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Anharmonic Effect on Heat Capacity of Solids up to the Critical Temperature of Lattice Instability

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Anharmonic contribution to the thermal energy is evaluated for solids at temperatures higher than Debye temperature, with the assumption that anharmonic effects are expressed by the pseudoshift in the angular frequency of normal mode. Here the angular frequencies are assumed to depend on the mean thermal energy as well as on the volume. Both the thermal and caloric equations of state are derived systematically from the same partition function of this extended quasiharmonic treatment. Heat capacity is calculated as a function of temperature on the basis that the frequency shift occurs through the "vibrational elongation" introduced by Ida in the theory of lattice instability. The calculation describes a qualitatively correct curve of heat capacity. It is again shown that the lattice will be unstable above a critical temperature because of anharmonicity.

1. INTRODUCTION

RECENTLY, Ida[1] pointed out that a lattice instability is caused by anharmonicity at high temperature. According to his theory, the thermal energy of a lattice cannot exceed a critical value however great the amplitudes of lattice vibration may be, because there are pseudoshifts in angular frequencies associated with the increase in the amplitudes. The critical temperature was evaluated there by equating the upper limit of energy per normal mode to kT (k is the Boltzmann constant, and T is the temperature), but it was not taken into account that the thermal energy itself also deviates from kT because of anharmonicity. In the present paper we attempt to construct a theory that describes the anharmonic contributions to thermodynamical properties, consistently including the deviation of the thermal energy from kT. The examination of the treatment in a previous paper will be done in Sec. 4.

Usual caloric measurements give the data of the heat capacity C_p at constant pressure, while the heat capacity C_v at constant volume is more desirable for the comparison with theory. The conversion of C_p into C_v can be made, in principle, by use of a well-known thermodynamic relation between C_p and C_v. A small correction for thermal expansion is also necessary.[2] Although there is no question of this process itself, the ambiguity of the thermodynamic data required for the conversion tends to produce a fairly large uncertainty in C_v. In spite of this difficulty, it has been reported in some cases that C_v exceeds the value expected from the harmonic theory. It is believed that this *excess* heat capacity arises from the electronic heat,[3] the formation of lattice defects,[4–9] and anharmonicity. Recent careful investigations by Brooks and his co-workers[10,11] show that anharmonicity should have the most important contribution to the excess heat capacity for some metals. The theoretical approach to the anharmonic contribution is, however, not so advanced. There are some analyses for the case where the potential energy of lattice is very well known.[12–16] Some semiempirical relations are also used to analyze the anharmonic effect on C_v.[2,17–19]

The exact evaluation of anharmonic effects is a very difficult problem. The usual treatment is based on the theory in which cubic and quartic terms in the potential energy are considered to be small perturbations.[13,20] Although a simple expression can be obtained for the *thermal* equation of state from the quasiharmonic assumption,[21] the caloric equation of state, i.e., the relation between temperature and energy, is usually evaluated by considering directly the complicated terms involving the coupling parameters of higher orders. This treatment of the caloric equation is, however, very disadvantageous because of great mathematical difficulties, poor physical insight, and restricted data of coupling parameters. Hence it is attractive to

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examine whether the quasiharmonic approximation can include the caloric equation of state as well as the thermal equation of state. Recently the idea that the anharmonic contribution to free energy is also expressed by a pseudoshift of angular frequency was used by Pastine[22] to calculate thermodynamic properties for sodium metal. On the other hand, some efforts have been made to justify this *extended* quasiharmonic treatment on the basis of the perturbation theory.[23–26] This problem was also investigated with the aid of phonon thermodynamic Green's functions.[27] Although it has been shown by these works that the extended quasiharmonic treatment is successful at least partially, a systematic investigation of this kind of quasiharmonic treatment has not yet been made. In Secs. 2 and 3 of the present paper we shall study what thermodynamic relations are derived from a simple assumption about the pseudoshift of angular frequency. Both the thermal and the caloric equation of state will be obtained from the same partition function the usual manner of statistical mechanics. Throughout this paper we shall consider only the case of higher-than-Debye temperatures.

2. PARTITION FUNCTION OF QUASIHARMONIC SYSTEMS

The potential energy of a lattice can be expanded in a series in terms of the displacements of atoms from the equilibrium positions as

$$U=U_0+U_2+U_{ah}\,, \qquad (2.1)$$

where U_0 is the constant term, U_2 is the sum of quadratic terms, and U_{ah} denotes the terms of higher orders. If U_{ah} vanishes, the system is reduced to an assembly of $3N$ independent oscillators (N is the number of atoms), and the energy can be written as

$$E=U_0+\sum_{i=1}^{3N}(n_i+\tfrac{1}{2})\hbar\omega_i\,, \qquad (2.2)$$

where ω_i is the angular frequency of ith normal mode, and n_i is the quantum number ($n_i=0, 1, 2,\ldots$). For a completely harmonic system, any ω_i is independent of the dimension of the lattice. In the quasiharmonic treatment it is assumed that the displacements of atoms are so small that U_{ah} is negligibly small, compared with U_2, in considering the motion of atoms, but that the coupling parameters involved in U_2 depend on the initial state about which U is expanded. Thus ω_i is considered to be a function of the volume. Thermal expansion is interpreted by this kind of treatment. Further, it is suggested by some authors[22–26] that the effect of anharmonicity on the caloric properties can also be treated by a pseudoshift of ω_i. In this treatment we must recognize that ω_i depends not only on the volume, but also on the temperature. We begin our study by considering the physical meaning of this suggestion.

We may understand that the pseudoshift of ω_i at elevated temperatures is essentially of a purely dynamic origin; the shift is caused by some interaction among normal modes from anharmonicity. Since the strength of the interaction depends on the amplitudes of the lattice vibration, the shift may be determined by the state of the excitation of lattice. It is thus considered most generally that ω_i depends on each n_i. Remembering, however, that there are so many normal modes that statistical treatment is possible, we can expect that ω_i is effectively determined by a few of the quantities that represent, on the average, the degree of excitation. Here we adopt the simplest assumption that ω_i depends only on the mean energy ϵ of normal modes:

$$\omega_i=\omega_i(v,\epsilon)\,, \qquad (2.3)$$

which provides our starting point. In Eq. (2.3) the dependence of ω_i on the volume v (per atom) is also included. The relation between temperature and energy is derived from the function $\omega_i(v,\epsilon)$ in the manner of statistical mechanics. The partition function Z is evaluated as

$$Z=\int e^{-\beta E}g(E)dE\,, \qquad (2.4)$$

where $\beta=1/kT$. The state density $g(E)$ is defined so that $g(E)dE$ equals the number of quantum-mechanical states between E and $E+dE$. In the quasiharmonic treatment, $g(E)dE$ may be replaced by the number of distinct sets $(n_1,n_2,\ldots,n_{3N})$ satisfying

$$E-U_0\leqq\sum_{i=1}^{3N}n_i\hbar\omega_i(v,\epsilon)\leqq E-U_0+dE\,, \qquad (2.5)$$

where zero-point energy is neglected. Here we should notice that ϵ is related to E:

$$E=U_0+3N\epsilon. \qquad (2.6)$$

In the case where $3N\epsilon$ is sufficiently larger than any value of $\hbar\omega_i$, the number of the sets corresponding to Eq. (2.5) can be easily evaluated (Appendix A), and thus we have

$$g(E)=[\prod_{i=1}^{3N}\hbar\omega_i(v,\epsilon)]^{-1}\frac{(E-U_0)^{3N-1}}{(3N-1)!}\,, \qquad (2.7)$$

which is applicable to higher-than-Debye temperatures. In the integration in Eq. (2.4), v is regarded as a fixed parameter. Substituting Eq. (2.7) into Eq. (2.4), we

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have

$$Z=\left[(3N-1)!\prod_{i=1}^{3N}\hbar\omega_i(v,0)\right]^{-1}$$

$$\times\int(E-U_0)^{3N-1}e^{-\beta E}\xi(v,\epsilon)^{-3N}dE, \quad (2.8)$$

where

$$\xi(v,\epsilon)=\left[\prod_{i=1}^{3N}\omega_i(v,\epsilon)/\omega_i(v,0)\right]^{1/3N}. \quad (2.9)$$

Using Eq. (2.6), we can rewrite Eq. (2.8) as

$$Z=\frac{(3N)^{3N}}{(3N-1)!}e^{-\beta U_0}\left[\prod_{i=1}^{3N}\hbar\omega_i(v,0)\right]^{-1}$$

$$\times\int_0^\infty\epsilon^{-1}[X(v,\epsilon,\beta)]^{3N}d\epsilon, \quad (2.10)$$

where

$$X(v,\epsilon,\beta)=\epsilon e^{-\beta\epsilon}[\xi(v,\epsilon)]^{-1}. \quad (2.11)$$

Only the expression of Z for large N has meaning in the evaluation of macroscopic properties.

We shall consider the asymptotic form of Eq. (2.10) for infinitely large N. The function $[X(v,\epsilon,\beta)]^{3N}$ for large N will have a very steep maximum at the value ϵ_e that maximizes $X(v,\epsilon,\beta)$ itself, and the integral in Eq. (2.10) must be determined almost entirely by the behavior of $X(v,\epsilon,\beta)$ in the vicinity of ϵ_e. Thus we can expect the following expression of Z, neglecting some factors independent of N:

$$Z\sim\frac{(3N)^{3N-1/2}}{(3N-1)!}e^{-\beta U_0}\left[\prod_{i=1}^{3N}\hbar\omega_i(v,0)\right]^{-1}[X(v,\epsilon_e,\beta)]^{3N}. \quad (2.12)$$

A more exact derivation of Eq. (2.12) is shown in Appendix B. The values of ϵ_e are determined by the condition that $X(v,\epsilon,\beta)$ is maximum at $\epsilon=\epsilon_e$, i.e.,

$$(\partial X/\partial\epsilon)_{v,\beta}=0, \quad (2.13)$$

where the subscripts v, β denote the partial derivative at constant v and constant β. From Eq. (2.11), Eq. (2.13) yields

$$\frac{1}{\epsilon}-\beta=\left(\frac{\partial}{\partial\epsilon}\ln\xi\right)_v. \quad (2.14)$$

We shall find that this is an important equation, which gives the relation between temperature and energy.

3. THERMODYNAMIC RELATIONS

We shall obtain thermodynamic relations from the partition function Z of Eq. (2.12) and show that anharmonic effects on various properties can be evaluated from the function $\xi(v,\epsilon)$. The mean energy ϵ for a given temperature is calculated from the relation $E=-(\partial\ln Z/\partial\beta)_v$. Using Eq. (2.13), we have

$$\epsilon=\epsilon_e. \quad (3.1)$$

Equation (3.1) means that ϵ is determined so as to maximize $X(v,\epsilon,\beta)$, or to satisfy Eq. (2.14), for a given v and β. The Helmholtz free energy F is calculated as

$$F=U_0+\frac{1}{\beta}\sum_{i=1}^{3N}\ln\hbar\omega_i(v,0)+\frac{3N}{\beta}(\beta\epsilon-1-\ln\epsilon+\ln\xi). \quad (3.2)$$

In the derivation of Eq. (3.2), Stirling's theorem $\ln n!=n\ln n-n$ is used. Equation (3.2) is also written as

$$F=U_0-\frac{1}{\beta}\sum_{i=1}^{3N}\ln\frac{\epsilon}{\hbar\omega_i(v,\epsilon)}+3N\left(\epsilon-\frac{1}{\beta}\right). \quad (3.3)$$

Comparing Eq. (3.3) with the relation $F=E-S/k\beta$, we have the following expression for the entropy S:

$$S=k\left[\sum_{i=1}^{3N}\ln\frac{\epsilon}{\hbar\omega_i(v,\epsilon)}+3N\right]. \quad (3.4)$$

We notice that Eq. (3.4) can also be obtained from the relation $S=k\ln g(E)$.

The thermal equation of state is determined by the relation $P=-(\partial F/\partial V)_\beta$, where P is the pressure, and V is the total volume, i.e.,

$$V=Nv. \quad (3.5)$$

Using Eq. (3.2), we have

$$P=-\frac{dU_0}{dV}+\frac{3\gamma_0}{\beta v}-\frac{3}{\beta}\left[\beta\left(\frac{\partial\epsilon}{\partial v}\right)_\beta-\frac{1}{\epsilon}\left(\frac{\partial\epsilon}{\partial v}\right)_\beta\right.$$

$$\left.+\left(\frac{\partial}{\partial v}\ln\xi\right)_\beta\right], \quad (3.6)$$

where

$$\gamma_0=-\frac{1}{3N}\sum_{i=1}^{3N}d\ln Vd[\ln\omega_i(v,0)]. \quad (3.7)$$

The last term in the right-hand side of Eq. (3.6) is rewritten as

$$\left(\frac{\partial}{\partial v}\ln\xi\right)_\beta=\left(\frac{\partial}{\partial v}\ln\xi\right)_\epsilon+\left(\frac{\partial\epsilon}{\partial v}\right)_\beta\left(\frac{\partial}{\partial\epsilon}\ln\xi\right), \quad (3.8)$$

and hence, using Eq. (2.14), we find Eq. (3.6) is reduced to

$$P=-\frac{dU_0}{dV}+\frac{3}{\beta v}\left[\gamma_0-\left(\frac{\partial\ln\xi}{\partial\ln v}\right)_\epsilon\right]. \quad (3.9)$$

Remembering Eq. (2.9), we can rewrite Eq. (3.9) as

$$P=-(dU_0/dV)+(3\gamma'/\beta v), \quad (3.10)$$

where

$$\gamma'=-\frac{1}{3N}\sum_{i=1}^{3N}\left(\frac{\partial\ln\omega_i(v,\epsilon)}{\partial\ln v}\right)_\epsilon. \quad (3.11)$$

Equation (3.10) is analogous to the Mie-Grüneisen equation of state,[21] but, as is shown later [see Eq. (3.18)], γ' does not always agree with the Grüneisen parameter γ specified by

$$\gamma = VK\alpha/C_v, \tag{3.12}$$

where K is the isothermal bulk modulus, and α is the thermal expansivity.

The heat capacity C_v is obtained from the relation

$$C_v = 3N\left(\frac{\partial\epsilon}{\partial T}\right)_v = -3Nk\beta^2\left(\frac{\partial\epsilon}{\partial\beta}\right)_v. \tag{3.13}$$

The quantity $(\partial\epsilon/\partial\beta)_v$ is given by differentiating both sides of Eq. (2.14) with respect to β. Thus

$$C_v = 3Nk\beta^2\left[\frac{1}{\epsilon^2} + \left(\frac{\partial^2}{\partial\epsilon^2}\ln\xi\right)_v\right]^{-1}. \tag{3.14}$$

To obtain the expression of isothermal bulk modulus K, we differentiate Eq. (3.10) with respect to V. After simple calculations, we have

$$K = V\frac{d^2U_0}{dV^2} + \frac{3}{\beta}\left[\frac{\gamma'}{v} - \left(\frac{\partial\gamma'}{\partial v}\right)_\epsilon - \left(\frac{\partial\epsilon}{\partial v}\right)_\beta\left(\frac{\partial\gamma'}{\partial\epsilon}\right)_v\right]. \tag{3.15}$$

The above equation can also be written as

$$K = V\frac{d^2U_0}{dV^2} + \frac{3}{\beta}\left\{\frac{\gamma_0}{v} - \frac{d\gamma_0}{dv} + v\left(\frac{\partial^2\ln\xi}{\partial v^2}\right)_\epsilon - v\epsilon^2\left(\frac{\partial^2\ln\xi}{\partial v\partial\epsilon}\right)^2\left[1+\epsilon^2\left(\frac{\partial^2\ln\xi}{\partial\epsilon^2}\right)_v\right]^{-1}\right\}, \tag{3.16}$$

which is a convenient form to evaluate K from a given function $\xi(v,\epsilon)$. The differentiation of Eq. (3.10) with respect to T gives a relation involving α. Comparing the resulting relation with Eq. (3.15), we have

$$K\alpha = \frac{3k}{v}\left(\gamma' - \frac{vC_v}{3Nk\beta}\times\frac{\partial^2\ln\xi}{\partial\epsilon\partial v}\right). \tag{3.17}$$

Coupling Eqs. (3.12) and (3.17), we obtain

$$\gamma = \frac{3Nk}{C_v}\gamma' - \frac{v}{\beta}\times\frac{\partial^2\ln\xi}{\partial\epsilon\partial v}, \tag{3.18}$$

which predicts the difference between γ and γ'.

In the *usual* quasiharmonic treatment, in which the dependence of ω_i on ϵ is not taken into account, $\xi(v,\epsilon)$ is always equal to unity. In this case we have the relations corresponding to the Dulong-Petit law,

$$\epsilon = 1/\beta \quad\text{and}\quad C_v = 3Nk, \tag{3.19}$$

from Eqs. (2.14), (3.1), and (3.14). We also find that expression (3.3) agrees with the high-temperature form of F given by the harmonic approximation, and that relation (3.10) becomes identical with the Mie-Grüneisen equation of state. It is also noted that Eq. (3.18) gives only $\gamma' = \gamma$ in this case.

4. ANHARMONIC EFFECT THROUGH VIBRATIONAL ELONGATION

We have an approximate method to evaluate $\xi(v,\epsilon)$. It was shown in my previous paper (I) that the time average of interatomic distances becomes larger than the equilibrium distances as a result of lattice vibration. The fractional increase of interatomic distance is called "vibrational elongation" and denoted by Q. The quantity Q can be written in terms of the amplitudes of lattice vibration [Eq. (10) in I], or in terms of the energy ϵ_i of each normal mode. If each ϵ_i can be replaced by the mean value ϵ, and if a linear dispersion relation [Eq. (11) in I]

$$\omega_i = c_s f \tag{4.1}$$

is assumed (f is the length of the wave vector), we have the following expression of Q:

$$Q = \frac{\epsilon}{15m}\left(\frac{1}{c_1^2} + \frac{4}{c_2^2}\right), \tag{4.2}$$

where m is the mass of atoms, and c_1 and c_2 correspond to the sound velocities for longitudinal and transverse lattice waves, respectively. In I we replaced ϵ involved in (4.2) by kT to determine approximately the temperature corresponding to the lattice instability. Here we can examine the relation between ϵ and T more exactly, using the discussions in Secs. 2 and 3. We assume, as in I, that anharmonicity affects c_s through Q analogously to thermal expansion, and that this effect is expressed by a unique parameter b as

$$c_s = c_{s0}e^{-bQ}, \tag{4.3}$$

where c_{s0} depends only on the volume. From Eqs. (4.1) and (4.3) we have

$$\omega_i(v,\epsilon) = \omega_i(v,0)e^{-q/2}, \tag{4.4}$$

where

$$q = 2bQ, \tag{4.5}$$

and hence we obtain the expression of $\xi(v,\epsilon)$:

$$\ln\xi(v,\epsilon) = -\tfrac{1}{2}q. \tag{4.6}$$

The relation between q and ϵ is given by substituting Eq. (4.3) into (4.2), as follows:

$$qe^{-q} = h\epsilon, \tag{4.7}$$

where

$$h = \frac{2b}{15m}\left(\frac{1}{c_{10}^2} + \frac{4}{c_{20}^2}\right). \tag{4.8}$$

The quantity h is considered to be a function of v only.

From (4.6), Eq. (2.14) yields

$$1/\epsilon - \beta = -\tfrac{1}{2}(\partial q/\partial\epsilon)_v. \tag{4.9}$$

Evaluating $(\partial q/\partial \epsilon)_v$ from Eq. (4.7), we have

$$(1/\epsilon)-\beta=-\tfrac{1}{2}he^q/(1-q). \tag{4.10}$$

It is convenient to introduce new variables θ and u specified as

$$\theta=h/\beta, \tag{4.11}$$

$$u=h\epsilon. \tag{4.12}$$

The quantities θ and u are proportional to temperature and energy, respectively, when the volume is kept constant. In terms of θ and u, Eqs. (4.7) and (4.10) are written as

$$qe^{-q}=u, \tag{4.13}$$

$$(1/u)-(1/\theta)=-\tfrac{1}{2}e^q/(1-q). \tag{4.14}$$

The values of u and q as a function of θ were computed numerically from Eqs. (4.13) and (4.14) with the aid of a FACOM 270-30 computer and are given in Table I. The q-θ curve has a maximum corresponding to the upper limit of lattice stability at constant volume, and the critical point is given by $q_c=0.4563$ and $\theta_c=0.2037$. The heat capacity C_v can be computed from Eq. (3.14). After some simple calculations we have

$$C_v=3Nk\left[\left(\frac{\theta}{u}\right)^2-4\left(\frac{u}{\theta}\right)\left(1-\frac{\theta}{u}\right)^2\right]^{-1}. \tag{4.15}$$

Numerical values of $C_v/3Nk$ are also given as a function of θ in Table I.

The thermal equation of state is given by calculating $(\partial q/\partial v)_\epsilon$ from Eq. (4.7). Substituting the resulting expression into Eq. (3.9), we have

$$P=-\frac{dU_0}{dV}+\frac{3}{\beta v}\left[\gamma_0+\left(\frac{u}{\theta}-1\right)\frac{d\ln h}{d\ln v}\right]. \tag{4.16}$$

The volume dependences of dU_0/dV, γ_0, and $d\ln h/d\ln v$ must be known to determine the P-β-V relations by Eq. (4.16). Here, for a rough estimation, we again use the same simplified assumptions that are adopted in I. First we use the series expansion up to the linear term as the expression dU_0/dV:

$$dU_0/dV=-P+K_0(v-v_0)/v_0, \tag{4.17}$$

where v_0 is the volume at $T=0$, and K_0 is the bulk modulus at $T=0$ and $v=v_0$. The volume v_0 is determined so that the equation $-dU_0/dV=P$ is satisfied at $v=v_0$. Assuming that the effect of Q on the shift of ω_i is equivalent to that of the fractional increase of lattice dimension, and remembering Eq. (4.3) [see also Eq. (14) in I], we have

$$\omega_i(v,0)=\omega_i(0,0)\exp\left(-\tfrac{1}{3}b\frac{v-v_0}{v_0}\right). \tag{4.18}$$

TABLE I. Thermal energy u, heat capacity $C_v/3Nk$, and vibrational elongation q as a function of temperature θ at constant volume.

θ	u	$C_v/3Nk$	q
0	0	1.000	0
0.02	0.0202	1.022	0.0206
0.04	0.0409	1.047	0.0427
0.06	0.0621	1.078	0.0664
0.08	0.0841	1.116	0.0922
0.10	0.1069	1.165	0.1205
0.12	0.1308	1.231	0.1523
0.14	0.1563	1.326	0.1888
0.16	0.1842	1.482	0.2324
0.18	0.2166	1.810	0.2893
0.20	0.2637	3.742	0.3892
0.2037	0.2891	∞	0.4563

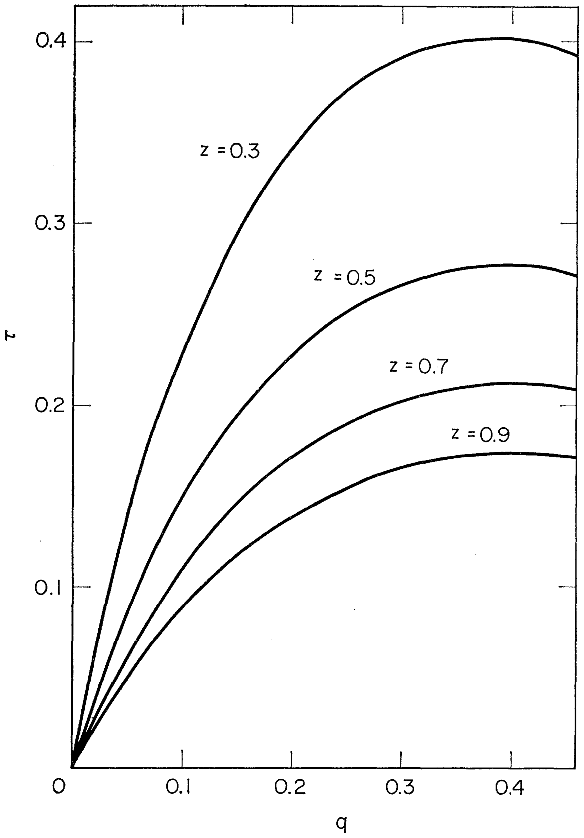

FIG. 1. Relations between the reduced vibrational elongation q and the reduced temperature τ at constant pressure. Curves are obtained for various z by use of (4.26).

Thus we have approximately, from Eq. (3.7),

$$\gamma_0=\tfrac{1}{3}b. \tag{4.19}$$

If b is not strongly dependent on volume, we obtain from Eq. (4.8)

$$h=h_0[1+\tfrac{2}{3}b\,(v-v_0)/v_0]. \tag{4.20}$$

Thus we have

$$d\ln h/d\ln v=\tfrac{2}{3}b. \tag{4.21}$$

Using Eqs. (4.17), (4.19), and (4.21), and noting Eqs. (4.13) and (4.14), we rewrite (4.16) as

$$\frac{v-v_0}{v_0}=\frac{b}{K_0v_0\beta}\frac{1}{1-q}, \tag{4.22}$$

which corresponds to Eq. (26) in I. From Eqs. (4.11), (4.20), and (4.22), we have

$$\frac{\theta\beta}{h_0}=1+\frac{2b^2}{3\beta K_0v_0}\frac{1}{1-q}. \tag{4.23}$$

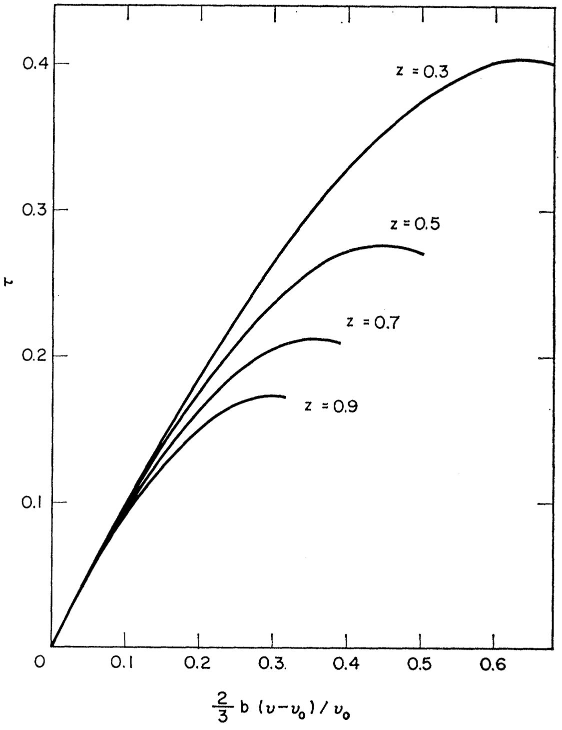

FIG. 2. Relations between the reduced volume $\frac{2}{3}b(v-v_0)/v_0$ and the reduced temperature τ at constant pressure. Curves are obtained for various z by use of (4.25) and (4.26).

Since θ is not always proportional to T at constant pressure, we introduce a new variable τ [see Eq. (28) in I], as

$$\tau=2b^2/3v_0K_0\beta. \tag{4.24}$$

Then Eqs. (4.22) and (4.23) yield, respectively,

$$\tfrac{2}{3}b\frac{v-v_0}{v_0}=\frac{\tau}{1-q}, \tag{4.25}$$

$$\frac{\theta}{z\tau}=1+\frac{\tau}{1-q}, \tag{4.26}$$

where

$$z=3v_0K_0h_0/2b^2. \tag{4.27}$$

TABLE II. $\mathrm{Mi}_1(z)$.

z	$\mathrm{Mi}_1(z)$	q_m
0	∞	0
0.1	0.8450	0.3546
0.2	0.5344	0.3700
0.3	0.4022	0.3801
0.4	0.3260	0.3876
0.5	0.2756	0.3935
0.6	0.2395	0.3983
0.7	0.2122	0.4023
0.8	0.1908	0.4058
0.9	0.1734	0.4088
1.0	0.1591	0.4114
1.1	0.1470	0.4137
1.2	0.1367	0.4158
1.5	0.1130	0.4209

Coupling Eq. (4.26) with (4.13) and (4.14), we obtain the values of q, θ, and u as a function of τ, and thus the value of $(v-v_0)/v_0$ with use of Eq. (4.25). The q-τ curves, given in Fig. 1 for various z, have a maximum, which corresponds to a limit of lattice stability under constant pressure. We write the maximum value τ_m as a function of z as

$$\tau_m=\mathrm{Mi}_1(z) \tag{4.28}$$

analogously to $\mathrm{Mi}(z)$ in I. The values of $\mathrm{Mi}_1(z)$ given in Table II are slightly different from $\mathrm{Mi}(z)$. The difference reflects the appreciation of the temperature-energy relation in the present treatment. Temperature dependences of the volume are drawn in Fig. 2 for various z.

5. DISCUSSION

First we shall examine the results obtained in Sec. 4 in comparison with observations. Equation (4.28) coupled with (4.24) gives a critical temperature, above which the lattice is not stable. In Table III we give the values of the critical temperature with the melting point observed for cubic materials. Although the calculated values are fairly scattered because the equation of state is too simplified, it seems that the agreement becomes better than in Tables II and III of Ref. 1. To examine Eq. (4.15) for heat capacity, we plot against θ some experimental values[7,10,11,28] with the theoretical curve, as is shown in Fig. 3. In plotting experimental data, we determine the relation between θ and T by assuming that T/T_m is equal to τ/τ_m. When C_v is not obtainable, only the data of C_p are given in Fig. 3. The theory explains that heat capacity increases rapidly close to the melting point, deviating from a linear relation. Quantitatively, however, it seems that the theoretical value overestimates the anharmonic effect, even if we assume all the excess heat in experimental data is caused by anharmonicity. Equation (3.10) is almost identical with the Mie-Grüneisen equation of state, except when the temperature is close to the critical point. Quantitative examination requires more

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[28] N. S. Rasor and J. D. McClelland, J. Phys. Chem. Solids **15**, 17 (1960).

TABLE III. Critical temperatures of lattice instability for cubic materials calculated from (4.28) coupled with (4.24). Data sources and the arrangement of data for the calculation are mentioned in Sec. 5 and in Tables II and III in Ref. 1.

	T_m (°K) (calc)	T_m (°K) (obs)
Li	375	453
Na	328	371
K	373	337
Cu	1497	1356
Ag	1069	1234
Au	890	1336
Al	1088	933
Pb	517	600
Mo	6723	2893
Ta	4259	3300
LiF	1390	1112
LiCl	1072	886
NaCl	1017	1073
NaBr	1006	1028
KF	1184	1153
KCl	948	1043
KBr	836	1003
KI	858	1046
RbBr	1017	955
RbI	584	915
MgO	3685	3073
TlBr	642	733
CaF_2	1785	1633

careful treatment than in Eq. (4.25), and more precise experimental determination of thermal expansion near the melting point.

If we use the perturbation theory to evaluate anharmonic contribution to heat capacity,[13] cubic and quartic terms among U_{ah} should give only the contribution that changes linearly with temperature. One may thus think that the rapid increase in C_v close to the critical temperature is caused by increasing contribution of higher than fourth-order terms. This opinion, however, is not completely correct. It is rather because of the *cooperation* of different modes that C_v deviates from a linear relation. Once the anharmonic interaction among various modes reduces ω_i according to Eq. (4.4), the amplitude of vibration, or q, must be increased to compensate the decrease of ω_i and to keep the energy constant [see Sec. 3 in I]. Therefore, ω_i is again reduced by this secondary increase of q. The anharmonic effect is thus amplified similarly to the case of well-known cooperative phenomena. Since each energy level becomes lower as a result of the anharmonic interaction, the intervals between energy levels are more reduced by the cooperation among the modes. This means that the entropy is rapidly increased in the vicinity of the critical energy at which the cooperation becomes rapidly stronger so that lattice instability occurs. That is the reason why heat capacity is increased as we approach the critical temperature.[29] Here it should be added that the increase of heat capacity close to the melting point has also been explained by the formation of lattice defects.[4–9] It is not clear at present whether the overestimation of excess heat capacity means some essential inadequacy of the theory or simply the roughness of the present treatment.

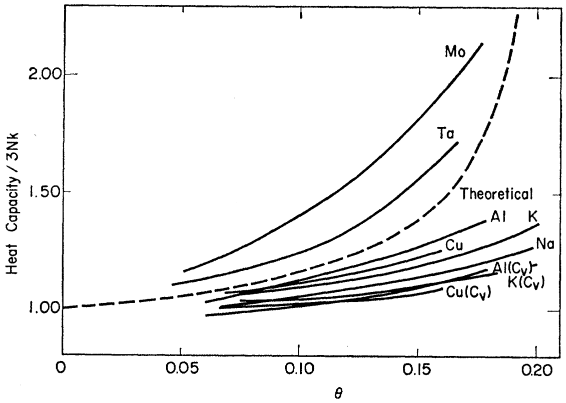

FIG. 3. Heat capacity as a function of the reduced temperature θ. The theoretical curve expresses the value of C_v given by (4.15). The experimental curves without the mark of C_v are the data of C_p. Data sources are Refs. 7 (Na, K), 10 (Cu), 11 (Al), and 28 (Ta, Mo).

Our expression (3.3) of F involves the term $3N(\epsilon-1/\beta)$, being different from that used by Barron[25] or Pastine[22]; the latter has the same form as the expression for a harmonic lattice. The distinction between the two treatments arises from the assumption in ours, that the frequency shift should have a purely dynamic origin. According to a formal treatment, different pseudoshifts of ω_i must be assumed to understand anharmonic behavior, depending on different thermodynamical quantities.[22,25] This self-inconsistency seems to be caused by a formalism that is too simple, in which the expression for the harmonic lattice is also used for anharmonic crystals without any modification, except that the frequency in the expression is regarded as temperature-dependent. If the extended quasi-harmonic treatment has the meaning beyond simple mathematical convenience, the true shift of ω_i must be uniquely determined, and various thermodynamical quantities should be obtained from this *substantial* shift. Our formulation in this paper is based on this philosophy. In addition, it is interesting that, while the term $3N(\epsilon-1/\beta)$ plays an important role in deriving the expression (3.14) of heat capacity, the effect of this term does not appear explicitly in the expression (3.10) for the thermal equation of state. The concept of vibrational elongation may give a physical picture to our philosophy, even if it is an approximate picture. It is known that the shift of ω_i can be actually observed by the experiments of neutron scattering.[23,27,30] The examination of our theory in

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[29] With regard to the discussion to connect the energy-entropy relation with thermodynamic properties, one may refer to F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Co., New York, 1940), p. 478.

[30] L. Bohlin and T. Högberg, J. Phys. Chem. Solids **29**, 1805 (1968).

comparison with this experimentation is interesting, but it is too complicated a problem to consider here.

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APPENDIX A: STATE DENSITY OF QUASIHARMONIC SYSTEMS

We shall derive here expression (2.7) of $g(E)$ by evaluating the number of distinct sets $(n_1,n_2,\dots,n_{3N})$ belonging to the region of Eq. (2.5). If we fix the energy E, or ϵ, $g(E)$ is concerned with only the value of ω_i corresponding to the fixed ϵ in question. Thus we can determine $g(E)$ as follows. First we evaluate the number $g_M(E')dE'$ of distinct sets $(n_1,n_2,\dots,n_M)$ that satisfy

$$E'\leqq\sum_{i=1}^{M} n_i a_i\leqq E'+dE', \tag{A1}$$

regarding each a_i as *constant*, and then we equate $g(E)$ to $g_M(E')$, putting $E'=E-U_0$, $M=3N$, and $a_i=\hbar\omega_i(v,\epsilon)$. If we know the function $G_M(E')$ defined by the number of the sets $(n_1,n_2,\dots,n_M)$ that are included in the region

$$\sum_{i=1}^{M} n_i a_i\leqq E', \tag{A2}$$

we can obtain $g_M(E')$ as

$$g_M(E')=dG_M(E')/dE', \tag{A3}$$

where each a_i is kept constant at the differentiation. The integer n_M extends from zero to $[E'/a_M]$ (the symbol $[x]$ denotes the maximum integer that is equal to, or smaller than x), when every a_i is positive. Thus we have

$$G_M(E')=\sum_{n_M=0}^{[E'/a_M]} G_{M-1}(E'-a_M n_M). \tag{A4}$$

If E'/a_M is sufficiently larger than unity, we can replace the summation by an integral. Introducing the variable $x_M=E'-a_M n_M$, we have

$$G_M(E')=\frac{1}{a_M}\int_0^{E'} G_{M-1}(x_M)dx_M. \tag{A5}$$

Using Eq. (A5) successively, we have finally

$$G_M(E')=(\prod_{i=2}^{M} a_i)^{-1}\int_0^{E'} dx_M\int_0^{x_M} dx_{M-1}\cdots \times\int_0^{x_3} dx_2 G_1(x_2). \tag{A6}$$

Noting $G_1(E')=E'/a_1$, we have

$$G_M(E')=(\prod_{i=1}^{M} a_i)^{-1}\frac{E'^M}{M!}. \tag{A7}$$

Using Eq. (A3), we obtain $g_M(E')$ and thus $g(E)$ in Eq. (2.7).

APPENDIX B: ASYMPTOTIC FORM OF EQ. (2.10)

We shall evaluate the asymptotic form of the integral

$$I_M=\int_0^\infty \epsilon^{-1}[X(\epsilon)]^M d\epsilon \tag{B1}$$

for infinitely large M. For simplicity we assume that the function $X(\epsilon)$ is not negative for any ϵ and it has a maximum at $\epsilon=\epsilon_e$ so that

$$X'(\epsilon_e)=0 \quad\text{and}\quad X''(\epsilon_e)<0. \tag{B2}$$

Putting $Y(\epsilon)=X(\epsilon)/X(\epsilon_e)$, we have

$$I_M=M^{-1/2}[X(\epsilon_e)]^M J_M, \tag{B3}$$

where

$$J_M=M^{1/2}\int_0^\infty \epsilon^{-1}[Y(\epsilon)]^M d\epsilon. \tag{B4}$$

For an arbitrary positive number δ, J_M is divided into the sum of the three integrals over the regions $\epsilon_e-\delta\leqq\epsilon\leqq\epsilon_e+\delta$, $0\leqq\epsilon\leqq\epsilon_e-\delta$, and $\epsilon_e+\delta\leqq\epsilon<\infty$. Since $Y(\epsilon)$ is smaller than unity for any ϵ belonging to the last two regions, the contributions of these two integrals can be made as small as we want, if we take sufficiently large M. Here it is of course assumed that the integral in Eq. (B4) converges for any positive integer M. Thus,

$$\lim_{M\to\infty} J_M=\lim_{M\to\infty} M^{1/2}\int_{\epsilon_e-\delta}^{\epsilon_e+\delta} \epsilon^{-1}[Y(\epsilon)]^M d\epsilon. \tag{B5}$$

Noting $Y(\epsilon_e)=1$, $Y'(\epsilon_e)=0$, and $Y''(\epsilon_e)<0$ [see Eq. (B2)], we can expand the function $\ln Y(\epsilon)$ about $\epsilon=\epsilon_e$ as

$$\ln Y(\epsilon)=-\tfrac{1}{2}|Y''(\epsilon_e)|(\epsilon-\epsilon_e)^2+\cdots. \tag{B6}$$

If a sufficiently small value is chosen as δ, the quadratic term in Eq. (B6) can express $\ln Y(\epsilon)$ for ϵ between $\epsilon_e-\delta$ and $\epsilon_e+\delta$ with sufficient accuracy, and the integral in Eq. (B5) can be replaced by

$$M^{1/2}\epsilon_e^{-1}\int_{\epsilon_e-\delta}^{\epsilon_e+\delta} e^{-(M/2)|Y''(\epsilon_e)|(\epsilon-\epsilon_e)^2}d\epsilon,$$

which is reduced for large M to

$$M^{1/2}\epsilon_e^{-1}\int_{-\infty}^{\infty} e^{-(M/2)|Y''(\epsilon_e)|(\epsilon-\epsilon_e)^2}d\epsilon.$$

Therefore we have

$$\lim_{M\to\infty} J_M=\epsilon_e^{-1}[2\pi/|Y''(\epsilon_e)|]^{1/2}. \tag{B7}$$

Then, using Eq. (B3), we have the asymptotic form

$$I_M\sim\epsilon_e^{-1}\left[\frac{2\pi X(\epsilon_e)}{|X''(\epsilon_e)|}\right]^{1/2}M^{-1/2}[X(\epsilon_e)]^M. \tag{B8}$$

Now we find that the factor $\epsilon_e^{-1}[2\pi X(\epsilon_e)/|X''(\epsilon_e)|]^{1/2}$ is neglected in the expression of Eq. (2.12).

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One-Phonon Excited States of Solid H_2 and D_2 in the Ordered Phase[*][†]

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Optical-phonon frequencies of ordered solid H_2 and D_2 have been calculated using a Lennard-Jones intermolecular potential derived from measurements of gas-phase properties. Good agreement with experiment is obtained. Density-of-states functions and phonon dispersion curves in three directions have also been computed.

INTRODUCTION

THE lattice dynamics of solid hydrogen and deuterium cannot be treated by the traditional harmonic approximation.[1] The molecules are so light and the intermolecular forces so weak that the zero-point kinetic energy is equal to about half of the sublimation energy,[2] and the harmonic approximation, when attempted, gives imaginary energies of excitation.[3]

Nosanow and Werthamer[4] have developed a means of treating the lattice dynamics of such crystals and have reported reasonable agreement between calculated and experimental sound velocities in solid ^{3}He and ^{4}He. We report here the application of this method to the calculation of phonon frequencies and density-of-states functions for the fcc phases of orthohydrogen and paradeuterium. A similar calculation has recently been done for hexagonal hydrogen by Mertens and Biem.[5]

The approach of Nosanow and Werthamer assumes a ground-state wave function of the form

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)=\prod_i \phi_0(\mathbf{r}_i-\boldsymbol{\tau}_i)\prod_{k<1} f(|\mathbf{r}_k-\mathbf{r}_1|), \tag{1}$$

where $\phi_0(\mathbf{r}-\boldsymbol{\tau})$ is a function of one molecule at $\mathbf{r}$, the equilibrium position of which is a lattice point τ, and the short-range correlation functions $f(\rho)=\exp(-K[(\sigma/\rho)^{12}-(\sigma/\rho)^6])$. Here K is a variational parameter and the intermolecular potential $v(\rho)=4\epsilon[(\sigma/\rho)^{12}-(\sigma/\rho)^6]$, with[6] $\epsilon=37.00$°K and $\sigma=2.928$ Å. An approximate treatment[7] has shown that for solid helium an appropriate ground-state one-particle function is

$$\phi_0(\mathbf{r})=(A/\pi)^{3/4}e^{-Ar^2/2}. \tag{2}$$

The effect of the short-range correlations may be looked upon as a replacement of the assumed intermolecular potential $v(\rho)$ by an effective potential[4]

$$W(\rho)\cong[v(\rho)-(\hbar^2/2\mu)\nabla^2\ln f(\rho)]f^2(\rho), \tag{3}$$

where μ is the molecular mass. By using linear response theory and several approximations, it is found that the

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