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.[1]

Contents

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[1]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 gaseuos 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 paticle, 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 constrains, 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 Γ 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 $(q_1, \cdots, q_{3N}, p_1, \cdots, p_{3N})$. (q, p) represents some point in Γ. As time passes, the point 'swims' in Γ. From here onwards, when we say 'phase space of the system' we will be talking about Γ, i.e., the region of allowed states.

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

Hence, the region Γ forms an ensemble. Every point in Γ 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. The volume of the cube is given by h_0^{3N}.

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

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

Note. A unit cell represents a 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

$$\mathcal{N} \int_\Gamma \rho(q, p, t) \frac{d^{3N}q \; d^{3N}p}{h_0^{3N}} = 1$$

$$\implies \mathcal{N} = \frac{1}{\int_\Gamma \rho(q, p, t) \frac{d^{3N}q \; d^{3N}p}{h_0^{3N}}}$$

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).

$$\langle F \rangle_E = \frac{\int_\Gamma F \; \rho(q, p, t) \frac{d^{3N}q \; d^{3N}p}{h_0^{3N}}}{\int_\Gamma \rho(q, p, t) \frac{d^{3N}q \; d^{3N}p}{h_0^{3N}}}$$

$$= \frac{\int_\Gamma F \rho(q, p, t) d^{3N}q \; d^{3N}p}{\int_\Gamma \rho(q, p, t) d^{3N}q \; d^{3N}p}$$

The denominator is for normalization purposes.

Note. The ensemble average of a macroscopic parameter does not depend on h_0.

In actual experiments, we measure the

Definition 6 (Time average).

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

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