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

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

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

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;

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

$$= 10^{19} \text{ keys.}$$

So, the 10 monkeys typed out

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

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

$$\underbrace{\underbrace{10^{29} \text{ characters}}_{\text{\# of keys pressed by the 10 monkeys.}} \; \underbrace{\frac{1 \text{ hamlet}}{10^{5} \text{ characters}}}_{\text{\# of Hamlet characters}}}_{\text{Possible Hamlets.}} \; \underbrace{10^{-164345}}_{\text{Prob of Having the correct Hamlet out of the random set}} = 10^{-164321}$$

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.

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

$Z \to$ Canonical partition function.

as we do not have a potential term:

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

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

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

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

The free energy

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

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

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

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

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

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.

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

$$PV = Nk_BT$$

Lastly, the chemical potential.

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

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

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.

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

Now, the partition function is a bit different.

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

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

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

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

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

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

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

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

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

Then, the free energy

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

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

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

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

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

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

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

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

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

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 $H = \langle E + PV \rangle$

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

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

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

The same argument as before

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

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

so

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

5 Ideal Gas in the Grand Canonical ensemble.

a) the Grand Partition function

$$\Xi(T,\mu,V) = \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{\frac{1}{N!} \int \prod_i^N \left(\frac{d^3\vec{q}_i \, d^3\vec{p}_i}{h^3} \right) \exp\left[-\beta \sum_i \frac{p_i^2}{2m} \right]}_{\text{canonical Distribution}}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \quad \text{with} \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$= \exp\left(e^{\beta\mu} \frac{V}{\lambda^3} \right) \longrightarrow \text{using } e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

So, the grand potential

$$G(T,\mu,V) = -k_B T \ln(\Xi) = -k_B T \, e^{\beta\mu} \frac{V}{\lambda^3}$$

and using $G = E - TS - \mu N = -PV$.

$$P = -\frac{G}{V} = -\left.\frac{\partial G}{\partial V}\right|_{\mu,T} = \frac{k_B T \, e^{\beta\mu}}{\lambda^3}$$

and the number of particles;

$$N = -\left.\frac{\partial G}{\partial \mu}\right|_{T,V} = \frac{e^{\beta\mu} V}{\lambda^3}$$

from these equations one can get the equation of state

$$P = k_B T N/V$$

from the equation of N

$$\frac{\lambda^3 N}{V} = e^{\beta\mu} \longrightarrow \mu = k_B T \ln\left(\frac{\lambda^3 N}{V} \right) = k_B T \ln\left(\frac{P\lambda^3}{k_B T} \right)$$

Grand partition Function of a two level system.

$$\Xi = \sum_N e^{\beta\mu N} \sum_i e^{-\beta E_i}$$

$$= \underbrace{e^{\beta\mu\times 0} \cdot e^{-\beta E_0}}_{\substack{\text{Not occupied} \\ E_0=0}} + \underbrace{e^{\beta\mu} e^{-\beta E_1}}_{\substack{\text{occupied} \\ \text{Not excited state} \\ E_1=0}} + \underbrace{e^{\beta\mu} e^{-\beta E_2}}_{\substack{\text{occupied} \\ \text{excited} \\ E_2=\epsilon}}$$

$$= 1 + \lambda \times 1 + \lambda \times e^{-\beta\epsilon}$$

$$= 1 + \lambda + \lambda e^{-\beta\epsilon}$$

the number of particles

$$\langle N \rangle = \frac{0\times 1 + (1)\times(\lambda + \lambda e^{-\beta\epsilon})}{\Xi} = \frac{\lambda + \lambda e^{-\beta\epsilon}}{\Xi}$$

the number of particles with energy ϵ

$$\langle N(\epsilon) \rangle = \frac{0\times 1 + 0\times\lambda + 1\times\lambda e^{-\beta\epsilon}}{\Xi} = \frac{\lambda e^{-\beta\epsilon}}{\Xi}$$

the average of energy

$$\langle \epsilon \rangle = \frac{0\times 1 + 0\times\lambda + \epsilon\lambda e^{-\beta\epsilon}}{\Xi} = \epsilon \langle N(\epsilon) \rangle = \frac{\epsilon\lambda e^{-\beta\epsilon}}{\Xi}$$

Then,

$$\Xi = \sum_N e^{\beta\mu N} \sum_i e^{-\beta E_i} = e^{0} e^{-\beta E_i} + e^{\beta\mu 1} e^{-\beta E_1} + e^{\beta\mu 1} e^{-\beta E_2} + e^{\beta\mu 2} e^{-\beta E_3}$$

$$= 1 + \lambda + \lambda e^{-\beta\epsilon} + \lambda^2 e^{-\beta\epsilon}$$

The only new term including two particles.