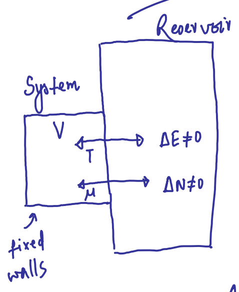
Grand Canonical Ensemble : (μ, V, T)

T: $\Delta E \neq 0$ "Thermal interaction with Reservoir"

V: fixed walls "No mechanical work"

μ: $\Delta N \neq 0$ "Exchange of particles with Reservoir"



Microstate : $\nu \equiv \{\vec{q_i}, \vec{p_i}\} \in N_\nu$

$$p(\nu, N_\nu) = \frac{e^{-\beta[H(\nu) - \mu N_\nu]}}{\mathcal{Z}(\mu, V, T)} \qquad \text{(1)}$$

, Energy scale = $H(\nu) - \mu N_\nu$

Grand Canonical Partition function:

$$\mathcal{Z}(\mu, V, T) = \sum_{\nu, N_\nu} e^{-\beta[H(\nu) - N_\nu \mu]}$$

"Unrestricted sum"

$$= \sum_{N_\nu = 0}^{\infty} e^{\beta \mu N_\nu} \sum_{\nu | N_\nu} e^{-\beta H(\nu)}$$

"Restricted sum"

$$\mathcal{Z}(\mu, V, T) = \sum_{N_\nu = 0}^{\infty} e^{\beta\mu N_\nu} \underbrace{Z(N_\nu, V, T)}_{\text{Canonical partition } f^n} \qquad \text{(1')}$$

Computing $N = \langle N_\nu \rangle = \sum_{\nu, N_\nu} N_\nu \, \underline{p(\nu, N_\nu)}$

$$= \frac{\sum_{\nu, N_\nu} N_\nu \, e^{-\beta[H(\nu) - \mu N_\nu]}}{\mathcal{Z}(\mu, V, T)}$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial}{\partial(\beta\mu)} \mathcal{Z}$$

$$N = \frac{1}{\beta}\cdot\frac{\partial}{\partial\mu}\ln \mathcal{Z}(\mu, V, T)$$

Compute fluctuations of N: $\langle N^2\rangle_c = \langle N^2\rangle - \langle N\rangle^2$

$$= \frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial(\beta\mu)^2} - \left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial(\beta\mu)}\right)^2$$

$$= \frac{\partial}{\partial(\beta\mu)}\left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial(\beta\mu)}\right)$$

$$= \frac{\partial}{\partial(\beta\mu)}\underbrace{\frac{\partial}{\partial(\beta\mu)}\ln \mathcal{Z}(\mu, V, T)}$$

$$= \frac{\partial}{\partial(\beta\mu)} N \sim N$$

Hence $\langle N^2\rangle_c \sim N$ "Variance"

$\langle N^2\rangle_c^{1/2} \sim N^{1/2}$ "Standard deviation"

Ratio of width/mean $\sim N^{1/2}/N \sim 1/N^{1/2} \xrightarrow[N\to\infty]{} 0$

"Ensemble equivalent to Micro-canonical Ensemble"

Develop connections with thermodynamics:

$$\mathcal{Z}(\mu, V, T) = \sum_{N_\nu=0}^{\infty} e^{\beta\mu N_\nu} Z(N_\nu, V, T)$$

$\longrightarrow$ Canonical partition function.

Since $N \to \infty$, the distribution is sharp "$\frac{\langle N^2\rangle_c^{1/2}}{\langle N\rangle_c} \xrightarrow[N\to\infty]{} 0$"

We can approximate $\mathcal{Z}(\mu, V, T)$ by largest summand!

"Saddle point approximation"

$$\mathcal{Z}(\mu, V, T) \simeq e^{\beta\mu N^*} Z(N^*, V, T)$$ "N^* maximizes $\mathcal{Z}$"

$$\simeq e^{\beta\mu N^*} e^{-\beta F(\epsilon^*)}$$ ... $F(\epsilon^*)$ is the Helmholtz free energy of system.

$$\simeq e^{-\beta(F - \mu N)}$$ ..... dropped * symbol for convenience.

$$\mathcal{Z}(\mu, V, T) \simeq e^{-\beta(E - TS - \mu N)} \quad (2)$$

Defining $(E - TS - \mu N) = \mathcal{G}$ "Grand potential"

$$\mathcal{Z}(\mu, V, T) = e^{-\beta \mathcal{G}}$$

$$\boxed{\mathcal{G} = -\frac{1}{\beta} \ln \mathcal{Z}(\mu, V, T)}$$

For thermodynamic quantities:

$$\mathcal{G} = E - TS - \mu N$$

$$d\mathcal{G} = \underline{dE - TdS} - S\,dT \underline{- \mu dN} - N d\mu$$

$$d\mathcal{G} = -P dV - S dT - N d\mu$$

..... 1st law: $T dS = dE + P dV - \mu dN$

$$P = -\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{\mu, T}$$

$$S = -\left.\frac{\partial \mathcal{G}}{\partial T}\right|_{V, \mu}$$

$$N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{V, T}$$