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appeared after prolonged heating. A very small endotherm occurred at the clearing point.

Earlier two of the authors[3] reported a similar solid–solid transition in cholesteryl acetate. Several DSC curves were run on this mesomorphic compound for comparison. An endotherm was observed at the crystalline modification. The positron lifetime in the case of the acetate ester increased at a temperature corresponding to this endothermic transition. This is just the opposite of the results observed for cholesteryl propionate.

Each compound was also studied by the technique of x-ray powder diffraction. The first trace of each substrate was taken before heating. Examination of the patterns showed that the long spacings were very intense relative to the short spacings in cholesteryl propionate, whereas just the opposite was true in cholesteryl acetate. The second trace of each ester was obtained after they were heated without melting for 24 h at a temperature just above the first endothermic transition previously discussed. It was found that the long spacings decreased greatly in relative intensity while the short spacings were very much intensified in the propionate ester. Just the opposite effect was revealed in the acetate compound.

The implications in the prior descriptions are clear. The crystal modification in the cholesteryl propionate caused a decrease of the free volume[4] in the molecular lattice and therefore an increase in the annihilation rate of the orthopositronium. The free volume increased in the cholesteryl acetate at the solid–solid transition accounting for the decrease in the annihilation rate.

The authors are grateful to Dr. T. H. Hughes and Mr. L. W. Clements for their aid in obtaining the powder diffraction patterns.

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Entropy for Small Classical Crystals*

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Interest is growing in computer calculations of small-system thermodynamic properties. It is, therefore, desirable to know how to extrapolate the small-system computer results to the large-system thermodynamic limit. In this note, we show that the entropy for any finite periodic harmonic crystal lies below the large-system limit by a term proportional to $(\ln N)/N$, where N is the number of particles in the crystal.

It is especially useful to study a "harmonic crystal," one in which the potential energy contains no terms higher than quadratic in the displacements of the particles from their lattice sites. This is first because in a real crystal, terms higher than the quadratic ones are negligible at low enough temperatures and can be treated as perturbations at higher temperatures. Second, the *exact* entropy S of a harmonic crystal can be calculated from its vibration frequencies $S/k \equiv \ln\prod(ekT/h\nu_i)$, where k and h are Boltzmann's and Planck's constants; T is the absolute temperature; and the so-called "normal mode frequencies" $\{\nu_i\}$ are the $D(N-1)$ nonzero frequencies with which an N-particle D-dimensional crystal can vibrate. These frequencies can be calculated by straightforward methods for periodic crystals of up to several thousand particles; this is the exact Born–von Kármán approach.

We can simplify the equations giving the entropy for N-particle crystals by quoting the difference between the exact entropy and an approximation. The approximation to the entropy, not exact, is Einstein's, in which the product of frequencies is approximated by the $D(N-1)$ power of the "Einstein frequency," the frequency at which one particle would vibrate if all of the others were fixed at their lattice sites. The difference between the exact Born–von Kármán frequencies and the Einstein approximation shows the effect of many-body correlations. If we define the excess entropy $S_{\text{exact}} - S_{\text{Einstein}} \equiv S^e$, S^e is just k times the logarithm of the product $\prod(\nu_{\text{Einstein}}/\nu_i)$.

In one dimension, the distribution of frequencies of an N-body periodic crystal with nearest-neighbor interactions is known.[1] From it, one finds for the excess entropy

$$(S^e/Nk)_{1-D} = 0.34657 - (\ln N)/N + \cdots, \qquad (1)$$

where the dots here and in the following equations indicate omitted terms of order $(1/N)$.

In two or three dimensions the frequency distribution is more complicated and only numerical work has been carried out. Beyerlein and Salsburg[2] recently published a study of the thermodynamics of small periodic two-dimensional crystals with nearest-neighbor interactions and a hexagonal lattice structure with six nearest-neighbors per particle. By analyzing the results that they tabulated, I noticed the relation

$$(S^e/Nk)_{2-D} = 0.27326 - (\ln N)/N + \cdots. \qquad (2)$$

Notice that the coefficient of the number-dependent $(\ln N)/N$ term is the same in one and in two dimensions. To see whether or not this dependence is generally valid, I calculated the exact Born–von Kármán entropies for the two close-packed three-dimensional periodic crystals with nearest-neighbor interactions.[3] The results showed that both close-packed lattices, face-centered cubic and hexagonal close-packed, have the *same* number dependence already found in one and two dimensions, $-(\ln N)N$; so this is evidently valid

for *all* crystals;

$$(S^e/Nk)_{\mathrm{FCC}}=0.24689-(\ln N)/N+\cdots,$$
$$(S^e/Nk)_{\mathrm{HCP}}=0.24541-(\ln N)/N+\cdots. \quad (3)$$

The slight extra stability of the face-centered lattice over the hexagonal one shows up even in this simple calculation.[4]

As a warning it should be pointed out that the easy way of calculating the entropy, summing the logarithms of the frequencies, is not the *best* way, where best means closest to the thermodynamic limit. If, for example, the entropy for the one-dimensional nearest-neighbor periodic harmonic crystal is evaluated directly from the configurational integral, rather than from the exact frequency distribution, one finds that the coefficient of the $(\ln N)/N$ term is $-\frac{1}{2}$ rather than -1.

I would like to thank George Jelinek and Richard Grover for educational discussions and advice. Warren Cunningham energetically extracted the normal mode frequencies from the computing machinery at Livermore.

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van der Waals Coefficients for the Ground and Metastable States of He and Li^+

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The van der Waals coefficients describing the long-range interactions between metastable helium and various gases are important parameters affecting the efficiency of thermal Penning ionization process.[1] A similar mechanism can operate for ionization by positive ions, although the interaction is then dominated by the polarization force.

Recently,[2] accurate representations of the frequency-dependent dipole polarizability of the metastable states of helium have been derived from which accurate values of the van der Waals coefficients for many gas mixtures can be obtained. Similar calculations can be carried through for the positive ion of lithium.

Table I. van der Waals coefficients for mixtures of alkali metals, metastable helium, and atomic and molecular hydrogen.

	He $(2,{}^1S)$	He $(2,{}^3S)$
$H_2(\parallel)$	198.3	135.9
$H_2(\perp)$	140.3	96.5
H_2[a]	159.6	109.6
H	129.4	88.2
Li	3 500	2090
Na	3 660	2220
K	5 940	3480
Rb	6 440	3760
Cs	7 980	4610
He$(2\,{}^1S)$	11 280	5837
He$(2\,{}^3S$	5 837	3291

[a] Orientation average.

According to the Casimir–Polder formula,[3] the van der Waals interaction between a pair of spherically symmetric atomic systems a and b can be written as

$$V(R)=-\frac{3}{\pi R^6}\int_0^\infty \alpha_a(i\omega)\alpha_b(i\omega)\,d\omega, \quad (1)$$

where R is the interatomic distance and $\alpha(\omega)$ is the dipole polarizability at the frequency ω.

Accurate variational calculations of $\alpha(\omega)$ for the $1\,{}^1S$, $2\,{}^1S$, and $2\,{}^3S$ states of helium have been reported recently,[2] and we have applied the procedures there described to calculate $\alpha(\omega)$ for the $1\,{}^1S$, $2\,{}^1S$, and $2\,{}^3S$ states of Li^+.

There are available accurate theoretical representations of $\alpha(\omega)$ for atomic hydrogen[4] and for lithium.[5] Semiempirical representations have been constructed

Table II. van der Waals coefficients for mixtures of various gases with the ground and metastable states of Li^+.

	Li^+ $(1\,{}^1S)$	Li^+ $(2\,{}^1S)$	Li^+ $(2\,{}^3S)$
$H_2(\parallel)$	0.8608	50.42	38.12
$H_2(\perp)$	0.6775	36.00	27.36
H_2[a]	0.7386	40.81	20.95
N_2	1.9	90	69
CH_4	2.5	140	105
He$(1\,{}^1S)$	0.302	11.12	8.61
He$(2\,{}^1S)$	6.01	1900	1070
He$(2\,{}^3S)$	4.24	1090	655
Ne	0.660	21.7	16.8
Ar	1.87	85.6	65.5
Kr	2.58	127	96.9
Xe	3.42	199	150
H	0.4931	32.44	24.31
Li	3.32	706	447
Na	3.60	751	481
K	4.86	1170	723
Rb	5.21	1260	780
Cs	6.09	1540	941
$Li^+(1\,{}^1S)$	0.0782	1.672	1.320
$Li^+(2\,{}^1S)$	1.672	366.0	244.2
$Li^+(2\,{}^3S)$	1.320	224.2	146.8

[a] Orientation average.