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Use of Computer Experiments to Locate the Melting Transition and Calculate the Entropy in the Solid Phase[*]

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Modern computers can accurately simulate the behavior of idealized systems of several hundred particles, but they have trouble in studying the melting process in which small-system surface effects make the transition irreversible. It is here suggested that a thermodynamically reversible path linking the solid and fluid phases can be obtained by using a periodic "external field" to stabilize the solid phase at low density. The properties of the artificially stabilized solid at low density are studied theoretically, and two practical schemes are outlined for determining the melting parameters by using computer-calculated entropies.

I. INTRODUCTION

Monte Carlo[1,2] and molecular dynamic[3–5] calculations are two popular computer methods for obtaining thermodynamic data under conditions in which exact statistical-mechanical calculations are difficult. In *pure* phases, either fluid or solid, the computer techniques can measure pressure and energy to within a percent of limiting thermodynamic values. In or near density–temperature regions where two phases can coexist, the computer calculations become inefficient. Distortions due to boundary effects become important in a two-phase system. Both density and energy fluctuations become large. In addition, the decay time for such fluctuations increases by orders of magnitude so that convergent thermodynamic averages cannot easily be obtained.

Volume and temperature are the usual independent variables for Monte Carlo computer work; volume and total energy are the independent variables for dynamic calculations. In either case the pressure, calculated from the virial theorem, together with the energy or temperature averages can be put in the form of an equation of state relating E, T, P, and V. Such an equation of state can be measured accurately only for pure phases.

In order to calculate the conditions under which two phases coexist, the $ETPV$ relations for the pure phases are not enough; the difference between the *entropies* of the two phases is also required.[6] Calculating entropy differences between two different thermodynamic states requires an integration of $dS=(1/T)dE+(P/T)dV$ along a thermodynamically reversible path linking the two states. To connect the gas and liquid phases, one can use a path which avoids the two-phase region by going above the critical point in temperature. To connect the fluid and solid phases is not so easy. The melting transition persists even at high temperature, and unlike the gas–liquid transition, cannot be avoided by heating the system.

Computer "experiments" with systems of a few hundred particles show distortion in the melting–freezing transition.[2–4] If one slowly decreases the density of a solid-phase system, then the system will change suddenly, at constant volume, from solid to fluid. Often this change is *not* reversible; i.e., going the other way, compressing a fluid to higher densities, leads not to a crystalline solid, but to a glassy state instead (see Fig. 1). Assuming that at high density a solid phase, not a glass, is thermodynamically stable, failure to observe the solid can only be due to surface effects.[7]

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

[1] W. W. Wood and J. D. Jacobson, Proc. Joint Computer Conf. San Francisco, March 1959, 261 (1959).

[2] W. W. Wood, "Monte Carlo Calculations of the Equation of State of Systems of 12 and 48 Hard Circles," Los Alamos Sci. Lab. Rept. LA-2827, 1963.

[3] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).

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

[5] A. Rahman, Phys. Rev. **136**, A405 (1964).

[6] See Gibbs' interesting discussion of this point in *The Collected Works of J. Willard Gibbs* (Yale University Press, New Haven, 1957), Vol. 1, p. 37.

[7] J. E. Mayer and W. W. Wood, J. Chem. Phys. **42**, 4268 (1965).

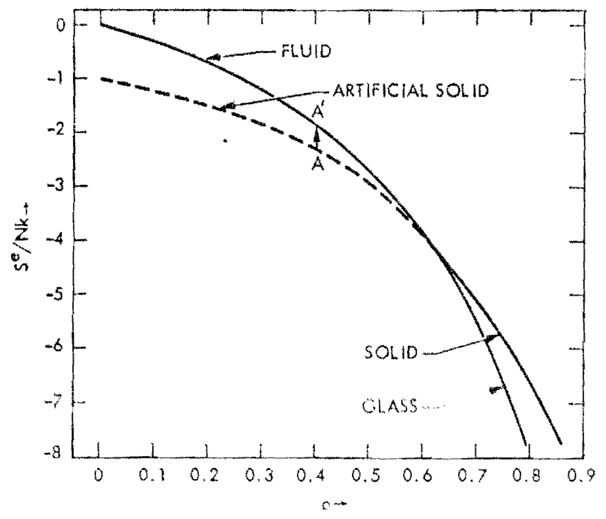

FIG. 1. Excess entropy S^e as a function of density ρ at fixed energy. For infinite thermodynamic systems, only the fluid and solid phases can be observed, and the two phases can coexist over a density range near the intersection of the two curves. In computer calculations with small systems, attempts to compress the fluid to solid-phase densities result in metastable glassy states. In the text, it is explained how generating the artificial solid states, indicated by dashes, can locate the melting transition. The properties of the artificial solid can be related to those of the real one either by following the entire dashed line or by converting the artificial solid to a fluid ($A \rightarrow A'$) by using an external field. The figure was drawn using approximate data for the hard-sphere system (the entropy excess was measured relative to an ideal gas at the same density and temperature, and volume units were chosen such that $\rho = 1$ at close packing).

It takes so much free energy to form a surface between two phases that even in a system containing 500 particles, a solid-phase nucleus cannot be formed.

This paper develops two ways to avoid the *discontinuous* change from solid to fluid. The first method is to prevent the melting transition from taking place at all by applying an external field, stabilizing the solid phase, at all densities. Each particle is held in a private cell; this artificial constraint can be thought of as the effect of an external field of infinite strength.[8]

The second method is to allow the melting transition to occur, but to force it to take place gradually and *reversibly*, instead of discontinuously, by a two-step process: first, using the infinite-strength external field already mentioned, the solid can be expanded to a reasonably low density; then the field strength can be gradually reduced to allow the system to "melt" in a reversible way. Both methods permit the exact calculation of the solid-phase entropy.

The three-dimensional hard-sphere system has been studied extensively by both the Monte Carlo and molecular-dynamic techniques,[9] and the pressure has been accurately determined in the pure-solid and pure-fluid phases. The hard-sphere model is of particular interest in the solid–fluid transition region, because the model gives a qualitative description of melting in real systems.[10] So far, however, computer attempts to accurately locate the two-phase region for hard spheres have failed. For the two phases to co-exist, it is necessary to consider larger systems (or possibly make much longer runs) than is now practical with present computers. Because of the difficulty in treating the interesting hard-sphere model, it is an appropriate test case for external-field calculations. In this paper we derive the basic equations needed for the hard-sphere calculation and evaluate the low-density limiting properties of the artificial hard-sphere solid. These latter results should prove valuable in extrapolating computer results from intermediate densities to the low-density limit. We expect to report on numerical work on the hard-sphere system at a later date.

II. ARTIFICIAL SOLID

The idea of locating the melting transition by studying a system which cannot melt is not so strange as it appears. By confining the center of each particle in an N-particle system to its own cell, of volume V/N, at *all* densities, the solid phase can be artificially extended to cover the entire density range. Particles in the artificial single-occupancy solid can collide both with the walls which confine each particle to its cell and with other nearby particles. At high density, particles are usually confined by their neighbors alone, rather than by cell walls. Each particle stays near the center of its cell, and the single-occupancy cell system faithfully represents the properties of a perfect solid. At low density, collisions with cell walls become appreciable—these collisions prevent the artificial solid from melting. That is, these collisions keep the particles ordered within the lattice of individual cells and prevent the diffusion throughout the entire system which is characteristic of particles in a normal fluid. Instead of melting, the cell system artificially continues solid-phase thermodynamic properties to low density.

At low-enough density all of the thermodynamic properties of either the constrained cell system or the unconstrained real system can be calculated exactly. We want to show how this low-density limit, coupled with computer-generated thermodynamic properties for the *artificial* cell system spanning the whole density range, can be used to calculate the entropy in the *real* solid phase.

To examine the differences between the artificial solid and the real system in a quantitative way, we first write down the configurational integrals which connect the thermodynamic properties of these systems with the microscopic potential-energy function $\Phi(\mathbf{r}^N)$. For the real system, the configurational inte-

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[8] J. G. Kirkwood, J. Chem. Phys. **18**, 380 (1950), used a constrained system of this kind as the first step in his derivation of the Lennard-Jones–Devonshire cell theory.

[9] A summary of recent work will shortly appear in *The Physics of Simple Liquids*, H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, Eds. (North-Holland Publ. Co., Amsterdam, to be published).

[10] J. S. Rowlinson, Mol. Phys. **8**, 107 (1964).

gral Q_N has the form

$$Q_N \equiv \exp[-(\bar{\Phi}/kT)+(S/k)] \equiv (N!)^{-1} \int \exp\left(\frac{-\Phi(\mathbf{r}^N)}{kT}\right) d\mathbf{r}^N. \quad (1)$$

The configurational entropy S and the average potential energy $\bar{\Phi}$ can be evaluated from the configurational integral $Q_N(T)$. The integration in Eq. (1) is carried out over the coordinates of all N particles in the system. The *single-occupancy*[8,11] configurational integral Q_{so} for the artificial solid differs from Q_N; the potential energy in the single-occupancy system contains an extra cell-wall term Φ_{cw}, which constrains each particle to lie within its own cell. This extra term modifies both the average potential energy $\bar{\Phi}$ and the configurational entropy S. Using Δ to indicate the difference, real-system property minus artificial-solid property, the single-occupancy configurational integral Q_{so} has the form

$$Q_{so} \equiv \exp[-(\bar{\Phi}/kT)+(S/k)+(\Delta\bar{\Phi}/kT)-(\Delta S/k)] \equiv \int \exp\left(-\frac{\Phi(\mathbf{r}^N)}{kT}\right) \exp\left(-\frac{\Phi_{cw}(\mathbf{r}^N)}{kT}\right) d\mathbf{r}^N. \quad (2)$$

In the integration in Eq. (2), each of the particles is confined by the cell-wall potential to a particular cell. Thus the factor of $(N!)^{-1}$ included in Eq. (1) has been automatically offset in Eq. (2) by restricting the integration to only one of the $N!$ different permutations of the N particles in N cells.

At low density both $\bar{\Phi}$ and $\Delta\bar{\Phi}$ approach zero; the two configurational integrals approach limits $Q_N \rightarrow (Ve/N)^N$ and $Q_{so} \rightarrow (V/N)^N$, and ΔS attains its maximum value $\Delta S \rightarrow Nk$. At high density the entropy difference, the so-called "communal entropy," goes to zero. Just how ΔS changes with density is not known in detail. The view that the entire communal entropy of Nk makes its appearance at melting, thus "explaining" the entropy of fusion, is by now obsolete.[4,11]

If the solid-phase configurational integral could itself be measured by a computer, then there would be no point in introducing the single-occupancy system. *In principle* the configurational integral could be calculated by taking random configurations of N particles in a volume V and averaging $\exp(-\Phi/kT)$ over these configurations. *In practice* one cannot measure configurational integrals at interesting densities, because almost all configurations of an N-particle system picked at random will have two or more particles so close together that the weight of that configuration is negligibly small.[12] The larger the system under consideration, the more serious this limitation becomes. It is, however, possible to determine accurate derivatives of Q with respect to external parameters. $(\partial \ln Q/\partial V)_T$ and $(\partial \ln Q/\partial T)_V$ are proportional to the average pressure P and the average potential energy $\bar{\Phi}$. Both averages can be measured in computer experiments. Then, knowing Q theoretically at low density, the derivative can be integrated to the solid-phase density of interest.

The derivative of Q with respect to V can be evaluated numerically by a direct application of the virial theorem.[2,3] For a D-dimensional system with a pairwise-additive potential energy $\Phi \equiv \sum \phi(\mathbf{r}_{ij})$, the virial theorem has the form

$$PV/NkT = N^{-1}(\partial \ln Q/\partial \ln V)_T = 1-[\langle \sum \mathbf{r}_{ij}\cdot \nabla\phi(\mathbf{r}_{ij})\rangle/\langle NDkT\rangle]. \quad (3)$$

All distinct pairs of particles $1 \leq i < j \leq N$ are included in the sum. The angle brackets correspond dynamically to a time average. For a Monte Carlo calculation, the time average is replaced by a configuration-space average. In the event that the forces are short range and the density is high, so that particles interact effectively only with z equivalent nearest neighbors, Eq. (3) can be simplified to

$$PV/NkT \doteq 1-\tfrac{1}{2}z\langle \mathbf{r}_{12}\cdot\nabla\phi(\mathbf{r}_{12})\rangle/\langle DkT\rangle, \quad (4)$$

where z is the coordination number of the lattice, and Particles 1 and 2 occupy nearest-neighbor cells.

Since the artificial cell walls partitioning the system make no contribution to the pressure themselves, the single-occupancy configurational integral can be calculated from the pressure using either Monte Carlo or molecular dynamics. The constraint of singly occupied cells is taken into account by rejecting any Monte Carlo moves which would take the center of a particle outside its cell, or in the dynamic case, by reflecting the component of velocity normal to a cell wall whenever the center of a particle reaches the wall.

To compute the entropy of the artificially stabilized solid at any density, $\rho \equiv N/V$, simply compute the integral, at constant energy,

$$\frac{S(\rho)}{Nk} = \frac{S_o(\rho_o)}{Nk} + \int_{\rho}^{\rho_0} \frac{P}{(\rho^2 kT)} d\rho, \quad (5)$$

where S_o is the entropy at ρ_o, chosen low enough so that S_o can be calculated. This does *not* mean zero density. The low-density limit can be calculated analytically by performing an f-function expansion[13] of the integrand of Q_{so}. For nearest-neighbor interactions, one finds the result

$$Q_{so} = (V/N)^N \exp\left[\tfrac{1}{2}(Nz)\rho^2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 f_{12} + \text{higher-order terms}\right], \quad (6)$$

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

[12] E. Byckling, Physica 27, 1030 (1961).

[13] This kind of expansion has been considered before by many authors, usually with the idea of calculating thermodynamic properties at liquid densities! See, for some hard-disk calculations, E. G. D. Cohen and B. C. Rethmeier, Physica 24, 959 (1958).

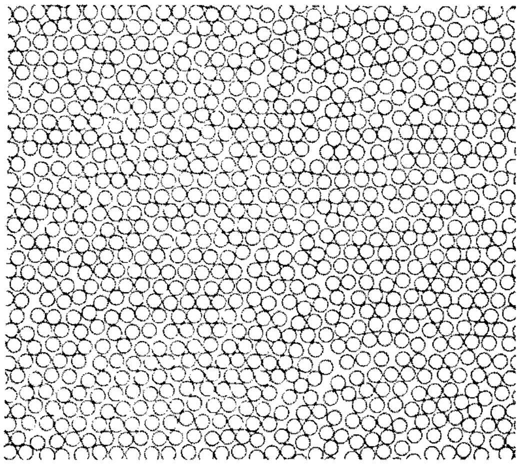

FIG. 2. A "snapshot" picture of a typical Monte Carlo configuration of 870 disks in the solid phase, expanded about 27% from close packing. The figure shows clearly the absence of long-range order in the two-dimensional solid phase. The displacement of the disks from their "lattice sites" is large. The configuration shown could not occur in the single-occupancy cell system. This figure was kindly furnished by W. W. Wood (see Ref. 9).

where Particles 1 and 2 occupy neighboring cells and the Mayer f-function f_{12} is equal to $\exp[-\phi(\mathbf{r}_{12})/kT]-1$. For a short-range potential function $\phi(\mathbf{r})$, the integral in Eq. (6) is at low density[14] proportional to the area of the cell wall separating Particles 1 and 2, $\sim(V/N)^{1-1/D}$ in D dimensions.

The procedure just outlined for evaluating the solid-phase entropy makes the assumption that the communal entropy $\Delta S=S-S_{\text{so}}$ is negligibly small in the solid phase. This is certainly valid provided that in the actual solid phase, particles remain localized within half a particle diameter of their most likely position at the cell center. The extent to which this localization prevails depends very strongly on the number of dimensions D. In one or two dimensions,[15] even at the highest densities, particles are not localized but instead move cooperatively back and forth over distances large with respect to the nearest-neighbor spacing. Thus the mean-squared displacement of a particle from its lattice site should diverge in one or two dimensions. Striking confirmation of the irregular structure and lack of long-range order, in the two-dimensional solid phase, can be seen in one of Wood's "snapshot" pictures of the computer-generated 870-disk solid, reproduced in Fig. 2. Of course, the fact that the mean-squared displacement diverges does not necessarily mean that thermodynamic properties calculated with a finite displacement (forced on a system by using cells) will be very different from those of a real system with a diverging displacement. In fact, thermodynamic properties are not very sensitive to these low-frequency motions. In the most extreme case, a one-dimensional hard-rod system, the mean-squared displacement is proportional to the number of particles N, and yet a comparison of Q_N and Q_{so} for this system shows that both the entropy and the pressure differences vanish near close packing.[11] The discrepancy is small at high density and must be much smaller in two or three dimensions; in our three-dimensional applications we will ignore it.

Since three-dimensional solids generally melt at a linear expansion of order 10% from an effective "close-packed" volume, the root-mean-squared displacement from the center of a cell should remain small with respect to the cell diameter even at melting; in three dimensions, the single-occupancy approximation should be accurate throughout the solid phase. Experimentally, the field-ion microscope pictures show that over periods long with respect to a molecular vibration time, particles are localized in three-dimensional solids.[16] Thus, the single-occupancy configurational integral, which can be connected to low-density thermodynamic properties, should realistically represent a three-dimensional system in the solid phase.

III. EXTERNAL FIELD OF VARIABLE STRENGTH

As an alternative to the evaluation of the single-occupancy configurational integral at many densities, one can instead connect the artificial solid phase with the fluid phase at some convenient sufficiently low density by using an external field of varying strength. In Fig. 1 the thermodynamic path joining Points A and A' could be used to make the solid-fluid connection. The "external field" is chosen so that when turned on at full strength, the system is forced into the single-occupancy configuration, with one particle per cell. At vanishing field strength the system behaves normally. We expect then to be able to go *reversibly* between the solid and fluid phases by varying the field strength.

To set up the field, imagine a cell structure of N cells superimposed on the volume V. To stabilize singly occupied cells, as opposed to empty or multiply occupied ones, we introduce an external field which furnishes an absorption energy, $-\epsilon$, per singly occupied cell. The absorption energy is added to the usual potential energy of the system $\Phi(\mathbf{r}^N)$. The total absorption energy for a configuration with ν singly occupied cells is $-\nu\epsilon$. Increasing the external field strength parameter ϵ increases the average number of singly occupied cells $\bar{\nu}$. For such a system the generalized configurational integral, depending on the field strength, can be written

$$Q_N(\epsilon)\equiv(N!)^{-1}\int\exp\left(-\frac{\Phi(\mathbf{r}^N)}{kT}\right)\exp\left(\frac{\epsilon\nu(\mathbf{r}^N)}{kT}\right)d\mathbf{r}^N. \qquad (7)$$

As ϵ approaches zero, $Q_N(\epsilon)$ reduces to the uncon-

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[14] At low density the integral reduces to, apart from a proportionality constant, a surface-tension integral considered and worked out for hard spheres, by A. Bellemans, Physica **28**, 493 (1962).

[15] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., London, 1958), Sec. 125.

[16] R. H. Good, Jr., and E. W. Müller, *Encyclopedia of Physics*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1956) Vol. 21, p. 176.

strained configurational integral for the real system Q_N. In the opposite limit, for ϵ large, $Q_N(\epsilon)$ approaches $\exp(\epsilon N/kT)Q_{\mathrm{so}}$ as all N cells become singly occupied. The two special cases, $\epsilon=0$ and $\epsilon\rightarrow\infty$, can be used to establish the useful identity

$$-\frac{\Delta\bar{\Phi}}{NkT}+\frac{\Delta S}{Nk}\equiv N^{-1}\ln\left(\frac{Q_N}{Q_{\mathrm{so}}}\right)=(kT)^{-1}\int_0^\infty\left(\frac{N-\bar{\nu}}{N}\right)d\epsilon, \quad (8)$$

where $\bar{\nu}=\bar{\nu}(\epsilon)$ depends on the field strength and temperature. We expect that as long as the chosen density is not too high, $\bar{\nu}$ could be determined by computer calculations, and that the transition could be made to occur reversibly, even for a small system. It seems likely that there is a critical density (analogous to the magnetic Curie temperature) below which the transition from artificial solid to fluid is continuous and above which the transition is discontinuous. Assuming that at sufficiently low density the transition from solid to fluid takes place *reversibly* for small systems, one can calculate the entropy in the solid phase by a two-step process: first, the single-occupancy pressure is measured from solid-phase density down to a density low enough for the field-induced transition to take place reversibly; next, the external field is gradually reduced in strength, at fixed density, to zero. The entropy changes for the two steps, added together, give the total entropy difference between the initial solid-phase state and lower-density fluid. The density at which the transition becomes reversible would have to be determined empirically. If it turns out to be extremely low, say one-tenth of close packing, then there is no advantage in using a variable external field. If, however, the transition becomes reversible at about half of close packing, the amount of numerical calculation needed could be reduced by using a variable external field.

The field strength required to "freeze" a low-density fluid should be of the order kT and should decrease at higher density when the cells are more likely to be singly occupied even without the help of an external field. In the low-density limit, we can evaluate the configurational integral in the presence of an external field by the usual variational technique

$$Q_N(\epsilon)\rightarrow N!(V/N)^N\sum_{\{N_j\}}\exp(N_1\epsilon/kT)\prod_{j=0}^{\infty}[(j!)^{N_j}N_j!]^{-1}, \quad (9)$$

where the sum is over all sets of N_j satisfying the restrictions $\sum N_j=\sum jN_j=N$. (N_j is the number of cells containing exactly j particles. *Two* restrictions occur, because we set both the number of cells $\sum N_j$ and the number of particles $\sum jN_j$ equal to N, to make a single-occupancy system occur when the external field is strong.) The solution[17] of this problem, in the large-system low-density limit, is

$$\begin{aligned} Q_N(\epsilon)&=(V/N)^N[\exp(\epsilon/kT)+e-1]^N,\\ N_j/N&=\{(j!)[\exp(\epsilon/kT)+e-1]\}^{-1}, \qquad \text{for } j\neq 1,\\ &=\exp(\epsilon/kT)[\exp(\epsilon/kT)+e-1]^{-1}, \qquad \text{for } j=1. \end{aligned} \quad (10)$$

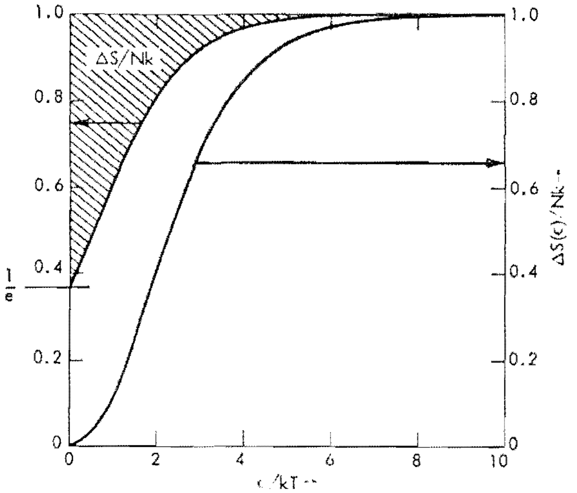

FIG. 3. An exact low-density calculation shows how the entropy difference $\Delta S(\epsilon)$ between an artificially stabilized solid and an ideal gas varies with the strength of the stabilizing external field. When the field is at full strength, all N cells are singly occupied. When the field is turned off, the artificial system reduces to the real one, and the fraction of cells singly occupied $\bar{\nu}/N$ is $1/e$. The shaded area is numerically equal to the communal entropy and illustrates the low-density limit of the integration indicated by Eq. (8) of the text.

In Fig. 3 both the entropy and the number of singly occupied cells are shown as functions of field strength. Notice that even at zero density a field strength of $4kT$ is sufficient to make over 96% of the cells singly occupied. At higher densities, weaker fields would be adequate.

In numerical applications it is reasonable to expect that the communal entropy, calculated in the way just outlined, could be determined with an error of order $0.01Nk$. In typical applications this would allow the phase transition pressure to be determined within about 1%.

IV. APPLICATION TO HARD SPHERES

To the extent that attractive forces can be idealized as forming a uniform background of negative energy and repulsive forces can be replaced by an energy-independent collision diameter, the hard-sphere system can be used to represent real systems. The hard-sphere system is probably the simplest which can reproduce melting qualitatively and is therefore of particular theoretical interest.

Because of its simplicity and intrinsic interest, the hard-sphere model has been extensively investigated

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[17] The same mathematical problem has no doubt been solved many times before. For a mathematically more general case, see N. G. Van Kampen, Phys. Rev. 135, A362 (1964).

by both the Monte Carlo and molecular-dynamic methods. So far, however, in systems containing up to 500 particles, it has not been possible to observe coexisting solid and fluid phases. At linear expansions of about 14% from close packing, the solid phase melts irreversibly[18] to the fluid, and attempts to compress the fluid back to solid-phase densities have always resulted in the generation of a metastable glassy phase.

The small size of the systems studied is responsible for these unsatisfactory results. The dependence of the transition on the number of particles has been estimated. The deviation from the large-system thermodynamic limit is reasonably small, of order $(\ln N)/N$,[19] but without a definite value for the transition pressure for some finite N, the extrapolation to infinite systems cannot be carried out. Instead, one must use entropy estimates from slowly converging theories[20] or use *ad hoc* assumptions[21] to connect the thermodynamic properties of the solid and fluid phases.

A fluid-phase equation of state for hard spheres, accurate over the whole density range, is already available.[22] Thus, the entropy of the single-occupancy hard-sphere system can be determined from Eq. (8) by measuring the change in the number of singly occupied cells with field strength. Then an integration along the single-occupancy isotherm ($TdS=PdV$ on a hard-sphere isotherm) would establish the entropy of the hard-sphere solid and allow the melting transition to be accurately located.

At the low-density limit, the configurational integral expansion indicated in Eq. (6) can be carried out analytically for hard spheres, at least through the first term. The integral corresponds to the average overlap of two spheres occupying neighboring cells and is the cell-system analog of the second virial coefficient.

For one-, two-, and three-dimensional hard spheres, respectively, one finds for the integral $\int d\mathbf{r}_1 \int d\mathbf{r}_2 f_{12}$: $-\frac{1}{2}\sigma^2$, $-\frac{2}{9}\sqrt{3}\sigma^4 x^{-1/2}$, and $-(\pi\sqrt{2}\sigma^6/16)x^{-2/3}$, where σ is the sphere diameter, and x is the density divided by the density at close packing. Using the density expansion of the configurational integral Q_N, one can use these results to calculate the communal entropy in the low-density limit

$$\Delta S/Nk = 1-1.00000x-O(x^3), \qquad \text{one dimension;}$$

$$= 1-1.81380x+1.53960x^{3/2}-O(x^2), \qquad \text{two dimensions;}$$

$$= 1-2.96192x+3.33216x^{4/3}-O(x^{5/3}), \qquad \text{three dimensions.} \tag{11}$$

The low-density limiting cases, Eq. (11), coupled with Monte Carlo or dynamic values of the single-occupancy pressure from low density to solid-phase densities will make it possible to determine the transition pressure and densities of the coexisting phases.

An investigation of the two-dimensional hard-disk system probably would not yield any new thermodynamic information, because the 870-disk transition has already been located.[4] It would nevertheless be of some interest to investigate the hard-disk single-occupancy system in the solid phase to find out if the qualitative difference in mean-squared displacement between the real system and the artificial one causes noticeable differences between their thermodynamic properties.

V. SUMMARY

Two different ways have been suggested to locate the melting transition accurately by using computer-generated thermodynamic properties of an artificial single-occupancy solid. The first method is to calculate the pressure of the artificial solid over the whole density range and by integration to calculate the entropy of the solid at high density, where the entropy difference vanishes between the actual solid and the artificial one. The second method avoids the low-density part of the integration by connecting the artificial solid to the real system at fixed density by turning on an external field reversibly. Computer results for the hard-sphere system, augmented by the low-density limiting results described in this paper, should make it possible to accurately locate the hard-sphere melting transition and to determine how the communal entropy varies with density. If this program is successful it would be logical to try the same techniques for more general force laws and for more complicated solid–solid transitions.

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[18] Some unpublished dynamic data, provided by B. J. Alder, indicate that a 500-sphere system "melts" at an expansion of 50% from close packing. The melting occurs in both the face-centered and hexagonal versions of the hard-sphere crystal. The transition is only "irreversible" in the context of times short enough for computer calculations, of course.

[19] W. G. Hoover and B. J. Alder, J. Chem. Phys. 46, 686 (1967).

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

[21] M. Ross and B. J. Alder, Phys. Rev. Letters 16, 1077 (1966).

[22] Either the integral of the Padé approximant to the hard-sphere pressure, or for simplicity, a Padé approximant to the entropy itself can be used. The former approximant can be found in F. H. Ree and W. G. Hoover, J. Chem. Phys. 40, 939 (1964).