

Now find the Helmholtz free energy

$$A(T, N) = -k_B T \ln \Omega_N \\ = -\epsilon N - k_B T \{ \ln N_0! - \ln N! - \ln (N_0 - N)! \}$$

$$= -\epsilon N - k_B T \left\{ N_0 \ln N_0 - N_0 \right. \\ \left. - N \ln N + N \right. \\ \left. - (N_0 - N) \ln (N_0 - N) + (N_0 - N) \right\} \\ = -\epsilon N - k_B T \{ N_0 \ln N_0 - N \ln N - (N_0 - N) \ln (N_0 - N) \}$$

$$\mu = \left(\frac{\partial A}{\partial N} \right)_T = -\epsilon + k_B T \left\{ \ln N + N \left(\frac{1}{N} \right) \right. \\ \left. - \ln (N_0 - N) - \frac{(N_0 - N)}{(N_0 - N)} \right\}$$

$$\mu = -\epsilon + k_B T \ln \left(\frac{N}{N_0 - N} \right)$$

$$\frac{N}{N_0 - N} = e^{\beta(\epsilon + \mu)}$$

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

Fraction occupied is

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

and we do the same calculation, but in the grand canonical ensemble

let $\{\alpha\}$ 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:

$$\mathcal{Z} = \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu N_{\alpha})}$$

E_{α} is total energy of state α

N_{α} is the number of occupied ~~state~~ sites in state α

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 α 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:

$$\alpha = \{s_i\} \Rightarrow E_{\alpha} = -\epsilon \sum_i s_i$$

$$N_{\alpha} = \sum_i s_i$$

The partition function can then be written as

$$\mathcal{Z} = \sum_{\{s_i\}} e^{-\beta[-\epsilon \sum_i s_i - \mu \sum_i s_i]} = \sum_{\{s_i\}} e^{\beta(\epsilon + \mu) \sum_i s_i}$$

We can factor the exponential since the degrees of freedom s_i are non-interacting with each other

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

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

Now we compute the grand potential

$$\Sigma(T, \mu) = -k_B T \ln \mathcal{Z}$$

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

The average number of adsorbed particles is then

$$N = - \left(\frac{\partial \Sigma}{\partial \mu} \right)_T = \frac{k_B T N_0 \beta e^{\beta(\epsilon + \mu)}}{(1 + e^{\beta(\epsilon + \mu)})}$$

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

This is the same result as we found using the canonical ensemble, as it must be!

Step ② Now we compute the chemical potential μ 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

$\mathcal{Z} = e^{zQ_1}$ where $z = e^{\beta\mu}$ and Q_1 is the one particle partition function

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

where $\lambda \equiv \sqrt{\frac{h^2}{2\pi m k_B T}}$ is called the "thermal wavelength"

$$-pV = \Sigma = -k_B T \ln \mathcal{Z} = -k_B T z Q_1$$

$$p = \frac{k_B T}{V} z Q_1 = \frac{k_B T}{V} z \frac{V}{\lambda^3}$$

$$p = \frac{k_B T}{\lambda^3} z$$

$$z = e^{\beta\mu} = \frac{\lambda^3 p}{k_B T}$$

or we could get $\mu(T, p)$ using the canonical ensemble

$$Q_N = \frac{1}{N!} Q_1^N$$

using Stirling approx

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

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

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

to write μ in terms of p and T we then need

$$p = - \left(\frac{\partial A}{\partial V} \right)_{T, N} = k_B T \frac{N}{Q_1} \left(\frac{\partial Q_1}{\partial V} \right)_T$$

$$\approx k_B T \frac{N \lambda^3}{V} \frac{1}{\lambda^3} = k_B T \frac{N}{V} \quad \text{ideal gas law!}$$

$$\text{so we can write } \frac{V}{N \lambda^3} = \frac{k_B T}{p \lambda^3} \quad \text{and so}$$

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

or

$$Z = e^{\beta \mu} = \frac{p \lambda^3}{k_B T}$$

same as found by grand canonical ensemble

step ③ substitute μ from step ②
into result from step ①

$$\frac{N}{N_0} = \frac{1}{1 + e^{-\beta\mu} e^{-\beta\epsilon}}$$

$$= \frac{1}{1 + \frac{k_B T}{p \lambda^3} e^{-\beta\epsilon}}$$

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

Note: as $T \rightarrow 0$, $\frac{N}{N_0} \rightarrow 1$ as expected

as $T \rightarrow \infty$, $\frac{N}{N_0} \rightarrow 0$ 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 orthonormal basis wave functions $|\varphi_n\rangle$. Define

$$\langle \varphi_m | \varphi_n \rangle = \delta_{mn}$$

$$|\psi^k\rangle = \sum_n a_n^k |\varphi_n\rangle$$

a_n^k is probability amplitude for $|\psi^k\rangle$ to be in state $|\varphi_n\rangle$.

$|a_n^k|^2$ is probability for $|\psi^k\rangle$ to be found in state $|\varphi_n\rangle$

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

$$\begin{aligned} \langle \hat{X} \rangle &= \frac{1}{M} \sum_{k=1}^M \sum_{n,m} a_n^k a_m^{k*} \langle \varphi_m | \hat{X} | \varphi_n \rangle \\ &= \frac{1}{M} \sum_k \sum_{n,m} a_n^k a_m^{k*} X_{mn} \end{aligned}$$

where $X_{mn} \equiv \langle \varphi_m | \hat{X} | \varphi_n \rangle$ is the matrix of \hat{X} in the basis $|\varphi_n\rangle$.

We can now define the density matrix that describes the ensemble

$$f_{nm} \equiv \frac{1}{M} \sum_{k=1}^M a_n^k a_m^{k*}$$

f_{nm} is just the matrix of the density operator $\hat{\rho}$ in the basis $|\varphi_n\rangle$

$$\hat{\rho} \equiv \sum_{n,m} |\varphi_n\rangle f_{nm} \langle \varphi_m|$$

We can write for ensemble averages

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

$$= \sum_{n,m} \langle \varphi_n | \hat{\rho} | \varphi_m \rangle \langle \varphi_m | \hat{X} | \varphi_n \rangle$$

$$= \sum_n \langle \varphi_n | \hat{\rho} \hat{X} | \varphi_n \rangle$$

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

Note: f_{nn} is the probability that a state, selected at random from the ensemble, will be found to be in $|\varphi_n\rangle$

$$\begin{aligned} \text{tr } \hat{\rho} &= \sum_n \rho_{nn} = \frac{1}{M} \sum_{k=1}^M \sum_n a_n^k a_n^{k*} \\ &= \frac{1}{M} \sum_{k=1}^M \sum_n |a_n^k|^2 \\ &= 1 \end{aligned}$$

Also

$$\begin{aligned} \rho_{nm} &= \frac{1}{M} \sum_k a_n^k a_m^{k*} \\ \Rightarrow \rho_{mn}^* &= \frac{1}{M} \sum_k a_m^{k*} a_n^k = \rho_{nm} \end{aligned}$$

So $\hat{\rho}$ is an Hermitian operator

$\Rightarrow \rho_{nn}$ 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 $\text{tr}[\hat{\rho} \hat{X}]$. 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 eqn
 \hat{H} is Hamiltonian

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

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

$$\begin{aligned}\langle \alpha | \hat{H} \hat{p} | \beta \rangle &= E_{\alpha} \langle \alpha | \hat{p} | \beta \rangle \\ &= \langle \alpha | \hat{p} \hat{H} | \beta \rangle = E_{\beta} \langle \alpha | \hat{p} | \beta \rangle\end{aligned}$$

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

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

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

$$\hat{H} |\alpha\rangle = E_{\alpha} |\alpha\rangle, \quad \hat{p} |\alpha\rangle = p_{\alpha} |\alpha\rangle$$

$$\text{or } \langle \alpha | \hat{H} | \beta \rangle = E_{\alpha} \delta_{\alpha\beta}, \quad \langle \alpha | \hat{p} | \beta \rangle = p_{\alpha} \delta_{\alpha\beta}$$

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