We will take advantage of two properties to instead develop a statistical connection between microscopic & bulk properties.

Ensemble method & ergodic hypothesis

Definitions (reminder)

- **Macrostate** - thermodynamic state of the system, e.g. \( N, V, E \) or \( N, V, T \) or \( n, \rho, T \)
- **Microstate** - \( x, y, z, \rho_x, \rho_y, \rho_z \) if every atom configuration of system, e.g.

**Ergodicity** - long enough time, system explores all microstates.

Spatis "correct" amount of time in each one (more later)

Ensemble method - if had many copies of system, average over copies gives same result as ten or one copy.
Suppose a system has $m$ possible states.

A total copy of system

```
1 2 3 ...
```

let $N_i$ be the number in state $i$

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

$$\sum N_i \Xi = \Xi N_1, N_2, ... N_m \Xi$$

prob of each state $1-m$

$$\Xi \Pi \Xi = \Xi \Pi_1, ... , \Pi_m \Xi = \Xi \frac{N_1}{A}, \frac{N_2}{A}, ..., \frac{N_m}{A} \Xi$$

Ensemble average of property $Y$

$$\langle Y \rangle = \frac{1}{m} \sum_{i=1}^{m} y_i \Pi_i$$

Should be same as time avg $$\langle Y \rangle_t = \frac{1}{N_t} \sum_{j=1}^{N_t} y_j(t_j)$$
An ensemble is a collection of copies of a system all in the same microstate. A "microcanonical" ensemble is one with constant \( N, V, E \) - isolated system obeying Newton's equations \( F = ma \), conserve \( E \).

How often does each microstate occur? Equilibrium maximizes entropy!

\[
S = k_B \ln W , \quad \text{but what is } W \left( N_1, V, E \right) \quad \text{for an ensemble}
\]

\[
N_1 \text{ copies in state } 1, \quad N_2 \text{ copies in state } 2, \ldots
\]

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

\[
W = \frac{A!}{N_1! N_2! N_3! \ldots N_m!} \quad \text{(multinomial)}
\]

For \( A \) & \( N_i \) large:

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

\[
\frac{1}{k_B} \frac{dS}{dN_i} = 0 \quad \text{for all} \ N_i
\]

\[
\frac{1}{k_B} \frac{dS}{dN_i} = \frac{\partial (A \ln A)}{\partial N_i} - \frac{\partial}{\partial N_i} \left( \sum_{N_i} \ln N_i \right) = 0
\]

Only includes

\[
A = \sum_{N_i} N_i
\]

\[
\frac{1}{k_B} \frac{dA}{dN_i} = \frac{\partial A}{\partial N_i}
\]

\[
= A \frac{\partial \ln A}{\partial N_i} + \frac{\partial A}{\partial N_i} \ln A - \frac{N_i}{N_i} - \ln N_i
\]

\[
= 1 + \ln A - 1 - \ln N_i
\]

\[
= \ln A - \ln N_i
\]

Smallest for \( N_j \) all maximized

But can't make all \( N_j \) max simultaneously

because \( \sum N_j = m \), need

a constraint
Turns out (see pg 312-313)

Lagrange Multipliers for constraint

Instead, find when

\[ I = f(x) - \alpha (\text{constraint}) \text{ is max} \]

\[ I = k \ln \omega - \alpha \left( \sum_{i=1}^{n} N_i - A \right) = 0 \]

\[ \frac{\partial I}{\partial N_i} = \ln A - \ln N_i - \alpha = 0 \quad \forall N_i \]

\[ \alpha = \ln \left( \frac{A}{N_i} \right) \text{ is a constant} \]

\[ N_i = e^{-\alpha} \quad \forall N_i \]

find \( \lambda \) by enforcing constraint

\[ \sum_{i=1}^{n} N_i = A = \sum_{i=1}^{m} A e^{-\alpha} \implies e^\lambda = m \]

\[ P_i = \frac{N_i}{\sum N_i} = \frac{1}{m} \text{ equal distribution} \]
Chapter 10 - Canonical Ensemble

Consider bunch of copies of system

\[ N, U, E \text{ overall} \]

Know heat transfers until have same temp

\[ S = k \ln W \]

but now

\[ \tilde{N}, \tilde{U}, \tilde{T} \]

so for one system,

\[ \tilde{N} = A \tilde{N}_i \text{ at } \tilde{T} \]

\[ \tilde{N} = A \tilde{N}_i \text{ at } \tilde{T} \]

\[ \tilde{E} = \sum_{i=1}^{N_i} \tilde{E}_i \]

Max S w/ E constraint & \( \sum \tilde{N}_i = A \text{ sun} \) own states
\[ S_{1/k_B} = \ln A - \alpha (\sum N_i - A) - \beta (\sum E_i - e_t) \]

\[ \frac{\partial S_{1/k_B}}{\partial N_j} = \ln \frac{A}{N_j} - \alpha - \beta E_j = 0 \]

and so \( N_j = e^\alpha e^{-\beta E_j} \cdot A \)

\[ \sum_j N_j = A = A \sum_j e^{-\alpha e^{-\beta E_j}} \]

so \( e^\alpha = \sum_j e^{-\beta E_j} \)

This means \( P_j = \frac{N_j}{A} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \)

\[ Q = \sum_{j=1}^{m} e^{-\beta E_j} \] is “partition function”

for canonical ensemble & \( e^{-\beta E_j} \)

is the Boltzmann factor (relative weight)
for micro canonical ensemble
\[ \beta F = 1 \quad \text{(like } \varepsilon_j = 0 \text{ for } \beta = 0) \]
and \[ Q = \frac{1}{Z} \beta F_i = \frac{1}{Z} \beta = \alpha \]

Average of \( y \)
\[ \langle y \rangle = \frac{1}{Z} \sum_{i=1}^{\beta} y_i \]
\[ \langle y \rangle = \frac{1}{Z} \sum_{i=1}^{\beta} y_i e^{-\beta \varepsilon_i} / \alpha \]
\[ \langle y \rangle < (3) > = \frac{1}{Z} \sum_{i=1}^{\beta} \varepsilon_i e^{-\beta \varepsilon_i} / \alpha \]

Turns out can show by connection to classical thermos that
\[ \beta = \frac{1}{k_B T} \]
so
\[ Q = \frac{1}{Z} e^{-\beta\varepsilon_i / k_B T} \]
can get other therm quantities from this function
\[ \frac{\partial m}{\partial \varepsilon} \times \frac{\partial \theta}{\partial \varepsilon} \] if we consider
\[ \frac{\partial \theta}{\partial \varepsilon} = \frac{1}{\partial\theta / \partial \beta} \]
\[ u = -e \ln \Theta \]

Also, \[
\frac{\partial f}{\partial \theta} = \frac{e}{\Theta} = \frac{\theta}{e} \frac{\partial \Theta}{\partial \beta} = \frac{\partial f}{\partial \beta} \left( \frac{\partial \beta}{\partial \theta} \right)^{-1} = \left( \frac{k_B T^2}{\Theta} \right) \frac{\partial f}{\partial \Theta} \]

so \[ u = k_B T^2 \frac{\partial \ln \Theta}{\partial T} \]

\[ \overline{\text{Gibbs Entropy}} \]

\[ S = -k_B \sum p_i \ln p_i \]

\[ = -k_B \sum p_i \left[ -\beta E_i - \ln \Theta \right] \]

\[ = k_B \beta \sum E_i \beta e_i + \ln \Theta \]

\[ = k_B \beta + k_B \ln \Theta \]
\[ T = \left( \frac{\partial u}{\partial s} \right)_v = \frac{\left( \frac{\partial u}{\partial \theta} \right)_v}{\left( \frac{\partial s}{\partial \beta} \right)_v} \]

\[ \frac{\partial S}{\partial \beta} = k_B (U + \beta \frac{\partial u}{\partial \beta} + \left( \frac{\partial \ln \theta}{\partial \beta} \right)_v) \]

\[ = k_B \beta \left( \frac{\partial u}{\partial \beta} \right)_v \]

So, \[ T = \frac{1}{k_B \beta} \Rightarrow \beta = \frac{1}{k_B T} \cdot \]