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High-Density Equation of State for Hard Parallel Squares and Cubes*

WILLIAM G. HOOVER
University of California, Lawrence Radiation Laboratory, Livermore, California

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High-density systems of hard parallel squares and cubes enclosed in rigid containers are considered. Evaluation of the exact volume-dependence of the configurational integral shows that such systems obey the free-volume equation of state. Low order deviations from the free-volume theory, found by Salsburg and Wood in an analogous calculation for hard circles and spheres, are not found for squares and cubes.

I. INTRODUCTION

ONE of the chief responsibilities of statistical mechanics is to derive the equation of state corresponding to a given interparticle force law. The problem of calculating the low-density equation of state for particles with pairwise-additive forces was solved formally by Mayer.[1] He showed that each of the virial coefficients B_k in the number density ($\rho \equiv N/V$) expansion of the equation of state,

$$PV/NkT = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + B_5\rho^4 + \cdots, \quad (1)$$

is equal to a sum of integrals over the coordinates of k particles. For mathematically convenient potentials it has been possible to calculate the first seven virial coefficients[2,3]; for realistic potentials, coefficients higher than the fourth have not been evaluated.[4] A recent reformulation of Mayer's recipe for calculating the B_k has increased the potential accuracy of Monte Carlo determination of virial coefficients and has led to reliable values of B_5 and B_6 for hard spheres.[5]

At moderate and high densities the virial expansion is useless for making equation of state calculations. Aside from the difficulty of calculating high-order virial coefficients, the radius of convergence of the series given in (1) is unknown.[6] For hard potentials, in which we are particularly interested, Monte Carlo and molecular dynamics have made possible the determination of accurate equation of state data (for finite periodic systems) over a wide density range.[7]

At very high densities, theoretical equation of state calculations have been intuitive and approximate. Only recently did Salsburg and Wood rigorously demonstrate the asymptotic form of the equation of state for finite systems of hard circles and spheres.[8] They showed that d-dimensional hard spheres obey, within terms of order unity and $1/N$, the equation of state predicted by the free-volume theory.

$$PV/NkT(\text{f.v.}) = V^{1/d}/(V^{1/d} - V_0^{1/d}), \quad (2)$$

$$PV/NkT(\text{spheres}) = [PV/NkT(\text{f.v.})][1 - N^{-1}] + O(1). \quad (3)$$

V_0 is the close-packed volume. Although (3) was proved to hold for spheres only over a density range which goes to zero as N increases, Salsburg and Wood feel that (3) is valid for infinite systems as well. We will show that a similar situation exists for hard squares and cubes confined to a rigid container, with the difference that no correction terms to the free-volume theory appear. The following sections are devoted to the proof and discussion of these results.

2. HIGH-DENSITY EQUATION OF STATE

In this section it is shown that the configurational integral for N d-dimensional cubes of unit side-length is, near close-packing, proportional to the (Nd)th power of the "free length," $\lambda \equiv V^{1/d} - N^{1/d}$. This relation,

$$Q_N \equiv \int \exp\left(\frac{-\Phi_N}{kT}\right) d\mathbf{r}^N = \kappa(V^{1/d} - N^{1/d})^{Nd}, \quad (4)$$

where κ is a volume-independent function of N, establishes the free-volume equation of state (2) for these systems. V is the volume and Φ_N the total potential energy of the N-particle system. This result is restricted to the density range for which λ lies between 0 and 1, and is in this way analogous to Salsburg and Wood's work with d-dimensional spheres. There are two main differences between the cube and sphere calculations:

(i) A rigid container is used in the cube calculations; Salsburg and Wood used a periodic container.

(ii) The exact volume dependence of the configurational integral is evaluated for cubes, and no deviation from free-volume theory is found; Salsburg and Wood

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[1] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chap. 13.

[2] 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.

[3] W. G. Hoover and A. G. De Rocco, J. Chem. Phys. **36**, 3141 (1962).

[4] See J. S. Rowlinson, Mol. Phys. **6**, 429 (1963), and references cited therein.

[5] F. H. Ree and W. G. Hoover, J. Chem. Phys. **40**, 939 (1963).

[6] Some lower bounds on the radius of convergence of the virial series have been obtained. See J. L. Lebowitz and O. Penrose (to be published).

[7] See the recent report by W. W. Wood, *Monte Carlo Calculations of the Equation of State of Systems of 12 and 48 Hard Circles* (Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico, 1963), Report LA-2827.

[8] Z. W. Salsburg and W. W. Wood, J. Chem. Phys. **37**, 798 (1963).

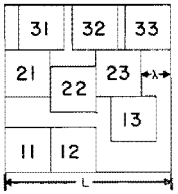

FIG. 1. 9-particle system of parallel hard squares. $V=121/9$, $L=11/3$, $N=9$, $n=3$, $\lambda=2/3$, $V/V_0=121/81$. Some of the coordinates in the configuration shown are $x_{11}=y_{11}=x_{21}=0$; $y_{31}=y_{32}=x_{33}=y_{33}=\lambda$; $x_{13}=y_{22}=\lambda/2$; etc.

evaluated the asymptotic volume dependence for spheres and were therefore unable to evaluate low-order deviations from free-volume theory.

Only one case, two-dimensional for clarity, will be worked out in detail. Extension to other cases (cubes in a parallelepiped container, for example) requires more notation but no new ideas. Consider a rigid-square container of side-length $L=V^{1/2}$, and place $N=n^2$ hard parallel squares within it. We assume that once the particles are in the box no diffusion (movement through the nearest-neighbor cage) is possible. This implies the restriction $0<\lambda\equiv L-n<1$. The particles are labeled by a double set of indices, i and j, giving their relative positions in the box. Particle i, j is in the ith row (counted from the bottom) and jth column (counted from the left) of the box at close packing. Our coordinates $x_{i,j}$ and $y_{i,j}$ measure the displacement of particle i, j from the configuration in which all particles are as close as possible (without overlapping) to the lower left-hand corner of the box. Thus for each particle i, j the following inequalities apply:

$$0\leq x_{i,j}\leq\lambda; \qquad 0\leq y_{i,j}\leq\lambda. \tag{5}$$

The coordinate system is illustrated for a nine-particle system in Fig. 1.

The restrictions that no particles overlap can be expressed in terms of a set of inequalities further bounding the coordinates:

$$x_{i,j}\leq x_{i,j+1}; \qquad y_{i,j}\leq y_{i+1,j}; \tag{6}$$

$$x_{i,j}\leq x_{i+1,j+1} \text{ or } \qquad y_{i,j}\leq y_{i+1,j+1}, \tag{7a}$$

$$x_{i+1,j}\leq x_{i,j+1} \quad \text{or} \quad y_{i,j+1}\leq y_{i+1,j}. \tag{7b}$$

The inequalities (7) make the overlap of second-nearest neighbors impossible, while inequalities (6) prevent all other overlaps. The configurational integral is given by the expression,

$$Q_N=\prod_{i=1}^{n}\prod_{j=1}^{n}\int_0^\lambda dx_{i,j}\int_0^\lambda dy_{i,j}, \tag{8}$$

(6) and (7),

where the integration is to be performed subject to the restrictions (6) and (7). From (8) we see the configurational integral as that part of a $2N$-dimensional hypercube of side-length λ which satisfies (6) and (7). Furthermore, each of the $(2N)!$ linear orderings of the $2N$ variables $\{x_{i,j}\}$ and $\{y_{i,j}\}$ corresponds to a particular region of the hypercube. (One of the 18! linear orderings for the system in Fig. 1 is $x_{11}<x_{12}<x_{13}<x_{21}<x_{22}<x_{23}<x_{31}<x_{32}<x_{33}<y_{11}<y_{21}<y_{31}<y_{12}<y_{22}<y_{32}<y_{13}<y_{23}<y_{33}$.) Each such region has volume $\lambda^{2N}/(2N)!$. Thus the configurational integral is just the total volume of the hypercube multiplied by that fraction of all linear orderings, denoted by κ, of the coordinates satisfying (6) and (7). This establishes (4), and the free-volume equation of state follows by differentiation:

$$P/kT=\frac{\partial\ \ln Q_N}{\partial V}=\frac{\partial\ \ln[\kappa\lambda^{2N}]}{\partial V}=\frac{NV^{-1/2}}{(V^{1/2}-N^{1/2})}. \tag{9}$$

The configurational entropy, $S=k\ \ln Q_N$, remains unknown because the acceptable fraction of orderings, κ, is unknown. An upper bound, $S(\max)$, can be calculated by ignoring inequalities (7), but retaining inequalities (6). This corresponds to integrating over some configurations in which second-nearest neighbors overlap, but no others do. $Q_N(\max)$ then becomes the product of $2n$ identical one-dimensional integrals, each of value $\lambda^n/n!$:

$$Q_N(\max)=(L-n)^{2N}/(n!)^{2n}. \tag{10}$$

Using Stirling's approximation for $n!$ gives $S(\max)=k\ \ln Q_N(\max)=2Nk\ \ln(\lambda e/n)$. This is just twice the configurational entropy for the corresponding one-dimensional gas.

3. DISCUSSION

The question of whether or not the high-density equation of state for finite systems is also correct for thermodynamic "infinite" systems remains open. Our main conclusion, that finite systems of squares and cubes in rigid containers obey the free-volume theory exactly is in itself useful information. Monte Carlo experiments can easily be designed for such systems, and the exact result is a powerful check on these experiments. Also, we expect that the form of the equation of state will be similar for systems with periodic boundary conditions, and measurements of the deviations between rigid and periodic systems would be of interest. It should be pointed out that for systems of the size conveniently treated by Monte Carlo and molecular dynamics, our result spans a considerable density range. It is exact for 100 two-dimensional particles with $V/V_0<1.21$, and for 1000 three-dimensional particles with $V/V_0<1.331$.

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