

TITLE: REVISION OF THE STATISTICAL MECHANICS OF PHONONS TO
INCLUDE PHONON LINE WIDTHS

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Revision of the Statistical Mechanics of Phonons
to Include Phonon Line Widths*

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1. Introduction

Zubarev[1] in 1960 obtained the "smeared" Bose-Einstein (B-E) function in order to take into account the fact that the eigenenergy associated with a fixed phonon wave vector q and fixed polarization index j is not precisely defined but instead, is smeared by phonon-phonon and phonon-electron interactions. The ratio $\Gamma(qj)/\omega(qj)$ is often quite small, i.e., of the order of 0.01 or less, where Γ is the phonon linewidth and ω is the eigenenergy. However, in strongly anharmonic crystals Γ/ω may be as large as 0.3 at certain points of the Brillouin zone. In such dramatic cases one would suspect that such phonon linewidths would have some observable effect on the thermodynamic properties. Zubarev represented the effect of "smearing" on the statistical properties by the infinite integral[1],

$$\bar{n} = \int_{-\infty}^{\infty} d\omega [\exp(\beta\hbar\omega) - 1]^{-1} L(\omega; \bar{\omega}, \Gamma) , \quad (1)$$

$$L(\omega; \bar{\omega}, \Gamma) = (\Gamma/\pi) [(\omega - \bar{\omega})^2 + \Gamma^2]^{-1} , \quad (2)$$

in which we have deleted the indices (q, j) for convenience. The term in square brackets in (1) is the usual B-E function, while in L , the usual Lorentzian function, $\bar{\omega}$ is the average or center frequency of the distribution.

Equation (1) is not usable as it stands. However, we have found a single formula which is the exact equivalent of (1) by the use of contour methods. We obtain for the average B-E function,

$$\bar{n} = (e^{\bar{x}} \cos \gamma - 1) / (e^{2\bar{x}} - 2 e^{\bar{x}} \cos \gamma + 1) - \sum_{\ell=1}^{\infty} 8 \ell \pi \bar{x} \gamma / [(-4 \ell^2 \pi^2 + \bar{x}^2 + \gamma^2)^2 + 16 \ell^2 \pi^2 \bar{x}^2] , \quad (3)$$

where $\bar{x} = \beta \hbar \bar{\omega}$, $\gamma = \beta \hbar \Gamma$, and $\beta = 1/kT$. The summation part of (3) is due to poles on the imaginary axis of the ω -plane. When we use (3) to derive the specific heat and entropy, we find that the entropy slope $\partial S/\partial T \rightarrow \infty$ as $T \rightarrow 0$ K, due to the summation part of (3). The first part of (3) is well behaved. Accordingly, the use of (1) is proven to be invalid.

2. A New Approach

Since we have shown that (3), which is equivalent to (1), is invalid, we have tried using the statistical mechanical expressions for the phonon partition function, entropy, and free energy, in the place of the B-E function in (1).

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Use of the two former functions leads to summations similar to that in (3) which are invalid. However, use of the phonon free energy per mode $f = \hbar \omega/2 + kT \ln[1 - \exp(-\beta \hbar \omega)]$ in (1) instead of the B-E function leads to a result that is well behaved at all temperatures. The purpose of this work is to derive the expression for the average free energy per mode \bar{f} for a crystal having large phonon linewidths and to test the properties of the thermodynamic functions derivable from \bar{f} .

The procedure is to insert f in (1) and to assume ω is complex. The line integration is accomplished by contour integration over the ω -plane. The counterclockwise contour for the upper half plane consists of a line ϵ above the real axis (with small semicircle at the origin) plus a large positive semicircle. Poles occur at $\omega = +2n\pi i (kT/\hbar)$; $n=1,2,\dots$, but the residues are zero for all n . The clockwise contour for the lower half plane consists of a line ϵ below the real axis (with small semicircle at origin) plus the large negative semicircle. Poles occur at $\omega = -2n\pi i (kT/\hbar)$; $n=1,2,\dots$, but, again, all of the residues are zero. The only residues of importance are at the poles $\omega = \bar{\omega} + i\Gamma$ (upper half plane) and $\omega = \bar{\omega} - i\Gamma$ (lower half plane). Results for the two half planes are averaged as discussed by Morse and Feshbach [2], a procedure which leads to,

$$\bar{f} = \hbar \bar{\omega}/2 + (kT/2) \ln [1 - 2 \exp(-\bar{x}) \cos \gamma + \exp(-2\bar{x})] \quad (4)$$

where $\bar{x} = \hbar \bar{\omega}/kT$ and $\gamma = \hbar \Gamma/kT$. This same procedure was used in deriving \bar{n} in (3) from (1).

3. Thermodynamic Applications

The specific heat per mode is obtained by the formula $c_v = -T \partial^2 \bar{f} / \partial T^2$. However, the exact form of c_v depends on the assumption made as to the temperature dependence of the anharmonic shift $\Delta(q_j)$ and half width $\Gamma(q_j)$. Maradudin and Fein [3] derived expressions for Δ and Γ and found approximations suitable for the very low temperature range and for the high temperature range with $T >$ Debye Θ . At low temperatures, Δ and Γ are nearly independent of T while at high temperatures they vary linearly with T . They also calculated formulas for Δ and Γ for high temperatures based on an anharmonic potential function (Morse potential) which, in turn, was based on the heat of sublimation of lead. Using their data, we thus have a basis for testing the possible validity of (4), at least for the case of crystalline lead. Thus, for the high temperature approximation, we may write,

$$\begin{aligned} \Delta &= dT; & \bar{x} &= \hbar \omega_0/kT + \hbar d/k = x_0 + \delta; \\ \Gamma &= gT; & \gamma &= \hbar g/k, \end{aligned} \quad (5)$$

where ω_0 is the harmonic (or quasi-harmonic) eigentfrequency. Using (5) in (4), we obtain the mode specific heat,

$$c_v = k x_0^2 e^{\bar{x}} [(e^{2\bar{x}} + 1) \cos \gamma - 2e^{\bar{x}}] / (e^{2\bar{x}} - 2e^{\bar{x}} \cos \gamma + 1)^2 \quad (6)$$

Since γ is small in the high temperature approximation, we may replace $\cos \gamma$ by $(1 - \gamma^2/2)$. The shift Δ is also small and we may replace $\exp(\bar{x})$ by $\exp(x_0)(1 + \delta + \delta^2/2)$. Thus, (6) can be rewritten in the form,

$$\begin{aligned} c_v/k &= x^2 e^x / (e^x - 1)^2 - \delta x^2 e^x (e^x + 1) / (e^x - 1)^3 \\ &+ (1/2)(\delta^2 + \gamma^2) x^2 e^x (e^{2x} + 4e^x + 1) / (e^x - 1)^4, \end{aligned} \quad (7)$$

in which x now denotes $x_0 = \hbar \omega_0/kT$. The leading term in (7) is the ordinary harmonic specific. When integrated over the spectrum, this leads to the Dulong-Petit value of $3R$ per mole for $T >$ Debye Θ . Upon expanding

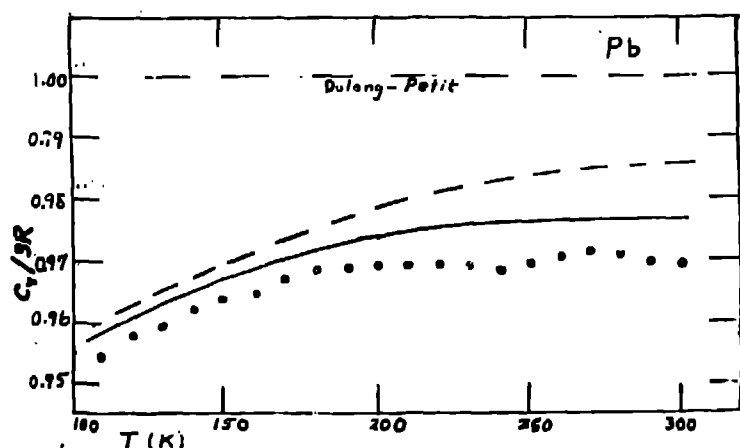


Fig. 1. Specific heat of lead. (Dashed curve) Theory with shift correction only. (solid curve) Theory with both shift and width corrections. (solid circles) Experimental data of Meads, Forsyth and Giauque, J. Am. Chem. Soc: 63, 1902 (1941).

further for the high temperature approximation, we observe that (7) can be expressed in the form,

$$c_v/k = c_{\text{har}}/k - (2\delta/x)(1 - x^4/40) + (3\delta^2/x^2 - 3\gamma^2/x^2)(1 + x^4/720) \quad (8)$$

Brockhouse, et al [4] have measured $\Gamma(qj)$ for lead by neutron scattering methods and find for the longitudinal mode at the [100] zone boundary and at 425 K the half width $\Gamma = 1.35$ tHz while the largest phonon frequency ω_L is 20.6 tHz, i.e., $\Gamma_{\text{max}}/\omega_L = 0.0655$. Thus, in view of (5), we may write $\Gamma(T) = (0.0655)(T/425)\omega_L$. For interior points we make the further approximation, $\Gamma(qj) = (0.0655)(T/425)\omega_L[\omega(qj)/\omega_L]$. Thus, $\gamma(qj) = (0.0655)(T/425)[h\omega(qj)/kT] = (0.0655)(T/425)x$.

Since (4) and (7) correspond to the case in which volume $V = V(0 \text{ K})$, we need only the cubic and quartic shifts while the shift due to thermal expansion does not enter. Following Ref. [3], we have for the quartic shift in lead, $\Delta_4 = (0.0151)(T/\Theta_\infty)\omega_L \lambda(qj)$, where $\lambda =$ reduced frequency and $\lambda_{\text{max}} = 2$ and $\lambda/\lambda_{\text{max}} = \omega/\omega_L$. Thus $\Delta_4 = (0.0302)(T/\Theta_\infty)\omega(qj)$ so that $\delta = (0.0302)(T/\Theta_\infty)x$. Since the cubic contribution is about five times smaller, we make little error by assuming a similar formula. Based on [3], we approximate Δ_3 by $(-0.0034)(T/\Theta_\infty)\omega(qj)$. Thus, the net δ becomes $(+0.0134)(T/\Theta_\infty)x$, when one takes into account the fact that the shift in free energy is exactly one half that in neutron scattering theory[5]. Substituting in (8) leads to,

$$c_v/k = c_{\text{har}}/k - (0.0268)(\Theta_0/\Theta_\infty)(1/x - x^3/240) + 3(0.0134)^2(\Theta_0/\Theta_\infty)^2(1/x^2) - (0.0129)(T/425)[1 + x^4/720] \quad (9)$$

where $\Theta_0 = h\omega_L/k = 15 \text{ K}$. Integrating over a Debye spectrum, we obtain

$$C_V/3R - C_{\text{har}}/3R = -0.0392(\Theta_0/\Theta_\infty)(\Theta/T) - (0.0129)(T/425)^2 \quad (10)$$

The results shown in Fig. 1 indicate that inclusion of the phonon line width in the statistical mechanics of phonons improves the agreement with experiment.

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