UNIT IIIA

EQUILIBRIUM —A Microscopic Understanding

Equilibrium, the condition attained by every isolated system, is a state for which all fundamentally intensive properties are spatially uniform and temporally constant. From a macroscopic perspective, we observe that isolated systems attain equilibrium but we cannot provide a fundamental explanation of how or why. With a microscopic approach, i.e., a study of the behavior of the system's particles, we can examine both the condition of equilibrium and explain the spontaneous processes that drive isolated systems toward equilibrium. In addition, microscopic analysis provides a means of calculating properties from knowledge of the energy levels accessible to particles of the system. In many instances these predicted properties are more accurate, less expensive to obtain, and much more easily extrapolated over wide ranges of conditions than properties obtained by macroscopic measurement. Equally significant, microscopic models give insight into why a particular substance exhibits its characteristic macroscopic properties.

I. THE BEHAVIOR OF INDIVIDUAL PARTICLES

Although real systems are invariably composed of large numbers of particles, we choose not to begin our study with such large groups. Rather we will study single particles, then small groups, and finally we will statistically extrapolate our findings to real systems. Our first task is to select a *particle*.

A. The Particle

The term *particle* is used to mean some part, component, subdivision, entity, etc., the concept of which facilitates the understanding of the nature of matter. Depending on the questions that a study seeks to answer, the system particles might be stars, planets, billiard balls, raindrops, molecules, atoms, ions, electrons, photons, mesons, and so on. Thermodynamics defines the particle to be the largest system subdivision, the knowledge of whose individual behavior is sufficient to predict the statistical overall behavior of the group, i.e., the system's thermodynamic properties.

Example 1. As we have stated, the choice of a system particle depends upon the system definition and the question(s) to be answered. Suppose the system is the sixteen balls of a game of pool. (a) What is a suitable choice of particle definition for the player? The manufacturer of the balls must design a process that transforms molten plastic into a hard spherical ball. The rate at which the ball is cooled must be controlled to prevent distortion. (b) What is a suitable choice of particle definiton for the designer?

(a) To the player, the particle is obvious. To make a shot he must know in what manner, in what direction, and how hard to hit the cue ball. His shot will involve energy interactions between the balls and its dissipation via frictional processes.

(b). The designer must account for the rate of change in the internal energy of the balls. In solids, this results primarily from changes in amplitude of vibration of the molecules about their fixed positions within the crystal. Since the engineer must obtain information concerning these motions, he chooses the molecules as the particles.

Notice the player is unconcerned about the finer detail of the internal structure of the balls. The designer is similarly unconcerned about the finer detail of the structure of the molecule. Each has chosen the largest particle consistent with the question to which he sought an answer.

A further difference between the perspective of the player and the designer is the detail of their study of the chosen particles. The pool player endeavors to understand the details of the motion of each ball on every shot—deterministic mechanics. The designer, on the other hand, is not interested in the detailed behavior of individual molecules. He seeks a general knowledge of the collective behavior of the group, or of the *typical* behavior of the individual.[1] This latter perspective is the method of Statistical Mechanics.

In Exmp. 1 it was possible to select a single type of particle (the balls, the molecules). In many cases it is necessary to consider more than one distinct particle type. In the study of gases at moderate temperatures, for example, we may select the molecule as the particle without ignoring the vibration of the atoms within the molecule, or excitation of the electrons; these phenomena are treated as part of the molecular model. As the temperature is increased, we will find that atoms are separated from the molecule (dissociation) and electrons from their atoms (ionization). Since these phenomena divide the molecule into its separate components, we can no longer study these events using the molecule as the particle of our study. We must now choose the separate species, that is, the electrons and the ions, as the distinct particles of our study.

Exercise 1. The resistivity of electrical conductors is a primary consideration in the design of transmission lines. What is a suitable choice of particle(s) to study material resistance to electrical current?

B. Quantum Mechanics

Engineering students are trained in applications of dynamics. Application is primarily to macroscopic objects, whose speeds are much less than that of light and whose total energies are much greater than those of Planckian quanta. Therefore, neither relativistic nor quantum effects need to be included and only the special case of the Newtonian limit is treated, i.e., Classical Mechanics. The thermodynamic properties of systems arise from the dynamic behavior of "very small" particles. The energy of these particles is not, in general, much greater than the Planckian quanta. Therefore, it is usually not possible to implement statistical mechanics to obtain properties without the more accurate methods of

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[1] Indeed, if the detailed individual behavior were known, the amount of data would be so staggering that it could only be sampled statistically.

quantum mechanics.[2] The major distinction between quantum mechanics and classical mechanics is that quantum mechanics hypothesizes that energy changes of systems occur in discrete rather than continuous amounts. The concept of discrete energy levels can be established by investigating the time-independent Schroedinger equation and the implications of its solution.

Note to the Student. The following paragraphs introduce some concepts of quantum mechanics that are used in statistical thermodynamics. The Schroedinger equation and its solution are presented for a simple yet realistic and important case. The formulation of the Schroedinger equation and the techniques of its solution are not objectives of this unit. The implications of the solution, i.e., that it predicts discrete energy magnitudes for particles and provides a means of calculating these energies, are of paramount importance. Study this material to be convinced that these conclusions are correct. The examples and exercises are intended to reinforce concepts. The post unit exam does not contain problems similar to the numerical exercises included in this section.

The time-independent Schroedinger equation is a second-order partial differential equation which in cartesian coordinates has the form

$$\frac{h^2}{8\pi^2 m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+[\varepsilon - V(x,y,z)]\,\psi(x,y,z)=0$$

where h is Planck's constant ($h = 6.625 \cdot 10^{-27}$ erg-s particle), m^* is the mass of the particle, ε is the energy of the particle, and $V(x,y,z)$ is the potential in the domain of the particle at point (x,y,z). The dependent variable, $\psi(x,y,z)$, is the particle's *wave function*. It is related to the particle's *position probability* by

$$P(x,y,z) = |\psi(x,y,z)|^2 \qquad \text{(IIIA-1)}$$

The position probability for a particle, is the probability that its center of mass will be at the position (x,y,z).[3]

As an example solution of the Schroedinger equation, we solve the case of a *point particle* in a field-free rectangular box of dimension $L_x \cdot L_y \cdot L_z$.[4] A field-free space is one for which the potential function, $V(x,y,z)$, is zero. Particles in such spaces are called *free particles*. The Schroedinger equation for this system is

$$\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}+\frac{8\pi^2 m^*\varepsilon}{h^2}\psi(x,y,z)=0 \qquad \text{(IIIA-2a)}$$

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[2] Though the Newtonian limit is not applicable in general, we will find that each particle model has a characteristic temperature above which the Newtonian approximation is adequate (IIIC).

[3] Predicting particle position in time requires the time-dependent form of the Schroedinger equation.

[4] The point particle implies vanishing size.

To solve this equation for $\psi(x,y,z)$ we must specify six boundary conditions.[5] These conditions result from the reasoning that as x approaches 0 or L_x (or as y and z approach 0 or L_y and L_z) the position probability must vanish since the particle cannot leave the box. Noticing that whenever the position probability is zero so also is the wave function (eqn. IIIA-1), the boundary conditions for our example are

$$\begin{array}{lll} \psi(0,y,z) = 0 & \psi(x,0,z) = 0 & \psi(x,y,0) = 0 \\ \psi(L_x,y,z) = 0 & \psi(x,L_y,z) = 0 & \psi(x,y,L_z) = 0 \end{array} \qquad \text{(IIIA-2b)}$$

A solution of eqns. IIIA-2 is presented in Ref. 5, pgs. 127-130. It yields a family of solutions

$$\psi_{\ell,m,n}(x,y,z) = A \sin\left(\frac{\ell\pi x}{L_x}\right) \sin\left(\frac{m\pi y}{L_y}\right) \sin\left(\frac{n\pi z}{L_z}\right) \qquad \text{(IIIA-3)}$$

corresponding to all nonzero positive integer values of the *quantum numbers*, $\ell,m,n = 1,2,3,\ldots$, and all combinations.[6,7] The following problems verify the validity of this solution by assuring that it satisfies both the boundary conditions (Exer. 2) and the equation (Exmp. 2).

Exercise 2. Show that the wave functions, $\psi_{\ell,m,n}(x,y,z)$, (eqn. IIIA-3), satisfy the boundary conditions, (eqns. IIIA-2b), provided ℓ, m, and n are integers.

Example 2. Determine if the proposed solution, eqn. IIIA-3, satisfies the Schroedinger equation as specialized for the example of a point particle in a field-free box. Determine the restrictions imposed on the energy by the form of the solution.

To establish the conditions for which $\psi_{\ell,m,n}(x,y,z)$ satisfies the Schroedinger equation we need only substitute the proposed wave functions into the equation and perform the indicated partial differentiations. Thus for the first term

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

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[5]Two boundary conditions are required for each of the second-order derivatives.

[6]The quantity A is an integration constant. Its values are determined through the requirement that the integral of the squared wave function over the dimensions of the box must equal one, i.e., the probability of the particle being in the box is one. The result is $A = (8/L_xL_yL_z)^{\frac{1}{2}}$.

[7]Note that negative values of ℓ,m,n are not included. No new solutions are obtained with negatives since $\sin(-\ell\pi x/L_x) = -\sin(\ell\pi x/L_x)$ and the minus is taken by A. Also neither ℓ,m, nor n are zero since this makes the probability zero for all x,y,z, which implies that the particle is not in the box.

Ans. 1. In determining electrical resistivity one must consider both the charge carriers and the scattering centers which interfere with their motion through the media. In this case, the analysis includes the *free electrons* and the vibrating lattice points or *molecules* of the solid.

Performing the inner differentiation we obtain

$$\frac{\partial}{\partial x}\left[A\left(\frac{\ell\pi}{L_x}\right)\cos\left(\frac{\ell\pi x}{L_x}\right)\sin\left(\frac{m\pi y}{L_y}\right)\sin\left(\frac{n\pi z}{L_z}\right)\right]$$

Differentiating again,

$$\frac{\partial^2\psi_{\ell,m,n}(x,y,z)}{\partial x^2} = -A\left(\frac{\ell\pi}{L_x}\right)^2\sin\left(\frac{\ell\pi x}{L_x}\right)\sin\left(\frac{m\pi y}{L_y}\right)\sin\left(\frac{n\pi z}{L_z}\right) = -\left(\frac{\ell\pi}{L_x}\right)^2\psi_{\ell,m,n}(x,y,z)$$

Similarly,

$$\frac{\partial^2\psi_{\ell,m,n}(x,y,z)}{\partial y^2} = -\left(\frac{m\pi}{L_y}\right)^2\psi_{\ell,m,n}(x,y,z) \qquad \frac{\partial^2\psi_{\ell,m,n}(x,y,z)}{\partial z^2} = -\left(\frac{n\pi}{L_z}\right)^2\psi_{\ell,m,n}(x,y,z)$$

Finally, adding these second partial derivatives as they appear in eqn. IIIA-2a,

$$\left\{-\left[\left(\frac{\ell\pi}{L_x}\right)^2+\left(\frac{m\pi}{L_y}\right)^2+\left(\frac{n\pi}{L_z}\right)^2\right]+\frac{8\pi^2m^*}{h^2}\varepsilon\right\}\psi_{\ell,m,n}(x,y,z) = 0$$

Since this product equals zero, either the quantity within brackets equals zero or $\psi(x,y,z)$ equals zero. The latter possibility is ignored since it implies that $P(x,y,z) = |\psi(x,y,z)|^2$ equals zero for all x,y, and z. This is to say that the probability that the particle at a point is zero for <u>all</u> points within the box. The alternative is that the bracketed terms equal zero. This gives an expression for the allowed values of the energy. See eqn. IIIA-4 below.

We have verified that the assumed wave function, eqn. IIIA-3, is a valid solution for the free particle in a box subject to the specified restrictions on the energy. This function can be used to predict the position probability of the particle in terms of its energy. Neither the wave function nor the position probability is necessary for the statistical determination of the thermodynamic properties. Yet some students may find a more thorough investigation of the character of eqn. IIIA-3, especially as it relates to our macroscopic experience, helpful in understanding its meaning. Such an elaboration is presented in Appendix IIIA-A.

In Exmp. 2 we found that the free particle in a box could acquire only certain discrete energy magnitudes.

$$\varepsilon_{\ell,m,n} = \frac{h^2}{8m^*}\left[\left(\frac{\ell}{L_x}\right)^2+\left(\frac{m}{L_y}\right)^2+\left(\frac{n}{L_z}\right)^2\right] \qquad \text{(IIIA-4)}$$

where $\ell,m,n = 1,2,3,\ldots$, and all possible combinations. The possible energies of the particle, ε, are written as $\varepsilon_{\ell,m,n}$ to emphasize that they are discrete, or quantized. We call the values ascribed to ℓ,m, and n for any specific $\varepsilon_{\ell,m,n}$ the *quantum numbers of that energy state*. Furthermore, the specified energy states $\varepsilon_{\ell,m,n}$ are the only possible states for the particle and the corresponding $\psi_{\ell,m,n}(x,y,z)$ are the only possible wave functions. These energy states and wave functions are called the *allowed* energies and wave functions.

Example 3. Electrical conduction in metals is dependent on the motion and energy exchange processes of its free electrons. Free electrons can be modeled as point particles in a field free box. The box in this case is the conducting element. The energy levels in a circular wire can be approximated as

$$\varepsilon \sim \frac{h^2}{8m_e^*}\left(\frac{\ell^2 + m^2}{D^2} + \frac{n^2}{L^2}\right)$$

where D is the diameter and L the length of the wire. Scattering processes that change the radial component of the velocity will necessarily involve a change in the quantum numbers ℓ and/or m. Calculate the minimum change in the electron energy for such a process and the corresponding discrete change in the electron's translational velocity for a 10-micron diameter wire.

The minimum discrete energy change would correspond to one integer in the magnitude of the ℓ and m quantum numbers squared, $(\ell^2 + m^2)_2 - (\ell^2 + m^2)_1 = 1$

$$\Delta\varepsilon_{min} = \frac{h^2}{8m_e^* D^2} = \frac{(6.625)^2 \cdot 10^{-54}\ \text{erg}^2\text{s}^2}{8 \cdot (9.109) \cdot 10^{-28}\ \text{g} \cdot 10^{-6}\ \text{cm}^2} = 6.023 \cdot 10^{-21}\ \text{erg}$$

The relationship to the velocity is in terms of the kinetic energy of the electron $\varepsilon = m_e^*(\hat{V}^2/2)$; so

$$\Delta\hat{V}_{min} = \left(\frac{2\Delta\varepsilon_{min}}{m_e^*}\right)^{\frac{1}{2}} = \frac{h}{2Dm_e^*} = \frac{6.625 \cdot 10^{-27}\ \text{erg-s}}{2 \cdot 10^{-3}\ \text{cm} \cdot 9.109 \cdot 10^{-28}\ \text{g}} = 3{,}637\ \text{cm/s}$$

Thus, though the discrete energy change is numerically small we nevertheless obtain large minimum radial velocity change. It is clear from this example that quantum mechanics is significant in determining electrical conductivity.

Exercise 3. While discrete energy changes are significant for some microscopic particles, they are insignificant for all macroscopic objects. Consider a billiard ball moving on a *frictionless* table. A frictionless billiard table can be modeled as a two-dimensional field-free box. The energies of the balls in such a system can be inferred from eqn. IIIA-4 to be

$$\varepsilon_{2\text{-dim.}} = \frac{h^2}{8m^*}\left(\frac{\ell^2}{L_x^2} + \frac{m^2}{L_y^2}\right)$$

Ans. 2. The function, (x,y,z), satisfies the boundary conditions at the limits of x for all y and z. At x = 0

$$\psi_{\ell,m,n}(0,y,z) = A \sin\left(\frac{\ell\pi}{L_x} \cdot 0\right) \sin\left(\frac{m\pi y}{L_y}\right) \sin\left(\frac{n\pi z}{L_z}\right)$$

which is zero, since sin (0) = 0. At $x = L_x$ we have

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

The only nontrivial way this can equal zero is if $\sin(\ell\pi L_x/L_x) = 0$. Thus ℓ must be an integer. Similarly, the boundary conditions for y and z are satisfied provided m and n are integers.

The minimum energy is determined by $\ell = 1$, $m = 1$. This energy is kinetic, $(1/2)m^*\hat{V}^2$. Intuitively we expect the minimum speed of the ball to equal zero. Treat the ball as a point particle of mass 250 g on a table of dimensions 1.2 m by 2.7 m. Calculate the minimum speed of the ball. Calculate the time required for the ball to move a minimum detectable macroscopic increment, 10^{-7} cm, at this speed.

Note to the Student. Unlike the previous section, thorough familiarity with the meaning of the terms defined and discussed in this section is essential to accomplish the objectives of this unit.

C. Energy States, Energy Levels, and Degeneracy

The solution of the Schroedinger equation for a particle in a field-free box resulted in an expression for the discrete energies of the particle, eqn. IIIA-4. The energy states of the particle are dependent on the dimensions of the box (L_x, L_y, L_z). The general concepts are more easily assimilated in terms of the simpler geometry of a cubic box. Within a cube, the discrete energy states of the particle can be written as a function of the mass of the particle and the volume of the cube.[8]

$$\varepsilon_{\ell,m,n} = \frac{h^2}{8m^*V^{2/3}}(\ell^2+m^2+n^2) = \varepsilon_{\ell,m,n}(m^*,V) = B_o(\ell^2+m^2+n^2) \qquad \text{(IIIA-5)}$$

To save writing the physical constant $(h^2/8m^*V^{2/3})$ is named B_o.

Every set of quantum numbers (ℓ,m,n) identifies a distinct energy state. Since the minimum value of each quantum number is one, the minimum energy magnitude (the first *level*) that a particle can possess is $3\,B_o$. The next higher energy level is $\varepsilon_2 = 6\,B_o$. There are three states in this level: (1,1,2), (1,2,1) and (2,1,1). Though the energy of the states is the same, they remain distinct. The behavior of particles residing in different states is the same, they remain distinct. The behavior of particles residing in different states of the same level is different.[9] The number of states in a level is called its *degeneracy*,

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[8]for a cubic box $L_x = L_y = L_z$, $L^3 = V$, and $L^2 = V^{2/3}$. Thus eqn IIIA-4 can be simplified as

$$\left(\frac{\ell^2}{L_x^2} + \frac{m^2}{L_y^2} + \frac{\ell^2}{L_z^2}\right) = \frac{1}{L^2}(\ell^2 + m^2 + n^2) = \frac{1}{V^{2/3}}(\ell^2 + m^2 + n^2)$$

[9]The only energy form available to a particle within a field-free box is kinetic energy. Kinetic energy (a scalar quantity) is proportional to particle speed, i.e., the magnitude of the particle velocity (a vector quantity). Total kinetic energy can be written as a sum of its x,y, and z components. For each energy magnitude there may exist more than one quantum set, ℓ,m, and n. These integers prescribe how the total kinetic energy of the state is distributed among the three coordinate directions. Since the energy of the particle is proportional to velocity, one might ask of our solution, "What is the velocity vector for a particle in quantum state (1,1,2)?" The stationary state Schroedinger equation cannot be used to specify this vector exactly. The vector can lie in any quadrant. Its z component energy will be twice its x or y component. To specify the direction of motion, we would require a solution of the complete, time-dependent equation. However, since the particle's energy is independent of its direction of motion, we can disregard considerations of direction in our studies.

g. Thus, the second level has a degeneracy of three, $g_2 = 3$. The first level has only one state, $g_1 = 1$. This level is said to be *non-degenerate*. This is typical, higher energy levels often have larger degeneracies.

Table IIIA-1 presents the states, levels, and degeneracies for the first several levels of a particle in a cubical box. The quantum numbers corresponding to the states in each successive level are listed. The degeneracy of a level is the number of possible permutations of those quantum numbers as shown. The first energy level where more than one non-permuted set has the same energy is level number 14. The two sets of quantum numbers are (1,1,5) and (3,3,3). The level number is designated as j. Thus for this level j = 14 and the energy, ε_{14}, equals 27 B_o. The following exercise will aid in seeing the relationships of the table.

TABLE IIIA-1: ENERGY STATES, ENERGY MAGNITUDES, AND LEVELS, AND ENERGY LEVEL DEGENERACIES FOR A PARTICLE WITHIN A FIELD-FREE CUBE

Quantum Numbers	Energy, ε_j	Degeneracy, g_j
(1,7,12), (3,4,13), (3,8,11), (5,5,12), (7,8,9), ... and all permutations	$\varepsilon_{140} = 194\ B_0$	$g_{140} = ?$
⋮	⋮	⋮
(1,1,5), (1,5,1), (5,1,1) (3,3,3)	$\varepsilon_{14} = 27\ B_0$	$g_{14} = 4$
(1,3,4), (3,1,4), (1,4,3) (3,4,1), (4,1,3), (4,3,1)	$\varepsilon_{13} = 26\ B_0$	$g_{13} = 6$
(2,2,4), (2,4,2), (4,2,2)	$\varepsilon_{12} = 24\ B_0$	$g_{12} = 3$
(2,3,3), (3,2,3), (3,3,2)	$\varepsilon_{11} = 22\ B_0$	$g_{11} = 3$
(1,2,4), ... , ...	$\varepsilon_{10} = 21\ B_0$	$g_{10} = ?$
(1,3,3), (3,1,3), (3,3,1)	$\varepsilon_9 = 19\ B_0$	$g_9 = 3$
(1,1,4), (1,4,1), (4,1,1)	$\varepsilon_8 = (?)B_0$	$g_8 = 3$
(?), ...	$\varepsilon_7 = 17\ B_0$	$g_7 = ?$
(1,2,3), (1,3,2), (2,1,3) (2,3,1), (3,1,2), (3,2,1)	$\varepsilon_6 = 14\ B_0$	$g_6 = 6$
(2,2,2)	$\varepsilon_5 = 12\ B_0$	$g_5 = 1$
(1,1,3), (1,3,1), (3,1,1)	$\varepsilon_4 = 11\ B_0$	$g_4 = 3$
(1,2,2), (2,1,2), (2,2,1)	$\varepsilon_3 = 9\ B_0$	$g_3 = 3$
(1,1,2), (1,2,1), (2,1,1)	$\varepsilon_2 = 6\ B_0$	$g_2 = 3$
(1,1,1)	$\varepsilon_1 = 3\ B_0$	$g_1 = 1$

Exercise 4. Several blanks have been left in Table IIIA-1. To assure your understanding of the relationship between the quantum numbers, energy states, energy levels, and degeneracy, determine the missing quantities: the quantum numbers for level seven and its degeneracy, $g_7 = ?$; the energy of level eight, $\varepsilon_8 = ?$; the degeneracy of level ten, $g_{10} = ?$ All distinct sets of quantum numbers for level 140 are listed. Find its degeneracy, $g_{140} = ?$

We summarize the definitions presented above.

STATE - (Energy State): A distinct condition of the system specified by the quantum numbers. Each state has an energy magnitude associated with it, $\varepsilon_{\ell,m,n}$ (often abbreviated ε_i).

Ans. 3. The minimum energy is

$$\varepsilon_{min} = \frac{(6.625 \cdot 10^{-34}\ \text{J s})^2}{8 \cdot 0.250\ \text{kg}} \cdot \left[\frac{1}{(1.2\ \text{m})^2} + \frac{1}{(2.7\ \text{m})^2}\right] = 1.83 \cdot 10^{-69}\text{J}$$

From which

$$\hat{V}_{min} = \frac{2\varepsilon_{min}}{m^*} = 4.0 \cdot 10^{-37}\ \text{m/s}.$$

At this rate, it would take approximately 10^{24} years before our displacement measuring device could detect its motion.

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STATE - (Energy State): A distinct condition of the system specified by the quantum numbers. Each state has an energy magnitude associated with it, $\varepsilon_{\ell,m,n}$ (often abbreviated ε_i).

Ans. 3. The minimum energy is

$$\varepsilon_{min} = \frac{(6.625 \cdot 10^{-34}\ \text{J s})^2}{8 \cdot 0.250\ \text{kg}} \cdot \left[\frac{1}{(1.2\ \text{m})^2} + \frac{1}{(2.7\ \text{m})^2}\right] = 1.83 \cdot 10^{-69}\text{J}$$

From which

$$\hat{V}_{min} = \frac{2\varepsilon_{min}}{m^*} = 4.0 \cdot 10^{-37}\ \text{m/s}.$$

At this rate, it would take approximately 10^{24} years before our displacement measuring device could detect its motion.

LEVEL - (Energy Level): In general, an allowed discrete energy magnitude. Level, when associated with the integer, j, implies an ordering of energy magnitudes. Thus, there are (j-1) levels with discrete energy magnitudes less than the magnitude of the jth level. The first energy level is ε_1, the second ε_2, etc. The notation ε_j represents any energy level, j = 1,2,.... With each energy level there is associated at least one, and frequently many energy states, i.e., distinct sets of the numbers ℓ,m, and n.

DEGENERACY - (The Degeneracy of an Energy Level): The number, g, of energy states, all of which possess equal discrete energies, i.e., the number of states at a given level is called the degeneracy of that level. Thus, g_j for a fixed integer, j, implies the number of energy states in the jth level.

Thus far our introduction to quantum mechanics has been limited to systems composed of only one particle. Since the particles we have in mind are molecules, atoms, electrons, etc., we realize that the concepts developed must be extended to systems with more than one, indeed, very large numbers of particles. In the following paragraphs we discuss some of the complications that such systems present to our theory.

II. GROUP PARTICLE BEHAVIOR

The macroscopic properties of systems result from individual particle behaviors. These behaviors cannot be considered individually since the particles experience continuous interactions (collisions) among themselves. In this section, we explain why it is that even while the distribution of particles among states and levels changes continually under the agitation of collisions (i.e., as the particles exchange energies), their macroscopic properties in equilibrium remain constant. To reconcile constant properties with incessantly changing particle distributions, we must study the possible and probable distributions of the particles within the available energy states and levels under prescribed system conditions.

A. Macrostate Distributions

We will consider the properties of systems with certain fixed conditions or constraints. Basically, these conditions ensure that the systems do not exchange mass or energy with the surroundings, i.e., the systems are isolated. In terms of the particles of a system, isolation requires that:

(i) the space occupied by the particles be permanently fixed in shape and size—the volume, V, of the system is constant;

(ii) the system contains a fixed group of particles (number and identity). For convenience we will consider only systems with a single type of particle, N in number.

(iii) there are no energy transfers to these particles from sources outside of the system. Therefore, the internal energy, U, of the system is constant.[10]

[10]We are considering an isolated system in a fixed stationary position. Hence, the kinetic and potential energy terms need not be included.

If a single particle were constrained as an isolated system, it could only be in a single energy level, $U = \varepsilon_j$. The only spontaneous processes that could occur to the particle would be changes among the g_j states of the jth level. This is not the case in isolated systems of more than one particle. In them we recognize the possibility (indeed probability) that there can be more than one distribution of the N particles among the levels which will satisfy the constraint on total system energy. Each of these distributions describes a net condition of the microscopic particles within the macroscopic system. Each allowed distribution is called a *macrostate* of the system. The macrostates are differentiated from one another by the subscript i. Thus $n_{j,i}$ is that distinct distribution of particles among j levels designated as the ith macrostate. The constraints on allowed $n_{j,i}$ are

$$U = \sum_{j=1}^{J} n_{j,i}\varepsilon_j \qquad N = \sum_{j=1}^{J} n_{j,i} \qquad \text{(IIIA-6a,b)}$$

Hence, a macrostate is defined as a distribution of particles among the levels that satisfies the constraint equations, IIIA-6. It is specified by a set of numbers $(n_{1,i}, n_{2,i}, n_{3,i}, \ldots, n_{j,i}, \ldots, n_{J,i})$. We distinguish macrostates by Roman numerals (I, II, III,...,i, ...I^*). Not only can the system exist in any of I^* allowed macrostate distributions, but it changes from one allowed macrostate to another very frequently as the particles interact (collide) with one another. Collisions between particles permit exchanges of energy and effect alterations in particle distribution.

At any instant properties are determined by the macrostate present. For real systems, the number of particles is very large and macrostates change with such extreme rapidity that during a finite time the system will visit a great many of its macrostates. The observable, time average properties depend upon the sequence and duration of macrostates present during observation. Our approach to the prediction of properties must consider these macrostates and their probabilities. First we must determine the macrostate distributions by solving eqns. IIIA-6. This will depend upon rules governing their solution.

In Section I we solved the Schroedinger equation for a single-point particle in a field-free box. We established the energy states (and levels) available to it. Now we want to treat a system of many particles. How does the solution of the Schroedinger equation change when it is solved for a few and then many particles simultaneously? Are the energy state and level magnitudes altered? The answer to this question depends upon the type of particles present.

Ans. 4. Quantum numbers of ε_7 are (2,2,3), (2,3,2) and (3,2,2); $g_7 = 3$; $\varepsilon_8 = 18\ B_o$, $g_{10} = 6$, $g_{140} = 27$.

Dependent Particles. Continuing our consideration of the particle in a box, the energy states accessible to the single-point particle are those of translation. This model can provide a basis for the consideration of gaseous behavior. But when more than one molecule is present in the box, it is no longer field free. A potential field acts between the particles as a result of their dipole interactions (see Unit ICS). As a result, the potential, V, appearing in the Schroedinger equation is no longer zero. This potential is, in fact, dependent on the position of all of the molecules present in the box, $V = V(x_1, \ldots V(x_1, y_1, z_1, y_2, z_2, \ldots; x_N, y_N, z_N)$. In these instances the Schroedinger equation must be solved simultaneously for the N particles and the allowed energies will not be the same as those for the original single particle, $\varepsilon_j(\text{one}) \neq \varepsilon_j(\text{many})$.

One can imagine that the simultaneous solution of the Schroedinger equation for a system of particles is not a simple matter. The usual procedure is to account for the effect of the dependence of particles by successively treating cases of increasing numbers of particles and examining the changes in behavior as each more accurate model is solved. Physical situations for which the first-order (single-particle), solution for the energy states gives accurate representations of properties of actual systems are not uncommon.

Independent Particles. Whenever the energy states and levels accessible to the many particles of a real system are the same as those for a single particle under the same conditions, $\varepsilon_j(\text{one}) = \varepsilon_j(\text{many})$, that system is composed of independent particles. This requires that the potential acting on each particle is, at most, dependent on its position, $V(x,y,z)$. For example, the molecules of a gas can be treated as independent particles whenever the total translational kinetic energy of the collection dominates the total potential energy associated with the fields between the particles. These conditions prevail in gaseous systems when the pressure is low, so that the distance between particles is comparatively large, or when the temperature is high, so that the average molecular kinetic energy is high.[11] Lattice vibrations of atoms in a solid can also be modeled as independent (Unit IIID). This approximation is valid not because the potential energy between the atoms is negligible but because the potential can be written in terms of a constant "mean" position of the neighboring atoms. Thus the potential is independent of the motions of the neighbors.

The independent particle approximation accurately predicts the properties of many important physical systems. It will allow us to apply statistical principles to groups of particles and it will not impair our subsequent understanding of equilibrium or the second law of thermodynamics. We will continue this assumption throughout Units III.

As defined, the macrostates of a given isolated system constitute all possible solutions of eqns. IIIA-6. Thus to determine a macrostate one must specify the internal energy, U, the number of particles, N, and the energy levels for the system $(\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_j, \ldots, \varepsilon_J)$. One of the great frustrations of the science of statistical thermodynamics is that no technique to determine the full set of macrostate distributions has been found except trial and error. Fortunately, through our development, we will find a characteristic

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[11]We will see in Unit IIIC that a gaseous system of independent particles is a perfect gas (see also Unit ID).

pattern that relates macrostate distributions to system properties. Once this pattern is understood, we will be able to avoid the tedium of trial-and-error procedures.

Since macrostate distributions cannot be found analytically, our examination of procedure and results, and the discovery of trends must be accomplished in terms of examples.[12] For consistency and simplicity, we will use the energy levels and degeneracies developed for the particle in a cubic box. The energy levels of this system were written in terms of the constant, B_o $[(\equiv h^2/(8m^*V^{2/3})]$, and the quantum numbers ℓ,m, and n = 1,2,3,..., and all possible combinations, as

$$\varepsilon_j = \varepsilon_{\ell,m,n} = B_o(\ell^2 + m^2 + n^2) \qquad \text{(IIIA-5)}$$

or specifically ε_j/B_o =.3,6,9,11,12,14,17,18,19,21,22,24,... (see Table IIIA-1). In this example the internal energy of the system must be an integral multiple of B_o, $U = L\ B_o$. And, since the minimum energy of any single particle is 3 B_o, the minimum total energy is $U_{min} = 3\ NB_o$. Thus $L \geq 3\ N$. Subject to these constraints, we propose to draw physical conclusions by considering successively larger numbers of point particles isolated in a cubic box. As a smallest example consider the following.

Example 4. Determine the macrostate distributions of a system of three particles with a total energy of 27 B_o isolated within a cubic box.

This problem will require trial and error to determine all distinct sets of $n_{j,i}$ that satisfy the constraints, eqns. IIIA-6.

$$N = 3 = \sum_{j=1} n_{j,i} \qquad \text{and} \qquad U = 27\ B_o = \sum_{j=1} n_{j,i}\varepsilon_j$$

To begin, we can divide the 27 B_o energy evenly among the three particles. Thus each particle would have 9 B_o and Table IIIA-1 shows this to be acceptable. Thus macrostate I is

$$\text{I.}\quad n_{1,I} = n_{2,I} = 0,\quad n_{3,I} = 3,\quad n_{4,I} = n_{5,I} = \ldots = n_{J,I} = 0$$

$$\text{Check:}\quad 0\cdot 3\ B_o + 0\cdot 6\ B_o + 3\cdot 9\ B_o + 0\cdot 11\ B_o + 0\cdot 12\ B_o = 27\ B_o$$

We have established a first macrostate and that the levels above or below level 3 can possess at most two particles for any macrostate. If level four has two particles their energy is 22 B_o and the third particle must have 5 B_o. This is not possible; 5 B_o is not an allowed energy. Trying two particles in level five we find that the third particle in level one satisfies the constraint equations.

$$\text{II.}\quad n_{1,II} = 1,\quad n_{2,II} = n_{3,II} = n_{4,II} = 0,\quad n_{5,II} = 2,\quad n_{6,II} = \ldots = 0$$

$$\text{Check:}\quad 1\cdot 3\ B_o + 0\cdot 6\ B_o + \ldots + 2\cdot 12\ B_o + \ldots = 27\ B_o$$

Two particles cannot occupy levels above level five. Now we try two particles in level two. This requires the third to have 15 B_o which is not allowed. However, two particles in level one and one in level ten constitute a macrostate.

[12]Whereas examples are generally intended to be supplements to the text, in Unit IIIA important concepts are established by means of example.

III. $n_{1,III} = 2;\quad n_{2,III} = n_{3,III} = \ldots = n_{9,III} = 0;\quad n_{10,III} = 1$

Check: $2 \cdot 3\ B_o + 0 \cdot 6\ B_o + \ldots + 1 \cdot 21\ B_o = 27\ B_o$

This macrostate has bracketed the potentially occupied levels. No higher levels can be occupied in this system. Also, that constitutes all the macrostates with two particles in the same state.

An additional macrostate is found by reexamining macrostate I. If one particle's energy is reduced by 3 B_o and one increased 3 B_o, we have macrostate IV.

IV. $n_{2,IV} = n_{3,IV} = n_{5,IV} = 1;\quad n_{1,IV} = n_{4,IV} = n_{6,IV} = \ldots = 0$

Check: $0 + 1 \cdot 6\ B_o + 1 \cdot 9\ B_o + 0 + 1 \cdot 12\ B_o + 0 = 27\ B_o$

Similarly consider macrostate III if one of the particles in the lowest energy is increased 3 B_o and the other is reduced to level 8, we have macrostate V.

V. $n_{1,V} = n_{2,V} = n_{8,V} = 1;\quad n_{3,V} = n_{4,V} = \ldots = n_{7,V} = n_{9,V} = 0$

Because we have used a patterned method of looking, it is clear that no others exist. These are the five macrostates of our example.

The trial-and-error determination of macrostates for 3 particles is relatively easy because our selection of system energy limited the potentially occupied levels to only the lowest ten of the infinite array. In the course of the unit we will consider the characteristics of systems with successively larger numbers of particles and eventually extrapolate to draw conclusions about real systems. In the process, to maintain as much commonality as possible throughout the systems of our study, we choose to hold the average energy per particle, $\bar{\varepsilon}$, fixed at a constant value, $\bar{\varepsilon} = U/N = 9\ B_o$. Therefore as we proceed to larger systems the total energy will increase in proportion. What about the number of levels accessible to the system?

In the 3 particle example the 10th was the highest level occupied. For a 30 particle example the total energy is 270 B_o. This means that the highest level occupied would be $\varepsilon_{129} = 180\ B_o$ ($n_{1,I} = 28$, $n_{2,I} = 1$, $n_{129,I} = 1$). Thus the number of levels accessible to particles increases very rapidly with increased total energy (or system size). This in turn, vastly increases the number of macrostates. A 4 particle system would have 14 possible energy levels and 14 macrostates. Since our principal purpose is to investigate increased numbers of particles we will facilitate the process by arbitrarily limiting our systems to the lowest five levels, Fig. IIIA-1. In the figure, states and levels of increased energy are placed higher on the page in analogy with greater energy. The existence of more than one energy

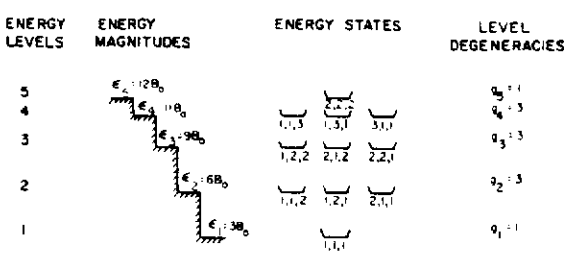


Fig. IIIA-1: A Schematic Representation of the Energy States of a 5-Energy Level System

state at a level is represented by several cups at the level. Each cup represents a state, they are subscripted with their quantum numbers to indicate that they are distinct.

Exercise 5. Determine the macrostates of a system of 3 particles, energy 27 B_o, when the levels are limited to 3 B_o, 6 B_o, 9 B_o, 11 B_o, and 12 B_o, as shown in Fig. IIIA-1.

Exercise 6. Given a system with 4 particles and 36 B_o energy to which only the five lowest energy levels of Table IIIA-1 are accessible, write the constraint equations and determine the macrostate distributions. (Answers in Table IIIA-2.)

TABLE IIIA-2: THE MACROSTATES OF A 4 PARTICLE, 36 B_o ENERGY SYSTEM WITH 5 ENERGY LEVELS

Macrostate	j	= 1	2	3	4	5	$\sum_{j=1}^{5} n_{j,i}$	$\sum_{j=1}^{5} n_{j,i}\varepsilon_j$
I	$n_{j,I}$	= 0	1	2	0	1	4	$36B_o$
II	$n_{j,II}$	= 1	0	0	3	0	4	$36B_o$
III	$n_{j,III}$	= 0	0	4	0	0	4	$36B_o$
IV	$n_{j,IV}$	= 0	2	0	0	2	4	$36B_o$
V	$n_{j,V}$	= 1	0	1	0	2	4	$36B_o$
	ε_j	= $3B_o$	$6B_o$	$9B_o$	$11B_o$	$12B_o$		

B. Microstates

In the three and four particle examples we found several solutions to the constraint equations, IIIA-6, i.e., several macrostates. Since each macrostate constitutes a distinct arrangement of the particles among the levels, we could expect the different macrostates to display different characteristics or properties. As collisions occur and macrostates change very rapidly, time average properties will be associated with macrostate properties in proportion to the probability of existence of each macrostate. Therefore we must be able to predict the probability of allowed macrostates.

A macrostate description specifies only the distribution of particles among levels. But most levels contain several states (those with $g_j \geq 2$). Therefore, most macrostates encompass several arrangements of particles among the states in the degenerate levels. Since these arrangements are elements of a macrostate set, they are called *microstates* of that macrostate. A *microstate* is a *unique arrangement* of particles *among the energy states* which satisfies the system constraints (eqns. IIIA-6). While macrostate determination is independent of particle characteristics (for given N, U, and ε_j), microstate counting procedures vary with the type of particle. We will first study distinguishable particles.

Distinguishable vs. Indistinguishable Particles. One cannot distinguish between like microscopic particles. One nitrogen atom is the same as any other nitrogen atom.[13] Nor can we tell one copper atom from another. Microscopic particles appear identical. However, within a crystal of copper we can distinguish the atoms by virtue of their fixed positions. This is the distinguishability of particles. The like particles constituting the lattice points of solids are dis-

[13]We exclude other isotopes.

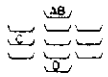
tinguishable since their positions are fixed. The statistics obeyed by *distinguishable particles* is called *MAXWELL-BOLTZMANN* (M-B) *STATISTICS* and we will call a distinguishable particle a *Boltzon*.[14]

To determine the probability of a macrostate relative to other macrostates, we must determine the number of microstates of each macrostate. In systems of distinguishable particles a microstate description contains the detail of not only which states of a degenerate level are occupied but also, precisely which particles occupy each state.

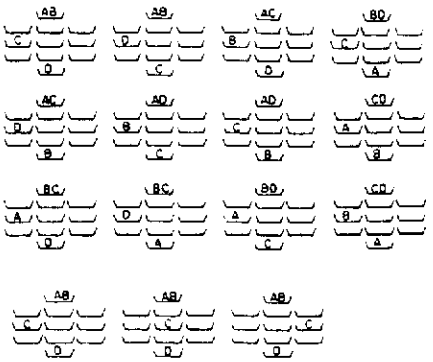
Boltzon macrostate probabilities. Any number of Boltzons can occupy a particular energy state so long as the arrangement is consistent with the system constraints, eqns. IIIA-6. To illustrate the concept of Boltzon microstates consider the 4 particle system of Exer. IIIA-6, whose macrostate distributions are listed in Table IIIA-2. What are the allowed microstates if the 4 particles are distinguishable Boltzons, designated A, B, C and D? (See Exmp. 5.)

Example 5. Consider a system of 4 Boltzons occupying the 5 levels of Fig. IIIA-1 with a total energy of 36 B_o. Determine how many microstates exist in macrostate V, Table IIIA-2.

The first arrangement of macrostate V is shown on the schematic distribution of states and levels at the right. Each distinguishable particle is designated as to which state it occupies. This is one microstate.



Other microstates are represented by simply listing all possible rearrangements among the occupied energy states (including the original in the upper-left-hand corner).



Each of the microstates generated by particle interchange has its level three particle in its (1,2,2) (left) energy state. Since this particle could just as well occupy the (2,1,2) (center) or (2,2,1) (right) energy state of the third level, each above distribution is one of three possibilities. Thus the total number of microstates of macrostate V equals 36. We designate the numbers of microstates in a macrostate as W_i where i = I,II,...; etc. This example has determined that $W_V = 36$.

In Exmp. 5 we showed that there are 36 microstates in Macrostate V of Table IIIA-2. We also found that it is tedious to determine the microstates of a macrostate by listing them. The principles involved are those of combinations and permutations. An equation that determines the number of microstates for the ith macrostate of N Boltzons distributed as $n_{j,i}$ among J levels with degeneracies g_j is (Ref. 5, Sects. 2.6 and 3.2)

$$W_i^{MB} = N! \prod_j^J \frac{g_j^{n_{j,i}}}{n_{j,i}!} = N! \left[\left(\frac{g_1^{n_{1,i}}}{n_{1,i}!}\right)\left(\frac{g_2^{n_{2,i}}}{n_{2,i}!}\right)\cdots\left(\frac{g_J^{n_{J,i}}}{n_{J,i}!}\right)\right] \qquad \text{(IIIA-7a)}$$

[14]Two indistinguishable particle statistics are considered below.

Example 6. Macrostate V, Table IIIA-2 was shown to have 36 microstates. The particle distribution is: $n_{1,V} = 1$, $n_{2,V} = 0$, $n_{3,V} = 1$, $n_{4,V} = 0$ and $n_{5,V} = 2$. The level degeneracies are $g_1 = 1$, $g_2 = g_3 = g_4 = 3$ and $g_5 = 1$. Verify that eqn. IIIA-7a yields 36 microstates for this macrostate.

$$W_V^{MB} = 4! \cdot \left[\left(\frac{1^1}{1!}\right) \left(\frac{3^0}{0!}\right) \left(\frac{3^1}{1!}\right) \left(\frac{3^0}{0!}\right) \left(\frac{1^2}{2!}\right)\right] = 4 \cdot 3 \cdot 2 \cdot 1 \cdot \left[\left(\frac{1}{1}\right)\left(\frac{1}{1}\right)\left(\frac{3}{1}\right)\left(\frac{1}{1}\right)\left(\frac{1}{2}\right)\right] = 36$$

Thus once the macrostate distributions have been determined (by trial and error), repeated application of eqn. IIIA-7 permits the determination of all I^* values of W_i with relative ease. The total number of microstates accessible in all I^* macrostates is

$$W = \sum_{i=1}^{I^*} W_i \qquad \text{(IIIA-8)}$$

The evaluation of W_i and W permit the evaluation of the required macrostate probabilities on the basis of a single underlying assumption.

THE EQUAL PROBABILITY AXIOM: ALL MICROSTATES ACCESSIBLE TO A SYSTEM UNDER GIVEN CONDITIONS ARE EQUALLY PROBABLE.

This assumption leads us directly to an understanding of the concept of equilibrium and ultimately to the formulation of the second law of thermodynamics (Unit IIIB). Thus the assumption is equivalent to a statement (but not a derivation) of the second law. Though the assumption seems credible, it is properly viewed as a postulate whose validity rests on the correspondence between predicted behavior and physical observations.

With the assumption that all microstates are equally probable, we can write the *probability of any macrostate*, p_i, as

$$p_i = \frac{W_i}{W} \qquad \text{(IIIA-9)}$$

This definition facilitates the determination of which macrostates will appear with greatest frequency in the system.

Exercise 7. Table IIIA-2 presents the 5 macrostate distributions for 4 particles in the 5 levels of Fig. IIIA-1 with a total energy of 36 B_o. If the particles are Boltzons, determine W_i for each of the 5 macrostates ($W_I = 36$, see Exmps. 5 and 6), as well as the total number of microstates, W, and the probability of each macrostate, p_i. The answers to this exercise are compiled in Table IIIA-3.

Exer. 7 concludes the development that results in the determination of Boltzon macrostate probabilities. The following section extends these methods to indistinguishable particles.

Ans. 5. I. $n_{3,I} = 3$; II. $n_{2,II} = 1$, $n_{3,II} = 1$, $n_{5,II} = 1$; III. $n_{1,III} = 1$, $n_{5,III} = 2$, all unlisted levels equal zero.

Indistinguishable particle macrostate probabilities. We found that most of the microstates of Maxwell-Boltzmann systems are simply interchanges of position of the distinguishable particles (A, B, ...) among the energy states. For a system of indistinguishable particles (a liquid or gas) particle position swapping does not result in new distinct distributions. Therefore, we expect fewer microstates for indistinguishable systems. In our previous consideration of distinguishable particles (Boltzons), we placed no limit on the number of particles that could occupy a state. There are two classifications of indistinguishable particles. One shares this characteristic with Boltzons. The other is restricted to at most one particle per state.

> The Pauli Exclusion Principle and its Significance. Indistinguishable particles are classed as symmetric or antisymmetric depending upon whether they contain an even or an odd number of subatomic components (that is, the total number of electrons, protons, and neutrons). The necessity for this distinction arises from the experimental fact that particles with an even number of subatomic components (symmetric particles) behave differently from those with an odd number of subatomic components (antisymmetric particles).[15] These differences can be accounted for by the postulate that each energy state of systems of antisymmetric particles is reserved for at most one particle at any instant, whereas any number of symmetric particles can occupy the same energy state simultaneously. This postulate is called the Pauli Exclusion Principle. It is an effect of the symmetry of the individual particle wave functions and the manner in which they combine to give the group wave function. If the individual wave functions are odd and two particles are placed in one state, the group wave function and therefore the probability of such an arrangement, vanishes. If the individual particle wave functions are even and two particles are placed in one state, the group wave function does not vanish. To make this point more rigorously, it is necessary to study the effect of matrix multiplication of individual wave functions to obtain group results. The interested student may wish to read Ref. 5, Sect. 5.10.

For application we require only knowledge of the additional restriction. Antisymmetric indistinguishable particle systems can have no more than one particle per state. Symmetric indistinguishable particle systems like distinguishable particles (Boltzons) can have any number of particles per state. Two statistical methods have been developed to predict the behaviors of the two classes of indistinguishable particles. These are *BOSE-EINSTEIN STATISTICS* for symmetric particles and *FERMI-DIRAC STATISTICS* for antisymmetric particles. Applications to systems of indistinguishable particles require that we be able to differentiate systems of symmetric particles, *Bosons*, from systems of antisymmetric particles, *Fermions*. This differentiation is accomplished by simply counting the number of subatomic components composing the particle, i.e., its total number of electrons, protons, and neutrons. The procedure is the same for all particles whether they be molecules, atoms, or electromagnetic and acoustical waves.

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[15]We will subsequently find (Unit IIIC) that the differences vanish in each system at its own characteristic high temperature.

Example 7. The following are examples of classification of indistinguishable particles as symmetric (even) or antisymmetric (odd) and the selection of an appropriate statistic.

(i) The common isotope of helium, He^4, has two electrons, two protons, and two neutrons. Its total number of subatomic components is 6—even, therefore He^4 particles are symmetric particles, Bosons. The statistics applicable to He^4 particles is the Bose-Einstein statistics.

(ii) The rare helium isotope, He^3, has one less neutron than He^4; therefore its number of substomic components is 5 which is an odd number. Conclusion: He^3 particles obey the statistics of antisymmtric particles, i.e., Fermi-Dirac statistics.

The markedly different properties of these very similar gases at low temperatures are explained and predicted by their respective statistical procedures.

(iii) All homonuclear, diatomic gases are composed of two identical atoms. The particle is the gas molecule.[16] The atoms come in pairs, e.g., O_2, N_2, etc. Thus their total numbers of subatomic parts are even numbers and these particles are Bosons, symmetric. They obey Bose-Einstein statistics.

(iv) Consider a heteronuclear diatomic gas. The hydrogen of hydrogen chloride, HCl, contributes 1 proton and 1 electron. The normal chlorine atom has 17 + 17 + 18. The total for HCl, 54, is even. Hydrogen chloride particles are symmetric—Bose-Einstein Statistics. Other heteronuclear diatomic gases may be antisymmetric.

Symmetry characteristics of particles are of practical significance to the studies of helium, hydrogen, electrons, and other particles as light or lighter than these, at practical temperatures and in principle to heavier particles at unattainably low temperatures.

Exercise 8. Classify each of the following particles as Bosons or Fermions. (a) diatomic hydrogen, H_2; (b) the hydrogen atom, H; (c) the hydrogen ion, H^+; (d) an electron, e^-; (e) a photon; (f) a phonon (photon and phonon are the names given to the massless particles of electromagnetic and acoustic radiation, respectively).

We are now able to classify indistinguishable particles as Bosons or Fermions. Further, we recognize that neither the counting procedures nor the combinatorial relationships illustrated for Boltzons (eqn. IIIA-7a) are applicable to these particles. Formulas for counting microstates of macrostates of indistinguishable particle systems have been derived (Ref. 5, Sect. 3.2). For Bosons and Fermions, respectively, they are

$$W_i^{BE} = \prod_j^J \frac{(g_j + n_{j,i} - 1)!}{(g_j-1)!\ n_{j,i}!} \qquad W_i^{FD} = \prod_j^J \frac{g_j!}{n_{j,i}!(g_j-n_{j,i})!} \qquad \text{(IIIA-7b,7c)}$$

Application of these formulas is illustrated in the following example and exercise. The macrostates of the 4 particle example, Table IIIA-2, will be used. (Macrostate

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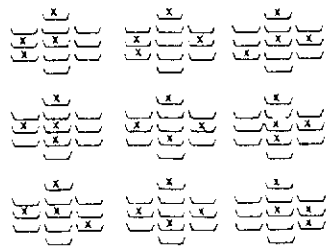
[16]Recall that the term particle refers to the entire entity, not to its parts separately. Subsequent considerations (Unit IIIC) treating the components of gaseous molecules will depend on the evenness or oddness of portions of the total particle.

determinations depend on the number of particles and total energy but not on particle type.)

Example 8. Determine the number of microstates and the probability of each macrostate of the 4 particle system, Table IIIA-2, when the particles are Fermions.

Macrostate I. The distribution of Fermions in macrostate I is represented at the right. The Fermions are represented by indistinguishable X's and no more than one X is permitted in any state.[17] This gives a total of only 9 microstates.



Macrostate II. To determine this number of microstates we apply eqn. IIIA-7c

$$W_{II}^{FD} = \left(\frac{1!}{1!(1-1)!}\right)\cdot\left(\frac{3!}{0!(3-0)!}\right)\cdot\left(\frac{3!}{0!(3-0)!}\right)\cdot\left(\frac{3!}{3!(3-3)!}\right)\cdot\left(\frac{1!}{0!(1-0)!}\right) = 1$$

Macrostates III, IV, and V. Inspection of these distributions reveals that they require two particles in at least one state ($n_{3,III} = 4$, $g_3 = 3$; $n_{5,IV} = 2$, $g_5 = 1$; $n_{5,V} = 2$, $g_5 = 1$). Therefore, these macrostates have no microstates.[18,19]

$$W_{III}^{FD} = W_{IV}^{FD} = W_{V}^{FD} = 0$$

And the total number of microstates is

$$W^{FD} = \sum_{i=1}^{5} W_i^{FD} = 9 + 1 + 0 + 0 + 0 = 10$$

and the macrostate probabilities are

$$p_I^{FD} = 0.9; \qquad p_{II}^{FD} = 0.1; \qquad p_{III}^{FD} = p_{IV}^{FD} = p_V^{FD} = 0$$

Exercise 9. Determine the number of microstates and the probability of each of the macrostates for the 4 particle system, Table IIIA-2, with the particles treated as Bosons. (Answers in Table IIIA-3.)

Table IIIA-3 summarizes the probability results for the 4 particle example which has been repeated for Boltzons, Bosons, and Fermions.[20] Notice the pattern $W_i^{MB} > W_i^{BE} > W_i^{FD}$ We would expect Boltzons to have more microstates than Bosons since Boltzons are distinguishable. (New microstates occur due to interchanging of particles.) Bosons have more

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[17]A similar figure for Bosons would include additional microstates with the two particles on the 3rd level sharing each of the 3 states.

[18]Application of eqn. IIIA-7c to macrostates in which $g_j > n_{j,i}$ will call for negative factorials. Interpret such a condition as precluding the macrostate, $W_i = 0$.

[19]In some texts the macrostates of zero probability are not counted among the system macrostates.

[20]The macrostates appear in the table in the order of decreasing probability. This is not happenstance. They were arranged in that manner deliberately for our subsequent convenience. See property determinations below.

microstates than Fermions because any number of Bosons can occupy an energy state.[21] This concludes our discussion of macrostate probability determination. Since the concept of a macrostate, microstate, and microstate probability are important to our next topic, the determination of thermodynamic properties, a summary of terms is appropriate.

TABLE IIIA-3: MICROSTATES AND PROBABILITIES OF MACROSTATES FOR SYSTEMS OF FOUR BOLTZONS, BOSONS, AND FERMIONS

Macrostate	W_i^{M-B}	p_i^{MB}	W_i^{B-E}	p_i^{BE}	W_i^{F-D}	p_i^{FD}
I	324	0.537	18	0.346	9	0.9
II	108	0.178	10	0.192	1	0.1
III	81	0.134	15	0.289	0	0
IV	54	0.090	6	0.115	0	0
V	36	0.060	3	0.058	0	0
Total	603	1.000	52	1.000	10	1.0

Macrostate. When a system of N particles has a total energy U and occupies an array of energy levels $\varepsilon_j (j = 1,2,3,\ldots,J)$, its particles can be distributed over this array in any manner that satisfies

$$U = \sum_{j=1}^{J} n_{j,i}\varepsilon_j \qquad \text{and} \qquad N = \sum_{j=1}^{J} n_{j,i}$$

The solutions of these equations are the particle distributions over the levels, $n_{j,i}$. Each of these $i = 1,2,3,\ldots,I^*$ solutions is a macrostate.

Microstates. A microstate is a more detailed description of the particle distribution than a macrostate. It specifies not only how many particles are in each level, but also in which energy states they reside. In the case of distinguishable particles, a microstate also specifies which particle is in which state. A microstate distribution completely specifies every distinct characteristic of the particles among the accessible energy states.

Macrostate Probabilities. It is not important that microstate particle distributions be specified, only that the number of microstates in each macrostate, W_i, be determined. Eqn. IIIA-7a,b, or c permits this determination for Boltzons, Bosons, and Fermions, respectively. This determination allows the macrostate probabilities to be determined.

$$p_i = \frac{W_i}{\sum_{i=1}^{I^*} W_i} \qquad \text{(IIIA-9)}$$

[21] For macrostates in which no level holds more than a single particle, $W_i^{BE} = W_i^{FD}$.

Ans. 8. (a) All diatomic molecules necessarily are even; Boson. (b) One electron, one proton, also even; Boson. (c) One proton, odd; Fermion. (e) A single electron is odd; Fermion. This recognition may help put the Bohr electron shell model in better prespective. As you recall, the first shell can contain at most 2 electrons, the second 8, the third 18, and so on. It is now recognizable that the shells correspond to levels with the first shell having 2 states. It will hold no more than 2 electrons since both states would then hold a particle. And the Pauli exclusion principle will permit no more than one electron to occupy a state. (e) and (f) Waves are massless. They have no electrons, protons, or neutrons. Zero is an even number; Bosons.

C. Properties

The properties of a macroscopic system result from the microscopic behaviors of the particles of which it is composed. Specifically, the "instantaneous" properties of an isolated system are those of the macrostate in which it resides at that instant. The magnitudes of the energy levels, ε_j, and the distribution of particles among the levels, $n_{j,i}$, are sufficient information to determine properties. System properties are related to the energies of occupied levels by a functional relationship, say $\lambda(\varepsilon_j)$. For a specific macrostate an intensive property per particle is written

$$\bar{\lambda}_i = \frac{1}{N} \sum_{j=1}^{J} n_{j,i} \lambda(\varepsilon_j) \qquad \text{(IIIA-10a)}$$

An extensive property is written as

$$\bar{\Lambda}_i = N\bar{\lambda}_i = \sum_{j=1}^{J} n_{j,i} \lambda(\varepsilon_j) \qquad \text{(IIIA-10b)}$$

Example 9. The system of 4 particles restricted to 5 energy levels was found to have five macrostates as listed in Table IIIA-2. Calculate the intensive macrostate property that corresponds to the particle energy relation, $\lambda(\varepsilon_j) = \varepsilon_j^{\frac{1}{2}}$ for macrostate I.

Before we determine the value of this property, let us consider its significance. Our energy levels have been chosen consistently as those of the particle in a box. The particle in a box is a model for the translational kinetic energy of gaseous particles, $\varepsilon_j = (m^*\hat{V}_j^2/2)$. Thus our function is linearly proportional to particle velocity, $\lambda(\varepsilon_j) = \varepsilon_j^{\frac{1}{2}} \sim V$. Therefore, it is proportional to the gaseous particle momentum. The pressure in a gas is a measure of momentum exchange at an interface. The property to be determined is proportional to the pressure of the particle in a box. We will call this property the *pseudopressure*. The pseudopressure of macrostate I is determined by means of the substitution of its distribution ($n_{1,I} = 0$, $n_{2,I} = 1$, $n_{3,I} = 2$, $n_{4,I} = 0$, $n_{5,I} = 1$) into eqn. IIIA-10 a.

$$\overline{\varepsilon_I^{\frac{1}{2}}} = \frac{1}{N} \sum_{j=1}^{5} n_{j,I} \varepsilon_j^{\frac{1}{2}} = \frac{B_o^{\frac{1}{2}}}{4} (0 \cdot 3^{\frac{1}{2}} + 1 \cdot 6^{\frac{1}{2}} + 2 \cdot 9^{\frac{1}{2}} + 0 \cdot 11^{\frac{1}{2}} + 1 \cdot 12^{\frac{1}{2}}) = 2.97840\ B_o^{\frac{1}{2}}$$

Exercise 10. Use a calculator to determine the pseudopressure for macrostates II to V for the 4 particle example. Five place accuracy is needed below to emphasize differences. (The answers are listed in Table IIIA-4.)

The previous example and exercise have illustrated the manner in which macrostate properties are calculated. Our interest is in observed properties. Real systems shift from microstate to microstate with extreme rapidity under the action of particle collisions. These microstate shifts give rise to the appearance of a sequence of different macrostates. The system properties are those of the "then present" macrostate; thus the instantaneous properties vary in time. Though macrostate shifts do not necessarily occur with each collision (microstates of the same macrostate can occur in sequence), their frequency of change is sufficiently rapid that no observational technique can detect the

properties of a single macrostate.[22] Rather, the observed properties are the time average of many microstate and macrostate changes. If the time span is sufficient, the assumption of equal microstate probability will allow the calculation of the long time or *"ensemble" average properties* on the basis of a weighted average over the macrostates.[23] Each macrostate contributes to the ensemble average system property in proportion to its probability. We designate ensemble average properties with a (^), for either intensive or extensive properties.

$$\hat{\lambda} = \sum_{i=I}^{I^*} p_i \bar{\lambda}_i \quad \text{or} \quad \hat{\Lambda} = \sum_{i=1}^{I^*} p_i \bar{\Lambda}_i \qquad \text{(IIIA-11)}$$

Macrostate average properties, like macrostate distributions, are identical for all three statistics. However, ensemble average properties and hence observed properties vary with particle type for the same macrostate possibilities.

Example 10. Calculate the ensemble average pseudo-pressure $\hat{\varepsilon}^{\frac{1}{2}}$, for the 4 particle system of Boltzons, Table IIIA-2. (Five place accuracy will be required to establish differences.)

The macrostate probabilities, p_i^{MB} are listed in Table IIIA-3 and repeated in Table IIIA-4 along with macrostate average pseudo-pressures. Substitution into eqn. IIIA-11 gives

$$\hat{\varepsilon}^{\frac{1}{2}} = \sum_{i=1}^{5} p_i \overline{\varepsilon_i^{\frac{1}{2}}} = [0.537 \cdot 2.9784 + 0.179 \cdot 2.9205 + 0.134 \cdot 3.0000 + 0.090 \cdot 2.9568 + 0.060 \cdot 2.9151]\, B_o^{\frac{1}{2}} = 2.9649\, B_o^{\frac{1}{2}}$$

Exercise 11. Use the macrostate probabilities, p_i^{B-E} and p_i^{F-D}, and macrostate average pseudopressures listed in Table IIIA-4 to compute the ensemble average pseudopressure for a system of 4 Bosons and 4 Fermions. (The answers are listed in Table IIIA-4.)

TABLE IIIA-4: CHARACTERISTICS OF 4 PARTICLE SYSTEMS OF BOLTZONS, BOSONS, AND FERMIONS

Macrostate	$\bar{\varepsilon}_i^{\frac{1}{2}}/B_o^{\frac{1}{2}}$	p_i^{MB}	$\frac{\lvert\hat{\varepsilon}^{\frac{1}{2}} - \bar{\varepsilon}_i^{\frac{1}{2}}\rvert^{MB}}{\hat{\varepsilon}^{\frac{1}{2}}}$	p_i^{BE}	$\frac{\lvert\hat{\varepsilon}^{\frac{1}{2}} - \bar{\varepsilon}_i^{\frac{1}{2}}\rvert^{BE}}{\hat{\varepsilon}^{\frac{1}{2}}}$	p_i^{FD}	$\frac{\lvert\hat{\varepsilon}^{\frac{1}{2}} - \bar{\varepsilon}_i^{\frac{1}{2}}\rvert^{FD}}{\hat{\varepsilon}^{\frac{1}{2}}}$
I	2.9784	0.5373	0.4553%	0.3461	0.3741%	0.9	0.1951%
II	2.9205	0.1791	1.4982%	0.1921	1.5779%	0.1	1.7533%
III	3.0000	0.1343	1.1838%	0.2885	1.1020%	0	--
IV	2.9568	0.0895	0.2735%	0.1154	0.3542%	0	--
V	2.9151	0.0597	1.6810%	0.0577	1.7605%	0	--
		1.000	$\left(\frac{\hat{\varepsilon}^{\frac{1}{2}}}{B_o^{\frac{1}{2}}}\right)^{MB} = 2.9649$	1.000	$\left(\frac{\hat{\varepsilon}^{\frac{1}{2}}}{B_o^{\frac{1}{2}}}\right)^{BE} = 2.9673$	1.00	$\left(\frac{\hat{\varepsilon}^{\frac{1}{2}}}{B_o^{\frac{1}{2}}}\right)^{FD} = 2.9726$

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[22] As a specific illustration of the magnitude of the collision rate, in one cm^3 of air at STP there are on the order of 10^{28} collisions/s.

[23] A more formal treatment of statistical thermodynamics introduces the probability distribution in terms of the instantaneous condition of an ensemble of identical system replicas. Our isolated system model is known as a microcanonical ensemble. The equivalence between the instantaneous distribution of the ensemble and the long time trace of a single system is termed the ergodic hypothesis (see Ref. 7).

GROUP PARTICLE BEHAVIOR

The examples and exercises of this section have used the pseudopressure of the 4 particle example to illustrate the determination of properties. Table IIIA-4 summarizes these results for comparison. It demonstrates that the statistics dependent macrostate probabilities (p_i^{MB}, p_i^{BE}, and p_i^{FD}) influence the ensemble average (i.e., observable) property. While our very small and unrealistic example shows these differences to be slight, certain real systems exhibit behaviors sufficiently different to merit the distinctions between distinguishable, Boltzons, versus indistinguishable— symmetric, Bosons, and indistinguishable— antisymmetric, Fermions. A case in point is the remarkable properties of the Boson, He^4, in its liquid state below 2.172 K. This liquid exhibits unique properties, a so-called superfluidity, that are quite different from the ordinary liquid properties of the very similar Fermion, He^3. Superconductivity, a similar phenomenon, is a manifestation of Boson-type behavior exhibited by free electron pairs that occur in some conductors. Other effects of particle type are considered in more detail in Units IIID and IIIE.

Our present interest is not to explore the differences of the three types of particle behavior. Rather, it is the development of the concept and conditions of equilibrium attained by all isolated systems.

Note to the Student. The preceding section has developed operational procedures for calculation of distributions, probabilities, and properties in small systems. This provides necessary background for extension to real systems. On the basis of these concepts, we will build an understanding of the nature of, and processes that lead to equilibrium. This is the primary objective of Unit IIIA. Students who are not confident of the operational techniques so far developed may find the following comprehensive exercise helpful.

Exercise 12. Consider a system of 4 independent particles of total energy 8 C (where C is a constant with units of energy). Three energy levels are accessible to the particles, 1 C, 2 C, and 3 C their degeneracies are $g_1 = 1$, $g_2 = 2$, $g_3 = 3$, respectively. Answer the following questions:

I. Macrostate Determination (Trial and Error)

a. Determine the macrostates of this system.

b. Calculate the pseudopressure for each macrostate, $\overline{\varepsilon_i^{\frac{1}{2}}}$.

II. Determination of Particle Type. For each of the following particle descriptions, classify the particles as Boltzons, Bosons, or Fermions. (M is molecular weight).

a. System "A" is composed of four He^4 molecules, M = 4.

b. System "B" is composed of four particles. Each of them is a diatomic molecule composed of one atom of deuterium (1 proton, 1 neutron and 1 electron) and one atom of normal hydrogen, M = 3.

c. System "C" is composed of 4 particles all of the same molecular weight, M = 3. These 4 particles are: a He^3 atom; a molecule of deuterium; a cluster of 3 neutrons, and an "extra" heavy hydrogen atom (1 proton, 2 neutrons, 1 electron).

Verify your answers to parts I and II before proceeding.

III. Determination of Systems Characteristics. For one or more of the systems "A", "B" and "C".

a. Determine the number of microstates per macrostate, (W_i), and the total number

of microstates, W. (Use the appropriate counting formula, eqn. IIIA-7a,b, or c).

b. Calculate the macrostate probabilities, p_i.

c. Calculate the ensemble average pseudopressure, $\hat{\varepsilon}^{\frac{1}{2}}$.

d. Calculate the deviation between the ensemble average and more probable macrostate pseudo-pressures

$$\left[\left|\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon^{\frac{1}{2}}_{mp}}\right| / \hat{\varepsilon}^{\frac{1}{2}}\right] \%$$

III. EQUILIBRIUM

A four particle example has been developed extensively (Tables IIIA-2, 3, and 4). Included in the tabulation of its properties are the deviations of the macrostate's pseudopressure from the ensemble average pseudopressure, $|\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon^{\frac{1}{2}}}|/\hat{\varepsilon}^{\frac{1}{2}}$ (Table IIIA-4). When these deviations are compared for each of three statistics we find that the most probable macrostate's pseudopressure is a close approximation of the average, $\overline{\varepsilon^{\frac{1}{2}}_{mp}} \approx \hat{\varepsilon}^{\frac{1}{2}}$.[24] As this tiny system has only 5 macrostates and the most probable macrostate rather dominates its probability distribution, it is not unexpected that the most probable macrostate's properties would be close to the probability-weighted average properties. But our purpose in this section is to determine those characteristics of systems small enough to be studied in detail, that are maintained or enchanced as we extrapolate to realistically large systems.[25] We will find that as N increases I^* increases geometrically. As a result, the probability of individual macrostates, including the most probable, decreases. The most probable macrostate does not dominate the probability distribution of real systems. Yet, we will also find that the correspondence between the properties of the most probable macrostate and the ensemble average properties gets better and better as system size increases. The following section demonstrates how this trend is evidenced and explains why. With the help of this study we can recognize the meaning of equilibrium.

A. Extrapolation to Large Systems

In this section we extend the conclusions drawn from the 4 particle example, Table IIIA-4, by considering successively larger Boltzon systems with the same average energy per particle in the same 5 energy levels. For a six particle system, Table IIIA-5, we

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[24]In the case of the Boltzon systems, the next to least probable macrostate is even closer. In large systems it is not unusual for several macrostates to be closer to the average than the most probable. This has no particular significance. The emphasis is on the observation that the easily identified most probable is always a close approximation.

[25]Trial and error determination of macrostate distributions is inconceivable in real systems. There are 10^{19} molecules/cm^3 in air at STP. The 30-particle example, see Table IIIA-7 below, required a large fraction of an hour in execution time on a large computer to find its macrostate distributions.

TABLE IIIA-5: A 6 PARTICLE SYSTEM OF BOLTZONS

	MACROSTATE					w_i	p_i	R_i	$\overline{\varepsilon_i^{1/2}}/B_o^{1/2}$	$\frac{\lvert\hat{\varepsilon}_i^{1/2} - \overline{\varepsilon^{1/2}}\rvert}{\varepsilon^{1/2}}$ %
i	$n_{1,i}$	$n_{2,i}$	$n_{3,i}$	$n_{4,i}$	$n_{5,i}$					
I	0	2	1	3	0	43,740	0.505	5.05	2.975	0.333
II	1	0	2	3	0	14,580	0.168	1.68	2.946	0.605
III	1	1	0	3	1	9,720	0.112	1.12	2.932	1.088
IV	0	1	4	0	1	7,290	0.084	0.84	2.985	0.697
V	0	2	2	0	2	7,290	0.084	0.84	2.971	0.212
VI	1	0	3	0	2	1,620	0.018	0.18	2.943	0.727
VII	1	1	1	0	3	1,080	0.012	0.12	2.928	0.726
VIII	0	0	6	0	0	729	0.008	0.08	3.000	1.212
IX	0	3	0	0	3	540	0.006	0.06	2.956	0.273
X	2	0	0	0	4	15	0.0001	0.001	2.886	2.631
						86,604	1.000	Avg. 1.00	$\hat{\varepsilon}^{1/2}/B_o^{1/2} = 2.964$	Avg. 0.850

find that p_{mp} is reduced from that of the 4 particle system. Yet observe that the pseudo-pressure deviation is also reduced ($N = 4$, $p_{mp} = 0.537$, $|\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon_{mp}^{\frac{1}{2}}}|/\hat{\varepsilon}^{\frac{1}{2}} = 0.442$; $N = 6$, $p_{mp} - 0.505$, $|\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon_{mp}^{\frac{1}{2}}}|/\hat{\varepsilon}^{\frac{1}{2}} = 0.333$). An understanding of why this somewhat paradoxical trend occurs can be achieved by defining *relative macrostate probability*, R_i. In terms of the smaller, 4 particle system with its 5 macrostates, if macrostates were equally probable then each would have a probability of 1 in 5 or 0.20. But macrostates are not equally probable. Thus, the most probable macrostate appears (0.537/0.20 =) 2.68 times its "fair share." Or more formally,

$$R_i \equiv p_i I^* \qquad \text{(IIIA-12)}$$

Macrostates with relative probability above one exceed "fair share" probability; those below one are relatively unlikely. Macrostates with large relative probability are disproportionately likely. In the 6 particle example the first three macrostates have relative probabilities above one. The most probable macrostate exceeds its fair share by almost twice the factor of the 4 particle example ($R_{mp,6} = 5.05$; $R_{mp,4} = 2.68$). Therefore, even though the absolute probabilities are lower in the larger system, the distribution is more distorted in favor of its high probability macrostates.

Ans. 12. There are three macrostates, $I^* = 3$. Their distributions and pseudo-pressures are shown at right.

i	$n_{1,i}$	$n_{2,i}$	$n_{3,i}$	$\overline{\varepsilon_i^{1/2}}/C$	w_i^A	p_i^A	w_i^B	p_i^B	w_i^C	p_i^C
I	2	0	2	1.3660	6	0.300	0	0	54	0.2524
II	1	2	1	1.3901	9	0.450	1	1.0	144	0.6729
III	0	4	0	1.4142	5	0.250	0	0	16	0.0747
					20		1		214	

II. (a) He^4 is composed of 2 neutrons, 2 protons, and 2 electrons; thus these 4 indistinguishable particles are Bosons. (b) Indistinguishable molecules composed of normal and heavy hydrogen atoms have an odd number of substomic components and are Fermions. (c) the correct answer is Boltzons, since each of the 4 particles is distinguishable from the others.

III. The number of microstates and their probabilities are shown in the table. In addition the pseudo-pressure deviations are: (A) 1.3889, 0.0876%; (B) 1.3901, 0.0%; (C) 1.3858, 0.310%.

In Table IIIA-6 the effect of further increases in system size on system characteristics is summarized. First, as expected, larger systems have more macrostates per particle than smaller systems. ($N = 4$, $I^*/N = 1.25$; $N = 30$, $I^*/N = 13.9$). The number of microstates increases even more rapidly with the addition of particles. And, as expected, the *absolute probability* of the *most probable macrostate decreases with increased system size;* but the *relative probability increases.* Thus, in larger systems the distribution of probability is increasingly *distorted toward more probable macrostates,* i.e., those with high relative probability. In that sense the larger system is spending more, not less, time in high-probability macrostates. But not in *the* most probable, which is simply one member of the group of high-probability macrostates.

TABLE IIIA-6: EFFECT OF SIZE ON SYSTEMS OF BOLTZONS

N	I*	I*/N	W	W/N	P_{MP}	R_{MP}	$\frac{\lvert\hat{\varepsilon}^{\frac{1}{2}}_{MP} - \overline{\varepsilon^{\frac{1}{2}}}\rvert}{\hat{\varepsilon}^{\frac{1}{2}}}$ %
4	5	1.25	$6.03 \cdot 10^{2}$	$1.5 \cdot 10^{2}$	0.537	2.68	0.442
6	10	1.66	$8.66 \cdot 10^{5}$	$1.4 \cdot 10^{4}$	0.505	5.05	0.333
10	28	2.80	$1.06 \cdot 10^{9}$	$1.1 \cdot 10^{8}$	0.313	8.75	0.329
14	60	4.28	$1.17 \cdot 10^{13}$	$0.8 \cdot 10^{12}$	0.153	9.18	0.267
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
30	419	13.9	$2.65 \cdot 10^{29}$	$0.9 \cdot 10^{28}$	0.064	26.71	0.209
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.

N = No. of particles, I* = Total no. of macrostates, W = Total no. of microstates. All systems have average energy $9\,B_0$ and the same 5 levels.

What about properties? To see the relationship between the group of probable macrostates and those of the system consider the 30-particle example. Since it has 419 macrostates we present only an extract of its data, Table IIIA-7. The characteristics of the most, 10th, 20th, 219th-most and the least probable macrostates are listed. None of the individual macrostates is very probable. But the relative probability of even the twentieth most probable macrostate is quite large, $R_{XX} = 6.78$. Thus, though the system will rarely be found in any specified individual macrostate, it is very likely to be found within the group of high relative probability macrostates. Table IIIA-7 shows that the system spends 87.6% of its time in one of the 42 most probable macrostates, Group 1, and 98.1% in the first 84, Groups 1 and 2.

TABLE IIIA-7: SUMMARY OF PROPERTIES OF A 30-PARTICLE SYSTEM OF BOLTZONS

$I^* = 419$ $\quad W = 2.648 \cdot 10^{29}$ $\quad \hat{\varepsilon}^{\frac{1}{2}} = 2.9644\, B_0^{\frac{1}{2}}$

i	$n_{1,i}$	$n_{2,i}$	$n_{3,i}$	$n_{4,i}$	$n_{5,i}$	P_i	R_i	$\left(\frac{\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon^{\frac{1}{2}}_i}}{\hat{\varepsilon}^{\frac{1}{2}}}\right)$ %
I	1	7	10	9	3	$6.39 \cdot 10^{-2}$	$2.64 \cdot 10^{1}$	0.209
X	3	5	7	12	3	$2.71 \cdot 10^{-2}$	$1.13 \cdot 10^{1}$	0.334
XX	1	7	11	6	5	$1.62 \cdot 10^{-2}$	$6.78 \cdot 10^{0}$	0.185
CCIX	5	0	13	6	6	$3.01 \cdot 10^{-6}$	$1.26 \cdot 10^{-3}$	0.663
CDIXX	10	0	0	0	20	$1.13 \cdot 10^{-22}$	$4.73 \cdot 10^{-22}$	2.62

Groups of Macrostates	Number of Microstates	Total Probability	$\left[\frac{\sum_{i=1}^{42}\left(\hat{\varepsilon}^{\frac{1}{2}} - \overline{\varepsilon^{\frac{1}{2}}_i}\right)^2}{42[\hat{\varepsilon}^{\frac{1}{2}}]^2}\right]^{\frac{1}{2}}$ %
1	$2.32 \cdot 10^{29}$	$8.76 \cdot 10^{-1}$	0.298
2	$2.81 \cdot 10^{28}$	$1.05 \cdot 10^{-1}$	0.382
3	$3.86 \cdot 10^{27}$	$1.45 \cdot 10^{-2}$	0.564
4	$7.09 \cdot 10^{26}$	$2.6 \cdot 10^{-3}$	0.570
5	$1.09 \cdot 10^{26}$	$2.6 \cdot 10^{-3}$	0.570
6	$1.31 \cdot 10^{25}$	$5.0 \cdot 10^{-5}$	0.849
7	$1.16 \cdot 10^{24}$	$4.4 \cdot 10^{-6}$	0.855
8	$1.03 \cdot 10^{23}$	$3.9 \cdot 10^{-7}$	1.01
9	$2.73 \cdot 10^{22}$	$1.0 \cdot 10^{-8}$	1.17
10	$1.34 \cdot 10^{19}$	$5.2 \cdot 10^{-11}$	15.3

Notice that the distributions of the three probable macrostates listed are similar to one another in form; each has a rather "disordered" distribution among the states.

The two improbable macrostate distributions, in contrast, are bunched more tightly among the levels.[26] They are more "ordered." As the distributions of the probable macrostates are similar, so are their properties. Since the system spends time disproportionately in the probable macrostates, the ensemble average is determined predominantly by the properties of these macrostates. Correspondingly the pseudopressure deviations of the probable macrostates listed are small. Indeed this is true for each member of Group 1. Its RMS deviation is 0.298%. And the RMS deviation of each successively less probable group is increased. With this illustration we see how and why the most probable macrostate's properties can converge toward the ensemble average properties as the system size increases. The most probable macrostate is simply one member of the group of probable macrostates. The last column of Table IIIA-6 shows a continuous decrease in pseudopressure deviation as system size increases. It is not difficult to project that in real systems, $\overline{\varepsilon^{\frac{1}{2}}_{mp}} \rightarrow \varepsilon^{\frac{1}{2}}$. This conclusion eliminates the necessity for determining the macrostate distributions by trial and error. *We only need the distribution of the most probable macrostate*, $n_{j,mp}$. We will be able to determine this distribution analytically, Unit IIIB. We follow this procedure to determine properties in the remainder of Units III.

We have considered the relationship between macrostate probability and properties in successively larger isolated systems in order to achieve an understanding of the behavior of real systems. We conclude this extrapolation with a summary.

> Equilibrium. The macrostate probability in a real system is dominated by a tiny proportion of the macrostates, those with high relative probability. These macrostates constitute the *equilibrium group*. Individually, none of these macrostates is particularly probable, but collectively their probability is overwhelming. The macrostates of the equilibrium group are similar to one another; they are characterized by their disorder and they have essentially the same properties. As a result the long-time or ensemble average properties of the system are indistinguishable from those of the equilibrium group macrostates. A system is in equilibrium when its observed properties are the same as the long time average.
>
> Nonequilibrium. An isolated system is out of equilibrium when its properties are *observed* to deviate from the long time, ensemble average. Such an observation requires that the system traverse a sequence of macrostates that includes a large proportion of improbable nonequilibrium macrostates. The sequence must be of sufficient duration that observation of the property deviation is possible.

The test of equilibrium is the absence of property deviations. This implies property measurement. Our illustrative energy states are those of a simple compressible media.[27] Its measurable properties are pressure, temperature, and volume. But in an

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[26]The lowest and highest levels are nondegenerate; therefore they are less occupied.

[27]The levels of the particle in a box are governed by its volume, $\varepsilon_j = \varepsilon_j(V)$. The energy levels of other types of single media would be dependent on their displacement variable, $\varepsilon_j = \varepsilon_j(\bar{X})$, or variables in complex media, $\varepsilon_j = \varepsilon_j(\bar{X}_k)$.

isolated system volume is fixed. Only specific volume, or its reciprocal— density, could be observed to deviate. Deviations can only be measured in terms of specific volume, pressure, or temperature. These are intensive properties, they are defined, and must be measured, locally. Thus equilibrium, i.e., an absence of property deviations in an isolated system of identical particles, requires that the intensive properties be spatially uniform as well as temporally invariant.[28,29] As a consequence we recognize that each spatial subdivision of an isolated system of identical particles in equilibrium contains the same proportion of the constrained energy and number of particles. Moreover, the properties in that subdivision are the same as they would be if it were itself an isolated system.

B. Approach to Equilibrium

Our development has been premised on the hypothesis that macrostate sequences are governed by pure chance. Thus, over long times the probability of a sequence that passes through a series of nonequilibrium macrostates for a period long enough to exhibit property deviation is nil.[30,31] But it is unrealistic to limit our consideration to systems that have been isolated for long times. Indeed, our primary interest is energy exchange. Typically a system's energy is altered by heat or work occurring at a localized position on the boundary. Once the energy transport is concluded the system can be considered isolated. But when the transport has been rapid, the system is left with a surplus or deficit

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[28]We are ignoring the effect of extrinsic fields imposed on the system, e.g., gravity. In the presence of an extrinsic field the equilibrium distribution might be nonuniform but it is still uniquely defined, e.g., hydrostatic pressure variation.

[29]A system of identical particles requires that each has the same accessible energy states. This eliminates multiphase systems from consideration. For example, particles in a solid have one set of accessible states while those in a surrounding vapor have another set. The more general procedures of a Grand Canonical Ensemble are required to extend our consideration to such cases.

[30]In the previously considered 30 particle system, if we assume 10^3 collisions/s the least probable macrostate would occur once every three years. Random probability would expect the system to exist in the less probable 80% of the macrostates 19 times per second. If we assume that a measurable deviation would require that the system exist in one of the less probable 80% of the macrostates 20% of the time for a period of 0.1 s, we could only expect such a sequence once every 6,767 years.

[31]Our development has concerned macrostates of the entire system, not the spatial distribution in subsystems. It is theoretically conceivable that a property might deviate locally while corresponding regions deviated in the opposite sense in such a manner that the ensemble average property over the whole system was constant. But one intuitively recognizes that this probability is even smaller than that of other events already found negligible.

in its energy density locally in the region of transfer.[32] Thus the end result of the energy exchange process is a nonequilibrium isolated system. Initially the macrostate sequence of such a system is not governed by pure chance; it begins in an improbable nonequilibrium macrostate.

How long a microstate sequence is necessary before the long time probability takes over and the properties become those of the equilibrium group? This question can be answered intuitively by considering a physical example. When a tuning fork is struck, it is placed in a nonequilibrium state. Its vibrating prongs indicate a high energy density in these localized regions and the single frequency, in-phase vibration of the fork prongs indicate the presence of an ordered nonequilibrium macrostate. After the strike, the fork evolves toward equilibrium. The energy, initially localized in the vibrating prongs, is distributed throughout the material by means of particle collisions. The redistributed energy is manifest primarily in multifrequency and multidirection (i.e., highly disordered) vibration of the atoms in the metallic lattice. Equilibrium macrostates are achieved and the fork ceases to ring. Our experience is that this redistribution occurs quite rapidly. And that once the vibration stops, it never starts again spontaneously. Thus an isolated tuning fork goes from its initial improbable macrostate to more probable equilibrium macrostates in a continuous irreversible sequence.[33] This is the qualitative manner in which equilibrium is obtained. A more quantitative description of the process can be obtained through a detailed consideration of the collision processes of a small model system.

Note to the Student. The following quantitative illustration establishes the inevitability of a rapid approach to equilibrium through the study of transition probabilities, Table IIIA-8. Neither the determination nor the use of these probabilities is an objective of the unit. This section is intended to help the student recognize the processes which lead to equilibrium macrostates are overwhelmingly probable.

The mechanism of microstate change is collisions between particles. These collisions are restricted by the requirement that the energy and number of particles are conserved during each collision.[34] Each macrostate can be reached from every other as a result of

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[32]Electric and magnetic polarization work processes penetrate the boundary and are performed throughout the system's interior. In that sense, they can leave the energy density in the system spatially uniform. Yet they are still apt to terminate in a low-probability nonequilibrium macrostate. For example, microwaves penetrate the receiver, distributing the energy they deliver; but they promote particle vibration at a single frequency. This corresponds to ordered nonequilibrium macrostates.

[33]In fact, the tuning fork is not isolated. As it rings, it emits sound. A more rigorous statement of this example would place the vibrating fork in a vacuum. It would then be isolated. The processes and description for these circumstances are otherwise the same.

[34]Momentum must be conserved as well; but our discussion has omitted its consideration

a single collision involving two or more particles. But collisions involving more than two particles are sufficiently infrequent that they can be neglected. Under this assumption some macrostates cannot be reached from others by a single collision. However, the net collision probabilities remain representative.

As a specific illustration, consider two particle collisions occurring in a system of 6 Boltzons with 4 energy levels (3, 6, 9 and 12 B_o with degeneracies 1, 3, 3, and 1, respectively). The total energy of the 6 particle system is 54 B_o, and the average energy per particle is 9 B_o. The 7 macrostate distributions of this system, along with their probabilities and relative probabilities are listed in Table IIIA-8.[35] It also presents the *transition probability matrix* for this system. The elements of this matrix are the probabilities that a two-particle collision occurring to the system while it is in the macrostate of that row will result in the macrostate of that column. Thus the probability of transition from macrostate I to II is $p_{I-II} = 0.172$ and that from macrostate I to III is $p_{I-III} = 0.030$, etc. The elements of each row add to one.[36] The diagonal elements represent the probabilities of two particle collisions that leave the system in its original macrostate. Zeros represent the fact that macrostates of that column cannot be reached by a single two-particle collision from the macrostate of that row.

TABLE IIIA-8: MACROSTATES AND TRANSITION PROBABILITIES OF A SYSTEM OF 6 BOLTZONS

	INITIAL MACROSTATE						PROBABILITY OF OUTCOME OF TWO PARTICLE COLLISION						
i	$n_{1,i}$	$n_{2,i}$	$n_{3,i}$	$n_{4,i}$	P_i	R_i	I	II	III	IV	V	VI	VII
I	0	1	4	1	.390	2.73	.746	.172	.030	0	.043	0	0
II	0	2	2	2	.390	2.73	.185	.713	.031	.042	0	.030	0
III	1	0	3	2	.087	0.61	.215	.162	.515	.108	0	0	0
IV	1	1	1	3	.058	0.40	0	.323	.162	.449	0	.054	.012
V	0	0	6	0	.039	0.27	.400	0	0	0	.600	0	0
VI	0	3	0	3	.029	0.20	0	.443	0	.098	0	.459	0
VII	2	0	0	4	.008	0.06	0	0	0	.864	0	0	.136

$\epsilon_1 = 3B_o$ $\epsilon_2 = 6B_o$ $\epsilon_3 = 9B_o$ $\epsilon_4 = 12B_o$
$g_1 = 1$ $g_2 = 3$ $g_3 = 3$ $g_4 = 1$

[35]This system is an abbreviation of the 6 particle system considered earlier with the original fourth level, 11 B_o, eliminated. Macrostates with this level occupied (I, II, and III of Table IIIA-5) cannot be reached from the other macrostates by 2 particle collisions. The 7 macrostates of Table IIIA-8 are the last 7 of Table IIIA-5.

[36]The probabilities are the proportion of ways a two-particle collision can produce each possible type of macrostate. In row 1, for example, there are 156 two-particle collisions which leave macrostate I unchanged, 36 which produce macrostate II, 8-III, 0-IV, 9-V, 0-VI, and 0-VII, total is 209. Thus, $p_{I-I} = 156/209 = 0.746$ etc.

The elements on the diagonal (the no change probabilities) are on the average the largest elements of the matrix. In general, their value decreases as we proceed from the most to the least probable macrostates. The elements on the diagonal separate collisions that result in more probable macrostates (below the diagonal) from those that result in less probable macrostates (above the diagonal). Notice that the matrix is symmetric with respect to its zeros. (Macrostate IV cannot be reached from macrostate I, $p_{I-IV} = 0$ via a two-particle collision. Conversely, macrostate I cannot be reached from IV, $p_{IV-I} = 0$). For nonzero terms each probability of change to a more probable macrostate is larger than its counterpart above the diagonal pair (e.g., $p_{III-I} = 0.215 > p_{I-III} = 0.030$). Thus it is recognized that the system tends toward more probable macrostates as collisions occur. The ratio of the sum of the below-diagonal to the above-diagonal probabilities is 5.46, indicating a better than 5 to 1 tendency that any macrostate change will be toward more probable macrostates. It was pointed out above that an isolated system that has just undergone interaction is likely to be in an improbable, nonequilibrium macrostate. The transition probability matrix indicates that after relatively few collisions it is very probable that the system will have evolved to a high probability, equilibrium macrostate. Furthermore, the transition table shows that once equilibrium is achieved, a spontaneous return to nonequilibrium states is extremely improbable. Consider the following example.

Example 11. After an interaction, the 6 particle system of Table IIIA-8 is found in the least probable macrostate, VII. Determine the highest probability sequence of macrostate changes that result in the most probable macrostate, the probability of that sequence and the probability of the converse sequence.

Starting in macrostate VII the most probable result of a single collision is macrostate IV, $p_{VII-IV} = 0.864$. In row IV the most probable individual result of collision is no change, $p_{IV-IV} = 0.449$, though the system is more likely to change to one of the two accessible more probable macrostates ($p_{IV-III} + p_{IV-II} = 0.162 + 0.323 = 0.485$). The most probable change is from IV to II, $p_{IV-II} = 0.323$. In fact, macrostate II is one of the two equal probability most probable macrostates. In that sense, the very high probability of no change in macrostates II and I, $p_{II-II} = 0.713$, $p_{I-I} = 0.746$, is supportive of the maintenance of equilibrium. The change to macrostate I is the most probable change, $p_{II-I} = 0.185$. The probability of this sequence is

$$p_{VII-IV-II-I} = 0.864 \cdot 0.343 \cdot 0.185 = 0.548 \cdot 10^{-1}$$

Even though this is the most probable sequence of change, it is not very probable. No individual sequence of occurrences is. The reverse sequence is much less likely.

$$p_{I-II-IV-VII} = p_{I-II} \cdot p_{II-IV} \cdot p_{IV-VII} = 0.172 \cdot 0.042 \cdot 0.012 = 0.867 \cdot 10^{-4}$$

In fact, the system is $p_{VII-IV-II-I}/p_{I-II-IV-VII} = 6.32 \cdot 10^{2}$ times more likely to go from the least to most probable macrostate by this sequence than vice versa.

The preceding example reminds us that collisions occur in sequence. A product of the ratios of below to above the diagonal transition probabilities $\prod_{\substack{i,j \\ i \neq j}} p'_{ij}/p_{ji}$ might be more meaningfully compare than their sum. This ratio, $8.34 \cdot 10^{6}$, strongly indicates the

inevitability of processes that lead to equilibrium in this 6 particle system. In more realistic, larger systems these trends are even more pronounced.

SUMMARY QUESTIONS

We summarize this unit, particularly the last and most important section, with several questions.

1. Distinguish between dependent and independent particles.

2. On what basis are particles classified as Boltzons, Bosons, or Fermions?

3. Describe macrostates and microstates and distinguish between them.

4. How do the properties of microstates within a single macrostate compare?

5. How frequently (answer qualitatively) and by what mechanism does a "real" system change, (a) microstate? (b) macrostate?

6. What are the orders of magnitude of the absolute and relative probabilities of the most probable macrostate in a real system?

7. Compare the relative macrostate probability and the nature of particle distributions over the levels for the macrostates of the equilibrium group, one to another and to the remaining macrostates.

8. How do the properties of the macrostates of the equilibrium group compare, (a) with one another? (b) with the most probable? (c) with the ensemble average?

9. Consider a system which has been isolated for some time. How likely is it to be in one of the equilibrium group macrostates? Relatively how frequently will the system encounter one of the nonequilibrium macrostates? Relatively how frequently will the system spontaneously go through a sequence of nonequilibrium macrostates long enough that there is a measurable fluctuation in its properties?

10. Consider an isolated system immediately after an energy interaction. How likely is it to be in an equilibrium group macrostate?

11. If an isolated system is released from a nonequilibrium macrostate describe its subsequent time trace through the macrostates.

ANSWERS TO SUMMARY QUESTIONS

Students whose answers were equivalent to the following should proceed immediately to evaluation. Incorrect answers will provide a guide to where further study is needed.

1. The energy levels of dependent particles are affected by the instantaneous position or motion of other particles in the system. The energy levels of independent particles are not so affected.

2. Boltzons are distinguishable particles (lattice points in a solid). Bosons and Fermions are indistinguishable particles. Bosons have an even number of subatomic components, Fermions an odd number.

3. Macrostates are allowed distributions over the levels, $n_{j,i}$ that satisfy the constraints on the number of particles and energy. Microstates specify, additionally, in which states the particles reside and in the case of distinguishable particles which particle is in which state.

4. Since each microstate within a given macrostate has the same distribution over the levels, they have the same properties.

Answers continued bottom of next page.

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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

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

---

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.

where ℓ, m = 1,2,3,..., and all possible combinations. These functions can be sketched in three dimensions.[37] The energy levels for a free particle within a rectangular plane are

$$\varepsilon_{\ell,m} = \frac{h^2}{8m^*}\left[\left(\frac{\ell}{L_x}\right)^2 + \left(\frac{m}{L_y}\right)^2\right]$$

Let us consider the first few energy levels, wave functions, and probability distributions for a free particle confined within a plane.

The lowest energy level of this particle corresponds to the set of quantum numbers (1, 1) or ℓ = 1 and m = 1. This particle's wave function is

$$\psi_{1,1}(x,y) = A \sin\left(\frac{\pi x}{L_x}\right) \sin\left(\frac{\pi y}{L_y}\right)$$

and its probability distribution is

$$P_{1,1}(x,y) = A^2 \sin^2\left(\frac{\pi x}{L_x}\right) \sin^2\left(\frac{\pi y}{L_y}\right)$$

Fig. IIIA-A1 shows a sketch of these functions versus x and y. It is seen in the sketch of $P_{1,1}(x,y)/A^2$ that with this lowest energy it is probable that the particle will be at or near the center of the plane.

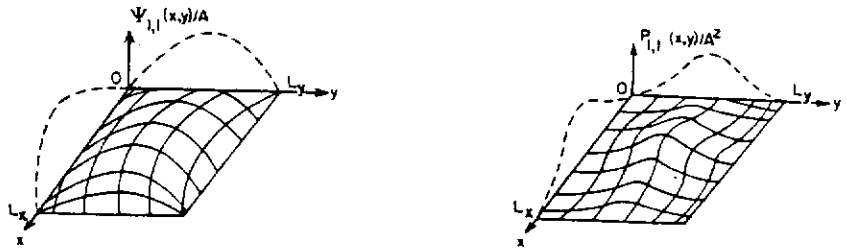

Fig. IIIA-A1. The Wave Function and Probability Distribution for a Particle of Minimum Energy in a Plane

Two higher energy levels for the particle correspond to the quantum number sets, ℓ = 1, m = 2, ℓ = 2, m = 1. For the quantum set (1, 2) the energy is

$$\varepsilon_{1,2} = \frac{h^2}{8m^*}\left[\left(\frac{1}{L_x}\right)^2 + \left(\frac{2}{L_y}\right)^2\right]$$

The wave function and probability distribution for the quantum set (1, 2) are

$$\psi_{1,2}(x,y) = A \sin\left(\frac{\pi x}{L_x}\right) \sin\left(\frac{2\pi y}{L_y}\right)$$

and

$$P_{1,2}(x,y) = A^2 \sin^2\left(\frac{\pi x}{L_x}\right) \sin^2\left(\frac{2\pi y}{L_y}\right)$$

[37]The three-dimensional box would require four-dimensional sketches.

Fig. IIIA-A2 shows these functions for the plane $0 \leq x \leq L_x$, $0 \leq y \leq L_y$.

Exercise A1. Sketch the wave function and probability distribution for the quantum set (2, 1).

An inspection of Fig. IIIA-A2 shows that the probability that the particle will be on the line $y = L_y/2$ is zero.[38] The fact that such lines exist is inconsistent with our macroscopic expectations of particle behavior. It is absurd to think that there are lines on a billiard table upon which we will never observe a billard ball as it moves. To

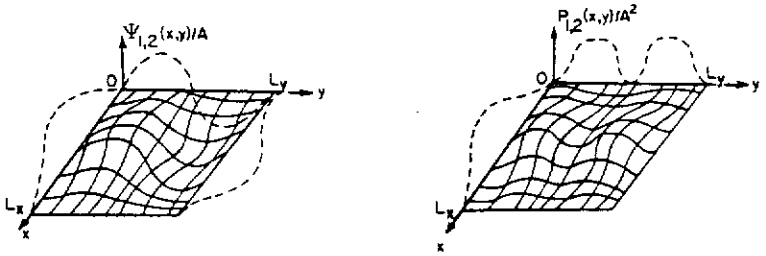

Fig. IIIA-A2. The Wave Function and Probability Distribution for a Particle in State (1, 2) in a Plane

resolve this apparent paradox we must extend the concept of the probability distribution function to particles whose energies are relatively enormous in comparison to the initial energy levels we have pictured. Fig. IIIA-A3 shows that in this limit the probability distribution will resemble an array of infinitesimally small hills distributed over the xy plane. Although these hills are separated by lines of zero probability, they are so close together that one cannot distinguish between the zones of "allowed" particle position and the grid of excluded lines. Thus the effective position probability is uniform over the plane and in the limit of energetic particles, the Quantum Mechanical prediction is consistent with intuition, i.e., the ball is uniformly likely to be anywhere on the table.

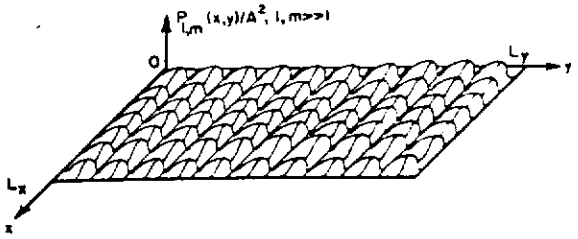

Fig. IIIA-A3. A Representative Probability Distribution for a Particle of "High" Energy Confined Within a Plane

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[38]The line of zero probability does not imply that the particle is trapped on one half. A solution of the unsteady state Schroedinger equation shows that the particle can move across the line.