Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 40, No. 7, 2048–2049, 1 April 1964
Printed in U. S. A.

On the Signs of the Hard Sphere Virial Coefficients*

FRANCIS H. REE AND WILLIAM G. HOOVER
Lawrence Radiation Laboratory, University of California, Livermore, California 94551

(Received 5 December 1963)

THE question, whether or not a central hard potential will give any negative virial coefficients, is an unsettled problem. Temperley[1] has calculated virial coefficients B_n for hyperdimensional hard cubes (angle-dependent potential). He found that B_4 in five dimensions and B_5 in four dimensions are negative for these systems. He then conjectured that a hard "three-dimensional gas" would give negative B_6 or B_7. At that time there was no evidence that B_n for spheres and cubes could differ in sign. In fact, as suggested by Zwanzig,[2] inequalities which apply to individual integrals can be used to bound certain sphere integrals in terms of cube integrals. Unfortunately, these inequalities are so weak that they cannot be used to determine the signs of any of the B_n's for $n>3$. By now it is known that sphere and cube virial coefficients *do* differ in sign as well as in magnitude. B_6 is positive for hard spheres,[3] while, in support of Temperley's conjecture, B_6 is negative for hard cubes.[4] Furthermore, two approximate equations of state, derived from Percus–Yevick integral equation, have *all* positive B_n for hard spheres.[5] Likewise, the approximate equations of state obtained by Reiss, Frisch, Lebowitz, and Helfand[6] give *all* positive B_n for both hard discs and spheres. Therefore, there arises a question: Is the central hard potential sufficient to make all the B_n positive? We have investigated this question by increasing the number of dimensions in which the hard hyperspheres are allowed to move and by calculating B_4 for the corresponding hard hyperspheres.

In any number of dimensions, for a pairwise-additive potential function ϕ, B_4 can be written[3] in terms of Mayer f functions, $f\equiv \exp(-\phi/kT)-1$, and $\tilde{f}$-functions, $\tilde{f}\equiv \exp(-\phi/kT)$:

$$B_4=\tfrac{1}{4}U-\tfrac{3}{8}V, \tag{1}$$

$$U=\iiint f_{12}f_{13}f_{14}f_{23}f_{24}f_{34}d\mathbf{r}_2d\mathbf{r}_3d\mathbf{r}_4, \tag{2}$$

$$V=\iiint f_{12}\tilde{f}_{13}f_{14}f_{23}\tilde{f}_{24}f_{34}d\mathbf{r}_2d\mathbf{r}_3d\mathbf{r}_4, \tag{3}$$

where Particle 1 is placed at the origin. The integrals (2) and (3) can be calculated by a Monte Carlo method.[7] These values are listed in Table I along with the expected deviations for d-dimensional hard spheres ($1\leq d\leq 9$). We note that B_4 in eight dimensions is negative. This shows that a central hard potential *can* give negative B_n. Table I also shows that the first integral (2) depends upon dimensions as $\sim(3/5)^d$, while the negative term (3), after initial irregularity, decreases more slowly and (in eight and nine dimensions) is large enough to give negative B_4. Our conclusion from this investigation of spherically symmetric particles is that Temperley's remarks can be applied to such systems, although his conjecture of negative B_n for hard spheres will not be verified before B_9 or B_{10}. As Temperley has pointed out, negative B_n may have a bearing on the observed[8] hard-sphere phase transition, because an isotherm with negative curvature can be obtained from the virial series only if some B_n's are negative.

TABLE I. Fourth virial coefficients B_4 for multidimensional hard-sphere gases.

Dimensions (d)	B_4/B_2^3	B_2[a]	U/B_2^3	V/B_2^3	q[b]
1	1	1	4	0	...
2	0.5324(3)[c]	$\pi/2$	2.196 (1)	0.04392(8)	10
3	0.2869	$2\pi/3$	1.2669	0.0794	...
4	0.1527(5)	$\pi^2/4$	0.759 (2)	0.0986 (5)	15
5	0.0758(3)	$4\pi^2/15$	0.460 (1)	0.1050 (6)	28
6	0.0328(4)	$\pi^3/12$	0.284 (1)	0.1017 (5)	15
7	0.0098(2)	$8\pi^3/105$	0.1788(6)	0.0930 (4)	43
8	−0.0026(2)	$\pi^4/48$	0.1138(4)	0.0827 (3)	81
9	−0.0084(2)	$16\pi^4/945$	0.0729(4)	0.0709 (4)	75

[a] The sphere diameter is set equal to unity.
[b] The number of batches of independent Monte Carlo trial configurations, $f_{12}=f_{23}=f_{34}=-1$; each of the batches contains 100 000 trial configurations for $d>3$, and 10^6 trial configurations for $d=2$.
[c] The number appearing in parentheses is the mean-square expected deviation in the last digit preceding it; for instance, 0.5324(3) = 0.5324±0.0003. The mean square deviation is obtained from $\langle(\langle I\rangle-I)^2/q(q-1)\rangle^{1/2}$, where $\langle\ \rangle$ denotes the expectation operator, and $\langle I\rangle$ is the cumulative average value over q independent calculations of I.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] H. N. V. Temperley, Proc. Phys. Soc. (London) **B70**, 536 (1957).
[2] R. W. Zwanzig, J. Chem. Phys. **24**, 855 (1956).
[3] F. H. Ree and W. G. Hoover, J. Chem. Phys. **40**, 939 (1964).
[4] W. G. Hoover and A. G. De Rocco, J. Chem. Phys. **36**, 3141 (1962).
[5] E. Thiele, J. Chem. Phys. **39**, 474 (1963).
[6] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959); E. Helfand, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **34**, 1037 (1961).
[7] For detail of the Monte Carlo calculation, we refer to F. H. Ree and W. G. Hoover, UCRL-7519-T (unpublished report).
[8] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).