and

$$H = E + PV = G + TS. \tag{16}$$

The specific heat at constant volume, C_V, and the one at constant pressure, C_P, would be given by

$$C_V \equiv T \left(\frac{\partial S}{\partial T} \right)_{N,V} = \left(\frac{\partial E}{\partial T} \right)_{N,V} \tag{17}$$

and

$$C_P \equiv T \left(\frac{\partial S}{\partial T} \right)_{N,P} = \left(\frac{\partial (E + PV)}{\partial T} \right)_{N,P} = \left(\frac{\partial H}{\partial T} \right)_{N,P}. \tag{18}$$

1.4 The classical ideal gas

To illustrate the approach developed in the preceding sections, we shall now derive the various thermodynamic properties of a classical ideal gas composed of monatomic molecules. The main reason why we choose this highly specialized system for consideration is that it affords an explicit, though asymptotic, evaluation of the number $\Omega(N, V, E)$. This example becomes all the more instructive when we find that its study enables us, in a most straightforward manner, to identify the Boltzmann constant k in terms of other physical constants; see equation (3). Moreover, the behavior of this system serves as a useful reference with which the behavior of other physical systems, especially real gases (with or without quantum effects), can be compared. And, indeed, in the limit of high temperatures and low densities the ideal-gas behavior becomes typical of most real systems.

Before undertaking a detailed study of this case it appears worthwhile to make a remark that applies to all *classical* systems composed of *noninteracting* particles, irrespective of the internal structure of the particles. This remark is related to the explicit dependence of the number $\Omega(N, V, E)$ on V and hence to the *equation of state* of these systems. Now, if there do not exist any spatial correlations among the particles, that is, if the probability of any one of them being found in a particular region of the available space is completely independent of the location of the other particles,[9] then the total number of ways in which the N particles can be spatially distributed in the system will be simply equal to the product of the numbers of ways in which the individual particles can be accommodated in the same space independently of one another. With N and E fixed, each of these numbers will be directly proportional to V, the volume of the container; accordingly, the total number of ways will be directly proportional to the Nth power of V:

$$\Omega(N, E, V) \propto V^N. \tag{1}$$

[9]This will be true if (i) the mutual interactions among particles are negligible, and (ii) the wave packets of individual particles do not significantly overlap (or, in other words, the quantum effects are also negligible).

Combined with equations (1.3.9) and (1.3.10), this gives

$$\frac{P}{T} = k\left(\frac{\partial \ln \Omega(N,E,V)}{\partial V}\right)_{N,E} = k\frac{N}{V}. \tag{2}$$

If the system contains n moles of the gas, then $N = nN_A$, where N_A is the *Avogadro number*. Equation (2) then becomes

$$PV = NkT = nRT \quad (R = kN_A), \tag{3}$$

which is the famous *ideal-gas law*, R being the *gas constant* per mole. Thus, for any classical system composed of noninteracting particles the ideal-gas law holds.

For deriving other thermodynamic properties of this system, we require a detailed knowledge of the way Ω depends on the parameters N, V, and E. The problem essentially reduces to determining the total number of ways in which equations (1.1.1) and (1.1.2) can be mutually satisfied. In other words, we have to determine the total number of (independent) ways of satisfying the equation

$$\sum_{r=1}^{3N} \varepsilon_r = E, \tag{4}$$

where ε_r are the energies associated with the various degrees of freedom of the N particles. The reason why this number should depend on the parameters N and E is quite obvious. Nevertheless, this number also depends on the "spectrum of values" that the variables ε_r can assume; it is through this spectrum that the dependence on V comes in. Now, the energy eigenvalues for a *free, nonrelativistic* particle confined to a cubical box of side L ($V = L^3$), under the condition that the wave function $\psi(r)$ vanishes everywhere on the boundary, are given by

$$\varepsilon(n_x, n_y, n_z) = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2); \quad n_x, n_y, n_z = 1, 2, 3, \ldots, \tag{5}$$

where h is Planck's constant and m the mass of the particle. The number of distinct eigenfunctions (or microstates) for a particle of energy ε would, therefore, be equal to the number of independent, positive-integral solutions of the equation

$$\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{8mV^{2/3}\varepsilon}{h^2} = \varepsilon^*. \tag{6}$$

We may denote this number by $\Omega(1, \varepsilon, V)$. Extending the argument, it follows that the desired number $\Omega(N, E, V)$ would be equal to the number of independent, positive-integral solutions of the equation

$$\sum_{r=1}^{3N} n_r^2 = \frac{8mV^{2/3}E}{h^2} = E^*, \quad \text{say.} \tag{7}$$

An important result follows straightforwardly from equation (7), even before the number $\Omega(N,E,V)$ is explicitly evaluated. From the nature of the expression appearing on the right side of this equation, we conclude that the volume V and the energy E of the system enter into the expression for Ω in the form of the combination $(V^{2/3}E)$. Consequently,

$$S(N,V,E) \equiv S\left(N, V^{2/3}E\right). \tag{8}$$

Hence, for the constancy of S and N, which defines a *reversible adiabatic* process,

$$V^{2/3}E = \text{const.} \tag{9}$$

Equation (1.3.11) then gives

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = \frac{2}{3}\frac{E}{V}, \tag{10}$$

that is, the pressure of a system of nonrelativistic, noninteracting particles is precisely equal to two-thirds of its energy density.[10] It should be noted here that, since an explicit computation of the number Ω has not yet been done, results (9) and (10) hold for *quantum* as well as *classical* statistics; equally general is the result obtained by combining these, namely

$$PV^{5/3} = \text{const.}, \tag{11}$$

which tells us how P varies with V during a *reversible adiabatic* process.

We shall now attempt to evaluate the number Ω. In this evaluation we shall explicitly assume the particles to be *distinguishable,* so that if a particle in state i gets interchanged with a particle in state j the resulting microstate is counted as distinct. Consequently, the number $\Omega(N,V,E)$, or better $\Omega_N(E^*)$ (see equation (7)), is equal to the number of positive-integral lattice points lying on the surface of a $3N$-dimensional sphere of radius $\sqrt{E^*}$.[11] Clearly, this number will be an extremely irregular function of E^*, in that for two given values of E^* that may be very close to one another, the values of this number could be very different. In contrast, the number $\Sigma_N(E^*)$, which denotes the number of positive-integral lattice points lying *on or within* the surface of a $3N$-dimensional sphere of radius $\sqrt{E^*}$, will be much less irregular. In terms of our physical problem, this would correspond to the number, $\Sigma(N,V,E)$, of microstates of the given system consistent with *all* macrostates characterized by the specified values of the parameters N and V but having energy *less*

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[10]Combining (10) with (2), we obtain for the classical ideal gas: $E = \frac{3}{2}NkT$. Accordingly, equation (9) reduces to the well-known thermodynamic relationship: $V^{\gamma-1}T = \text{const.}$, which holds during a *reversible adiabatic* process, with $\gamma = \frac{5}{3}$.

[11]If the particles are regarded as *indistinguishable,* the evaluation of the number Ω by counting lattice points becomes quite intricate. The problem is then solved by having recourse to the theory of "partitions of numbers"; see Auluck and Kothari (1946).

than or equal to E; that is,

$$\Sigma(N, V, E) = \sum_{E' \leq E} \Omega(N, V, E') \tag{12}$$

or

$$\Sigma_N(E^*) = \sum_{E^{*'} \leq E^*} \Omega_N(E^{*'}). \tag{13}$$

Of course, the number Σ will also be somewhat irregular; however, we expect that its asymptotic behavior, as $E^* \to \infty$, will be a lot smoother than that of Ω. We shall see in the sequel that the thermodynamics of the system follows equally well from the number Σ as from Ω.

To appreciate the point made here, let us digress a little to examine the behavior of the numbers $\Omega_1(\varepsilon^*)$ and $\Sigma_1(\varepsilon^*)$, which correspond to the case of a single particle confined to the given volume V. The *exact* values of these numbers, for $\varepsilon^* \leq 10,000$, can be extracted from a table compiled by Gupta (1947). The wild irregularities of the number $\Omega_1(\varepsilon^*)$ can hardly be missed. The number $\Sigma_1(\varepsilon^*)$, on the other hand, exhibits a much smoother asymptotic behavior. From the geometry of the problem, we note that, *asymptotically*, $\Sigma_1(\varepsilon^*)$ should be equal to the volume of an octant of a three-dimensional sphere of radius $\sqrt{\varepsilon^*}$, that is,

$$\lim_{\varepsilon^* \to \infty} \frac{\Sigma_1(\varepsilon^*)}{(\pi/6)\varepsilon^{*3/2}} = 1. \tag{14}$$

A more detailed analysis shows that, to the next approximation (see Pathria, 1966),

$$\Sigma_1(\varepsilon^*) \approx \frac{\pi}{6}\varepsilon^{*3/2} - \frac{3\pi}{8}\varepsilon^*; \tag{15}$$

the correction term arises from the fact that the volume of an octant somewhat overestimates the number of desired lattice points, for it includes, partly though, some points with one or more coordinates equal to zero. Figure 1.2 shows a histogram of the actual values of $\Sigma_1(\varepsilon^*)$ for ε^* lying between 200 and 300; the theoretical estimate (15) is also shown. In the figure, we have also included a histogram of the actual values of the corresponding number of microstates, $\Sigma_1'(\varepsilon^*)$, when the quantum numbers n_x, n_y, and n_z can assume the value zero as well. In the latter case, the volume of an octant somewhat underestimates the number of desired lattice points; we now have

$$\Sigma_1'(\varepsilon^*) \approx \frac{\pi}{6}\varepsilon^{*3/2} + \frac{3\pi}{8}\varepsilon^*. \tag{16}$$

Asymptotically, however, the number $\Sigma_1'(\varepsilon^*)$ also satisfies equation (14).

Returning to the N-particle problem, the number $\Sigma_N(E^*)$ should be *asymptotically* equal to the "volume" of the "positive compartment" of a $3N$-dimensional sphere of
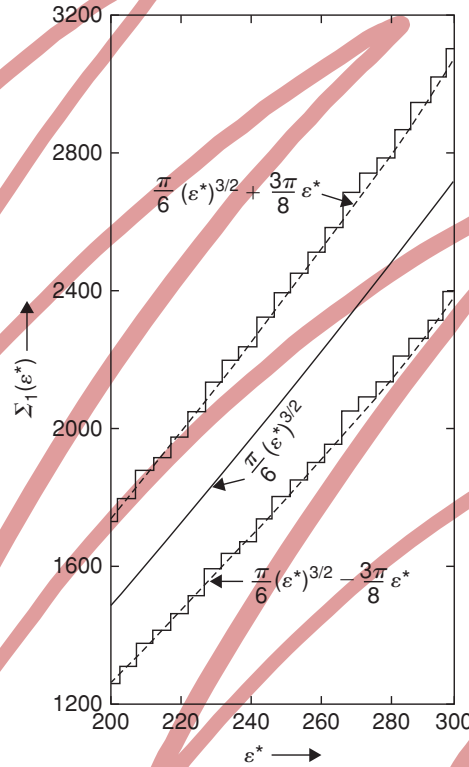
FIGURE 1.2 Histograms showing the actual number of microstates available to a particle in a cubical enclosure; the lower histogram corresponds to the so-called Dirichlet boundary conditions, while the upper one corresponds to the Neumann boundary conditions (see Appendix A). The corresponding theoretical estimates, (15) and (16), are shown by dashed lines; the customary estimate, equation (14), is shown by a solid line.

radius $\sqrt{E^*}$. Referring to equation (C.7a) of Appendix C, we obtain

$$\Sigma_N(E^*) \approx \left(\frac{1}{2}\right)^{3N} \left\{ \frac{\pi^{3N/2}}{(3N/2)!} E^{*3N/2} \right\}$$

which, on substitution for E^*, gives

$$\Sigma(N,V,E) \approx \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. \tag{17}$$

Taking logarithms and applying Stirling's formula, (B.29) in Appendix B,

$$\ln(n!) \approx n\ln n - n \quad (n \gg 1), \tag{18}$$

we get

$$\ln \Sigma(N,V,E) \approx N \ln \left[\frac{V}{h^3} \left(\frac{4\pi mE}{3N} \right)^{3/2} \right] + \frac{3}{2}N. \tag{19}$$

For deriving the thermodynamic properties of the given system we must somehow fix the precise value of, or limits for, the energy of the system. In view of the extremely irregular nature of the function $\Omega(N,V,E)$, the specification of a precise value for the energy of the system cannot be justified on physical grounds, for that would never yield well-behaved expressions for the thermodynamic functions of the system. From a practical point of view, too, an absolutely isolated system is too much of an idealization. In the real world, almost every system has some contact with its surroundings, however little it may be; as a result, its energy cannot be defined sharply.[12] Of course, the effective width of the range over which the energy may vary would, in general, be small in comparison with the mean value of the energy. Let us specify this range by the limits $\left(E - \frac{1}{2}\Delta \right)$ and $\left(E + \frac{1}{2}\Delta \right)$ where, by assumption, $\Delta \ll E$; typically, $\Delta/E = O(1/\sqrt{N})$. The corresponding number of microstates, $\Gamma(N,V,E;\Delta)$, is then given by

$$\Gamma(N,V,E;\Delta) \simeq \frac{\partial \Sigma(N,V,E)}{\partial E} \Delta \approx \frac{3N}{2} \frac{\Delta}{E} \Sigma(N,V,E), \tag{17a}$$

which gives

$$\ln \Gamma(N,V,E;\Delta) \approx N \ln \left[\frac{V}{h^3} \left(\frac{4\pi mE}{3N} \right)^{3/2} \right] + \frac{3}{2}N + \left\{ \ln \left(\frac{3N}{2} \right) + \ln \left(\frac{\Delta}{E} \right) \right\}. \tag{19a}$$

Now, for $N \gg 1$, the first term in the curly bracket is negligible in comparison with any of the terms outside this bracket, for $\lim_{N \to \infty} (\ln N)/N = 0$. Furthermore, for any reasonable value of Δ/E, the same is true of the second term in this bracket.[13] Hence, for all practical purposes,

$$\ln \Omega \simeq \ln \Gamma \approx \ln \Sigma \approx N \ln \left[\frac{V}{h^3} \left(\frac{4\pi mE}{3N} \right)^{3/2} \right] + \frac{3}{2}N. \tag{20}$$

We thus arrive at the baffling result that, for all practical purposes, the actual width of the range allowed for the energy of the system does not make much difference; the energy could lie between $\left(E - \frac{1}{2}\Delta \right)$ and $\left(E + \frac{1}{2}\Delta \right)$ or equally well between 0 and E. The reason underlying this situation is that the rate at which the number of microstates of the system

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[12]Actually, the very act of making measurements on a system brings about, inevitably, a contact between the system and its surroundings.

[13]It should be clear that, while Δ/E is much less than 1, it must not tend to 0, for that would make $\Gamma \to 0$ and $\ln \Gamma \to -\infty$. A situation of that kind would be too artificial and would have nothing to do with reality. Actually, in most physical systems, $\Delta/E = O(N^{-1/2})$, whereby $\ln(\Delta/E)$ becomes of order $\ln N$, which again is negligible in comparison with the terms outside the curly bracket.

increases with energy is so fantastic, see equation (17), that even if we allow *all* values of energy between zero and a particular value E, it is only the "immediate neighborhood" of E that makes an overwhelmingly dominant contribution to this number! And since we are finally concerned only with the logarithm of this number, even the "width" of that neighborhood is inconsequential!

The stage is now set for deriving the thermodynamics of our system. First of all, we have

$$S(N,V,E) = k \ln \Gamma = Nk \ln \left[\frac{V}{h^3} \left(\frac{4\pi mE}{3N} \right)^{3/2} \right] + \frac{3}{2} Nk, \qquad (21)^{[14]}$$

which can be inverted to give

$$E(S,V,N) = \frac{3h^2 N}{4\pi m V^{2/3}} \exp\left(\frac{2S}{3Nk} - 1 \right). \qquad (22)$$

The temperature of the gas then follows with the help of formula (1.3.10) or (1.3.13), which leads to the energy–temperature relationship

$$E = N\left(\frac{3}{2} kT \right) = n\left(\frac{3}{2} RT \right), \qquad (23)$$

where n is the number of moles of the gas. The specific heat at constant volume now follows with the help of formula (1.3.17):

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} Nk = \frac{3}{2} nR. \qquad (24)$$

For the equation of state, we obtain

$$P = -\left(\frac{\partial E}{\partial V} \right)_{N,S} = \frac{2}{3} \frac{E}{V}, \qquad (25)$$

which agrees with our earlier result (10). Combined with (23), this gives

$$P = \frac{NkT}{V} \quad \text{or} \quad PV = nRT, \qquad (26)$$

which is the same as (3). The specific heat at constant pressure is given by, see (1.3.18),

$$C_P = \left(\frac{\partial (E+PV)}{\partial T} \right)_{N,P} = \frac{5}{2} nR, \qquad (27)$$

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[14]Henceforth, we shall replace the sign $\approx$, which characterizes the *asymptotic* character of a relationship, by the sign of equality because for most physical systems the asymptotic results are as good as exact.

so that, for the ratio of the two specific heats, we have

$$\gamma = C_P/C_V = \frac{5}{3}. \tag{28}$$

Now, suppose that the gas undergoes an *isothermal* change of state ($T = $ const. and $N = $ const.); then, according to (23), the total energy of the gas would remain constant while, according to (26), its pressure would vary inversely with volume (Boyle's law). The change in the entropy of the gas, between the initial state i and the final state f, would then be, see equation (21),

$$S_f - S_i = Nk \ln(V_f/V_i). \tag{29}$$

On the other hand, if the gas undergoes a *reversible adiabatic* change of state ($S = $ const. and $N = $ const.), then, according to (22) and (23), both E and T would vary as $V^{-2/3}$; so, according to (25) or (26), P would vary as $V^{-5/3}$. These results agree with the conventional thermodynamic ones, namely

$$PV^\gamma = \text{const.} \quad \text{and} \quad TV^{\gamma-1} = \text{const.,} \tag{30}$$

with $\gamma = \frac{5}{3}$. It may be noted that, thermodynamically, the change in E during an adiabatic process arises solely from the external work done by the gas on the surroundings or vice versa:

$$(dE)_{\text{adiab}} = -PdV = -\frac{2E}{3V}dV; \tag{31}$$

see equations (1.3.4) and (25). The dependence of E on V follows readily from this relationship.

The considerations of this section have clearly demonstrated the manner in which the thermodynamics of a macroscopic system can be derived from the multiplicity of its microstates (as represented by the number Ω or Γ or Σ). The whole problem then hinges on an asymptotic enumeration of these numbers, which unfortunately is tractable only in a few idealized cases, such as the one considered in this section; see also Problems 1.7 and 1.8. Even in an idealized case like this, there remains an inadequacy that could not be detected in the derivations made so far; this relates to the *explicit* dependence of S on N. The discussion of the next section is intended not only to bring out this inadequacy but also to provide the necessary remedy for it.

1.5 The entropy of mixing and the Gibbs paradox

One thing we readily observe from expression (1.4.21) is that, contrary to what is logically desired, the entropy of an ideal gas, as given by this expression, is *not* an extensive