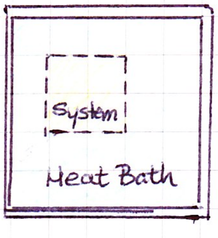
Lecture 20 Grand Canonical Partition Function

Consider a system that can exchange particles with a heat bath.



For every N, there exists a set of quantum states $\{N_1, N_2, N_3, \ldots N_r, \ldots\}$

Solve the Schrodinger equation for any number of particles in the system. Isolated system = System + H.B.
The total number of particles is conserved.

$$E_{Nr} + E_2 = E_0 = \text{constant} \qquad N + N_2 = N_0 = \text{constant}$$
$$E_2 = E_0 - E_{Nr} \qquad N_2 = N_0 - N$$

one particle has a huge number of quantum states. The system is in a definite state N_r

Statistical Weight: $\Omega_2(N_2, E_2) = \Omega_2(E_0 - E_{Nr}, N_0 - N)$

All states of the same, definite energy, are equally probable. $P_{Nr} \propto \Omega_2(E_2, N_2)$

For a given energy, the Boltzmann definition of entropy is $S_2(E_0 - E_{Nr}, N_0 - N) = k\ln\Omega_2$

$$\Omega_2 = e^{S_2(E_0 - E_{Nr}, N_0 - N)/k} \qquad p_{Nr} \propto e^{S_2(E_0 - E_{Nr}, N_0 - N)/k}$$

Take a Taylor expansion of S_2 about (E_0, N_0)

$$S_2 = S_2(E_0, N_0) - E_{Nr}\left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=E_0} - N\left.\frac{\partial S_2}{\partial N_2}\right|_{N_2=N_0} - \cancel{\frac{E_{Nr}^2}{2!}\left.\frac{\partial^2 S_2}{\partial E_2^2}\right|_{E_2=E_0}}^{\,0} + \cancel{\frac{N^2}{2!}\left.\frac{\partial^2 S_2}{\partial N_2^2}\right|_{N_2=N_0}}^{\,0} - + \cdots$$

only keep 1^{ST} order terms

$$S_2(E_0 - E_{Nr}, N_0 - N) = S_2(E_0, N_0) - \frac{E_{Nr}}{T} + \frac{N\mu}{T}$$

$$P_{Nr} \propto e^{\frac{1}{k}[S_2(E_0,N_0) - E_{Nr}/T + N\mu/T]} = (\text{Constant})e^{\beta(\mu N - E_{Nr})} \qquad \sum_{Nr} p_{Nr} = 1$$

$$\hookrightarrow (\text{Constant}) = \frac{1}{\sum_{Nr} e^{\beta(\mu N - E_{Nr})}}$$

$$\boxed{\text{Grand Canonical Partition Function} \quad \mathcal{Z} \equiv \sum_{Nr} e^{\beta(\mu N - E_{Nr})}}$$

$$P_{Nr} = \frac{1}{\mathcal{Z}} e^{\beta(\mu N - E_{Nr})}$$

the probability of finding the quantum state in the state N_r when it is in equilibrium with a heat bath

<u>Once you get the probabilities, you can get the averages.</u>

$$\bar{N} = \sum_{Nr} N\, p_{Nr} = \sum_{Nr} N \frac{1}{\mathcal{Z}} e^{\beta(\mu N - E_{Nr})}$$

$$\frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\mathcal{Z}}\sum e^{\beta(\mu N - E_{Nr})}(\beta N) = \beta \sum N p_{Nr} = \beta \bar{N}$$

$$\bar{N} = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

You can do many things with the Grand Canonical Function. In one homework problem, you get the relative fluctuation $\frac{1}{\sqrt{N}}$

Read Ch. 11 Mandl, that comes from the statistical mechanics of ideal gases.