Extension of Debye's theory of specific heats of solids

2008 J. Phys.: Condens. Matter 20 295207

(http://iopscience.iop.org/0953-8984/20/29/295207)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 295207 (5pp) doi:10.1088/0953-8984/20/29/295207

Extension of Debye's theory of specific heats of solids

Xian-Zhi Wang

Institute for Theoretical Physics, Department of Physics, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 17 March 2008, in final form 14 May 2008
Published 26 June 2008
Online at stacks.iop.org/JPhysCM/20/295207

Abstract
Van Hove's theory of singularities tells us that for three-dimensional lattices the phonon frequency distribution function has square-root singularities and hence is continuous. Using this fact and Weierstrass's theorem, we extend Debye's theory of specific heats of three-dimensional solids to arbitrary phonon frequency spectra. It is found that in the low-temperature limit both the specific heat and thermal expansion coefficient exhibit the T^3 law and the Grüneisen's law is valid. In the high-temperature limit, the thermal expansion coefficient approaches a volume-dependent constant and Grüneisen's law is valid. At intermediate temperatures Grüneisen's law is invalid.

1. Introduction

The evaluation of the vibrational specific heat of a solid is an old problem dating back to Einstein [1] and Debye [2]. The specific heat of the lattice of a solid can be obtained if the phonon frequency distribution function $g(\omega)$ is known. Here $g(\omega)$ is defined such that $g(\omega)\mathrm{d}\omega$ is the fractional number of frequencies in the range between ω and $\omega + \mathrm{d}\omega$. Theoretically, $g(\omega)$ can be obtained by use of the Born–Karman method [3]. Unfortunately, the evaluations of $g(\omega)$ are in general very complicated [4–9]. The analytical expressions for $g(\omega)$ are available only for one-dimensional (1D) [3] and two-dimensional (2D) lattices [7]. Experimentally $g(\omega)$ can be obtained by use of x-ray [10, 11] and neutron [12] scattering methods. Since it is widely believed that phonons play a significant role in the mechanism of high-temperature superconductivity [13], researchers' interest in phonons has revived.

Since experimentally it is easier to obtain the specific heat than to obtain $g(\omega)$, researchers tried to obtain $g(\omega)$ inversely by use of the experimental data of the specific heat. Using the Fourier transform, Montroll [4] and independently Lifshitz [14] obtained an exact solution of the inverse problem. Using the Möbius inverse formula, Chen [15, 16] also obtained an exact solution of the inverse problem. Although the exact solution is available, it is in practice still difficult to obtain $g(\omega)$ [17, 18]. In this paper, we will apply Weierstrass's theorem to this problem and further develop Debye's theory.

2. Low-temperature limit

The specific heat can be expressed as

$$C_V(T) = k_B \int_0^{\omega_m} \frac{(\hbar\omega/k_B T)^2 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} g(\omega)\mathrm{d}\omega, \quad (1)$$

where T is the temperature, ω_m is the maximum possible frequency, $\hbar$ is Planck's constant and k_B is Boltzmann's constant. $g(\omega)$ satisfies the normalization condition

$$\int_0^{\omega_m} g(\omega)\mathrm{d}\omega = 3rN, \quad (2)$$

where N is the number of unit cells in the lattice, r is the number of atoms per unit cell.

Let us write $g(\omega) = g_a(\omega) + g_o(\omega)$. Here $g_a(\omega)$ and $g_o(\omega)$ are the contributions of three acoustic modes and $3r - 3$ optical modes to the frequency spectrum, respectively. For small ω, we may expand for acoustic mode σ,

$$\omega(\sigma, \vec{k}) = \omega(\sigma, k, \theta, \phi) = u(\sigma, \theta, \phi)k\left[1 + \sum_{i=1}^{\infty} \tau_{2i}(\sigma, \theta, \phi)k^{2i}\right], \quad (3)$$

where $\vec{k} = (k, \theta, \phi)$ is the wavevector and $u(\sigma, \theta, \phi)$ and $\tau_{2i}(\sigma, \theta, \phi)$ are determined by the second derivative of the potential of the crystal with respect to atomic displacements evaluated at equilibrium positions.

From equation (3), we can calculate $g_a(\omega)$. $g_a(\omega)$ can be expanded as a power series in ω^2,

$$g(\omega) = g_a(\omega) = \sum_{j=1}^{\infty} b_{2j}\omega^{2j}, \qquad \omega \ll \omega_m, \quad (4)$$

where b_{2j} are determined by $u(\sigma,\theta,\phi), \tau_2(\sigma,\theta,\phi), \ldots, \tau_{2j}(\sigma,\theta,\phi), \sigma = 1, 2, 3$. For example, b_2 and b_4 are given by

$$b_2 = \frac{V}{8\pi^3}\sum_{\sigma=1}^{3}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \frac{\sin\theta}{[u(\sigma,\theta,\phi)]^3} \equiv \frac{3V}{2\pi^2\bar{u}^3}, \quad (5)$$

$$b_4 = -\frac{5V}{8\pi^3}\sum_{\sigma=1}^{3}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \frac{\tau_2(\sigma,\theta,\phi)}{[u(\sigma,\theta,\phi)]^5}. \quad (6)$$

Let us show that Van Hove's singularities cannot invalidate the low-frequency expansion equation (4). Van Hove's singularities are caused by the existence of the critical points satisfying $\partial\omega/\partial\vec{k} = 0$ in the $\vec{k}$-space [19]. In the low-frequency regime, the first-order term of equation (3) is much larger than the higher-order terms and so we have $\partial\omega/\partial\vec{k} \neq 0$. Hence no Van Hove's singularities occurs and the low-frequency expansion is valid.

In the low-temperature limit, only the low-frequency phonons are excited and equation (4) becomes useful. This gives [24]

$$C_V(T) = 9rNk_B\left(\frac{T}{T_D}\right)^3 \sum_{j=1}^{\infty} \frac{b_{2j}\omega_m^{2j-2}}{b_2} \times (2j+2)!\zeta(2j+2)\left(\frac{T}{T_m}\right)^{2j-2}, \qquad T \ll T_m, \quad (7)$$

where $\zeta(x) = \sum_{n=1}^{\infty} n^{-x}$ is the usual Riemann zeta function.

3. Extension

Let us extend the above low-frequency expansion equation (4) to the whole range of frequency. Van Hove's theory of singularities [19–21] tells us that for three-dimensional (3D) lattices $g(\omega)$ has square-root singularities and hence is continuous for $0 \leqslant \omega \leqslant \omega_m$. $g(\omega)$ shows the Debye acoustic spectrum for small frequencies, displays a few finite maxima for intermediate frequencies and approaches zero at the maximum frequency. We have

$$g(\omega = 0) = g(\omega = \omega_m) = 0. \quad (8)$$

Van Hove's results agree with numerical and experimental results of $g(\omega)$ [22, 23].

Since $g(\omega)$ has square-root singularities, we cannot expand it by use of the Fourier series and the Legendre polynomials. Let us make use of Weierstrass's theorem [25], which states that if $f(x)$ is continuous on the closed interval $[a, b]$, there exists a sequence of polynomials $P_n(x)$ such that

$$\lim_{n\to\infty} P_n(x) = f(x), \quad (9)$$

where

$$P_n(x) = \sum_{j=0}^{n} a_{nj}x^j. \quad (10)$$

This theorem tells us that there exists a set of coefficients $a_{nj}, n = 0, \ldots, \infty, j = 0, \ldots, n$ such that $\sum_{j=0}^{n} a_{nj}x^j$ tends uniformly to $f(x)$ as $n \to \infty$.

Make a transformation

$$x \in [a, b] \to y = \frac{x-a}{b-a} \in [0, 1], \qquad f(x) \to F(y) = \frac{f(x)-f(a)}{f(b)-f(a)} - \frac{x-a}{b-a}, \quad (11)$$

such that $F(y)$ is continuous on the closed interval $[0, 1]$, with $F(0) = F(1) = 0$. Using Bernstein's polynomials $\mathcal{B}_n(F, y)$ [25], we obtain

$$F(y) = \lim_{n\to\infty} \mathcal{B}_n(F, y), \quad (12)$$

where

$$\mathcal{B}_n(F, y) \equiv \sum_{i=1}^{n}\left[C_n^i F\left(\frac{i}{n}\right)\right] y^i(1-y)^{n-i} = \sum_{i=1}^{n} C_n^i F\left(\frac{i}{n}\right)\sum_{j=0}^{n-i}(-1)^{n-i-j}C_{n-i}^j y^{n-j} = \sum_{j=1}^{n} A_{nj}y^j, \quad (13)$$

with

$$A_{nj} = \sum_{i=1}^{j}(-1)^{j-i}C_{n-i}^{n-j}C_n^i F\left(\frac{i}{n}\right). \quad (14)$$

Since $g(\omega)$ is an even function of ω, we may define the dimensionless phonon frequency distribution function as

$$G(\omega^2/\omega_m^2) = \frac{g(\omega)}{b_2\omega_m^2}. \quad (15)$$

We find that $G(y)$ is continuous on the closed interval $[0, 1]$, with $G(0) = G(1) = 0$ and $G(y) = y$ for $y \ll 1$. Making use of Bernstein's polynomials, we obtain

$$\frac{g(\omega)}{b_2\omega_m^2} = G(\omega^2/\omega_m^2) = \lim_{n\to\infty}\mathcal{B}_n\left(G, \frac{\omega^2}{\omega_m^2}\right) = \lim_{n\to\infty}\sum_{j=1}^{n}\Lambda_{nj}\left(\frac{\omega^2}{\omega_m^2}\right)^j, \qquad 0 \leqslant \omega \leqslant \omega_m, \quad (16)$$

where

$$\Lambda_{nj} = \sum_{i=1}^{j}(-1)^{j-i}C_{n-i}^{n-j}C_n^i G\left(\frac{i}{n}\right) = \sum_{i=1}^{j}(-1)^{j-i}C_{n-i}^{n-j}C_n^i \frac{g\left(\sqrt{\frac{i}{n}}\omega_m\right)}{b_2\omega_m^2}. \quad (17)$$

Equation (16) is an extension of equation (4).

Substitution of equation (16) into (2) gives

$$\frac{\omega_D}{\omega_m} = \left[\lim_{n\to\infty}\sum_{j=1}^{n}\frac{3\Lambda_{nj}}{1+2j}\right]^{1/3}, \quad (18)$$

where $\omega_D = (9rN/b_2)^{1/3}$ is the usual Debye cut-off frequency.

Making use of equation (16), we obtain the canonical partition function Z, the internal energy E and the specific heat

C_V as

$$\ln Z = -\frac{E_0}{k_B T} + 9rN \lim_{n\to\infty} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{\sum_{l=1}^{n} 3\Lambda_{nl}/(1+2l)} \times \left[(2j)!\zeta(2j+2)\left(\frac{T}{T_m}\right)^{2j+1} - \sum_{i=0}^{2j} i! C_{2j}^{i} \left(\frac{T}{T_m}\right)^{i+1} \mathcal{W}_{i+2}(e^{-T_m/T}) \right], \quad (19)$$

$$E = E_0 + 9rNk_B T \lim_{n\to\infty} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{\sum_{l=1}^{n} 3\Lambda_{nl}/(1+2l)} \times \left[(2j+1)!\zeta(2j+2)\left(\frac{T}{T_m}\right)^{2j+1} - \sum_{i=0}^{2j+1} i! C_{2j+1}^{i} \left(\frac{T}{T_m}\right)^{i} \mathcal{W}_{i+1}(e^{-T_m/T}) \right], \quad (20)$$

$$C_V(T) = 9rNk_B \lim_{n\to\infty} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{\sum_{l=1}^{n} 3\Lambda_{nl}/(1+2l)} \times \left[(2j+2)!\zeta(2j+2)\left(\frac{T}{T_m}\right)^{2j+1} - (2j+2)!\left(\frac{T}{T_m}\right)^{2j+1} \mathcal{W}_{2j+2}(e^{-T_m/T}) - \left(\frac{T}{T_m}\right)^{-1} \mathcal{W}_0(e^{-T_m/T}) - \sum_{i=0}^{2j} (i+1)!(C_{2j+1}^{i} + C_{2j+1}^{i+1}) \left(\frac{T}{T_m}\right)^{i} \mathcal{W}_{i+1}(e^{-T_m/T}) \right], \quad (21)$$

where $E_0 = E(T=0)$, $T_m = \hbar\omega_m/k_B$, $T_D = \hbar\omega_D/k_B$ is the usual Debye temperature and the Bose–Einstein function $\mathcal{W}_\delta(x)$ is defined as

$$\mathcal{W}_\delta(x) = \sum_{i=1}^{\infty} \frac{x^i}{i^\delta}, \qquad 0 < x < 1, \quad (22)$$

with $\zeta(\delta) = \mathcal{W}_\delta(1)$.

As is well known, the thermodynamic functions of a 3D ideal Bose gas are expressible in terms of Bose–Einstein functions,

$$P = \frac{2E}{3V} = \frac{k_B T}{\lambda^3} \mathcal{W}_{5/2}(e^{\mu/k_B T}), \qquad N/V = \frac{1}{\lambda^3} \mathcal{W}_{3/2}(e^{\mu/k_B T}), \quad (23)$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ is the usual thermal wavelength and μ is the chemical potential. It is interesting to notice that the thermodynamic functions of 3D solids involve Bose–Einstein functions.

In the low-temperature limit, equation (21) reduces to

$$C_V = 9rNk_B \left(\frac{T}{T_D}\right)^3 \times \lim_{n\to\infty} \sum_{j=1}^{n} \Lambda_{nj}(2j+2)!\zeta(2j+2)\left(\frac{T}{T_m}\right)^{2j-2}, \qquad T \ll T_m. \quad (24)$$

Comparing equation (24) with (7), we obtain

$$\lim_{n\to\infty} \Lambda_{nj} = \frac{b_{2j}\omega_m^{2j-2}}{b_2}. \quad (25)$$

Equation (25) is only valid for sufficiently small j. The reason is that for sufficiently small j only acoustic modes make a contribution to Λ_{nj}. For sufficiently large j, both acoustic and optical modes make a contribution to Λ_{nj}.

At high temperatures, let us use the expansion

$$\frac{x}{e^x - 1} = 1 - \frac{1}{2}x - \sum_{i=1}^{\infty} (-1)^i \frac{B_i}{(2i)!} x^{2i}, \quad (26)$$

where B_i are Bernoulli's numbers, with $B_1 = 1/6$, $B_2 = 1/30$, $B_3 = 1/42$, $B_4 = 1/30$, $B_5 = 5/66, \ldots$. We obtain for $T \gg T_m$

$$\ln Z = -\frac{E_0}{k_B T} + 3rN \left\{ \ln(T/T_m) + \lim_{n\to\infty} \left[\frac{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)^2}{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)} + 3\frac{T_m}{T} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{2(2j+2)} + \sum_{i=1}^{\infty} \frac{(-1)^i B_i}{(2i)!(2i)} \left(\frac{T_m}{T}\right)^{2i} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{2i+2j+1} \right] \right\}, \quad (27)$$

$$E = E_0 + 3rNk_B T \left\{ 1 - 3\lim_{n\to\infty} \left[\frac{T_m}{T} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{2(2j+2)} - \sum_{i=1}^{\infty} \frac{(-1)^i B_i}{(2i)!} \left(\frac{T_m}{T}\right)^{2i} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{2i+2j+1} \right] \right\}, \quad (28)$$

$$C_V = 3rNk_B \left\{ 1 + 3\sum_{i=1}^{\infty} \frac{(-1)^i (2i-1) B_i}{(2i)!} \left(\frac{T_m}{T}\right)^{2i} \times \left[\lim_{n\to\infty} \sum_{j=1}^{n} \frac{\Lambda_{nj}}{2i+2j+1} \right] \right\}. \quad (29)$$

4. Thermal expansion coefficient

Making use of equations (19) and (20), we obtain the pressure P, the compression coefficient K and the thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_P$ as

$$P = k_B T \frac{\partial \ln Z}{\partial V} = -\frac{dE_0}{dV} - \frac{\partial \ln \omega_m}{\partial V}(E - E_0) + 9rNk_B T \lim_{n\to\infty} \sum_{j=1}^{n} \left[\frac{\partial}{\partial V} \frac{\Lambda_{nj}}{\sum_{l=1}^{n} 3\Lambda_{nl}/(2l+1)} \right] \times \left[(2j)!\zeta(2j+2)\left(\frac{T}{T_m}\right)^{2j+1} - \sum_{i=0}^{2j} i! C_{2j}^{i} \left(\frac{T}{T_m}\right)^{i+1} \mathcal{W}_{i+2}(e^{-T_m/T}) \right], \quad (30)$$

$$K = -V\left(\frac{\partial P}{\partial V}\right)_T \cong V\frac{d^2 E_0}{dV^2} \equiv K_0, \quad (31)$$

$$\alpha K = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial \ln \omega_m}{\partial V} C_V$$

$$+ 9rNk_B \lim_{n\to\infty} \sum_{j=1}^{\infty} \left[\frac{\partial}{\partial V} \frac{\Lambda_{nj}}{\sum_{l=1}^{n} 3\Lambda_{nl}/(2l+1)} \right] \times \left[(2j)!(2j+2)\zeta(2j+2) \left(\frac{T}{T_m}\right)^{2j+1} - \sum_{i=0}^{2j} i!(i+2)C_{2j}^{i} \left(\frac{T}{T_m}\right)^{i+1} \mathcal{W}_{i+2}(e^{-T_m/T}) - \sum_{i=0}^{2j} i!C_{2j}^{i} \left(\frac{T}{T_m}\right)^{i} \mathcal{W}_{i+1}(e^{-T_m/T}) \right]. \quad (32)$$

Grüneisen's law states that the ratio α/C_V is independent of temperature. We see that Grüneisen's law is invalid at finite temperatures.

In the low-temperature limit, both C_V and α exhibit the T^3 law and Grüneisen's law is valid,

$$C_V = 216\zeta(4)rNk_B \left(\frac{T}{T_D}\right)^3, \qquad T \ll T_m, \quad (33)$$

$$\frac{\alpha}{C_V} = -\frac{1}{K_0}\frac{\partial \ln \omega_D}{\partial V} = \frac{1}{3K_0}\frac{\partial \ln b_2}{\partial V}, \qquad T \ll T_m. \quad (34)$$

At high temperatures, we obtain by use of equations (27)–(29)

$$P = k_B T \frac{\partial \ln Z}{\partial V} = -\frac{dE_0}{dV} - \frac{\partial \ln \omega_m}{\partial V}(E - E_0) + 3rNk_B T \lim_{n\to\infty} \left[\frac{\partial}{\partial V} \frac{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)^2}{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)} + 3\frac{T_m}{T} \sum_{j=1}^{n} \frac{1}{2(2j+2)} \frac{\partial \Lambda_{nj}}{\partial V} + \sum_{i=1}^{\infty} \frac{(-1)^i B_i}{(2i)!(2i)} \left(\frac{T_m}{T}\right)^{2i} \sum_{j=1}^{n} \frac{1}{2i+2j+1} \frac{\partial \Lambda_{nj}}{\partial V} \right], \quad (35)$$

$$K = -V\left(\frac{\partial P}{\partial V}\right)_T \cong V\frac{d^2 E_0}{dV^2} \equiv K_0, \quad (36)$$

$$\alpha K = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial \ln \omega_m}{\partial V} C_V + 3rNk_B \lim_{n\to\infty} \frac{\partial}{\partial V} \frac{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)^2}{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)} - 3rNk_B \lim_{n\to\infty} \sum_{i=1}^{\infty} \frac{(-1)^i (2i-1) B_i}{(2i)!(2i)} \times \left(\frac{T_m}{T}\right)^{2i} \sum_{j=1}^{n} \frac{1}{2i+2j+1} \frac{\partial \Lambda_{nj}}{\partial V}. \quad (37)$$

In the high-temperature limit, α approaches a volume-dependent constant and Grüneisen's law is valid,

$$\frac{\alpha K_0}{C_V} = \frac{\alpha K_0}{3rNk_B} = -\frac{\partial \ln \omega_m}{\partial V} + \lim_{n\to\infty} \frac{\partial}{\partial V} \frac{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)^2}{\sum_{j=1}^{n} \Lambda_{nj}/(2j+1)}, \qquad T \gg T_m. \quad (38)$$

5. The corresponding law

Retaining the lowest-order term in equation (16), equation (21) reduces to the Debye result,

$$C_V = 3rNk_B 3\left[24\zeta(4)\left(\frac{T}{T_D}\right)^3 - \left(\frac{T}{T_D}\right)^{-1} \mathcal{W}_0(e^{-T_D/T}) - 4\mathcal{W}_1(e^{-T_D/T}) - 12\left(\frac{T}{T_D}\right)\mathcal{W}_2(e^{-T_D/T}) - 24\left(\frac{T}{T_D}\right)^2 \mathcal{W}_3(e^{-T_D/T}) - 24\left(\frac{T}{T_D}\right)^3 \mathcal{W}_4(e^{-T_D/T}) \right] \equiv 3rNk_B\phi(T/T_D). \quad (39)$$

Here $\phi(T/T_D)$ is a universal function of T/T_D. The specific heats of solids are the same if the solids are in corresponding states, i.e. have the same values of T/T_D (the corresponding law).

For the general phonon frequency spectrum, equation (21) may be written as

$$C_V = 3rNk_B\psi(\{\Lambda_{nj}\}, T/T_m). \quad (40)$$

Here $\psi(\{\Lambda_{nj}\}, T/T_m)$ is not a universal function of T/T_m and the corresponding law is in general invalid. Nevertheless, the specific heats of two solids are the same at the same values of T/T_m if their respective dimensionless phonon frequency distribution functions $g(\omega)/b_2\omega_m^2 = G(\omega^2/\omega_m^2)$ are the same function of ω^2/ω_m^2.

6. Possible application

Let us discuss possible application of our results.

(1) The experimental data of $g(\omega)$ can be obtained by use of x-ray [10, 11] and neutron [12] scattering methods. Since the experimental data are discrete, a fitting function must be used. The Van Hove's theory of singularities and Weierstrass's theorem guarantee that we should use a polynomial $P_n(\omega^2) = \sum_{j=1}^{n} a_{nj}\omega^{2j}$ to fit $g(\omega)$. The more experimental data we use, the more accurate $g(\omega)$ we obtain.

Particularly, if $g(\sqrt{i/n}\omega_m)$ $(i = 1, 2, \ldots, n-1)$ are obtained experimentally, $g(\omega)$ can be obtained approximately by use of the approximate formula

$$g(\omega) \approx \sum_{j=1}^{n} \left[\sum_{i=1}^{j} (-1)^{j-i} C_{n-i}^{n-j} C_n^i g\left(\sqrt{\frac{i}{n}}\omega_m\right) \right] \left(\frac{\omega^2}{\omega_m^2}\right)^j. \quad (41)$$

The obtained $g(\omega)$ will become more and more accurate as n becomes larger and larger. As $n \to \infty$, the obtained $g(\omega)$ approaches the actual phonon spectrum.

(2) The discrete data of the specific heat can be obtained experimentally. The Van Hove's theory of singularities and Weierstrass's theorem guarantee that the fitting function of $g(\omega)$ should be a polynomial $P_n(\omega^2) = \sum_{j=1}^{n} a_{nj}\omega^{2j}$, which implies that the fitting function of C_V should be

$$C_V(T) \approx 9rNk_B \sum_{j=1}^{n} \frac{a_{nj}\omega_m^{2j}}{\sum_{l=1}^{n} 3a_{nl}\omega_m^{2l}/(1+2l)} \times (T/T_m)^{2j+1} \int_0^{T_m/T} \frac{x^{2j+2}e^x}{(e^x-1)^2} dx. \quad (42)$$

Using this function to fit the experimental data of C_V, the coefficients a_{nj} can be obtained. Hence $g(\omega)$ can be obtained approximately.

7. Conclusion

Van Hove's theory of singularities tells us that for 3D lattices the phonon frequency distribution function $g(\omega)$ has square-root singularities and is continuous for $0 \leqslant \omega \leqslant \omega_m$. Using this fact and Weierstrass's theorem as well as Bernstein's polynomials, we extend Debye's theory of specific heats of 3D solids to arbitrary frequency spectra. We obtain the analytical expressions of the thermodynamic functions involving Bose–Einstein functions. For the general phonon frequency spectra, the corresponding law is in general invalid. Nevertheless, the specific heats of two solids are the same at the same values of T/T_m if their respective dimensionless frequency distributions function $g(\omega)/b_2\omega_m^2 = G(\omega^2/\omega_m^2)$ are the same function of ω^2/ω_m^2. In the low-temperature limit, both specific heat and thermal expansion coefficient exhibit the T^3 law and Grüneisen's law is valid. In the high-temperature limit, the thermal expansion coefficient approaches a volume-dependent constant and Grüneisen's law is valid. At intermediate temperatures Grüneisen's law is invalid.

Finally, we should point out that the theory presented in this paper is invalid for 1D and 2D lattices. The reason is that for 1D lattices $g(\omega)$ have inverse square-root singularities and for 2D lattices $g(\omega)$ have logarithmic singularities; $g(\omega)$ diverge at these singularities.

References

[1] Einstein A 1907 *Ann. Phys.* **22** 180
[2] Debye P 1912 *Ann. Phys.* **39** 789
[3] Born M and von Karman T 1912 *Phys. Z.* **13** 297
[4] Montroll E W 1942 *J. Chem. Phys.* **10** 218
[5] Montroll E W 1943 *J. Chem. Phys.* **11** 481
[6] Montroll E W and Peaslee D C 1944 *J. Chem. Phys.* **12** 98
[7] Montroll E W 1947 *J. Chem. Phys.* **15** 575
[8] Peresada V I 1968 *Sov. Phys.—JETP* **26** 389
[9] Hendricks J B, Riser H N and Clark C B 1963 *Phys. Rev.* **130** 1377
[10] Walker C B 1956 *Phys. Rev.* **103** 547
[11] Bosak A and Krisch M 2005 *Phys. Rev.* B **72** 224305
[12] Stewart A T and Brockhouse B N 1958 *Rev. Mod. Phys.* **30** 250
[13] Douglas F J *et al* 2007 *Nature* **446** E5
[14] Lifshitz I M 1954 *Zh. Eskp. Teor. Fiz.* **26** 551
[15] Chen N X 1990 *Phys. Rev. Lett.* **64** 1193
Chen N X and Rong E Q 1998 *Phys. Rev.* E **57** 1302
[16] Ming D M, Wen T, Dai J X, Dai X X and Evenson W E 2000 *Phys. Rev.* E **62** R 3019
[17] Hague J P 2005 *J. Phys.: Condens. Matter* **17** 2397
[18] Wen T, Ma G C, Dai X X, Dai J X and Evenson W E 2003 *J. Phys.: Condens. Matter* **15** 225
[19] Van Hove L 1953 *Phys. Rev.* **89** 1189
[20] Ziman J M 1972 *Principles of the Theory of Solids* (London: Cambridge) pp 49–51
[21] Landau L D and Lifshitz E M 1980 *Statistical Physics* (New York: Pergamon) Part 1, Section 70
[22] Münster A 1974 *Statistical Thermodynamics* vol II (Berlin: Springer) chapter XI
[23] Jones W and March N H 1973 *Theoretical Solid State Physics* vol 1 (London: Wiley) pp 214–48
[24] Weiss G 1959 *Prog. Theor. Phys. Japan* **22** 526
[25] Lorentz G G 1966 *Approximation of Functions* (New York: Holt, Rinehart and Winston)