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Cell Theories for Hard Particles*

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The consequences of each of the three approximations made by Kirkwood in deriving the Lennard-Jones–Devonshire cell theory are elucidated by a comparison with exact results in the one-dimensional case of hard rods. This comparison gives an explicit calculation of the one-dimensional communal entropy and shows that the single-occupancy approximation is exact at close packing, although it does not lead to thermodynamic properties which are analytic functions of density. For two- and three-dimensional systems, numerical results show that the cell-theory entropy predictions are more accurate than in one dimension because the particles are more localized. The more-than-one-particle-per-cell theories provide simple and rigorous lower bounds on the entropy, but the convergence to the thermodynamic limit by considering more and more particles is slow.

I. INTRODUCTION

Cell theories have gained in interest recently because it could be shown that the pressure for particles with hard-core potentials is given correctly in the limit of close packing.[1–3] This result was first suggested by numerical experiments.[4] These numerical experiments have also yielded the result, through integration of the equation of state, that in both two and three dimensions the entropy is also nearly correctly given at close packing by the Lennard-Jones–Devonshire cell theory.[5] It was therefore thought worthwhile to reexamine the foundation of the cell models in the hope of developing theories which could account for the small deviations.

The physical reason that the pressure is given correctly in the limit is that the only characteristic volume on which the partition function can depend is the volume of the system less the volume of the particles, the *free volume*. The N-particle partition function is proportional to the Nth power of the free volume. This functional form is sufficient to determine the pressure, but not the entropy, for which the coefficient multiplying this functional form is required. This coefficient depends sensitively on the cooperative motions possible in the system, since the magnitude of the effective free volume is determined by how localized a particle is. It is therefore surprising that the entropy is given so well by the cell theory, and this work was undertaken in an effort to understand this result. A further incentive for establishing the absolute entropy at close packing is that it would enable one to draw the tie line between the solid and fluid branches of the hard-particle equation of state.[6] Once the limiting properties have been theoretically determined, it might be possible to go on and show that away from close packing, the partition function, and hence the thermodynamic properties, are rigorously expressible in a power series in the free volume,[7] just as at low densities it can be proved that they are expressible in a power series in the reciprocal of the free volume.[8]

Kirkwood[9] showed that the Lennard-Jones–Devonshire cell theory could be derived from the partition function by making three separate approximations. First, it was necessary to impose a fixed-cell structure on the system and to require that no particle leave its private cell. This so-called single-occupancy approximation can be expected to be exact only in the limit of close packing. Second, it was assumed that the correlation between the motions of neighboring particles could be neglected. This "product of singlet distribution functions" approximation cannot be a very good approximation at high density. It is only rigorously valid in the limit of very low density where the particles are far enough apart to be independent. It can thus be predicted that, just as the self-consistent Hartree–Fock wavefunctions overestimate the energy, the self-consistent singlet distribution function, treating all particles alike, will considerably overestimate the free energy of a classical system. Hence, it might be expected that it is better not to choose the self-consistent solution but to choose a solution more in keeping with the product approximation; namely, the one where all neighboring particles are localized at their most probable position, at the centers of their cells, and hence uncorrelated with the central particle. This

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third approximation does then lead to the Lennard-Jones–Devonshire cell theory, which is nearly quantitatively successful for disks and spheres at high density.

Each of these approximations has been quantitatively evaluated in the one-dimensional hard-rod system for which the exact partition function is known.[10] This is an appropriate system from the point of view that a particle is always confined to a cell formed by its neighbors. It is this feature of the theory, however, which restricts its applicability in higher dimensions to the solid phase. From the point of view of the second and third of the above approximations, the hard-rod system presents a particularly severe test. This is because a particle is less localized if it has fewer neighbors to restrict its motion. The singlet distribution function, for example, can be shown in one dimension to have an infinite half-width in the thermodynamic limit. This means that a particle moves over distances large compared to the nearest-neighbor distance. It is, however, not clear whether for disks and spheres the singlet distribution function is bounded either. Localization in the hard-rod system is also less because of the absence of any potential minimum in the interaction. Thus, the Lennard-Jones–Devonshire theory should be more valid for real systems at low temperature, since the intermolecular potential localizes the particles.[11]

In order to obtain the exact thermodynamic properties in the limit of close packing, it is necessary to work out the single-occupancy partition function without further approximations. Although this task can be carried out in one dimension, in higher dimensions this does not seem possible. Instead, successively more particles per cell are considered in the hope that the resulting scheme converges rapidly to the thermodynamic limit. The cell-cluster theory[12] is such an attempt, but it gets bogged down in a difficult combinatorial problem. An alternative scheme[13] in which this problem is avoided and an identity is written which gives the partition function as a product of ratios of partition functions appears to converge very rapidly. However, this result is deceptive. The correction to the single-particle cell theory, which is always the first approximation, is known to be small for hard disks and spheres. The second approximation, the ratio of the two-particle to the square of the one-particle partition function, is indeed very close to 1; however, the correction is very small compared to the small correction needed to reproduce the numerically established results for the entropy. Another approach is to carry out Kirkwood's three-approximation scheme, outlined above for one particle, for successively more particles per cell and ascertain its convergence. This is discussed for the hard-rod system in the third section of this report.

Since all these schemes show slow convergence—that is, it is difficult to represent with a few-particle partition function the highly cooperative motions present in dense systems—an alternative approach is to incorporate into a simple few-particle model some of the correlations present. Such an empirical approach is represented by the correlated cell model for disks.[7] By having some of the particles perfectly correlated and others not at all, the model simulates quite successfully the cooperative motion necessary for melting. In addition, this model almost quantitatively accounts for the correction of the equation of state away from close packing.

II. ONE-PARTICLE CELL THEORIES

The starting point of any classical high-density theory is the configurational integral, Q_N, the volume-dependent part of the partition function

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

$$= \int_V \exp\left(\frac{-\Phi}{kT}\right) d\mathbf{r}^N \qquad (1)$$

(ordered).

The total potential energy of the system, Φ, is a function of the coordinates of all of the particles $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N$. For the hard particles considered in this paper Φ is either zero or infinity for a particular choice of $\mathbf{r}^N$. The particles are restricted to lie within the volume V throughout the integration. In the second form of the configurational integral, the N particles are to be ordered in any one of $N!$ equivalent ways. Any convenient ordering, such as $x_1 < x_2 < \cdots < x_N$, can be used; in approximate theories the particles are often ordered by confining them to individual cells.

Particles in the solid phase *are* ordered ("distinguishable") and confined to small volumes of the order of the volume per particle by their nearest neighbors. Dynamically, the center of each particle sweeps out, as time goes on, a microscopic "free volume." Although there is no rigorous relation linking this physically imagined free volume to the N-particle partition function, one expects, intuitively, that this free volume will approximately equal the Nth root of the configurational integral, $(Q_N)^{1/N} \approx v_f$. This idea was the basis for the cell and free-volume theories.[11–14]

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[11] J. Barker, *Lattice Theories of the Liquid State* (Macmillan Co., New York, 1963). This book should be consulted for a description of cell-theory calculations and extensive references to original papers.

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

[14] 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); **A165**, 1 (1938); **A169**, 317 (1939); **A170**, 464 (1939).

In order to derive a cell theory from the configurational integral, Kirkwood[9] divided the volume V into N equal cells. Kirkwood's first approximation is to ignore the contributions of all but the single-occupancy configurational integral, $Q_1(N)$,

$$Q_1(N)\equiv\int_V \exp\left(\frac{-\Phi}{kT}\right)d\mathbf{r}^N \qquad (2)$$

$$(k\text{th particle in } k\text{th cell}).$$

It is anticipated that at very high density doubly occupied cells will be rare, assuming that the cell structure is chosen wisely, and that the approximation $Q_N \approx Q_1(N)$ will be accurate in this limit.

In order to analyze the single-occupancy approximation in detail, $Q_1(N)$ for hard rods is worked out below. The system of N rods has a total length V so that each rod is confined to a cell of length $V/N\equiv\lambda\equiv\rho^{-1}$. For convenience, the length of a hard rod is set equal to unity. With this choice of units the length per particle, λ, and the density, ρ, both approach unity at close packing. In the single-occupancy configurational integral the coordinate of the jth rod, x_j, is restricted to the jth cell: $(j-1)\lambda<x_j<j\lambda$. By introducing Mayer's f functions,[8] $1+f_{j,j+1}\equiv\exp(-\phi_{j,j+1}/kT)$, for $j=N-1$, $N-2$, $N-3$, $\cdots$, the following relation is obtained:

$$Q_1(N)=Q_1(N-1)Q'_1(1)+Q_1(N-2)Q'_1(2)$$
$$+Q_1(N-3)Q'_1(3)+\cdots, \qquad (3)$$

where the prime indicates that all k particles in $Q'_1(k)$ are not only restricted to their cells but also linked to their nearest neighbors by f functions

$$Q'_1(k)\equiv\int\prod_{j=1}^{k-1}f_{j,j+1}\prod_{j=1}^{k}dx_j\,. \qquad (4)$$

$Q'_1(k)$ is zero when the k particles can no longer overlap, that is, for densities less than $(k-2)/(k-1)$. Thus the sum of products in Eq. (3) truncates, giving a closed-form recursion relation for $Q_1(N)$ in terms of the integrals $Q'_1(k)$. These latter can be evaluated by making a change of variable

$$Q'_1(k)=(-)^{k-1}[(k-1)-(k-2)\lambda]^k/k!. \qquad (5)$$

With the help of these $Q'_1(k)$, a generating function can be written for the single-occupancy configurational integral

$$\sum_{N=0}^{\infty}Q_1(N)z^N=\left\{\sum_{k=0}^{L}z^k\,\frac{[(k-2)\lambda-(k-1)]^k}{k!}\right\}^{-1}, \qquad (6)$$

where L is $2+[\rho/(1-\rho)]$ and the brackets $[\ ]$ indicate the greatest integer function. Each of the configurational integrals on the left-hand side of Eq. (6) is evaluated at the particular value of the density appearing on the right-hand side, so that Eq. (6) is *not* a grand partition function. The analytic form of the single-occupancy partition function changes at densities of $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, $\frac{4}{5}$, $\cdots$. Thus $Q_1(N)$ is not analytic at these densities and the thermodynamic properties derived from $Q_1(N)$ have discontinuous derivatives characteristic of phase transitions. In the thermodynamic limit this conceptually simple partition function thus produces an infinite number of fictitious phase transitions. In the thermodynamic limit, $Q_1(N)$ is related to the smallest zero, z_0, of the polynomial appearing on the right-hand side of Eq. (6):

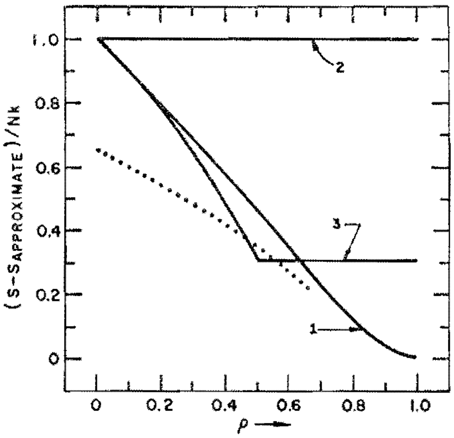

FIG. 1. The error made in calculating the hard-rod entropy, using 1, 2, or all 3 of Kirkwood's approximations. Curve 1 shows the *communal entropy*, the error resulting from the single-occupancy approximation alone. Curve 2 is the entropy error resulting from the solution of Kirkwood's approximate integral equation. Curve 3 is the entropy error incurred after all three approximations, the Lennard-Jones–Devonshire cell-theory error. The dotted curve shows the error obtained using the double-occupancy approximation to the partition function.

$$\lim_{N\to\infty}Q_1(N)=[z_0(\lambda)]^{-N}. \qquad (7)$$

The differences in entropy and pressure between the exact[10] configurational integral and the single-occupancy configurational integral are plotted in Figs. 1 and 2, respectively. The difference in entropy is the *communal entropy* which has not previously been calculated for interacting particles. It is shown to be a monatomic, smoothly decreasing function of the density. The entropy from the single-occupancy configurational integral is, as it must be, always too small. The pressure is also too small, with the greatest discrepancy, about 30%, occurring near three-fourths the close-packed density. Both the pressure and entropy discrepancies vanish at close packing, making the single-occupancy partition function exact in that limit.

For low densities, $0<\rho<\frac{1}{2}$, the smallest zero in the denominator of the generating function given by Eq. (6) is found by solving a quadratic equation

$$z_0=\lambda-(\lambda^2-2)^{1/2}=2-\sqrt{2}+(\lambda-2)(1-\sqrt{2})$$
$$+(\lambda-2)^2\sqrt{2}/4-(\lambda-2)^3\sqrt{2}/4+\cdots, \qquad (8)$$

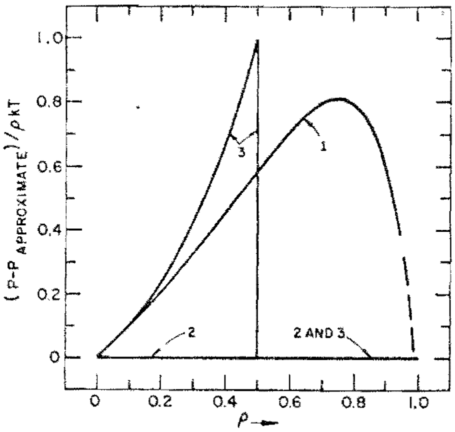

FIG. 2. The error made in calculating the hard-rod compressibility factor (PV/NkT) using 1, 2, or all 3 of Kirkwood's approximations. Curve 1 shows the error resulting from the single-occupancy approximation alone. Curve 2 shows the result obtained from Kirkwood's approximate integral equation. Curve 3 is the result according to the Lennard-Jones–Devonshire cell theory (all three approximations).

so that the pressure from the single-occupancy configurational integral is given by the expressions

$$PV/NkT=\lambda(\lambda^2-2)^{-1/2}=(1-2\rho^2)^{-1/2}$$
$$=1+\rho^2+\tfrac{3}{2}\rho^4+\tfrac{5}{2}\rho^6+\cdots$$
$$=\sqrt{2}\lambda[\tfrac{1}{2}-\tfrac{1}{2}(\lambda-2)$$
$$+\tfrac{5}{8}(\lambda-2)^2-\cdots]. \quad (9)$$

The even-numbered virial coefficients are all zero in this density range. In the next-higher density range, $\frac{1}{2}<\rho<\frac{2}{3}$, the analytic form of $Q_1(N)$ changes, according to Eq. (6). In this region z_0 is given by the expression

$$z_0=2-\sqrt{2}+(\lambda-2)(1-\sqrt{2})+\tfrac{1}{4}(\lambda-2)^2\sqrt{2}$$
$$-\tfrac{1}{12}(\lambda-2)^3(28-17\sqrt{2})+\cdots, \quad (10)$$

which should be compared to Eq. (8). The pressure has the form

$$PV/NkT=\sqrt{2}\lambda[\tfrac{1}{2}-\tfrac{1}{2}(\lambda-2)+(\sqrt{2}-\tfrac{7}{8})(\lambda-2)^2-\cdots],$$
$$[\tfrac{1}{2}<\rho<\tfrac{2}{3}]. \quad (11)$$

Comparison of Eq. (9) with Eq. (11) shows that the curvature of the single-occupancy isotherm, $\partial^2P/\partial V^2$, changes discontinuously at half the close-packed density, and from Eq. (6) it is clear that successively higher derivatives will have discontinuities at successively higher densities.

Although an analytical single-occupancy treatment for two- and three-dimensional hard particles is difficult to carry out, even at low density, the three qualitative effects found in one dimension have analogs in the higher dimensional cases too: (1) The analytic form of $Q_1(N)$ will change as the density increases and more complicated clusters become possible; (2) the single-occupancy approximation becomes exact at close-packing for hard parallel squares and cubes,[15] and this is also likely true for disks and spheres but a proof is lacking; and (3) the pressure derived from $Q_1(N)$ can be shown to have no virial expansion; the first deviations from ideality are proportional to $\rho^{3/2}$ and $\rho^{4/3}$ in two and three dimensions, respectively.

Kirkwood's second approximation, unlike the first, is rather poor at high density. This approximation states that the probability distribution function for N particles in their cells is a product of single-cell single-particle distribution functions

$$P_N(\mathbf{r}^N)=\prod_{\text{cells}} P_1(\mathbf{r}_k) \quad (12)$$

(kth particle in kth cell).

$P_1(\mathbf{r})$ is to be chosen to minimize the Helmholtz free energy; this leads to an integral equation for the determination of $P_1(\mathbf{r})$. For hard particles it is not necessary to consider the integral equation at all. The solution of the minimization problem is simplified in this case because minimizing the free energy corresponds to maximizing the entropy. The entropy is proportional to the logarithm of the volume in each cell for which the probability density is nonvanishing. For hard spheres Wood pointed out that $P_1(\mathbf{r})$ is nonvanishing in those parts of the cell separated by at least half of a particle diameter from the cell boundary. In order for hard rods to be independent of one another, no particle can be allowed within distance $\frac{1}{2}$ of its cell walls, so that the solution of the minimization problem in this case is equivalent to the configurational integral

$$Q_N=[(V/N)-1]^N \quad (13)$$

(first and second approximations).

This result should be compared with the exact result, $e^N[(V/N)-1]^N$. Interestingly enough, in one dimension the error introduced in the pressure by the first approximation (as shown in Fig. 2) is exactly offset by the second approximation, so that the pressure obtained from Eq. (13) is exact at any density. However, the error introduced by the second approximation in the entropy contributes a constant net entropy error of Nk at any density. Because correlations, particularly at the highest densities, are important for hard particles, the product approximation is poor.

It is only in one dimension that the first two approximations exactly offset each other, yielding the exact equation of state. The molecular dynamics studies indicate that at high density the pressure can be ex-

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[15] The argument given on p. 226 of the last paper of Ref. 3 can be applied to hard parallel squares and cubes to prove this statement.

panded in powers of the relative free volume α,

$$PV/NkT=(D/\alpha)+C_0+C_1\alpha+C_2\alpha^2+\cdots, \qquad (14)$$

where α is $(V/V_0)-1$ and V_0 is the close-packed volume. In D dimensions, Wood[16] found that the free-volume equation of state, $PV/NkT=(1-\rho^{-1/D})^{-1}$, results when the first two approximations are made. This equation of state reproduces the first term, D/α, in Eq. (14) correctly. However, the constant term is in error when calculated by this free-volume equation of state. The value of C_0 from molecular dynamics data[5] is 1.9 instead of 1.5 for disks, and 2.5 instead of 2.0 for spheres. In two or more dimensions this two-approximation free-volume equation of state is also known to be qualitatively wrong at low density, since it does not lead to the virial series.

It is clear that the entropy derived from the first two approximations is a rigorous lower bound on the correct entropy, for all of the configurations counted in the solution of Kirkwood's integral equation *do* contribute to the correct Q_N, but many other configurations are left out by these approximations. The entropy error at close packing is Nk in one dimension, about $1.4Nk$ for disks, and about $2Nk$ for spheres. Thus, the product approximation neglects important correlations at high density.

The results of the minimization procedure just referred to are in fact less accurate than those obtained from the Lennard-Jones–Devonshire cell theory, which requires one additional approximation. In order to get the Lennard-Jones–Devonshire cell theory Kirkwood makes his third approximation, assuming that $P_1(\mathbf{r})$ is a delta function located at the center of the cell. This approximation is sensible provided the particles are localized, as they are at low temperatures in real systems where the molecules make small oscillations about their equilibrium positions. The initial step in solving by iteration the integral equation mentioned above is to substitute the delta-function guess into the integral equation. This first iteration generates exactly the Lennard-Jones–Devonshire theory. Thus, the free volume per particle is evaluated by placing all neighboring particles at the centers of their cells. This is, of course, inconsistent in that the particles are not all treated alike in evaluating the free volume. For hard particles the choice that $P_1(\mathbf{r})$ is a delta function might appear particularly poor. Wood[16] found in fact that the iteration scheme starting from this choice does not converge.

For hard rods the delta-function approximation gives, for all densities greater than half the close-packed density, a free volume of $2[(V/N)-1]$, and this *is* in fact the average free volume. It is also, however, exactly twice the true solution of Kirkwood's integral equation. After applying all three approximations the entropy is too low by $Nk\ln\frac{1}{2}e$ while the pressure is unchanged from the two-approximation stage. The entropy discrepancy has thus been reduced from Nk to $0.307Nk$ and the pressure remains exact. At densities less than half of close packed, the free volume from all three approximations is V/N, the pressure is ideal, and the entropy is too low by $Nk[1+\ln(1-\rho)]$.

The effect in two or three dimensions is similar. The entropy is increased (near close packing) by $DNk\ln 2$ in D dimensions over the exact solution of the integral equation. The discrepancy between this entropy prediction and the exact entropy at close packing is not known precisely, but it is evidently quite small. Preliminary estimates from molecular dynamics indicate that the high-density Lennard-Jones–Devonshire entropy is slightly too low $(0.06Nk)$ for hard disks and slightly too high $(\sim 0.1Nk)$ for hard spheres. Thus, a vast improvement has resulted over the two-approximation scheme where the discrepancies were $1.4Nk$ and $2Nk$. However, for hard disks and spheres the pressure does not remain unchanged, as for hard rods. PV/NkT is increased a little. C_0 increases from 1.500 to 1.556 for disks, and from 2.000 to 2.125 for spheres. A comparison of the values of C_0 to the ones obtained from molecular dynamics[5] (1.9 and 2.5, respectively), shows that the delta-function approximation improves the pressure too. The details of these molecular dynamics results will be published soon.

III. MORE-PARTICLE CELL THEORIES

Squire and Salsburg[17] generalized Kirkwood's approach by dividing the volume V into $N/2$ identical cells, each of which is doubly occupied. Their first approximation is

$$Q_N=Q_2(N), \qquad (15)$$

where $Q_2(N)$ is the double-occupancy configurational integral. For hard rods, just as in the single-occupancy case, it is possible to derive a closed-form recursion relation for $Q_2(N)$ and to find a generating function for $Q_2(N,\lambda)$. In the low-density case, $0<\rho<\frac{2}{3}$, one finds the result

$$\sum_{\substack{N=0\\ \text{even}}}^{\infty} Q_2(N)z^N = \frac{1+\frac{1}{2}z^2}{[1-(2\lambda^2-2\lambda)z^2+(\lambda^2-\frac{5}{3}\lambda+\frac{5}{8})z^4-\frac{1}{144}z^6]}, \qquad (16)$$

where λ is again the volume per particle, V/N.

The entropy from the double-occupancy partition function is the dotted line plotted in Fig. 1. Although the results are closer to the exact entropy than the single-occupancy results, the improvement is greatest at low density. It appears that at high density the

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

[17] D. R. Squire and Z. W. Salsburg, J. Chem. Phys. **35**, 486 (1961). The correlated cell model of Ref. 7 is essentially a two-dimensional analog of the three-dimensional hard-sphere model obtained here.

properties of $Q_2(N)$ resemble those of $Q_1(N)$ more closely than those of Q_N. This is an indication that quantitative results in the solid phase will not be obtained with a few-particle model. Many particles are necessary to reproduce the cooperative motion and correlations present in a dense infinite system.

The virial expansion for the double-occupancy configurational integral can be derived from Eq. (16) by expanding the smallest zero of the cubic polynomial as a power series in ρ. The resulting virial expansion,

$$PV/NkT=1+\tfrac{1}{2}\rho+\tfrac{3}{4}\rho^2+\tfrac{5}{8}\rho^3+\tfrac{5}{6}\rho^4+\cdots, \qquad (17)$$

gives a second virial coefficient within 50% of the correct value, unity, as opposed to the value zero for the single-occupancy case.

Squire and Salsburg[17] derive an integral equation for the distribution function for two particles in a cell, based on the minimization of the Helmholtz free energy, under the restriction

$$P_N(\mathbf{r}^N)=\prod_{\text{cells}} P_2(\mathbf{r}^2). \qquad (18)$$

The solution of this integral equation must be self-consistent (all particles treated alike). Squire and Salsburg did not actually solve this integral equation for $P_2(\mathbf{r}^2)$, but it is clear that the results would be analogous to the one-particle theory. Again each particle must stay at least one diameter distant from particles in neighboring cells, so that the problem involves the partition function for two particles confined to a rigid box. In one dimension the result is

$$Q_N=2^{N/2}[(V/N)-1]^N \qquad (19)$$

(first and second approximations),

so that the entropy has increased by $0.347Nk$ over the one-particle entropy at this stage, but is still too low, over the entire density range, by $0.653Nk$. The geometry involved in this problem is complicated for disks and spheres, but for hard parallel squares or cubes it is easy to show that the increase in entropy over the single-occupancy theory at the same two-approxiamtion stage is also $0.347Nk$. For squares and cubes the known rigorous lower bounds on the entropy near close packing[3] show that the double-occupancy result lies further from the correct entropy than in one dimension; thus the convergence to the thermodynamic limit, obtained by considering bigger and bigger cells, is slower in two and three dimensions than in one.

Although it is tedious to obtain multiple-occupancy configurational integrals for greater numbers of particles per cell,[18] it is possible to consider the effect of the first two approximations combined for the general hard-rod case, M particles per cell with

$$P_N(\mathbf{r}^N)=\prod_{\text{cells}} P_M(\mathbf{r}^M). \qquad (20)$$

The probability distribution function maximizing the entropy gives the approximation

$$Q_N=M^N[(V/N)-1]^N(M!)^{-N/M}. \qquad (21)$$

In the limit of large M, Eq. (21) passes over to the exact configurational integral, as it must. It is noteworthy that the pressure from Eq. (21) is correct for any M, while the entropy rises monotonically with M to the correct value. The guess that $P_M(\mathbf{r}^M)$ is a product of M delta functions is always better than the true solution of the integral equation, for any value of M. For M as large as 10, however, the error in the entropy from the delta-function approximation is still of the order of $0.1Nk$. This indicates that extension of the free-volume theories by considering bigger and bigger systems of particles confined to rigid containers converges so slowly that analytic work is ruled out.

IV. CONCLUSIONS

That the Lennard-Jones–Devonshire cell model predicts the thermodynamic properties of hard spheres remarkably well is a surprising result. For real solids it was to be expected that the model would be a very good approximation at low temperature because the attractive potential localizes the molecules. In that case the first and third approximations of single occupancy and localization at the cell centers are quite realistic. The accuracy of the second approximation, that the particles move independently in the vicinity of these cell centers (shown to be accurate in the case of real solids at low temperature by harmonic oscillator calculations[19]) gives a clue as to why the cell model works so well for spheres too. The reason is that the thermodynamic properties are only sensitive to the high-frequency motions in the solid. The low-frequency cooperative motions do not affect the thermodynamic properties much, although an instability to a long-wavelength shear mode no doubt leads to melting. Thus, even for spheres the cell model nicely approximates the surroundings of a typical particle, on a short time scale and in the solid phase. One can thus conclude that for *any* pair potential and at all temperatures the Lennard-Jones–Devonshire cell model is the best quick route to accurate solid-phase thermodynamic properties.

In view of the above it should, however, not be surprising that the cell model does not predict the one-particle distribution function well. The exact distribution function can be worked out analytically in one dimension; it does not have the sharp boundaries and

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flat top predicted by the cell model. To calculate distribution functions accurately or to predict melting transitions, it is clearly necessary to consider highly cooperative motions. The inclusion of correlations is, of course, also necessary if the prediction of thermodynamic properties from the cell model is to be improved upon. It will be difficult to make further progress from such a good starting point. The attempt to treat a two- or three-dimensional system more accurately by making only the single-occupancy approximation fails, except in one dimension, because the simplification of single occupancy is not enough to permit an analytic treatment.

The slow convergence of systematic more-particles-per-cell theories is partly due to boundary effects. In molecular dynamics or Monte Carlo calculations, which are after all just such theories treated numerically, it was found that much more rapid convergence to the thermodynamic results was obtained with periodic boundaries than with rigid boundaries. Another advantage of periodic boundary conditions is the automatic introduction of additional correlations between the particles. An attempt in this direction, the correlated cell model for two disks, leads to significant improvements over the Lennard-Jones–Devonshire model. The correlated cell model not only predicted melting at the correct density, but gave an almost exact solid-phase equation of state.

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Isenthalpic Solidification and the Specific Heat of Supercooled Liquid Phosphorus

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Isenthalpic solidification of a unary (one-component) supercooled liquid results in either two-phase invariant equilibrium or in single-phase univariant equilibrium, depending on the degree of supercooling prior to solidification.

When postsolidification univariant equilibrium obtains, a determination of the specific heat at constant pressure, $C_p{}^l$, of the supercooled phase relative to the stable, solid phase can be made by measuring the adiabatic temperature rise during recalescence.

Values of $C_p{}^l$ for highly supercooled phosphorus over the temperature range −1° to +18°C have been determined with this method. No evidence for the changes in molecular association deduced from earlier viscosity data on supercooled phosphorus was found in the temperature variation of the specific-heat function. The enthalpy and specific-heat values determined for supercooled liquid phosphorus agree with published values for the stable liquid above the normal melting point, $T_e=44$°C.

INTRODUCTION

A NUMBER of recent investigations on both the equilibrium and transport properties of various pure monatomic liquids have shown that these properties vary in a smooth and continuous manner as a liquid is cooled from the region of stability above the thermodynamic melting point into the supercooled state. The effects of clustering, or extended local order—if present at all in these supercooled liquids—appear to be below present levels of experimental detection for equilibrium properties such as x-ray structure (atomic radical distribution),[1] specific heat,[2] and mass density[3]; and for transport properties such as electrical[4] and thermal[5] conductivity, and viscosity.[6] Nonetheless, a substantial body of experimental data also exists which indicates various properties exhibiting anomalous behavior in the vicinity of the melting point; these so-called precrystallization phenomena were discussed recently by Turnbull[7] in a comprehensive paper on the liquid state and the liquid–solid transition. Turnbull's words are so apt, that we quote from Ref. 7 directly:

"We note that the thermodynamic crystallization temperature is not an intrinsic property of either the crystalline or the amorphous phase but is rather the temperature at which two quite independent functions

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