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On the Anharmonic Contribution to the Specific Heat of Monatomic Face-Centered Cubic Crystals

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We have presented a method for an exact calculation of the two lowest-order, cubic (F_3) and quartic (F_4), perturbation terms in the Helmholtz free energy (F) of an anharmonic crystal in the high temperature limit. The method is applicable to a nearest-neighbor central force model of a monatomic fcc crystal for any phenomenological two-body potential $\phi(r)$. The calculation of F_3 and F_4 requires a knowledge of the six dimensionless Brillouin zone (BZ) sums, as a function of a parameter a_1 depending on the first and second derivatives of $\phi(r)$. These sums are calculated to a high degree of accuracy for a mesh size of 308,000 points in the whole BZ in the range $-0.1 \leq a_1 \leq +0.1$ in steps of 0.02. The linear temperature dependent anharmonic contribution to the specific heat at constant volume, calculated for the elements Pb, Ag, Ni, Cu, Al, Ca, and Sr, from the Morse and Rydberg potentials, is found to be positive in all cases, with the exception of Pb. In this case the Morse potential gives a negative sign. The predictions of theory are in agreement with experiments where the data is available (e.g., Cu, Al, and Pb).

KEY WORDS: Helmholtz free energy; anharmonic fcc crystal; specific heat; perturbation theory; Brillouin zone sums.

1. INTRODUCTION

During the past 20 years, many calculations have been performed of the two lowest-order anharmonic free energy (F_3 and F_4) terms of rare gas anharmonic crystals. For an exhaustive review of the calculations of F_3 and F_4 for rare gas solids, see [1]. F_3 and F_4 arise from the cubic and quartic terms in the Taylor series expansion of the crystal potential energy. In the high tempera-

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ture limit ($T > \theta_D$), where θ_D is the Debye temperature, F_3 and F_4 both contribute to C_v (specific heat at constant volume), a term linear in temperature (T), i.e.,

$$C_v(\text{anharmonic}) \equiv C_v^A = 3R\left\{-\frac{2}{3}\left[a_3(v) + a_4(v)\right]\right\}K_B T \tag{1}$$

where the volume dependent coefficients $a_3(v)$ and $a_4(v)$ in Eq. (1) are obtained from F_3 and F_4, respectively, K_B is the Boltzmann constant, and R is the gas constant.

One of the earlier calculations of $a_3(v)$ and $a_4(v)$ was carried out in the high temperature (HT) limit by Stern [2] for a special nearest-neighbor model of bcc Na crystal. The next exhaustive calculations of $a_3(v)$ and $a_4(v)$ in the HT limit were performed by Maradudin et al. [3] for a nearest-neighbor central force model of a fcc crystal in the leading-term approximation. The leading-term approximation involves retaining only the highest-order radial derivative in each of the expressions for the cartesian tensor derivatives of the two-body potential $\phi(r)$, which occurs in the mathematical expressions for F_3 and F_4. Maradudin et al. [3] also corrected an error in the $a_3(v)$ calculation by Stern [2] and performed their calculations at $v = v_0$, corresponding to the volume (v_0) at the minimum in $\phi(r)$ at the nearest neighbor distance (r_0), i.e., $\phi'(r_o) = 0$.

In this paper, we present a calculation of F_3 and F_4 for the monatomic fcc structure, using the central force model potential, $\phi(r)$, without making the leading term approximation. The error [4] introduced in F_3 and F_4 in this approximation is 0.3% and 40%, respectively. Here we do not assume $\phi'(r_0) = 0$. Thus our calculations of F_3 and F_4 have been carried out for a set of values of the ratio $a_1 \equiv \phi'/[r(\phi'' - \phi'/r)]$ [5], where ϕ' and ϕ'' are the first and second radial derivatives of $\phi(r)$. This ratio serves to characterize the various nearest-neighbor potentials $\phi(r)$, and, in addition, for a given potential $\phi(r)$, its variation can represent changes in the lattice constant a_0 and hence the variation of F_3 and F_4 with volume. In other words, we obtian $a_3(v)$ and $a_4(v)$ at any volume for a given potential $\phi(r)$.

Often the parameters of the phenomenological potentials such as the Morse and Rydberg potentials of Girifalco and Weizer [6] and Varshni and Bloore [7], respectively, are determined by considering "all" neighbor interactions. For these potentials the ratio a_1 is negative. Most cases are taken care of if we restrict a_1 to the range $-0.1 \leq a_1 +0.1$. The calculations of F_3 and F_4 presented in this paper are in this range of a_1 in steps of 0.02. The range of a_1 in [5] was $-0.02 \leq a_1 \leq 0.1$, which is not adequate for the above potentials.

In Sec. 2, we present a summary of the expressions for F_3 and F_4 in terms of dimensionless sums. These dimensionless sums are functions of the frequency $\omega(\mathbf{q}\,j)$ for a wave vector $\mathbf{q}$ and branch index j. $\omega(\mathbf{q}\,j)$ are obtained by diagonalizing the dynamical matrix $D_{\alpha\beta}(\mathbf{q})$, which depends on the ratio a_1. Hence the dimensionless sums also depend on the ratio a_1.

The calculation of these dimensionless sums as a function of a_1 is presented in Sec. 3. As an example, calculations of F_3 and F_4 and C_v^A for a number of materials are presented in Sec. 4 where, given any $\phi(r)$ such as Morse or Rydberg potentials, it is shown how to find the value of the dimensionless sums required in the calculation of F_3 and F_4.

A discussion of the numerical results obtained in this paper for a number of materials (Pb, Ag, Ni, Cu, Al, Ca, Sr) and the validity of the nearest-neighbor model for metals are presented in Sec. 5, where it is concluded that the model used in this paper has its usefulness in metals involving large ion cores, such as Cu.

2. EXPRESSIONS FOR F_3 AND F_4 AND THE RATIO a_1

A complete derivation of the expressions for F_3 and F_4 in computational form for the "all" neighbor interaction potential $\phi(r)$, without making any approximation, for a monatomic fcc or bcc structure can be found in Shukla and Taylor [8]. Hence there is little point in repeating this derivation here. For our purposes we can write the expression for F_4, for a nearest-neighbor central force model of an fcc crystal [4], in the following form:

$$F_4 = \frac{N(K_BT)^2}{64\,|B(r_0)|^2}\left[D(r_0)S4A + \frac{2C(r_0)}{r_0}S4B + \frac{4B(r_0)}{r_0^2}S4C\right] \tag{2}$$

where N is the Avogadro number; $S4A$, $S4B$, and $S4C$ are the dimensionless single whole Brillouin zone sums; K_B and T have been defined in Eq. (1); and $B(r_0)$, $C(r_0)$, and $D(r_0)$ are the various combinations of the first four derivatives of $\phi(r)$ evaluated at r_0, and their expressions in terms of these derivatives are given by

$$B(r_0) = \phi''(r_0) - \frac{1}{r_0}\phi'(r_0) \tag{3}$$

$$C(r_0) = \phi'''(r_0) - \frac{3}{r_0}\phi''(r_0) + \frac{3}{r_0^2}\phi'(r_0) \tag{4}$$

$$D(r_0) = \phi^{\text{iv}}(r_0) - \frac{6}{r_0}\phi'''(r_0) + \frac{15}{r_0^2}\phi''(r_0) - \frac{15}{r_0^3}\phi'(r_0) \tag{5}$$

where r_0 is the nearest-neighbor distance (r_n).

The expression for F_3 is more complicated than F_4. For a nearest-neighbor central force model of an fcc crystal, the complete expression for F_3 can be written in the following form [4]:

$$F_3 = -\frac{N(K_B T)^2[C(r_0)]^2}{(96)(32)[B(r_0)]^3}[S3A + 6(RBC)S3B + (RBC)^2 S3C] \tag{6}$$

where $S3A$, $S3B$, and $S3C$ are dimensionless double Brillouin zone sums. $RBC = 2B(r_0)/r_0C(r_0)$, and the other symbols have been defined earlier in connection with Eq. (2).

The expressions for the dimensionless sums $S4A$, $S4B$, and $S4C$ arising in F_4 are given in full in Ref. [8]. We will not reproduce them here, but, in order to see how they depend on the ratio a_1, let us consider the full expression for $S4A$ for a nearest-neighbor fcc crystal [3,8]:

$$S4A = \frac{12}{N^2}\left[\sum_{\mathbf{q}j} \frac{[e_x(\mathbf{q}\,j) + e_y(\mathbf{q}\,j)]^2}{\lambda^2(\mathbf{q}\,j)}\left[1 - \cos\frac{a_0}{2}(q_x + q_y)\right]\right]^2 \tag{7}$$

where the summations over the wave vector $\mathbf{q}$ and j are over the whole first Brillouin zone and branch index, respectively; $e_\alpha(\mathbf{q}\,j)$ are the eigenvector components ($\alpha = x,y,z$), and $\lambda(\mathbf{q}\,j)$ are the dimensionless frequencies to be determined from the dynamical matrix $D_{\alpha\beta}(\mathbf{q})$. For a potential $\phi(r)$ and the nearest-neighbor fcc crystal, the diagonal, $D_{xx}(\mathbf{q})$ and the off-diagonal, $D_{xy}(\mathbf{q})$, matrix elements are given by [9]

$$MD_{xx}(\mathbf{q}) = 2B(r_0)[2 - C_x(C_y + C_z) + 2a_1(3 - C_xC_y - C_{yC_z} - C_zC_x)] \tag{8}$$

$$MD_{xy}(\mathbf{q}) = 2B(r_0)S_xS_y \tag{9}$$

where, in Eqs. (8) and (9), $C_i = \cos a_0q_i$, $S_i = \sin a_0q_i (i = x,y,z)$; M is the atomic mass; and $B(r_0)$ and the ratio a_1 have been defined above.

The eigenvalue equation is given by

$$\sum_\beta D_{\alpha\beta}(\mathbf{q})e_\beta(\mathbf{q}\,j) = \omega^2(\mathbf{q}\,j)e_\alpha(\mathbf{q}\,j) \tag{10}$$

where $\alpha, \beta = x,y,z$, and $j = 1,2,3$.

The dimensionless frequencies $\lambda(qj)$ in Eq. (7) are obtained from the scaling procedure

$$\omega^2(\mathbf{q}\,j) = \frac{2B(r_0)}{M}\lambda^2(\mathbf{q}\,j) \tag{11}$$

Clearly then, $\lambda(\mathbf{q}\,j)$ depends on the ratio a_1, and thus $S4A$ depends on a_1. Similarly, the other dimensionless sums $S4B$ and $S4C$ in F_4 depend on a_1.

In the same manner one can see that the other sums $S3A$, $S3B$, and $S3C$, involving double Brillouin zone summations and triple branch index summations in the expression for F_3, Eq. (6), also depend on a_1. The expressions for $S3A$, etc., are lengthy and we do not reproduce them here. They can be obtained from Refs. [3, 4, 8]

3. CALCULATION OF THE DIMENSIONLESS SUMS

The dimensionless sums $S4A$, $S4B$, $S4C$, and $S3A$, $S3B$, $S3C$ can be calculated by the method described in Shukla and Wilk [4]. In Ref. [4], these sums were calculated for $a_1 = 0$. The calculation requires the knowledge of the following tensorial Brillouin zone sums for a direct lattice vector $\mathbf{r}^l$:

$$S_{xx}(\mathbf{l}) = \sum_{\mathbf{q}j} \frac{e_x(\mathbf{q}\,j)e_x(\mathbf{q}\,j)}{\lambda^2(\mathbf{q}\,j)} \cos(\mathbf{q}\cdot\mathbf{r}^l) \tag{12}$$

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

The other two-diagonal and off-diagonal tensors, viz., $S_{yy}(\mathbf{l})$, $S_{zz}(\mathbf{l})$, $S_{xz}(\mathbf{l})$, and $S_{yz}(\mathbf{l})$ are obtained from the above by proper interchange of the indices. It has been shown in Ref. [4] how to reduce the whole Brillouin sums in Eqs. (12) and (13) to the 1/48th portion of the zone and eliminate the j summation, using the following simple version of Born's theorem [10]:

$$\sum_{j} \frac{e_\alpha(\mathbf{q}\,j)e_\beta(\mathbf{q}\,j)}{\lambda^2(\mathbf{q}\,j)} = [H^{-1}(\mathbf{q})]_{\alpha\beta}$$

where $[H^{-1}(\mathbf{q})]_{\alpha\beta}$ is the $\alpha\beta$ element of the inverse dynamical matrix defined by Eqs. (8) and (9) with $2B(r_0)/M = 1$.

Our procedure in computing $S4A$, $S4B$, $S4C$, and $S3A$, $S3B$, $S3C$ was to first calculate and store $S_{\alpha\beta}(\mathbf{l})$ for a sufficient number of direct lattice vectors $\mathbf{l}$. This was done for 11 values of a_1 in the range $-0.1 \le a_1 \le +0.1$ in steps of 0.02. $S_{\alpha\beta}(\mathbf{l})$ are then obtained from Eqs. (12) and (13). In the actual calculation of $S4A$, $S4B$, $S4C$, and $S3A$, $S3B$, $S3C$, the appropriate sum was selected as needed by comparing the direct lattice vector in the argument of $S_{\alpha\beta}(\mathbf{l})$ with those of the stored general set of direct lattice vectors.

In all the calculations, we have used a simple cubic mesh of wave vectors with $\mathbf{q} = \pi\mathbf{p}/La_0$ and boundaries of the 1/48th portion of the first Brillouin

Table I. Dimensionless Sums, $S4A$, $S4B$, and $S4C$, for Different Values of a_1

a_1	$S4A$	$S4B$	$S4C$
0.10	6.6424	36.1406	32.8783
0.08	7.3575	40.1996	36.9149
0.06	8.2049	45.0390	41.7913
0.04	9.2219	50.8877	47.7716
0.02	10.4613	58.0712	55.2378
0.00	12.0000	67.0682	64.7629
−0.02	13.9544	78.6124	77.2455
−0.04	16.5105	93.8898	94.1752
−0.06	19.9855	114.9579	118.2144
−0.08	24.9771	145.7607	154.6527
−0.10	32.7935	195.1482	215.9211

zone defined by $L \geq p_x \geq p_y \geq p_z \geq 0$, $p_x + p_y + p_z \leq 1.5L$, where p_x, p_y, p_z and L are integers and a_0 is the lattice constant. This yields $4L^3$ points in the whole zone. In Ref. [4], the step length $L = 7$, corresponding to 1372 points in the whole zone, was used in computing $S4A$, $S4B$, $S4C$ and $S3A$, $S3B$, $S3C$ for $a_1 = 0$. Here, in this paper, we have calculated these sums for $L = 30$, which corresponds to 308,000 points in the whole zone. We have presented in Tables I and II the sums $S4A$, $S4B$, $S4C$ and $S3A$, $S3B$, $S3C$, respectively, for 11 values of a_1 in the range $-0.1 \leq a_1 \leq +0.1$ in steps of 0.02.

4. CALCULATION OF F_3, F_4 AND C_v^A

The cubic and quartic terms of the Helmholtz freen energy, F_3 and F_4, can be calculated from Eqs. (2)–(6) presented in Sec. 3 for any two-body

Table II. Dimensionless Sums, $S3A$, $S3B$, and $S3C$, for Different Values of a_1

a_1	$S3A$	$S3B$	$S3C$
0.10	70.5913	38.4839	305.3829
0.08	82.3512	44.7611	356.0845
0.06	97.0710	52.5874	419.5128
0.04	115.8116	62.5078	500.2258
0.02	140.1570	75.3319	605.0335
0.00	172.5623	92.3066	744.5057
−0.02	217.0117	115.4410	935.8389
−0.04	280.3586	148.1617	1208.742
−0.06	375.3332	196.7660	1618.819
−0.08	528.2631	274.0925	2282.677
−0.10	803.4675	410.8234	3493.464

potential $\phi(r)$ in the following manner. First we find the derivatives $\phi'(r)$ and $\phi''(r)$ of $\phi(r)$ and then compute the ratio a_1, defined by

$$a_1 = \left.\frac{(\phi'/r)}{(\phi'' - \phi'/r)}\right|_{r=r_0} \tag{14}$$

For this value of a_1, the values of the dimensionless sums $S4A$, $S4B$, $S4C$ and $S3A$, $S3B$, $S3C$, which are functions of a_1, are obtained by interpolation from the Tables I and II, respectively. Next, we obtain the other derivatives of $\phi(r)$ and compute $B(r_0)$, $C(r_0)$ and $D(r_0)$ from Eqs. (3)–(5). Finally, with all this, F_4 and F_3 are easily computed from Eqs. (2) and (6), respectively. The anharmonic contribution to C_v from F_3 and F_4 is obtained from the following:

$$C_v^A = -T\frac{\partial^2}{\partial T^2}(F_3 + F_4) = 3RAK_BT = 3RBT, \quad \text{where } B = AK_B \tag{15}$$

As an example of the above description of finding F_3, F_4, and C_v^A for a given $\phi(r)$ from Tables I and II, we consider the following two widely used phenomenological potentials: (a) the Morse potential, $\phi_M(r)$, and (b) the Rydberg potential, $\phi_R(r)$, defined by

$$\phi_M(r) = D[\exp\{-2\alpha(r - \gamma_0)\} - 2\exp\{-\alpha(r - \gamma_0)\}] \tag{16}$$

$$\phi_R(r) = -D[1 + \alpha(r - \gamma_0)]\exp[-\alpha(r - \gamma_0)] \tag{17}$$

where the potential parameters D, α, and γ_0, appearing in $\phi_M(r)$ and $\phi_R(r)$, have been determined for a number of monatomic fcc materials by Girifalco and Weizer [6] and Varshni and Bloore [7], respectively.

Following the procedure outlined above, we have calculated numerical values of a_1, F_3, F_4, $F = F_3 + F_4$, and the anharmonic coefficient B in Eq. (15) for the elements Pb, Ag, Ni, Cu, Al, Ca, and Sr. These results for $\phi_M(r)$ and $\phi_R(r)$ potentials [6, 7] are presented in Tables III and IV, respectively.

5. DISCUSSION

The method presented in this paper of an exact calculation of the two lowest-order perturbation terms in the Helmholtz free energy (F) of an anharmonic crystal, viz., F_3 and F_4, is applicable to a nearest-neighbor central force model of a monatomic fcc crystal in the high temperature limit. Given any phenomenological two-body potential $\phi(r)$, F_3 and F_4 and their contribution to C_v^A can be calculated from the equations given in the previous sections. We performed these calculations for seven elements (Pb, Ag, Ni, Cu, Al, Ca,

Table III. Cubic, F_3, quartic, F_4, the total free energy, F, and the coefficient, B, in $C_v^A/3R = BT$, for the Morse Potential[a]

Elements	a_1	F_3	F_4	$F = F_3 + F_4$	B
Pb	−0.048	−0.34940	0.37142	0.02202	−2.027
Ag	−0.052	−0.24382	0.23984	−0.00399	0.367
Ni	−0.067	−0.17853	0.13487	−0.04367	4.019
Cu	−0.069	−0.21816	0.15615	−0.06201	5.707
A*l*	−0.076	−0.27377	0.17132	−0.10245	9.429
Ca	−0.083	−0.45473	0.23819	−0.21654	19.929
Sr	−0.084	−0.48558	0.25233	−0.23325	21.467

[a] F_3, F_4, and F are in units of $10^{12}\,N(K_BT)^2$ erg^{-1} and B is in units of 10^{-6}/K.

and Sr), employing the Morse and Rydberg phenomenological potentials. In all our calculations we have used the Morse and Rydberg potential parameters determined by Girifalco and Weizer [6], and Varshni and Bloore [7], respectively. The value of the parameter b quoted in Table II of Ref. [7] for Ca is in error. The correct value communicated to the author by Y. P. Varshni is $b = 1.1884$. This value has been used in the present calculations of F_3, F_4, and B for Ca.

It is interesting to note that both the potentials predict a positive anharmonic contribution for C_v in six elements, viz., Ag, Ni, Cu, Al, Ca, and Sr, but for Pb the signs are opposite.

There are two sets of predictions of C_v^A from the experimental data on the heat capacity in Al [11, 12]. The prediction of C_v^A being positive from both the potentials agrees with Brooks and Bingham [11]. Leadbetter [12] predicts a negative C_v^A. Currently we are analyzing this situation in Al, and the results of our findings will be reported later. For Pb the two potentials give opposite results: positive C_v^A from Rydberg and negative C_v^A from Morse. The

Table IV. Cubic, F_3, quartic, F_4, the total free energy, F, and the coefficient, B, in $C_v^A = BT$, for the Rydberg Potential[a]

Elements	a_1	F_3	F_4	$F = F_3 + F_4$	B
Pb	−0.042	−0.32612	0.31132	−0.01479	1.362
Ag	−0.049	−0.22106	0.18480	−0.03626	3.337
Ni	−0.062	−0.16057	0.10514	−0.05543	5.101
Cu	−0.064	−0.19458	0.11932	−0.07525	6.926
A*l*	−0.071	−0.24209	0.12706	−0.11503	10.587
Ca	−0.078	−0.39899	0.17110	−0.22789	20.974
Sr	−0.078	−0.42799	0.18358	−0.24440	22.494

[a] F_3, F_4, and F are in units of $10^{12}\,N(K_BT)^2$ erg^{-1} and B is in units of 10^{-6}/K.

latter prediction is in agreement with the analysis (experimental) of Leadbetter [12]. For Cu the prediction of the sign of C_v^A from both the potentials agrees with that of Brooks' [13] analysis of the experimental heat capacity data.

Now the question arises: Is the nearest-neighbor model useful in the calculations of the above type? It would seem that for metallic crystals the nearest-neighbor central force (nncf) model is inadequate if the volume dependent terms arising from the electron gas effects are not included in the potential function. As a matter of fact, the interatomic forces, even in such simple metals as Na, K, etc., are long range and oscillatory and, in addition, they change as the crystal volume changes. The calculation of F_3 and F_4 in such cases is very time consuming, with the additional difficulty of convergence of the sums arising in F_4. A full description of the method of F_3 and F_4 calculation and a discussion of the convergence difficulties can be found in the paper of Shukla and Taylor [8]. In such cases the nncf model has very little or no usefulness.

On the other hand, in another report [14] on the anharmonic calculations in metals such as copper, where the interatomic forces are known to exist primarily between nearest-neighbor atoms, due to the overlap of the $3d$ orbitals on adjacent atoms (overlap energy), the nncf model was found to be useful. The nncf model is to some extent justified in metals like Cu as seen by a direct calculation [15, 16] of the electron-ion contribution to the forces, which indicates that the convergence is rapid, and by the fit to experimental phonon dispersion curves given by a nearest-neighbor model [17]. In the nncf model of Cu employed by Cowley and Shukla [14], the overlap energy was represented by a Born-Mayer term of the type

$$V_{\mathrm{BM}}(r) = \alpha \exp\,[\rho(\gamma_0 - r)/\gamma_0] \tag{18}$$

where α, ρ, and γ_0 are potential parameters. The total energy was taken as $V_{\mathrm{BM}}(r)$ plus the volume dependent electron gas contributions describing the kinetic, correlation, and exchange energies. It was shown in this work that the volume dependent electronic energy terms can be included in the potential function, acting between nearest neighbors, if the parameter α in $V_{\mathrm{BM}}(r)$ is volume dependent. The method presented in this paper of the F_3 and F_4 calculation is applicable to the above type of potentials in Cu as well as other similar potentials in monatomic fcc structures.

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