

FYS2160 — Oblig 5

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Exercise 1

a) The partition function is defined by

$$Z = \sum_{\text{All states } i} e^{-\varepsilon_i/kT}$$

where ε_i is the energy of the state i .

We are now looking at one particle with motion described by the states $n_x = 0, 1, 2, \dots$, and the energy of state n_x is $\varepsilon(n_x) = an_x^2$, where $a = h^2/(8mL^2)$. The partition function for this particle is then

$$Z_{1,x} = \sum_{n_x=0}^{\infty} e^{-an_x^2/kT}$$

As discussed on the previous week's project, in the high-temperature limit, the above expression can be approximated by an integral (see figure 1). This leads us to

$$\begin{aligned} Z_{1,x} &\approx \int_0^{\infty} e^{-an_x^2/kT} dn_x \\ \lambda^2 \equiv a/kT &\rightarrow = \int_0^{\infty} e^{-\lambda^2 n_x^2} dn_x \\ &= \frac{\sqrt{\pi}}{2\lambda} \\ &= \frac{1}{2} \sqrt{\frac{kT\pi}{h^2} 8mL^2} \\ &= \sqrt{\frac{2\pi mkT}{h^2}} L \end{aligned} \tag{1}$$

where I used the solution to the integral given in the exercise:

$$\int_0^{\infty} e^{-\lambda^2 x^2} dx = \frac{\sqrt{\pi}}{2\lambda}$$

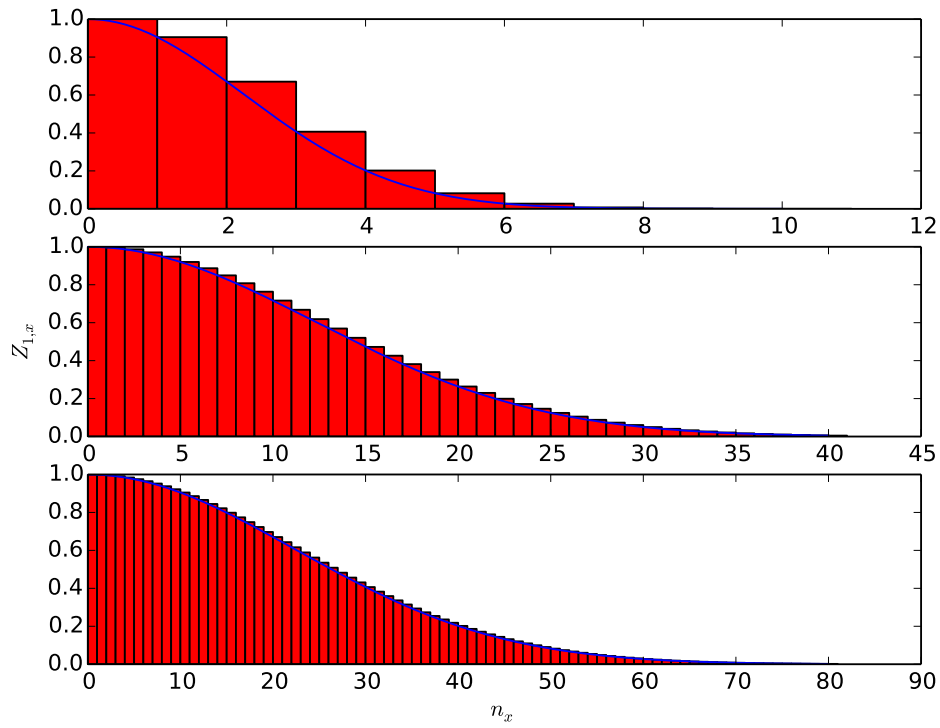


Figure 1: Illustration that the partition function becomes more and more equal an integral for high temperatures. The figure shows three plots with the terms in the partition function plotted on the x -axis and for increasing temperatures down (top is lowest temperature, bottom is highest).

b) For 2 particles moving in one direction, the partition function would read

$$\begin{aligned}
Z_{2,x} &= \sum_{n_{x_1}=0}^{\infty} \sum_{n_{x_2}=0}^{\infty} e^{-[\varepsilon(n_{x_1})+\varepsilon(n_{x_2})]/kT} \\
&= \sum_{n_{x_1}=0}^{\infty} \sum_{n_{x_2}=0}^{\infty} e^{-\varepsilon(n_{x_1})/kT} e^{-\varepsilon(n_{x_2})/kT} \\
&= \sum_{n_{x_1}=0}^{\infty} e^{-\varepsilon(n_{x_1})/kT} \sum_{n_{x_2}=0}^{\infty} e^{-\varepsilon(n_{x_2})/kT} \\
&= Z_{1,x}^2
\end{aligned}$$

In the general case, we get

$$Z_{N,x} = Z_{1,x}^N$$

Note, however, that this is for a gas which is made up of distinguishable particles. The ideal gas in question, can, however, be assumed to be made up of indistinguishable particles, meaning we can swap any two particles in different states and still have the same gas. Some particle states have therefore been counted twice, resulting in¹

$$Z_{N,x} = \frac{1}{N!} Z_{1,x}^N = \frac{1}{N!} \left(\frac{2\pi m kT}{h^2} \right)^{N/2} L^N \quad (2)$$

c) The total average energy of the gas is

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

where $\beta = 1/(kT)$. Using the partition function in eq. (2), we get

$$\begin{aligned}
U &= - \left[\frac{1}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{N/2} L^N \right]^{-1} \frac{\partial}{\partial \beta} \left[\frac{1}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{N/2} L^N \right] \\
&= - \left[\frac{1}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{N/2} L^N \right]^{-1} \left[\frac{1}{N!} \left(\frac{2\pi m}{h^2} \right)^{N/2} L^N \right] \frac{\partial}{\partial \beta} \beta^{-N/2} \\
&= -\beta^{N/2} \left(-\frac{N}{2} \right) \beta^{-N/2-1} \\
&= \frac{N}{2\beta} = \frac{1}{2} N kT
\end{aligned}$$

d) For the canonical system, we found the quantity called Helmholtz free energy: $F = E - TS$. Where F can be calculated by

$$F = -kT \ln Z$$

¹Following the derivation in section 6.6 of Schroeder's book on thermal physics (2000), we ignore the fact that interchanging to particles with the same states, have not, in fact, been counted twice. This is an approximation which, to a great extent, is valid for low density gases.

Taking the differential of F we obtain

$$\begin{aligned} dF &= dE - SdT - TdS \\ &= dE - SdT - dE - PdV + \mu dN \\ \Rightarrow S &= - \left(\frac{\partial F}{\partial T} \right)_{V,N} \end{aligned}$$

So, all we need to do is calculate $F_{N,x}$:

$$\begin{aligned} F_{N,x} &= -kT \ln Z_{N,x} \\ &= -kT \ln \left[\frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{N/2} L^N \right] \\ &= -kT \left[-\ln N! + \frac{N}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + N \ln L \right] \end{aligned}$$

and so, the entropy is

$$\begin{aligned} S &= -\frac{\partial}{\partial T} \left[kT \left[\ln N! - \frac{N}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) - N \ln L \right] \right]_{N,V} \\ &= -k \ln N! + \frac{Nk}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{NkT}{2} \frac{h^2}{2\pi mkT} \frac{2\pi mk}{h^2} \\ &= -k \ln N! + \frac{Nk}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{Nk}{2} \end{aligned}$$

- e) Opening for the possibility that the particles can move freely in 2 dimensions, the energy associated with each particle is

$$\varepsilon(n_x, n_y) = an_x^2 + an_y^2$$

The partition function for one particle then reads

$$\begin{aligned} Z_{1,x,y} &= \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} e^{-an_x^2/kT} e^{-an_y^2/kT} \\ &= \sum_{n_x=0}^{\infty} e^{-an_x^2/kT} \sum_{n_y=0}^{\infty} e^{-an_y^2/kT} \end{aligned}$$

We recognize that the first sum in the above expression is the same as for one particle moving in one dimension, which can be evaluated as in eq. 1. We also recognize that the second sum above has the same value as the first, leading to the partition function being:

$$Z_{1,x,y} = Z_{1,x}^2 \quad (3)$$

Following the same set of steps as in ex. b), we find that for N particles, the partition function is

$$Z_{N,x,y} = Z_{1,x}^{2N} \quad (4)$$

which in turn implies that the total average energy of the ideal gas is

$$U = -\frac{1}{Z} \frac{\partial Z_{n,x,y}}{\partial \beta} = \dots = NkT$$

and the entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\ \dots = -k \ln N! + Nk + Nk \ln \left(\frac{2\pi mkT}{h^2}\right) - 2Nk \ln L$$

where Helmholtz free energy is

$$F = -kT \left[-\ln N! + N \ln \left(\frac{2\pi mkT}{h^2}\right) + 2N \ln L \right]$$

f) The energy of this system is

$$\varepsilon_{3D} = an_x^2 + an_y^2 + \varepsilon_{z0}$$

So the partition function is

$$\begin{aligned} Z_{1,3D} &= \sum_{\text{all states}} e^{\varepsilon_{3D}/kT} \\ &= \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} e^{an_x^2/kT} e^{an_y^2/kT} e^{\varepsilon_{z0}/kT} \\ &= \sum_{n_x=0}^{\infty} e^{an_x^2/kT} \sum_{n_y=0}^{\infty} e^{an_y^2/kT} e^{\varepsilon_{z0}/kT} \\ &= Z_{1,2D} e^{\varepsilon_{z0}\beta} \end{aligned}$$

where $Z_{1,2D}$ is the partition function for one particle the two dimensional case in eq. 3 and ε_{z0} is the energy for the ground state for motion in the z -direction. For N particles:

$$\begin{aligned} Z &= \frac{1}{N!} Z_{1,3D}^N \\ &= \frac{1}{N!} Z_{1,2D}^N e^{N\varepsilon_{z0}\beta} \\ &= Z_{N,2D} e^{N\varepsilon_{z0}\beta} \end{aligned}$$

where again, $Z_{N,2D}$ is the partition function for N particles in the two dimensional case in eq. 4.

g) Using the above expression for the partition function in three dimensions, the energy can be

calculated as

$$\begin{aligned}
U &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\
&= -\frac{1}{Z} \frac{\partial}{\partial \beta} \left(Z_{N,2D} e^{N\varepsilon_{z0}\beta} \right) \\
&= -\frac{1}{Z} \left[e^{N\varepsilon_{z0}\beta} \frac{\partial}{\partial \beta} Z_{N,2D} + Z_{N,2D} \frac{\partial}{\partial \beta} e^{N\varepsilon_{z0}\beta} \right] \\
&= -\frac{1}{Z} \left[e^{N\varepsilon_{z0}\beta} (-U_{2D} Z_{N,2D}) + Z_{N,2D} N\varepsilon_{z0} e^{N\varepsilon_{z0}\beta} \right] \\
&= -\frac{1}{Z_{N,2D} e^{N\varepsilon_{z0}\beta}} Z_{N,2D} e^{N\varepsilon_{z0}\beta} (N\varepsilon_{z0} - U_{2D}) \\
&= U_{2D} - N\varepsilon_{z0} \\
&= NkT - N\varepsilon_{z0}
\end{aligned}$$

End of oblig 5