# 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

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

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

$\Rightarrow$ __Indistinguishable__

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

__Distinguishable__

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

## 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.

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

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
$$\left. \begin{array}{l} \dfrac{p}{k_B T} = z f(T) \\[2mm] \dfrac{N}{V} = z f(T) \end{array} \right\} \Rightarrow pV = N k_B T$$

Ideal gas law! - independent of what $f$ is!

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

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

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

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

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

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

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

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

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

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

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

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

$\left(\begin{array}{l} \text{if } Q_1 \propto V, \text{ then} \\ \text{series would not} \\ \text{converge!} \end{array}\right)$

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

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

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

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

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

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

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

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

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

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

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

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

to get

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

# 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 $\rho$,
becomes a density operator or density matrix.

In QM, the states of the ~~state~~ system are
given by wave functions $|\psi\rangle$. Suppose
we ~~this~~ 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:

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

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

So
$$\rho_{nm}^* = \rho_{mn} \implies \hat{\rho} \text{ is Hermitian }, \; \hat{\rho} = \hat{\rho}^\dagger$$
$$\implies \hat{\rho} \text{ can be diagonalized}$$

For the average of any observable

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

$$= \sum_k p_k \; \langle \psi^k | n \rangle \langle n | X | m \rangle \langle m | \psi^k \rangle$$
$$\quad _{m,n}$$

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

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

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

$\Rightarrow$ 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

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

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

$\Rightarrow$ $\langle \alpha | \hat{\rho} | \beta \rangle = 0$ 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

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

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

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 useful 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 $\hat{H}^0$, 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 $\langle \hat{X} \rangle = tr(\hat{X} \hat{\rho})$ in an operator form that is indep of its representation in any particular basis.

## Microcanonical ensemble:

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

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

## Canonical ensemble:

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

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