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# Studies in Molecular Dynamics. V. High-Density Equation of State and Entropy for Hard Disks and Spheres*

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The equations of state for periodic systems of hard disks and hard spheres in the solid phase have been accurately determined and used to evaluate the coefficients in the expansion of the pressure in powers of the relative free volume, $\alpha=(V-V_0)/V_0$, where $V_0$ is the close-packed volume. For disks $pV/NkT=2/\alpha+1.90+0.67\alpha+O(\alpha^2)$ and for spheres $pV/NkT=3/\alpha+2.56+0.56\alpha+O(\alpha^2)$. These coefficients are compared to cell models, and those models which include correlations between neighboring particles work best. An equivalent expansion of other thermodynamic properties requires the entropy constant to be evaluated in the close-packed limit. This constant is obtained here by integrating the equation of state over the entire density region. The Lennard-Jones–Devonshire cell-theory estimates of the entropy constant are nearly correct; that is, the cell-theory estimate is too small by $0.06Nk$ for disks and too large by $0.24Nk$ for spheres. The pressure difference and hence the entropy difference between the hexagonal and face-centered cubic packings of spheres could not be detected, and thus the relative stability of these two phases remains an open question.

## I. INTRODUCTION

Although the low-density expansion of the thermodynamic properties in terms of the virial coefficients is well known, a similar expansion of high-density properties is poorly established. Part of the reason for this is that for real molecules no high-density asymptotic limit exists about which to expand. To be sure, there exists a natural low-temperature limit about which a power series in temperature can be developed, but the high-density analog of the virial series is an expansion in the relative free volume $\alpha=(V-V_0)/V_0$, where $V_0$ is the close-packed volume. Only artificial molecules with a hard core have such a close-packed limit, although real molecules at high density and temperature can be considered to have an effective hard core.

On computers, however, it is possible to study hard-core particles and show empirically that in the limit of close-packing $pV/NkT$ behaves as $D/\alpha$, where $D$ is the dimensionality of the system. Subsequently this was proven to be exact for finite systems of spheres.[1] This result has long been known to be exact for hard rods[2] and could also be proven for some artificial models even for infinite systems.[3] However an extension of the proof to infinite systems of spheres and a systematic expansion beyond the asymptotic term are both lacking.

Empirical determination of the nature as well as the coefficients of this expansion require precise equation-of-state data because of the dominant asymptotic term. The method of molecular dynamics is particularly suitable for obtaining the high precision required because the use of the virial theorem removes the uncertainties involved in extrapolating the pair distribution to its value at contact of the spheres in the usual Monte Carlo calculations. The high precision is also required to establish the dependence of the expansion coefficients on the number of particles so that the infinite-system expansion coefficients can be estimated. These can then be used as a testing ground for approximate theories of the solid, particularly the various cell theories. These coefficients present, however, primarily a formidable challenge to the theoretician to establish their exact formulation and subsequently their evaluation.

The expansion of the equation of state at high densities does not permit an equivalent expansion of all thermodynamic properties unless the multiplicative constant in the partition function is also calculated. This additional constant, obtained here by integrating the equation of state generated by molecular dynamics all the way from the ideal-gas limit to the close-packed limit, is for hard particles directly related to the entropy at close packing. It provides a further sensitive test for models of the solid state.

Finally, an accurate equation of state for hard spheres gives some hope that the minute difference in thermodynamic properties between hexagonal and face-centered-cubic crystal structures can be established. Such a determination could then decide the intriguing question of the relative stability of these two phases.

## II. PRESSURE

The pressure can be calculated from either the virial theorem or the measured collision rate. The equivalence of these two methods has already been described[4] and thus only the virial-theorem pressure, which has smaller

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TABLE I. Dynamic equation of state for hard disks at high density.

| $V/V_0$ | $N$ | Collisions (millions) | $pV/NkT$ |
|---|---|---|---|
| 1.01 | 7968 | 22.0 | 201.911±0.006 |
| 1.01 | 3944 | 4.0 | 201.908±0.027 |
| 1.01 | 1920 | 2.0 | 201.907±0.036 |
| 1.01 | 870 | 1.8 | 201.905±0.02 |
| 1.03 | 870 | 1.5 | 68.586±0.012 |
| 1.07 | 870 | 2.8 | 30.515±0.004 |
| 1.10 | 870 | 1.8 | 21.965±0.006 |
| 1.10 | 72 | 0.2 | 21.951±0.005 |
| 1.15 | 870 | 2.0 | 15.340±0.014 |
| 1.20 | 7968 | 22.0 | 12.069±0.008 |
| 1.20 | 3944 | 7.2 | 12.070±0.002 |
| 1.20 | 1920 | 2.7 | 12.069±0.005 |
| 1.20 | 870 | 0.3 | 12.065±0.011 |
| 1.20 | 72 | 0.2 | 12.051±0.002 |
| 1.25 | 870 | 2.0 | 10.170±0.013 |

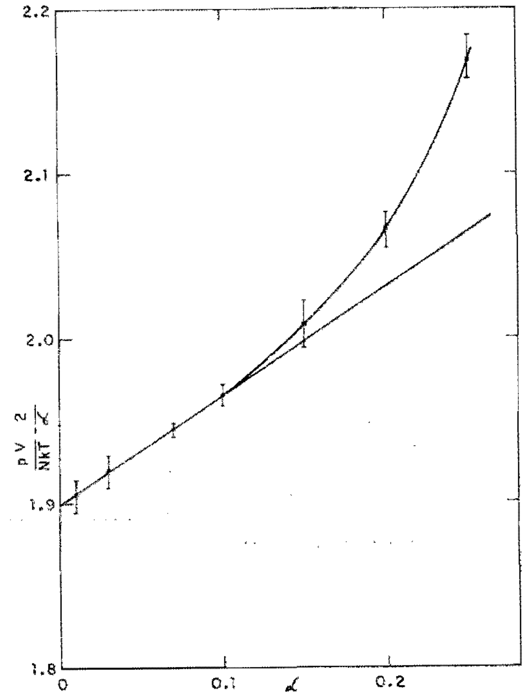

FIG. 1. High-density equation of state for 870 hard disks. The intercept and slope of the straight line shown yield, respectively, $C_0$ and $C_1$. The vertical bars indicate the statistical uncertainty.

fluctuations, has been tabulated. The results are shown in Table I for disks and Table II for spheres.

The uncertainties quoted in these tables are standard deviations from the mean obtained by dividing each run into about 10 batches after the initial part of the run was discarded. The initially perfect lattice configuration took about 20–30 sound-traversal times to relax to equilibrium during which the pressure was observed to be slightly too high.

Most of the results tabulated are for periodic systems of 870 disks and 500 face-centered spheres. Sample data for smaller and larger systems and for hexagonal-packed spheres are also included. These show that the pressure is insensitive to the number of particles (the center of mass is kept fixed) and to the geometry of the hard-sphere lattice. Since the face-centered and hexagonal structures differ only in the arrangement of the first and second neighbors but not in their coordination number and spacing, the small difference in their thermodynamic properties is not unexpected. This is because thermodynamic properties are primarily sensitive to the short-range few-particle (high-fre-

TABLE II. Dynamic equation of state for hard spheres at high density.

| $V/V_0$ | $N^a$ | Collisions (millions) | $pV/NkT$ |
|---|---|---|---|
| 1.005[b] | 4000 | 5.0 | 604.067±0.050 |
| 1.005[b] | 2048 | 2.4 | 604.074±0.106 |
| 1.01 | 500 | 1.0 | 302.560±0.04 |
| 1.02 | 500 | 0.3 | 152.573±0.05 |
| 1.05 | 500 | 0.4 | 62.582±0.01 |
| 1.05 | 512 | 0.3 | 62.581±0.03 |
| 1.15 | 500 | 0.5 | 22.638±0.01 |
| 1.15 | 108 | 0.2 | 22.630±0.002 |
| 1.20 | 500 | 0.3 | 17.680±0.01 |
| 1.25 | 500 | 0.5 | 14.720±0.009 |
| 1.3448 | 500 | 0.3 | 11.542±0.006 |
| 1.42 | 4000 | 3.0 | 10.170±0.010 |
| 1.42 | 2048 | 2.2 | 10.169±0.010 |
| 1.42 | 500 | 0.6 | 10.163±0.023 |
| 1.42 | 108 | 0.1 | 10.10±0.04 |
| 1.42 | 512 | 0.5 | 10.156±0.013 |

[a] All systems are face-centered except the 512 systems which are hexagonal.

[b] This number is actually $(1.01)^{1/2}$.

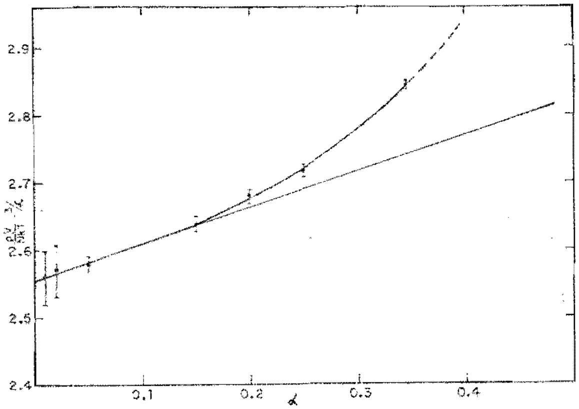

FIG. 2. High-density equation of state for 500 hard spheres. The intercept and slope of the straight line shown yield, respectively, $C_0$ and $C_1$. The vertical bars indicate the statistical uncertainty.

quency) correlations and these are nearly the same in the two crystal structures. It is for this same reason that the number dependence of the results is found to be so small. The data do permit, however, as discussed in the last section, the determination of an upper bound for the free-energy difference between the two crystal structures.

From the high-density equation of state it can be seen that $D/\alpha$ is a good approximation to $pV/NkT$. Figures 1 and 2 illustrate that $(pV/NkT)-(D/\alpha)$ is a well-behaved function that can be expanded in a power series in the relative free volume of the following form:

$$pV/NkT=(D/\alpha)+C_0+C_1\alpha+C_2\alpha^2+C_3\alpha^3+\cdots. \quad (1)$$

The coefficients $C_0$ and $C_1$ are, respectively, the intercept and slope of the data plotted in Figs. 1 and 2. The best estimates of these coefficients are given in Table III. The uncertainty in the data prevents reliable evaluation of the higher coefficients even though positive deviations become evident in both two and three dimensions for $\alpha$ greater than 0.1.

The above expansion is the high-density analog of the low-density virial expansion. Since this series has not been justified theoretically, comparison can only be made at present to various models of the solid. These models are all variations of cell theories. The best known of these is the Lennard-Jones–Devonshire (LJD) cell theory[5] which ignores all correlation between neighboring particles by keeping the nearest neighbors localized at their most probable positions, the lattice sites. Because all particles are not treated on an equal footing, the LJD theory is not self-consistent. Self-consistency is attained by letting each particle share equally the free space available, which leads to the self-consistent free-volume (SCFV) equation of state[6]

$$pV/NkT=[1-(V_0/V)^{1/D}]^{-1}. \quad (2)$$

Another cell theory, called here the correlated-cell theory,[7] takes as the opposite extreme to the LJD theory the view that some of the neighboring particles are completely correlated with the central particle. Finally, comparison will be made to the cell-cluster theory[8] of which the LJD model is the zero-order approximation. In this theory, cells of increasingly larger number of particles are systematically evaluated.

The values of $C_0$ and $C_1$ for both disks and spheres from molecular dynamics are compared in Table III to those evaluated by the above cell theories. The correlated-cell and cell-cluster models give results quite close to dynamic values. Tables IV and V give a more detailed comparison of the equations of state at interpolated values of $V/V_0$. The accuracy of the correlated-cell model is shown in these tables to be such that $pV/NkT$ deviates by no more than 0.5 at any solid density from the computer results in either two or three dimensions. The poorer agreement of either the LJD or SCFV model is due to the too-regular shape of the free volume of the cell. As a result, the pressure predicted by those models is too low. Density fluctuations and/or correlations lead to a more complex free volume which grows more rapidly as the system expands. This leads to a higher pressure since the pressure is proportional to the volume derivative of the free volume. Thus the correlated-cell model owes its success to the spikes added to the LJD free volume, two for disks and four for spheres. These spikes grow in size more rapidly than the LJD part of the free volume as the density is reduced, and thus the pressure is higher.

## III. ENTROPY

Although there exist statistical-mechanical expressions for the thermodynamic quantities requiring derivatives of the partition function (such as the pressure and the internal energy), no similar expression is available for the free energy. The free energy, or equivalently, the entropy, involves evaluation of the partition function itself. Traditionally the entropy is evaluated in statistical mechanics by thermodynamic manipulation of the pressure and internal energy. For hard particles the entropy may thus be obtained from an integration of the pressure with respect to the volume. The entropy at close packing is then obtained by an integration of the equation of state all the way from the perfect gas to the high-density limit. From a knowledge of the entropy at close packing coupled with the expansion of the equation of state given in the last section, it is then possible to expand all thermodynamic properties in terms of the relative free volume.

Although there exist alternative and more direct ways to evaluate the entropy and free energy, these methods all prove impractical, at least at high density. The excess chemical potential over that of a perfect gas can easily be related to the probability of successfully adding an additional particle to the system.[9] At high densities, however, that probability becomes so small that without enormously long runs, the excess chemical potential cannot be obtained very accurately, and, in any case, in the solid phase this method is not applicable. Another way would be to measure the pair

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[5] By the phrase "Lennard-Jones–Devonshire cell theory" we mean the unsmoothed free volume, first tabulated for hard spheres by R. J. Buehler, R. H. Wentorf, J. O. Hirschfelder, and C. F. Curtiss, J. Chem. Phys. **19**, 61 (1951). The two-dimensional analog of the Lennard-Jones–Devonshire cell theory is discussed in Ref. 7.

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

TABLE III. Coefficients in the high-density expansion of the thermodynamic properties of hard disks and spheres.

| | Disks | | | Spheres | | |
|---|---|---|---|---|---|---|
| | $S_0$ | $C_0$ | $C_1$ | $S_0$ | $C_0$ | $C_1$ |
| Dynamics | +0.06±0.01 | 1.90±0.01 | 0.67±0.07 | −0.24±0.04 | 2.56±0.02 | 0.56±0.08 |
| SCFV | −1.386 | 1.500 | −0.125 | −2.079 | 2.000 | −0.222 |
| LJD | 0.000 | 1.556 | −0.086 | 0.000 | 2.125 | −0.149 |
| Correlated | −0.059 | 1.889 | 0.765 | −0.059 | 2.333 | 0.167 |
| Cell cluster | +0.011 | 1.90 | ... | −0.2165[a]<br>−0.2157[b] | 2.449[a]<br>2.458[b] | ... |

[a] Face-centered lattice—three-particle cluster for $S_0$, two-particle cluster for $C_0$.

[b] Hexagonal close-packed lattice—three-particle cluster for $S_0$, two particle cluster for $C_0$.

TABLE IV. Interpolated values of the equation of state of hard disks compared to various models, and the entropy in the solid phase.

| | | $pV/NkT$ | | | |
|---|---|---|---|---|---|
| $\alpha$ | $\Delta S/Nk$[a] | Dynamics | SCFV | LJD | Correlated cell |
| 0.01 | −0.0010 | 201.905 | 201.499 | 201.555 | 201.897 |
| 0.02 | −0.0019 | 101.912 | 101.498 | 101.554 | 101.905 |
| 0.03 | −0.0027 | 68.585 | 68.163 | 68.220 | 68.580 |
| 0.04 | −0.0036 | 51.925 | 51.495 | 51.552 | 51.923 |
| 0.05 | −0.0042 | 41.933 | 41.494 | 41.551 | 41.932 |
| 0.06 | −0.0049 | 35.273 | 34.826 | 34.884 | 35.276 |
| 0.07 | −0.0054 | 30.519 | 30.063 | 30.121 | 30.524 |
| 0.08 | −0.0059 | 26.956 | 26.490 | 26.549 | 26.964 |
| 0.09 | −0.0064 | 24.186 | 23.711 | 23.770 | 24.198 |
| 0.10 | −0.0067 | 21.972 | 21.488 | 21.548 | 21.998 |
| 0.15 | −0.0075 | 15.354 | 14.816 | 14.877 | 15.397 |
| 0.20 | −0.0061 | 12.084 | 11.477 | 11.541 | 12.172 |
| 0.25 | −0.0015 | 10.171 | 9.472 | 9.537 | 10.345 |

[a] $\Delta S/Nk$ is the configurational entropy relative to the close-packed limit $=(S/Nk)-[S_0+2\ \ln\alpha+\ln(V_0/N)]$.

TABLE V. Interpolated values of the equation of state of hard spheres compared to various models, and the entropy in the solid phase.

| | | $pV/NkT$ | | | |
|---|---|---|---|---|---|
| $\alpha$ | $\Delta S/Nk$ | Dynamics | SCFV | LJD | Correlated cell |
| 0.01 | −0.004 | 302.559 | 301.998 | 302.124 | 302.335 |
| 0.02 | −0.009 | 152.564 | 151.996 | 152.122 | 152.337 |
| 0.03 | −0.013 | 102.568 | 101.993 | 102.121 | 102.339 |
| 0.04 | −0.017 | 77.573 | 77.991 | 77.119 | 77.341 |
| 0.05 | −0.021 | 62.577 | 61.989 | 62.118 | 62.343 |
| 0.06 | −0.025 | 52.582 | 51.987 | 52.116 | 52.345 |
| 0.07 | −0.029 | 45.445 | 44.842 | 44.972 | 45.204 |
| 0.08 | −0.032 | 40.093 | 39.483 | 39.614 | 39.850 |
| 0.09 | −0.036 | 35.932 | 35.314 | 35.446 | 35.685 |
| 0.10 | −0.040 | 32.605 | 31.979 | 32.111 | 32.355 |
| 0.15 | −0.056 | 22.640 | 21.969 | 22.105 | 22.369 |
| 0.20 | −0.071 | 17.683 | 16.960 | 17.099 | 17.387 |
| 0.25 | −0.084 | 14.736 | 13.950 | 14.094 | 14.408 |
| 0.30 | −0.093 | 12.801 | 11.942 | 12.089 | 12.435 |
| 0.35 | −0.101 | 11.452 | 10.505 | 10.656 | 11.040 |

[a] $\Delta S/Nk$ is the configurational entropy relative to the close-packed limit $=(S/Nk)-[S_0+3\ \ln(2\alpha/3)+\ln(V_0/N)]$.

distribution at zero separation for two particles which do not interact with each other but which do interact normally with the other particles in the system.[10] The difficulty with this scheme is that the distribution function at small distances is hard to measure accurately.

A variation of the above methods (all of which alter the interaction between particles by either coupling particles differently or equivalently adding an external field) can, however, be used to measure the entropy in the solid phase. This is the calculation of the equation of state under the constraint of single occupancy.[11] This method, although still requiring the cumbersome integration of an equation of state (or equivalently integrating over a coupling constant), avoids the uncertainty caused by integrating the actual equation of state through the melting transition into the solid phase. This uncertainty is caused by the distortion of the phase-transition region in molecular dynamics studies of small systems which do not allow the tie line connecting the solid and fluid phases to be determined accurately. The single-occupancy constraint circumvents this difficulty and hence allows the tie line to be determined by artificially stabilizing the solid phase to low density. The equation of state can then be reliably integrated into the actual solid-phase region, where, at high enough density, the entropy will accurately represent the real one, since the single-occupancy approximation becomes more precise as the density increases.

The entropy is determined here by integrating the equation of state from the low-density limit to the volume of interest,

$$\frac{S}{Nk}=\ln\frac{Ve}{N}-(2N)^{-1}\ln 2\pi N-\int_{V/V_0}^{\infty}\left(\frac{pV_0}{NkT}-\frac{V_0}{V}\right)d\,\frac{V}{V_0}, \tag{3}$$

where the ideal-gas entropy $N^{-1}\ln(V^N/N!)$ has been used as the reference state. The first two terms on the right-hand side of the above expression represent the Stirling approximation to order $N^{-1}\ln N$ of the perfect-gas term. Retention of the logarithmic term is necessary in precise work. Numerical integration of the equation of state can be avoided over most of the fluid range by using a Padé approximant to the configurational integral which is chosen to be consistent with the first six virial coefficients; for disks

$$Q_N=\frac{V^N}{N!}\exp\left(-N\left[\frac{1-0.2781515x+0.0059612x^2}{1-0.6691537x+0.0901912x^2}\right]\right), \tag{4}$$

and for spheres

$$Q_N=\frac{V^N}{N!}\exp\left(-N\left[\frac{1-0.1107519x+0.0046923x^2}{1-0.4232519x+0.0413087x^2}\right]\right), \tag{5}$$

where $x$ is the product of the second virial coefficient and the number density, that is, $(\frac{1}{2}\pi\sigma^2)N/V$ for disks and $(\frac{2}{3}\pi\sigma^3)N/V$ for spheres. The pressure and entropy calculated from the Padé approximants are given in Table VI and VII and compared to those given by the cell theory, Born–Green theory,[12] and Percus–Yevick[13] theory. The comparison illustrates the well-known fact that cell theories are poor in the fluid state, and that the integral equations give relatively good entropies except at the highest fluid densities inasmuch as they reproduce the first few virial coefficients accurately.

From the end of the validity of the Padé approximant to the freezing density of the fluid, that is, about the highest 10% of the fluid pressure range, the equation-of-state integral was performed numerically. Although the freezing density for 870 disks has been accurately located[14] by molecular dynamics calculations, the same could not be achieved for a system of spheres because the fluid and solid phases could not be made to coexist for small numbers of spheres. The tie line for spheres

TABLE VI. Thermodynamic functions for hard disks in the fluid phase as determined from the Padé approximant. $S(\mathrm{P})$ and $S(\mathrm{FV})$ are the entropies according to the Padé approximant and to the self-consistent free-volume theory, respectively. $S(\mathrm{I})$ is the configurational entropy of an ideal gas at the same number density.

| Density $(V_0/V)$ | Padé $pV/NkT$ | SCFV $pV/NkT$ | $\frac{S(\mathrm{P})-S(\mathrm{FV})}{Nk}$ | $\frac{S(\mathrm{P})-S(\mathrm{I})}{Nk}$ |
|---|---|---|---|---|
| 0.00 | 1.000 | 1.000 | 0.000 | 0.000 |
| 0.05 | 1.098 | 1.288 | 0.412 | −0.094 |
| 0.10 | 1.211 | 1.462 | 0.565 | −0.195 |
| 0.15 | 1.343 | 1.632 | 0.675 | −0.305 |
| 0.20 | 1.498 | 1.809 | 0.762 | −0.424 |
| 0.25 | 1.683 | 2.000 | 0.831 | −0.555 |
| 0.30 | 1.904 | 2.211 | 0.888 | −0.698 |
| 0.35 | 2.173 | 2.449 | 0.934 | −0.857 |
| 0.40 | 2.501 | 2.721 | 0.967 | −1.035 |
| 0.45 | 2.909 | 3.038 | 0.982 | −1.234 |
| 0.50 | 3.423 | 3.414 | 0.993 | −1.461 |
| 0.55 | 4.083 | 3.870 | 0.985 | −1.721 |
| 0.60 | 4.947 | 4.436 | 0.953 | −2.025 |
| 0.65 | 6.107 | 5.161 | 0.898 | −2.384 |
| 0.70 | 7.708 | 6.122 | 0.806 | −2.818 |
| 0.75 | 9.999 | 7.464 | 0.666 | −3.354 |

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TABLE VII. Thermodynamic functions for hard spheres in the fluid phase as determined from the Padé approximant. $S(\mathrm{P})$ and $S(\mathrm{FV})$ are the configurational entropies according to the Padé approximant and to the self-consistent free-volume theory, respectively. $S(\mathrm{I})$ is the configurational entropy of an ideal gas at the same number density. BG and PY represent, respectively, the results from the Born-Green and Percus-Yevick theories.

| Density $(V_0/V)$ | Padé $pV/NkT$ | SCFV $pV/NkT$ | $\frac{S(\mathrm{P})-S(\mathrm{FV})}{Nk}$ | $\frac{S(\mathrm{P})-S(\mathrm{I})}{Nk}$ | $\frac{S(\mathrm{BG})-S(\mathrm{I})}{Nk}$ | $\frac{S(\mathrm{PY})-S(\mathrm{I})}{Nk}$ |
|---|---|---|---|---|---|---|
| 0.00 | 1.000 | 1.000 | 0.000 | 0.000 | 0.00 | 0.000 |
| 0.05 | 1.163 | 1.583 | 1.223 | −0.155 | −0.16 | −0.155 |
| 0.10 | 1.359 | 1.866 | 1.545 | −0.326 | −0.33 | −0.326 |
| 0.15 | 1.598 | 2.134 | 1.758 | −0.516 | −0.51 | −0.514 |
| 0.20 | 1.888 | 2.408 | 1.911 | −0.726 | −0.72 | −0.722 |
| 0.25 | 2.244 | 2.702 | 2.018 | −0.961 | −0.94 | −0.954 |
| 0.30 | 2.682 | 3.025 | 2.096 | −1.225 | −1.20 | −1.211 |
| 0.35 | 3.225 | 3.387 | 2.136 | −1.524 | −1.47 | −1.499 |
| 0.40 | 3.903 | 3.799 | 2.141 | −1.864 | −1.78 | −1.822 |
| 0.45 | 4.756 | 4.279 | 2.108 | −2.253 | −2.10 | −2.188 |
| 0.50 | 5.841 | 4.847 | 2.033 | −2.702 | −2.45 | −2.602 |
| 0.55 | 7.234 | 5.535 | 1.907 | −3.226 | −2.82 | −3.076 |
| 0.60 | 9.048 | 6.387 | 1.720 | −3.843 | −3.19 | −3.622 |
| 0.65 | 11.444 | 7.476 | 1.458 | −4.577 | −3.62 | −4.255 |

had thus to be estimated from other considerations. One of the most convincing of these is the comparison of molecular dynamics behavior of a small number of simulated argon molecules to the melting behavior of the actual system.[15] This showed that the highest density at which the fluid could be generated on the computer from the initial solid configuration (which corresponds for 500 hard spheres to a value of $V/V_0=1.50$) leads to a freezing density for an infinite hard-sphere system of $V/V_0=1.49$, since by analogy the argon melting volume was about 1% smaller than the highest transition density. The melting density of the solid corresponding to the freezing density is $V/V_0=1.35$ as illustrated in Fig. 3. A strong argument in favor of this melting-density value is furnished by the Lindemann melting rule[16] which predicts for all real face-centered-cubic crystals that $V/V_0=1.37\pm0.01$ at melting, where the maximum amplitude of motion is interpreted as the mean radius of the exact LJD free volume. Confidence in the validity of Lindemann's rule for hard particles is based on the correct prediction of the melting volume for disks.

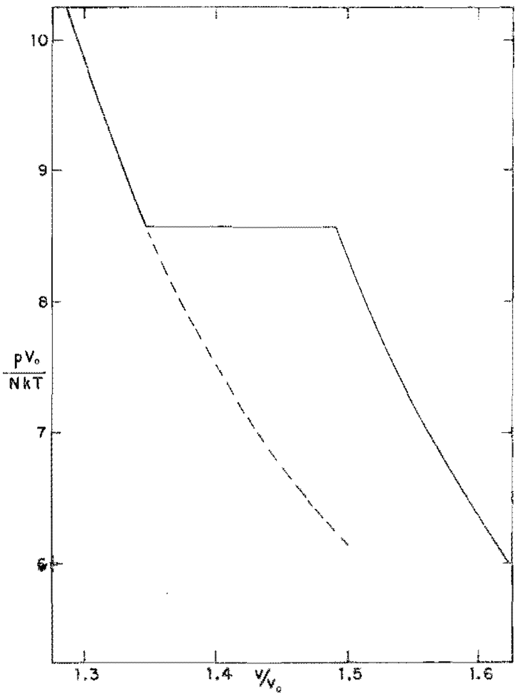

FIG. 3. Equation of state for hard spheres in the vicinity of the phase transition with the tie line drawn in.

Continuation of the integration of the equation of state over the solid region is more conveniently done if the reference state is changed since the pressure and hence the entropy become infinite in the close-packed limit. As the reference state the LJD cell theory is chosen. Here, as previously discussed, the asymptotically correct volume-dependent part of the partition function is multiplied by the volume per particle at close packing: $(V_0/N)^N(2\alpha/D)^{DN}$. The multiplying factor of the volume per particle, though of the correct dimensions, does not have the correct coefficient. Thus the power-series expansion in the relative free volume of the partition function must be written as

$$Q_N=(V_0/N)^N(2\alpha/D)^{DN}\times\exp[N(S_0+S_1\alpha+S_2\alpha^2+\cdots)], \quad (6)$$

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

[16] F. A. Lindemann, Physik. Z. **11**, 609 (1910).

TABLE VIII. Entropy calculations.

| $V/V_C$ | $S/Nk - (S/Nk)_{\text{ideal}}$ | $S/Nk - \ln(V_0/N) - D\ln(2\alpha/D)$ |
|---|---|---|
| | 870 disks | |
| $\infty$ | $-0.005$ | |
| 1.312 (fluid) | $-3.504$ | |
| 1.266 (solid) | $-3.823$ | 0.061 |
| 1.000 | | 0.060 |
| | 500 spheres | |
| $\infty$ | $-0.008$ | |
| 1.49 (fluid) | $-4.92$ | |
| 1.35 (solid) | $-6.01$ | $-0.34$ |
| 1.00 | | $-0.24$ |

where $\exp(NS_0)$ is the correction factor at close packing. It is written in this form so that the constant $S_0$ measures the deviation of the close-packing entropy from that predicted by the LJD theory. The higher coefficients in powers of $\alpha$ can be easily related to the coefficients in the pressure expansion:

$$S_1 = C_0 - D,$$

$$2S_2 = C_1 - C_0 + D,$$

$$3S_3 = C_2 - C_1 + C_0 - D, \text{ etc.}$$

Graphical integration of the difference between the molecular dynamics and LJD equation of state in the solid phase permits the evaluation of $S_0$. These entropy calculations are summarized in Table VIII for 870 disks and 500 spheres. The reference state in the fluid phase is the ideal-gas state and is taken to be the infinite-system ideal entropy so that the low-density limiting entropy consists of the small $N^{-1}\ln 2\pi N$ term for 870 and 500 particles, respectively. Values of the entropy at the freezing volume obtained by integrating the fluid branch are shown. The table also contains the entropy of fusion obtained by integrating across the tie line. At the melting volume the reference state is changed to that of the LJD theory by subtracting $\ln[(V_0/V)e^{-1}(2\alpha/D)^D]$. Subsequent integration over the solid phase leads to the values of $S_0$ shown. The entropy in the solid phase is shown in more detail in Tables IV and V, where the reference state is the actual entropy of the solid at close packing.

The uncertainty in the value of $S_0$ is indicated in Table III. For both disks and spheres the inaccuracy in the equation of state leads to an error of 0.005 in the entropy for both the solid and fluid phase. For disks there is a small additional error of 0.001 due to the uncertainty of locating the tie line, thus leading to a maximum total uncertainty of 0.01. Confidence in this error analysis is gained from the preliminary single-occupancy calculation of the entropy at melting density, $-3.838$, which is within 0.015 of the results given in Table VIII. For spheres the error caused by the tie line location is less certain. A reasonable estimate of the error in locating the freezing density is $V/V_0 = 1.49 \pm 0.01$, leading to an entropy uncertainty of 0.03 and to a maximum total error in $S_0$ of 0.04. The preliminary single-occupancy entropy at the melting volume, $-6.0$, is again within the error limits quoted.

Before comparing the value of $S_0$ to that predicted by various theories, the question of the dependence of the entropy calculation on the number of particles must be discussed in order to obtain thermodynamically significant values. As has already been observed from the pressure data for different sized systems in Tables I and II, the number dependence of the solid equation of state is hidden within the statistical accuracy of the results, once the system is larger than about 100 particles. Similar observations were made previously about the fluid equation of state. Thus, the most significant number dependence of the entropy in the fluid phase is the correction of $N^{-1}\ln 2\pi N$ due to the Stirling approximation. Even this correction should, however, be absent in the solid phase, since the localization (or distinguishability) of the particles removes the $N!$ factor. That this is indeed so has been shown in a previous paper in this series[4] where the dependence of the location of the tie line on the number of particles was discussed. The location of the tie line is governed by the communal entropy of the number of particles in the periodic cell, which means in effect that there is also a Stirling approximation correction which exactly cancels that of the fluid phase. An alternative way to understand this result is from the elastic-continuum view which can be applied once the system is large enough. From a continuum standpoint certain long wavelength modes are left out in any calculation of finite systems which contribute again an entropy of order $N^{-1}\ln N$. This contribution occurs, however, for the reference state as well, so that the entropy differences are unaffected to first order between finite and infinite systems.

## IV. DISCUSSION

The over-all impression of the comparison presented in Table III between the molecular dynamics results and those of various cell models is that the cell theories are good first-order approximations to solid-state properties. The basis for the accuracy of the cell models lies in the observation that the short-range, few-particle correlations are of primary importance to the thermodynamic properties.

The accuracy of the LJD theory in calculating the entropy at close packing for disks is schematically demonstrated in Fig. 4. The actual free volume is only 6% larger than for the LJD theory. The self-consistent theory, however, has a free volume which is only $\frac{1}{4}$ of that for the LJD theory, and thus is badly in error, because the particles are not as localized as required by the self-consistency criterion. In one dimension localization is even less, as might be expected, so that even the LJD theory restricts the accessible free volume too much. The actual entropy at close packing is 0.307 larger than the LJD results.[17] On the other hand, in three dimensions the situation is reversed, namely the LJD theory predicts too large a free volume by 22%; however, the self-consistent free volume is still too small by a factor of about 6. These results reflect the enhanced localization as the number of nearest neighbors and the number of dimensions increases.

The correlated cell model, considering its simplicity, gives the best results. One of the primary reasons for this is that this model predicts phase transitions at approximately the right density and is thus believed to contain the qualitatively correct mechanism for melting. Furthermore, the quantitative aspects of the equation of state are remarkably good, as can be seen from the calculations of $C_0$ and $C_1$. The value of the entropy at close packing is also quite accurate. There is an element of arbitrariness in the calculation of $S_0$ which does not exist for the equation of state. The value of $S_0$ has been calculated here in the spirit of the molecular dynamics calculation in which the correlated cell is considered as a two-particle model with periodic boundary conditions and a fixed center of mass.

The final comparison is to the cell-cluster theory. This theory is the only systematic attempt to calculate corrections to the LJD theory by adding on a series of correction terms involving cells containing two, three, four, etc., particles. The initial formulation[18] of this theory got bogged down in the evaluation of some complicated combinatorial factors. The first correction term could, however, be calculated and did not improve agreement with the machine results. A reformulation of this theory[8] made the combinatorial problem manageable, and the first four correction terms have been evaluated with the result[19] that for disks $S_0$ changes from 0.00000 to 0.01386 to $-0.00047$ to $+0.00686$ to 0.01108 as increasingly larger clusters are considered. The difficulty that these results present is that although they show indeed small corrections to the LJD theory and seemingly good convergence, the deviation from the LJD theory is almost an order of magnitude smaller than the molecular dynamics calculations.

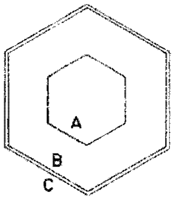

FIG. 4. Schematic diagram of the relative sizes of the hard-disk free volume. (A) Self-consistent free volume (SCFV); (B) Lennard-Jones–Devonshire free volume (LJD); (C) Free volume computed from molecular dynamics data.

In order to resolve this discrepancy, the molecular dynamic results have been carefully examined and the error quoted for disks is conservative. Although an error of 0.01 in entropy appears small, it represents in terms of the equation of state a considerable change. The extrapolation to infinite system was estimated to yield at most a correction of 0.006 and in the direction of making the discrepancy larger. This is because any finite system is likely to underestimate the entropy relative to an infinite system. Thus the seemingly good convergence of the cluster series must be questioned. Because surface contributions of these small clusters are larger, it was previously suggested that a better behaved series might be obtained if only the most compact clusters of a given size are considered. Although this is indeed the case, judged by the series 0.0000, 0.00231, 0.00682, 0.01065, and 0.01178, the final result is still far from the molecular dynamics answer. The surface argument suggests that this series ought to be extrapolated to infinity by $N^{-1/2}$ in two dimensions. Because the extrapolation from the largest cluster of five so far considered to infinite systems is so large, the cell-cluster and molecular dynamic results cannot be considered inconsistent.

The slow convergence of the cell-cluster series must be ascribed to the slow disappearance of the boundary effect if hard walls made up of particles are used. Partial evidence in support of this view has been obtained from a comparison of molecular dynamics calculation of 870 disks with periodic and with hard walls of particles boundary conditions. Even for such a large system of particles, the equations of state differ considerably; for example, the tie line is considerably displaced. In general the hard walls of particles can be said to induce more solidlike character into the system compared to the periodic boundary condition case and thus the entropy of the system is lowered. This argument may account for the lower $S_0$ values of the cell-cluster theory in two dimensions, and suggests that a cell-cluster calculation involving a periodic boundary may converge more rapidly. Certainly the molecular dynamic calculation with periodic boundary conditions indicate no strong number dependence, and the correlated cell results indicate that even for such a very small system already accurate results are obtained.

The cell-cluster theory gives encouragingly good results for the equation of state as the comparison for $C_0$ shows.[20] The difference between $C_0$ for face-centered cubic and hexagonal close packing is realistically small in the low-order cluster expansion worked out so far. Although the cell-cluster theory predicts that the

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

[18] Z. W. Salsburg, E. G. D. Cohen, B. C. Rethmeier, and J. de Boer, Physica **23**, 407 (1957).

[19] Z. W. Salsburg, W. G. Rudd, and F. H. Stillinger, J. Chem. Phys. **47**, 4534 (1967). The first three of these numbers can be calculated from results given in Ref. 8.

[20] The hard-sphere and hard-disk values for $C_0$ were kindly furnished by Z. W. Salsburg.

hexagonal lattice is more stable,[21] the molecular dynamics calculation gives no detectable difference in $C_0$ and the difference in $S_0$ can be no larger than 0.04, the uncertainty in the solid-state entropy calculation.

Although this paper has emphasized comparison of the hard-particle results in the solid to various models, it must be pointed out that very useful comparison to experiment can also be made. For example, the entropy of fusion for spheres calculated to be $1.17Nk$ agrees closely with that for rare gases. In fact, the hard-sphere model of solids, representing the anharmonic extreme, is likely to be a more accurate model of solids at high temperature, that is near melting, than the conventional harmonic-oscillator treatments.

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[21] F. H. Stillinger and Z. W. Salsburg, J. Chem. Phys. **46,** 3962 (1967).