1 Introduction

In this notes I want to 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

Free particle with energy \( E = \frac{p^2}{2m} \) \hspace{1cm} (1)

and a

Harmonic oscillator with energy \( E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 \) \hspace{1cm} (2)

Applications to solid state physics are briefly discussed. The central input is that thermodynamics tells us that in thermal equilibrium the probability \( P_i \) to find a systems in state \( i \) with energy \( E_i \) is given by the Boltzmann distribution (or canonical distribution)

\[
P_i = \frac{e^{-\beta E_i}}{Z} \quad \text{with} \quad \beta = \frac{1}{k_B T} \quad \text{and the partition function} \quad Z = \sum_i e^{-\beta E_i}
\]

In particular, we find that for \( T = 0 \), the system is always in its ground state with lowest energy. In the following, the two indefinite integrals

\[
\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad \text{and} \quad \int_{-\infty}^{\infty} dx x^2 e^{-ax^2} = \sqrt{\frac{\pi}{4a^3}} \quad \text{for} \quad a > 0
\]

are frequently used.

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 \( \delta p \) around \( p_0 \). Then the partition function reads

\[
Z_1 = \int_{-\infty}^{\infty} dp e^{-\beta p^2/2m} = \sqrt{\frac{2m\pi}{\beta}}
\]

The expectation value for the kinetic energy is

\[
\left\langle \frac{p^2}{2m} \right\rangle = \frac{1}{Z_1} \int_{-\infty}^{\infty} dp \frac{p^2}{2m} e^{-\beta p^2/2m} = \sqrt{\frac{\beta}{2m\pi}} \frac{1}{2m} \sqrt{\frac{\pi(2m)^3}{4\beta^3}} = \frac{1}{2\beta} = \frac{k_B T}{2}
\]
For three dimensions, we have

\[
Z_3 = \int_{-\infty}^{\infty} d^3p \, e^{-\beta p^2/2m} = \left( \int_{-\infty}^{\infty} dp_x \, e^{-\beta p_x^2/2m} \right) \left( \int_{-\infty}^{\infty} dp_y \, e^{-\beta p_y^2/2m} \right) \left( \int_{-\infty}^{\infty} dp_z \, e^{-\beta p_z^2/2m} \right) = Z_1^3
\]

and

\[
\langle \frac{p^2}{2m} \rangle = \langle \frac{p_x^2}{2m} \rangle + \langle \frac{p_y^2}{2m} \rangle + \langle \frac{p_z^2}{2m} \rangle
\]

with

\[
\langle \frac{p_x^2}{2m} \rangle = \frac{1}{Z_3} \left( \int_{-\infty}^{\infty} dp_x \, \frac{p_x^2}{2m} e^{-\beta p_x^2/2m} \right) \left( \int_{-\infty}^{\infty} dp_y \, e^{-\beta p_y^2/2m} \right) \left( \int_{-\infty}^{\infty} dp_z \, e^{-\beta p_z^2/2m} \right) = \frac{k_B T}{2}
\]

and similarly for \( \langle \frac{p_y^2}{2m} \rangle \) and \( \langle \frac{p_z^2}{2m} \rangle \). Adding up these contributions provides

\[
\langle \frac{p^2}{2m} \rangle = \frac{3k_B T}{2}
\]

This can be directly extended to \( N \) particles and we find

In thermal equilibrium a system on \( N \) free particles in \( D \) dimensions has the internal energy

\[
E = ND \frac{k_B T}{2}
\]

which is precisely \( k_B T/2 \) for each degree of freedom

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

\[
c_v = \frac{dE}{dT} = ND \frac{k_B}{2}
\]

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

### 2.2 Harmonic oscillator

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

\[
Z = \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \, e^{-\beta(p^2/2m+m\omega^2x^2)/2} = \sqrt{\frac{2m\pi}{\beta}} \sqrt{\frac{2\pi}{\beta m\omega^2}}
\]

and

\[
\langle \frac{p^2}{2m} + \frac{m\omega^2x^2}{2} \rangle = k_B T
\]

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

\[
E = k_B T
\]

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

\[
\frac{c_v}{N_{\text{atoms}}} = 3k_B
\]
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 \(m = 55.845 \times 1.66 \times 10^{-27} \text{kg} = 9.27 \times 10^{-26} \text{kg}\) we thus estimate a specific heat of \(3k_B/m = 447 \text{ J/(K kg)}\). This is actually a surprisingly good approximation for the experimental value of about 440 J/(K kg) at room temperature.

2.3 Comment on phase space

Tactically, 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

\[
Z = \int_0^\infty dE \, e^{-\beta E} = 1/\beta \quad \text{and} \quad \langle E \rangle = \int_0^\infty dE \, E \, e^{-\beta E} / Z = k_B T,
\]

for all systems. Thus one wonders, why the choice of space and momentum is the right one? The reason lies in classical mechanics, where one obtains one set of (generalized) momentum and position for each degree of freedom. Thus these variables (as well as other pairs obtained by canonical transformations) stand out.\(^1\)

3 Quantum Physics

3.1 Harmonic oscillator

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

\[
Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \frac{e^{\beta \hbar \omega/2}}{1 - e^{-\beta \hbar \omega}}
\]

and the average energy

\[
\langle E_n \rangle = \frac{1}{Z} \sum_{n=0}^{\infty} E_n e^{-\beta E_n} = -\frac{1}{Z} \frac{\partial Z(\beta)}{\partial \beta} = \ldots = \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}
\]

This provides the specific heat

\[
C_V = \frac{d}{dT} \langle E_n \rangle = k_B \frac{\beta^2 (\hbar \omega)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}
\]

The results 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 \(\omega(q) = c|q|\), where \(c\) is the sound velocity (actually these are three branches with different and direction-dependent velocities). Assuming for simplicity, that all modes with \(\hbar \omega(q) < k_B T\) provide \(k_B\) to the specific heat, while those with higher frequency do not participate at all, be obtain that the specific heat is just given by \(3k_B\) times the number of \(q\) values satisfying \(|q| < k_B T/(\hbar c)\). 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 at \(T^3\) if the temperature approaches the absolute zero, which is known as the Debye law.

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

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

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right)$$

with energy

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \quad \text{for} \quad n = 1, 2, \ldots$$

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 $\hbar / \sqrt{2\pi m K_B T^2}$) we may replace the sum by an integral, as $e^{-\alpha x^2}$ 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 high 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 $k_B T$, the classical result for the specific heat is recovered for a single particle. Otherwise, if the $k_B T$ becomes smaller than 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

Note that the are some factors $\pi$ changed, in order to match other conventions
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 level

\[
E_F = \frac{\hbar^2 \pi^2 N^2}{8mL^2}
\]

in one dimension

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 \( n_x^2 + n_y^2 + n_z^2 \leq n_{\text{max}}^2 \), and their number can be estimated by \( \pi n_{\text{max}}^3/6 \).

**Question 1:** Derive this number!

Taking into account spin, this allows to accommodate \( N = \pi n_{\text{max}}^3/3 \) electrons and we find

\[
E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{L^3}\right)^{2/3}
\]

for a cube with length \( L \) in three dimensions.

For an electron density \( 2/(3\text{Å})^3 \) we obtain \( E_F = 6 \text{ eV} \), 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 \( k_B T = 25 \text{ meV} \), we find that the vast majority of electron is frozen in and does not contribute to the specific heat. Thus \( c_v \) is much smaller than the value \( N^3 k_B/2 \) 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

\[
c_v \approx N_{\text{excitable}} \frac{3}{2} k_B = \frac{9}{2} k_B \frac{k_B T}{E_F}
\]

More detailed calculations provide an additional factor \( \pi^2/9 \), see [1]. The main point is that the specific heat is strongly reduced by the ratio \( 3k_B T/E_F \) (i.e. 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 degenerate systems is strongly reduced compared to the classical result.

4 References