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!

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

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

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0 \qquad \frac{\partial \rho}{\partial t} = 0$$

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

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.

$$\rho(q_i, p_i) = Const.$$

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

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

$$\langle \mathrm{f} \rangle = \frac{\iint_{\text{all phase space}} \mathrm{f(q,p)}\rho(\mathrm{q,p;t})\mathrm{d}^{3N}\mathrm{q}\mathrm{d}^{3N}\mathrm{p}}{\iint_{\text{all phase space}} \rho(\mathrm{q,p;t})\mathrm{d}^{3N}\mathrm{q}\mathrm{d}^{3N}\mathrm{p}}$$

$$= \frac{\rho \iint_{\text{all phase space}} \mathrm{f(q,p)} d^{3N}q d^{3N}p}{\rho \iint_{\text{all phase space}} d^{3N}q d^{3N}p}$$

$$= \frac{\iint_{\text{all phase space}} \mathrm{f(q,p)} d^{3N}q d^{3N}p}{\iint_{\text{all phase space}} d^{3N}q d^{3N}p} = \frac{1}{\omega} \iint_{\text{all phase space}} \mathrm{f(q,p)} d\omega$$

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*.

$$\rho = \begin{cases} const. & \text{Over the relevant region} \\ 0 & \text{Outside the relevant region} \end{cases}$$

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.

$$\rho(q, p) = \rho[H(q, p)]$$

Condition (11) is then identically satisfied.

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

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

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

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

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

$$= \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial H}\{-\dot{p}_i\dot{q}_i + \dot{q}_i\dot{p}_i\}\right) = 0 \quad ☺$$

$$\frac{\partial \rho}{\partial t} = 0 \quad \Leftrightarrow \quad \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

$q, p = const.$

$$\frac{d\rho}{dt} = \left(\frac{\partial \rho}{\partial t}\right)_{q_i, p_i} + \sum_{i=1}^{3N}\left(\left(\frac{\partial \rho}{\partial q_i}\right)_{p_j, t}\dot{q}_i + \left(\frac{\partial \rho}{\partial p_i}\right)_{q_i, t}\dot{p}_i\right) = 0$$

$\rho \neq \rho(t)$ $\qquad$ $\rho \neq \rho(t)$

$$\vec{\nabla}.(\rho\vec{v}) \begin{cases} > 0 \rightarrow \frac{\partial \rho}{\partial t} > 0 \rightarrow \text{Increasing density at (q,p)} \\ < 0 \rightarrow \frac{\partial \rho}{\partial t} < 0 \rightarrow \text{Decreasing density at (q,p)} \end{cases}$$

The functional form ρ(q,p)= ρ[H(q, p)] 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

$$\rho(q, p) \propto \exp[H(q, p)/kT]$$

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

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

$$(E - \tfrac{1}{2}\Delta) \leq H(q, p) \leq (E + \tfrac{1}{2}\Delta)$$

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

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

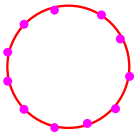
where the primed integration extends only over that part of the phase space which conforms to condition (1). It is clear that ω will be a function of the parameters N, V, E and Δ.

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

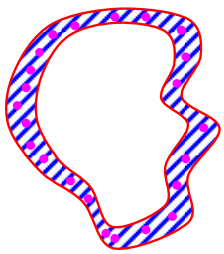
$$\left.\begin{aligned} \rho(q, p) &= \text{const.} \quad \text{if } (E - \tfrac{1}{2}\Delta) \leq H(q, p) \leq (E + \tfrac{1}{2}\Delta) \\ &0 \qquad \text{otherwise} \end{aligned}\right\}$$

$$H(q, p) = E_0$$

$$q^2 + p^2 = cte.$$



$$(E - \tfrac{1}{2}\Delta) \leq H(q, p) \leq (E + \tfrac{1}{2}\Delta)$$



$\rho = cte.$

Equal a priori probabilities of everything such as energy

H is independent of q and p

Hypersurface

$(E - \frac{1}{2}\Delta) \leq H(q, p) \leq (E + \frac{1}{2}\Delta)$

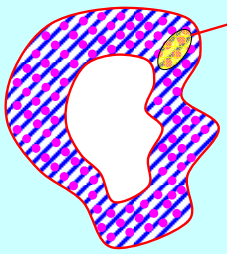
Hypershell

H is **nearly** independent of q and p

Approximately

Equal a priori probabilities

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



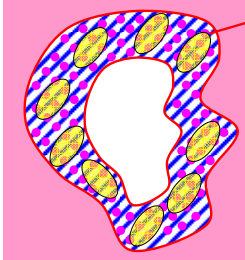
$d\omega$

Expectation value of the number of the representative points in a volume element of dω =

$$= \rho(q,p) d^3q d^3p$$
$$= \rho(q,p) d\omega$$
$$\propto d\omega$$

$\rho(q,p) = cte.$

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

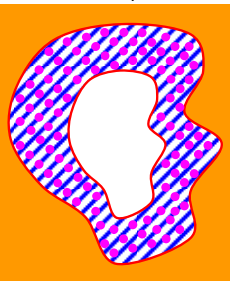


$d\omega$

Probability of finding a representative point in a given volume element dω =

Probability of finding a representative point in an equivalent volume element dω located anywhere

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



Probability of finding a representative point in the hypershel =

Probability of finding a representative point located anywhere in the hypershel

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.

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

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

$$\langle f \rangle = \langle f \rangle_{ensemble} = \langle \langle f \rangle_{ensemble} \rangle_{time}$$

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

$$\langle f \rangle = \langle \langle f \rangle_{ensemble} \rangle_{time} = \langle \langle f \rangle_{time} \rangle_{ensemble}$$

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

$$\langle f \rangle = \langle \langle f \rangle_{long-time} \rangle_{ensemble} = \langle f \rangle_{long-time}$$

According to ensemble theory

$$\langle f \rangle = \langle \langle f \rangle_{long-time} \rangle_{ensemble} = \langle f \rangle_{long-time}$$

According to ensemble theory

Is this removing the ensemble averge trivial?

N0, it is possible only if the system is ergodic.

Homework: Prepare an introduction (around 3 or 4 pages) to the chaos and chaotic systems.

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

$$\langle f \rangle = \langle f \rangle_{long-time} = \langle f \rangle_{\exp}$$

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.

Microcanonical Ensemble ⟺ Thermodynamics

To do this, we observe that there exists a direct correspondence between the various microstates of the given system and the various locations m the phase space.

Various Microstates ⟺ Various locations in the phase space

The volume co (of the allowed region of the phase space) is, therefore, a direct measure of the multiplicity Γ of the microstates accessible to the system.

Allowed volume of the phase space **ω** ⟺ Microstates accessible to the system **Γ**

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,

$$\omega_0 = ? \qquad \left(\frac{\omega}{\omega_0}\right)_{asymp.} = \Gamma$$

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

$$S = k \ln \Gamma = k \ln\left(\frac{\omega}{\omega_0}\right)$$

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.

$$\omega = \int d\omega = \int d^{3N} q d^{3N} p \longrightarrow (qp)^{3N} \longrightarrow (L)^{3N} \longrightarrow (\hbar)^{3N}$$