PHYSICAL REVIEW B VOLUME 21, NUMBER 2 15 JANUARY 1980

Thermal behavior of the Debye-Waller factor and the specific heat of anharmonic crystals

Raimundo Alexandre Tavares Lima
Centro Brasileiro de Pesquisas Físicas (CNPq), Avenida Wenceslau Braz 71, Rio de Janeiro, Brazil and Departamento de Física, Universidade Federal de São Carlos, Via Washington Luiz, Km 235, 13.560 São Carlos, S. Paulo, Brazil

Constantino Tsallis
Centro Brasileiro de Pesquisas Físicas (CNPq), Avenida Wenceslau Braz 71, Rio de Janeiro, Brazil

(Received 9 August 1979)

We study, within the framework of the variational method in statistical mechanics, the influence of the cubic and quartic crystalline anharmonicity on the classical and quantum thermal behavior of the specific heat, Debye temperature Θ, Debye-Waller factor W, crystalline expansion, and phonon spectrum. The systems we mainly focalize are the single oscillator, the monoatomic linear chain, and the simple cubic crystal. The trial Hamiltonian is a harmonic one, therefore the various anharmonic influences are mainly absorbed into the renormalization of $\Theta(T)$. Several differences between the classical and quantum results are exhibited. Satisfactory qualitative agreement with experience was obtained in the low-temperature regime, in particular on what concerns the existence of a minimum in $\Theta(T)$ which has been observed in Cu, Al, Ag, Au, and Pb. For the intermediate-temperature regime the customary linear behavior of $W(T)$ [hence $\Theta(T)$ almost constant] is reobtained. Finally, in the high-temperature regime, the present treatment leads to a $\sqrt{T}$ dependence for the W factor, which implies the wrong curvature with respect to experimental data. A possible explanation of this disagreement might be related to the melting phenomenon, which is not covered by the present theory.

I. INTRODUCTION

After the starting point given by the works of Debye[1] in 1914, Faxen[2] in 1918, and Waller[3] in 1923, a great quantity of theoretical and experimental work has been dedicated to the study of the thermal behavior of x-ray (neutron, γ-ray, etc.) scattering by a vibrating regular lattice. Various improvements have been introduced, through different generalizations of the historical "single-atom harmonic perfect crystal", by taking into account the anharmonicity of the crystal, the presence of more than one atom per unit cell, the existence of different kinds of defects (impurities, dislocations, and others) in the crystalline periodicity, the quantum effects, etc.

Let us recall that the scattered intensity I we are talking about is proportional, for a single-atom crystal, to $e^{-2W(T)}$ where $W(T)$ is the so-called (temperature-dependent) Debye-Waller factor. If we call T_0 a reference temperature, it obviously holds that

$$I(T)/I(T_0)=\exp\{-2[W(T)-W(T_0)]\}. \tag{1}$$

It is customary to introduce a quantity designated $Y(T, T_0)$ through

$$W(T_0)-W(T)=(\sin^2\theta/2\lambda^2)Y(T, T_0) \tag{2}$$

or

$$Y(T,T_0)=(\lambda^2/\sin^2\theta)\ln[I(T)/I(T_0)]. \tag{2$'$}$$

In quite general situations, $Y(T,T_0)$ *does not* depend either on the incident wavelength λ or on the scattering angle θ. Let us also recall that, within the quantum harmonic hypothesis, we have

$$W=f(T)/\Theta_D, \tag{3}$$

where $f(T)$ is a well-known function (see, for example, Ref. 4) which tends to be constant in the limit $T\to 0$, and increases linearly with T in the (classical) limit $T\to\infty$; the characteristic Debye temperature Θ_D separates these two regimes. We remark that expression (2′) is well adapted for obtaining $Y(T, T_0)$ directly from experience; consequently, the assumption of validity of relation (3) leads in general to a *temperature-dependent* "Debye temperature" which we shall designate $\Theta_{DW}(T)$. Furthermore, always within the quantum harmonic hypothesis, we know that the vibrational contribution to the constant-volume specific heat is given by

$$C_v=g(T/\Theta_D), \tag{4}$$

where $g(x)$ is a well-known function (see for example Ref. 5) which behaves as x^d [d is the space dimensionality) in the limit $T\to 0$ and tends to be constant in the (classical) limit $T\to\infty$, Θ_D being once more the characteristic temperature which separates the two regimes. If we now assume the validity of relation (4) and try to fit experimental data, we obtain (quite generally) another *temperature-dependent* Debye temperature which we shall note $\Theta_{SH}(T)$. Usually $\Theta_{DW}(T)$ and $\Theta_{SH}(T)$ do not exactly coincide, hence there is *no hope* for any theory which (explicitly or implicitly) adopts a quasiharmonic framework to simultaneously interpret, with accuracy, scattering *and* specific-heat experimental data. This criticism holds for most available theories, and our own treatment does not escape it. Nevertheless, partial success is of course not excluded, as will become clear later on.

The W factors of copper (in the range 4–500 °K[6]) and aluminum (in the range 4–400 °K[7]) have been measured and interpreted within central-force models. However, it is known[8] that these models are inadequate to explain, over the entire wavelength region, other vibrational properties. For what concerns copper, DeWames *et al.*[8] calculated, by using several sets of force constants,[9–11] its W factor; they concluded that the experimental accuracy is not high enough to spot the most adequate among them.

The anharmonic contribution to the W factor has been taken into account in several works. For instance, Owen and Williams[12] have phenomenologically introduced the anharmonicity of a single-atom crystal through a characteristic temperature $\Theta(T)=\Theta(T_0)[1-\alpha\gamma(T-T_0)]$, where T_0 is a reference temperature, γ is the Grüneisen constant, and α is the cubic thermal-expansion factor.

This procedure leads to a Y parameter which reasonably fits the experimental data (in range 300 –900 °K) for gold and copper, but not those for aluminum. Maradudin and Flinn[13] have explicitly introduced, within a classical framework, the cubic and quartic anharmonic contributions to the W factor; they obtained, besides the usual linear (in T) harmonic term, corrections in T^2 and T^3, which allow for a satisfactory fit to experimental data in what concerns the Y factor, but not in what concerns $\Theta_{\mathrm{SH}}(T)$.[14] Since then there has been a renewal of interest in calculating the W factor.[15–24,29] In particular there was some success[15–17] in interpreting at the same time, the frequency spectra and W-factor measurements in cubic metals.

In the present work we study, by taking into account the cubic and quartic anharmonicity, within a variational statistical framework, the thermal behavior of the frequency spectrum, the crystalline expansion, the Debye-Waller factor, and finally the specific heat of single-atom crystals. In particular, this theory predicts for the W factor: (a) a small temperature dependence in the limit $T\rightarrow 0$; (b) a linear dependence for intermediate temperatures; (c) a $\sqrt{T}$ dependence in the limit $T\rightarrow\infty$. Furthermore, it becomes possible to interpret the minimum of $\Theta_{\mathrm{SH}}(T)$ observed by Horton and Schiff[14] and Flinn and McManus[7] in Cu, Al, Ag, Au, Pb.

In Sec. II we perform, in order to demonstrate the kind of approximation we use, the classical and quantum calculation of the thermal expansion and thermally renormalized vibration frequency associated with a single anharmonic oscillator; in Sec. III we establish the same physical quantities for a first-neighbor linear chain. In Sec. IV we present, for a single oscillator as well as for a one-, two-, and three-dimensional crystal, the results obtained for the vibrational contribution to the constant-volume specific heat; in Sec. V we discuss, for a three-dimensional crystal, the thermal behavior of the Debye-Waller factor; finally in Sec. VI we conclude and compare the predictions of the present theory with available experimental information.

II. SINGLE OSCILLATOR

Introduction

In order to present the problem and exhibit the nature of our approximation, we shall discuss in the present section a single anharmonic oscillator (with cubic and quartic contributions) within the framework of the variational method in both classical and quantum statistical mechanics. We shall focus on the thermal behavior of the renormalized frequency and of the expansion. We shall assume the following Hamiltonian:

$$H=p^2/2m+\tfrac{1}{2}m\omega^2x^2-cx^3+bx^4\,, \tag{5}$$

where ω, c, and b are real positive quantities (ω and c are conventional; b is introduced to ensure stability). According to the relative values of ω, b, and c the potential energy might present one or two minima. The two-minima possibility might lead, in the case of systems of interacting oscillators, to structural phase transitions. As this eventuality lies beyond the scope of the present paper, we shall impose the existence of only one minimum, hence

$$c^2\leqslant\tfrac{16}{9}m\omega^2b\,. \tag{6}$$

Furthermore, by introducing the variables

$$x=\eta+u\,,$$

$$\eta=\langle x\rangle$$

where $\langle x\rangle$ is the thermal mean value, the Hamiltonian (1) can be re-written in a convenient form for variational purposes with a trial Hamiltonian given by

$$H_0=p^2/2m+\tfrac{1}{2}m\Omega^2u^2\,. \tag{7}$$

The variational free energy $\overline{F}$ (not to be confused with the exact free energy) is given by[25]

$$\overline{F}=F_0+\langle H-H_0\rangle_0\,, \tag{8}$$

where F_0 and $\langle\ldots\rangle_0$ denote, respectively, the free energy and the canonical mean value associated with H_0.

Classical statistics

Introducing (5) and (7) into (8) leads to

$$\begin{aligned}\overline{F} = F_0 + \tfrac{1}{2}m\omega^2\eta^2 - c\eta^3 + b\eta^4 \\ + (\tfrac{1}{2}m\omega^2 - 3c\eta + 6b\eta^2 - \tfrac{1}{2}m\Omega^2)\langle u^2\rangle_0 \\ + 3b\langle u^2\rangle_0^2, \qquad (9)\end{aligned}$$

where we have used that $\langle u^4\rangle_0 = 3\langle u^2\rangle_0^2$. Next we impose the minimization equations $\partial\overline{F}/\partial\Omega = 0$ and $\partial\overline{F}/\partial\eta = 0$, which lead to

$$\nu^2(\nu^2 - 1 + 6C\lambda - 12B\lambda^2) - 12Bt = 0\,, \qquad (10a)$$

$$\nu^2(\lambda - 3C\lambda^2 + 4B\lambda^3) - (3C - 12B\lambda)t = 0\,, \qquad (10b)$$

where we have used the relations

$$\frac{\partial F_0}{\partial\Omega} = \Omega^2\langle u^2\rangle_0$$

$$\tfrac{1}{2}m\Omega^2\langle u^2\rangle_0 = \tfrac{1}{2}k_BT\,,$$

(classical equipartition) and have introduced the reduced variables

$$\nu \equiv \Omega/\omega; \quad \lambda \equiv \eta(m\omega/\hbar)^{1/2}\,;$$

$$t \equiv k_BT/\hbar\omega; \quad B \equiv b\hbar/m^2\omega^3; \quad C = c(\hbar/m^3\omega^5)^{1/2}\,.$$

The constant $\hbar$ has been artificially introduced in order to make easier the comparison with the quantum case. The restriction (6) becomes

$$C^2 \leqslant \tfrac{16}{9}B\,. \qquad (6')$$

Equations (10a) and (10b) implicitly give $\nu(t)$ and $\lambda(t)$ (see Fig. 1), whose asymptotic behaviors are $\nu \sim 1 + (6B - 9C^2)t$, $\lambda \sim 3Ct$ in the limit $t \to 0$, and

$$\nu \sim (12Bt)^{1/4}\left\{1 + \frac{(12B)^{-1/2}}{4}\left(1 - \frac{3C^2}{4B}\right)t^{-1/2} + \frac{(12B)^{-1}}{32}\left(1 - \frac{3C^2}{4B}\right)^2 t^{-1} + \left[\frac{(12B)^{1/2}}{4}L^2 - \frac{3}{32}(12B)^{-3/2}\left(1 - \frac{3C}{4B}\right)\right]t^{-3/2}\right\},$$

$$\lambda \sim \lambda_\infty - Lt^{-1/2} + \tfrac{1}{2}(12B)^{1/2}(1 - 3C^2/4B)t^{-1} - (12B)^{-1}(1 - 3C^2/4B)Lt^{-3/2},$$

in the limit $t \to \infty$ with $\lambda_\infty \equiv C/4B$ and

$$L \equiv [C/8\sqrt{3}\,B^{3/2}](1 - C^2/2B).$$

Note that within restriction (6′), it is $L > 0$.

Quantum statistics

The trial Hamiltonian (7) may be rewritten in terms of boson operators

$$H_0 = \hbar\Omega(B^\dagger B + \tfrac{1}{2}) \qquad (7')$$

with the well-known transformation

$$x = (\hbar/2m\Omega)^{1/2}(B^\dagger + B)\,,$$

$$p = i(\tfrac{1}{2}\hbar m\Omega)^{1/2}(B^\dagger - B)\,,$$

which must be defined in terms of the renormalized frequency.[26]

The expression (9) still holds with

$$F_0 = k_BT\ln\left(2sh\frac{\hbar\Omega}{2k_BT}\right)$$

and

$$\langle u^2\rangle_0 = \frac{\hbar}{2m\Omega}\coth\left(\frac{\hbar\Omega}{2k_BT}\right).$$

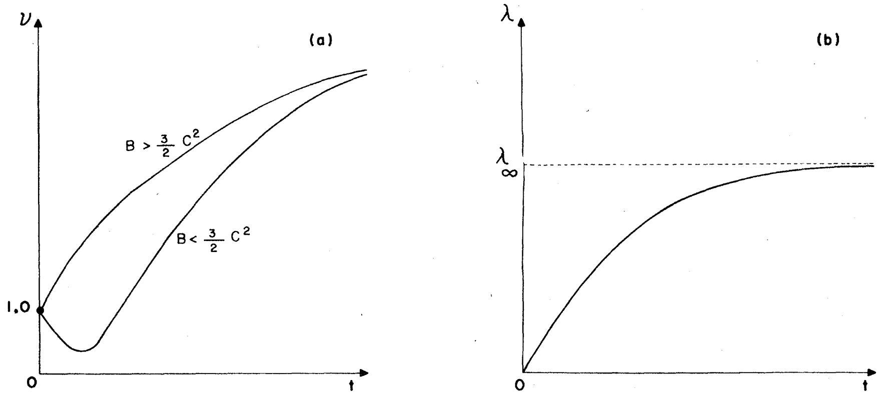

FIG. 1. Classical thermal behavior of the: (a) reduced renormalized frequency; and (b) reduced linear-expansion parameter. The saturation value denoted by λ_∞ is $C/4B$. In the limit $t \to 0$, $\nu \sim 1 + (6B - 9C^2)t$ and $\lambda \sim 3Ct$; in the limit $t \to \infty$, $\nu \sim (12bt)^{1/4}$ and $\lambda \sim \lambda_\infty - Lt^{1/2}$.

The minimization equations $\partial\bar{F}/\partial\Omega=0$ and $\partial\bar{F}/\partial\eta=0$ now become

$$\nu^2(\nu^2-1+6C\lambda-12B\lambda^2)-6B\coth(\nu/2t)=0\,, \tag{11a}$$

$$\nu(\lambda-3C\lambda^2+4B\lambda^3)+\tfrac{1}{2}(12B\lambda-3C)\coth(\nu/2t)=0\,. \tag{11b}$$

The ν and λ thermal behaviors are given, in the limit $t\to 0$, by

$$\nu\sim\nu_0+C_\nu e^{-\nu_0/t},\quad \lambda\sim\lambda_0+C_\lambda e^{-\nu_0/t}\,,$$

with

$$\nu_0(\lambda_0-3C\lambda_0^2+4B\lambda_0^3)+\tfrac{1}{2}(12B\lambda_0-3C)=0\,,$$

$$\nu_0^3-\nu_0+6C\lambda_0\nu_0-12B\lambda_0^2\nu_0-6B=0\,,$$

$$C_\nu\equiv\frac{12B\nu_0^3-18\nu_0(C-4B\lambda_0)^2}{2\nu_0^5+6B\nu_0^2-(3C-12B\lambda_0)^2}\,,$$

$$C_\lambda\equiv\frac{6\nu_0^2(C-4B\lambda_0)}{2\nu_0^3+6B-(3C-12B\lambda_0)^2}\,.$$

As expected, Eqs. (11a) and (11b) reproduce (10a) and (10b) in the classical limit $t\to\infty$. Within this limit we have the following behaviors:

$$\nu\sim(12Bt)^{1/4}\{1+\tfrac{1}{4}(12B)^{-1/2}(1-3C^2/4B)t^{-1/2}+\tfrac{1}{32}(12B)^{-1}(1-3C^2/4B)^2t^{-1}$$
$$+[\tfrac{1}{4}(12B)^{1/2}L^2-\tfrac{3}{32}(12B)^{-3/2}(1-3C^2/4B)^3+\tfrac{1}{48}(12B)^{1/2}]t^{-3/2}\}\,,$$

$$\lambda\sim\lambda_\infty-Lt^{-1/2}+(12B)^{-1/2}(1-3C/4B)t^{-1}-(12B)^{-1}(1-3C^2/4B)^2Lt^{-3/2}\,,$$

where, for ν, we have exhibited the quantum correction with respect to the classical behavior. It is remarkable that, within a high asymptotic order, classical and quantum results coincide [the same occurs with $\lambda(t)$].

The solutions $\nu(t)$ and $\lambda(t)$ of (11a) and (11b) are represented in Fig. 2. Analysis of ν_0, λ_0, C_ν, and C_λ shows that, within the restriction (6′) and depending on the relative values of B and C, we have (see Fig. 3):

$$\nu_0\gtreqless 1\,,\quad \lambda_0\geqslant 0,\quad C_\nu\gtreqless 0,\quad C_\lambda\geqslant 0\,.$$

The fact that, in contrast to the classical situation, we have, at vanishing temperatures, $\nu_0\neq 1$ and $\lambda_0\neq 0$, is clearly a consequence of the energy of the fundamental state being $\frac{1}{2}\hbar\Omega_0$ above the bottom of the potential.

III. LINEAR CHAIN

Introduction

In this section we discuss, within the variational framework, a cyclic linear chain made of N identical first-neighbor interacting oscillators. Once more we shall be interested in the thermal behavior of the crystalline expansion and frequency spectrum. We shall assume the Hamiltonian

$$H=\sum_{j=1}^{N}\left(\frac{p_j^2}{2m}+\tfrac{1}{2}m\omega^2(x_{j+1}-x_j)^2-c(x_{j+1}-x_j)^3+b(x_{j+1}-x_j)^4\right) \tag{12}$$

with the constants ω, c, and b satisfying the same restrictions as for the single-oscillator case.

By introducing the new variables $x_j=u_j+\eta$, the Hamiltonian becomes

$$H=\sum_{j=1}^{N}\frac{p_j^2}{2m}+(\tfrac{1}{2}m\omega^2-3c\eta+6b\eta^2)(u_{j+1}-u_j)^2$$
$$+b(u_{j+1}-u_j)^4+N(\tfrac{1}{2}m\omega^2\eta^2-c\eta^3+b\eta^4)+\cdots\,. \tag{12′}$$

where the dots represent odd terms in $(u_{j+1}-u_j)$. Then, through the Fourier transformation given by

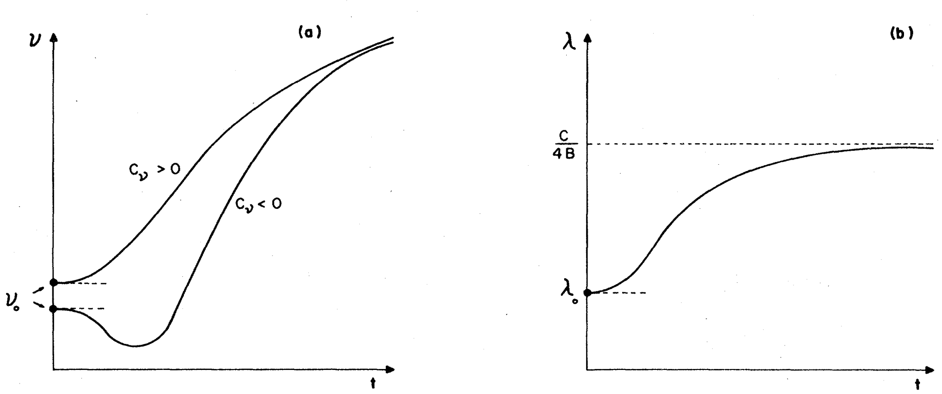

FIG. 2. Quantum behavior of the: (a) reduced renormalized frequency; (b) linear-expansion parameter. In the limit $t\to 0$, it is $\nu\sim\nu_0+C_\nu e^{-\nu_0/t}$ and $\lambda\sim\lambda_0+C_\lambda e^{-\nu_0/t}$; in the limit $t\to 0$, the classical asymptotic behaviors are re-obtained (see Fig. 1).

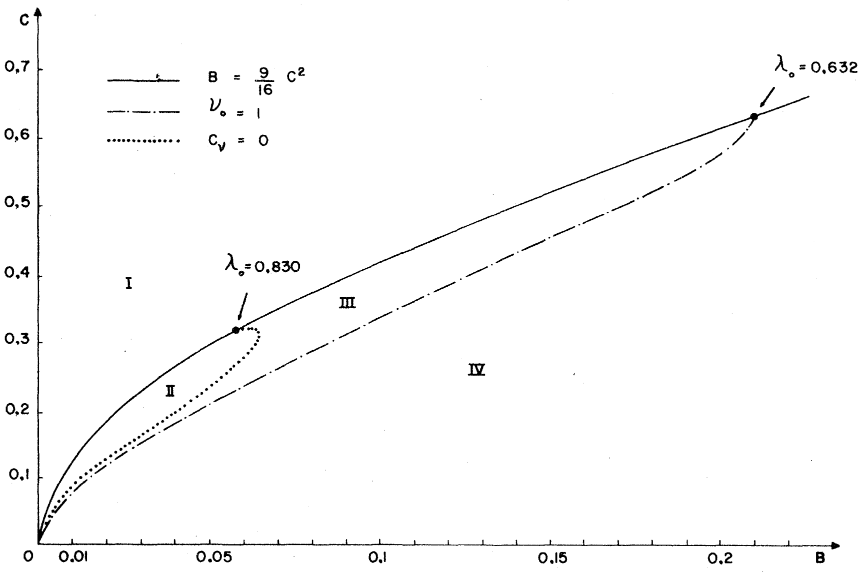

FIG. 3. Mapping of the B-C space according the cases $C_\nu \gtrless 0$ and $\nu_0 \gtrless 1$. The region I is forbidden by condition (6′); region II corresponds to $C_\nu < 0$ and $\nu_0 < 1$; region III corresponds to $C_\nu > 0$ and $\nu_0 < 1$; region IV corresponds to $C_\nu > 0$ and $\nu_0 > 1$.

$$u_j = \frac{1}{\sqrt{N}} \sum_q x_q e^{-iqj}\,, \quad p_j = \frac{1}{\sqrt{N}} \sum_q p_q e^{-iqj}$$

(q runs over all of the first Brillouin zone), the Hamiltonian takes the following form:

$$H = \sum_q \left[\frac{|p_q|^2}{2m} + 2(\tfrac{1}{2} m\omega^2 - 3c\eta + 6b\eta^2)(1 - \cos q)|x_q|^2 \right]$$
$$+ \frac{3b}{2N} \sum_{\substack{qq' \\ q''}} [(e^{-iq} - 1)(e^{-i(q+q')} - 1)(e^{-iq''} - 1)(e^{-i(q''-q')} - 1) x_q x_{q+q'} x_{q''} x_{q''-q'}] + N(\tfrac{1}{2} m\omega^2\eta^2 - c\eta^3 + b\eta^4) + \cdots\,, \quad (12'')$$

where the dots stand for the corresponding odd terms in $(u_{j+1} - u_j)$ on (12′).

We now introduce the following trial Hamiltonian:

$$H_0 = \sum_q \left(\frac{|p_q|^2}{2m} + \tfrac{1}{2} m\Omega_q |x_q|^2 \right). \quad (13)$$

Classical statistics

The use of relations (8), (12″), and (13) leads to the following expression for the variational free energy:

$$\bar{F} = F_0 + \sum_q \left([(m\omega^2 - 6c\eta + 12b\eta^2)(1 - \cos q) - \tfrac{1}{2} m\Omega_q^2)] \langle |x_q|^2 \rangle_0 + \frac{6b}{N} (1 - \cos q)^2 \langle |x_q|^2 \rangle_0^2 \right)$$
$$+ \frac{12b}{N} \sum_{qq'} (1 - \cos q)(1 - \cos q') \langle |x_q|^2 \rangle_0 \langle |x_{q'}|^2 \rangle_0 + N(\tfrac{1}{2} m\omega^2\eta^2 - c\eta^3 + b\eta^4). \quad (14)$$

Then the minimization of $\bar{F}$ with respect to Ω_q and η leads to

$$\mu^2(\mu^2 - 1 + 6C\lambda - 12B\lambda) - 12Bt = 0\,, \quad (15a)$$

$$\mu^2(\lambda^2 - 3C\lambda^2 + 4B\lambda^3) - (3C - 12B\lambda)t = 0\,, \quad (15b)$$

where we have used the classical equipartition principle and the phonon frequency spectrum

$$\Omega_q^2 = 2\omega^2\mu^2(1 - \cos q)\,, \quad (16)$$

and we have introduced the same reduced variables of Sec. II.

We remark that, within the substitution $\mu \to \nu$, Eqs. (15a) and (15b) rigorously reproduce Eqs. (10a) and (10b). However, it should be clear that μ represents the renormalized longitudinal sound velocity, while ν is the renormalized frequency of a single oscillator.

Quantum statistics

In order to study the quantum statistics of the Hamiltonian (12″), we shall put it into a second-quantization form through use of the transformation

$$x_q=\left(\frac{\hbar}{2m\Omega_q}\right)^{1/2}(B^\dagger_{-q}+B_q)\,,$$

$$p_q=i\left(\frac{\hbar m\Omega_q}{2}\right)^{1/2}(B^\dagger_q-B_{-q})\,,$$

where

$$[B_q, B^\dagger_{q'}]=\delta_{qq'}\,.$$

This procedure leads to a free energy

$$\overline{F}=F_0+\sum_q\left(\frac{1-6C\lambda+12B\lambda^2}{\mu_q}(1-\cos q)-\tfrac{1}{2}\mu_q\right)Y_q+\frac{12B}{N}\left(\sum_q(1-\cos q)\frac{Y_q}{\mu_q}\right)^2+N(\tfrac{1}{2}\lambda^2-C\lambda^3+B\lambda^4)\,,\tag{17}$$

where $\overline{F}$ and F_0 are given in $\hbar\omega$ units and

$$\overline{F}=t\sum_q\ln[2\sinh(\mu_q/2t)]\,,$$

$$Y_q\equiv\langle B^\dagger_q B_q+\tfrac{1}{2}\rangle_0=\tfrac{1}{2}\coth(\mu_q/2t)\,,$$

$$\mu_q\equiv\Omega_q/\omega\,.$$

From the conditions $\partial\overline{F}/\partial\mu_q=0$ and $\partial\overline{F}/\partial\lambda=0$, we obtain

$$\mu(\mu^2-1+6C\lambda-12B\lambda^2)-\frac{12B}{N}\sum_q\sin q\,\coth\left(\frac{\mu\sin q}{t}\right)=0\,,\tag{18a}$$

$$\mu(\lambda-3C\lambda^2+4B\lambda^3)-\frac{3C-12B\lambda}{N}\sum_q\sin q\,\coth\left(\frac{\mu\sin q}{t}\right)=0\,.\tag{18b}$$

As expected, these equations reproduce (15a) and (15b) in the classical limit $t\to\infty$. On the other hand, in the limit $t\to 0$, we obtain

$$\mu(\mu^2-1+6C\lambda-12B\lambda^2)\sim\frac{24B}{\pi}+\frac{2\pi B}{\nu_0^2}t^2\tag{19a}$$

$$\mu(\lambda-3C\lambda^2+4B\lambda^3)\sim\frac{6C-24B\lambda}{\pi}+\frac{\pi(C-4B\lambda_0)}{\nu_0^2}t^2\,,\tag{19b}$$

where we have used the quasicontinuum limit ($N\to\infty$). These equations lead to

$$\mu\sim\mu_0+C_\mu t^2\,,\quad \lambda\sim\lambda_0+C_\lambda t^2\,,$$

with

$$\mu_0(\mu_0^2-1+6C\lambda_0-12B\lambda_0^2)=24B/\pi\,,$$

$$\mu_0(\lambda_0-3C\lambda_0^2+4B\lambda_0^3)=(6C-24B\lambda_0)/\pi\,,$$

$$C_\mu\equiv\frac{\pi^2[2B\mu^2-3(C-4B\lambda_0)^2]}{2\mu_0[\pi\mu_0^2(\mu_0^2+12B/\pi)-18(C-4B\lambda_0)^2]}\,,$$

$$C_\lambda\equiv\frac{\pi^2(C-4B\lambda_0)}{2[\pi\mu_0^2(\mu_0^2+12B/\pi)-18(C-4B\lambda_0)^2]}\,.$$

We remark that, through the transformations

$$\mu_0\to\nu_0,\quad C_\mu\to(\pi^2/24\nu_0^2)C_\nu\,,$$

$$B\to\tfrac{1}{4}\pi B,\quad C_\lambda\to\frac{\pi^{3/2}}{12\nu_0^2}C_\lambda\,,$$

$$C\to\tfrac{1}{2}\sqrt{\pi}\,C\,,$$

$$\lambda_0\to(2/\sqrt{\pi})\lambda_0\,,$$

the above relations exactly reproduce the ones we obtained in Sec. II.

IV. SPECIFIC HEAT

Introduction

Let us now calculate the constant-"volume" specific heat C_v for both the single-oscillator and the linear-chain cases. Within the variational approximation it is

$$C_v=\frac{\partial}{\partial T}\langle H\rangle_0\tag{20}$$

Single oscillator

Within classical statistics, expression (20) may be rewritten as follows

$$C_v=k_B\left(1-\frac{t}{\nu}\frac{\partial\nu}{\partial t}\right),\tag{21}$$

where we have used (10a) and (10b). Note that the thermal expansion enters only indirectly, through its influence on $\nu(t)$. Furthermore, if ν monotonously increases (with t), then C_v monotonously decreases; if ν presents a minimum (see Fig. 2a), then C_v presents a maximum (see Fig. 4). Its asymptotic behaviors are

$$C_v\sim\tfrac{3}{4}k_B\left(1+\frac{1-3C^2/4B}{6(12B)^{1/2}}t^{-1/2}\right)\tag{22}$$

in the limit $t\to\infty$, and

$$C_v\sim k_B[1-(6B-9C^2)t]\tag{22'}$$

in the limit $t\to 0$.

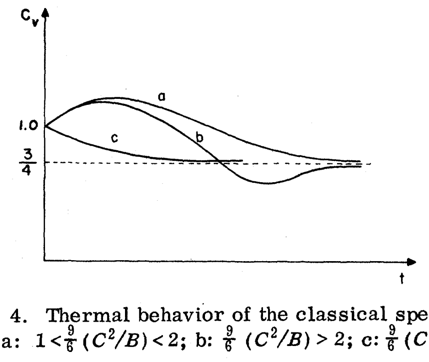

FIG. 4. Thermal behavior of the classical specific heat. a: $1<\frac{9}{6}(C^2/B)<2$; b: $\frac{9}{6}(C^2/B)>2$; c: $\frac{9}{6}(C^2/B)<1$.

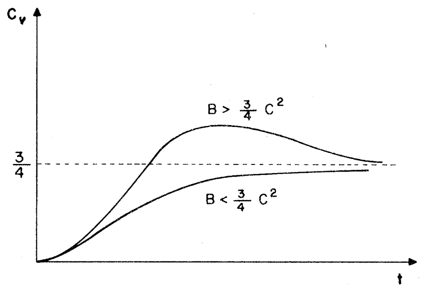

FIG. 5. Thermal behavior of the quantum specific heat for both cases $B \lessgtr \frac{3}{4}C^2$.

The discussion of these asymptotic behaviors leads to three different cases (see Fig. 4). Within quantum statistics, expression (20) becomes

$$C_v = \tfrac{1}{2}k_B \nu \frac{\partial}{\partial t}\left(\coth\frac{\nu}{2t}\right), \tag{23}$$

where we have used (11a) and (11b). The asymptotic behavior in the limit $t \to 0$ is

$$C_v \sim 4\nu_0 (e^{-\nu_0/t}/t)\,,$$

while in the limit $t \to \infty$, it is still given by expression (22) (see Fig. 5).

Linear chain

The classical specific heat for this case is given by

$$C_v = Nk_B\left(1 - \frac{t}{\mu}\,\frac{\partial \mu}{\partial t}\right), \tag{24}$$

which differs from the single-oscillator case only by a factor N. In the quantum case we obtain, through use of Eqs. (18a) and (18b),

$$C_v = k_B \mu \frac{\partial}{\partial t} \sum_q \sin\frac{q}{2}\, \coth\left(\frac{\mu}{t}\sin\frac{q}{2}\right). \tag{25}$$

Clearly, expression (25) reproduces (24) in the classical limit. On the other hand, in the limit $t \to 0$, we have

$$C_v \sim (N\pi k_B/3\mu_0)t\,. \tag{26}$$

The temperature dependence of C_v is shown in Fig. 6.

If we compare Eqs. (11a) and (11b) with (18a) and (18b) we observe a great similarity between them. The difference consists in the fact that, while in the first case (single oscillator) the temperature dependence appears explicitly in the unique coth term; in the second one (linear chain), it appears through an integral on coth terms. Therefore it is clear that for a d-dimensional crystal we shall obtain a d-dimensional integral over the same type of coth terms. Hence, in the limit $t \to 0$, the asymptotic behavior (26) will become $C_v \propto t^d$, as in the well-known *harmonic* Debye case. At high temperature, all cases (for any value of d) are expected to present the same type of asymptotic behavior. Let us conclude by saying that these considerations lead to

$$\mu \sim \mu_0 + C_\mu t^{d+1} \quad (t \to 0) \tag{27a}$$

$$\mu \propto t^{1/4} \quad (t \to \infty)\,, \tag{27b}$$

where C_μ is related, for any value of $d \geq 1$, to C_v through a transformation similar to the one we exhibited in Sec. III C.

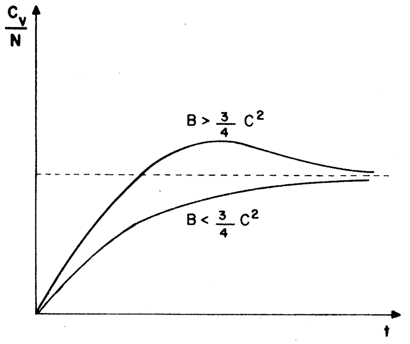

FIG. 6. Thermal behavior of the quantum specific heat of a linear chain for both cases $B \lessgtr \frac{3}{4}C^2$.

V. DEBYE-WALLER FACTOR

Let us recall that the amplitude of scattered x-rays (and other similar beams) is given by

$$e^{-W} = \langle \exp[i\vec{K}\cdot(\vec{u}_j - \vec{u}_{j'})]\rangle\,, \tag{28}$$

where $\vec{K} = \vec{k} - \vec{k}'$ is the scattering vector, u_j is the displacement of the jth atom from its equilibrium position, and $\langle \ldots \rangle$ denotes the thermal canonical average. In any quasiharmonic approximation the probability distribution of the displacements is Gaussian in both classical and quantum treatments (see, for example, Ref. 27). Hence (see for example Ref. 28),

$$e^{-W} = \exp\{-\tfrac{1}{2}\langle[\vec{K}\cdot(\vec{u}_j - \vec{u}_{j'})]^2\rangle_0\}\,, \tag{28$'$}$$

where now $\langle \ldots \rangle_0$ denotes thermal average with a Gaussian law. Within the variational treatment we are dealing with, we obtain

$$W = \tfrac{1}{6}K^2\langle(\vec{u}_j - \vec{u}_{j'})^2\rangle_0 = \frac{K^2}{6}\sum_q \langle |u_q|^2\rangle_0\,,$$

where we have performed a Fourier transformation. Within the quasicontinuum limit and the Debye approximation, we obtain for $d = 3$ (see also Ref. 24)

$$W = \frac{3}{2}\,\frac{K^2\hbar^2 T^2}{mk_B[\Theta(T)]^3}\int_0^{\Theta(T)/T}\left(\frac{1}{e^z - 1} + \frac{1}{2}\right) z\, dz\,, \tag{29}$$

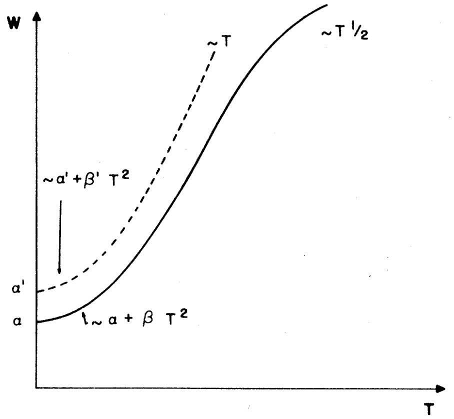

FIG. 7. Thermal behavior of the quantum Debye-Waller factor of a three-dimensional crystal in both harmonic (dashed line) and anharmonic (continuous line) cases. α' might be greater than α (as in this figure) or not, depending on the values of B and C.

where m is the mass of the atom and $\Theta(T)$ is the thermally renormalized Debye temperature. Therefore, the anharmonic influence appears exclusively through $\Theta(T)$, which is given by

$$\Theta(T) = \frac{\hbar \Omega_D(T)}{k_B} = 2\hbar a q_D \omega \mu(T) , \tag{30}$$

where a is the characteristic crystalline parameter, Ω_D is the Debye frequency, and q_D is the Debye wave vector. By using relations (27a), (27b), (29), and (30) we finally obtain

$$W \sim \tfrac{1}{16} (K^2/a^2 q_D)(3k_B/b)^{1/2} T^{1/2}$$

in the limit $T \rightarrow \infty$, and

$$W \sim \alpha + \beta T^2 + \gamma T^4$$

in the limit $T \rightarrow 0$, where

$$\alpha \equiv \frac{3K^2\hbar}{16 m a q_D \omega \mu_0} , \quad \beta \equiv \frac{3\pi^2 k_B K^2}{96 m \hbar a^3 q_D^3 \omega^3 \mu_0} , \quad \gamma \equiv \frac{-C_\mu \alpha}{\mu_0} .$$

In Fig. 7 we present typical harmonic and anharmonic Debye-Waller factors as functions of temperature.

VI. CONCLUSION

The purpose of the present work was to study the influence of (cubic and quartic) anharmonicity of real crystals on the thermal behavior of some relevant physical quantities [constant-volume specific heat, thermally renormalized Debye temperature (Θ), Debye-Waller factor (W), crystalline expansion, phonon spectrum]. The calculations were performed within the framework of the variational method in statistical mechanics, which in a relatively simple and unified manner provides the thermal dependence, for the *whole range* of temperatures, of the above quantities. Precisely, our methodology consisted in first presenting the single-oscillator case, then the linear chain, and finally we generalized some of our results to d-dimensional monoatomic crystals. Because of our harmonic choice for the trial Hamiltonian, most of the physical quantities were given, as functions of temperature, by relations formally equal to those customary for the purely harmonic case, and the anharmonic influence was mainly absorbed into the renormalization of $\Theta(T)$.

For what concerns the low-temperature regime, the present treatment succeeded in providing forms of $\Theta(T)$ which qualitatively fit well experimental data. In particular we obtained (for a defined region of the space of the harmonic and anharmonic elastic constants) the minimum of $\Theta(T)$ which is typical[7,14] of Cu, Al, Ag, Au, and Pb.

For the intermediate-temperature regime, we obtained the customary (Refs. 7, 12, 14, 18, 23, 29) linear dependence of the W and Y factors [in other words, $\Theta(T)$ approximatively constant].

Finally, in the high-temperature regime, the present treatment leads to a $\sqrt{T}$ dependence for for the W factor, which implies the *wrong* curvature when comparison is made with experimental results for Al (Ref. 12) and Na (Refs. 23, 29). Nevertheless, let us point out that the high-temperature regime practically coincides with the region just below the melting point where the phase-transition effects, *not included* in the present treatment, are expected to be important (in the sense of accelerating the increase of the W factor with temperature). More precisely, Al and Na were, respectively, studied[12,23,29] in the regions 300–900 °K and 100–370 °K (we recall that their melting points are, respectively, 933 and 371 °K). Furthermore, it is significant that several other substances (which were observed in regions relatively far from their melting points) *did not deviate* from the linear increase of $W(T)$; namely, Cu [observed in the 300–900 °K region (Ref. 12); melting point 1356 °K], Au [300–900 °K (Ref. 12); 1336 °K], Fe [200–1100 °K (Refs. 18, 23, 29), 1809 °K], Mo [100–500 °K (Ref. 23); 2890 °K], and Cr [100–500 °K (Ref. 23); 2130 °K].

ACKNOWLEDGMENTS

One of us (C.T.) acknowledges early useful comments of A. Craievich on the subject and R.A.T.L. acknowledges a fellowship from Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil.

[1] P. Debye, Ann. Physik 43, 49 (1914).
[2] H. Faxén, Ann. Physik 54, 615 (1918).
[3] I. Waller, Z. Phys. 17, 398 (1923).
[4] Mikkail A. Krivoglass, *Theory of X-Ray and Thermal-Neutron Scattering by Real Crystals* (Plenum, New York, 1969), Chap. VI.
[5] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University, Cambridge, 1965), Chap. 2.
[6] P. A. Flinn, G. M. McManus, and J. A. Rayne, Phys. Rev. 123, 809 (1961).
[7] P. A. Flinn, and G. M. McManus, Phys. Rev. 132, 2458 (1963).
[8] R. E. DeWames, T. Wolfram, and G. W. Lehman, Phys. Rev. 131, 528 (1963).
[9] E. H. Jacobsen, Phys. Rev. 97, 654 (1955).
[10] G. W. Lehman, T. Wolfram, and R. E. DeWames, Phys. Rev. 128, 1593 (1962).
[11] H. C. White, Phys. Rev. 112, 1097 (1958).
[12] E. A. Owen and R. W. Williams, Proc. R. Soc. London A 188, 509 (1947).
[13] A. A. Maradudin and P. A. Flinn, Phys. Rev. 129, 2529 (1963).
[14] G. K. Horton and H. Schiff, Proc. R. Soc. London A 250, 248 (1959).
[15] K. C. Sharma and S. K. Joshi, Phys. Rev. 136, A419 (1964).
[16] N. Singh and P. K. Sharma, Phys. Rev. B 4, 1141 (1971).
[17] J. Prakash and M. P. Hemkar, J. Phys. Soc. Jpn. 34, 1583 (1973).
[18] H. C. Haworth, Phys. Mag. 5, 1229 (1960).
[19] F. H. Herbstein, Adv. Phys. 10, 313 (1961).
[20] V. Synecek, H. Chessin, and M. S. Simerska, Acta Crystallogr. A 26, 108 (1970).
[21] J. Prakash, L. P. Pathak, and M. P. Hemkar, Aust. J. Phys. 28, 63 (1975).
[22] L. A. Bertolo and M. M. Shuka, Phys. Status Solidi B 77, 433 (1976).
[23] M. Kumar and M. P. Hembar, Acta Phys. Pol. A 53, 543 (1978).
[24] L. P. Pathak, J. Prakash, V. P. Singh, and P. Hemkar, Aust. J. Phys. 28, 63 (1975).
[25] R. P. Feynman, *Statistical Mechanics* (Benjamin, New York, 1972), Chap. 2.
[26] C. Tsallis and J. W. Valle, Rev. Bras. Física 9, (3) (1979).
[27] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), Chap. III.
[28] C. Tsallis, Nuovo Cimento B 34, 411 (1976).
[29] A. M. Ozorio de Almeida and Caticha Ellis, Phys. Status Solidi B 75, 657 (1976).