Worksheet 7 - Solutions

1. The Meaning of "Never"

Let us consider to have $N_{monkeys} = 10^{10}$.

we need to count how likely it is to have 10^5 characters in one specific order, having 44 possibilities for each character.

$$\left(\frac{1}{44}\right)^{100000} = \frac{1}{44^{100.000}}$$

but if we use that

$$\log_{10} 44 \approx 1{,}64345$$

$$\hookrightarrow 44 \approx 10^{1{,}64345}$$

So, the probability is

$$\left(\frac{1}{44}\right)^{100.000} = 10^{-164345}$$

b) Now, knowing the writing speed, we have that since of the begining of the universe;

$$(\text{age of universe}) \times \frac{10 \text{ keys}}{\text{second}} = 10^{18} \cancel{s} \left(\frac{10 \text{ keys}}{\cancel{s}}\right)$$

$= 10^{19}$ keys.

So, the 10 monkeys typed out

$$10^{19} \text{ keys} \times 10^{10} \text{ monkeys} = 10^{29} \text{ keys}.$$

So

$$10^{29} \text{ Characters typed out} \times 10^{-164345} \text{ Prob of having a hamlet} = 10^{-164316}$$

2 Time for a large fluctuation.

1) The number of accesible states

$$S = k_B \ln(\Omega) \longrightarrow \Omega = e^{\frac{S}{k_B}}$$

and the Sackur-Tetrode equation;

$$\frac{S}{k_B N} = \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right] + \frac{5}{2}.$$

$$= \ln\left[\frac{n_q}{n}\right] + \frac{5}{2}$$

when $n = \frac{N}{V}$ and $n_q = \left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}$

$$n_q^{2/3} = \frac{4\pi m}{3h^2}\frac{U}{N} = \frac{\cancel{4}^{2} \times m(\text{proton}) \times \left(\cancel{\tfrac{3}{2}} k_B T\right) \cancel{4\pi} \cdot \cancel{N}}{(\cancel{2}\cancel{\pi}_{\pi} \hbar)^2 \ \cancel{3} \ \cancel{N}}$$

$$= \frac{2 \ m_{proton} \times k_B \ T}{\pi \ \hbar^2}$$

$$= \frac{2 \ \frac{938 \ MeV}{c^2} \times 0{,}8617 \times 10^{-4} \frac{eV}{\cancel{K}} \ 300 \cancel{K}}{\pi \left(6.5821 \times 10^{-22} \ MeV \cdot s\right)^2}$$

$$= \frac{2 \times 938 \times 0{,}8617 \times 300}{\pi \ 6.5821^2} \times 10^{-4} \times 10^{44} \ \frac{\cancel{MeV}}{c^2} \ eV \ \frac{1}{MeV^{\cancel{2}} s^2}$$

$$\approx \frac{484964.76}{136.} \times \frac{10^{44}}{c^2 s^2} \ \frac{\cancel{eV}}{10^6 \cancel{eV}}$$

$$= 3563 \frac{10^{38}}{\cancel{s^2}} \frac{1}{\left(3 \times 10^8 \, m/\cancel{s}\right)^2}$$

$$= \frac{3563}{m^2} \frac{10^{38-16}}{9} = 396 \times 10^{22} \; 1/m^2$$

$$n_q^{2/3} = 396 \times 10^{22} \; m^{-2}$$

$$n_q = \left(396 \times 10^{22}\right)^{3/2} \; m^{-3}$$

$$= 7880 \times \frac{10^{33}}{m^{-3}} = 7{,}88 \frac{10^{30}}{m^{-3}}$$

and from the ideal gas equation of state.

$$PV = N k_B T$$

$$\frac{V}{N} = \frac{k_B T}{P}$$

$$\Rightarrow \frac{P}{k_B T} = \frac{N}{V} = \frac{1{,}013 \times 10^5 \, \cancel{N}/m^2}{1{,}381 \times 10^{-23} \frac{\cancel{J}}{\cancel{K}} \; 300 \, \cancel{K}} \times \frac{\cancel{J} \, \cancel{s^2}}{\cancel{kg} \, \cancel{m^2}} \frac{\cancel{kg} \, \cancel{m}}{\cancel{s^2}} \times \frac{1}{\cancel{N}}$$

$$= n$$

$$= 0{,}002445 \times 10^{28} \frac{1}{m^3} = 2{,}445 \times 10^{25} \; 1/m^3$$

so, for $1L = 10^{-3} \, m^3$

$0{,}1L = 10^{-4} \, m^3$

$$V/n = N = 2{,}445 \times 10^{25} \frac{1}{\cancel{m^3}} \; 10^{-4} \, \cancel{m^3}$$

$$= 2{,}445 \times 10^{21}$$

$$\frac{S}{k_B N} = \ln\left[\frac{n_q}{n}\right] + \frac{5}{2}$$

$$= \ln\left[\frac{7{,}88 \times 10^{30}}{2{,}445 \times 10^{25}}\right] + \frac{5}{2}$$

$$= \ln\left[3{,}22\ 10^{5}\right] + \frac{5}{2}$$

$$\frac{S}{k_B} = 2{,}445 \times 10^{21}\left[\ln\left(3{,}22\ 10^{5}\right) + \frac{5}{2}\right]$$

$$= \frac{5}{2} \times \left(2{,}445 \times 10^{21}\right) + \ln\left[\left(3{,}22 \times 10^{5}\right)^{(2{,}445 \times 10^{21})}\right]$$

so

$$\Omega = e^{S/k_B} = e^{\frac{5}{2}(2{,}445 \times 10^{21})} \left(3{,}22 \times 10^{5}\right)^{(2{,}445 \times 10^{21})}$$

$$\approx e^{3{,}71 \times 10^{22}}$$

b) At $V = 0,05\,L$ with the same temperature.
$nq = cte$ and the concentration doubles
So, the entropy gets reduced by

$$\Delta S = -N k_B \log(2) \approx -1.70 \times 10^{21}$$

Then $$S + \Delta S = 3,54 \times 10^{22}$$

$$\Omega_2 = \exp\left(3,54 \times 10^{22}\right)$$

3) And

$$\frac{\Omega_2}{\Omega_1} = \exp\left(\frac{\Delta S}{k_B}\right) = \exp\left(-1,70 \times 10^{21}\right) \approx 10^{-7,36 \times 10^{20}} \quad *$$

d) There are approx $\pi \times 10^7$ secs in 1 year. So

$$\text{freq colls} = 2,7 \times 10^{21} \times 10^{10} \times \frac{\pi \times 10^7}{y} = 8,5 \times 10^{38} \frac{1}{y}$$

$$= 8,5 \times 10^{38} \frac{1}{y} \approx 10^{39}\ 1/y$$

e) from $(*)$, it happens once every

$$\frac{\Omega_1}{\Omega_2} \approx 10^{7 \times 10^{20}} \quad \text{times}$$

only 1 every Ω_1/Ω_2 such state exists.

$$t = \frac{\Omega_1}{\Omega_2} \frac{1}{f_c} = 10^{7 \times 10^{20}} \Big/ 10^{39}\ 1/y = 10^{7 \times 10^{21}} \text{ years}$$

3 Ideal Gas in the Canonical ensemble*

let us start by considering a macrostate $M \equiv (T, V, N)$

* The canonical ensamble is characterised by its constant temperature.

Now the energy of the system changes, but its average and fluctuations are well defined and known,

$$P(\mu) = p(\{\vec{p}_i, \vec{q}_i\}) = \underbrace{\frac{1}{Z}}_{\text{Canonical partition function}} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] \times \begin{cases} 1 & \text{for } \{q_i\} \in \text{Box} \\ 0 & \text{otherwise} \end{cases}$$

as we do not have a potential term:

$$Z(T, V, N) = \underbrace{\frac{1}{N!}}_{\text{undistinguishable particles}} \int \underbrace{\frac{d\vec{q}_1 d\vec{q}_2 \cdots d\vec{q}_n d\vec{p}_1 \cdots d\vec{p}_n}{h^{3N}}}_{\text{phase space minimum volume}} e^{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}}$$

$$= \frac{1}{N! h^{3N}} \underbrace{\left[\prod_{i=1}^{N} \int_{-\infty}^{\infty} d\vec{p}_i \, e^{-\beta \frac{p_i^2}{2m}}\right]}_{\text{Gaussion integral} \, = (2\pi m k_B T)^{3N/2}} \times \prod_{i=1}^{N} \underbrace{\int_{\text{Box}} d\vec{q}_i}_{V^N}$$

$$= \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda(T)^3}\right)^N \quad \text{with} \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Once we have the partition function, Z, we can compute the thermodynamics.

The free energy

$$F = -k_B T \ln(Z) = -k_B T \ln\left[\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\right]$$

$$= -k_B T\left[N\ln(V) \underbrace{- N\ln(N) + N}_{\text{Stirling formula.}} - \frac{3N}{2}\ln(\lambda^2)\right]$$

$$= -k_B T N\left[\ln\left(\frac{V}{N}\right) \underbrace{-1}_{\begin{array}{l} -1 = -\ln(e) \\ = \ln(1/e) \end{array}} - \frac{3}{2}\ln\left(\frac{h^2}{2\pi m k_B T}\right)\right]$$

$$= -k_B T N\left[\ln\left(\frac{Ve}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

let us use this expression to compute more thermodynamics.
We have that F is an equation of state;

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$\hookrightarrow -S = \left.\frac{\partial F}{\partial T}\right|_{V,N} ; \quad -P = \left.\frac{\partial F}{\partial V}\right|_{T,N} ; \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}$$

$$-S = \frac{\partial F}{\partial T}\Big|_{V,N} = -Nk_B\left[\ln\left(\frac{Ve}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$-Nk_BT\left(\frac{3}{2}\frac{1}{T}\right)$$

$\frac{3}{2}Nk_BT = E \equiv$ internal energy

$$= \frac{F - E}{T}$$

To get the equation of state, we might use the equation for pressure.

$$-P = \frac{\partial F}{\partial V}\Big|_{T,N} = -\frac{Nk_BT}{V}$$

$$\boxed{PV = Nk_BT}$$

lastly, the chemical potential.

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V} = -k_BT\left[\ln\left(\frac{Ve}{N}\right) + \frac{3}{2}\left(\frac{2\pi m k_BT}{h}\right)\right] + k_BT\cancel{N}\left(\frac{1}{\cancel{N}}\right)$$

$$= \frac{F}{N} + k_BT = \frac{E - TS + PV}{N}$$

4 The ideal gas in the isobaric ensemble.

We have a similar situation as before, but now one has to add the correct Lagrange multiplier.

$$\rho(\{\vec{p}_i, \vec{q}_i\}, V) = \frac{\exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta P V\right]}{Z} \times \begin{cases} 1 \text{ for } \{q_i\} \in \text{Box}(V). \\ 0 \quad \text{otherwise} \end{cases}$$

Now, the partition function is a bit different.

$$Z(N,T,P) = \underbrace{\frac{1}{N!}}_{\text{undistinguishable particles}} \int_0^\infty dV \int \frac{d\vec{q}_1 \, d\vec{q}_2 \cdots d\vec{q}_n \, d\vec{p}_1 \cdots d\vec{p}_n}{\underbrace{h^{3N}}_{\text{phase space minimum volume}}} e^{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}} e^{-\beta P V}$$

$$= \frac{1}{N! \, h^{3N}} \underbrace{\left[\prod_{i=1}^{N} \int_{-\infty}^{\infty} d\vec{p}_i \, e^{-\beta \frac{p_i^2}{2m}} \right]}_{\text{Gaussian integral.}} \times \int_0^\infty dV \, e^{-\beta P V} \underbrace{\prod_{i=1}^{N} \int_{\text{Box } V} d\vec{q}_i}_{V^N}$$

$$= \frac{1}{\lambda(T)^{3N}} \left[\frac{1}{N!} \int_0^\infty dV \, V^N e^{-\beta P V} \right]$$

$$u = \beta P V \qquad \frac{u}{\beta P} = V$$

$$du = \beta P \, dV$$

$$\frac{du}{\beta P} = dV$$

$$= \frac{1}{\lambda(T)^{3N}} \left[\frac{1}{N!} \int_0^\infty \frac{du}{\beta P} \left(\frac{u}{\beta P} \right)^N e^{-u} \right]$$

$$= \frac{1}{\lambda(T)^{3N}} \left[\cancel{\frac{1}{N!}} \frac{1}{(\beta P)^{N+1}} \underbrace{\int_0^\infty du \, u^N e^{-u}}_{\cancel{\Gamma(N+1) = N!}} \right]$$

$$\boxed{\mathcal{Z}(N, T, P) = \frac{1}{\lambda(T)^{3N} (\beta P)^{N+1}}}$$

Then, the free energy

$$G = -k_B T \ln \mathcal{Z} = k_B T \ln \left(\lambda(T)^{3N} (\beta P)^{N+1} \right)$$

$$= k_B T \left[3N \ln(\lambda) + (N+1) \ln(\beta P) \right]$$

$$= k_B T \left[3N \ln(\lambda) + (N+1) \left(\ln(\beta) + \ln(P) \right) \right]$$

$$= k_B T N \left[3 \ln(\lambda) + \ln(P) + \ln(\beta) \right]$$

$$+ k_B T \ln(\beta) + k_B T \ln(P)$$

$$= k_B T N \left[\frac{3}{2} \ln\left(\frac{h^2 \beta}{2\pi m}\right) + \ln(P) + \ln(\beta) \right]$$

$$+ k_B T \ln(\beta) + k_B T \ln(P)$$

$$= k_B T N \left[\ln(P) - \frac{5}{2} \ln(k_B T) + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m}\right) \right]$$

$$+ k_B T \ln(P\beta)$$

in the same way we did in the Canonical case.

$$dG = -S\,dT + V\,dP + \mu\,dN.$$

The Volume

$$V = \left.\frac{\partial G}{\partial P}\right|_{T,N} = \frac{N k_B T}{P} + \frac{k_B T}{P}$$

$$= \frac{(N+1) k_B T}{P}$$

as $N \gg 1$

$N+1 \approx N$

$$\approx \frac{N k_B T}{P} \rightarrow PV = N k_B T$$

The enthalpy $H = \langle E + PV \rangle$

$$H = -\frac{\partial \ln Z}{\partial \beta} = \frac{-\partial}{\partial \beta}\left(\beta G\right)$$

$$= -\frac{\partial}{\partial \beta}\left(\frac{G}{k_B T}\right)$$

$$= \frac{5}{2} N k_B T - \frac{k_B T}{P}$$

The same argument as before

$$N k_B T >> \frac{1}{P}$$

$$H \simeq \frac{5}{2} k_B T N$$

so

$$C_P = \frac{dH}{dT} = \frac{5}{2} N k_B$$