

Melting Transition and Communal Entropy for Hard Spheres*

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In order to confirm the existence of a first-order melting transition for a classical many-body system of hard spheres and to discover the densities of the coexisting phases, we have made a Monte Carlo determination of the pressure and absolute entropy of the hard-sphere solid. We use these solid-phase thermodynamic properties, coupled with known fluid-phase data, to show that the hard-sphere solid, at a density of 0.74 relative to close packing, and the hard-sphere fluid, at a density of 0.67 relative to close packing, satisfy the thermodynamic equilibrium conditions of equal pressure and chemical potential at constant temperature. To get the solid-phase entropy, we integrated the Monte Carlo pressure-volume equation of state for a "single-occupancy" system in which the center of each hard sphere was constrained to occupy its own private cell. Such a system is no different from the ordinary solid at high density, but at low density its entropy and pressure are both lower. The difference in entropy between an unconstrained system of particles and a constrained one, with one particle per cell, is the so-called "communal entropy," the determination of which has been a fundamental problem in the theory of liquids. Our Monte Carlo measurements show that communal entropy is nearly a linear function of density.

I. INTRODUCTION

There has been little trustworthy theoretical progress toward locating a transition for hard spheres. The approximations necessary before numbers can be extracted from fundamental theories make the results suspect. On experimental grounds, however, the evidence for a hard-sphere phase transition is persuasive. Bridgman's pioneering high-pressure measurements of the melting line¹ convinced him that at sufficiently high pressure molecules of any "shape" would crystallize. His work indicated that repulsive forces, even working alone, could produce an ordered solid if the usual "glue" of attractive forces holding the solid together were replaced by external pressure. Rice later found that when glass spheres were randomly thrown together the density did not exceed about 85% of the theoretical density for the crystalline solid.² Thus he could reason

that the disordered fluid phase must be thermodynamically unstable, with respect to the solid, at high enough density. The machine experiments³ in which many-body systems of hard spheres were simulated on a fast computer indicated that an order-disorder transition did occur near a 15% linear expansion from close packing.

The computer experiments⁴ have so far provided the only quantitative information for hard spheres in the transition region. Although the hard-sphere systems studied were too small for the solid and fluid phases to coexist together, both phases could be generated separately and, at constant pressure, differed in density by about 10%. Thus, unless the disordered phase were always stable, a first-order transition would have to link the two.

From thermodynamics we know that, at any pressure

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¹ P. W. Bridgman, *Phys. Rev.* **3**, 126, 153 (1914).

² O. K. Rice, *J. Chem. Phys.* **12**, 1 (1944). See also A. E. R. Westman and H. R. Hugill, *J. Am. Ceram. Soc.* **13**, 767 (1930) and G. D. Scott, *Nature* **188**, 908 (1960).

³ W. W. Wood, F. R. Parker, and J. D. Jacobson, *Nuovo Cimento Suppl.* **9**, 133 (1958); T. E. Wainwright and B. J. Alder, *ibid.*, 116 (1958).

⁴ A summary, including fairly recent work, can be found in *The Physics of Simple Liquids*, H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, Eds. (North-Holland Publ. Co., Amsterdam, 1968), (to be published).

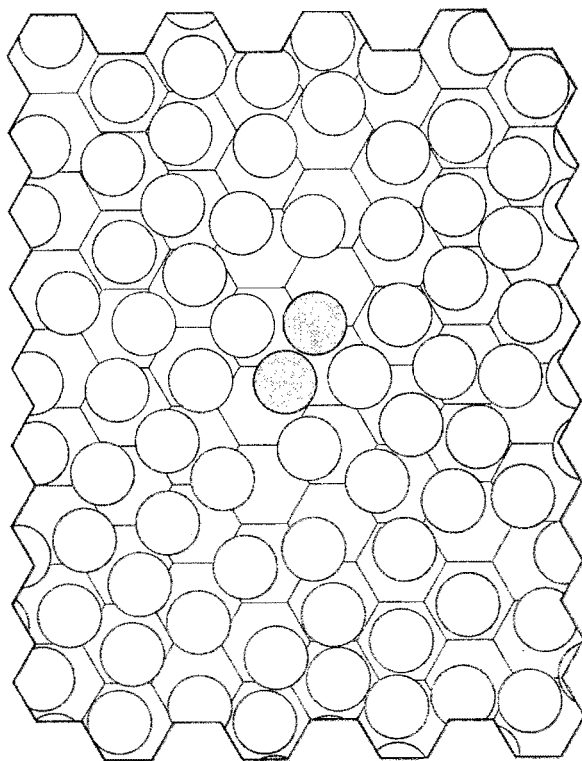


FIG. 1. A sample configuration of a 72-disk single-occupancy system. Two of the disks have been shaded to show that even with the restriction of the center of each disk to its own cell, particles occupying second-neighbor cells can interact.

and temperature, the phase with lowest chemical potential will be stable. Pressure is just a momentum flux and can be directly measured for any state. It is not so easy to calculate chemical potential in a computer experiment. This difficulty arises because the entropy, a part of the chemical potential, is not a "dynamical variable." That is, entropy is not a function of coordinates and velocities which can be time or phase averaged. Entropy and chemical potential must be measured relative to a "standard state" by integrating along a reversible path joining the standard state to the state of interest. Of course, if one could *estimate* the entropy accurately, *a priori*, this would take the place of a measurement; in practice, however, intuitive guesses of entropy are too crude, often being in error by $\sim Nk$ or so, which is the magnitude of the difference in entropy between solid and fluid.

We previously suggested a way of measuring the solid-phase entropy for hard-sphere systems, using computer experiments.⁵ The present paper describes the results of those experiments. Our idea was to calculate the thermodynamic properties, both pressure and entropy, for a constrained "single-occupancy" system of hard spheres. Because a three-dimensional system is

hard to depict graphically, the simpler two-dimensional hard-disk single-occupancy system is shown instead in Fig. 1. The whole volume is divided up into similar "Wigner-Seitz" cells and the center of each particle is restricted to stay within its own cell. This system behaves like a solid at high density, when the root-mean-squared displacement of a particle from the center of its cell is small with respect to the cell width. At low density the system represents an artificial extension of the solid. In the absence of the cell boundaries such a solid would be either metastable or unstable.

Besides verifying the reality of the three-dimensional hard-sphere transition, we also carried out the same kind of calculation for two-dimensional hard disks, for which Alder and Wainwright have already⁶ located the phase transition. Our results show that the two states joined by a van der Waals loop in the Alder-Wainwright equation of state do have the same chemical potential, and are therefore in thermodynamic equilibrium.

In our single-occupancy extension of the *solid* to low density, we do not allow the density fluctuations which characterize fluids. Exactly the same kind of unrealistic restriction has long been adopted,⁷ for sake of expediency, in formulating approximate theories of the *liquid* phase. In these approximate "cell-model" treatments, "liquid" particles were constrained to occupy individual cells and, to make further progress possible, their motions in these cells were ultimately taken independent of each other. Since the symmetry and long-range order of a solid are obviously inappropriate to a liquid model, it was natural to wonder—How bad will the results be?

For a short time it was hoped that simply adding an entropy Nk to the cell-model entropy would be enough to convert the cell-model "liquid" to a realistic liquid. This hope was born when it was noticed that the entropy gained by an ideal gas, if partitions dividing its container into N singly occupied cells are destroyed, was about the same as the experimental entropy of melting,⁸ $\sim Nk$.

Rice's valid objection⁹ that the entropy of melting depends strongly on pressure demolished these simple ideas. Evidently melting is more complicated than the ideal-gas model suggested. Therefore the difference in entropy between the fluid unconstrained system and the constrained system, with cells, can come in slowly as density is reduced from the melting density. This entropy difference has consistently been called the *communal entropy* by various workers,⁸⁻¹⁰ although Kirkwood's rigorous definition of the term did not come until 15 years after its introduction.¹⁰ We have studied

⁶ B. J. Alder and T. E. Wainwright, *Phys. Rev.* **127**, 359 (1962).

⁷ H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.* **41**, 249 (1937); J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* **A163**, 53 (1937).

⁸ J. O. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.* **5**, 896 (1937).

⁹ O. K. Rice, *J. Chem. Phys.* **6**, 476 (1938).

¹⁰ J. G. Kirkwood, *J. Chem. Phys.* **18**, 380 (1950).

⁵ W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **47**, 4873 (1967).

exactly the same system Kirkwood incorporated into his mathematical definition. We find that the communal entropy is a nearly linear function of density, just as in the one-dimensional hard-core case.¹¹ Up to about two-thirds of the close-packed density, the results for hard spheres, hard disks, and hard rods are all very nearly alike.

An interesting property of the three-dimensional single-occupancy system is that it can exhibit *mechanical* instability (very large compressibility). The unrestricted solid phase, on the other hand, ordinarily melts due to *thermodynamic* instability; i.e., it dissolves in a liquid which has slightly lower chemical potential. In our single-occupancy system we prolong the life of the solid phase to densities so low that the mechanical instability can be seen. At that point only the cell walls prevent the unstable solid from shaking itself apart. The difference between *mechanical* and *thermodynamic* instability is clearcut in this case. Frenkel¹² emphasized that melting is thermodynamic and does not depend upon a mechanism characteristic of the solid phase alone.

In Sec. III we tabulate all of our pressure and entropy data for hard-sphere and hard-disk systems of 12–780 particles. We try to make our extrapolation to infinite systems plausible, and we discuss the assumptions and errors inherent in our work. In Sec. IV our results are summarized and some of their implications are pointed out.

II. LOCATION OF THE MELTING TRANSITION

Even in large systems of macroscopic size glasses and other metastable states are encountered. In the theoretical "infinite system" fluctuations sufficiently large to annihilate the metastable states are always available. In systems of finite size, especially the small ones which can be treated on a computer, both the region over which metastable phases can occur, and the time for which they persist, can be large. Precisely these difficulties have complicated the search for the hard-sphere phase transition in small systems.

The machine experiments showed that over a range of densities it was possible to generate either the fluid or the solid phase on the computer. Most runs were started from a perfect crystal, obviously unstable at low enough density; at densities less than two-thirds of the close-packed density this solid would melt spontaneously but sometimes only after many thousands of collisions per particle. In rare cases the fluid would evidently freeze again. Thus the solid phase was extended from high density where it was at least

metastable into the low-density region where it was unstable thermodynamically.

Due to the irregular nature of a fluid's structure it is not easy to invent an unbiased initial condition for a fluid run. In practice the fluid was extended to higher and higher densities by gradually increasing the particle diameter in a system that was initially in the fluid phase. Under these conditions the system did not crystallize; instead a high-pressure high-density glassy extension of the fluid isotherm was generated. Since the two curves which could be generated on a pressure–volume plot, the fluid and solid isotherms, were separated by about 10% in density, a first-order phase transition between the two, at some pressure, seemed likely. The problem was to locate the densities of the coexisting phases. Only a thermodynamic comparison of chemical potentials of the two phases could settle this point.

In the fluid phase both the pressure and the entropy are known. Up to two-thirds of close-packing, the pressure and entropy are given within 1% and $0.01Nk$, respectively, by various approximate expressions based on the virial series, so-called "Padé approximants." In the solid phase the pressure is now known quite well,¹³ and by integration the entropy in the solid phase is also known, except for an additive constant. It is this additive constant which is crucial. In the pictorial terms of the cell theory this constant gives the *size* of the free volume in units of the free length. We determined this entropy constant by extending the solid phase through its region of metastability and on to low density. In the hard-sphere case each particle was confined to a Wigner–Seitz cell of a face-centered cubic lattice. The sides of these dodecahedral cells are pieces of planes drawn midway between nearest-neighbor lattice sites and perpendicular to the line joining these lattice sites. For hard disks the geometry is simpler; the hexagonal Wigner–Seitz cells can be seen in Fig. 1.

Aside from the restriction that the center of each sphere was not allowed to leave its cell, the calculation of the pressure proceeded just as in the usual Monte Carlo hard-sphere calculations.^{3,4}

We measured $(\partial S/\partial V)_{N,T} = P/T$ up to three-fourths the close-packed density (which we found to be safely within the stable solid phase), and then integrated from the known low-density limit to establish the value of the previously unknown entropy constant in the solid, with an expected error of $0.015Nk$.

Now, knowing the entropy in the solid phase, we could calculate the transition pressure and the densities of the coexisting phases. We found that for hard spheres in the thermodynamic limit the equilibrium pressure is $(8.27 \pm 0.13)NkT/V_0$, where V_0 is the volume at close packing. The densities of the coexisting phases relative

¹¹ W. G. Hoover and B. J. Alder, *J. Chem. Phys.* **45**, 2361 (1966).

¹² J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, Inc., New York, 1955) (a republication of the 1946 English translation published by Oxford University Press), Chap. 3.

¹³ B. J. Alder, W. G. Hoover, and D. Young, "Studies in Molecular Dynamics. V. High-Density Equation of State and Entropy for Hard Disks and Spheres," *J. Chem. Phys.* (to be published).

to the close-packed density are 0.736 ± 0.003 (solid) and 0.667 ± 0.003 (fluid). The fluid density seems to agree well with Ross and Alder's empirical rule¹⁴ that the fluid side of the tie line should be associated with the highest density at which the solid melts in computer experiments.

If instead of using measured solid-phase thermodynamic properties, the Lennard-Jones-Devonshire cell model for the solid phase were used, then the predicted transition pressure would have been slightly too low.¹⁵ If Kirkwood's self-consistent theory¹⁶ or Rice's estimate² for the entropy constant were used, then the pressure would have been grossly in error.

In order to verify the consistency of the previous machine calculations with ours, we also investigated the two-dimensional single-occupancy hard-disk system. Since with 870 disks Alder and Wainwright had already found a van der Waals loop linking the solid and fluid states, we wanted to calculate independently the chemical potential of the two states linked by their tie line to check that their van der Waals loop linked together equilibrium states of the system. The test was passed.¹⁷

A second reason for interest in the hard-disk single-occupancy system is that long-wavelength density fluctuations are more important in two dimensions than in three, so that the restriction of particles to cells might conceivably reduce the entropy of the solid phase in two dimensions. It is evident from our results that the entropy lost in this way is at most $0.01Nk$. Our single-occupancy equation of state in two dimensions joins smoothly onto that which Alder and Wainwright measured without the single-occupancy restriction.

Aside from possible errors in our extrapolation from systems of a few hundred particles to the hypothetical "infinite" system, there is one effect which we have consciously ignored: the thermodynamic effect of vacancies. In the equilibrium solid phase, at any density, some fraction of the crystal's lattice sites will be empty. Although not strictly zero, the fraction is small. As soon as the free energy of vacancy formation exceeds $55kT$, the average number of vacancies in a mole of crystal would be $(6 \times 10^{23})e^{-55}$, less than one.

¹⁴ M. Ross and B. J. Alder, *Phys. Rev. Letters* **16**, 1077 (1966).

¹⁵ Using Eq. (8) of the text to represent the fluid, and using the unsmoothed free volume calculated by R. J. Buehler, R. H. Wentorf, Jr., J. O. Hirschfelder, and C. F. Curtiss, *J. Chem. Phys.* **19**, 61 (1951), we find that the fluid at $V/V_0 = 1.515$ is in equilibrium with the LJD solid at $V/V_0 = 1.349$. The equilibrium pressure predicted is $PV_0/NkT = 7.928$, slightly too low.

¹⁶ W. W. Wood, *J. Chem. Phys.* **20**, 1334 (1952).

¹⁷ Alder and Wainwright's 870-disk tie line extends from $V/V_0 = 1.266$ to $V/V_0 = 1.312$ with $PV_0 = 7.72NkT$. Using the Padé-approximant entropy at $V/V_0 = 1.40$, and integrating numerically to $1.312V_0$, we find $(PV/NkT) - (S/Nk) + \ln(V_0/N) = 12.356 \pm 0.01$ for the fluid. Using our own single-occupancy data, interpolated to $V/V_0 = 1.266$ and adjusting for the difference between the dynamic and Monte Carlo equations of state [W. G. Hoover and B. J. Alder, *J. Chem. Phys.* **46**, 686 (1967)], we found for the single-occupancy solid $(PV/NkT) - (S/Nk) + \ln(V_0/N) = 12.372 \pm 0.03$. The discrepancy 0.016 is within the combined error limits.

Experimental and theoretical results both suggest that the Lennard-Jones-Devonshire cell model could furnish an approximate prediction of the number and effect of vacancies. This has been shown most recently by Squire¹⁸ in a direct Monte Carlo calculation of the number of vacancies present in crystalline argon. For hard spheres the cell theory predicts that the fraction of vacancies is¹⁹ of order $\exp(-PV/NkT)$, or about 10^{-5} at melting. The corresponding contribution to the entropy would be of order $0.0001Nk$ and we feel safe in ignoring it. This point could be checked quantitatively by a Monte Carlo calculation such as Squire's. We conclude, subject to the uncertainties in our extrapolation to infinite systems, that both hard spheres and hard disks have a first-order melting transition at linear expansions of $10\frac{1}{2}\%$ (spheres) and 12% (disks) from close packing.

III. COMMUNAL ENTROPY AND THE SINGLE-OCCUPANCY CONFIGURATIONAL INTEGRAL

The vagueness of the communal entropy definitions prior to Kirkwood's time caused some interesting misunderstandings.²⁰ The term was introduced by Hirschfelder, Stevenson, and Eyring.⁸ They provided no operational definition of communal entropy, referring only to an entropy Nk due to "communal sharing of the volume," which sharing occurs in the liquid, but not the solid.

Rice's communal entropy² is well defined for hard particles without short-range attractive forces and represents the difference in entropy between an unconstrained N -body system, and a constrained system in which not only the centers, but also the leading edges, of the hard particles must stay within the cells. Rice²¹ expected that the solid phase would have a communal entropy nearly equal to $3Nk$.

Kirkwood's communal entropy is precisely defined for any kind of force law. He compares two many-body systems, the first unconstrained, the second restricted to have the center of each particle stay within its cell.¹⁰ It is exactly this restricted system which we are studying, and so it is Kirkwood's communal entropy that we calculate.

¹⁸ D. R. Squire and W. G. Hoover, *Bull. Am. Phys. Soc.* **12**, 1142 (1967).

¹⁹ This result follows from the work of F. H. Stillinger, Z. W. Salsburg, and R. L. Kornegay, *J. Chem. Phys.* **43**, 932 (1965).

²⁰ O. K. Rice, *J. Chem. Phys.* **14**, 348 (1946); H. S. Frank, *ibid.* **14**, 350 (1946).

²¹ In his 1944 paper² Rice cites Tonks' calculation [L. Tonks, *Phys. Rev.* **50**, 955 (1936)] of the partition function for a one-dimensional hard-rod system. Tonks' result shows that for the one-dimensional system the actual entropy is greater than that of a cell system by Nk . It should be emphasized that the cells Rice had in mind constrain not just the centers of the particles, but also the leading edges. Rice expected that since motions in the x , y , and z directions are to a first approximation independent the communal entropy in three dimensions would be $3Nk$ relative to a system with edge-constraining cells. The interference is, however, far from negligible. At high density the hard-sphere "communal entropy" envisioned by Rice is actually about $1.86Nk$.

So long as we are interested only in classical systems, the momentum distribution does not depend upon whether or not we constrain our particles with cells. The momenta contribute only a multiplicative factor of $(2\pi mkT)^{DN/2}$ to the classical canonical partition function in D dimensions. The remaining factor in the partition function is the integration over the coordinates of all N particles, \mathbf{r}^N , of the Boltzmann factor $\exp(-\Phi/kT)$, where Φ is the total potential energy of the system, a function of \mathbf{r}^N . In our hard-sphere case $\exp(-\Phi/kT)$ is either zero or one for every configuration. The integral over coordinates is the *configurational integral*, denoted by Q_N ,

$$Q_N \equiv (N!)^{-1} \int \exp\left(-\frac{\Phi}{kT}\right) d\mathbf{r}^N \equiv \exp\left(-\frac{A}{kT}\right). \quad (1)$$

For an ideal gas Φ is zero whenever all N particles lie within their container, of volume V , and the configurational integral is $V^N/N!$, $\sim (Ve/N)^N$ for large N . The configurational Helmholtz free energy is denoted by A .

Now the configurational integral (1) contains all configurations, crystalline, fluid, and intermediate, which the N particles can assume. If we restrict ourselves to only those configurations for which the particles form a given lattice we obtain a smaller configurational integral. We make such a restriction by constructing a network of Wigner-Seitz cells centered on the lattice sites of a perfect face-centered cubic crystal. Any configuration which has one particle in each of these cells

will be included in our single-occupancy configurational integral, Q_{so} . Other configurations will be left out. If we indicate the restriction to single occupancy by putting an extra cell-wall energy into the Hamiltonian, Φ_{cw} , which is zero if all the cells are singly occupied, and infinite otherwise, and if we indicate the single-occupancy restriction by the subscript so , we can write the definition of the single-occupancy configurational integral as follows:

$$\begin{aligned} Q_{so} &\equiv (N!)^{-1} \int \exp\left(-\frac{\Phi}{kT}\right) \exp\left(-\frac{\Phi_{cw}}{kT}\right) d\mathbf{r}^N \\ &\equiv \exp\left(-\frac{A_{so}}{kT}\right) \leq Q_N. \end{aligned} \quad (2)$$

For an ideal gas Q_{so} is $(V/N)^N$, smaller than Q_N by a factor of $\sim e^N$.

Since we are here restricting ourselves to hard particles, $-A/T$ is the same as the configurational entropy S . Defining also $S_{so} \equiv -A_{so}/T$, Kirkwood's communal entropy, $\Delta S \equiv S - S_{so}$, can be written in terms of the configurational integrals,

$$\Delta S \equiv k \ln(Q_N/Q_{so}). \quad (3)$$

At densities so low that the ideal-gas values are sufficiently accurate, the communal entropy is Nk . At slightly higher densities, up to about one-tenth of close packing, it is worthwhile to use the series expansions generated by using a Mayer f -function expansion,⁵

$$\begin{aligned} \Delta S/Nk &= 1 - 2.96192(\rho/\rho_0) + 3.33216(\rho/\rho_0)^{4/3} - \dots \quad (\text{spheres}), \\ &1 - 1.81380(\rho/\rho_0) + 1.53960(\rho/\rho_0)^{3/2} - \dots \quad (\text{disks}), \\ &1 - 1.00000(\rho/\rho_0) + 0.00000(\rho/\rho_0)^2 - \dots \quad (\text{rods}), \end{aligned} \quad (4)$$

where (ρ/ρ_0) is the density relative to the close-packed density. At the opposite extreme, high density, where vacancies are squeezed out and the root-mean-squared displacement of a particle from its most likely position is small (at least in three dimensions²²) the communal entropy is zero.

Little theoretical progress has been made toward calculating the communal entropy at interesting liquid-phase densities. This is because such a calculation entails comparing two different N -body problems, both of which are intractable analytically, except in the relatively simple one-dimensional case.²³ Modern computing machinery, more efficient than a previous

simulation of the N -body problem,²⁴ makes the N -body problems tractable.

One obtains the pressure-volume equations of state by differentiating the two configurational integrals, (1) and (2), with respect to volume. Using Green's technique²⁵ of introducing dimensionless variables to simplify the differentiation, one finds, for the single-occupancy system

$$P_{so}/\rho kT \equiv \rho^{-1}(\partial \ln Q_{so}/\partial V)_{N,T} = 1 + b\rho g_{so}. \quad (5)$$

The number density N/V is indicated by ρ , and g_{so} indicates the probability of finding two particles in contact, relative to that in an ideal gas at the same density. The second virial coefficient, 2^{D-1} times the

²² See Sec. 4 of Chap. 3 in Frenkel's book Ref. 12 for a lucid discussion of the diverging mean-square displacement found for one- and two-dimensional "solid" phases.

²³ For hard rods Tonks (Ref. 21) calculated the unconstrained partition function. The single-occupancy partition function is worked out in Ref. 11.

²⁴ W. E. Morrell and J. H. Hildebrand, J. Chem. Phys. 4, 224 (1936).

²⁵ H. S. Green, *Molecular Theory of Fluids* (North-Holland Publ. Co., Amsterdam, 1952).

TABLE I. Equation of state for single-occupancy systems of 32, 108, 256, and 500 hard spheres. The compressibility factor PV/NkT is given as a function of the density relative to the close-packed density. The column headed Padé gives the compressibility factor from the approximate expression (8) of the text. The expected error for the data listed below ranges between 0.5% and 1% in $[(PV/NkT) - 1]$. Systems indicated with an asterisk (*) included *third-neighbor* interactions. Only first- and second-neighbor interactions were included in the other data.

ρ/ρ_0	Padé	32	32*	108	256	500	500*
0.050	1.163	1.082		1.078			
0.100	1.359	1.220		1.211			
0.150	1.598	1.408		1.407			
0.200	1.888	1.658		1.644			
0.250	2.244	1.970		1.971	1.962		1.961
0.300	2.682	2.342		2.346			
0.350	3.225	2.860		2.862			
0.400	3.903	3.530		3.515			
0.450	4.756	4.357		4.377			
0.500	5.841	5.394	5.368	5.333	5.403	5.372	5.396
0.550	7.234	6.649	6.752	6.725	6.688	6.715	6.767
0.600	9.048	8.273	8.390	8.371	8.378	8.400	8.523
0.625	10.161	8.975	8.484	9.349	9.490	9.495	9.315
0.650	11.444	8.368	8.433	8.885	9.263	9.290	9.253
$\frac{2}{3}$	12.412	8.616	8.683	9.024	9.297	9.313	9.304
0.700	14.667	9.487	9.438	9.787	9.956	10.104	10.088
0.725	16.699	10.258	10.171	10.760	10.765	10.717	10.870
0.750	19.094	11.403	11.273	11.590	11.841	11.910	11.791

volume of a single particle for D -dimensional hard spheres, is indicated by b . If the unconstrained configurational integral (1) is differentiated with respect to V , the identity $P/kT \equiv (\partial \ln Q_N / \partial V)_{N,T}$ leads to (5) without the subscripts.

The fluid-phase equation of state and entropy are already well known for hard spheres and disks except near the phase transition. To obtain communal entropy, $S - k \ln Q_{so}$, we need to calculate P_{so} , using the Monte Carlo procedure described by Wood²⁶ to obtain g_{so} .

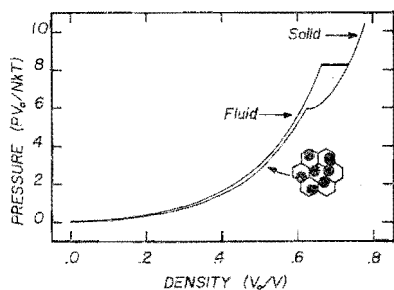


FIG. 2. Hard-sphere equations of state. The fluid and solid isotherms are joined by a tie line connecting states of equal chemical potential. The single-occupancy isotherm constitutes a smooth extension of the solid-phase isotherm to low density. The fluid curve shown here is actually taken from the Padé approximant (8) in the text, since that curve fits the accurate computer data. PV_0/NkT is 8.27 at the transition. The densities, relative to close-packing, of the coexisting phases are 0.667 (fluid) and 0.736 (solid).

²⁶ Besides Ref. 4 see W. W. Wood "Monte Carlo Calculations of the Equation of State of Systems of 12 and 48 Hard Circles," Los Alamos Scientific Laboratory Rept. LA-2827, July 1963.

Then we integrate to find Q_{so} ,

$$Q_{so} = \left(\frac{V}{N}\right)^N \exp \left[-N \int_0^{\rho} \left(\frac{P_{so}}{\rho kT} - 1 \right) d \ln \rho \right]. \quad (6)$$

Since it is easier to write a Monte Carlo program than a dynamic one, and since dynamics has no advantages, except possibly at very high density,²⁷ we have used Monte Carlo simulation throughout, setting up the systems with periodic boundaries and confining each particle's center to its own cell.

Our calculation is the same as that Wood ably describes²⁶ for the system without walls, except for two

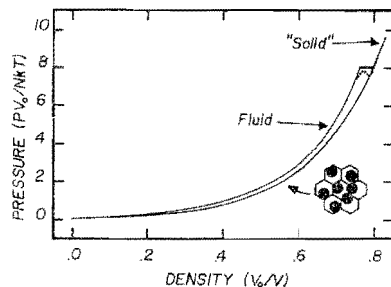


FIG. 3. Hard-disk equations of state. The fluid and solid isotherms are joined by a tie line connecting states of equal chemical potential. The fluid curve is based on the Padé approximant (9) given in the text. The tie line shown at $PV_0/NkT = 8.08$ is an estimate for infinite systems of hard disks. The van der Waals loop found by Alder and Wainwright⁶ is shown as a series of dots.

²⁷ The high-density data in Ref. 13 seem to be much more precise than the results obtained by *straightforward* Monte Carlo calculations. More imaginative Monte Carlo procedures cut down this gap [W. W. Wood, J. Chem. Phys. **48**, 415 (1968)].

differences. We reject any move which would take a sphere (disk) outside its dodecahedral (hexagonal) cell. We also ignore, in some of the three-dimensional calculations, the possibility of overlaps between spheres occupying third nearest-neighbor cells. Such overlaps are mathematically possible, for all densities greater than $0.19245\rho_0$. Since these interactions can certainly be ignored in the solid phase, the value of Q_{so} obtained in the solid is independent of whether or not third-neighbor interactions are included. Nevertheless we undertook to assess their importance by making a complete equation of state determination for 32 spheres including third-neighbor interactions. The isotherm showed no statistically significant change (see Table I). Fairly extensive data including third-neighbor interactions for 500 spheres are also included in Table I. In the *hexagonal* close-packed lattice, which we did not investigate, not only the third neighbors, but also the fourth and fifth neighbors can interact at high enough density.

We investigated systems of 32, 108, 256, and 500 hard spheres as well as 12, 72, and 780 hard disks.²⁸ Most of our data were accumulated at densities greater than half of close-packing because at lower densities the

TABLE II. Equation of state for single-occupancy systems of 12, 72, and 780 hard disks. The compressibility factor PV/NkT is given as a function of density relative to the close-packed density. The column headed Padé gives the compressibility factor from the approximate expression (9) of the text. The expected error in $[(PV/NkT) - 1]$ ranges between 0.5% and 1%.

ρ/ρ_0	Padé	12	72	780
0.050	1.098	1.026	1.026	1.026
0.100	1.211	1.077	1.076	1.075
0.150	1.343	1.146	1.146	1.145
0.200	1.498	1.249	1.243	1.241
0.250	1.683	1.373	1.378	1.373
0.300	1.904	1.543	1.537	1.541
0.350	2.173	1.747	1.762	1.761
0.400	2.501	2.032	2.052	2.051
0.450	2.909	2.430	2.401	2.423
0.500	3.423	2.893	2.896	2.876
0.550	4.083	3.447	3.495	3.501
0.600	4.947	4.121	4.291	4.351
0.625	5.482	4.624	4.786	4.829
0.650	6.107	5.087	5.397	5.426
0.675	6.840	5.582	6.075	6.079
0.700	7.708	6.073	6.797	6.791
0.725	8.745	6.640	7.405	7.475
0.750	9.999	7.307	8.132	8.271
0.775	11.530	8.052	8.910	9.096
0.800	13.426	9.034	9.875	10.141

²⁸ The hard-sphere systems were all cubic in shape with the usual periodic boundaries. The 72-disk system is composed of 8 rows of 9 disks each, the ratio of height to width of the system being $(4/9)\sqrt{3} = 0.76980$; the 780-disk system is composed of 30 rows of 26 disks each the ratio of height to width being $(15/26)\sqrt{3} = 0.99926$.

TABLE III. Entropy, relative to an ideal gas at the same density and temperature, for hard spheres. The column headed Padé gives values from the approximant (8) in the text. This describes the hard-sphere fluid accurately over the density range for which the fluid phase is stable. The column headed single occupancy gives the result of numerical integration of the data listed in Table I, using Eq. (6) of the text. The communal entropy is the difference between the first two columns except in the two-phase region. The expected error in the last two columns is 0.015 at the highest density given.

Density	$S^e(\text{Padé})/Nk$	S_{so}^e/Nk	$\Delta S/Nk$
0.00	0.000	-1.000	1.000
0.05	-0.155	-1.061	0.906
0.10	-0.326	-1.155	0.829
0.15	-0.516	-1.278	0.762
0.20	-0.726	-1.428	0.702
0.25	-0.961	-1.608	0.647
0.30	-1.225	-1.816	0.591
0.35	-1.524	-2.061	0.537
0.40	-1.864	-2.352	0.488
0.45	-2.253	-2.695	0.442
0.50	-2.702	-3.101	0.399
0.55	-3.226	-3.583	0.357
0.60	-3.843	-4.155	0.312
0.65	-4.577	-4.806	0.229
0.66	-4.741	-4.933	0.192
0.67	-4.911	-5.058	0.148
0.68	-5.088	-5.184	0.107
0.69	-5.272	-5.311	0.072
0.70	-5.463	-5.440	0.044
0.71	-5.662	-5.570	0.023
0.72	-5.870	-5.703	0.009
0.73	-6.087	-5.838	0.001
0.74	-6.313	-5.978	0.000

number dependence is not statistically significant. Indeed in the low-density single-occupancy system $[(P_{so}/\rho kT) - 1]$ can be shown to be *independent* of the number of particles. By contrast in the unconstrained system $(P/\rho kT) - 1$ lies below the infinite-system limit by a factor $(N-1)/N$.

Our lowest density data agree quantitatively with the theoretical N -independent expansion of P_{so} ,

$$P_{so}/\rho kT = 1 + 2.30940(\rho/\rho_0)^{3/2} \quad (\text{disks}) \\ = 1 + 4.44288(\rho/\rho_0)^{4/3} \quad (\text{spheres}). \quad (7)$$

Figures 2 and 3 show that both the sphere and the disk single-occupancy isotherms lie surprisingly close to the fluid-phase isotherms. The sphere and disk results differ qualitatively from each other, however. The sphere results suggest a cusp in the single-occupancy isotherm at a 60% expansion from close-packing. The cusp occurs at the density at which the cell walls begin to be important in holding the crystal together. At this "cusp" the solid becomes *mechanically* unstable; without the cell walls it would rapidly disintegrate. A theory of melting based only on solid-phase properties would predict melting at the cusp density rather than at the

TABLE IV. Entropy, relative to an ideal gas at the same density and temperature, for hard disks. The column headed Padé gives values from the approximant (9) in the text. The column headed single occupancy gives the result of numerical integration of the data listed in Table II, using Eq. (6) of the text and corrected to the infinite-system thermodynamic limit. The communal entropy up to 0.761 times the close-packed density is obtained from the difference between these two columns. At higher density we used a tie line with $PV_0/NkT=8.08$ linking a fluid at a density of 0.761 with a solid at a density of 0.798. The expected error in the last two columns is 0.01 at the highest density given.

Density	$S^e(\text{Padé})/Nk$	S_{so}^e/Nk	$\Delta S/Nk$
0.00	0.000	-1.000	1.000
0.05	-0.094	-1.017	0.923
0.10	-0.195	-1.049	0.854
0.15	-0.305	-1.092	0.787
0.20	-0.424	-1.146	0.722
0.25	-0.555	-1.214	0.659
0.30	-0.698	-1.296	0.598
0.35	-0.857	-1.395	0.538
0.40	-1.035	-1.515	0.480
0.45	-1.234	-1.660	0.426
0.50	-1.461	-1.832	0.371
0.55	-1.721	-2.039	0.318
0.60	-2.025	-2.292	0.267
0.65	-2.384	-2.600	0.216
0.70	-2.818	-2.977	0.159
0.75	-3.354	-3.430	0.076
0.76	-3.477	-3.528	0.051
0.77	-3.606	-3.630	0.027
0.78	-3.742	-3.735	0.011
0.79	-3.885	-3.843	0.002
0.80	-4.036	-3.956	0.000

higher melting density determined by *thermodynamic* instability of the solid phase. The fact that the effect is sudden in three dimensions but gradual in two may be due to the absence of true long-range order in the two-dimensional "solid."

We used graphical integration to calculate entropy at higher densities for the various sized systems. Rather than tabulate all of these results for finite N separately, we undertook an extrapolation to infinite systems. The extrapolation is based on the guess²⁹ that at high density the configurational integral Q_N (or equivalently Q_{so}) is of the form $(V/N)v_f^{N-1}$, where v_f is a free volume which

TABLE V. High-density comparison of exact and unsmoothed Lennard-Jones-Devonshire entropies. The difference $(S_{ex,ot} - S_{LJD})/Nk$ is tabulated.

	Hard spheres	Oscillators
One dimension	0.30685	0.34657
Two dimensions	0.050	0.27326
Face-centered cubic	-0.216	0.24689
Hexagonal close packed	-0.216 ^a	0.24541

^a The estimate for the hexagonal close-packed spheres is based on the fact that the solid-phase isotherms for the two kinds of packings, cubic and hexagonal, show no significant differences (see Ref. 13). Also, the cell-cluster calculations of Rudd, Salsburg, Yu, and Stillinger (see Ref. 31) indicate that the entropy difference between the two packings is of order 0.001Nk.

²⁹ The guess is consistent with and suggested by the results of Z. W. Salsburg and W. W. Wood, J. Chem. Phys. 37, 798 (1962).

is nearly independent of N . As long as v_f does not depend on the number of particles one expects that S/Nk for an N -particle system lies above that for the infinite system by $\ln(V/Nv_f)/N$. Our results at the highest densities studied, for both spheres and disks, followed this relation and we could therefore extrapolate to $N = \infty$. Our pressure data for spheres and disks appear in Tables I and II. The entropies, obtained by integration, are given in Tables III and IV.

Using the coexistence tie line determined in the preceding section one can calculate the entropy of the two-phase hard-sphere system between the densities of $0.667\rho_0$ (all fluid) and $0.736\rho_0$ (all solid). In the pure fluid we used a Padé-approximant description of the hard-sphere system³⁰:

$$Q_N(\text{fluid}) = (Ve/N)^N \times \exp \left[-Nb\rho \left(\frac{1 - 0.110751866b\rho + 0.00469232b^2\rho^2}{1 - 0.423251866b\rho + 0.04130870b^2\rho^2} \right) \right]. \quad (8)$$

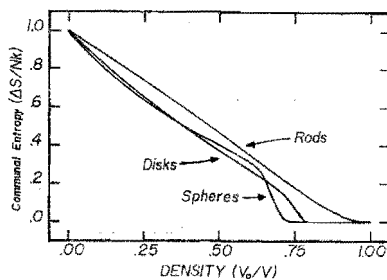


FIG. 4. The communal entropy (entropy due to the presence of density fluctuations) for one-, two-, and three-dimensional hard spheres. The communal entropy approaches zero at the solid side of the phase transition. For disks the solid-phase density chosen was 0.798 relative to the close-packed density. For spheres the solid-phase density is 0.736.

The entropies in the two-phase region and from (8) were then compared with the single-occupancy entropies to obtain the hard-sphere communal entropy $\Delta S/Nk \equiv (S - S_{so})/Nk$. The communal entropy is tabulated in Table III. The isotherms, both fluid and single-occupancy, are shown for spheres in Fig. 2 and for disks in Fig. 3.

A comparison of the 870-disk isotherm^{6,17} with the Padé-approximant equation of state for disks analogous to (8),

$$Q_N(\text{fluid}) = (Ve/N)^N \times \exp \left[-Nb\rho \left(\frac{1 - 0.2781515b\rho + 0.0059612b^2\rho^2}{1 - 0.6691537b\rho + 0.0901912b^2\rho^2} \right) \right], \quad (9)$$

³⁰ The expressions (8) and (9) were set up to reproduce the first six virial coefficients for hard spheres and disks. Although the seventh virial coefficient is now known as well [F. H. Ree and W. G. Hoover, J. Chem. Phys. 46, 4181 (1967)] the present expressions are sufficiently exact for our purposes.

shows noticeable disagreement at densities higher than three-fourths of close packing. Without measurements on much larger systems it is not possible to guess whether (i) the Padé approximant gives a poor approximation to the fluid equation of state near the phase transition, or (ii) negative curvature is introduced into the finite hard-disk system isotherm by the nearby van der Waals loop, with the curvature going away and the agreement with the Padé approximant improving in larger systems. By analogy with the three-dimensional system, where the Padé approximant seems useful all the way up to the freezing density, we have chosen to use the Padé approximant to represent the hard-disk fluid phase. The communal entropy so calculated for disks appears in Table IV. All of the communal entropy data for spheres and disks, as well as the analytic results for rods¹¹ are plotted in Fig. 4.

The most striking feature of our communal entropy results is the linearity of communal entropy with density. Up to about six-tenths of the close-packed density, the one-, two-, and three-dimensional systems all resemble one another closely. This suggests that in cell-model calculations a linear, rather than constant, correction term be added to simulate the effect of many-body correlations.

IV. SUMMARY

Our calculations confirm the existence of a definite first-order phase transition for hard-sphere particles. This is in accord with the experimental evidence that the melting curve can be followed to pressures so high that attractive forces are negligible. The hard-sphere solid and fluid phases are in thermodynamic equilibrium over a density interval from 0.667 ± 0.003 to 0.736 ± 0.003 times the close-packed density, and at a pressure of $(8.27 \pm 0.13)\rho_0 kT$. Because we have corrected our results to take into account the finite number of particles considered we expect the thermodynamic-limit phase transition to lie within the stated confidence limits. In this connection it is reassuring to see the good agreement between the entropy we calculate in the hard-sphere solid and Salsburg's high-density cell-cluster calculation of the hard-sphere entropy.³¹

The results for disks are less consistent with cell-cluster theory. Our data combined with the high-density dynamic data¹³ suggest that the hard-disk entropy lies $(0.05 \pm 0.01)Nk$ above the Lennard-Jones-Devonshire entropy near close packing. Using the Alder-Wainwright tie line instead, the prediction is

$(0.06 \pm 0.01)Nk$. These two values disagree with the fifth-order cell-cluster³¹ prediction of $(0.01 \pm ?)Nk$. If one assumes that the many-body machine calculations are substantially correct one comes to the conclusion that the cell-cluster theory for some unknown reason converges better in three dimensions than in two.

Perhaps a clue to understanding this difference can be found in the variation of long-range order with dimensionality. A three-dimensional crystal has a fixed lattice within which the particles carry out small vibrations. On the other hand, in two dimensions cooperative modes allow large displacements at all densities; the entire lattice is less localized and particles collide more frequently with the cell walls. The increased localization in three dimensions may be responsible for the better convergence of the cell theories.

Although we considered only hard particles in these calculations, there is no reason to expect any difficulty in extending such calculations, at high temperature at least, to more complicated systems. At low temperature the Born-von Kármán lattice-dynamics starting point would be better. In a dense fluid, the simplest approach is probably to calculate the constant-volume integral of $(1/T)dE$ from the high-temperature limit.

Our results suggest also that cruder calculations can be quite useful. In particular the finding that the communal entropy decreases almost linearly with density suggests a way to modify cell-model treatments of the liquid state.

Since the simple Lennard-Jones-Devonshire cell model with one particle moving in the field of its fixed neighbors provides a quick estimate of high-density thermodynamic properties, we would like to check the accuracy of that model. In the high-density limit, depending on the temperature, one expects a situation intermediate between purely harmonic forces and the purely anharmonic hard-sphere forces. A comparison of the cell-model predictions with the accurate many-body results for spheres and harmonic oscillators is presented in Table V.³² Ignoring low-temperature quantum effects, we conclude that the Lennard-Jones-Devonshire entropy, in the solid phase, will lie within $0.3Nk$ of the correct entropy.

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³¹ The most recent cell-cluster estimate for the hard-disk entropy near close packing is based on clusters containing up to five disks: $(S_{\text{Disks}} - S_{\text{LJD}})/Nk = 0.0111$ [Z. W. Salsburg, W. G. Rudd, and F. H. Stillinger, Jr., *J. Chem. Phys.* **47**, 4534 (1967)]. The most recent cell-cluster estimate for the face-centered hard-sphere entropy near close-packing includes clusters of up to three spheres: $(S_{\text{FCC}} - S_{\text{LJD}})/Nk = -0.2165$ [Z. Salsburg (private communication) of the results of a calculation by Rudd, Salsburg, Yu, and Stillinger].

³² The entropy differences near close-packing for hard-sphere systems combine our data with high-density data from Ref. 13. The results for (nearest-neighbor) oscillator systems in one, two, and three dimensions come from E. G. D. Cohen, J. de Boer, and Z. W. Salsburg (1 dimension) *Physica* **23**, 389 (1957); A. Beyerlein and Z. W. Salsburg (2 dimensions) *J. Chem. Phys.* **47**, 3763 (1967); and W. G. Hoover (3 dimensions), "Entropy for Small Classical Crystals," *J. Chem. Phys.* (to be published).