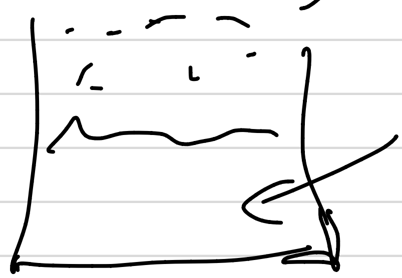
Other Ensembles:

Constant Pressure &

Constant Chemical Potential

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



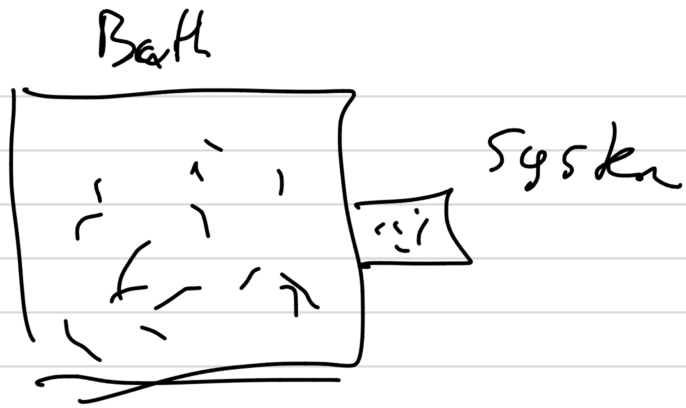
important → density/properties depend on external pressure

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

[changing # of species $A, B, \ldots$ and also maybe them 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

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

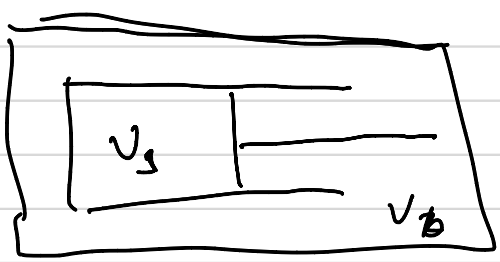
$S_{bath} = k_B \log \Omega_{bath} \Rightarrow$

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

& # states of bath where sys has state

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

Similarly:



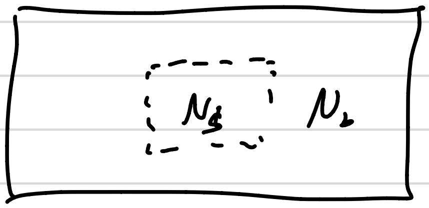
$V = V_b + V_s$

@ eq $P_1 = P_2$

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

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

Similarly



$N = N_s + N_b$

equil @ equal μ

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

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

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

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

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

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

Grand Canonical:

$\Omega_b \to P(\mu, V, T) \propto e^{-\beta\mathcal{E} + \beta\mu N}$ [note, μ 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 λ ~ 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 $\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \log \mathcal{Z}(\lambda, V, T)$

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

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

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

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

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

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

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

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/ $\langle N^2 \rangle$

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

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

$$\langle N \rangle = \langle \sum_N e^{\mu \beta N} \cdot N / Z \rangle_E \Rightarrow \text{"} \langle N \rangle Z \text{"}$$

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

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

$$\Rightarrow k_B T \frac{\partial}{\partial \mu} \langle N \rangle = \langle N^2 \rangle - \langle N^2 \rangle = \sigma_N^2 \quad \text{※ FDT}$$

$$\langle N \rangle = k_B T \frac{\partial}{\partial \mu} \log Z = \frac{\partial}{\partial \mu} (k_B T \log Z)$$

nontrivial

$$\text{so } \sigma_N^2 = (k_B T)^2 \frac{\partial^2}{\partial \mu^2} \log Z = k_B T V \frac{\partial^2 P}{\partial \mu^2}$$

Non-trivial to make this useful

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

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

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

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

Pressure

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

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

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

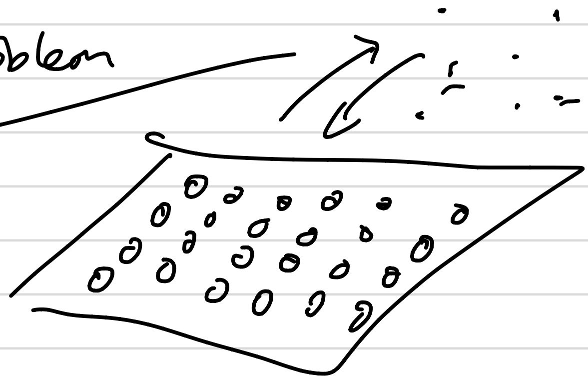
Back to $\sigma_N^2 = k_BT\,V\frac{\partial^2 P}{\partial \mu^2} = k_BTV\frac{\partial}{\partial \mu}\left(\frac{\partial P}{\partial \mu}\right)$

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

$$= k_BTV\,\frac{-1}{v^2}\cdot\underbrace{\left(\frac{1}{v}\frac{\partial v}{\partial P}\right)}_{-K_T}$$

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

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

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

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

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

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

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

$PV = Nk_BT$

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

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

$$= \frac{P\Lambda^3\beta}{1/q_s + P\Lambda^3\beta} = \frac{P}{P + \frac{1}{\Lambda^3\beta q_s}}$$

$$\rightarrow P_0 = \frac{k_BT}{q_s}\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}$$

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