General Physics II at EPFL

(2018-2019 SS, Wed 17:15-19:00 and Thu 8:15-10:00, Exercise Thu 10:15-12:00)

Thermodynamic (3rd week)

Boltzmann Factor

Microstates and Macrostates

Imagine a system with two coins: Coin-A and Con-B. If you toss them, there are four possible states with equal probabilities, 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 four states are called microstates. All the microstates can be realised with an equal probability. However, a more relevant states are macrostates, which are

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 two. Therefore, the probability for the second macrostate to be realised is twice larger than 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 are described by more global quantities such as a volume, pressure and thermal energy and a set of different microstates give a same macrostate. All the microstates have an equal probability to be realised. The probability to be realised for a particular macrostate is proportional to the number of microstates giving that macrostate. We denote Ω to be the number of microstates for a particular macrostate.

Thermal Equilibrium and Definition of Temperature

Let us consider the two systems, which are in thermal connect but isolated from their surroundings, i.e. they can exchange thermal energies between the two but not with outside. The first system has 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. most likely.

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

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

It follows that

$$\frac{d}{dE_1}\left[\Omega_1(E_1)\Omega_2(E_2)\right] = \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) + \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_1}$$
$$= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) + \Omega_1(E_1)\frac{dE_2}{dE_1}\frac{d\Omega_2(E_2)}{dE_2}$$

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

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

or

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

By noting

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

it follows that

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

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

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

with k being the Boltzmann constant.

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

$$P_r(E_r) \propto \Omega'(E^0 - E_r)$$

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', $E_r << E^0$. The Taylor expansion of $f(x_0 + x)$ for $\varepsilon = x/x_0 << 1$, is given by

$$f(x_0 + x) = f(x_0 + x_0\varepsilon) \approx f(x_0) + \left(\frac{df}{d\varepsilon}\right)_{\varepsilon=0}\varepsilon$$

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

$$\frac{d}{d\varepsilon} = \frac{dx}{d\varepsilon}\frac{d}{dx} = x_0\frac{d}{dx} = x_0\frac{d}{d(x_0 + x)}$$

it follows that

$$f(x_0 + x) \approx f(x_0) + \left(\frac{df}{d(x_0 + x)}\right)_{\varepsilon=0}\varepsilon x_0 = f(x_0) + \left(\frac{df}{d(x_0 + x)}\right)_{x=0} x$$

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

$$\ln\Omega\left(E^0 - E_r\right) \approx \ln\Omega\left(E^0\right) - \left(\frac{d\ln\Omega\left(E^0 - E_r\right)}{d\left(E^0 - E_r\right)}\right)_{E_r=0} E_r$$

Since

$$\left(\frac{d\ln\Omega\left(E^0 - E_r\right)}{d\left(E^0 - E_r\right)}\right)_{E_r=0} = \frac{1}{kT}$$

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

$$\ln\Omega\left(E^0 - E_r\right) \approx \ln\Omega\left(E^0\right) - \frac{E_r}{kT}$$

thus

$$\Omega\left(E^0 - E_r\right) = Ce^{-E_r/kT}$$

where C is a constant. It follows that

$$P_r\left(E_r\right) \propto e^{-E_r/kT}$$

The term, $e^{-E/kT}$, is called a Boltzmann factor.

Velocity components and velocity distribution of molecule

Maxwell Distribution (391)

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

$$E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right)$$

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

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

which is a Gauss distribution.

A Gauss distribution in one dimension is generally given by

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

where x_0 is the mean

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

and σ variance, i.e.

$$Var(x) \equiv \left\langle\left(x - x_0\right)^2\right\rangle$$

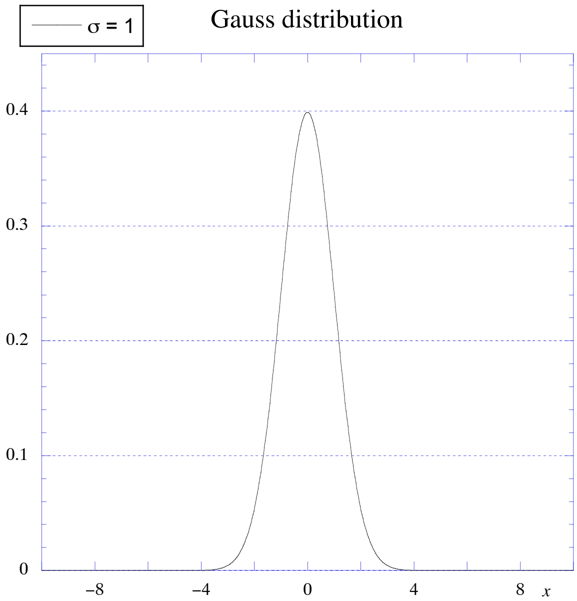
leading to

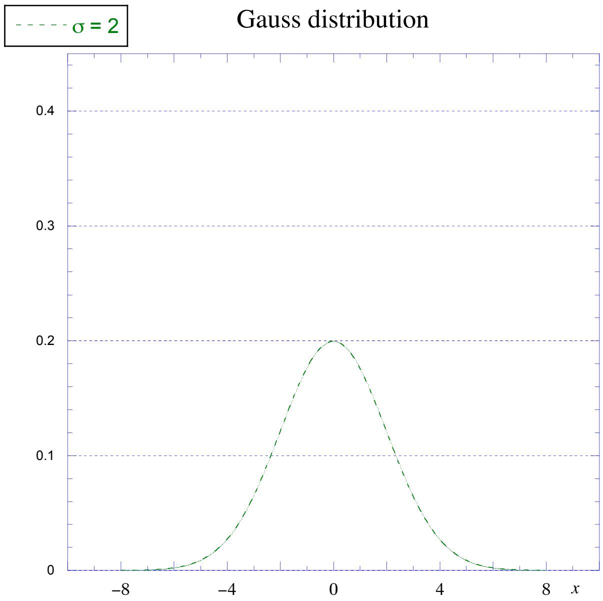
$$\left\langle\left(x - x_0\right)^2\right\rangle = \int_{-\infty}^{\infty}\left(x - x_0\right)^2 G_{\sigma,x_0}(x)dx = \int_{-\infty}^{\infty} x'^2 G_{\sigma,x_0}\left(x' + x_0\right)dx = \frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{\infty} x'^2 \exp\left[-\frac{x'^2}{2\sigma^2}\right]dx = \sigma^2$$

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

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

An important characteristics of a Gauss distribution is that the probability for x to be between $x_0 - \sigma$ and $x_0 + \sigma$ is ~68.2%. Equally for between $x_0 - 2\sigma$ and $x_0 + 2\sigma$, ~95.4%, and for between $x_0 - 3\sigma$ and $x_0 + 3\sigma$, ~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

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

Integration over θ and ϕ gives

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

where

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

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

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

Similarly, v_{rms} is given by

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

Using the integrals given in the next section,

$$I_2(a) = \int_0^{\infty} x^2 \exp\left(-ax^2\right) dx = \frac{\sqrt{\pi}}{4} a^{-3/2}$$

$$I_4(a) = \int_0^{\infty} x^4 \exp\left(-ax^2\right) dx = \frac{3\sqrt{\pi}}{8} a^{-5/2}$$

we obtain

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

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

$$\int_0^\infty v^2 F(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^4 \exp\left(-\frac{m}{2kT}v^2\right)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{3\sqrt{\pi}}{8}\left(\frac{m}{2kT}\right)^{-5/2} = \frac{3}{2}\left(\frac{m}{2kT}\right)^{-1} = \frac{3kT}{m}$$

i.e.

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

which was needed in the previous section.

Equally, by using

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

we obtain

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

thus the average velocity is given by

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

Lastly, the most probable velocity v_{mp} given

$$\frac{d}{dv}F\left(v = v_{\text{mp}}\right) = 0$$

From $F(v)$, it follows that

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

thus

$$\exp\left(-\frac{m}{2kT}v_{\text{mp}}^2\right) - \frac{mv_{\text{mp}}^2}{2kT}\exp\left(-\frac{m}{2kT}v_{\text{mp}}^2\right) = 0\,.$$

leading to

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

therefore,

$$v_{\text{mp}} = \sqrt{\frac{2kT}{m}}$$

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

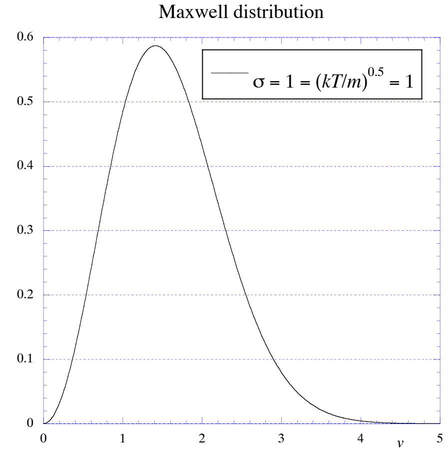
It is interesting to remark that

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

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

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

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


Maxwell distribution
σ = 1 = (kT/m)^0.5 = 1
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
v
5

Special subject on distributions

Let us consider a variable x, which can take a value between x_l to x_u. The variable x can be **discrete**, such as the number of population in the Swiss towns and villages, or **continuous** such as the absolute value of the speed of cars on the road. We then make n measurements of x, i.e. $x_1, x_2, \cdots$ to x_n.

Average and root mean squared are given by

$$\langle x \rangle = \frac{1}{n}\sum_{i=1}^{n} x_i$$

and

$$\sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2},$$

respectively, and a probability to have a value x_i by

$$P(x_i) = \frac{1}{n} x_i$$

leading the average to be

$$\langle x \rangle = \sum_{i=1}^{n} P(x_i)$$

One can "bin" x with a finite interval, dx, and denote $n(x_i)dx$ to be the number of measurements where x is between x_i and $x_i + dx$. Then the average becomes

$$\langle x \rangle = \frac{1}{n}\sum_{i=1}^{n} x_i n(x_i)\, dx = \frac{1}{n}\sum_{x=x_l}^{x_u} x n(x)\, dx = \sum_{x=x_l}^{x_u} xP(x)\, dx$$

For continuous variable, in the limit of $n \to \infty$ and $dx \to 0$, $n(x)$ (so as $P(x)$) becomes a smooth function of x. Then the sum can be replaced by the integral, i.e.

$$\langle x \rangle = \frac{1}{N}\int_{x_l}^{x_u} xn(x)dx = \int_{x_l}^{x_u} xP(x)dx$$

Some Tricks for Integral

Here are some useful notes on the integration.

$$I_n(a) = \int_0^\infty x^n \exp\left(-ax^2\right)dx$$

For $n = 0$, by introducing $x' = \sqrt{a}x$

$$I_0(a) = \int_0^\infty \exp\left(-ax^2\right)dx = \frac{1}{\sqrt{a}}\int_0^\infty \exp\left(-x'^2\right)dx'$$

We now consider the following integral:

$$\int_0^\infty \exp\left(-x^2\right)dx \int_0^\infty \exp\left(-y^2\right)dy = \int_0^\infty \int_0^\infty \exp\left(-x^2\right)\exp\left(-y^2\right)dxdy = \int_0^\infty \int_0^\infty \exp\left[-\left(x^2 + y^2\right)\right]dxdy$$

By changing to the polar coordinate system, $x = r\cos\phi$, $y = r\sin\phi$, and $dxdy = rdrd\phi$, we have

$$\int_0^\infty \int_0^\infty \exp\left[-\left(x^2 + y^2\right)\right]dxdy = \frac{1}{4}\int_0^\infty \int_0^{2\pi} r\exp\left(-r^2\right)drd\phi = \frac{\pi}{2}\int_0^\infty r\exp\left(-r^2\right)dr = -\frac{\pi}{4}\exp\left(-r^2\right)\Big]_{r=0}^{\infty} = \frac{\pi}{4}$$

leading to

$$\int_0^\infty \exp\left(-x^2\right)dx = \frac{\sqrt{\pi}}{2}$$

Finally, we obtain

$$I_0(a) = \int_0^\infty \exp(-ax^2)dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

For $n = 1$, it follows that

$$I_1(a) = \int_0^\infty x\exp(-ax^2)dx = -\frac{1}{2a}\exp(-ax^2)\Big]_0^\infty = \frac{1}{2a}$$

and for $n = 2$,

$$I_2(a) = \int_0^\infty x^2\exp(-ax^2)dx = -\frac{d}{da}I_0(a) = -\frac{\sqrt{\pi}}{2}\frac{d}{da}a^{-1/2} = \frac{\sqrt{\pi}}{4}a^{-3/2}$$

For n = 3 and 4 , we have

$$I_3(a) = \int_0^\infty x^3\exp(-ax^2)dx = -\frac{d}{da}I_1 = -\frac{1}{2}\frac{d}{da}a^{-1} = \frac{1}{2}a^{-2}$$

$$I_4(a) = \int_0^\infty x^4\exp(-ax^2)dx = -\frac{d}{da}I_2(a) = \frac{\sqrt{\pi}}{4}\frac{d}{da}a^{-3/2} = \frac{3\sqrt{\pi}}{8}a^{-5/2}$$