CHAPTER 2

ELEMENTS OF ENSEMBLE THEORY

In THE preceding chapter we noted that, for a given *macrostate* (N, V, E), a statistical system, at any time t, is equally likely to be in any one of an extremely large number of distinct *microstates*. As time passes, the system continually switches from one microstate to another, with the result that, over a reasonable span of time, all one observes is a behavior "averaged" over the variety of microstates through which the system passes. It may, therefore, make sense if we consider, at a *single* instant of time, a rather large number of systems–all being some sort of "mental copies" of the given system–which are characterized by the same macrostate as the original system but are, naturally enough, in all sorts of possible microstates. Then, under ordinary circumstances, we may expect that the average behavior of any system in this collection, which we call an *ensemble*, would be identical with the time-averaged behavior of the given system. It is on the basis of this expectation that we proceed to develop the so-called *ensemble theory*.

For classical systems, the most appropriate workshop for developing the desired formalism is the *phase space*. Accordingly, we begin our study of the various ensembles with an analysis of the basic features of this space.

2.1. Phase space of a classical system

The microstate of a given classical system, at any time t, may be defined by specifying the *instantaneous* positions and momenta of all the particles constituting the system. Thus, if N is the number of particles in the system, the definition of a microstate requires the specification of $3N$ position coordinates $q_1, q_2, \ldots, q_{3N}$ and $3N$ momentum coordinates $p_1, p_2, \ldots, p_{3N}$. Geometrically, the set of coordinates (q_i, p_i), where $i = 1, 2, \ldots, 3N$, may be regarded as a point in a space of $6N$ dimensions. We refer to this space as the *phase space*, and the phase point (q_i, p_i) as a *representative point*, of the given system.

Of course, the coordinates q_i and p_i are functions of the time t; the precise manner in which they vary with t is determined by the canonical equations of motion,

$$\left.\begin{aligned}\dot{q}_i &= \frac{\partial H(q_i, p_i)}{\partial p_i}\\ \dot{p}_i &= -\frac{\partial H(q_i, p_i)}{\partial q_i}\end{aligned}\right\} \quad i = 1, 2, \ldots, 3N, \tag{1}$$

where $H(q_i, p_i)$ is the *Hamiltonian* of the system. Now, as time passes, the set of coordinates (q_i, p_i), which also defines the microstate of the system, undergoes a continual change. Correspondingly, our representative point in the phase space carves out a *trajectory* whose direction, at any time t, is determined by the *velocity vector* $\boldsymbol{v} \equiv (\dot{q}_i, \dot{p}_i)$, which in turn is given by the equations of motion (1). It is not difficult to see that the trajectory of the representative point must remain within a limited region of the phase space; this is so because a finite volume V directly limits the values of the coordinates q_i, while a finite energy E limits the values of both the q_i and the p_i [through the Hamiltonian $H(q_i, p_i)$]. In particular, if the total energy of the system is known to have a *precise* value, say E, the corresponding trajectory will be restricted to the "hypersurface"

$$H(q_i, p_i) = E \tag{2}$$

of the phase space; on the other hand, if the total energy may lie anywhere in the range $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$, the corresponding trajectory will be restricted to the "hypershell" defined by these limits.

Now, if we consider an ensemble of systems (i.e. the given system, along with a large number of mental copies of it) then, at any time t, the various members of the ensemble will be in all sorts of possible microstates; indeed, each one of these microstates must be consistent with the given macrostate which is supposed to be common to all members of the ensemble. In the phase space, the corresponding picture will consist of a swarm of representative points, one for each member of the ensemble, all lying within the "allowed" region of this space. As time passes, every member of the ensemble undergoes a continual change of microstates; correspondingly, the representative points constituting the swarm continually move along their respective trajectories. The overall picture of this movement possesses some important features which are best illustrated in terms of what we call a *density function* $\rho(q, p; t)$. This function is such that, at any time t, the number of representative points in the "volume element" $(d^{3N}q\, d^{3N}p)$ around the point (q, p) of the phase space is given by the product $\rho(q, p; t)\, d^{3N}q\, d^{3N}p$.[1] Clearly, the density function $\rho(q, p; t)$ symbolizes the manner in which the members of the ensemble are distributed over all possible microstates at different instants of time. Accordingly, the *ensemble average* $\langle f \rangle$ of a given physical quantity $f(q, p)$, which may be different for systems in different microstates, would be given by

$$\langle f \rangle = \frac{\int f(q, p)\rho(q, p; t)\, d^{3N}q\, d^{3N}p}{\int \rho(q, p; t)\, d^{3N}q\, d^{3N}p}. \tag{3}$$

The integrations in (3) extend over the whole of the phase space; however, it is only the populated regions of the phase space ($\rho \neq 0$) that really contribute. We note that, in general, the ensemble average $\langle f \rangle$ may itself be a function of time.

An ensemble is said to be *stationary* if ρ does not depend explicitly on time, i.e. at all times

$$\frac{\partial \rho}{\partial t} = 0. \tag{4}$$

Clearly, for such an ensemble the average value $\langle f \rangle$ of *any* physical quantity $f(q, p)$ will be independent of time. Naturally, a stationary ensemble qualifies to represent a system in *equilibrium*. To determine the circumstances under which eqn. (4) may hold, we have to make a rather detailed study of the movement of the representative points in the phase space.

2.2. Liouville's theorem and its consequences

Consider an arbitrary "volume" ω in the relevant region of the phase space and let the "surface" enclosing this volume be denoted by σ; see Fig. 2.1. Then, the rate at which the number of representative points in this volume increases with time is written as

$$\frac{\partial}{\partial t} \int_{\omega} \rho \, d\omega, \tag{1}$$

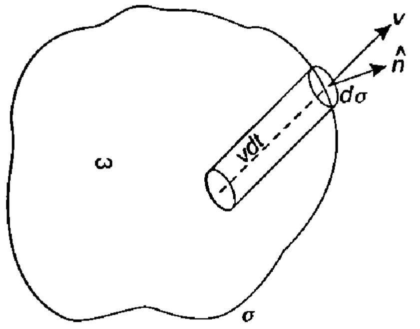

FIG. 2.1. The "hydrodynamics" of the representative points in the phase space.

where $d\omega \equiv (d^{3N}q \, d^{3N}p)$. On the other hand, the *net* rate at which the representative points "flow" out of ω (across the bounding surface σ) is given by

$$\int_{\sigma} \rho(\boldsymbol{v} \cdot \hat{\boldsymbol{n}}) \, d\sigma; \tag{2}$$

here, $\boldsymbol{v}$ is the velocity vector of the representative points in the region of the surface element $d\sigma$ while $\hat{\boldsymbol{n}}$ is the (outward) unit vector normal to this element. By the divergence theorem, (2) can be written as

$$\int_{\omega} \operatorname{div}(\rho \boldsymbol{v}) \, d\omega; \tag{3}$$

of course, the operation of divergence here means the following:

$$\operatorname{div}(\rho \boldsymbol{v}) \equiv \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho \dot{p}_i) \right\}. \tag{4}$$

In view of fact that there are no "sources" or "sinks" in the phase space and hence the total number of representative points remains conserved,[2] we have, by (1) and (3),

$$\frac{\partial}{\partial t}\int_{\omega} \rho \, d\omega = -\int_{\omega} \operatorname{div}(\rho \boldsymbol{v}) \, d\omega, \tag{5}$$

that is,

$$\int_{\omega} \left\{ \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{v}) \right\} d\omega = 0. \tag{6}$$

Now, the necessary and sufficient condition that integral (6) vanish for all arbitrary volumes ω is that the integrand itself vanish *everywhere* in the relevant region of the phase space. Thus, we must have

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{v}) = 0, \tag{7}$$

which is the *equation of continuity* for the swarm of the representative points.

Combining (4) and (7), we obtain

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) + \rho \sum_{i=1}^{3N} \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = 0. \tag{8}$$

The last group of terms vanishes identically because, by the equations of motion, we have, for all i,

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H(q_i, p_i)}{\partial q_i \partial p_i} \equiv \frac{\partial^2 H(q_i, p_i)}{\partial p_i \partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}. \tag{9}$$

Further, since $\rho \equiv \rho(q_i, p_i; t)$, the remaining terms in (8) may be combined to form the "total" time derivative of ρ, with the result that

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0. \tag{10}$$ [3]

Equation (10) embodies the so-called *Liouville's theorem* (1838). According to this theorem, the "local" density of the representative points, *as viewed by an observer moving with a representative point*, stays constant in time. Thus, the swarm of the representative points moves in the phase space in essentially the same manner as an incompressible fluid moves in the physical space!

A distinction must be made, however, between eqn. (10) on one hand and eqn. (2.1.4) on the other. While the former derives from the basic mechanics of the particles and is therefore *quite generally* true, the latter is only a requirement for equilibrium which, in a given case, may or may not be satisfied. The condition that ensures simultaneous validity of the two equations is clearly

$$[\rho, H] = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0. \tag{11}$$

Now, one possible way of satisfying (11) is to assume that ρ, which is already assumed to have no explicit dependence on time, is *independent* of the coordinates (q, p) as well, i.e.

$$\rho(q, p) = \text{const.} \tag{12}$$

over the relevant region of the phase space (and, of course, is zero everywhere else). Physically, this choice corresponds to an ensemble of systems which at *all* times are *uniformly* distributed over all possible microstates. The ensemble average (2.1.3) then reduces to

$$\langle f \rangle = \frac{1}{\omega} \int_{\omega} f(q, p)\, d\omega; \tag{13}$$

here, ω denotes the total "volume" of the relevant region of the phase space. Clearly, in this case, *any* member of the ensemble is equally likely to be in *any* one of the various possible microstates, inasmuch as *any* representative point in the swarm is equally likely to be in the neighborhood of *any* phase point in the allowed region of the phase space. This statement is usually referred to as the postulate of "equal *a priori* probabilities" for the various possible microstates (or for the various volume elements in the allowed region of the phase space); the resulting ensemble is referred to as the *microcanonical ensemble.*

A more general way of satisfying (11) is to assume that the dependence of ρ on (q, p) comes only through an explicit dependence on the Hamiltonian $H(q, p)$, i.e.

$$\rho(q, p) = \rho[H(q, p)]; \tag{14}$$

condition (11) is then identically satisfied. Equation (14) provides a class of density functions for which the corresponding ensemble is stationary. In Chap. 3 we shall see that the most natural choice in this class of ensembles is the one for which

$$\rho(q, p) \propto \exp[-H(q, p)/kT]. \tag{15}$$

The ensemble so defined is referred to as the *canonical ensemble.*

2.3. The microcanonical ensemble

In this ensemble the macrostate of a system is defined by the number of molecules N, the volume V and the energy E. However, in view of the considerations expressed in Sec. 1.4, we may prefer to specify a range of energy values, say from $(E - \frac{1}{2}\Delta)$ to $(E + \frac{1}{2}\Delta)$, rather than a sharply defined value E. With the macrostate specified, a choice still remains for the systems of the ensemble to be in *any one* of a large number of possible microstates. In the phase space, correspondingly, the representative points of the ensemble have a choice to lie *anywhere* within a "hypershell" defined by the condition

$$\left(E - \tfrac{1}{2}\Delta\right) \le H(q, p) \le \left(E + \tfrac{1}{2}\Delta\right) \tag{1}$$

The volume of the phase space enclosed within this shell is given by

$$\omega = \int' d\omega \equiv \int' (d^{3N}q\, d^{3N}p), \tag{2}$$

where the primed integration extends only over that part of the phase space which conforms to condition (1). It is clear that ω will [illegible] function of the parameters N, V, E and Δ.

Now, the microcanonical ensemble is a collection of systems for which the density function ρ is, at all times, given by

$$\left.\begin{array}{lll}\rho(q, p) = \text{const.} & \text{if } (E - \frac{1}{2}\Delta) \le H(q, p) \le (E + \frac{1}{2}\Delta) \\ \quad 0 & \text{otherwise}\end{array}\right\}. \tag{3}$$

Accordingly, the expectation value of the number of representative points lying in a volume element $d\omega$ of the relevant hypershell is simply proportional to $d\omega$. In other words, the *a priori* probability of finding a representative point in a given volume element $d\omega$ is the same as that of finding a representative point in an equivalent volume element $d\omega$ located *anywhere* in the hypershell. In our original parlance, this means an equal *a priori* probability for a given member of the ensemble to be in *any one* of the various possible microstates. In view of these considerations, the ensemble average $\langle f \rangle$, as given by eqn. (2.2.13), acquires a simple physical meaning. To see this, we proceed as follows.

Since the ensemble under study is a stationary one, the ensemble average of any physical quantity f will be independent of time; accordingly, taking a time average thereof will not produce any new result. Thus

$$\begin{aligned}\langle f \rangle &\equiv \text{ the ensemble average of } f \\ &= \text{the time average of (the ensemble average of } f).\end{aligned}$$

Now, the processes of time averaging and ensemble averaging are completely independent, so the order in which they are performed may be reversed without causing any change in the value of $\langle f \rangle$. Thus

$$\langle f \rangle = \text{ the ensemble average of (the time average of } f).$$

Now, the time average of any physical quantity, taken over a sufficiently long interval of time, must be the same for *every* member of the ensemble, for after all we are dealing with only *mental copies* of a given system.[4] Therefore, taking an ensemble average thereof should be inconsequential, and we may write

$$\langle f \rangle = \text{ the long-time average of } f,$$

where the latter may be taken over *any* member of the ensemble. Furthermore, the long-time average of a physical quantity is all one obtains by making a measurement of that quantity on the given system; therefore, it may be identified with the value one expects to obtain through experiment. Thus, we finally have

$$\langle f \rangle = f_{\text{exp}}. \tag{4}$$

This brings us to the most important result: *the ensemble average of any physical quantity f is identical with the value one expects to obtain on making an appropriate measurement on the given system.*

The next thing we look for is the establishment of a connection between the mechanics of the microcanonical ensemble and the thermodynamics of the member systems. To do this, we observe that there exists a direct correspondence between the various microstates of the given system and the various locations in the phase space. The volume ω (of the allowed region of the phase space) is, therefore, a direct measure of the multiplicity Γ of the microstates accessible to the system.

To establish a numerical correspondence between ω and Γ, we need to discover a *fundamental volume* ω_0 which could be regarded as "equivalent to one microstate". Once this is done, we may say that, asymptotically,

$$\Gamma = \omega/\omega_0. \tag{5}$$

The thermodynamics of the system would then follow in the same way as in Secs 1.2–1.4, viz. through the relationship

$$S = k \ln \Gamma = k \ln (\omega/\omega_0), \quad \text{etc.} \tag{6}$$

The basic problem then consists in determining ω_0. From dimensional considerations, see (2), ω_0 must be in the nature of an "angular momentum raised to the power $3N$". To determine it exactly, we consider certain simplified systems, both from the point of view of the phase space and from the point of view of the distribution of quantum states.

2.4. Examples

We consider, first of all, the problem of a classical ideal gas composed of monatomic particles; see Sec. 1.4. In the microcanonical ensemble, the volume ω of the phase space accessible to the representative points of the (member) systems is given by

$$\omega = \int' \ldots \int' (d^{3N}q\, d^{3N}p), \tag{1}$$

where the integrations are restricted by the conditions that (i) the particles of the system are confined in physical space to volume V, and (ii) the total energy of the system lies between the limits $(E - \frac{1}{2}\Delta)$ and $(E + \frac{1}{2}\Delta)$. Since the Hamiltonian in this case is a function of the p_i alone, integrations over the q_i can be carried out straightforwardly; these give a factor of V^N. The remaining integral is

$$\underset{\left(E-\frac{1}{2}\Delta\right) \le \sum_{i=1}^{3N}(p_i^2/2m) \le \left(E+\frac{1}{2}\Delta\right)}{\int \cdots \int} d^{3N}p = \underset{2m\left(E-\frac{1}{2}\Delta\right) \le \sum_{i=1}^{3N} y_i^2 \le 2m\left(E+\frac{1}{2}\Delta\right)}{\int \cdots \int} d^{3N}y,$$

which is equal to the volume of a $3N$-dimensional hypershell, bounded by hyperspheres of radii

$$\sqrt{[2m(E + \tfrac{1}{2}\Delta)]} \quad \text{and} \quad \sqrt{[2m(E - \tfrac{1}{2}\Delta)]}.$$

For $\Delta \ll E$, this is given by the thickness of the shell, which is almost equal to $\Delta(m/2E)^{1/2}$, multiplied by the surface area of a $3N$-dimensional hypersphere of radius $\sqrt{(2mE)}$. By eqn. (7) of Appendix C, we obtain for this integral

$$\Delta\left(\frac{m}{2E}\right)^{1/2}\left\{\frac{2\pi^{3N/2}}{[(3N/2)-1]!}(2mE)^{(3N-1)/2}\right\},$$

whence

$$\omega \simeq \frac{\Delta}{E} V^N \frac{(2\pi mE)^{3N/2}}{[(3N/2)-1]!}. \tag{2}$$

Comparing (2) with (1.4.17, 17a), we obtain the desired correspondence, viz.

$$(\omega/\Gamma)_{\text{asymp}} \equiv \omega_0 = h^{3N};$$

see also Problem 2.9. Quite generally, if the system under study has N' degrees of freedom, the desired conversion factor is

$$\omega_0 = h^{N'}. \tag{3}$$

In the case of a single particle, $N' = 3$; accordingly, the number of microstates available would asymptotically be equal to the volume of the allowed region of the phase space divided by h^3. Let $\Sigma(P)$ denote the number of microstates available to a free particle confined to volume V of the physical space, its momentum p being less than or equal to a specified value P. Then

$$\Sigma(P) \approx \frac{1}{h^3}\underset{p\le P}{\int\cdots\int}(d^3q\,d^3p) = \frac{V}{h^3}\frac{4\pi}{3}P^3, \tag{4}$$

whence we obtain for the number of microstates with momentum lying between p and $p + dp$

$$g(p)\,dp = \frac{d\Sigma(p)}{dp}\,dp \approx \frac{V}{h^3}4\pi p^2\,dp. \tag{5}$$

Expressed in terms of the particle energy, these expressions assume the form

$$\Sigma(E) \approx \frac{V}{h^3}\frac{4\pi}{3}(2mE)^{3/2} \tag{6}$$

and

$$a(\varepsilon)\,d\varepsilon = \frac{d\Sigma(\varepsilon)}{d\varepsilon}\,d\varepsilon \approx \frac{V}{h^3}2\pi(2m)^{3/2}\varepsilon^{1/2}\,d\varepsilon. \tag{7}$$

The next case we shall consider here is that of a one-dimensional *simple harmonic oscillator*. The classical expression for the Hamiltonian of this system is

$$H(q, p) = \frac{1}{2}kq^2 + \frac{1}{2m}p^2, \tag{8}$$

where k is the spring constant and m the mass of the oscillating particle. The space coordinate q and the momentum coordinate p of the system are given by

$$q = A\cos(\omega t + \phi), \qquad p = m\dot{q} = -m\omega A\sin(\omega t + \phi), \tag{9}$$

A being the amplitude and ω the (angular) frequency of vibration:

$$\omega = \sqrt{(k/m)}. \tag{10}$$

The energy of the oscillator is a constant of the motion, and is given by

$$E = \tfrac{1}{2}m\omega^2A^2. \tag{11}$$

The phase-space trajectory of the representative point (q, p) of this system is determined by eliminating t between expressions (9) for $q(t)$ and $p(t)$; we obtain

$$\frac{q^2}{(2E/m\omega^2)} + \frac{p^2}{(2mE)} = 1, \tag{12}$$

which is an ellipse, with axes proportional to $\sqrt{E}$ and hence area proportional to E; to be precise, the area of this ellipse is $2\pi E/\omega$. Now, if we restrict the oscillator energy to the interval $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$, its representative point in the phase space will be confined to the region bounded by elliptical trajectories corresponding to the energy values $(E + \frac{1}{2}\Delta)$ and $(E - \frac{1}{2}\Delta)$. The "volume" (in this case, the area) of this region will be

$$\int_{\left(E-\frac{1}{2}\Delta\right) \le H(q,p) \le \left(E+\frac{1}{2}\Delta\right)} \cdots \int (dq\,dp) = \frac{2\pi\left(E+\frac{1}{2}\Delta\right)}{\omega} - \frac{2\pi\left(E-\frac{1}{2}\Delta\right)}{\omega} = \frac{2\pi\Delta}{\omega}. \tag{13}$$

According to quantum mechanics, the energy eigenvalues of the harmonic oscillator are given by

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega; \quad n = 0, 1, 2, \ldots \tag{14}$$

In terms of phase space, one could say that the representative point of the system must move along one of the "chosen" trajectories, as shown in Fig. 2.2; the area of the phase space between two consecutive trajectories, for which $\Delta = \hbar\omega$, is simply $2\pi\hbar$.[5] For arbitrary values of E and Δ, such that $E \gg \Delta \gg \hbar\omega$, the number of eigenstates within the allowed energy interval is very nearly equal to $\Delta/\hbar\omega$. Hence, the area of the phase space equivalent to one eigenstate is, asymptotically, given by

$$\omega_0 = (2\pi\Delta/\omega)/(\Delta/\hbar\omega) = 2\pi\hbar = h. \tag{15}$$

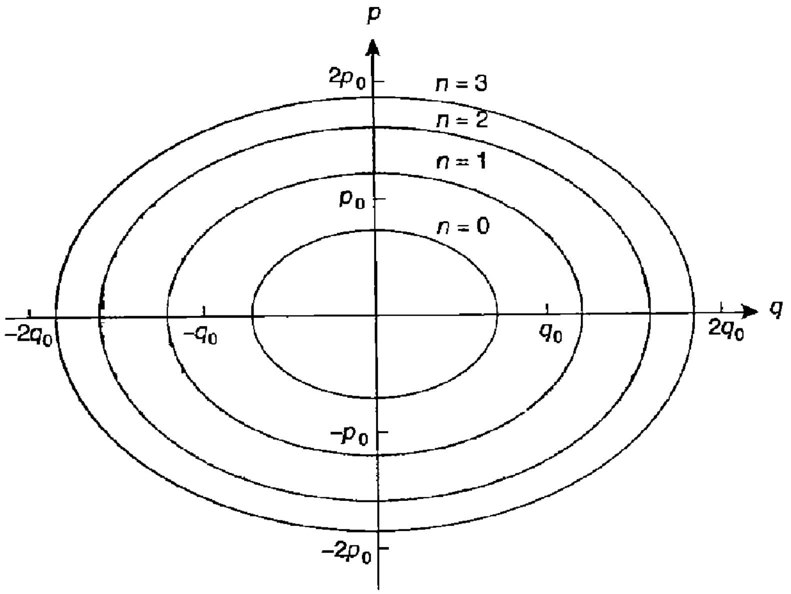

FIG. 2.2. Eigenstates of a linear harmonic oscillator, in relation to its phase space.

If, on the other hand, we consider a system of N harmonic oscillators along the same lines as above, we arrive at the result: $\omega_0 = h^N$ (see Problem 2.7). Thus, our findings in these cases are consistent with our earlier result (3).

2.5. Quantum states and the phase space

At this stage we would like to say a few words on the central role played here by the Planck constant h. The best way to appreciate this role is to recall the implications of the Heisenberg uncertainty principle, according to which we cannot specify *simultaneously* both the position and the momentum of a particle exactly. An element of uncertainty is inherently present and can be expressed as follows: assuming that all conceivable uncertainties of measurement are eliminated, even then, by the very nature of things, the product of the uncertainties Δq and Δp in the *simultaneous* measurement of the canonically conjugate coordinates q and p would be of order $\hbar$:

$$(\Delta q \Delta p)_{\min} \sim \hbar. \tag{1}$$

Thus, it is impossible to define the position of a representative point in the phase space of the given system more accurately than is allowed by condition (1). In other words, around any point (q, p) in the (two-dimensional) phase space, there exists an area of order $\hbar$ within which the position of the representative point cannot be pin-pointed. In a phase space of $2N$ dimensions, the corresponding "volume of uncertainty" around any point would be of order $\hbar^{N}$. Therefore, it seems reasonable to regard the phase space as made up of elementary cells, of volume $\sim \hbar^{N}$, and to consider the various positions within such a cell as non-distinct. These cells could then be put into one-to-one correspondence with the quantum-mechanical states of the system.

It is, however, obvious that considerations of uncertainty alone cannot give us the *exact* value of the conversion factor ω_0. This could only be done by an *actual* counting of microstates on one hand and a computation of volume of the relevant region of the phase space on the other, as was done in the examples of the previous section. Clearly, a procedure along these lines could not be possible until after the work of Schrödinger and others. Historically, however, the first to establish the result (2.4.3) was Tetrode (1912) who, in his well-known work on the chemical constant and the entropy of a monatomic gas, assumed that

$$\omega_0 = (zh)^{3N} \tag{2}$$

where z was supposed to be an unknown numerical factor. Comparing theoretical results with the experimental data on mercury, Tetrode found that z was very nearly equal to unity; from this he concluded that "it seems rather plausible that z is *exactly* equal to unity, as has already been taken by O. Sackur (1911)".[6]

In the extreme relativistic limit, the same result was established by Bose (1924). In his famous treatment of the photon gas, Bose made use of Einstein's relationship between the momentum of a photon and the frequency of the associated vibration, namely

$$p = \frac{h\nu}{c}, \tag{3}$$

and observed that, for a photon confined to a three-dimensional cavity of volume V, the relevant "volume" of the phase space,

$$\int (d^3q\, d^3p) = V4\pi p^2\, dp = V(4\pi h^3 \nu^2/c^3)\, d\nu, \tag{4}$$

would correspond exactly to the Rayleigh expres

$$V(4\pi\nu^2/c^3)\,d\nu, \tag{5}$$

for the number of normal modes of a radiation oscillator, *provided that* we divide phase space into elementary cells of volume h^3 and put these cells into one-to-one correspondence with the vibrational modes of Rayleigh. It may, however, be added that a two-fold multiplicity of these states ($g = 2$) arises from the spin orientations of the photon (or from the states of polarization of the vibrational modes); this requires a multiplication of both expressions (4) and (5) by a factor of 2, leaving the conversion factor h^3 unchanged.

Problems

2.1. Show that the volume element

$$d\omega = \prod_{i=1}^{3N}(dq_i\,dp_i)$$

of the phase space remains *invariant* under a canonical transformation of the (generalized) coordinates (q, p) to any other set of (generalized) coordinates (Q, P).

[*Hint*: Before considering the most general transformation of this kind, which is referred to as a *contact* transformation, it may be helpful to consider a *point* transformation–one in which the new coordinates Q_i and the old coordinates q_i transform only among themselves.]

2.2. (a) Verify *explicitly* the invariance of the volume element $d\omega$ of the phase space of a single particle under transformation from the Cartesian coordinates (x, y, z, p_x, p_y, p_z) to the spherical polar coordinates $(r, \theta, \phi, p_r, p_\theta, p_\phi)$.

(b) The foregoing result seems to contradict the intuitive notion of "equal weights for equal solid angles", because the factor $\sin\theta$ is invisible in the expression for $d\omega$. Show that if we average out any physical quantity, whose dependence on p_θ and p_ϕ comes only through the kinetic energy of the particle, then as a result of integration over these variables we do indeed recover the factor $\sin\theta$ to appear with the sub-element $(d\theta\,d\phi)$.

2.3. Starting with the line of zero energy and working in the (two-dimensional) phase space of a classical rotator, draw lines of constant energy which divide phase space into cells of "volume" h. Calculate the energies of these states and compare them with the energy eigenvalues of the corresponding quantum-mechanical rotator.

2.4. By evaluating the "volume" of the relevant region of its phase space, show that the number of microstates available to a rigid rotator with angular momentum $\leq M$ is $(M/\hbar)^2$. Hence determine the number of microstates that may be associated with the quantized angular momentum $M_j = \sqrt{\{j(j+1)\}}\,\hbar$, where $j = 0, 1, 2, \ldots$ or $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$. Interpret the result physically.

[*Hint*: It simplifies to consider motion in the variables θ and φ, with $M^2 = p_\theta^2 + (p_\phi/\sin\theta)^2$.]

2.5. Consider a particle of energy E moving in a one-dimensional potential well $V(q)$, such that

$$m\hbar\left|\frac{dV}{dq}\right| \ll \{m(E-V)\}^{3/2}.$$

Show that the allowed values of the momentum p of the particle are such that

$$\oint p\,dq = \left(n + \tfrac{1}{2}\right)h,$$

where n is an integer.

2.6. The generalized coordinates of a simple pendulum are the angular displacement θ and the angular momentum $ml^2\dot{\theta}$. Study, both mathematically and graphically, the nature of the corresponding trajectories in the phase space of the system, and show that the area A enclosed by a trajectory is equal to the product of the total energy E and the time period τ of the pendulum.

2.7. Derive (i) an *asymptotic* expression for the number of ways in which a given energy E can be distributed among a set of N one-dimensional harmonic oscillators, the energy eigenvalues of the oscillators being $(n + \frac{1}{2})\hbar\omega$; $n = 0, 1, 2, \ldots$, and (ii) the corresponding expression for the "volume" of the relevant region of the phase space of this system. Establish the correspondence between the two results, showing that the conversion factor ω_0 is precisely h^N.

2.8. Following the method of Appendix C, replacing eqn. (C.4) by the integral

$$\int_0^\infty e^{-r} r^2 \, dr = 2,$$

show that

$$V_{3N} = \underset{0 \le \sum_{i=1}^{N} r_i \le R}{\int \cdots \int} \prod_{i=1}^{N} (4\pi r_i^2 \, dr_i) = (8\pi R^3)^N / (3N)!.$$

Using this result, compute the "volume" of the relevant region of the phase space of an extreme relativistic gas ($\varepsilon = pc$) of N particles moving in three dimensions. Hence, derive expressions for the various thermodynamic properties of this system and compare your results with those of Problem 1.7.

2.9. (a) Solve the integral

$$\underset{0 \le \sum_{i=1}^{3N} |x_i| \le R}{\int \cdots \int} (dx_1 \ldots dx_{3N})$$

and use it to determine the "volume" of the relevant region of the phase space of an extreme relativistic gas ($\varepsilon = pc$) of $3N$ particles moving in one dimension. Determine, as well, the number of ways of distributing a given energy E among this system of particles and show that, asymptotically, $\omega_0 = h^{3N}$.

(b) Compare the thermodynamics of this system with that of the system considered in Problem 2.8.

Notes

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[1] Note that (q, p) is a further abbreviation of $(q_i, p_i) \equiv (q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N})$.

[2] This means that in the ensemble under consideration neither are any new members being admitted nor are any old ones being expelled.

[3] We recall that the *Poisson bracket* $[\rho, H]$ stands for the sum

$$\sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right),$$

which is identical with the group of terms in the middle of (8).

[4] To provide a *rigorous* justification for this assertion is not trivial. One can readily see that if, for any particular member of the ensemble, the quantity f is averaged only over a *short* span of time, the result is bound to depend upon the relevant "subset of microstates" through which the system passes during that time. In the phase space, this will mean an averaging over only a "part of the allowed region". However, if we employ instead a sufficiently long interval of time, the system may be expected to pass through *almost* all possible microstates "without fear or favor"; consequently, the result of the averaging process would depend only upon the macrostate of the system, and not upon a subset of microstates. Correspondingly, the averaging in the phase space would go over *practically* all parts of the allowed region, again "without fear or favor". In other words, the representative point of our system will have traversed each and every part of the allowed region *almost* uniformly. This statement embodies the so-called *ergodic theorem* or *ergodic hypothesis*, which was first introduced by Boltzmann (1871). According to this hypothesis, the trajectory of a representative point passes, in the course of time, through *each and every* point of the relevant region of the phase space. A little reflection, however, shows that the statement as such requires a qualification; we better replace it by the so-called *quasi-ergodic hypothesis*, according to which the trajectory of a representative point

traverses, in the course of time, *any neighborhood of any point* of the relevant region. For further details, see ter Haar (1954, 1955), Farquhar (1964).

Now, when we consider an ensemble of systems, the foregoing statement should hold for every member of the ensemble; thus, *irrespective of the initial (and final) states* of the various systems, the long-time average of any physical quantity f should be the same for every member system.

[5] Strictly speaking, the very concept of phase space is invalid in quantum mechanics because there it is wrong, in principle, to assign to a particle the coordinates q and p *simultaneously*. Nevertheless, the ideas discussed here are tenable in the correspondence limit.

[6] For a more satisfactory proof, see Sec. 5.5, especially eqn. (5.5.22).

CHAPTER 3

THE CANONICAL ENSEMBLE

IN THE preceding chapter we established the basis of ensemble theory and made a somewhat detailed study of the microcanonical ensemble. In that ensemble the macrostate of the systems was defined through a fixed number of particles N, a fixed volume V and a fixed energy E [or, preferably, a fixed energy range $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$]. The basic problem then consisted in determining the number $\Omega(N, V, E)$, or $\Gamma(N, V, E; \Delta)$, of *distinct* microstates accessible to the system. From the asymptotic expressions of these numbers, complete thermodynamics of the system could be derived in a straightforward manner. However, for most physical systems, the mathematical problem of determining these numbers is quite formidable. For this reason alone, a search for an alternative approach within the framework of the ensemble theory seems necessary.

Physically, too, the concept of a fixed energy (or even an energy range) for a system belonging to the real world does not appear satisfactory. For one thing, the total energy E of a system is hardly ever measured; for another, it is hardly possible to keep its value under strict physical control. A far better alternative appears to be to speak of a fixed temperature T of the system–a parameter which is not only directly observable (by placing a "thermometer" in contact with the system) but also controllable (by keeping the system in contact with an appropriate "heat reservoir"). For most purposes, the precise nature of the reservoir is not very relevant; all one needs is that it should have an infinitely large heat capacity, so that, irrespective of energy exchange between the system and the reservoir, an overall constant temperature can be maintained. Now, if the reservoir consists of an infinitely large number of mental copies of the given system we have once again an ensemble of systems–this time, however, it is an ensemble in which the macrostate of the systems is defined through the parameters N, V and T. Such an ensemble is referred to as a *canonical* ensemble.

In the canonical ensemble, the energy E of a system is variable; in principle, it can take values anywhere between zero and infinity. The question then arises: what is the probability that, at any time t, a system in the ensemble is found to be in one of the states characterized by the energy value E_r?[1] We denote this probability by the symbol P_r. Clearly, there are two ways in which the dependence of P_r on E_r can be determined. One consists in regarding the system as in equilibrium with a heat reservoir at a *common* temperature T and studying the statistics of the energy exchange between the two. The other consists in regarding the system as a member of a canonical ensemble (N, V, T), in w[illegible] an energy $\mathcal{E}$ is being shared by $\mathcal{N}$ identical systems constituting the ensemble, and studying the statistics of this sharing process. We expect that in the thermodynamic limit the final result in either case would be the same. Once P_r is determined, the rest follows without difficulty.

3.1. Equilibrium between a system and a heat reservoir

We consider the given system A, immersed in a very large heat reservoir A'; see Fig. 3.1. On attaining a state of mutual equilibrium, the system and the reservoir would have a *common* temperature, T say. Their energies, however, would be variable and, in principle, could have, at any time t, values lying anywhere between 0 and $E^{(0)}$, where $E^{(0)}$ denotes the energy of the composite system $A^{(0)} (\equiv A + A')$. If, at any particular instant of time, the system A happens to be in a state characterized by the energy value E_r, then the reservoir would have an energy E'_r such that

$$E_r + E'_r = E^{(0)} = \text{const.} \tag{1}$$

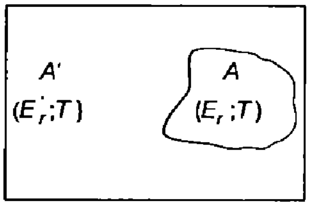

FIG. 3.1. A given system A immersed in a heat reservoir A'; in equilibrium, the two have a common temperature T.

Of course, since the reservoir is supposed to be much larger than the given system, any *practical* value of E_r would be a very small fraction of $E^{(0)}$; therefore, for all practical purposes,

$$\frac{E_r}{E^{(0)}} = \left(1 - \frac{E'_r}{E^{(0)}}\right) \ll 1. \tag{2}$$

With, the state of the system A having been specified, the reservoir A' can still be in *any one* of a large number of states compatible with the energy value E'_r. Let the number of these states be denoted by $\Omega'(E'_r)$. The prime on the symbol Ω emphasizes the fact that its functional form will depend upon the nature of the reservoir; of course, the details of this dependence are not going to be of any particular relevance to our final results. Now, the larger the number of states available to the reservoir, the larger the probability of the reservoir assuming that particular energy value E'_r (and, hence, of the system A assuming the corresponding energy value E_r). Moreover, since the various possible states (with a given energy value) are *equally likely* to occur, the relevant probability would be directly proportional to this number; thus,

$$P_r \propto \Omega'(E'_r) \equiv \Omega'(E^{(0)} - E_r). \tag{3}$$

In view of (2), we may carry out an expansion of (3) around the value $E'_r = E^{(0)}$, i.e. around $E_r = 0$. However, for reasons of convergence, it is essential to effect the expansion of its logarithm instead:

$$\ln \Omega'(E'_r) = \ln \Omega'(E^{(0)}) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E'=E^{(0)}} (E'_r - E^{(0)}) + \cdots$$

$$\simeq \text{const} - \beta' E_r, \tag{4}$$

where use has been made of formula (1.2.3), whereby

$$\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \equiv \beta; \tag{5}$$

note that, in equilibrium, $\beta' = \beta = 1/kT$. From (3) and (4), we obtain the desired result:

$$P_r \propto \exp(-\beta E_r). \tag{6}$$

Normalizing (6), we get

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{7}$$

where the summation in the denominator goes over *all* states accessible to the system A. We note that our final formula (7) bears no relation whatsoever to the physical nature of the reservoir A'.

We now examine the same problem from the ensemble point of view.

3.2. A system in the canonical ensemble

We consider an ensemble of $\mathcal{N}$ identical systems (which may be labelled as $1, 2, \ldots, \mathcal{N}$), sharing a total energy $\mathscr{E}$; let $E_r (r = 0, 1, 2, \ldots)$ denote the energy eigenvalues of the systems. If n_r denotes the number of systems which, at any time t, have the energy value E_r, then the set of numbers $\{n_r\}$ must satisfy the obvious conditions

$$\left.\begin{aligned} \sum_r n_r &= \mathcal{N} \\ \sum_r n_r E_r &= \mathscr{E} = \mathcal{N} U, \end{aligned}\right\} \tag{1}$$

where $U (= \mathscr{E}/\mathcal{N})$ denotes the average energy per system in the ensemble. Any set $\{n_r\}$ which satisfies the restrictive conditions (1) represents a possible mode of distribution of the total energy $\mathscr{E}$ among the $\mathcal{N}$ members of the ensemble. Furthermore, any such mode can be realized in a number of ways, for we may effect a reshuffle among those members of the ensemble for which the energy values are different and thereby obtain a state of the ensemble which is distinct from the original one. Denoting the number of different ways of doing so by the symbol $W\{n_r\}$, we have

$$W\{n_r\} = \frac{\mathcal{N}!}{n_0! n_1! n_2! \ldots}. \tag{2}$$

In view of the fact that all possible states of the ensemble, which are compatible with conditions (1), are *equally likely* to occur, the frequency with which the distribution set $\{n_r\}$ may appear will be directly proportional to the number $W\{n_r\}$. Accordingly, the "most probable" mode of distribution will be the one for which the number W is a maximum. We denote the corresponding distribution set by $\{n_r^*\}$; clearly, the set $\{n_r^*\}$ must also satisfy conditions (1). As will be seen in the sequel, the probability of appearance of other modes of distribution, however little they may be differing from the most probable mode, is extremely low! Therefore, for all practical purposes, the *most probable distribution set* $\{n_r^*\}$ is the only one we have to contend with.

However, unless this is mathematically demonstrated, one must take into account *all* possible modes of distribution, as characterized by the various distribution sets $\{n_r\}$, along with their respective weight factors $W\{n_r\}$. Accordingly, the *expectation values*, or *mean values*, $\langle n_r\rangle$ of the numbers n_r would be given by

$$\langle n_r\rangle = \frac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}}, \tag{3}$$

where the primed summations go over all distribution sets that conform to conditions (1). In principle, the mean value $\langle n_r\rangle$, as a fraction of the total number $\mathcal{N}$, should be a natural analogue of the probability P_r evaluated in the preceding section. In practice, however, the fraction $n_r^*/\mathcal{N}$ is also the same.

We now proceed to derive expressions for the numbers n_r^* and $\langle n_r\rangle$, and to show that, in the limit $\mathcal{N} \to \infty$, they are identical.

(i) *The method of most probable values.* Our aim here is to determine that distribution set which, while satisfying conditions (1), maximizes the weight factor (2). For simplicity, we work with $\ln W$ instead:

$$\ln W = \ln(\mathcal{N}!) - \sum_r \ln(n_r!). \tag{4}$$

Since in the end we propose to resort to the limit $\mathcal{N} \to \infty$, the values of n_r (which are going to be of any practical significance) would also, in that limit, tend to infinity. It is, therefore, justified to apply the Stirling formula, $\ln(n!) \approx n \ln n - n$, to (4) and write

$$\ln W = \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r. \tag{5}$$

If we shift from the set $\{n_r\}$ to a slightly different set $\{n_r + \delta n_r\}$, then expression (5) would change by an amount

$$\delta(\ln W) = -\sum_r (\ln n_r + 1)\,\delta n_r. \tag{6}$$

Now, if the set $\{n_r\}$ is maximal, the variation $\delta(\ln W)$ should vanish. At the same time, in view of the restrictive conditions (1), the variations δn_r themselves must satisfy the conditions

$$\left.\begin{aligned} \sum_r \delta n_r &= 0 \\ \sum_r E_r\,\delta n_r &= 0. \end{aligned}\right\} \tag{7}$$

The desired set $\{n_r^*\}$ is then determined by the method of *Lagrange multipliers*,[2] by which the condition determining this set becomes

$$\sum_r \{-(\ln n_r^* + 1) - \alpha - \beta E_r\}\,\delta n_r = 0, \tag{8}$$

where α and β are the Lagrangian undetermined multipliers that take care of the restrictive conditions (7). In (8), the variations δn_r become completely arbitrary; accordingly, the only way to satisfy this condition is that all its coefficients must vanish identically, i.e. for *all r*,

$$\ln n_r^* = -(\alpha + 1) - \beta E_r,$$

whence

$$n_r^* = C \exp(-\beta E_r), \tag{9}$$

where C is again an undetermined parameter. To determine C and β, we subject (9) to conditions (1), with the result that

$$\frac{n_r^*}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{10}$$

the parameter β being a solution of the equation

$$\frac{\mathcal{E}}{\mathcal{N}} = U = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}. \tag{11}$$

Combining statistical considerations with thermodynamic ones, see Sec. 3.3, we can show that the parameter β here is exactly the same as the one appearing in Sec. 3.1, i.e. $\beta = 1/kT$.

(ii) *The method of mean values.* Here we attempt to evaluate expression (3) for $\langle n_r \rangle$, taking into account the weight factors (2) and the restrictive conditions (1). To do this, we replace (2) by

$$\tilde{W}\{n_r\} = \frac{\mathcal{N}!\,\omega_0^{n_0}\omega_1^{n_1}\omega_2^{n_2}\ldots}{n_0!\,n_1!\,n_2!\ldots}, \tag{12}$$

with the understanding that in the end all the ω_r will be set equal to unity, and introduce a function

$$\Gamma(\mathcal{N}, U) = \sum_{\{n_r\}}{}' \tilde{W}\{n_r\}. \tag{13}$$

where the primed summation, as before, goes over all distribution sets that conform to conditions (1). Expression (3) can then be written as

$$\langle n_r \rangle = \omega_r \frac{\partial}{\partial \omega_r}(\ln \Gamma)\bigg|_{\text{all } \omega_r = 1} \tag{14}$$

Thus, all we need to know here is the dependence of the quantity $\ln \Gamma$ on the parameters ω_r. Now

$$\Gamma(\mathcal{N},U)=\mathcal{N}!\sum_{\{n_r\}}{}'\left(\frac{\omega_0^{n_0}}{n_0!}\cdot\frac{\omega_1^{n_1}}{n_1!}\cdot\frac{\omega_2^{n_2}}{n_2!}\cdots\right), \tag{15}$$

but the summation appearing here cannot be evaluated explicitly because it is restricted to those sets only which conform to the pair of conditions (1). If our distribution sets were restricted by the condition $\sum_r n_r=\mathcal{N}$ alone, then the evaluation of (15) would have been trivial; by the multinomial theorem, $\Gamma(\mathcal{N})$ would have been simply $(\omega_0+\omega_1+\cdots)^{\mathcal{N}}$. The added restriction $\sum_r n_rE_r=\mathcal{N}U$, however, permits the inclusion of only a "limited" number of terms in the sum–and that constitutes the real difficulty of the problem. Nevertheless, we can still hope to make some progress because, from a physical point of view, we do not require anything more than an *asymptotic* result–one that holds in the limit $\mathcal{N}\to\infty$. The method commonly used for this purpose is the one developed by Darwin and Fowler (1922a,b, 1923), which itself makes use of the *saddle-point method* of integration or the so-called *method of steepest descent.*

We construct a *generating function* $G(\mathcal{N},z)$ for the quantity $\Gamma(\mathcal{N},U)$:

$$G(\mathcal{N},z)=\sum_{U=0}^{\infty}\Gamma(\mathcal{N},U)z^{\mathcal{N}U} \tag{16}$$

which, in view of eqn. (15) and the second of the restrictive conditions (1), may be written as

$$G(\mathcal{N},z)=\sum_{U=0}^{\infty}\left[\sum_{\{n_r\}}{}'\frac{\mathcal{N}!}{n_0!n_1!\ldots}\left(\omega_0z^{E_0}\right)^{n_0}\left(\omega_1z^{E_1}\right)^{n_1}\ldots\right]. \tag{17}$$

It is easy to see that the summation over *doubly* restricted sets $\{n_r\}$, followed by a summation over all possible values of U, is equivalent to a summation over *singly* restricted sets $\{n_r\}$, viz. the ones that satisfy only one condition: $\sum_r n_r=\mathcal{N}$. Expression (17) can, therefore, be evaluated with the help of the multinomial theorem, with the result

$$\begin{aligned}G(\mathcal{N},z)&=\left(\omega_0z^{E_0}+\omega_1z^{E_1}+\cdots\right)^{\mathcal{N}}\\&=[f(z)]^{\mathcal{N}},\ \text{say}.\end{aligned} \tag{18}$$

Now, if we suppose that the E_r (and hence the total energy values $\mathcal{E}=\mathcal{N}U$) are all integers, then, by (16), the quantity $\Gamma(\mathcal{N},U)$ is simply the coefficient of $z^{\mathcal{N}U}$ in the expansion of the function $G(\mathcal{N},z)$ as a power series in z. It can, therefore, be evaluated by the method of residues in the complex z-plane.

To make this plan work, we assume to have chosen, *right at the outset*, a unit of energy so small that, to any desired degree of accuracy, we can regard the energies E_r (and the prescribed total energy $\mathcal{N}U$) as integral multiples of this unit. In terms of this unit, any energy value we come across will be an integer. We further assume, without loss of generality, that the sequence $E_0,E_1,\ldots$ is a *nondecreasing* sequence, *with no common divisor*;[3] also, for the sake of simplicity, we assume that $E_0=0$.[4] The solution now is

$$\Gamma(\mathcal{N},U)=\frac{1}{2\pi i}\oint\frac{[f(z)]^{\mathcal{N}}}{z^{\mathcal{N}U+1}}dz, \tag{19}$$

where the integration is carried along any closed contour around the origin; of course, we should stay *within* the circle of convergence of the function $f(z)$, so that a need for analytic continuation does not arise.

First of all we examine the behavior of the integrand as we proceed from the origin along the real positive axis, remembering that all our ω are virtually equal to unity and that $0 = E_0 \leq E_1 \leq E_2 \cdots$. We find that the factor $[f(z)]^{N}$ starts from the value 1 at $z = 0$, increases monotonically and tends to infinity as z approaches the circle of convergence of $f(z)$, wherever that may be. The factor $z^{-(NU+1)}$, on the other hand, starts from a positive, infinite value at $z = 0$ and decreases monotonically as z increases. Moreover, the relative rate of increase of the factor $[f(z)]^{N}$ itself increases monotonically while the relative rate of decrease of the factor $z^{-(NU+1)}$ decreases monotonically. Under these circumstances, the integrand must exhibit a minimum (and no other extremum) at some value of z, say x_0, within the circle of convergence. And, in view of the largeness of the numbers N and NU, this minimum may indeed be very steep!

Thus, at $z = x_0$ the first derivative of the integrand must vanish, while the second derivative must be positive and, hopefully, very large. Accordingly, if we proceed through the point $z = x_0$ in a direction orthogonal to the real axis, the integrand must exhibit an equally steep maximum.[5] Thus, in the complex z-plane, as we move along the real axis our integrand shows a minimum at $z = x_0$, whereas if we move along a path parallel to the imaginary axis but passing through the point $z = x_0$, the integrand shows a maximum there. It is natural to call the point x_0 a *saddle point*; see Fig. 3.2. For the contour of integration we choose a circle, with center at $z = 0$ and radius equal to x_0, hoping that on integration along this contour only the immediate neighborhood of the sharp maximum at the point x_0 will make the most dominant contribution to the value of the integral.[6]

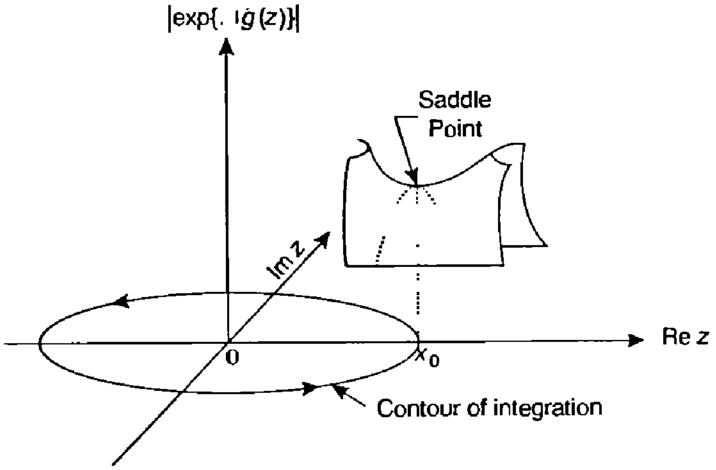

FIG. 3.2. The saddle point.

To carry out the integration we first locate the point x_0. For this we write our integrand as

$$\frac{[f(z)]^{N}}{z^{NU+1}} = \exp[N g(z)]. \tag{20}$$

where

$$g(z) = \ln f(z) - \left(U + \frac{1}{\mathcal{N}}\right) \ln z, \tag{21}$$

while

$$f(z) = \sum_r \omega_r z^{E_r}. \tag{22}$$

The number x_0 is then determined by the equation

$$g'(x_0) = \frac{f'(x_0)}{f(x_0)} - \frac{\mathcal{N}U + 1}{\mathcal{N}x_0} = 0 \tag{23}$$

which, in view of the fact that $\mathcal{N}U \gg 1$, can be written as

$$U \approx x_0 \frac{f'(x_0)}{f(x_0)} = \frac{\sum_r \omega_r E_r x_0^{E_r}}{\sum_r \omega_r x_0^{E_r}}. \tag{24}$$

We further have

$$\begin{aligned} g''(x_0) &= \left(\frac{f''(x_0)}{f(x_0)} - \frac{[f'(x_0)]^2}{[f(x_0)]^2}\right) + \frac{\mathcal{N}U + 1}{\mathcal{N}x_0^2} \\ &\approx \frac{f''(x_0)}{f(x_0)} - \frac{U^2 - U}{x_0^2}. \end{aligned} \tag{25}$$

It will be noted here that, in the limit $\mathcal{N} \to \infty$ and $\mathscr{E}(\equiv \mathcal{N}U) \to \infty$, *with U staying constant*, the number x_0 and the quantity $g''(x_0)$ become independent of $\mathcal{N}$.

Expanding $g(z)$ about the point $z = x_0$, along the direction of integration, i.e. along the line $z = x_0 + iy$, we have

$$g(z) = g(x_0) - \tfrac{1}{2} g''(x_0) y^2 + \cdots;$$

accordingly, the integrand (20) might be approximated as

$$\frac{[f(x_0)]^{\mathcal{N}}}{x_0^{\mathcal{N}U+1}} \exp\left[-\frac{\mathcal{N}}{2} g''(x_0) y^2\right]. \tag{26}$$

Equation (19) then gives

$$\begin{aligned} \Gamma(\mathcal{N}, U) &\simeq \frac{1}{2\pi i} \frac{[f(x_0)]^{\mathcal{N}}}{x_0^{\mathcal{N}U+1}} \int_{-\infty}^{\infty} \exp\left[-\frac{\mathcal{N}}{2} g''(x_0) y^2\right] i\,dy \\ &= \frac{[f(x_0)]^{\mathcal{N}}}{x_0^{\mathcal{N}U+1}} \cdot \frac{1}{\{2\pi \mathcal{N} g''(x_0)\}^{1/2}}, \end{aligned} \tag{27}$$

whence

$$\frac{1}{\mathcal{N}} \ln \Gamma(\mathcal{N}, U) = \{\ln f(x_0) - U \ln x_0\} - \frac{1}{\mathcal{N}} \ln x_0 - \frac{1}{2\mathcal{N}} \ln \{2\pi \mathcal{N} g''(x_0)\}. \tag{28}$$

In the limit $\mathcal{N} \to \infty$ (with U staying constant), the last two terms in this expression tend to zero, with the result

$$\frac{1}{\mathcal{N}} \ln \Gamma(\mathcal{N}, U) = \ln f(x_0) - U \ln x_0. \tag{29}$$

Substituting for $f(x_0)$ and introducing a new variable β, defined by the relationship

$$x_0 \equiv \exp(-\beta), \tag{30}$$

we get

$$\frac{1}{\mathcal{N}} \ln \Gamma(\mathcal{N}, U) = \ln \left\{ \sum_r \omega_r \exp(-\beta E_r) \right\} + \beta U. \tag{31}$$

The expectation value of the number n_r then follows from (14) and (31):

$$\frac{\langle n_r \rangle}{\mathcal{N}} = \left[\frac{\omega_r \exp(-\beta E_r)}{\sum_r \omega_r \exp(-\beta E_r)} + \left\{ -\frac{\sum_r \omega_r E_r \exp(-\beta E_r)}{\sum_r \omega_r \exp(-\beta E_r)} + U \right\} \omega_r \frac{\partial \beta}{\partial \omega_r} \right]_{\text{all } \omega_r = 1} \tag{32}$$

The term inside the curly brackets vanishes identically because of (24) and (30). It has been included here to emphasize the fact that, for a fixed value of U, the number $\beta (\equiv -\ln x_0)$ in fact depends upon the choice of the ω_r; see (24). We will appreciate the importance of this fact when we evaluate the mean square fluctuation in the number n_r; in the calculation of the expectation value of n_r, this does not really matter. We thus obtain

$$\frac{\langle n_r \rangle}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{33}$$

which is identical with expression (10) for $n_r^*/\mathcal{N}$. The physical significance of the parameter β is also the same as in that expression, for it is determined by eqn. (24), with all $\omega_r = 1$, i.e. by eqn. (11) which fits naturally with eqn. (33) because U is nothing but the ensemble average of the variable E_r:

$$U = \sum_r E_r P_r = \frac{1}{\mathcal{N}} \sum_r E_r \langle n_r \rangle. \tag{34}$$

Finally, we compute fluctuations in the values of the numbers n_r. We have, first of all,

$$\langle n_r^2 \rangle \equiv \frac{\sum'_{\{n_r\}} n_r^2 W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}} = \frac{1}{\Gamma} \left(\omega_r \frac{\partial}{\partial \omega_r} \right) \left(\omega_r \frac{\partial}{\partial \omega_r} \right) \Gamma \Bigg|_{\text{all } \omega_r = 1}; \tag{35}$$

see eqns (12)–(14). It follows that

$$\langle (\Delta n_r)^2 \rangle \equiv \langle \{ n_r - \langle n_r \rangle \}^2 \rangle = \langle n_r^2 \rangle - \langle n_r \rangle^2 = \left(\omega_r \frac{\partial}{\partial \omega_r} \right) \left(\omega_r \frac{\partial}{\partial \omega_r} \right) (\ln \Gamma) \Bigg|_{\text{all } \omega_r = 1}. \tag{36}$$

Substituting from (31) and making use of (32), we get

$$\frac{\langle(\Delta n_r)^2\rangle}{\mathcal{N}} = \omega_r \frac{\partial}{\partial\omega_r}\left[\frac{\omega_r \exp(-\beta E_r)}{\sum\limits_r \omega_r \exp(-\beta E_r)} + \left\{-\frac{\sum\limits_r \omega_r E_r \exp(-\beta E_r)}{\sum\limits_r \omega_r \exp(-\beta E_r)} + U\right\}\omega_r \frac{\partial\beta}{\partial\omega_r}\right]_{\text{all } \omega_r=1} . \qquad (37$$

We note that the term in the curly brackets would not make any contribution because it is identically zero, *whatever the choice of the* ω_r. However, in the differentiation of the first term, we must not forget to take into account the *implicit* dependence of β on the ω_r, which arises from the fact that unless the ω are set equal to unity the relation determining β does contain ω_r; see eqns (24) and (30), whereby

$$U = \left.\frac{\sum\limits_r \omega_r E_r \exp(-\beta E_r)}{\sum\limits_r \omega_r \exp(-\beta E_r)}\right|_{\text{all } \omega_r=1} . \qquad (38$$

A straightforward calculation gives

$$\left.\left(\frac{\partial\beta}{\partial\omega_r}\right)_U\right|_{\text{all } \omega_r=1} = \frac{E_r - U}{\langle E_r^2\rangle - U^2}\frac{\langle n_r\rangle}{\mathcal{N}} . \qquad (39$$

We can now evaluate (37), with the result

$$\frac{\langle(\Delta n_r)^2\rangle}{\mathcal{N}} = \frac{\langle n_r\rangle}{\mathcal{N}} - \left(\frac{\langle n_r\rangle}{\mathcal{N}}\right)^2 + \frac{\langle n_r\rangle}{\mathcal{N}}(U - E_r)\left.\left(\frac{\partial\beta}{\partial\omega_r}\right)_U\right|_{\text{all } \omega_r=1}$$

$$= \frac{\langle n_r\rangle}{\mathcal{N}}\left[1 - \frac{\langle n_r\rangle}{\mathcal{N}} - \frac{\langle n_r\rangle}{\mathcal{N}}\frac{(E_r - U)^2}{\langle(E_r - U)^2\rangle}\right] . \qquad (40$$

For the relative fluctuation in n_r, we have

$$\left\langle\left(\frac{\Delta n_r}{\langle n_r\rangle}\right)^2\right\rangle = \frac{1}{\langle n_r\rangle} - \frac{1}{\mathcal{N}}\left\{1 + \frac{(E_r - U)^2}{\langle(E_r - U)^2\rangle}\right\} . \qquad (41$$

As $\mathcal{N} \to \infty$, $\langle n_r\rangle$ also $\to \infty$, with the result that the relative fluctuations in n tend to zero; accordingly, the (canonical) distribution becomes infinitely sharp an with it the mean value, the most probable value–in fact, any values of n_r th appear with nonvanishing probability–become essentially the same. And that is t reason why two wildly different methods of obtaining the canonical distributi followed in this section have led to identical results.

3.3. Physical significance of the various statistical quantities in the canonical ensemble

We start with the *canonical distribution*

$$P_r \equiv \frac{\langle n_r\rangle}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{1}$$

where β is determined by the equation

$$U = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} = -\frac{\partial}{\partial\beta}\ln\left\{\sum_r \exp(-\beta E_r)\right\} \tag{2}$$

We now look for a general recipe to extract information about the various macroscopic properties of the given system on the basis of the foregoing statistical results. For this we recall certain thermodynamic relationships involving the Helmholtz free energy $A(= U - TS)$, namely

$$dA = dU - T\,dS - S\,dT = -S\,dT - P\,dV + \mu\,dN, \tag{3}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} \qquad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}, \tag{4}$$

and

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V} = -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V} = \left[\frac{\partial(A/T)}{\partial(1/T)}\right]_{N,V} \tag{5}$$

where the various symbols have their usual meanings. Comparing (5) with (2), we infer that there exists a close correspondence between the quantities that enter through the statistical treatment and the ones that come from thermodynamics, viz.

$$\beta = \frac{1}{kT}, \qquad \ln\left\{\sum_r \exp(-\beta E_r)\right\} = -\frac{A}{kT}, \tag{6}$$

where k is a universal constant yet to be determined; soon we shall see that k is indeed the *Boltzmann constant.*

Equations (6) constitute the most fundamental result of the canonical ensemble theory. Customarily, we write it in the form

$$A(N, V, T) = -kT \ln Q_N(V, T), \tag{7}$$

where

$$Q_N(V, T) = \sum_r \exp(-E_r/kT). \tag{8}$$

The quantity $Q_N(V, T)$ is referred to as the *partition function* of the system; sometimes, it is also called the "sum-over-states" (German: *Zustandssumme*). The dependence of Q on T is quite obvious. The dependence on N and V comes through the energy eigenvalues E_r; in fact, any other parameters that might govern the values E_r should also appear in the argument of Q. Moreover, for the quantity $A(N, V, T)$ to be an extensive property of the system, $\ln Q$ must also be an extensive quantity.

Once the Helmholtz free energy is known, the rest of the thermodynamic quantities follow straightforwardly. While the entropy, the pressure and the chemical potential are obtained from formulae (4), the specific heat at constant volume follows from

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V} \tag{9}$$

and the Gibbs free energy from

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\left(\frac{\partial A}{\partial N}\right)_{V,T} = N\mu; \tag{10}$$

see Problem 3.5.

At this stage it appears worthwhile to make a few remarks on the foregoing results. First of all, we note from eqns (4) and (6) that the pressure P is given by

$$P = -\frac{\sum_r \frac{\partial E_r}{\partial V}\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{11}$$

so that

$$P\,dV = -\sum_r P_r\,dE_r = -dU. \tag{12}$$

The quantity on the right-hand side of this equation is clearly the change in the average energy of a system (in the ensemble) during a process that alters the energy levels E_r, leaving the probabilities P_r unchanged. The left-hand side then tells us that the volume change dV provides an example of such a process, and the pressure P is the "force" accompanying that process. The quantity P, which was introduced here through the thermodynamic relationship (3), thus acquires a mechanical meaning as well.

Next, about the entropy. Since $P_r = Q^{-1}\exp(-\beta E_r)$, it follows that

$$\langle \ln P_r\rangle = -\ln Q - \beta\langle E_r\rangle = \beta(A - U) = -S/k,$$

with the result that

$$S = -k\langle \ln P_r\rangle = -k\sum_r P_r \ln P_r. \tag{13}$$

This is an extremely interesting relationship, for it shows that the entropy of a physical system is *solely* and *completely* determined by the probability values P_r (of the system being in different dynamical states accessible to it)!

From the very look of it, eqn. (13) appears to be of fundamental importance; indeed, it admits of a number of interesting conclusions. One of these relates to a system in its ground state ($T = 0$ K). If the ground state is unique, then the system is sure to be found in this particular state and in no other; consequently, P_r is equal to 1 for this state and 0 for all others. Equation (13) then tells us that the entropy of the system is precisely zero, which is essentially the content of the *Nernst heat theorem* or the *third law of thermodynamics*.[7] We also infer that vanishing entropy and perfect statistical order (which implies complete predictability about the system) go together. As the number of accessible states increases, more and more of the P become nonzero; the entropy of the system thereby increases. As the number of states becomes exceedingly large, most of the P-values become exceedingly small (and their logarithms assume large, negative values); the net result is that the entropy becomes exceedingly large. Thus, the largeness of entropy and the high degree of statistical disorder (or unpredictability) in the system also go together.

It is because of this fundamental connection between entropy on one hand and lack of information on the other that formula (13) became the starting point of the pioneering work of Shannon (1948, 1949) in the theory of communication.

It may be pointed out that formula (13) applies in the microcanonical ensemble as well. There, for each member system of the ensemble, we have a group of Ω states, all *equally likely* to occur. The value of P_r is, then, $1/\Omega$ for each of these states and 0 for all others. Consequently,

$$S = -k\sum_{r=1}^{\Omega}\left\{\frac{1}{\Omega}\ln\left(\frac{1}{\Omega}\right)\right\} = k\ln\Omega, \tag{14}$$

which is precisely the central result in the microcanonical ensemble theory; see eqn. (1.2.6) or (2.3.6).

3.4. Alternative expressions for the partition function

In most physical cases the energy levels accessible to a system are *degenerate*, i.e. one has a group of states, g_i in number, all belonging to the same energy value E_i. In such cases it is more useful to write the partition function (3.3.8) as

$$Q_N(V,T) = \sum_i g_i \exp(-\beta E_i); \tag{1}$$

the corresponding expression for P_i, the probability that the system be in a state with energy E_i, would be

$$P_i = \frac{g_i \exp(-\beta E_i)}{\sum_i g_i \exp(-\beta E_i)}. \tag{2}$$

Clearly, the g_i states with a common energy E_i are all equally likely to occur. As a result, the probability of a system having energy E_i becomes proportional to the multiplicity g_i of this level; g_i thus plays the role of a "weight factor" for the level E_i. The actual probability is then determined by the weight factor g_i as well as by the Boltzmann factor $\exp(-\beta E_i)$ of the level, as we have in (2). The basic relations established in the preceding section remain unaffected.

Now, in view of the largeness of the number of particles constituting a given system and the largeness of the volume to which these particles are confined, the consecutive energy values E_i of the system are, in general, very close to one another. Accordingly, there lie, within a reasonable interval of energy $(E, E + dE)$, a very large number of energy levels. One may then regard E as a *continuous* variable and write $P(E)\,dE$ for the probability that the given system, as a member of the canonical ensemble, may have its energy in the range $(E, E + dE)$. Clearly, this will be given by the product of the relevant single-state probability and the number of energy states lying in the specified range. Denoting the latter by $g(E)\,dE$, where $g(E)$ denotes the *density of states* around the energy value E, we have

$$P(E)\,dE \propto \exp(-\beta E) g(E)\,dE \tag{3}$$

which, on normalization, becomes

$$P(E)\,dE = \frac{\exp(-\beta E) g(E)\,dE}{\int\limits_0^\infty \exp(-\beta E) g(E)\,dE} \tag{4}$$

The denominator is clearly another expression for the partition function of the system:

$$Q_N(V, T) = \int\limits_0^\infty e^{-\beta E} g(E)\,dE. \tag{5}$$

The expression for $\langle f \rangle$, the expectation value of a physical quantity f, may now be written as

$$\langle f \rangle \equiv \sum_i f_i P_i = \frac{\sum\limits_i f(E_i) g_i e^{-\beta E_i}}{\sum\limits_i g_i e^{-\beta E_i}} \rightarrow \frac{\int\limits_0^\infty f(E) e^{-\beta E} g(E)\,dE}{\int\limits_0^\infty e^{-\beta E} g(E)\,dE}. \tag{6}$$

Before proceeding further, we take a closer look at eqn. (5). With $\beta > 0$, the partition function $Q(\beta)$ is just the Laplace transform of the density of states $g(E)$. We may, therefore, write $g(E)$ as the inverse Laplace transform of $Q(\beta)$:

$$g(E) = \frac{1}{2\pi i} \int\limits_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q(\beta)\,d\beta \quad (\beta' > 0) \tag{7}$$

$$= \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} e^{(\beta' + i\beta'')E} Q(\beta' + i\beta'')\,d\beta''. \tag{8}$$

where β is now treated as a complex variable, $\beta' + i\beta''$, while the path of integration runs parallel to, and to the right of, the imaginary axis, i.e. along the straight line Re $\beta = \beta' > 0$. Of course, the path may be continuously deformed so long as the integral converges.

3.5. The classical systems

The theory developed in the preceding sections is of very general applicability. It applies to systems in which quantum-mechanical effects are important as well as to those that can be treated classically. In the latter case, our formalism may be written in the language of the phase space; as a result, the summations over quantum states get replaced by integrations over phase space.

We recall the concepts developed in Secs 2.1 and 2.2, especially formula (2.1.3) for the ensemble average $\langle f \rangle$ of a physical quantity $f(q, p)$, namely

$$\langle f \rangle = \frac{\int f(q, p)\rho(q, p)\, d^{3N}q\, d^{3N}p}{\int \rho(q, p)\, d^{3N}q\, d^{3N}p}, \tag{1}$$

where $\rho(q, p)$ denotes the density of the representative points (of the systems) in the phase space; we have omitted here the explicit dependence of the function ρ on time t because we are interested in the study of equilibrium situations only. Evidently, the function $\rho(q, p)$ is a measure of the probability of finding a representative point in the vicinity of the phase point (q, p), which in turn depends upon the corresponding value $H(q, p)$ of the Hamiltonian of the system. In the canonical ensemble,

$$\rho(q, p) \propto \exp\{-\beta H(q, p)\}; \tag{2}$$

cf. eqn. (3.1.6). The expression for $\langle f \rangle$ then takes the form

$$\langle f \rangle = \frac{\int f(q, p) \exp(-\beta H)\, d\omega}{\int \exp(-\beta H)\, d\omega}. \tag{3}$$

where $d\omega\,(\equiv d^{3N}q\, d^{3N}p)$ denotes a volume element of the phase space. The denominator of this expression is directly related to the partition function of the system. However, to write the precise expression for the latter, we must take into account the relationship between a volume element in the phase space and the corresponding number of distinct quantum states of the system. This relationship was established in Secs 2.4 and 2.5, whereby an element of volume $d\omega$ in the phase space corresponds to

$$\frac{d\omega}{N! h^{3N}} \tag{4}$$

distinct quantum states of the system.[8] The appropriate expression for the partition function would, therefore, be

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(q, p)}\, d\omega; \tag{5}$$

it is understood that the integration in (5) goes over the *whole* of the phase space.

As our first application of this formulation, we consider the example of an ideal gas. Here, we have a system of N identical molecules, assumed to be monatomic (so that there are no internal degrees of motion to be considered), confined to a space of volume V and in equilibrium at temperature T. Since there are no intermolecular interactions to be taken into account, the energy of the system is wholly kinetic:

$$H(q, p) = \sum_{i=1}^{N} (p_i^2/2m). \tag{6}$$

The partition function would then be

$$Q_N(V,T) = \frac{1}{N!h^{3N}} \int e^{-(\beta/2m)\sum_i p_i^2} \prod_{i=1}^{N} (d^3q_i\, d^3p_i). \tag{7}$$

Integrations over the space coordinates are rather trivial; they yield a factor of V^N. Integrations over the momentum coordinates are also quite easy, once we note that integral (7) is simply a product of N identical integrals. Thus, we get

$$Q_N(V,T) = \frac{V^N}{N!h^{3N}} \left[\int_0^\infty e^{-p^2/2mkT} (4\pi p^2\, dp) \right]^N \tag{8}$$

$$= \frac{1}{N!} \left[\frac{V}{h^3} (2\pi mkT)^{3/2} \right]^N ; \tag{9}$$

here, use has been made of eqn. (B.13a). The Helmholtz free energy is then given by, using Stirling's formula (B.29),

$$A(N,V,T) \equiv -kT \ln Q_N(V,T) = NkT \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right\} - 1 \right]. \tag{10}$$

The foregoing result is identical with eqn. (1.5.8), which was obtained by following a very different procedure. The simplicity of the present approach is, however, striking. Needless to say, the complete thermodynamics of the ideal gas can be derived from eqn. (10) in a straightforward manner. For instance,

$$\mu \equiv \left(\frac{\partial A}{\partial N} \right)_{V,T} = kT \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right\}, \tag{11}$$

$$P \equiv -\left(\frac{\partial A}{\partial V} \right)_{N,T} = \frac{NkT}{V} \tag{12}$$

and

$$S \equiv -\left(\frac{\partial A}{\partial T} \right)_{N,V} = Nk \left[\ln \left\{ \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right\} + \frac{5}{2} \right] \tag{13}$$

These results are identical with the ones derived previously, namely (1.5.7), (1.4.2) and (1.5.1a), respectively. In fact, the identification of formula (12) with the ideal-gas law, $PV = nRT$, establishes the identity of the (hitherto undetermined) constant k as the *Boltzmann constant*; see eqn. (3.3.6). We further obtain

$$U \equiv -\left[\frac{\partial}{\partial \beta} (\ln Q) \right]_{E_r} \equiv -T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_{N,V} \equiv A + TS = \frac{3}{2} NkT, \tag{14}$$

and so on.

At this stage we have an important remark to make. Looking at the form of eqn. (8) and the manner in which it came about, we may write

$$Q_N(V,T) = \frac{1}{N!} [Q_1(V,T)]^N , \tag{15}$$

where $Q_1(V, T)$ may be regarded as the partition function of a *single* molecule in the system. A little reflection shows that this result obtains essentially from the fact that the basic constituents of our system are non-interacting (and hence the total energy of the system is simply the sum of their individual energies). Clearly, the situation will not be altered even if the molecules in the system had internal degrees of motion as well. What is essentially required for eqn. (15) to be valid is the absence of interactions among the basic constituents of the system (and, of course, the absence of quantum-mechanical correlations).

Going back to the ideal gas, we could as well have started with the density of states $g(E)$. From eqn. (1.4.17), and in view of the Gibbs correction factor, we have

$$g(E) = \frac{\partial \Sigma}{\partial E} \approx \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{\{(3N/2)-1\}!} E^{(3N/2)-1}. \tag{16}$$

Substituting this into eqn. (3.4.5), and noting that the integral involved is equal to $\{(3N/2)-1\}!/\beta^{3N/2}$, we readily obtain

$$Q_N(\beta) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}. \tag{17}$$

which is identical with (9). It may also be noted that if one starts with the single-particle density of states (2.4.7), namely

$$a(\varepsilon) \approx \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}. \tag{18}$$

computes the single-particle partition function,

$$Q_1(\beta) = \int_0^\infty e^{-\beta\varepsilon} a(\varepsilon)\, d\varepsilon = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} \tag{19}$$

and then makes use of formula (15), one arrives at the same result for $Q_N(V, T)$.

Lastly, we consider the question of determining the density of states, $g(E)$, from the expression for the partition function, $Q(\beta)$, assuming that the latter is already known; indeed, expression (9) for $Q(\beta)$ was derived without making use of any knowledge regarding the function $g(E)$. According to eqn. (3.4.7) and (9), we have

$$g(E) = \frac{V^N}{N!}\left(\frac{2\pi m}{h^2}\right)^{3N/2} \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} \frac{e^{\beta E}}{\beta^{3N/2}}\, d\beta \quad (\beta' > 0). \tag{20}$$

Noting that, for all positive n,

$$\frac{1}{2\pi i} \int_{s'-i\infty}^{s'+i\infty} \frac{e^{sx}}{s^{n+1}}\, ds = \begin{cases} \dfrac{x^n}{n!} & \text{for} \quad x \geq 0 \\ 0 & \text{for} \quad x \leq 0, \end{cases} \tag*{(21)[9]}$$

eqn. (20) becomes

$$g(E) = \begin{cases} \dfrac{V^N}{N!}\left(\dfrac{2\pi m}{h^2}\right)^{3N/2} \dfrac{E^{(3N/2)-1}}{\{(3N/2)-1\}!} & \text{for} \quad E \geq 0 \\ 0 & \text{for} \quad E \leq 0, \end{cases} \tag{22}$$

which is indeed the correct result for the density of states of an ideal gas; cf. eqn. (16). The foregoing derivation may not appear particularly valuable because in the present case we already knew the expression for $g(E)$. However, cases do arise where the evaluation of the partition function of a given system and the consequent evaluation of its density of states turn out to be quite simple, whereas a direct evaluation of the density of states from first principles happens to be rather involved. In such cases, the method given here can indeed be useful; see, for example, Problem 3.15 in comparison with Problems 1.7 and 2.8.

3.6. Energy fluctuations in the canonical ensemble: correspondence with the microcanonical ensemble

In the canonical ensemble, a system can have energy anywhere between zero and infinity. On the other hand, the energy of a system in the microcanonical ensemble is restricted to a very narrow range. How, then, can we assert that the thermodynamic properties of a system derived through the formalism of the canonical ensemble would be the same as the ones derived through the formalism of the microcanonical ensemble? Of course, we do expect that the two formalisms yield identical results, for otherwise our whole scheme would be marred by inner inconsistency. And, indeed, in the case of an ideal classical gas the results obtained by following one approach were precisely the same as the ones obtained by following the other approach. What is the underlying reason for this equivalence?

The answer to this question is obtained by examining the *actual* extent of the range over which the energies of the systems (in the canonical ensemble) have a significant probability to spread; that will tell us the extent to which the canonical ensemble *really* differs from the microcanonical one. To do this, we write down the expression for the mean energy,

$$U \equiv \langle E \rangle = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{1}$$

and differentiate it with respect to the parameter β, holding the energy values E_r constant; we obtain

$$\begin{aligned} \frac{\partial U}{\partial \beta} &= -\frac{\sum_r E_r^2 \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} + \frac{\left[\sum_r E_r \exp(-\beta E_r\right]^2}{\left[\sum_r \exp(-\beta E_r)\right]^2} \\ &= -\langle E^2 \rangle + \langle E \rangle^2, \end{aligned} \tag{2}$$

whence it follows that

$$\langle(\Delta E)^2\rangle \equiv \langle E^2\rangle - \langle E\rangle^2 = -\left(\frac{\partial U}{\partial \beta}\right) = kT^2\left(\frac{\partial U}{\partial T}\right) = kT^2 C_V. \tag{3}$$

Note that we have here the specific heat *at constant volume*, because the partial differentiation in (2) was carried out with the E_r kept constant! For the relative root-mean-square fluctuation in E, eqn. (3) gives

$$\frac{\sqrt{[\langle(\Delta E)^2\rangle]}}{\langle E\rangle} = \frac{\sqrt{(kT^2 C_V)}}{U}, \tag{4}$$

which is $O(N^{-1/2})$, N being the number of particles in the system. Consequently, for large N (which is true for every statistical system) the relative r.m.s. fluctuation in the values of E is quite negligible! Thus, for all practical purposes, a system in the canonical ensemble has an energy equal to, or almost equal to, the mean energy U; the situation in this ensemble is, therefore, practically the same as in the microcanonical ensemble. That explains why the two ensembles lead to practically identical results.

For further understanding of the situation, we consider the manner in which energy is distributed among the various members of the (canonical) ensemble. To do this, we treat E as a continuous variable and start from expression (3.4.3), namely

$$P(E)dE \propto \exp(-\beta E)g(E)dE. \tag{3.4.3}$$

The probability density $P(E)$ is given by the product of two factors: (i) the Boltzmann factor, which monotonically decreases with E, and (ii) the density of states, which monotonically increases with E. The product, therefore, has an extremum at some value of E, say E^*.[10] The value E^* is determined by the condition

$$\frac{\partial}{\partial E}\left\{e^{-\beta E}g(E)\right\}\bigg|_{E=E^*} = 0,$$

that is, by

$$\frac{\partial \ln g(E)}{\partial E}\bigg|_{E=E^*} = \beta. \tag{5}$$

Recalling that

$$S = k\ln g \quad \text{and} \quad \left(\frac{\partial S(E)}{\partial E}\right)_{E=U} = \frac{1}{T} = k\beta.$$

the foregoing condition implies that

$$E^* = U. \tag{6}$$

This is a very interesting result, for it shows that, irrespective of the physical nature of the given system, the most probable value of its energy is identical with its mean value. Accordingly, if it is advantageous, we may use one instead of the other.