Statistical Ensemble

Property of collection of molecules

Statistical thermo- important properties average over molecular configurations:

phase, optical properties, electronic properties

→ In a particular state
State (macro) set of thermo variables $N, V, E, N_i, V_i, T$

$N_1, N_2, N_3, P_i, T$

$d + 2$ variables to define a state

Microstate particular arrangement of $N_{\text{tot}}$ atoms particular velocity/momentum

$6N_{\text{tot}}$ degrees of freedom
State $N, V, E$

$x, y, z$ inside a "box" of size $L_x \cdot L_y \cdot L_z = N$

Energy $\varepsilon_{\text{total}} = KE + PE$

$$\frac{1}{2} m (u_x^2 + u_y^2) \leq \varepsilon_{\text{total}}$$

1 atom in 2d

(bohrs constraints)
Averages

Enumerate every state of system possible states is $2 \cdot 2 \cdot 2 \cdots 2 = 2^N$ distinguishable states $\frac{2^N}{N!}$

$C_6H_{12} \rightarrow 2$ important states

$N$ molecules
- $m$ boat
- $N-m$ chair

$E = m \cdot E_{\text{boat}} + (N-m)E_{\text{chair}}$
Enumerate states

Average of \( O(\text{state}) \)

\[
\langle 0 \rangle = \sum_{i=1}^{M_{\text{states}}} O_i \cdot P_i 
\]

or

\[
\langle 0 \rangle = \int dx_1 dy_1 dz_1 \ldots dx_m dy_m dz_m \\
\frac{d^3p_1}{d^{3}p_1} \frac{d^3p_2}{d^{3}p_2} \ldots \frac{d^3p_n}{d^{3}p_n} \\
\delta^{3n}(\vec{p} - \vec{p}_1) \ldots \delta^{3n}(\vec{p} - \vec{p}_n) \delta^{3n}(\vec{x} - \vec{x}_1) \ldots \delta^{3n}(\vec{x} - \vec{x}_m) \\
\theta(C X, \vec{p}_1) \ldots \theta(C X, \vec{p}_n) 
\]
How likely is each microstate → depends on type of state

$N, V, E$

Microcanonical Ensemble

Isolated

$N, V, T$

Canonical Ensemble
N, U, E - isolated

Newton's equations:
\[ F = ma \]

\[ \vec{F} = m \vec{a} \]

know \( x_{0} \rightarrow p_{0} \)

[Diagram with variables and equations]
Ensemble "many" copies of system all in possible correct proportion A copies.

How likely is state $K$?

$$P_k = \frac{M_k}{\sum_{k=1}^{\# \text{ possible}} M_k = A}$$
Microcanonical Ensemble

Every microstate equally likely

$N, V, E$

\[\begin{array}{c}
\cdot \\
\cdot \\
X
\end{array}\]
Entropy: \[ S = k_B \ln W \]

Statistically, a state ensemble will maximize entropy.
\[ W = \frac{A!}{M_1! M_2! M_3! \ldots M_k!} \] (multinomial distrib)

A copies
order them in \( A! \)

\# possible states, can't distinguish \( M_1, M_2 \ldots \)

Maximize \( S : \frac{\partial S}{\partial M_k} = 0 \) for each \( k \)

\( \Rightarrow \) makes \( M_k \) as large as possible for every \( k \)
Maximize $f(x)$ subject to

$$h(x) = h$$

$$g(x, \alpha) = f(x) - \alpha (h(x) - A)$$

Maximize $g$ instead of $f$

Lagrange multipliers

$$\frac{\partial g}{\partial x} = \frac{\partial f(x)}{\partial x} - \frac{\partial}{\partial x} \alpha (h(x) - h) = 0$$

$$\frac{\partial g}{\partial \alpha} = 0 = h(x) - h \Rightarrow h(x) = h$$
\[ W = \frac{100,000!}{M_H! \cdot M_T!} \]

\[ \frac{\partial \ln W}{\partial M_H} = 0 \]

\[ \frac{\partial \ln W}{\partial M_T} = 0 \]

\[ \frac{\partial g}{\partial \alpha} = 0 \Rightarrow M_H + M_T = 100,000 \]
Classic Example

\[ f(x, y) = x + y \]

where is this max or min

\[ \frac{\partial f}{\partial x} = 1 \quad \frac{\partial f}{\partial y} = 1 \]

If \[ x^2 + y^2 = 1 \]
\[ y(x, y) = \frac{f(x, y) - \alpha (x^2 + y^2 - 1)}{x + y} \]

\[ \frac{\partial g}{\partial x} = 1 - 2\alpha x^2 = 0 \quad \Rightarrow \quad x^* = \frac{1}{2} \alpha \]

\[ \frac{\partial g}{\partial y} = 1 - 2\alpha y^2 = 0 \quad \Rightarrow \quad y^* = \frac{1}{2} \alpha \]

\[ \frac{\partial g}{\partial \alpha} = x^2 + y^2 - 1 = 0 \]

\[ \frac{1}{4\alpha^2} + \frac{1}{4\alpha^2} - 1 = 0 \quad \Rightarrow \quad \alpha = \pm \frac{1}{2} \]

\( f \) is max at \( \frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2} \) if \( x^2 + y^2 = 1 \).
Canonical Ensemble (ch 10)

A copies

→ can exchange energy

\[ N, V, E \]

whole thing isolated

How likely is a microstate
\[ S(M_1, M_2, \ldots, M_n) \]
\[ = -\alpha \left( \sum M_i - A \right) \]
\[ - \beta \left( \sum M_i \varepsilon_i - \varepsilon_{\text{tot}} \right) \]

Maximize: \( P_i = \frac{M_i}{A} \alpha e^{-\beta \varepsilon_i} \)

\[ P_i = e^{-\beta \varepsilon_i} \frac{\sum_{i=1}^{\#} e^{-\beta \varepsilon_i}}{\sum_{i=1}^{\#} e^{-\beta \varepsilon_i}} \]

\[ \sum_{i=1}^{\#} P_i = 1 \]
\[ Q = \sum_i e^{-\beta E_i} = \sum_i e^{-E_i/k_BT} \]

Partition function

\[ \varepsilon_n = h\nu \left( \frac{1}{2} + n \right) \]

turns out \( \beta = \frac{1}{k_BT} \)
\[ w_i = e^{-\beta e_i} \]

Relative weight

\[ p_i = w_i / Q = \frac{e^{-\beta e_i}}{\sum_i e^{-\beta e_i}} \]