

Fundamentals of Engineering Physics 2019

Week 11.

* Statistical Physics

IV-1

Ch.2. Basic Probability Concepts

⊗ Statistical Ensembles :

In many cases, the particular outcome resulting from a single experiment cannot be predicted with certainty. Although it's not possible to make statements about a single experiment, it may still be possible to make significant statements about the outcomes of a large number of similar experiments. \longrightarrow "statistical description of the system!"

Instead of focusing attention on the single system "A" of interest, we contemplate an assembly (or **ensemble**) consisting of some very large number N of 'similar' systems.

"Ensemble"

- * Those N systems are 'similar' in the sense that each system satisfies the same conditions known to be satisfied by the system A .
- * Suppose that a particular outcome of the experiment is labeled by " r " and that there are, among the N systems of the ensemble, N_r systems which exhibit this outcome. Then,

$$P_r \equiv \frac{N_r}{N} \quad (\text{as } N \rightarrow \infty) \quad \text{is called} \quad (1)$$

the probability of occurrence of the outcome r .

- * Although the outcome of the experiment on a single system cannot be predicted, the task of a statistical theory is then that of predicting the probability of occurrence of each of the possible outcomes of the experiment.

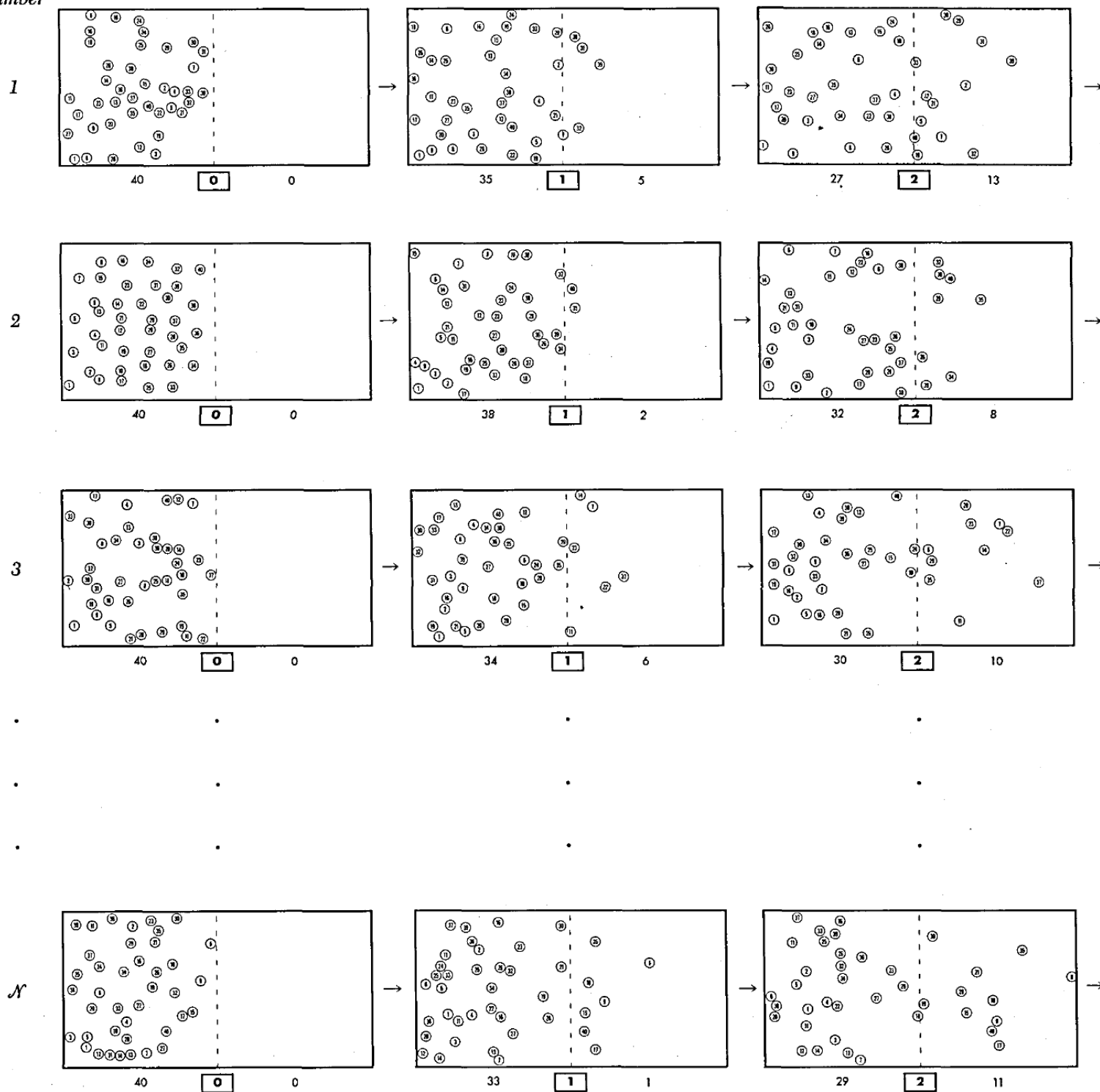


Fig. 2.3 Computer-made pictures showing a statistical ensemble of systems. This ensemble was constructed to represent a system consisting of 40 particles in a box when the information available about the system is the following: All particles are

known to be in the left half of the box at some initial time corresponding to the frame $j \approx 0$, but nothing else is known about their positions or velocities.

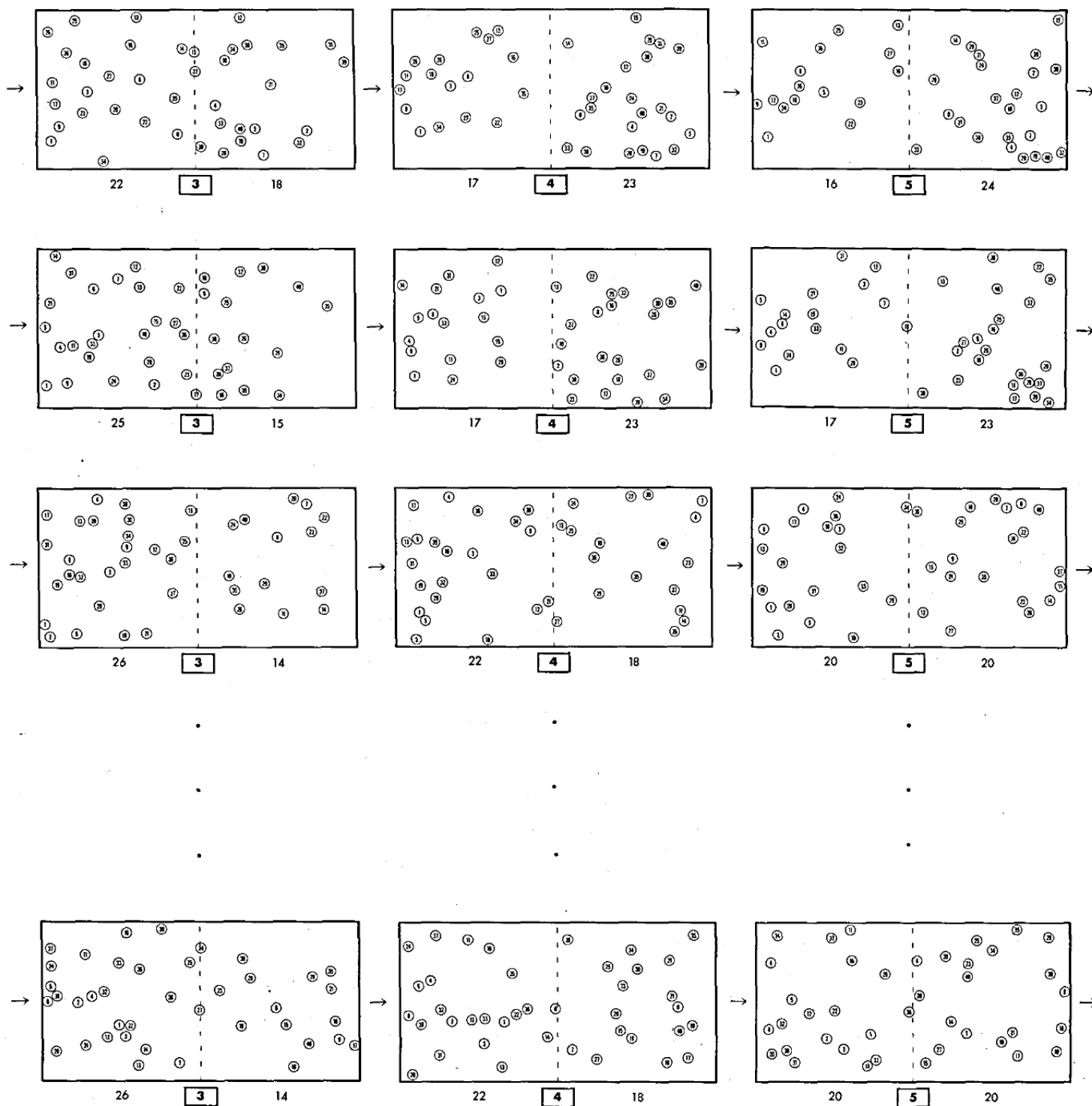


Fig. 2.3 (cont.)

The evolution in time of the k th system in the ensemble can be followed by looking horizontally at the successive frames $j = 0, 1, 2, \dots$ for this system. Statistical statements about the

system at any time corresponding to the j th frame can be made by looking vertically at all the systems in their j th frame and doing the counting necessary to determine probabilities.

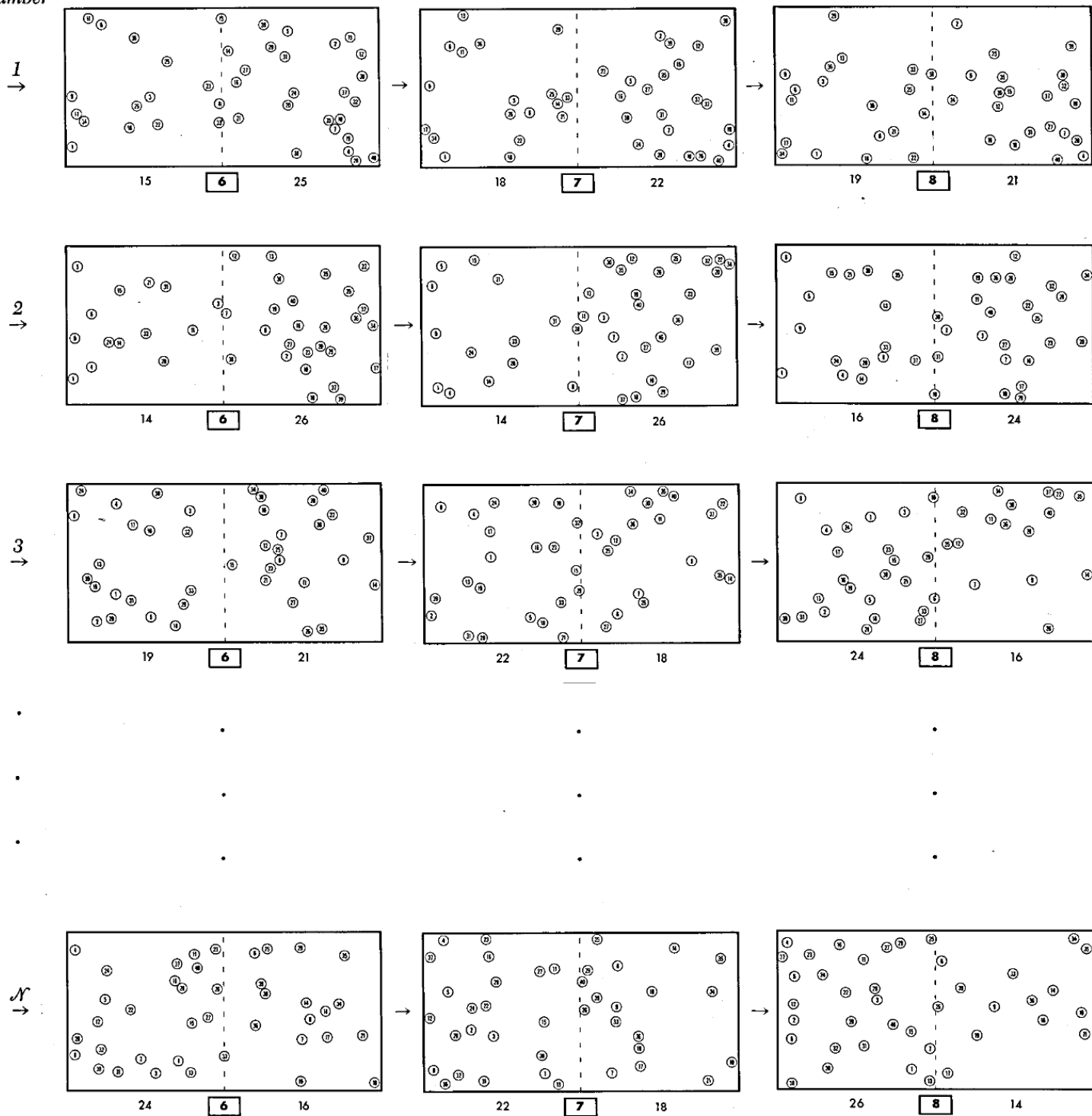


Fig. 2.4 Continuation of Fig. 2.3. The ensemble has by now become time-independent, i.e., the system has attained equilibrium.

Example

Consider an ideal gas of N molecules in a box,

* Initially, at time t_0 , all particles are in the left half of the box.

Let the probability $p(t)$ that a particular ptl is on the left ^{half} at time t :

" $q(t)$: " ^{right half} "

Then, $p(t_0) = 1$ and $q(t_0) = 0$ for any ptl .

* As time goes ~~on~~ on, all these probabilities change until the molecules become uniformly distributed throughout the box so that $p(t) = q(t) \Rightarrow 1/2$.

* Thereafter the probabilities remain unchanged in time, i.e., the ensemble become time-independent and the system has attained equilibrium.

* "An isolated macroscopic system is said to be in equilibrium if a statistical ensemble of such system is time-independent."

Reading Assignment

- * Read "Summary of Definitions" on page 90 and make sure you understand those.

Homework

Problem 2.7 on page 92.

" 2.20 " 97.

Ch. 3. Statistical Description of Systems of Ptls

IV-8

3.1.

In a quantum-mechanical description, the most precise possible measurement on a system always shows this system to be in some ~~one microscopic~~ one of a set of discrete quantum states characteristic of the system.

(*) The microscopic state of a system can thus be described completely by specifying the particular quantum state in which the system is found.

(*) Each quantum state of an isolated system is associated with a definite value of its energy and is called an energy level.

(*) A quantum state of the system with the lowest energy:
Ground State
Other states with higher energies: Excited States.

r	σ	M	E
1	+1	μ_0	$-\mu_0 B$
2	-1	$-\mu_0$	$+\mu_0 B$

Table 3.1 Quantum states of a single spin $\frac{1}{2}$ having a magnetic moment μ_0 and located in a magnetic field \mathbf{B} . Each state of the system can be labeled by an index r , or alternatively, by the quantum number σ . The magnetic moment (along the “up” direction specified by the field \mathbf{B}) is denoted by M ; the total energy of the system is denoted by E .

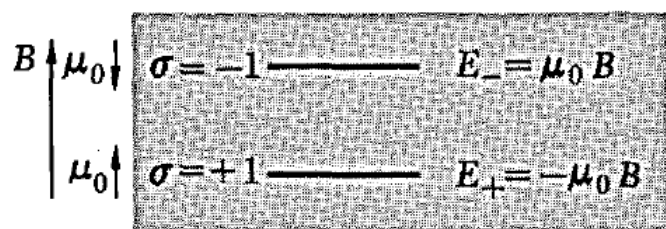


Fig. 3.2 Diagram showing the two energy levels of a spin $\frac{1}{2}$ having a magnetic moment μ_0 and located in a magnetic field \mathbf{B} . The state where the magnetic moment points “up,” so that its direction is parallel to \mathbf{B} , is denoted by $\sigma = +1$ (or simply by $+$); that where it points “down” is denoted by $\sigma = -1$ (or simply by $-$).

(i) Single spin

Consider a single particle, assumed to be fixed in position, which has spin $\frac{1}{2}$ and a magnetic moment of magnitude μ_0 . As already discussed in Sec. 1.3, this moment will be found to point either “up” or “down” (i.e., parallel or antiparallel) with respect to any specified direction. The system consisting of this single spin thus has only two quantum states which we shall label by a *quantum number* σ . We can then denote the state where the magnetic moment of the particle points up by $\sigma = +1$, and the state where it points down by $\sigma = -1$.

If the particle is in the presence of a magnetic field \mathbf{B} , this field specifies the

direction of physical interest in the problem. The energy E of the system then is lower when the magnetic moment is aligned parallel to the field rather than antiparallel to it. The situation is analogous to that of a bar magnet located in an external magnetic field. Thus, when the magnetic moment points up (i.e., parallel to the field \mathbf{B}), its magnetic energy is simply $-\mu_0 B$. Conversely, when the moment points down (i.e., antiparallel to the field \mathbf{B}), its magnetic energy is simply $\mu_0 B$. The two quantum states (or energy levels) of the system then correspond to different energies.

† The hydrogen atom is likely to be a familiar example of a system described in terms of discrete energy levels. Transitions of the atom between states of different energy give rise to the sharp spectral lines emitted by the atom. A description in terms of energy levels is, of course, equally applicable to any atom, molecule, or system consisting of many atoms.

‡ In some cases there may be a relatively small number of quantum states of the same energy equal to the lowest possible energy of the system. The ground state of the system is then said to be *degenerate*.

(ii) Ideal system of N spins

Consider a system consisting of N particles, assumed to be fixed in position, where each particle has spin $\frac{1}{2}$ and a magnetic moment μ_0 . The system is located in an applied magnetic field \mathbf{B} . The interaction between the particles is assumed to be almost negligible.†

The magnetic moment of each particle can point either up or down with respect to the field \mathbf{B} . The orientation of the i th moment can thus be specified by the value of its quantum number σ_i so that $\sigma_i = +1$ when this moment points up and $\sigma_i = -1$ when it points down. A particular state of the whole system can then be specified by stating the orientation of

each of the N moments, i.e., by specifying the values assumed by the set of quantum numbers $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$. Thus one can enumerate, and label by some index r , all the possible states of the whole system. This is done in Table 3.2 for the special case where $N = 4$. The total magnetic moment of the system is simply equal to the sum of the magnetic moments of the individual spins. Since the interaction between these spins is almost negligible, the total energy E of the system is also simply equal to the sum of the energies of the individual spins.

(iii) Particle in a one-dimensional box

Consider a single particle, of mass m , free to move in one dimension. The particle is supposed to be confined within a box of length L , so that the particle's position coordinate x must lie in the range $0 \leq x \leq L$. Within this box the particle is subject to no forces.

In a quantum-mechanical description, the particle has wave properties associated with it. The particle confined within the box and bouncing back and forth between its walls is thus represented by a wave function ψ in the form of a standing wave whose amplitude must vanish at the boundaries of the box (since ψ itself must vanish outside the box).‡ The wave function thus must be of the form

$$\psi(x) = A \sin Kx \quad (1)$$

(where A and K are constants) and must satisfy the boundary conditions

$$\psi(0) = 0 \quad \text{and} \quad \psi(L) = 0. \quad (2)$$

The expression (1) obviously satisfies the condition $\psi(0) = 0$. In order that it also satisfy the condition $\psi(L) = 0$, the constant K must be such that

$$KL = \pi n$$

or

$$K = \frac{\pi}{L} n, \quad (3)$$

where n can assume any of the integral values§

$$n = 1, 2, 3, 4, \dots \quad (4)$$

r	σ_1	σ_2	σ_3	σ_4	M	E
1	+	+	+	+	$4\mu_0$	$-4\mu_0 B$
2	+	+	+	-	$2\mu_0$	$-2\mu_0 B$
3	+	+	-	+	$2\mu_0$	$-2\mu_0 B$
4	+	-	+	+	$2\mu_0$	$-2\mu_0 B$
5	-	+	+	+	$2\mu_0$	$-2\mu_0 B$
6	+	+	-	-	0	0
7	+	-	+	-	0	0
8	+	-	-	+	0	0
9	-	+	+	-	0	0
10	-	+	-	+	0	0
11	-	-	+	+	0	0
12	+	-	-	-	$-2\mu_0$	$2\mu_0 B$
13	-	+	-	-	$-2\mu_0$	$2\mu_0 B$
14	-	-	+	-	$-2\mu_0$	$2\mu_0 B$
15	-	-	-	+	$-2\mu_0$	$2\mu_0 B$
16	-	-	-	-	$-4\mu_0$	$4\mu_0 B$

Table 3.2 Quantum states of an ideal system of 4 spins $\frac{1}{2}$, each having a magnetic moment μ_0 and located in a magnetic field \mathbf{B} . Each quantum state of the whole system is labeled by the index r , or equivalently, by the set of 4 numbers $\{\sigma_1, \sigma_2, \sigma_3, \sigma_4\}$. For the sake of brevity, the symbol $+$ indicates $\sigma = +1$ and the symbol $-$ indicates $\sigma = -1$. The total magnetic moment (along the “up” direction specified by \mathbf{B}) is denoted by M ; the total energy of the system is denoted by E .

The constant K in (1) is the *wave number* associated with the particle; it is related to the wavelength λ (the so-called *de Broglie wavelength* associated with the particle) by the relation

$$K = \frac{2\pi}{\lambda}. \quad (5)$$

Hence (3) is equivalent to

$$L = n \frac{\lambda}{2}$$

and represents merely the familiar condition that standing waves are obtained when the length of the box is equal to some integral multiple of half-wave-lengths.

The momentum p of the particle is related to K (or λ) by the famous de Broglie relation

$$p = \hbar K = \frac{h}{\lambda} \quad (6)$$

where $\hbar \equiv h/2\pi$ and h is Planck's constant. The energy E of the particle is simply its kinetic energy, since there is no potential energy due to external forces. Hence E can be expressed in terms of the velocity v or momentum $p = mv$ of the particle as

$$E = \frac{1}{2}mv^2 = \frac{1}{2} \frac{p^2}{m} = \frac{\hbar^2 K^2}{2m}. \quad (7)$$

The possible values (3) of K then yield the corresponding energies

$$E = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} n \right)^2 = \frac{\pi^2 \hbar^2}{2m} \frac{n^2}{L^2}. \quad (8)$$

Equivalently, we could have discussed the whole problem from a more mathematical point of view by starting from the fundamental Schrödinger equation for the wave function ψ . For a free particle in one dimension this equation is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi.$$

The functional form (1) satisfies this equation provided that the energy E is related to K by (7). The condition (2) that the wave function must vanish at the boundaries of the box leads again to (3) and hence to the expression (8) for the energy.

The possible quantum states of the particle in the box thus can be specified by the possible values (4) of the quantum number n . The corresponding discrete energies of these states (i.e., the corresponding energy levels of the particle) are then given by (8).

The relation (8) shows that the separation in energy between successive quantum states of the particle is very small if the length L of the box is of macroscopic size. The lowest possible energy of the particle, i.e., its ground-state energy, corresponds to the state $n = 1$. Note that this ground-state energy does not vanish.†

The wave function of the particle now represents a standing wave in three dimensions. Thus it is of the form

$$\psi = A(\sin K_x x)(\sin K_y y)(\sin K_z z) \quad (9)$$

where the constants K_x, K_y, K_z can be regarded as the three components of a vector \mathbf{K} , the *wave vector* of the particle. According to the de Broglie relation the momentum of the particle is then given by

$$\mathbf{p} = \hbar \mathbf{K} \quad (10)$$

so that the relationship between the magnitude of p and the magnitude of K (or the wavelength λ) is the same as in (6). The energy of the particle is then given by

$$\begin{aligned} E &= \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2 \mathbf{K}^2}{2m} \\ &= \frac{\hbar^2}{2m} (K_x^2 + K_y^2 + K_z^2). \end{aligned} \quad (11)$$

Equivalently, it can be immediately verified that ψ in (9) is indeed a solution of the time-independent Schrödinger equation for a free particle in three dimensions,

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

provided that E is related to \mathbf{K} by (11).

The fact that ψ must vanish at the boundaries of the box imposes the conditions that

$\psi = 0$ at the planes

$$\left. \begin{aligned} x &= 0, & y &= 0, & z &= 0, \\ x &= L_x, & y &= L_y, & z &= L_z. \end{aligned} \right\} \quad (12)$$

The expression (9) vanishes properly when $x = 0$, $y = 0$, or $z = 0$. To make it vanish for $x = L_x$, $y = L_y$, or $z = L_z$, the constants K_x, K_y, K_z must satisfy the respective conditions

$$K_x = \frac{\pi}{L_x} n_x, \quad K_y = \frac{\pi}{L_y} n_y, \quad K_z = \frac{\pi}{L_z} n_z, \quad (13)$$

where each of the numbers n_x, n_y , and n_z can assume any of the positive integral values

$$n_x, n_y, n_z = 1, 2, 3, 4, \dots \quad (14)$$

Any particular quantum state of the particle can then be designated by the values assumed by the set of quantum numbers $\{n_x, n_y, n_z\}$. Its corresponding energy is, by (11) and (13), equal to

$$E = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right). \quad (15)$$

Ideal Gas of N particles in a box

- * Consider a system consisting of N ptls confined within the box,
 - Interaction between ptls is negligible \rightarrow ideal gas.

* Total Energy:
$$E = \epsilon_1 + \epsilon_2 + \dots + \epsilon_i + \dots + \epsilon_N$$

energy of ptl 1, 2, ..., i , ..., N

- ⊛ Since the state of each such ptl can be specified by the values of its 3 quantum numbers n_{ix} , n_{iy} , and n_{iz} , each possible quantum state of the entire gas can be specified by the values assumed by the $3N$ quantum numbers

$$\{ n_{1x}, n_{1y}, n_{1z}; n_{2x}, n_{2y}, n_{2z}; \dots; n_{Nx}, n_{Ny}, n_{Nz} \}$$

- ⊗ Each possible quantum state of a system can be specified by some set of f quantum numbers. This number f , called the number of degrees of freedom of the system, is equal to the number of independent coordinates (including spin coordinates).

The microscopic state of a system can be described by specifying the particular quantum state r in which the system is found.