

Worksheet 7 - Solutions

1. The Meaning of "Never."

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

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

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

but if we use that

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

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

So, the probability is

$$\left(\frac{1}{44}\right)^{100000} = 10^{-164345}$$

b) Now, knowing the writing speed, we have that since of the beginning 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

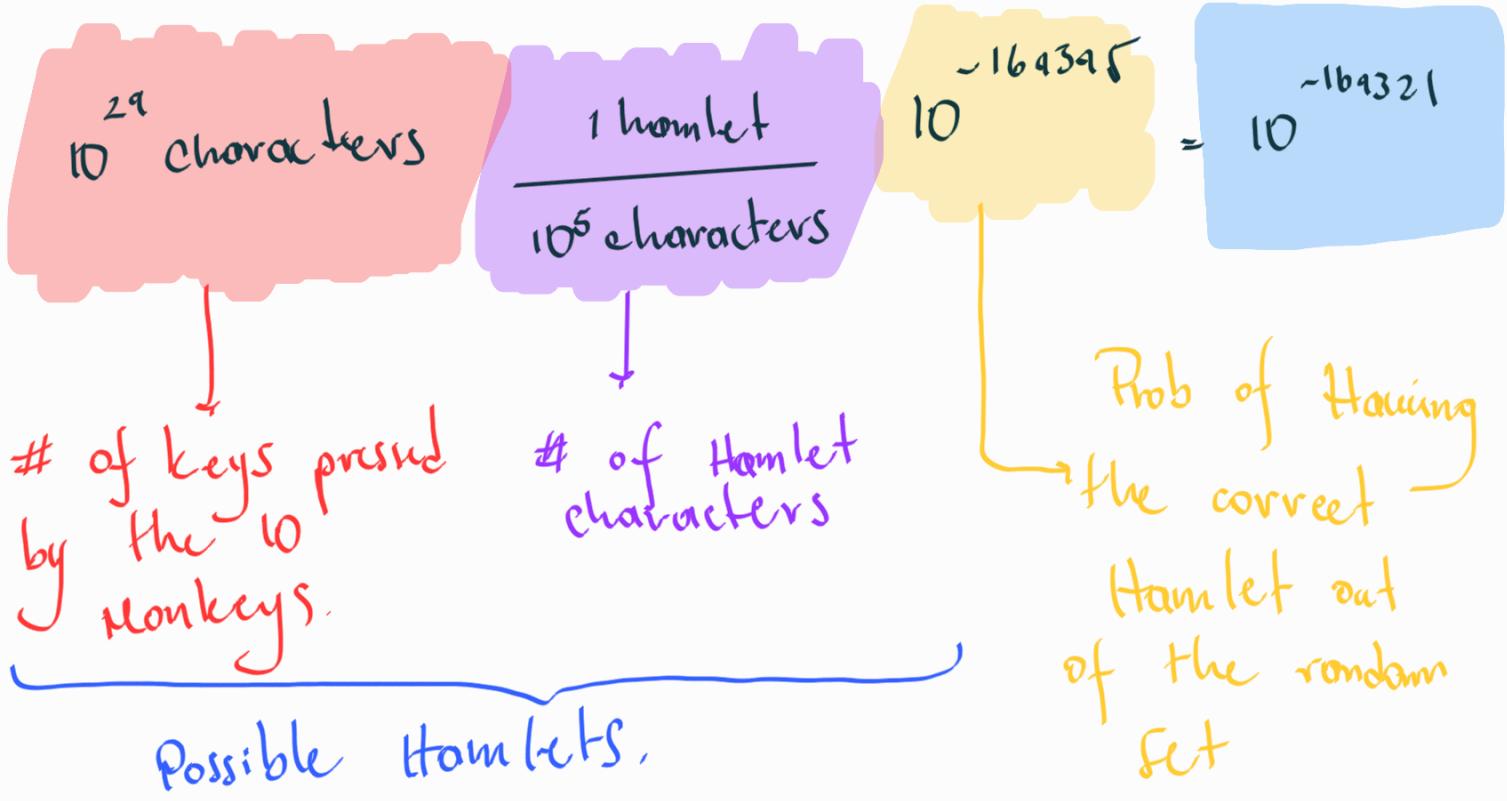
$$10^{19} \text{ keys} \times 10^0 \text{ monkeys} = 10^{29} \text{ keys.}$$

So

$$10^{29} \text{ keys typed out} \times \frac{1 \text{ hamlet}}{10^5 \text{ characters}}$$

$$= 10^{24} \text{ possible "Hamlets".}$$

As we saw before, the "Chance" of getting a Hamlet is $10^{-164345}$, so



2 Time for a large fluctuation.

1) The number of accessible states

$$S = k_B \ln(\omega_U) \quad \underbrace{\omega_U = e^{\frac{S}{k_B}}$$

and the Sackur-Tetrode equation;

$$\begin{aligned} \frac{S}{k_B N} &= \ln \left[\frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right] + \frac{5}{2} \\ &= \ln \left[\frac{n_q}{n} \right] + \frac{5}{2} \\ \text{when } n &= \frac{N}{V} \quad \text{and} \quad n_q = \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \end{aligned}$$

$$\begin{aligned} n_q^{2/3} &= \frac{4\pi m}{3h^2} \quad \frac{U}{N} = \frac{2 \times m(\text{proton})}{(\cancel{\pi} \cancel{h^2})^2} \times \frac{(\cancel{\pi} \cancel{k_B T})}{\cancel{N}} \cancel{\pi} \cdot \cancel{h^2} \\ &= \frac{2 \times m_{\text{proton}} \times k_B T}{\pi h^2} \\ &= \frac{2 \frac{938 \text{ MeV}}{c^2} \times 0,8617 \times 10^{-4} \frac{\text{eV}}{\text{K}}}{\pi (6.5821 \times 10^{-22} \text{ MeV} \cdot \text{s})^2} \quad 300 \text{ K} \\ &= \frac{2 \times 938 \times 0,8617 \times 300}{\pi 6.5821^2} \times 10^{-4} \times 10^{44} \quad \cancel{\frac{\text{MeV}}{c^2}} \frac{\text{eV}}{10^6 \cancel{\text{eV}}} \frac{1}{\text{MeV}^2 \text{s}^2} \\ &\approx \frac{484964.76}{136} \times \frac{10^{44}}{c^2 s^2} \end{aligned}$$

$$= 3563 \times \frac{10}{8^2} = \frac{1}{(3 \times 10^8 m/s)^2}$$

$$= \frac{3563}{m^2} \times \frac{10}{9} = 396 \times 10^{22} \text{ } 1/m^2$$

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

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

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

and from the ideal gas equation of state.

$$PV = Nk_B T$$

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

$$\Rightarrow \frac{P}{k_B T} = \frac{N}{V} = \frac{1,013 \times 10^5 \text{ } \cancel{N/m^2}}{1.381 \times 10^{-23} \cancel{\frac{J}{K}} \times 300 \cancel{K}} \times \frac{\cancel{J s^2}}{\cancel{kg} \cancel{m^2}} \times \frac{\cancel{kg} \cancel{m}}{\cancel{s^2}} \times \frac{1}{\cancel{N}}$$

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

so, for $1L \approx 10^{-3} \text{ } m^3$
 $0,1L = 10^{-4} \text{ } m^3$

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

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

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

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

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

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

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

$$S_{k_B} = \frac{5}{2} (2,445 \times 10^{21}) (3,22 \times 10^5)^{(2,445 \times 10^{21})}$$

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

$$\approx e,$$

b) At $V = 0.05 \text{ L}$ with the same temperature, $nq = nc$ and the concentration doubles so, the entropy gets reduced by

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

$$\text{Then } S + \Delta S = 3.59 \times 10^{22}$$

$$\omega_2 = \exp(3.59 \times 10^{22})$$

c) And

$$\frac{\omega_2}{\omega_1} = \exp\left(\frac{\Delta S}{k_B}\right) = \exp(-1.70 \times 10^{21}) \approx 10^{-7.36 \times 10^{20}} *$$

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

$$\begin{aligned} \text{freq. collis} &= 2.7 \times 10^{21} \times 10^{10} \times \underbrace{\frac{\pi \times 10^7}{y}}_{= 8.5 \times 10^{38} \frac{1}{y}} = 8.5 \times 10^{38} \frac{1}{y} \\ &\approx 10^{39} \frac{1}{y} \end{aligned}$$

e) from (*), it happens once every

$$\frac{\omega_1}{\omega_2} \approx 10^{7 \times 10^{20}} \text{ times}$$

only 1 energy ω_1/ω_2 such state exists.

$$t = \frac{\omega_1}{\omega_2} \frac{1}{f_C} = 10^{7 \times 10^{20}} / 10^{39} \frac{1}{y} = 10^{7 \times 10^{21}} \text{ years}$$

3 Ideal Gas in the Canonical ensemble

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

* The canonical ensemble is characterised by its constant temperature.

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

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

↓
Canonical partition function.

as we do not have a potential term:

$$Z(T, V, N) = \frac{1}{N!} \int \frac{d\vec{q}_1 d\vec{q}_2 \dots d\vec{q}_N d\vec{p}_1 \dots d\vec{p}_N}{h^{3N}} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}$$

↓
undistinguishable particles ↓
phase space minimum volume

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

↓
 V^N

Gaussian integral.

$$= (2\pi m k_B T)^{3N/2}$$

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

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

The free energy

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

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

$$= -k_B T N \left[\ln \left(\frac{V}{N} \right) - 1 - \frac{3}{2} \ln \left(\frac{\hbar^2}{2\pi m k_B T} \right) \right]$$

$$-1 = -\ln(e)$$

$$= \ln(1/e)$$

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

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

$$dF = -SdT - PdV + \mu dN$$

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

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

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

$\underbrace{\frac{3}{2} Nk_B T = E \equiv \text{internal energy}}$

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

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

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

$$PV = Nk_B T$$

lastly, the chemical potential.

$$\mu = \frac{\partial F}{\partial N} \Big|_{T,V} = -k_B T \left[\ln \left(\frac{V_e}{N} \right) + \frac{3}{2} \left(\frac{2\pi m k_B T}{h^2} \right) \right] + k_B T \delta \left(\frac{f_1}{N} \right)$$

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

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.

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

Now, the partition function is a bit different.

$$\mathcal{Z}(N, T, P) = \frac{1}{N! h^{3N}} \int_0^\infty \int \frac{d\vec{q}_1 d\vec{q}_2 \dots d\vec{q}_N d\vec{p}_1 \dots d\vec{p}_N}{h^{3N}} e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} e^{-\beta PV}$$

↓
Undistinguishable particles

↓
phase space
minimum volume

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

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

$$U = \beta P V \quad \frac{U}{\beta P} = V$$

$$dU = \beta P dV$$

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

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

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

$\Gamma(N+1) = N!$

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

Then, the free energy

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

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

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

$$\begin{aligned}
&= k_B T N \left[3 \ln(\lambda) + \ln(P) + \ln(\beta) \right] \\
&\quad + k_B T \ln(\beta) + k_B T \ln(P) \\
&= k_B T N \left[\frac{3}{2} \ln\left(\frac{h^2 \beta}{2\pi m}\right) + \ln(P) + \ln(\beta) \right] \\
&\quad + k_B T \ln(\beta) + k_B T \ln(P) \\
&= k_B T N \left[\ln(P) - \frac{5}{2} \ln(k_B T) + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m}\right) \right] \\
&\quad + k_B T \ln(P\beta)
\end{aligned}$$

in the same way we did in the Canonical case.

$$dG = -SdT + VdP + \mu dN.$$

The Volume

$$\begin{aligned}
V &= \left. \frac{\partial G}{\partial P} \right|_{T, \mu} = \frac{N k_B T}{P} + \frac{k_B T}{P} \\
&= \frac{(N+1) k_B T}{P} \quad \text{as } N \gg 1 \\
&\approx \frac{N k_B T}{P} \rightarrow PV = N k_B T
\end{aligned}$$

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

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

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

The same argument as before

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

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

so

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