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APPENDIX IIIA-A

THE SIGNIFICANCE OF THE PROBABILITY DISTRIBUTION

Note to the Student. The concepts of this appendix are presented for general understanding of the wave function and its magnitude squared, the position probability.

A free particle within a box of dimensions L_x by L_y by L_z can possess any of an infinite number of discrete energy magnitudes. Each of these allowed energy levels corresponds to one or more sets of quantum numbers ℓ, m, and n, and each set has an associated wave function. The wave function for the quantum numbers ℓ, m, and n is written as

$$\psi_{\ell,m,n}(x,y,z) = A \sin\left(\frac{\ell\pi x}{L_x}\right) \sin\left(\frac{m\pi y}{L_y}\right) \sin\left(\frac{n\pi z}{L_z}\right)$$

If we restrict the particle to remain not only within the box but also within some plane of constant z, the wave function, $\psi(x,y,z)$, becomes

$$\psi_{\ell,m}(x,y) = A \sin\left(\frac{\ell\pi x}{L_x}\right) \sin\left(\frac{m\pi y}{L_y}\right)$$

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5. Changes in microstate and macrostate occur by means of particle collisions. With almost every collision the system changes microstate. Collisions occur with extreme rapidity so microstate change is very rapid. Frequently the succeeding microstate will belong to the same macrostate; thus macrostate changes, though very frequent, are not as quick as microstate changes. (See the diagonal of Table IIIA-8.)

6. The number of macrostates in a real system is so vast that even the most probable macrostate has a very low probability. But, on a relative basis the most probable macrostate appears many times more frequently than an average macrostate. Its relative probability is very high.

7. The equilibrium group consists of the macrostates of high relative probability. Their relative probabilities are all much higher than an average macrostate. The distribution of particles in macrostates of the equilibrium group are disordered among the levels. The lower the probability of a macrostate the more ordered its distribution over levels.

8. Since the distributions of the macrostates of the equilibrium group are about the same, so are their properties. The most probable macrostate is a member of the equilibrium group and shares its characteristics. The ensemble average is dominated by the properties of the probable equilibrium group.

9. Collectively the equilibrium group is overwhelmingly probable. Nevertheless, individual macrostates which are not members of the equilibrium group occur occasionally. The probability that the system will spontaneously go through a sequence of nonequilibrium macrostates for a measurable period is incredibly minute.

10. Immediately after an energy interaction, it is almost certain that a system will be in a nonequilibrium macrostate.

11. An isolated system which is not in equilibrium will evolve rapidly toward probable equilibrium macrostates as collisions occur. Once in equilibrium the system will jump around among the macrostates of the equilibrium group.