Fluctuation of the energy

Recall that in the canonical ensemble we had

$$\langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = -k_B \frac{\partial \langle E \rangle}{\partial (1/T)} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}$$

$$= k_B T^2 C_V$$

$\qquad\qquad\qquad \underleftarrow{\text{specific heat at constant volume}}$

We now want to see how the fluctuation of N in the grand canonical ensemble will effect the fluctuation of E.

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

$\qquad\qquad\qquad\qquad\qquad \underleftarrow{\text{fugacity } z = e^{\beta \mu}}$

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

$$= \sum_i \rho_i E_i = \langle E \rangle$$

and

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

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

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

So

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

In above it was crucial that derivates were taken at constant $z = e^{\beta \mu}$

Note $\sigma_E^2 = -\left(\dfrac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V}$ E is extensive so $\sim N$

β is intensive

so $\sigma_E^2 \sim N$

then $\dfrac{\sigma_E}{\langle E \rangle} \sim \dfrac{\sqrt{N}}{N} \sim \dfrac{1}{\sqrt{N}} \to 0$ as $N \to \infty$

We now want to write σ_E in terms of more familiar response functions. To do so we want to take our derivative $\left(\dfrac{\partial \langle E \rangle}{\partial T}\right)_{z,V}$ at constant z and rewrite in terms of derivatives at constant N.

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

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

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

Now $\left(\dfrac{\partial \langle E \rangle}{\partial T}\right)_{N,V} = C_V$ specific heat at constant volume

so this first term in $(*)$ is same as in the canonical ensemble. The second term gives the additional fluctuations in E that arise because N is fluctuating

For the second term one can show

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

proof left to the reader

Then

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

where the last step comes from our earlier calculation of σ_N

So finally

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

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

↑ as in canonical ensemble

↑ additional fluctuations in E due to fluctuations in N

Note, $C_V \sim N$ extensive

$$\frac{\partial \langle E \rangle}{\partial N} \sim \frac{extensive}{extensive} \sim intensive$$

$$\sigma_N^2 \sim N \quad extensive$$

So $\sigma_E^2 \sim N$ is extensive and

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \quad as \ we \ saw \ before$$

Proof

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{\partial}{\partial T}\left[\frac{1}{\mathcal{Z}}\sum_i e^{-\beta E_i} z^{N_i} N_i\right]_{z,V}$$

$$= \frac{1}{\mathcal{Z}}\sum_i e^{-\beta E_i} z^{N_i} N_i \left(\frac{E_i}{k_B T^2}\right)$$

$$- \frac{1}{\mathcal{Z}^2}\left(\sum_i e^{-\beta E_i} z^{N_i} N_i\right)\left(\sum_i e^{-\beta E_i} z^{N_i}\left(\frac{E_i}{k_B T^2}\right)\right)$$

$$= \frac{1}{k_B T^2}\left(\langle NE\rangle - \langle N\rangle\langle E\rangle\right)$$

while

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

$$= \frac{1}{T}\frac{1}{\mathcal{Z}}\sum_i e^{-\beta E_i} e^{\beta \mu N_i} \beta N_i E_i$$

$$- \frac{1}{T}\frac{1}{\mathcal{Z}^2}\left(\sum_i e^{-\beta E_i} e^{\beta \mu N_i} E_i\right)\left(\sum_i e^{-\beta E_i} e^{\beta \mu N_i} \beta N_i\right)$$

$$= \frac{1}{k_B T^2}\left(\langle NE\rangle - \langle E\rangle\langle N\rangle\right)$$

So $$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial \langle E\rangle}{\partial \mu}\right)_{T,V}$$

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

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

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

$\Rightarrow$ <u>Indistinguishable</u>

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

<u>Distinguishable</u>

$$\mathcal{L} = \sum_{N=0}^{\infty} (z Q_1)^N = \frac{1}{1 - z Q_1} \quad \leftarrow \text{must have}$$
$$z Q_1 < 1 \quad \text{for series to converge}$$

Indistinguishable :
$$-pV = \sum = -k_B T \ln \mathcal{L} = -k_B T \, z Q_1$$

$$p = \frac{k_B T}{V} z Q_1 \qquad\qquad z = e^{\beta \mu}$$

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

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

Ideal gas

For a single gas of particles

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

$$= V f(T)$$

will have this form even for a more complicated gas in which the particles may have internal degrees of freedom.

$$\mathcal{L} = e^{z Q_1} = e^{z V f(T)} \qquad \ln \mathcal{L} = z V f(T)$$

grand potential $\quad \Sigma = -k_B T \ln \mathcal{L} = -k_B T z V f(T) = -pV$

$$p = k_B T z f(T) \qquad\qquad z = e^{\beta \mu}$$

$$N = -\frac{\partial \Sigma}{\partial \mu} = -\frac{\partial \Sigma}{\partial z} \frac{\partial z}{\partial \mu} = k_B T V f(T) \beta e^{\beta \mu}$$

$$= z V f(T)$$

Combine the above
$$\begin{array}{l} \dfrac{p}{k_B T} = z f(T) \\[2mm] \dfrac{N}{V} = z f(T) \end{array} \Bigg\} \Rightarrow pV = N k_B T$$

Ideal gas law!
independent of what
f is!

$$E = -\left(\frac{\partial}{\partial \beta} \ln \mathcal{Z}\right)_{\mathcal{Z}, V} = k_B T^2 \left(\frac{\partial}{\partial T} \ln \mathcal{Z}\right)_{\mathcal{Z}, V}$$

$$= k_B T^2 \, z V \frac{df}{dT} = k_B T^2 N \, \frac{(df/dT)}{f} = k_B T^2 N \left(\frac{\partial \ln f}{\partial T}\right)$$

use $N = z \, V f$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N, V} = 2 k_B T N \frac{\partial \ln f}{\partial T} + k_B T^2 N \frac{\partial^2 \ln f}{\partial T^2}$$

Note, for harmonic degrees of freedom (i.e. $\vec{p}$, or harmonic internal degrees of freedom, such as internal vibrations of molecule) $f \propto T^n$ for some power n (for single particle, $n = 3/2$)

$$\Rightarrow \frac{\partial \ln f}{\partial T} = \frac{\partial}{\partial T}(n \ln T) = \frac{n}{T}$$

$$\frac{\partial^2 \ln f}{\partial T^2} = \frac{-n}{T^2}$$

and so

ideal gas law

$$E = n k_B T N = n p V \Rightarrow \frac{E}{V} = n p$$

$$C_V = 2 n k_B N + k_B T^2 N \left(\frac{-n}{T^2}\right) = n k_B N$$

Helmholtz free energy

$$A = \Sigma + \mu N = -k_B T z V f(T) + k_B T (\ln z) z V f$$

$$= z V k_B T f(T) \left[\ln z - 1 \right]$$

$$= N k_B T \left[\ln z - 1 \right]$$

$$A(T, V, N) = N k_B T \left[\ln \left(\frac{N}{V f(T)} \right) - 1 \right]$$

above agrees with direct result from canonical ensemble:

$$Q_N = \frac{V^N f^N}{N!} \Rightarrow A = -k_B T \ln Q_N = -k_B T \ln \left(\frac{V^N f^N}{N!} \right)$$

$$= -k_B T \, N \ln V f + k_B T (N \ln N - N)$$

$$= -N k_B T + N k_B T \ln \left(N / V f \right)$$

entropy

$$S = -\left(\frac{\partial A}{\partial T} \right)_{V, N} = N k_B \left[\ln \left(\frac{N}{V f(T)} \right) - 1 \right]$$

$$- N k_B T \frac{d (\ln f)}{dT}$$

For distinguishable particles

- corresponds to situation where particles are <u>localized</u> - so we can distinguish them by their spatial location.

Now expect $Q_1 = \phi(T)$ is not proportional to V as the particles are localized.

$$\mathcal{L} = \frac{1}{1 - z Q_1} = \frac{1}{1 - z \phi(T)}$$

(if $Q_1 \propto V$, then series would not converge!)

$$\Sigma = -k_B T \ln \mathcal{L}$$

$$N = -\frac{\partial z}{\partial \mu} \frac{\partial \Sigma}{\partial z} = -\beta e^{\beta \mu} (-k_B T) \frac{1}{\mathcal{L}} \frac{\partial \mathcal{L}}{\partial z}$$

$$= z \cdot (1 - z\phi) \frac{(+\phi)}{(1 - z\phi)^2} = \frac{z\phi}{1 - z\phi}$$

$$N = \frac{z\phi}{1 - z\phi} \quad \Rightarrow \quad (1 - z\phi)N = z\phi$$

$$N = z\phi(1 + N)$$

$$z\phi = \frac{N}{1+N} \simeq 1 - \frac{1}{N} \quad \text{for } N \gg 1$$

$$E = -\left(\frac{\partial}{\partial \beta} \ln \mathcal{L}\right)_{z,V} = k_B T^2 \left(\frac{\partial}{\partial T} \ln \mathcal{L}\right)_{z,V}$$

$$= k_B T^2 (1 - z\phi) \frac{+ z \, d\phi/dT}{(1 - z\phi)^2}$$

$$E = \frac{k_B T^2 \, z(d\phi/dT)}{1 - z\phi} = k_B T^2 N \frac{(d\phi/dT)}{\phi} = k_B T^2 N \left(\frac{d \ln \phi}{dT}\right)$$

$$A = \Sigma + \mu N = -k_B T \ln\left(\frac{1}{1-z\phi}\right) + k_B T (\ln z) N$$

$$= k_B T \left[\ln(1-z\phi) + \cancel{k_B T} N \ln z \right]$$

use $\quad 1 - z\phi \approx 1/N \quad$ and $\quad z \approx 1/\phi$

to get

$$A = -k_B T N \ln \phi(T) + 0(\ln N)$$

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

$$S(N_1, N_2, N_3) \qquad N_i \text{ adjust to maximize } S$$

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

Now if N_3 __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.

$$\text{or if} \quad dN_3 = -n_3 \, dN$$
$$dN_1 = n_1 \, dN$$
$$dN_2 = n_2 \, dN$$

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

$$\Rightarrow \quad \mu_1 n_1 + \mu_2 n_2 - \mu_3 n_3 = 0$$
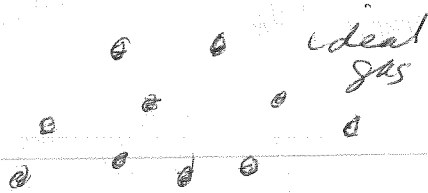
$$\boxed{\mu_1 n_1 + \mu_2 n_2 = \mu_3 n_3}$$

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

~~atom + photon ← atom~~

~~atom + photon ← atom → photon = 0~~

Example

Consider an ideal gas ⟨ o o o o o o o ⟩ adsorption sites
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 <u>same</u>
temperature and <u>equal</u> 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.

(left margin, rotated)
Let "A" be a gas atom, "B" be an adsorbed atom
$A \leftrightarrow B \Rightarrow \mu_A = \mu_B$

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 $\dfrac{N_0!}{N!\,(N_0-N)!}$. So the canonical partition function is

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