Thermodynamics Lecture Notes: Chapter 5

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Contents

5 Statistical Thermodynamics II

5.1 Microstates and Macrostates

Imagine a system with two coins: Coin-A and Coin-B. If you toss them, there are four possible states with equal probabilities, $\frac{1}{4}$, namely

- Coin-A head and Coin-B head
- Coin-A head and Coin-B tail
- Coin-A tail and Coin-B head
- Coin-A tail and Coin-B tail

Each of the four states is called microstate. All microstates can be realised with an equal probability. However, more relevant states are macrostates, which could be for example:

- Both coins are head
- One of the coins is head
- None of the coins is head

where the first and last macrostates contain one microstate and the second one contains two microstates. Therefore, the probability for the second macrostate to be realised is twice as large as for the other two.

In thermodynamics, a microstate of a gas can be defined by the position and velocity of the every gas molecule, a macrostate is described by more global quantities such as a volume, pressure and temperature. A set of different microstates may give the same macrostate. All the microstates have an equal probability to be realised. The probability to realise a particular macrostate is proportional to the number of microstates resulting in that macrostate.

We denote Ω to be the number of microstates for a particular macrostate.

5.2 Microstates and thermal equilibrium (definition of Temperature)

Let us consider two thermodynamic systems, which are in thermal contact, but isolated from their surroundings, i.e. they can exchange thermal energy between them but not with the outside. The first system has the energy E_1 and the second system E_2. The total energy, $E = E_1 + E_2$, is constant, since there is no energy exchange with outside. Therefore, E_1 alone is enough to determine the microstates of the joint system.

We denote that $\Omega_1(E_1)$ as the number of the microstates in the first system and $\Omega_2(E_2)$ for the second system. The total system then has $\Omega_1(E_1)\Omega_2(E_2)$ microstates. When the total system reaches equilibrium, E_1 and E_2 become stable. The system appears to take a macroscopic configuration that maximises the number of microstates, which corresponds to the highest probability, i.e. the most likely.

Since $\Omega_1(E_1)\Omega_2(E_2)$ is maximum,

$$\frac{d}{dE_1}\left[\Omega_1(E_1)\Omega_2(E_2)\right] = 0 \tag{1}$$

It follows that

$$\begin{aligned} \frac{d}{dE_1}\left[\Omega_1(E_1)\Omega_2(E_2)\right] &= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) + \frac{d\Omega_2(E_2)}{dE_1}\Omega_1(E_1) \\ &= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) + \frac{d\Omega_2(E_2)}{dE_2}\frac{dE_2}{dE_1}\Omega_1(E_1) \end{aligned} \tag{2}$$

From $E = E_1 + E_2 =$ constant, $dE = dE_1 + dE_2 = 0$, thus $dE_1 = -dE_2$. Then we have,

$$\frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2} = 0 \tag{3}$$

or

$$\frac{1}{\Omega_1(E_1)}\frac{d\Omega_1(E_1)}{dE_1} = \frac{1}{\Omega_2(E_2)}\frac{d\Omega_1(E_2)}{dE_2} \tag{4}$$

By noting

$$\frac{d\ln f(x)}{dx} = \frac{df(x)}{dx}\frac{d\ln f(x)}{df(x)} = \frac{1}{f(x)}\frac{df(x)}{dx} \tag{5}$$

It follows that

$$\frac{d\ln\Omega_1(E_1)}{dE_1} = \frac{d\ln\Omega_2(E_2)}{dE_2} \tag{6}$$

which is the equilibrium condition. In thermodynamics, this means that two systems are at the same temperature. Therefore, the temperature is defined as

$$\frac{1}{kT} = \frac{d\ln\Omega}{dE} \tag{7}$$

with k being the Boltzmann constant.

5.3 Boltzmann Factor

We consider a small system A in thermal contact with a heat reservoir A', which means A' is much larger than A, and denote $P_r(E_r)$ to be the probability to find A in any one particular microstate r of energy E_r.

The energy of the total system, A+A', E_0 is constant. It follows that

$$P_r(E_r) \propto \Omega'(E_0 - E_r) \tag{8}$$

where $\Omega'(E_0 - E_r)$ is the number of microstates accessible by A' when its energy is $E_0 - E_r$. Since A is much smaller than A', $E_r \ll E_0$. The Taylor expansion of $f(x_0+x)$ for $\epsilon = \frac{x}{x_0} \ll 1$, is given by

$$f(x_0 + x) = f(x_0 + \epsilon x_0) \approx f(x_0) + \frac{df}{d\epsilon}\epsilon \tag{9}$$

where higher order in ϵ is neglected. Since $x = \epsilon x_0$ and x_0 is a constant,

$$\frac{d}{d\epsilon} = \frac{dx}{d\epsilon}\frac{d}{dx} = x_0 \frac{d}{dx} = x_0 \frac{d}{d(x_0 + x)} \tag{10}$$

It follows that

$$f(x_0 + x) \approx f(x_0) + \frac{df}{d(x_0 + x)} \epsilon x_0 = f(x_0) + \frac{df}{d(x_0 + x)} x \tag{11}$$

If we take $f(x_0 + x)$ to be $\ln \Omega'(E_0 - E_r)$, where $x_0 = E_0$ and $x = -E_r$, we obtain

$$\ln \Omega'(E_0 - E_r) \approx \ln \Omega'(E_0) - \frac{d \ln \Omega'(E_0 - E_r)}{d(E_0 - E_r)}\Big|_{E_r=0} E_r \tag{12}$$

Since

$$\frac{d \ln \Omega'(E_0 - E_r)}{d(E_0 - E_r)}\Big|_{E_r=0} = \frac{1}{kT} \tag{13}$$

T being the temperature of the reservoir A', which is also the temperature of A when they are in thermal equilibrium, and

$$\ln \Omega'(E_0 - E_r) \approx \ln \Omega'(E_0) - \frac{E_r}{kT}, \tag{14}$$

we obtain

$$\Omega'(E_0 - E_r) = C \exp(-\frac{E_r}{kT}) \tag{15}$$

where C is a constant. It follows that

$$P_r(E_r) \propto e^{-\frac{E_r}{kT}} \tag{16}$$

The term $e^{-\frac{E}{kT}}$ is called Boltzmann factor.

5.4 Maxwell-Boltzmann distribution of velocities of gas particles

Maxwell Distribution

The energy of a gas molecule with a mass m and velocity $\vec{v} = (v_x, v_y, v_z)$ is given by,

$$E = \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) \tag{17}$$

Using the Boltzmann factor, $e^{-\frac{E}{kT}}$, the probability to have a velocity between $\vec{v} = (v_x, v_y, v_z)$ and $\vec{v} + d\vec{v} = (v_x + dv_x, v_y + dv_y, v_z + dv_z)$ is given by

$$f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)\right] dv_x dv_y dv_z \tag{18}$$

which is a Gauss distribution.

A Gauss distribution in one dimension is generally given by

$$G_{\sigma,x_0}(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right) \tag{19}$$

where x_0 is the mean

$$\langle x \rangle = \int_{-\infty}^{\infty} x G_{\sigma,x_0}(x) dx = x_0 \tag{20}$$

and σ^2 the variance, i.e.

$$Var(x) \equiv \langle (x-x_0)^2 \rangle \tag{21}$$

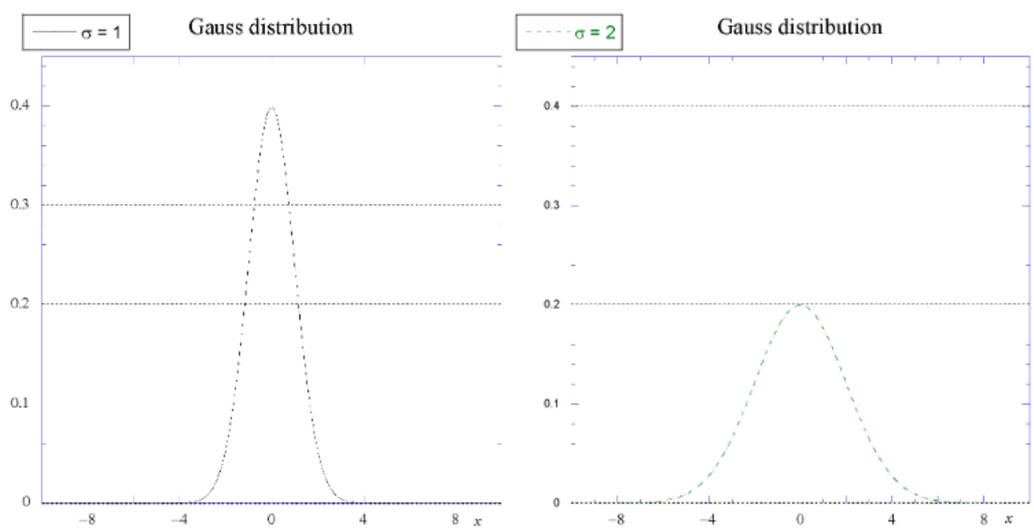
leading to

$$\langle (x-x_0)^2 \rangle = \int_{-\infty}^{\infty} (x-x_0)^2 G_{\sigma,x_0}(x) dx = \int_{-\infty}^{\infty} (x-x_0)^2 \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right) dx = \sigma^2 \tag{22}$$

So the distribution of the velocity components are given by the Gauss distribution with

$$x_0 = 0, \text{ and } \sigma^2 = \frac{m}{kT} \tag{23}$$

An important characteristic of a Gauss distribution is that the probability for x to be between $x_0 - \sigma$ and $x_0 + \sigma$ is $\sim 68.2\%$. Between $x_0 - 2\sigma$ and $x_0 + 2\sigma$, the probability for x is $\sim 95.4\%$, and between $x_0 - 3\sigma$ and $x_0 + 3\sigma$, it is 99.7%.



By recalling, $v^2 = v_x^2 + v_y^2 + v_z^2$ and $dv_x dv_y dv_z = v^2 \sin\theta dv d\theta d\phi$, it follows that

$$\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)\right) dv_x\, dv_y\, dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m}{2kT}v^2\right) v^2 \sin\theta dv d\theta d\phi \tag{24}$$

Integration over θ and ϕ gives then

$$
\begin{aligned}
F(v)dv &= \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp(-\frac{m}{2kT}v^2)dv \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi \\
&= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp(-\frac{m}{2kT}v^2)dv
\end{aligned}
\tag{25}
$$

where

$$
F(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \tag{26}
$$

gives the probability distribution of the velocity, v.

Using $F(v)$, called the Maxwell distribution of speeds, the average velocity, $\langle v \rangle$, is given by

$$
\langle v \rangle = \int_0^{\infty} vF(v)dv \tag{27}
$$

Similarly, v_{rms} is given by

$$
v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\int_0^{\infty} v^2 F(v)dv} \tag{28}
$$

Using the integrals discussed in the "Mathematical Notes",

$$
\begin{aligned}
I_2(a) &= \int_0^{\infty} x^2 \exp(-ax^2)dx = \frac{\sqrt{\pi}}{4} a^{-\frac{3}{2}} \\
I_4(a) &= \int_0^{\infty} x^4 \exp(-ax^2)dx = \frac{3\sqrt{\pi}}{8} a^{-\frac{5}{2}}
\end{aligned}
\tag{29}
$$

we obtain

$$
\begin{aligned}
\int_0^{\infty} F(v)dv &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{\infty} v^2 \exp\left(-\frac{m}{2kT}v^2\right) dv \\
&= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{\sqrt{\pi}}{4} \left(\frac{m}{2kT}\right)^{-3/2} = 1
\end{aligned}
\tag{30}
$$

i.e. the probability function, $F(v)$, is properly normalised, and

$$
\begin{aligned}
\int_0^{\infty} v^2 F(v)dv &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{\infty} v^4 \exp\left(-\frac{m}{2kT}v^2\right) dv \\
&= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{3\sqrt{\pi}}{8} \left(\frac{m}{2kT}\right)^{-5/2} = \frac{3kT}{m}
\end{aligned}
\tag{31}
$$

i.e.

$$
v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\int_0^{\infty} v^2 F(v)dv} = \sqrt{\frac{3kT}{m}} \tag{32}
$$

which was needed in the previous section.

Equally, by using

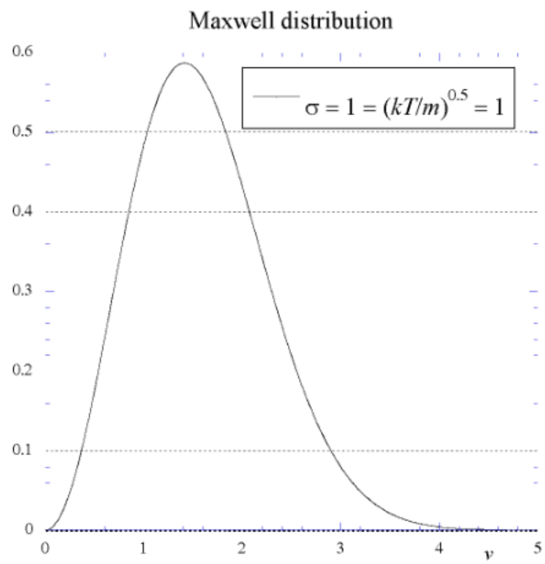
$$
I_3(a) = \int_0^{\infty} x^3 \exp(-ax^2)dx = \frac{1}{2} a^{-2} \tag{33}
$$

we obtain

$$\begin{aligned}\int_0^\infty vF(v)dv &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{m}{2kT}v^2\right) dv \\ &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{m}{2kT}\right)^{-2} = \sqrt{\frac{8kT}{\pi m}}\end{aligned} \tag{34}$$

Thus, the average velocity is given by

$$\langle v \rangle = \int_0^\infty vF(v)dv = \sqrt{\frac{8kT}{\pi m}} \tag{35}$$



Lastly, the most probable velocity v_{mp} is given by:

$$\frac{d}{dv}F(v = v_{mp}) = 0 \tag{36}$$

From $F(v)$, it follows that

$$\frac{dF(v)}{dv} = 8\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left[v \exp\left(-\frac{m}{2kT}v^2\right) - \frac{mv^3}{2kT} \exp\left(-\frac{m}{2kT}v^2\right)\right] \tag{37}$$

thus,

$$\exp(-\frac{m}{2kT}v_{mp}^2) - \frac{mv_{mp}^2}{2kT} \exp(-\frac{m}{2kT}v_{mp}^2) = 0 \tag{38}$$

leading to

$$\frac{mv_{mp}^2}{2kT} = 1 \tag{39}$$

and therefore, we obtain

$$v_{mp} = \sqrt{\frac{2kT}{m}}. \tag{40}$$

Note that the trivial solution, $v = 0$, corresponds to the minimum.

It is interesting to remark that

$$v_{mp} = \sqrt{\frac{2kT}{m}} \approx 1.414\sqrt{\frac{kT}{m}}, \quad \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \approx 1.596\sqrt{\frac{kT}{m}}, \quad v_{rms} = \sqrt{\frac{3kT}{m}} \approx 1.732\sqrt{\frac{kT}{m}} \tag{41}$$

i.e. the three velocities are not so far apart. It is interesting to note that

$$v_{rms}^2 = \frac{3kT}{m} = 3\sigma^2 \tag{42}$$

where σ is the standard deviation of the Gauss distribution giving the probability distribution of the velocity components.