Grand Canonical Ensemble

Byungjoon Min

Department of Physics, Chungbuk National University

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Open Systems

Grand Canonical Ensemble describe an equilbrium system which can exchange energy and particles with a heat bath. The probability distribution P_i depends on not only its energy but also the number of particles, $P_i \sim e^{-\beta(E_i - \mu N_i)}$.

Maximum Entropy

The probability distribution maximizes entropy with three constraints: the normalization $\sum_i P_i = 1$, the average energy $\sum_i P_i E_i = \langle E \rangle$, and the average number of particles $\sum_i P_i N_i = \langle N \rangle$. Applying the Lagrange multilier, we obtain

$$\delta[S - \lambda(\sum_i P_i - 1) - \beta(\sum_i P_i E_i - \langle E \rangle) - \alpha(\sum_i P_i N_i - \langle N \rangle)$$

$$= \sum_i [-\log P_i - C - \beta E_i - \alpha N_i] = 0.$$

Maximum Entropy

Finally, we obtain

$$P_n = \frac{e^{-\beta(E_n - \mu N_n)}}{\sum_i e^{-\beta(E_i - \mu N_i)}} = \frac{1}{Q} e^{-\beta(E_n - \mu N_n)},$$

where the normalization factor Q is called as "grand partition function",

$$Q(T, V, \mu) = \sum_i e^{-\beta(E_i - \mu N_i)}.$$

Grand Free Energy and $\langle N \rangle$

We define grand free energy as

$$\Phi(T, V, \mu) = -kT \log Q = \langle E \rangle - TS - \mu N.$$

The expectation number of particles for a system is

$$\langle N \rangle = \frac{kT}{Q} \frac{\partial Q}{\partial \mu} = -\frac{\partial \Phi}{\partial \mu}.$$

Chemical Potential

The chemical potential is like a pressure pushing particles into the system:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V,T}.$$

We can also interpret the chemical potential like the temperature for thermal equilibrium:

$$\begin{aligned}\delta S &= \frac{\partial S}{\partial E}dE + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial N}dN \\ &= \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN.\end{aligned}$$

Thus, if we have two systems with different $\mu_A > \mu_B$, particles move from A to B until they will be the same.