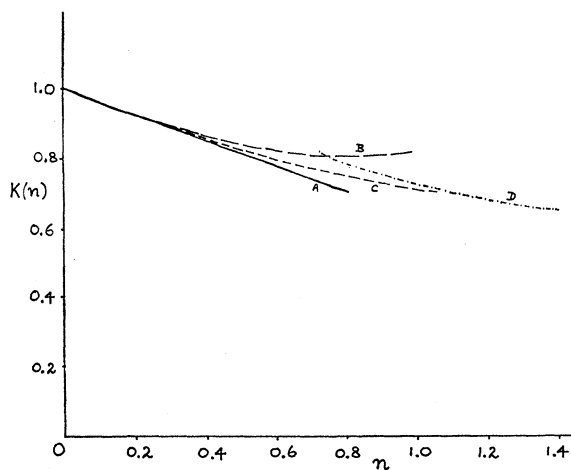


Fig. 1. Plot of the integral $K(n)$, defined by Eq. (2) of the text, as a function of the number density n for a hard sphere gas. Curve A represents Eq. (24a) derived from the arguments of the present paper; curve B represents Eq. (24b) discussed earlier by Nijboer and Van Hove²; curve C is drawn from numerical data given by Kirkwood, Maun, and Alder⁸; and curve D represents the expression (24c) for the high-density limit. (For close packing of the spheres the magnitude of n is $\sqrt{2}$).

⁸ J. G. Kirkwood, E. K. Maun, and B. J. Alder, J. Chem. Phys. 18, 1040 (1950).

than does curve *B* for the lower densities (curve *B* moves away from curve *C* beyond about $n=0.4$, while curve *A* moves away beyond about $n=0.5$) no simple conclusions can be drawn as to the range of validity of the leading terms (24a) of the density expansion for K since curve *C* is based on the simple form of the Kirkwood superposition approximation (5) whereas curve *A* is based on the improved form (7). Finally, in Fig. 1, curve *D* is a plot of the high-density form of $K(n)$ which can be represented approximately by

$$K_D \sim 0.722n^{-\frac{1}{2}}. \quad (24c)$$

The expansions (24a) and (24b) apply for low densities, whereas (24c) applies for the high-density region (where n is of the order of the density for close packing of the hard spheres) so that the region of intermediate densities must be approached properly by adding more terms to the expansion (24a). It is a happy accident, however, that curve *D* and curve *B* [derived equivalently from the first three terms of (24a) or from (24b)] do cross in the region $|n| \sim 0.7$. The effect of the cubic term in (24a) in reducing the final numerical value of K becomes more marked as the density increases with the result that the curves *A* and *D* do not cross. Curve *C*, on the other hand, meets rather smoothly with curve *D* for large n (~ 1.2). Presumably the addition of the corresponding quadruplet term to the expansion (24a), which will carry a positive sign, will

again ensure a common point between this expansion and the expression (24c), but at the present time the most precise information about the intermediate density range ($0.5 \leq n \leq 1.2$, say) is still very probably the numerical data of Kirkwood, Maun, and Alder. From a purely arithmetic point of view, the empirical addition of the term $+0.099n^4$ to the expansion series (24a) for $K_A(n)$ reproduces the curve *C* numerically fairly well. This modified curve K_A then crosses the curve K_D in the region $n \sim 1.2$, and the gradients of these curves at this junction are not too different.

The value (23) which follows from the arguments set down above is approximate in that it is derived on the basis of the modified superposition approximation (7) under the restricted assumption $X_i = \text{constant}$. The accuracy of the calculation cannot be directly assessed, because virtually nothing is known independently about the exact form of the functions X_i . However, the case of I_2 is important since a direct test is possible here; the restriction $X_1 = \text{constant}$ is found to be adequate for information about I_2 accurate to 1 or 2%. This does not, unfortunately, allow the conclusion to be drawn that the value (23) is also reliable to a few percent. The function X_1 occurs in two integrals in the calculation of Ξ_3 , whereas it occurs in only one in the calculation of Ξ_2 ; also the additional assumption is made in calculating Ξ_3 that $X_2 = \text{constant}$. It should be made clear, however, that if the functions X_i are known exactly then the arguments developed above are exact.