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New results for virial coefficients of hard spheres in D dimensions

NATHAN CLISBY[1] and BARRY M McCOY[2]
[1]ARC Centre of Excellence for Mathematics and Statistics of Complex Systems, 139 Barry Street, The University of Melbourne, Victoria 3010, Australia
[2]C.N. Yang Institute for Theoretical Physics, Stony Brook University, Stony Brook, NY 11794-3840, USA
E-mail: N.Clisby@ms.unimelb.edu.au; mccoy@insti.physics.sunysb.edu

Abstract. We present new results for the virial coefficients B_k for $k \leq 10$ for hard spheres in dimensions $D = 2, \ldots, 8$.

Keywords. Hard spheres; virial expansion; Ree–Hoover diagrams.

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1. Introduction

The low density virial expansion of the pressure

$$\frac{P}{k_{\mathrm{B}}T} = \sum_{k=1}^{\infty} B_k \rho^k \quad \text{with} \quad B_1 \equiv 1 \tag{1}$$

for the hard sphere gas of particles of diameter σ in D dimensions defined by the two-body potential

$$U(\mathbf{r}) = \begin{cases} +\infty, & |\mathbf{r}| < \sigma \\ 0, & |\mathbf{r}| > \sigma \end{cases} \tag{2}$$

is one of the oldest systems studied in statistical mechanics. The problem was first studied analytically by van der Waals [1], Boltzmann [2], and van Laar [3] who computed the coefficients up through B_4. The computation of B_4 for $D = 2$ was first done in 1964 by Rowlinson [4] and Hemmer [5] and very recently these analytic computations for B_4 have been extended to $D = 4, 6, 8, 10, 12$ by the present authors [6], and by Lyberg [7] for $D = 5, 7, 9, 11$. Analytic results for B_3 and B_4 in dimensions $D = 2, \ldots, 8$ are summarized in table 1, in the form of

Table 1. Exact results for B_3 and B_4.

D	B_3/B_2^2	B_4/B_2^3
2	$\frac{4}{3}-\frac{\sqrt{3}}{\pi}$	$2-\frac{9\sqrt{3}}{2\pi}+\frac{10}{\pi^2}=0.5322318\cdots$
3	$\frac{5}{8}$	$\frac{219\sqrt{2}}{2240\pi}+\frac{2707}{4480}-\frac{4131}{4480\pi}\arccos\left(\frac{1}{3}\right)=0.2869495\cdots$
4	$\frac{4}{3}-\frac{\sqrt{3}}{\pi}\frac{3}{2}$	$2-\frac{27\sqrt{3}}{4\pi}+\frac{832}{45\pi^2}=0.1518460\cdots$
5	$53/2^7$	$\frac{3888425\sqrt{2}}{16400384\pi}+\frac{25315393}{32800768}-\frac{67183425}{32800768\pi}\arccos\left(\frac{1}{3}\right)=0.07597248\cdots$
6	$\frac{4}{3}-\frac{\sqrt{3}}{\pi}\frac{9}{5}$	$2-\frac{81\sqrt{3}}{10\pi}+\frac{38848}{1575\pi^2}=0.03336314\cdots$
7	$289/2^{10}$	$\frac{159966456685\sqrt{2}}{435894091776\pi}+\frac{299189248759}{290596061184}-\frac{292926667005}{96865353728\pi}\arccos\left(\frac{1}{3}\right)=0.009864946\cdots$
8	$\frac{4}{3}-\frac{\sqrt{3}}{\pi}\frac{279}{140}$	$2-\frac{2511\sqrt{3}}{280\pi}+\frac{17605024}{606375\pi^2}=-0.002557868\cdots$

B_k/B_2^{k-1} where

$$B_2=\frac{\sigma^D\pi^{D/2}}{2\Gamma(1+\frac{D}{2})}. \tag{3}$$

All other computations for the hard sphere gas are by means of computer. This work was initiated in the 1950s for hard discs by Metropolis *et al* [8] and for hard spheres by Rosenbluth and Rosenbluth [9]. Subsequently B_6 and B_7 were computed by Ree and Hoover [10–12] during the 1960s and B_8 was computed by Janse van Rensberg [13] in 1993. Computations for $D > 3$ were initiated in 1964 by Ree and Hoover [14] who computed B_4 for $D = 4, \ldots, 11$. The coefficients B_5 and B_6 for $D = 4$ and 5 were computed by Bishop, Masters and Clarke [15] in 1999, and Bishop, Masters and Vlasov [16] have recently calculated B_7 in $D = 4, 5$ and B_8 in $D = 4$.

In a series of papers [17–19], we have extended these numerical computations by computing virial coefficients up through B_{10} in $D = 2, 3, \ldots, 8$. We use the method of Ree–Hoover diagrams as evaluated by Monte Carlo integration. The details are given in [19]. Our results are given in table 2.

It is well-known for hard spheres in D dimensions that for some sufficiently large k which depends on D there are some Ree–Hoover diagrams for B_k which vanish identically for geometric reasons. We give (a lower bound on) the number of non-vanishing Ree–Hoover diagrams in table 3.

2. Behavior of B_k for large k

It is apparent from table 2 that negative virial coefficients occur. This was first observed for B_4 in [14]. We note that B_4 changes sign between $D = 7$ and $D = 8$,

Table 2. Numerical values of virial coefficients. Values for B_7 for $D > 5$, B_8 for $D > 4$, B_9, and B_{10} are new, and other values improve on published literature results except for the results for B_5 for $D = 2, 3$ which are due to Kratky [20].

D	B_5/B_2^4	B_6/B_2^5	B_7/B_2^6	B_8/B_2^7	B_9/B_2^8	B_{10}/B_2^9
2	0.33355604(1)*	0.1988425(42)	0.1148728(43)	0.0649930(34)	0.0362193(35)	0.0199537(80)
3	0.110252(1)*	0.03888198(91)	0.01302354(91)	0.0041832(11)	0.0013094(13)	0.0004035(15)
4	0.0357041(17)	0.0077359(16)	0.0014303(19)	0.0002888(18)	0.0000441(22)	0.0000113(31)
5	0.0129551(13)	0.0009815(14)	0.0004162(19)	−0.0001120(20)	0.0000747(26)	−0.0000492(48)
6	0.0075231(11)	−0.0017385(13)	0.0013066(18)	−0.0008950(30)	0.0006673(45)	−0.000525(16)
7	0.0070724(10)	−0.0035121(11)	0.0025386(16)	−0.0019937(28)	0.0016869(41)	−0.001514(14)
8	0.00743092(93)	−0.0045164(11)	0.0034149(15)	−0.0028624(26)	0.0025969(38)	−0.002511(13)

Table 3. Number of Mayer and Ree–Hoover integrals.

	Order								
	2	3	4	5	6	7	8	9	10
Mayer	1	1	3	10	56	468	7123	194066	9743542
RH	1	1	2	5	23	171	2606	81564	4980756
RH/Mayer	1	1	0.667	0.500	0.410	0.365	0.366	0.420	0.511
RH, $D = 1$	1	1	1	1	1	1	1	1	1
RH, $D = 2$	1	1	2	4	15	73	$\gtrsim$647	$\gtrsim$8417	$\gtrsim$110529
RH, $D = 3$	1	1	2	5	22	161	>2334	>60902	
RH, $D = 4$	1	1	2	5	23	169	>2556	>76318	

B_6 changes sign between $D = 5$ and 6, and B_8 and B_{10} change sign between $D = 4$ and $D = 5$. This suggests that for large k the coefficient B_k may become negative for dimensions smaller than 5. In particular, if for $D = 2$ or $D = 3$ there were a value of k such that B_k changed sign then approximate equations of state obtained from the first ten virial coefficients would be wholly inadequate to obtain the radius of convergence of the virial series.

The most important property of the virial coefficients B_k is not their actual numerical values for k less than some finite number but rather their asymptotic behavior as $k \to \infty$ because it is the asymptotic value which determines the radius of convergence. Of course no finite number of virial coefficients can give information on the $k \to \infty$ behavior unless there is some *a priori* reason to expect that the values of k are already in the asymptotic $k \to \infty$ regime.

We see in table 3 the dramatic effect that the number of non-zero Ree–Hoover integrals in two dimensions is far less than that of the number of biconnected graphs with non-zero star content. At $k = 10$ in $D = 2$ we estimate that only 0.022 of the Ree–Hoover diagrams with non-zero coefficients have non-zero integrals. This reduction as $k \to \infty$ in the number of non-vanishing Ree–Hoover diagrams gives one criterion for the size of k needed for B_k to be in the asymptotic region.

Criterion 1

The number of non-zero Ree–Hoover diagrams has approached its large k behavior.

For $k = 10$ this criterion may only be fulfilled for $D = 2$ and is surely not fulfilled at all for $D \geq 5$.

Our second criterion has been presented in our previous paper [17].

Criterion 2

The loose packed diagrams (defined to be those with the number of $\tilde{f}$ bonds near their maximum value) numerically dominate B_k as $k \to \infty$.

The validity of this criterion has been studied in detail in [17]. Here it was seen that for $D = 3$ and $k \geq 12$ the criterion is well satisfied and that as D increases the criterion is satisfied for smaller values of k. However, for $D = 2$ the criterion was not satisfied even for k as large as 17.

We thus conclude that there is no dimension in which both of these criteria are simultaneously fulfilled though in $D = 3$ and $D = 4$ it is possible that they both hold for some moderate values of k such as 12–14.

3. Ratio analysis

Even though we have argued that $k = 10$ may not be sufficiently large to see the true asymptotic behavior of B_k it is still of interest to determine what results are obtained if well-known methods are used to estimate the radius of convergence from the first ten virial coefficients.

One such way of estimating the radius of convergence is the analysis of the ratios of coefficients [21,22] where we plot $B_k \rho_{\rm cp}/B_{k-1}$ vs. $1/k$ (and we have normalized the virial coefficients to the density $\rho_{\rm cp}$ of the closest packed lattice). The ratio extrapolated to $1/k \to 0$ will give the radius of convergence of the series ρ_R which may also be expressed in terms of the packing fraction $\eta = B_2\rho/2^{D-1}$. If the slope of the interpolated points approaches zero for large k then the leading singularity is a pole on the positive real axis, if the slope is non-zero then the divergence is algebraic.

The plot of $B_k \rho_{\rm cp}/B_{k-1}$ vs. $1/k$ for $D = 2$ is given in figure 1. Here we observe smoothly falling ratios which extrapolate to a radius of convergence greater than the closest packed density $\rho_{\rm cp}$.

We plot the ratios for $D \geq 5$ in figures 2 and 3. In this case the first few virial coefficients are positive, and then alternate in sign to the order calculated. We propose the scenario that there is a singularity on the positive real axis that dominates the series initially, but at higher order another singularity (or singularities) in the complex plane or negative real axis competes with the original singularity and hence the new singularity must be at a smaller radius. If the leading singularity is on the negative real axis then the ratio plot will smoothly converge to some negative value, otherwise the ratios will oscillate.

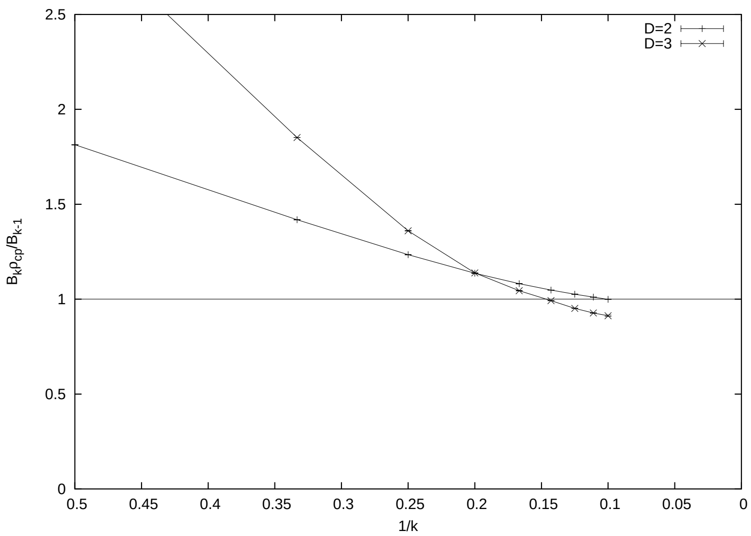

Figure 1. Ratio plot for virial coefficients in dimensions $D = 2, 3$.

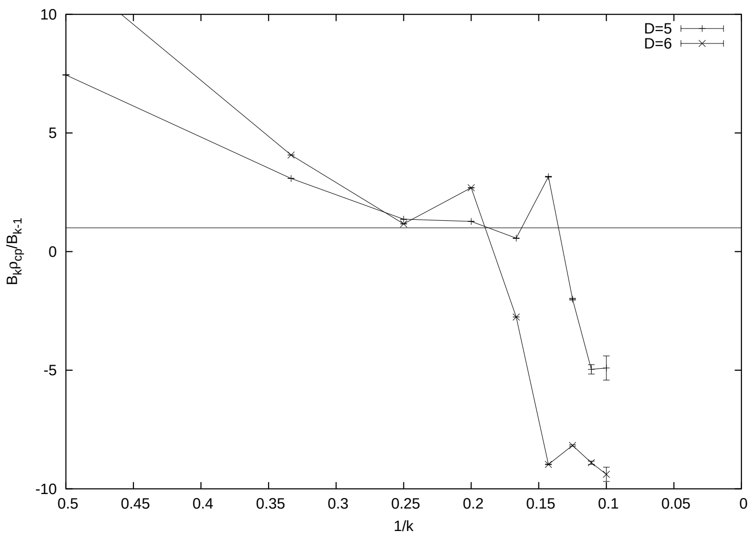

Figure 2. Ratio plot for virial coefficients in dimensions $D = 5, 6$.

We plot the ratios for $D = 4$ in figure 4 and observe that despite the absence of negative virial coefficients and the poor accuracy of B_{10}, an oscillation is developing in the ratio plot in exactly the same way as for $D \geq 5$. Extrapolation of the series [19] via the methods of Dlog Padés and differential approximants as explained by Guttmann [22], suggests that negative coefficients for $D = 4$ may occur for k not much greater than 12.

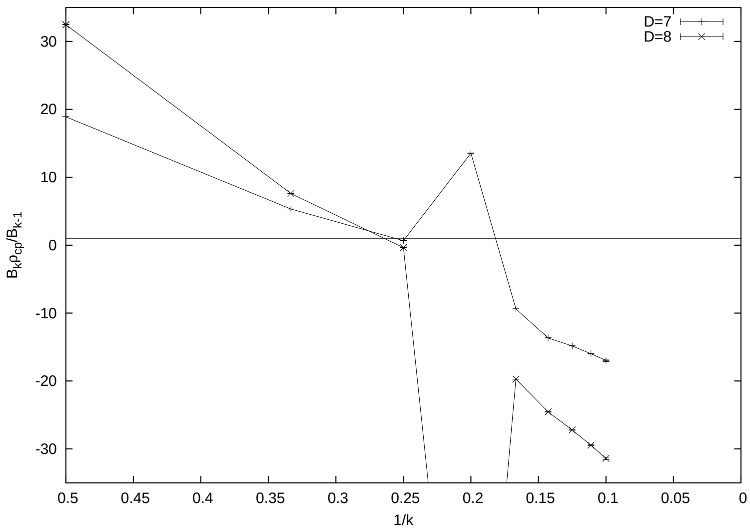

Figure 3. Ratio plot for virial coefficients in dimensions $D = 7, 8$.

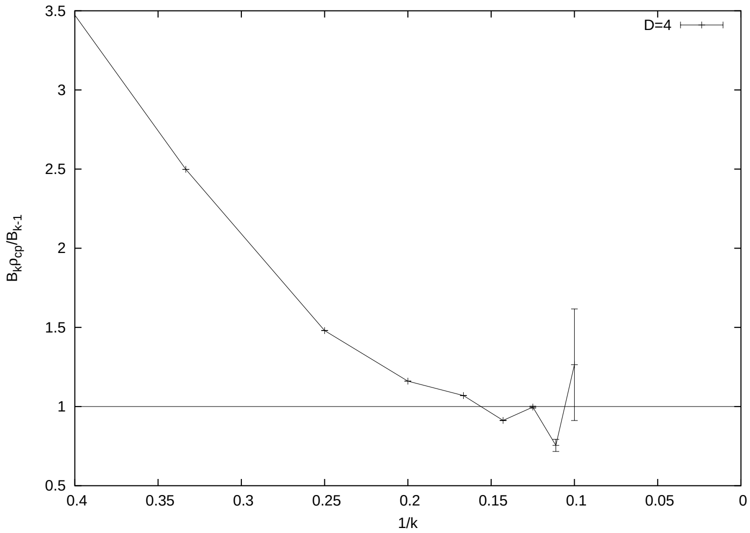

Figure 4. Ratio plot for virial coefficients in dimension $D = 4$.

The case $D = 3$ is plotted in figures 1 and 5. These ratios do not show the large oscillations of $D = 4$ but close inspection reveals that the slopes are not increasing monotonically as they were for $D = 2$. This may indicate that the plot for $D = 3$ is displaying very small amplitude oscillations, which will eventually result in oscillations in the sign of the coefficients.

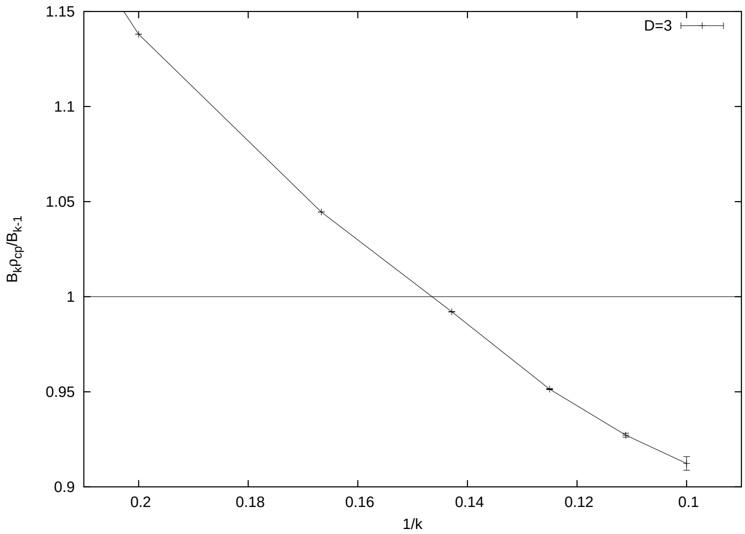

Figure 5. Ratio plot for virial coefficients in dimension $D = 3$ over a small domain to show non-monotonic behavior of the second derivative.

4. Differential approximants

We have analyzed the virial coefficients of table 2 by using differential approximants using the FORTRAN program NEWGRQD given in Guttmann [22]. Our results for the leading singularity on the real positive axis in dimensions $D = 2, 3, 4$ are tabulated in table 4. More detailed analysis will be found in [19]. The notation $L, M; N$ refers to an inhomogeneous first-order differential approximant, which is the solution of

$$zP_M(z)f'(z) + Q_L(z)f(z) = R_N(z), \tag{4}$$

where the subscript denotes the order of the polynomial, and $f(z)$ is the function that is to be approximated.

One can see from tables 4 and 5 that there appears to be a singularity on the positive real axis close to the space filling density $\eta = 1$ for dimensions $D = 2, 3, 4$. The kind of singularity is not so clear, for $D = 2$ there seems to be an algebraic singularity with exponent $\phi \simeq -1.75$, but for $D = 3, 4$ it is not possible to give a good estimate for the exponent.

5. Conclusion

In table 2 above, we have reported the first computations of the virial coefficients B_9 and B_{10} for hard spheres in dimensions $D = 2, \ldots, 8$, and showed that B_8 is negative for $D \geq 5$. The coefficient B_{10} is negative for $D > 4$ and at $D = 4$ the ratios

Table 4. Singularities from differential approximants on the positive real axis for $D = 2, 3, 4$. Blank entries are due to defective approximants.

Differential	$D=2$		$D=3$		$D=4$	
approximant	$B_2\rho_{\text{sing}}$	ϕ	$B_2\rho_{\text{sing}}$	ϕ	$B_2\rho_{\text{sing}}$	ϕ
3,3;0	1.987	−1.790	4.068	−2.818	7.995	−3.520
3,4;0	1.984	−1.774	3.830	−2.329	6.843	−2.478
4,3;0	1.984	−1.774	3.714	−2.043	5.551	−1.207
4,4;0	1.987	−1.788	3.732	−2.090	7.249	−2.871
4,5;0	1.988	−1.795	3.675	−1.899	6.985	−2.583
5,4;0	1.988	−1.795	3.720	−2.056	6.721	−2.229
2,2;1	1.946	−1.575	3.659	−2.014	6.888	−2.593
2,3;1	1.970	−1.695	3.787	−2.246	5.412	−2.922
3,2;1	1.966	−1.677	4.038	−2.953	8.332	−4.368
3,3;1	2.021	−2.076	3.811	−2.298	7.296	−2.920
3,4;1	1.981	−1.756	3.786	−2.241	6.764	−2.389
4,3;1	1.978	−1.740	3.708	−2.024	4.663	−3.708
2,1;2	1.945	−1.572	3.676	−2.054	–	–
2,2;2	1.967	−1.682	3.641	−1.987	7.715	−3.531
2,3;2	2.008	−1.900	3.799	−2.269	7.277	−2.916
3,2;2	–	–	3.874	−2.468	7.250	−2.899
3,3;2	1.971	−1.679	3.773	−2.210	7.308	−2.920
2,1;3	1.959	−1.628	3.599	−1.889	6.802	−2.680
2,2;3	1.984	−1.784	3.747	−1.956	7.508	−3.404
2,3;3	1.982	−1.778	3.777	−2.110	7.003	−2.539
3,2;3	1.981	−1.770	3.779	−2.034	–	–

Table 5. Approximate position of singularities with exponents.

D	$B_2\rho_{\text{sing}}$	η_{sing}	ϕ
1	1.00	1.00	−1.00
2	1.98	0.99	−1.75
3	3.75	0.94	−2.1
4	7.00	0.88	−3.00

of sucessive coefficients oscillate in such a way as to suggest that negative values may occur for $k = 12$–14. For $D = 2, 3$ analysis of the first 10 virial coefficients leads to a radius of convergence greater than close packing. This is in agreement with the conclusions reached in the previous studies [13] based on eight or fewer virial coefficients. The meaning of this is controversial and we argue that the true large k behavior is not seen in the first 10 coefficients. A more complete analysis and discussion is given in [19].

Acknowledgments

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