Review of (N,V,E) ensemble

Thus far: $\Omega(N,V,E)$ → number of microstates in (N,V,E) "microcanonical" ensemble

All microstates <u>equally</u> probable.

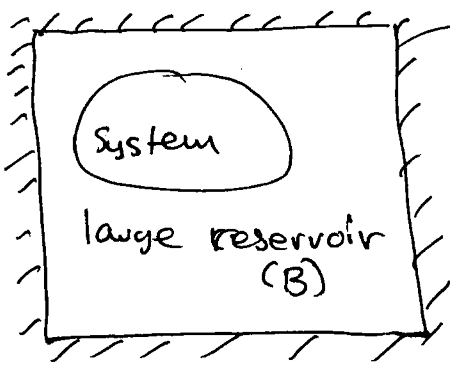
Probability of each state: $\mathcal{P}_m = \dfrac{\delta_{E_m,E}}{\Omega(E,V,N)}$

$$\delta_{E_m,E} = \begin{cases} 1 & \text{if } E_m = E \\ 0 & \text{otherwise} \end{cases}$$

Define "<u>Partition function</u>" as the normalization factor for probabilities of microstates - here

$$\Omega(E,V,N) = \sum_{\substack{\text{all states} \\ m \text{ at } V,N}} \delta_{E_m,E}$$

Constant (N,V,T) ensemble



total system (T) at (E_T, V_T, N_T) conditions

$$\Omega_T(E_T) = \sum_E \Omega_E \, \Omega_B(E_T - E)$$

[any microstate of the system, m, can be coupled with any microstate of the bath, l]

$$\mathcal{P}_{lm} = \frac{\delta_{E_{lm},E}}{\Omega_T(E_T)}$$ ← bath at l, system at m

$$\mathcal{P}_m = \sum_{\text{all } l} \mathcal{P}_{lm} = \frac{\Omega_B(E_T - E_m)}{\Omega_T(E_T)}$$

[Since there are $\Omega_B(E_T - E_m)$ states for the bath]

$$\ln \mathcal{P}_m = \ln \Omega_B(E_T - E_m) + \underbrace{\text{const.}}_{\text{does not depend on } E}$$

Taylor expand: $k_B \ln \Omega_B(E_T - E_m) = S_B(E_T - E_m) =$

$$= S_B(E_T) - E_m \frac{\partial S_B}{\partial E_B} + \cdots = S_B(E_T) - \beta E_m + \cdots$$

$\beta = \dfrac{1}{k_B T}$ ← the common temperature of the bath and the system; bath is much bigger than the system, so that energy exchange does not influence its temperature

$$\therefore \ln P_m = -\beta E_m + \text{const.} \Rightarrow \boxed{P_m \propto e^{-\beta E_m}}$$

$e^{-\beta E}$ is called the "Boltzmann factor"

The normalizing factor for the probabilities is:

$$\boxed{Q(N,V,T) = \sum_{\substack{\text{all states } m \\ \text{at } N,V}} e^{-\beta E_m}}$$

"Canonical" partition function Q

Then $P_m = \dfrac{\exp(-\beta E_m)}{Q}$

$$\langle E \rangle = \sum_m P_m E_m = \frac{1}{Q} \sum_m E_m e^{-\beta E_m} \qquad (1)$$

Consider the derivative $\left.-\dfrac{\partial \ln Q}{\partial \beta}\right)_{N,V} =$

$$= -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -\frac{1}{Q}\cdot\left[\sum_m -E_m e^{-\beta E_m}\right] = \langle E \rangle$$

Compare to

$$\left[\frac{\partial (A/T)}{\partial T}\right]_{V,N} = -\frac{A}{T^2} + \left.\frac{\partial A}{\partial T}\right)_{V,N} \frac{1}{T} = -\frac{A}{T^2} - \frac{S}{T} = -\frac{A+TS}{T^2} = -\frac{E}{T^2}$$

Thus, $\boxed{A = -k_B T \ln Q}$

$y^{(0)} = S(E,V,N)$

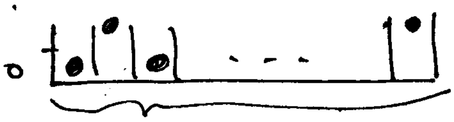
var.	der.
E	$1/T$
V	P/T
N	$-\mu/T$

$y^{(1)} = S - \frac{E}{T} = -\frac{A}{T}$

var.	der.
$1/T$	$-E$
V	P/T
N	$-\mu/T$

The "partition function" for each ensemble obeys a similar relationship: $\boxed{\begin{array}{l} y^{(0)} = k_B \ln \Omega \\ y^{(1)} = k_B \ln Q \end{array}}$

Example 16.1



N slots

Each particle can have energy 0 or ε

Have already derived in microcanonical (N,V,E) ensemble – see Lecture 2

$$S = N k_B \left[-x \ln x - (1-x)\ln(1-x) \right]$$

where $x = \frac{E}{N}$

$$E = N\varepsilon \cdot \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

Now, consider the system in the (N,V,T) ensemble:

$$Q = \sum_m e^{-\beta E_m} = \sum_m e^{-\beta \sum_{i=1}^{N} \varepsilon_i} = \sum_{\varepsilon_1 = 0,\varepsilon} \sum_{\varepsilon_2 = 0,\varepsilon} \cdots \sum_{\varepsilon_N = 0,\varepsilon} e^{-\beta \sum_i \varepsilon_i}$$

e.g., for $N=2$ $\quad Q = e^{-\beta 0 - \beta 0} + e^{-\beta 0 - \beta\varepsilon} + e^{-\beta\varepsilon - \beta 0} + e^{-\beta\varepsilon - \beta\varepsilon}$

Because the particles are not interacting, the sum can be rewritten as

$$Q = \left(\sum_{\varepsilon_1 = 0,\varepsilon} e^{-\beta\varepsilon_1} \right) \left(\sum_{\varepsilon_2 = 0,\varepsilon} e^{-\beta\varepsilon_2} \right) \cdots \left(\sum_{\varepsilon_N = 0,\varepsilon} e^{-\beta\varepsilon_N} \right)$$

e.g. for $N=2$ $\quad Q = \left(e^{-\beta 0} + e^{-\beta\varepsilon}\right)\cdot\left(e^{-\beta 0} + e^{-\beta\varepsilon}\right)$

$$\therefore \quad Q = \left(1+e^{-\beta\varepsilon}\right)^N \Rightarrow A = -k_BT\ln Q = -Nk_BT\ln\left(1+e^{-\beta\varepsilon}\right)$$

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial \beta} = -N\frac{-\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} \Rightarrow \langle E\rangle = N\varepsilon\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

{same result as previously, except now the energy can fluctuate}

[This "trick" of separating out partition functions for independent (non-interacting) degrees of freedom is <u>extremely general</u>, as discussed below.]

<u>Independent Molecules</u>

$$E(x_1, x_2, \dots x_N) = \underbrace{\varepsilon_1(x_1, \dots x_k) + \varepsilon_2(x_{k+1}, \dots x_N)}_{\text{independent terms}}$$

$$Q(T,V,N) = \sum_{x_1}\sum_{x_2}\dots\sum_{x_N} e^{-\beta\varepsilon_1(x_1\dots x_k)} e^{-\beta\varepsilon_2(x_{k+1}\dots x_N)}$$

$$= \left[\sum_{x_1}\dots\sum_{x_k} e^{-\beta\varepsilon_1(x_1\dots x_k)}\right]\left[\sum_{x_{k+1}}\dots\sum_{x_N} e^{-\beta\varepsilon_2(x_{k+1}\dots x_N)}\right]$$

$$= Q_1(T,V,N)\,Q_2(T,V,N)$$

E.g., this implies that the translational partition function (depends on velocities) can always be separated out from the configurational part (depends on positions).

For multiple independent molecules,

$$Q = \prod_i q_i \quad \text{where} \quad q_i \equiv \sum_{x_i} e^{-\beta\varepsilon_i(x_i)}$$ molecular partition function

If all molecules are identical,

$Q = q^N$ (distinguishable) or

$Q = q^N / N!$ (indistinguishable)

Binary mixture of A + B (no interactions) $Q = \dfrac{q_A^{N_A} q_B^{N_B}}{N_A! \, N_B!}$

An Interacting System (Example 16.2)

$\underline{\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\uparrow}$

1-dimensional Ising model

$$E = -J \sum_{\substack{i,j \\ \text{nearest neighbors}}} \sigma_i \sigma_j$$

$$\sigma_i = \begin{cases} +1 & \uparrow \\ -1 & \downarrow \end{cases} \qquad Q = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{\beta J(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \cdots + \sigma_{N-1}\sigma_N)}$$

Transform $t_i = \sigma_{i-1}\sigma_i \rightarrow \sigma_i = \dfrac{t_i}{\sigma_{i-1}}$ $\quad t_i = \pm 1$

$$Q = \sum_{\sigma_1=\pm 1} \underbrace{\left(\sum_{t_2=\pm 1} \cdots \sum_{t_N=\pm 1} e^{\beta J(t_2 + t_3 + \cdots + t_N)} \right)}_{\text{this is separable, } t\text{'s don't interact}}$$

$$= \sum_{\sigma_1=\pm 1} \left(\sum_{t=\pm 1} e^{\beta J t} \right)^{N-1} = 2\left(e^{-\beta J} + e^{+\beta J}\right)^{N-1}$$

$$A = -k_B T \ln Q = -k_B T(N-1)\ln\left(e^{-\beta J} + e^{\beta J}\right) \cancel{- k_B T \ln 2}$$

small as $N \to \infty$

$$\Rightarrow A \simeq -k_B T N \ln\left[e^{-\beta J} + e^{\beta J}\right]$$

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = -NJ \frac{e^{\beta J} - e^{-\beta J}}{e^{\beta J} + e^{-\beta J}}$$

$\begin{cases} \text{as } T \to \infty & \langle E \rangle \to 0 \\ T \to 0 & \langle E \rangle \to -NJ \end{cases}$