Solid State Physics IV -Part II : Macroscopic Quantum Phenomena

Koji Usami*

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We review the *classic* examples of *macroscopic quantum phenomena*, which are *not* the main concern of the lecture. As examples, we study the *phonon concept* appeared in investigating the specific heat of insulators and the *flux quantization* appeared as a result of the macroscopic wave function of superconducting metals. The main theme of the lecture is, however, to discuss the *second quantum revolution*, after which the macroscopic quantum systems become the controllable objects and quantum mechanics is needed not only for explaining the phenomena but also *for manipulating the objects at our disposal*.

Introduction

A. Phonon concept - specific heat of insulators

1. The law of Dulong and Petit - a classical model of specific heat due to lattice vibrations

Let us begin with considering simple one-dimensional harmonic oscillator. The Hamiltonian can be given by

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 q^2,$$
 (1)

where m and ω are the mass and the angular frequency of the oscillator, respectively, with $m\omega^2 = \kappa$ is the spring constant. q and p are the displacement coordinate and its conjugate momentum of the harmonic oscillator. Since each of these terms in the Hamiltonian is quadratic the equipartition theorem leads to

(Mean kinetic energy)
$$\equiv \bar{K} = \frac{1}{2m}\bar{p}^2 = \frac{1}{2}k_{\rm B}T$$
 (2)

(Mean potential energy)
$$\equiv \bar{V} = \frac{1}{2}m\omega^2\bar{q^2} = \frac{1}{2}k_{\rm B}T,$$
 (3)

so that

(Mean total energy)
$$\equiv \bar{E} = \bar{K} + \bar{V} = \frac{1}{2m}\bar{p}^2 + \frac{1}{2}m\omega^2\bar{q}^2 = k_{\rm B}T.$$
 (4)

Thus the specific heat for the one-dimensional harmonic oscillator is

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = k_{\rm B}.\tag{5}$$

It is straightforward to extend the above result to three-dimensional harmonic oscillator. The resultant specific heat is

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = 3k_{\rm B}.\tag{6}$$

Next let us consider a simple solid with Avogadro's number N_a of atoms per mole. The simple-minded model of this solid can be just an ensemble of N_a three-dimensional harmonic oscillators with the mean total energy per mole of

$$\bar{E} = \sum_{i=1}^{3N_{\rm a}} \left(\frac{1}{2m} \bar{p_i^2} + \frac{1}{2} m \omega^2 \bar{q_i^2} \right) = 3N_{\rm a} k_{\rm B} T = 3RT \tag{7}$$

^{*}Electronic address: usami@qc.rcast.u-tokyo.ac.jp

and the specific heat of

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = 3N_{\rm a}k_{\rm B} = 3R,\tag{8}$$

where $R \equiv N_{\rm a}k_{\rm B}$ is the gas constant. This is nothing but the law of Dulong and Petit. From the two constants $k_{\rm B}$ and $N_{\rm a}$ the specific heat of the simple-minded solid would be

$$c_V = 3R = 24.94 \left[\text{J/mol} \cdot \text{K} \right] \text{ or} \tag{9}$$

$$= 5.961 \left[\text{cal/mol} \cdot \text{K} \right], \tag{10}$$

a constant value irrespective of the temperature. This conclusion of Dulong and Petit is in stark contrast to the experimental fact that the specific heats for many solid state substances fall well below the Dulong-Petit value as the temperature drops.

A. Einstein, in 1907, proposed a brilliant idea that the discrepancy can be resolved if the then new Planckian energy quanta concept is applied to the specific heat, the birth of "phonon" concept!

2. Einstein's specific heat - ensemble of independent quantum harmonic oscillators

Let us quantize the one-dimensional harmonic oscillator first. The Hamiltonian can then be given by

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{q}^2,$$
(11)

where \hat{p} and \hat{q} are the quantum-mechanical momentum operator and the position operator, respectively. Now we define the annihilation operator and the creation operator as

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{q} + \frac{i}{m\omega} \hat{p} \right), \tag{12}$$

$$\hat{a}^{\dagger} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{q} - \frac{i}{m\omega} \hat{p} \right), \tag{13}$$

then, we have

$$\hat{H} = \hbar\omega \left(\hat{a}\hat{a}^{\dagger} + \frac{1}{2} \right) \tag{14}$$

$$= \hbar\omega\left(\hat{n} + \frac{1}{2}\right). \tag{15}$$

Thus we succeed in quantizing the harmonic oscillator, which has the discretized energies of $E_n = \hbar \omega \left(n + \frac{1}{2}\right)$ where n is the expectation value of the hermitian operator $\hat{n} \equiv \hat{a}^{\dagger} \hat{a}$. Inspection tells us that the discreteness of the energy (energy "quanta"), in fact, demands the well-known commutation relations,

$$[\hat{q}, \hat{p}] = i\hbar, \tag{16}$$

or

$$\left[\hat{a}, \hat{a}^{\dagger}\right] = 1,\tag{17}$$

which means that the position \hat{q} and the momentum \hat{p} of harmonic oscillators cannot be precisely assigned although they can take continuum of expectation values (as opposed to the quantized energy E_n).

From Eq. (15) the mean total energy of the quantum harmonic oscillator is

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z = \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1}\right),\tag{18}$$

where $\beta = \frac{1}{k_{\rm B}T}$ and Z is the partition function defined by

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega} \frac{1}{1 - e^{-\beta\hbar\omega}}.$$
(19)

Thus the specific heat for the one-dimensional quantum harmonic oscillator is

$$c_{V} = \left(\frac{\partial \bar{E}}{\partial T}\right)_{V} = \left(\frac{\partial \bar{E}}{\partial \beta}\right)_{V} \left(\frac{\partial \beta}{\partial T}\right) = -\frac{1}{k_{\rm B}T^{2}} \left(\frac{\partial \bar{E}}{\partial \beta}\right)_{V} = -\frac{\hbar\omega}{k_{\rm B}T^{2}} \left(-\frac{\hbar\omega e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^{2}}\right)$$

$$= k_{\rm B} \left(\beta\hbar\omega\right)^{2} \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^{2}}$$
(20)

It is straightforward to extend the above result to three-dimensional quantum harmonic oscillator. The resultant specific heat is

$$c_V = 3k_{\rm B} \left(\beta\hbar\omega\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}.$$
(21)

Comparing to the one for the classical harmonic oscillator, Eq. (6), there is extra factor $(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$, which varies as the temperature changes.

The Einstein's model of solid is simply an ensemble of independent $N_{\rm a}$ three-dimensional quantum harmonic oscillators; thus the mean total energy per mole is

$$\bar{E} = 3N_{\rm a}\hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right),\tag{22}$$

and the specific heat is

$$c_{V} = \left(\frac{\partial \bar{E}}{\partial T}\right)_{V} = 3N_{\rm a}k_{\rm B} \left(\beta\hbar\omega\right)^{2} \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^{2}}$$
$$= 3R \left(\frac{\Theta_{\rm E}}{T}\right)^{2} \frac{e^{\frac{\Theta_{\rm E}}{T}}}{\left(e^{\frac{\Theta_{\rm E}}{T}}-1\right)^{2}}.$$
(23)

where $\frac{\Theta_{\rm E}}{T} \equiv \beta \hbar \omega$ and $\Theta_{\rm E}$ is called the Einstein temperature. In the high temperature limit c_V in Eq. (23) approaches the classical Dulong-Petit value, 3R, while in the low temperature limit c_V becomes $3R \left(\frac{\Theta_{\rm E}}{T}\right)^2 e^{-\frac{\Theta_{\rm E}}{T}}$, i.e., exponential decrease as $T \to 0$. Experimentally the specific heat approaches zero more gently than this, that is, $c_V \propto T^3$ as $T \to 0$.

The discrepancy indeed stems from the fact that in solids atoms (or ions) are rigidly bound to each other so that Einstein's independent harmonic oscillator model fails to capture the truth of the reality. Nevertheless, the very simple Einstein's quantum model of specific heat helps stimulate the thought that the deviation of the experimentally measured specific heats from the law of Dulong and Petit would reveal the profound quantum nature of reality.

3. Debye's specific heat - model of interacting particles

Solid is a system where the interaction between particles (atoms, ions) is sufficiently strong (due to covalent/molecular/ionic bonding) so that they become arranged in a lattice of definite crystal structure (spontaneous symmetry breaking). The potential energy of such a system is no longer separable but dependent on the interrelation between constituent particles' displacements. If we write the potential energy as V = $V(q_{1x}, q_{2x}, \cdot, q_{N_ax}; q_{1y}, \cdots, q_{N_ay}; q_{1z}, \cdots, q_{N_az})$ the potential energy can be expanded in Taylor's series as

$$V = V_0 + \sum_{i=1}^{N_a} \sum_{\alpha = x, y, z} \left(\frac{\partial V}{\partial q_{i\alpha}} \right) q_{i\alpha} + \frac{1}{2} \sum_{i, j=1}^{N_a} \sum_{\alpha, \beta = x, y, z} \left(\frac{\partial^2 V}{\partial q_{i\alpha} \partial q_{j\beta}} \right) q_{i\alpha} q_{j\beta} + \cdots,$$
(24)

where V_0 corresponds to the potential energy in the equilibrium configuration of the particles. The second term corresponds to the force and vanishes at the equilibrium. Omitting the irrelevant V_0 in the dynamics of the lattice vibration and the higher order terms in q than second (the harmonic approximation) the Hamiltonian of the lattice vibration becomes

$$\hat{H} = \frac{1}{2} \sum_{i=1}^{N_{\rm a}} \sum_{\alpha=x,y,z} \frac{1}{2m} \hat{p}_{i\alpha}^2 + \frac{1}{2} \sum_{i,j=1}^{N_{\rm a}} \sum_{\alpha,\beta=x,y,z} D_{i\alpha,j\beta} \hat{q}_{i\alpha} \hat{q}_{j\beta}.$$
(25)

The complicated potential energy term reflects the fact that the particles interact so that they do not behave like independent particles, which Einstein tacitly assumes in his model.

It is, however, possible to factorize the Hamiltonian, Eq. (25), into independent quasi-particles' Hamiltonians. Let the displacement coordinates (or the quantum-mechanical position operators), $\hat{q}_{i\alpha}$, be transformed in the form,

$$\hat{q}_{i\alpha} = \sum_{r=1}^{3N_{a}} B_{i\alpha,r} \hat{u}_{r}.$$
(26)

A proper choice of the matrix $B_{i\alpha,r}$ leads to

$$\hat{H} = \sum_{r=1}^{3N_{\rm a}} \left(\frac{1}{2} m \dot{\hat{u}}_r^2 + \frac{1}{2} m \omega_r^2 \hat{u}_r^2 \right).$$
(27)

The new variables \hat{u}_r is called the "normal coordinates" of the system of the interacting particles. The form of the Hamiltonian, Eq. (27), is identical to Eq. (7), i.e., 3N independent harmonic oscillators, but having a varying normal-mode angular frequency ω_r for each \hat{u}_r . The mean total energy per mole in Einstein model, Eq. (22), is then modified into

$$\bar{E} = \sum_{r=1}^{3N_{\rm a}} \hbar \omega_r \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega_r} - 1} \right). \tag{28}$$

As we shall learn next week, the low frequency limit (or long wavelength limit, or elastic continuum limit) we have a linear dispersion relation $\omega = c_s k$ between the normal-mode angular frequency ω and wave vector k, where c_s is an "effective" sound velocity. In this elastic continuum limit the identity, $\sum_{r=1}^{3N_a} = 3V \int \frac{dk^3}{(2\pi)^3}$, can be used and the mean total energy, Eq. (28), can then be rewritten as an integral form;

$$\bar{E} = 3V \int \frac{d\mathbf{k}^3}{(2\pi)^3} \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$$

$$= 3V \int_0^{k_{\rm D}} \frac{4\pi k^2 dk}{(2\pi)^3} \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$$

$$= \int_0^{\omega_{\rm D}} \frac{3V}{2\pi^2} \frac{\omega^2 d\omega}{c_s^3} \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right),$$
(29)

where the last step we used the assumed dispersion relation, $\omega = c_s k$. Here ω_D is called the Debye angular frequency and defined so as to yield the correct total number of $3N_a$ normal modes, i.e.,

$$\int_{0}^{\omega_{\rm D}} \frac{3V}{2\pi^2} \frac{\omega^2 d\omega}{c_s^3} = 3V \int \frac{d\mathbf{k}^3}{(2\pi)^3} = \sum_{r=1}^{3N_{\rm a}} = 3N_{\rm a},\tag{30}$$

which leads to

$$\frac{V}{2\pi^2 c_s^3} \omega_{\rm D}^3 = 3N_{\rm a}$$
(31)

or

$$\omega_{\rm D} = c_s \left(6\pi^2 \frac{N_{\rm a}}{V} \right). \tag{32}$$

TABLE I: Specific heats -Classical / Quantum theories

	Radiation (Boson)	Lattice vibration (Boson)	Free electron (Fermion)
Number of degrees of freedom	Infinite	Limited by Debye temperature	Limited by Fermi temperature
Classical Theory	Rayleigh-Jeans	Dulong-Petit	Drude
Quantum Theory	Planck/Stefan-Boltzmann	Einstein/Debye	Sommerfeld

Einstein's specific heat, Eq. (23), is accordingly modified into

$$c_{V} = \left(\frac{\partial \bar{E}}{\partial T}\right)_{V} = \frac{3V}{2\pi^{2}} \frac{1}{c_{s}^{3}} \int_{0}^{\omega_{\mathrm{D}}} \frac{\hbar^{2} \omega^{4} e^{\beta \hbar \omega}}{\left(e^{\beta \hbar \omega} - 1\right)^{2}} \frac{1}{k_{\mathrm{B}} T^{2}} d\omega$$
$$= k_{\mathrm{B}} \frac{3V}{2\pi^{2}} \frac{1}{c_{s}^{3}} \int_{0}^{\omega_{\mathrm{D}}} \frac{\left(\beta \hbar \omega\right)^{2} e^{\beta \hbar \omega}}{\left(e^{\beta \hbar \omega} - 1\right)^{2}} \omega^{2} d\omega$$
$$= k_{\mathrm{B}} \frac{3V}{2\pi^{2} (c_{s} \beta \hbar)^{3}} \int_{0}^{\beta \hbar \omega_{\mathrm{D}}} \frac{x^{4} e^{x}}{\left(e^{x} - 1\right)^{2}} dx, \tag{33}$$

where $x = \beta \hbar \omega$. Using $V = 6\pi^2 N_{\rm a} \left(\frac{c_{\rm s}}{\omega_{\rm D}}\right)^3$, which deduced from Eq. (32), Debye's specific heat can be expressed in the similar form to Eq. (23); that is,

$$c_V = 3N_a k_B \frac{3}{(\beta \hbar \omega_D)^3} \int_0^{\beta \hbar \omega_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$= 3R \frac{3}{\left(\frac{\Theta_D}{T}\right)^3} \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx,$$
 (34)

where $\frac{\Theta_{\rm D}}{T} \equiv \beta \hbar \omega$ and $\Theta_{\rm D}$ is called the Debye temperature. In the high temperature limit c_V in Eq. (33) approaches the classical Dulong-Petit value, 3R, like the Einstein model. In the low temperature limit, however, upper limit of the integral $\frac{\Theta_D}{T}$ can be replaced by ∞ so that the integral becomes constant (a mathematical formula says it is $\frac{4\pi^4}{15}$). Thus Debye's specific heat at low temperature limit is

$$c_V = 3R \frac{4\pi^2}{5} \left(\frac{T}{\Theta_{\rm D}}\right)^3. \tag{35}$$

which agrees with the experimentally observed behavior of specific heats, that is, $c_V \propto T^3$ as $T \to 0$,

4. Einstein/Debye, Planck, Sommerfeld, ...

We have studied the models of specific heat due to lattice vibration and learned that to explain the measured specific heats the Planckian energy quanta concept, that is, phonons, has to be introduced. The seemingly dull activity of investigating heat capacities indeed reveals a deep and beautiful quantum nature of physics! It is thus worth to further explore other specific heats. The table A4 summarizes the classical and quantum theories of specific heats.

Flux quantization -superconductivity [5] в.

The Schrödinger equation of a charged particle in an electromagnetic field A and ϕ can be given by

$$i\hbar \frac{\partial}{\partial t}\psi(\mathbf{r},t) = \mathcal{H}\psi(\mathbf{r},t)$$
$$= \frac{1}{2m} \left(-i\hbar\nabla - q\mathbf{A}\right) \left(-i\hbar\nabla - q\mathbf{A}\right)\psi + q\phi\psi$$
(36)

Since the probability density $P(\mathbf{r}, t)$ in quantum mechanics is given in terms of the wave function $\psi(\mathbf{r}, t)$ by

$$P(\mathbf{r},t) = \psi^*(\mathbf{r},t)\psi(\mathbf{r},t),\tag{37}$$

the probability current $\boldsymbol{J}(\boldsymbol{r},t)$ can be obtained by

$$\frac{\partial}{\partial t}P(\boldsymbol{r},t) = -\nabla \cdot \boldsymbol{J}(\boldsymbol{r},t), \qquad (38)$$

which leads to

$$\boldsymbol{J}(\boldsymbol{r},t) = \frac{1}{2} \left(\left(\frac{-i\hbar\nabla - q\boldsymbol{A}}{m} \psi \right)^* \psi + \psi^* \left(\frac{-i\hbar\nabla - q\boldsymbol{A}}{m} \psi \right) \right).$$
(39)

We new consider the wave function $\psi(\mathbf{r})$ in Eq. (36) as a *macroscopic* one by identifying it as an *order parameter* of a superconducting metal;

$$\psi(\boldsymbol{r},t) = \sqrt{\rho(\boldsymbol{r})}e^{i\theta(\boldsymbol{r})},\tag{40}$$

where ρ is the charge density and θ is the *phase*. Equation. (39) is then nothing but the simpler form of the *Ginzburg-Landau* equation, which can be explicitly given in terms of ρ and θ by

$$\boldsymbol{J}(\boldsymbol{r}) = \frac{\hbar}{m} \left(\nabla \theta(\boldsymbol{r}) - \frac{q}{\hbar} \boldsymbol{A}(\boldsymbol{r}) \right) \rho(\boldsymbol{r}).$$
(41)

Without the first term the Eq. (41) would be the London equation;

$$\boldsymbol{J}(\boldsymbol{r}) = \frac{q}{m} \rho(\boldsymbol{r}) \boldsymbol{A}(\boldsymbol{r}), \tag{42}$$

which explains the perfect conductivity as well as the Meissner effect.

The existence of the θ term in Eq. (41) produces an even more remarkable phenomenon, *flux quantization*. Let us consider a superconducting ring under the magnetic field. Since the superconducting current flows only near the surface down to the *London penetration depth* $\frac{1}{\lambda}$, where

$$\lambda = \sqrt{\frac{q}{\epsilon_0 c^2 m} \rho(\mathbf{r})},\tag{43}$$

the interior current of the ring should be zero. From Eq. (41) this situation leads to

$$\hbar \nabla \theta(\mathbf{r}) = q \mathbf{A}(\mathbf{r}). \tag{44}$$

Taking the line integral along the interior of the ring, we have, from the single-valuedness of the wave function,

$$\hbar \underbrace{\oint \nabla \theta(\mathbf{r}) \cdot d\mathbf{s}}_{2\pi n} = q \underbrace{\oint \mathbf{A}(\mathbf{r}) \cdot d\mathbf{s}}_{\Phi}, \tag{45}$$

and reach the conclusion that the flux Φ has to be *quantized* as

$$\Phi = \frac{2\pi\hbar}{q}n\tag{46}$$

with n being any integers $(0,1,2,\cdots)$ and q turning out to be 2e reflecting the fact that the electrons pairing up as the *Cooper pairs* and being condensed in the ground state (BCS state) in the superconducting metals.

Plan

- 1. Harmonic oscillators, coupled harmonic oscillators, and boson fields [2014/12/08]
- 2. Damped harmonic oscillators [2014/12/15]
- 3. Cavity cooling [2014/12/22]
- 4. Two level systems [2015/01/05]
- 5. Cavity QED and circuit QED [2015/01/19]
- 6. Hybrid quantum systems [2015/01/26]

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