Statistical connection between microscopic & macroscopic properties

Microscopic (atomistic) - molecular properties

$x, y, z$ of each atom or $V_x, V_y, V_z$...

Spin of each of each atom

Macroscopic (Thermodynamic)

$T, P, \text{ heat capacity }, \text{ coefficient of thermal expansion}$
Macrostates - characterizes the thermodynamic system \( N, V, T \) or \( N, p, T \)

Microstate - particular configuration of your system

\[ N_{H_2O}, \quad U = 1 \text{ cal} \]
\[ V = 1 \text{ liter} \]
\[ T = 25°C \]

\[ x, y, z, z_1, z_2, \ldots, z_N \]
Ergodicity explores all accessible states in finite time.

Ergodic hypothesis systems are big enough that they're effectively ergodic.

Billiard Ball Problem
Ensemble Method: If you have many copies of a system, average a property over that ensemble. The same answer as 1 system far $t \to \infty$. 

\[
\langle \text{d}z \rangle
\]

\[+\]

\[
\text{ensemble} \quad \downarrow
\]

\[
N, V, T
\]

\[\text{average}\]
have been talking about continuous systems meaning \( x, y, z \)

start with discrete systems discrete number of possible states

Consider a system that can be in \( M \) microstates

A total copies

\[
\begin{align*}
\text{state} & \rightarrow \\
1 & \rightarrow 5 \\
2 & \rightarrow 7 \\
3 & \rightarrow 11 \\
& \cdots \\
A & \rightarrow M/3
\end{align*}
\]
$N_i$ is the # in state $i$

$$\sum_{i=1}^{m} N_i = A$$

$$\prod_{i=1}^{m} N_i = \prod N_1, N_2, \ldots, N_m$$

$$\prod p_i z = \prod P_1, \ldots, P_m z = \prod \frac{N_1}{A}, \frac{N_2}{A}, \ldots, \frac{N_m}{A}$$

$m = 6$
Ensemble Average

Property \( y_i \) for each \( i \)

\[
\langle y \rangle_{\text{ensemble}} = \frac{1}{m} \sum_{i=1}^{m} y_i \cdot P_i
\]

Contrast to a time average

\( y(t_1), y(t_2), \ldots, y(t_{N_t}) \)

\[
\langle y \rangle_{\text{time}} = \frac{1}{N_t} \sum_{i=1}^{N_t} y(t_i)
\]
Microcanonical Ensemble

Ensemble where every copy has the same $N, U, E$ - isolated system

All molecules follow Newton's equations

$F = ma$

or Schrödinger equation

Both case $E$ is constant
Learned previously that entropy
\[ S = k \ln \Omega \]

is a thermodynamic potential for \( N, U, E \) systems.

\( S \) is maximized at equilibrium.
Copies of this system maximize entropy.

\[ \Rightarrow P_1, P_2 \ldots P_m \] for our system.
\[ S = k_B \ln W \]

\( N \) copies and \( N_1 \) in state 1

\( N_2 \) in state 2...

\[ w = \frac{A!}{N!N_2!N_3!N_4!...N_m!} \quad (\text{multinomial distribution}) \]

\[ \sum_{i=1}^{m} N_i = A \]

\[ A \& \{N_i\} \text{ large} \]

Sterling's approximation is okay
\[ \omega = \frac{A!}{N_1!N_2!N_3!N_4! \cdots N_m!} \]

\[ S = k_B \ln W = (A \ln A - \sum_{i=1}^{m} (N_i \ln N_i - N_i)) - A \]

\[ S_{kB} = A \ln A - \sum_{i=1}^{m} N_i \ln N_i \]

\[ \frac{\partial S_{kB}}{\partial N_i} = 0 \]
\( S \approx \frac{A \ln A - \frac{m}{2} N_i \ln N_i}{k_B} \)

\[
\frac{\partial S / k_B}{\partial N_j} = A \left( \frac{\partial \ln A}{\partial N_j} + \frac{\partial A}{\partial N_j} \right) \ln A \\
- \frac{N_j}{N_i} - 1 \cdot \ln N_j
\]

\( A = \frac{m}{2} N_i \)

\( \frac{\partial A}{\partial N_j} = 1 \)

Maximize \( S \) to get 

\( S \to 0 \)

\( \ln A - \ln N_j = \ln \left( \frac{A}{N_j} \right) \)
Want to maximize all $N_j$

but $\sum_{j=1}^{m} N_j = A$ < constraint

Method of Lagrange Multipliers

$f(X) \leftarrow$ want to find max or min with a constraint

$\max_{\text{or} \min} I = f(X) - \lambda (\text{constraint})$
$$S = k \ln w \quad \omega / \text{constraint}$$

$$\sum_{i=1}^{m} N_i = A \Rightarrow \left( \sum_{i=1}^{m} N_i - A \right) = 0$$

$$I = k \ln w - \alpha \left( \sum_{i=1}^{m} N_i - A \right)$$

$$\frac{\partial I}{\partial N_{j}} = \ln A - \ln N_{j} - \alpha = 0 \quad \text{for every } N_{j}$$

$$\alpha = \ln \left( \frac{A}{N_{j}} \right) \iff N_{j} = Ae^{-\alpha}$$
\[ N_j = Ae^{-\alpha} \]
\[ \sum_{i=1}^{\infty} N_j - A = 0 \leftarrow \text{constraint} \]
\[ \sum_{i=1}^{\infty} Ae^{-\alpha} = A \Rightarrow mAe^{-\alpha} = A \]
\[ e^\alpha = m \quad \alpha = \ln(m) \]
\[ P_i = \frac{N_i}{A} = \frac{Ae^{-\alpha}}{A} = \frac{1}{e^\alpha} = \frac{1}{m} \]
Chapter 10: Canonical Ensemble

A system of interest has constant

\[ N, U, T \]

\[ N = A \tilde{N}, V = A \tilde{V}, \varepsilon = \frac{A}{N} \varepsilon_i \]

\[ N, U, E \] overall heat transfers until each system has same \( T \)

\[ \tilde{N}, \tilde{U}, T \]
Whole system is \( N_i, \epsilon \)

Maximize \( S = k \ln(\epsilon) \)

Constraints:

1. \( \sum_{i=1}^{m} N_i = A \)

2. \( \sum_{i=1}^{m} \epsilon_i = \epsilon_{\text{total}} \)

Lagrange multipliers (2 constraints)

\[ S = k \ln(\epsilon) - \alpha (\sum N_i - A) - \beta (\sum \epsilon_i) \]
Energy constraint

\[ E_{\text{total}} = \sum_{i=1}^{N} N_i E_i \]

\[ S = k \ln \omega - \alpha (\sum N_i - A) \]
\[ - \beta (\sum Z N_i E_i - 3 + \text{total}) \]

\[ \frac{\partial S}{\partial N_i} = \ln \left( \frac{A/N_i}{N_i} \right) - \alpha - \beta E_i = 0 \]
\[ \ln \left( \frac{A}{N_i} \right) - \alpha - \beta \varepsilon j = 0 \]
\[ N_j = e^{-\alpha} e^{-\beta \varepsilon j}. A \]
\[ \sum_{j=1}^{m} N_j = A = A e^{-\alpha} \sum_{j=1}^{m} e^{-\beta \varepsilon j} \]
\[ 1 = e^{-\alpha} \sum_{j=1}^{m} e^{-\beta \varepsilon j} \]
\[ e^{\alpha} = \sum_{j=1}^{m} e^{-\beta \varepsilon j} \]
\[ P_j = \frac{N_j}{A} = e^{-\alpha} e^{-\beta \varepsilon j} \]
\[ P_j = e^{-\beta \varepsilon j} \frac{1}{\sum_{j=1}^{m} e^{-\beta \varepsilon j}} \]
\[ P_j = \frac{e^{-\beta E_j}}{\sum_{i=1}^{N} e^{-\beta E_i}} \]

\[ Q = \sum_{i=1}^{N} e^{-\beta E_i} \]

"partition function"

\[ e^{-\beta E_j} \] is called Bolzmann factor (relative weight)
for Microcanonical
Bolzmann factor = 1 like $\beta = 0$

\[ Q = \sum_{i=1}^{m} \beta E_i = m \]

\[ \langle y \rangle = \sum_{i=1}^{m} y_i P_i = \sum_{i=1}^{m} y_i e^{-\beta E_i} / Q \]

\[ \langle 3 \rangle = \sum_{i=1}^{m} e^{i \cdot e^{-\beta E_i}} / Q \]

$\beta = \frac{1}{k_B T}$
can derive thermodynamic quantities from the partition function

\[
\langle 3 \rangle = \sum_{i=1}^{m} \frac{e^{-\beta E_i}}{Q}
\]

\[
-\frac{\partial Q}{\partial \beta} = \sum_{i=1}^{m} E_i e^{-\beta E_i}
\]

\[
\frac{\partial \log Q}{\partial x} = \frac{1}{x} \frac{dx}{dQ}
\]
\[-\frac{\partial \ln \Omega}{\partial \beta} = \sum_{i=1}^{\Omega} e^{-\beta E_i} = \langle E \rangle\]

\[\langle E \rangle = -\frac{\partial \ln \Omega}{\partial \beta}\]
Gibbs Entropy \[ S = k_B \ln \omega \text{ micro} \]

\[
S = -k_B \sum_{i=1}^{m} p_i \ln p_i; \quad \sum_i p_i y_i = \langle y \rangle
\]

\[
p_i = \frac{e^{-\beta E_i}}{\theta}
\]

\[
= -k_B \sum_i p_i [-\beta E_i - \ln \theta]
\]

\[
= k_B \beta \sum_i p_i E_i + k_B \ln \theta
\]

\[
= k_B \beta \langle E \rangle + k_B \ln \theta
\]

\[
\downarrow \text{entropy}
\]
\[ S = k_B \beta \langle \varepsilon \rangle + k_B \ln \theta \]

\[ T = \left( \frac{\partial u}{\partial s} \right)_v = \frac{\partial u}{\partial s} \]