Introduction

1.1. The scope of statistical physics

There are many cases in the study of physics where an exact treatment of the properties of a given physical system is rendered impracticable because of the large number of components· involved. As an example of such a case consider the behavior of the molecules in a gas. At standard temperature and pressure one cubic centimeter of a gas will contain about 2×10^{19} molecules. It would be theoretically possible to write down all the classical equations of motion of these molecules provided that their positions and velocities at some instant of time, and the factors determining their energies; are known. These equations and the calculation of the subsequent motion of the gas molecules would not, however, be very rewarding even if they could be interpreted from the volume of paper which they would occupy. Because of this it is the purpose of statistical physics to enable the macroscopic properties of such a gas to be described in terms of the microscopic properties of the molecules without involving the detailed calculation of the motions of the individual molecules.

In any experimental measurement which may be performed on the gas the result obtained will, in general, be an average value of some mechanical or thermodynamic property of the gas such as the pressure or the temperature. The most detailed measurement likely to be made on the gas molecules, in practice, is one which would involve the distribution of the molecular velocities over the range of values from zero to infinity. It therefore follows from both theoretical and experimental considerations that any useful study of the behavior of the gas will have to be made with the aid of statistical methods. However, the very generality of the first and second laws of thermodynamics restricts the information which may be obtained from their application. It will thus be seen necessary to subject the gas to a more detailed statistical analysis if further information about the nature of the gas, and about thermodynamic properties in general, is required.

In order to obtain statistical results for the mechanical and thermodynamic properties of the systems under consideration it will, of course, be necessary to introduce certain assumptions as a basis for the theory.

1.2. Description of the assemblies-phase space

Those bodies which can be treated by the methods of statistical physics will generally be composed of a large number of independent, or almost independent, components. In many cases these components will be individual particles such as electrons or photons or, in the case of a gas, individual atoms or molecules. However, in some cases, the components may be quite complex systems and, as will be seen, it is useful for certain applications to consider complete assemblies of particles as themselves forming the components of a larger physical body.

In order that the discussion given here shall be as general as ·possible, and also to follow common usage in this subject, the individual components of any physical body will be .referred to as ***systems***·. The physical body in question will then be considered as an *assembly* of these systems, which may themselves be complex. In the introductory chapters only those assemblies which consist of structure less (i.e. single particle), non-interacting systems will be considered while the more general case of systems which have an internal structure and which may be subject to interactions with other systems will be treated later.

The state of an assembly at a given instant of time may be defined by specifying the position and either the momentum or velocity of each of the component systems. (It will be seen later that, mathematically, the definition in terms of the momentum is most convenient.) The position and momentum may be specified in Cartesian coordinates by taking the position as(x, y, z) in Euclidean space while the corresponding components of the momentum (p_x, p_y, p_z) specify the 'position' of the system in momentum space. The state of a system is thus precisely defined by the six coordinates(x, y, z, p_x, p_y, p_z) and it is, therefore, convenient to consider the system to be moving in a six-dimensional space which is termed phase space or Γ-space.

As it is convenient to define an element of volume in Euclidean space so that a system with coordinates in the range x to $x+dx$, y to $y+dy$ and z to $z+dz$ lies within the volume

$$dV = dxdydz$$

it is also convenient to define an element of volume in phase space so that a system with its position and momentum coordinates in the range x to $x+dx$, y to $y+dy$, z to $z+dz$, to lies within a volume.

$$d\Gamma = dxdydzdp_xdp_ydp_z \qquad \textbf{1.1}$$

The kinetic energy of a system which has its coordinates lying within this volume $d\Gamma$ will be

$$\epsilon = \frac{p_x^2+p_y^2+p_z^2}{2m} \qquad 1.2$$

Where m is the mass of the system and the velocities are assumed to be non-relativistic.

As the state of a single system is defined in terms of six coordinates so it is possible to define the state of an assembly of *N* systems in terms of *6N* coordinates-3N position coordinates and *3N* momentum coordinates. It is sometimes convenient to allow these *6N* coordinates to define mathematically a 6N-dimensional phase space-a Γ_{6N} The coordinates of the system *i* may be written as (x_i, y_i, z_i, p_{xi}, p_{yi}, p_{zi}) and the coordinates of the assembly are then made up from all such sets with the suffix *i* running from 1 to *N.* If the coordinates are taken to be in the range x_i to x_i+dx_i, p_{xi} to $p_{xi}+dp_{xi}$ and so on for each of the *6N* coordinates then the 'point' representing the assembly in Γ_{6N} space will be.

$$\begin{aligned} d\Gamma_{6N} &= dx_1dy_1dz_1dp_{x1}dp_{y1}dp_{z1}\cdot\ldots \\ &\quad \cdot\ldots\cdot dx_idy_idz_idp_{xi}dp_{yi}dp_{zi} \\ &\quad \cdot\ldots\cdot dx_Ndy_Ndz_Ndp_{xN}dp_{yN}dp_{zN} \\ &= \prod_{i=1}^{N} dx_idy_idz_idp_{xi}dp_{yi}dp_{zi} && 1.3a \\ &= \prod_{i=1}^{N} (d\Gamma)_i && 1.3b \end{aligned}$$

where $(d\Gamma)_i$ is the volume element of the six-dimensional phase space for the ith system.

The kinetic energy of an assembly which has its coordinates within the volume $d\Gamma_{6N}$ will be given by.

$$\begin{aligned} E &= \epsilon_1+\epsilon_2+\ldots+\epsilon_i+\ldots\epsilon_N \\ &= \sum_{i=1}^{N} \epsilon_i \\ &= \sum_{i=1}^{N} \frac{p_{xi}^2+p_{yi}^2+p_{zi}^2}{2m} && 1.4 \end{aligned}$$

It will be seen in the subsequent discussion that a definition of the state of an assembly rather less detailed than that given above can lead to useful statistical results. However, even in this less detailed representation, it will be found useful to express the results in terms of the phase space coordinates.