Constant Pressure & Chemical Potential

So far we mainly discussed situations @ const $N, V, \& T$ (which is very important). However many expts actually done @ const P:

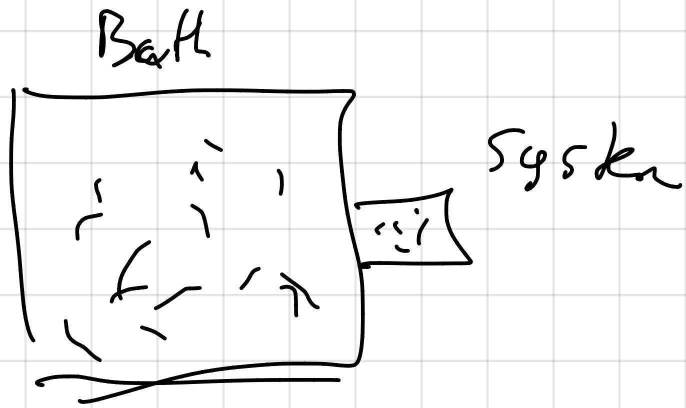
important → density/properties depend on external pressure

Additionally, N isn't always constant, especially when there are chemical reactions

[changing # of species $A, B, \ldots$ and also maybe then absorb from gas, eg]

How do we deal with this?

Reminder:



exchange energy, $\mathcal{E} = \mathcal{E}_b + \mathcal{E}_{system}$ conserved

If system very small

$$S_{bath}(N_{bath}, V_{bath}, \mathcal{E}_{bath}) \approx S_b(\mathcal{E}) + \underbrace{\left(\frac{\partial S_b}{\partial \mathcal{E}_b}\right)_{N,V}}_{1/T} \underbrace{(\mathcal{E}_b - \mathcal{E})}_{-\mathcal{E}_{sys}} + \cdots$$

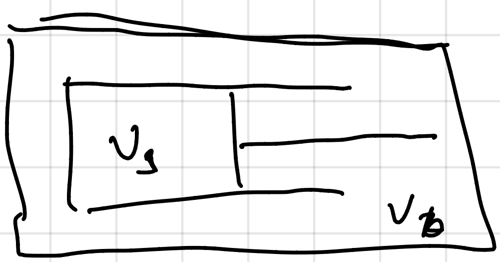
$S_{bath} = k_B \log \Omega_{bath} \Rightarrow$

$$\Omega_{bath} \approx e^{S_b(\mathcal{E})/k_B} e^{-\mathcal{E}_{sys}/k_BT} \propto e^{-\mathcal{E}_{sys}/k_BT}$$

& # states of bath where sys has state

$(N_{sys}, V_{sys}, T) = \Omega_{bath} = Q(N, V, T)$

Similarly:



$V = V_b + V_s$

@ eq $P_1 = P_2$

$$S_{bath}(N_{bath}, V_{bath}, \mathcal{E}_{bath}) \approx S_{bath}(V) + \underbrace{\left(\frac{\partial S}{\partial V_b}\right)_{N,\mathcal{E}}}_{+P/T} \underbrace{(V_b - V)}_{-V_{sys}} + \cdots$$

$$\Omega_b \propto e^{-\beta P V}, \quad (N, P, \mathcal{E})$$

Similarly

$N = N_s + N_b$

equil @ equal μ

$$S_b(N_b, V_b, E_b) \approx S_b(N) + \underbrace{\left(\frac{\partial S_b}{\partial N_b}\right)}_{-\mu/T}\underbrace{(N_b - N)}_{-N_{sys}} + \cdots$$

$$\Omega_b \propto e^{+\beta\mu N} \quad [\mu, V, E]$$

Now combine transformation from $E \to T$ w/ these to get $\Omega = P(N,P,T) \propto e^{-\beta E - \beta P V}$

$$\Delta(N,P,T) = \frac{1}{V_0}\int_0^\infty dV \int_{-\infty}^{\infty} dp \int_V dq \; e^{-\beta(\mathcal{H}(p,q) + PV)}$$

$$\approx \frac{1}{V_0}\int_0^\infty dV \; e^{-\beta P V}\, \Omega(N,V,T)$$

$$G = -k_B \log \Delta(N,P,T)$$

Isothermal! Isobaric

Grand canonical:

$$\Omega_b \to P(\mu, V, T) \propto e^{-\beta E + \beta\mu N} \quad \text{[note, } \mu \text{ can be pos or neg]}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{+\beta\mu N}\, \Omega(N, V, T)$$

$$\Omega(\mu, V, T) = -k_B T \log \mathcal{Z}(\mu, V, T) = -PV$$

(grand potential)

[Note; $e^{\beta\mu}$ sometimes called $\lambda \sim$ activity (fugacity), $\Delta\mu = k_B T \ln \lambda_2/\lambda_1$

These other ensembles are interesting because they allow for fluctuations in the quantities (V for isobaric, N for Grand) meaning the system is "compressible"

Eg

$$\langle N \rangle = k_B T \left(\frac{\partial}{\partial \mu} \log \mathcal{Z}(\mu, V, T) \right)$$

and

$$\frac{\partial}{\partial \mu} = \frac{\partial \lambda}{\partial \mu} \frac{\partial}{\partial \lambda} = \beta \lambda \, \partial/\partial\lambda$$

so

$$\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log \mathcal{Z}(\lambda, V, T)$$

$$\sqrt{\frac{h^2}{2\pi m}} \cdot \beta^{1/2}$$

$$\shortparallel$$

Ideal Gas

recall $Q(N,V,T) = \frac{1}{N!}\left(V/\Lambda^3\right)^N$, $\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$

$$\text{so } \mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(V/\Lambda^3\right)^N \lambda^N = \exp\left(\frac{V\lambda}{\Lambda^3}\right)$$

$$PV = k_B T \log \mathcal{Z} = k_B T \cdot \frac{V\lambda}{\Lambda^3} = k_B T \langle N \rangle$$

$$\text{but } \langle N \rangle = \lambda \frac{\partial}{\partial \lambda}\left(\log\left(\exp\left(\frac{V\lambda}{\Lambda^3}\right)\right)\right) = \frac{V\lambda}{\Lambda^3}$$

$$\text{so } \boxed{PV = \langle N \rangle RT}$$

$$\left[\frac{\partial \Lambda}{\partial \beta} = \frac{1}{2} \beta^{-1/2} \sqrt{\frac{h^2}{2\pi m}} = \frac{1}{2} \cdot \beta^{-1} \Lambda \right.$$

$$\text{and } \langle E \rangle = -\frac{\partial}{\partial \beta} \log \mathcal{Z} = -\frac{\partial}{\partial \beta}\left(\frac{V\lambda}{\Lambda^3}\right) = V\lambda \cdot 3 \Lambda^{-4} \frac{\partial \Lambda}{\partial \beta} = \frac{3}{2} \langle N \rangle k_B T$$

(sackr tetrode -exercise?)

What about fluctuations now

$$\sigma_N^2 = \langle N^2\rangle - \langle N\rangle^2$$

Lets start w/ $\langle N^2\rangle$

$$= \left\langle \sum_N N^2 P(N)\right\rangle_E = \left\langle \sum_N N^2 \frac{e^{-\beta E} e^{+\mu N\beta}}{Z}\right\rangle_E$$

$$= \frac{1}{Z}\left\langle \sum_N N \frac{1}{\beta}\frac{\partial}{\partial\mu} e^{\mu N\beta}\right\rangle = \frac{k_BT}{Z}\left\langle \frac{\partial}{\partial\mu}\sum_N N e^{\mu\beta N}\right\rangle_E$$

$$\langle N\rangle = \left\langle \sum_N e^{\mu\beta N}\cdot N / Z\right\rangle_E \Rightarrow \text{“}\langle N\rangle Z\text{”}$$

$$\langle N^2\rangle = \frac{k_BT}{Z}\frac{\partial}{\partial\mu}\left(\langle N\rangle Z\right) = \frac{k_BT}{Z}\cdot\left(\langle N\rangle\frac{\partial}{\partial\mu}Z + Z\frac{\partial}{\partial\mu}\langle N\rangle\right)$$

$$= \langle N^2\rangle + k_BT\frac{\partial}{\partial\mu}\langle N\rangle$$

$$\Rightarrow k_BT\frac{\partial}{\partial\mu}\langle N\rangle = \langle N^2\rangle - \langle N^2\rangle = \sigma_N^2 \quad \ast\ \text{FDT}$$

$$\langle N\rangle = k_BT\frac{\partial}{\partial\mu}\log Z = \frac{\partial}{\partial\mu}\left(k_BT\log Z\right)$$

nontrivial

so $\sigma_N^2 = (k_BT)^2\frac{\partial^2}{\partial\mu^2}\log Z = k_BTV\frac{\partial^2 P}{\partial\mu^2}$

Non-trivial to make this useful

$a(T,v) = \frac{F(N,V,T)}{N}$, $v = V/N$ (only depends on intensive variables)

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N}(aN) = a + \frac{\partial a}{\partial N}N = a + N\left(\frac{\partial a}{\partial(V/N)}\right)\frac{\partial(V/N)}{\partial N} = a - v\frac{\partial a}{\partial v}$$

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

$$\frac{\partial \mu}{\partial v} = \frac{\partial}{\partial v}\left(a - v\frac{\partial a}{\partial v}\right) = \frac{\partial a}{\partial v} - v\frac{\partial^2 a}{\partial v^2} - \frac{\partial a}{\partial v} = -v\frac{\partial^2 a}{\partial v^2}$$

Pressure

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial (NF/N)}{\partial V} = -N\frac{\partial a}{\partial v}\frac{\partial (V/N)}{\partial V} = -\frac{\partial a}{\partial v}$$

$$\frac{\partial P}{\partial v} = -\frac{\partial a^2}{\partial v^2} \Rightarrow \boxed{\frac{\partial \mu}{\partial v} = v\frac{\partial P}{\partial v}}$$

Also: $\left(\frac{\partial P}{\partial \mu}\right)_{T,V} = \frac{\partial}{\partial \mu}\left(\frac{k_BT}{V}\ln Z\right) = \frac{1}{V}\frac{\partial}{\partial \mu}\left(k_BT\ln Z\right) = \langle N\rangle/V = \frac{1}{v}$

Back to $\sigma_N^2 = k_BT\,V\frac{\partial^2 P}{\partial \mu^2} = k_BT\,V\frac{\partial}{\partial \mu}\left(\frac{\partial P}{\partial \mu}\right)$

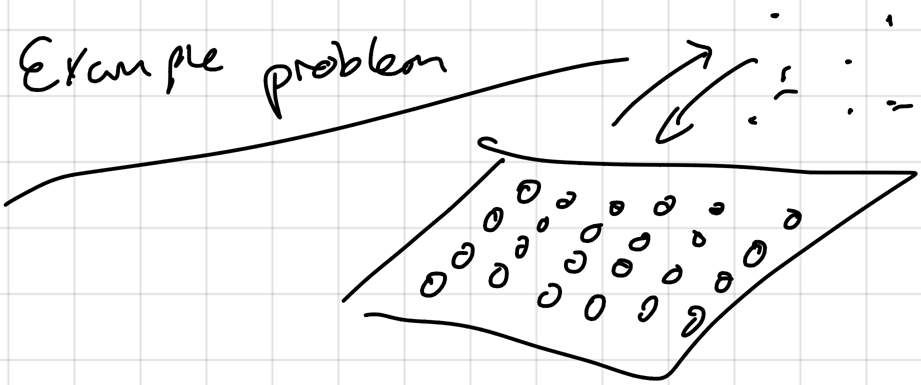
$$= k_BT\,V\left(\frac{\partial v}{\partial \mu}\right)\frac{\partial}{\partial v}\underbrace{\left(\frac{\partial P}{\partial \mu}\right)}_{1/v} = k_BT\,V\cdot\frac{-1}{v^2}\cdot\frac{\partial v}{\partial \mu}$$

$$= k_BT\,V\,\frac{-1}{v^2}\cdot\left(\frac{1}{v}\frac{\partial v}{\partial P}\right)$$

$$\boxed{\sigma_N^2 = \frac{k_BT\langle N\rangle^2}{V}\cdot \kappa}$$

$-\kappa_T$

Example problem



@ eq when $\mu_{gas} = \mu_{substrate}$

if site occupied or unoccupied & each site has partition function 1 when unoc & q otherwise

$$Q(N, M, T) = \binom{M}{N} q^N$$

$$Z = \sum_{N=0}^{M} e^{\mu N \beta} Q(N) = \sum_{N=0}^{M} \binom{M}{N} (e^{\mu\beta} q)^N (1)^{M-N}$$

$$= (1 + q e^{\mu\beta})^M$$

$$\langle N \rangle = k_B T \frac{\partial \log Z}{\partial \mu} = k_B T M \frac{\partial}{\partial \mu} \log(1 + q e^{\mu\beta})$$

$$= \cancel{k_B} T M \cdot \frac{q \cancel{\beta} e^{\mu\beta}}{1 + q e^{\mu\beta}}$$

$$\langle N \rangle / M = \theta = \frac{q e^{\mu\beta}}{1 + q e^{\mu\beta}}$$

For the gas $\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$, $A = -k_BT\ln Z$

$$Z = \frac{1}{N!}\Big(\underbrace{V/\Lambda^3}_{q_g}\Big)^N$$

$$\mu_g = -k_BT\frac{\partial}{\partial N}\left(\ln\left(\frac{1}{N!}\Big(\overbrace{\frac{V}{\Lambda^3}}^{q_g}\Big)^N\right)\right)$$

$$= -k_BT\frac{\partial}{\partial N}\left(N\ln q_g - N\log N + N\right)$$

$$= -k_BT\left(\ln q_g + 1 - (1 + \log N)\right)$$

$$= -k_BT\ln(q_g/N)$$

$PV = Nk_BT$

$$\Theta = \frac{q_s/(q_g/N)}{1 + (q_s/(q_g/N))} = \frac{(q_g/N)^{-1}}{1/q_s + (q_g/N)^{-1}}$$

$q_g = \frac{V}{\Lambda^3} \Rightarrow$

$$q_g/N = \left(\frac{V}{N}\right)\cdot\frac{1}{\Lambda^3} = \frac{k_BT}{P\Lambda^3}$$

$$= \frac{P\Lambda^3\beta}{1/q_s + P\Lambda^3\beta} = \frac{P}{P + \frac{1}{\Lambda^3\beta q_s}} \rightarrow P_0 = \frac{k_BT}{q_s}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}$$

$$= \frac{P}{P+P_0}$$