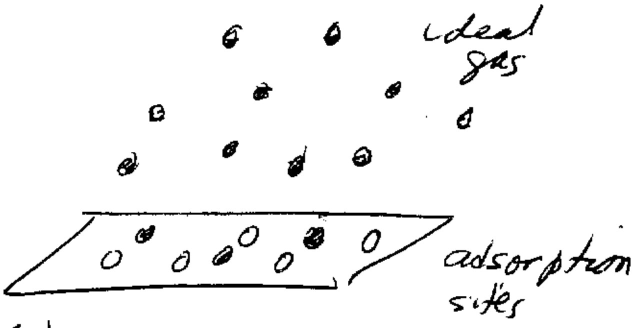
Exaple



Consider an ideal gas at temperature T and pressure p that is in equilibrium with a surface containing N_0 adsorption sites. Each adsorption site can hold at most one particle of the gas. The binding energy of a particle to the adsorption site is $-\epsilon$. What is the fraction of occupied adsorption sites as a function of T and p?

Solution: Regard the ideal gas and the gas of adsorbed particles as two seperate systems. Since these two systems are in equilibrium with each other, and can exchange particles between each other, they must be at the same temperature and equal chemical potential.

To solve the problem we

① Find the number N of occupied adsorption sites assuming the gas of adsorbed particles is at temperature T and chemical potential μ

② Find the chemical potential $\mu(T,p)$ of the ideal gas at temperature T, pressure p.

③ Insert μ from ② into result from ① since the chemical potentials of the two systems must be equal. From this we can get (N/N_0) as function of T and p.

step ① We can do this using either the canonical or grand canonical ensembles

canonical ensemble - compute Q_N

let $\{\alpha\}$ be the set of states of adsorbed particles that have exactly N sites occupied and the rest empty.

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

In general case, E_α will depend on the state α. But here $E_\alpha = -\epsilon N$ is the same for all states - it does not matter which of the sites are occupied since they all have the same binding energy $-\epsilon$.

$$Q_N = e^{+\beta\epsilon N} \sum_\alpha$$

the sum is now over all states with exactly N occupied sites. The number of ways to choose which N of the N_0 sites are occupied is $\frac{N_0!}{N!\,(N_0-N)!}$. So the canonical partition function

is

$$Q_N = \frac{N_0!}{N!\,(N_0-N)!}\, e^{\beta\epsilon N}$$

Now for the Helmholtz free energy

$$\begin{aligned} A(T,N) &= -k_B T \ln Q_N \\ &= -\epsilon N - k_B T \left\{ \ln N_0! - \ln N! - \ln (N_0 - N)! \right\} \\ &= -\epsilon N - k_B T \left\{ N_0 \ln N_0 - N_0 \right. \\ &\qquad - N \ln N + N \\ &\qquad \left. - (N_0 - N) \ln (N_0 - N) + (N_0 - N) \right\} \\ &= -\epsilon N - k_B T \left\{ N_0 \ln N_0 - N \ln N - (N_0 - N) \ln (N_0 - N) \right\} \end{aligned}$$

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

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

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

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

fraction occupied is

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

now we do the same calculation, but in the <u>grand canonical ensemble</u>

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:

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

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:

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

$$N_\alpha = \sum_i s_i$$

The partition function can then be written as

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

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

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

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

Now we compute the grand potential

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

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

The average number of adsorbed particles is then

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

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

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

$$\mathcal{L} = e^{zQ_1} \quad \text{where} \quad z = e^{\beta\mu} \quad \text{and}$$

Q_1 is the one particle partition function

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

$$= V \sqrt{\frac{2\pi m k_B T}{h^2}}^{\,3} = \frac{V}{\lambda^3}$$

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

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

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

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

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

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

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

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

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

Note: as $T \to 0$, $\frac{N}{N_0} \to 1$ 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 $\rho(q_i, p_i)$ such that thermodynamic averages of an observable X are given by

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

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 $\rho(q_i p_i)$ 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

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

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

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

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

a_n^k is probability <u>amplitude</u> 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

$$\langle \hat{X} \rangle = \frac{1}{M} \sum_{k=1}^{M} \sum_{n,m} a_n^k a_m^{k*} \langle \varphi_m | \hat{X} | \varphi_n \rangle$$

$$= \frac{1}{M} \sum_k \sum_{n,m} a_n^k a_m^{k*} X_{mn}$$

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

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

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

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

We can write for ensemble averages

$$\begin{aligned} \langle \hat{X} \rangle &= \sum_{n,m} \rho_{nm} X_{mn} \\ &= \sum_{n,m} \langle \varphi_n | \hat{\rho} | \varphi_m \rangle \langle \varphi_m | \hat{X} | \varphi_n \rangle \\ &= \sum_n \langle \varphi_n | \hat{\rho} \hat{X} | \varphi_n \rangle \\ &= \mathrm{tr}\left[\hat{\rho} \hat{X} \right] \end{aligned}$$

tr = "trace"

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

$$\operatorname{tr}\hat{\rho} = \sum_n \rho_{nn} = \frac{1}{M}\sum_{k=1}^{M}\sum_n a_n^k a_n^{k*}$$

$$= \frac{1}{M}\sum_{k=1}^{M}\sum_n |a_n^k|^2$$

$$= 1$$

Also

$$\rho_{nm} = \frac{1}{M}\sum_k a_n^k a_m^{k*}$$

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

so $\hat{\rho}$ is an Hermitean operator

$\Rightarrow$ ρ_{nn} can be diagonalized and its eigenvalues are real.

So a quantum mechanical ensemble is described by a Hermitean density matrix $\hat{\rho}$ such that $\operatorname{tr}\hat{\rho} = 1$, and ensemble averages are given by $\operatorname{tr}[\hat{\rho}\hat{X}]$. 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 $\hat{\rho}$ 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

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

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

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

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.

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

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

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