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# Free Energy of the fcc and hcp Lattices under First- and Second-Neighbor Harmonic Interactions*

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The harmonic contribution to the high-temperature expansion of the Helmholtz free energy was calculated for the hcp and fcc lattices for an arbitrary analytic central pair potential with interactions extending to first and second neighbors. The numerical method used was not the usual extrapolation based upon a sampling of points in the first Brillouin zone but rather an extrapolation of the properties of finite crystals to the thermodynamic limit ($N \rightarrow \infty$).

## 1. INTRODUCTION

The face centered cubic structure was the only known crystalline form of argon until 1964. In that year, using a powder $x$-ray diffraction technique, Barrett and Meyer [1] observed a metastable hexagonal close packed phase in coexistence with the fcc phase. It was found that a 1 % impurity was sufficient to stabilize the hcp phase [2].

Optical bi-refringence [3] and electron diffraction [4] studies on very pure argon samples indicated the hcp phase does indeed coexist with the fcc phase below the triple point. Recent electron diffraction studies on very thin films of solid argon found that an fcc, an hcp, a mixture of fcc-hcp, or an amorphous phase could exist depending on the film thickness and condensation conditions [5].

Due to the great similarity of the fcc and hcp packings, quite precise theoretical work is necessary to obtain quantitative differences in the thermodynamic

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properties of the two lattices, but the relatively short range van der Waals interactions in solid argon should render the system relatively amenable to precise theoretical investigations. Several informative reviews of this problem have appeared in recent years [6–9].

Lattice energy calculations for Lennard-Jones and related potentials favor the hcp lattice for stability [10–11]. Even though the zero-point vibrational energy under first neighbor interactions favors the fcc lattice for stability, its effect is insufficient to counterbalance the lattice energy difference [12]. The effects of anharmonic interactions have been explored, especially for the fcc lattice under first neighbor interactions [13–16]. Many body interactions have also been considered in an attempt to explain the relative stability, but their effects have been quite small [17–19].

In order to perform meaningful calculations, an accurate interaction potential must be known. Alder and Paulson [20] have pointed out that small changes in the interaction potential can result in either the fcc or hcp lattice having the lower lattice energy. Barron [21] has discussed intermolecular potentials with regard to anharmonic crystals, and a many body interaction potential has been proposed by Klein and Munn [22]. Dymond and Alder [23] have recently calculated a numerical pair potential for Ar which fits known data quite well. Experimental work on the $Ar_2$ molecule [24] may soon aid in the elucidation of the interaction potential.

Thus, despite the relative theoretical simplicity which one assumes for rare gas crystals, we are in fact confronted with a complex problem. Each consideration or contribution can be extremely crucial. A survey of the literature [9] shows, however, that even the harmonic model has not been analyzed carefully enough to say what the harmonic contributions are to the relative stability of the fcc and hcp phases.

It is the purpose of the present work to calculate the harmonic contribution to to the Helmholtz free energy for the fcc and hcp lattices. The calculations were performed for an arbitrary central, pairwise-additive, analytic potential since an accurate interaction potential for argon has not been well characterized. Moreover, since the differences in the two lattices are quite small, the effect of both first- and second-neighbor interactions were considered.

Most studies of the harmonic model focus attention on the phonon frequency distribution function $g(\nu)$. The numerical extrapolation method most often employed consists of solving the secular equation at a relatively small number of mesh points in the irreducible section of the first Brillouin zone and then by interpolation or extrapolation estimating the solutions over the entire Brillouin zone. Details of these techniques can be found in many references [25].

An alternative technique, seldom used, is to calculate the properties of a finite crystal of $N$ particles exactly for various values of $N$ and then extrapolate to $N = \infty$.

This technique can make use of the analysis of asymptotic $N$ dependence to help the extrapolation [26] and was chosen as the procedure for this investigation.

## 2. HARMONIC ANALYSIS

Consider a three dimensional lattice with Born–Von Karman boundary conditions which contains $N$ interacting particles. Let $\mathbf{R}_i^0$ be the vector from the origin of a Cartesian coordinate system to lattice site $i$. Figure 1 illustrates the situation in which particles $i$ and $j$ are displaced from their lattice sites by amounts $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively.

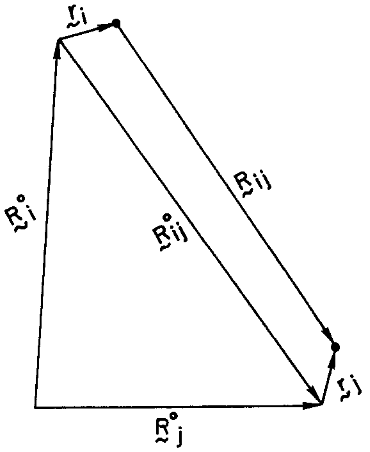

FIG. 1. Situation in which particles $i$ and $j$ are displaced from their lattice sites by amounts $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively. The dots indicate the instantaneous positions of the two particles.

Assuming central forces and pairwise interactions, we may define a potential

$$U_N = \sum_{(ij)} \Phi(R_{ij}). \tag{2.1}$$

Although triplet and higher-order interactions are neglected here, their effects have been the subject of recent investigations [17–19].

We obtain in the harmonic approximation [27]

$$U_N = U_N^{(0)} + \tfrac{1}{2}k_1 \mathbf{r} \cdot \mathsf{M} \cdot \mathbf{r}, \tag{2.2}$$

where $\mathbf{r} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$, $\mathsf{M}$ is a dynamical matrix with eigenvalues $(\nu_\alpha/\nu_0)^2$, $\nu_\alpha$

$1 \leqslant \alpha \leqslant 3N - 3$ are the $3N - 3$ normal vibrational modes for the system,

$$\nu_0 = \frac{1}{2\pi} \sqrt{k_1/m}, \qquad k_1 = \Phi''(R_0) - \Phi'(R_0)/R_0 ,$$

$R_0$ being the first-neighbor equilibrium separation.

The anharmonic terms which are neglected in Eq. (2.2) account for several interesting phenomena [13–16].

The Helmholtz free energy for the system is given as

$$A_N = U_N^{(0)} + F_N , \tag{2.3}$$

where $U_N^{(0)}$ is the lattice energy at absolute zero and $F_N$ is the harmonic free energy. At sufficiently high temperatures [28, 29]

$$F_N/NkT = (3 - 3/N)\ln(\Theta/T) + \frac{1}{2N}\ln |\mathsf{M}|' + \sum_{n=1}^{\infty} \frac{B_{2n}}{(2n)(2n)!}(\Theta/T)^{2n}\frac{1}{N}\operatorname{tr}(\mathsf{M}^n), \tag{2.4}$$

where $\Theta = h\nu_0/k$ and $|\mathsf{M}|'$ is restricted to exclude the three translational modes.

To facilitate the numerical calculation of the terms in Eq. (2.4), the matrix $\mathsf{M}$ can be block diagonalized by standard techniques [30, 31].

## 3. Numerical Results

Under first- and second-neighbor interactions, the matrix elements of $\mathsf{M}$ depend linearly on three-dimensionless parameters

$$\begin{aligned} l_1 &= \Phi'(R_0)/(k_1 R_0), \\ l_2 &= \Phi'(\sqrt{2}R_0)/(k_1 \sqrt{2}R_0), \\ k_2 &= \Phi''(\sqrt{2}R_0)/k_1 - l_2 . \end{aligned} \tag{3.1}$$

As such,

$$\frac{1}{N}\operatorname{tr}\mathsf{M}^n = \sideset{}{'}\sum_{C_1,C_2,C_3=0}^{n} b^{(n)}_{C_1C_2C_3} l_1^{C_1} l_2^{C_2} k_2^{C_3}, \qquad C = C_1 + C_2 + C_3 \leqslant n. \tag{3.2}$$

As shown by Isenberg [32], the coefficients $b^{(n)}_{C_1C_2C_3}$ for sufficiently large finite lattices are exactly the same as for the infinite lattice. A consideration of the form of the dynamical matrix $\mathsf{M}$ insures for the fcc lattice that $b^{(n)}_{C_1C_2C_3}\,2^{n+C}$ is an integer and insures for the hcp lattice that $b^{(n)}_{C_1C_2C_3}18^{n-C}$ is an integer.

TABLE 1

Twenty moments for the fcc lattice under first neighbor interactions. The results can be compared to those of Isenberg [32] by noting that $b_{000}^{(n)} = 3 \cdot 8^n \mu_{2n}$.

| $n$ | $b_{000}^{(n)}$ |
|---|---|
| 0 | 3. |
| 1 | 12. |
| 2 | 60. |
| 3 | 342. |
| 4 | 2109. |
| 5 | 13647. |
| 6 | 91059. |
| 7 | 620273.1/4 |
| 8 | 4288065.9/16 |
| 9 | 29977872.3/4 |
| 10 | 211452231.9/16 |
| 11 | 1502586690.21/32 |
| 12 | 10745522619.51/128 |
| 13 | 77276408636.11/128 |
| 14 | 558533729674.7/8 |
| 15 | 4055463913213.43/512 |
| 16 | 29570777955997.3401/4096 |
| 17 | 216463329635910.951/1024 |
| 18 | 1590348447544759.193/2048 |
| 19 | 11724314853646673.1231/4096 |

Using this result, the first twenty moments for the fcc lattice under first-neighbor interactions were computed exactly from the numerical results of Isenberg [32]. These moments are listed in Table I and were utilized by Gordon and Wheeler [33] to obtain rigorous upper and lower bounds to some thermodynamic quantities.

The exact values of coefficients $b_{C_1C_2C_3}^{(n)}$ were calculated for both the fcc and hcp lattices and are given in Table II for $n \leqslant 6$. Garland and Jura [34] have calculated these coefficients for the fcc lattice for the special case $l_1 = l_2 = 0$. For $n \leqslant 3$, the coefficients are identical for the two lattices as shown by Barron and Domb [35].

In a similar manner we obtain the expansion

$$\frac{1}{N} \ln | \mathsf{M} |' = \sum_{C_1, C_2, C_3 = 0} a_{C_1C_2C_3} l_1^{C_1} l_2^{C_2} k_2^{C_3}. \tag{3.3}$$

Unlike the coefficients $b_{C_1C_2C_3}^{(n)}$ of Eq. (3.2), the coefficients $a_{C_1C_2C_3}^{(n)}$ for the infinite lattice must be obtained by extrapolation. These coefficients for $C \leqslant 3$ were computed for systems of 1000, 8000, and 27 000 particles. The extrapolated coefficients are given in Table III. The coefficient $a_{000}$ has been computed by several techniques [26, 33, 36], and all the values obtained agree with our results.

## TABLE 2

The exact coefficients $b^{(n)}_{C_1C_2C_3}$, $1 \leqslant n \leqslant 6$, of Eq. (3.2) for the fcc and hcp lattices of infinite size. A dash indicates the coefficient for the hcp lattice is equal to the coefficient for the fcc lattice. For $n \leqslant 3$, the coefficients are the same for the two lattices

| $C_2C_1C_3$ | b(hcp)<br>b(fcc) |
|---|---|
| n = 1 | |
| 0 0 0 | 12 |
| 0 0 1 | 6 |
| 0 1 0 | 36 |
| 1 0 0 | 18 |
| n = 2 | |
| 0 0 0 | 60 |
| 0 0 1 | 48 |
| 0 0 2 | 18 |
| 0 1 0 | 312 |
| 0 1 1 | 144 |
| 0 2 0 | 468 |
| 1 0 0 | 144 |
| 1 0 1 | 84 |
| 1 1 0 | 432 |
| 2 0 0 | 126 |
| n = 3 | |
| 0 0 0 | 342 |
| 0 0 1 | 360 |
| 0 0 2 | 216 |
| 0 0 3 | 60 |
| 0 1 0 | 2412 |
| 0 1 1 | 1800 |
| 0 1 2 | 648 |
| 0 2 0 | 6336 |
| 0 2 1 | 2736 |
| 0 3 0 | 6336 |
| 1 0 0 | 1080 |
| 1 0 1 | 1008 |
| 1 0 2 | 396 |
| 1 1 0 | 5472 |
| 1 1 1 | 3024 |
| 1 2 0 | 8208 |
| 2 0 0 | 1512 |
| 2 0 1 | 972 |
| 2 1 0 | 4536 |
| 3 0 0 | 972 |

TABLE 2 (*continued*)

| $c_2c_1c_3$ | b(fcc) | b(hcp) | $c_2c_1c_3$ | b(fcc) | b(hcp) |
|---|---|---|---|---|---|
| n = 4 | | | | | |
| 0 0 0 | 2109 | 2108 1/6 | 1 0 2 | 6336 | --- |
| 0 0 1 | 2760 | 2766 2/3 | 1 0 3 | 1800 | --- |
| 0 0 2 | 2148 | 2134 2/3 | 1 1 0 | 56016 | 56101 1/3 |
| 0 0 3 | 960 | --- | 1 1 1 | 49824 | 49781 1/3 |
| 0 0 4 | 210 | --- | 1 1 2 | 19008 | --- |
| 0 1 0 | 18576 | 18565 1/3 | 1 2 0 | 143424 | --- |
| 0 1 1 | 18288 | 18341 1/3 | 1 2 1 | 75456 | --- |
| 0 1 2 | 10656 | 10613 1/3 | 1 3 0 | 143424 | --- |
| 0 1 3 | 2880 | --- | 2 0 0 | 15264 | 15157 1/3 |
| 0 2 0 | 66456 | 66434 2/3 | 2 0 1 | 15552 | --- |
| 0 2 1 | 46656 | 46698 2/3 | 2 0 2 | 6300 | 6278 2/3 |
| 0 2 2 | 16272 | 16229 1/3 | 2 1 0 | 75456 | --- |
| 0 3 0 | 117360 | --- | 2 1 1 | 46656 | --- |
| 0 3 1 | 47808 | --- | 2 2 0 | 113184 | --- |
| 0 4 0 | 88020 | --- | 3 0 0 | 15552 | --- |
| 1 0 0 | 8280 | 8301 1/3 | 3 0 1 | 10728 | --- |
| 1 0 1 | 10224 | 10138 2/3 | 3 1 0 | 46656 | --- |
| | | | 4 0 0 | 8046 | --- |

TABLE 2 (*continued*)

| $C_2C_1C_3$ | b(fcc) | b(hcp) | $C_2C_1C_3$ | b(fcc) | b(hcp) |
|---|---|---|---|---|---|
| n = 5 | | | | | |
| 0 0 0 | 13647 | 13632 5/12 | 1 1 2 | 388080 | 386586 2/3 |
| 0 0 1 | 21501 | 21639 1/6 | 1 1 3 | 108000 | --- |
| 0 0 2 | 20490 | 20234 1/6 | 1 2 0 | 1862640 | 1867760 |
| 0 0 3 | 11850 | 11740 | 1 2 1 | 1584000 | 1582293 1/3 |
| 0 0 4 | 4200 | --- | 1 2 2 | 589680 | 588826 2/3 |
| 0 0 5 | 756 | --- | 1 3 0 | 3209760 | --- |
| 0 1 0 | 144150 | 143870 5/6 | 1 3 1 | 1612800 | --- |
| 0 1 1 | 176520 | 178030 | 1 4 0 | 2407320 | --- |
| 0 1 2 | 133920 | 132753 1/3 | 2 0 0 | 149040 | 146906 2/3 |
| 0 1 3 | 58800 | 58386 2/3 | 2 0 1 | 200160 | 196533 1/3 |
| 0 1 4 | 12600 | --- | 2 0 2 | 126000 | 125573 1/3 |
| 0 2 0 | 644580 | 643380 | 2 0 3 | 36360 | 36146 2/3 |
| 0 2 1 | 596880 | 600933 1/3 | 2 1 0 | 969120 | 964426 2/3 |
| 0 2 2 | 339840 | 336933 1/3 | 2 1 1 | 954000 | 952933 1/3 |
| 0 2 3 | 90000 | 89573 1/3 | 2 1 2 | 378000 | 376720 |
| 0 3 0 | 1556280 | 1554893 1/3 | 2 2 0 | 2419200 | --- |
| 0 3 1 | 1033920 | 1036480 | 2 2 1 | 1440720 | --- |
| 0 3 2 | 351360 | 348906 2/3 | 2 3 0 | 2419200 | --- |
| 0 4 0 | 2075760 | --- | 3 0 0 | 198720 | 195520 |
| 0 4 1 | 802440 | --- | 3 0 1 | 214560 | --- |
| 0 5 0 | 1245456 | --- | 3 0 2 | 88920 | 88280 |
| 1 0 0 | 64560 | 65022 1/2 | 3 1 0 | 960480 | --- |
| 1 0 1 | 100320 | 98565 | 3 1 1 | 643680 | --- |
| 1 0 2 | 80220 | 79013 1/3 | 3 2 0 | 1440720 | --- |
| 1 0 3 | 36000 | --- | 4 0 0 | 160920 | --- |
| 1 0 4 | 7980 | --- | 4 0 1 | 117180 | --- |
| 1 1 0 | 542160 | 545466 2/3 | 4 1 0 | 482760 | --- |
| 1 1 1 | 639360 | 634986 2/3 | 5 0 0 | 70308 | --- |

TABLE 2 (*continued*)

| $C_2C_1C_3$ | b(fcc) | b(hcp) | $C_2C_1C_3$ | b(fcc) | b(hcp) |
|---|---|---|---|---|---|
| n = 6 | | | | | |
| 0 0 0 | 91059 | 90900 125/144 | 1 0 2 | 944280 | 912571 1/3 |
| 0 0 1 | 168624 | 170283 13/18 | 1 0 3 | 544320 | 534485 1/3 |
| 0 0 2 | 191007 | 187515 3/4 | 1 0 4 | 191520 | --- |
| 0 0 3 | 134544 | 131811 1/9 | 1 0 5 | 34776 | --- |
| 0 0 4 | 61776 | 61149 1/9 | 1 1 0 | 5094540 | 5159623 |
| 0 0 5 | 18144 | --- | 1 1 1 | 7570080 | 7473363 7/9 |
| 0 0 6 | 2772 | --- | 1 1 2 | 5946480 | 5839796 4/9 |
| 0 1 0 | 1123749 | 1119553 7/9 | 1 1 3 | 2633760 | 2617621 1/3 |
| 0 1 1 | 1657980 | 1682747 8/9 | 1 1 4 | 574560 | --- |
| 0 1 2 | 1541160 | 1523236 | 1 2 0 | 21750120 | 21944568 |
| 0 1 3 | 878400 | 863960 8/9 | 1 2 1 | 24544080 | 24432560 |
| 0 1 4 | 307440 | 304652 4/9 | 1 2 2 | 14644800 | 14529152 |
| 0 1 5 | 54432 | 54432 | 1 2 3 | 4008960 | 3998240 |
| 0 2 0 | 6023295 | 5995531 2/9 | 1 3 0 | 50533200 | 50719248 |
| 0 2 1 | 6926040 | 7033264 2/3 | 1 3 1 | 41179680 | 41146912 |
| 0 2 2 | 5144940 | 5088840 | 1 3 2 | 15007680 | 14948032 |
| 0 2 3 | 2232000 | 2195768 8/9 | 1 4 0 | 65871360 | --- |
| 0 2 4 | 471240 | 468253 1/3 | 1 4 1 | 31690080 | --- |
| 0 3 0 | 18196800 | 18128960 | 1 5 0 | 39522816 | --- |
| 0 3 1 | 15917040 | 16097968 | 2 0 0 | 1424385 | 1395924 13/18 |
| 0 3 2 | 8892720 | 8772976 | 2 0 1 | 2412360 | 2314650 8/9 |
| 0 3 3 | 2318400 | 2288768 | 2 0 2 | 1947600 | 1895143 1/3 |
| 0 4 0 | 33299280 | 33244176 | 2 0 3 | 872640 | 867520 |
| 0 4 1 | 21029760 | 21124992 | 2 0 4 | 195300 | 193810 2/9 |
| 0 4 2 | 6991920 | 6903856 | 2 1 0 | 11436480 | 11331616 |
| 0 5 0 | 35743104 | --- | 2 1 1 | 14871600 | 14613520 |
| 0 5 1 | 13174272 | --- | 2 1 2 | 9218880 | 9156928 |
| 0 6 0 | 17871552 | --- | 2 1 3 | 2617920 | 2602560 |
| 1 0 0 | 506682 | 513152 5/6 | 2 2 0 | 37728720 | 37622416 |
| 1 0 1 | 961650 | 937256 | 2 2 1 | 35916480 | 35850560 |

TABLE 2 (*continued*)

| $C_2C_1C_3$ | b(fcc) | b(hcp) |
|---|---|---|
| n = 6 (continued) | | |
| 2 2 2 | 13955760 | 13898096 |
| 2 3 0 | 63380160 | --- |
| 2 3 1 | 36383040 | --- |
| 2 4 0 | 47535120 | --- |
| 3 0 0 | 2377800 | 2291448 |
| 3 0 1 | 3360960 | 3269184 |
| 3 0 2 | 2134080 | 2118720 |
| 3 0 3 | 623280 | 615408 |
| 3 1 0 | 14923440 | 14716272 |
| 3 1 1 | 15716160 | 15699648 |
| 3 1 2 | 6402240 | 6356160 |
| 3 2 0 | 36383040 | --- |
| 3 2 1 | 23686560 | --- |
| 3 3 0 | 36383040 | --- |
| 4 0 0 | 2500200 | 2437416 |
| 4 0 1 | 2812320 | --- |
| 4 0 2 | 1186740 | 1174836 |
| 4 1 0 | 11843280 | --- |
| 4 1 1 | 8436960 | --- |
| 4 2 0 | 17764920 | --- |
| 5 0 0 | 1687392 | --- |
| 5 0 1 | 1282536 | --- |
| 5 1 0 | 5062176 | --- |
| 6 0 0 | 641268 | --- |

TABLE 3

Listed below are the extracted coefficients $a_{c_1c_2c_3}$ of Eq. (3.3). Values for both the fcc and hcp lattices are given.

| $C_1$ | $C_2$ | $C_3$ | $a$(fcc) | $a$(hcp) |
|---|---|---|---|---|
| 0 | 0 | 0 | 1.8325536 | 1.8340288 |
| 1 | 0 | 0 | 5.3835 | 5.3705 |
| 0 | 1 | 0 | 3.1237 | 3.0984 |
| 0 | 0 | 1 | 1.0395 | 1.0252 |
| 2 | 0 | 0 | −11.196 | −11.099 |
| 0 | 2 | 0 | −5.0010 | −4.7810 |
| 0 | 0 | 2 | −0.70722 | −0.64973 |
| 1 | 1 | 0 | −13.798 | −13.464 |
| 1 | 0 | 1 | −4.7363 | −4.5767 |
| 0 | 1 | 1 | −3.4054 | −3.1866 |
| 3 | 0 | 0 | 34.501 | 33.827 |
| 0 | 3 | 0 | 13.764 | 12.404 |
| 0 | 0 | 3 | 0.84842 | 0.69747 |
| 2 | 1 | 0 | 67.838 | 64.653 |
| 2 | 0 | 1 | 24.260 | 22.860 |
| 1 | 2 | 0 | 51.098 | 47.203 |
| 0 | 2 | 1 | 14.581 | 12.663 |
| 1 | 0 | 2 | 7.4458 | 6.5988 |
| 0 | 1 | 2 | 5.8837 | 4.9561 |
| 1 | 1 | 1 | 36.243 | 32.613 |

## 4. An Example Calculation

Consider the pair potential [10]

$$\Phi(R_{ij}) = \epsilon(R^*/R_{ij})^{12} - 2\epsilon(R^*/R_{ij})^6. \tag{4.1}$$

Following Kihara and Koba [11], we shall determine the first-neighbor separation $R_0$ by minimizing $U_N^{(0)}$ at absolute zero, neglecting the zero-point vibrational energy. This yields

$$\begin{aligned} U_N^{(0)}/N\epsilon &= C_6{}^2/2C_{12}\,, \\ V/NR^{*3} &= (C_{12}/2C_6)^{1/2}, \\ k_1 &= 12\epsilon\eta R^{*-2}C_6^{4/3}C_{12}^{-7/3}, \\ k_2 &= (7C_6 - 32C_{12})/2^6\eta, \\ l_1 &= (-C_6 + C_{12})/\eta, \\ l_2 &= (-C_6 + 8C_{12})/2^7\eta, \end{aligned} \tag{4.2}$$

where $\eta = 14C_6 - 8C_{12}$.

From the results of Section 3, we find, where $\Delta$ = hcp–fcc,

$$(kT)^{-1}\Delta(F_N/N) = 2.62 \times 10^{-3} + 4.57 \times 10^{-5}(\Theta_{\mathrm{fcc}}/T)^2 + 3.65 \times 10^{-6}(\Theta_{\mathrm{fcc}}/T)^4 + 4.76 \times 10^{-7}(\Theta_{\mathrm{fcc}}/T)^6 + \cdots, \qquad (4.3)$$

which converges for $T > 0.865\ \Theta_{\mathrm{fcc}}$. It is interesting to note that $\Delta F_N$ is essentially a classical result in the region of convergence.

Since $\Delta V < 0$, the hcp lattice is stable at higher pressures than is the fcc lattice. For the two lattices to coexist at a fixed temperature and pressure,

$$\Delta G = 0 = \Delta A + P\Delta V. \qquad (4.4)$$

The transition pressure for $T > 0.865\ \Theta_{\mathrm{fcc}}$ is then given as

$$P = -80.2(\epsilon/R^{*3}) + [243 + 4.24(\Theta_{\mathrm{fcc}}/T)^2]\, kT/R^{*3}. \qquad (4.5)$$

Using the values $\epsilon = 1.69 \times 10^{-14}$ erg and $R^* = 3.82Å$ for argon in the fcc structure [6], we find $\Theta_{\mathrm{fcc}} = 36.6°$ K. Equation (4.5) then predicts the fcc lattice to be the stable form of argon for $T > \Theta_{\mathrm{fcc}}$ with a possibility of a phase transition to the hcp structure occurring at pressures of the order of $10^{10}$ dynes/cm$^2$.

The errors in the example calculation resulting from the choice of interaction potential and from the determination of the parameters at absolute zero rather than at the temperature in question are no doubt quite large. The main point of the example is to point out that $\Delta F_N$ depends significantly on second-neighbor harmonic interactions. As such, any attempt to explain the stability of the two lattices should include the effects of second-neighbor harmonic interactions. The results of Section 3 should prove quite useful in this regard.

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