

## Determination of Virial Coefficients from the Potential of Mean Force\*

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A relation between the potential of mean force at zero separation and the excess chemical potential is derived for "hard" molecules. Application to hard spheres shows that of the Percus-Yevick, Kirkwood, convolution, and Born-Green-Yvon integral equations, only the Kirkwood equation gives the correct *third* virial coefficient.

IN this article we derive a new relation (between the potential of mean force<sup>1</sup> and the excess chemical potential) which may be used to obtain virial coefficients from the radial distribution function. The relation is valid whenever each term  $\phi(r_{ij})$  in the total potential energy  $\Phi(\mathbf{r}^N)$  has the possible values 0 and  $\infty$  only.<sup>2</sup>

Consider the definitions of the potential of mean force  $\Psi(r)$  and of the radial distribution function  $g(r)$ :

$$\exp[-\Psi(r)/kT] \equiv g(r) \equiv \frac{V^2 \int \exp[-\Phi(\mathbf{r}^N)/kT] d\mathbf{r}^{N-2}}{\int \exp[-\Phi(\mathbf{r}^N)/kT] d\mathbf{r}^N} \quad (1)$$

The denominator in (1) is  $N!$  times the configurational integral  $Q_N$ . Multiply (1) by  $\exp[\phi(r)/kT]$  and pass to the limit  $r \rightarrow 0$ . In this limit, so long as the molecules are hard, we may replace  $\phi(r_{1k}) + \phi(r_{2k})$  by  $\phi(r_{2k})$  in the integral over  $d\mathbf{r}^{N-2} \equiv d\mathbf{r}_3 \cdots d\mathbf{r}_N$ . Thus we have, after taking the limit,

$$\exp[-\Psi(0)/kT + \phi(0)/kT] = \frac{V^2 \int \exp[-\Phi(\mathbf{r}^{N-1})/kT] d\mathbf{r}^{N-2}}{N! Q_N} \quad (2)$$

The numerator of (2) is  $(N-1)!V$  times the configurational integral  $Q_{N-1}$ . Using the relations<sup>3</sup>  $Q_{N-1}/Q_N = z = \rho \exp(-\sum \beta_n \rho^n)$ , where  $z$  is the fugacity divided by  $kT$ , and  $\beta_n \equiv -(n+1)B_{n+1}/n$ , where  $\beta_n$  is the  $n$ th irreducible cluster integral<sup>4</sup> and  $B_n$  is the  $n$ th

virial coefficient, we see from (2) that the potential of mean force at zero separation is related to the excess chemical potential  $\mu^E$  by the equation,

$$\begin{aligned} \Psi(0) - \phi(0) &= -\mu^E \equiv kT \sum_{n=1} \beta_n \rho^n \\ &= -kT \sum_{n=1} (n+1) B_{n+1} \rho^n / n. \end{aligned} \quad (3)$$

From number density ( $\rho \equiv N/V$ ) expansions of  $\exp[\phi(r)/kT]g(r)$ , number density expansions of  $\Psi(r) - \phi(r)$  may be obtained; inserting the latter into the new relation (3), equating equal powers of  $\rho$ , and letting  $r \rightarrow 0$ , one obtains the virial coefficients. For those systems for which (3) is valid, the above procedure is an alternative to inserting the number density expansion of  $g(r)$  into the Ornstein-Zernicke relation<sup>5</sup> (and solving for  $P/kT$ )

$$kT(\partial\rho/\partial P)_{N,T} = 1 + \rho \int [g(r) - 1] d\mathbf{r}, \quad (4)$$

TABLE I. Fourth virial coefficient for hard spheres according to various approximations. Unit volume is  $4 \times$  the molecular volume.

	Eq. (3)	Eq. (4)	Eq. (5)
Exact <sup>a</sup>	0.28695	0.28695	0.28695
Percus-Yevick	0.07812	0.29687 <sup>b</sup>	0.25000 <sup>b</sup>
Kirkwood	0.20919	0.44182 <sup>c</sup>	0.13996 <sup>c</sup>
Convolution	0.89062	0.20919 <sup>d</sup>	0.44531 <sup>d</sup>
Born-Green-Yvon	... <sup>e</sup>	0.34241 <sup>f</sup>	0.22522 <sup>g</sup>

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<sup>1</sup> T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 193.

<sup>2</sup> This statement is stronger than is implied by the symbols  $\phi(r_{ij})$  and  $\Phi(\mathbf{r}^N)$ . The new relation holds even for an angle-dependent pair potential (provided it is of the "hard" 0 or  $\infty$  type) with the modification that in the limit to which (3) refers, hard ellipsoids, for example, would be merged in a common orientation. Because (3) is applied only to hard spheres in this work, we prefer to suppress the angle dependence here to simplify the notation. In a forthcoming publication we will apply the new relation to systems of parallel hard lines, squares, and cubes, and illustrate its graphical interpretation.

<sup>3</sup> See, for example, J. de Boer, *Reports on Progress in Physics* (The Physical Society, London, 1949), Vol. 12, p. 339.

<sup>4</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), p. 287.

<sup>a</sup> For references see G. E. Uhlenbeck and G. W. Ford, *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (Interscience Publishers, Inc., New York, 1962), Vol. 1, p. 182. This article is a valuable reference on the application of graph theory to the equation of state and the radial distribution function.

<sup>b</sup> See reference 7, reference 11, reference 1, p. 213, and G. S. Rushbrooke and H. I. Scoles, *Proc. Roy. Soc. (London)* **A216**, 203 (1953).

<sup>c</sup> See reference 12.

<sup>d</sup> See reference 9 and K. Hiroike, *J. Phys. Soc. Japan* **13**, 1497 (1958).

<sup>e</sup> For the Born-Green-Yvon equation  $\Psi(0) - \phi(0)$  is not simply related to combinations of hard-sphere cluster integrals; because of this difficulty we have not made the (tedious) calculation of  $B_4(\text{BGY})$  according to (3).

<sup>f</sup> See reference 11.

<sup>g</sup> See reference 1, p. 213, footnote 1.

<sup>5</sup> See reference 3, p. 365.

or the virial theorem<sup>6</sup>

$$P/kT = \rho - (\rho^2/6kT) \int g(r) (d\phi/dr) r dr, \quad (5)$$

and equating equal powers of  $\rho$ . As is well known, the values of a particular  $B_n$  obtained from an *approximate*  $g(r)$  using (4) and (5) are not generally the same. For this reason it was of interest to investigate the virial coefficients derived from (3).

For a system of hard spheres, we obtained number density expansions of the approximate  $g(r)$ 's satisfying the Percus-Yevick,<sup>7</sup> Kirkwood,<sup>8</sup> convolution,<sup>9</sup> and Born-Green-Yvon<sup>10</sup> integral equations. The analytical expressions derived by Nijboer and Van Hove<sup>11</sup> were

<sup>6</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 134.

<sup>7</sup> J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**, 1 (1958).

<sup>8</sup> J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

<sup>9</sup> This equation has been derived by many authors (independently). See, for a listing, footnote 1 of G. S. Rushbrooke and P. Hutchinson, *Physica* **27**, 647 (1961).

<sup>10</sup> M. Born and H. S. Green, *Proc. Roy. Soc. (London)* **A188**, 10 (1946); J. Yvon, *Actualités scientifiques et industrielles* (Hermann & Compagnie, Paris, 1935), Vol. 203.

<sup>11</sup> B. R. A. Nijboer and L. Van Hove, *Phys. Rev.* **85**, 777 (1952). In order to calculate  $B_3$  according to (3) it was necessary to calculate  $\chi'(r)$  for  $0 \leq r \leq 1$ , using the notation of this reference. We found

$$\chi'(r) = \pi^2 [(r^6/630) - (r^4/10) - (r^3/24) + (r^2/2) - (5/9)].$$

used for the integrals of the doubly rooted graphs appearing in the coefficients of the first two powers of  $\rho$ . Using (3), we obtain for  $B_3$   $-\frac{1}{12}$ ,  $\frac{5}{8}$ ,  $\frac{5}{4}$ , and  $\frac{5}{6}$ , respectively, from the four integral equations. (The exact value of  $B_3$  is  $\frac{5}{6}$  in these conventional units, molecular volume  $\equiv \frac{1}{4}$ .) We note that only the Kirkwood integral equation gives the correct  $B_3$  if (3) is used. By contrast, it is well known that all four integral equations give the correct  $B_3$  (but *not*  $B_4$ ) if either (4) or (5) is used.

In Table I we list fourth virial coefficients  $B_4$  for hard spheres calculated from three of the four integral equations using (3);  $B_4$  from the Kirkwood integral equation using (4) and (5) (apparently an original calculation<sup>12</sup>); and, for comparison, the exact  $B_4$  and published values arising from the three other integral equations using (4) and (5).

The results in the table bear out the conclusions we have reached in our hard-cubes work: The Percus-Yevick integral equation, together with (4), gives the best results at densities where the virial expansion is useful; determination of virial coefficients from the Kirkwood equation gives more reliable results if (3), rather than (4) or (5), is used.

<sup>12</sup> Stell's detailed and identical independent calculation [G. Stell, *J. Chem. Phys.* **36**, 1817 (1962)] appeared just after we had submitted this article.

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