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# Validity of nearest-neighbor interaction and leading-term approximation in lattice-anharmonicity calculations of monatomic bcc structures

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The validity of the nearest-neighbor central-force interaction (NNCF) and the leading-term approximation (LTA) in lattice anharmonicity calculations of monatomic bcc structures is investigated. Calculations are made of the lowest-order cubic ($F_3$) and quartic ($F_4$) anharmonic contributions to the Helmholtz free energy and the specific heat at constant volume ($C_V^A$) for Na from a number of central-force two-body potentials obtained by Cochran, Price *et al.*, and the Morse potential of Lloyd. Excellent results for $C_V^A$ are obtained with exact calculations for the nearest-neighbor anharmonic interaction. However, the good agreement is destroyed when more neighbors are included in the anharmonic interaction in the exact calculation. For example, the two-neighbor anharmonic interaction produces an almost exact cancellation of $F_3$ and $F_4$ for the Cochran and Ashcroft-Singwi potentials and $C_V^A(\text{calc}) = -C_V^A(\text{expt})/4$ for the Morse potential of Lloyd. The inclusion of the third neighbor in the anharmonic interaction in the exact calculation gives $C_V^A(\text{calc}) = C_V^A(\text{expt})/8$ for the Cochran potential and $C_V^A(\text{calc}) = -C_V^A(\text{expt})/8$ for the Ashcroft-Singwi potential. This behavior in $C_V^A$ is due to a very low value of $F_4$ for the exact NNCF calculation and in this case it is even negative for the Ashcroft-Singwi potential. The second neighbors make a large positive contribution to $F_4$ but do not change the value of $F_3$ dramatically from its nearest-neighbor value. The results indicate that the NNCF and LTA approximations are totally unreliable in the calculations of $F_3$, $F_4$, and $C_V^A$.

Recently, a paper has been published on the calculation of the lattice anharmonicity of alkali metals.[1] In this paper, the authors have calculated the cubic ($F_3$) and quartic ($F_4$) terms of the Helmholtz free energy ($F$), and their contributions to the specific heat at constant volume ($C_v^A$), in the high-temperature limit. Representing the latter contribution by $(C_v/3Nk_B) = 1 + AT$, where $N$ is the Avogadro number, $k_B$ is the Boltzmann constant, and $T$ is temperature, the coefficient $A$ was calculated by including the effect of thermal expansion. The authors claim to find good agreement with the experimental values[2] of $A$ for all the alkali metals.

These anharmonic calculations of $F_3$, $F_4$, and the coefficient $A$ have been carried out in the high-temperature limit employing two approximations: (a) nearest-neighbor central-force (NNCF) interaction, and (b) leading-term approximation. The meaning of approximation (a) is obvious, where a two-body potential $V(r)$ is assumed and only nearest neighbors are considered in the calculation of $F_3$, $F_4$, and the coefficient $A$. The approximation (b) involves retaining only the highest-ordered radial derivative of $V(r)$ in evaluating each of the Fourier transforms of the third- and fourth-rank Cartesian tensors, required in the calculation of $F_3$ and $F_4$. Hence the name leading-term approximation. The authors have concluded that "a potential which may be adequate in estimating the effects of anharmonicity may not be essentially suitable to describe the harmonic properties."

The errors introduced in the $F_3$ and $F_4$ calculation, for an NNCF model of an fcc crystal in approximation (b), have been estimated previously[3] for a Lennard-Jones potential $V(r)$. They are of the order of less than 1% in $F_3$ and about 40% in $F_4$. The purpose of this paper is to examine the usefulness and validity of the two aforementioned approximations in the calculation of the lattice anharmonicity of alkali metals and body-centered-cubic structure in general, and also to clarify once again the meaning of "the coefficient $A$ was calculated by including the effect of thermal expansion." Although it has been shown before[4] that it is erroneous to include thermal-expansion effects in the calculation of $C_v$ and still call it $C_v$, obviously the point needs further clarification.

A general method of the calculation of $F_3$ and $F_4$, with anharmonic interactions extending to any number of neighbors and without making the leading-term approximation, has been given by Shukla and Taylor.[5] In their work, calculations of $F_3$ and $F_4$ for Na and K were carried out for a large number of volumes, in each case considering anharmonic interactions up to 23 neighbors. They also pointed out the difficulties associated with the convergence of $F_3$ and $F_4$ especially if one chooses to calculate them from $V(r)$ generated in real space which for large distances has Friedel oscillations of the type $\cos(2k_F r + \theta)/r^3$, where $k_F$ is the Fermi radius and $\theta$ is the phase factor. The potential used in Ref. 1, from Shyu and Gaspari,[6] shows oscillations of the above type. These oscillations occur due to the singularity in the slope of the dielectric function of the electron gas at twice the Fermi radius ($k_F$). Hence in the present work we will not repeat the derivations of $F_3$ and $F_4$ as they can be obtained from Shukla and Taylor.[5] Here, it is sufficient to note that in the high-temperature limit $F_3$ and $F_4$ can be written from Ref. 5, in the following form:

$$F_3 = -N(k_B T)^2 (f_{3a}S_{3a} + f_{3b}S_{3b} + f_{3c}S_{3c}), \qquad (1)$$

$$F_4 = N(k_B T)^2 (f_{4a}S_{4a} + f_{4b}S_{4b} + f_{4c}S_{4c}), \qquad (2)$$

where in Eq. (1) the functions $f_{3a}$, $f_{3b}$, and $f_{3c}$ depend on the various combination of derivatives of $V(r)$ evaluated at different positions of the neighbors to be included in the calculation. The functions $S_{3a}$, $S_{3b}$, and $S_{3c}$ represent the double-Brillouin-zone and triple-branch-index summations. The symbols appearing in Eq. (2) have similar meanings except that $S_{4a}$, $S_{4b}$, $S_{4c}$ represent the single Brillouin-zone and branch-index summations. The mathematical expressions for the symbols appearing in Eqs. (1) and (2) can be obtained from the results derived in Sec. III of Ref. 5.

To investigate the validity of the use of the nearest-neighbor model and the leading-term approximation we have chosen to calculate $F_3$ and $F_4$ for Na from the Morse potential derived by Lloyd,[7] the Cochran potential,[8] and the now widely used Ashcroft potential employed in the calculations of Price, Singwi and Tosi.[9] We include in this paper the results for $F_3$, $F_4$, and $C_v^A$ for Na calculated from the Morse and Cochran potentials, because both these potentials were used previously[10] in the calculation of $F_3$, $F_4$, and $C_v^A$ for Na in approximations (a) and (b).

We present in Table I the results of our full calculations without any approximations such as (a) or (b) mentioned before for all three potentials. The number of neighbors included in the harmonic and anharmonic interactions are also given in this table.

For example, with the Cochran potential, interactions up to five neighbors are included in the harmonic dynamical matrix in obtaining the eigenvalues $\omega(\vec{q}j)$ and eigenvectors $\vec{e}(\vec{q}j)$ for a mode $\vec{q}j$. These $\omega(\vec{q}j)$ and $\vec{e}(\vec{q}j)$ are then used in the $F_3$ and $F_4$ calculations by the method of Shukla and Taylor[5] where we include up to three shells in the anharmonic interaction. The corresponding $F_3$ and $F_4$ results are presented in Table I, columns 4 and 5, respectively. The last two columns contain the total $F = F_3 + F_4$ and the coefficient $A$ in $C_v^A$. The results for the other potentials are also presented.

In a similar fashion we present in Table I the results for $F_3$, $F_4$, and $C_v^A$ for all three potentials in approximations (a) and (b). To avoid any confusion, we wish to reiterate again that the approximations (a) and (b) are only used in the anharmonic calculation and not in setting up the dynamical matrix in obtaining $\omega(\vec{q}j)$ and $\vec{e}(\vec{q}j)$.

From the results presented in Table I we can draw the following conclusions for all the three potentials. The nearest-neighbor central-force

TABLE I. Cubic ($F_3$), quartic ($F_4$), the total free energy ($F$), and the coefficient $A$ in $C_v^A = 3Nk_BAT$ for three potentials of Na. $F_3$, $F_4$, and $F$ are in units of $10^{12}N(k_BT)^2$ erg$^{-1}$ and $A$ is in units of $10^{-4}$/K.

| Type of potential | Number of terms in harmonic interaction | Number of terms in anharmonic interaction | $F_3$ | $F_4$ | $F = F_3 + F_4$ | $A$ |
|---|---|---|---|---|---|---|
| | | Results of full calculation | | | | |
| Morse potential of Lloyd | 2 | 1 | −1.5298 | 0.7811 | −0.7487 | 0.689 |
| | 2 | 2 | −1.6803 | 2.1953 | 0.5150 | −0.474 |
| Cochran | 5 | 1 | −1.9669 | 0.0604 | −1.9065 | 1.755 |
| | 5 | 2 | −2.4594 | 2.3814 | −0.0780 | 0.072 |
| | 5 | 3 | −2.4912 | 2.2741 | −0.2171 | 0.200 |
| Ashcroft-type Singwi potential | 10 | 1 | −2.2548 | −0.0863 | −2.3411 | 2.155 |
| | 10 | 2 | −3.0243 | 3.0059 | −0.0184 | 0.017 |
| | 10 | 3 | −3.0768 | 3.3824 | 0.3056 | −0.281 |
| | | Results of calculations in approximations (a) and (b) | | | | |
| Lloyd | 2 | 1 | −1.3407 | 2.7604 | 1.4197 | −1.307 |
| Cochran | 5 | 1 | −1.5309 | 2.4522 | 0.9213 | −0.848 |
| Singwi | 10 | 1 | −1.6884 | 2.5325 | 0.8441 | −0.777 |

model coupled with the leading-term approximation, i.e., approximations (a) and (b), give a negative sign for the coefficient $A$ in $C_v^A$. The experimental value of $A$ by Martin[2] is of course positive. When anharmonic interactions are restricted to the nearest neighbors only, the full calculation for the Cochran and Singwi potentials yields the positive values of $A$ which is in surprisingly good agreement with the experimental value[2] of $1.69\times10^{-4}/$ K, whereas the Morse potential of Lloyd gives a positive lower value, i.e., approximately $A$(expt)/2.4. However, for both Cochran and Singwi potentials, when anharmonic interactions are extended to two shells, $A$ becomes very small but remains positive, whereas the Morse potential of Lloyd gives negative $A$. When three shells are included in the anharmonic interaction, the Cochran potential gives $A \sim A$(expt)/8 but the Singwi potential gives a negative $A$. We can understand this behavior in the magnitude and sign of the coefficient $A$ for the three potentials because for all of them there are wide variations in the value of $F_4$. For example, $F_4$ is a factor of 30 smaller in absolute terms than $F_3$ for the Singwi and Cochran potentials, and for the former it is even negative.

The inclusion of second neighbors in the anharmonic interaction does not change $F_3$ substantially but $F_4$ increases by a factor of 40 from its nearest-neighbor value and changes sign for the Singwi potential. In both cases $F_3$ and $F_4$ almost cancel each other, thus giving a low value for the coefficient $A$ in $C_v^A$.

It is clear from the above discussion that the nearest-neighbor central-force model in the anharmonic calculations of bcc alkali metals gives misleading results. The NNCF results of the full calculation have no relationship to the results obtained in approximations (a) and (b).

Now we turn our attention to the other point mentioned before, i.e., in Ref. 1 the coefficient $A$ was calculated by including the effect of thermal expansion. The arguments first presented in Ref. 10 and again used in Ref. 1 are as follows.

The total Helmholtz free energy can be written as[11]

$$F(V,T)=\Phi_{\mathrm{st}}(V)+F_{\mathrm{qh}}(V,T)+\lambda^2F_a(V)T^2, \tag{3}$$

where $\Phi_{\mathrm{st}}$ is the energy of the static crystal, $F_{\mathrm{qh}}$ is the quasi harmonic Helmholtz free energy, $\lambda$ is the Van Hove expansion parameter, and the last term in Eq. (3) is the sum of $F_3$ and $F_4$ with $F_a$ as the volume-dependent term. We note that the first two terms in Eq. (3) also depend on crystal volume $v$. By replacing $v$ or the nearest-neighbor distance $r$ with $r_0(1+\epsilon)$, where $\epsilon$ is the thermal strain parameter and $r_0$ is the value of $r$ with $\epsilon=0$, Eq. (3) can be expanded to $O(\epsilon^2)$ as

$$F(\epsilon,T)=\Phi_{\mathrm{st}}(0)+\Phi_1\epsilon^2+F_{\mathrm{qh}}(0,T)+F_1T\epsilon +\lambda^2F_a(0)T^2\,, \tag{4}$$

where $\Phi_1$ and $F_1$ are the first derivatives of $\Phi_{\mathrm{st}}$ and $F_{\mathrm{qh}}$ with respect to $\epsilon$ evaluated at $\epsilon=0$. Since $\epsilon$ is of $O(\lambda)$, Eq. (4) is correct to $O(\lambda^2)$.

From Eq. (4) we can evaluate both the equilibrium value of $\epsilon$ and $C_v$ by the following two equations:

$$\left(\frac{\partial F}{\partial\epsilon}\right)_T=0 \quad \text{at } P=0\,,$$

$$C_v=-T\left(\frac{\partial^2F}{\partial T^2}\right)_v=-T\left(\frac{\partial^2F}{\partial T^2}\right)_\epsilon\,,$$

where $P$ is the pressure, and the subscripts $v$ and $\epsilon$ imply the constancy of $v$ and hence that of $\epsilon$. Using these differentiations we find from Eq. (4),

$$\epsilon=-\frac{F_1T}{2\Phi_1}\,, \tag{5}$$

$$C_v=C_{\mathrm{qh}}-2\lambda^2F_a(0)T\,, \tag{6}$$

where $C_{\mathrm{qh}}$ is the quasiharmonic contribution to $C_v$, the second term is the anharmonic contribution from the $F_3$ and $F_4$ terms, and there are no contributions at all to the lowest order.

The procedure followed in Refs. 10 and 1 is to first substitute for $\epsilon$ from Eq. (5) into Eq. (4) and then perform the temperature differentiations to get $C_v$. When this procedure is followed one finds

$$F(\epsilon,T)=\Phi_{\mathrm{st}}(0)+F_{\mathrm{qh}}(0,T)+\lambda^2F_a(0)T^2-\frac{F_1^2T^2}{4\Phi_1} \tag{7}$$

and the extra contribution to the heat capacity from the last term in Eq. (7) is $F_1^2T/2\Phi_1$.

Obviously then substituting for $\epsilon$ in $F(\epsilon,T)$ before taking temperature derivatives means that the derivatives are not obtained at constant volume (i.e., at constant $\epsilon$) but at constant zero pressure. In other words, one obtains $C_p$ rather than $C_v$. Since Martin has derived the coefficient $A$ in $C_v^A$ from the analysis of $C_v$(expt), there is no justification of the comparison of the coefficient $A$ calculated in Ref. 1 with that of Martin.

Finally, we note the following. Since there are two ingredients of any anharmonic calculation at least to $O(\lambda^2)$, (1) the first four derivatives of $V(r)$ evaluated at various neighbors positions and (2) the knowledge of $\omega(\vec{q}j)$ and $\epsilon(\vec{q}j)$ which are the zero-order solutions of the harmonic Hamiltonian $(H_0)$, it is difficult to see the usefulness of the anharmonic calculation if the zero-order solutions are not adequate as in Ref. 1. Of course, the accurate calculation of the anharmonic results, for a given potential, may still be poor in spite of good agreement of $\omega(\vec{q}j)$ with the measured experimental values. This then indicates the inadequate representation of the third and fourth derivatives by that potential or the inadequacy of the $O(\lambda^2)$ perturbation theory. It may be then necessary to go to $O(\lambda^4)$ perturbation theory.[3,12]

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[1] P. C. Trivedi, H. O. Sharma, and L. S. Kothari, Phys. Rev. B 18, 2668 (1978).

[2] D. L. Martin, Phys. Rev. 139, A150 (1965).

[3] R. C. Shukla and L. Wilk, Phys. Rev. B 10, 3660 (1974).

[4] E. R. Cowley, J. Phys. C 6, L125 (1973).

[5] R. C. Shukla and Roger Taylor, Phys. Rev. B 9, 4116 (1974).

[6] W. Shyu and G. D. Gaspari, Phys. Rev. 163, 667 (1967).

[7] P. Lloyd, Aust. J. Phys. 17, 269 (1964).

[8] W. Cochran, Proc. R. Soc. London A276, 308 (1963).

[9] D. L. Price, K. S. Singwi, and M. P. Tosi, Phys. Rev. B 2, 2983 (1970).

[10] P. C. Trivedi, J. Phys. F 1, 262 (1971).

[11] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N.Y.) 15, 360 (1961).

[12] R. C. Shukla and E. R. Cowley, Phys. Rev. B 3, 4055 (1971).