Pressure: $P = -\frac{\partial F}{\partial V} = \frac{N k_B T}{V} \Rightarrow PV = N k_B T$ as expected

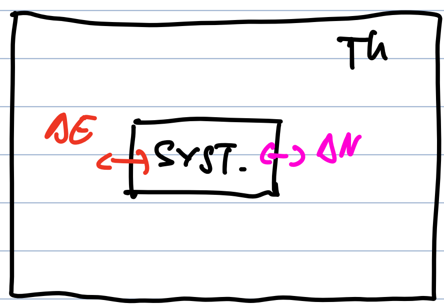
$\Rightarrow$ Same physics in both ensemble in the thermodynamic limit

3.3) The grand canonical ensemble

3.3.1) Changing ensemble

Let us now consider open systems, that can exchange particles and energy with a reservoir.

1



System + Thermostat isolated

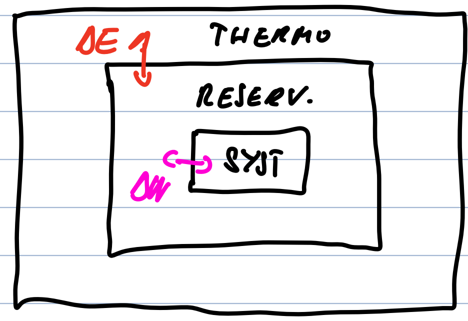
$$\left.\begin{aligned} E(q_{th}) + E(q_s) &= E \\ N(q_{th}) + N(q_s) &= N \end{aligned}\right\} \text{microcanonical ensemble}$$

Microstate $\{q_s, q_{th}\}$

$$P(q_s, q_{th}) = \frac{1}{\Omega(E,N)} \delta_{N_{th}+N_s, N} \, \delta_{E_{th}+E_s, E}$$

Thermostat $\gg$ syst

2



System + Reservoir exchange ΔE with reservoir

$$\left.\begin{aligned} &\text{Temperature } T_{th} \\ &N(q_s) + N(q_{res}) = N \end{aligned}\right\} \text{canonical ensemble}$$

Microstate $\{q_s, q_{res}\}$

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

Thermostat $\gg$ reservoir $\gg$ syst

Macro state: fixing q_{syst} & computing $P(q_s)$

* Route 1 & 2 are equivalent in the limits of large thermostat & reservoirs, with <u>finite</u> systems (still large enough to neglect interaction energy). Here: follow 1

2

$$P(q_s) = \sum_{q_{res} | N_s + N_{res} = N} \frac{1}{Z_{tot}(T,N)} e^{-\beta E(q_{res})} e^{-\beta E(q_s)} \quad ; \beta = \frac{1}{k_B T_{th}}$$

$$= e^{-\beta E(q_s)} \frac{1}{Z_{tot}(T,N)} \underbrace{\sum_{q_{res} | N_{res} = N - N_s} e^{-\beta E(q_{res})}}_{Z_{res}(T, N-N_s)}$$

$$P(q_s) = e^{-\beta E(q_s)} \frac{Z_{res}(T, V_{res}, N-N_s)}{Z_{tot}(T, V_{tot}, N_{tot})} \rightarrow e^{-\beta \underbrace{F_{res}(T, V_{res}, N-N_s)}_{F_{res}(T, V_{res}, N) - N_s \frac{\partial F_{res}}{\partial N}}}$$

$$P(q_s) = e^{-\beta E(q_s)} e^{\beta N_s \frac{\partial F_{res}}{\partial N}\big|_{T, V_{res}, N}} \cdot \frac{Z_{res}(T, V_{res}, N)}{Z_{tot}(T, V_{tot}, N)}$$

Chemical potential of the reservoir: $\mu_{res} = \dfrac{\partial F_{res}(T, V_{res}, N_{tot})}{\partial N}$

Fugacity: $z = e^{\beta\mu}$

Grand canonical partition function: $Q = \dfrac{Z_{tot}(T, V_{tot}, N)}{Z_{res}(T, V_{res}, N)}$

$\Rightarrow$ Grand canonical distribution function

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

Normalization: $Q = \sum_{q_s} e^{-\beta E(q_s) + \beta\mu N(q_s)} = \sum_N e^{\beta\mu N} \sum_{q_s | N(q_s) = N} e^{-\beta E}$

$$= \sum_N e^{\beta\mu N} Z_c(T, V, N) = \sum_{N,E} e^{\beta\mu N - \beta E + \beta T S_m}$$

Grand potential: $\boxed{G = -kT \ln Q}$

3.3.2) Fluctuations and large V limit

N is now a fluctuating quantity, set by the chemical potential

$\mu = \frac{\partial F}{\partial N}$. Since $F \propto N$, $\mu \underset{N\to\infty}{\sim} \mathcal{O}(1) \Rightarrow$ intensive quantity,

like the temperature.

To take the large system limit, we can now only send V to ∞, keeping T & μ constant.

Fluctuations of N:

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

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

[the $\frac{\partial}{\partial(-\beta)}$ of the canonical ensemble becomes $\frac{\partial}{\partial(\beta\mu)}$ here...]

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

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

$$\psi^{(n)}(\lambda)\Big|_{\lambda=0} = \frac{1}{\beta^n}\frac{\partial^n}{\partial \mu^n}\left[Q(\mu)\right] = \frac{\partial^n}{\partial(\beta\mu)^n}\left[-\beta G\right]$$

. Typical fluctuations

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

$$\langle N^2 \rangle_c = -\frac{1}{\beta}\partial_\mu^2 G|_T = kT \frac{\partial}{\partial \mu}\langle N \rangle$$

The typical fluctuations thus scale as $\sqrt{\langle N^2 \rangle_c} \propto \sqrt{\langle N \rangle} \ll \langle N \rangle$

as $V\to\infty$ and the relative fluctuations of N are small. 4
like those of E in the canonical ensemble.

Large V limit:

$$* \sum_{N,E} e^{\beta\mu N-\beta E+\beta T S_m(E,N,V)} \sim e^{\beta\mu N^*-\beta E^*+\beta T S_m(E^*,N^*,V)}$$

where N^* & E^* maximize $\Psi_\alpha(N,E,V)=\mu N-E+TS_m(E,N,V)$

$$\frac{\partial\Psi}{\partial E}=0 \Rightarrow -1+T\frac{\partial S_m}{\partial E}=0 \Rightarrow \left.\frac{\partial S_m(E,N,V)}{\partial E}\right|_{E^*,N^*}=\frac{1}{T}$$

$$\frac{\partial\Psi}{\partial N}=0 \Rightarrow \mu+T\frac{\partial S_m}{\partial N}=0 \Rightarrow \left.\frac{\partial S_m(E,V,N)}{\partial N}\right|_{E^*,N^*}=-\frac{\mu}{T} \quad (*)$$

$$* \text{ But also } Q=\sum_N e^{\beta\mu N} Z_c(N,V,T)=\sum_N e^{\beta\mu N-\beta F(N,V,T)}$$

$$\Rightarrow N^*=\underset{N}{\operatorname{argmax}}\left[\mu N-F(N,V,T)\right] \Rightarrow \mu-\left.\frac{\partial F(N,V,T)}{\partial N}\right|_{N^*}=0 \quad (**)$$

$\Rightarrow$ we start to see a lot of similarly looking relaxations that are consistent $\Rightarrow$ thermodynamic relaxations.

Proof of consistency:

$$F(N,V,T)=E^*-TS_m(E^*,N,V) \text{ when } \left.\frac{\partial S_m}{\partial E}\right|_{E^*,N}=\frac{1}{T}$$

$$\frac{\partial F}{\partial N}=\frac{\partial E^*}{\partial N}-T\frac{\partial S_m}{\partial N}-T\frac{\partial S_m}{\partial E^*}\cdot\frac{\partial E^*}{\partial N}=-T\frac{\partial S_m(E^*,N,V)}{\partial N} \Rightarrow \text{consistent!}$$

3.3.3) Thermodynamics

So far, we have ignored the variations of F & S with N

$$\Rightarrow dF = \frac{\partial F}{\partial V} dV + \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial N} dN = -p\,dV - S\,dT + \mu\,dN$$

$$dS = \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial N} dN = \frac{p}{T} dV + \frac{1}{T} dE - \frac{\mu}{T} dN$$

$\Rightarrow$ 1st principle $\boxed{dE = T\,dS - p\,dV + \mu\,dN}$

grand potential $G = E - TS - \mu N = F - \mu N$

$$\Rightarrow dG = dF - \mu\,dN - N\,d\mu = -S\,dT - p\,dV - N\,d\mu$$

Entropy $S = -\left.\frac{\partial G}{\partial T}\right|_{V,\mu}$ Pressure $p = -\left.\frac{\partial G}{\partial V}\right|_{T,\mu}$

All these definitions are consistent with canonical & microcanonical ones in the large V limit.

3.3.4) Ideal gas

Ideal gas

Grand partition function $Q = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N$

$$= \sum_N \frac{1}{N!} \left(\frac{V e^{\beta\mu}}{\lambda^3}\right)^N = \exp\left[\frac{V e^{\beta\mu}}{\lambda^3}\right] = e^{\frac{Vz}{\lambda^3}}$$

Fugacity $z = e^{\beta\mu}$

$P_{GC}(N) = \frac{1}{N!}\left(\frac{Vz}{\lambda^3}\right)^N e^{-\frac{V}{\lambda^3}z} \Rightarrow$ Poisson distribution of parameter

$$\langle N \rangle = \frac{V}{\lambda^3} z$$

$\Rightarrow$ Makes sense for a non interacting gas.

$\Rightarrow z$ controls the average density $\frac{\langle N \rangle}{V}$

$$\Rightarrow \mu = kT \ln\left[\frac{\Lambda^3 \langle N\rangle}{V}\right]$$

Grand potential

$$G = -kT \frac{V z}{\Lambda^3}$$

Pressure $P = -\frac{\partial G}{\partial V} = kT\frac{z}{\Lambda^3} = kT\frac{\langle N\rangle}{V} \Rightarrow EOS$

Can also do S, F, etc. $\Rightarrow$ consistent with canon & micro when $V \to \infty$

3.4) Thermodynamics

3.4.1) Thermodynamic variables

3 extensive variables, E, V, N & 3 intensive vars, T, p, μ.

$\Rightarrow 2^3 - 1 = 7$ ensembles with at least one extensive observable.

All these ensembles lead to thermodynamic potentials

$$\left.\begin{array}{l} (E,V,N) \to S_m \\ (T,V,N) \to F \\ (T,V,\mu) \to G \end{array}\right\} \text{etc.}$$

In the large size limit, all ensembles lead to consistent thermodynamics provided the variables are related by the saddle point relations*.

e.g. $\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V \Rightarrow U(T,V,N)$ constrains the variables.

$F = U - TS \Rightarrow$ the Legendre transform constrains the potentials.

$\Rightarrow$ Thermodynamic variables are NOT independent.

Experiments: what you can measure

Ensemble: what you can predict

* & the thermo potentials have the right convexity properties.