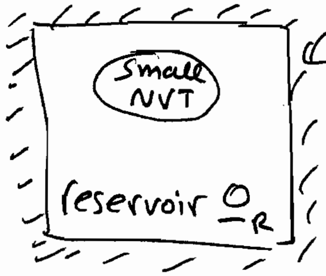
Canonical Ensemble: Const. (N, V, T)

We have seen that all microstates are equally probable at const. U, V, N. How about other ensembles?



Total system: UVN constant

Ω states all equally probable

Assume small system is at microstate ν, with energy U_ν

Reservoir can be at any one of $\Omega_R(U - U_\nu)$ states

$$P_\nu \propto \Omega_R(U - U_\nu) = \exp\left[\ln \Omega_R (U - U_\nu)\right] \quad \Rightarrow$$

$$\ln \Omega_R(U - U_\nu) = \underbrace{\ln\left[\Omega_R(U)\right]}_{\text{constant, indep. of } \nu} - U_\nu \underbrace{\frac{\partial \ln \Omega_R}{\partial U}}_{\beta \text{ of reservoir imposed on small system}} + \ldots$$

$$\boxed{P_\nu \propto \exp(-\beta U_\nu)}$$ Boltzmann statistics

Normalization factor ("partition function") $\quad Q = \sum_\nu \exp(-\beta U_\nu)$

Probability of a certain energy in small system at NVT conditions

$$P(U) = \frac{\Omega(U) \cdot \exp(-\beta U)}{Q(N,V,T)}$$

this is now $\Omega(U)$ of the small system

$$\langle U \rangle = \frac{1}{Q} \cdot \sum_\nu U_\nu \exp(-\beta U_\nu) \quad \text{mean energy}$$

$\langle U \rangle$ is related to a derivative of $\ln Q$:

$$\ln Q = \ln\left[\sum_\nu \exp(-\beta U_\nu)\right] \Rightarrow$$

$$\frac{\partial \ln Q}{\partial \beta} = \frac{1}{Q}\sum_\nu \frac{\partial \exp(-\beta U_\nu)}{\partial \beta} = -\frac{1}{Q}\sum_\nu U_\nu e^{-\beta U_\nu}$$

$$= -\sum_\nu U_\nu P_\nu = -\langle U \rangle$$

Recall F.E. for entropy S:

$$\frac{dS}{k_B} = \beta dU + \beta P dV - \beta \mu dN = d(\ln \Omega) = y^{(0)}$$

$$y^{(1)} = -U d\beta + \beta P dV - \beta\mu dN = d(\ln Q)$$

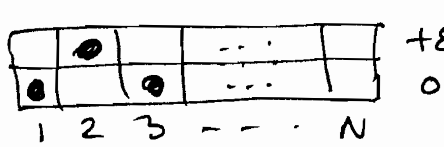
↳ 1st Legendre transformation of S

$$y^{(1)} = y^{(0)} - x_1 \xi_1 \Rightarrow \quad \ln Q = \frac{S}{k_B} - \frac{U}{k_B T} = -\frac{U-TS}{k_B T}$$

$$\Rightarrow \boxed{\ln Q = -\frac{A}{k_B T} = -\beta A}$$

$$\left.\frac{\partial \ln Q}{\partial V}\right)_{T,N} = \beta P \quad ; \quad \left.\frac{\partial \ln Q}{\partial N}\right)_{T,V} = -\beta\mu$$

<u>Example</u>: 2-state system of N particles



$$Q = \sum_\nu e^{-\beta U_\nu} =$$

$$= \sum_{l_1, l_2, \ldots l_N = 0,1} \exp\left[-\beta \sum_{i=1}^{N} \varepsilon l_i\right] =$$

($l_i = 0$ or 1 to describe state)

$$= \sum_{l_1, l_2, \ldots l_N} \left[\prod_{i=1}^{N} \exp(-\beta \varepsilon l_i)\right] =$$

$$= \prod_{i=1}^{N} \sum_{l_i = 0,1} e^{-\beta\varepsilon l_i} = \left(1 + e^{-\beta\varepsilon}\right)^N$$

$\therefore \ln Q = N \ln(1+e^{-\beta\varepsilon})$

$$\langle u \rangle = -\left.\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = N\frac{\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{N\varepsilon}{1+e^{\beta\varepsilon}}$$

recall previous result in uVN ensemble:

$$\beta\varepsilon = \ln\frac{N-M}{M} \Rightarrow \frac{N}{M}-1 = e^{\beta\varepsilon} \Rightarrow M = \frac{N}{1+e^{\beta\varepsilon}} \Rightarrow M\varepsilon = u = \frac{N\varepsilon}{1+e^{\beta\varepsilon}}$$

At the same conditions, results for observable quantities are the same in all ensembles <u>at the thermodynamic limit</u> $N\to\infty$

For small systems, $O(1/N)$ differences.

<u>Generalized ensembles</u>

A similar derivation for P_ν and the partition function can be made for <u>any</u> Legendre transform of the Fundamental Equation.

$$y^{(0)} = \frac{S}{k_B} \qquad y^{(k)} = \frac{S}{k_B} - \xi_1 x_1 - \xi_2 x_2 - \dots - \xi_k x_k$$

x: variable of S

ξ: corr. derivative of S

Partition Function of ensemble corresponding to $y^{(k)} = \ln \Xi$

$$\Xi = \sum_{\text{all microstates}} \exp(-\xi_1 x_1 - \xi_2 x_2 - \dots \xi_k x_k)$$

$$P_\nu = \frac{\exp(-\xi_1 x_1 - \xi_2 x_2 - \dots \xi_k x_k)}{\Xi}$$

Grand Canonical (μVT) ensemble

Useful for phase equilibrium calculations

$$\frac{dS}{k_B} = +\underline{\beta\, dU} + \beta P\, dV - \underline{\beta\mu\, dN}$$

transform

U, N fluctuate

$$\frac{d \ln \Xi_{\mu VT}}{k_B} = -U\, d\beta + N\, d(\beta\mu) + \beta P\, dV$$

$$\left.\frac{\partial \ln \Xi_{\mu VT}}{\partial \beta}\right)_{\mu, V} = -\langle U \rangle \qquad \left.\frac{\partial \ln \Xi_{\mu VT}}{\partial (\beta\mu)}\right)_{T, V} = \langle N \rangle$$

$$\Xi_{\mu VT} = \sum_{N_\nu = 0,1,2,\ldots\infty} \; \sum_{\substack{\text{all microstates } \nu \\ \text{for given } N_\nu}} \exp(-\beta U_\nu + \beta\mu N_\nu)$$

Constant Pressure (PNT) ensemble

$$\frac{dS}{k_B} = \underbrace{\beta\, dU + \beta P\, dV}_{\text{transform}} - \beta\mu\, dN$$

U, V fluctuate

$$\frac{d \ln \Xi_{PNT}}{k_B} = -U\, d\beta - V\, d(\beta P) - \beta\mu\, dN$$

$$\left.\frac{\partial \ln \Xi_{PNT}}{\partial \beta}\right)_{P, N} = -\langle U \rangle \qquad \frac{\partial \ln \Xi_{PNT}}{\partial (\beta P)} = -\langle V \rangle$$

$$\Xi_{PNT} = \sum_{\substack{\text{all possible} \\ \text{volumes } V_\nu}} \; \sum_{\substack{\text{all microstates } \nu \\ \text{at given volume}}} \exp(-\beta U_\nu - \beta P V_\nu)$$