Introduction To Statistical Mechanics

Statistical formulation of the mechanical systems

To analyze such systems some statistical ideas and laws of mechanics (applicable) will be combined. This will be the basis of "statistical mechanics".

1. Specification of the State of a System

Consider any system of particles, no matter how complicated (e.g. an assembly of weakly interacting harmonic oscillators, a gas, a liquid, an automobile). We know that the particles in any such system (i.e., the electrons, atoms, or molecules composing the system) can be described in terms of the laws of quantum mechanics. Specifically, the system can then be described by a wave function $\psi\left(q_1,....q_f\right)$ which is a function of some set of f coordinates (including possible spin variables) required to characterize the system. The number f is the "number of degrees of freedom" of the system. A particular quantum state of the system is then specified by giving the values of some set of f quantum numbers. This description is complete since, if ψ is thus specified at any time t, the equations of motion of quantum mechanics allow prediction of ψ at any other time.

Example: Describe single particle spin in magnetic system?

Solution: Consider a system consisting of a single particle, considered fixed in position, but having a spin $\frac{1}{2}$ (i.e., intrinsic spin angular momentum $\frac{1}{2}\hbar$). In a quantum-mechanical description the state of this particle is specified by the projection m of its spin along some fixed axis (which we shall choose to call the z - axis). The quantum number m can then assume the two values $m=\frac{1}{2}$ or $m=-\frac{1}{2}$; i.e., roughly speaking, one can say that the spin can point either "up" or "down" with respect to the z - axis.

Example: Describe single particle spin in magnetic system?

Solution: Consider a system consisting of N particles considered fixed in position, but each having spin $\frac{1}{2}$. Here N may be large, say of the order of Avogadro's number $N_a = 6\times10^{23}$. The quantum number m of each particle can then assume the two values $\frac{1}{2}$ or $-\frac{1}{2}$. The state of the entire system is then specified by stating the values of the N quantum numbers $m_1,....,m_N$ which specify the orientation of the spin of each particle.

Example: Describe one-dimensional simple harmonic quantum oscillator?

Solution: Consider a system consisting of a one-dimensional simple harmonic oscillator whose position coordinate is 'x'. The possible quantum states of this oscillator can be specified by a quantum number n such that the energy of the oscillator can be expressed as

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega$$

Where ω is the classical angular frequency of oscillation. Here the quantum number n can assume any integral value $n = 0,1,2,....$

Example: Describe N weakly interacting one-dimensional simple harmonic oscillators?

Solution: Consider a system consisting of N weakly interacting one-dimensional simple harmonic oscillators. The quantum state of this system can be specified by the set of numbers $n_1,.....,n_N$ where the quantum number n, refers to the i^{th} oscillator and can assume any value $0,1,2,....$

Example: Describe Single particle (without spin) confined within a rectangular box?

Solution: Consider a system consisting of a single particle (without spin) confined within a rectangular box (so that the particle's coordinates lie within the ranges $0 \le x \le L_x, 0 \le y \le L_y, 0 \le z \le L_z$), but otherwise subject to no forces. The wave function ψ of the particle (of mass m) must then satisfy the Schrödinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{2y^2}+\frac{\partial^2}{2z^2}\right)=E\psi \qquad (1)$$

and, to guarantee confinement of the particle within the box, ψ must vanish at the walls. The wave function having these properties has the form

$$\psi=\sin\left(\pi\frac{n_x x}{L_x}\right)\sin\left(\pi\frac{n_y y}{L_y}\right)\sin\left(\pi\frac{n_z z}{L_z}\right) \qquad (2)$$

This satisfies (2.1.1), provided that the energy E of the particle is related to n_x, n_y, n_z by

$$E=\frac{\hbar^2}{2m}\pi^2\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right) \qquad (3)$$

Also $\psi=0$ properly when $x=0$ or $x=L_x$, when $y=0$ or $y=L_y$, and when $z=0$ or $z=L_x$, provided that the three numbers n_x, n_y, n_z assume any discrete integral values. The state of the particle is then specified by stating the values assumed by these three quantum numbers n_x, n_y, n_x while Eq. (3) gives the corresponding value of the quantized energy.

A single particle in one dimension: "Phase Space"

Let us start with a very simple case – a single particle in one dimension. This system can be completely described in terms of its position coordinate q and its corresponding momentum p. (This specification is complete, since the laws of classical mechanics are such that a knowledge of q and p at any other time). It is possible to represent the situation geometrically by drawing Cartesian axes labelled by q and p. Specification of q and p then equivalent to specifying a point in this two-dimensional space (commonly called "phase space"). As the coordinate and momentum of the particle charge in time, this representative point moves through this phase space.

$$\boxed{\delta q \delta p = h_0}$$

where h_0 is some small constant having the dimensions of angular momentum.

Summary: The microscopic state or "microstate" of a system of particles can be simply specified in the following way:

(a) Enumerate in some convenient order, and label with some index $r(r=1,2,3,....)$, all the possible quantum sates of the system. The state of the system is then described by specifying the particular state r in which the system is found.

(b) If it is desired to use the approximation of classical mechanics, the situation is quite analogous.

(c) After the phase space for the system has been sub-divided into suitable cells of equal size, one can enumerate these cells in some convenient order and label them with some index $r(r=1,2,3,....)$.

(d) The state of the system is then described by specifying the particular cell r in which the representative point of the system is located.

The quantum mechanical and classical descriptions are thus very similar, a cell in phase space in the classical discussion being analogous to a quantum state in the quantum-mechanical discussion.