Grand Canonical partition function for non-interacting systems

\[ \mathcal{Z} = \sum_{N=0}^{\infty} z^N \Phi_N(T, V) \]

for non-interacting particles we saw

\[ \Phi_N(T, V) = \frac{1}{N!} \left[ \Phi_1(T, V) \right]^N \]

indistinguishable particles (as in ideal gas)

\[ = \left[ \Phi_1(T, V) \right]^N \]

distinguishable particles (as in paramagnetic spins)

\[ \Rightarrow \text{Indistinguishable} \]

\[ \mathcal{Z} = \sum_{N=0}^{\infty} \frac{(z \Phi_1)^N}{N!} = e^{z \Phi_1} \]

\[ \text{Distinguishable} \]

\[ \mathcal{Z} = \sum_{N=0}^{\infty} (z \Phi_1)^N = \frac{1}{1 - z \Phi_1} \quad \text{we must have} \quad z \Phi_1 < 1 \quad \text{for series to converge} \]
Ideal Gas

For a simple gas of particles

\[ Q_i = \int d^3p \int d^3r \frac{e^{-\beta p/2m}}{\hbar^3} = (2\pi m k_B T)^{3/2} \frac{V}{\hbar^3} \]

\[ = V f(T) \]

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

\[ Z = e^{\frac{2\pi Q_i}{\hbar^3}} = e^{2V f(T)} \]

\[ \ln Z = z V f(T) \]

grand potential

\[ \Sigma = -k_B T \ln Z = -k_B T z V f(T) = -p V \]

\[ \hat{p} = k_B T z f(T) \]

\[ z = e^{\beta \mu} \]

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

\[ = z V f(T) \]

Combine the above

\[ \frac{\hat{p}}{k_B T} = z f(T) \]

\[ \Rightarrow \quad pV = Nk_B T \]

\[ \frac{N}{V} = z f(T) \]

Ideal gas laws independent of what \( f \) is!
\[ E = -\left( \frac{\partial}{\partial T} \ln f \right)_V = k_B T^2 \left( \frac{\partial}{\partial T} \ln f \right)_V \]

\[ = k_B T^2 V \frac{df}{dT} = k_B T^2 N \frac{df}{dT} f = k_B T^2 N \frac{\partial \ln f}{\partial T} \]

and \( N = z V f \)

\[ C_V = \frac{\partial E}{\partial T} = 2 k_B T N \frac{\partial \ln f}{\partial T} + k_B T^2 N \frac{\partial^2 \ln f}{\partial T^2} \]

Note, for harmonic degrees of freedom (i.e., harmonic internal degrees of freedom, such as vibrational degrees of freedom) \( f \propto T^n \) for some power \( n \) (for single particle, \( n = 3/2 \))

\[ \Rightarrow \frac{\partial \ln f}{\partial T} = \frac{\partial}{\partial T} \left( n \ln T \right) = \frac{n}{T} \]

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

\[ \text{ideal gas law} \]

And so

\[ E = n k_B T N = n p V \Rightarrow \frac{E - n p}{V} \]

\[ C_V = 2 n k_B N + k_B T^2 N \left( -\frac{n}{T^2} \right) = n k_B N \]
Helmholtz free energy

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

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

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

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

above agrees with direct result from canonical ensemble:

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

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

\[ = -Nk_B T + Nk_B T \ln \left( N/V f \right) \]

entropy

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

\[ -Nk_B T \frac{d (\ln f)}{dT} \]
For distinguishable particles

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

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

\[
L = \frac{1}{1 - zQ_1} = \frac{1}{1 - z\phi(T)} \quad (\text{if } Q_1 \propto V, \text{ then series would not converge!})
\]

\[
\Sigma = -k_B T \ln L
\]

\[
N = -\frac{\partial}{\partial \mu} \frac{\partial}{\partial z} \ln z = -\beta e^{\beta \mu} (-k_B T) \frac{1}{L} \frac{\partial^2 z}{\partial z^2}
\]

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

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

\[
N = \frac{z \phi}{1 - z \phi} = \frac{z \phi}{1 + N}
\]

\[
z \phi = \frac{N}{1 + N} \propto 1 - \frac{1}{N} \quad \text{for } N \gg 1
\]

\[
E = -\left( \frac{\partial}{\partial \mu} \ln z \right)_{z, V} = k_B T^2 \left( \frac{\partial}{\partial T} \ln z \right)_{z, V}
\]

\[
= k_B T^2 \frac{z(1 - z \phi)}{(1 - z \phi)^2}
\]

\[
E = k_B T^2 \frac{z(\frac{d \phi}{dT})}{1 - z \phi} = k_B T^2 N \frac{(d \phi/dT)}{\phi} = k_B T^2 N \left( \frac{d \ln \phi}{dT} \right)
\]
\[ A = \mu N + \mu N = -k_B T \ln \left( \frac{1}{1-z\phi} \right) + k_B T (\ln z) N \]

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

Use \( 1 - z\phi \approx \frac{1}{N} \) and \( z \approx \frac{1}{\phi} \) to get

\[ A = -k_B T N \ln \phi(T) + O(\ln N) \]
Chemical equilibrium

Suppose \( n_1A_1 + n_2A_2 \leftrightarrow n_3A_3 \)

chemical reaction among species \( A_1, A_2, A_3 \)

What determines equilibrium concentrations of \( A_1, A_2, A_3 \)?

Consider total entropy as function of \( N_1, N_2, N_3 \)

numbers of \( A_1, A_2, A_3 \)

\[ S(N_1, N_2, N_3) \] \( \Rightarrow \) \( N_i \) adjust to maximize \( S \)

\[ \frac{dS}{dT} = \sum \frac{\partial S}{\partial N_i} dN_i \]

(all species \( \rightarrow \) equilibrate at common \( T \))

Now if \( N_3 \) changes, let \( -dN \)

Then \( N_1 \) and \( N_2 \) increase by \( \frac{n_1}{n_3} \) \( dN \) and \( \frac{n_2}{n_3} \) \( dN \)

respectively.

or if \( dN_1 = -n_1 dN \)

\[ dN_2 = n_2 dN \]

\[ dN_3 = -n_3 dN \]

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 \( \mu_i(T, V, N_i) \) satisfy this condition.
Quantum Ensembles

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

$$\langle X \rangle = \int \! d g_i d p_i \, X(g_i, p_i) \rho(g_i, p_i)$$

In quantum mechanics, the density function $\rho$ becomes a density operator or density matrix.

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

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

we define the density matrix as

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

If $\{|\psi\rangle\}$ 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:

\[ f_{nm}^* = \sum_k \langle \psi_k^* | n \rangle \ p_k \ \langle m | \psi_k \rangle \]

\[ = \sum_k \langle m | \psi_k \rangle \ p_k \ \langle \psi_k^* | n \rangle = f_{mn} \]

So \[ f_{nm} = f_{mn} \Rightarrow \hat{f} \] is Hermitian, \[ \hat{f} = \hat{f}^\dagger \]

\[ \Rightarrow \hat{f} \] can be diagonalized.

For the average of any observable

\[ \langle \hat{X} \rangle = \sum_k p_k \ \langle \psi_k^* | \hat{X} | \psi_k \rangle \]

\[ = \sum_k p_k \ \langle \psi_k^* | n \rangle \langle n | \hat{X} | m \rangle \langle m | \psi_k \rangle \]

\[ = \sum_{m,n} X_{nm} f_{mn} = \text{trace} (\hat{X} \hat{f} ) \]

If we take \[ \hat{X} = \hat{1} \] identity operator, then we get the normalization condition

\[ 1 = \text{trace} \hat{f} = \sum_n f_{nn} \]

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

\[ i \frac{\partial \hat{f}}{\partial t} = [\hat{H}, \hat{f}] \]

quantum analogue of liouville's eqn.
⇒ if \( \hat{\beta} \) is to describe a stationary equilibrium, it is necessary that \( \hat{\beta} \) commutes with \( \hat{A} \), 
\[ [\hat{A}, \hat{\beta}] = 0, \]
so \( \partial \hat{\beta} / \partial t = 0. \)

⇒ \( \hat{\beta} \) is diagonal in the basis formed by the energy eigenstates. If these states are \( |\alpha \rangle \)
then
\[ \langle \alpha | \hat{\beta} | \beta \rangle = E_{\alpha} \langle \alpha | \hat{\beta} | \beta \rangle \]
\[ = \langle \alpha | \hat{\beta} \hat{H} | \beta \rangle = E_{\beta} \langle \alpha | \hat{\beta} | \beta \rangle \]

\[ E_{\alpha} \langle \alpha | \hat{\beta} | \beta \rangle = E_{\beta} \langle \alpha | \hat{\beta} | \beta \rangle \]
⇒ \( \langle \alpha | \hat{\beta} | \beta \rangle = 0 \) unless \( E_{\alpha} = E_{\beta} \)

So \( \hat{\beta} \) only couples eigenstates of equal energy (i.e., degenerate states), but since \( \hat{\beta} \) is Hermitian, it is diagonalizable ⇒ we can always take appropriate linear combinations of degenerate eigenstates to make eigenstates of \( \hat{\beta} \). In this basis \( \hat{\beta} \) is diagonal.

\[ \hat{H} |\alpha \rangle = E_{\alpha} |\alpha \rangle, \quad \hat{\beta} |\alpha \rangle = \beta_{\alpha} |\alpha \rangle \]

or
\[ \langle \alpha | \hat{H} | \beta \rangle = E_{\beta} \delta_{\alpha \beta}, \quad \langle \alpha | \hat{\beta} | \beta \rangle = \beta_{\alpha} \delta_{\alpha \beta} \]

\[ \delta_{\alpha \beta} = \begin{cases} 1, & \alpha = \beta \\ 0, & \alpha \neq \beta \end{cases} \quad \text{Kronecker delta} \]
Even though a stationary $\hat{\phi}$ is diagonal in the basis of energy eigenstates, we can always express it in terms of any other complete basis states.

$$S_{nm} = \langle n | \hat{\phi} | m \rangle = \sum_{\alpha} \langle n | \alpha \rangle \langle \alpha | \hat{\phi} | \psi \rangle \langle \psi | m \rangle$$

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

In this basis, $\hat{\phi}$ 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 smaller $\hat{H}_0$, but not the full $\hat{H}$. In this case it may be convenient to express $\hat{\phi}$ in terms of the eigenstates of $\hat{H}_0$ and treat $\hat{H}_1$ as perturbation. In general it is useful to have the above representation for $\hat{\phi}$ and

$$\langle \hat{\xi} \rangle = \text{tr} (\hat{\xi} \hat{\phi})$$

as an operator form that is indeped of $\hat{H}$.

**Microcanonical ensemble:**

$$\hat{\phi} = \sum_{\alpha} \alpha \langle \alpha | \varrho_{\alpha} <\alpha|$$

with $\varrho_{\alpha} = \begin{cases} \text{const} & E \leq E_{\alpha} \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$

and $\sum_{\alpha} \varrho_{\alpha} = 1$

**Canonical ensemble:**

$$\hat{\phi} = \sum_{\alpha} \alpha \langle \alpha | \varrho_{\alpha} <\alpha|$$

with $\varrho_{\alpha} = \frac{e^{-\beta E_{\alpha}}}{\Theta_N}$

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

$$\hat{P} = \frac{e^{-\beta \hat{H}}}{Q_N} \quad \langle \hat{X} \rangle = \frac{\text{tr} (\hat{X} e^{-\beta \hat{H}})}{\text{tr} (e^{-\beta \hat{H}})}$$

Grand Canonical ensemble

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

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

$$\hat{P} = \frac{e^{-\beta (\hat{H} - \mu \hat{N})}}{Z}$$

with $Z = \text{tr} (e^{-\beta (\hat{H} - \mu \hat{N})}) = \sum_{\alpha,N} e^{-\beta (E_\alpha - \mu N)}$

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

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

$$\sum_{N=0}^\infty z^N Q_N$$