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1 Basic concepts of Statistical Mechanics

Consider a physical system composed of N identical particles confined in a volume V. For a macroscopic system, N is of the order of Avogadro number $N_A \approx 6.022 \times 10^{23}$ per mole. In this view, all the analysis in statistical mechanics are carried out in the so-called thermodynamic limit. It is defined as: both number of particles N and volume V of the system tends to infinity whereas the density of particles $\rho = N/V$ remains finite.

$$N \to \infty, \quad V \to \infty, \quad \rho = N/V = \text{ finite.} \tag{1.1}$$

In this limit, the extensive properties of the system become directly proportional to the size of the system (N or V), while the intensive properties become independent of the size of the system. The particle density becomes an important parameter for all physical properties of the system.

In order to develop a microscopic theory of a macroscopic system, it is necessary to specify the state of micro-particles, atoms or molecules as a first step. Next is to construct the macro-state from the micro-states of N number of particles when N is very large. Finally, one needs to extract the macroscopic properties in terms of the micro-states of a macroscopic system. In this section, all these essential definitions will be given.

1.1 Specification of states:

The specification of the state of a particle depends on the nature of the particle, *i.e.* whether the particle's dynamics is described by classical mechanics or by quantum mechanics.

The dynamics of a classical system is determined by its Hamiltonian $\mathcal{H}(p,q)$ where q and P are the generalized position and momentum conjugate variables. The motion of a particle is described by the canonical Hamilton's equation of motion

$$\dot{q}_i = \frac{\partial \mathcal{H}(p,q)}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial \mathcal{H}(p,q)}{\partial q_i}; \quad i = 1, 2, \cdots, N \tag{1.2}$$

The state of a single particle at any time is then given by the pair of conjugate variables (q_i, p_i) . The state of a system composed of N particles is then completely and uniquely defined by $3N$ canonical coordinates $q_1, q_2, \cdots, q_{3N}$ and $3N$ canonical momentum $p_1, p_2, \cdots, p_{3N}$.

These $6N$ variables constitute a $6N$ -dimensional Γ -space or phase space of the system and each point of the phase space represents a state of the system. Each single particle constitutes a 6 -dimensional μ -space. Γ -space is evidently built up of N such 6 -dimensional μ -space of each particle.

The locus of all the points in Γ -space satisfying the condition $\mathcal{H}(p, q) = E$, total energy of the system, defines a surface called energy surface. Specification of states of quantum particles will be discussed later.

1.2 Counting of Microstates:

It is important to enumerate the number of microstates for a given macrostate (N, V, E) of a system. For a classical particle, the microstate is specified by a phase point. Consider an infinitesimal change in the position and momentum coordinates in the phase space. The phase point of this particle then under go a small displacement in the phase space and the microscopic state of the system will be modified. However, if the change in the microstate is so small that it is not measurable by the most accurate experiment, then it can be assumed that there is no change in the macroscopic state of the system. Thus, the state of a system is given by a small volume element $\delta\Omega$ of the Γ -phase space. If $\delta q \delta p = h$, then

$$\delta\Omega = \delta q_1 \delta q_2 \cdots \delta q_{3N} \delta p_1 \delta p_2 \cdots \delta p_{3N} = h^{3N} \tag{1.3}$$

By Heisenberg's uncertainty principle in quantum mechanics it can be shown that h is the Planck's constant. Thus, the number of states of a system of N particles of energy $\leq E$ is given by

$$\Gamma = \frac{1}{h^{3N}} \int d\Omega = \frac{1}{h^{3N}} \iint d^{3N}q d^{3N}p \tag{1.4}$$

The number of microstates is then proportional to the volume of the phase space.

The counting of number of microstates however depends on the distinguishable and indistinguishable nature of the particles. If the constituent particles are distinguishable, the two microstates corresponding to the interchange of two particles of different energy are distinct microstates.

On the other hand, if the constituent particles are indistinguishable, these two microstates are not distinct microstates.

Thus, for a system of N indistinguishable, identical classical particles having different energy states, the number of microstates is then given by

$$\Gamma = \frac{1}{h^{3N}N!}\iint d^{3N}q d^{3N}p \tag{1.5}$$

Consider a system of N particles of total energy E and corresponds to a macrostate (N, V, E). If the particles are distributed among the different energy levels as, n_i particles in the energy level ϵ_i, the following conditions has to be satisfied

$$N = \sum_i n_i \qquad \text{and} \qquad E = \sum_i n_i \epsilon_i \tag{1.6}$$

The total number of possible distributions of N such particles is then given by

$$\frac{N!}{\prod n_i!} \tag{1.7}$$

If the particles are distinguishable, then all these permutations would lead to distinct microstate whereas if the particles are indistinguishable, these permutations must be regarded as one and the same microstate.

1.3 Equal a priori probability:

As it is already seen that for a given macrostate (N, V, E), there is a large number of possible microstates of the system. In case of classical non-interacting system, the total energy E can be distributed among the N particles in a large number of different ways and each of these different ways corresponds to a microstate. In case of a quantum system, the various different microstates are identified as the independent solutions $\Psi\left(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N\right)$ of the Schrödinger equation of the system, corresponding to an eigenvalue E. In any case, to a given macrostate of the system there exists a large number of microstates and it is assumed in statistical mechanics that at any time t the system is equally likely to be in any one of these microstates. This is generally referred as the postulate of equal a priori probability for all microstates of a given macrostate of the system.

Equal a priori probability postulate is one of the two fundamental postulates in Statistical Mechanics.

1.4 Statistical ensembles:

The microstate of a macroscopic system is specified by a point in $6N$ -dimensional phase space where N is of the order of Avogadro number $\left(10^{23}\right)$. At any time t the system is equally likely to be in any one of the large number of microstates corresponding to a given macrostate (N, V, E).

As the dynamical system evolves with time, the system moves from one microstate to another. After a sufficiently long time, the system passes through a large number of microstates. The behaviour of the system then can be obtained as averaged over those microstates through which the system passes.

Thus, in a single instant of time, one could consider a collection of large number of replicas (mental copies) of the original system characterized by the same macrostate but could be in any of the possible microstates to obtain the average behaviour of the system.

This collection of large number of copies of the same system is called an ensemble. It is expected that the ensemble averaged behaviour of a system would be identical with the time averaged behaviour of the given system.

Since the values of (q, p) at any instant are different for a system of an ensemble, they are represented by different points in the phase space. Thus, the ensemble will be represented by a cloud of phase points in the phase space. As time passes, every member of the ensemble undergoes a continuous change in microstates and accordingly the system moves from one place to another on the phase space describing a phase trajectory.

The density of the cloud of phase points at a particular place then may vary with time or at a given time the density may vary place to place. It must be emphasized here that the systems of an ensemble are independent systems, that is, there is no interaction between them and hence the trajectories do not intersect.

1.5 Phase point density:

Since a phase point corresponds to a microstate of a system and its dynamics is described by the phase trajectory, the density of phase points $\rho(p, q)$ is then determining the number of microstates per unit volume, that is, the probability to find a state around a phase point (p, q). The phase point density $\rho(p, q)$ is given by

$$\rho(p, q) = \frac{\text{Number of states}}{\text{Volume element}} \tag{1.8}$$

At any time t, the number of representative points in the volume element $d^{3N}qd^{3N}p$ around the point (p, q) of the phase space is then given by

$$\rho(p, q)d^{3N}qd^{3N}p \tag{1.9}$$

The density function $\rho(p, q)$ then represents the manner in which the members of the ensemble are distributed over all possible microstate at different instant of time.

1.6 Statistical average and mean values:

Consider any physical property of the system $X(p, q)$, which may be different in different microstates for a system. The macroscopic value of X must be the average of it over all possible microstates corresponding to a given macrostate. The ensemble average or the statistical average $\langle X \rangle$ of the physical quantity X at a given instant of time, is defined as

$$\langle X \rangle = \frac{\int X(p,q)\rho(p,q)d^{3N}qd^{3N}p}{\int \rho(p,q)d^{3N}qd^{3N}p} \tag{1.10}$$

where $\rho(p, q)$ is the density of phase points. Note that the integration is over the whole phase space. However, it is only the populated region of phase space that really contribute.

The mean value $\bar{X}$ of the physical quantity X depends how it evolves with time t In a sufficiently long time, the phase trajectory passes through all possible phase points. If the duration of time is T, the mean value is defined as

$$\bar{X} = \lim_{T\to\infty} \frac{1}{T} \int_0^T X(t)dt \tag{1.11}$$

The statistical average $\langle X \rangle$ and the mean value $\bar{X}$ are equivalent. This is known as ergodic hypothesis.

Ergodic hypothesis is the second fundamental postulate of statistical mechanics.

1.7 Condition of Equilibrium:

By Liouville's theorem, the total time derivative of the phase point density $\rho(p,q)$, in absence of any source and sink in the phase space, is given by

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} = 0 \tag{1.12}$$

where

$$\{\rho, \mathcal{H}\} = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) \tag{1.13}$$

is known as Poisson bracket of the density function ρ and the Hamiltonian $\mathcal{H}$ of the system. Thus, the cloud of phase points moves in the phase space like an incompressible fluid.

The ensemble is considered to be in statistical equilibrium if $\rho(p,q)$ has no explicit dependence on time at all points in the phase space, *i.e.*,

$$\frac{\partial \rho}{\partial t} = 0 \tag{1.14}$$

Under the condition of equilibrium is then

$$\{\rho, \mathcal{H}\} = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right) = 0 \tag{1.15}$$

and it will be satisfied only if ρ is independent of P and q. That is

$$\rho(p, q) = \text{constant} \tag{1.16}$$

which means that the representative points are distributed uniformly over the phase space. The condition of statistical equilibrium then requires no explicit time dependence of the phase point density $\rho(p, q)$ as well as independent of the coordinates (p, q).