where we have used Stirling's formula since N is large. Here the factor $N!$ corresponds simply to the number of possible permutations of the particles, permutations which are physically meaningless when the particles are identical. It was precisely this factor which we had to introduce in an *ad hoc* fashion in Sec. 7·3 to save ourselves from the nonphysical consequences of the Gibbs paradox. What we have done in this section is to justify the whole discussion of Sec. 7·3 as being appropriate for a gas treated properly by quantum mechanics in the limit of sufficiently low concentration or high temperature. The partition function is automatically correctly evaluated by (9·8·9), there is no Gibbs paradox, and everything is consistent.

A gas in the classical limit where (9·8·6) is satisfied is said to be "nondegenerate." On the other hand, if the concentration and temperature are such that the actual FD or BE distribution (9·8·1) must be used, the gas is said to be "degenerate."

IDEAL GAS IN THE CLASSICAL LIMIT

9·9 *Quantum states of a single particle*

Wave function To complete the discussion of the statistical problem it is necessary to enumerate the possible quantum states s and corresponding energies ϵ_s of a single noninteracting particle. Consider this particle to be nonrelativistic and denote its mass by m, its position vector by $\mathbf{r}$, and its momentum by $\mathbf{p}$. Suppose that the particle is confined within a container of volume V within which the particle is subject to no forces. Neglecting for the time being the effect of the bounding walls, the wave function $\Psi(\mathbf{r},t)$ of the particle is then simply described by a plane wave of the form

$$\Psi = Ae^{i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)} = \psi(\mathbf{r})\, e^{-i\omega t} \tag{9·9·1}$$

which propagates in a direction specified by the "wave vector" $\boldsymbol{\kappa}$ and which has some constant amplitude A. Here the energy ϵ of the particle is related to the frequency ω by

$$\epsilon = \hbar\omega \tag{9·9·2}$$

while its momentum is related to its wave vector $\boldsymbol{\kappa}$ by the de Broglie relation

$$\mathbf{p} = \hbar\boldsymbol{\kappa} \tag{9·9·3}$$

Thus one has

$$\epsilon = \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2\kappa^2}{2m} \tag{9·9·4}$$

The basic justification for these statements is, of course, the fact that Ψ must satisfy the Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \mathcal{H}\Psi \tag{9·9·5}$$

Since one can choose the potential energy to be zero inside the container, the Hamiltonian $\mathcal{H}$ reduces there to the kinetic energy alone; i.e.,

$$\mathcal{H} = \frac{1}{2m}p^2 = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla\right)^2 = -\frac{\hbar^2}{2m}\nabla^2$$

where $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Putting $$\Psi = \psi\, e^{-i\omega t} = \psi\, e^{-(i/\hbar)\epsilon t} \qquad (9\cdot 9\cdot 6)$$

where ψ does not depend on time, (9·9·5) reduces to the time-independent Schrödinger equation

$$\mathcal{H}\psi = \epsilon\psi \qquad (9\cdot 9\cdot 7)$$

or $$\nabla^2\psi + \frac{2m\epsilon}{\hbar^2}\psi = 0 \qquad (9\cdot 9\cdot 8)$$

Equation (9·9·7) shows that ϵ corresponds to the possible values of $\mathcal{H}$ and is thus the energy of the particle. The wave equation (9·9·8) has solutions of the general form

$$\psi = A\, e^{i(\kappa_x x + \kappa_y y + \kappa_z z)} = A\, e^{i\boldsymbol{\kappa}\cdot\mathbf{r}} \qquad (9\cdot 9\cdot 9)$$

where $\boldsymbol{\kappa}$ is the constant "wave vector" with components κ_x, κ_y, κ_z. By substitution of (9·9·9) into (9·9·8) one finds that the latter equation is satisfied if

$$-(\kappa_x^2 + \kappa_y^2 + \kappa_z^2) + \frac{2m\epsilon}{\hbar^2} = 0$$

Thus $$\epsilon = \frac{\hbar^2\kappa^2}{2m} \qquad (9\cdot 9\cdot 10)$$

and ϵ is only a function of the magnitude $\kappa \equiv |\boldsymbol{\kappa}|$ of $\boldsymbol{\kappa}$. Since

$$\mathbf{p}\psi = \frac{\hbar}{i}\nabla\psi = \hbar\boldsymbol{\kappa}\psi$$

one obtains then the relations (9·9·3) and (9·9·4).

Up to now we have considered only the translational degrees of freedom. If the particle also has an intrinsic spin angular momentum, the situation is scarcely more complicated; there is then simply a different function ψ for each possible orientation of the particle spin. For example, if the particle has spin $\frac{1}{2}$ (e.g., if it is an electron), then there are two possible wave functions $\psi_\pm$ corresponding to the two possible values $m = \pm\frac{1}{2}$ of the quantum number specifying the orientation of the particle's spin angular momentum.

Boundary conditions and enumeration of states The wave function ψ must satisfy certain boundary conditions. Accordingly, not all possible values of $\boldsymbol{\kappa}$ (or $\mathbf{p}$) are allowed, but only certain discrete values. The corresponding energies of the particle are then also quantized by virtue of (9·9·4).

The boundary conditions can be treated in a very general and simple way in the usual situation where the container enclosing the gas of particles is large enough that its smallest linear dimension L is much greater than the de Broglie wavelength $\lambda = 2\pi/|\boldsymbol{\kappa}|$ of the particle under consideration.* It is then physically clear that the detailed properties of the bounding walls of the container (e.g., their shape or the nature of the material of which they are made) must become of negligible significance in describing the behavior of a particle located well within the container.† To make the argument more precise, let us consider any macroscopic volume element which is large compared to λ and which lies well within the container so that it is everywhere removed from the container walls by distances large compared to λ. The actual wave function anywhere within the container can always be written as a superposition of plane waves $(9 \cdot 9 \cdot 1)$ with all possible wave vectors $\boldsymbol{\kappa}$. Hence one can regard the volume element under consideration as being traversed by waves of the form $(9 \cdot 9 \cdot 1)$ traveling in all possible directions specified by $\boldsymbol{\kappa}$, and with all possible wavelengths related to the magnitude of $\boldsymbol{\kappa}$. Since the container walls are far away (compared to λ), it does not really matter just how each such wave is ultimately reflected from these walls, or which wave gets reflected how many times before it passes again through the volume element under consideration. The number of waves of each kind traversing this volume element should be quite insensitive to any such details which describe what happens near the container walls and should be substantially unaffected if the shape or properties of these walls are modified. Indeed, it is simplest if one imagines these walls moved out to infinity, i.e., if one effectively eliminates the walls altogether. One can then avoid the necessity of treating the problem of reflections at the walls, a problem which is really immaterial in describing the situation in the volume element under consideration. It does not matter whether a given wave enters this volume element after having been reflected somewhere far away, or after coming in from infinity without ever having been reflected at all.

The foregoing comments show that, for purposes of discussing the properties of a gas anywhere but in the immediate vicinity of the container walls, the exact nature of the boundary conditions imposed on each particle should be unimportant. One can therefore formulate the problem in a way which makes these boundary conditions as simple as possible. Let us therefore choose the basic volume V of gas under consideration to be in the shape of a rectangular parallelepiped with edges parallel to the x, y, z axes and with respective edge lengths equal to L_x, L_y, L_z. Thus $V = L_x L_y L_z$. The simplest boundary conditions to impose are such that a traveling wave of the form $(9 \cdot 9 \cdot 1)$ is indeed an exact solution of the problem. This requires that the wave $(9 \cdot 9 \cdot 1)$ be able to propagate indefinitely without suffering any reflections. In order to make the boundary conditions consistent with this simple situation, one can neglect

* This condition is ordinarily very well satisfied for essentially all molecules of a gas since a typical order of magnitude, already estimated in Sec. 7·4, is $\lambda \approx 1$ Å for an atom of thermal energy at room temperature.

† Note that the fraction of particles near the surface of the container, i.e., within a distance λ of its walls, is of the order of $\lambda L^2/L^3 = \lambda/L$ and is thus ordinarily utterly negligible for a macroscopic container.

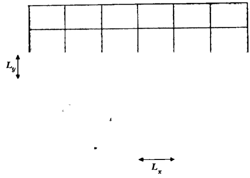

Fig. 9·9·1 The volume under consideration (indicated in darker gray) is here considered embedded in an array of similar volumes extending throughout all space. Wall effects are thus effectively eliminated.

completely the presence of any container walls and can imagine that the volume of gas under consideration is embedded in an infinite set of similar volumes in each of which the physical situation is exactly the same (see Fig. 9·9·1). The wave function must then satisfy the conditions

$$\left.\begin{aligned} \psi(x + L_x, y, z) &= \psi(x,y,z) \\ \psi(x, y + L_y, z) &= \psi(x,y,z) \\ \psi(x, y, z + L_z) &= \psi(x,y,z) \end{aligned}\right\} \qquad (9\cdot 9\cdot 11)$$

The requirement that the wave function be the same in any of the parallelepipeds should not affect the physics of interest in the one volume under consideration if its dimensions are large compared to the de Broglie wavelength λ of the particle.

Remark Suppose that the problem were one-dimensional so that a particle moves in the x direction in a container of length L_x. Then one can eliminate the effects of reflections by imagining the container to be bent around in the form of a circle as shown in Fig. 9·9·2. If L_x is very large, the curvature is quite negligible so that the situation inside the container is substantially the same as before. But the advantage is that there are now no container walls to worry about. Hence traveling waves described by (9·9·1) and going around without reflection are perfectly good solutions of the problem. It is only necessary to note that the points x and $x + L_x$ are now coincident; the requirement that the wave function be single-valued implies the condition

$$\psi(x + L_x) = \psi(x) \qquad (9\cdot 9\cdot 12)$$

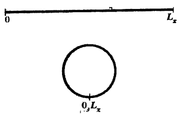

Fig. 9·9·2 A one-dimensional container of length L_x bent into a circle by joining its ends.

This is precisely the analog of (9·9·11) in one dimension. Indeed, one could regard the condition (9·9·11) as resulting from the attempt to eliminate reflections in three dimensions by imagining the original parallelepiped to be bent into a doughnut in four dimensions. (This is, admittedly, difficult to visualize.)

This point of view, which describes the situation in terms of simple traveling waves satisfying the periodic boundary conditions (9·9·11), is very convenient and mathematically exceedingly easy. By virtue of (9·9·1) or (9·9·9)

$$\psi = e^{i\boldsymbol{\kappa}\cdot\mathbf{r}} = e^{i(\kappa_x x + \kappa_y y + \kappa_z z)}$$

To satisfy (9·9·11) one must require that

$$\kappa_x(x + L_x) = \kappa_x x + 2\pi n_x \qquad (n_x \text{ integral})$$

or

$$\left.\begin{aligned} \kappa_x &= \frac{2\pi}{L_x} n_x \\ \text{Similarly,} \quad \kappa_y &= \frac{2\pi}{L_y} n_y \\ \text{and} \quad \kappa_z &= \frac{2\pi}{L_z} n_z \end{aligned}\right\} \qquad (9\cdot 9\cdot 13)$$

Here the numbers n_x, n_y, n_z are *any* set of integers—positive, negative, or zero.

The components of $\boldsymbol{\kappa} = \mathbf{p}/\hbar$ are thus quantized in discrete units. Accordingly (9·9·4) yields the possible quantized particle energies

$$\epsilon = \frac{\hbar^2}{2m}(\kappa_x^2 + \kappa_y^2 + \kappa_z^2) = \frac{2\pi^2\hbar^2}{m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \qquad (9\cdot 9\cdot 14)$$

Note that for any kind of macroscopic volume where L_x, L_y, L_z are large, the possible values of the wave-vector components given by (9·9·13) are very closely spaced. There are thus very many states of the particle (i.e., very many possible integers n_x) corresponding to any small range $d\kappa_x$ of a wave-vector component. It is easy to do some counting. For given values of κ_y and κ_z, it follows by (9·9·13) that the number Δn_x of possible integers n_x for which κ_x lies in the range between κ_x and $\kappa_x + d\kappa_x$ is equal to

$$\Delta n_x = \frac{L_x}{2\pi} d\kappa_x \qquad (9\cdot 9\cdot 15)$$

The number of translational states $\rho(\boldsymbol{\kappa})\, d^3\boldsymbol{\kappa}$ for which $\boldsymbol{\kappa}$ is such that it lies in the range between $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa} + d\boldsymbol{\kappa}$ (i.e., in the range such that its x component is between κ_x and $\kappa_x + d\kappa_x$, its y component between κ_y and $\kappa_y + d\kappa_y$, and its z component between κ_z and $\kappa_z + d\kappa_z$) is then given by the product of the numbers of possible integers in the three component ranges. Thus

$$\rho\, d^3\boldsymbol{\kappa} = \Delta n_x\, \Delta n_y\, \Delta n_z = \left(\frac{L_x}{2\pi} d\kappa_x\right)\left(\frac{L_y}{2\pi} d\kappa_y\right)\left(\frac{L_z}{2\pi} d\kappa_z\right) = \frac{L_x L_y L_z}{(2\pi)^3}\, d\kappa_x\, d\kappa_y\, d\kappa_z$$

or

$$\rho\, d^3\kappa = \frac{V}{(2\pi)^3}\, d^3\kappa \tag{9·9·16}$$

where $d^3\kappa \equiv d\kappa_x\, d\kappa_y\, d\kappa_z$ is the element of volume in "κ space." Note that the density of states ρ is independent of κ and proportional to the volume V under consideration; i.e., the number of states *per unit volume*, with a wave number κ (or momentum $p = \hbar\kappa$) lying in some given range, is a constant independent of the magnitude or shape of the volume.

Remark Note that (9·9·3) yields for the number of translational states $\rho_p\, d^3p$ in the momentum range between p and $p + dp$ the expression

$$\rho_p\, d^3p = \rho\, d^3\kappa = \frac{V}{(2\pi)^3}\frac{d^3p}{\hbar^3} = V\frac{d^3p}{h^3} \tag{9·9·17}$$

where $h = 2\pi\hbar$ is the ordinary Planck's constant. Now $V\, d^3p$ is the volume of the classical six-dimensional phase space occupied by a particle in a box of volume V and with momentum between p and $p + dp$. Thus (9·9·17) shows that subdivision of this phase space into cells of size h^3 yields the correct number of quantum states for the particle.

Various other relations can be deduced from the result (9·9·16). For example, let us find the number of translational states $\rho_\kappa\, d\kappa$ for which κ is such that its magnitude $|\kappa|$ lies in the range between κ and $\kappa + d\kappa$. This is obtained by summing (9·9·16) over all values of κ in this range, i.e., over the volume in κ space of the portion of spherical shell lying between radii κ and $\kappa + d\kappa$. Thus

$$\rho_\kappa\, d\kappa = \frac{V}{(2\pi)^3}(4\pi\kappa^2\, d\kappa) = \frac{V}{2\pi^2}\kappa^2\, d\kappa \tag{9·9·18}$$

Remark Since ϵ depends only on $\kappa = |\kappa|$, (9·9·18) gives immediately, corresponding to this range of κ, the corresponding number of translational states $\rho_\epsilon\, d\epsilon$ for which the energy of the particle lies between ϵ and $\epsilon + d\epsilon$. From the equality of states one has

$$|\rho_\epsilon\, d\epsilon| = |\rho_\kappa\, d\kappa| = \rho_\kappa \left|\frac{d\kappa}{d\epsilon}\right| d\epsilon = \rho_\kappa \left|\frac{d\epsilon}{d\kappa}\right|^{-1} d\epsilon$$

By (9·9·4) one then obtains

$$\rho_\epsilon\, d\epsilon = \frac{V}{2\pi^2}\kappa^2 \left|\frac{d\kappa}{d\epsilon}\right| d\epsilon = \frac{V}{4\pi^2}\frac{(2m)^{\frac{3}{2}}}{\hbar^3}\epsilon^{\frac{1}{2}}\, d\epsilon \tag{9·9·19}$$

Alternative discussion It is, of course, possible to adopt a slightly more complicated point of view which does take into account explicitly reflections occurring at the walls of the container. Since the exact boundary conditions are immaterial let us, for simplicity, assume that the container is in the shape of a rectangular parallelepiped with walls located at $x = 0$ and $x = L_x$, $y = 0$ and $y = L_y$, and $z = 0$ and $z = L_z$. Let us further assume that these walls are perfectly reflecting, i.e., that the potential energy U of the particle equals $U = 0$ inside the box and $U = \infty$ outside the box. Then the wave function ψ must satisfy the requirement that

$$\psi = 0 \qquad \begin{cases} \text{whenever } x = 0 \text{ or } L_x \\ \qquad\quad\; y = 0 \text{ or } L_y \\ \qquad\quad\; z = 0 \text{ or } L_z \end{cases} \tag{9·9·20}$$

The *particular* solution $\psi = e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}$ of (9·9·9) represents a traveling wave and does *not* satisfy the boundary conditions (9·9·20). But one can construct suitable linear combinations of (9·9·9) (all of which automatically also satisfy the Schrödinger equation (9·9·8)) which do satisfy the boundary conditions (9·9·20). What this means physically is that in this box with perfectly reflecting parallel walls standing waves are set up which result from the superposition of traveling waves propagating back and forth.* Mathematically, since $e^{i\kappa_x x}$ is a solution of (9·9·8), so is $e^{-i\kappa_x x}$. The combination

$$(e^{i\kappa_x x} - e^{-i\kappa_x x}) \propto \sin \kappa_x x \tag{9·9·21}$$

vanishes properly when $x = 0$. It can also be made to vanish for $x = L_x$, provided one chooses κ_x so that

$$\kappa_x L_x = \pi n_x$$

where n_x is any integer. Here the possible values n_x should be restricted to the positive set

$$n_x = 1, 2, 3, \ldots$$

since a sign reversal of n_x (or κ_x) just turns the function (9·9·20) into

$$\sin(-\kappa_x)x = -\sin \kappa_x x$$

which is not a distinct new wave function. Thus a standing wave solution is specified completely by $|\kappa_x|$.

Forming standing waves analogous to (9·9·21) also for the y and z directions, one obtains the product wave function

$$\psi = A(\sin \kappa_x x)(\sin \kappa_y y)(\sin \kappa_z z) \tag{9·9·22}$$

where A is some constant. This satisfies the Schrödinger equation (9·9·8) and also the boundary conditions (9·9·20) provided that

$$\kappa_x = \frac{\pi}{L_x} n_x, \qquad \kappa_y = \frac{\pi}{L_y} n_y, \qquad \kappa_z = \frac{\pi}{L_z} n_z \tag{9·9·23}$$

* Simple standing waves of the form (9·9·21) would not be set up if the walls of the container were not exactly parallel. Hence our previous discussion in terms of traveling waves criss-crossing the volume in all directions, in a manner insensitive to the precise boundary conditions, affords a more convenient and general point of view.

where n_x, n_y, n_z are any *positive* integers. The possible energies of the particle are then given by

$$\epsilon = \frac{\hbar^2}{2m}\kappa^2 = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

For given values of κ_y and κ_z, the number of translational states with κ_x in the range between κ_x and $\kappa_x + d\kappa_x$ is now equal to

$$\Delta n_x = \frac{L_x}{\pi}\,d\kappa_x \tag{9·9·24}$$

The number of translational states with $\mathbf{\kappa}$ in the range between $\mathbf{\kappa}$ and $\mathbf{\kappa} + d\mathbf{\kappa}$ is then given by

$$\rho\, d^3\mathbf{\kappa} = \Delta n_x\, \Delta n_y\, \Delta n_z = \left(\frac{L_x}{\pi}\,d\kappa_x\right)\left(\frac{L_y}{\pi}\,d\kappa_y\right)\left(\frac{L_z}{\pi}\,d\kappa_z\right)$$

or

$$\rho\, d^3\mathbf{\kappa} = \frac{V}{\pi^3}\,d^3\mathbf{\kappa} \tag{9·9·25}$$

The number of translational states $\rho_\kappa\, d\kappa$ for which $\mathbf{\kappa}$ is such that its *magnitude* lies in the range between κ and $\kappa + d\kappa$ is obtained by summing (9 9·25) over all values of $\mathbf{\kappa}$ in this range, i.e., over the volume in $\mathbf{\kappa}$ space of the portion of spherical shell lying between radii κ and $\kappa + d\kappa$ *and* located in the first octant where $\kappa_x, \kappa_y, \kappa_z > 0$ so as to satisfy (9·9 23). Thus (9·9·25) yields

$$\rho_\kappa\, d\kappa = \frac{V}{\pi^3}\left(\frac{4\pi\kappa^2\, d\kappa}{8}\right) = \frac{V}{2\pi^2}\,\kappa^2\, d\kappa \tag{9·9·26}$$

This is the *same* result as was obtained in (9·9 18). The reason is simple. By (9·9·24) there are, compared to (9·9·15), twice as many states lying in a given interval $d\kappa_x$, but since only positive values of κ_x are now to be counted, the number of such intervals is decreased by a compensating factor of 2.

By (9·9·26) it also follows that $\rho_\epsilon\, d\epsilon$ is the same as in (9 9 19). This just illustrates the result (which can also be established by rather elaborate general mathematical arguments)* that this density of states should be the same irrespective of the shape of the container or of the exact boundary conditions imposed on its surface, so long as the de Broglie wavelength of the particle is small compared to the dimensions of the container.

9 · 10 *Evaluation of the partition function*

We are now ready to calculate the partition function Z of a monatomic ideal gas in the classical limit of sufficiently low density or sufficiently high temperature. By (9·8 9) one has

$$\ln Z = N(\ln \zeta - \ln N + 1) \tag{9·10 1}$$

where

$$\zeta \equiv \sum_r e^{-\beta\epsilon_r} \tag{9 10·2}$$

* See, for example, R. Courant and D. Hilbert, "Methods of Mathematical Physics," vol. I, pp. 429–445, Interscience Publishers, New York, 1953.