

## Chapter II

# Statistics of Closed Systems

### 2.1 Liouville's Theorem and the Microcanonical Density Function

We start again with classical systems, whose motion can be pictured in the gamma-space or phase space, described in section 1.2. The principal theorem regarding the change of the density function  $\rho(\{p_i(t)\},\{q_i(t)\},t)$  – or for short  $\rho(p,q,t)$  – is due to Liouville<sup>1</sup>. The basic statement of the theorem is found in standard texts on classical mechanics, like Goldstein's book.<sup>2</sup> Let us consider the motion of a number of points  $dN$  in the phase space from a time  $t_1$  to a later time  $t_2$ . If  $d\Omega$  is the associated volume in the phase space, then we clearly have

$$dN = \rho(p_1, q_1, t_1) d\Omega_1 = \rho(p_2, q_2, t_2) d\Omega_2. \quad (2.1-1)$$

According to classical mechanics  $d\Omega$  is a Poincaré invariant, since the Jacobian of the canonical transformation  $\{p_{i,1}\},\{q_{i,1}\} \rightarrow \{p_{i,2}\},\{q_{i,2}\}$  is unity (Goldstein, Op.Cit. p. 403, 393)<sup>3</sup>; hence,  $d\Omega_1 = d\Omega_2$ . Equation (2.1-1) therefore entails that  $\rho$  remains unchanged when we follow along the trajectories of the system points, i.e.,

$$d\rho/dt = 0. \quad (2.1-2)$$

We note that  $d/dt$  stands for the total derivative, which in this connection is usually referred to as the *convected or hydrodynamic derivative*. Equation (2.1-2) indicates that the flow of system points in phase space is like that of an 'incompressible fluid'.

We obtain another form of Liouville's theorem when we apply the chain rule for  $d\rho/dt$ . We then have

$$\frac{d\rho(p,q,t)}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{rN} \left[ \left( \frac{\partial\rho}{\partial p_i} \right) \dot{p}_i + \left( \frac{\partial\rho}{\partial q_i} \right) \dot{q}_i \right] = 0. \quad (2.1-3)$$

Upon applying Hamilton's equations, see (1.1-7), we find the result,

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<sup>1</sup> J. Liouville "Note sur la théorie de variation de constantes arbitraires", J. Math. Pures et Appl. (9) **3**, 342 (1838).

<sup>2</sup> H. Goldstein, "Classical Mechanics", 2<sup>nd</sup> Ed., Wiley, New York 1980.

<sup>3</sup> This follows from the *symplectic condition* for canonical transformations,  $M\tilde{M} = J$ , where  $M$  is the Jacobian matrix and  $J = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$  is the symplectic matrix; clearly,  $|\text{Det } M| = 1$ .

$$\frac{\partial \rho}{\partial t} = -\{\rho, \mathcal{H}\}, \quad (2.1-4)$$

where the curly bracket denotes the Poisson bracket with its usual definition,

$$\{A, B\} = \sum_{i=1}^{rN} \left[ \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right]. \quad (2.1-5)$$

We now proceed to find a form for  $\rho$  in the microcanonical ensemble. In equilibrium statistical mechanics ‘statistical equilibrium’ implies that the ensemble picture is the same at all times, i.e., the local derivative of the density function,  $\partial \rho / \partial t$  is zero. Thus also,

$$\{\rho, \mathcal{H}\} = 0, \quad (2.1-6)$$

indicating that  $\rho$  is a proper constant of motion. Therefore,  $\rho$  must have the following form,

$$\rho(p, q) = f[\mathcal{H}(p, q), \varphi_2(p, q), \varphi_3(p, q), \dots, \varphi_{2rN-1}(p, q)], \quad (2.1-7)$$

where the  $\varphi$ 's are the constants of motion introduced in Section 1.1. As we pointed out there, however, these constants of motion are wholly unknown; only  $\varphi_1(p, q) \equiv \mathcal{H}(p, q)$  is defined in the ensemble. Consequently, the other  $\varphi$ 's must be ‘talked away!’ In classical physics this is accomplished with *ergodic theory*, which has a long history, from the founders of kinetic theory, Maxwell and Boltzmann, to more recent very mathematical considerations by Oxtoby and Ulam; we shall briefly dwell on these in the next section.

Taking it for granted that  $\rho$  is only a functional of  $\mathcal{H}$ , we proceed to fix its form. Given that for a closed system  $\mathcal{H}$  is conserved, it follows that all systems have a trajectory that lies on the energy surface  $\mathcal{H}(p, q) = \mathcal{E}$ . So we conclude that  $\rho$  will have the form,

$$\rho(p, q) = C \delta[\mathcal{H}(p, q) - \mathcal{E}], \quad (2.1-8)$$

where  $C$  is a constant, determined by normalization, as follows. For the volume element in phase space we write

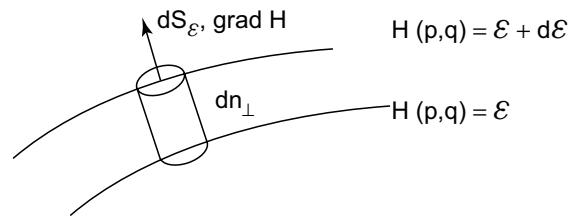
$$d\Omega = d\mathcal{E} dS_{\mathcal{E}} / |\text{grad}_{\Omega} \mathcal{H}| \equiv d\mathcal{E} dM_{\mathcal{E}}, \quad (2.1-9)$$

where  $dM_{\mathcal{E}}$  is called the differential surface measure.

A pictorial explanation is given in Fig. 2-1. One easily notes the relations, employing the definition of generalized gradient in curvilinear coordinates,

$$\begin{aligned} d\Omega &= dS_{\mathcal{E}} dn_{\perp}, \\ d\mathcal{E} &= |\text{grad}_{\Omega} \mathcal{H}| dn_{\perp}, \end{aligned} \quad (2.1-10)$$

which result in (2.1-9).

Fig. 2-1. Volume  $\Delta\Omega$  between two energy surfaces.

We thus have from (2.1-8) and (2.1-9)

$$\begin{aligned} \int \rho d\Omega &= C \int \delta[\mathcal{H}(p, q) - \mathcal{E}] d\Omega \\ &= C \int d\mathcal{E}' \oint dM_{\mathcal{E}'} \delta(\mathcal{E}' - \mathcal{E}) = C M_{\mathcal{E}} = 1. \end{aligned} \quad (2.1-11)$$

It follows that  $1/C$  is equal to the surface measure  $M_{\mathcal{E}}$ ; hence,  $\rho$  is given by<sup>†</sup>

$$\rho(p, q) = \frac{1}{M_{\mathcal{E}}} \delta[\mathcal{H}(p, q) - \mathcal{E}]. \quad (2.1-12)$$

This is the exact form, indicating that the density is confined to the energy surface, where it is a constant (no ‘loading’).

Yet, for many practical computations, the energy is given a ‘leeway’  $\delta\mathcal{E}$ . Denoting the volume between the neighbouring energy surfaces  $\mathcal{E}$  and  $\mathcal{E} + \delta\mathcal{E}$  by  $\Delta_{\mathcal{E}}\Omega$ , we then write

$$\rho(p, q) = \begin{cases} 1/\Delta_{\mathcal{E}}\Omega & , \quad \mathcal{E} \leq \mathcal{H}(p, q) \leq \mathcal{E} + \delta\mathcal{E}, \\ 0 & \text{elsewhere.} \end{cases} \quad (2.1-13)$$

From normalization we now have

$$\Delta_{\mathcal{E}}\Omega = M_{\mathcal{E}}\delta\mathcal{E}. \quad (2.1-14)$$

## 2.2 The Ergodic Hypothesis

When one looks through Maxwell’s and Boltzmann’s collected papers, it becomes clear just how much these authors were concerned with the justification of the use of ensemble averages for kinetic computations. Many modern books, in which phase-space averages are ‘justified’ by the *ad hoc* postulate of equal *a priori* probabilities, should do well to refer to the original work of the pioneers. Boltzmann states the

<sup>†</sup> Rather than boxing equations, we have resorted to using **bold numbers** for very basic results.

ergodic hypothesis<sup>4</sup> as follows:<sup>5</sup> “The great irregularity of the thermal motion and the variety of extrinsic forces acting on bodies make it probable that, in virtue of the motion which we call heat, the atoms of bodies take on all positions and velocities compatible with the equation of energy.” Maxwell states the same idea in more detail:<sup>6</sup> “The only assumption which is necessary for the direct proof [of Boltzmann’s law] is that the system, if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy.” Clearly he came close to the enunciation of the ergodic hypothesis as it is nowadays phrased: *For a conservative system the path of the system in phase space passes through all points of the energy surface and in such a manner that this surface is covered uniformly.*

Whereas the first part of the statement seems plausible for a curve that never crosses itself (see Section 1.2) the latter part is more sticky. To clarify this point, Boltzmann derives a formula for the time interval which the phase point during its motion spends on a given element of the energy surface. First he computes the time  $dt$  that it takes for the system to move through an element of the independent variables, i.e., those  $p$ ’s and  $q$ ’s which remain time-dependent after all others are fixed by the integrals of motion, cf. Eq. (1.1-8); this calculation is straightforward, using “Jacobi’s method of the last multiplier”. From here he proceeds in an obscure way to obtain the time spent by a representative point of the system on an element  $dS$  of its energy surface. The asserted result is,

$$\lim_{T \rightarrow \infty} dt / T \propto dS / |\text{grad}_{\mathcal{E}} \mathcal{H}| = dM_{\mathcal{E}} . \tag{2.2-1}$$

If this were true, the desired result is obtained, viz., that the time average over the trajectory of one system equals the ensemble average for all systems:

$$\begin{aligned} \overline{F(p, q)} &= \lim_{T \rightarrow \infty} \int_0^T F[p(t), q(t)] dt / T = C \oint F(p, q) dM_{\mathcal{E}} \\ &= C \int d\mathcal{E}' \oint F(p, q) dM_{\mathcal{E}} \delta(\mathcal{E}' - \mathcal{E}) = \langle F(p, q, ) \rangle . \end{aligned} \tag{2.2-2}$$

However, it is certain that Boltzmann’s proof was fallacious. Critique on the ergodic hypothesis was voiced by many authors in the early twentieth century, among which Rosenthal and Plancherel.<sup>7</sup> From a point of view of measure theory the impossibility of the hypothesis is clear: No trajectory which cannot have multiple points can fill out a multi-dimensional surface.<sup>8</sup> Slightly better fared the quasi-ergodic hypothesis, which states that *the trajectory will come arbitrarily close to any point on the energy*

<sup>4</sup> The name stems from the Greek  $\epsilon\rho\gamma\omicron\sigma$  = work.

<sup>5</sup> L. Boltzmann, Wiener Berichte **63**<sup>2</sup>, 679, 1871, or his collected papers No. 19.

<sup>6</sup> J.C. Maxwell, Proc. Cambridge Phil. Soc. **12**, 547 (1879); also collected papers **2**, p. 713.

<sup>7</sup> A. Rosenthal, Ann. der Physik, **42**, 796 (1913); M. Plancherel, Ann. der Physik **42**, 1061 (1913).

<sup>8</sup> A.I. Khintchine, “Mathematical Foundations of Statistical Mechanics”, Dover, New York, 1949, p. 53.

surface. However, although Fermi showed that this is true for a large class of systems, the statement (2.2-1) remained elusive.

A more rewarding avenue was taken by Birkhoff and in a somewhat weaker form by von Neumann, both in 1931. They showed the equivalence of (2.2-2) for the condition that the energy surface is ‘metrically indecomposable’. The latter property entails that  $S_g$  cannot be decomposed into two parts  $S_1$  and  $S_2$ , both of positive measure, and both invariant under the transformation group  $p_i(t), q_i(t) \rightarrow p'_i(t), q'_i(t)$ . The essential argument has now been moved to another question, viz., which systems have a metrically transitive transformation group? In 1941 Oxtoby and Ulam showed that ‘almost every’ continuous transformation satisfies this criterion.<sup>9</sup>

For those who are mathematically inclined it is gratifying, that with the help of modern measure theory the alleged result of the founders has finally been shown to be correct for ‘almost all’ systems. However, classical systems have little place in present-day many-body quantum physics. As we will see in the next section, in most quantum systems the Hamiltonian  $\mathcal{H}$  is the only constant of motion, whose states span the entire relevant Hilbert space. Therefore  $\rho$  can only be a functional of  $\mathcal{H}$ .

### 2.3 Von Neumann’s Theorem and the Microcanonical Density Operator

The road for quantum statistics is beset with less trouble. Following the developments of Section 1.2, we have for the density operator in an arbitrary basis of many-body states  $\{|\gamma\rangle\}$

$$\rho_{\gamma\gamma'}(t) = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M c_{\gamma}^i(t) c_{\gamma'}^{i*}(t). \quad (2.3-1)$$

With  $|\Psi^i(t)\rangle$  being the dynamical state of system ‘ $i$ ’ in the ensemble, and with  $c_{\gamma}^i(t) = \langle \gamma | \Psi^i(t) \rangle$  being its projection on  $|\gamma\rangle$  we have from  $\hbar i \partial |\Psi^i\rangle / \partial t = \mathcal{H} |\Psi^i\rangle$  by insertion of the closure property  $\sum_{\gamma''} |\gamma''\rangle \langle \gamma''| = 1$ ,

$$\begin{aligned} \hbar i \sum_{\gamma''} (\partial / \partial t) |\gamma''\rangle \langle \gamma''| \Psi^i(t) &= \mathcal{H} \sum_{\gamma''} |\gamma''\rangle \langle \gamma''| \Psi^i(t), \quad \text{or,} \\ \hbar i \sum_{\gamma''} (\partial / \partial t) |\gamma''\rangle c_{\gamma''}^i(t) &= \mathcal{H} \sum_{\gamma''} |\gamma''\rangle c_{\gamma''}^i(t). \end{aligned} \quad (2.3-2)$$

Taking the scalar product with  $|\gamma\rangle$  and noting  $\langle \gamma | \gamma'' \rangle = \delta_{\gamma\gamma''}$ , this gives the transformed Schrödinger equation in the basis  $\{|\gamma\rangle\}$ ,

$$\hbar i (\partial / \partial t) c_{\gamma}^i(t) = \sum_{\gamma''} \mathcal{H}_{\gamma\gamma''} c_{\gamma''}^i(t). \quad (2.3-3)$$

<sup>9</sup> I. Oxtoby and S. Ulam, Ann. of Math. **42**, 874 (1941).

Differentiating (2.3-1), this yields,

$$\begin{aligned} \frac{\partial \rho_{\gamma\gamma'}}{\partial t} &= \lim_{M \rightarrow \infty} \frac{1}{M} \sum_i \left[ \frac{\partial c_{\gamma}^i}{\partial t} c_{\gamma'}^{i*} + c_{\gamma}^i(t) \frac{\partial c_{\gamma'}^{i*}}{\partial t} \right] \\ &= \frac{1}{\hbar i} \sum_{\gamma''} \left[ \mathcal{H}_{\gamma\gamma''} \rho_{\gamma''\gamma'} - \rho_{\gamma\gamma''} \mathcal{H}_{\gamma''\gamma'} \right] = \frac{1}{\hbar i} [\mathcal{H} \rho - \rho \mathcal{H}]_{\gamma\gamma'}. \end{aligned} \quad (2.3-4)$$

Since this holds for the matrix elements, it holds for the operators themselves. We thus obtained von Neumann's theorem,

$$\frac{\partial \rho}{\partial t} = -\frac{1}{\hbar i} [\rho, \mathcal{H}], \quad (2.3-5)$$

where  $[\rho, \mathcal{H}]$  is the commutator. Notice the minus sign compared to the well-known Heisenberg equation of motion.<sup>10</sup> The result is similar to the Liouville equation (2.1-4), derived earlier. We clearly have the correspondence  $\{\rho, \mathcal{H}\} \rightarrow (1/\hbar i)[\rho, \mathcal{H}]$ ; this was to be expected from the general quantum condition  $\{A, B\} = (1/\hbar i)[A, B]$ , see Dirac.<sup>11</sup>

The formal solution of (2.3-5) is easily given. If  $\mathcal{H}$  does not explicitly depend on time we have,

$$\begin{aligned} \rho(t) &= e^{-i\mathcal{H}t/\hbar} \rho(0) e^{i\mathcal{H}t/\hbar} = e^{-i\mathcal{L}t} \rho(0) \\ &= U(t, 0) \rho(0) U^\dagger(t, 0), \end{aligned} \quad (2.3-6)$$

where  $U$  is the evolution operator and where  $\mathcal{L}$  is the Liouville (super)-operator. We note that, if  $\rho(0)$  commutes with  $\mathcal{H}$ , so does  $\rho(t)$ .

For an ensemble in statistical equilibrium  $\partial \rho / \partial t = 0$ , so that  $[\rho, \mathcal{H}] = 0$ . It follows that  $\rho$  is a constant of motion; we write

$$\rho = f(\mathcal{H}). \quad (2.3-7)$$

There is now no need to include other constants of motion, since, except for pathological cases, they only span a subspace of the Hilbert space for  $\mathcal{H}$ . We now use the *spectral resolution*<sup>12</sup> (decomposition theorem, see e.g., Messiah<sup>13</sup>):

$$\mathcal{H} = \sum_{\eta} |\eta\rangle \langle \eta| \mathcal{E}_{\eta} \quad \text{and} \quad f(\mathcal{H}) = \sum_{\eta} |\eta\rangle \langle \eta| f(\mathcal{E}_{\eta}). \quad (2.3-8)$$

<sup>10</sup> The density operator is not a Heisenberg operator, but a Schrödinger operator. Also note that we used the symbol  $\partial/\partial t$  for the appropriate derivative.

<sup>11</sup> P.A.M. Dirac, "The Principles of Quantum Mechanics", 4<sup>th</sup> Ed., Oxford University Press, 1958, p. 87.

<sup>12</sup> F. Riesz and B.Sz. Nagy, "Leçons d'analyse fonctionnelle", 4<sup>th</sup> Ed., Gauthiers-Villars, Paris, 1965, Chapter 11.

<sup>13</sup> A. Messiah, "Quantum Mechanics", Vol. I, North Holland, Amsterdam, 1961, pp.260-272; translated from A. Messiah, "Mécanique Quantique", Dunod, Paris, 1958.

Now  $\rho$  can be represented by its diagonal part, see (1.2-8),

$$\rho = \sum_{\eta} |\eta\rangle p(\eta) \langle \eta|. \quad (2.3-9)$$

From (2.3-7) – (2.3-9) we find,

$$p(\eta) = f(\mathcal{E}_{\eta}^{\circ}), \quad |\eta\rangle \in \mathcal{E}. \quad (2.3-10)$$

The restrictions on the accessible states  $|\eta\rangle$  entail that  $f(\mathcal{E}_{\eta}^{\circ})$  must be taken to be a delta-function

$$p(\eta) = A \delta(\mathcal{E}_{\eta}^{\circ} - \mathcal{E}). \quad (2.3-11)$$

Let us write

$$\sum_{\eta} \dots \rightarrow \int d\mathcal{E}_{\eta}^{\circ} \chi(\mathcal{E}_{\eta}^{\circ}) \dots, \quad (2.3-12)$$

where  $\chi(\mathcal{E}_{\eta}^{\circ})$  is the density of states; the approximation is near-exact, since for a macroscopic system the states are very dense. From (2.3-11), (2.3-12) and normalization we have

$$\sum_{\eta} p(\eta) = A \int \chi(\mathcal{E}_{\eta}^{\circ}) \delta(\mathcal{E}_{\eta}^{\circ} - \mathcal{E}) d\mathcal{E}_{\eta}^{\circ} = A \chi(\mathcal{E}) = 1. \quad (2.3-13)$$

This fixes both  $p(\eta)$  and  $\rho$ :

$$\begin{aligned} p(\eta) &= \frac{1}{\chi(\mathcal{E})} \delta(\mathcal{E}_{\eta}^{\circ} - \mathcal{E}), \\ \rho &= \sum_{\eta} |\eta\rangle \frac{1}{\chi(\mathcal{E})} \delta(\mathcal{E}_{\eta}^{\circ} - \mathcal{E}) \langle \eta|. \end{aligned} \quad (2.3-14)$$

The latter expression can again be summed with the decomposition theorem (2.3-8); we then obtain the final form,

$$\rho = \frac{1}{\chi(\mathcal{E})} \delta[\mathcal{H} - |\mathcal{E}|], \quad (2.3-15)$$

where  $|\mathcal{E}|$  is the identity operator. Obviously, Equation (2.3-15), containing a delta function of an operator, is a symbolic expression, its true meaning being just (2.3-14). Clearly, the expressions for the classical density function  $\rho(p, q)$  and the quantum density operator  $\rho$  are very similar, with the surface measure  $M_g$  being replaced by the density of states  $\chi(\mathcal{E})$ .

Again, we can also allow for a certain tolerance  $\delta\mathcal{E}$ . Then, let  $\Delta\Gamma(\mathcal{E}) = \chi(\mathcal{E})\delta\mathcal{E}$  be the number of states in this interval, i.e., the number of states  $|\eta\rangle$  with energies  $\mathcal{E} \leq \mathcal{E}_{\eta}^{\circ} \leq \mathcal{E} + \delta\mathcal{E}$ . We refer to  $\Delta\Gamma(\mathcal{E})$  as the *microcanonical partition function*. Then (2.3-15) takes the alternate form,

$$\rho = \begin{cases} \sum_{\eta} |\eta\rangle \frac{1}{\Delta\Gamma(\mathcal{E})} \langle\eta|, & |\eta\rangle \in (\mathcal{E} \leq \mathcal{E}_{\eta} \leq \mathcal{E} + \delta\mathcal{E}) \\ 0, & \text{all other } |\eta\rangle. \end{cases} \quad (2.3-16)$$

To be noted is that we did not appeal to ergodic theory for the quantum case. This indicates the superiority of the quantum treatment. A device like spectral resolution is non-existing in classical mechanics. The very complex arguments of Oxtoby and Ulam, involving metrical decomposition of the energy surface, come close, however, to the considerations of spectral resolution theory of quantum operators, which, for its mathematical validity relies on very extensive properties of linear operator theory, especially when such operators are not necessarily bounded in the Hilbert space; see in particular Ref.12 [also, Ref. 49 of Chapter XVI].

### 2.4 Macro-Probability in Classical and Quantum Statistics

In the previous sections we obtained the density function, or operator, for a microcanonical ensemble. The next step is to find the macro-probability for the specification of the  $a$ -variables in a system, see Section 1.5 . Suppose we have the state variables  $\{a_i(t)\}$ ,  $i = 1 \dots P$ . Let these variables lay in the domain

$$\mathcal{D}(\mathbf{a}) = \begin{cases} a_1 \leq a_1(p, q) \leq a_1 + da_1 \\ \vdots \\ a_P \leq a_P(p, q) \leq a_P + da_P \end{cases} \quad (2.4-1)$$

This specification delineates a volume  $\Delta\Omega(\mathbf{a})$  in phase space, called the *accessible volume in phase space*,

$$\Delta\Omega(\mathbf{a}) = \int_{\mathcal{D}(\mathbf{a})} d\Omega . \quad (2.4-2)$$

The situation is pictured in Fig. 2-2.

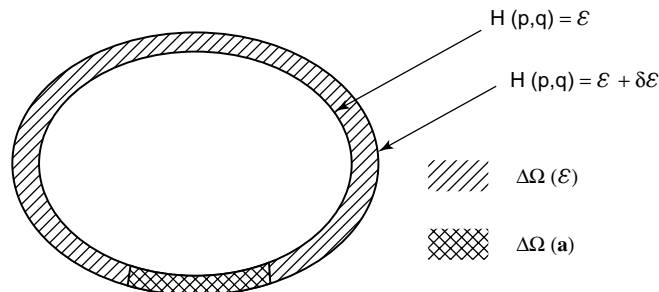


Fig. 2-2. Accessible volume for a specification (2.4-1).

We introduce a density function  $G(\{a_i\})$  by

$$\Delta\Omega(\mathbf{a}) = \int_{\mathcal{D}(\mathbf{a})} d\Omega = G(\{a_i\}) da_1 da_2 \dots da_p. \quad (2.4-3)$$

For the probability of the specification (2.4-1) we clearly have

$$W(\{a_i\}) da_1 da_2 \dots da_p = \Delta\Omega(\mathbf{a}) / \Delta_{\mathcal{E}}\Omega. \quad (2.4-4)$$

With (2.4-3) we obtain for the probability density function (pdf):

$$W(\{a_i\}) = G(\{a_i\}) / \Delta_{\mathcal{E}}\Omega. \quad (2.4-4')$$

This is the basic result for macro-probability in classical statistical mechanics.

However, if the  $a$ 's are extensive variables, they are most likely fixed in the ensemble. We may then consider subsystems in which the  $a$ 's fluctuate, as discussed in Section 1.5. Accordingly we write, dividing the composite system into two subsystems, noting  $da_i = da_i^I = -da_i^{II}$ ,

$$\begin{aligned} \Delta\Omega(\mathbf{a}) &= \int_{\mathcal{D}(\mathbf{a})} d\Omega^I d\Omega^{II} \sim G(\{a_i^I\}) G(\{a_i^{II}\}) \prod_k da_k \\ &= G(\{a_i^I\}) G(\{a_i^c - a_i^I\}) \prod_k da_k. \end{aligned} \quad (2.4-5)$$

The reader notices that (2.4-5) is a dimensional failure, since we have  $P$  factors  $da$  too few on the rhs. This is not as grave as it looks, however. Taking the example of a hypersphere, let  $\Delta\Omega(a) = Ca^{\lambda N}$ , then  $(d/da)\Delta\Omega(a) = G(a) = C\lambda Na^{\lambda N-1}$ ; or

$$\Delta\Omega(a) / G(a) = a / \lambda N \approx \delta a. \quad (2.4-6)$$

This indicates that  $\ln(\prod da_i) = \mathcal{O}(\ln N) \equiv \hat{c}$ . Henceforth, constants that vanish logarithmically will always be denoted by  $\hat{c}$ . The result (2.4-5) therefore reads more properly,

$$\Delta\Omega(\mathbf{a}) = \hat{c} G(\{a_i^I\}) G(\{a_i^c - a_i^I\}) \prod_k da_k \quad (2.4-7)$$

leading to the pdf,

$$W(\{a_i\}) = \hat{c} G(\{a_i^I\}) G(\{a_i^c - a_i^I\}) / \Delta\Omega(\mathcal{E}, \{a_i^c\}). \quad (2.4-8)$$

As a direct extension, consider  $K$  subsystems with  $\sum_{\alpha} a_i^{\alpha} = a_i^c$ . Then, similar to (2.4-8),

$$W(\mathbf{a}^1 \dots \mathbf{a}^{K-1}) = \hat{c} \prod_{\alpha=1}^K G(\mathbf{a}^{\alpha}) / \Delta\Omega(\mathcal{E}, \mathbf{a}^c). \quad (2.4-9)$$

These results are rapidly reformulated for quantum statistics. Let  $a_1 \dots a_p$  be coarse grained (commuting) macroscopic fluctuating variables. Since [see (1.5-5)]

$$a_i = \sum_J a_i^{(J)} \sum_{\eta \in \Delta \mathcal{E}^J} \{|\eta\rangle\langle\eta|\}_i \quad (2.4-10)$$

we only need to count the energy cells  $J$  corresponding to the specification for the  $a_i$  to be in  $(a_i, a_i + da_i)$  and the number of states in each cell. The *accessible number of quantum states* will be denoted by  $\Delta\Gamma(\mathbf{a})$ . This leads to a density of states in  $a$ -space  $\Delta\Gamma(\mathbf{a}) = \chi(\mathbf{a}) \Pi_i da_i$ . The macro-probability density function is then given by

$$W(\{a_i\}) = \chi(\{a_i\}) / \Delta\Gamma(\mathcal{E}). \quad (2.4-11)$$

More likely, the  $a$ 's will be pertaining to subsystems. The analogues of (2.4-8) and (2.4-9) are:

$$W(\{a_i\}) = \hat{c} \chi(\{a_i^I\}) \chi(\{a_i^c - a_i^I\}) / \Delta\Gamma(\mathcal{E}, \{a_i^c\}) \quad (2.4-12)$$

$$W(\mathbf{a}^1, \dots, \mathbf{a}^{K-1}) = \hat{c} \prod_{\alpha=1}^K \chi(\mathbf{a}^\alpha) / \Delta\Gamma(\mathcal{E}, \mathbf{a}^c). \quad (2.4-13)$$

Some authors<sup>14</sup> absorb the constant  $1/\Delta\Gamma(\mathcal{E})$ , together with  $\hat{c}$ , in a 'big' constant  $C$

$$C = \hat{c} [1 / \Delta\Gamma(\mathcal{E})]. \quad (2.4-14)$$

This constant does not, however, vanish logarithmically! We shall refer to the quantity  $W/C \equiv \tilde{W}$  as the 'thermodynamic probability'. Equations (2.4-12) and (2.4-13) then read:

$$\tilde{W}(\{a_i\}) \approx \chi(\{a_i^I\}) \chi(\{a_i^c - a_i^I\}), \quad (2.4-15)$$

$$\tilde{W}(\mathbf{a}^1, \dots, \mathbf{a}^{K-1}) \approx \prod_{\alpha=1}^K \chi(\mathbf{a}^\alpha). \quad (2.4-16)$$

We note that  $\tilde{W}$  is a huge number and that the thermodynamic probability *is not normalized*. Yet it is useful for some considerations, as we will see later.

*Note.* Quite often a semiclassical computation of  $\Delta\Gamma(\mathcal{E})$  and  $\Delta\Gamma(\mathbf{a})$  can be made. Let  $\Delta\Omega$  be the relevant volume in phase space. According to Heisenberg's uncertainty principle  $p$  and  $q$  cannot be specified to within  $\sim h$ , i.e.,  $\prod_i^{rN} \Delta p_i \Delta q_i \sim h^{rN}$ . In addition the particles can be permuted, since in quantum mechanics they are indistinguishable. Therefore, the smallest volume in phase space, within which all points represent the same motion, is a *microcell*  $\mathbf{\Delta}\Omega = h^{rN} N!$  We thus surmise the following connection between accessible volume in phase space and accessible number of quantum states,

$$\Delta\Gamma = \Delta\Omega / \mathbf{\Delta}\Omega = \Delta\Omega / h^{rN} N!. \quad (2.4-17)$$

<sup>14</sup> See e.g. L.D. Landau and E.M. Lifshitz, "Statistical Physics", Addison Wesley 1958, p.21, Eqs. (6.5) and (6.6).

Ter Haar<sup>15</sup>, however, has pointed out that the uncertainty-principle argument leaves much to be desired, since actually  $\Delta p_i \Delta q_i \geq h/4\pi$ . Instead, the result follows from the connection between the Schrödinger  $q$ - and Schrödinger  $p$ -representations. From Parseval's theorem the amplitudes  $\phi(q)$  and  $A(k)$ , [ $p = \hbar k$ ] are related by

$$\begin{aligned} \int \phi^*(q)\phi(q)d\Omega_q &= \frac{1}{(2\pi)^{rN}} \int A^*(k)A(k)d^{rN}k \\ &= \frac{1}{(2\pi\hbar)^{rN}} \int A^*(p)A(p)d\Omega_p = 1. \end{aligned} \quad (2.4-18)$$

According to ter Haar, the total volume in phase space corresponding to one stationary state is obtained by multiplying the probability in  $q$ -space with that in  $p$ -space and integrating over all phase space, while in addition the particles must be allowed to be permuted. We then obtain, using both equalities in (2.4-18):

$$\Delta\Omega = N! \iint \phi^*(q)\phi(q) A^*(p)A(p)d\Omega_q d\Omega_p = N!h^{rN}, \quad (2.4-19)$$

which is the desired result.

## 2.5 Examples of Extension in Phase Space and of Accessible Number of Quantum States

We have already remarked that the microcanonical ensemble is a poor one for actual calculations. On the other hand, it is difficult to grasp the results of the previous section without a few examples. We shall consider the simple problems of finding the energy probability density function for a subsystem of a perfect gas and for an assembly of harmonic oscillators.

### 2.5.1 Ideal Gas

Let us consider a mono-atomic ideal gas of  $N$  particles with energy  $\mathcal{E}$  and volume  $V$ . The accessible volume in phase space is

$$\Delta\Omega(\mathcal{E}, V, N) = \iint d\Omega_q d\Omega_p = V^N \int_{\mathcal{D}} dp_1 \dots dp_{3N}, \quad (2.5-1)$$

where  $\mathcal{D}$  is the domain bounded by

$$\mathcal{E} \leq \sum_{i=1}^{3N} p_i^2 / 2m \leq \mathcal{E} + \delta\mathcal{E}. \quad (2.5-2)$$

We will also write

<sup>15</sup> D. ter Haar, "Elements of Statistical Mechanics", Rinehart, New York 1954, p. 60.

$$\Delta\Omega(\mathcal{E}, V, N) = V^N \delta\mathcal{E} \frac{d}{d\mathcal{E}} \int_{\mathcal{D}'} dp_1 \dots dp_{3N}, \quad (2.5-2')$$

where  $\mathcal{D}'$  is the domain bounded by  $\sum_{i=1}^{3N} p_i^2 \leq 2m\mathcal{E}$ . Clearly,  $\int_{\mathcal{D}'} \Pi_i dp_i$  is the volume of a hypersphere.

To obtain this we consider the integral

$$I = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} e^{-(x_1^2 + x_2^2 + \dots + x_\nu^2)} dx_1 \dots dx_\nu = \left[ \int_{-\infty}^{\infty} e^{-x^2} dx \right]^\nu = \pi^{\nu/2}. \quad (2.5-3)$$

We also compute this integral using ‘polar coordinates’. Let  $r^{\nu-1} A_\nu$  be the area of a hypersphere, where  $A_\nu$  is a geometry factor (such as  $4\pi$  if  $\nu = 3$ ); then we have,

$$I = \int_0^\infty e^{-r^2} r^{\nu-1} A_\nu dr = \frac{1}{2} A_\nu \int_0^\infty e^{-t} t^{\frac{1}{2}\nu-1} dt = \frac{1}{2} A_\nu \Gamma(\nu/2), \quad (2.5-3')$$

where  $\Gamma(y)$  is the generalized factorial or gamma function. Comparing (2.5-3) and (2.5-3') we find

$$A_\nu = 2\pi^{\frac{1}{2}\nu} / \Gamma(\frac{1}{2}\nu). \quad (2.5-4)$$

So, for the volume of a hypersphere with radius  $R$  we get,

$$V_\nu(R) = \int_0^R r^{\nu-1} A_\nu dr = R^\nu \pi^{\frac{1}{2}\nu} / \Gamma(\frac{1}{2}\nu + 1). \quad (2.5-5)$$

Setting  $\nu = 3N$ ,  $R = \sqrt{2m\mathcal{E}}$ , we find for (2.5-2')

$$\Delta\Omega(\mathcal{E}, V, N) = V^N \delta\mathcal{E} \frac{d}{d\mathcal{E}} \frac{(2\pi m\mathcal{E})^{3N/2}}{\Gamma(\frac{3}{2}N + 1)} = V^N \delta\mathcal{E} \frac{2\pi m (2\pi m\mathcal{E})^{\frac{3}{2}N-1}}{\Gamma(\frac{3}{2}N)}. \quad (2.5-6)$$

For the number of accessible quantum states we then obtain,

$$\Delta\Gamma(\mathcal{E}, V, N) = V^N \delta\mathcal{E} \frac{2\pi m (2\pi m\mathcal{E})^{\frac{3}{2}N-1}}{\Gamma(\frac{3}{2}N) \Gamma(N+1) h^{3N}}. \quad (2.5-7)$$

Since  $\Delta\Gamma = \chi \delta\mathcal{E}$  this yields for the density of states,

$$\chi(\mathcal{E}, V, N) = \frac{V^N 2\pi m (2\pi m\mathcal{E})^{\frac{3}{2}N-1}}{\Gamma(\frac{3}{2}N) \Gamma(N+1) h^{3N}}. \quad (2.5-8)$$

We now consider a small subsystem with attributes  $\mathcal{E}'$ ,  $V'$  and  $n$ . Only energy exchange is considered, i.e.,  $V'$  and  $n$  are fixed. From Equation (2.4-12) we find for the energy pdf of the subsystem,

$$W(\mathcal{E}') = \hat{c} \frac{V'^n (V - V')^{N-n} (2\pi m)(2\pi m \mathcal{E}')^{\frac{3}{2}n-1} [(2\pi m(\mathcal{E} - \mathcal{E}'))^{\frac{3}{2}(N-n)-1}]}{V^N \delta \mathcal{E} (2\pi m \mathcal{E})^{\frac{3}{2}N-1} h^{3n}} \quad (2.5-9)$$

$$\times \frac{\Gamma(\frac{3}{2}N)\Gamma(N+1)}{\Gamma(\frac{3}{2}n)\Gamma(n+1)\Gamma[\frac{3}{2}(N-n)]\Gamma(N-n+1)}.$$

We shall only keep the essential terms associated with the subsystem. Thus we write

$$W(\mathcal{E}') = C \frac{V'^n (2\pi m)(2\pi m \mathcal{E}')^{\frac{3}{2}n-1} [2\pi m(\mathcal{E} - \mathcal{E}')]^{\frac{3}{2}N-1}}{\Gamma(\frac{3}{2}n)\Gamma(n+1)(2\pi m \mathcal{E})^{\frac{3}{2}N-1} h^{3n}}. \quad (2.5-10)$$

For the terms in  $\mathcal{E}'$  we have logarithmically

$$(\frac{3}{2}N - 1) \ln \left( 1 - \frac{\mathcal{E}'}{\mathcal{E}} \right) \sim -(\frac{3}{2}N) \frac{\mathcal{E}'}{\mathcal{E}}. \quad (2.5-11)$$

Employing equipartition,  $\mathcal{E} = \frac{3}{2} N k_B T$ , we arrive at

$$W(\mathcal{E}') = C \frac{V'^n (2\pi m)(2\pi m \mathcal{E}')^{\frac{3}{2}n-1}}{\Gamma(\frac{3}{2}n)\Gamma(n+1)h^{3n}} e^{-\mathcal{E}'/k_B T} = C \chi(\mathcal{E}') e^{-\mathcal{E}'/k_B T}. \quad (2.5-12)$$

## 2.5.2 An Assembly of Oscillators

### (a) Semiclassical

We consider an assembly of  $N$  independent harmonic oscillators. The energy is given by

$$\mathcal{E} = \sum_{i=1}^N (n_i + \frac{1}{2}) \hbar \omega = (K + N/2) \hbar \omega, \quad (2.5-13)$$

where  $K$  is a sum of integers. We assume that the energy is quasi-continuous, with spacing for oscillator energy  $g(\Delta \mathcal{E}) = \Delta \mathcal{E} / \hbar \omega$ . For the total number of states we find,

$$\Delta \Gamma(\mathcal{E}, N) = \delta \mathcal{E} \frac{d}{d\mathcal{E}} \left( \frac{1}{\hbar \omega} \right)^N \int_{\mathcal{O}} d\mathcal{E}_1 d\mathcal{E}_2 \dots d\mathcal{E}_N, \quad (2.5-14)$$

where  $\mathcal{O}$  is the domain

$$\mathcal{E}_1 + \mathcal{E}_2 + \dots + \mathcal{E}_N \leq \mathcal{E}. \quad (2.5-15)$$

The result is easily obtained with the Dirichlet integral<sup>16</sup>:

<sup>16</sup> R.C. Tolman, "The Principles of Statistical Mechanics", Oxford University Press, 1938, p. 656.

$$\Delta\Gamma(\mathcal{E}, N) = \left(\frac{1}{\hbar\omega}\right)^N \frac{1}{\Gamma(N)} \mathcal{E}^{N-1} \delta\mathcal{E}. \tag{2.5-16}$$

The Dirichlet integral is as follows. Let  $\mathcal{E}$  be the domain bounded by

$$\sum_{j=1}^{\nu} (x_j / a_j)^{r_j} \leq \mathcal{E}, \quad \text{all } x_j, a_j, r_j > 0. \tag{2.5-17}$$

Then

$$\int_{\mathcal{E}} \dots \int x_1^{i_1-1} x_2^{i_2-1} \dots x_{\nu}^{i_{\nu}-1} dx_1 dx_2 \dots dx_{\nu} = \frac{\left(\prod_{j=1}^{\nu} a_j^{i_j}\right) \left(\prod_{j=1}^{\nu} \Gamma(i_j / r_j)\right) (\mathcal{E})^{\sum_{j=1}^{\nu} (i_j / r_j)}}{\left(\prod_{j=1}^{\nu} r_j\right) \left(\Gamma\left[\sum_{j=1}^{\nu} (i_j / r_j) + 1\right]\right)}. \tag{2.5-18}$$

In our example  $i_1 \dots i_{\nu} = 1$ ,  $a_1 \dots a_{\nu} = 1$ ,  $r_1 \dots r_{\nu} = 1$ ,  $\mathcal{E} = \mathcal{E}$ . The result (2.5-16) then easily follows.

Again we can consider a subsystem and apply (2.4-12). We leave it up to the reader to obtain once more the form of the far rhs of (2.5-12).

We now indicate another method to evaluate integrals like (2.5-14). So consider

$$I(\mathcal{E}, N) = \int_{\emptyset} \dots \int d\varepsilon_1 d\varepsilon_2 \dots d\varepsilon_N. \tag{2.5-19}$$

To rid ourselves of the energy constraint we take the Laplace transform (with  $N \rightarrow n$ ):

$$\begin{aligned} \Phi(s) &= \int_0^{\infty} d\mathcal{E} e^{-s\mathcal{E}} \int_{\emptyset} \dots \int d\varepsilon_1 d\varepsilon_2 \dots d\varepsilon_n \\ &= \int_0^{\infty} d\mathcal{E} e^{-s\mathcal{E}} \int_0^{\mathcal{E}} d\varepsilon_n \int_0^{\mathcal{E}-\varepsilon_n} d\varepsilon_{n-1} \dots \int_0^{\mathcal{E}-\varepsilon_n-\dots-\varepsilon_2} d\varepsilon_1. \end{aligned} \tag{2.5-20}$$

*Intermezzo*

To handle the above Laplace transform – of a type frequently occurring in statistical mechanics – we discuss the convolution theorem. Let  $A_i(s) = \mathcal{L}[a_i(t)]$  denote the Laplace transform; the inverse will be denoted by the symbol  $\mathcal{L}^{-1}$ . The inverse for two or three factors is given by the convolution theorems,

$$\mathcal{L}^{-1}[A_1(s)A_0(s)] = \int_0^t d\tau a_1(\tau) a_0(t - \tau), \tag{2.5-21}$$

$$\mathcal{L}^{-1}[A_2(s)A_1(s)A_0(s)] = \int_0^t d\tau_2 \int_0^{t-\tau_2} d\tau_1 a_2(\tau_2) a_1(\tau_1) a_0(t - \tau_2 - \tau_1).$$

For a product of  $(n + 1)$  factors one may prove by induction,

$$\begin{aligned} \mathcal{L}^{-1}[A_n(s)\dots A_0(s)] &= \int_0^t d\tau_n \int_0^{t-\tau_n} d\tau_{n-1} \dots \int_0^{t-\tau_n-\dots-\tau_2} d\tau_1 \\ &\times a_n(\tau_n) a_{n-1}(\tau_{n-1}) \dots a_1(\tau_1) a_0(t - \sum_i \tau_i). \end{aligned} \quad (2.5-22)$$

Needless to say, that we can also give the inverse statement,

$$\begin{aligned} \mathcal{L}\left[\int_0^t d\tau_n \int_0^{t-\tau_n} d\tau_{n-1} \dots \int_0^{t-\tau_n-\dots-\tau_2} d\tau_1 a_n(\tau_n) a_{n-1}(\tau_{n-1}) \dots a_1(\tau_1) a_0(t - \sum_i \tau_i)\right] \\ = A_n(s) \dots A_0(s). \end{aligned} \quad (2.5-23)$$

An important modification appears when we make the substitution of variables

$$\tau_n = t - \theta_n, \quad \tau_{n-1} = \theta_n - \theta_{n-1}, \quad \dots \quad \tau_1 = \theta_2 - \theta_1. \quad (2.5-24)$$

Equation (2.5-23) then goes over into

$$\begin{aligned} \mathcal{L}\left[\int_0^t d\theta_n \int_0^{\theta_n} d\theta_{n-1} \int_0^{\theta_{n-1}} d\theta_{n-2} \dots \int_0^{\theta_2} d\theta_1 \right. \\ \left. \times a_n(t - \theta_n) a_{n-1}(\theta_n - \theta_{n-1}) \dots a_1(\theta_2 - \theta_1) a_0(\theta_1)\right] = A_n(s) \dots A_0(s). \end{aligned} \quad (2.5-24)$$

The repeated integral on the left-hand-side is called a *time-ordered integral*, since  $t > \theta_n > \theta_{n-1} \dots > \theta_1$ . These results will often be needed.

We now return to Equation (2.5-20). For this case  $t \rightarrow \mathcal{E}$ ,  $\varepsilon_i \rightarrow \tau_i$ ; all  $(N + 1)$  factors  $a_i$  are 1. Hence,  $A(s) = 1/s$ . The result is therefore

$$\Phi(s) = 1/s^{N+1}, \quad (2.5-25)$$

with inversion

$$I(\mathcal{E}, N) = \mathcal{E}^N / \Gamma(N + 1). \quad (2.5-26)$$

Whence,

$$\chi(\mathcal{E}, N) = \left(\frac{1}{\hbar\omega}\right)^N \frac{d}{d\mathcal{E}} I(\mathcal{E}, N) = \left(\frac{1}{\hbar\omega}\right)^N \frac{\mathcal{E}^{N-1}}{\Gamma(N)}, \quad (2.5-27)$$

in full accord with (2.5-16).

### (b) Quantum Mechanical

An exact result is also readily obtained. With the energy quantization given by (2.5-13) we have

$$n_1 + n_2 + \dots + n_N = K, \quad (2.5-28)$$

where  $K = \mathcal{E} / \hbar\omega - N / 2$ . The question is now: what is the possible number of sets  $\{n_i\}$  concordant with (2.5-28)? This problem will be met later in Bose-Einstein statistics. We can also formulate the question as follows: In how many ways can we distribute  $K$  entities over  $N$  boxes, with no limit to the number of entities  $n_i$  per box, except that  $n_i$  cannot exceed  $K$ . The usual way to solve this is to put the  $K$  entities on a row, after which we put in  $(N - 1)$  partitions to form the ‘boxes’; see Fig. 2-3.



Fig. 2-3 : the boxes problem.

In this example there are five boxes with 2,3,0,4 and 2 particles in them. Clearly, altogether we have  $K+N-1$  objects on a line, divided into groups of  $K$  and  $N-1$ . The number of states we have realised is

$$\Delta\Gamma(\mathcal{E}, N) = \frac{(K + N - 1)!}{K!(N - 1)!} = \frac{[(\mathcal{E} / \hbar\omega) + \frac{1}{2}N - 1]!}{[(\mathcal{E} / \hbar\omega) - \frac{1}{2}N]!(N - 1)!}. \quad (2.5-29)$$

Dividing by  $\delta\mathcal{E} = \hbar\omega$  we find the density of states,

$$\chi(\mathcal{E}, N) = \left(\frac{1}{\hbar\omega}\right) \frac{(K + N - 1)!}{K!(N - 1)!} = \left(\frac{1}{\hbar\omega}\right) \frac{[(\mathcal{E} / \hbar\omega) + \frac{1}{2}N - 1]!}{[(\mathcal{E} / \hbar\omega) - \frac{1}{2}N]!(N - 1)!}. \quad (2.5-30)$$

This is the exact answer. To re-obtain the semiclassical result, assume that  $\mathcal{E}$  is very large. Then we have,

$$\begin{aligned} & \frac{[(\mathcal{E} / \hbar\omega) + \frac{1}{2}N - 1]!}{[(\mathcal{E} / \hbar\omega) - \frac{1}{2}N]!} \\ & \sim [(\mathcal{E} / \hbar\omega) + \frac{1}{2}N - 1] \times \dots \times [(\mathcal{E} / \hbar\omega) - \frac{1}{2}N + 1] \sim (\mathcal{E} / \hbar\omega)^{N-1}. \end{aligned} \quad (2.5-31)$$

When this is substituted in (2.5-30) the semiclassical result (2.5-27) follows, noting that  $\Gamma(N) = (N - 1)!$

### 2.5.3 A General Form for $\Delta\Gamma(\mathcal{E}, V, N)$ in the Microcanonical Ensemble

We suppose that the Hamiltonian can be expressed in the generalized coordinates and momenta:

$$\mathcal{H} = \sum_{i=1}^{rN} p_i^2 / 2b_i + \mathcal{V}(q_1 \dots q_{rN}), \quad (2.5-32)$$

where the kinetic energy includes translational and internal degrees of freedom. Then define,

$$\Omega(\mathcal{E}, V, N) = \int_{\Sigma_i(p_i^2/2b_i) + \mathcal{V} \leq \mathcal{E}} d\Omega_p d\Omega_q. \quad (2.5-33)$$

We set

$$p_i^2/2b_i = \varepsilon_i, \quad dp_i = d\varepsilon_i \sqrt{b_i/2\varepsilon_i}. \quad (2.5-34)$$

Thus,<sup>17</sup>

$$\Omega(\mathcal{E}, V, N) = \int d\Omega_q \int_{\Sigma_i \varepsilon_i \leq \mathcal{E} - \mathcal{V}(q)} \dots \int d\varepsilon_1 \dots d\varepsilon_{rN} \prod_{j=1}^{rN} \left( \frac{b_j}{2\varepsilon_j} \right)^{\frac{1}{2}} 2^{rN}. \quad (2.5-35)$$

We take the Laplace transform, noting  $\mathcal{E} \geq \mathcal{V}(q)$ :

$\Phi(s, V, N)$

$$\begin{aligned} &= \int d\Omega_q \int_{\mathcal{V}(q)}^{\infty} e^{-s\mathcal{E}} d\mathcal{E} \int_0^{\mathcal{E} - \mathcal{V}(q)} d\varepsilon_{rN} \int_0^{\mathcal{E} - \mathcal{V}(q) - \varepsilon_{rN}} d\varepsilon_{rN-1} \dots \int_0^{\mathcal{E} - \mathcal{V}(q) - \varepsilon_{rN} \dots - \varepsilon_2} d\varepsilon_1 2^{rN} \prod_{j=1}^{rN} \left( \frac{b_j}{2\varepsilon_j} \right)^{\frac{1}{2}} \\ &= 2^{rN} \int d\Omega_q e^{-s\mathcal{V}(q)} \int_0^{\infty} e^{-s\tilde{\mathcal{E}}} d\tilde{\mathcal{E}} \int_0^{\tilde{\mathcal{E}}} \left( \frac{b_{rN}}{2\varepsilon_{rN}} \right)^{\frac{1}{2}} d\varepsilon_{rN} \int_0^{\tilde{\mathcal{E}} - \varepsilon_{rN}} \left( \frac{b_{rN-1}}{2\varepsilon_{rN-1}} \right)^{\frac{1}{2}} d\varepsilon_{rN-1} \dots \\ &\times \int_0^{\tilde{\mathcal{E}} - \varepsilon_{rN} \dots - \varepsilon_2} \left( \frac{b_1}{2\varepsilon_1} \right)^{\frac{1}{2}} d\varepsilon_1. \end{aligned} \quad (2.5-36)$$

[We set  $\tilde{\mathcal{E}} = \mathcal{E} - \mathcal{V}(q)$ .] Leaving the integral  $\int d\Omega_q \exp[-s\mathcal{V}(q)]$  aside, the rest is amenable to the convolution theorem (2.5-23), with  $rN$  factors  $(b_i/2\varepsilon_i)^{\frac{1}{2}}$  and one factor  $1 \rightarrow 1/s$ . For the former we have, going back to a Gaussian integral,

$$\int_0^{\infty} e^{-s\varepsilon_i} \left( \frac{b_i}{2\varepsilon_i} \right)^{\frac{1}{2}} d\varepsilon_i = \int_0^{\infty} e^{-sp_i^2/2b_i} dp_i = \frac{1}{2} \sqrt{\frac{2\pi b_i}{s}}. \quad (2.5-37)$$

Accordingly  $\Phi(s, V, N)$  is given by,

$$\Phi(s, V, N) = \int d\Omega_q e^{-s\mathcal{V}(q)} \sqrt{\frac{2\pi b_{rN}}{s}} \sqrt{\frac{2\pi b_{rN-1}}{s}} \dots \sqrt{\frac{2\pi b_1}{s}} \frac{1}{s}. \quad (2.5-38)$$

The inverse is obtained as – see footnote 19 of Chapter I,

$$\Omega(\mathcal{E}, V, N) = (2\pi)^{\frac{1}{2}rN} \prod_{j=1}^{rN} \sqrt{b_j} \int_{\Omega_q=0}^{\mathcal{V}=\mathcal{E}} d\Omega_q [\mathcal{E} - \mathcal{V}(q)]^{\frac{1}{2}rN} / \Gamma(\frac{1}{2}rN + 1). \quad (2.5-39)$$

<sup>17</sup> The resulting integral must be multiplied by  $2^{rN}$  to allow for both positive and negative values of the  $p_i$ 's.

From this we have for the microcanonical partition function,

$$\begin{aligned} \Delta\Gamma(\mathcal{E}, V, N) &= \frac{(2\pi)^{\frac{1}{2}rN} \delta\mathcal{E}}{h^{rN} \Gamma(N+1) \Gamma(\frac{1}{2}rN+1)} \prod_{j=1}^{rN} \sqrt{b_j} \\ &\times \frac{d}{d\mathcal{E}} \int_{\Omega_q=0}^{\mathcal{V}=\mathcal{E}} d\Omega_q [\mathcal{E} - \mathcal{V}(q)]^{\frac{1}{2}rN}. \end{aligned} \quad (2.5-40)$$

This is a very general result, from which we can obtain the entropy (see next chapter). Of course, the final integral is far from trivial! It was first approximated for real gases by Streiter and Mayer.<sup>18</sup>

## 2.6 Problems to Chapter II

2.1 Consider a perfect classical gas of charged particles (charge  $q$ ) in a constant magnetic field  $\mathbf{B} = B\hat{\mathbf{k}}$ , for which the Landau vector potential  $\mathbf{A} = (0, Bx, 0)$  applies. Show that the Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^N [p_{i,x}^2 + (p_{i,y} \pm m\omega_c q_{i,x})^2 + p_{i,z}^2] / 2m, \quad (1)$$

where  $\omega_c = |q|B/mc$  is the cyclotron frequency. The system is part of a microcanonical ensemble. Make a change of variables

$$Q_i = q_i, \quad P_{i,x} = p_{i,x}, \quad P_{i,y} = p_{i,y} \pm m\omega_c q_{i,x}, \quad P_{i,z} = p_{i,z}. \quad (2)$$

Find the Jacobian and the accessible volume in phase space  $\Delta_g \Omega(\mathcal{E}, V, N)$ .

Show that it does not depend on the magnetic field (nor do any thermodynamic properties depend on  $\mathbf{B}$ ; this failure for a classical gas to yield diamagnetism is known as the Bohr–van Leeuwen theorem, see Chapter VI).

2.2 Consider a system of (semi)-classical harmonic oscillators,

$$\mathcal{H} = \sum_i^N \left( p_i^2 / 2m + \frac{1}{2} m\omega^2 q_i^2 \right). \quad (3)$$

(a) Compute the volume occupied in phase space,  $\Delta_g \Omega$ , by making a change of variables, such that the volume is that between two hyperspheres [do *not* use the Dirichlet integral].

(b) Next find the associated number of accessible quantum states,  $\Delta_g \Gamma$ , noting that harmonic oscillators are *distinguishable* objects, so that the factor  $N!$  in the microcell volume must be omitted. Compare your result with Eq. (2.5-27).

<sup>18</sup> S.F. Streiter and J.E. Mayer, J. Chem. Physics **7**, 1025 (1939).

(c) Obtain the associated entropy  $S = k_B \ln \Delta_g \Gamma$ . Find the temperature  $T$  and obtain the classical equipartition result  $\mathcal{E} = Nk_B T$ .

2.3 Consider a perfect classical gas in an adiabatic enclosure, which is divided into two subsystems,  $v$  and  $V - v \gg v$ . We assume that the two subsystems are separated by an adiabatically lined impermeable moveable piston, so that there is free volume exchange but no energy or particle exchange. Show that the probability density function (pdf) is a gamma distribution,

$$W(v) = C v^{n-1} e^{-Nv/V}, \quad (4)$$

where  $n$  and  $N - n \gg n$  are particle numbers in the two subsystems. Find the moments  $\langle v^k \rangle$  and the variance  $\text{var } v$ .

2.4 In the same problem as above, assume that  $v$  and  $V - v$  are of comparable size. Show that  $W(v)$  is a beta distribution and express the moments  $\langle v^k \rangle$  and the variance  $\text{var } v$  as beta functions, making no approximations. Compare the answers with those of problem 2.3.

2.5 At *extremely* low temperatures the relevant eigenvalue spectrum of any system becomes discrete. Using Kronecker deltas rather than Dirac delta functions, restate the expressions for  $p(\eta)$  and  $\rho$  for a microcanonical ensemble

2.6 The von Neumann equation  $\partial \rho / \partial t + (1/\hbar)[\rho, \mathcal{H}] = 0$  is often written as

$$\partial \rho / \partial t + i\mathcal{L}\rho = 0, \quad (2.3-5')$$

where  $\mathcal{L}$  is the *superoperator* (i.e., an operator acting on an operator) defined by  $\mathcal{L}K = (1/\hbar)[\mathcal{H}, K]$ . The solutions of the ordinary commutator form and of the superoperator form are indicated in (2.3-6):

$$\rho(t) = e^{-i\mathcal{H}(t-t_0)/\hbar} \rho(t_0) e^{i\mathcal{H}(t-t_0)/\hbar}, \quad \text{or} \quad \rho(t) = e^{-i\mathcal{L}(t-t_0)} \rho(t_0). \quad (2.3-6')$$

Show by series expansion that the two solutions are identical, given the definition of the superoperator  $\mathcal{L}$  stated above.<sup>19</sup>

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<sup>19</sup> Louisell states the following general theorem: Let  $A$  and  $B$  be two generally non-commuting operators of the same Hilbert space and let  $\xi$  be a parameter, then:

$$e^{\xi A} B e^{-\xi A} = B + \xi[A, B] + \frac{\xi^2}{2!}[A, [A, B]] + \frac{\xi^3}{3!}[A, [A, [A, B]]] + \dots, \quad (5)$$

cf. W. Louisell "Radiation and Noise in Quantum Electronics", McGraw-Hill, 1964, Section 3.2, theorem 3.