The specific heat of an anharmonic phonon system

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Abstract. The effect of on-site anharmonicity in a one-dimensional phonon system is studied by calculating the specific heat at low temperatures. The formula for the specific heat is derived by applying the path integral method to the expression for the partition function.

1. Introduction

It is well known that for many phenomena in solid state physics the harmonic approximation can be considered as completely satisfactory. In molecular crystals, however, such an approximation may not be adequate. For example, each molecule can have large anharmonicity. It is necessary then to treat the problem beyond the harmonic approximation. One possible way has been described in our earlier work [1]. It was shown there that, starting from the classical Hamiltonian which includes cubic and quartic terms, it is possible to derive a model Hamiltonian, which is essentially a Bose version of the Hubbard model with attractive interactions. This model Hamiltonian is

$$H = \sum_{l=1}^{N} (\varepsilon b_l^+ b_l - \Gamma_l b_l^+ b_l^+ b_l b_l) + \Delta \sum_{l=1}^{N} (b_{l+1}^+ b_l + b_{l+1} b_l^+) \qquad (1.1)$$

where ε is the observed energy difference between the lowest two states of the uncoupled oscillators [1]. Γ_l and Δ are constants describing the anharmonicity at site l and the strength of the nearest-neighbour interaction, respectively, and b_l and b_l^+ are the destruction and creation operators at site l. The b_l operators obey Bose statistics, i.e. $[b_l, b_{l'}^+] = \delta_{ll'}$. During the derivation of equation (1.1), two steps were important.

(i) It was assumed that ε is much larger than Γ_l, Δ and the strength of the cubic anharmonicity in the classical Hamiltonian.

(ii) Only the lowest-order phonon-conserved term was kept after the canonical transformation.

The important parameter characterising the anharmonicity is $x \equiv W/\Gamma$, where $W = 4\Delta$ which is the phonon bandwidth. There is a broad spectrum of values for the parameter x as has already been discussed in [1]. Only two limiting cases of x were explicitly discussed in [1]: they are $x \to 0$ and $x \to \infty$. The corresponding limiting expressions for the free energy were studied. Furthermore, for small x, the localisation of the multi-

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vibrational excitations with random Γ_l has also been investigated [2]. However, the important case of arbitrary x has not been studied. In this paper, we assume that $\Gamma_l = \Gamma$, a constant for the whole lattice and examine the effect of arbitrary Γ on the one-phonon spectrum. Because of the presence of the on-site energy ε, the optical phonon system is considered. The contribution of Γ will be present mainly through the renormalisation of the site energy. Also Γ acts as the scattering centre for the phonon system. In § 2, formal mathematical description to find an expression of the partition function in terms of the Green function will be outlined. An approximate way of finding the Green function will be presented and the expression of the free energy will be given in § 3. Finally in § 4 the results on the specific heat will be discussed.

2. Formal derivation of the partition function

Using commutation relations for the b_l operators, we can rewrite the Hamiltonian (1.1) as

$$H = H_0 - V \tag{2.1}$$

where

$$H_0 = \sum_{l=1}^{N} E_l n_l + \Delta \sum_{l=1}^{N} (b_{l+1}^+ b_l + b_{l+1} b_l^+) \tag{2.2}$$

and

$$V = \sum_{l=1}^{N} \Gamma_l n_l n_l \tag{2.3}$$

where $E_l = \varepsilon + \Gamma_l$ and $n_l = b_l^+ b_l$. E_l is the renormalised site energy. Equation (2.3) expresses the scattering potential for the phonon system defined by equation (2.2). It depends on the population n_l at site l. As we shall see later, the population contributes to the thermodynamical quantities through its thermal average. Furthermore, the low-temperature case will be of interest. The thermal average of n_l is a small quantity and $\Gamma\langle n_l n_l \rangle$ will not exceed the fundamental site energy.

Using the well known formulae [3], the expression for the partition function can be written as

$$Z = \mathrm{Tr}\left[\exp(-\beta H_0)\, T \exp\left(\int_0^\beta \mathrm{d}\tau \sum_{l=1}^{N} \Gamma_l n_l^2(\tau) \right) \right] \tag{2.4}$$

where T is the ordering operator with respect to τ.

The next step will be to divide the interval $[0, \beta]$ into P factors, i.e. $\beta = P\Delta\tau$. Within each subinterval $\Delta\tau$, we can apply the Gaussian identity

$$\exp(a^2) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}z}{\sqrt{4\pi}} \exp(-\tfrac{1}{4}z^2 + az)$$

where in our case $a^2 = \Delta\tau\, \Gamma_l n_l^2(\tau)$. After changing variables

$$z_l(\tau)/\sqrt{4\pi} = \sqrt{\Delta\tau/\beta}\; \xi_l(\tau)$$

one can express the exponential term in equation (2.4) as follows:

$$\prod_{l=1}^{N} \prod_{\tau=1}^{P} \exp(-\Delta\tau \, \Gamma_l n_l(\tau) n_l(\tau))$$

$$= \prod_{l=1}^{N} \int D\xi_l(\tau) \exp\left[-\sum_{l=1}^{N} \int_0^\beta d\tau \left(\frac{\pi}{\beta} \xi_l^2(\tau) - 2\sqrt{\frac{\pi}{\beta}} \, \Gamma_l n_l(\tau) \xi_l(\tau) \right) \right]$$

and the measure $D\xi_l(\tau)$ is defined as

$$D\xi_l(\tau) = \lim_{\Delta\tau \to 0} \left(\prod_\tau \sqrt{\frac{\Delta\tau}{\beta}} \, d\xi_l(\tau) \right).$$

The above trick allows us to write the partition function as

$$Z = Z_0 \prod_l \int D\xi_l(\tau) \exp\left(-\frac{\pi}{\beta} \int_0^\beta \sum_l \xi_l^2(\tau) \, d\tau \right) Z(\xi_l) \qquad (2.5)$$

and

$$Z(\xi_l) \equiv \left\langle T \exp\left(2 \sum_l \sqrt{\frac{\pi\Gamma_l}{\beta}} \int_0^\beta d\tau \, \xi_l(\tau) n_l(\tau) \right) \right\rangle_0 \qquad (2.6)$$

where the average $\langle \cdots \rangle_0$ is defined as

$$\langle \cdots \rangle_0 = (1/Z_0) \, \text{Tr}[\exp(-\beta H_0) \cdots] \qquad (2.7)$$

and Z_0 is the partition function corresponding to H_0. To evaluate the above average, we define

$$c_l \equiv 2\sqrt{\pi\Gamma_l/\beta} \qquad (2.8)$$

and follow the method in [4, 5] by introducing the coupling constant λ via $c_l \to \lambda c_l$. Differentiating with respect to λ gives

$$\frac{\partial}{\partial\lambda} \{\ln[Z_\lambda(\xi_l)]\} = -\sum_l c_l \int_0^\beta d\tau \, \xi_l(\tau) \langle n_l(\tau) \rangle_\lambda. \qquad (2.9)$$

The new average is defined as

$$\langle \cdots \rangle_\lambda \equiv \left\langle T \cdots \exp\left(-\lambda \sum_l c_l \int_0^\beta d\tau \, n_l(\tau) \xi_l(\tau) \right) \right\rangle_0$$

$$\times \left[\left\langle T \exp\left(-\lambda \sum_l c_l \int_0^\beta d\tau \, n_l(\tau) \xi_l(\tau) \right) \right\rangle_0 \right]^{-1}. \qquad (2.10)$$

Equation (2.9) expresses the partition function explicitly in terms of the scattering contribution of the anharmonicity c_l and the average population $\langle n_l(\tau) \rangle_\lambda$ in which the

additional contribution of Γ will appear in E through the thermal average. The latter can be evaluated by introducing the following Green function:

$$G_{ij}(\tau, \tau') \equiv - \langle T_\tau b_i(\tau) b_j^+(\tau') \rangle_\lambda \qquad (2.11)$$

which is related to average population as $\langle n_l(\tau) \rangle_\lambda = -G_{ll}(\tau, \tau^+)$. The Green function $G_{ij}(\tau, \tau')$ satisfies the Dyson equation

$$G_{ij}(\tau, \tau') = G_{ij}^0(\tau - \tau') + \lambda \sum_{l=1}^N c_l \int_0^\beta \mathrm{d}\tau'' \, G_{il}^0(\tau - \tau'') \xi_l(\tau'') G_{lj}(\tau'', \tau'). \qquad (2.12)$$

Its Fourier transform with respect to 'time' τ is given as

$$G_{ij}(\tau, \tau') = \sum_{n,n'} G_{ij}(n, n') \exp(-i\omega_n \tau + i\omega_{n'} \tau') \qquad (2.13)$$

and where $\omega_n = (2\pi/\beta)n$. It should be noted that n in equation (2.13) is a dummy variable used for the Fourier transform.

The Fourier-transformed Dyson equation is then

$$G_{ij}(n, n') = G_{ij}^0(n)\delta_{nn'} + \lambda \sum_{ll'} \sum_{n''} G_{il'}^0(n) c_l \xi_l(n - n'') G_{l,j}(n'', n') \qquad (2.14)$$

with the Fourier transform of the field $\xi_l(\tau)$ being

$$\xi_l(n - n'') = \int_0^\beta \mathrm{d}\tau \, \xi_l(\tau) \exp[i(\omega_n - \omega_{n''})\tau]. \qquad (2.15)$$

Now, equation (2.9) can be written in terms of the Fourier transform of the Green function

$$\frac{\partial}{\partial \lambda} \{\log[Z_\lambda(\xi)]\} = - \sum_l \sum_{n,n'} G_{ll}(n, n') \xi_l(n' - n). \qquad (2.16)$$

The above formal expression for the partition function and the Dyson equation (2.14) are our starting formulae to derive the expressions of free energy and specific heat. In § 3, we shall solve G_{ll} by using the static approximation.

3. Static approximation

This approximation consists of taking the $\xi_l(\tau)$ to be time independent, i.e.

$$\xi_l(\tau) \equiv \xi_{l0} = \text{constant.} \qquad (3.1)$$

This is equivalent to the case that each frequency mode is independent of the other (equation (2.15)).

In this approximation, the Dyson equation is

$$G_{ij}(n) = G_{ij}^0(n) + \lambda \sum_{l=1}^N G_{il}^0(n) \eta_l G_{lj}(n) \qquad (3.2)$$

where $\eta_l \equiv \beta c_l \xi_{l0}$ and $G_{ij}(n) \equiv G_{ij}(n, n)$.

On the assumption that only the nearest-neighbour Green functions are non-zero, the above equation generates the following system of algebraic equations (we have dropped the n dependence):

$$G_{ii}(1 - \lambda\eta_i G_{ii}^0) - \lambda\eta_{i+1}G_{i,i+1}^0 G_{i+1,i} - \lambda\eta_{i-1}G_{i,i-1}^0 G_{i-1,i} = G_{ii}^0$$

$$- G_{ii}\lambda\eta_i G_{i+1,i}^0 + (1 - \lambda\eta_{i+1}G_{i+1,i+i}^0)G_{i+1,i} = G_{i+1,i}^0$$

$$- G_{ii}\lambda\eta_i G_{i-1,i}^0 + (1 - \lambda\eta_{i-1}G_{i-1,i-1}^0)G_{i-1,i} = G_{i-1,i}^0. \tag{3.3}$$

The above set of coupled equations can be solved by standard method. Using the results from Appendix 1 and the notation $G_{ii}^0 = G_{i\pm1,i\pm1}^0 \equiv G_D$ and $G_{i\pm1,i}^0 \equiv G_0$, we obtain

$$G_{ii} = [G_D(1 - \lambda\eta G_D) + 2\lambda\eta G_0^2]/[(1 - \lambda\eta G_D)^2 - 2\lambda^2\eta^2 G_0^2] \tag{3.4}$$

where $\eta_l \equiv \eta$ = constant because of the assumption that Γ_l = constant.

In this static approximation the partition function is

$$\frac{\partial}{\partial\lambda}\{\ln[Z_\lambda(\xi)]\} = -\sum_{l=1}^{N}\sum_{n=-\infty}^{+\infty} \eta G_{ll}(n). \tag{3.5}$$

Substituting (3.4) into (3.5), integrating over λ and finally putting $\lambda = 1$, one has

$$Z(\xi) = \tfrac{1}{2}N \sum_{n=-\infty}^{+\infty} \ln\{[1 - \eta G_D(n)]^2 - 2\eta^2 G_0^2(n)\} \tag{3.6}$$

where

$$G_D(n) = -(1/\beta)[1/(E - i\omega_n)][1 + 2\Delta^2/(E - i\omega_n)^2] \tag{3.7}$$

$$G_0(n) = (1/\beta)[1/(E - i\omega_n)][\Delta/(E - i\omega_n)]. \tag{3.8}$$

From equation (2.5) the change in the free energy per site in the static approximation is

$$\Delta F = -\frac{1}{\beta}\ln\int_{-\infty}^{+\infty} d\xi \exp(-\pi\xi^2) Z(\xi) \tag{3.9}$$

where $Z(\xi)$ is given by equation (3.6).

By assuming that $\Delta \ll E$ in the frequency sum in equation (3.6) and performing the steepest descent integration for small ξ with equations (3.7) and (3.8), we finally have

$$\Delta F = -\Gamma\{1/[\exp(\beta E) - 1] - \Delta^2\beta^2 \exp(\beta E)[\exp(\beta E) + 1]/[\exp(\beta E) - 1]^3\}^2. \tag{3.10}$$

4. Specific heat

We can use the results in § 3 and Appendix 2 to evaluate analytically the expression for low-temperature specific heat. Using the standard definition, the specific heat per site in the case with $\Gamma = 0$ is

$$C_V^0 = \frac{1}{\pi}\int_0^\pi dx \frac{[\tfrac{1}{2}\beta(\varepsilon + 2\Delta\cos x)]^2}{\sinh^2[\tfrac{1}{2}\beta(\varepsilon + 2\Delta\cos x)]}. \tag{4.1}$$

Taking the low-temperature limit ($\beta\Delta \to \infty$), one finds that

$$C_V^0 = 1/(2\sqrt{\pi})\,(\beta^2/\sqrt{\beta\Delta})\,(\varepsilon - 2\Delta)^2 \exp[-\beta(\varepsilon - 2\Delta)]. \tag{4.2}$$

Except for the factor $1/\sqrt{\beta\Delta}$, C_V^0 in equation (4.2) is just for a two-level system which
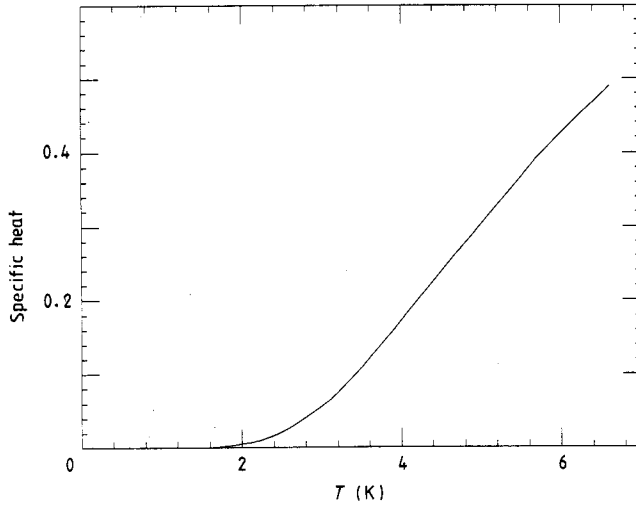
Figure 1. Specific heat in the case with $\Gamma = 0$ (Boltzmann constant $k_B = 1$; site energy $\varepsilon = 20.0$; $\Delta = 0.5$).

is expected from optical phonon system. The factor $1/\sqrt{\beta\Delta}$ is obtained through the integration of x, where $x = ka$ (Appendix 2). For $\Gamma \neq 0$, using equation (3.10), one has for the leading temperature term

$$\Delta C_V = 6E\Gamma\Delta^2\beta^4 \exp(-\beta E) \tag{4.3}$$

where Γ appears also in E.

We have performed numerical integration of equation (4.1) using $\varepsilon = 20$ which is equivalent to 0.1 eV, the optical phonon energy and $\Delta = 0.5$. The result is shown in figure 1. As the temperature (T) increases, C_V^0 increases monotonically at low temperatures.

By examining the expressions given in equations (4.2) and (4.3), we find that the term $(\varepsilon - 2\Delta)^2$ dominates the total $C_V(= C_V^0 + \Delta C_V)$ for physically reasonable values of Δ and Γ. It becomes extremely difficult to see the effect of Γ in ΔC_V if C_V is plotted as a function of T. So we plot the ratio of $\Delta C_V/C_V^0$ as a function of temperature using equations (4.3) and (4.1) (figure 2). For $\Delta = 0.5$, we used two values of Γ (full curve for $\Gamma = 0.2$ and broken curve for $\Gamma = 5.0$). At low temperatures $(T < 2.4 \text{ K})$, the effect of temperature is rather small. Consequently, the two curves nearly coincide. For $T > 2.4 \text{ K}$, more phonons are excited. The phonon–phonon interaction due to Γ increases. It causes the broken curve with $\Gamma = 5.0$ to increase more rapidly than the full curve with $\Gamma = 0.2$.

We have also increased Δ to the value of 2.0 and constructed a plot for an intermediate Γ value of 0.5 (dotted curve). For low temperatures $(T < 2.8 \text{ K})$, it is difficult to excite phonons with large Δ. So ΔC_V is smaller than the cases with smaller Δ. For high temperatures the dominant contribution to the specific heat is due to the scattering among the phonons and at a given temperature it is dominated by the largest value of Γ. As shown in figure 2 the dotted curve falls between the two other curves ($\Gamma = 0.2$ and $\Gamma = 5.0$).
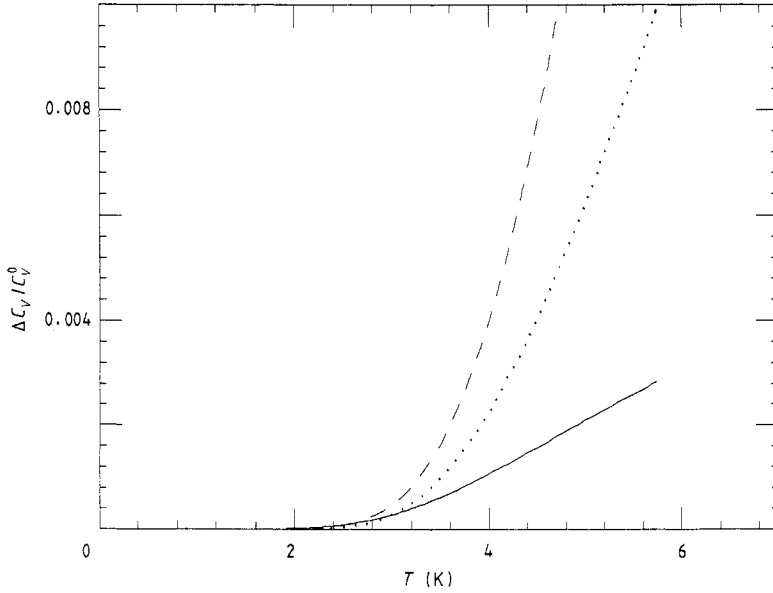
Figure 2. Plot of $\Delta C_V/C_V^0$ as a function of temperature ($k_B = 1$; site energy $\varepsilon = 20.0$): ———, $\Gamma = 0.2$, $\Delta = 0.5$; ———, $\Gamma = 5.0$, $\Delta = 0.5$; $\cdots\cdots$, $\Gamma = 0.5$, $\Delta = 2.0$.

Appendix 1. Zero-order Green function

The zero-order Green function $G_{ij}^0(u)$ corresponds to $c_l = 0$ and is defined as

$$G_{ij}^0(\tau) = -\langle T_\tau b_i(\tau) b_j^+(0)\rangle_0. \tag{A1.1}$$

The appropriate zero-order Hamiltonian reads

$$H_0 = \sum_l E b_l^+ b_l + \Delta \sum_l (b_{l+1}^+ b_l + b_{l+1} b_l^+) \tag{A1.2}$$

where $E = \varepsilon + \Gamma$.

The diagonalisation of (A1.2) is performed by the transformation

$$b_l = \frac{1}{\sqrt{N}} \sum_k b_k \exp(\mathrm{i}kal). \tag{A1.3}$$

The result of diagonalisation is well known:

$$H_0' = \sum_k \Omega_k b_k^+ b_k \tag{A1.4}$$

and $\Omega_k = E + 2\Delta \cos ka$.

Using definition (A1.1) and following [6], one easily finds that

$$G_{ij}^0(\tau) = -\frac{1}{N} \sum_k \exp[\mathrm{i}ka(l-j)] \exp(-u\Omega_k) [N_k + \theta(\tau)] \tag{A1.5}$$

where $N_k = [\exp(\beta\Omega_k) - 1]^{-1}$ and $\theta(\tau)$ is the step function.

In § 3, we needed the inverse Fourier transform of (A1.5) which is defined as

$$G_{ij}^0(n) = \frac{1}{\beta} \int_0^\beta d\tau \, \exp(i\omega_n \tau) \, G_{ij}(\tau) \tag{A1.6}$$

and $\omega_n = (2\pi/\beta)n$. Simple integration gives

$$G_{ij}^0(n) = \frac{1}{\beta N} \sum_k \exp[ika(l-j)] \frac{1}{i\omega_n - \Omega_k}. \tag{A1.7}$$

The above sum is then replaced by an integral as $(a \equiv L/N)$

$$\sum_k \rightarrow \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk. \tag{A1.8}$$

Using the result from [7], one finally finds that

$$G_{ij}^0(n) = (-1/\beta N)\{1/[(E - i\omega_n)^2 - 4\Delta^2]^{1/2}\}$$
$$\times [\sqrt{(E - i\omega_n)^2 - 4\Delta^2} - (E - i\omega_n)]/2\Delta\}^{|l-j|}. \tag{A1.9}$$

Appendix 2. Free energy for $\Gamma = 0$

For $\Gamma = 0$, we can use the result from [8]:

$$F_0 = \frac{1}{\beta} \sum_k \ln[2 \sinh\left(\tfrac{1}{2}\beta\Omega_k\right)] \tag{A2.1}$$

where $\Omega_k = \varepsilon + 2\Delta \cos ka$. Using again equation (A1.8), the free energy per site is

$$\tilde{F}_0 \equiv \frac{F_0}{N} = \frac{1}{\beta} \frac{1}{\pi} \int_0^\pi dx \, \ln\{2 \sinh[\tfrac{1}{2}\beta(\varepsilon + 2\Delta \cos x)]\}. \tag{A2.2}$$

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