1

$$Z(T) = \int dE\, e^{-\beta F_L(T,E)} \; ; \quad F_L(T,E) = E - T S_m(E)$$

$$\sim e^{-\beta F_L(T,E^*)} \quad \text{when} \quad E^* = \underset{E}{\operatorname{argmin}}\, F_L(T,E)$$

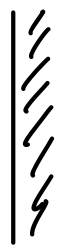
$$\Rightarrow \frac{1}{T} = \frac{\partial S_m}{\partial E}\Big|_{E^*}$$

$$\Rightarrow F(T) = -k_B T \ln Z = F_L(T,E^*) = E^* - T S_m(E^*)$$

Gibbs entropy

$$S_G = -k_B \sum_q p(q) \ln p(q) = \frac{\langle E \rangle - F(T)}{T} \underset{N \to \infty}{\sim} S_m(E^*)$$

Mechanical pressure on a wall



$x = L$

$$\leftrightarrow V_w(x_i - L)$$

$$P = \frac{1}{A} \left\langle \sum_i V_w'(x_i - L) \right\rangle = -\frac{\partial F}{\partial V}$$

Consistency with microcanonical ensemble

$$F(T,V) = E^*(T,V) - T\, S_m(E^*(T,V), V)$$

$$\Rightarrow \frac{\partial F}{\partial V} = \frac{\partial E^*}{\partial V} - T\left[\underbrace{\frac{\partial S_m}{\partial E^*}}_{\frac{1}{T}} \frac{\partial E^*}{\partial V} + \frac{\partial S_m}{\partial V}\right] = -T\frac{\partial S_m}{\partial V} \Rightarrow \text{as in the microcanonical ensemble!}$$

$$= -P$$

From free energy to entropy

We have characterized $\frac{\partial F}{\partial V}(T,V)$. What about $\frac{\partial F}{\partial T}$?

$$\frac{\partial}{\partial T}\left(-kT\ln Z\right) = -k\ln Z - kT\,\partial_T \ln Z$$

$$\frac{\partial}{\partial T} = \frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta} = -\frac{1}{k_B T^2}\frac{\partial}{\partial\beta} \Rightarrow \frac{\partial F}{\partial T} = \frac{F}{T} + \frac{1}{T}\overbrace{\partial_\beta \ln Z}^{\sim \langle E\rangle} = \frac{F - \langle E\rangle}{T} = -S_G(T)$$

$$\underset{N\to\infty}{\sim} -S_m(E^*)$$

$$\Rightarrow \frac{\partial F}{\partial T} = -S$$

1st law

Is this consistent with the first law?

$$dF(T,V) = \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial V}dV = -S\,dT - P\,dV \qquad (1)$$

we also know that $F = E^* - TS \Rightarrow dF = dE^* - TdS - SdT$ (2)

(1) & (2) $\Rightarrow dE^* = TdS - PdV$ which is consistent with the 1st law that we derived in the microcanonical ensemble.

Summary

For finite systems, micro & cano ensembles are very different (just think about the fluctuations of E)

As $N \to \infty$, the concentration of measures leads to an ensemble equivalence. The thermodynamic potentials & laws that one can define in each ensemble coincide, upon relating correctly the control parameters. Here, through $\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{E^*}$.

Conclusion: Whatever ensemble your experiences lives in, you can use your favourite ensemble to account/predict experimental result, provided you use the right thermodynamic relation between control parameters.

Check on ideal gas

Micro: $S_m = N k_B \ln\left[\frac{Ve}{N}\left(\frac{4\pi m e E}{3 N h^2}\right)^{3/2}\right]$

Cano: $F = -N k_B T \ln\left[\frac{Ve}{N\Lambda^3}\right] = -N k_B T \ln\left[\frac{Ve}{N}\right] + \frac{3}{2} N k_B T \ln\left[\frac{h^2}{2\pi m k_B T}\right]$

$$S_c = -\frac{\partial F}{\partial T} = N k_B \ln\left[\frac{Ve}{N}\right] - \frac{3}{2} N k_B \ln\left[\frac{h^2}{2\pi m k_B T}\right] + \frac{3}{2} N k_B \overset{=1}{\ln e} = N k_B \ln\left[\frac{Ve}{N}\left(\frac{2\pi m e k_B T}{h^2}\right)^{3/2}\right]$$

Thermodynamic relation $\frac{1}{T} = \frac{\partial S_m}{\partial E}\Big|_{E^*} = \frac{3}{2} N k_B \frac{1}{E^*} \Rightarrow k_B T = \frac{2E^*}{3N} \Rightarrow S_c(T) = S_m(E^*)$

Pressure $P = -\frac{\partial F}{\partial V} = \frac{N k_B T}{V}$ $\Rightarrow$ as in micro

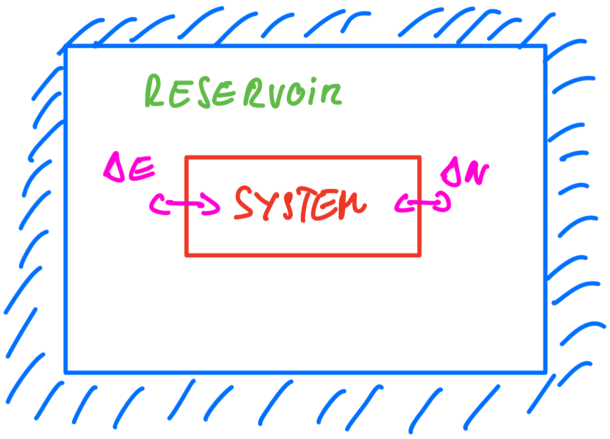
$\Rightarrow$ Same physics in both ensembles in the large N limit

3.3) The grand canonical ensemble

3.3.1) Exchanging particles

Let us now consider a system that can exchange particles (& energy) with reservoir(s).

1

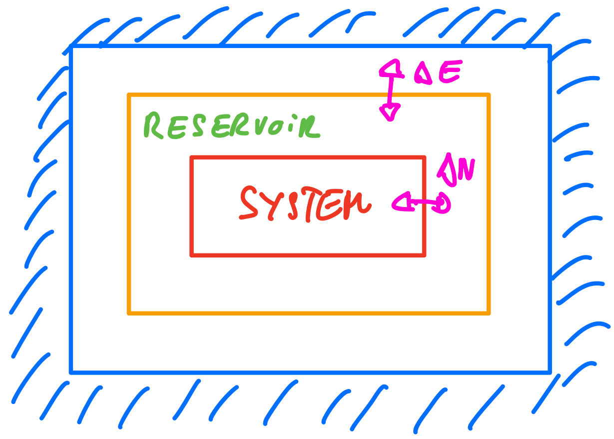


Syst + reserv. in microcanonical ensemble

$$E(q_r) + E(q_s) = E$$

$$N(q_r) + N(q_s) = N$$

$$P(q_s, q_r) = \frac{1}{\Omega_{tot}(E,N)} \delta_{N_r + N_s, N} \, \delta_{E_r + E_s, E}$$



Syst + reservoir in canonical ensemble

$$N(q_r) + N(q_s) = N$$

$$P(q_s, q_r) = \frac{1}{Z(T,N)} e^{-\beta[E(q_s) + E(q_r)]}$$

Microstate $\{q_s, q_r\}$ $\longrightarrow$ Macrostate q_s $\xrightarrow{\text{reservoir} \gg \text{system}}$ $P(q_s) = ?$

Both routes are equivalent.

Route 1 repeats the micro $\rightarrow$ cano derivation with a new variable.

Here, follow 2

$$P(\varphi_s) = \sum_{\varphi_r} \frac{1}{Z_{tot}(T,N)} e^{-\beta E(\varphi_r)} e^{-\beta E(\varphi_s)} \quad , \quad \frac{1}{T} = \frac{\partial S_{tot}}{\partial E_{tot}} \simeq \frac{\partial S_r}{\partial E_r} = \frac{1}{T_r}$$

$$= \frac{e^{-\beta E(\varphi_s)}}{Z_{tot}} \underbrace{\sum_{\varphi_r | N_r = N - N_s} e^{-\beta E(\varphi_r)}}_{Z_r(T_r, V_r, N-N_s) = e^{-\beta F_r(T_r, V_r, N-N_s)}}$$

$$\simeq e^{-\beta F(T_r, V_r, N) + \beta N_s \frac{\partial F_r}{\partial N}}$$

We then define the **chemical potential** of the reservoir $\mu_r = \frac{\partial F_r}{\partial N}$

and the **fugacity** $z = e^{\beta\mu}$.

One then finds the **grand canonical distribution**

$$P(\varphi_s) = \frac{1}{Q} e^{-\beta E(\varphi_s) + \beta\mu N(\varphi_s)}$$

where $Q = \frac{Z_{tot}(T, V_{tot}, N)}{Z_{res}(T, V_{tot}, N)} = \sum_{\varphi_s} e^{-\beta E(\varphi_s) + \beta\mu N(\varphi_s)}$ is the

grand canonical partition function. Q can be conveniently written as

$$Q = \sum_N e^{\beta\mu N} \sum_{\varphi_s | N(\varphi_s) = N} e^{-\beta E} = \sum_N e^{\beta\mu N} Z(T,V,N) = \sum_N z^N Z(T,V,N)$$

useful for algebra

$$= \sum_N e^{\beta\mu N - \beta F} = \sum_{N,E} e^{\beta[\mu N - E + TS]}$$

useful for saddle point & thermodynamics

Grand potential $\boxed{G = -k_B T \ln Q}$

3.3.2) Fluctuations & large-V limit

N is now a fluctuating quantity, whose statistics are controlled by μ.
Since F is extensive, $\mu = \frac{\partial F}{\partial N}$ is intensive, as the temperature.

To take a large system limit, we can only send V to ∞.

Fluctuations of N:

moment generating function $\langle N^n \rangle = \frac{1}{Q} \frac{\partial^n Q}{\partial (\beta\mu)^n} = \frac{1}{Q} \left(z \frac{\partial}{\partial z} \right)^n Q$

Using $\frac{\partial}{\partial \beta\mu} = \frac{1}{\beta} \frac{\partial z}{\partial \mu} \frac{\partial}{\partial z} = z \frac{\partial}{\partial z}$ $\Rightarrow$ $\langle N \rangle = z \frac{\partial}{\partial z} \ln Q = \frac{\partial}{\partial \beta\mu} \ln Q$

Cumulant generating function $\langle N^n \rangle_c = \frac{1}{\beta^n} \frac{\partial^n}{\partial \mu^n} (-\beta G) = -\beta \left(z \frac{\partial}{\partial z} \right)^n G$

$$\langle e^{\lambda N} \rangle = \frac{Q(\mu + \frac{\lambda}{\beta})}{Q(\mu)} \Rightarrow \varphi(\lambda) = \ln Q(\mu + \tfrac{\lambda}{\beta}) - \ln Q(\mu)$$

$$\Rightarrow \varphi^{(n)}(\lambda)\Big|_{\lambda=0} = \frac{1}{\beta^n} \frac{\partial^n}{\partial \mu^n} (-\beta G)$$

Typical fluctuations

$$\langle N \rangle = -\partial_\mu G$$

$$\langle N^2 \rangle_c = -\frac{1}{\beta} \partial_\mu^2 G = \frac{1}{\beta} \partial_\mu \langle N \rangle \Rightarrow \sqrt{\langle N^2 \rangle_c} \sim \sqrt{\langle N \rangle}$$

The typical fluctuations of N are much smaller than its average value