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Number Dependence of Small-Crystal Thermodynamic Properties. I*

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The approach of small-crystal thermodynamic properties to the large-crystal limit of thermodynamics is studied numerically. We calculate the number dependence of the vibrational entropy for two- and three-dimensional crystallites by direct integration of the canonical partition function. A simple functional representation of the data shows that small-crystal entropies lie within 10% of the predictions of macroscopic thermodynamics.

I. INTRODUCTION

The intrinsic "number dependence" of thermodynamic properties is important in two kinds of calculations. One can either try to deduce large-system properties from those of small systems, or one can estimate small-system properties from thermodynamics. The small-to-large extrapolation is routinely carried out in analyzing the results of computer experiments on small systems.¹ The systems are usually periodic and the number dependence of their "intensive" thermodynamic quantities is usually of order $1/N$ or $\ln N/N$ for N particles. The reverse problem of large-to-small extrapolation is more difficult; this is the ambitious goal of nucleation theorists who must estimate the properties of individual drops or crystallites from gross thermodynamic information.

The effects of small-system number dependence are minimized in the periodic boundary case. Small systems with free boundaries have a larger more complicated number dependence due to the presence of surface effects. In addition to the $1/N$ and $\ln N/N$ terms typical of periodic crystals one finds "surface" and "edge" corrections of order $(1/N)^{1/3}$ and $(1/N)^{2/3}$. In bulk-phase calculations one wants to calculate per particle intensive properties. The small-system deviations are then simply a nuisance which must be recognized and allowed for. In nucleation theory one instead deals specifically with small systems; clusters containing only a few molecules are sufficient to "nucleate" a growing phase. The so-called "critical nucleus" of a new phase is one large enough to grow spontaneously, rather than to subside, after initial formation from thermal fluctuations. In typical applications the minimum size of the critical nucleus is 100 molecules, so that small- N corrections to the predictions of bulk-phase thermodynamics are significant. The corrections are crucial in rate calculations because the rate at which nuclei are formed is directly

proportional to the critical-nucleus partition function. An error of only $\frac{1}{2}kT$ per molecule in the Helmholtz free energy leads to an error of order 10^{10} in the nucleation rate!

For several decades, it has been common to use classical thermodynamics to estimate partition functions for small crystals and liquid droplets.² But about 10 years ago this use of thermodynamics began to be questioned. How well *does* classical thermodynamics describe systems of 100 particles? This question remains a subject of controversy and discussion³ and is not likely to be resolved theoretically, for the errors in good theoretical calculations of bulk-phase thermodynamic properties are often as large as $\frac{1}{4}NkT$. Direct measurement of nucleation rates has not so far been achieved. The rates inferred from nozzle expansion experiments⁴ are apparently inconsistent with those inferred from cloud chamber experiments.⁵

The importance of "nonthermodynamic terms"—that is, the difference between actual small-system properties and those estimated by macroscopic thermodynamics—*can* be determined by a numerical study of the simplest possible case incorporating them. Accordingly we have evaluated the thermodynamic properties of classical, close-packed, defect-free harmonic crystals, with nearest-neighbor interactions, over a wide range of crystal sizes ($N \leq 500$). For such crystals the *energy* can be determined by counting the number of nearest-neighbor pairs. The *entropy* is not a local property but rather a collective one and has to be determined by evaluating the corresponding partition function. We have worked out the partition functions for small crystals in two independent ways: (1) The traditional approach of lattice dynamics in which the dynamical matrix is diagonalized and the partition function is expressed as a product of normal-mode partition functions; (2) direct evaluation of the partition function for a crystal constrained from translational and rotational motion. The latter method

has been seldom used but deserves greater use because it is (1) faster and (2) readily applicable to free energy calculations for quantum crystals, surfaces, vacancies, and dislocations. Direct evaluation involves working out a single determinant. Matrix diagonalization is considerably slower.

To follow the trend with dimensionality from the understood but artificial one-dimensional crystal to the more realistic and complicated three-dimensional case, we include also intermediate two-dimensional results.

The model and methods used to treat it are described in Sec. II. Numerical results, and the conclusions which we draw from them appear in Secs. III and IV.

II. HARMONIC CRYSTAL CALCULATIONS

In a nearest-neighbor "harmonic" crystal the interaction energy of two neighboring particles i and j is taken to be quadratic in the relative particle displacements ($\delta \equiv \delta_i - \delta_j$) from the minimum-energy separation ($\Delta \equiv \mathbf{r}_i - \mathbf{r}_j$),

$$\phi_{ij} \equiv -\epsilon + \frac{1}{2}\kappa(\delta \cdot \Delta)^2 / \Delta^2. \quad (1)$$

Provided that the displacements are small, so that terms of order δ^3 and higher can be ignored, the potential (1) is equivalent to the Hooke's law potential $\phi_{\text{Hooke}} = -\epsilon + \frac{1}{2}\kappa(|\Delta + \delta| - \Delta)^2$. In our work we consider the triangular close-packed lattice in two dimensions (in which each particle has no more than six nearest neighbors) and the face-centered-cubic close-packed lattice in three dimensions (in which each particle has no more than 12 nearest neighbors). All nearest-neighbor pairs of particles interact with the potential (1) so that ϵ and κ are constants. In classical harmonic crystals the thermodynamic energy is independent of κ and the entropy is independent of ϵ .

The thermodynamic properties of an N -particle crystal in a volume V at temperature T follow from the canonical partition function:

$$Z(N, V, T) = \exp(-\Phi_o/kT) Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}. \quad (2)$$

Φ_o is the static-lattice potential energy, $-\epsilon$ times the number of nearest-neighbor pairs; Z_{trans} , Z_{rot} , and Z_{vib} are the translational, rotational, and vibrational partition functions. For *classical* crystals the various partition functions are:

$$\begin{aligned} Z_{\text{trans}} &= V(2\pi Nm kT)^{(1/2)D} / h^D \text{ in } D \text{ dimensions;} \\ Z_{\text{rot}} &= (2\pi/\sigma)(2\pi I kT)^{1/2} / h \text{ for } D=2; \\ Z_{\text{rot}} &= (8\pi^2/\sigma)(2\pi I kT)^{3/2} / h^3 \text{ for } D=3; \\ Z_{\text{vib}} &= \prod (kT/h\nu). \end{aligned} \quad (3)$$

The symbols in (3) have their usual meaning. In the rotational partition functions σ is the symmetry number and I the moment of inertia. For our three-dimensional crystals the three moments of inertia are all equal (because of the particular shapes we

choose, tetrahedra and cubes) so that $I_1 = I_2 = I_3 = I$. In the vibrational partition functions there are $N-1$, $2N-3$, and $3N-6$ terms in the frequency product in one, two, and three dimensions, respectively. The vibrations together with the rotational and translational contributions give the equipartition energy of $\frac{1}{2}kT + 0 + (N-1)kT$ for $D=1$, $kT + \frac{1}{2}kT + (2N-3)kT$ for $D=2$, and $\frac{3}{2}kT + \frac{3}{2}kT + (3N-6)kT$ for $D=3$. The total energy is this thermal part plus the static lattice contribution, the number of nearest-neighbor pairs times $-\epsilon$.

The entropy, unlike the energy, depends on the vibration frequencies. It is usually calculated by diagonalizing the dynamical matrix and forming the frequency product $\prod (kT/h\nu)$. For a classical crystal the individual frequencies are not required and the product of frequencies can be found most simply by direct integration of the canonical partition function. The integration is carried out by noting that if the potential energy can be written as a nonvanishing quadratic form in the particle coordinates, $Q = \Phi(\delta_1, \delta_2, \dots, \delta_N)$, then the partition function is proportional to the inverse square root of the determinant of the coefficients in Q :

$$\begin{aligned} Z &= \exp(-\Phi_o/kT) \Lambda^{-DN} \int \dots \int \exp(-Q/kT) d\delta_1 \dots d\delta_N \\ &= \exp(-\Phi_o/kT) \Lambda^{-DN} (\pi kT)^{(1/2)DN} (\det)^{-1/2}, \end{aligned} \quad (4)$$

where Λ is the deBroglie wavelength $h/(2\pi m kT)^{1/2}$. The simple expression (4) is not actually useful as it stands for crystals with either free or periodic boundaries. In both cases \det vanishes. The vanishing corresponds to the existence of displacements for which the quadratic form furnishes no restoring force: translation of the crystal, or, in the free boundary case, rotation of the crystal. To use (4) these singular motions have to be constrained and the constraint can be applied in *any convenient way*. In particular, in the three-dimensional case, it is convenient to fix one of the particles at the origin ($\delta_x = \delta_y = \delta_z = 0$), eliminating translation; a second particle can then be fixed along the x axis at an average distance r from the origin ($\delta_y = \delta_z = 0$; x unrestricted), eliminating two rotational degrees of freedom; finally a third particle can be constrained to the plane $z=0$ ($\delta_z = 0$; x and y unrestricted), eliminating the last rotational degree of freedom. If this last particle lies an average distance s from the x axis then the configurational integration over the six coordinates can be carried out to give $V(4\pi r^2)(2\pi s)/\sigma$, where σ is again the rotational symmetry number appearing in (3), the number of equivalent configurations of the N atoms occurring during the integration over the coordinates just described. The remaining integration over the $3N-6$ coordinates can then be carried out by determinant evaluation. The new determinant \det' is just the original one with the six rows and columns (three rows and columns in two dimensions) corres-

TABLE I. Excess entropies for two-dimensional harmonic classical crystals with nearest-neighbor interactions. The crystals are of two shapes, triangular with $N = \frac{1}{2}L(L+1)$, and parallelogram with $N = L^2$ where L is the number of particles on a side. The excess entropy tabulated is $(1/N) \sum \ln(\nu_E/\nu)$ where the sum is over the $2N-3$ vibrational frequencies remaining when translation and rotation are omitted. The infinite crystal Einstein frequency is defined by the relation $(2\pi\nu_E)^2 = 3\kappa/m$.

Triangles		Parallelograms	
N	S^e/Nk	N	S^e/Nk
1	0.000000	1	0.000000
3	0.231049	4	0.325336
6	0.487107	9	0.507150
10	0.558987	16	0.536027
15	0.574103	25	0.530242
21	0.569629	36	0.515540
28	0.558044	49	0.499239
36	0.544188	64	0.483618
45	0.530049	81	0.469343
55	0.516455	100	0.456521
66	0.503725	121	0.445065
78	0.491952	144	0.434833
91	0.481124	169	0.425673
105	0.471186	196	0.417445
120	0.462064	225	0.410027
136	0.453683	256	0.403311
153	0.445969	289	0.397209
171	0.438855	324	0.391642
190	0.432280	361	0.386546
210	0.426189	400	0.381865
231	0.420534	441	0.377551
253	0.415271	484	0.373563
∞	0.27326	∞	0.27326

ponding to the frozen degrees of freedom omitted. The advantage of this determinant method is speed. Once \det' is obtained Z can be calculated:

$$Z = \exp(-\Phi_0/kT) \Lambda^{-DN} (\pi kT)^{\frac{1}{2}D(N-1)} V R (\det')^{-1/2},$$

where R is $(2\pi r)/\sigma$ in two dimensions and $(4\pi r^2) \times (2\pi s)/\sigma$ in three dimensions.

The \det' is most efficiently obtained by using the LU (lower-upper) method in which the $3N-6$ by $3N-6$ matrix is factored into a lower triangular matrix L and an upper triangular matrix U with $U_{ii}=1$. Then the matrix product LU gives the determinant, $\det' = \prod L_{ii}$. The factorization of the matrix into two triangular matrices can be carried out efficiently using the Crout algorithm,⁶ modified to take advantage of the symmetric nature of Q and the relatively sparse "band" structure of the matrix which results from restricting interactions to nearest neighbors. With the simple harmonic potential a face-centered crystal of 500 atoms (corresponding to a 1494×1494 determinant) required less than a minute

of (CDC 7600) computer time. Matrix diagonalization would have required a few hours time.

III. RESULTS

We expected to find that the Helmholtz free energy depends on size in a relatively simple way and on shape in a relatively complicated way. To separate size dependence from shape dependence we began by studying many crystals of the same shape but different sizes. Then, by comparing results for different shapes, we could distinguish between the intrinsic number dependence and the extraneous shape-dependent number dependence.

Numerical results are more easily interpreted for two-dimensional crystals because relatively larger crystals (in terms of the fraction of particles on the surface) can be studied and because an empirical series of correction terms to the bulk phase limit should converge more rapidly in two dimensions than in three dimensions. We first considered two-dimensional crystals in the form of equilateral triangles and parallelograms. For such crystals the number of particles, static-lattice energy, and moments of inertia are all simple polynomials in the number of particles on a side of the crystal L :

$$\begin{array}{ll} \text{Triangles} & \text{Parallelograms} \\ N = \frac{1}{2}L(L+1), & N = L^2, \\ \Phi_0 = -\frac{3}{2}\epsilon L(L-1), & \Phi_0 = -\epsilon(3L-1)(L-1), \\ I = m\Delta^2 \binom{L+2}{4}, & I = m\Delta^2 L \binom{L+1}{3}, \end{array}$$

where Δ is the nearest-neighbor separation in the static lattice. These expressions can be used to generate expansions in powers of $N^{-1/2}$.

We expected that the entropy results would be more complicated, and certainly not simple closed-form expressions, because crystal vibrations are collective rather than local. From the periodic-crystal results⁷ we know that logarithmic terms as well as terms of order $N^{1/2}k$ should contribute to the entropy. The existence of logarithmic contributions of order $k \ln N$ follows from the Debye model when the lower limit of integration over the frequency distribution function is cut off at a frequency of order $N^{-1/D}$, corresponding to the maximum wavelength; the exact value of the coefficient of the $k \ln N$ contribution to the entropy is uncertain without actual calculations. In the periodic case, with all surface terms absent, the entropy term was found to be $-k \ln N$ in one, two, and three dimensions. In the free boundary case,⁸ the one-dimensional contribution is smaller, $-\frac{1}{2}k \ln N$.

The excess entropies calculated from determinants (and checked, using lattice dynamics, for the smaller crystals) are given in Tables I and II.

The excess entropy is measured relative to the entropy obtained from the Einstein approximation, $Z_{\text{vib}} = (kT/h\nu_{\text{Einstein}})^{D(N-\frac{1}{2})}$, where ν_{Einstein} is the bulk-phase Einstein frequency. The tabulated results can be described or fitted numerically in several different ways, all of which suggest coefficients of the $k \ln N$ term lying within 10% of -1 . As an extrapolation formula, useful for predicting the properties of even larger crystals, we believe the most reasonable choice is that which converges to the known thermodynamic limit and which also fits the data from the largest crystals we studied. With the assumption that the coefficient of $k \ln N$ in the excess entropy is -1 we have the results:

$$S^e/Nk = 0.27326 + 2.82N^{-1/2} - 3.42N^{-1} - \ln N/N$$

(triangles),

$$S^e/Nk = 0.27326 + 2.65N^{-1/2} - 3.52N^{-1} - \ln N/N$$

(parallelograms).

These expressions, fitted to large-crystal data alone give S^e/Nk within 0.01 for crystals as small as $N=15$. The ratio of the triangle surface coefficient (2.82) to the parallelogram surface coefficient (2.65) agrees, as it should, with the surface area ratio for the two shapes $(9/8)^{1/2} \doteq 1.06$.

In three dimensions the deviations of small-crystal entropies from the large-crystal thermodynamic limit are larger. From Table II we see that the per particle excess entropy in the largest crystals we studied lies about $\frac{1}{2}k$ above the thermodynamic limit, 5 times the discrepancy found in two dimensions for the same number of particles.

Just as in two dimensions N , Φ_0 , and I can be expressed as simple sidelength polynomials. We studied both tetrahedra (12 crystals) and cubes (5 crystals). The tetrahedra were specially selected because the relatively many accessible crystal sizes offered the best chance for determining the coefficient of the $k \ln N$ term in the entropy. The three-dimensional static-lattice properties for the two crystal shapes are as follows:

<i>Tetrahedra</i>	<i>Cubes</i>
$N = \frac{1}{6}L(L+1)(L+2)$,	$N = \frac{1}{2}L^3$,
$\Phi_0 = -\epsilon(L-1)L(L+1)$,	$\Phi_0 = -3\epsilon L(L-1)^2$,
$I = m\Delta^2 \binom{L+3}{5}$,	$I = m\Delta^2 \frac{1}{4}L^2 \binom{L+1}{3}$.

In the cube case L is the (even) number of particles along a diagonal of one cube face. Just as in two

TABLE II. Excess entropies for three-dimensional harmonic classical crystals with nearest-neighbor interactions. The crystals are of two shapes, tetrahedra, with $N = (L+2)(L+1)L/6$, and cubes with $N = L^3/2$, where L is the number of particles along a side in the tetrahedral case and the number of particles on the diagonal of a 100 face of the cube in the cubic case. The excess entropy tabulated is $(1/N) \sum \ln(\nu_{\text{E}}/\nu)$ where the sum is over the $3N-6$ vibrational frequencies remaining when translation and rotation are omitted. The infinite crystal Einstein frequency is defined by the relation $(2\pi\nu_{\text{E}})^2 = 4\kappa/m$.

Tetrahedra		Cubes	
<i>N</i>	S^e/Nk	<i>N</i>	S^e/Nk
1	0.000000		
4	0.606504	4	0.606504
10	1.222688	32	1.254043
20	1.285044	108	1.002204
35	1.225431	256	0.833150
56	1.142891	500	0.721976
84	1.062498	∞	0.24689
120	0.990510		
165	0.927692		
220	0.873233		
286	0.825970		
364	0.784778		
455	0.748679		
∞	0.24689		

dimensions the numerical data were analyzed as series in $N^{-1/D}$ with an additional $\ln N/N$ term. The results, although less clearcut than the two-dimensional ones, are consistent with a contribution of $-1.5k \ln N$ to the excess entropy, so that a reasonable guess for the general D -dimensional logarithmic term is $-\frac{1}{2}kD \ln N$.

In the accompanying paper⁹ Abraham and Kortzeborn show that the free energy results for small crystals can be analyzed approximately in terms of additive contributions from particles with coordination numbers 12, 11, 10, ..., with different characteristic excess entropies for each coordination number. In the tetrahedral case, for instance, the only coordination numbers present other than 12 are 9, 6, and 4. The Abraham-Kortzeborn description is also consistent with a $-\frac{1}{2}kD \ln N$ contribution to the excess entropy. Using that guess, our representations of the entropy for the largest three-dimensional crystals are

$$S^e/Nk = 0.24689 + 3.83N^{-1/3} + 2.74N^{-2/3} - 10.4N^{-1} - \frac{3}{2} \ln N/N \text{ (tetrahedra),}$$

$$S^e/Nk = 0.24689 + 3.70N^{-1/3} + 2.83N^{-2/3} - 8.8N^{-1} - \frac{3}{2} \ln N/N \text{ (cubes).}$$

Just as in the two-dimensional case, the large-crystal approximations give S^e/Nk within 0.01 for crystals

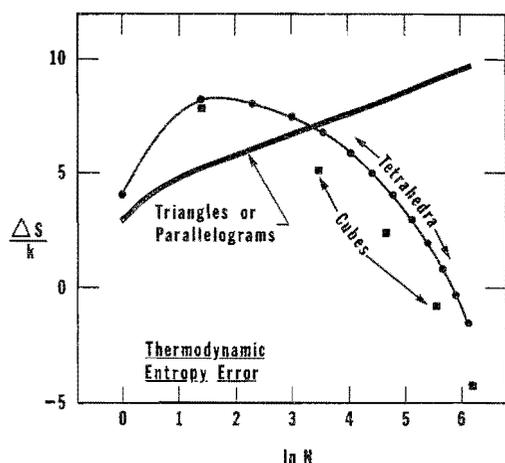


FIG. 1. Entropy error, $\Delta S \equiv$ thermodynamic prediction less exact entropy, for two- and three-dimensional classical close-packed harmonic crystals. On the scale of the figure the results for triangular crystals are indistinguishable from those for parallelograms. The results for cubes and tetrahedra show a shape dependence of order k , much too small to be measured by present-day experiments.

of more than about 10 particles. Additional terms of order $N^{-4/3}$ or $N^{-5/3}$ do not significantly improve the accuracy of these expressions.

The source of the logarithmic term is indeed the long-wavelength cutoff of the finite-crystal frequency distribution function. It is just sufficient to *cancel* the N dependence of the translational partition function:

$$Z_{\text{trans}} \propto N^{(1/2)D}.$$

Why the coefficient in the vibrational entropy should be $-\frac{1}{2}D$ and why the rotational terms make no corresponding contribution to the entropy are unclear.

IV. RELATION TO NUCLEATION THEORY

The primary usefulness of our exact results is to aid the intuition in dealing with nucleation problems. The question which needs to be settled is whether or not the classical approach of writing the thermodynamic properties of small liquid drops or crystallites as rigid-body terms plus surface terms is worthwhile. If the classical thermodynamic approach were inaccurate then separate microscopic calculations would have to be made for each new small system of interest.

In the simplest models, such as those we considered in this paper and including also crystals with long-range forces and lattice relaxation, there is no difficulty in calculating how *energy* depends on crystal size. The primary difficulty in nucleation theory has been in assessing the small-system effect on *entropy*. Our numerical results are quite interesting from this standpoint. If we identify "thermodynamic" information with the first two terms in the per particle entropy (the bulk and surface terms) then we can examine how serious the neglect of the remaining "nonthermodynamic" terms would be.

Figure 1 illustrates the error made if the thermodynamic approximation (translation+rotation+bulk+surface) to the small-crystal entropy is used. We see that this simplest possible estimate for the entropy always lies within $10k$ of the correct result. The terms of order $N^{-2/3}$, N^{-1} , and $\ln N/N$ partially cancel one another. Present experiments are so crude that rate errors of order e^{10} incurred by the thermodynamic estimate can be neglected. We conclude that until experiments which measure nucleation rates are perfected the present macroscopic thermodynamic theory is entirely adequate.

In the accompanying paper Abraham and Kortzeborn use a different definition of the "thermodynamic" entropy based on adding up contributions from 12-, 11-, 10-, ...-fold coordinated particles. Their definition tends to increase the discrepancy between the exact entropy and the thermodynamic approximation to it. We feel that our definition of thermodynamic entropy is a reasonable one with the added advantage that it applies equally well to liquids.

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or not the simple macroscopic theory works as well for liquids as for crystals. Dr. McGinty was kind enough to send us preprints of the results he forecast in *J. Chem. Phys.* **55**, 580 (1971).

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