New Quantum Theory and New Meaning of Specific Heat of a Solid

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Abstract

In this article, we consider the specific heat of a monatomic solid in the view point of the new quantum theory. Thereby we can clarify a new meaning of specific heat. At last, we give a new meaning of the Debye model of specific heat of a solid.

Introduction

In this article, we consider the molar heat of a monatomic solid in the view point of the new quantum theory. We get a reasonable explanation of the molar heat of a monatomic solid. It gives a new explanation of the Debye's model of specific heat of a solid. In the old quantum theory, there are Einstein's theory of specific heat at 1907 and Debye's theory of specific heat at 1912. But they are different from ours with respect to the standing point. The new quantum theory was originated by Y. Ito [2]-[4] at 1998-2000. As for the new quantum theory, we refer the papers [1]-[8] of the references.

1. Axiom of the new quantum theory

Here we remember the axiom of the new quantum theory which is the basis of this article. As for this we refer Ito[2], [3], Ito-Kayama[6],[7] and Ito-Kayama-Kamoshita[8].

Axiom I (quantum system). A quantum system Ω is defined to be a probability space (Ω, B, P). Here Ω is a set of microparticles ρ, B is a σ-algebra of subsets of Ω and P is a completely additive probability measure on B.

Axiom II (quantum state). The (quantum) state of a quantum system $\Omega = \Omega(B, P)(= (\Omega, B, P))$ is defined to be the state of the quantum probability distribution of the position variables $r(\rho)$ and the momentum variables $p(\rho)$ of microparticles ρ which compose the quantum system. Here, we consider the orthogonal coordinate systems of n-dimensional Euclidean space R^n and its dual space R_n. Here we put $n = dM$, where d denotes the dimension of the physical space and M denotes the number of particles which compose one elementary event ρ.

(II_1) The quantum probability distribution of the position variables $r = r(\rho)$ is determined by an L^2-density ψ on R^n such that it satisfies the condition

$$\int_{R^n} |\psi(r)|^2 dr = 1,$$

where dr denotes the Lebesgue measure on R^n.

(II_2) The quantum probability distribution of the momentum variable $p = p(\rho)$ is determined by the Fourier transform $\hat{\psi}$ of ψ. Here we put

$$\hat{\psi}(p) = (2\pi\hbar)^{-n/2} \int \psi(r) e^{-i(p \cdot r)/\hbar} dr,$$

$$\psi(r) = (2\pi\hbar)^{-n/2} \int \hat{\psi}(p) e^{i(p \cdot r)/\hbar} dp,$$

$$r = (x_1, x_2, \cdots, x_n), \ \ p = (p_1, p_2, \cdots, p_n),$$

$$p \cdot r = p_1 x_1 + p_2 x_2 + \cdots + p_n x_n.$$

Here we put $\hbar = \dfrac{h}{2\pi}$ and h is the Planck constant.

(II_3) We put

$$\mu(A) = \int_A |\psi(r)|^2 dr$$

for a Lebesgue measurable set A in R^n. Then we assume that

$$P(\{\rho \in \Omega; r(\rho) \in A\}) = \mu(A).$$

Then, $\mu(A)$ denotes the probability of the event "$r(\rho)$ belongs to A". Thereby, we have the probability space $(R^n, \mathcal{M}_n, \mu)$, where $\mathcal{M}_n$ is the family of all Lebesgue measurable sets in R^n.

(II$_4$) We put

$$\nu(B) = \int_B |\hat{\psi}(\boldsymbol{p})|^2 d\boldsymbol{p}$$

for a Lebesgue measurable set B in $\boldsymbol{R}_n$. Then we assume that

$$P(\{\rho \in \Omega; \boldsymbol{p}(\rho) \in B\}) = \nu(B).$$

Then, $\nu(B)$ denotes the probability of the event "$\boldsymbol{p}(\rho)$ belongs to B". Thereby, we have the probability space $(\boldsymbol{R}_n, \mathcal{N}_n, \nu)$, where $\mathcal{N}_n$ is the family of all Lebesgue measurable sets in $\boldsymbol{R}_n$.

Axiom III (motion of a quantum system). We call the time evolution of the L^2-density $\psi(\boldsymbol{r}, t)$ of a quantum system the motion of the quantum system. The law of the motion of the quantum system is described by the Schrödinger equation. We call the Schrödinger equation the equation of motion of the quantum system.

A Schrödinger equation is defined by an equation of the form

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi.$$

We call the operator H a Hamiltonian, which has a various form corresponding to each quantum system. H is assumed to be a self-adjoint operator on some Hilbert space $\mathcal{H}$.

2. Physical setting of the system and the problem

We consider a monatomic solid spreaded infinitely. Every atom of the solid is oscillating by the cause of heat. Approximately we may consider every atom as a harmonic oscillator near the equilibrium point. We wish to consider the specific heat of this solid.

We consider the specific heat as molar heat. It is $3N$ times of the specific heat with respect to one degree of freedom of oscillation, where N is the Avogadro's number.

3. Setting of the mathematical model

We use the notation in chapter 1. Let $\Omega = \Omega(\boldsymbol{B}, P)$ be the probability space which represents the quantum system considered here. An elementary event ρ of Ω is a harmonic oscillator which oscillates harmonically in the 1-dimensioanl Euclidean space $\boldsymbol{R}^1$. Here we consider one degree of freedom of the 3-dimensional harmonic oscillator. Then we denote the position variable of a harmonic oscillator ρ by $x = x(\rho)$, and the momentum variable of ρ by

$p = p(\rho)$. Here we put $n = dM = 1$ because the space dimension is $d = 1$, the number of harmonic oscillators which compose an elementary event ρ is $M = 1$. The variable x changes in the space $\boldsymbol{R}^1$ and the variable p changes in its dual space $\boldsymbol{R}_1$. Then by the axiom II, the L^2-density $\psi(x)$ determines the quantum probability distribution law of the position variable x and its Fourier transform $\hat{\psi}(p)$ determines the quantum probability distribution law of the momentum variable p. The total energy of each harmonic oscillator ρ is determined by the classical mechanics. Its value is

$$\frac{1}{2m}p(\rho)^2 + \frac{m}{2}\omega(\rho)^2 x(\rho)^2.$$

Here the first term is the kinetic energy of the harmonic oscillator ρ and the second term is the potential energy of the harmonic oscillator ρ. $\omega(\rho)$ is the angular frequency of the harmonic oscillator ρ and m is the mass of the harmonic oscillator.

This energy variable is considered as a quantum random variable defined on the probability space Ω which represents the quantum system. The evaluation of the expectation value of this energy variable, namely the energy expectation value, is carried out by using the axiom II.

Namely we use the relation

$$P(\{\rho \in \Omega; x(\rho) \in A\}) = \int_A |\psi(x)|^2 dx,$$

$$P(\{\rho \in \Omega; p(\rho) \in B\}) = \int_B |\hat{\psi}(p)|^2 dp$$

for a subset A in $\boldsymbol{R}^1$ and a subset B in $\boldsymbol{R}_1$. Further we assume that the $\omega(\rho)$ is a random variable whose probability distribution law is given by a probability density $D(\omega)$ such as

(1) $0 \leq D(\omega) \leq \infty$.

(2) $\displaystyle\int_0^\infty D(\omega)d\omega = 1$.

(3) $\displaystyle\int_0^\infty \omega D(\omega)d\omega < \infty$.

Then we have the energy expectation value $\overline{E}$:

$$\overline{E} = E\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2\right]$$

$$= \int_0^\infty E\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2; \omega(\rho) = \omega\right] D(\omega)d\omega.$$

Then, for an admissible L^2-density ψ, we have

$$E\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2; \omega(\rho) = \omega\right]$$

$$= E\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega^2 x(\rho)^2\right]$$

$$= E\left[\frac{1}{2m}p(\rho)^2\right] + E\left[\frac{1}{2}m\omega^2 x(\rho)^2\right]$$

$$= \int \frac{1}{2m}p^2|\hat{\psi}(p)|^2 dp + \int \frac{1}{2}m\omega^2 x^2|\psi(x)|^2 dx$$

$$= \int \left\{\frac{\hbar^2}{2m}\left|\frac{d\psi(x)}{dx}\right|^2 + \frac{1}{2}m\omega^2 x^2|\psi(x)|^2\right\} dx.$$

Here we use the Plancherel formula for Fourier transformation.

Here we denote this conditional energy expectation value by

$$J[\psi;\omega] = \int \left\{\frac{\hbar^2}{2m}\left|\frac{d\psi(x)}{dx}\right|^2 + \frac{1}{2}m\omega^2 x^2|\psi(x)|^2\right\} dx.$$

We call $J[\psi;\omega]$ the conditional energy functional.

Here we assert the following principle.

Principle I (variational principle). The true physical state of the quantum system is realized as a state such that the energy expectation value of the quantum system takes its stationary value under some conditions.

From this principle, we can choose the true L^2-density for each quantum system. So that we consider the following problem.

Problem 1. Find out the L^2-density ψ for which conditional energy expectation value $J[\psi;\omega]$ takes its stationary value under the condition that

$$\int |\psi(x)|^2 dx = 1.$$

4. Mathematical analysis

Solving the problem 1 in chapter 3 under the condition that $\omega(\rho) = \omega$ is fixed by the way similar to Ito-Kayama-Kamoshita [8], we have the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right)\psi(x) = \mathcal{E}\psi(x)$$

as the Euler equation. Here $\mathcal{E}$ is the Lagrange's unknown constant. Namely, the function ψ which is the solution of the problem is obtained as a solution of the above Schrödinger equation. As solutions of the above eigenvalue problem, we have the eigenfunctions $\psi_n(x)$ corresponding to the eigenvalues $\mathcal{E}_n$ for $n = 0, 1, 2, \cdots$.

Namely we have

$$\mathcal{E}_n = \left(n + \frac{1}{2}\right)\hbar\omega,$$

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!}} \sqrt{\frac{1}{\pi} \cdot \frac{m\omega^2}{\hbar}} H_n\left(\sqrt{\frac{m}{\hbar}}\omega x\right) \cdot \exp\left[-\frac{1}{2}\frac{m}{\hbar}\omega^2 x^2\right],$$
$$(n = 0, 1, 2, \cdots).$$

Here we put

$$H_n(x) = (-1)^n e^{x^2} \cdot \frac{d^n}{dx^n} e^{-x^2}.$$

Then we have

$$J[\psi_n; \omega] = \left(n + \frac{1}{2}\right)\hbar\omega, (n = 0, 1, 2, \cdots).$$

Let $\mathcal{S}(\mathbf{R}^1)$ be the space of all rapidly decreasing C^∞-functions on $\mathbf{R}^1$. Then for the system of eigenfunctions $\{\psi_n\}_{n=0}^\infty$, we have the following. (see Kuroda [10], Chapter 4).

Theorem 1. *The system of eigenfunctions $\{\psi_n\}_{n=0}^\infty$ is a complete orthonormal system in $\mathcal{S}(\mathbf{R}^1)$.*

By virtue of theorem 1, for any $\psi \in \mathcal{S}(\mathbf{R}^1)$, there exists only one sequence $\{c_n\}_{n=0}^\infty$ of complex numbers such that we can expand $\psi(x)$ as $\psi(x) = \sum_{n=0}^\infty c_n\psi_n(x)$. Here this series converges also in the space $L^2(\mathbf{R}^1)$.

If the true physical state of the total quantum system Ω is determined by some L^2-density $\psi(x)$ at the initial time point, then we can expand $\psi(x)$ by using $\{\psi_n\}_{n=0}^\infty$ as above. Then we have the conditional energy expectation value

$$J[\psi; \omega] = \sum_{n=0}^\infty |c_n|^2 J[\psi_n; \omega] = \sum_{n=0}^\infty |c_n|^2 \left(n + \frac{1}{2}\right)\hbar\omega.$$

Further, since the function $\psi(x)$ satisfies the normalization condition $\int_{-\infty}^\infty |\psi(x)|^2 dx = 1$, we have

$$\sum_{n=0}^\infty |c_n|^2 = 1.$$

Then the sequence $\{c_n\}_{n=0}^\infty$ is a rapidly decreasing sequence. (see Kuroda [10], p.81). Here, using the experimental facts, we assume

$$|c_n|^2 = (1 - \exp\left[-\frac{\hbar\omega}{k_B T}\right])(\exp\left[-\frac{\hbar\omega}{k_B T}\right])^n, (n = 0, 1, 2, \cdots).$$

Here T is the absolute temperature and k_B is the Boltzmann constant. Therefore we have the conditional energy expectation value

$$J[\psi; \omega] = \sum_{n=0}^\infty |c_n|^2 J[\psi_n; \omega]$$

$$= \left(1 - \exp\left[-\frac{\hbar\omega}{k_B T}\right]\right) \hbar\omega \sum_{n=0}^{\infty} \left(\frac{1}{2} + n\right) \left(\exp\left[-\frac{\hbar\omega}{k_B T}\right]\right)^n$$

$$= \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\exp\left[\frac{\hbar\omega}{k_B T}\right] - 1}$$

The L^2-density $\psi(x)$ at the initial time point can be expanded as follows:

$$\psi(x) = \sum_{n=0}^{\infty} c_n \sqrt{\frac{1}{2^n n!}} \sqrt{\frac{1}{\pi} \cdot \frac{m\omega^2}{\hbar}} H_n\left(\sqrt{\frac{m}{\hbar}}\omega x\right) \cdot \exp\left[-\frac{1}{2}\frac{m}{\hbar}\omega^2 x^2\right].$$

Here we follow the method of separation of variables in the reverse. At first we consider the function

$$\psi_n(x,t) = \psi_n(x) \exp\left[-i\frac{\mathcal{E}_n}{\hbar}t\right].$$

Then we differentiate with respect to the time variable t and we have

$$i\hbar\frac{\partial\psi_n(x,t)}{\partial t} = \mathcal{E}_n\psi_n(x)\exp\left[-i\frac{\mathcal{E}_n}{\hbar}t\right].$$

Here we put

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m}{2}\omega^2 x^2.$$

Then we have

$$H\psi_n(x) = \mathcal{E}_n\psi_n(x), (n = 0, 1, 2, \cdots).$$

Thereby we have

$$i\hbar\frac{\partial\psi_n(x,t)}{\partial t} = H\psi_n(x) \cdot \exp\left[-i\frac{\mathcal{E}_n}{\hbar}t\right]$$

$$= H\psi_n(x,t).$$

Therefore, considering the function

$$\psi(x,t) = \sum_{n=0}^{\infty} c_n\psi_n(x,t),$$

we have

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = H\psi(x,t).$$

This is the Schrödinger equation of the time evolution of the total quantum system Ω. This shows that this quantum system satisfies the axiom III in

chapter 1. Therefore we have the energy expectation value of the total quantum system Ω:

$$\overline{E} = E\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2\right]$$

$$= \int_0^\infty J[\psi;\omega]D(\omega)d\omega$$

$$= \int_0^\infty \left\{\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\exp\left[\frac{\hbar\omega}{k_B T}\right] - 1}\right\} D(\omega)d\omega$$

$$= \frac{1}{2}\hbar\overline{\omega} + \int_0^\infty \frac{\hbar\omega}{\exp\left[\frac{\hbar\omega}{k_B T}\right] - 1} D(\omega)d\omega.$$

Here $\overline{\omega}$ is the mean of angular frequency:

$$\overline{\omega} = \int_0^\infty \omega D(\omega)d\omega.$$

For considering the specific heat of the solid, we should evaluate the derivative $\frac{d\overline{E}}{dT}$.

$$\frac{d\overline{E}}{dT} = \frac{d}{dT}\int_0^\infty \frac{\hbar\omega}{\exp\left[\frac{\hbar\omega}{k_B T}\right] - 1} D(\omega)d\omega.$$

The density $D(\omega)$ of angular frequency should be determined for each solid concretely.

5. Consideration and conclusion

On the true physical system, the quantum system $\Omega = \Omega(B, P)$ of 1-dimensional harmonic oscillators is decomposed into subsystems as follows:

$$\Omega = \bigcup_\omega \Omega(\omega),$$

$$\Omega(\omega) = \{\rho \in \Omega; \omega(\rho) = \omega\}.$$

Then we have the probability space $\{\Omega(\omega), B(\omega), P_\omega\}$ for every ω. Then, for every angular frequency ω, the subsystem $\Omega(\omega)$ is decomposed into characteristic subsystems as follows:

$$\Omega(\omega) = \sum_{n=0}^\infty \Omega_n(\omega), \text{(direct sum)}.$$

Then, for every $A \in \boldsymbol{B}(\omega)$, we have

$$P_\omega(A) = \sum_{n=0}^{\infty} P_\omega(\Omega_n(\omega)) P_{\Omega_n(\omega)}(A).$$

Here $P_{\Omega_n(\omega)}(A)$ denotes the conditional probability. Then, for $n = 0, 1, 2, \cdots$, the probability space $\{\Omega_n(\omega), \boldsymbol{B}(\omega) \cap \Omega_n(\omega), P_{\Omega_n(\omega)}\}$ is said to be the n-th characteristic quantum system.

Here we assume that, for $n = 0, 1, 2, \cdots$,

$$P_\omega(\Omega_n(\omega)) = |c_n|^2 = \left(1 - \exp\left[-\frac{\hbar\omega}{k_B T}\right]\right) \left(\exp\left[-\frac{\hbar\omega}{k_B T}\right]\right)^n$$

holds.

Then, for $A \subset \boldsymbol{R}^1$ and $B \subset \boldsymbol{R}_1$, we have

$$\sum_{n=0}^{\infty} P_\omega(\Omega_n(\omega)) = \sum_{n=0}^{\infty} |c_n|^2 = 1,$$

$$P_{\Omega_n(\omega)}(\{\rho \in \Omega_n(\omega); x(\rho) \in A\}) = \int_A |\psi_n(x)|^2 dx,$$

$$P_{\Omega_n(\omega)}(\{\rho \in \Omega_n(\omega); p(\rho) \in B\}) = \int_B |\hat{\psi}_n(p)|^2 dp.$$

Therefore, for every ω, the conditional energy expectation value of the characteristic quantum system $\Omega_n(\omega)$ is

$$E_{\Omega_n(\omega)}\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2; \omega(\rho) = \omega\right]$$

$$= \int \left\{\frac{\hbar^2}{2m}\left|\frac{d\psi_n(x)}{dx}\right|^2 + \frac{1}{2}m\omega^2 x^2 |\psi_n(x)|^2\right\} dx$$

$$= J[\psi_n; \omega] = \left(n + \frac{1}{2}\right)\hbar\omega.$$

Then we have

$$E\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2; \omega(\rho) = \omega\right]$$

$$= \sum_{n=0}^{\infty} P_\omega(\Omega_n(\omega)) E_{\Omega_n(\omega)}\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2; \omega(\rho) = \omega\right]$$

$$= \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\exp\left[\frac{\hbar\omega}{k_B T}\right] - 1}$$

Therefore we have the energy expectation value $\overline{E}$ of the total quantum system Ω:

$$\overline{E} = E\left[\frac{1}{2m}p(\rho)^2 + \frac{1}{2}m\omega(\rho)^2 x(\rho)^2\right]$$

$$= \int_0^\infty J[\psi;\omega]D(\omega)d\omega$$

$$= \frac{1}{2}\hbar\overline{\omega} + \int_0^\infty \frac{\hbar\omega}{\exp\left[\frac{\hbar\omega}{k_BT}\right] - 1}D(\omega)d\omega.$$

Here we put

$$\overline{\omega} = \int_0^\infty \omega D(\omega)d\omega.$$

In the monatomic solid, each atom has 3 degree of freedom as a harmonic oscillation, so that if we consider the molar heat C of the considered monatomic solid, we have

$$C = 3N\frac{d\overline{E}}{dT}.$$

Here N is the Avogadro's number.

Here we consider the Debye model of the specific heat of the monatomic solid. So that we put

$$D(\omega) = \begin{cases} \dfrac{3}{\omega_D^3}\omega^2 & , (\omega < \omega_D), \\ 0 & , (\omega > \omega_D). \end{cases}$$

Here ω_D denotes the Debye frequency.

Then we have the molar heat C as follows:

$$C = 3N\frac{d\overline{E}}{dT}$$

$$= \frac{9N}{\omega_D^3}\frac{d}{dT}\int_0^{\omega_D} \frac{\hbar\omega^3}{\exp\left[\frac{\hbar\omega}{k_BT}\right] - 1}d\omega.$$

$$= \frac{9N}{\omega_D^3}\frac{\hbar^2}{k_BT^2}\int_0^{\omega_D} \frac{\omega^4 \exp\left[\frac{\hbar\omega}{k_BT}\right]}{\left(\exp\left[\frac{\hbar\omega}{k_BT}\right] - 1\right)^2}d\omega$$

$$= \frac{9N}{\omega_D^3}k_B^4\left(\frac{T}{\hbar}\right)^3\int_0^{\{\hbar\omega_D\}/\{k_BT\}} \frac{x^4e^x}{(e^x - 1)^2}dx$$

$$= 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T} \frac{x^4e^x}{(e^x - 1)^2}dx.$$

Here we put

$$\theta_D = \frac{\hbar\omega_D}{k_B}.$$

We call θ_D to be the Debye temperature. This gives the new meaning of the specific heat for the Debye model of a solid.

The Debye model shows the good coincidence between the theoretical result and the experimental result. The Debye model gives a very good model of the true physical phenomena.

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