General Concepts of Statistical Mechanics

There are two ways of thinking about statistical mechanics, the classical approach and the quantum approach. We will start with the classical approach. However, this has some obstacles which we overcome be making it "semi-classical":

i) we introduce the semiclassical constant h for counting microstates

ii) we consider all identical particles as indistinguishable (they are distinguishable in classical physics) in order to ensure entropy is extensive.

However, this semiclassical approach still does not agree with the 3rd Law of TD; we need a quantum approach to fix this. But let's first learn more about the classical approach:

Newtonian Approach for Ideal Gas of Point-like Particles

How much energy is in an ideal gas? Well, if we take the Newtonian approach, we can simply sum the energy of each point-like particle. $K = \frac{1}{2}mv^2 \Rightarrow K = \frac{p^2}{2m}$

$$\therefore \quad E(q,p) = \sum_{i=1}^{N} \frac{|p_i|^2}{2m} \qquad \begin{array}{ll} p_i = (p_{ix}, p_{iy}, p_{iz}) & \text{momentum} \\ q_i = (q_{ix}, q_{iy}, q_{iz}) & \text{position} \end{array}$$

For a closed system Σp_i = constant and the equations of motion are simply Newton's Laws.

Macrostates and Microstates

A macrostate is a specific set of values of the macroscopic observables (eg. P, T, etc.)

A microstate is a complete microscopic specification of the system, and thus of a macrostate. Subject to macroscopic constraints (eg. constant energy, pressure etc.). Not observable.

For an ideal gas, a microstate corresponds to the full specification of the positions and momenta of N point-like particles, i.e $6N$ ($3N$ position + $3N$ momentum) variables.

Example:

Coin tossing

If we toss 3 coins, the number of heads (H) is a macrostate, an observable quantity. The microstates are the complete specification of which coins are heads.

	Num. Heads
T T T	0
T T H	1
T H T	1
H T T	1
H T H	2
H H T	2
H H H	3

Each microstate is equally likely with 1/8 probability.

Each macrostate is <u>not</u> equally likely. eg. $P(H=1) = 3/8$

NB:// $H_1 H_2 T \equiv H_2 H_1 T$ since H_1, H_2 are indistinguishable

As explained before, we take $H_1 \equiv H_2$ since their intrinsic property (heads) is the same. Similarly: $e^- \equiv e^-$ but $e^- \not\equiv e^+$

This is a key difference between classical and quantum approaches! How they deal with identical particles:

	non-identical	identical
classical	distinguishable	distinguishable
quantum	distinguishable	indistinguishable

Example:

consider 3 distinguishable particles which can be in any of the states α, β, γ. (α, β, γ)

A macrostate is given by a set of 3 numbers. eg. if all the particles are in α, then macrostate is $(3, 0, 0)$

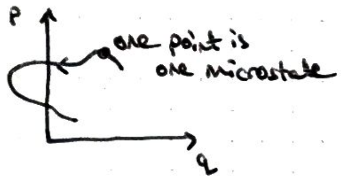
Since the particles are distinguishable, a macrostate can have many microstates. The number of microstates a macrostate has is called its "statistical weight"

$(3, 0, 0)$ has weight 1

$(2, 1, 0)$ has weight 3

Phase Space

An ideal gas with N particles has 3N degrees of freedom, 1N for each dimension of movement.
The space of 3N coordinates and 3N momenta is called "phase space". It is hard to visualise in 3D since we can't really plot 3N momenta against 3N coordinates, but in 1D:



Each point corresponds to a particular set of values (q, p), i.e a particular microstate.
The path represents the motion of the system for a constant energy E. But this is only for the classical approach, we will discuss the semi-classical approach later.

Suppose we are interested in measuring a macroscopic observable $F(t)$ over a time period t_0. The time average is given by:

$$\overline{F}_{t_0} = \frac{1}{t_0} \int_0^{t_0} F(t)\, dt$$

for $t_0 \gg \tau_{relax}$ (the relaxation time of system), there is minimal fluctuation is $F(t)$ which agrees with the Ergodic hypothesis:

"The system explores the accessible phase space, and all permissible values are chosen at some point"

Since there is minimal fluctuation, we can make an assumption:

$$\overline{F}_{t_0} \approx \langle F \rangle$$

statistical average over the ensemble.

An ensemble is a set of many replicas of our system, i.e trials of the system.

If we take $\rho(p,q)$ to be the statistical distribution then:

$$\langle F \rangle = \int_{\substack{\text{phase} \\ \text{space}}} F(p,q)\,\rho(p,q)\,dp\,dq$$

We can generalise this to N_{df} degrees of freedom but this is a little tricky.

Since $\rho(p,q)$ is a statistical distribution, we require:

$$\int_{\substack{\text{phase} \\ \text{space}}} \rho(p,q)\,dp\,dq = 1$$

So how do we determine this distribution? Well, this is a fundamental problem in statistical mechanics and relies on the "principle of equal a priori probabilities", the most important postulate in stat mech:

> An isolated system is equally likely to be found in any of its accessible microstates.

This is somewhat related to the ergodic hypothesis, since if the system explores all of phase-space, then there is no reason any point would be more likely than another.

The word "accessible" in the principle means possible microstates after the physical constraints are taken into account.
An if all of these microstates are equally likely, then determining the statistical distribution is the same as determining which microstates are accessible.

Fluctuations for Systems of Many Particles

What is the probability that a single measurement of the observable quantity could deviate from its average value? This is given by the fractional deviation:

$$\boxed{\frac{\sigma_F}{\langle F \rangle} = \frac{\sqrt{\langle F^2 \rangle - \langle F \rangle^2}}{\langle F \rangle}}$$

This is also called relative fluctuation and is $\sim \frac{1}{\sqrt{N}}$ due to central limit theorem

The probability of observing a fluctuation which is larger than the experimental error is negligible.

A First Problem in Classical Stat Mech

Consider a discrete system with macroscopic observable x. The different values of x are denoted by x_i, where i takes discrete values. The weight of each macrostate x_i is denoted by W_i. Due to the "principle of equal a priori probabilities", each microstate is equally likely so prob. of a macrostate is:

$$P_i = \frac{W_i}{\sum_i W_i}$$

If we consider a classical system described by position q and momentum p, we have some problems. The probability of any macrostate is 0 since we can't have a precise point p or q. We can only look at a range, say $x_i \to x_i + \Delta x_i$

Δx_i can be interpreted to be experimental error.

A macrostate corresponds to a region in phase space:

$$\Delta p \Delta q = \int_{x_i \to x_i + \Delta x_i} dp\, dq$$

we integrate over the region in which the macrostate exists

So the probability of being in a particular macrostate region is:

$$\boxed{P(X_i, X_i+\Delta X_i) = \int_{\Delta p \Delta q} \rho(p,q)\, dp\, dq}$$

where $\Delta p \Delta q$ is the region of phase space corresponding to our macrostate.

This isn't as simple as $\dfrac{\Delta p \Delta q}{\text{total volume of phase space}}$ since not all of the phase space is accessible, depending on the system constraints.

Accessibility information is contained in $\rho(p,q)$ the stat. distribution

We now encounter our first problem in classical stat mech.
With discrete macrostates, the statistical weight was well-defined; we simply count the number of microstates for X_i.

But with this continuous range, how many microstates are in $X_i \to X_i + \Delta X_i$?

We can reasonably assume it is proportional to volume $\Delta p \Delta q$ of phase space but we don't know the constant of proportionality. Let's therefore introduce the constant, $1/h^{N_{df}}$; we can find the value later with experiments! N_{df} is the number of degrees of freedom

So statistical weight of macrostate is given by:

$$\boxed{\Delta W(X_i, X_i+\Delta X_i) = \frac{\Delta p \Delta q\,(X_i, X_i+\Delta X_i)}{h^{N_{df}}}}$$

Since W is dimensionless, h has dimensions of $p \times q$ i.e angular momentum

By introducing h, we are introducing a minimum volume to phase space. i.e for 1 microstate, $\Delta W = 1$ so $\Delta p \Delta q$ is a finite quantity. So we divide phase space into "cells" in each of which exists a microstate, hence allowing us to count microstate in a continuous macrostate!

Hence, classical stat mech is necessarily semiclassical!