# Essential Notes on Statistical Mechanics

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# I.  INTRODUCTION

Statistical Mechanics is a branch of physics that uses statistical methods and probability theory to explain the behavior of a large number of particles in a system, for example, a vessel containing a gas or a liquid. It provides a bridge between the microscopic world of individual atoms or molecules and the macroscopic properties (temperature, volume, pressure, ... ) of the system. Statistical Mechanics has applications in various fields, including thermodynamics, condensed matter physics, and quantum mechanics. It plays a crucial role in understanding phenomena such as phase transitions, heat conduction, and the behavior of gases and liquids.

# II.  FUNDAMENTAL CONCEPTS

For the understanding of Statistical Mechanics, it is essential to clarify the numerous definitions and notions involved. Here, we summarise some of the most useful definitions.

- ❑ **Particle.** The smallest unit studied in Statistical Mechanics, for example, an atom or a molecule. The position and momentum of the $i$th particle are denoted by the three-dimensional vectors $\mathbf{r}_i$ and $\mathbf{p}_i = m_i \mathbf{v}_i$, where $m$ is the mass and $v$ is the velocity of the particle.

- ❑ **System.** Collection of $N$ interacting or non-interacting particles. The system is defined by the tuple

$$\mathbf{x} = \{\mathbf{r}, \mathbf{p}\} = \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \ \mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N\} \,. \tag{1}$$

  Note that the notation $\mathbf{r}$ and $\mathbf{p}$ without subscripts denotes the tuples

$$\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\} \,, \tag{2}$$

  and

$$\mathbf{p} = \{\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N\} \,. \tag{3}$$

- ❑ **Surroundings.** The surroundings of a system encompass everything external to the system boundaries that are not explicitly included in the definition of the system.

These external components may interact with the system, exchanging energy, matter, or both. The interaction between system and surroundings determines the type of system:

➤ Isolated system: no interaction between system and surroundings;

➤ Closed system: can exchange energy with its surroundings;

➤ Open system: can exchange both energy and matter with its surroundings.

❑ **Microstate.** A specific configuration of the system characterized by positions and momenta of the particles: $\mathbf{r}_i, \mathbf{p}_i \ \forall i = 1, 2, \ldots, N$.

❑ **Macrostate.** The macrostate of a system, is the set of macroscopic variables that fix the macroscopic state of the system, for example, Energy $E$, Temperature $T$, Volume $V$, Pressure $P$, Number of particles $N$, chemical potential $\mu$.

❑ **Ensemble.** The set of possible microstates accessible to the macroscopic state. In other words, given a macrostate characterized by specific macroscopic properties (e.g. number of particles $N$, volume $V$, and energy $E$), the ensemble is the collection of all possible microstates (i.e. all possible configurations of particles) that determine the macrostate. Examples of ensembles are:

➤ Microcanonical ensemble $(N, V, E)$: Collection of the microstates that determine an isolated system, hence with fixed Number of particles, volume and energy. The systems belonging to the microcanonical ensemble obey Hamilton's equations of motion.

➤ Canonical ensemble $(N, V, T)$: Collection of the microstates that determine a closed system with fixed number of Particles, volume and temperature. In this case, the total energy $E$ of the system varies due to exchanges with the surroundings to maintain a constant temperature.

➤ Grand canonical ensemble $(\mu, V, T)$: Collection of the microstates that determine an open system with fixed chemical potential, volume, and temperature. Here, the system can exchange matter with its surroundings, so the number of particles changes. However, it is required that the exchange maintains a constant chemical potential, a physical property of thermodynamic systems that indicates how the

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energy of a system changes when the number of particles in the system is altered. It reflects the system's inclination to exchange particles with its surroundings.

## III.   PROBABILITY DISTRIBUTIONS IN STATISTICAL MECHANICS

The number of microstates determining a specific macrostate is typically very large, for example, there are approximately $2.44 \times 10^{22}$ molecules in 1 liter of air at 1 atm pressure and temperature 298 K (room temperature). For this reason, it is unfeasible to study the dynamics of every single particle in a thermodynamic system; instead, it is reasonable to use statistical tools.

For this purpose, we introduce the concept of <u>probability distribution</u> $\pi(\mathbf{x})$, a mathematical function that describes the probability that a particular configuration of the system (a microstate), at equilibrium, possesses a specific physical property. In this context, by equilibrium we mean the situation in which the macroscopic properties defining the ensemble do not evolve over time. However, individual systems in the ensemble can change their microstate. Depending on which ensemble is being investigated, it is convenient to define the probability distribution with respect to different physical properties.

### A.   Microcanonical ensemble

For the microcanonical ensemble, with conserved quantities $(N, V, E)$, the probability distribution $\pi(\mathbf{x})$ is defined

$$\pi(\mathbf{x}) = \frac{1}{\Omega(E)} \, . \tag{4}$$

The quantity $\Omega(E)$ represents the volume of phase space accessible to the system at a given energy level $E$ and is given by the $6N$-dimensional integral over the phase space

$$\Omega(E) = \int d\mathbf{x}^N \, \delta(\mathcal{H}(\mathbf{x}) - E) \, , \tag{5}$$

where $\delta$ is the $\delta$-function and $\mathcal{H}(x)$ is the Hamiltonian function

$$\mathcal{H}(\mathbf{x}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \, . \tag{6}$$

Eq. 4 expresses the probability that a certain microstate possesses the energy $E$ and it is based on the postulate of equal a prior probability: For an isolated system in equilibrium, all accessible microscopic states are equally probable.

A consequence of the a priori probability equality postulate is that if a system of the ensemble $(N, V, E)$ evolves over an infinite span of time, it will visit all configurations associated with energy $E$. A system that satisfies this property is said to be ergodic.

We now discuss the example of a one-dimensional harmonic oscillator of mass $m$ moving along the axis of positions $r$ and momenta $p$ with Hamiltonian function

$$\mathcal{H}(r, p) = \frac{1}{2} \frac{p^2}{m} + \frac{1}{2} r^2, \quad , \tag{7}$$

with equations of motion

$$\begin{cases} \dot{r} &= \dfrac{p}{m} \\ \dot{p} &= -r \end{cases} . \tag{8}$$

In fig. 1-(a), we show the component $r(t)$ of the solution, which is a sinusoidal function, and the total energy $E(t)$, which is constant over time; in fig. 1-(b), we show the complete solution $\{r(t), p(t)\}$ on the phase space, which is a closed circle. We, therefore, note that only a small portion of the phase space is visited by the trajectory. Let us now imagine that we have a very long trajectory and that we discretize the phase space with a very fine grid. Then, we count how many times the trajectory visits each grid mesh. In other words, we construct the two-dimensional histogram, which is an approximation of the distribution $\pi(r, p)$. The result is shown in fig. 1-(c). If the trajectory is sufficiently long, net of defects due to the discretization of the grid and the trajectory, the resulting distribution is constant along the generated trajectory, in agreement with eq. 4. However, this may seem counterintuitive. If we imagine an oscillator moving along an axis without friction or other external forces, we observe that the oscillator spends most of its time along the extremes, i.e., where it slows down. Conversely, the time spent around the equilibrium point is less, as the oscillator passes quickly. Therefore, if we wanted to sketch a distribution representing the time spent by the oscillator in space, we would have to draw a parabola-like curve, not a constant straight line. This curve, reported in fog. 1-(d), is actually the marginal distribution along the axis of momenta

$$\pi_r(r) = \int dp \, \pi(r, p) . \tag{9}$$

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It expresses the fact that near the extremes, there is a greater number of possible states that satisfy the condition $H(x) = E$. This observation is important, as it shows how by projecting the probability distribution of the system onto a specific coordinate, i.e. by reducing dimensionality, we can obtain unexpected results.
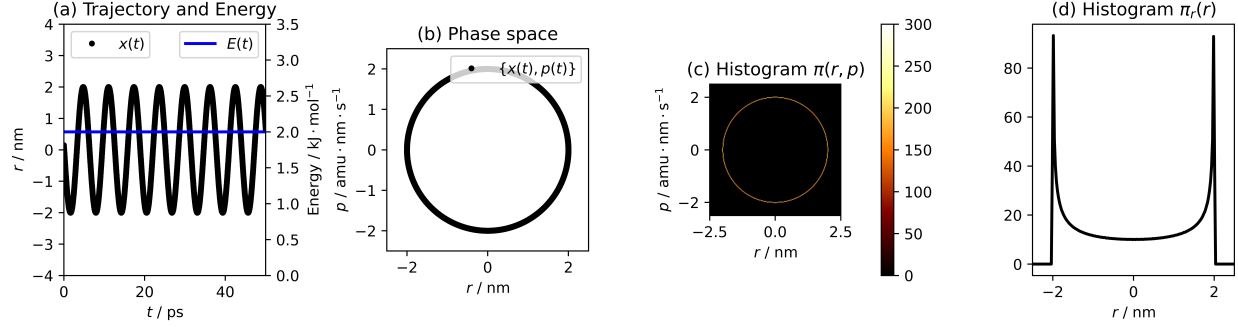


FIG. 1. Harmonic oscillator

## B.    Canonical ensemble

A system belonging to the canonical ensemble can interact with its surroundings by exchanging energy to maintain a constant temperature. In this case, the probability distribution is given by the Boltzmann distribution

$$\pi(\mathbf{x}) = \frac{1}{Z} \exp\left(-\beta\mathcal{H}(\mathbf{x})\right) , \tag{10}$$

where the partition function $Z$ acts as a normalization constant

$$Z = \int d\mathbf{x}^N \exp\left(-\beta\mathcal{H}(\mathbf{x})\right) . \tag{11}$$

In eq.10, we introduced

$$\beta = \frac{1}{k_B T} , \tag{12}$$

where $k_B$ is the Boltzmann constant and $T$ is the temperature of the macrocanonical ensemble. The Boltzmann distribution describes the probability of finding the system in a particular configuration such that the temperature is $T$.

Let us now see how the example of the harmonic oscillator changes when it can interact with the environment to maintain a constant temperature. In fig. reffig:fig2-(a), we show the solution of the equations of motion in phase space. Again, we observe a trajectory that draws

circles, however, it is highly irregular and appears to be dominated by stochastic motion. In fig. 2-(b,c), we show the energy and temperature. The former is erratic, while the latter, net of statistical fluctuations, is constant. If, on the other hand, we considered the complete system consisting of the oscillator and its surroundings, the energy would be constant. If, on the other hand, we considered the complete system consisting of the oscillator and its surroundings, the energy would be constant. In fig. 2-(d), we show the two-dimensional histogram built over the phase space. In this case, we observe that the distribution covers a larger phase space area, however, it is not constant, but it approximates the Boltzmann distribution defined in eq. 10. From the Boltzmann distribution, we fnally deduce that the most accessible states are those that take on the lowest energy levels.
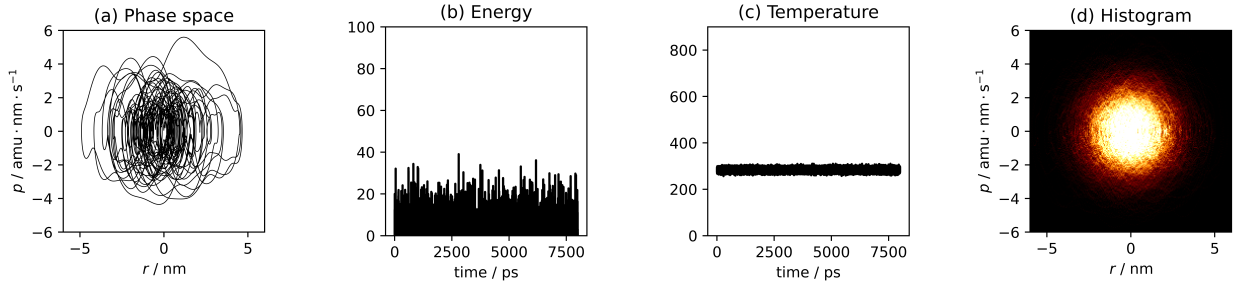


FIG. 2. Harmonic oscillator in thermal equilibrium.