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Pressure and Entropy for Hard Particles at High Density*

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A hard-particle model is introduced. For this model it is possible to calculate the thermodynamic limit of both the pressure and the entropy at high (solid-phase) densities. The model embodies both the simplicity associated with a nearest-neighbor lattice-gas interaction, and the realism of a *continuous* configuration space.

The volume of the system is divided into V cells, with particles in nearest-neighbor cells interacting as hard parallel squares (cubes, in the three-dimensional case). When written in terms of the cell occupation numbers the configurational integral for this system bears a superficial resemblance to a lattice-gas partition function. It is possible to calculate the maximum term in the lattice-gas partition function explicitly. This makes it possible to establish tight bounds on the continuum configurational integral; these bounds show that the free-volume form of the pressure and the entropy is *exact* at high density.

At close packing, where the upper and lower bounds coincide, the absolute entropy is determined. It is shown that the communal entropy vanishes at close packing, and cannot be fully excited for densities greater than half the close-packed density.

I. INTRODUCTION

ALTHOUGH a rigorous series development of the high-density thermodynamic properties, analogous to the low-density virial series, is not yet known,[1] considerable progress toward establishing the asymptotic form of both the pressure and the entropy has been made. It appears that for continuum (as opposed to lattice) particles, with a hard-core repulsion, the thermodynamic properties approach the "free-volume" form at high density. In the one-dimensional case (hard rods) the pressure is the reciprocal of the free volume per particle, and the entropy per particle is, within an additive constant, the logarithm of this free volume—in D dimensions the "free-volume pressure" and the "free-volume entropy" are D times as great. The free volume has been suggested as an expansion parameter at high density.[2]

The early computer experiments for finite systems of hard disks[3] and spheres[4] indicated that the free-volume form of the pressure, D times the one-dimensional pressure, is correct at high density. This was later *proved* to be the case for *finite* systems with either periodic[5] or rigid[6] boundary conditions. For hard squares and cubes it was discovered that the entropy has the free-volume form in the thermodynamic limit (infinite systems)[7]; an effort to obtain an equally strong result for the pressure,[8] a difficult undertaking even for the simple hard-square potential, was less successful.

In order to demonstrate that the free-volume form of the pressure, as well as the entropy, really is correct at high density, we here introduce a model, very similar to the hard-parallel-square model,[9] for which it is possible to establish the thermodynamic properties exactly, in the limit of close packing. Whereas for hard parallel squares the entropy at close packing could be determined only within an uncertainty of order Nk (making it impossible to deduce the equation of state),[8] for the present model it is possible to calculate the absolute entropy at close packing, with no error of finite order, and so to establish the free-volume equation of state. In addition, it is shown that the communal

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[1] For certain lattice gases it *is* possible to write down an expansion of the high-density equation of state. In the lattice case the pressure is proportional to the logarithm of the free volume, rather than to the reciprocal of the free volume. See the article by D. S. Gaunt and M. E. Fisher, J. Chem. Phys. **43**, 2840 (1965). For a comparison of hard-core lattice and continuum systems see the article by W. G. Hoover, B. J. Alder, and F. H. Ree, J. Chem. Phys. **41**, 3258 (1964).

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

[3] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[4] M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. **22**, 881 (1954). Similar results at high density have recently been obtained by A. Rotenburg, J. Chem. Phys. **42**, 1126 (1965). Accurate results for both hard disks and hard spheres, allowing the deviations from the free-volume theory and various cell models to be determined within 1%–2%, will soon be published by B. J. Alder and W. G. Hoover.

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

[6] W. G. Hoover, J. Chem. Phys. **40**, 937 (1964), cubes. The work in Ref. 5 was concerned with "locked-in" configurations, and periodic boundary conditions were used. Because I did not realize that locked-in configurations could also be achieved with squares and cubes, I studied rigid boundaries instead. In Sec. V of the present paper a locked-in configuration of squares is shown to which the methods of Salsburg and Wood could be applied.

[7] W. G. Hoover, J. Chem. Phys. **43**, 371 (1965).

[8] M. E. Fisher, J. Chem. Phys. **42**, 3852 (1965). Fisher shows that because the pressure is known to be a nonincreasing function of the volume, it is possible to bound the pressure once bounds on the entropy are given. The entropy bounds must be rather tight to make this undertaking successful. For squares, Fisher obtained the result, $0.253/\alpha < PV/NkT < 6.848/\alpha$. The present effort to obtain tighter bounds on the solid-phase pressure was stimulated by Fisher's paper.

[9] See, for example, the article by W. G. Hoover and A. G. De Rocco, J. Chem. Phys. **36**, 3141 (1962).

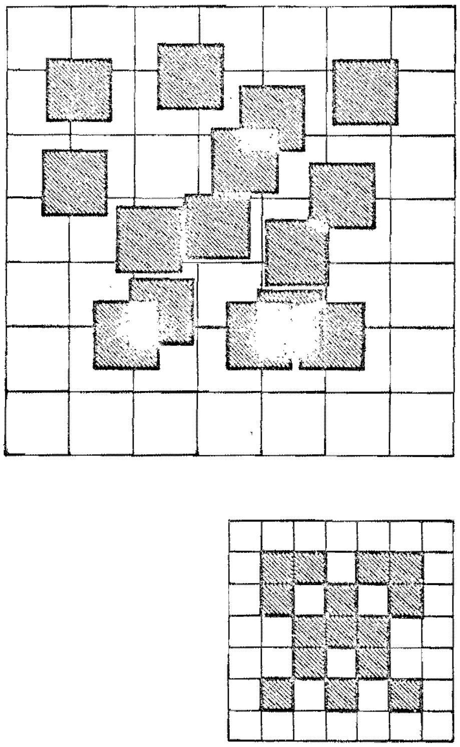

FIG. 1. A configuration of 15 model particles in 49 cells. The larger drawing illustrates the diagonal overlaps (heavy shading) which are allowed for this potential, and which distinguish it from the hard-parallel-square potential. The smaller drawing shows the lattice configuration (shaded squares are occupied) to which the continuum configuration corresponds. The boundary cells have all been left unoccupied in this configuration in order that the figure could be used to illustrate the calculation of $Q_N(\omega)$ as discussed in Sec. III.

entropy vanishes at close packing, just as in the one-dimensional hard-rod case,[10] and bounds on the communal entropy are established.

II. MODEL SYSTEM

For convenience, we restrict our attention to a two-dimensional model system. Systems of higher dimensionality require nothing new. Let the volume V be divided into V cells of unit area, checkerboard fashion. N particles, also of unit area, are placed in the volume with, at most, one particle per cell. The model closely resembles the hard-parallel-square model. In a system of hard parallel squares, interactions can occur between particles in both nearest-neighbor and second-nearest-neighbor cells; in the model system particles in nearest-neighbor cells interact as hard parallel squares of unit side length, but particles in higher-neighbor cells do not interact. Thus, the treatment of "diagonal" interactions (along the diagonals of the checkerboard grid) is the only difference between the two systems. A representative configuration of a model system is shown in Fig. 1. Notice the allowed "overlap"—without interaction—of particles in second-neighbor cells. In the smaller drawing those cells which are occupied in the configuration shown are indicated by shading. The restriction to nearest-neighbor interactions, borrowed from the Ising problem, results in a marked simplification of the continuum problem at high density.[11]

Because in the present model system some of the repulsive hard-square interactions are omitted, it can be anticipated that the model isotherm lies *below* that for hard parallel squares. This is certainly true in an "average" sense, for the work of compressing the model system to a particular density is less than the work of compressing a hard-square system to the same density (because the entropy for squares is, at every density, less than that of the model system).[12] The low-density virial series[13] confirm this observation:

$$\begin{aligned} \text{Model:}\quad & PV/NkT=1+1.5000\rho+1.6667\rho^2\\ &\quad +1.5625\rho^3+1.4667\rho^4+\cdots,\\ \text{Disks:}\quad & PV/NkT=1+1.8138\rho+2.5727\rho^2\\ &\quad +3.1759\rho^3+3.61_3\rho^4+\cdots,\\ \text{Squares:}\quad & PV/NkT=1+2.0000\rho+3.0000\rho^2\\ &\quad +3.6667\rho^3+3.7222\rho^4+\cdots. \qquad (1) \end{aligned}$$

P and T are pressure and temperature, respectively; k is Boltzmann's constant. For comparison purposes, the hard-disk result is given in units comparable to those for the model system and for hard squares; the number density, $\rho(\equiv N/V)$, is unity at close packing.

At high density, in the solid phase, these series expansions are not useful (they may not even converge to the true pressure), but we expect that, just as at low density, the model pressure lies below the hard-square and hard-disk pressures. To make this more plausible, consider the bounds on the entropy, S, which were previously obtained for the hard-square system[7]:

$$2\ln\alpha-0.3863-\tfrac{1}{2}\alpha+O(\alpha^2)<S/Nk<2\ln\alpha+2;$$
$$\alpha\equiv(V/V_0)-1. \qquad (2)$$

The parameter α, introduced in (2), is the relative free volume, the ratio of the unoccupied volume, $V-V_0$, to

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[10] The one-dimensional communal entropy is calculated by W. G. Hoover and B. J. Alder, in "Cell Theories for Hard Particles" (to be published).

[11] The low-density virial series is, however, more difficult to calculate for the model system. Because the potential depends upon where a particle is in its cell, an additional integration must be carried out. Also, the virial coefficient integrals do not factor, for the model system, in as nice a way as do the corresponding integrals for hard parallel squares.

[12] This is because all configurations acceptable for hard parallel squares are also acceptable for the model system, but *not vice versa*.

[13] The integrals contributing to these virial coefficients for the model system are listed in the Appendix. Recent calculations of the exact grand partition functions for systems containing up to 25 particles confirm the coefficients. The grand partition functions, along with machine calculations for larger systems will be published by W. G. Hoover and F. H. Ree. A better upper bound than (14), derived from the Cauchy inequality, will also be discussed in that paper.

the close-packed volume, V_0. The relative free volume approaches zero at close packing, and is the natural high-density expansion parameter for hard-core systems. From a mathematical viewpoint[8] there is no guarantee that the pressure is bounded by the derivatives of the entropy bounds (2), but because the bounds were derived by considering configurations typical of the dense solid, we expect on physical grounds to find the actual pressure bounded by the derivatives of the entropy bounds:

$$(2/\alpha)+\tfrac{3}{2}+O(\alpha)<PV/NkT_{\text{squares}}<(2/\alpha)+2. \quad (3)$$

It is interesting to note, in support of this surmise, that the accurate machine results for hard disks[4] lie, at high density, within these bounds for squares:

$$PV/NkT_{\text{disks}}=(2/\alpha)+1.8_6+O(\alpha). \quad (4)$$

The three-dimensional case is analogous: the hard-sphere pressure lies between the derivatives of the hard-cube entropy bounds.

In Sec. III of the present paper, bounds on the entropy for the model system are derived. Differentiation of these bounds, using Stirling's approximation, suggests that the following inequalities may hold for the model:

$$(2/\alpha)+\ln\alpha+O(1)<PV/NkT_{\text{model}}<(2/\alpha)+1.1621+O(\alpha). \quad (5)$$

Notice that these latter (nonrigorous) bounds both lie below the (nonrigorous) hard-square lower bound from (3). This again is consistent with our expectation that the model isotherm lies below the hard-square isotherm at all densities.

III. ENTROPY

The configurational entropy S is related to the configurational integral, Q_N, by the equation,

$$\frac{S}{k}=\ln Q_N\equiv\ln\left[(N!)^{-1}\int e^{-\Phi/kT}d\mathbf{r}^N\right], \quad (6)$$

where the integration is over the coordinates, $\mathbf{r}^N$, of all the particles, restricted to the interior of the volume V, and Φ is the total potential energy of the system.

Along with the checkerboard grid of cells it is convenient to introduce the occupation numbers, $\{\omega_i\}$, with the ith occupation number equal to 0 if the ith cell is empty, and equal to 1 if the ith cell contains a particle (as do the shaded cells in Fig. 1). A typical set of the ω_i [containing, by the single-occupancy restriction, $(V-N)$ zeros and N ones] is abbreviated ω. The introduction of the occupation numbers allows the configurational integral to be written as a sum of restricted integrals, $Q_N(\omega)$. For a particular choice of ω, Particle 1 is confined to the first occupied cell, Particle 2 to the second, and so on:

$$Q_N(\omega)=\int e^{-\Phi/kT}d\mathbf{r}^N, \quad (7)$$

(jth particle confined to the jth occupied cell).

For any choice of ω the two-dimensional integral $Q_N(\omega)$ factors into a product of simple one-dimensional integrals; this is the simplification which results from the lack of diagonal (second-nearest-neighbor) interactions. For hard parallel squares the diagonal interactions serve to couple the x and y integrations.

Let us indicate the integrals in the x and y directions by $q_x(\omega)$ and $q_y(\omega)$, respectively. Then, introducing the restricted integrals, the configurational integral can be written

$$Q_N=\sum_\omega Q_N(\omega)=\sum_\omega q_x(\omega)\,q_y(\omega); \quad (8)$$

the factor of $(N!)^{-1}$ in the definition of Q_N has been taken into account by choosing the particular ordering (1 of $N!$ possible orderings) specified in (7). The one-dimensional integrals are easily worked out.[14] A group of j particles in a line of adjacent cells, preceded and succeeded by empty cells, contributes a factor of $(j!)^{-1}$ to q. In the configuration shown in Fig. 1, for example, the x integration gives a factor of $(1/2!)^2$ from the second row, and $(1/3!)$ from the fourth. The y integration gives $(1/2!)^5$, each of the columns except the first and last containing a single group of two adjacent particles. (Isolated particles contribute a factor of unity.) Thus, for the configuration shown, $Q_{15}(\omega)=q_x(\omega)\,q_y(\omega)=(\frac{1}{24})(\frac{1}{32})=(\frac{1}{768})$.

How to carry out the sum in (8) explicitly, including all of the ways of distributing N particles in V cells, is unknown. We anticipate that at high density a single term in the sum, provided it is wisely chosen, will provide not only a lower bound, but also a good approximation to the entire sum. The results cited previously[7] show that at high density the *maximum term* $\bar{Q}_N(\omega)$ in the sum (8) *is* a good approximation to the configurational integral. In fact, because there are precisely $V!/[N!(V-N)!]$ terms in the sum, the maximum term not only is a lower bound, but also provides an upper bound:

$$\bar{Q}_N(\omega)<Q_N<[V!/N!(V-N)!]\bar{Q}_N(\omega). \quad (9)$$

This same equation holds also for hard parallel squares [although with a *different* $\bar{Q}_N(\omega)$]. In fact the *upper* bound obtained for the model system is also an upper bound for squares (but only slightly better than that previously found).[7] Because the binomial coefficient in (9), the configurational sum for an ideal lattice gas, approaches unity at close packing the two bounds (9) are asymptotically equal at high density.

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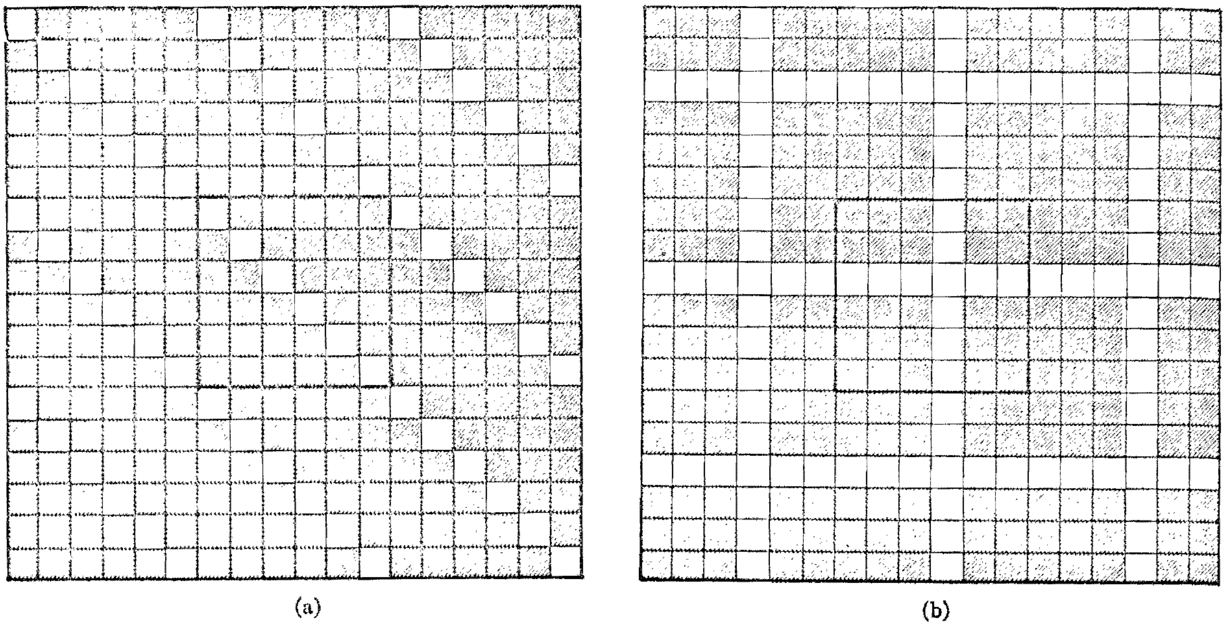
[14] See Eq. (3.1) of L. K. Runnels, J. Chem. Phys. **42**, 217 (1965), for example. See also a theorem on more general integrals of this type on p. 377 of W. G. Hoover and F. H. Ree, J. Chem. Phys. **43**, 375 (1965).


(a) (b)

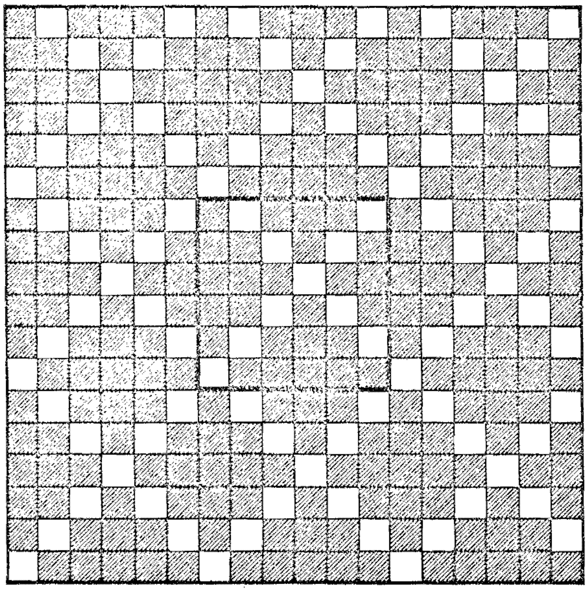

(c)

FIG. 2. Representatives of three classes of configurations which contribute to the model configurational integral are shown in this figure. (a) Strip domains, $\rho=30/36$; (b) square domains, $\rho=25/36$; (c) diamond domains, $\rho=26/36$. Only the first, a "strip domain," makes an important contribution to the high-density properties. In the center of each drawing is an outlined area of 36 cells, which if repeated throughout space (just as if periodic boundary conditions were used) would give the configuration of the infinite system.

It is clear that the maximum term, $\bar{Q}_N(\omega)$, cannot be larger than the square of the maximum one-dimensional term, and, in fact, it is exactly equal to the square, $\bar{Q}_N(\omega)=\bar{q}_x(\omega)\bar{q}_y(\omega)$. For a density $\rho=m/(m+1)$, where m is any positive integer, the configuration corresponding to this maximum term is a set of parallel "strips" of width m running through the system [see Fig. 2(a), for the case $m=5$]. In three dimensions the maximum term corresponds to sheets of thickness m. For densities of the form $m/(m+1)$ the bounds from (9) are shown as dots in Fig. 3. For densities lying between two such values, the maximum term is constructed by using strips of two different widths. In general, the maximum term has the form[15]

$$\bar{Q}_N(\omega)=(n!)^{2[(n+2)N-(n+1)V]}[(n+1)!]^{2[nV-(n+1)N]}, \qquad (10)$$

where n is the greatest integer in $\rho/(1-\rho)$. The entropy bounds obtained by inserting (10) in (9) are the heavy lines shown in Fig. 4. In that figure the bounds in terms of the *excess entropy* $S^e[S^e(\rho)\equiv S(\rho)-S_{\text{ideal}}(\rho)]$ are plotted. The thermodynamic properties from (10)

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[15] This result is not restricted to the case of a square or rectangular container. For any shape (without a pathologically large boundary) the maximum term is the same, and a function of density only.

are the following:

$$S/Nk=2[\rho^{-1}n\ln(n+1)-\rho^{-1}\ln n!+\ln n!-(n+1)\ln(n+1)], \quad (11)$$

$$PV_0/NkT=2[n\ln(n+1)-\ln n!]. \quad (12)$$

In D dimensions the 2's in (11) and (12) are replaced by D's. It is noteworthy that the pressure from (12) remains constant as the density is increased from $m/(m+1)$ to $(m+1)/(m+2)$. Because density fluctuations have been ignored in computing the configurational integral (we don't know how to include them) the resulting isotherm has an artificial stair-step character, with different parts of the system existing in equilibrium (same pressure) at the two coexisting densities. Because, at least in the solid phase, the effect of introducing fluctuations in the density is an *increase* in the pressure,[16] one might expect that the pressure given by (12) lies below the true pressure. This is *not* the case at lower densities. The pressure predicted by (12) at half the close-packed density, with $n=1$, $PV_0/NkT=2\ln 2=1.386$, can be compared with the estimate from the virial series (1):

$$PV_0/NkT=0.500+0.375+0.208+0.098+0.046+\cdots$$
$$=1.227+\cdots\doteq 1.30; \qquad (\rho=\tfrac{1}{2}). \quad (13)$$

The first five virial coefficients predict 1.227, so that (12), obtained by differentiating the entropy lower bound (11), crosses the model isotherm at least once and is therefore *not* a lower bound on the pressure.

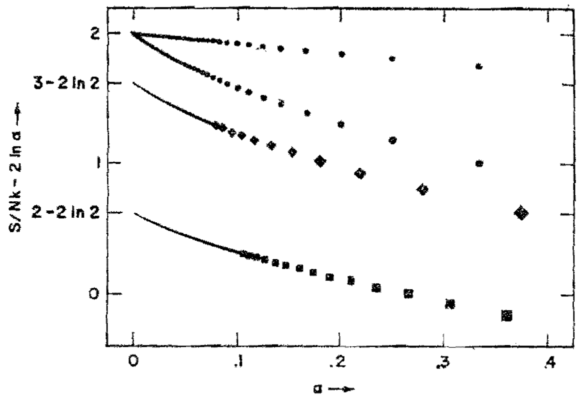

FIG. 3. The upper and lower bounds on the model-system entropy, obtained by taking the exact maximum term in the corresponding lattice partition function, are shown as a series of bullets (● ● ●). For clarity, a heavy line is drawn in as the points become closely spaced, using the high-density expansion of the bounds. The results for the entropy lower bounds using square (■) and diamond (◆) domains are also shown in the figure. The latter types of domains make negligible contributions to the entropy at high density.

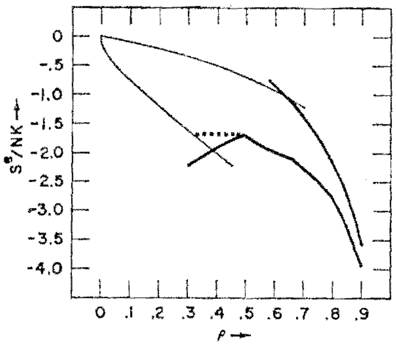

FIG. 4. Bounds on the excess entropy $[S^e(\rho)\equiv S(\rho)-S_{\text{ideal gas}}(\rho)]$ obtained by using strips of two different widths are shown as heavy lines. The two light lines, the best bounds at lower densities, are derived in Ref. 7. The upper bound at low density is the one-dimensional free-volume entropy; the lower bound is essentially a two-dimensional cell-model entropy. An improved lower bound, indicated by a series of dots in the figure, follows from the observation that the excess entropy for the model system is a decreasing function of density, $\partial S^e/\partial\rho<0$.

At high density (small α) terms of order α^2 and higher can be ignored, and then, using (10) for $\bar{Q}_N(\omega)$, the bounds (9) give, whether $\rho/(1-\rho)$ is an integer or not, the result

$$2\ln\alpha+2+\alpha\ln\alpha-\alpha\ln 2\pi<S/Nk<2\ln\alpha+2+\alpha(1-\ln 2\pi), \qquad (\text{small } \alpha). \quad (14)$$

In D dimensions (14) has the form

$$D\ln\alpha+D+\tfrac{1}{2}D\alpha\ln\alpha<S/Nk<D\ln\alpha+D+(\tfrac{1}{2}D-1)\alpha\ln\alpha, \qquad (\text{small } \alpha).$$

The difference between the upper and lower bound is of course just the configurational entropy for an ideal lattice gas, the logarithm of the number of ways N indistinguishable particles can be distributed on V sites.

Evidently the distribution of terms around the maximum is sharply peaked. To see this, consider two other possible terms, $Q_N(\omega)$, which at first glance appear to be likely candidates for the maximum term in the sum. We call the configurations to which they correspond "square domains" and "diamond domains." Typical configurations are shown in Parts (b) and (c) of Fig. 2, and the lower bounds which they yield for the entropy are included in Fig. 3. At close packing, the three kinds of domains considered give the following lower bounds:

$$\text{Strips:} \qquad S/Nk>2\ln\alpha+2,$$
$$\text{Squares:} \qquad S/Nk>2\ln\alpha+2-2\ln 2, \quad (15)$$
$$\text{Diamonds:} \qquad S/Nk>2\ln\alpha+3-2\ln 2, \quad (15)$$

so that contributions to the partition function from the square and diamond configurations can be ignored at high density.

Because the entropy near close packing is now known exactly for the model system, a calculation of the position of the phase transition would be possible if the equations of state for the high-density and low-density

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[16] See the argument presented on p. 1444 of B. J. Alder and T. E. Wainwright, J. Chem. Phys. 33, 1439 (1960).

phases were known. For hard spheres the situation is reversed. The solid-phase and fluid-phase isotherms are known quite accurately, but the absolute entropy in the solid phase can only be estimated.[4]

Notice (see Fig. 4) that for densities greater than half of close packing, the upper and lower entropy bounds are separated by less than Nk. This means that the *communal entropy* (the actual entropy minus the *best* N-cell single-occupancy entropy) cannot be fully excited at higher densities. Incidentally, the fact that the lower bound, derived from a single configuration, is exact at close packing proves that the communal entropy vanishes there. This is also the case in the one-dimensional hard-rod system, where the communal entropy has been calculated exactly.[10] At high density the communal entropy for the present system is bounded above by the ideal-lattice-gas entropy and below by zero. For hard disks we can prove only that the communal entropy lies between zero and $Nk[\ln(\frac{4}{3})+\frac{1}{3}\ln 4]$ at close packing.[17]

Notice that the entropy at close packing, $S/Nk=2\ln\alpha+2$, is quite a bit higher than the best estimates for squares $(2\ln\alpha+0.2)$ and disks[18] $(2\ln\alpha+0.1)$, showing that many additional configurations become accessible if second-nearest-neighbor overlaps are allowed. This difference in entropies at close packing has the following meaning: PV_0/NkT for disks minus PV_0/NkT for the model system, integrated over (V/V_0) from close packing to infinity, is about 1.9.

In addition to the bounds calculated from the strip configurations, two other kinds of bounds are of interest here, because they are better than the strip bounds at low density. A lower bound,

$$Q_N^{1/N}>(\rho^{-\frac{1}{2}}-1)^2e, \tag{16}$$

obtained previously for squares,[6] but equally valid for the present model, is the best lower bound for densities less than 0.38746. An upper bound,

$$Q_N^{1/N}<(\rho^{-1}-1)e, \tag{17}$$

is also valid for both squares and for the model system, and is the best upper bound for densities less than 0.63361. The bounds on the excess entropy from (16) and (17) are shown as light lines in Fig. 4.

In the next section we use Fisher's method[8] to establish bounds on the equation of state for the model system.

IV. PRESSURE

Observing that the entropy is a convex function of the volume $[\partial^2S/\partial V^2=\partial(P/T)/\partial V<0]$, Fisher established the following inequalities[8]:

$$[S^-(V+\Delta)-S^+(V)]/\Delta\leq P/T$$
$$\leq[S^+(V)-S^-(V-\Delta)]/\Delta, \tag{18}$$

where S^+ and S^- are upper and lower bounds on the entropy, and Δ is an arbitrary positive number. Using the upper and lower bounds (14) and choosing the best possible Δ, namely

$$\Delta/\alpha=(-\alpha\ln\alpha)^{\frac{1}{2}}, \tag{19}$$

we establish the equation-of-state bounds:

$$\frac{2-2(-\alpha\ln\alpha)^{\frac{1}{2}}}{\alpha}<\frac{PV}{NkT}<\frac{2+2(-\alpha\ln\alpha)^{\frac{1}{2}}}{\alpha}, \tag{20}$$

so that the free-volume form of the pressure is exact for our model, in the following sense:

$$[P-P(fv)]/P\leq O(-\alpha\ln\alpha)^{\frac{1}{2}}. \tag{21}$$

In D dimensions (20) has the following form:

$$\frac{D-(\frac{1}{2}D+1)(-\alpha\ln\alpha)^{\frac{1}{2}}}{\alpha}\leq\frac{PV}{NkT}\leq\frac{D+(\frac{1}{2}D+1)(-\alpha\ln\alpha)^{\frac{1}{2}}}{\alpha}. \tag{22}$$

Although at low and at high density the model potential has properties similar to the hard-square and hard-disk systems, it is entirely possible that any transition between an ordered solid phase and a disordered fluid phase will be modified qualitatively, reflecting the neglect of second-neighbor interactions.

V. DISCUSSION

The major accomplishment of this work is the rigorous demonstration that *in the thermodynamic limit* a dense system of simple hard-core particles obeys the free-volume equation of state. The relative deviation is at most, of order $(-\alpha\ln\alpha)^{\frac{1}{2}}$. For the model system both the pressure and the entropy are characterized more precisely than was possible for hard parallel squares. Although a rigorous proof of the correctness of free-volume form is not yet possible in the general case, we expect that other hard-core potentials obey it too, at high density.

The *deviations* from the free-volume form are of primary interest now that the dominant term in the pressure, D/α, is established. The computer experiments on systems of hard disks and spheres[4] indicate that an expansion in powers of α is likely for both the entropy and the pressure. This implication is subject to the two limitations of the machine results: (1) an analytic form is lacking, so that the exact nature of singularities cannot be determined; and (2) the calculations cover only a limited region of the solid-phase phase space, that region corresponding to an expanded,

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[17] In order to insure single occupancy for disks it is necessary to choose cells which are three-fourths the area per disk at close packing. Then, at close packing, the upper and lower bounds on the hard-disk configurational integral differ by the entropy of an ideal lattice gas at a density three-fourths of close packing.

[18] The estimates for disks and squares are given in "Studies in Molecular Dynamics. V. High-Density Equation of State for Hard Disks and Spheres," to be published by W. G. Hoover and B. J. Alder.

perfect lattice, without vacancies or other imperfections. It has been suggested that the presence of such defects might make a contribution to thermodynamic properties which, although small, might not have an expansion in powers of α.[19] The results found for our model suggest that, at worst, the deviations from the free-volume form of the pressure include terms of the form $\alpha^i(\ln\alpha)^j$.

An approximation to the low-density virial equation of state, introduced by Ree and Hoover,[20] is of particular interest in connection with the present model. If one computes the contribution of all the complete graphs to the pressure, as outlined in Ref. 20, one finds that this class of diagrams predicts the high-density equation of state, $PV/NkT=(2/\alpha)+\ln\alpha$ for the model system. This is in contrast to the situation for hard parallel squares, where the same approximation gives a pressure (incorrectly[21]) diverging as $1/\alpha^2$. The fact that the low- and high-density series for the model system are apparently related is reminiscent of a hard lattice gas studied earlier.[1] Fisher and Gaunt found that both the low- and the high-density coefficients in the fugacity series for a nearest-neighbor lattice gas could be obtained from a single modified series.[22] For the present model, the second and third approximations of Ref. 20 to the pressure (the latter approximation is exact through the fifth virial coefficient) predict the same high-density form.

The fact that the maximum term in the high-density model configurational integral can be computed with a small system, using periodic boundary conditions, shows that these boundary conditions are a good choice in the solid phase. It is only in the phase-transition region, characterized by density fluctuations if the transition is first order, that a small system cannot represent thermodynamic behavior accurately.

The maximum term shows how the ordered solid phase might break up at melting. Diagonal cracks spread throughout the system, having the effect of breaking the large system into many small independent subsystems. It might be pointed out that the disparity in interparticle spacing between (1) particles separated by a diagonal crack and (2) particles in the same strip is not great. The average spacing is essentially the particle length in both cases. The average spacing *in excess of the particle length* is twice as large between particles in neighboring strips as for particles in the same strip. Whether or not the melting mechanism found here predominates when higher-neighbor interactions are included is not known.

The precise geometrical form of the maximum term depends strongly on the interparticle potential. The configuration which is the maximum term for the model system makes no contribution to the hard-parallel-square configurational integral. In the latter case the maximum term undoubtedly corresponds to the square domains shown in Fig. 2(b).

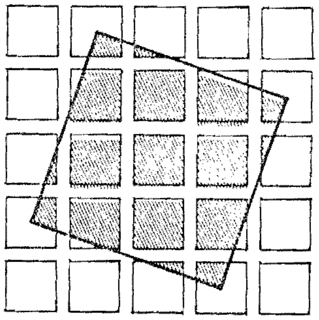

FIG. 5. A locked-in configuration of 10 hard parallel squares with periodic boundary conditions. As long as any one of the particles is fixed, no diffusion can occur.

It is possible that the exact knowledge of the entropy for this model system will be of use in judging the rapidity of convergence of small-system results and approximation schemes to the thermodynamic limit. The entropy for a small system differs from the thermodynamic entropy by a term proportional to the surface of the small system. Careful consideration of this surface entropy must be made in any extrapolation procedure (such as that proposed in Ref. 19) designed to estimate the entropy for infinite systems.

The piecewise-smooth lower entropy bound from the strip domains has one nonphysical feature worth noticing: the excess entropy *increases* with density for densities less than half of close packing. The reason for this is the omission of density fluctuations, resulting in a pressure that, in an average sense, is too low. The pressure of the model system is known to be greater than that of an ideal gas (this can be seen most easily by considering the virial theorem, which gives the pressure as an ideal term *plus* a contribution proportional to the collision rate). Therefore the excess entropy *decreases* as density increases. Thus the lower bound can be improved slightly in the low-density region, $0.32618<\rho<\frac{1}{2}$. The improved bound is indicated in Fig. 4 by a series of dots. Our knowledge of the entropy is now accurate within 0.6 Nk over the entire density range.

Either Monte Carlo or dynamic computer experiments could be carried out on the present model system. The absolute entropy would then be useful in linking the ordered and disordered branches of the isotherm, as well as in providing a check on the numerical integration of the machine-generated isotherm. A possible objection to the use of hard squares or similar potentials in computer experiments is that with standard periodic boundaries, rotation of rows or columns of particles around the periodic torus could occur, contributing a spurious surface entropy term. To avoid this effect it is possible to generate locked-in configurations, even for square particles. A typical configuration of this kind, for 10 hard parallel squares, is shown in Fig. 5.

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[19] F. H. Stillinger, Z. W. Salsburg, and R. L. Kornegay, J. Chem. Phys. **43**, 932 (1965).

[20] See Eq. (10) in the article by F. H. Ree and W. G. Hoover, J. Chem. Phys. **41**, 1635 (1964).

[21] A high-density equation of state of the form $PV/NkT=\alpha^{-2}$ would contradict the entropy bounds established in Ref. 6.

[22] See the article by Gaunt and Fisher cited in Ref. 1.

APPENDIX

In this appendix we catalog the absolute values of the star integrals contributing to the first five virial coefficients for the model potential. These integrals were calculated primarily as a check, because the simplest route to the virial coefficients for this system is through the modified star integrals discussed in Ref. 20. The ordering of the star integrals is the same as that used in Ref. 9, and the integrals have all been multiplied by 18 to give integer values.

$n=2$: 54,

$n=3$: 90,

$n=4$: 215, 166, 126,

$n=5$: 512, 376, 375, 336, 303, 273, 242, 216, 189, 162.

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Kinetic Theory of Nuclear Spin Relaxation in Gases

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A theory of nuclear spin relaxation in linear molecules is developed for dilute gases and mixtures. The main assumptions used are those often employed in the kinetic theory of dilute gases: (1) binary collisions, (2) no correlation between the effects of successive binary collisions, and (3) classical mechanics for the molecular translational and rotational motion. The calculations result in expressions relating the spin relaxation times to the rotational angular momentum transfered by collisions. Using the results, it is possible to calculate the spin relaxation times for any given intermolecular potential which includes angle-dependent terms.

1. INTRODUCTION

Nuclear spins are weakly coupled to molecular rotation by a number of mechanisms,[1] so that when collisions disturb the molecular rotation, the motion of the nuclear spins is indirectly influenced. Therefore, studies of nuclear spin relaxation should be able to provide quantitative information about intermolecular torques. Molecular hydrogen has received considerable attention, both theoretically[2] and experimentally.[3] The case of hydrogen is, however, unique in that the intermolecular torques are very weak and the rotational levels are very widely spaced. This fortunate combination of circumstances permits the use of quantum-mechanical perturbation theory for the coupling of rotation to translation in hydrogen, even for collisions at small impact parameters. Since these conditions are not satisfied in most other gases, the perturbation method is of limited usefulness in calculating nuclear spin relaxation times. In this paper we develop a nonperturbative method of calculation, which is valid for intermolecular torques of any size. Because we use classical mechanics for this calculation, the present results are not accurate for hydrogen, but should be quite accurate for all gases heavier than hydrogen. Thus the present work complements the range of validity of the earlier calculations.

In the kinetic theory of spin relaxation, we treat only binary collisions, so that the results are appropriate in the limit of a dilute gas. It is also convenient to neglect any correlation between the effects of successive binary collisions (assumption of "molecular chaos"). Classical mechanics is used to describe the rotational and translational motion. Quantum corrections should be small for most gases, becoming negligible as the temperature and the moment of inertia increase. For simplicity we consider the limit of extreme narrowing (persistence of molecular rotation short compared to the Larmor period of the nuclear spins). The case of linear molecules is considered in detail, but the same methods may be applied to symmetric tops and asymmetric molecules.

The spin relaxation times in a dilute gas are found to depend only on the net changes produced by collisions, in the molecular rotational-angular-momentum vector, but not on the details of the trajectory during a collision. The result is analogous to the fact that in a dilute gas transport effects, such as diffusion and viscosity, depend only on the net change in translational momentum produced by a collision, and not on the details of a collision trajectory.

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