The central application of statistical mechanics rests on the assumption that the average of a property over a large number of systems will give the same value as the thermodynamic quantity of interest. We can distinguish between mechanical properties such as pressure, energy, volume etc. and non-mechanical properties such as entropy. Although there are a large number of particles and an extremely large number of quantum states accessible to even a small system, the state of the system can be characterized by just a few thermodynamic variables. These statements are known as the Gibbs postulate:

The ensemble average of a property corresponds to the thermodynamic quantity.

For example, the average energy corresponds to the internal energy, the average pressure corresponds to the thermodynamic pressure, etc. To accomplish the kind of averaging needed to calculate the pressure, for example, we must consider a large number of systems. The concept of a collection of systems, or an ensemble was first introduced by Gibbs. An ensemble consists of a very large number of systems, each constructed to be a replica on the macroscopic level. We will introduce several types of ensemble in this course depending on which variables are held fixed. Corresponding to each ensemble there is a partition function that represents the average number of states accessible at a given temperature.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ensemble Name</th>
<th>Fixed Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>Microcanonical</td>
<td>N, V, E</td>
</tr>
<tr>
<td>Q</td>
<td>Canonical</td>
<td>N, V, T</td>
</tr>
<tr>
<td>D</td>
<td>Isobaric-isothermal</td>
<td>N, P, T</td>
</tr>
<tr>
<td>Q</td>
<td>Grand canonical</td>
<td>m, V, T</td>
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</tbody>
</table>

The magnitude of the partition function, \( W(E) \) for the microcanonical ensemble is the same as the degeneracy of the system at the given energy, \( E \). The principle of equal a priori probabilities states that each and every quantum state of the system must be represented an equal number of times. Another way to put this is to state that in an isolated system (\( N, V, E, \) fixed) any one of the \( W \) possible quantum states is equally likely. The partition function \( W \) of the microcanonical ensemble is the same as the thermodynamic probability \( W \) introduced in the Boltzmann equation for the statistical entropy, \( S = k \ln W \). The same equation holds for the microcanonical ensemble, \( S = k \ln W \) and thus represents a direct thermodynamic connection between the partition function and the entropy. The difficulty with
application of this information is that it is very difficult to obtain a set of molecules at a constant energy. In spite of this experimental difficulty, the microcanonical ensemble is useful for illustrating the number of degenerate (equal energy) states in systems of interest. The conclusion from these investigations will be that the number of quantum states accessible to a system is vast and that provides the motivation for application of statistical techniques to the calculation of average quantities, fluctuations and transport properties.

**Molecular motion: the quantum view**

We consider the three types of molecular motion

1. translation
2. vibration
3. rotation

From quantum mechanics we have

\[ H Y = E Y \]

where \( H \) is the hamiltonian

where \( h = h/2p \), that is, Planck's constant divided by \( 2p \). The hamiltonian comprises both the kinetic and potential energy of the system. For the purposes of statistical mechanics it is the energy levels and their degeneracy that are of interest. The wavefunctions, \( Y \) do not appear in averages and are therefore not given below.

**Translation**

Translation is calculated using the particle-in-a-box treatment.

Setting the potential \( U(x) = 0 \) over the range \( x = 0 \) to \( a \) and \( U(x) \) equal to infinity outside this range, for one dimension the hamiltonian,

the energy levels are

\[ \text{energy levels} \]
The extension to three dimensions is easily made and is shown below.

**Vibration**

The classical Hooke’s law potential is $\frac{1}{2} kx^2$ and this is exactly what is used as the potential in the quantum mechanical hamiltonian. In one dimension this becomes

The energy levels are

where $W = (k/m)^{1/2}$.

** Rotation**

The rigid rotor hamiltonian is

The energy levels are

$I$ is the moment of inertia of the rotor.

The essence of statistical mechanics is to connect these quantum mechanical energy levels to the macroscopically measured thermodynamic energies, pressure, and entropy. There are two important aspects of these energy levels. First, there is a ladder of increasing energy states. Second, in some cases there is a degeneracy associated with the states. For the rigid rotor solutions the degeneracy is $2J + 1$. In the case of the solutions for the particle-in-a-box there is an enormous degeneracy because of the three dimensional solution. This is important for understanding ensembles and the strategy of statistical mechanics.
The degeneracy of translational energy levels is very large

The solution of the particle-in-a-box problem in three dimensions is

The degeneracy is given by the number of ways that the integer \( M = \frac{8ma^2e}{h^2} \) can be written as the sum of squares of three positive integers. The degeneracy becomes a smooth function for large \( M \). Consider a three-dimensional space spanned by \( n_x, n_y, \) and \( n_z \). There is a one-to-one correspondence between energy states given by above energy equation and the points in this space. A radius in this space is given by \( R^2 = n_x^2 + n_y^2 + n_z^2 \) so that \( R = (\frac{8ma^2e}{h^2})^{1/2} \).

We wish to calculate the number of lattice points that are at some fixed distance from the origin in this space. In practice, this means that we want the number of states between energy \( e \) and \( e + de \). To obtain the total number of states with energy less than \( e \) we consider the volume of one octant (recall that the quantum numbers must be positive). This number of states is:

The number of states between \( e \) and \( e + de \) is

Expand \( e + de \) about \( de = 0 \) as follows

Keeping only the first two terms we have
This derivation is valid for the degeneracy of single particle. A simple calculation taking $E = \frac{3kT}{2} \gg 6 \times 10^{-21}$ J, $m = 10^{-25}$ kg, $a = 1$ m and $dE = 10^{-9}$ gives $W(E, dE) \gg 10^{44}$ for a single particle in a of one part per billion about the energy $E$.

For an $N$ particle system, the degeneracy is tremendously greater. To see this consider $N$ noninteracting particles in a cube. The energy of the system is

Defining the space of the quantum numbers as an $N$-dimensional sphere, the number of states with energy less than $E$ is

where $\Gamma(n)$ is the gamma function. The number of states between $E$ and $E + \Delta E$ is

Even though there are a large number of levels and we will assume that they are all equally probable, there is an energetic constraint on the system. This leads to the concept of a most probable distribution among these levels. Although the microcanonical ensemble is useful for illustrating the number of levels, the most convenient ensemble for determining the most probable distribution is the canonical ensemble (constant $N$, $V$, and $T$).