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

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

Ideal gas

For a single gas of particles

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

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

$$\mathcal{Z} = e^{zQ_1} = e^{zVf(T)} \qquad \ln \mathcal{Z} = zVf(T)$$

grand potential $\Sigma = -k_BT \ln \mathcal{Z} = -k_BTzV f(T) = -pV$

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

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

Combine the above

$$\left.\begin{aligned} \frac{p}{k_BT} &= zf(T) \\ \frac{N}{V} &= zf(T) \end{aligned}\right\} \Rightarrow pV = Nk_BT$$

Ideal gas law! independent of what f is!

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

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

use $N = zVf$

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

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

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

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

and so

ideal gas law

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

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

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:

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

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

$$= -N k_B T + N k_B T \ln (N/Vf)$$

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 localized - 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.

$$\mathcal{L} = \frac{1}{1 - zQ_1} = \frac{1}{1 - z\phi(T)}$$

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

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

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

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

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

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

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

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

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

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

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

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

use $1 - z\phi \simeq 1/N$ ad $z \simeq 1/\phi$
to get

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

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 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 ~~2~~ N_3 ~~changes by~~ decreases by $-dN$

Then N_1 and N_2 <u>increase</u> 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
$$-\frac{\mu_1}{T} dN_1 - \frac{\mu_2}{T} dN_2 - \frac{\mu_3}{T} dN_3 = 0$$

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

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

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

~~neutral atom + photon ⇔ atom~~

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

Quantum Ensembles

Classical ensemble was a probability distribution in phase space $\rho(q_i, p_i)$ such that averages were

$$\langle X \rangle = \prod_i \int dp_i \, dq_i \; X(q_i, p_i)\, \rho(q_i, p_i)$$

In quantum mechanics, the density function ρ becomes a density operator or density matrix.

In QM, the states of the ~~state~~ system are given by wave functions $|\psi\rangle$. Suppose we ~~have~~ have a system which we know has probability p_k to be in state $|\psi^k\rangle$. Then the average of some observable would be

$$\langle \hat{X} \rangle = \sum_k p_k \langle \psi^k | \hat{X} | \psi^k \rangle$$

Note this is an incoherent sum. Not a coherent superposition of different states $|\psi^k\rangle$

we define the density ~~matrix as~~ operator as

$$\hat{\rho} = \sum_k |\psi^k\rangle p_k \langle \psi^k|$$

If $\{|n\rangle\}$ are a complete set of basis states (for example the energy eigenstates) then the density matrix is

$$\rho_{nm} = \langle n | \hat{\rho} | m \rangle = \sum_k \langle n | \psi^k \rangle p_k \langle \psi^k | m \rangle$$

Note:

$$\rho_{nm}^* = \sum_k \langle \psi^{k*} | n \rangle p_k \langle m | \psi^k \rangle \qquad p_k \text{ is } \underline{\text{real}}$$

$$= \sum_k \langle m | \psi^k \rangle p_k \langle \psi^k | n \rangle = \rho_{mn}$$

So

$$\rho_{nm}^* = \rho_{mn} \Rightarrow \hat{\rho} \text{ is Hermitean}, \ \hat{\rho} = \hat{\rho}^\dagger$$
$$\Rightarrow \hat{\rho} \text{ can be diagonalized}$$

For the average of any observable

$$\langle \hat{X} \rangle = \sum_k p_k \langle \psi^k | X | \psi^k \rangle$$

$$= \sum_{\substack{k \\ m,n}} p_k \langle \psi^k | n \rangle \langle n | X | m \rangle \langle m | \psi^k \rangle$$

$$= \sum_{m,n} X_{nm} \rho_{mn} = \text{trace}(\hat{X} \hat{\rho})$$

If we take $\hat{X} = \hat{\mathbb{I}}$ identity operator, then we get the normalization condition

$$1 = \text{trace}\,\hat{\rho} = \sum_n \rho_{nn}$$

As for any operator in the Heisenberg picture, its equation of motion is

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \qquad \text{quantum analogue of Liouville's eqn}$$

$\Rightarrow$ if $\hat{\rho}$ is to describe a stationary equilibrium, it is necessary that $\hat{\rho}$ commutes with $\hat{H}$, $[\hat{H}, \hat{\rho}] = 0$, so $\partial\hat{\rho}/\partial t = 0$.

$\Rightarrow$ $\hat{\rho}$ is diagonal in the basis formed by the energy eigenstates. If these states are $|\alpha\rangle$ then

$$\langle\alpha|\hat{H}\hat{\rho}|\beta\rangle = E_\alpha \langle\alpha|\hat{\rho}|\beta\rangle$$
$$= \langle\alpha|\hat{\rho}\hat{H}|\beta\rangle = E_\beta \langle\alpha|\hat{\rho}|\beta\rangle$$

$$E_\alpha \langle\alpha|\hat{\rho}|\beta\rangle = E_\beta \langle\alpha|\hat{\rho}|\beta\rangle$$

$$\Rightarrow \quad \langle\alpha|\hat{\rho}|\beta\rangle = 0 \quad \text{unless } E_\alpha = E_\beta$$

So $\hat{\rho}$ only couples eigenstates of equal energy (ie degenerate states) but since $\hat{\rho}$ is Hermitian, it is diagonalizeable $\Rightarrow$ we can always take appropriate linear combinations of degenerate eigenstates to make eigenstates of $\hat{\rho}$. In this basis $\hat{\rho}$ is diagonal.

$$\hat{H}|\alpha\rangle = E_\alpha|\alpha\rangle \quad , \quad \hat{\rho}|\alpha\rangle = \rho_\alpha|\alpha\rangle$$

or

$$\langle\alpha|\hat{H}|\beta\rangle = E_\alpha \delta_{\alpha\beta} \quad , \quad \langle\alpha|\hat{\rho}|\beta\rangle = \rho_\alpha \delta_{\alpha\beta}$$

$$\delta_{\alpha\beta} = \begin{cases} 1 & \alpha = \beta \\ 0 & \alpha \neq \beta \end{cases} \quad \text{Kronecker delta}$$

Even though a stationary $\hat{\rho}$ is diagonal in the basis of energy eigenstates, we can always express it in terms of any other complete basis states

$$\rho_{nm} = \langle n|\hat{\rho}|m\rangle = \sum_{\alpha\beta} \langle n|\alpha\rangle\langle\alpha|\hat{\rho}|\beta\rangle\langle\beta|m\rangle$$

$$= \sum_{\alpha} \langle n|\alpha\rangle \rho_\alpha \langle\alpha|m\rangle$$

in this basis, $\hat{\rho}$ need not be diagonal

This will be usefull because we may not know the exact eigenstates for $\hat{H}$. If $\hat{H} = \hat{H}^0 + \hat{H}^1$ we might know the eigenstates of the simpler H^0, but not the full $\hat{H}$. In this case it may be convenient to express $\hat{\rho}$ in terms of the eigenstates of $\hat{H}^0$ and treat $\hat{H}^1$ in perturbation. In general it is useful to have the above representation for $\hat{\rho}$ and $\langle\hat{X}\rangle = \mathrm{tr}(\hat{X}\hat{\rho})$ in an operator form that is indep of its representation in any particular basis

Microcanonical ensemble:

$$\hat{\rho} = \sum_\alpha |\alpha\rangle\rho_\alpha\langle\alpha| \quad \text{with } \rho_\alpha = \begin{cases} \text{const} & E \le E_\alpha \le E+\Delta \\ 0 & \text{otherwise} \end{cases}$$

$$\text{and } \sum_\alpha \rho_\alpha = 1$$

Canonical ensemble:

$$\hat{\rho} = \sum_\alpha |\alpha\rangle\rho_\alpha\langle\alpha| \quad \text{with } \rho_\alpha = \frac{e^{-\beta E_\alpha}}{Q_N}$$

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

can also write $Q_N = \sum_\alpha e^{-\beta E_\alpha} = \sum_\alpha \langle\alpha| e^{-\beta \hat{H}} |\alpha\rangle$

$$= \text{trace}\left(e^{-\beta \hat{H}}\right)$$

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Q_N} \qquad \langle \hat{X} \rangle = \frac{\text{tr}\left(\hat{X} e^{-\beta \hat{H}}\right)}{\text{tr}\left(e^{-\beta \hat{H}}\right)}$$

Grand Canonical ensemble

Here $\hat{\rho}$ is an operator in a space that includes wavefunctions with any number of particles N.

$\hat{\rho}$ should commute with both $\hat{H}$ (so it is stationary) and with $\hat{N}$ (so it doesn't mix states with different N)

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathcal{L}}$$

with $\mathcal{L} = \text{trace}\left(e^{-\beta(\hat{H} - \mu\hat{N})}\right) = \sum_{\alpha, N} e^{-\beta(E_\alpha - \mu N)}$

$$\langle \hat{X} \rangle = \frac{\text{tr}\left(\hat{X} e^{-\beta \hat{H}} e^{+\beta\mu\hat{N}}\right)}{\text{tr}\left(e^{-\beta\hat{H}} e^{\beta\mu\hat{N}}\right)}$$

$$= \frac{\sum_{N=0}^{\infty} z^N \langle \hat{X} \rangle_N Q_N}{\sum_{N=0}^{\infty} z^N Q_N}$$