Fluctuations - We want to show that the grand canonical distribution is indeed sharply peaked about the average $\langle E\rangle$ and $\langle N\rangle$

Particle Number

We had $\langle N\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}(\ln \mathcal{Z})$

$$\Rightarrow \quad \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{1}{\beta^2}\frac{\partial^2(\ln\mathcal{Z})}{\partial\mu^2}$$

$$= \frac{1}{\beta^2}\frac{\partial}{\partial\mu}\left(\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu}\right) = \frac{1}{\beta^2}\left[\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\mu^2} - \frac{1}{\mathcal{Z}^2}\left(\frac{\partial\mathcal{Z}}{\partial\mu}\right)^2\right]$$

Now $\frac{1}{\beta\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu} = \frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial\mu} = \langle N\rangle$

and $\frac{1}{\beta^2\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\mu^2} = \frac{1}{\beta^2}\frac{\frac{\partial^2}{\partial\mu^2}\sum_i e^{-\beta E_i}e^{\beta\mu N_i}}{\mathcal{Z}} = \langle N^2\rangle$

so $\frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{1}{\beta^2}\frac{\partial^2\ln\mathcal{Z}}{\partial\mu^2} = \langle N^2\rangle - \langle N\rangle^2$

$\sigma_N^2 \equiv \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} \sim N$ as μ, β _intensive_

so $\frac{\sigma_N}{\langle N\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0$ as $N \to \infty$

fluctuations in N vanish as $N \to \infty$

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 $\quad N d\mu = V dp - S dT$

$$d\mu = v\,dp - (S/N)\,dT$$

$\Rightarrow$ at constant T, $d\mu = v\,dp$

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

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

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

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

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

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

κ_T is isothermal compressibility ∼ const except perhaps at a phase transition

Energy

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

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

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

Now

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

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

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

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

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

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 rewrite the second term above, one can show that

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

proof left to the reader

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

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

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

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

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

for non-interacting particles we saw

$$Q_N(T,V) = \frac{1}{N!}\left[Q_1(T,V)\right]^N$$ indistinguishable particles (as in ideal gas)

$$= \left[Q_1(T,V)\right]^N$$ distinguishable particles (as in paramagnetic spins)

$\Rightarrow$ Indistinguishable

$$\mathcal{L} = \sum_{N=0}^{\infty} \frac{(zQ_1)^N}{N!} = e^{zQ_1}$$

Distinguishable

$$\mathcal{L} = \sum_{N=0}^{\infty} (zQ_1)^N = \frac{1}{1-zQ_1}$$ $\leftarrow$ must have $zQ_1 < 1$ for series to converge

Indistinguishable : $-pV = \Sigma = -k_BT \ln \mathcal{L} = -k_BT\, zQ_1$

$$p = \frac{k_BT}{V}\, zQ_1 \qquad z = e^{\beta\mu}$$

also $N = -\frac{\partial \Sigma}{\partial \mu} = k_BT \frac{\partial z}{\partial \mu} Q_1 = k_BT \cdot \beta\, zQ_1$

$$= zQ_1$$

$\Rightarrow$ $p = \frac{k_BTN}{V}$ 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 equilib 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

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

$$dS = 0 = \sum_i \frac{\partial S}{\partial N_i} dN_i = \sum_i -\frac{\mu_i}{T} dN_i$$ (all species in equilib 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.

or if
$$dN_3 = -n_3 dN$$
$$dN_1 = n_1 dN$$
$$dN_2 = n_2 dN$$

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

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

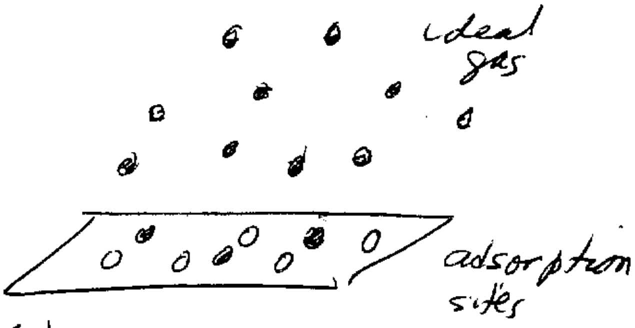
$$\boxed{\mu_1 n_1 + \mu_2 n_2 = \mu_3 n_3} \longleftarrow$$

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

~~atom + photon ⇔ atom~~

~~$\Rightarrow \mu_{atom} + \mu_{photon} = \mu_{atom} \Rightarrow \mu_{photon} = 0$~~

Exaple



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.

step ① We can do this using either the canonical or grand canonical ensembles

canonical ensemble - compute Q_N

Let $\{\alpha\}$ be the set of states of adsorbed particles that have exactly N sites occupied and the rest empty.

$$Q_N = \sum_{\alpha} e^{-\beta E_\alpha}$$

In general case, E_α will depend on the state α. But here $E_\alpha = -\epsilon N$ is the same for all states - it does not matter which of the sites are occupied since they all have the same binding energy $-\epsilon$.

$$Q_N = e^{+\beta\epsilon N} \sum_{\alpha}$$

the sum is now over all states with exactly N occupied sites. The number of ways to choose which N of the N_0 sites are occupied is $\frac{N_0!}{N!\,(N_0-N)!}$. So the canonical partition function

is

$$Q_N = \frac{N_0!}{N!\,(N_0-N)!}\, e^{\beta\epsilon N}$$

Now find the Helmholtz free energy

$$A(T,N) = -k_B T \ln Q_N$$
$$= -\epsilon N - k_B T \left\{ \ln N_0! - \ln N! - \ln (N_0 - N)! \right\}$$

$$= -\epsilon N - k_B T \left\{ N_0 \ln N_0 - N_0 - N \ln N + N - (N_0 - N) \ln (N_0 - N) + (N_0 - N) \right\}$$

$$= -\epsilon N - k_B T \left\{ N_0 \ln N_0 - N \ln N - (N_0 - N) \ln (N_0 - N) \right\}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_T = -\epsilon + k_B T \left\{ \ln N + N\left(\frac{1}{N}\right) - \ln (N_0 - N) - \frac{(N_0 - N)}{(N_0 - N)} \right\}$$

$$\mu = -\epsilon + k_B T \ln \left(\frac{N}{N_0 - N} \right)$$

$$\frac{N}{N_0 - N} = e^{\beta(\epsilon + \mu)}$$

$$N = \frac{N_0 e^{\beta(\epsilon+\mu)}}{1 + e^{\beta(\epsilon+\mu)}} = \frac{N_0}{1 + e^{-\beta(\epsilon+\mu)}}$$

fraction occupied is

$$\boxed{\frac{N}{N_0} = \frac{1}{1 + e^{-\beta(\epsilon+\mu)}}}$$

now we do the same calculation, but in the <u>grand canonical ensemble</u>

let $\{\alpha\}$ be the set of states of adsorbed particles, where the number of adsorbed particles is free to be anything from zero to N_0. The grand partition function is:

$$\mathcal{L} = \sum_{\alpha} e^{-\beta(E_\alpha - \mu N_\alpha)}$$

E_α is total energy of state α

N_α is the number of occupied ~~state~~ sites in state α

For adsorption site i define a variable s_i such that

$$s_i = \begin{cases} 1 & \text{if site } i \text{ is occupied} \\ 0 & \text{if site } i \text{ is empty} \end{cases}$$

a particular state α can then be specified by giving the values 1 or 0 of each of the N_0 variables s_i

In terms of these variables we have for the energy and number of adsorbed particles:

$$\alpha = \{s_i\} \Rightarrow \quad E_\alpha = -\epsilon \sum_i s_i$$

$$N_\alpha = \sum_i s_i$$

The partition function can thus be written as

$$\mathcal{L} = \sum_{\{s_i\}} e^{-\beta\left[-\epsilon \sum_i s_i - \mu \sum_i s_i\right]} = \sum_{\{s_i\}} e^{\beta(\epsilon+\mu)\sum_i s_i}$$

we can factor the exponential since the degrees of freedom s_i are non-interacting with each other

$$\mathcal{Z} = \sum_{\{s_i\}} \prod_{i=1}^{N_0} e^{\beta(\epsilon+\mu)s_i} = \prod_{i=1}^{N_0} \left[\sum_{s_i=0,1} e^{\beta(\epsilon+\mu)s_i} \right]$$

$$= \prod_{i=1}^{N_0} \left[1 + e^{\beta(\epsilon+\mu)} \right] = \left[1 + e^{\beta(\epsilon+\mu)} \right]^{N_0}$$

Now we compute the grand potential

$$\Sigma(T,\mu) = -k_B T \ln \mathcal{Z}$$

$$= -k_B T N_0 \ln\left[1 + e^{\beta(\epsilon+\mu)} \right]$$

The average number of adsorbed particles is then

$$N = -\left(\frac{\partial \Sigma}{\partial \mu}\right)_T = \frac{k_B T N_0 \, \beta e^{\beta(\epsilon+\mu)}}{\left(1 + e^{\beta(\epsilon+\mu)}\right)}$$

$$\boxed{N = \frac{N_0}{1 + e^{-\beta(\epsilon+\mu)}}}$$

this is the same result as we found using the canonical ensemble, as it must be!

Step ② Now we compute the chemical potential μ of the ideal gas at temperature T and pressure P.

We will use the grand canonical ensemble. Since particles in the gas are non-interacting we have

$$\mathcal{L} = e^{zQ_1} \quad \text{where} \quad z = e^{\beta\mu} \quad \text{and}$$

Q_1 is the one particle partition function

$$Q_1 = \frac{\int d^3p \int d^3r}{h^3}\, e^{-\beta p^2/2m} = \frac{V}{h^3} \sqrt{\frac{2\pi m}{\beta}}^{\,3}$$

$$= V \sqrt{\frac{2\pi m k_B T}{h^2}}^{\,3} = \frac{V}{\lambda^3}$$

where $\lambda \equiv \sqrt{\frac{h^2}{2\pi m k_B T}}$ is called the "thermal wavelength"

$$-pV = \Sigma = -k_B T \ln \mathcal{L} = -k_B T\, z Q_1$$

$$p = \frac{k_B T}{V} z Q_1 = \frac{k_B T}{V} z \frac{V}{\lambda^3}$$

$$p = \frac{k_B T}{\lambda^3} z$$

$$z = e^{\beta\mu} = \frac{\lambda^3 p}{k_B T}$$

step ③ substitute μ from step ②
into result from step ①

$$\frac{N}{N_0} = \frac{1}{1 + e^{-\beta\mu} e^{-\beta\epsilon}}$$

$$= \frac{1}{1 + \frac{k_B T}{p\lambda^3} e^{-\beta\epsilon}}$$

$$\boxed{\frac{N}{N_0} = \left[1 + \frac{k_B T}{P}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{-\epsilon/k_B T}\right]^{-1}}$$

Note: as $T \to 0$, $\frac{N}{N_0} \to 1$ as expected

as $T \to \infty$ $\frac{N}{N_0} \to 0$ as expected