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Bounds on the Configurational Integral for Hard Parallel Squares and Cubes*

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Upper and lower bounds on the configurational integral for hard parallel squares and cubes are obtained. These bounds are valid over the entire density range and apply to infinite (thermodynamic) systems. Both the upper bound and the lower bound approach the free-volume form at high density.

This strong result proves rigorously that the free-volume form is correct for these systems in the thermodynamic limit.

I. INTRODUCTION

IN 1902 Gibbs pointed out that all of the thermodynamic properties of a system can be derived from the corresponding partition function. It is understandable that since then much effort has been expended in trying to calculate partition functions for various systems of interest.

In the classical case the partition function is a product of two terms, the momentum integral and the configurational integral. The momentum integral can generally be evaluated analytically. The configurational integral, on the other hand, is incredibly complicated for two- or three-dimensional systems. For even the simplest "realistic" force law, hard-core repulsion, an exact evaluation of the configurational integral appears out of the question. A part of this complexity carries through even to the simplest possible caricature of a continuum system, the so-called[1] "lattice gas." For a two-dimensional hard-core lattice gas with nearest-neighbor attractions, Onsager was able to evaluate the configurational sum (the lattice analog of the configurational integral) at half the close-packed density. The evaluation for even this simple two-dimensional model required some unusually sophisticated mathematics; the three-dimensional nearest-neighbor lattice-gas problem has defied exact treatment.

In view of the complete lack of exact results on configurational integrals for two- and three-dimensional continuum systems, it is worthwhile to investigate the simpler problem of bounding such integrals. We have discovered how to calculate both upper and lower bounds on the configurational integrals for hard parallel squares and cubes. Unlike a previous upper bound,[2] these new bounds are valid for infinite systems and span the entire density range. Our method of attack is to bound the integrals for two- and three-dimensional systems in terms of integrals for one-dimensional systems. A pleasing feature of the bounds that result is that both the upper bound and the lower bound approach the free-volume form at high density.

II. MODEL

We limit our explicit treatment to the two-dimensional system, hard parallel squares. The generalization to three dimensions (hard parallel cubes) should be obvious enough. We quote only the results for cubes.

Consider a system of $N(\equiv n^2)$ hard parallel squares of unit side length, confined to a rigid box of side length v and volume $V(\equiv v^2)$. Indicating the pair sum of all the interparticle potential-energy functions by Φ, we write the configurational integral Q_N in the following form

$$N!Q_N \equiv \prod_{i=1}^{N}\left[\int\int dx_i dy_i\right] e^{-\Phi/kT} \equiv \int e^{-\Phi/kT} d\mathbf{r}^N. \qquad (1)$$

Boltzmann's constant and the absolute temperature are indicated by k and T, respectively. Because Φ/kT takes on only the two values, zero and infinity, for hard parallel squares, Q_N is temperature-independent. The potential energy of the wall forces is taken into account in the integration limits. Each of the particle coordinates in the set $\{x_i, y_i\} \equiv \mathbf{r}^n$ lies between $\frac{1}{2}$ and $(v-\frac{1}{2})$.

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[1] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 7.

[2] W. G. Hoover, J. Chem. Phys. **40**, 937 (1964).

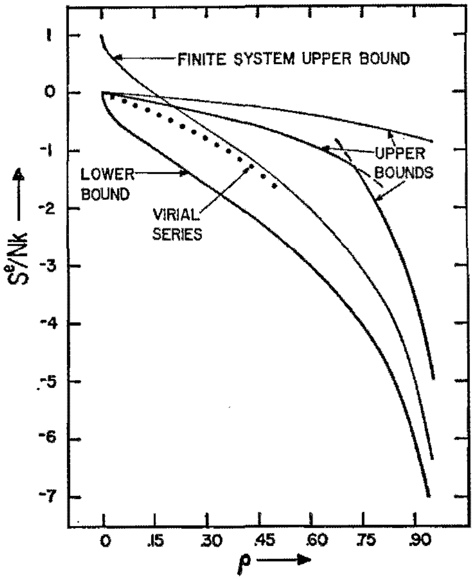

FIG. 1. Excess entropy for the various bounds discussed in the text for hard parallel squares. The low-density virial expansion of the excess entropy [from Eq. (2)] is shown as a series of dots. The heavy lines represent bounds [from Eqs. (8), (9), and (13)] which are valid even in the thermodynamic limit. An upper bound derived only for finite systems (in Ref. 2) is shown as the steeper of the two light curves. The other light curve, an upper bound for infinite systems, comes from Eq. (5). (See also Ref. 6.)

At low density the configurational integral can be expanded as a power series in the number density $\rho(\equiv N/V)$.

$$\ln(Q_N)^{1/N}=1-\ln\rho-\left(2\rho+\tfrac{3}{2}\rho^2+\tfrac{11}{9}\rho^3+\tfrac{67}{72}\rho^4+\frac{121\rho^5}{200}+\frac{17\,827\rho^6}{64\,800}+\cdots\right). \quad (2)$$

This series[3] converges reasonably well for densities up to half of close packing. The configurational excess entropy[4] according to (2) is plotted (dotted line) in Fig. 1. This excess entropy is defined by the equation,

$$S^e/Nk\equiv\ln\rho-1+\ln(Q_N)^{1/N}. \quad (3)$$

The excess entropy is always negative for repulsive potentials and approaches minus infinity at close packing.

At high density the only rigorous results concerning Q_N are for finite systems.[2,5] For hard parallel squares, with $\rho\geq(1-v^{-1})^2$, it has been shown[2] that Q_N is proportional to $[(v-n)/n]^{2N}$, and that the proportionality constant is independent of ρ and less than e^{2N}. The excess entropy for this finite-system upper bound is also plotted (steeper of the light lines) in Fig. 1.

In the following sections we obtain upper and lower bounds on Q_N which are valid over the entire density range.

III. UPPER BOUNDS

The obvious way to obtain an upper bound on the configurational integral, Q_N, is to delete some part of the nonnegative potential-energy function Φ before carrying out the integration. Any such deletion produces an upper bound by including in the bounding integral configurations in which pairs of particles overlap. We find three different upper bounds on Q_N in this section, and each of them exploits the idea of including not only all configurations which contribute to the configurational integral (those for which Φ is zero), but also some configurations in which particles overlap.

It is convenient to divide the system into a square "checkerboard" grid of V cells, such that each cell has unit volume. This choice of cells makes multiple occupancy of any cell impossible, so that any configuration contributing to Q_N will have exactly N of the V cells occupied.

To express distributions of particles in the cells in a quantitative way, we define the occupation numbers $\{\omega_i\}$, with ω_i equal to zero if the ith cell is unoccupied, and equal to one if the ith cell is occupied. For any acceptable configuration the sum of the ω_i's must be N, because each of the N particles must lie in one and only one cell. There are exactly $V!/[N!(V-N)!]$ different sets of ω_i which contribute to Q_N. We use the abbreviation ω to stand for a typical set. For each ω we have a corresponding integral $Q_N(\omega)$, obtained by constraining Particle 1 to the first occupied cell, Particle 2 to the second, and so on. Notice that this particular ordering of the particles is only one of $N!$ different possibilities (each of which would give the same integral). We choose only one ordering, rather than all $N!$ possible orderings, in order to take into account the factor $(N!)^{-1}$ which appears in Q_N. In terms of the restricted integrals, Q_N has the following form:

$$Q_N=(N!)^{-1}\int e^{-\Phi/kT}d\mathbf{r}^N$$

$$=\sum_{\omega}Q_N(\omega)=\sum_{\omega}\int e^{-\Phi/kT}d\mathbf{r}^N$$

$$[j\text{th particle in the }j\text{th occupied cell}]. \quad (4)$$

Each of the restricted integrals $Q_N(\omega)$ is less than or equal to 1. (This is because each of the N particles is restricted to a cell of unit volume for a particular choice of ω.) We get our first upper bound by ignoring *all* interactions between particles in neighboring cells,

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[3] The series comes from the virial series given in W. G. Hoover and A. G. De Rocco, J. Chem. Phys. **36**, 3141 (1962).

[4] The excess entropy we consider here is relative to an ideal gas at the same *number density*. The excess entropy in Ref. 3 is relative to an ideal gas at the same *pressure* and is therefore larger than the excess entropy in the present paper by $Nk\ln(PV/NkT)$.

[5] Z. W. Salsburg and W. W. Wood, J. Chem. Phys. **37**, 798 (1962).

and using the bound $Q_N(\omega)\leqslant 1$ for all ω. Inserting this inequality into (4) gives the result:

$$Q_N < V!/[N!(V-N)!]. \tag{5}$$

This bound is a special case of some general inequalities relating lattice and continuum partition functions.[6]

We can improve upon the bound (5) quite a bit. If it were not for the possibility of second-nearest-neighbor interactions (interactions along the diagonals of the checkerboard grid), we could factor the two-dimensional integral $Q_N(\omega)$ into two one-dimensional integrals, $q_x(\omega)\times q_y(\omega)$. Because the second-nearest-neighbor interactions *are* present we have instead the relation,

$$Q_N(\omega)\leqslant q_x(\omega)\times q_y(\omega). \tag{6}$$

Now observe that the sum of the one-dimensional q's, summed over all ω, is strictly less than the configurational integral[7] for N hard rods of unit side length confined to a line of length V:

$$\sum_\omega q_x(\omega)=\sum_\omega q_y(\omega)<(V-N)^N/N!. \tag{7}$$

[By using appropriate "screw" boundary conditions we could obtain an equality rather than the inequality (7).] As before, notice that each of the $q_x(\omega)$ and $q_y(\omega)$ lies between zero and one. Using this fact together with (5) and (6) produces a second bound on Q_N:

$$Q_N<\sum_\omega q_x(\omega)q_y(\omega)<\sum_\omega q_x(\omega)<(V-N)^N/N!. \tag{8}$$

At low density, (8) is the best bound we obtain. For densities greater than $\rho=0.73106[=e/(1+e)]$, we improve this bound, as follows:

$$Q_N<\sum_\omega q_x(\omega)q_y(\omega)<[\sum_\omega q_x(\omega)][\sum_\omega q_y(\omega)] < [(V-N)^N/N!]^2. \tag{9}$$

Notice that to obtain this bound we have included many configurations which don't really exist by summing up the x and y integrals *before* forming the product. One might therefore expect that the bound could be improved by finding the maximum term of the form $q_x(\omega)q_y(\omega)$. It turns out that this maximum term has exactly the same value, at high density, as does the sum of all terms, squared, which we used in (9).

The excess entropies from the bounds (5), (8), and (9) are all shown in Fig. 1. Notice that the bound (5) exceeds the bound (8) at all densities. The bound (9) becomes better as the density increases, and, as we can see, has the correct asymptotic form near close packing.

IV. LOWER BOUND

Now we turn to the determination of a lower bound for Q_N. We get such a bound by including in the bound only a part of the configurations which contribute to Q_N; other configurations are left out.

Again, in order to account for the factor of $(N!)^{-1}$ in Q_N, we begin by ordering the particles. Let us indicate the coordinates of the $N(\equiv n^2)$ particles by a double set of indices, i and j (with $1\leqslant i, j\leqslant n$). To order the particles we first partition them into n columns, requiring that the following inequalities be satisfied for all j:

$$\{x_{ij}<x_{i',j+1}\} \qquad \text{for} \quad 1\leqslant i, i'\leqslant n. \tag{10a}$$

The second subscript indicates the column in which Particle ij lies. Within each column we use the first subscript to order the y coordinates:

$$\{y_{ij}<y_{i+1,j}\} \qquad \text{for} \quad 1\leqslant i<n. \tag{10b}$$

There are exactly $N!$ possible (and equivalent) orderings of the kind represented by (10) so that, arbitrarily choosing this one, (10), we can write Q_N as a restricted integral:

$$Q_N=(N!)^{-1}\int e^{-\Phi/kT}d\mathbf{r}^N=\int_{(10)} e^{-\Phi/kT}d\mathbf{r}^N, \tag{11}$$

where the restrictions on the integration variables are indicated by the (10) next to the integral sign. Now we observe that if we strengthen the inequalities somewhat:

$$\{x_{ij}+1<x_{i',j+1}\} \qquad \text{for} \quad 1\leqslant i, i'\leqslant n, \tag{12a}$$

$$\{y_{ij}+1<y_{i+1,j}\} \qquad \text{for} \quad 1\leqslant i<n, \tag{12b}$$

no overlaps of the particles can occur, so that each of the configurations which satisfies the restrictions (12) contributes to Q_N. We are guaranteed by (12a) that particles in adjacent columns cannot overlap (in the x direction), and by (12b) that particles in the same column cannot overlap (in the y direction). The integral corresponding to the restrictions (12) can be evaluated, and this gives us a lower bound on Q_N:

$$Q_N=\int_{(10)} e^{-\Phi/kT}d\mathbf{r}^N>\int_{(12)} d\mathbf{r}^N=\int_{(12a)} dx^N\int_{(12b)} dy^N$$
$$=[(v-n)^N(n!)^n/N!][(v-n)^n/n!]^n=(v-n)^{2N}/N!. \tag{13}$$

The excess entropy for this lower bound is also shown in Fig. 1.

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[6] W. G. Hoover, B. J. Alder, and F. H. Ree, J. Chem. Phys. **41**, 3528 (1964).

[7] K. F. Herzfeld and M. G. Mayer, J. Chem. Phys. **2**, 38 (1934); also see L. Tonks, Phys. Rev. **50**, 955 (1936). Tonks' paper presents a plausibility argument for the free-volume equation of state for spheres and disks.

V. DISCUSSION

A glance at Fig. 1 shows that our knowledge of the absolute entropy is imprecise, with an uncertainty of order $\pm Nk$ at some densities. Near close packing, however, the excess entropy approaches minus infinity, and the finite uncertainty becomes a negligible fraction of the entropy. The chief result of this paper is that:

> *The entropy for systems of hard parallel squares and cubes, in the thermodynamic limit, approaches the free-volume form at high density,* $[S-S(fv)]/S=[O(1)]/\ln(1-\rho)$.

To establish this result we expand the bounds (9) and (13) in terms of the high-density parameter $\alpha(\equiv\rho^{-1}-1)$:

$$2\ln\alpha+1-2\ln 2-\tfrac{1}{2}\alpha+\tfrac{3}{16}\alpha^2-\cdots<\ln(Q_N)^{1/N}<2\ln\alpha+2. \quad (14)$$

For cubes, the bounds analogous to (9) and (13) are the following:

$$(V^{\frac{1}{3}}-N^{\frac{1}{3}})^{3N}/N!<Q_N<(V-N)^{3N}/(N!)^3; \quad (15)$$

or, in terms of α,

$$3\ln\alpha+1-3\ln 3-\alpha+\tfrac{7}{18}\alpha^2-\cdots<\ln(Q_N)^{1/N}<3\ln\alpha+3. \quad (16)$$

Thus, we see that in D dimensions, $\ln(Q_N)^{1/N}$ approaches the ubiquitous free-volume form, $D\ln\alpha+O(1)$.

This same form has turned up in almost every approximate treatment of the high-density partition function for hard-core models. In addition to the work cited in Refs. 2 and 5, various cell models,[8] Wood's solution of Kirkwood's free-volume integral equation for hard spheres,[9] and the machine calculations for hard spheres and disks[8,10] all have this limiting form at high density. In view of this, it is very reassuring and significant that this same form *is exact* in a case which can be worked out rigorously.

It is interesting to see that all of the simple theories, as well as the machine results give an expansion of the form

$$\ln(Q_N)^{1/N}=D\ln\alpha+h_0+h_1\alpha+h_2\alpha^2+\cdots. \quad (17)$$

If such an expansion exists in the thermodynamic limit, as seems likely, then our result would also imply the free-volume form of the equation of state at high density:

$$PV/NkT=D/\alpha+C_0+C_1\alpha+C_2\alpha^2+\cdots. \quad (18)$$

Although we cannot *prove* that this expansion exists it is still worthwhile to point out that the upper and lower bounds for Q_N, derived for cubes and squares, when differentiated to obtain the pressure, give results which bound the high-density equations of state for hard spheres and disks.[11]

We expect to discuss the high-density entropy and equation of state for both spheres and disks in detail in forthcoming papers.[10]

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I would like to thank Berni J. Alder for some stimulating conversations on the subject of this paper.

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[8] B. J. Alder, W. G. Hoover, and T. E. Wainwright, Phys. Rev. Letters **11**, 241 (1963).

[9] W. W. Wood, J. Chem. Phys. **20**, 1334 (1952).

[10] W. G. Hoover, B. J. Alder, and T. E. Wainwright (to be published).

[11] Considerably weakened forms of our upper bounds can be obtained for spheres and disks. [See Eq. (5) in R. W. Zwanzig, J. Chem. Phys. **24**, 855 (1956).] This is not a very powerful method, however. The best *lower* bound that we can obtain for spheres and disks (in the thermodynamic limit) is identical with the entropy derived from Wood's solution of Kirkwood's free-volume integral equation. In a preprint, "Bounds for the Derivatives of the Free Energy and the Pressure of a Hard-Core System near Close Packing," M. E. Fisher shows how to establish such lower bounds for general hard-core systems. He also proves that cubes and squares satisfy the free-volume equation of state within a *multiplicative* factor of order unity.