EXACT ANALYTICAL FORMULA FOR A FIFTH VIRIAL COEFFICIENT OF A HARD-SPHERE MIXTURE AT INFINITE DILUTION FOR SMALL DIAMETER RATIOS

Stanislav LABÍK

Department of Physical Chemistry, Institute of Chemical Technology, Prague, 166 28 Prague, Czech Republic; e-mail: labik@vscht.cz

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Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.

A new exact analytical formula for the fifth partial virial coefficient, $B_5^{[1]}$, of the additive hard-sphere mixture (i.e., for four spheres having diameters of σ_1 and one sphere having a diameter of σ_2), for small diameter ratios ($s = \sigma_2/\sigma_1$), is derived. The derivation method is based on simple geometrical arguments and uses as the only input three first terms in the density expansion of the radial distribution function.
Keywords: Statistical thermodynamics; Hard-sphere mixture; Virial coefficients.

The virial expansion in powers of density for the fluid is

$$z = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \qquad (1)$$

where $z = pV/(Nk_\mathrm{B}T)$, k_B is the Boltzmann constant, B_n are the virial coefficients and ρ is the number density, $\rho = N/V$ (refs[1,2]).

For a mixture, the virial coefficients are composition-dependent. For a binary mixture, the following equation is applicable

$$B_n(s) = \sum_{i=0}^{2} \binom{n}{i} B_n^{[i]}(s) x_1^{n-i} x_2^{i} \qquad (2)$$

where x_1 and x_2 are the molar fractions of particles 1 and 2, respectively. For a hard-sphere mixture, the partial virial coefficients, $B_n^{[i]}(s)$, depend on the hard-sphere diameters, σ_1 and σ_2. Throughout this paper, we take the

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first diameter of the spheres, σ_1, as a unit of length. Thus, the values of $B_n^{[i]}(s)$ depend only on the diameter ratio, $s = \sigma_2/\sigma_1$.

In principle, the virial coefficients can be calculated for any order. Unfortunately, calculation of higher order coefficients becomes increasingly difficult, as both the number of integrals and their dimensionality rapidly increase. Up to now, only the second and third virial coefficients for the hard-sphere mixture have been exactly determined[3,4].

For the fourth virial coefficients, an analytical expression ($B_4^{[1]}$) for the partial coefficient, with three large spheres at diameters of 1 and one small sphere at a diameter of s, was found only at a small diameter ratio, $s < 2/\sqrt{3} - 1 \doteq 0.1547$ (ref.[5])

$$B_4^{[1]}(s) = \left(\frac{\pi}{6}\right)^3 \left[-\frac{9}{56}s^9 - \frac{81}{56}s^8 - \frac{162}{35}s^7 - \frac{27}{5}s^6 + \right.$$
$$\left. + \frac{27}{40}s^5 + \frac{27}{8}s^4 + \frac{21}{4}s^3 + 9s^2 + \frac{9}{4}s + \frac{1}{4}\right] \qquad (3)$$

and, due to a symmetry condition[6]

$$B_4^{[i]}(s) = s^9 B_4^{[n-i]}(1/s) \qquad (4)$$

we can also obtain $B_4^{[3]}(s)$ for $s > \sqrt{3}/(2 - \sqrt{3}) \doteq 6.464$.

Other exact analytical expressions are unknown. Values of $B_4^{[3]}(s)$ for other diameter ratios and for higher virial coefficients, up to $B_7(s)$, are available from numerical integrations[7–12].

The aim of this work is to propose a new method for the derivation of an exact analytical expression for $B_5^{[1]}(s)$, at small values of s. The possibility of its extension to greater diameter ratios and higher virial coefficients is briefly discussed.

THEORY

The dimensionless chemical potential of the infinitely diluted hard sphere is obtained from Eqs. (*1*) and (*2*) using a standard thermodynamic route, giving

$$\beta\mu_1^{\infty}(s) = \sum_{n=2}^{\infty} \frac{n}{n-1} B_n^{[1]}(s)\rho^{n-1} \qquad (5)$$

where $\mu_1^\infty(s)$ is the residual chemical potential of an infinitely diluted hard sphere of diameter s in the system of spheres having diameters of 1 and $\beta = 1/(k_B T)$.

The same chemical potential is related to the probability of the successful insertion of a trial particle (diameter = s) in the NVT ensemble, $P(s)$ [13]

$$\beta\mu_1^\infty(s) = -\ln[P(s)]\,. \tag{6}$$

The probability, $P(s)$, can be determined by

$$P(s) = 1 - \frac{\overline{V}_{\text{exc}}(s)}{V} \tag{7}$$

where $\overline{V}_{\text{exc}}(s)$ is the volume of merged regions that are excluded to the centre of a trial particle by spheres (Fig. 1).

The excluded volume is given as

$$\overline{V}_{\text{exc}}(s) = \sum_i \overline{V}_{\text{exc}}^{[i]}(s) - \sum_{i<j} \overline{V}_{\text{exc}}^{[i\cap j]}(s) + \sum_{i<j<k} \overline{V}_{\text{exc}}^{[i\cap j\cap k]}(s) - \ldots \tag{8}$$

where $\overline{V}_{\text{exc}}^{[i]}(s)$ is the volume excluded by the ith sphere, $\overline{V}_{\text{exc}}^{[i\cap j]}(s)$ is the volume of the excluded intersecting regions of the ith and jth spheres, and so on.

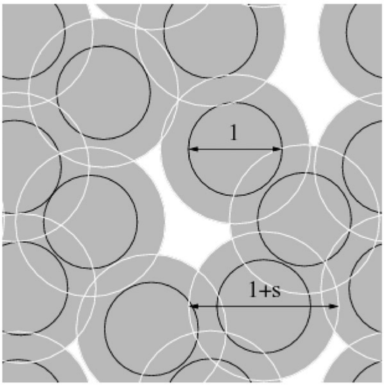


FIG. 1
The volume excluded to the centre of a trial particle. The shadow region is the union of spheres, with diameters equal to 1 + s, excluded to the centre of a trial particle

The excluded volume of a single sphere is given by

$$\overline{V}_{\mathrm{exc}}^{[i]}(s) = \frac{2\pi}{3}(1+s)^3 \tag{9}$$

and the volume of the intersection of excluded regions for two spheres is given by

$$\overline{V}_{\mathrm{exc}}^{[i\cap j]}(s) = 4\pi\int_1^{1+s} \Delta V^{[2]}(s,r)\,p(r)r^2\,\mathrm{d}r \tag{10}$$

where $p(r)$ is the average probability density that the centres of two spheres are at distance r and $\Delta V^{[2]}(s,r)$ is the volume of the intersection of two spheres, having diameters $1 + s$, with centres at a distance of $r < 1 + s$

$$\Delta V^{[2]}(s,r) = \frac{\pi}{12}(r+2+2s)(r-1-s)^2\,. \tag{11}$$

The integration range is limited by two conditions

$$p(r) = 0 \quad \text{for} \quad r < 1$$

and

$$\Delta V^{[2]}(s,r) = 0 \quad \text{for} \quad r > 1 + s\,.$$

For a diameter ratio of $s < 2/\sqrt{3} - 1$, the intersection of excluded regions for three or more spheres equals zero. This means that the term $\overline{V}_{\mathrm{exc}}^{[i\cap j\cap k]}(s)$ and the following terms in Eq. (*8*) may be omitted.

For an infinite system, the probability density, $p(r)$, is equal to

$$p(r) = \frac{g(r)}{V} \tag{12}$$

where $g(r)$ is the radial distribution function. Provided that we know the radial distribution function, Eqs (*6*)–(*12*) give a simple way to obtain the chemical potential at infinite dilution and, thus, the partial virial coefficients, $B_n^{[1]}(s)$.

The radial distribution function may be approximated by a density expansion having coefficients expressed as a sum of cluster integrals of the

Mayer f function[1,2]. When combined with Eqs (*6*)–(*12*), the 0th order approximation

$$g(r) = 1 \qquad (13)$$

yields

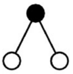
$$\beta\mu_1^{\infty}(s) = -\ln\left[1 - \frac{\pi}{6}(1+s)^3\rho + \frac{\pi^2 s^3}{72}(12 + 15s + 6s^2 + s^3)\rho^2\right]. \qquad (14)$$

The Maclaurin expansion of Eq. (*14*) in density, together with Eq. (*5*), yields correct second and third partial virial coefficients, $B_2^{[1]}(s)$ and $B_3^{[1]}(s)$, respectively.

The 1st order approximation

$$g(r) = 1 + \rho g_1(s) \qquad (15)$$

where $g_1(s)$ is given as the convolution of the Mayer f functions

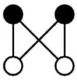
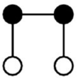
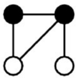
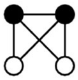
$g_1(s) =$  $= \dfrac{\pi}{12}(r+4)(r-2)^2$ (*16*)

is valid for $r \le 2$. This leads to the exact formulae for partial virial coefficients up to $B_4^{[1]}(s)$.

The 2nd order approximation

$$g(r) = 1 + \rho g_1(s) + \rho^2 g_2(s) \qquad (17)$$

where $g_2(s)$ is also known analytically[14]

$g_2(r) = \Big(\dfrac{1}{2}$  $+$  $+\,2$  $+\dfrac{1}{2}$  $\Big)$ (*18*)

$$= \frac{\pi^2}{1260r}(r^7 - 63r^5 + 210r^4 + 315r^3 - 1806r^2 + 1645r - 162) +$$

$$+\frac{\pi}{2}\left[\left(-\frac{3}{280}r^4 + \frac{41}{420}r^3\right)\sqrt{3-r^2} + \left(-\frac{23}{15}r + \frac{36}{35r}\right)\arccos\left(\frac{r}{\sqrt{12-3r^2}}\right) +\right.$$

$$+\left(\frac{3}{560}r^6-\frac{1}{15}r^4+\frac{1}{2}r^2+\frac{2}{15}r-\frac{9}{35r}\right)\arccos\left(\frac{r^2+r-3}{\sqrt{12-3r^2}}\right)+$$

$$+\left(\frac{3}{560}r^6-\frac{1}{15}r^4+\frac{1}{2}r^2-\frac{2}{15}r+\frac{9}{35r}\right)\arccos\left(\frac{-r^2+r+3}{\sqrt{12-3r^2}}\right)\Bigg]\tag{19}$$

is valid for $1 \le r \le \sqrt{3}$. This yields the exact analytical formula for the fifth partial virial coefficient

$$B_5^{[1]}(s)=\left(\frac{\pi}{6}\right)^4\left\{\frac{11268}{175\pi}(s+1)^3\left[\arcsin\left(\frac{\sqrt{3}(s+1)}{3}\right)-\arcsin\left(\frac{\sqrt{3}}{3}\right)\right]+\right.$$

$$+\frac{576}{875\pi}(65s^3+111s^2+27s+17)\left[\arcsin\left(\frac{\sqrt{3}(1-2s)}{3(1-s)}\right)-\arcsin\left(\frac{\sqrt{3}}{3}\right)\right]-$$

$$-\frac{576}{875\pi}(65s^3+279s^2+363s+113)\left[\arcsin\left(\frac{\sqrt{3}(5+2s)}{3(3+s)}\right)-\arcsin\left(\frac{5\sqrt{3}}{9}\right)\right]+$$

$$+\frac{9}{3500\pi}(s^7+7s^6-3s^5-85s^4+215s^3+1233s^2+1531s-1139)\times$$

$$\times(s+1)^5\arcsin\left(\frac{\sqrt{3}(s^2+3s-1)}{3\sqrt{3-2s-s^2}}\right)-$$

$$-\frac{216}{875\pi}(23s^2+46s-49)(s+1)^5\arcsin\left(\frac{\sqrt{3}(s+1)}{3\sqrt{3-2s-s^2}}\right)-$$

$$-\frac{9}{3500\pi}(s^7+7s^6-3s^5-85s^4+215s^3+849s^2+763s+1933)\times$$

$$\times(s+1)^5\arcsin\left(\frac{\sqrt{3}(s^2+s-3)}{3\sqrt{3-2s-s^2}}\right)-$$

$$-\frac{9}{3500\pi}(9080s^3+25254s^2+23268s+5843)\arcsin\left(\frac{1}{3}\right)-$$

$$-\frac{99}{700}s^{12}-\frac{297}{175}s^{11}-\frac{2781}{350}s^{10}-\frac{135}{7}s^{9}-\frac{20997}{700}s^{8}-\frac{32958}{875}s^{7}-\frac{3573}{125}s^{6}+$$

$$+\frac{7074}{875}s^{5}+\frac{5049}{700}s^{4}-\frac{4234}{175}s^{3}-\frac{61773}{3500}s^{2}-\frac{19263}{1750}s-\frac{15997}{700}+$$

$$+\frac{3}{61250\pi}[(105s^{10}+1050s^{9}+2555s^{8}-4760s^{7}-40954s^{6}-108524s^{5}-$$

$$-241510s^{4}-465800s^{3}+413153s^{2}+1599922s+375323)\sqrt{2-2s-s^{2}}+$$

$$+\sqrt{2}(204400s^{3}-548814s^{2}-1710828s-375323)]\,. \qquad (20)$$

The derivation of Eq. (*20*) was carried out by very careful usage of the computer algebraic system Maple[15].

RESULTS AND DISCUSSION

To verify the final results given by Eq. (*20*), several tests were performed. Limiting behaviour at small values of *s*, which is discussed in detail in the literature[6], was fully reproduced. Values of $B_s^{[1]}(s)$ were compared with results from the numerical calculation in Table I. New data presented here are from results obtained recently by our calculations[12]. Older data are the best values obtained by various authors[7,9,10]. These results were found to coin-

TABLE I

Comparison of the analytical formula for $B_5^{[1]}(s)$, with values obtained by numerical integration. Numbers in parentheses are estimated standard deviations

s	Eq. (*20*)	New data[12]	Old data
0.05	0.026588443	0.026587(2)	0.0266(3)[7]
0.1	0.043506981	0.043514(4)	0.04321(7)[10]
0.15	0.066359196	0.066367(6)	–
0.2	0.095857076	0.095860(6)	0.0960(1)[9]

cide with each other, with deviations corresponding to the estimated uncertainties of the numerical integration. Strictly speaking, formula (*20*) is not valid for $s = 0.2$, because the intersection of excluded regions for three spheres may exist. By analogy with the fourth virial coefficients[16], we can expect that the contribution due to triple intersections may by neglected. This assumption is confirmed by the observed agreement with numerical integration.

The formula (*20*) for the fifth partial virial coefficient is substantially more complicated than for the second, third and fourth virial coefficients, being the 3rd, 6th and 9th polynomials in s, respectively. Nevertheless, the Maclaurin series of Eq. (*20*) shows that it is very close to the 12th polynomial in s. This is because the coefficients for powers of s equal to or greater than 13 are at least two orders of magnitude smaller than for previous ones.

The proposed method of calculation of partial virial coefficients is limited to a small diameter ratio, $s < 2/\sqrt{3} - 1$. In principle, this method could also be extended to greater diameter ratios. This would require knowledge of the intersection of three and four spheres, together with triplet and quadruplet distribution functions of the pure hard-sphere system. Moreover, the calculation would involve three-fold and six-fold integration and is probably beyond the present state of art in computer algebra. On the other hand, the method could be extended to higher virial coefficients if the higher terms in the density expansion of $g(r)$ are known. For example, the fourth term will give the sixth partial virial coefficient.

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REFERENCES

1. Hill T. L.: *Statistical Mechanics*. McGraw-Hill, New York 1956.
2. Uhlenbeck G. E., Ford G. W. in: *Studies in Statistical Mechanics* (J. de Boer and G. E. Uhlenbeck, Eds). North-Holland, Amsterdam 1962.
3. Kihara T.: *Rev. Mod. Phys.* **1955**, *27*, 412.
4. Kihara T., Miyoshi K.: *J. Stat. Phys.* **1975**, *13*, 337.
5. Blaak R.: *Mol. Phys.* **1998**, *95*, 695.
6. Barrio C., Solana J. R. in: *Theory and Simulation of Hard-Sphere Fluids and Related Systems*, Lect. Notes in Phys. 753 (A. Mulero, Ed.), p. 133. Springer, Berlin–Heideberg 2008.
7. Enciso E., Almarza N. G., Gonzalez M. A., Bermejo F. J.: *Phys. Rev. E* **1998**, *57*, 4486.
8. Saija F., Fiumara G., Giaquinta P. V.: *Mol. Phys.* **1997**, *92*, 1089.
9. Wheatley R. J., Saija F., Giaquinta P. V.: *Mol. Phys.* **1998**, *94*, 877.

10. Vlasov A. Yu., You X. M., Masters A. J.: *Mol. Phys.* **2002**, *100*, 3313.
11. Vlasov A. Yu., Masters A. J.: *Fluid Phase Equilib.* **2002**, *212*, 183.
12. Labík S., Kolafa J.: *Mol. Phys.,* submitted.
13. Labík S., Smith W. R.: *Mol. Simul.* **1994**, *12*, 23.
14. Nijboer B. R. A., van Hover L.: *Phys. Rev.* **1952**, *85*, 777.
15. Monagan M. B., Geddes K. O., Heal K. M., Labahn G., Vorkoetter S. M., McCarron J., DeMarco P.: *Maple 9 Advanced Programming Guide*. Maplesoft, Waterloo (ON) 2003.
16. Labík S., Kolafa J.: *Phys. Rev. E* **2009**, *8*, 051122.