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High-temperature heat capacity of an anharmonic crystal to order λ^4

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The thermal-expansion contribution to the high-temperature heat capacity of an anharmonic crystal to $O(\lambda^4)$ is obtained. It is found that an additional term of $O(\lambda^4)$ contributes to the T^2 coefficient of heat capacity at constant volume. The heat capacity at constant pressure has also been calculated to the same order and the difference $c_p - c_v$ is shown to be consistent with that obtained from the exact thermodynamic identity.

Recently,[1-5] there has been interest in the study of higher-order anharmonic contributions to the Helmholtz free energy of a crystal. In fact, all anharmonic contributions to $O(\lambda^4)$ to the free energy have been calculated for simple models.[3,4,6] The thermal strain parameter and the heat capacity at constant volume have been obtained from the free-energy expression to $O(\lambda^2)$ by Maradudin *et al.*[6] The thermal-expansion contribution to the heat capacity to $O(\lambda^2)$ has been described by Trivedi[7] and Brown.[8] This contribution has been clarified in detail by Cowley.[9] Aggarwal and Pathak[4] have discussed c_v to $O(\lambda^4)$. However, they have not considered the thermal-expansion contributions to c_v. In this paper, we discuss the effect of thermal expansion to the high-temperature heat capacity. It has been found that there is an extra contribution of $O(\lambda^4)$ to c_v which arises due to thermal expansion. This modifies the coefficient of T^2 in the expression for the high-temperature heat capacity obtained by Aggarwal and Pathak.[4] The expressions for the heat capacity at constant pressure and the thermal strain parameter have also been obtained and the difference $c_p - c_v$ has been shown to be consistent with that obtained from the exact thermodynamic identity.

The Helmholtz free energy at high temperatures for an anharmonic crystal can be formally written

$$F = \Phi_{\mathrm{st}} + F_{\mathrm{qh}} + \lambda^2 F_a T + \lambda^4 F_b T^3 , \qquad (1)$$

where Φ_{st} is the static energy of the crystal, and F_{qh} is the quasiharmonic free energy. The coefficients F_a and F_b include the anharmonic contributions in the lowest and next higher order, respectively. These have been calculated for a central force nearest-neighbor model of a fcc crystal. The contributions $\Phi_{\mathrm{st}}, F_{\mathrm{qh}}, F_a, F_b$ all involve the potential derivatives evaluated at equilibrium distance, which itself depends on the temperature. In order to obtain the potential derivatives at a particular defined temperature (say 0 °K), we express

$$r = r_0(1+\epsilon) , \qquad (2)$$

where r_0 is the equilibrium distance in the static lattice and ϵ is the thermal strain parameter. It is of $O(\lambda)$ in the first approximation.

We now expand the coefficients in Eq. (1) as a power series in ϵ and retain terms to $O(\lambda^4)$. The expression for free energy can be seen to be

$$F(\epsilon, T) = \Phi_{\mathrm{st}}(0) + F_{\mathrm{qh}}(0, T) + \lambda^2[\epsilon^2\Phi_1 + \epsilon F_1 T + F_a(0) T^2] + \lambda^4[\epsilon^3\Phi_2 + \epsilon^2 F_2 T + \epsilon F_{a1} T^2 + F_b(0) T^3]. \qquad (3)$$

It is easy to see that Φ_1, Φ_2; F_1, F_2, and F_{a1} are related to the derivatives of $\Phi_{\mathrm{st}}(r)$; $F_{\mathrm{qh}}(r, T)$, and $F_a(r)$, respectively, evaluated at r_0. For example,

$$\Phi_{\mathrm{st}}(r) \equiv \Phi_{\mathrm{st}}(r_0 + r_0\epsilon) \cong \Phi_{\mathrm{st}}(0) + r_0\epsilon \Phi'_{\mathrm{st}}\big|_{r_0} + \tfrac{1}{2}\lambda^2 r_0^2 \epsilon^2 \Phi''_{\mathrm{st}}\big|_{r_0} + \tfrac{1}{6}\lambda^4 r_0^3 \epsilon^3 \Phi'''_{\mathrm{st}}\big|_{r_0} . \qquad (4)$$

The second term in expansion (4) is taken to be zero. $\Phi''_{\mathrm{st}}|_{r_0}$ and $\Phi'''_{\mathrm{st}}|_{r_0}$ involve second and third derivatives of $\Phi(r)$, respectively. As Φ''' is known to be of $O(\lambda)$, the last term in expansion (4) is of $O(\lambda^4)$. We have thus defined, in Eq. (3),

$$\Phi_1 = \tfrac{1}{2} r_0^2 \Phi''_{\mathrm{st}}\big|_{r_0} \quad \text{and} \quad \Phi_2 = \tfrac{1}{6} r_0^3 \Phi'''_{\mathrm{st}} .$$

Similar expressions can be obtained for other coefficients in Eq. (3).

The thermal-strain parameter can be calculated using $(\partial F/\partial\epsilon)_T = 0$, which gives

$$\epsilon = \lambda\alpha T + \lambda^3 \beta T^2 , \qquad (5)$$

where

$$\alpha = - F_1/2\,\Phi_1$$

and

$$\beta = -\frac{1}{2\Phi_1}\left(F_{a1} + \frac{3}{4}\frac{F_1^2\Phi_2}{\Phi_1^2} - \frac{F_1 F_2}{\Phi_1}\right). \qquad (6)$$

The heat capacity at constant volume is defined as

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

from which we obtain

$$c_v = c_h - 2\lambda^2 F_a(0) T - 2\lambda^4[\alpha F_{a1} + 3F_b(0)] T^2 . \qquad (7)$$

In obtaining Eq. (7), we have substituted for ϵ in the expression obtained by calculating $-T(\partial^2 F/\partial T^2)_\epsilon$

and have retained terms to $O(\lambda^4)$ only. c_h is the harmonic part of c_v. In Eq. (7) the first term in brackets (i.e., $-2\alpha F_{a1}T^2$) is the extra term arising as a result of thermal expansion. We also calculate c_p at constant zero pressure to check the consistency of our results. This is obtained by substituting the zero-pressure value of ϵ, i.e., Eq. (5) into Eq. (3) and using $c_p = -T(\partial^2 F/\partial T^2)_p$. In this way we obtain

$$c_p = c_h - 2\lambda^2 T[\alpha^2\Phi_1 + \alpha F_1 + F_a(0)] - 6\lambda^4 T^2[\alpha^3\Phi_2 + 2\alpha\beta\Phi_1 + F_1\beta + \alpha^2 F_2 + F_{a1}\alpha + F_b(0)] \,. \qquad (8)$$

Therefore, the expression for $c_p - c_v$ becomes

$$c_p - c_v = \lambda^2 \frac{F_1^2}{2\Phi_1} T + \lambda^4 \left(\frac{2F_1F_{a1}}{\Phi_1} + \frac{3}{4}\frac{F_1^3\Phi_2}{\Phi_1^3} - \frac{3}{2}\frac{F_1^2F_2}{\Phi_1^2} \right) T^2 \,, \qquad (9)$$

where we have substituted for α and β.

The above result for $c_p - c_v$ can be seen to be consistent with exact thermodynamic identity

$$c_p - c_v = \gamma^2 Tv/K \,, \qquad (10)$$

where γ and K are the volume expansion coefficient and the isothermal compressibility, respectively. In order to verify Eq. (10), we need to calculate γ and K to appropriate order. The volume expansion coefficient is obtained from Eq. (5) as

$$\gamma = \frac{1}{v}\lambda(\alpha + 2\lambda^2\beta T)\frac{\partial v}{\partial \epsilon} \,. \qquad (11)$$

The isothermal compressibility can be calculated from

$$\frac{1}{K} = v\left(\frac{\partial^2 U}{\partial v^2} - T\frac{\partial^2 S}{\partial v^2} \right) . \qquad (12)$$

In Eq. (12), U is the internal energy and S is the entropy. The inverse of compressibility, i.e., the bulk modulus, B can be rewritten in the form

$$B = v\left(\frac{\partial^2 U}{\partial \epsilon^2} - T\frac{\partial^2 S}{\partial \epsilon^2} \right)\left(\frac{\partial \epsilon}{\partial v} \right)^2 + v\left(\frac{\partial U}{\partial \epsilon} - T\frac{\partial S}{\partial \epsilon} \right)\frac{\partial^2 \epsilon}{\partial v^2} \,. \qquad (13)$$

Substituting for the internal energy and the entropy from the expressions

$$U = F - T\left(\frac{\partial F}{\partial T} \right)_v = F - T\left(\frac{\partial F}{\partial T} \right)_\epsilon \qquad (14a)$$

and

$$S = -\left(\frac{\partial F}{\partial T} \right)_v = -\left(\frac{\partial F}{\partial T} \right)_\epsilon \,, \qquad (14b)$$

we obtain the expression for B to $O(\lambda^2)$. This is given as

$$B = v[2\Phi_1 + 2\lambda^2 T(3\alpha\Phi_2 + F_2)]\left(\frac{\partial \epsilon}{\partial v} \right)^2 \,. \qquad (15)$$

The second term in Eq. (13) does not contribute to $O(\lambda^2)$. The bulk modulus to this order is sufficient for $c_p - c_v$ to be obtained to $O(\lambda^4)$. This is evident from Eqs. (11) and (10). With these expressions for B and γ, it can be easily seen that it is consistent with Eq. (9).

It is thus clear that the results obtained by us for c_v and c_p to $O(\lambda^4)$ are complete and correct. We conclude that thermal expansion does not contribute to c_v to $O(\lambda^2)$ as emphasized by Cowley.[9] But it makes a contribution of $O(\lambda^4)$.

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