Concepts for Specific Heat

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1 Introduction

These notes shall briefly explain general results for the internal energy and the specific heat for simple classical and quantum systems. The focus is on two model systems namely a

$$\text{Free particle with energy} \quad E = \frac{\mathbf{p}^2}{2m} \tag{1}$$

and a

$$\text{Harmonic oscillator with energy} \quad E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \,. \tag{2}$$

Applications to solid state physics are briefly discussed. The central input from thermodynamics is the probability P_i to find a systems in state i with energy E_i. In thermal equilibrium (i.e. in contact with a heat bath of temperature T), it is given by the *Boltzmann distribution* (or canonical distribution)

$$P_i = \frac{\mathrm{e}^{-\beta E_i}}{Z} \quad \text{with} \quad \beta = \frac{1}{k_B T} \quad \text{and the partition function} \quad Z = \sum_i \mathrm{e}^{-\beta E_i} \,.$$

In particular, we find that for $T = 0$, the system is always in its ground state with lowest energy. For finite temperatures, the system can be excited and the average energy is given by

$$U(T) = \sum_i E_i P_i = \sum_i \frac{E_i \mathrm{e}^{-\beta E_i}}{Z} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \,. \tag{3}$$

Here we evaluate U both for the classical and the quantum case and discuss the specific heat at constant volume $C_v = \frac{\partial U}{\partial T}$, where no work by compression or expansion is involved.

2 Classical Physics

2.1 Free particles

We start with a free particle in one dimension, which can take arbitrary momentum p. In this case the sum over i becomes an integral of p and $P(p_0)\delta p$ is the probability to find the system in the interval δp around p_0. Then the partition function reads

$$Z_1 = \int_{-\infty}^{\infty} \mathrm{d}p \, \mathrm{e}^{-\beta p^2/2m} = \sqrt{\frac{2m\pi}{\beta}} \quad \text{using the standard integral} \quad \int_{-\infty}^{\infty} \mathrm{d}x \, \mathrm{e}^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} \,.$$

The expectation value for the energy (3) provides

$$U_1 = -\sqrt{\frac{\beta}{2m\pi}} \frac{\partial}{\partial\beta} \sqrt{\frac{2m\pi}{\beta}} = \frac{k_B T}{2}$$

For three dimensions, we have

$$Z_3 = \int_{-\infty}^{\infty} \mathrm{d}^3 p \, e^{-\beta \mathbf{p}^2/2m} = \left(\int_{-\infty}^{\infty} \mathrm{d}p_x \, e^{-\beta p_x^2/2m} \right) \left(\int_{-\infty}^{\infty} \mathrm{d}p_y \, e^{-\beta p_y^2/2m} \right) \left(\int_{-\infty}^{\infty} \mathrm{d}p_z \, e^{-\beta p_z^2/2m} \right) = Z_1^3$$

and

$$U_3 = -\left(\frac{2m\pi}{\beta}\right)^{-3/2} \frac{\partial}{\partial\beta} \left(\frac{2m\pi}{\beta}\right)^{3/2} = \frac{3k_B T}{2} \, .$$

This can be directly extended to N particles and we find

> In thermal equilibrium a classical system on N free particles in D dimensions has the internal energy
>
> $$U = ND\frac{k_B T}{2} \tag{4}$$
>
> which is precisely $k_B T/2$ for each degree of freedom.

Then the specific heat (at constant volume) is given by

$$C_v = \frac{\partial U}{\partial T} = ND\frac{k_B}{2} \tag{5}$$

which holds, e.g., for ideal monoatomic gases.

2.2 Harmonic oscillator

In this case the energy (2) depends both on p and x and we have to integrate over both variables in order to get the correct distribution. We find

$$Z = \int_{-\infty}^{\infty} \mathrm{d}p \int_{-\infty}^{\infty} \mathrm{d}x \, e^{-\beta(p^2/2m + m\omega^2 x^2/2)} = \sqrt{\frac{2m\pi}{\beta}} \sqrt{\frac{2\pi}{\beta m\omega^2}} = \frac{2\pi}{\omega\beta}$$

and Eq. (3) provides

$$U = -\frac{\omega\beta}{2\pi} \frac{\partial}{\partial\beta} \frac{2\pi}{\omega\beta} = k_B T$$

Thus the average energy is just twice as large as for the free particle, as the energy is evenly distributed between the kinetic and potential energy. (This only holds for quadratic potentials!)

> In thermal equilibrium each oscillation mode has the internal energy
>
> $$U = k_B T \tag{6}$$

The atoms in a crystal have $3N_{\mathrm{atoms}}$ different oscillation modes as given by the vibration(phonon) spectrum. Thus we expect the specific heat

$$C_V = 3k_B N_{\mathrm{atoms}}$$

This is called the *Dulong-Petit law*, which is valid for solids at sufficiently high temperatures (as we will see below, room temperature is at the borderline for many substances). For iron, the atomic mass is $m = 55.845 \times 1.66 \times 10^{-27}\mathrm{kg} = 9.27 \times 10^{-26}\mathrm{kg}$ we thus estimate a specific heat per mass of $3k_B/m = 447$ J/(K kg). This is actually in surprisingly good agreement with the experimental value of about 440 J/(K kg) at room temperature.

2.3 Comment on phase space

Tacitly, it was assumed in the preceding subsections, that the probability should be evaluated for the variables momentum p_i and positions x_i. If one would use the energy to describe the states instead, we would find $Z = \int_0^\infty dE\, e^{-\beta E} = 1/\beta$ and $\langle E \rangle = \int_0^\infty dE\, E e^{-\beta E}/Z = k_B T$, for all systems. Thus one wonders, why the choice of space and momentum is the right one? The reason lies in classical Hamiltonian mechanics, which is based on a pair of position and (generalized) momentum coordinate for each degree of freedom to describe the state of the sytem. These variables (as well as other pairs obtained by canonical transformations) stand out, as they allow to predict the evolution of the system via the Hamilton equations (a generalization of Newtons law $m\mathbf{a} = \mathbf{F}$). [2]

3 Quantum Physics

3.1 Harmonic oscillator

Quantum physics tells us that the one-dimensional harmonic oscillator with angular frequency ω has discrete energies $E_n = (n + 1/2)\hbar\omega$ with $n = 0, 1, 2, \ldots$. We find the partition function

$$Z = \sum_{n=0}^\infty e^{-\beta E_n} = e^{\beta\hbar\omega/2} \sum_{n=0}^\infty e^{-\beta n\hbar\omega n} = \frac{e^{\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \quad \text{using} \sum_{n=0}^\infty a^n = \frac{1}{1-a} \quad \text{for } |a| < 1$$

and the average energy

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \ldots = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

This provides the specific heat

$$C_v = \frac{d}{dT}U = k_B \frac{\beta^2(\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

The result is plotted in Fig. 1. In the case $\beta\hbar\omega \gg 1$ (i.e. $k_B T \ll \hbar\omega$) this becomes vanishingly small, while for $\beta\hbar\omega \ll 1$ (i.e. $k_B T \gg \hbar\omega$) we obtain the classical result k_B. One says, that the degree of freedom freezes in around a temperature where $k_B T = \hbar\omega$.

As the energies of the phonons for solids are typically some tens of meV (while $k_B T = 25$ meV at room temperature, we expect modifications from the Dulong-Petit law addressed above. These become even more prominent, when lowering the temperature. The low-energy phonon spectrum is given by the acoustic phonons with a spectrum $\omega(\mathbf{q}) = c|\mathbf{q}|$, where c is the sound velocity (actually these are three branches with different and direction-dependent velocities). Assuming for simplicity, that all modes with $\hbar\omega(\mathbf{q}) < k_B T$ provide k_B to the specific heat, while those with higher frequency do not participate at all, we obtain that the specific heat is just given by $3k_B$ times the number of $\mathbf{q}$ values satisfying $|\mathbf{q}| < k_B T/(\hbar c)$. This number is proportional to the volume of a sphere, i.e., proportional to T^3. Thus the phonon part for the specific heat vanishes as T^3 if the temperature approaches the absolute zero, which is known as the *Debye law*.

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[2]Actually these canonical variables are the ones which also satisfy the canonical commutation relations $[\hat{p}_i, \hat{x}_j] = \delta_{ij}\frac{\hbar}{i}$ in quantum mechanics.
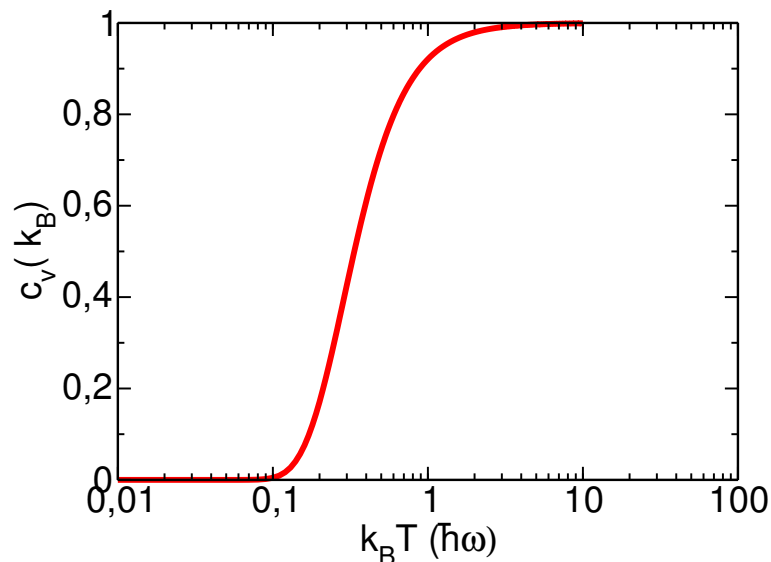
Figure 1: Specific heat of a phonon mode with angular frequency ω.

3.2 Single particle in a box

For a box of length L with infinite potentials outside, the eigenstates of the stationary Schrödinger equation are

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{with energy} \quad E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \quad \text{for} \quad n = 1, 2, \ldots$$

Thus we get the partition functions $Z = \sum_n e^{-\beta E_n}$. Now we set $\alpha = \beta\hbar^2\pi^2/2mL^2$. In the limit of $\alpha \ll 1$ (i.e. L is much larger than the thermal wavelength[3] $\hbar/\sqrt{2\pi mk_BT}$) we may replace the sum by an integral, as $e^{-\alpha n^2}$ changes only weakly between consecutive values of n. We obtain

$$Z \approx \int_0^\infty dx\, e^{-\alpha x^2} = \sqrt{\frac{\pi}{4\alpha}} \quad \text{and} \quad \langle E_n \rangle \approx \frac{1}{Z} \int_0^\infty dx\, \alpha x^2 e^{-\alpha x^2} = \frac{k_B T}{2}$$

This recovers the classical result. On the other hand for $\alpha \gg 1$, i.e. for low temperatures, the probabilities for P_n are vanishingly small for $n \geq 2$ and $P_1 = 1$. This we find

$$\langle E_n \rangle \approx E_1 = \frac{\hbar^2 \pi^2}{2mL^2}$$

In this case the specific heat becomes zero, in contrast to the result $k_B/2$ for high temperatures. Together with the preceding subsection this can be summarized as

Quantum physics provides discrete energy levels. If the spacing of these levels is small compared to k_BT, the classical result for the specific heat is recovered for a single particle. Otherwise, if k_BT becomes smaller than the spacing between the ground and first excited quantum level, the contribution to the specific heat vanishes. One says that the degree of freedom freezes in.

3.3 Many particles in a finite box

Next to the existence of discrete energy levels, the Pauli principle is another important consequence of quantum physics. It states that for systems of identical particles, each must be

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[3]Note a change in the factors π in order to match the conventional definition.

placed in a different level. Thus the lowest energy for N electrons in a one dimensional box is obtained by putting them into the levels $n = 1, 2, \ldots N/2$, where the electron spin allows to put two electron in each orbital level. The energy of the last filled level is denoted as the Fermi energy and we obtain

$$E_F = \frac{\hbar^2 \pi^2 N^2}{8mL^2} \quad \text{for a one-dimensional box}$$

which is actually a function of the one-dimensional electron density N/L. In the same spirit the three-dimensional case is treated. For a cube with length L the energy levels are $E_{n_x,n_y,n_z} = \frac{\hbar^2 \pi^2}{2mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$. Here one may use all combinations $n_x, n_y, n_z \geq 1$ with $n_x^2 + n_y^2 + n_z^2 \leq n_{\max}^2$. Geometrically, these are the points within a $1/8$ segment of a sphere of radius $n_{\max}$. As each point covers a volume $\Delta n_x \Delta n_y \Delta n_z = 1$, the volume of this sphere segment matches the number of points for large $n_{\max}$, where fluctuations at the surface become less relevant. thus we find $\pi n_{\max}^3/6$ different combinations (n_x, n_y, n_z). Taking into account spin, this allows to accommodate $N = \pi n_{\max}^3/3$ electrons and we find the Fermi energy

$$E_F = \frac{\hbar^2 \pi^2 n_{\max}^2}{2mL^2} = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{L^3} \right)^{2/3} \quad \text{for a cube with length } L \text{ in three dimensions.}$$

For an electron density $2/(3\text{Å})^3$ we obtain $E_F = 6$ eV, a typical value for a Fermi energy in a metal.

In order to be thermally excited, the electrons have to occupy levels above this Fermi energy. As E_F is huge compared to the thermal energy of $k_B T = 25$ meV, we find that the vast majority of electrons is frozen in and does not contribute to the specific heat. Thus C_v is much smaller than the value $N3k_B/2$ expected for a classical gas in three dimensions. In order to estimate the magnitude we assume, that only the states with $E_{n_x,n_y,n_z} \gtrsim E_F - 2k_B T$ contribute to the specific heat by thermal excitations (i.e. being partially excited to levels above E_F). Their number is

$$N_{\text{excitable}} = \frac{L^3 (2m)^{3/2}}{3\pi^2 \hbar^3} \left[E_F^{3/2} - (E_F - 2k_B T)^{3/2} \right] \approx \frac{L^3 (2m)^{3/2} \sqrt{E_F}}{2\pi^2 \hbar^3} 2k_B T = 3N \frac{k_B T}{E_F}$$

Assuming further that the excitably states contribute with the classical specific heat of free particles we find

$$C_v \approx N_{\text{excitable}} \frac{3}{2} k_B = \frac{9}{2} \frac{k_B^2}{E_F} T$$

The correct calculation provides an additional factor $\pi^2/9$, see [1]. The main point is that the specific heat is strongly reduced by the ratio $3k_B T/E_F$ (typically 1% at room temperature) and that it is proportional to the temperature.

> The Pauli principle restricts the possible excitations with low energy and thus the heat capacity of an electron gas with metallic density is strongly reduced compared to the classical result.

This actually solves the puzzle, why the Dulong-Petit value, solely based on the motion of the ions, is quite good for the specific heat of many materials at room temperature. As there are more electrons than ions, they should actually dominate the specific heat from a classical point of view. Due to the Pauli principle they are almost entirely frozen in!

References

[1] C. Kittel, *Introduction to Solid States Physics (seventh edition)* (John Wiley & Sons inc, New York, 1996)