

We can write σ_N^2 in terms of more familiar response functions as follows:

$$\sigma_N^2 = \frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T, V}$$

write $v \equiv V/N \Rightarrow N = V/v$

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T, V} = \left(\frac{\partial (V/v)}{\partial \mu} \right)_{T, V} = -\frac{V}{v^2} \left(\frac{\partial v}{\partial \mu} \right)_{T, V}$$

By Gibbs-Duhem relation $Nd\mu = Vdp - SdT$
 $d\mu = vdp - (v/N)dt$

\Rightarrow at constant T , $d\mu = vdp$

$$\Rightarrow \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T, V} = -\frac{V}{v^2} \left(\frac{\partial v}{\partial p} \right)_{T, V} = -\frac{N^2}{V} \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_{T, V}$$

now, since both v and p are intensive, they are independent of $V, N \Rightarrow \left(\frac{\partial v}{\partial p} \right)_{T, V} = \left(\frac{\partial v}{\partial p} \right)_{T, N} = \left(\frac{\partial (V/N)}{\partial p} \right)_{T, N} = \frac{1}{N} \left(\frac{\partial V}{\partial p} \right)_{T, N}$

$$\text{so } \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = \frac{N}{V} \left(\frac{\partial v}{\partial p} \right)_T = \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, N} = -\kappa_T$$

$$\text{so } \frac{\sigma_N^2}{\langle N \rangle^2} = \frac{1}{\beta N^2} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T, V} = \frac{k_B T}{N^2} \frac{N^2}{V} \kappa_T$$

$$= \frac{k_B T}{V} \kappa_T$$

$$\frac{\sigma_N}{\langle N \rangle} = \sqrt{\frac{k_B T \kappa_T}{V}}$$

κ_T is isothermal compressibility or ~~is~~ const except perhaps at a phase transition

Energy

$$\text{Write } \mathcal{Z} = \sum_i e^{-\beta(E_i - \mu N_i)} = \sum_i e^{-\beta E_i} z^{N_i}$$

$$\text{Then } -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{z, V} = -\frac{1}{\mathcal{Z}} \left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{z, V} = \frac{1}{\mathcal{Z}} \sum_i E_i e^{-\beta E_i} z^{N_i} = \langle E \rangle$$

$$\text{and } \left(\frac{\partial^2 \ln \mathcal{Z}}{\partial \beta^2}\right)_{z, V} = -\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z, V} = \frac{1}{\mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \beta^2}\right)_{z, V} - \frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{z, V}^2$$

Now

$$\frac{1}{\mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \beta^2}\right)_{z, V} = \frac{1}{\mathcal{Z}} \sum_i E_i^2 e^{-\beta E_i} z^{N_i} = \langle E^2 \rangle$$

$$\frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{z, V}^2 = \langle E \rangle^2$$

Note the important difference
in taking derivatives at
constant $z = e^{\beta \mu}$ rather
than at constant μ

So

$$-\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z, V} = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z, V} = \langle E^2 \rangle - \langle E \rangle^2 \equiv \sigma_E^2$$

Above expression involves derivative at constant $\underline{z} = e^{\beta \mu}$

We want to convert it to an expression at constant N

$$\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z, V} = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N, V} + \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T, V} \left(\frac{\partial N}{\partial T}\right)_{z, V}$$

Above follows from regarding E as a function of T, N, V and N as a function of z, V, T , and then applying the chain rule to differentiate

$$E(T, N, V) = E(T, N(z, V, T), V)$$

$$\left(\frac{\partial \langle E \rangle}{\partial T} \right)_{z, V} = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{\mu, V} + \left(\frac{\partial \langle E \rangle}{\partial N} \right)_{T, \mu} \left(\frac{\partial N}{\partial T} \right)_{z, V}$$

$$\uparrow$$

$$= C_V$$

this term is the same
one we had for energy
fluctuations in the
canonical ensemble



this term is the extra
fluctuation in energy
due to fluctuations in N
in the grand canonical ensemble

To ~~can~~ rewrite the ~~second~~ second term above, one can
show that

$$\left(\frac{\partial N}{\partial T} \right)_{z, V} = \frac{1}{T} \left(\frac{\partial \langle E \rangle}{\partial \mu} \right)_{T, V} = \frac{1}{k_B T^2} [\langle EN \rangle - \langle E \rangle \langle N \rangle]$$

proof left to the reader

$$\text{Then: } \left(\frac{\partial \langle E \rangle}{\partial \mu} \right)_{T, V} = \left(\frac{\partial \langle E \rangle}{\partial N} \right)_{T, V} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T, V} = \left(\frac{\partial \langle E \rangle}{\partial N} \right)_{T, V} \beta \sigma_N^2$$

last step comes from our earlier calculation of σ_N

So finally

$$\sigma_E^2 = k_B T^2 \left\{ C_V + \left(\frac{\partial \langle E \rangle}{\partial N} \right)_{T, \mu} \frac{1}{T} \left(\frac{\partial \langle E \rangle}{\partial N} \right)_{T, V} \beta \sigma_N^2 \right\}$$

$$\sigma_E^2 = k_B T^2 C_V + \left(\frac{\partial \langle E \rangle}{\partial N} \right)_{T, \mu}^2 \sigma_N^2$$

Note: $C_V \sim N$, $\frac{\partial \langle E \rangle}{\partial N} \sim \frac{N}{N} \sim 1$, $\sigma_N^2 \sim N$

So $\sigma_E^2 \sim N$ and $\frac{\sigma_E}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$

Grand Canonical partition function for non-interacting systems

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Q_N(T, V)$$

for non-interacting particles we saw

$$\begin{aligned} Q_N(T, V) &= \frac{1}{N!} [Q_1(T, V)]^N && \text{indistinguishable particles} \\ & && \text{(as in ideal gas)} \\ &= [Q_1(T, V)]^N && \text{distinguishable particles} \\ & && \text{(as in paramagnetic spins)} \end{aligned}$$

⇒ Indistinguishable

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{(z Q_1)^N}{N!} = e^{z Q_1}$$

Distinguishable

$$\mathcal{Z} = \sum_{N=0}^{\infty} (z Q_1)^N = \frac{1}{1 - z Q_1}$$

↪ must have $z Q_1 < 1$ for series to converge

Indistinguishable: $-pV = \Sigma = -k_B T \ln \mathcal{Z} = -k_B T z Q_1$

$$p = \frac{k_B T}{V} z Q_1$$

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

also $N = -\frac{\partial \Sigma}{\partial \mu} = k_B T \frac{\partial z Q_1}{\partial \mu} = k_B T \cdot \beta z Q_1$
 $= z Q_1$

⇒ $p = \frac{k_B T N}{V}$ ideal gas law no matter what Q_1 !

Chemical equilibrium

Suppose $n_1 A_1 + n_2 A_2 \leftrightarrow n_3 A_3$

chemical reaction among species A_1, A_2, A_3

What determines equilb concentrations of A_1, A_2, A_3 ?

Consider total entropy as function of N_1, N_2, N_3
numbers of A_1, A_2, A_3

$S(N_1, N_2, N_3)$ N_i adjust to maximize S

$$dS = 0 = \sum_i \frac{\partial S}{\partial N_i} dN_i = \sum_i -\frac{\mu_i}{T} dN_i \quad (\text{all species in equilb at common } T)$$

Now if N_3 ~~changes~~ by decreases by $-dN$
Then N_1 and N_2 increase by $\frac{n_1}{n_3} dN$ and $\frac{n_2}{n_3} dN$
respectively.

$$\text{or if } dN_3 = -n_3 dN$$

$$dN_1 = n_1 dN$$

$$dN_2 = n_2 dN$$

$$\text{So } -\frac{\mu_1}{T} dN_1 - \frac{\mu_2}{T} dN_2 - \frac{\mu_3}{T} dN_3 = 0$$

$$\Rightarrow \mu_1 n_1 + \mu_2 n_2 - \mu_3 n_3 = 0$$

$$\boxed{\mu_1 n_1 + \mu_2 n_2 = \mu_3 n_3}$$

~~interaction between atoms~~

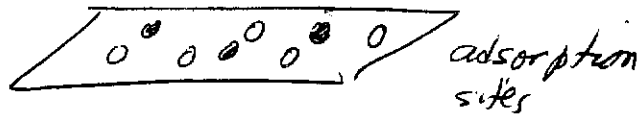
~~interaction between atoms~~

goal will be to
choose N_i such that
the $\mu_i(T, V, N_i)$
satisfy this condition

Example



Consider an ideal gas at temperature T and pressure p that is in equilibrium with a surface containing N_0 adsorption sites. Each adsorption site can hold at most one particle of the gas. The binding energy of a particle to the adsorption site is $-\epsilon$. What is the fraction of occupied adsorption sites as a function of T and p ?



Solution: Regard the ideal gas and the gas of adsorbed particles as two separate systems. Since these two systems are in equilibrium with each other, and can exchange particles between each other, they must be at the same temperature and equal chemical potential.

To solve the problem we

- ① Find the number N of occupied adsorption sites assuming the gas of adsorbed particles is at temperature T and chemical potential μ .
- ② Find the chemical potential $\mu(T, p)$ of the ideal gas at temperature T , pressure p .
- ③ Insert μ from ② into result from ① since the chemical potentials of the two systems must be equal. From this we can get (N/N_0) as function of T and p .