Now for the Helmholtz free energy

\[
A(T,N) = -k_B T \ln QN
\]

\[
= -\varepsilon N - k_B T \left\{ \ln N_0 - \ln N + \frac{1}{N} \right\}
\]

\[
= -\varepsilon N - k_B T \left\{ N_0 \ln N_0 - N_0 - N \ln N + N - \frac{1}{N} \right\}
\]

\[
= -\varepsilon N - k_B T \left\{ N_0 \ln N_0 - N_0 \ln N - (N_0 - N) \ln \frac{N}{N_0} \right\}
\]

\[
\mu = \frac{\partial A}{\partial N} \bigg|_T = -\varepsilon + k_B T \left\{ \ln N + N \left( \frac{1}{N} \right) - \ln(N_0 - N) - \frac{(N_0 - N)}{(N_0 - N)} \right\}
\]

\[
\mu = -\varepsilon + k_B T \ln \left( \frac{N}{N_0 - N} \right)
\]

\[
\frac{N}{N_0 - N} = e^\beta(\varepsilon + \mu)
\]

\[
N = \frac{N_0 e^\beta(\varepsilon + \mu)}{1 + e^\beta(\varepsilon + \mu)} = \frac{N_0}{1 + e^{-\beta(\varepsilon + \mu)}}
\]

Fraction occupied is

\[
\frac{N}{N_0} = \frac{1}{1 + e^{-\beta(\varepsilon + \mu)}}
\]
and we do the same calculation, but in the grand canonical ensemble.

Let \( \mathcal{E} \) 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:

\[
Z = \sum_{\mathcal{E}} e^{-\beta (E_\mathcal{E} - \mu N_\mathcal{E})}
\]

\( E_\mathcal{E} \) is the total energy of state \( \mathcal{E} \)

\( N_\mathcal{E} \) is the number of occupied sites in state \( \mathcal{E} \)

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 \( \mathcal{E} \) 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:

\[
\begin{align*}
\sum s_i & = N_\mathcal{E} \\
E_\mathcal{E} = -\sum_s s_i E_s & = -\sum s_i E_s \\
\end{align*}
\]

The partition function can then be written as:

\[
Z = \sum_{s_i} e^{-\beta \left[ -\sum_s s_i E_s + \mu \sum s_i \right]} = \sum_{s_i} e^{\beta (E + \mu) \sum s_i}
\]
we can factor the exponential since the degrees of freedom \( s_i \) are non-interacting with each other

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

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

Now we compute the grand potential

\[
\Sigma (T, \mu) = -k_B T \ln I
\]

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

The average number of adsorbed particles in thin

\[
N = -\frac{\partial \Sigma}{\partial \mu} = k_B T N_0 \frac{\beta e^{\beta (e + \mu)}}{(1 + e^{\beta (e + \mu)})^2}
\]

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

this is the same result as we found using the canonical ensemble, as it must be!
Step 2: Now we compute the chemical potential \( \mu \) 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

\[
Z = e^{z Q_1}
\]

where \( Z = e^{\mu \lambda^3} \) and \( \lambda^3 \) is the one particle partition function.

\[
Q_1 = \int \frac{d^3 p}{(2\pi \hbar)^3} e^{-\beta P^2/2m} = \frac{V}{\hbar^3} \sqrt{\frac{2\pi m k_B T}{\hbar^2}} \lambda^3
\]

\[
= \sqrt{\frac{2\pi m k_B T}{\hbar^2}} \lambda^3 = \frac{V}{\lambda^3}
\]

where \( \lambda = \sqrt{\frac{\hbar}{\sqrt{2\pi m k_B T}}} \) is called the "thermal wavelength."

\[
-pV = \mathcal{Z} = -k_B T \ln \mathcal{Z} = -k_B T \ln Q_1
\]

\[
P = \frac{k_B T}{V} \ln Q_1 = \frac{k_B T}{V} \frac{V}{\lambda^3} = k_B T \frac{V}{\lambda^3}
\]

\[
\mathcal{Z} = e^{\beta P} = \frac{\lambda^3 P}{k_B T}
\]
or we could get \( \mu(T, P) \) using the canonical ensemble

\[
Q_N = \frac{1}{N!} Q_1^n
\]

using stirling approx

\[
A = -k_B T \ln Q_N = -k_B T \left[ N \ln Q_1 - N \ln N + N \right]
\]

\[
\mu = \left( \frac{\partial A}{\partial N} \right)_{T, V} = -k_B T \left[ \ln Q_1 - \ln N - \frac{N}{N} + 1 \right]
\]

\[
= -k_B T \ln \left( \frac{Q_1}{N} \right)
\]

\[
\mu = -k_B T \ln \left( \frac{V}{N \lambda^3} \right) \text{ gives } \mu(T, V, N)
\]

to write \( \mu \) in terms of \( p \) and \( T \) we then need

\[
p = \left( \frac{\partial A}{\partial V} \right)_{T, N} = k_B T \frac{N}{Q_1} \left( \frac{\partial Q_1}{\partial V} \right)_{T}
\]

\[
= k_B T \frac{N \lambda^3}{V} \frac{1}{\lambda^3} = k_B T \frac{N}{V} \text{ ideal gas law!}
\]

so we can write \( \frac{V}{N \lambda^3} = \frac{k_B T}{p \lambda^3} \) and so

\[
\mu(T, P) = -k_B T \ln \left( \frac{k_B T}{p \lambda^3} \right)
\]

or

\[
z = e^\beta \mu = \frac{p \lambda^3}{k_B T} \text{ same as found by grand canonicalensemble}
Step 2: Substitute \( \mu \) from step 1 into result from step 1

\[
\frac{N'}{N_0} = \frac{1}{1 + e^{-\beta \mu} e^{-\beta \varepsilon}}
\]

\[
= \frac{1}{1 + \frac{k_B T}{p A^3} e^{-\beta e}}
\]

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

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
Quantum Ensembles

The classical ensemble was a probability distribution in phase space \( f(q_i, p_i) \) such that thermodynamic averages of an observable \( X \) are given by

\[
\langle X \rangle = \left( \prod_i \int dp_i dq_i \right) X(q_i, p_i) f(q_i, p_i)
\]

The ensemble interpretation of thermodynamics imagines that we make many (ideally infinitely many) copies of our system, each prepared identically as far as macroscopic parameters are concerned. The distribution \( f(q_i, p_i) \) is then the probability that a given copy will be found at coordinates \( (q_i, p_i) \) in phase space. The average \( \langle X \rangle \) above is the average over all copies of the system. The ergodic hypothesis states that this ensemble average over many copies will give the same result as averaging \( X \) over the time trajectory of the system in just one copy.

In quantum mechanics, states are described by wavefunctions \( | \psi \rangle \) rather than points in phase space \( (q_i, p_i) \). To describe a quantum ensemble imagine making many copies of the system. Let \( | \psi_k \rangle \) be the state of the system in copy \( k \).
The ensemble average of an observable operator \( \hat{X} \) would then be

\[
\langle \hat{X} \rangle = \frac{1}{M} \sum_{k=1}^{M} \langle \psi^k | \hat{X} | \psi^k \rangle
\]

where in the above we took \( M \) copies of the system to make our ensemble. In general \( M \rightarrow \infty \).

In quantum mechanics it is convenient to express wavefunctions as a linear superposition of some complete set of basis wave functions \( | \psi_n \rangle \). Define

\[
| \psi^k \rangle = \sum_n a_n^k | \psi_n \rangle
\]

\( a_n^k \) is probability amplitude for \( | \psi^k \rangle \) to be in state \( | \psi_n \rangle \).

\( |a_n^k|^2 \) is probability for \( | \psi^k \rangle \) to be found in state \( | \psi_n \rangle \).

Normalization \( \langle \psi^k | \psi^k \rangle = 1 \Rightarrow \sum_n |a_n^k|^2 = 1 \)

Now express \( \langle \hat{X} \rangle \) in terms of the basis states

\[
\langle \hat{X} \rangle = \frac{1}{M} \sum_{k=1}^{M} \sum_{n,m} a_n^k a_m^{k*} \langle \psi_m | \hat{X} | \psi_n \rangle
\]

\[
= \frac{1}{M} \sum_{k} \sum_{n,m} a_n^k a_m^{k*} X_{mn}
\]
where $X_{mn} = \langle \Phi_m | \hat{X} | \Phi_n \rangle$ is the matrix of
$\hat{X}$ in the basis $| \Phi_n \rangle$.

We can now define the density matrix that
describes the ensemble

$$ \rho_{nm} = \frac{1}{M} \sum_{k=1}^{M} a_k^* a_k \delta_{mn} $$

$\rho_{nm}$ is just the matrix of the density operator $\hat{\rho}$
in the basis $| \Phi_n \rangle$.

$$ \hat{\rho} = \sum_{n,m} \rho_{nm} | \Phi_n \rangle \langle \Phi_m | $$

We can write for ensemble averages

$$ \langle \hat{X} \rangle = \sum_{n,m} \rho_{nm} X_{mn} $$

$$ = \sum_{n,m} \langle \Phi_m | \hat{\rho} | \Phi_n \rangle \langle \Phi_m | \hat{X} | \Phi_n \rangle $$

$$ = \sum_{n} \langle \Phi_1 | \hat{\rho} | \hat{X} | \Phi_n \rangle $$

$$ = \text{tr} [ \hat{\rho} \hat{X} ] \quad \text{tr} = "trace" $$

Note: $\rho_{nm}$ is the probability that a state
selected at random from the ensemble, will
be found to be in $| \Phi_n \rangle$
\[ \text{tr} \hat{\rho} = \sum_n p_n = \frac{1}{M} \sum_{k=1}^{M} \sum_n a_n^k a_n^{k*} = \frac{1}{M} \sum_{k=1}^{M} \sum_n |a_n^k|^2 = 1 \]

Also
\[ f_{nm} = \frac{1}{M} \sum_k a_n^k a_m^{k*} \]
\[ \Rightarrow f_{mn}^{*} = \frac{1}{M} \sum_k a_m^{k*} a_n^k = f_{nm} \]

So \( \hat{\rho} \) is an Hermitian operator

\[ \Rightarrow f_{nm} \text{ can be diagonalized and its eigenvalues are real.} \]

So a quantum mechanical ensemble is described by a Hermitian density matrix \( \hat{\rho} \) such that \( \text{tr} \hat{\rho} = 1 \), and ensemble averages are given by \( \text{tr}[\hat{A} \hat{\rho}] \). What additional conditions must \( \hat{\rho} \) satisfy if it is to describe thermal equilibrium?

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 analog of Liouville's equation
\( \hat{H} \) is Hamiltonian
If \( \hat{\mathbf{p}} \) is to describe a stationary equilibrium, it is necessary that \( \hat{\mathbf{p}} \) commutes with \( \hat{\mathbf{A}} \), \( [\hat{\mathbf{A}}, \hat{\mathbf{p}}] = 0 \), so \( \partial \hat{\mathbf{p}} / \partial t = 0 \).

\( \Rightarrow \hat{\mathbf{p}} \) is diagonal in the basis formed by the energy eigenstates. If these states are \( |\alpha\rangle \) then

\[
\langle \alpha | \hat{\mathbf{H}} | \beta \rangle = E_\alpha \langle \alpha | \hat{\mathbf{p}} | \beta \rangle = \langle \alpha | \hat{\mathbf{p}} \hat{\mathbf{H}} | \beta \rangle = E_\beta \langle \alpha | \hat{\mathbf{p}} | \beta \rangle
\]

\( E_\alpha \langle \alpha | \hat{\mathbf{p}} | \beta \rangle = E_\beta \langle \alpha | \hat{\mathbf{p}} | \beta \rangle \)

\( \Rightarrow \langle \alpha | \hat{\mathbf{p}} | \beta \rangle = 0 \) unless \( E_\alpha = E_\beta \)

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

\( \hat{\mathbf{H}} |\alpha\rangle = E_\alpha |\alpha\rangle \), \( \hat{\mathbf{p}} |\alpha\rangle = \delta_{\alpha \beta} |\alpha\rangle \)

\( \Rightarrow \langle \alpha | \hat{\mathbf{H}} | \beta \rangle = E_\alpha \delta_{\alpha \beta} \), \( \langle \alpha | \hat{\mathbf{p}} | \beta \rangle = \delta_{\alpha \beta} \delta_{\alpha \beta} \)

\[\delta_{\alpha \beta} = \begin{cases} 1 & \text{if } \alpha = \beta \\ 0 & \text{if } \alpha \neq \beta \end{cases} \text{ Kronecker delta}\]