

# Statistical Mechanics

Based on lectures by Dr. Suvankar Dutta

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These notes are not endorsed by the lecturers, and I have modified them (often significantly) after lectures. They are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.<sup>1</sup>

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<sup>1</sup>This is how Dexter Chua describes his lecture notes from Cambridge. I could not have described mine in any better way.

# 1 Ensemble

**Definition 1** (Macroscopic variables). The variables of a system that can be controlled externally or determined experimentally. They are also called thermodynamic variables.

For e.g., volume, pressure, temperature, etc.

**Definition 2** (Microscopic variables). These parameters are not under any control.

For e.g., the coordinates of a molecule of a gaseous system.

**Definition 3** (Ensemble). Set of identical copies of the same system which are same at the macroscopic level but different at the microscopic level.

## 1.1 Phase Space

In the case of 1D motion of a single particle, the phase space is represented by the  $p, q$ -plane, where  $p, q$  represent the momentum and position of the particle, respectively. The collection of points  $(q, p)$  that are possible classical states of the particle is called the phase space trajectory (or surface) of the particle. This trajectory can be found by

$$E = \mathcal{H}(q, p) = \frac{p^2}{2m} + V(q)$$

where  $E$  represents the classically allowed energy states of the system.

**Example 1** (Classical Harmonic Oscillator). In this case  $E$  is a constant of motion and  $V(q) = -\frac{1}{2}m\omega^2 q^2$ . So we have

$$\frac{p^2}{2m} - \frac{1}{2}m\omega^2 q^2 = E$$

This is an ellipse in the  $p, q$ -plane. The direction of the trajectory depends on the boundary conditions.

Thus, the phase space trajectory tells us about the possible states of the particle (or, system) and how one state evolves into another.

Now, we extend this idea to  $N$  particles in 3 dimensions. This time instead of just two quantities  $p, q$ , we require the 3 position and 3 momentum coordinates of each of the  $N$  particles. Provided there are no additional constraints, in general, we require a  $6N$  dimensional phase space to describe the states of this system. Thus,  $E = \mathcal{H}$  represents a  $6N - 1$  dimensional hypersurface in this phase space.

**Note.**  $\mathcal{H}$  is a function of all the  $6N$  positions and momenta.

**Note.** If  $E$  is continuous, say we have energy between  $E$  and  $E + \Delta E$ , we get a  $6N$  dimensional region in the phase space.

## 1.2 Ensemble of a classical gas

We need to understand the ensemble for a gas of  $N$  particles in volume  $V$  and energy between  $E$  and  $E + \Delta E$ .

All the states of this system can be represented as a  $6N$  dimensional region  $\Gamma$  in the  $6N$  dimensional phase space.

Say, we have an initial state  $(q, p)$  of our system. Here,  $(q, p)$  is a shorthand notation for  $(q_1, \dots, q_{3N}, p_1, \dots, p_{3N})$ .  $(q, p)$  represents some point in  $\Gamma$ . As time passes, the point 'swims' in  $\Gamma$ .

From here onwards, when we say 'phase space' we will be talking about  $\Gamma$ , i.e., the region of allowed states.

Now, our system can be in any point (state) in  $\Gamma$  but its macroscopic properties would not change, i.e. energy would still lie between  $E$  and  $E + \Delta E$  and its volume would still be  $V$ .

Hence, the region  $\Gamma$  forms an ensemble. Every point in  $\Gamma$  is an ensemble member called a *microstate*. Each microstate represents the system at some point in time.

**Definition 4** (Unit cell in phase space). We assume that there exists some small hypercube in the phase space inside which all points represent the same state. Its volume is given by  $h_0^{3N}$ .

Ideally, this hypercube should be infinitesimally small as every point represents a different state. Hence, we will later take the limit as  $h_0 \rightarrow 0$ .

Also, the physics of our system (measurable quantities) should not depend on  $h_0$ .

**Note.** A unit cell represents a single microstate of the system as all points in it are equivalent.

**Note.**  $h_0$  has the dimension of angular momentum.

A differential volume in the phase space is given by

$$dq_1 \cdots dq_{3N} dp_1 \cdots dp_{3N} \equiv d^{3N}q d^{3N}p$$

The total number of microstates (unit cells) in this differential volume is then

$$\frac{d^{3N}q d^{3N}p}{h_0^{3N}}$$

Suppose, the probability of finding the system in a microstate  $(q, p)$  at time  $t$  is  $\rho(q, p, t)$ . All points within a differential volume element containing  $(q, p)$  effectively represent the same microstate. Hence, the ‘probability’ of finding the system in the volume  $d^{3N}q d^{3N}p$  is given by

$$\rho(q, p, t) \frac{d^{3N}q d^{3N}p}{h_0^{3N}}$$

**Note.** This probability is not normalized. To normalize this

$$\begin{aligned} \mathcal{N} \int_{\Gamma} \rho(q, p, t) \frac{d^{3N}q d^{3N}p}{h_0^{3N}} &= 1 \\ \Rightarrow \mathcal{N} &= \frac{1}{\int_{\Gamma} \rho(q, p, t) \frac{d^{3N}q d^{3N}p}{h_0^{3N}}} \end{aligned}$$

We want to calculate the average (over all the possible microstates) of any macroscopic property  $F(q, p, t)$  of the system. This average is called the

**Definition 5** (Ensemble average).

$$\begin{aligned} \langle F \rangle_E &= \frac{\int_{\Gamma} F \rho(q, p, t) \frac{d^{3N}q d^{3N}p}{h_0^{3N}}}{\int_{\Gamma} \rho(q, p, t) \frac{d^{3N}q d^{3N}p}{h_0^{3N}}} \\ &= \frac{\int_{\Gamma} F \rho(q, p, t) d^{3N}q d^{3N}p}{\int_{\Gamma} \rho(q, p, t) d^{3N}q d^{3N}p} \\ &= \int_{\Gamma} d^{3N}q d^{3N}p F P(q, p, t) \end{aligned}$$

$P$  is just the normalized version of  $\rho$ .

**Note.** The ensemble average of a macroscopic parameter does not depend on  $h_0$  which makes sense.

In actual experiments, we measure the

**Definition 6** (Time average).

$$\langle F \rangle_T = \lim_{T \rightarrow +\infty} \frac{1}{T} \int_0^T F(t) dt$$

**Note.** For the formulation of statistical mechanics to be valid, we must have  $\langle F \rangle_E = \langle F \rangle_T$ .

### 1.3 Ergodic Hypothesis

Let us look into the time average in detail. We assume that our observable  $F$  does not explicitly depend on time, i.e., a change in  $F$  is only caused by a change in the microstate and not by when we measure the same microstate.

$$\therefore \langle F \rangle_T = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T F(q(t), p(t)) dt$$

Let us now divide the phase space into  $M$  volume elements. Let the total time spent by the system in the  $i^{\text{th}}$  volume element, be  $T_i$ . Note that the system may visit the  $i^{\text{th}}$  volume element several times but we are only concerned with the total time it spends there. Clearly,

$$\sum_{i=1}^M T_i = T$$

Also, if we take these volume elements to be infinitesimally small,  $(q, p)$  does not change much inside each volume element. Let  $(q_i, p_i)$  be the state of the system in the  $i^{\text{th}}$  volume element.

$$\therefore \langle F \rangle_T = \lim_{T \rightarrow \infty} \frac{1}{T} \sum_{i=1}^M F(q_i, p_i) T_i$$

Now,  $\tilde{P}(i) = \frac{T_i}{T}$  is simply the probability of finding the system in the  $i^{\text{th}}$  volume element.

$$\therefore \langle F \rangle_T = \lim_{T \rightarrow \infty} \sum_{i=1}^M F(q_i, p_i) \tilde{P}(i)$$

In the continuous limit, instead of summing over  $M$  discrete volume elements we can take an integral over the phase space.

$$\therefore \langle F \rangle_T = \int_{\Gamma} d^{3N}q d^{3N}p F(q, p) \tilde{P}(q, p)$$

**Hypothesis** (Ergodic hypothesis). If one waits for a sufficient amount of time, the system visits all its possible microstates.

This means that in the limit  $T \rightarrow \infty$ , the system visits all the volume elements several times. Hence,

$$P(q, p) = \tilde{P}(q, p)$$

$$\therefore \langle F \rangle_E = \langle F \rangle_T$$

**Note.** There is no reason to assume that  $P(q, p) = \tilde{P}(q, p)$  a priori. While  $P$  is the probability that tells us how many microstates there is in some volume element,  $\tilde{P}$  tells us how much time the system spends in that volume element.

From the Ergodic hypothesis, it is clear that the time the system spends in a volume element of the phase space is proportional to the number of microstates in that volume element, provided we observe the system for a sufficiently long (ideally, infinite) amount of time. As a result the ensemble average (calculated in statistical mechanics) of an observable is equal to its time average (measured in experiment).

Thus, the Ergodic hypothesis forms the backbone of statistical mechanics.