Helmholtz free energy of an anharmonic crystal to $O(\lambda^4)$. II*

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Numerical calculations of the Helmholtz free energy F to $O(\lambda^2)$ and $O(\lambda^4)$ from all the diagrams have been carried out in the high-temperature limit without making the leading-term approximation for a monatomic face-centered cubic crystal with nearest-neighbor central-force interactions. The numbers obtained for some diagrams and the total $F(\lambda^4)$ can differ by as much as 47 and 33%, respectively from those obtained in the leading term approximation, indicating that this approximation is not very good as far as absolute magnitudes are concerned. However, the ratio $F(\lambda^4)/F(\lambda^2)$ is nearly the same as in the leading-term approximation, indicating that the convergence of the perturbation expansion is satisfactory up to one third of the melting temperature. Finally, the improved-self-consistent (ISC) scheme of selecting the most important diagrams is probably as good as doing perturbation theory to order λ^4.

I. INTRODUCTION

Recently Shukla and Cowley[1] have derived expressions for the Helmholtz free energy (F) of an anharmonic crystal to $O(\lambda^4)$ by means of the diagrammatic method, where λ is the Van Hove ordering parameter equal in magnitude to a typical atomic displacement divided by the nearest-neighbor distance. They also performed numerical calculations for all the diagrams for a crystal in which every atom is on a site of inversion symmetry for a nearest-neighbor central-force model of a face-centered-cubic (fcc) lattice in the high-temperature limit and in the leading-term approximation. The leading-term approximation involves retaining the highest-order radial derivative in the evaluation of the Cartesian tensor derivatives of the two-body potential.

For a Lennard-Jones 12-6 potential different contributions to F of $O(\lambda^4)$ were presented by Shukla and Cowley from the viewpoint of diagrams included in the first-order self-consistent (SC1), improved self-consistent (ISC), and the second-order self-consistent (SC2) phonon theories of lattice dynamics. Diagrams of $O(\lambda^2)$ and $O(\lambda^4)$ are presented in Figs. 1 and 2, respectively. Diagrams 2(a) and 2(b) are included in the SC1, 2(c) and 2(d) as well as 2(a) and 2(b) in the ISC, and all of the above plus 2(e) and 2(f) in the SC2. Diagrams 2(g) and 2(h) are not included in any of the different theories. Thus, to $O(\lambda^4)$, they concluded that none of the diagrams made a negligibly small contribution and that of the various approximate schemes for selecting the most important diagrams, only ISC gave a subtotal which was close to the total $F(\lambda^4)$. The convergence of the perturbation expansion appeared poor for temperatures greater than one-third of the melting temperature.

The contributions of $O(\lambda^4)$ were recently calculated by Aggarwal and Pathak[2] using both the leading-term and Ludwig approximations. Previous unpublished results[3] suggest that these approximations when applied to free-energy calculations do not produce good results. Leech and Reissland[4] and Feldman and Horton[5] have assessed the importance of not making the leading-term approximation and concluded that for terms of $O(\lambda^2)$ the errors were about 30% for the quartic and 4% for the cubic term, respectively.

In order to assess the convergence of the perturbation expansion and the accuracies of the subtotal for F obtained according to the above-mentioned schemes of selecting diagrams we have computed in the present paper the different contributions to F of $O(\lambda^2)$ and $O(\lambda^4)$ without making the leading-term approximation for the same model of fcc crystal as used by Shukla and Cowley.[1]

We can draw the following conclusions from our calculations. The numbers obtained for some diagrams [e.g., $F(2(b))$] and the total $F(\lambda^4)$ can vary by as much as 47% and 38%, respectively, from those obtained in the leading-term approximation, indicating that this approximation is not very good as far as absolute magnitudes are concerned. However, the ratio $F(\lambda^4)/F(\lambda^2)$ is nearly the same as in the leading-term approximation indicating that the convergence of the perturbation expansion is satisfactory up to one-third of the melting temperature. Finally, the ISC scheme of selecting the most important diagrams is probably as good as doing perturbation theory to order λ^4.

The relevant theory is summarized in Sec. II. The computation in the high-temperature limit, without making the leading-term approximation, is presented in Sec. III; Sec. IV contains the discussion and comparison with the similar numerical results obtained in the leading term approximation by Shukla and Cowley.[1] Finally Sec. V contains the

summary and conclusions.

II. THEORY

In the high-temperature limit, different terms of F to $O(\lambda^2)$ and $O(\lambda^4)$ have been derived previously,[1] and the corresponding diagrams are presented in Figs. 1 and 2, respectively. Using the notation $F(1(a))$, $F(1(b))$, etc., which means the free energy corresponding to the diagram (1(a)), (1(b)), etc., the expressions can be obtained from Table I of Shukla and Cowley.[1] All these expressions involve the anharmonic coefficient

$$V(\vec{k}_1 j_1, \vec{k}_2 j_2, \cdots, \vec{k}_m j_m)$$

defined by

$$V(\vec{k}_1 j_1, \vec{k}_2 j_2, \cdots, \vec{k}_m j_m) = \left(\frac{1}{n!}\right) N^{1-n/2} \Delta(\vec{k}_1 + \vec{k}_2 + \cdots + \vec{k}_m) \left(\frac{\hbar^n}{2^n \omega(\vec{k}_1 j_1)\omega(\vec{k}_2 j_2), \cdots, \omega(\vec{k}_m j_m)}\right)^{1/2} \times \Phi(\vec{k}_1 j_1, \vec{k}_2 j_2, \cdots, \vec{k}_m j_m), \quad (1)$$

$$\Phi(\vec{k}_1 j_1, \cdots, \vec{k}_m j_m) = \frac{1}{2M^{m/2}} \sum_{\vec{n}} \sum_{\alpha_1 \cdots \alpha_m} e_{\alpha_1}(\vec{k}_1 j_1) \cdots e_{\alpha_m}(\vec{k}_m j_m) \phi_{\alpha_1 \cdots \alpha_m}(n)(1 - e^{-2\pi i \vec{k}_1 \cdot \vec{r}_0^n}) \cdots (1 - e^{-2\pi i \vec{k}_m \cdot \vec{r}_0^n}), \quad (2)$$

where $\omega(\vec{k}_i j_i)$ and $\vec{e}(\vec{k}_i, j_i)$ are the eigenvalues and eigenvectors for the mode $\vec{k}_i j_i$ $(i = 1, 2, \cdots, m)$, $\phi_{\alpha_1, \cdots, \alpha_m}(n)$ is the mth-order tensor derivative of a two-body potential $\Phi(r)$, with $\alpha_1, \cdots, \alpha_m$ each running over the Cartesian indices x, y, z; $\vec{r}_0^n = \frac{1}{2} a_0[n_1, n_2, n_3]$, where n_1, n_2, n_3 are integers whose sum is even for a face-centered cubic lattice and a_0 is the lattice parameter. $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T is the temperature. M and N denote the atomic mass and number of unit cells in the crystal, respectively. $\Delta(\vec{k}_1 + \cdots + \vec{k}_m)$ is equal to unity if the sum of arguments is zero or a vector of reciprocal lattice, and zero otherwise.

Complete expressions (i.e., without making the leading-term approximation) for $\Phi(\vec{k}_1 j_1, \vec{k}_2 j_2, \vec{k}_3 j_3)$ and $\Phi(\vec{k}_1 j_1, \vec{k}_2 j_2, \vec{k}_3 j_3, \vec{k}_4 j_4)$ can be obtained from Maradudin *et al.*,[6] using Eqs. (2.12), (2.13), and (2.7) in their paper. After some lengthy algebra, but in a similar manner, one can derive complete expressions for $\Phi(\vec{k}_1 j_1, \vec{k}_2 j_2, \vec{k}_3 j_3, \vec{k}_4 j_4, \vec{k}_5 j_5)$ and $\Phi(\vec{k}_1 j_1, \vec{k}_2 j_2, \vec{k}_3 j_3, \vec{k}_4 j_4, \vec{k}_5 j_5, \vec{k}_6 j_6)$ needed in the calculation of $F(2(a))$ and $F(2(c))$.

III. NUMERICAL CALCULATIONS

The anharmonic free-energy contributions in the high-temperature limit were evaluated without making the leading term approximation for a face-centered cubic monatomic crystal with nearest-neighbor central-force interaction and $\phi'(r_0) = 0$, where r_0 is the nearest-neighbor distance.

In this case the elements of the harmonic dynamical matrix are given by

$$D_{xx}(\vec{k}) = [2\phi''(r_0)/M] \times [2 - \cos\pi a_0 k_x(\cos\pi a_0 k_y + \cos\pi a_0 k_z)], \quad (3)$$

$$D_{xy}(\vec{k}) = [2\phi''(r_0)/M] \sin\pi a_0 k_x \sin\pi a_0 k_y . \quad (4)$$

The other elements of the matrix can be obtained from the above by a change of labels. The eigenvalue equation is given by

$$\sum_{\beta} D_{\alpha\beta}(\vec{k}) e_\beta(\vec{k}j) = \omega^2(\vec{k}j) e_\alpha(\vec{k}j); \quad \alpha, \beta = x, y, z. \quad (5)$$

For convenience we introduce the dimensionless frequencies $\lambda(\vec{k}j)$ defined by

$$\lambda^2(\vec{k}j) = [M/2\phi''(r_0)]\omega^2(\vec{k}j) . \quad (6)$$

The eigenvectors $\vec{e}(\vec{k}j)$ satisfy the following relations:

$$\sum_{\alpha} e_\alpha(\vec{k}j) e_\alpha(\vec{k}j') = \delta_{jj'} , \quad (7)$$

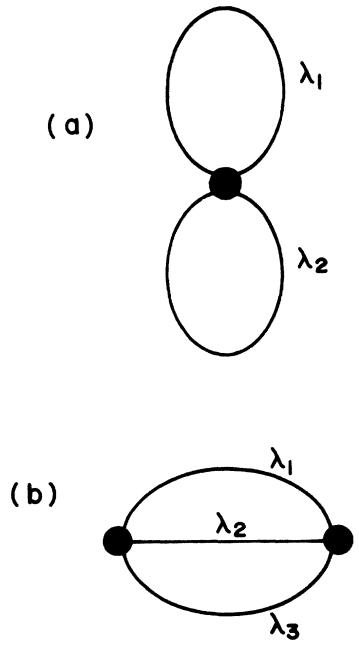

FIG. 1. Diagrams of order λ^2.

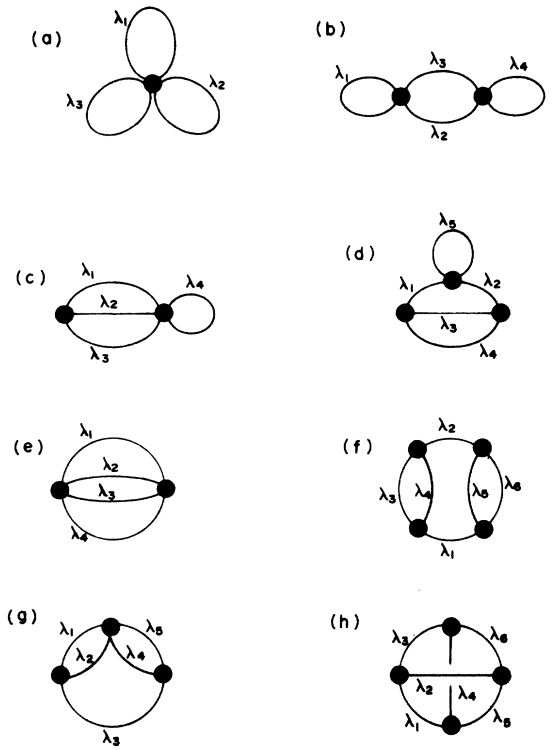

FIG. 2. Diagrams of order λ^4.

$$\sum_j e_\alpha(\vec{k}j)e_\beta(\vec{k}j) = \delta_{\alpha\beta}, \qquad j = 1, 2, 3, \tag{8}$$

and they transform under the point-group transformation according to the wave vector $\vec{k}$.

In all our calculations, we have eliminated the explicit knowledge of the eigenvalues $\omega(\vec{k}j)$ and eigenvectors $\vec{e}(\vec{k}j)$ by using the following simple version of the Born's theorem[7]

$$\sum_j \frac{e_\alpha(\vec{k}j)e_\beta(\vec{k}j)}{\omega^2(\vec{k}j)} = [D^{-1}(\vec{k})]_{\alpha\beta}, \tag{9}$$

where $D^{-1}(\vec{k})$ is the inverse of the harmonic dynamical matrix $D(\vec{k})$.

In order to evaluate the different free-energy contributions, we found it convenient to evaluate first the sums of the form

$$\sum_{\vec{q}j} \frac{e_\alpha(\vec{q}j)e_\beta(\vec{q}j)}{\lambda^2(\vec{q}j)} \cos(\vec{q}\cdot\vec{n}), \tag{10}$$

where the summation over $\vec{q} = \pi a_0 \vec{k}$ is over the whole Brillouin zone. This sum can be reduced from the whole zone to that of the $\frac{1}{48}$th portion in the following manner. Each of the 48 symmetry operations of a cube was applied to the vector $\vec{q}$ of the summand. Use was then made of the fact that $\vec{e}(\vec{q}j)$ transforms like $\vec{q}$ itself. Thus, 48 new summands (many identical) were produced, each of which when summed over $\vec{q}$ and j yielded the original sum. This is because the components q_x, q_y, q_z occur as for the original summand. If we add all these new summands together we obtain a term which is invariant under the 48 symmetry operations of a cube, meaning thereby that we need only sum this invariant total summand over $\frac{1}{48}$ of the Brillouin zone. The sums for the whole zone are obtained by multiplying with a weighting factor for each vector $\vec{q}$ to account for the number of $\vec{q}$'s equivalent to it by symmetry, special care being taken in assigning weighting factors for vectors on the zone boundaries. The result is 48 times the original sum. For example, we get the following:

$$S_{xx} = \sum_{\vec{q}j} \frac{e_x(\vec{q}j)e_x(\vec{q}j)}{\lambda^2(\vec{q}j)} \cos(\vec{q}\cdot\vec{n}), \tag{11}$$

$$S_{xx} = \sum_{\vec{q}}^{1/48} \tfrac{1}{6} W(\vec{q})[(D^{-1})_{xx}c_{xx}(c_{yy}c_{zz}+c_{zy}c_{yz}) + (D^{-1})_{yy}c_{yx}(c_{zy}c_{xz}+c_{xy}c_{zz}) + (D^{-1})_{zz}c_{zx}(c_{xy}c_{yz}+c_{yy}c_{xz})], \tag{12}$$

$$S_{xy} = \sum_{\vec{q}j} \frac{e_x(\vec{q}j)e_y(\vec{q}j)}{\lambda^2(\vec{q}j)} \cos(\vec{q}\cdot\vec{n}), \tag{13}$$

$$S_{xy} = -\sum_{\vec{q}}^{1/48} \tfrac{1}{6} W(\vec{q})[(D^{-1})_{xy}c_{zz}(s_{xx}s_{yy}+s_{xy}s_{yx}) + (D^{-1})_{yz}c_{xz}(s_{yx}s_{zy}+s_{zx}s_{yy}) + (D^{-1})_{xz}c_{yz}(s_{xx}s_{zy}+s_{xy}s_{zx})]. \tag{14}$$

Here, $c_{\alpha\beta} = \cos q_\alpha n_\beta$, $s_{\alpha\beta} = \sin q_\alpha n_\beta$, and $\alpha, \beta = x, y, z$. The summations $\sum_{\vec{q}}^{1/48}$ are over a $\frac{1}{48}$ portion of the entire Brillouin zone and $W(\vec{q})$ is the weighting factor for the vector $\vec{q}$. The factors

$$(D^{-1})_{xx},\ (D^{-1})_{yy},\ (D^{-1})_{zz},\ (D^{-1})_{xy},\ (D^{-1})_{yz},\ (D^{-1})_{xz},$$

are elements of the inverse of the dimensionless dynamical matrix and arise here by the use of Born's theorem. Other sums, S_{yy}, S_{zz}, etc. can be derived from the above by proper interchanges of the components n_x, n_y, n_z of the vector $\vec{n}$. Another type of sum which arises in the calculation of

$F(2(b))$ and $F(2(d))$ is

$$S_{\alpha\beta\gamma\delta}=\sum_{\vec{q}\,j_1j_2}\frac{e_\alpha(\vec{q}j_1)e_\beta(\vec{q}j_1)e_\gamma(\vec{q}j_2)e_\delta(\vec{q}j_2)}{\lambda^2(\vec{q}j_1)\lambda^2(\vec{q}j_2)}\cos(\vec{q}\cdot\vec{n}), \tag{15}$$

where each of α, β, γ, δ takes the values of x, y, z. As before we generate a summand which is invariant under the point group of a cube and then employ Born's theorem to eliminate the sums over j_1 and j_2, getting, for example,

$$S_{xxxx}=\sum_{\vec{q}\,j_1j_2}\frac{e_x^2(\vec{q}j_1)e_x^2(\vec{q}j_2)}{\lambda^2(\vec{q}j_1)\lambda^2(\vec{q}j_2)}\cos(\vec{q}\cdot\vec{n}), \tag{16}$$

$$S_{xxxx}=\sum_{\vec{q}}^{1/48}\tfrac{1}{6}W(\vec{q})\{[(D^{-1})_{xx}]^2c_{xx}(c_{yy}c_{zz}+c_{zy}c_{yz})+[(D^{-1})_{yy}]^2c_{yx}(c_{zy}c_{xz}+c_{xy}c_{zz})+[(D^{-1})_{zz}]^2c_{zx}(c_{xy}c_{yz}+c_{yy}c_{xz})\}, \tag{17}$$

$$S_{xxyy}=\sum_{\vec{q}\,j_1j_2}\frac{e_x^2(\vec{q}j_1)e_y^2(\vec{q}j_2)}{\lambda^2(\vec{q}j_1)\lambda^2(\vec{q}j_2)}\cos(\vec{q}\cdot\vec{n}), \tag{18}$$

$$S_{xxyy}=\sum_{\vec{q}}^{1/48}\tfrac{1}{6}W(\vec{q})[(D^{-1})_{xx}(D^{-1})_{yy}c_{zz}(c_{xx}c_{yy}+c_{yx}c_{xy})+(D^{-1})_{xx}(D^{-1})_{zz}c_{yz}(c_{zx}c_{xy}+c_{xx}c_{zy})$$
$$+(D^{-1})_{yy}(D^{-1})_{zz}c_{xz}(c_{yx}c_{zy}+c_{zx}c_{yy})], \tag{19}$$

$$S_{xxxy}=\sum_{\vec{q}\,j_1j_2}\frac{e_x^2(\vec{q}j_1)e_x(\vec{q}j_2)e_y(\vec{q}j_2)}{\lambda^2(\vec{q}j_1)\lambda^2(\vec{q}j_2)}\cos(\vec{q}\cdot\vec{n}), \tag{20}$$

$$S_{xxxy}=-\sum_{\vec{q}}^{1/48}\tfrac{1}{6}W(\vec{q})\{(D^{-1})_{xx}S_{xx}[(D^{-1})_{xy}s_{yy}c_{zz}+(D^{-1})_{xz}s_{zy}c_{yz}]+(D^{-1})_{yy}s_{yx}[(D^{-1})_{yz}s_{zy}c_{xz}+(D^{-1})_{xy}s_{xy}c_{zz}]$$
$$+(D^{-1})_{zz}s_{zx}[(D^{-1})_{xz}s_{xy}c_{yz}+(D^{-1})_{yz}s_{yy}c_{xz}]\}, \tag{21}$$

$$S_{xxyz}=\sum_{\vec{q}\,j_1j_2}\frac{e_x^2(\vec{q}j_1)e_y(\vec{q}j_2)e_z(\vec{q}j_2)}{\lambda^2(\vec{q}j_1)\lambda^2(\vec{q}j_2)}\cos(\vec{q}\cdot\vec{n}), \tag{22}$$

$$S_{xxyz}=-\sum_{\vec{q}}^{1/48}\tfrac{1}{6}W(\vec{q})[(D^{-1})_{xx}(D^{-1})_{yz}c_{xx}(s_{yy}s_{zz}+s_{zy}s_{yz})+(D^{-1})_{xz}(D^{-1})_{xy}c_{zx}(s_{xy}s_{yz}+s_{yy}s_{xz})$$
$$+(D^{-1})_{yy}(D^{-1})_{xz}c_{yx}(s_{zy}s_{xz}+s_{xy}s_{zz})], \tag{23}$$

$$S_{xyxy}=\sum_{\vec{q}\,j_1j_2}\frac{e_x(\vec{q}j_1)e_y(\vec{q}j_1)e_x(\vec{q}j_2)e_y(\vec{q}j_2)}{\lambda^2(\vec{q}j_1)\lambda^2(\vec{q}j_2)}\cos(\vec{q}\cdot\vec{n}), \tag{24}$$

$$S_{xyxy}=\sum_{\vec{q}}^{1/48}\tfrac{1}{6}W(\vec{q})\{[(D^{-1})_{xy}]^2c_{zz}(c_{xx}c_{yy}+c_{yx}c_{xy})+[(D^{-1})_{xz}]^2c_{yz}(c_{zx}c_{xy}+c_{xx}c_{zy})$$
$$+[(D^{-1})_{yz}]^2c_{xz}[c_{yx}c_{zy}+c_{zx}c_{yy}]\}, \tag{25}$$

$$S_{xyxz}=\sum_{\vec{q}\,j_1j_2}\frac{e_x(\vec{q}j_1)e_y(\vec{q}j_1)e_x(\vec{q}j_2)e_z(\vec{q}j_2)}{\lambda^2(\vec{q}j_1)\lambda^2(\vec{q}j_2)}\cos(\vec{q}\cdot\vec{n}) \tag{26}$$

$$S_{xyxz}=-\sum_{\vec{q}}^{1/48}\tfrac{1}{6}W(\vec{q})[(D^{-1})_{xy}(D^{-1})_{xz}c_{xx}(s_{yy}s_{zz}+s_{zy}s_{yz})+(D^{-1})_{xz}(D^{-1})_{yz}c_{zx}(s_{xy}s_{yz}+s_{yy}s_{xz})$$
$$+(D^{-1})_{yz}(D^{-1})_{xy}c_{yx}(s_{zy}s_{xz}+s_{xy}s_{zz})]. \tag{27}$$

Using these six sums we can, by suitably interchanging n_x, n_y, and n_z generate all 21 of the possible distinct sums of this type.

For computational purposes a simple cubic lattice of points in $\vec{k}$ space was used with $\vec{k}=\vec{p}/La_0$ and boundaries of the $\frac{1}{48}$ portion of the B. Z. defined by $L\geq p_x\geq p_y\geq p_z\geq 0$; $p_x+p_y+p_z<1.5L$, where p_x, p_y, p_z and L are integers. For $L=7$, this yields a mesh of 1372 points in the entire zone, including the origin (0, 0, 0). The previously discussed types of sums $S_{\alpha\beta}$, $S_{\alpha\beta\gamma\delta}$ were computed for $L=7$ in the reduced zone for a large number of vectors $\vec{n}$.[8] The origin was omitted from the sum over $\vec{k}$ and the sums were normalized by dividing them by a factor of 1371. Any remaining inaccuracy cancels out in the final results which all involve differences of the $S_{\alpha\beta}$ or $S_{\alpha\beta\gamma\delta}$.

In $F(1(a))$ and $F(2(b))$ if we substitute in full for the $\Phi(\vec{k}_1j_1,\ldots,\vec{k}_nj_n)$ function and factor out sums over different $\vec{k}_ij_i$, we get, respectively, a single and double summation over the nearest neighbors. In each case the summand is some function of the

sums $S_{\alpha\beta}$ and $S_{\alpha\beta\gamma\delta}$. For $F(1(a))$ we find

$$F(1(a)) = \frac{N(k_B T)^2}{64[\phi''(r_0)]^2}\left[D(r_0)S_{1A} + \frac{2C(r_0)}{r_0} S_{1B} + \frac{4B(r_0)}{r_0^2} S_{1C}\right], \quad (28)$$

where

$$B(r_0) = \left(\phi''(r) - \frac{1}{r}\phi'(r)\right)_{r=r_0}$$

$$C(r_0) = \left(\phi'''(r) - \frac{3}{r}\phi''(r) + \frac{3}{r^2}\phi'(r)\right)_{r=r_0},$$

$$D(r_0) = \left(\phi^{iv}(r) - \frac{6}{r}\phi'''(r) + \frac{15}{r^2}\phi''(r) - \frac{15}{r^3}\phi'(r)\right)_{r=r_0},$$

and the numerical values for the coefficients S_{1A}, S_{1B}, and S_{1C} are $S_{1A} = 12.00000$, $S_{1B} = 67.05850$, $S_{1C} = 64.73280$.

We note that if in sums like $S_{\alpha\beta}$ and $S_{\alpha\beta\gamma\delta}$ we put $\lambda(\vec{q}j) = 1$ and use Eq. (8) and $\sum_{\vec{q}} \cos(\vec{q}\cdot\vec{n}) = N\Delta(\vec{n})$, where $\Delta(\vec{n}) = 1$ for $\vec{n} = (0, 0, 0)$ and zero otherwise, we find

$$\sum_{\vec{q}j} e_\alpha(\vec{q}j)e_\beta(\vec{q}j)\cos(\vec{q}\cdot\vec{n}) = \delta_{\alpha\beta}N\Delta(\vec{n}),$$

$$\sum_{\vec{q}j_1j_2} e_\alpha(\vec{q}j_1)e_\beta(\vec{q}j_1)e_\gamma(\vec{q}j_2)e_\delta(\vec{q}j_2)\cos(\vec{q}\cdot\vec{n}) = \delta_{\alpha\beta}\delta_{\gamma\delta}N\Delta(\vec{n}).$$

Hence, if we put $\lambda(\vec{q}j) = 1$, which is equivalent to putting $(D^{-1})_{\alpha\beta} = \delta_{\alpha\beta}$, in our computer program for calculating, say, S_{1A}, S_{1B}, etc. and compute the result we can check this number against the analytical result which we can now easily obtain. Thus, we have a way of testing the accuracy of the terms being computed, such as S_{1A}, S_{1B}, and S_{1C}, as well as our summation procedure. All of the terms computed above and those which follow have been tested in this way. The analytically evaluated and the computed test sums were identical to at least seven significant figures.

$$F(2(a)) = \frac{N(k_B T)^3}{768[\phi''(r_0)]^3}\left(F(r_0)\, S_{3A} + \frac{2E(r_0)}{r_0} S_{3B} + \frac{4D(r_0)}{r_0^2} S_{3C} + \frac{8C(r_0)}{r_0^3} S_{3D}\right), \quad (29)$$

where

$$E(r_0) = \left(\phi^{v}(r) - \frac{10}{r}\phi^{iv}(r) + \frac{45}{r^2}\phi'''(r) - \frac{105}{r^3}\phi''(r) + \frac{105}{r^4}\phi'(r)\right)_{r=r_0},$$

$$F(r_0) = \left(\phi^{vi}(r) - \frac{15}{r}\phi^{v}(r) + \frac{105}{r^2}\phi^{iv}(r) - \frac{420}{r^3}\phi'''(r) + \frac{945}{r^4}\phi''(r) - \frac{945}{r^5}\phi'(r)\right)_{r=r_0},$$

and $C(r_0)$, $D(r_0)$ have been defined earlier.

The sums S_{3A}, etc. are given by $S_{3A} = 12$, $S_{3B} = 136.5878$, $S_{3C} = 395.3739$ and $S_{3D} = 273.9112$.

The expressions for $F(1(b))$, $F(2(c))$, and $F(2(e))$ each contain a Δ function of the type $\Delta(\vec{k}_1 + \cdots + \vec{k}_n)$. We can express the Δ function by

$$\Delta(\vec{k}) = \frac{1}{N}\sum_{\vec{n}} e^{ra_0 i\vec{k}\cdot\vec{n}},$$

the summation being over the N direct lattice vectors $\frac{1}{2}a\vec{n}$ of the "macrocrystal." For each of the above, we thus have a double summation over nearest-neighbor vectors from the two Φ functions as well as a summation over the N lattice vectors. The summands are again functions of the $S_{\alpha\beta}$.

The expressions are of the form

$$\sum_{\vec{n}}\sum_{\vec{n}_1}\sum_{\vec{n}_2} f(\vec{n}, \vec{n}_1, \vec{n}_2),$$

where $\vec{n}_1$, $\vec{n}_2$ range over the 12 nearest neighbors of the fcc crystal and $f(\vec{n}, \vec{n}_1, \vec{n}_2)$ can be expressed in terms of the $S_{\alpha\beta}$ for fixed $\vec{n}$, $\vec{n}_1$, and $\vec{n}_2$. The actual calculation was carried out as follows.[6] For a fixed vector $\vec{n}$ the sums over $\vec{n}_1$ and $\vec{n}_2$ were carried out. Then, noting that for each of the above three cases the result of summing over $\vec{n}_1$ and $\vec{n}_2$ was an expression having cubic symmetry in the components of $\vec{n}$; the result was multiplied by the multiplicity of the lattice vectors n. The range of n vectors was out to the first seven shells (i.e., up to the vector $\vec{n} = \langle 2, 2, 2\rangle$).

The expressions for $F(2(b))$ and $F(2(d))$ involve sums of the type $S_{\alpha\beta\gamma\delta}$ as well as $S_{\alpha\beta}$. In the case of $F(2(b))$ involving no Δ function there is only a double summation over nearest neighbors. In $F(2(d))$ there is only one Δ function and three Φ functions, so that we get a sum of the form

$$\sum_{\vec{m}}\sum_{\vec{n}_1}\sum_{\vec{n}_2}\sum_{\vec{n}_3} g(\vec{m}, \vec{n}_1, \vec{n}_2, \vec{n}_3),$$

where $\vec{n}_1$, $\vec{n}_2$, and $\vec{n}_3$ extend over nearest neighbors and m over general lattice vectors. Again the symmetry of the integrand required only one $\vec{m}$ from each shell. The remaining three contributions $F(2(f))$, $F(2(g))$, and $F(2(h))$ were computed by the scanning method. Let us define the following coefficients:

$$R_{BC} = \frac{2B(r_0)}{r_0 C(r_0)}, \quad R_{DE} = \frac{2D(r_0)}{r_0 E(r_0)}, \quad R_{CE} = \frac{4C(r_0)}{r_0^2 E(r_0)},$$

$$R_{BD} = \frac{B(r_0)}{r_0^2 D(r_0)}, \quad R_{CD} = \frac{C(r_0)}{r_0 D(r_0)}.$$

In the following, $B(r_0)$, $C(r_0)$, etc. will be written B, C, etc. The result for $F(1(b))$ is

$$F(1(b)) = -\frac{N(k_B T)^2 C^2}{(96)(32)[\phi''(r_0)]^3}\left[S_{2A} + 6(R_{BC})S_{2B}\right.$$

$$+(R_{BC})^2 S_{2C}] \,, \tag{30}$$

where $S_{2A} = 172.4021$, $S_{2B} = 92.13481$, and $S_{2C} = 742.5510$. For $F(2(c))$ we get

$$F(2(c)) = -\frac{N(k_B T)^3 CE}{(192)(32)[\phi''(r_0)]^4} \times [S_{4A} + (R_{DE})S_{4B} + (R_{CE})S_{4C} + (R_{BC})S_{4D} + (R_{BC})(R_{DE})S_{4E} + (R_{BC})(R_{CE})S_{4F}] \,, \tag{31}$$

where

$$S_{4A} = 172.4021 \,, \quad S_{4D} = 276.4044 \,,$$

$$S_{4B} = 1102.918 \,, \quad S_{4E} = 2067.663 \,,$$

$$S_{4C} = 1053.887 \,, \quad S_{4F} = 2914.453 \,.$$

Since 2(b) and 2(e), 2(f) and 2(h), and 2(g) and 2(d) involve the same types of derivatives we present them as follows. For $F(2(e))$ and $F(2(b))$ we have

$$F_\alpha = -\frac{N(k_B T)^3 D^2}{C_\alpha[\phi''(r_0)]^4}[C_{\alpha 1} + (R_{CD})C_{\alpha 2} + (R_{BD})C_{\alpha 3} + (R_{CD})^2 C_{\alpha 4} + (R_{BD})(R_{CD})C_{\alpha 5} + (R_{BD})^2 C_{\alpha 6}] \,, \tag{32}$$

$$C_{2B} = 1024 \,, \quad C_{2E} = 49152 \,,$$

$$C_{2B1} = 48.00000 \,, \quad C_{2E1} = 399.6699 \,,$$

$$C_{2B2} = 1072.936 \,, \quad C_{2E2} = 5188.788 \,,$$

$$C_{2B3} = 2069.772 \,, \quad C_{2E3} = 4798.0428 \,,$$

$$C_{2B4} = 6097.504 \,, \quad C_{2E4} = 25798.176 \,,$$

$$C_{2B5} = 19941.024 \,, \quad C_{2E5} = 61152.432 \,,$$

$$C_{2B6} = 26116.016 \,, \quad C_{2E6} = 73462.848 \,.$$

For $F(2(d))$ and $F(2(g))$ we have

$$F_\alpha = \frac{N(k_B T)^3}{C_\alpha[\phi''(r_0)]^5} DC^2[C_{\alpha 1} + (R_{BC})C_{\alpha 2} + (R_{BC})^2 C_{\alpha 3} + (R_{CD})C_{\alpha 4} + (R_{BC})(R_{CD})C_{\alpha 5} + (R_{BC})^2(R_{CD})C_{\alpha 6} + (R_{BD})C_{\alpha 7} + (R_{BC})(R_{BD})C_{\alpha 8} + (R_{BC})^2(R_{BD})C_{\alpha 9}] \,. \tag{33}$$

$$C_{2D} = 16384 \,, \quad C_{2G} = 2048 \,,$$

$$C_{2D1} = 689 \,, \quad C_{2G1} = 38.811986 \,,$$

$$C_{2D2} = 1167.954 \,, \quad C_{2G2} = 125.25767 \,,$$

$$C_{2D3} = 3115.2132 \,, \quad C_{2G3} = 106.36076 \,,$$

$$C_{2D4} = 3882.267 \,, \quad C_{2G4} = 126.11582 \,,$$

$$C_{2D5} = 6434.624 \,, \quad C_{2G5} = 468.04264 \,,$$

$$C_{2D6} = 17580.4979 \,, \quad C_{2G6} = 501.12368 \,,$$

$$C_{2D7} = 3816.3639 \,, \quad C_{2G7} = 58.468606 \,,$$

$$C_{2D8} = 6221.5498 \,, \quad C_{2G8} = 254.98396 \,,$$

$$C_{2D9} = 14149.1407 \,, \quad C_{2G9} = 363.06476 \,.$$

$F(2(d))$ was computed for only the three shells of m vectors $\langle 0, 0, 0\rangle$, $\langle 1, 1, 0\rangle$, and $\langle 2, 0, 0\rangle$. The total C_{2D1} for these shells was about 708, while the complete calculation gives about 689.[1] Hence, the numbers above are the result of scaling our numbers by the factor $\frac{689}{708}$. 108 wave vectors were used in the calculation of $F(2(g))$ and the sum was normalized by dividing it by the factor (107)(106)(106).

For $F(2(f))$ and $F(2(h))$ we have

$$F_\alpha = -\frac{N(k_B T)^3 C^4}{C_\alpha[\phi''(r_0)]^6}[C_{\alpha 1} + (R_{BC})C_{\alpha 2} + (R_{BC})^2 C_{\alpha 3} + (R_{BC})^3 C_{\alpha 4} + (R_{BC})^4 C_{\alpha 5}] \,, \tag{34}$$

$$C_{2F} = 4096 \,, \quad C_{2H} = 6144 \,,$$

$$C_{2F1} = 38.933938 \,, \quad C_{2H1} = 15.734122 \,,$$

$$C_{2F2} = 251.48430 \,, \quad C_{2H2} = 104.76075 \,,$$

$$C_{2F3} = 756.97021 \,, \quad C_{2H3} = 283.10868 \,,$$

$$C_{2F4} = 1135.8170 \,, \quad C_{2H4} = 394.57177 \,,$$

$$C_{2F5} = 780.02955 \,, \quad C_{2H5} = 256.81971 \,,$$

$C_{2F1}, \cdots, C_{2F5}$ were computed using 256 wave vectors in the whole zone and the resulting sums were normalized by the factor (255)(254)(254) while $C_{2H1}, \cdots, C_{2H5}$ were computed for 108 wave vectors and the normalization factor was (107)(106)(105).

IV. DISCUSSION

In order to compare the magnitudes of the various anharmonic contributions to the free energy we must have numbers for the coefficients $B(r_0)$, $C(r_0)$, etc. Hence, we must choose some form of two-body potential $\phi(r)$. Let us assume here the 12-6 potential:

$$\phi(r) = \epsilon[(r_0/r)^{12} - 2(r_0/r)^6] \,, \tag{35}$$

where we suppose that the minimum of $\Phi(r)$ occurs at the nearest-neighbor separation r_0. For the leading-term approximation (LTA) we retain only the terms containing the highest-ordered radial derivatives of $\phi(r)$ in each of $B(r)$, $C(r)$, etc. Evaluating these coefficients in terms of ϵ and r_0, and substituting into the free-energy expressions we find that the contributions of $O(\lambda^2)$, $F(1(a))$ and $F(1(b))$, are expressible in units of $N(k_B T)^2/\epsilon$, while those of $O(\lambda^4)$ are expressible in units of $N(k_B T)^3/\epsilon^2$. The full and LTA numbers are presented in columns 2 and 3 of Table I. In columns 4 and 5 are given the numbers arising from various classification schemes. SC1, ISC, SC2, $F(\lambda^4)$, and $F(\lambda^2)$ refer to the sums of the first two, first four, first six, first eight and last two numbers in each column, respectively.

An examination of Table I reveals that the LTA is not very good as far as absolute magnitudes are concerned. The deviations of the values from the

TABLE I. Anharmonic contributions to the free energy.

	Contribution		Partial total	
Diagram	Full	Leading	Full	Leading
$F(2(a))$	0.2049	0.3452		
$F(2(b))$	−0.6627	−1.2446	$F(SC1) = -0.4578$	$F(SC1) = -0.8994$
$F(2(c))$	−0.6012	−0.7320		
$F(2(d))$	(0.9146)	(1.3268)	$F(ISC) = -0.1444$	$F(ISC) = -0.3046$
$F(2(e))$	−0.2234	−0.2159		
$F(2(f))$	−0.3533	−0.3566	$F(SC2) = -0.7211$	$F(SC2) = -0.8771$
$F(2(g))$	0.5814	0.5981		
$F(2(h))$	−0.0912	−0.0961	$F(\lambda^4) = -0.2309$	$F(\lambda^4) = -0.3751$
$F(1(a))$	0.6910	0.9661		
$F(1(b))$	−0.3424	−0.3437	$F(\lambda^2) = 0.3486$	$F(\lambda^2) = 0.6224$

LTA range from 0.4% for $F(1(b))$ to 47% for $F(2(b))$. The largest contribution of $O(\lambda^4)$ in absolute magnitude comes from $F(2(d))$. With the exception of $F(2(e))$, for which there is a slight increase, the trend in Table I is a decrease in absolute magnitude in going from the LTA to the full-term numbers. The reductions of $F(\lambda^4)$ and $F(\lambda^2)$ are 38% and 44%, respectively. Of the various approximate schemes only $F(ISC)$ is close to $F(\lambda^4)$ in both full and LTA cases.

In order to assess the convergence of the perturbation expansion we examine the ratio of $F(\lambda^4)$ to $F(\lambda^2)$. We find that

$$F(\lambda^4)/F(\lambda^2) = -0.662(k_B T/\epsilon) \quad \text{(full)}, \tag{36a}$$

$$F(\lambda^4)/F(\lambda^2) = -0.603(k_B T/\epsilon) \quad \text{(LTA)}. \tag{36b}$$

For the inert-gas crystals the potential-well depth ϵ is approximately twice the melting temperature (T_m). Hence, substituting $\epsilon = 2k_B T_m$ and $T \sim T_m/3$ in Eq. (36) we find that $F(\lambda^4)$ is approximately $\frac{1}{10}$ of $F(\lambda^2)$ and of opposite sign in both cases indicating a satisfactory convergence if one uses the criterion of consecutive terms in an expansion being an order of magnitude (say, a factor of 10) smaller. It is interesting to note that $F(\lambda^4)$ is negative, indicating that if lowest order perturbation theory [i.e., $O(\lambda^2)$] is inadequate (e.g., the calculated C_v is lower than the experimental C_v in the high temperature range) the addition of all the terms of $O(\lambda^4)$ or only those included in the ISC scheme should help to improve the agreement.

V. SUMMARY AND CONCLUSIONS

We have calculated all of the contributions to the Helmholtz free energy of $O(\lambda^4)$ and $O(\lambda^2)$ without using the leading term approximation for a nearest-neighbor central-force model of a monatomic fcc crystal. For the Lennard-Jones potential, the ratio $F(\lambda^4)/F(\lambda^2)$ indicates a satisfactory convergence of the perturbation expansion up to approximately $\frac{1}{3}$ of the melting temperature. The leading-term approximation was found to be adequate only for estimating the ratio $F(\lambda^4)/F(\lambda^2)$. This approximation produced poor numbers for the total free energy as well as for some of the individual diagrams. Of the various classification schemes only ISC produced numbers close to $F(\lambda^4)$.

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