Chapter V

GIBBS FORMALISM--PHYSICAL DERIVATION

In this Chapter we present physical arguments by which the Gibbs formalism can be derived and justified, deliberately avoiding all use of probability theory. This will serve to convince us of the validity of Gibbs' formalism for the particular applications given by Gibbs, and will give us an intuitive physical understanding of the second law, as well as the physical meaning of the Kelvin temperature.

Later on (Chapter 9) we will present an entirely different derivation in terms of a general problem of statistical estimation, deliberately avoiding all use of physical ideas, and show that the identical mathematical formalism emerges. This will serve to convince us of the generality of the Gibbs methods, and show that their applicability is in no way restricted to equilibrium problems; or indeed, to physics.

It is interesting to note that most of Gibbs' important results were found independently and almost simultaneously by Einstein (1902); but it is to Gibbs that we owe the elegant mathematical formulation of the theory. In the following we show how, from mechanical considerations involving the microscopic state of a system, the Gibbs rules emerge as a description of equilibrium macroscopic properties. Having this, we can then reason backwards, and draw inferences about microscopic conditions from macroscopic experimental data. We will consider only classical mechanics here; however, none of this classical theory will have to be unlearned later, because the Gibbs formalism

lost none of its validity through the development of quantum theory. Indeed, the full power of Gibbs' methods has been realized only through their successful application to quantum theory.

5.1 Review of Classical Mechanics

In classical mechanics a complete description of the state of a system is given by specifying n coordinates $q_1 \ldots q_n$, and the corresponding velocities $\dot{q}_1 \ldots \dot{q}_n$. The equations of motion are then determined by a Lagrangian function which in simple mechanical problems is

$$L(q_i, \dot{q}_i) = T - V \tag{5-1}$$

where T and V are the kinetic and potential energies. In problems involving coupling of particles to an electromagnetic field, the Lagrangian function takes a more general form, as we will see later. In either case, the equations of motion are

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = 0. \tag{5-2}$$

The advantage of the Lagrangian form (5-2) over the original Newtonian form (to which it is completely equivalent in simple mechanical problems)

$$m\ddot{x}_i = -\frac{\partial V}{\partial x_i} \tag{5-3}$$

is that (5-2) holds for arbitrary choices of the coordinates q_i; they can include angles, or any other parameters which serve to locate a particle in space. The Newtonian equations (5-3), on the other hand, hold only when the x_i are rectangular (cartesian) coordinates of a particle.

Still more convenient for our purposes is the Hamiltonian form of the equations of motion. Define the momentum "canonically conjugate" to the coordinate q_i by

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i} \tag{5-4}$$

and a Hamiltonian function H by

$$H(q_1 p_1 \ldots q_n p_n) \equiv \sum_{i=1}^{n} p_i \dot{q}_i - L(q_1 \ldots \dot{q}_n) \tag{5-5}$$

the notation indicating that after forming the right-hand side of (5-5) the velocities $\dot{q}_i$ are eliminated mathematically, so that the Hamiltonian is expressed as a function of the coordinates and momenta only.

Problem (5.1). A particle of mass m is located by specifying $(q_1, q_2, q_3) = (r, \theta, z)$ respectively, where r, θ, z are a cylindrical coordinate system related to the cartesian x, y, z by $x + iy = r\, e^{i\theta}$, $z = z$. The particle moves in a potential $V(q_1, q_2, q_3)$. Show that the Hamiltonian in this coordinate system is

$$H(q_i p_i) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2m} + V(q_1, q_2, q_3) \tag{5-6}$$

and discuss the physical meaning of p_1, p_2, p_3.

Problem (5.2). Find the Hamiltonian for the same particle, in the spherical coordinate system $(q_1, q_2, q_3) = (r, \theta, \phi)$, related to the cartesian by $x + iy = r \sin\theta\, e^{i\phi}$, $z = r \cos\theta$, and again discuss the physical meaning of p_1, p_2, p_3.

In terms of the Hamiltonian, the equations of motion assume a more symmetrical form:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad\qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{5-7}$$

of which the first follows from the definition (5-5), while the second is equivalent to (5-2).

The above formulation of mechanics holds only when all forces are conservative; i.e. derivable from a potential energy function $V(q_1,\ldots,q_n)$, and in this case the Hamiltonian is numerically equal to the total energy (T + V). Often, in addition to the conservative forces we have non-conservative ones which depend on the velocities as well as the coordinates. The Lagrangian and Hamiltonian form of the equations of motion can be preserved if there exists a new potential function $M(q_i,\dot{q}_i)$ such that the non-conservative force acting on coordinate q_i is

$$F_i = \frac{d}{dt}\frac{\partial M}{\partial \dot{q}_i} - \frac{\partial M}{\partial q_i} \qquad (5\text{-}8)$$

We then define the Lagrangian as $L \equiv T - V - M$.

Problem (5.3). Show that the Lagrangian equations of motion (5-2) are correct with this modified Lagrangian. Find the new momenta and Hamiltonian. Carry this through explicitly for the case of a charged particle moving in a time-varying electromagnetic field $\vec{E}(x,y,z,t)$, $\vec{H}(x,y,z,t)$ for which the non-conservative force is given by the Lorentz force law,

$$\vec{F} = e[\vec{E} + \frac{1}{c}\vec{v} \times \vec{B}]$$

Hint: Express the potential M in terms of the vector and scalar potentials of the field $\vec{A}$, ϕ, defined by $\vec{B} = \vec{\nabla} \times \vec{A}$, $\vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\dot{\vec{A}}$. Notice that, since the potentials are not uniquely determined by E, H, there is no longer any unique connection between momentum and velocity; or between the Hamiltonian and the energy. Nevertheless, the Lagrangian and Hamiltonian equations of motion still describe the correct physical laws.

5.2 Liouville's Theorem

The Hamiltonian form (5-7) is of particular value because of the following property. Let the coordinates and momenta $(q_1 p_1 \ldots q_n p_n)$ be regarded as coordinates of a single point in a 2n-dimensional phase space. This point moves, by virtue of the equations of motion, with a velocity v whose components are $(\dot{q}_1 \dot{p}_1 \ldots \dot{q}_n \dot{p}_n)$. At each point of phase space there is specified in this way a particular velocity, and the equations of motion thus generate a continuous flow pattern in phase space, much like the flow pattern of a fluid in ordinary space. The divergence of the velocity of this flow pattern is

$$\begin{aligned} \text{div}(v) &= \sum_{i=1}^{n} \left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] \\ &= \sum_{i=1}^{n} \left[\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right] = 0 \end{aligned} \qquad (5\text{-}9)$$

so that the flow in phase space corresponds to that of an incompressible fluid.

In an incompressible flow, the volume occupied by any given mass of the fluid remains constant as time goes on and the mass of fluid is carried into various regions. An exactly analogous property holds in phase space by virtue of (5-9). Consider at time t = 0 any 2n-dimensional region Γ_o consisting of some possible range of initial conditions $q_i(0)$, $p_i(0)$ for a mechanical system, as shown in Fig. (5.1). This region has a total phase volume

$$\Omega(0) = \int_{\Gamma_o} dq_1 dp_1 \ldots dq_n dp_n \quad . \qquad (5\text{-}10)$$

In time t, each point $[q_1(0) \ldots p_n(0)]$ of Γ_o is carried, by the equations of motion, into a new point $[q_1(t) \ldots p_n(t)]$. The totality of all points which were originally in Γ_o now defines a new region Γ_t with phase volume

$$\Omega(t) = \int_{\Gamma_t} dq_1 \ldots dp_n$$

and from (5-9) it can be shown that

$$\Omega(t) = \Omega(0). \qquad (5\text{-}11)$$

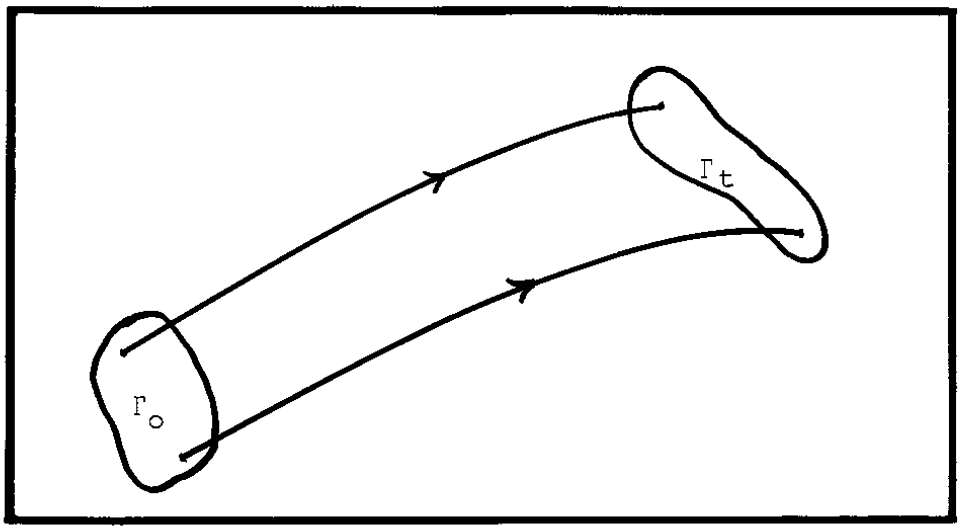

Figure 5.1. Volume-conserving flow in phase space.

An equivalent statement is that the Jacobian determinant of the transformation $[q_1(0)\ldots p_n(0)] \to [q_1(t)\ldots p_n(t)]$ is identically equal to unity:

$$\frac{\partial(q_{1t}\cdots p_{nt})}{\partial(q_{10}\cdots p_{n0})} = \begin{vmatrix} \frac{\partial q_{1t}}{\partial q_{10}} & \cdots & \frac{\partial p_{nt}}{\partial q_{10}} \\ \vdots & & \vdots \\ \frac{\partial q_{1t}}{p_{n0}} & \cdots & \frac{\partial p_{nt}}{p_{n0}} \end{vmatrix} = 1 \qquad (5\text{-}12)$$

Problem (5.4). Prove that (5-9), (5-11), and (5-12) are equivalent statements. (Hint: See A. I. Khinchin, "Mathematical Foundations of Statistical Mechanics", Chapter II.)

This result was termed by Gibbs the "Principle of conservation of extension-in-phase", and is usually referred to nowadays as Liouville's theorem. An important advantage of considering the motion of a system referred to phase space (coordinates and momenta) instead of the coordinate-velocity space of the Lagrangian is that in general no such conservation law holds in the latter space (although they amount to the same thing in the special case where all

the q_i are cartesian coordinates of particles and all forces are conservative in the sense of Problem 5.3).

Problem (5.5). Liouville's theorem holds only because of the special form of the Hamiltonian equations of motion, which makes the divergence (5-9) identically zero. Generalize it to a mechanical system whose state is defined by a set of variables $\{x_1, x_2, \ldots, x_n\}$ with equations of motion for $x_i(t)$:

$$\dot{x}_i(t) = f_i(x_1 \ldots x_n) \quad , \qquad i = 1, 2, \ldots, n \tag{5-13}$$

The jacobian (5-12) then corresponds to

$$J[x_1(0) \ldots x_n(0); t] \equiv \frac{\partial [x_1(t) \ldots x_n(t)]}{\partial [x_1(0) \ldots x_n(0)]} \tag{5-14}$$

Prove that in place of Liouville's theorem $J = 1 = \text{const.}$, we now have

$$J(t) = J(0) \exp \left[\int_0^t \sum_{i=1}^n \frac{\partial f_i [x_1(t) \ldots x_n(t)]}{\partial x_i(t)} \, dt \right] \tag{5-15}$$

5.3 The Structure Function

One of the essential dynamical properties of a system, which controls its thermodynamic properties, is the total phase volume compatible with various experimentally observable conditions. In particular, for a system in which the Hamiltonian and the energy are the same, the total phase volume below a certain energy E is

$$\Omega(E) = \int \theta[E - H(q_i p_i)] \, dq_1 \ldots dp_n \tag{5-16}$$

(When limits of integration are unspecified, we understand integration over all possible values of q_i, p_i.) In (5-16), $\theta(x)$ is the unit step function

$$\theta(x) \equiv \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases} \tag{5-17}$$

The differential phase volume, called the structure function, is given by

$$\rho(E) = \frac{d\Omega}{dE} = \int \delta[E - H(q_i p_i)]\ dq_1 \ldots dp_n \tag{5-18}$$

and it will appear presently that essentially all thermodynamic properties of the system are known if $\rho(E)$ is known, in its dependence on such parameters as volume and mole numbers.

Calculation of $\rho(E)$ directly from the definition (5-18) is generally very difficult. It is much easier to calculate first its Laplace transform, known as the partition function:

$$Z(\beta) = \int_0^\infty \rho(E)\ e^{-\beta E}\ dE \tag{5-19}$$

where we have assumed that all possible values of energy are positive; this can always be accomplished for the systems of interest by appropriately choosing the zero from which we measure energy. In addition, it will develop that full thermodynamic information is easily extracted directly from the partition function $Z(\beta)$, so that calculation of the structure function $\rho(E)$ is unnecessary for some purposes.

Using (1-18), the partition function can be written as

$$Z(\beta) = \int e^{-\beta H(q_i p_i)}\ dq_1 \ldots dp_n \tag{5-20}$$

which is the form most useful for calculation. If the structure function $\rho(E)$ is needed, it is then found by the usual rule for inverting a Laplace transform:

$$\rho(E) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} Z(\beta)\ e^{\beta E}\ d\beta \tag{5-21}$$

the path of integration passing to the right of all singularities of $Z(\beta)$, as in Fig. (5.2).

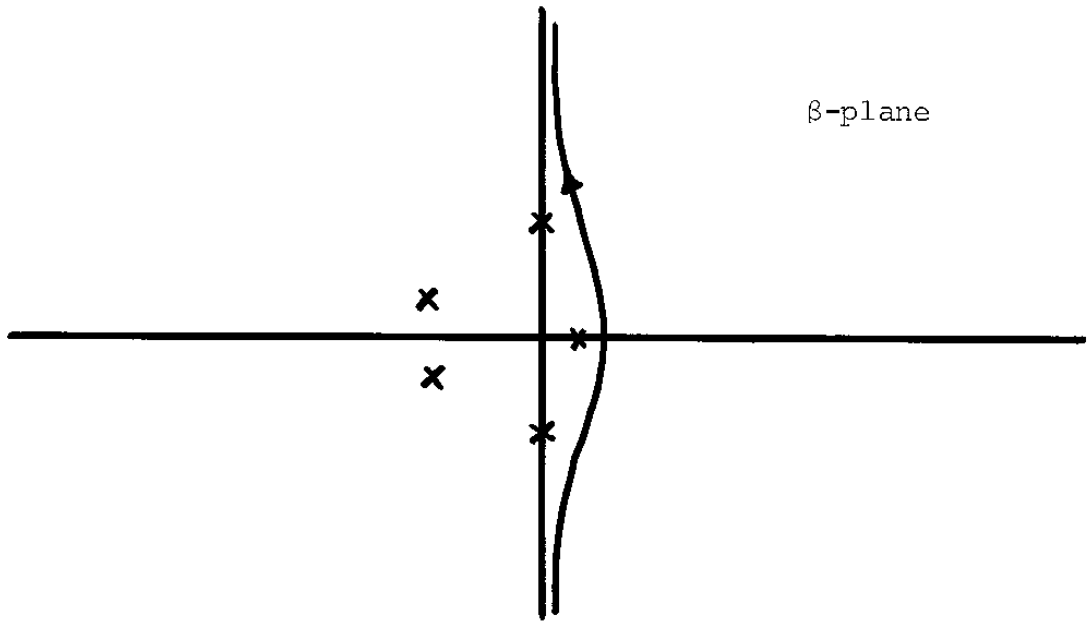

Figure 5.2. Path of integration in Equation (5-21).

To illustrate the above relations, we now compute the partition function and structure function in two simple examples.

Example 1. Perfect monatomic gas. We have N atoms, located by cartesian coordinates $q_1 \ldots q_N$, and denote a particular component (direction in space) by an index α, $\alpha = 1, 2, 3$. Thus, $q_{i\alpha}$ denotes the α'th component of the position vector of the i'th particle. Similarly, the vector momenta of the particles are denoted by $p_1 \ldots p_N$, and the individual components by $p_{i\alpha}$. The Hamiltonian is then

$$H_1 = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + u(q_i) \right] \tag{5-22}$$

where

$$p_i^2 \equiv \sum_{\alpha=1}^{3} p_{i\alpha}^2 \tag{5-23}$$

and the potential function u(q) defines the box of volume V containing the gas:

$$u(q) \equiv \begin{cases} u_o, & q_i \text{ in } V \\ \infty, & \text{otherwise} \end{cases} . \qquad (5\text{-}24)$$

The arbitrary additive constant u_o, representing the zero from which we measure our energies, will prove convenient later. The partition function is then

$$Z_1(\beta) = \prod_{i=1}^{N} \left[\int e^{-\frac{\beta p_i^2}{2m}} d^3p_i \int e^{-\beta u(q_i)} d^3q_i \right]$$

$$= \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \left(V e^{-\beta u_o} \right)^N \qquad (5\text{-}25)$$

and the structure function is

$$\rho_1(E) = \frac{V^N (2\pi m)^{3N/2}}{2\pi i} \int_{-i\infty}^{i\infty} \frac{e^{\beta(E-Nu_o)}}{\beta^{3N/2}} d\beta$$

If N is an even number, the integrand is analytic everywhere in the complex β-plane, except for the pole of order 3N/2 at the origin. If $E > Nu_o$, the integrand tends to zero very rapidly as $|\beta| \to \infty$ in the left half-plane $\mathrm{Re}(\beta) \leq 0$. The path of integration may then be extended to a closed one by addition of an infinite semicircle to the left, as in Fig. (5.3), the integral over the semicircle vanishing. We can then apply the Cauchy residue theorem

$$\frac{1}{2\pi i} \int_C \frac{f(z)\, dz}{(z-a)^{n+1}} = \frac{1}{n!} \frac{d^n}{da^n} f(a) \qquad (5\text{-}27)$$

where the closed contour C, illustrated in Fig. (5.4), encloses the point z = a once in a counter-clockwise direction, and f(z) is analytic everywhere on and within C.

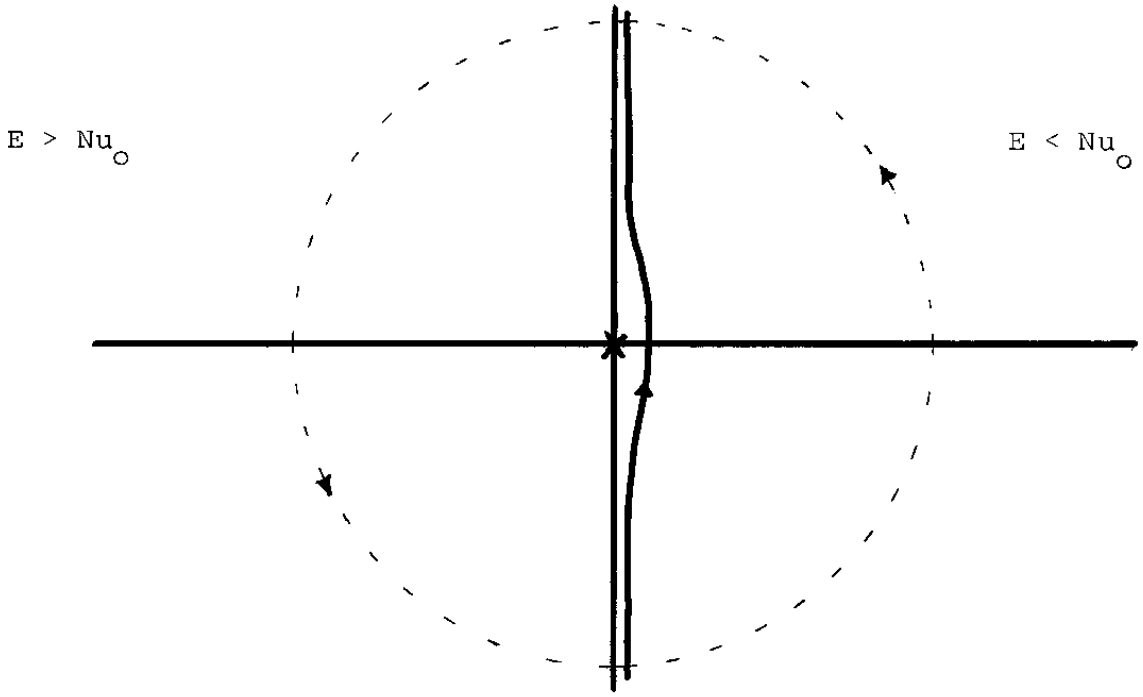

Figure 5.3. Extensions of integration path in Equation (5-26).

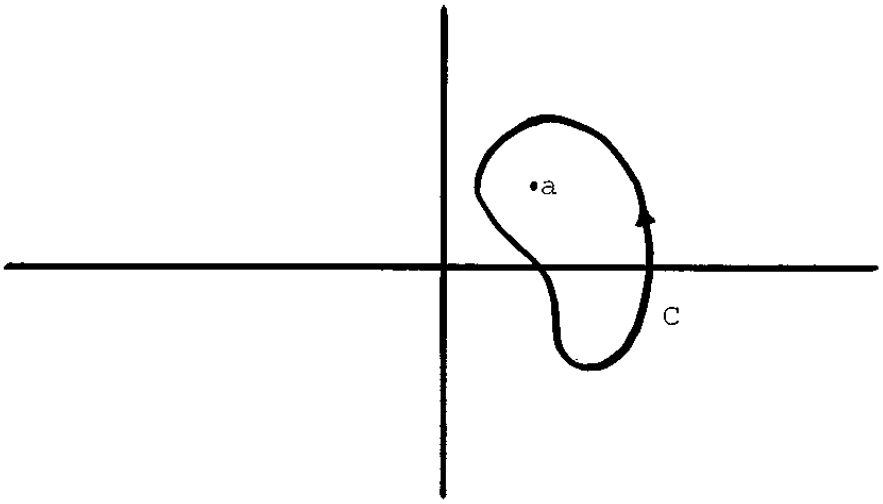

Figure 5.4. The Cauchy Residue Theorem.

This gives for (5-23),

$$\rho_1(E) = \frac{V^N (2\pi m)^{K+1}}{K!} \frac{d^K}{d\beta^K} e^{\beta(E-Nu_o)} \Bigg|_{\beta=0} . \qquad (5\text{-}28)$$

where $K \equiv (3N/2) - 1$. If $E < Nu_o$, the integrand of (5-26) tends to zero very

rapidly as $|\beta| \to \infty$ in the right half-plane $\mathrm{Re}(\beta) \geq 0$, so the path of integration may be completed by addition of the infinite semicircle to the right, also illustrated in Fig. (5.3). The integral over the semicircle is again zero, but the closed path now contains no singularities of the integrand, and by the Cauchy theorem the integral is now zero. Collecting results, we have for N even,

$$\rho_1(E) = \begin{cases} \dfrac{V^N (2\pi m)^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} (E - Nu_o)^{\frac{3N}{2} - 1}, & E > Nu_o \\ 0, & E < Nu_o \end{cases} \tag{5-29}$$

If N is odd, we have a second-order branch point, instead of a pole, at $\beta = 0$. We then add a branch cut along the negative real axis as shown in Fig. (5.5). If $E < Nu_o$, we can still complete the path to the right as in Fig. (5.3), and the integral is still zero.

If $E > Nu_o$ we cannot complete the path of integration C to the left because of the branch cut. We can, however, deform it to C_1 in Fig. (5.5), since the integrals over the two infinite quarter-circles C', C" still vanish. If we now make the change of variables $s = \beta(E - Nu_o)$, the integral (5-26) reduces to

$$\rho_1(E) = V^N (2\pi m)^{3N/2} (E - Nu_o)^{\frac{3N}{2} - 1} \frac{1}{2\pi i} \int_{C_1} e^s \, s^{-3N/2} \, ds \tag{5-30}$$

But this is just Hankel's integral representation of the Gamma function [Whittaker and Watson, (1927); Chap. 12]:

$$\frac{1}{\Gamma(z)} = \frac{1}{2\pi i} \int_{C_1} e^s \, s^{-z} \, ds \tag{5-31}$$

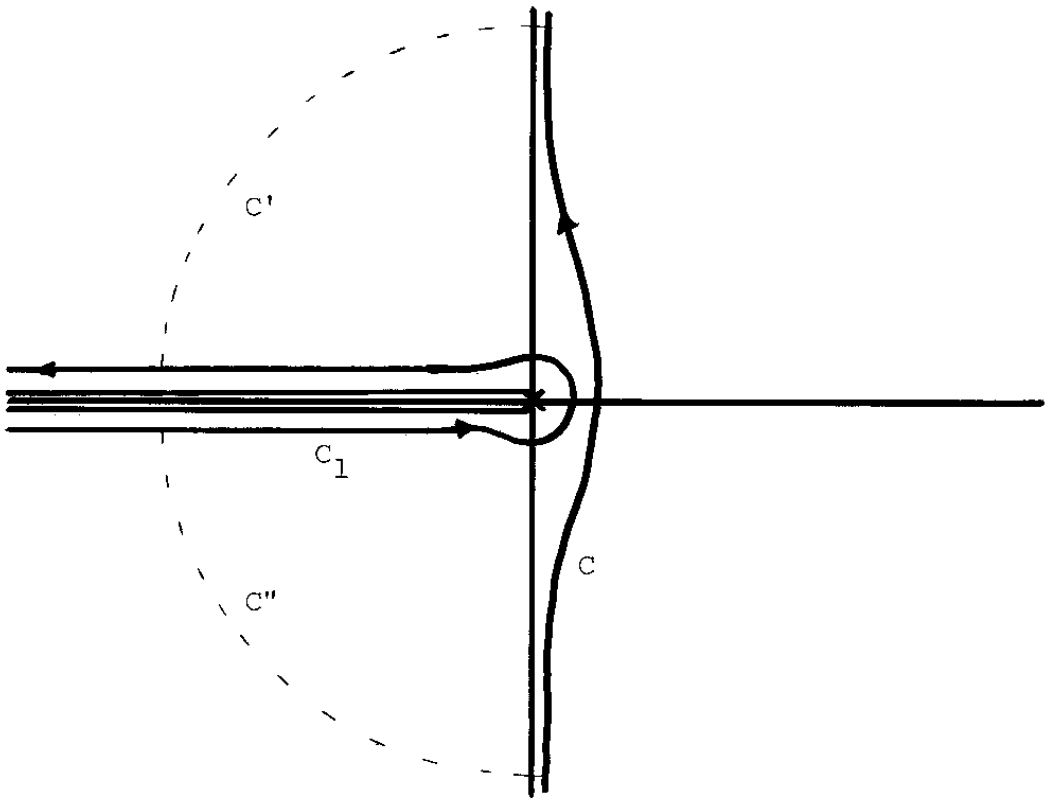

Figure 5.5. Path of integration for N odd.

which holds when z is any complex number. Therefore the previous result (5-29) actually holds for N even or odd, provided that for N odd we understand $\left(\frac{3N}{2} - 1\right)!$ as standing for its analytic generalization, $\Gamma(3N/2)$. The factorial notation is often more convenient than the Γ-function notation, and so we understand that the factorial of any number, real or complex, is defined by

$$x! \equiv \Gamma(x+1) \quad . \tag{5-32}$$

Example 2. Assembly of Harmonic Oscillators. We have N particles of mass m, and this time we label the cartesian coordinates and corresponding momenta by $\{q_1 \ldots q_n\}$, $\{p_1 \ldots p_n\}$, with n = 3N. The potential energy is a positive definite quadratic form in the q_i, so the Hamiltonian is

$$H_2(q_i p_i) = \sum_{i=1}^{n} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j=1}^{n} a_{ij} q_i q_j \geq 0 \tag{5-33}$$

where, without loss of generality, a_{ij} can be considered a symmetric matrix: $a_{ij} = a_{ji}$. The partition function is then

$$Z_2(\beta) = \left[\prod_{i=1}^{n} \int_{-\infty}^{\infty} e^{-\frac{\beta p_i^2}{2m}} dp_i\right]\left[\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\{-\frac{\beta}{2} \sum a_{ij} q_i q_j\} dq_1 \cdots dq_n\right]$$

$$= \left(\frac{2\pi m}{\beta}\right)^{n/2} \frac{(2\pi)^{n/2}}{\sqrt{\beta^n \det(a_{ij})}} \tag{5-34}$$

the formula for the integral over the q's being easily derived from the elementary integral

$$\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left[-\frac{1}{2} \sum_{k=1}^{n} a_k x_k^2\right] dx_1 \cdots dx_n = \prod_{k=1}^{n} \sqrt{\frac{2\pi}{a_k}} \tag{5-35}$$

by making the substitutions

$$x_k = \sum_{j=1}^{n} M_{kj} q_j \quad , \qquad \sum_{k=1}^{n} a_k M_{ki} M_{kj} = a_{ij} \tag{5-36}$$

where M is any matrix with nonvanishing determinant, and using the fact that the determinant of the product of matrices is the product of the determinants:

$$\det(a_{ij}) = [\det(M)]^2 \prod_{k=1}^{n} a_k \quad . \tag{5-37}$$

Better physical understanding of the result (5-34) is achieved by transformation of the Hamiltonian (5-33) to normal mode coordinates. The matrix a_{ij} is real and symmetric, and so by a well-known result of matrix theory [Margenau and Murphy (1943); Chap. 10] there exists an orthogonal matrix N,

$$\sum_{i=1}^{n} N_{ij} N_{ik} = \delta_{jk} \tag{5-38}$$

which diagonalizes a_{ij}:

$$(\tilde{N}\, A\, N)_{kl} = \sum_{i,j=1}^{n} a_{ij} N_{ik} N_{jl} = \lambda_k \delta_{kl} = m\omega_k^2 \delta_{kl} \tag{5-39}$$

The last step merely defines a new quantity ω_k. If now we introduce new coordinates Q_k, defined by

$$q_i = \frac{1}{\sqrt{m}} \sum_{k=1}^{n} N_{ik} Q_k \quad , \tag{5-40}$$

the potential energy reduces to

$$V = \frac{1}{2} \sum_{i,j=1}^{n} a_{ij} q_i q_j = \frac{1}{2} \sum_{k=1}^{n} \omega_k^2 Q_k^2 \tag{5-41}$$

The kinetic energy appears in the Lagrangian as

$$T = \sum_i \frac{1}{2} m \dot{q}_i^2 = \sum_{k=1}^{n} \dot{Q}_k^2 \tag{5-42}$$

where we used (5-40) and (5-38). The Lagrangian in terms of the new coordinates thus reduces to

$$L = \frac{1}{2} \sum_{k=1}^{n} \left[\dot{Q}_k^2 - \omega_k^2 Q_k^2 \right] \tag{5-43}$$

The momentum canonically conjugate to Q_k is therefore

$$P_k = \frac{\partial L}{\partial \dot{Q}_k} = \dot{Q}_k \tag{5-44}$$

and the Hamiltonian in the new coordinates is

$$H_2 = \frac{1}{2} \sum_{k=1}^{n} \left[P_k^2 + \omega_k^2 Q_k^2 \right] \tag{5-45}$$

This yields the equations of motion

$$\dot{Q}_k = \frac{\partial H}{\partial P_k} = P_k \tag{5-46}$$

$$\dot{P}_k = - \frac{\partial H}{\partial Q_k} = - \omega_k^2 Q_k \tag{5-47}$$

or

$$\ddot{Q}_k + \omega_k^2 Q_k = 0 \tag{5-48}$$

and so the ω_k are the normal mode oscillation frequencies of the system, Q_k is the corresponding normal coordinate. Taking the determinant of (5-39), we have

$$\det(a_{ij})\,[\det(N)]^2 = m^n \prod_{k=1}^{n} \omega_k^{\,2} \tag{5-49}$$

but $\det(N) = \pm 1$ from (5-38), and so the partition function (5-34) reduces to

$$Z_2(\beta) = \left(\frac{2}{\bar{\omega}\beta}\right)^n = \left(\frac{2}{\bar{\omega}\beta}\right)^{3N} \tag{5-50}$$

where $\bar{\omega}$ is the geometric mean of all the oscillation frequencies, defined by

$$\bar{\omega}^n = \prod_{k=1}^{n} \omega_k \tag{5-51}$$

As a check, note that (5-50) can be derived directly from the transformed Hamiltonian (5-45) by application of (5-20) and (5-35). This is an example of the fact that the partition function (5-20) is invariant under any canonical transformation $(q_i,p_i) \rightarrow (Q_k,P_k)$, so that in calculating $Z(\beta)$ we are at liberty to use any coordinate system that proves to be convenient mathematically.

Problem (5.6). In the Debye model of a crystal, lattice vibration modes are distributed in frequency with a density $\rho(\omega)$ proportional to ω^2; i.e. the number of modes in a frequency interval $d\omega$ is

$$\rho(\omega)\, d\omega = A\omega^2\, d\omega$$

up to a maximum frequency ω_{max}; and $\rho(\omega) = 0$ for $\omega > \omega_{max}$. Find the constant A in terms of ω_{max} and the number N of atoms in the crystal, and show that the geometrical mean frequency is

$$\bar{\omega} = \exp(-1/3)\ \omega_{max} = 0.716\ \omega_{max}$$

The structure function for the assembly of harmonic oscillators is now found immediately by the method of (5-28):

$$\rho_2(E) = \left(\frac{2\pi}{\hbar\omega}\right)^{3N} \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{e^{\beta E}}{\beta^{3N}}\, d\beta = \left(\frac{2\pi}{\hbar\omega}\right)^{3N} \frac{E^{3N-1}}{(3N-1)!} \tag{5-52}$$

In both examples, the structure function increases as a very high power of E. This is typical of all macroscopic systems, and it is an essential part of the reason they exhibit reproducible thermodynamic properties.

The phase volume relations can be visualized by means of semi-realistic diagrams like Fig. (5.6). The vertical coordinate represents the energy. Imagine a tapered vase filled with water up to a level equal to the energy of the system. The total volume of water needed to fill it to this level corresponds to the phase volume $\Omega(E)$, the surface area to the structure function $\rho(E)$. Because $\rho(E)$ increases as an enormously high power of E, the vase flares at an enormous rate, not possible to depict in the diagram. It is, in fact so rapid that practically all of the phase volume up to energy E is actually contained in a very small range δE just under the surface E. For example, if $\rho(E) = A\, E^{n-1}$, then $\Omega(E) = (E/n)\, \rho(E)$, and the energy shell δE contains half the phase volume $\Omega(E)$ if $\rho(E)\ \delta E = \frac{1}{2}\, \Omega(E)$, or

$$\frac{\delta E}{E} = \frac{1}{2n} \tag{5-53}$$

i.e., the half-volume shell, for a macroscopic system, has relative thickness of only about one part in 10^{24}. If we take the still very small energy shell of thickness $\delta E = E/\sqrt{n} \simeq 10^{-12}\, E$, we find that

$$\int_{E-\delta E}^{E} \rho(E)\, dE = \Omega(E) - \Omega\left(E - \frac{E}{\sqrt{n}}\right) \simeq \Omega(E)\left[1 - e^{-\sqrt{n}}\right] \tag{5-54}$$

so that only an infinitesimal fraction

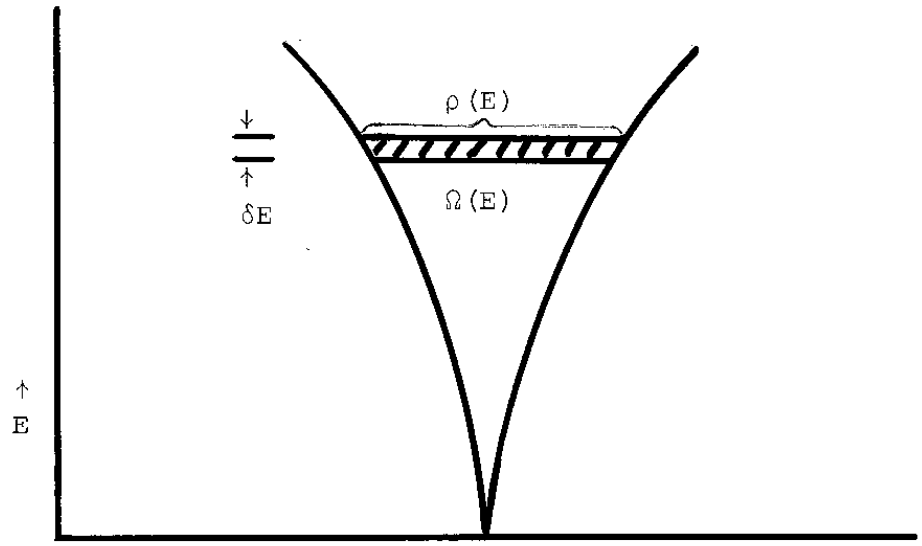

Figure 5.6. Representation of phase volume and structure function.

$$e^{-(10^{12})} \simeq 10^{-(4.3 \times 10^{11})}$$

of the phase volume $\Omega(E)$ lies below this energy shell. The suggested analogy to water filling a vase actually holds in a much more important sense, as we will see presently.

Problem (5.7). Calculate the structure function $\rho(E)$ for a spherical pendulum consisting of a mass m connected to the origin by a weightless rod of length L, for which the Lagrangian is

$$L(\theta,\phi,\dot{\theta},\dot{\phi}) = \frac{1}{2} mL^2\dot{\theta}^2 + \frac{1}{2} mL^2 \sin^2\theta \, \dot{\phi}^2 + mgL \cos\theta \ ,$$

θ being the angle the rod makes with the vertical, ϕ the azimuth angle.

5.4 Relation to Thermodynamics

Suppose we place two systems with structure functions $\rho_1(E) = A_1 E^{n_1}$, $\rho_2(E) = A_2 E^{n_2}$ in loose contact so that they can exchange energy, but not par-

ticles. Together they constitute a larger system with phase volume below total energy E given by

$$\Omega(E) = \int_0^E \rho_1(E_1)\Omega_2(E-E_1)\, dE_1 \tag{5-55}$$

or, differentiating with respect to E, the structure function of the combined system is

$$\rho(E) = \int_0^E \rho_1(E_1)\rho_2(E-E_1)\, dE_1 \tag{5-56}$$

Now for macroscopic systems the exponents n_1, n_2 are very large as we have seen. Therefore the integrand of (5-56) has a single enormously sharp peak, and practically all the contribution to the integral (5-56) comes from values of E_1 in the immediate neighborhood of this peak. The value of E_1 at the peak is found by differentiating:

$$\frac{d}{dE_1}\left[\rho_1(E_1)\rho_2(E-E_1)\right] = \rho_1'(E_1)\rho_2(E-E_1) - \rho_1(E_1)\rho_2'(E-E_1) = 0$$

or,

$$\frac{d \log \rho_1}{dE_1} = \frac{d \log \rho_2}{dE_2} \tag{5-57}$$

Let us investigate the sharpness of this peak. The logarithm of the integrand is

$$L(E_1) = \log\left[\rho_1(E_1)\rho_2(E-E_1)\right] = \log(A_1A_2) + n_1 \log E_1 + n_2 \log(E-E_1) \tag{5-58}$$

Expand this in a Taylor series about the value $E_1 = E_{10}$ which maximizes L(E), noting that $(E - E_{10}) = (n_2/n_1)\, E_{10}$;

$$L(E_1) = L_{max} - n_1\left[1 + \frac{n_1}{n_2}\right]\frac{(E_1 - E_{10})^2}{2!\, E_{10}^2} +$$

$$+ 2n_1\left[1 - \frac{n_1^2}{n_2^2}\right]\frac{(E_1 - E_{10})^3}{3!\ E_{10}^3}$$

$$- 3!\ n_1\left[1 + \frac{n_1^3}{n_2^3}\right]\frac{(E_1 - E_{10})^4}{4!\ E_{10}^4} + \ldots \qquad (5\text{-}59)$$

If the fractional deviation from the maximum is small; i.e. if

$$|E_1 - E_{10}| << E_{10}\frac{n_2}{n_1} \qquad (5\text{-}60)$$

then all the succeeding terms are very small compared to the term in $(E_1 - E_{10})^2$, and so a good approximation is

$$\rho_1(E_1)\rho_2(E-E_1) \simeq (\rho_1\rho_2)_{max}\exp\left[-n_1\left(1 + \frac{n_1}{n_2}\right)\frac{(E_1 - E_{10})^2}{2\ E_{10}^2}\right] \qquad (5\text{-}61)$$

Problem (5.8). As a check on the accuracy of the approximation (5-61), note that it leads to an approximate expression for $\rho(E)$ by using (5-56):

$$\rho(E) \simeq (\rho_1\rho_2)_{max}\int_{-\infty}^{\infty}\exp\left\{-n_1\left[1 + \frac{n_1}{n_2}\right]\frac{(E_1 - E_{10})^2}{2\ E_{10}^2}\right\}dE_1$$

$$= (\rho_1\rho_2)_{max}\sqrt{\frac{2\pi E_{10}^2 n_2}{n_1(n_1+n_2)}} \qquad (5\text{-}62)$$

Calculate the exact $\rho(E)$ from (5-56) and compare with (5-62). The following formulas will be useful here: (1) the Eulerian integral of the first kind, or complete Beta function, is

$$\int_0^1 x^a\ (1-x)^b dx = \frac{a!b!}{(a+b+1)!} \qquad (5\text{-}63)$$

(2) the Stirling approximation for factorials of large numbers is

$$\log N! = N \log N - N + \frac{1}{2} \log(2\pi N) + O\,\frac{1}{N} \tag{5-64}$$

The relative contribution of various ranges of E_1 to $\rho(E)$ may be seen from tables of the "error function":

$$\operatorname{erf} x \equiv \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2}\, dx \tag{5-65}$$

Some numerical values of erf x are:

x	erf x
0.0	0.00000
0.5	0.52050
1.0	0.84270
1.5	0.96611
2.0	0.99532
2.5	0.99959
3.0	0.99998
> 3	$1 - \frac{e^{-x^2}}{x\sqrt{\pi}}$

Suppose, for simplicity, that $n_1 = n_2 = 10^{24}$. Then, letting

$$x = \sqrt{n_1}\, \frac{E_1 - E_{10}}{E_{10}} = 10^{12}\, \frac{E_1 - E_{10}}{E_{10}}\ , \tag{5-66}$$

we see from the table that over 84 per cent of the integral

$$\int_0^E \rho_1(E_1)\rho_2(E-E_1)\, dE_1$$

is contributed by values of E_1 in the range

$$E_{10} \pm \frac{E_{10}}{\sqrt{n_1}} = E_{10}[1 \pm 10^{-12}] \tag{5-67}$$

Similarly, 99.998 per cent of the integral is contributed by values of E_1 in a range three times as wide: $E_{10}(1 \pm 3 \times 10^{-12})$. Values of E_1 which deviate from E_{10} by more than one part in a million contribute one part in

$$\frac{e^{-x^2}}{x\sqrt{\pi}} = \frac{\exp[-10^{12}]}{10^6\sqrt{\pi}} \simeq 10^{-(4.3 \times 10^{11})} \tag{5-68}$$

to the structure function of the combined system.

To state this remarkable situation in the most useful way of all for our purposes, suppose the phase point of a system is known to be in a small region $\delta\Omega$ of phase space, comprised within the energy shell of thickness δE. If $\delta\Omega$ contains as much as one part in $10^{10^{10}}$ of the total phase volume of this energy shell; i.e. if $\delta\Omega \geq 10^{-(10^{10})}\rho(E)\,\delta E$, then

$$\left\{\begin{array}{l}\text{the fraction of the phase volume } \delta\Omega \text{ in which } E_1 \\ \text{differs from } E_{10} \text{ by as much as one part in } 10^6, \\ \text{is necessarily less than } 10^{-(4 \times 10^{11})}\end{array}\right\} \tag{5-69}$$

Suppose that these two systems were initially given arbitrary energies $E_1(0)$, $E_2(0)$ and at time $t = 0$ were placed in contact so that the energies $E_1(t)$, $E_2(t)$ become redistributed. The systems being otherwise isolated, the total energy $E = E_1(t) + E_2(t)$ will remain constant. Now on the one hand we know (Liouville's theorem) that phase volume for the combined system is conserved in the time development. On the other hand, we have just seen that

the overwhelmingly greatest part of all the phase volume accessible to the system corresponds very accurately to one definite distribution of energy E_1, E_2, such that

$$\frac{\partial \log \rho_1}{\partial E_1} = \frac{\partial \log \rho_2}{\partial E_2} \tag{5-70}$$

Thus, if we are asked to predict the final distribution of energy reached after a long interaction time, it will be a pretty safe bet that the subsystems will divide up the available energy in such a way that (5-70) is satisfied.

To illustrate the reasoning here in a case where the numbers are much more modest, suppose the entire surface of the earth painted red, with the exception of one particular square centimeter, which is painted blue. Consider now the last nitrogen molecule emitted in the dying gasp of Julius Caesar. Evidently, we cannot predict very well just where it is now, but if we are asked to predict only whether it is at this moment over a red or blue area, it is a pretty safe bet that the answer is "red". Not because we believe that the nitrogen molecule has any tendency to prefer red regions, but only because there are so many more of them. Indeed, it would take an enormously strong tendency to avoid red regions, before there could be any difference in our conclusions; this is the analog of statement (5-69). The numbers here are much more modest, however, because the total surface area of the earth is only about 5×10^{18} cm^2. If the blue region were reduced to one square Angstrom, we would be concerned with numbers of about 5×10^{34}, still utterly negligible compared to those involved in (5-69).

As the reader can easily verify, this result holds for any number of systems in contact, so that they share a common energy; the overwhelmingly greatest part of all the phase volume of the combined system corresponds very

accurately to a particular distribution of energy among the subsystems such that

$$\frac{\partial \log \rho_1}{\partial E_1} = \frac{\partial \log \rho_2}{\partial E_2} = \frac{\partial \log \rho_3}{\partial E_3} = \cdots \tag{5-71}$$

We can hardly interpret this otherwise than that <u>equal $\partial \log \rho / \partial E$ means equal temperature</u>. In other words, we infer that the quantity

$$x \equiv \frac{\partial \log \rho(E,V)}{\partial E} = x(T) \tag{5-72}$$

must be some function of the Kelvin temperature T. To find what function it is, there is only one criterion. As we saw in Chapter 1, Sec. 1.8, in a closed system (i.e. no particles enter or leave), T^{-1} is defined as the integrating factor that converts the infinitesimal heat flow, $dQ = dE + P\,dV$, into an exact differential $dS = T^{-1}\,dQ$ of some state function $S(E,V)$, where P, V are the pressure and volume of our system. For convenience, call this integrating factor w:

$$T^{-1} = w = w(x) \tag{5-73}$$

then we can repeat the argument of Equations (1-20) - (1-28):

$$dS = w\,dQ = w\,dE + wP\,dV \tag{5-74}$$

so that

$$w = \left(\frac{\partial S}{\partial E}\right)_V \quad , \qquad wP = \left(\frac{\partial S}{\partial V}\right)_E \tag{5-75}$$

and the condition that dS is an exact differential is

$$\frac{\partial^2 S}{\partial E \partial V} = \frac{\partial^2 S}{\partial V \partial E}$$

or,

$$\left(\frac{\partial w}{\partial V}\right)_E = \left(\frac{\partial (wP)}{\partial E}\right)_V \tag{5-76}$$

This yields

$$w'(x)\left(\frac{\partial x}{\partial V}\right)_E = w(x)\left(\frac{\partial P}{\partial E}\right)_V + w'(x)P\left(\frac{\partial x}{\partial E}\right)_V$$

or, the function w(x) must satisfy

$$\frac{w'(x)}{w(x)} = \frac{\left(\frac{\partial P}{\partial E}\right)_V}{\left(\frac{\partial x}{\partial V}\right)_E - P\left(\frac{\partial x}{\partial E}\right)_V} \tag{5-77}$$

It is clear that this program will fail unless the right-hand side of (5-77) turns out to be a function of x alone; and we will not have succeeded in establishing a universal temperature scale unless the right-hand side of (5-77) is a universal function (i.e., the same function for all systems) of x. These properties are far from obvious from the form of (5-77).

We cannot solve (5-77) immediately because, although the derivatives in the denominator are known from (5-72) if $\rho(E,V)$ is known, we do not yet know how the pressure is related to these quantities. To investigate this, suppose we increase the volume (for example, by moving a piston). The system does work, and its energy decreases by

$$\Delta E = -\int_{V_o}^{V_1} P\, dV = E_1 - E_o \tag{5-78}$$

The original and final conditions can be visualized in the semirealistic manner of Fig. (5.6).

The system has an initial energy E_o which we suppose controlled to an accuracy δE_o. Thus at the start of the expansion, the system might be anywhere in the phase volume $\rho_o(E_o)\ \delta E_o$ depicted at the top of Fig. (5.7a). The

structure function $\rho(E,V)$ will depend on V in a manner qualitatively like Eq. (5-26); i.e. the expansion of V has the effect of widening the "vase" to the configuration of Fig. (5.7b).

We suppose that on repetitions of this experiment, the change in energy ΔE is reproducible. Not because we know of any law of physics which says that i must be so, but merely because thermodynamics is concerned only with reproducible phenomena. If the work ΔE varied widely on different repetitions of the experiment, then no one would think of applying thermodynamics to this process.

More generally, it is an experimental fact that with an easily attainable degree of control over experimental conditions, the observable behavior of most macroscopic systems is reproducible. This is a necessary condition for any general theory to be either useful or possible. Indeed, without this property of "macroscopic uniformity", our measuring instruments would not work predictably, and neither experimental nor theoretical physics would be possible.

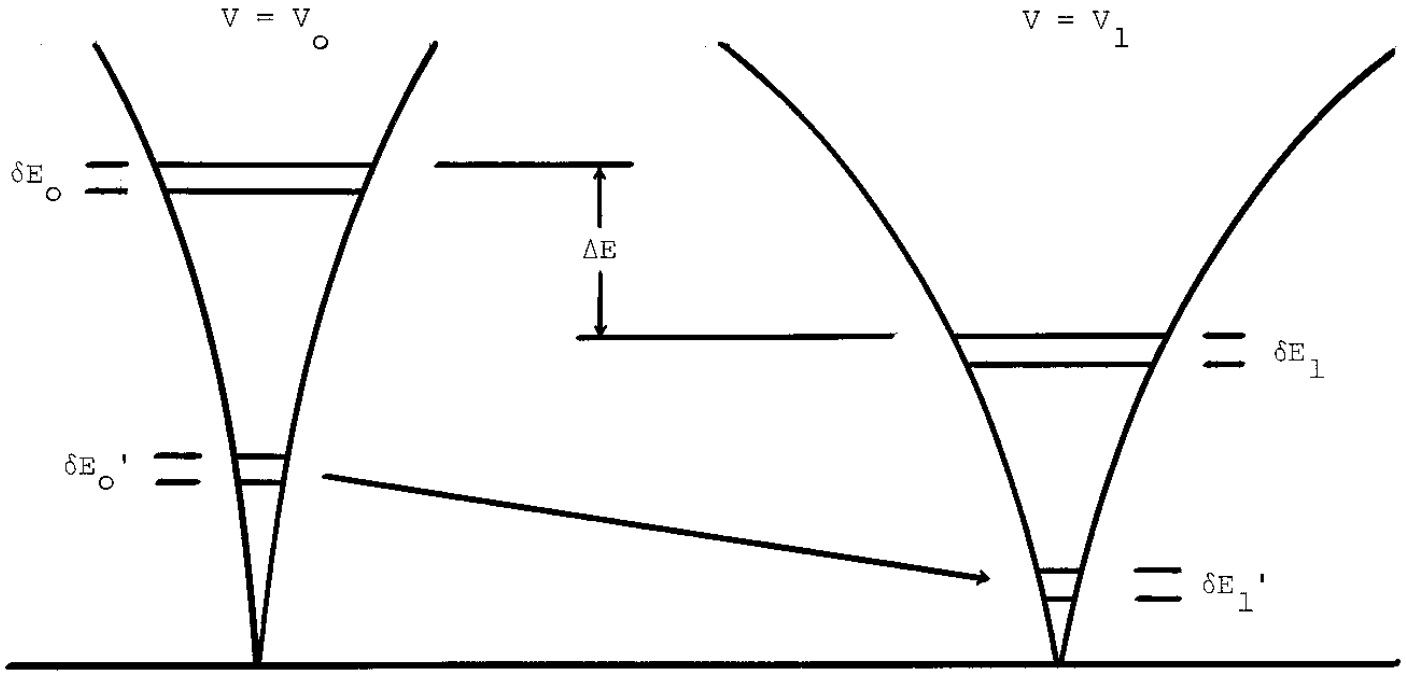

Figure 5.7. Phase volume relations before and after expansion.

We emphasize this because the fact itself is so commonplace to all of us that we might not notice that, from the standpoint of general dynamics, as exemplified in the Hamiltonian equations of motion, it is a rather surprising property. There is no known property of the Hamiltonian per se that would lead us to expect this. The fact that macroscopic experiments are reproducible is thus, from the standpoint of Hamiltonian mechanics, an entirely "new" fact, from which we should be able to draw new conclusions.

To find such a new conclusion, we might reason as follows. Referring to Fig. (5.7), if the change ΔE is reproducible, then it must be that practically every initial state in the shaded region of volume $\rho_o(E_o)\ \delta E_o$ leads to a final energy in the range ωE_1, of phase volume $\rho_1(E_1)\ \delta E_1$. But since phase volume is conserved by the equations of motion, the final volume must be as least large enough to accommodate all these points. Thus, a necessary condition for the process to be reproducible with the specified tolerances δE_o, δE_1 on initial and final energies, is

$$\rho_1(E_1)\ \delta E_1 \geq \rho_o(E_o)\ \delta E_o \tag{5-79}$$

But, because of the numerical situation noted above, (5-79) is not the most appropriate way of stating this condition. For, the exact phase volume corresponding to the energy increment δE is

$$\int_{E-\delta E}^{E} \rho(E)\ dE = \Omega(E) - \Omega(E-\delta E) \tag{5-80}$$

and if δE is so small that this is well approximated simply by $\rho(E)\ \delta E$, then δE must be far smaller than the tolerance with which we could hope to measure the energy experimentally. Indeed, if δE represents any reasonable experimental error, then (5-80) reduces, to enormously great accuracy, simply to $\Omega(E)$, so that (5-79) ought to be replaced by

$$\Omega_1(E_1) \geq \Omega_o(E_o) \tag{5-81}$$

Thus, (5-79) is not a realistic statement of any experimental fact.

In view of this, a weaker condition than (5-79), which exploits the same idea, will suffice for our purposes. Referring again to Fig. (5.7), it is surely a well-verified experimental fact that <u>if</u> the initial energy E_o leads reproducibly, and within experimental error, to the final energy E_1, then any lower initial energy $E_o' < E_o$, will lead to a lower final energy $E_1' < E_1$. In other words, any initial state in the phase volume $\rho_o(E_o)$ must lead to a final state in the phase volume $\rho_1(E_1)$. As before, this is possible only if the final phase volume is large enough to accommodate all these states, which leads again to the condition (5-81).

More generally, we see that an immediate consequence of Liouville's theorem is that in <u>any</u> reproducible process, the phase volume compatible with the final macroscopic state cannot be less than the phase volume which measures the accuracy with which we can reproduce the initial state:

$$\Omega_{\text{final}} \geq \Omega_{\text{initial}} \tag{5-82}$$

Evidently this must hold however we specify the initial and final states; i.e. instead of energy we may specify the observed pressure, stress, magnetization, angular momentum, or any other macroscopic properties. Furthermore, the result (5-82) must hold whether or not the initial and final states are equilibrium states.

Now suppose we compress the system from volume V_1 back to the original volume V_o. It will acquire a final energy E_2, and we shall have to do work $E_2 - E_1$. If this work done is experimentally reproducible, then exactly the same argument about phase volumes applies, and it is necessary that

$$\Omega_2(E_2) \geq \Omega_1(E_1) \tag{5-83}$$

If the expansion and compression are carried out rapidly, it will be found experimentally that the work required for compression is greater than that obtained from the expansion, so that $E_2 > E_o$; this is a particular case of the second law of thermodynamics. But in the limit where these processes are carried out so slowly that the system is at all times very close to equilibrium, E_2 approaches E_o, and we have a reversible process. But, if $E_2 = E_o$, comparison of (5-81) and (5-83) shows that

$$\Omega_o(E_o) = \Omega_1(E_1) \tag{5-84}$$

Under these conditions, the pressure P of (5-78) will be the thermal equilibrium value which we needed to find in order to solve (5-77).

Thus, the missing relation we need for (5-77) is

$$P = -\left(\frac{\partial E}{\partial V}\right)_{\Omega} = -\left(\frac{\partial E}{\partial V}\right)_{\log \Omega} \tag{5-85}$$

but let us cast it into a more useful form. For any macroscopic system we will have a result more or less like (5-29); or

$$\Omega(E) = AV^n E^m \quad , \qquad \rho(E) = mAV^n E^{m-1} \tag{5-86}$$

where n and m are of the order of Avogadro's number. But then

$$\begin{aligned} \log \Omega &\simeq n \log V + m \log E + \text{const.} \\ \log \rho &\simeq n \log V + (m-1) \log E + \text{const.} \end{aligned} \tag{5-87}$$

Now the condition ($\log \Omega$ = const.) on (5-85) imposes a relation between E and V which determines the value of the derivative. From (5-87) it is clear that the condition ($\log \rho$ = const.) imposes the same relation, to an accuracy of something like one part in 10^{24}. More specifically,

$$\left(\frac{\partial E}{\partial V}\right)_{\log \Omega} = -\frac{nE}{mV}$$

$$\left(\frac{\partial E}{\partial V}\right)_{\log \rho} = -\frac{nE}{(m-1)V} \tag{5-88}$$

and so, unless we propose to measure the pressure to better than 1 part in 10^{24} (which as we will see later is about 10^{12} times smaller than the spontaneous fluctuations continually taking place in P anyway), we can just as well write

$$P = -\left(\frac{\partial E}{\partial V}\right)_{\log \rho} \tag{5-89}$$

which is exactly the relation we need to complete the solution of (5-77).