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Entropy of fcc and hcp Lattices: Comparison of *H* Theorem Method with Vibrational Analysis

P. O. ESBJØRN, E. J. JENSEN, W. D. KRISTENSEN, J. W. MARTIN, AND
L. B. PEDERSEN

Department of Structural Properties of Materials,
Technical University of Denmark, Lyngby, Denmark

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The entropy of a Lennard–Jones model solid was calculated as a function of temperature, for both the fcc and hcp phases, using data derived from a molecular dynamics computer simulation. Two independent methods of calculation were used, one based on the Boltzmann H theorem and the other on the power spectrum method of Dickey and Paskin.

1. INTRODUCTION

The stability of crystal structures has been sometimes attributed to the relative energies of the different structures, the stable phase being the structure of lowest energy. For example, the cohesive energy of the solid phases of the inert gases has been carefully calculated to find the stable lattice type [1–4]. Similar studies have been made on alkali halide crystals [5, 6] and for a number of metals [7, 8]. No matter how exactly the cohesive energy is determined, however, the question of stability is not resolved. In fact stability and metastability are determined by the relative free energies, and it is the phase of lowest free energy which is in thermodynamic equilibrium.

The difference in Gibbs free energy between two phases at fixed temperature T and pressure P is expressed as

$$\Delta F = \Delta E + P\Delta V - T\Delta S, \tag{1}$$

where E is the internal energy, V the volume and S the entropy of the solid. A zero in the free energy difference ΔF for some temperature and pressure indicates a phase transition at that point. The presence of the entropy term $T\Delta S$ shows that only the low temperature structure is determined by the cohesive energy alone: at all finite temperatures the full free energy must be considered. This is especially important in systems where the enthalpy difference between two phases is nearly zero, that is

$$\Delta E + P\Delta V \simeq 0, \tag{2}$$

such as in the inert gases and the alkali halides. It is also true of the Lennard–Jones model solid. In such cases it is essential to include the entropy contribution to the free energy.

In this present work we investigate the entropies of the fcc and hcp phases of a simple model solid, with a first nearest neighbor central potential of the Lennard–Jones type. The model is described in detail in Section 2. Both fcc and hcp phases are stable against small deformations, and because of the restriction to first neighbor interactions they have the same static energies. Differences in entropy between them must, therefore, be investigated to determine which of them is the stable and which the metastable form.

The cause of this entropy difference lies in the vibrational characteristic of the two lattices. One way of approximately calculating the entropy is via the frequency spectrum $D(\omega)$ of the lattice vibrations. An expression for the vibrational entropy valid for the temperature range of interest (i.e., where quantum effects are negligible) is given by [9]

$$S(T) = k \int D(\omega)(1 + \ln(kT/\hbar\omega))\, d\omega, \tag{3}$$

where k is Boltzmann's constant and $D(\omega)$ is normalized to $3N$, the number of vibrational modes in a crystal containing N atoms. For a limited range of temperature the frequency spectrum can be obtained from a perturbation treatment of a harmonic analysis of the crystal, and the free energy and entropy derived from it [10–12]. On the other hand, the molecular dynamics technique [13, 14] allows us to compute the effective frequency spectrum, via the autocorrelation functions [15], at any temperature at which the model system can be simulated. Such calculations of the frequency spectra, using both lattice dynamics and molecular dynamics, to find the fcc and hcp phase entropies as a function of temperature are described in Sections 3 and 4.

There is a second method of calculating the entropy, which is described in Section 5 and which is independent of any form of vibrational analysis. This method is derived from Boltzmann's H theorem [16]: the entropy is found from phase space distribution functions which are measured directly in the course of a molecular dynamics simulation. Furthermore, this method can be used to monitor the progress of a simulation, so that thermodynamic averages are taken only in the equilibrized state of the system. It is shown in Sections 5 and 6 that this method increases the accuracy and reliability with which the entropy can be found. Finally in Section 7 the calculations of the fcc–hcp entropy difference by the two methods are described. It was found that the fcc system has the higher entropy and is, thus, the stable form.

2. THE MODEL

The Lennard–Jones model solid was used, in which the atoms interact via a pair potential

$$V(r) = \epsilon_0((r_0/r)^{12} - 2(r_0/r)^6). \tag{4}$$

This potential is computationally convenient, and in addition it represents quite well the interaction of inert gas atoms. To give substance to our calculations we took values of the parameters ϵ_0, r_0 to describe the solid phase of krypton. The chosen values of $\epsilon_0 = 3.104\ 10^{-21}\ J$ and $r_0 = 3.99\ 10^{-10}\ m$ reproduce the experimental lattice parameter and cohesive energy. The potential (4) was truncated between the first and second nearest neighbor distances. With either first or first and second neighbor interactions this model solid can occur in any close packed crystal structure, including the fcc and hcp lattices. All of these structures are statically stable, and satisfy the approximation (2).

A feature of the molecular dynamics method is that only systems containing a limited number of atoms can be studied (of the order of 1000–1500). The system can, however, be made effectively infinite by the use of periodic boundary conditions. In this case the atoms of the system must be confined to a parallelepiped region of space (this is trivial if they form a lattice), and this cell is then repeated to fill all of space. The computation is then confined to the atoms in this parallelepiped (referred to as the computational cell) together with as many atoms in the repeated cells as fall within the range of the interactions of the atoms of the computational cell. These atoms outside the computational cell are referred to as the ghost atoms, and it is usually necessary to take 100–500 ghost into the computational scheme. With the number of atoms typically involved in the molecular dynamics method, it is obvious that the repeat distance of the periodic boundaries (i.e., the dimensions of the computational cell) are of the order of ten atomic spacings, which is much smaller than that normally associated with periodic boundaries (macroscopic dimensions). The shape of the computational cell must, therefore, be chosen with care.

The system chosen for study in the fcc case contained 672 atoms. The computational cell was a rectangular box whose edges lay in the [111], [$1\bar{1}0$], and [$11\bar{2}$] directions. The system was, thus, built up from close packed planes of atoms, rectangular in section, stacked in the [111] direction. Each close packed plane contained eight close packed atom rows (the [$1\bar{1}0$] direction), and each row contained seven atoms. Twelve such planes were stacked together as shown in Fig. 1,

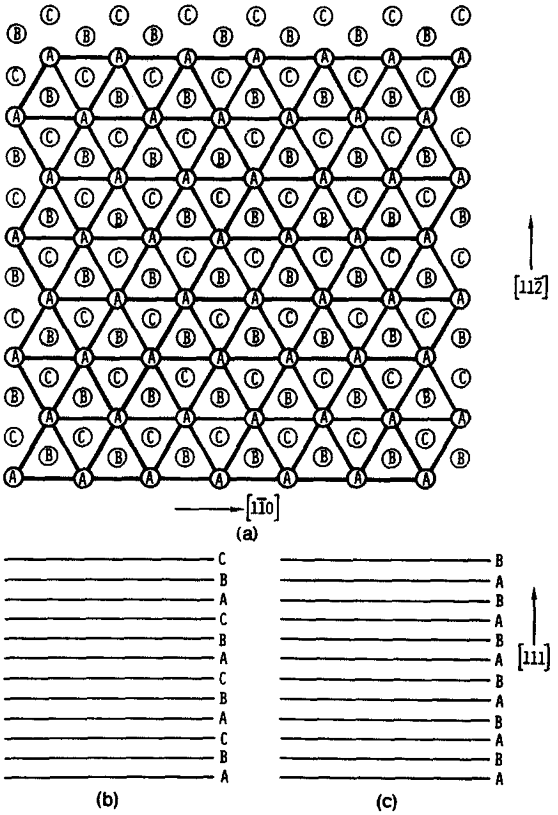

FIG. 1. (a) Those sections of the close packed planes (types A, B, and C) from which the 672 atom fcc and hcp systems were constructed; (b) The stacking sequence of the fcc system; (c) The stacking sequence of the hcp system.

so that the cell was as near to being a cube as the lattice structure permitted. The hcp system, which must be as nearly comparable to the fcc system as possible, was obtained from the fcc system by a simple restacking of the close packed (111) planes (Fig. 1). In this way the hcp and fcc systems were given equal numbers of atoms and computational cells of identical dimensions. In conventional notation the stacking sequence was *ABCABCABCABC* in the fcc case and *ABABABABAB* in the hcp system.

3. PERIODIC BOUNDARIES AND FREQUENCY SPECTRUM

The periodic boundaries of the model system prevent the molecular dynamics method from accurately measuring the frequency spectrum $D(\omega)$. The frequency spectrum is measured by sampling **k** space at many points in the first Brillouin zone, and constructing a histogram of the frequencies of the phonons with these **k** vectors. The net of allowed **k** vectors in this zone is determined by the periodic boundaries, and the total number of these vectors is equal to the number of atoms enclosed by the boundaries. Thus, in molecular dynamics simulations, with about 1000 atoms, we sample about 1000 points in **k** space. Thus, the integration (3) in finding the entropy is performed over a correspondingly coarse mesh of frequency. We, therefore, investigated the effect of the choice of periodic boundaries on the calculated frequency spectrum (and, hence, the entropy) by performing lattice dynamics calculations both on infinite systems, with a large sample of points in the Brillouin zone and on small systems.

The secular determinant for the fcc crystal with first neighbor interactions is given by de Launay [17], and the calculated 'infinite' frequency spectrum is shown in Fig. 2. In all some 10,000 points in the 1/48 Brillouin zone were sampled. The

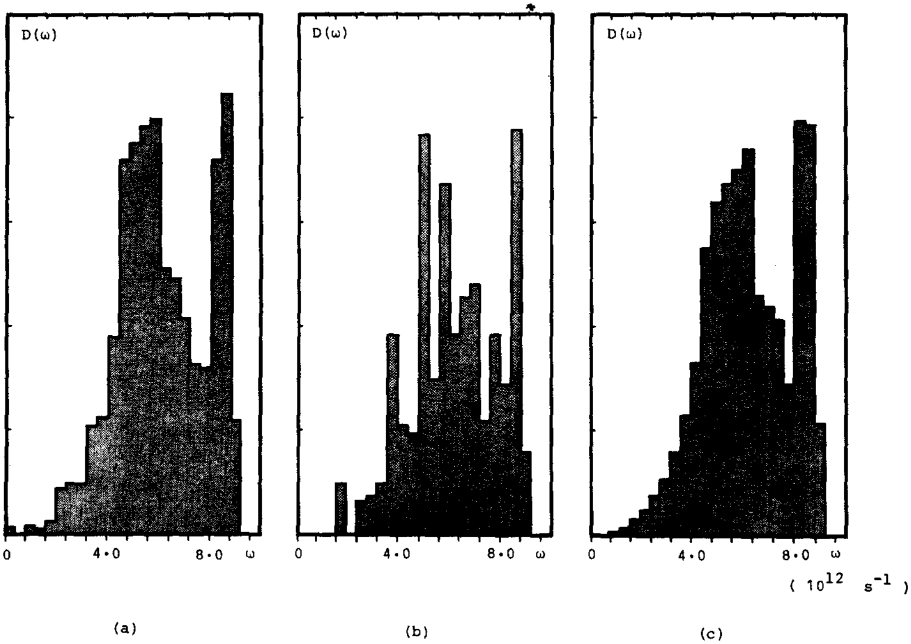

FIG. 2. The frequency spectrum of the fcc lattice: (a) the 672 atom system; (b) the 500 atom system; (c) the infinite system.

peaks corresponding to the transverse and longitudinal phonons are clearly seen. This was compared with the calculated spectra for 500 and 672 atom fcc systems, and the results are again plotted in Fig. 2. The 500 atom system had a cubic computational cell, with edges parallel to the cubic axes. The frequency spectrum deviated considerably from the infinite system. Much better results were obtained for the 672 atom system, which is that described in Section 2. The explanation lies in the different degrees of symmetry of the two smaller systems. The 500 atom system has in fact only 27 independent **k** vectors, and, hence, the effective integration mesh is very coarse. In the 672 atom case the degree of degeneracy is substantially reduced, as the **k** vectors are moved away from the symmetry planes.

The secular determinant in the hcp case was obtained from Slutsky and Garland's result [18], omitting the terms arising from the second neighbor interactions. The frequency spectrum of the 'infinite' system is plotted in Fig. 3, together with the frequency spectrum of the 672 atom hcp system described in Section 2. The two spectra have similar shapes: although the computational cell boundaries in this case lie in high symmetry directions, the hcp lattice has fewer symmetry elements than the fcc lattice.

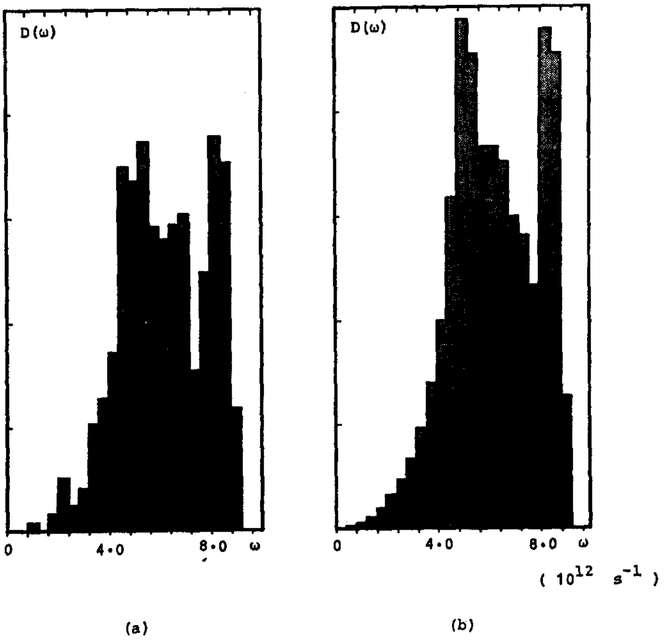

FIG. 3. The frequency spectrum of the hcp lattice: (a) the 672 atom system; (b) the infinite system.

4. MOLECULAR DYNAMICS AND POWER SPECTRUM

In the molecular dynamics simulation of the model systems described in Section 2, we define the power spectrum $f(\omega)$ as

$$f(\omega) = \int_0^\infty \gamma(t)\cos(\omega t)\,dt; \tag{5}$$

it is the Fourier transform of the velocity autocorrelation function $\gamma(t)$, which is defined by

$$\gamma(t) = \left\langle \sum_i \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \right\rangle \Big/ \left\langle \sum_i \mathbf{v}_i^2(0) \right\rangle. \tag{6}$$

Here $\mathbf{v}_i(t)$ the velocity of the i'th atom as a function of time, which is available directly from the molecular dynamics simulation. The angular brackets indicate that a thermodynamic average is taken. The most convenient way of achieving this is to average (6) over different origins in time.

Dickey and Paskin [15] have shown that for a collection of oscillators in thermodynamic equilibrium the power spectrum $f(\omega)$ is identical to the frequency spectrum $D(\omega)$. We assume that the average value of $f(\omega)$ at any temperature is equal to the average frequency spectrum, which is a justifiable assumption if the average frequency spectrum can be found within the computational time available (this is, of course, the real upper limit of the integral (5)). Dickey and Paskin also show by a numerical calculation that the power spectrum at very low temperatures is the same as the frequency spectrum derived from lattice dynamics.

The frequency spectrum which is found from (6) and (5) can then be used in the expression for the vibrational entropy (3), and the entropy of the model can thus be calculated. It is clear that this method of calculating the vibrational entropy involves several approximations of a numerical nature. First the velocity autocorrelation function is truncated after a time typically of the order of 10^{-11} s. This in itself prevents us from discovering the finer details of the frequency spectrum. Further the number of velocity autocorrelation functions used to calculate the mean autocorrelation function is limited to about 20, due to the finite length of time for which each simulation is carried out. Finally the use of (3) implies that the entropy calculation is based on a harmonic model. However, other contributions are effectively taken into account by the use of an average frequency spectrum measured at the temperature in question, and averaged over a sufficient length of time to incorporate the annihilation and creation of phonons of new frequencies by the anharmonic part of the potential.

Averaged velocity autocorrelation functions $\gamma(t)$ for the 672 atom fcc system at the temperatures 63 K and 111 K are shown in Fig. 4. Two features can be noted.

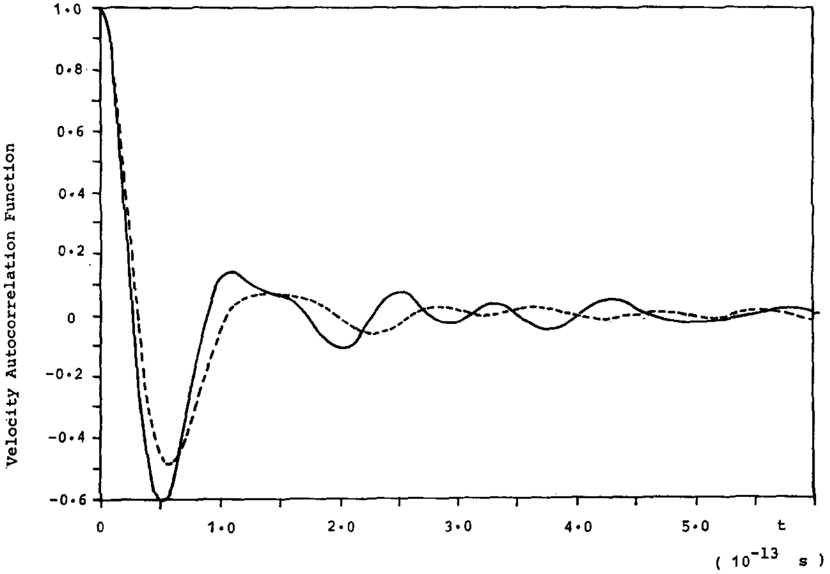

FIG. 4. Velocity autocorrelation function $\gamma(t)$ for the 672 atom fcc system. ——— 63 °K, - - - - - - 111 °K.

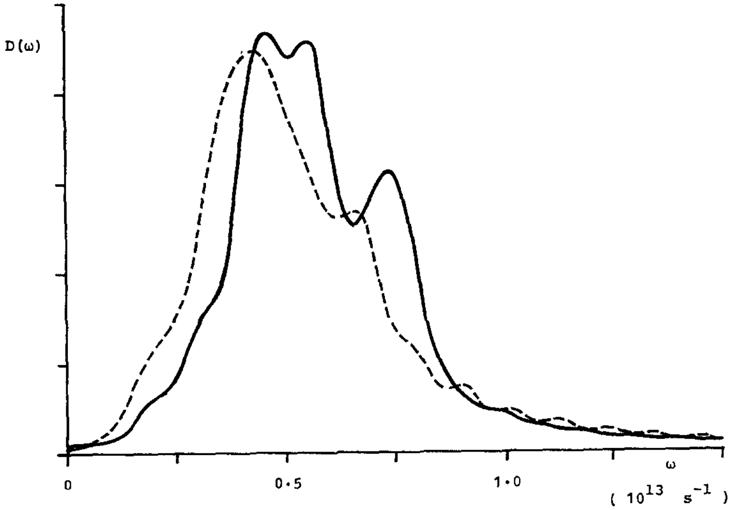

FIG. 5. Power spectrum $f(\omega)$ for the 672 atom fcc system. ——— 63 °K, - - - - - - 111 °K.

First, the correlations are markedly more persistent at the higher temperature. Secondly, the first minimum in $\gamma(t)$ has been shifted towards larger time for the higher temperature. This shift is mainly a consequence of the thermal expansion of the system, which gives rise to an overall reduction of the force constants. The frequency spectra derived from these autocorrelation functions are shown in Fig. 5. It is seen that the distribution shifts towards lower frequencies with increasing temperature, again because of the thermal expansion. Also the distinctive peaks of the longitudinal and transverse phonons, which are clearly visible at the lower temperature, become less marked at the higher temperature.

In Fig. 6 we show the frequency spectra of the 672 atom hcp system, at temperatures of 63 and 111 K, where similar changes with temperature are observed. On the other hand, the differences between the fcc and hcp systems, which are quite noticeable in the lattice dynamics spectra of Figs. 2 and 3, tend to disappear as the temperature is raised.

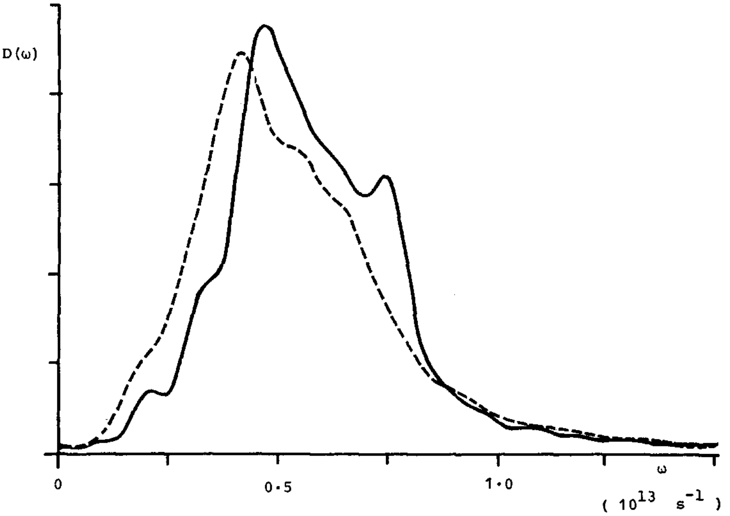

FIG. 6. Power spectrum $f(\omega)$ for the 672 atom hcp system. ——— 63 °K, - - - - - - 111 °K.

5. *H* THEOREM METHOD

Boltzmann's H function, which is simply related to the entropy of a system, is usually derived in connection with the ideals gas. In this case it is defined by [16]

$$H(t) = V \int \frac{N}{V} h(\mathbf{v}, t) \ln \left(\frac{N}{V} h(\mathbf{v}, t) \right) d^3 v, \tag{7}$$

where $h(\mathbf{v}, t)$ is the distribution function for the atomic velocities, here normalized to unity. Boltzmann's H theorem states that H, as a function of time, is minimized at thermodynamic equilibrium. If the system is not in equilibrium then $H(t)$ is found to continuously decrease until the system reaches equilibrium. The minimum, or equilibrium, value of $H(t)$ is connected to the maximum or equilibrium entropy. If we further include the possibility of a nonuniform space distribution in (7), then the expression for the H function is given by

$$H(t) = N \int h(\mathbf{v}, \mathbf{r}, t) \ln(Nh(\mathbf{v}, \mathbf{r}, t))\, d^3r\, d^3v, \tag{8}$$

where again h is normalized to unity.

The integral (8) can be found directly from molecular dynamics, where the positions and velocities of each atom as a function of time are recorded. However, to make (8) easier to evaluate we introduced two approximations, which were later checked by a test calculation. First, it was assumed that the distribution function $h(\mathbf{v}, \mathbf{r}, t)$ was separable into position and velocity distribution functions $g(\mathbf{r}, t)$ and $f(\mathbf{v}, t)$

$$h(\mathbf{v}, \mathbf{r}, t) = f(\mathbf{v}, t)\, g(\mathbf{r}, t), \tag{9}$$

which then gives for H

$$\begin{aligned} H(t) = {} & N \ln(N) + N \int g(\mathbf{r}, t) \ln(g(\mathbf{r}, t))\, d^3r \\ & + N \int f(\mathbf{v}, t) \ln(f(\mathbf{v}, t))\, d^3v. \end{aligned} \tag{10}$$

The second approximation was to assume that both g and f have spherical symmetry, so that they can be expressed as $g(r^2)$ and $f(v^2)$. Thus, dropping the constant term $N \ln(N)$ in (10), we can write H as the sum of finite elements [19]

$$H = N \left\{ \sum_j m_j \ln(m_j/(4\pi r_j^2\, \Delta r_j)) + \sum_j n_j \ln(n_j/(4\pi v_j^2\, \Delta v_j)) \right\}. \tag{11}$$

The elements m_j and n_j are the time averaged contributions from all the atoms to the distribution functions g and f in the ranges r_j to $r_j + \Delta r_j$ and v_j to $v_j + \Delta v_j$, respectively. The entropy, which is

$$S = -H \cdot k, \tag{12}$$

can be found from (11) provided we restrict the time averaging to the part of the simulation after equilibrium is achieved, as monitored by the minimum value of H being reached and maintained.

6. *H* THEOREM METHOD: A TEST CALCULATION

A simple test of the H theorem method was made by calculating the entropy change along an isotherm of the 672 atom fcc system. The system was held at a temperature of 63 K, and compressed from a lattice parameter $a_0 = 5.75\ 10^{-10}\ m$ to $5.73\ 10^{-10}\ m$.

The change in entropy can be calculated from the measured thermodynamic variables of the two states, which are also available from the molecular dynamics simulation. The change in enthalpy along the isotherm can be written in two ways

$$\begin{aligned} \Delta H &= \Delta E + \Delta(PV), \\ \Delta H &= T\,\Delta S + \int V\,dP, \end{aligned} \tag{13}$$

and, hence, an expression for the entropy change is

$$\Delta S = 1/T\left(\Delta E + \Delta(PV) - \int V\,dP\right). \tag{14}$$

With $T = 63$ K and measured values of $6.8\ 10^{-10}\ J$ for ΔH and $7.36\ 10^{-19}\ J$ for the integral in (14), the entropy change was found to be

$$\Delta S = -64.2\,k. \tag{15}$$

A corresponding value of ΔS was found by the H theorem method. The velocity distribution function was found in both cases to be Maxwell–Boltzmann in form, and reached its equilibrium form far more rapidly than the spatial distribution function $g(r^2)$. Hence, the change in entropy was entirely due to the contribution from $g(r^2)$, and the time taken to measure ΔS depended on the time taken to find the equilibrium form of g. Using the equilibrium values for g in (11) the change of entropy was calculated as

$$\Delta S = -65.4\,k \tag{16}$$

in excellent agreement with the independently obtained value (15). The contribution of $f(v^2)$ to ΔS was completely negligible.

These two results can also be compared with a value obtained on the basis of a vibrational analysis. The Einstein frequencies of the atoms in the two states of the system were found to have the ratio

$$(\omega_1/\omega_2)^2 = 0.9371, \tag{17}$$

and, hence, the entropy difference which is found from (3) is

$$\begin{aligned} \Delta S &= 3/2\, Nk \ln(\omega_1/\omega_2)^2 \\ &= -69.9\, k. \end{aligned} \tag{18}$$

The discrepancy here is, as expected, the largest, since we have crudely approximated the frequency spectrum. On the other hand, the close agreement of (15) and (16) shows that the approximations that were made in the form of the distribution functions f and g are justifiable.

7. ENTROPY CALCULATIONS ON fcc AND hcp SYSTEMS

Molecular dynamics runs for the fcc and hcp 672 atom systems were made at temperatures of 63, 80, 100, and 111 K in both cases. Each run was made at constant volume, and the pressure was determined during the course of the run. Pairs of (E, V) values were chosen so that pressure was close to zero in every case. The maximum pressure recorded was about 100 atmospheres; which gives rise to a change in the free energy, through the $P\Delta V$ term of (1), of about 4.5 10^{-24} J per atom, as compared with the zero pressure state. This correction will be seen to be small compared with the uncertainties in calculating the entropy and was neglected. More importantly, the pressure difference between the corresponding fcc and hcp runs was about 1 atm, so that corrections to the free energy difference arising from the pressure term were in fact quite negligible. These runs were then analyzed, first by the power spectrum method and then by the H theorem method.

The power spectrum was obtained from Eqs. (5) and (6), for a series of different truncations in the velocity autocorrelation function. From the power spectrum the entropy was calculated from Eq. (3), and the results for the four temperatures, as a function of truncation frequency, are shown in Fig. 7. The entropy differences between the two systems are shown in Fig. 8. It is seen that there is little dependence on the truncation frequency, provided it is greater than 1.0 10^{13} s^{-1}. The error on the mean of the entropy differences was determined from the values of ΔS obtained using different time origines for the velocity autocorrelation function. The first 500 cycles of each run were always excluded from consideration, so that a degree of equilibration had occurred before any averages were taken. The velocity autocorrelation functions were in fact determined from parts of the runs between cycle numbers 500 and 2500. The mean value of ΔS determined by this method was 0.011 k per atom, with an uncertainty of 0.02 k per atom, or somewhat more than the magnitude of ΔS itself.

The H function analysis used the same runs as the power spectrum case, but these runs were extended to a total of 6500 cycles (a time of 6.5 10^{-11} s). These runs

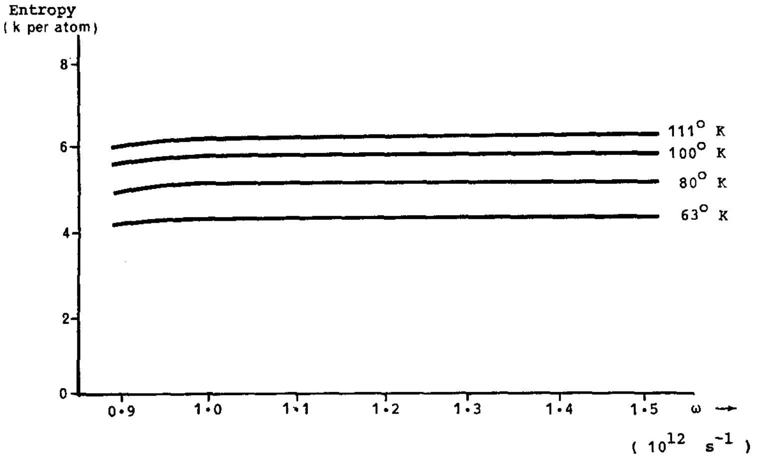

FIG. 7. Entropy of the fcc and hcp 672 atom systems at temperatures of 63, 80, 100, and 111 °K, versus truncation frequency in the power spectrum. Units are k per atom.

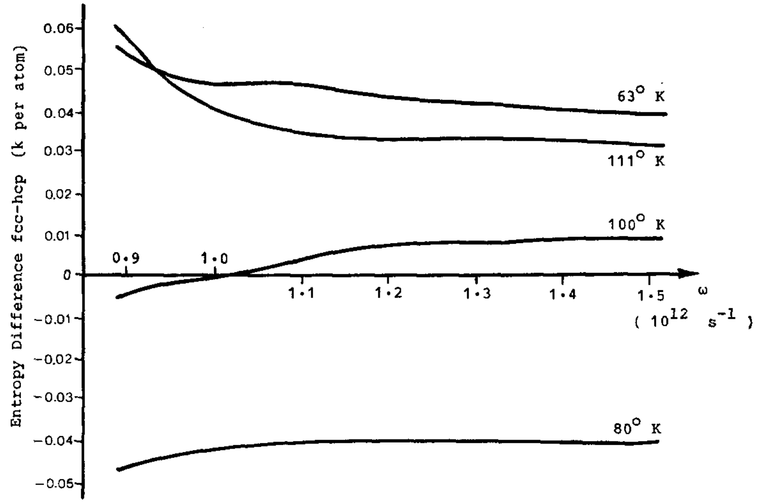

FIG. 8. Entropy difference between the fcc and hcp 672 atom systems at temperatures of 63, 80, 100, and 111 °K, versus truncation frequency in the power spectrum. Units are k per atom.

were divided into sequences of 500 cycles, and at the end of each sequence the entropy was calculated from (11), with m_j and n_j averaged both over the sequence just completed, and also over all the completed sequences (except for the first 500 cycles where some nonequilibrium features are expected to disappear).

It was found that the contributions to the entropy from the velocity distribution

n_j were constant throughout all the runs. This means that nonequilibrium features of the velocity distribution disappear within the first 500 cycles of beginning the simulation, and that fluctuations in this term have shorter periods than the 500 cycle time (5 10^{-12} s). The total entropy for the eight simulations is shown in Figs. 9–12. Here the entropy is calculated from the accumulated average of the distribu-

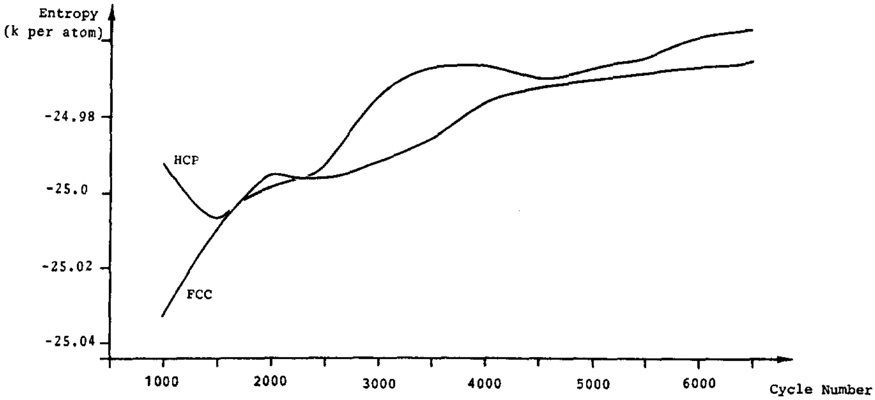

FIG. 9. Time development of the entropy as calculated from the H function for the fcc and hcp 672 atom systems at 63 °K. Units are k per atom.

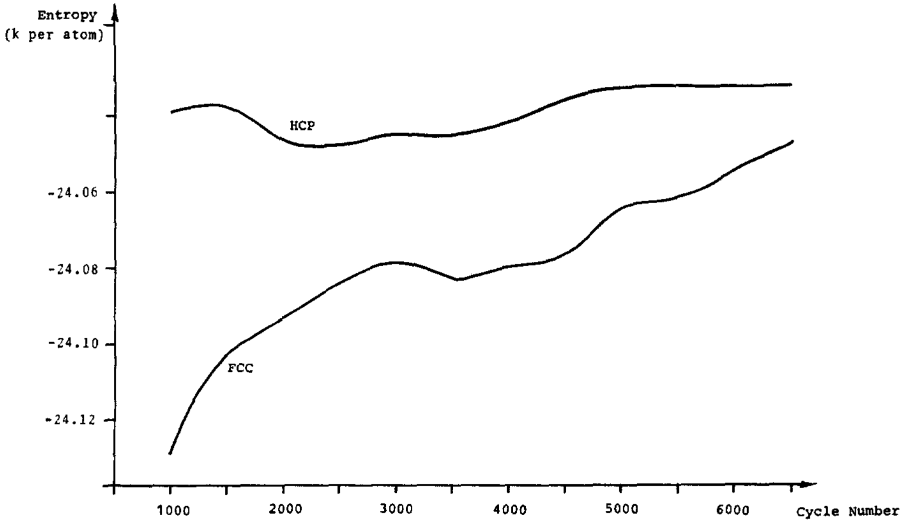

FIG. 10. Time development of the entropy as calculated from the H function for the fcc and hcp 672 atom systems at 80 °K. Units are k per atom.

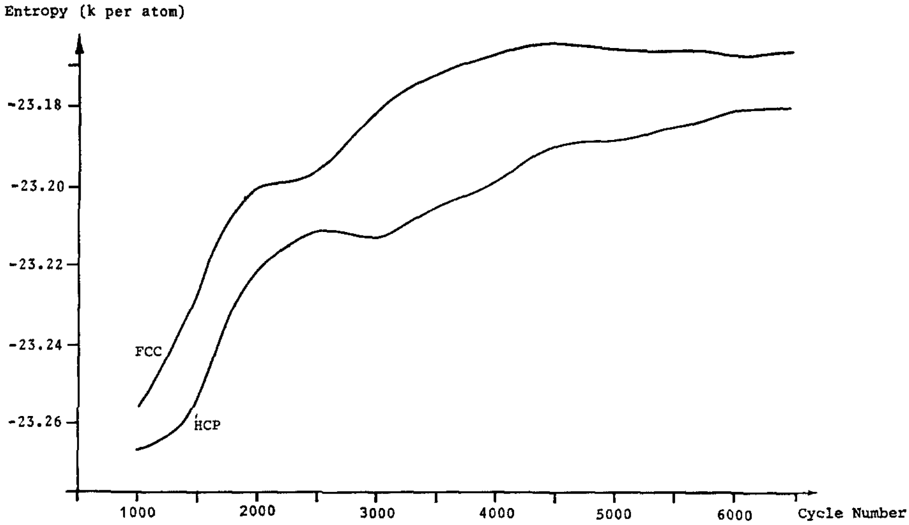

FIG. 11. Time development of the entropy as calculated from the *H* function for the fcc and hcp 672 atom systems at 100 °K. Units are *k* per atom.

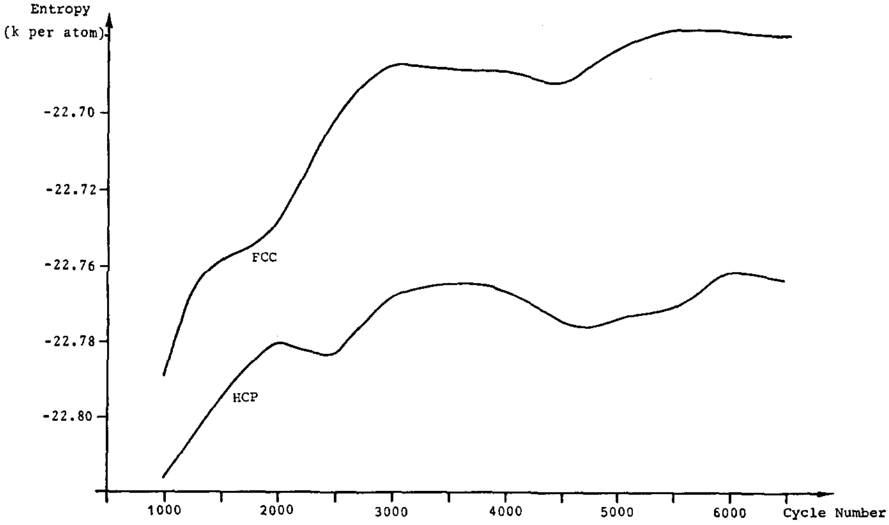

FIG. 12. Time development of the entropy as calculated from the *H* function for the fcc and hcp 672 atom systems at 111 °K. Units are *k* per atom.

tion functions. The change in calculated entropy with time is due to the space distribution function, and it is seen that here the initial conditions are remembered for many more than 500 cycles. The time development of the entropy, taken from the 500 cycle averages, shows fluctuations of the order of 0.04 k per atom with periods of order 2500 cycles. The time taken to reach equilibrium in m_j is also of this order. It is, therefore, important to delay taking thermodynamic averages until after this point.

The curves of Figs. 9–12 show the accumulated average value of the entropy, with the first 500 cycles excluded. The average value of the entropy must increase until equilibrium is reached, when it remains constant. The reason that the curves of Figs. 9–12 show a rising tendency even after 6500 cycles is due to the influence of the early, nonequilibrium values, which were retained in the accumulated average. The 500 cycle average showed that equilibrium was in fact achieved after about 2500 cycles. The accumulated average was plotted to suppress the fluctuations which arise when averaging over a relatively small number of cycles.

A comparison of the entropy calculations by the two methods is shown in Table 1.

TABLE I

The Entropy Change from the Value at 63 °K for the fcc and hcp Systems from the Power Spectrum and *H* Function Methods

	Power spectrum method		*H* function method		Thermodynamic value
T °K	$S(T)$–S(63 °K)		$S(T)$–S(63 °K)		$S(T)$–S(63 °K)
	fcc	hcp	fcc	hcp	
63	0	0	0	0	0
80	0.795	0.805	0.921	0.914	0.859
100	1.558	1.558	1.799	1.777	1.662
111	1.964	1.955	2.290	2.204	2.072

The thermodynamically obtained value is the same for the two systems. All entropies in units of k per atom.

Here is shown the increase in entropy with temperature for the two systems, referred to the base value at 63 K. The *H* function gives an entropy rise some 15% greater than that of the power spectrum method. We can use this table to give an independent test of the two methods. Since the specific heat c_p is very nearly constant in this temperature range, and can be measured directly from the molecular dynamics simulation, it is possible to use the thermodynamic relation,

$$(\partial S/\partial T)_p = c_p/T, \tag{19}$$

to calculate the entropy differences of Table 1 sufficiently accurately to distinguish between the two methods. These values are shown in the fifth column of the table, and it is seen that the exact values lie exactly halfway between those of the power spectrum method and those derived from the *H* function. Thus, the various approximations give rise to equal (but opposite) deviations. It is satisfying to note, however, that the deviation in all cases is less than 0.2 *k* per atom.

The entropy differences between the two phases, as calculated by the *H* function method, and averaged over the last 4500 cycles, are shown in Table 2. The dependence on temperature is only apparent: the constancy of the energy difference between the fcc and hcp systems reveals that the entropy difference is constant over this temperature range to within 0.0007 *k* per atom. This entropy difference should, however, be correctly given by the mean of the four values of Table 2. We obtain

$$\Delta S = 0.017 \pm 0.19 \text{ k per atom}; \tag{20}$$

the mean value, thus, lies in favor of a stable fcc and metastable hcp. This can be compared directly with the result of Hoover [20], who obtained from a lattice dynamics calculation an entropy difference of 0.00148 k per atom. Thus, our methods have produced a mean value some ten times larger than the harmonic analysis, although this is within the calculated uncertainty on our result. A comparison can also be made with the results of Huckaby and Salsburg [21] for the high temperature Helmholtz free energy difference. They also employed hcp and fcc

TABLE II

Entropy Difference of fcc and hcp Systems
Derived from *H* Function Method

T	ΔS
63	-0.012 ± 0.013
80	-0.0048 ± 0.018
100	0.012 ± 0.014
111	0.074 ± 0.017

All entropies in units of *k* per atom.

Lennard–Jones systems, for both first and first and second nearest neighbor interactions. With only first neighbor interactions, as we used, their free energy difference is equivalent to an entropy difference of 0.001475 k per atom, in excellent agreement with Hoover's result, and again within the error on the mean of our value.

Our aim in this paper has been to demonstrate the use of two methods, the power spectrum and H theorem method, in calculating the entropy of small model systems simulated by the molecular dynamics technique. In the examples chosen here to illustrate these methods, results have been obtained in agreement with those of harmonic analyses. However, the methods can also be applied in cases where harmonic analysis is inappropriate. The major criticism which can be made of our methods is their lack of accuracy, particularly when the difference of two large entropy values is required. In principle all that is required to improve the accuracy is a better thermodynamic averaging, which can be obtained with a longer period of simulation. However, we have already determined ΔS with an error on the mean of 0.02 k per atom and it is only the very small difference in the fcc–hcp first nearest neighbor system that means that such accuracy is insufficient in this case. In other systems such precision may well be acceptable.

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