

# LETTER TO THE EDITOR

## On the radial distribution function of a compressed gas of rigid spheres

From classical statistical mechanics it is known that the radial distribution function  $g(r)$  as well as the pressure  $p$  of a compressed gas may be expanded in powers of the density  $\rho$  as follows:

$$g(r) = \exp \{ - V(r)/kT \} \cdot \{ 1 + \rho g_1(r) + \rho^2 g_2(r) + \rho^3 g_3(r) + \dots \}, \quad (1)$$

$$p = \rho kT (1 + B_2 \rho + B_3 \rho^2 + B_4 \rho^3 + B_5 \rho^4 + \dots), \quad (2)$$

where  $r$  is the distance between two particles and  $V(r)$  is the intermolecular potential. The virial coefficients  $B_n$  and the functions  $g_n(r)$  can be expressed in terms of so-called cluster integrals<sup>1)</sup>. If the expansion (1) were known, the equation of state (2) could be obtained from either of the two well-known relations<sup>1)</sup>

$$p = \rho kT - 2\pi/3 \rho^2 \int_0^\infty dV/dr g(r) r^3 dr \quad (\text{virial theorem}), \quad (3)$$

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

On equating coefficients of equal powers of  $\rho$  on both sides of either (3) or (4), one can express  $B_{n+2}$  in terms of the function  $g_n(r)$ . In the simple case of rigid spheres (of unit diameter), to which we will confine ourselves in the following, we find in particular for  $B_5$  from (3) and (4) respectively

$$B_5 (\text{virial}) = 2\pi/3 g_3(1), \quad (5)$$

$$B_5 (\text{compr.}) = 1/5 (16B_2^4 - 36B_2^2 B_3 + 16B_2 B_4 - 9B_3^2) - 4\pi/5 \int_1^\infty g_3(r) r^2 dr. \quad (6)$$

For hard spheres  $g_1(r)$  can be found easily,  $g_2(r)$  has also been evaluated<sup>2)</sup>, but the calculation of  $g_3(r)$  and of higher terms would seem to require excessive labour. Of course, substitution of the exact function  $g_3(r)$  into (5) and (6) would lead to a unique value of  $B_5$ , cf. e.g. <sup>2)</sup> <sup>3)</sup>. As has been pointed out before<sup>2)</sup>, the consistency between the equations of state (3) and (4) (and also between the values (5) and (6)), which requires some special analytical property of the exact  $g(r)$ , will in general be destroyed when some approximate expression for the radial distribution function is used. It was shown that the superposition assumption of Kirkwood<sup>4)</sup> and Born and Green<sup>5)</sup> leads to an approximate function  $g'_2(r)$ , whose substitution into

formulae analogous to (5) and (6) yields the following values for  $B_4$  ( $^{1/4}b$  is the volume of each particle):

$$B'_4(\text{virial}) = 0.2252 b^3, \quad B'_4(\text{compr.}) = 0.3424 b^3, \quad (7)$$

whereas the exact value is

$$B_4 = 0.2869 b^3. \quad (8)$$

We have now applied (5) and (6) in order to obtain not only a further check on the superposition approximation, but also to test the so-called netted-chain approximation recently proposed by Rushbrooke and Scoins<sup>3</sup>). It will be evident that, even though we do not know the exact  $g_3(r)$  (or the exact  $B_5$ ), the deviations between the values (5) and (6) obtained for some approximation will provide an indication as to its quality.

The superposition assumption in the form as discussed by Born and Green<sup>5</sup>) leads to a non-linear integral equation for the approximate  $g'(r)$ , which in the case of hard spheres, when we put  $g'(r) = v(r) \exp \{-V(r)/kT\}$ , reduces to

$$\log v(r) = \pi \rho v(1) r^{-1} \int_{r-1}^{r+1} \{v(t) - 1\} t \{(t-r)^2 - 1\} dt, \quad (9)$$

where in the right-hand member  $v(t)$  has to be replaced by zero for  $t < 1$ . Analogously to (1) we put

$$v(r) = 1 + \rho g'_1(r) + \rho^2 g'_2(r) + \rho^3 g'_3(r) + \dots \quad (10)$$

When we introduce this expansion into (9) and equate the coefficients of equal powers of  $\rho$  on both sides, we can evaluate successively by means of simple integrations the functions  $g'_1(r)$ ,  $g'_2(r)$ ,  $g'_3(r)$ , etc. It was shown<sup>2</sup>) that  $g'_1(r) = g_1(r)$ ,  $g'_2(r)$  was found to deviate from  $g_2(r)$ . It leads to the values of  $B_4$  quoted in (7). We have now evaluated  $g'_3(r)$  and its substitution into (5) and (6) yields

$$B'_5(\text{virial}) = 0.0475 b^4, \quad B'_5(\text{compr.}) = 0.1335 b^4, \quad (11)$$

where in (6) the value  $B'_4(\text{compr.}) = 0.3424 b^3$  was used. We note that the approximate character of the function  $g'(r)$  becomes progressively more apparent when one considers higher powers of  $\rho$ . ( $B'_3(\text{compr.}) = B'_3(\text{virial})$ ,  $B'_4(\text{compr.}) \simeq 1.5 B'_4(\text{virial})$ ,  $B'_5(\text{compr.}) \simeq 2.8 B'_5(\text{virial})$ ). As mentioned above,  $B_5$  is not known exactly, but a preliminary estimate indicates that its value lies most probably between the values (11).

In a recent paper Rushbrooke and Scoins<sup>3</sup>) have proposed an alternative approximation  $g''_n(r)$  to the functions  $g_n(r)$ , which in the opinion of these authors is superior to the approximation  $g'_n(r)$  discussed above. In this so-called netted-chain approximation only the simplest of all the cluster integrals, by the sum of which the function  $g_n(r)$  can be expressed, are retained (namely those corresponding to a netted-chain), the sum of the remaining more complicated integrals being neglected. Indeed the function  $g''_2(r)$  obtained in this way gives a better approximation to the exact  $g_2(r)$  than the function  $g'_2(r)$  deduced under the superposition assumption. This is reflected in the values of  $B_4$  to which it leads<sup>2</sup>)<sup>3</sup>)

$$B''_4(\text{virial}) = 0.2500 b^3, \quad B''_4(\text{compr.}) = 0.2969 b^3. \quad (12)$$

We have now calculated  $g_3''(r)$ , which can be done by simple integrations again.

If we call  $f_{ij} = \exp \{-V(r)/kT\} - 1$ , we have <sup>3)</sup>

$$g_3''(r_{12}) = \int f_{23} f_{34} f_{45} f_{51} d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 + 3 \int f_{23} f_{34} f_{35} f_{45} f_{51} d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5 + \\ + \int f_{23} f_{24} f_{34} f_{45} f_{51} f_{41} d\mathbf{r}_3 d\mathbf{r}_4 d\mathbf{r}_5. \quad (13)$$

On introducing <sup>2)</sup>

$$g_1(r_{12}) = \int f_{13} f_{23} d\mathbf{r}_3 = 2\pi/3 (2 - \frac{3}{2} r_{12} + \frac{1}{8} r_{12}^3) \text{ for } r_{12} \leq 2, \quad (14) \\ = 0 \quad \text{for } r_{12} > 2,$$

we easily see that e.g. the last integral of (13) is simply ( $r = r_{12} > 1$ ,  $r_{14} = s$ ,  $r_{24} = t$ )

$$\int f_{14} g_1(s) f_{24} g_1(t) d\mathbf{r}_4 = 8\pi^3/9r \int_{r-1}^1 dt g_1(t) t \int_{r-t}^1 ds g_1(s) s ds. \quad (15)$$

The other terms can be evaluated in a similar way.

On substituting the resulting  $g_3''(r)$  into (5) and (6) we find

$$B_5''(\text{virial}) = -0.7132 b^4, \quad B_5''(\text{compr.}) = +0.5655 b^4 \quad (16)$$

The wide discrepancy between these values is in our view a proof of the inadequacy of the netted-chain approximation. This negative result does not seem so surprising, if we realize that the netted-chain approximation is obtained when the expansion of the direct correlation function, which is closely related to the function  $g(r)$ , is more or less arbitrarily cut off after the term in  $\varrho^2$  <sup>3)</sup>.

Finally it is interesting to observe that in the interval  $3 < r < 4$  the functions  $g_3'(r)$  and  $g_3''(r)$  coincide with the exact  $g_3(r)$ , because in this interval the only contributing cluster integral is the first integral in (13).

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