Ch2: Statistical Mechanics and the Statistical Approach to Thermodynamics

Mechanics \rightarrow Stat. Mech \rightarrow Thermodynamics
- Quantum or classical
- microscopic properties
- positions, momenta, energies of states
- mean values
- probabilities
- time vs ensemble averages
- observable or macroscopic prop.
- T-p-v-n dependence
- heat capacities
- phase changes
- chemical changes

Provides the foundation for many fields and applications: condensed matter physics, biological physics, material science, cloud physics, polymer physics, parts of solid state physics

To carry out this program, we will initially be concerned with characterizing macroscopic systems in terms of their microscopic states:
- What is a microstate? How many are there?
- How does the number of microstates affect behavior of macroscopic systems?
- What is the probability of being in a given microstate?
- How do we find mean values of observable properties?

States: unique arrangements of the constituents of a system
- An important property: States have energies $E$

Simple example of "states" of a system of 3 dice:

<table>
<thead>
<tr>
<th>States</th>
<th>E (total points)</th>
<th>$\Omega(E)$ = # of states with $E$</th>
<th>State label</th>
</tr>
</thead>
<tbody>
<tr>
<td>{1, 1, 1}</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>{1, 2, 1}</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>{2, 1, 1}</td>
<td>4</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>{1, 2, 2}</td>
<td>5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>{1, 1, 3}</td>
<td>5</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>{3, 1, 1}</td>
<td>5</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Individual particle states
1. Quantum Mechanical States are solutions to Schrödinger Eq.
   \[ H_N \psi_i = E_i \psi_i, \quad i = 1, 2, 3, \ldots \] states are discrete
   In principle, solving for all the \( E_i \) completely specifies the system
   In practice, "easy" to do for only a few relatively ideal systems

2. Classical Mechanical States are tiny subdivisions of "phase space"
   For \( N \) point particles, Hamiltonian mechanics is treated using
   \( 3N \) generalized coordinates \( \{ \theta \} \) and \( 3N \) generalized momenta \( \{ p \} \)
   This \( 6N \) dimensional space is referred to as phase space
   Classical states correspond to tiny cells of \( 6N \) dimensional "volume"
   A 2-d phase space example: \( lg \) and \( lp \)
   - subdivide the \( q-p \) plane into
   - many little cells of "area" \( dq \cdot dp \)
   - how "big" is a state \( dq \cdot dp = h_0 \)
   \( h_0 = \) a constant with dimensions of angular momentum
   Originally, \( h_0 \) could not be determined "a priori"
   Now we know from QM that \( h_0 = \hbar \) (Planck's constant)

3. Semi-classical states: a hybrid approach
   Use CM for translational degrees of freedom
   Use QM for internal degrees of freedom (vibration, rotation, electronic states)

   (classical)
   \[ f = \text{degrees of freedom} = \text{total \# of independent coordinates} \]
   needed to fully specify the configuration of a system
   \[ \begin{align*}
   &N \text{ monatomic particles (spinless)} \quad f = 3N \\
   &N \text{ diatomic molecules} \quad f = 6N = 3N(\text{com}) + N(\text{vib}) \\
   &N \text{ particles with } \nu \text{ internal dof} \quad f = N(3 + \nu) \\
   \end{align*} \]

A System = a small piece of the universe under study - need to specify boundaries, often it is isolated
isolated means its \( E, N, V \) are constant
Fundamental Postulate of Statistical Mechanics:
An isolated equilibrium system has equal probability for occupying any microstate consistent with its $E, N, S$

Let $S(E, V) =$ total # of microstates with energy $E \rightarrow E + SE$
in volume $V \rightarrow V + SV$

Then $P(E, V) = \frac{1}{S(E, V)} =$ probability of being in any particular microstate

Recall that an equilibrium state has constant, uniform properties:
- constant = no time dependence
- uniform = no spatial variation, unless there are applied external fields (gravity) or more than one phase

E.G.: Gas filling a container

<table>
<thead>
<tr>
<th>Gas and empty</th>
<th>remove partition</th>
<th>Gas expands, non-equilibrium</th>
<th>after a long time</th>
<th>uniform gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium initially</td>
<td>partition</td>
<td>gas fills volume, new equilibrium state</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The new equilibrium state (uniformly filled volume) is much more probable than the partly filled, partly empty, non-equilibrium state.

Equilibrium state = most probable macrostate for a given set of constraints, i.e., $E, V, N$

$= macrostate with largest # of microstates for a given $E, V, N$

- largest $S(E, V)$

How to tell when a system is in equilibrium? Sometimes it's not easy - just have to wait and monitor properties.

- time to reach equilibrium depends on the rates of different transport processes

Equilibrium averages:
- time average $\Rightarrow$ ensemble average of 1 system of many identical replicas

This assumed equivalence is known as

The Ergodic Hypothesis - very difficult to prove
Counting Microstates

Averaging: Say that \( \Omega(E, y_k) \) = \# of microstates with energy \( E \) such that a microscopic parameter \( y \) has a value \( y_k \). Then the probability of finding the value \( y_k \) is \( P(y_k) = \frac{\Omega(E, y_k)}{\Omega(E)} \)

\[
\Omega(E) = \sum_k \Omega(E, y_k)
\]

and mean value of \( y \) is \( \bar{y} = \sum_k y_k P(y_k) \)

The difficult problem is to calculate \( \Omega(E) \) - we are interested in microstates whose energy lies between \( E \) and \( E + \Delta E \). What is \( \Delta E \)?

Suppose we know the \( E \) values of all states roughly the energy levels are spaced by \( \Delta E \).

Choose \( E \gg \Delta E \) so that \( \Sigma(\Delta E) \) is a continuous, smooth function and to avoid limitations on precisely knowing \( E \) due to the uncertainty principle and instrumental resolution.

Often it is easier to calculate \( \Phi(E) = \text{total \# of states with energy} \leq E \)

then \( \Sigma(E, \nu) = \Phi(E+\Delta E) - \Phi(E) = \frac{d\Phi}{dE} \Delta E = \omega(E) \Delta E \)

\( \omega(E) = \text{density of states} \)

so \( \Sigma(E) = \omega(E) \Delta E \)

Examples:

(a) 1 particle in a 1-d "box", \( 0 \leq x \leq L \)

\( E = \frac{p^2}{2m} \quad p = \pm \sqrt{2mE} \)

each \( p \to E \)

\( \Phi(E) \propto \int_{-\sqrt{2mE}}^{\sqrt{2mE}} dp \int_0^L dx = 2Lp(E) = 2L\sqrt{2mE} \)

\( (\Sigma(E) \propto E^{-\nu/2}) \)
(a') If we had *f* such particles, weakly interacting,
\[ E = \sum_{i=1}^{f} E_i = f \bar{E} \rightarrow \text{act independently} \]

\[ \Phi(E) = \prod_{i} \Phi(E_i) \quad E_i \approx \bar{E} \]

\[ = \left( \prod_{i} \Phi(E_i) \right)^f = f^{f-1} \bar{E}^{f-1} = f^{f-1} \left( \frac{E}{\bar{E}} \right)^{f-1} \]

\[ \pi(E) = \frac{d}{dE} \Phi(E) = \frac{f}{\bar{E}} \left( \frac{E}{\bar{E}} \right)^{f-1} \frac{dE}{E} \]

\[ \uparrow \quad \text{a very strong function of } E \quad \text{and } \quad f \sim 10 \]

\[ \ln \pi(E) \sim \frac{f}{\bar{E}} \ln E + f \ln f \]

(b) H. D.
\[ E = \frac{p^2}{2m} + \frac{k_x^2}{2} \]

*elliptic*

\[ a = \sqrt{\frac{2E}{k}} \quad b = \sqrt{2mE} \]

\[ \Phi(e) = \iint dx dp = \text{area of ellipse} = \pi ab = 2\sqrt{\frac{m}{k}} E \]

(b') \[ \Phi(E) = \sum_{i} \Phi(E_i) \rightarrow \text{oscillators} \]

\[ \Phi(E) = \prod_{i} \Phi(E_i) = \prod_{i} \Phi(E) = \left( \Phi(E) \right)^f = \left( 2\sqrt{\frac{m}{k}} \frac{E}{f} \right)^f \]

\[ \pi(E) = f \left( 2\sqrt{\frac{m}{k}} \frac{E}{f} \right)^f \frac{dE}{E} \]

\[ \ln \pi(E) = f \ln E + \ldots \]