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A Semiclasical Treatment of Specific Heat of Solid

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固体の比熱の準古典的理論

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概　　要

固体も原子の集団であり，種々の諸性質は固体を構成する原子の相互作用及び運動状態により定まってくる。この小論に於ては，構成原子の振動運動モードの中に三種の音響モードが存在する事の一般証明を与える。次に，このモードを弾性振動のモードとみなすことによって，具体的に基準振動を導出する。これにより，底温における固体の比熱を導き，実験と比較する。さらに，低温（絶対温度で 20K）で，固体内に励起される phonon の絶対密度を計算しておく。これは，超電導現象の説明を定量的に与える可能性があって，我々の理論の極めて重要な結論である。

A Semiclasical Treatment of Specific Heat of Solid

Abstract:

The normal modes of phonon arised in solid are derived through regarding them to be elastic oscillations. The specific heat of solid is computed at low temperature and compared with data. The phonon number distribution are also derived.

§1 Introduction

A specific heat relates to the thermal vibrations in solid. In this paper, we propose a semiclassical treatment for the thermal vibrations contained in metal. Generally, the number of thermal vibrations in a given frequency range can be derived as follows [1-7].

Consider the solid to be a crystal lattice of atoms, each atom behaving as a harmonic oscillator. And we consider that the crystal has A atoms per unit cell and the unit cell is a rectangular solid of dimensions a_1, a_2, a_3, along three mutually perpendicular axes x_1, x_2, x_3. Then the position of any cell can be denoted by a vector $N=\sum_{i=1}^{3} n_i a_i \boldsymbol{e}_i$, where $\boldsymbol{e}_i$ denotes a unit vector along the direction of x_i axis. Since there are A atoms per cell, $3A$ additional coordinates must be given to designate the position of each atom. Let α and i correspond to an atom number and a Cartesian coordinate of an atom, respectively.

If we call the displacement of α atom from equilibrium of the coordinate in the N-th cell $Z_{\alpha i,N}$, the classical Hamiltonian for a crystal can be written as [3]

$$H=\frac{1}{2}\sum_{\alpha,i,N}\dot{Z}^2_{\alpha i,N}+\frac{1}{2}\sum_{\alpha,\beta}\sum_{N,M}\sum_{i,j}C^M_{\alpha i,\beta j}\,Z_{\alpha i,N}\,Z_{\beta j,N+M}\,, \tag{1}$$

and the classical equations of motion is

$$\ddot{Z}_{\alpha i,N}=-\sum_{\beta,M,j}C^M_{\alpha i,\beta j}\,Z_{\beta j,N+M}\,. \tag{2}$$

When all atoms of the crystal arbitrarily displace in the identical mannor $\boldsymbol{D}$, the force exerts on each atom is exactly zero, *i.e.*,

$$\sum_{\beta,M,j}C^M_{\alpha i,\beta j}\cdot D_j=0,$$

where D_j $(j=1, 2, 3)$ are arbitraly. Then we have

$$\sum_{\beta,M}C^M_{\alpha i,\beta j}=0. \tag{3}$$

In a given mode of oscillations, since one cell of the crystal is vibrating in a certain manner, all cells are vibrating the same way but with different phases. So we can write

$$Z_{\alpha i,N}=a_{\alpha i}(\boldsymbol{K})\exp i(\boldsymbol{K}\cdot\boldsymbol{N}-\omega t), \tag{4}$$

where $\boldsymbol{K}$ denotes the relative phase between cells. Moreover, $\boldsymbol{K}_i$ is written as

$$K_i=\frac{2\pi n_i}{L_i} \quad : \text{ integer number } n_i \text{ runs from } -L_i/a_i \text{ to } L_i/a_i,$$

where L_i is the total length of crystal in x_i direction. When we now want to find the normal modes of oscillations, we must solve the characteristic equation of a $3A$ by $3A$ matrix derived from substituting Eq. (4) to Eq. (2). The characteristic equation is

$$F(\omega^2,\boldsymbol{K})\equiv\det\left(\sum_M C^M_{\alpha i,\beta j}\cdot e^{i\boldsymbol{K}\cdot\boldsymbol{M}}-\omega^2\delta_{\alpha\beta}\delta_{ij}\right)=0. \tag{5}$$

Eq. (5) yields the $3A$ different normal modes of oscillations together with their dispersion relations. Among these $3A$ modes, there are three normal modes those frequencies tend to zero in propotional to $|\boldsymbol{K}|$ as $|\boldsymbol{K}|$ goes to zero, *i.e.* phonon modes. The proof is as follows:

When $\boldsymbol{K}=0$, Eq. (5) is written as

$$\det\left(\sum_M C^M_{\alpha i,\beta j}\right)-\omega^2\sum_{\gamma,k}\det\left(\sum_M C^M_{\alpha i,\beta j}\right)_{\gamma k}$$
$$+\omega^4\sum_{\gamma,k}\sum_{\delta,l}\det\left(\sum_M C^M_{\alpha i,\beta j}\right)_{\gamma k,\delta l}+O(\omega^6)=0, \tag{6}$$

where $(\sum_M C^M_{\alpha i,\beta j})_{\gamma k}$ denotes the $(3A-1)$ by $(3A-1)$ matrix obtained from the matrix $\sum_M C^M_{\alpha i,\beta j}$ by removing the γk-th row and γk-th column, and so on. From Eq. (3), we can easily shown that

$$\det\left(\sum_M C^M_{\alpha i,\beta j}\right)=\det\left(\sum_M C^M_{\alpha i,\beta j}\right)_{\gamma k}=\det\left(\sum_M C^M_{\alpha i,\beta j}\right)_{\gamma k,\delta l}=0. \tag{7}$$

Then we have known that when $\boldsymbol{K}$ is zero, there are three zero-frequency modes. Next, for sufficiently low frequnecy, by expanding the left hand side of Eq. (5) in Taylor series with respect to ω and $\boldsymbol{K}$, and neglecting the higher order terms in ω^2 and $|\boldsymbol{K}|$, we obtain

$$\begin{cases}\omega^2=\sum_{i,j}B_{ij}\cdot K_i K_j,\\ B_{ij}=-\dfrac{1}{2}(\partial^2 F/\partial K_i\partial K_j)_{\omega^2=K=0}/(\partial F/\partial\omega^2)_{\omega^2=K=0}.\end{cases} \tag{8}$$

If one diagonalizes the 3 by 3 matrix B through rotating the coordinate axes, one can get three independent linear dispersion relations between ω and $\boldsymbol{K}$. These are the phonon modes of oscillations in crystal.

§ 2 Derivation and quantization of normal modes in isotropic body

In preceeding section, we see that there are three low frequency modes in the crystal, *i.e.*, three phonon modes. It is well known that they are acoustic oscillations at least in low wave number $|\boldsymbol{K}|$. Then it has a significant physical meaning that we derivate the phonon modes by considering them to be elastic oscillations in solid.

Let us take a rectangular parallelepiped with sides a_1, a_2, a_3, and assume that the faces which are situated at $x_i=0$, a_i are constrained by the following boundary conditions:

$$\xi_i=0,\ \sigma_{ij}=0\ (i\neq j), \tag{9}$$

where ξ_i and σ_{ij} denotes displacement and stress tensor, respectively. It is necessary to note that the oscillations possible under these conditions are executed without any exchange of energy with the surroundings. The boundary condition (9) does not modify the macroscopic properties of the system from proper oscillation.

Hooke's low and Lagrangian of the system is

$$\sigma_{ij}=\lambda\cdot\delta_{ij}\sum_k \partial_k\xi_k+\mu(\partial_i\xi_j+\partial_j\xi_i), \tag{10}$$

$$L=\int d^3\boldsymbol{x}\,\frac{1}{2}\left[\rho\,\dot{\xi}^2-\frac{1}{2}\sum_{i,j}(\partial_i\xi_j+\partial_j\xi_i)\cdot\sigma_{ij}\right], \tag{11}$$

where we approximate that the solid is isotropic. $(\lambda,\ \mu)$ and ρ denote the Lamé's moduli, and the density of our solid, respectively.*) The minimum action principle on Lagrangian (11) gives the equations of motion of solid:

$$\rho\,\partial^2\xi_i/\partial t^2-\partial\sigma_{ij}/\partial x_j=0. \tag{12}$$

The solution of Eq. (12) compatible with the boundary condition (9) is written as [8]

$$\xi_l(\boldsymbol{K};\boldsymbol{x},t)=\frac{A_l(\boldsymbol{K})}{8i}\prod_{m=1}^{3}\left[\exp(i\,K_m\,x_m)\right.$$
$$\left.+(1-2\delta_{ml})\exp(-i\,K_m\,x_m)\right]e^{-i\omega(\boldsymbol{K})t}, \tag{13}$$

where

$$\boldsymbol{K}=\sum_{i=1}^{3}\boldsymbol{e}_i\frac{\pi\,n_i}{a_i}, \tag{14}$$

and the n_i are non-negative integers. On substituting the expression (13) in (12), we take the 3-by-3 characteristic equation:

$$\det\{\delta_{ij}\ \mu/\rho\cdot\boldsymbol{K}^2-(\lambda+\mu)\ K_i\,K_j/\rho-\omega(\boldsymbol{K})^2\,\delta_{ij}\}=0.$$

*) Strictly speaking, a crystal is in no way isotropic. In general, however, whether the solid is single crystal or not, it gives rise to no significant defference in thermodynamic property.

Since Eq. (15) yields the frequency values $\omega_1(\boldsymbol{K})=\omega_2(\boldsymbol{K})=\sqrt{\mu/\rho}\ |\boldsymbol{K}|$ and $\omega_3(\boldsymbol{K})=\sqrt{(\lambda+2\mu)/\rho}\ |\boldsymbol{K}|$, we can write the general motion of oscillation arises in solid as follows:

$$\begin{cases} \xi_l(\boldsymbol{x},t)=\sum_{i=1}^{3}\sum_{K} C^{(i)}(\boldsymbol{K})\,\xi_l^{(i)}(\boldsymbol{K};\boldsymbol{x},t), & (15)\\ \xi_l^{(i)}(\boldsymbol{K};\boldsymbol{x},t)=\frac{1}{8i}\,\mathrm{A}_l^{(i)}(\boldsymbol{K})\cdot\prod_{m=1}^{3}[\exp(i\,K_m x_m) \\ \quad +(1-2\delta_{ml})\exp(-i\,K_m x_m)]\exp[-i\,\omega_i(\boldsymbol{K})\,t], & (16)\end{cases}$$

where we normalized the vector $A^{(i)}(\boldsymbol{K})=\sum_l e_l\cdot A_l^{(i)}(\boldsymbol{K})$ as

$$A^{(i)}(\boldsymbol{K})\cdot A^{(j)}(\boldsymbol{K})=\delta_{ij}, \tag{17}$$

and the $C^{(i)}(\boldsymbol{K})$ are arbitrary constants. $\xi^{(i)}(\boldsymbol{K};\boldsymbol{x},t)(i=1,2,3)$ denote the three normal modes of vibrations of solid for a given wave vector $\boldsymbol{K}$, and correspond to the three phonon modes of crystal stated in Sec. 1.

Next we write

$$a_l^{(i)}(\boldsymbol{K};\boldsymbol{x})=\sqrt{\frac{8}{a_1 a_2 a_3}}\cdot\xi_l^{(i)}(\boldsymbol{K};\boldsymbol{x},t)\exp[i\,\omega_i(\boldsymbol{K})\,t], \tag{18}$$

$$Q^{(i)}(\boldsymbol{K})=\sqrt{\frac{\rho\, a_1 a_2 a_3}{8}}\ C^{(i)}(\boldsymbol{K})\exp[-i\,\omega_i(\boldsymbol{K})\,t]. \tag{19}$$

$a_l^{(i)}(\boldsymbol{K};\boldsymbol{x})$ and $Q^{(i)}(\boldsymbol{K})$ denote the vector of the eigenoscillation and the corresponding generalized coordinate, respectively. From Eqs. (15)−(18), it follows that

$$\xi_l(\boldsymbol{x},t)=\frac{1}{\sqrt{\rho}}\sum_{i=1}^{3}\sum_{K} a_l^{(i)}(\boldsymbol{K};\boldsymbol{x})\,Q^{(i)}(\boldsymbol{K};t),$$

$$\int_V d^3\boldsymbol{x}\cdot a^{(i)}(\boldsymbol{K};\boldsymbol{x})\cdot a^{(j)}(\boldsymbol{K}';\boldsymbol{x})=\delta_{ij}\cdot\delta_{KK'},$$

and the Lagrangian for our system is

$$L=\sum_{i=1}^{3}\sum_{K}\frac{1}{2}[\dot{Q}^{(i)}(\boldsymbol{K};t)^2-\omega_i(\boldsymbol{K})^2\cdot Q^{(i)}(\boldsymbol{K};t)^2]. \tag{20}$$

Thus it is shown that all sort of the internal motions of elastic solid can be described as certain sums of mutually independent harmonic oscillations which have frequencies $\omega_i(\boldsymbol{K})$, *i.e.* normal modes.

Next we perform to quantize the internal motion by introducing the canonical momentum, $P^{(i)}(\boldsymbol{K};t)$, which is conjugate with $Q^{(i)}(\boldsymbol{K};t)$, and imposing the canonical commutation relations on $P^{(i)}(\boldsymbol{K};t)$ and $Q^{(i)}(\boldsymbol{K};t)$. The $P^{(i)}(\boldsymbol{K};t)$ is

$$P^{(i)}(\boldsymbol{K};t)=\partial L/\partial\dot{Q}(\boldsymbol{K};t)=\dot{Q}(\boldsymbol{K};t), \tag{21}$$

then from Eqs. (20) and (21) the Hamiltonian of our system is written as

$$H=\sum_{i=1}^{3}\sum_{K}\frac{1}{2}[P^{(i)}(\boldsymbol{K};t)^2+\omega_i(\boldsymbol{K})^2\,Q^{(i)}(\boldsymbol{K};t)]. \tag{22}$$

The canonical commutation relations are

$$\begin{cases} [P^{(i)}(\boldsymbol{K};t),\ P^{(j)}(\boldsymbol{K}';t)]=[Q^{(i)}(\boldsymbol{K};t),\ Q^{(j)}(\boldsymbol{K}';t)]=0, \\ [P^{(i)}(\boldsymbol{K};t),\ Q^{(j)}(\boldsymbol{K}';t)]=-i\hbar\,\delta_{ij}\,\delta_{\boldsymbol{K}\boldsymbol{K}'}. \end{cases} \tag{23}$$

Eq. (23) yields the following form for our Hamiltonian (22):

$$H=\sum_{i=1}^{3}\sum_{\boldsymbol{K}}\left[m(i,\boldsymbol{K})+\frac{1}{2}\right]\cdot\hbar\,\omega_i(\boldsymbol{K}), \tag{24}$$

where $m(i,\boldsymbol{K})$ denotes nonnegative integer.

Then the states of internal motions of our solid can be adequately described by the set of the quantum numbers $m(i,\boldsymbol{K})$. It is a matter of course that this is true only when we regard the solid as an elastic continuous medium.

§ 3 Specific heat and frequency distribution in solid

In low temperature, the internal motion arised in solid contains only vibrations of phonon modes, which have linear dispersion relations. These are acoustic oscillations, and then we can treat them as elastic vibrations in solid, of which we gave a detailed account in preceding section. The energy of the system is

$$H=\sum_{i=1}^{3} m(i,\boldsymbol{K})\cdot\hbar\,\omega_i(\boldsymbol{K}), \tag{25}$$

where we neglect the zero-point energies. In other words, the energy levels of the system have a structure represented in Eq. (25).

Now, we consider a quantum state of the solid with N atoms as follows: The system consists of N pieces of fictitious particles, and the individual harmonic oscillator with frequency $\omega_i(\boldsymbol{K})$ provides the fictitious particle with one-particle energy levels:

$$\varepsilon(i,\boldsymbol{K};m_i)=m_i\cdot\hbar\,\omega_i(\boldsymbol{K}). \tag{26}$$

The N particles are distributed among these one-particle levels in a certain manner. Since it is reasonable to consider that the fictitious particles are mutually independent and correspond with the thermal excitations of solid, they are ideal bosons. As a result, we can derive the thermodynamic quantities of a solid by studying the ideal Bose gas in the level structure of Eq. (25), at least in low temperature.

It is well known that the Bose-Einstein condensation takes place for a Bose gas at sufficiently low temperature. In our fictitious Bose gas, the critical temperature T_c for the Bose condensation is

$$T_c=\frac{\hbar v}{k}\left\{\frac{\pi^2}{3[\zeta(3)]^2}\right\}^{1/3}, \tag{27}$$

where v and $\zeta(n)$ denote

$$v=\sqrt{\frac{\mu}{\rho}}\left[\frac{2}{3}+\frac{1}{3}\left(\frac{\mu}{\lambda+2\mu}\right)^{3/2}\right]^{-1/3},\quad \zeta(n)=\sum_{m=1}^{\infty}(1/m^n).$$

The values of T_c are 138 K for aluminum and 120 K for tungsten. For $T<T_c$, where our approaches make sense, the density of particles included in the energy levels belonging to the frequency range from ω to $\omega+d\omega$ is

$$dN(\omega)=\frac{3V}{2\pi^2 v^3}\sum_{m=1}^{\infty}\omega^2[\exp(m\hbar\omega/kT)-1]^{-1}d\omega, \tag{28}$$

where V represents the volume of the solid, $V=L_1\cdot L_2\cdot L_3$. And the energy of the system is

$$E=\int\hbar\omega\, dN(\omega)=\frac{3\cdot 3!\cdot[\zeta(4)]^2}{2\pi^2(v\hbar)^3}(kT)^4 V.$$

Then the specific heat is given by

$$C_v=\frac{36[\zeta(4)]^2}{\pi^2}V\left(\frac{kT}{v\hbar}\right)^3\cdot k=4.273\cdot V\left(\frac{kT}{v\hbar}\right)^3\cdot k. \tag{29}$$

In Fig. 1 we compare Eq. (29) with the experimental data[9] for $T<60$ K on tungsten. The Debye curve[10) 11)] with the theoretical charasteristic temperature $\theta_D=355$ K is also compared. Our theoretical values are slightly better agreement with data than those of Debye, which are just small as is commonly known.

Next we derive the phonon number arised in our solid. If a mode excited to the m th level, that is, if $\mathcal{E}(i, K; m)=m\hbar\omega_i(K)$, one says that there are m phonons with energy $\hbar\omega_i(K)$. From Eq. (28), we can immediatly write down the phonon number density dn for the frequency range from ω to $\omega+d\omega$ as

$$dn=\frac{3V}{2\pi^2 v^3}\cdot\sum_{m=1}^{\infty}m\omega^2\cdot[\exp(m\omega\hbar/kT)-1]^{-1}d\omega. \tag{30}$$

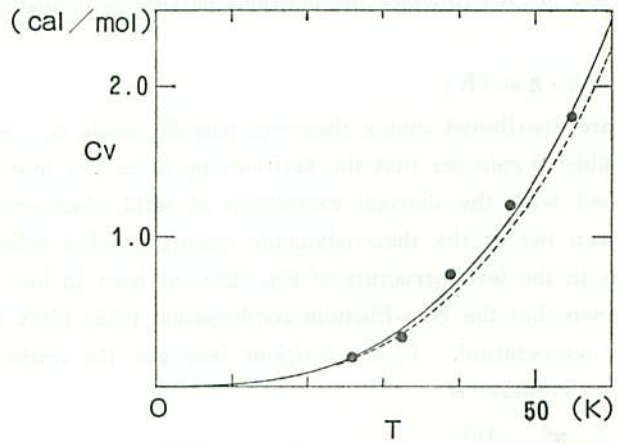

Fig. 1 Comparison between theory and the experimental data for tungsten. The solid curve of C_v are calculated from Eq. (29) by making use of the values $\mu=1.323\times10^{11}$ N/m^2 and $\lambda=1.80\times10^{12}$ N/m^2. The dotted curve represents the theoretical curve of Debye.

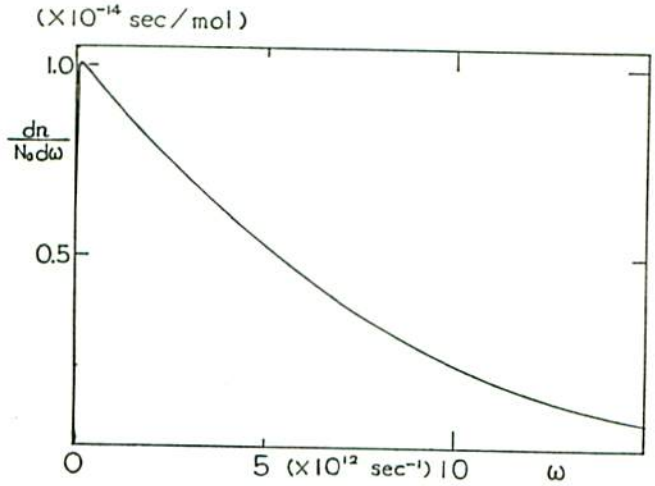

Fig. 2 The phonon spectra arised in one mol of tungsten at $T=20$K. N_0 denotes Avogadro's number.

In Fig. 2, the phonon number distribution for tungsten at $T=20$ K are plotted versus ω. It is well known that the phonons arised in metal at low temperature have a significant meang in connection with superconductivity. Some time later, we will give an account of the superconductor within the framwork of the present model.

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