Pravegaa Education

CSIR NET-JRF, GATE, IIT-JAM, JEST, TIFR and GRE for Physics
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Introduction To Statistical Mechanics

3. Basic Postulates

(a) An equilibrium situation is characterized by the fact that the probability of finding the system in any one state is independent of time (i.e., the representative ensemble is the same irrespective of time).

(b) An isolated system in equilibrium is equally likely to be in any of its accessible states.

(c) In classical mechanics, if phase space is subdivided into small cells of equal size, then an isolated system in equilibrium is equally likely to be in any of its accessible cells.

Example: Discuss probability of a spin being up vs. being down ?

Solution: In the previous example of a system of three spins, assume that the system is isolated. Its total energy is then known to have some constant value; suppose that it is known to be equal to $-\mu H$. As already mentioned, the system can then be in any of the following three states.

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$$(+ + -) \qquad (+ - +) \qquad (- + +)$$

The postulate asserts that when the system is in equilibrium it is equally likely to be found in any of these three states.

Note, that it is not true that a given spin is equally likely to point up or down, i.e., to be in any of its two possible states. (there is, of course, no paradox here, since a given spin is not an isolated system, but intersects with the other two spins). Indeed, it is seen that in the present example it is twice as probable that a give spin points up (is in a state of lower energy) than that it points down (is in a state of higher energy) 6 vs. 3.

Example: Consider a one-dimensional harmonic oscillator of mass m and spring constant k, and let us discuss it in terms of classical mechanics. Denote the displacement coordinate of the oscillator by x and its linear momentum by p.

(a) Discuss the Phase space is then two dimensional.

(b) Discuss phase curve.

Solution: (a) Phase space is then two dimensional The energy E of the oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

where the first term on the right is its kinetic, the second term its potential energy. For a constant energy E, equation describes an ellipse in phase space, i.e., in the px plane.

(b) Suppose one knows that the energy of the oscillator lies in the small range between E and $E + \delta E$. Then there are still many cells in phase space contained between the two ellipses corresponding to the respective energies E and $E + dE$, i.e., many different corresponding sets of values of x and p are possible for the oscillator is a representative ensemble. Given: oscillator is in equilibrium $E < E < E + dE$, then equal probability is there for any cell and x, p in this range.
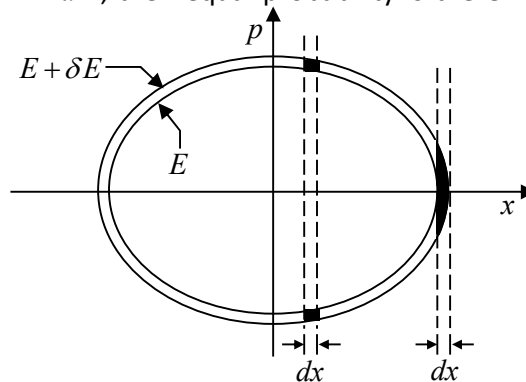
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Figure: Classical phase space for a one-dimensional harmonic oscillator with energy between E and $E + \delta E$. The accessible region of phase space constants of the area lying between the two ellipses.

Note: Another way of looking at the situation is the following. The time dependence of x and p for the oscillator is, by elementary mechanics, of the form

$$x = A\cos(\omega t + \varphi)$$
$$p = m\dot{x} = -mA\omega\sin(\omega t + \varphi)$$

where $\omega = \sqrt{\dfrac{k}{m}}$, while A and φ are constants. The total energy is given by

$$E = \frac{m\omega^2}{2}A^2\sin^2(\omega t + \varphi) + \frac{k}{2}A^2\cos^2(\omega t + \varphi) = \frac{1}{2}m\omega^2 A^2$$

This is indeed equal to a constant, and the above result determines the amplitude A in terms of E. But the phase angle φ is still quite arbitrary, depending on unknown initial conditions, and can assume any value in the range $0 < \varphi < 2\pi$. This gives rise to the many possible sets of values of x and p which correspond to the same energy.

BASIC POSTULATES

The Approach to Equilibrium:

Consider a situation where it is known that an isolated system is not equally likely to be found in any of the states accessible to it. Our fundamental postulate asserts that this situation cannot be one where equilibrium prevails. Thus one expects the situation to change with time. This means that in the representative statistical ensemble the distribution of systems over the accessible states will change in time; correspondingly, the mean values of various macroscopic parameters describing the system will also change.

When the system is known to be in such a state at any one time, it will not remain in this state indefinitely. Instead, there exists a finite probability that the system will at some later time be found in some of the other approximate states accessible to it, the transitions to these other states being caused by the presence of small residual interactions between the particles (interactions not taken into account in defining the approximate quantum states of the system).

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Example: Consider again the very simple of an isolated system of three spin $1/2$ in a large external magnetic field H . The approximate quantum states of the system can be labelled by the orientation of each spin with respect to this field ("up" or "down"). Suppose that this system has been prepared in such a way that it is known to be in the state $(++-)$ at some initial time; the system is then left to itself. What will happen to it?

Solution: Small interactions exist between the spins because the magnetic moment of one spin produces a small field $H_m (H_m < H)$ with which the moment of some other spin can interact. These interactions between the magnetic moments of the spins bring about transitions in which one spin flips from the "up" direction to the "down" direction while some other spin does the reverse; of course, such a mutual spin-flip leaves the total energy of the system unchanged. The net result is that, after a sufficiently long time, the system will be found with equal probability in any of its three accessible states $(+ + -), (+ - +)$ and $(- + +)$.

Example: In the figure, in which a gas of molecules is originally confined to the left half of a box, the right half being empty. Suppose now that the partition is removed at some initial time t . Discuss what will happen to the profile of density of molecules?

Solution: Steps:

(a) Immediately after this act, the molecules are certainly not distributed with equal probability over all their accessible states, since the molecules are all localized in the left half of the box whereas the right half, although now perfectly accessible, is empty.

(b) But it is clearly fantastically improbable that this situation will prevail for any length of time.
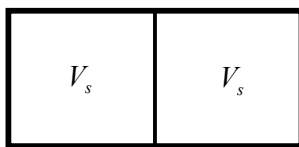
A system consisting of a box divided by a partition into two equal parts, each of volume V_s . The left side is filled with gas; the right side is empty.

(c) Indeed, as a result of collisions with the walls and with each other, the molecules will very quickly redistribute themselves over the entire volume of the box.

(d) The final equilibrium situation, where the density of molecules is uniform throughout the entire box, is thus attained quite rapidly.

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