Thermodynamics and Statistical Mechanics Lecture 1

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Overview

A **Macroscopic System** is a system of about 10^{23} particles or more. There are so many particles, that it is hopeless to predict the precise trajectory of all particles in the system from the basic laws of physics. There is no way to practically measure the microstate so we need a more powerful tool to deal with such systems.

The goal of statistical mechanics is to predict the macroscopic behavior of the system as described by the state of a few measurable macroscopic variables without having to solve the exact trajectory of all particles. In a system with 10^{23} particles, there would be about $10^{10^{23}}$ microstates.

Oddly enough, as a system gets larger and larger, with more and more particles, it does not matter which unit of measurements you use as they will all yield basically the same measurement. For example, take a system with $10^{10^{23}}$ microstates. When we change the units of measurement we use, we are simply scaling the value by some number. So let's use a very large unit with a magnitude of about 10^{23}.

$$\frac{10^{10^{23}}}{10^{23}} = 10^{10^{23}-23} \approx 10^{10^{23}}$$

The Fundamental Hypothesis of Statistical Mechanics: Over a very long period of time, the system will visit every accessible microstate with equal probability.

The following probability relation will be related to the micro-canonical ensemble, and I will go more in depth about that in a later document. All that is really needed to be known at this point is that P is probability, E is energy and N_{mic} is the amount of microstates in the system.

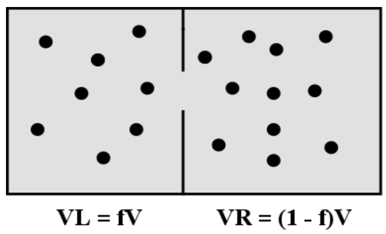
$$P_i = \frac{1}{N_{mic}(E)}$$

If we wanted to look into the probability that the system will be in a macrostate X, our probability relation will look something like:

$$P(X) = \frac{N_{mic}(X)}{N_{tot}}$$

Equilibrium will be the most probable macrostate.

Imagine a mysterious container that has two compartments yet allows particle exchange such as the following figure.



The probability of being in some state n can represented as:

$$P(n) = \binom{N}{n} f^n (1-f)^{N-n}$$

In a larger volume, there is a larger probability to find a particle there. The distribution of states will be sharply peaked at $f = n/N$ with a fluctuation of about $1/\sqrt{N}$.

Intensive quantities, like density and temperature, don't just change just by changing the size of the system we are looking at. If a room is 273 K, it won't matter much how many sections you subdivide the room into. The measurement of temperature should remain fairly constant.

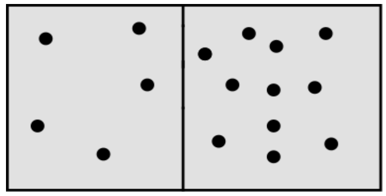
An important point to make is that equilibrium doesn't come from the dynamics of a system but from the statistics of the system. A drastically different state is statistically unfavorable and has low probability of occurring. The more drastic the difference, the more unlikely it is to occur.

We can say that the **Entropy** of some system can be defined as:

$$S(X) = k \log(N_{mic}(X))$$

with k being boltzmann's constant. Equilibrium will be the most probable state, or the state of maximum entropy.

Let's consider two compartments that can exchange energy, but not particles, which looks very similar to the following figure.



We can try to maximize entropy with respect to $\delta E = E_R - E_L$.

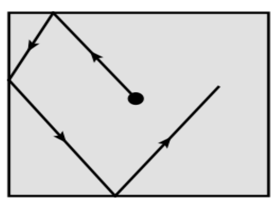
$$\frac{\partial S}{\partial \delta E} = \frac{\partial S_L}{\partial \delta E} + \frac{\partial S_R}{\partial \delta E} = 0$$

What we can learn about the system using this relation is that our temperature is related to the change in entropy in respect to a changing energy with constant volume and particles as:

$$\frac{1}{T} = (\frac{\partial S}{\partial E})_{V,N}$$

This is equation can be used to represent thermal equilibrium. Temperature is not a fundamental concept, but an emergent concept. It occurs as a result of more fundamental concepts. The arrow of time can also be considered an emergent concept.

If we are shown one particle moving in a box, such as the following figure, it will be impossible to know what direction time is flowing. We are stuck asking ourselves "Are we looking at this particle as it moves forward through time or are we watching the motion in reverse?"



If we were given a separate box of particles with most of the particles on the right and we watch the particles spread out and fill the box, such as in the following figure, we can use our intuition and understanding of physics to determine whether we are seeing the particles move forward or backward through time.