Lecture 2 - Microcanonical Ensemble

Last time:
\[ X = \{ x_1, \ldots, x_{3N}, p_1, \ldots, p_{3N} \} \text{ is microstate of the system} \]

A is an observable, \( A(x) \)

\[ \langle A \rangle = \int dx A(x) P(x) \] is value measured

\( P(x) \) depends only on Macrostate for constant \( N, V, T - P(x) = \frac{1}{Z} e^{-\beta H(x)} \)

\[ Z = \int dx e^{-\beta H(x)} \]

\[ \langle \mathcal{E} \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2} \frac{\partial^2}{\partial \beta^2} = \frac{1}{2Z} \int dx H(x)e^{-\beta H(x)} \]

\[ \mathcal{E} \] \( H = \frac{p^2}{2m} + \frac{1}{2} k x^2 \)
\( z = 2\pi \cdot \frac{1}{\beta \omega} \)

\[-\log z = -\log(2\pi/\omega) + \log(\beta)\]

\[\langle E \rangle = -\frac{\log \beta}{\beta} = \frac{1}{\beta} = k_B T\]

Average energy does not depend on \( \beta \) (or \( m \)). Very important physical fact

\( x \) is not always continuous

Eg quantum harmonic oscillator

\( E_n = \hbar \omega (n + \frac{1}{2}), \quad n=0, \ldots, \infty \)

\[ z = \sum_{i \in \text{states}} A_i \delta(z_i) \]

\[ \approx \sum_n E_n e^{-\beta E_n} / Z \]
Now let's return to a system of atoms or molecules we want to study

$N$ particles in closed isolated box

- no particle exchange
- no energy exchange

These $N$ particles follow Newton's laws, so if we know $X(t)$ we know $X$ at all times in theory.
If we know particle positions & momenta, we know everything.

Classical Mechanics:

\[
F_i = m_i a_i = m_i \dot{V}_i = m_i \ddot{x}_i
\]

\[
v = \dot{x} = \frac{dx}{dt}
\]

**integrate:**

\[
X(t) - X(0) = vt \quad \Rightarrow \quad d = vt
\]

\[
V(t) - V(0) = at \quad \Leftarrow \text{const } a
\]

\[
V_2 = V_1 + at
\]

\[
\dot{X}(t) = V_1 + at \quad \Rightarrow \quad d = V_1 t + \frac{1}{2} at^2
\]
Newton's laws conserve energy. So even if we cannot solve, $E$ stays constant [no external forces].

Macrostate: $N, U, E$

Microstate: any configuration $x = \mathcal{E}, x, \beta \beta$ where $x \in \text{box}$ (eq. $0 \leq x \leq L$) \iff

$H(x) = 3$

Express this constraint as $g(H(x) - 3)$
How many states are there?

“Count” every state where this is true. For continuous, this is an integral

$$\int dx \int dp \mathcal{S}(\mathcal{H}(x,p)-E) \propto$$

What is the probability of a state. Assumption: “equal a priori possibilities” - why should any one state be special?
So for $N, n, \epsilon$

$$P(X) = \begin{cases} \frac{1}{2} & \text{if } Z(x) = 3 \\ 0 & \text{otherwise} \end{cases}$$

$Z$ counts all allowed configurations.

If we can also take snapshots of dynamics, we would get representative configurations.
Ergodic - in principle, all possible configurations eventually visited.

If we have a long "movie" or "trajectory",

Take snapshots $X_i, P_i$, and to average, do

$$
\frac{1}{N_t} \sum_{i=1}^{N_t} A(X_i) = \langle A \rangle_{\text{time}}
$$

If ergodic

$$
\langle A \rangle = \langle A \rangle_{\text{time}}
$$