Thermodynamic Characteristics of 1D Structures

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In this paper 1D crystal lattice is analyzed within harmonic approximation, with one atom per elementary cell and nearest neighbor interaction included. For this type of crystal lattice dispersion relations are well known. Thermodynamic functions (specific heat and phonon thermal conductivity) are calculated via phonon density of states given in exact form. Thermodynamic variables are calculated for a whole temperature range. In limiting cases of low and high temperatures these thermodynamic variables can be found in analytic forms. For thermal conductivity the results of Callaway model for exact phonon density of states are compared with the results of Callaway model for Debye approximation of phonon density of states.

PACS: 63.20e, 63.20D, 63.20dk, 63.20kd, 63.20kg, 63.20kp, 65.40Ba, 66.30h

1. Introduction

In this paper 1D crystal lattice with one atom per elementary cell is analyzed. The nearest neighbor interaction within harmonic approximation is included. For such a model the dispersion relations are well known. Thermodynamic functions, such as specific heat of lattice and phonon thermal conductivity, are expressed via phonon density of states. In most simple cases, Einstein and Debye approximations are used for phonon density of states. In Einstein approximation the phonon density of states is expressed via Dirac δ function, while in Debye approximation the phonon density of states is of the ω^{d-1} type, where d is a dimension of the system. For the assumed 1D structure, it is useful to find thermodynamic characteristics by applying exact relation for phonon density of states and compare them with the results obtained by using Debye approximation. Such analysis of 1D structures can have both theoretical and practical implications for Q1D structures.

2. Specific heat

We shall consider 1D crystal lattice with one atom per elementary cell, consisting of N identical atoms of mass m positioned on average interatomic distance a, with interatomic forces characterized by elastic constant γ. Within harmonic approximation the dispersion relation is well known [1]

$$\omega = \omega_m \left| \sin \frac{ka}{2} \right|, \tag{1}$$

where $\omega_m = \sqrt{\gamma/m}$. By inserting dispersion relation (1) into general expression for phonon density of states [2]

$$g(\omega) = \frac{Na}{\pi} \left| \frac{dk}{d\omega} \right| \tag{2}$$

one obtains

$$g(\omega) = \begin{cases} \frac{2N}{\pi \sqrt{\omega_m^2 - \omega^2}}; \omega < \omega_m \\ 0; \omega > \omega_m \end{cases} \tag{3}$$

Then, by inserting phonon density of states (3) into expression for specific heat (per elementary cell) [3]

$$C_v = k_B \int_0^\infty \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar\omega}{k_B T}}}{(e^{\frac{\hbar\omega}{k_B T}} - 1)^2} g(\omega) \, d\omega \tag{4}$$

one obtains

$$C_v = \frac{2Nk_B}{\pi} \int_0^{\omega_m} \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar\omega}{k_B T}}}{(e^{\frac{\hbar\omega}{k_B T}} - 1)^2} \frac{1}{\sqrt{\omega_m^2 - \omega^2}} \, d\omega. \tag{5}$$

Further on, by applying substitutions $x = \hbar\omega/k_B T$, $\omega_m = k_B T x_m/\hbar$, $\hbar\omega_m = k_B\theta$, $x_m = \theta/T$ where θ is Debye temperature, expression (5) is transformed into

$$C_v = \frac{2Nk_B}{\pi} \int_0^{\frac{\theta}{T}} x^2 \frac{e^x}{(e^x - 1)^2} \frac{1}{\sqrt{(\frac{\theta}{T})^2 - x^2}} \, dx. \tag{6}$$

Expression (6) can be analytically solved for asymptotic low and high temperatures.

In the case of asymptotic high temperatures $\theta \ll T$ one obtains

$$\lim_{x \to 0} \left\{ x^2 \frac{e^x}{(e^x - 1)^2} \frac{1}{\sqrt{x_m^2 - x^2}} \right\} = \frac{1}{x_m};$$

$$C_v = \frac{2Nk_B}{\pi x_m} \int_0^{x_m} dx = \frac{2Nk_B}{\pi} = \text{const} \tag{7}$$

in accordance with Dulong-Petit law.

It is known empirically [4] that low-temperature dependence of the specific heat has the form $C_v \sim T^d$. So, it is interesting to find analytical expression for C_v at

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low temperatures in the case of 1D structures by applying exact expression for phonon density of states.
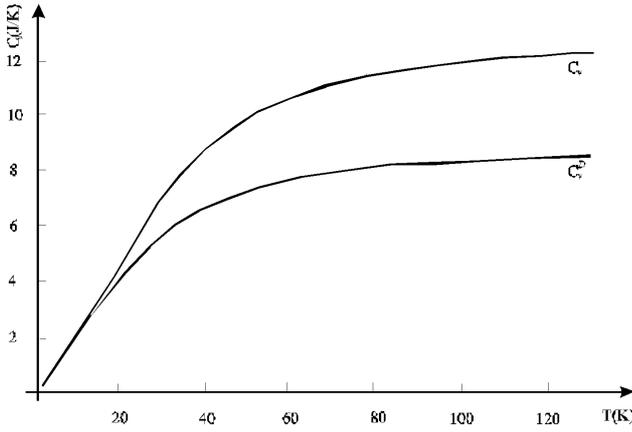

Fig. 1. Comparative presentation of specific heats.

In the case of asymptotic low temperatures $\theta \gg T$ it can be shown [5] that specific heat is linear function of temperature. By introducing function

$$f(x, x_m) = \frac{2}{\pi} \left[\frac{x/2}{\sinh(x/2)} \right]^2 \frac{1}{\sqrt{x_m^2 - x^2}} \qquad (8)$$

the expression for specific heat can be written as

$$C_v = Nk_B(I_1 + I_2); \quad I_1 = \int\limits_0^{qx_m} f(x, x_m)\,dx;$$

$$I_2 = \int\limits_{qx_m}^{x_m} f(x, x_m)\,dx; \quad 0 < q < 1. \qquad (9)$$

In expressions (9), integral I_2 exponentially tends to zero when $x \to \infty$, while integral I_1 becomes

$$I_1 = \frac{4T}{\pi x_m} \int\limits_0^\infty \left[\frac{x/2}{\sinh(x/2)} \right]^2 dr = \frac{2}{3}\pi^2 \frac{T}{x_m}, \qquad (10)$$

so specific heat finally obtains the form

$$C_v = \frac{\pi Nk_B^2}{3\hbar} \sqrt{\frac{m}{\gamma}} T. \qquad (11)$$

For wider temperature range the expression (6) can be solved numerically, by adopted values of the parameters [6]: $N = 10^{24}$, $a = 4 \times 10^{-10}$m, $v = 3,5 \times 10^3$m/s, $\omega_m = \frac{2v}{a} = 1,75 \times 10^{13}$ 1/s, $\theta = 134$ K.

It is interesting to compare values obtained for specific heat (6) with the values obtained for specific heat in Debye approximation. In the case of 1D structure the phonon density of states in Debye approximation is given by [2]

$$g(\omega) = \frac{Na}{\pi v} \qquad (12)$$

and in this case the specific heat can be found by numerical solving of equation

$$C_v^D = \frac{Nak_B^2}{\pi \hbar v} T \int\limits_0^{\frac{\theta}{T}} x^2 \frac{e^x}{(e^x - 1)^2}\,dx. \qquad (13)$$

From Fig. 1 it can be seen that specific heat calculated by using exact phonon density of states is above the one calculated in Debye approximation.

3. Thermal conductivity

The heat conductivity tensor in most general case can be found by using Kubo formula, which is an even correlation function on the operator of heat flux. In the first approximation, finding of the heat conductivity tensor can be reduced on solving Boltzmann transport equation.

In analysis of experimental data for heat conductivity of crystal lattice Callaway model is most frequently used [6], which takes into account various relaxation phonon processes. In this model for 3D case [9] a lot of approximations are made, restricting its application to low-temperature range:

1. Debye approximation for describing phonon spectra is used.

2. Only mean sound velocity is taken into account.

3. Phonon scattering on the surface is diffused (not mirror-like).

4. Normal tree-phonon scattering processes are realized for low frequency longitudinal phonons.

5. Relaxation time of U-processes is described similarly to relaxation time of normal processes.

6. Relaxation times of various relaxation phonon processes are considered additive.

7. Neither crystal anisotropy nor phonon polarization is not taken into account (difference between longitudinal and transversal phonons is not made).

In the case of 1D structure, we are starting from the expression for thermal conductivity (per unit volume) obtained from kinetic theory [7]

$$\kappa = \frac{1}{3} \int\limits_0^{\frac{\theta}{T}} v_s^2 C_v(x)\tau(x)\,dx, \qquad (14)$$

where v_s is phonon mean velocity, and τ is phonon relaxation time, which is a function of temperature and frequency.

Specific heat is given by expression (5), while phonon relaxation time has the form [6]

$$\tau^{-1}(T, \omega) = \frac{v_s}{L} + A\omega^4 + BT^3\omega^2. \qquad (15)$$

First term represents phonon relaxation time due to scattering on boundaries, second term represents phonon relaxation time due to scattering on dopants, and third term represents phonon relaxation time due to phonon-phonon scattering.

If we adopt substitution $x = \hbar\omega/k_\mathrm{B}T$, expression (14) on the basis of (5) and (15) becomes

$$\kappa = \frac{2Nk_\mathrm{B}v_s^2}{3\pi} \int\limits_0^{x_m} x^2 \frac{\mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \frac{1}{\sqrt{x_m^2 - x^2}}$$

$$\times \left(\frac{v_s}{L} + Dx^4 + Ex^2\right)^{-1} \mathrm{d}x, \qquad (17)$$

where

$$D = A(k_\mathrm{B}T/\hbar)^4, \quad E = BT^3(k_\mathrm{B}T/\hbar)^2. \qquad (18)$$

In the limiting case the expression for thermal conductivity can be found in analytic form. In the limit of high temperatures when $\theta << T$, one obtains

$$\kappa = \frac{2Nk_\mathrm{B}Lv_s}{3\pi\theta}T. \qquad (19)$$

In the limit of low temperatures when $\theta >> T$, expression (17) tends to zero. This means that contribution to thermal conductivity is negligible when phonon energy is much higher than $k_B T$ [8].

In the general case, the expression for thermal conductivity in wide temperature range can be found numerically.

The adopted values of the parameters are $A = 2.57 \times 10^{-44}$ s^3, $B = 2.77 \times 10^{-23}$ s/K, $L = 1.8 \times 10^{-3}$ m while other parameters are the same as in previous part.

If thermal conductivity is calculated by using Debye approximation for phonon density of states, one obtains

$$\kappa^D = \frac{Nak_\mathrm{B}^2 v_s}{3\pi\hbar}T$$

$$\times \int\limits_0^{\frac{\theta}{T}} x^2 \frac{\mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \frac{1}{v_s/L + Dx^4 + Ex^2} \mathrm{d}x. \qquad (20)$$

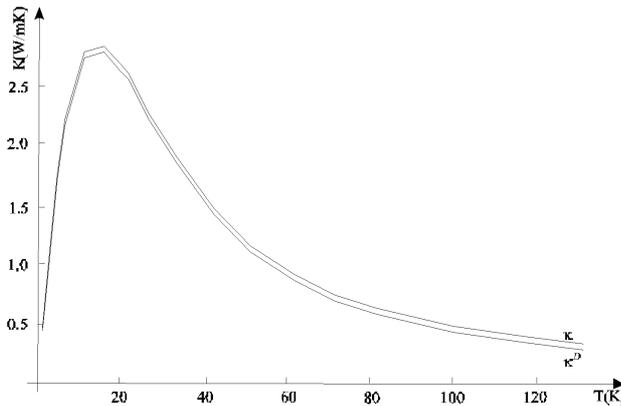Numerically calculated thermal conductivities are presented in Fig 2.

Fig. 2. Comparative presentation of thermal conductivities.

From Fig. 2 it can be seen that thermal conductivities, calculated in Debye approximation and by using exact phonon density of states, respectively, are surprisingly compatible, which suggests that relaxation processes are dominating in thermal conductivity and that influence of phonon density of states is not so significant, and hence in this case Debye approximation is quite correct.

All numerical calculations were done by using program package *Mathematica 7.0*.

4. Conclusion

In the case of most simple 1D structures, specific heat calculated in Debye approximation is underestimated in respect to that one calculated for the exact phonon density of states. On the other hand, thermal conductivities calculated in these two cases are surprisingly compatible, which suggests that influence of phonon density of states is not so significant and that relaxation processes are dominating in thermal conductivity. In further research, this idea will be examined on 2D and 3D structures.

Acknowledgement

References

[1] A. S. Davydov, *Solid State Theory,* Nauka, Moskva 1976, in Russian, p. 33.

[2] C. Kittel, *Introduction to Solid State Physics*, 7th ed., Wiley, New York 2006, p. 120.

[3] A. M. Kosevich, *The Crystal Lattice*, Wiley, Weinheim 2005, p. 46.

[4] Y. K. Godovskii, *Thermophysics of Polymers*, Himiya, Moskva 1982 (in Russian), p. 8.

[5] M. Mijatović, K. Trenčevski, *XII Yugoslav Symp. Condens. Matter Phys.*, Skopje 1992, p. 43.

[6] J. Callaway, *Quantum Theory of the Solid State,* 2nd ed., Academic, Boston 1991, p. 175.

[7] T. M. Tritt, *Thermal Conductivity Theory, Properties and Applications*, Kluwer/Plenum, New York 2004, p. 9.

[8] Zh. M. Zhang, *Nano/Microscale Heat Transfer*, Mc Graw Hill, New York 2007, p. 137.

[9] W-Q. Huang, K-Q. Chen, Z. Shuai, L. Wang, W. Hu, *Int. J. Mod. Phys. B* **19**, 1017 (2005).