

Statistical Mechanics: Lecture 1

Thermodynamics and microscopic laws

Thermodynamics describes the macroscopic properties of matter phenomenologically with the aid of equations of state which are derived empirically. For thermodynamics it is of no importance, how a certain equation of state comes about. This, of course, is consistent with the large universality of thermodynamics, namely that same laws of thermodynamics hold for different materials. However, this doesn't tell us what makes, say, the specific heat of one material different from the other. It is intuitively obvious that specific heat of one material is different from that of the other because microscopically the materials are different. The macroscopic quantities in materials must obviously be resulting from the microscopic properties. For example, the pressure of a gas is due to the collisions of the molecules with a surface, whereas temperature is directly given by the mean kinetic energy of the particles.

On the other end, the microscopic laws of physics describe the behaviour of individual particles with their interaction, very well. For classical particles we use Newton's equations of motion, and for quantum particles we use the Schrödinger equation. Although microscopic laws describe the behavior of particles accurately, they do not tell us how a huge collection of particles, of the order of 10^{23} , would behave *on the average*.

It is the task of statistical mechanics to answer this question, namely how microscopic behavior of particles or small constituents, leads to a particular macroscopic property of the material. Thus, statistical mechanics provides a connection between microscopic physics and thermodynamics.

One may take the view that microscopic laws describe the physics of one particles, and hence, they should describe the behavior of an assembly of particles (however large). A gas of N classical particles can be described by a set of coupled equations of motion

$$\begin{aligned}\frac{d^2\vec{r}_1}{dt^2} &= \frac{1}{m_1}\vec{F}_1(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) \\ \frac{d^2\vec{r}_2}{dt^2} &= \frac{1}{m_2}\vec{F}_2(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) \\ &\dots = \dots \\ \frac{d^2\vec{r}_N}{dt^2} &= \frac{1}{m_N}\vec{F}_N(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N)\end{aligned}\quad (1)$$

where \vec{r}_i is the position vector of the i 'th particle, with mass m_i , and \vec{F}_i is the force acting on it because of interaction with all other particles, and any external influence. A solution of these equations would allow us to know exact position and velocity of each particle at any future time. That information allows us to know the microscopic state (which we will henceforth call *microstate*) of the gas at every instant of time. Solving these coupled equations analytically is generally not possible. However, one can solve such equations numerically, using computers. However, for a realistic situation N is of the order of 10^{23} , and solving such a large number of equations numerically is beyond the capacity of any existing computer.

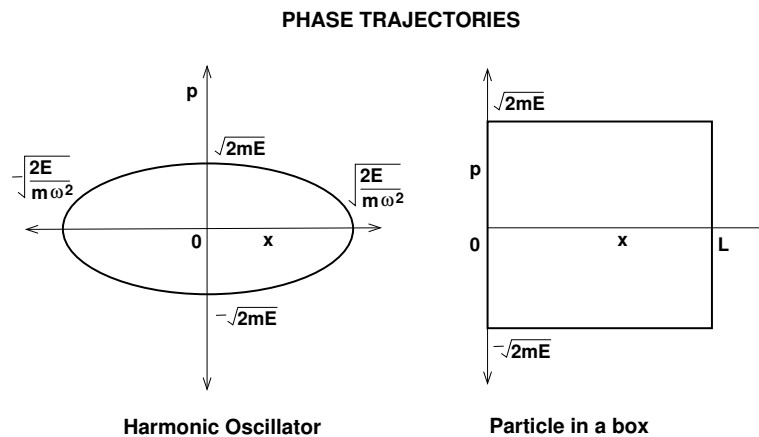
One should realize that for describing the macroscopic state of a gas, characterized by pressure, volume, temperature (which we will henceforth call *macrostate*), we do not need information on every microscopic detail which these coupled equations could provide. A huge number of microstates may correspond to the same, single microstate. We would,

for instance, be interested in knowing the pressure of the gas, and not bother about what a particular atom of the gas is doing at every instance. In other words, we only need some average macroscopic quantities, and not every microscopic detail. So, solving these coupled differential equations would anyway be an overkill, if at all we were able to solve them. We need a conceptually different approach to this problem.

Phase space

Let us first be more specific about the the concept of microstates. For a classical system it is sufficient to know at a time t all generalized coordinates $q_i(t)$ and momenta $p_i(t)$ to uniquely specify the state of motion of the system. Thus for a mechanical system we can interpret the set $\{q_i, p_i, i = 1, 2, \dots, N\}$ as the microstate of this system. For a single particle in one dimension, there is only one position variable x and one momentum variable p_x . If we plot x on the x-axis and p_x on the y-axis, a point on the graph will represent one state of the particle. As the particle moves in time, the point will follow a trajectory. We will call the space described by x and p_x , phase space, the point representing a particular value of x and p_x , a phase point, and the trajectory followed by the point, the phase trajectory. In this particular case, the phase space is 2-dimensional.

If a single particle moves in 3 dimensions, we would need 6 coordinate axes for x, y, z, p_x, p_y, p_z . For N particles in 3-dimensions, the phase space will be $6N$ -dimensional. So, the set $\{q_i, p_i\}$ can now be understood as a point in a $6N$ -dimensional phase space. A point in this phase space describes particular value of position and momentum



values of all N particles. Hence, a definite point in this phase space exactly corresponds to one microscopic state of motion of the whole system.

The trajectory in phase space is governed by Hamilton's equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

where the Hamiltonian $H(q(t), p(t))$ corresponds to the (possibly time-dependent) total energy of the system. It is a function of the phase-space point (q, p) , and of time. In a closed global system, in which the Hamiltonian does not depend explicitly on time, the total energy

$$E = H(p(t), q(t))$$

is a conserved quantity. Thus, the phase trajectory always moves on a constant-energy curve or multi-dimensional surface.

Statistical Ensembles

Each microstate of a N -particle gas is represented by a point in the $6N$ -dimensional phase space. So, if one considers all possible microstates which the gas can have, one will have

a huge collection of points in the phase space. This collection of points in the phase space, of all possible microstates of the system, is called an *ensemble*. Or one can imagine each point in the phase space representing an imaginary copy of the system, each in a different microstate. This collection of imaginary copies of the system, each in a different microstate, is called an ensemble. When the gas evolves in time, in the phase space it basically goes from one phase point to the next, in a specific sequence. Any macroscopic quantity of the gas which we measure, is not measured instantaneously. Rather it is measured over a finite time, which is very long compared to the time-scale of motion of the particles of the gas. So, the measured quantity is actually a time-averaged quantity.

The basic idea of statistical mechanics is the following. In doing a time-average of a quantity, one is basically looking at different values the quantity takes, as it goes from one microstate to the other, during its time evolution. And then one takes an average of all the values of the quantity. As far as taking the average is concerned, it is not important what the sequence in going from one microstate to the other is. One can just take the phase points of the ensemble, over which the system goes, and take the average. In other words, the time average can be replaced by the average over the whole ensemble.

To enable one to replace time-average by ensemble-average, some conditions have to be satisfied. First of all, average over the ensemble implicitly assumes that the system visits all phase points during its time evolution. Not only that, it is also assumed that all microstates are equally likely to be visited. So it better happen so in reality. If the system spends more time in certain microstates, and less in some others, our assumption will break down. This assumption constitutes, what is called, the *ergodic hypothesis*. The ergodic hypothesis says that, over long periods of time, the time spent by a system in some region of the phase space of microstates with the same energy is proportional to the phase-volume of this region, i.e., all accessible microstates are equiprobable over a long period of time. Ergodic hypothesis is a pillar of statistical mechanics, however, it cannot be proven in general. It is assumed to be true, and finds justification in the fact that statistical mechanics turns out to be a successful theory, in agreement with experiments.

We will first consider an isolated system, typically a gas enclosed in a box, which is thermally insulated. So, any time evolution of the system will be subject to the constraint that the total energy remains constant. Left for a long time, it is believed to be in equilibrium. We further assume that given an isolated system in equilibrium, it is found with equal probability in each of its accessible microstates. This is the *postulate of equal a priori probability*. This postulate is at the very core of statistical mechanics. Now each macrostate comprises of numerous microstates. For example, all the gas confined to only one half of the box, is a macrostate. There is a huge number of ways this can happen, by various arrangements of particles and their momenta. The gas uniformly occupying the whole volume of the box, is another macrostate. And again, there are a huge lot of microstates associated with this macrostate. Now each microstate is equally probable, but we never actually see a gas occupying only one half of its container. Why does that happen? It happens because the number of microstates associated with the gas occupying the whole volume are overwhelmingly large, compared to the microstates associated with the gas occupying only one half of the box.

One can get an idea of the numbers involved in such situations, by a simple example. Let there be an array of 4 noninteracting magnetic moments, each of which can only take values +1 or -1, in some suitable units. Now, assume that each magnetic moment is free to flip up and down, i.e., +1 or -1. We can use the total magnetic moment of the array to describe a macrostate. There is only one microstate associated with the macrostate with total magnetic moment 4, which is (+1+1+1+1). If one considers the macrostate with

total magnetic moment zero, the microstates associated with it are $(+1+1-1-1)$, $(-1-1+1+1)$, $(+1-1+1-1)$, $(-1+1-1+1)$, $(+1-1-1+1)$, $(-1+1+1-1)$, $(-1+1-1+1)$. So, there are 6 microstates associated with total magnetic moment 0, while only 1 with magnetic moment 4. One can easily see that if there were 10 magnetic moments, there would still be only one microstate associated with total magnetic moment 10. However, the number of microstates associated with total magnetic moment 0 in that case, will be overwhelmingly large. So, in a system of 10 magnetic moments which are freely flipping, one will almost never see magnetic moment 10, and the magnetic moment will appear to be zero or very small all the time.

A close analogy can be drawn from probability theory. Suppose there are different people doing 100 coin-tosses each. Almost all of them will get nearly equal number of heads and tails. It is next to impossible for anyone to obtain 100 heads or 100 tails. Probability of a 100 heads is $(1/2)^{100}$, which is infinitesimally small. Probability of *any* single configuration is also exactly the same. For example, the probability of getting alternate heads and tails for all 100 tosses is also $(1/2)^{100}$. However, the number of configurations in which the number of heads and tails are 50-50 is overwhelmingly large.

In the light of the above argument, we conclude that *equilibrium state is the one in which the number of microstates is maximum*. In reality, the system will go over all microstates, as the ergodic hypothesis states, but it will be mostly found in certain *macrostates*.

