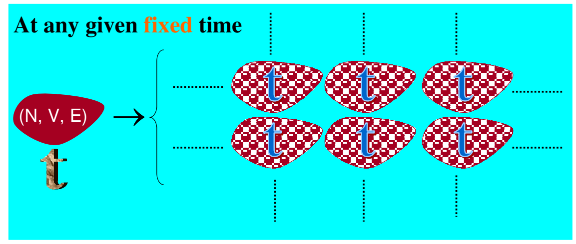
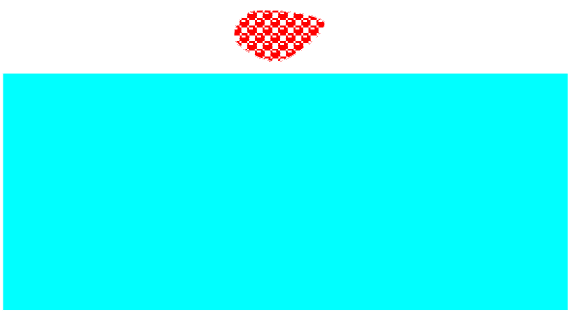
Chapter 2

ELEMENTS OF ENSEMBLE THEORY

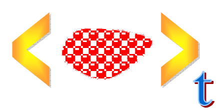
In the preceding chapter we noted that, for a given macrostate (TV, V, E), a statistical system, at any time t, is equally likely to be in any one of an extremely large number of distinct microstates.



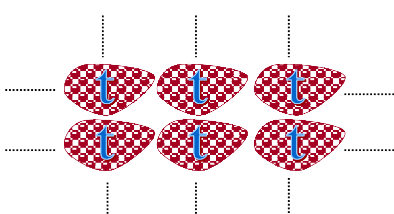
As time passes, the system continually switches from one microstate to another,



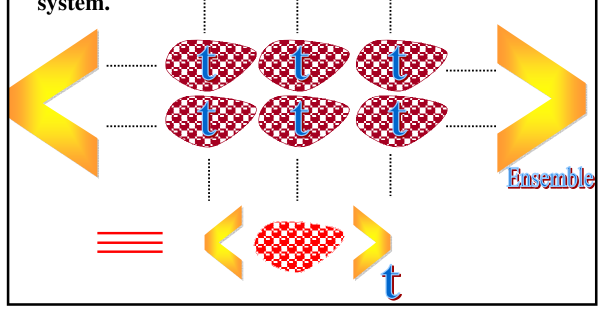
with the result that, over a reasonable span of time, all one observes is a behavior "averaged" over the variety of microstates through which the system passes.



It may, therefore, make sense if we consider, at a single instant of time, a rather large number of systems-all being some sort of "mental copies" of the given system-which are characterized by the same macrostate as the original system but are, naturally enough, in all sorts of possible microstates.



Then, under ordinary circumstances, we may expect that the average behavior of any system in this collection, which we call an ensemble, would be identical with the time-averaged behavior of the given system.



It is on the basis of this expectation that we proceed to develop the so-called ensemble theory.

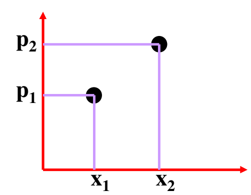
For classical systems, the most appropriate workshop for developing the desired formalism is the phase space.

Accordingly, we begin our study of the various ensembles with an analysis of the basic features of this space.

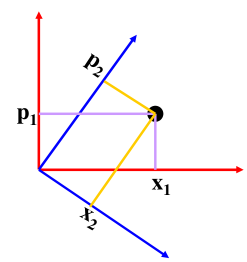
Phase space of a classical system

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

2 Particles in Two Dimensional Space



1 Particle in Four Dimensional Space



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

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

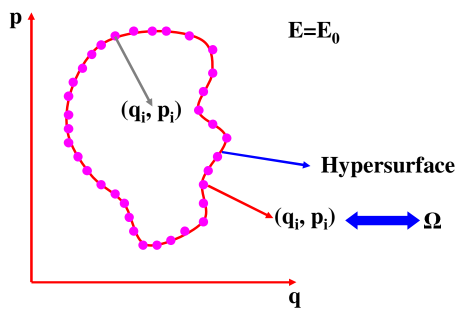
where $H(q_i, p_i)$ is the *Hamiltonian* of the system. Now, as time passes, the set of coordinates (q_i, p_i), which also defines the microstate of the system, undergoes a continual change. Correspondingly, our representative point in the phase space carves out a *trajectory* whose direction, at any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

$$H(q_i, p_i) = E$$

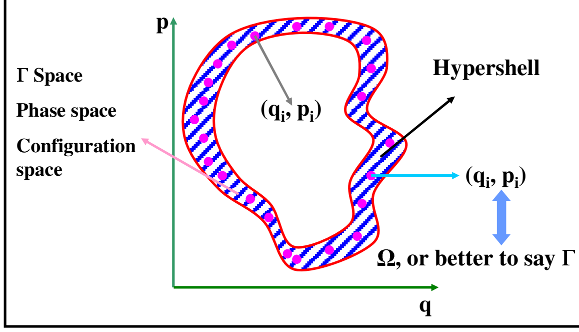
V is finite $\longrightarrow$ **q_i is limited**

E is finite $\longrightarrow$ **Both q_i and p_i are limited**

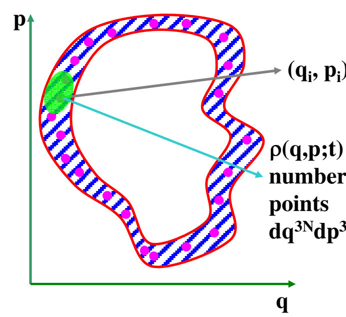
q=q(t), p=p(t)



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



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



ρ(q,p;t) dq^{3N}dp^{3N} is the number of representative points in the volume dq^{3N}dp^{3N}

Ensemble Theory

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

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

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

$$\frac{\partial \rho}{\partial t} = 0$$

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

Quantum Theory

$$\rho(x,t) = P(x,t) = |\Psi(x,t)|^2$$

$$\langle f \rangle = \frac{\iint\limits_{\text{all space}} f(x)|\Psi(x,t)|^2 d^3x}{\iint\limits_{\text{all space}} |\Psi(x,t)|^2 d^3x} = \iint\limits_{\text{all space}} f(x)|\Psi(x,t)|^2 d^3x$$

1

In Sherodinger picture of quantum mechanics the wave function is the fundamental variable, i.e. only wave function can vary with time. If the potential is not a function of time, V≠V(t), then time behavior of wave function can be separated as exp(-iEt/ħ), i.e. U_E(x) exp(-iEt/ħ). In this case |Ψ(x, t)|² will be independent of time. However, in general the potential is a function of time, V=V(t), hence it is impossible to separate time behavior of wave function from its position part.

In ensemble theory ρ(q,p;t), which plays the similar role of |Ψ(x, t)|² in quantum mechanics, determine representative points in phase space, and only its interoperation has changed, otherwise everything is similar to quantum mechanics. Indeed in both cases we have a distribution function and we talk about average values, i.e. <f>, that is expectations values and not absolute values.

Liouville's theorem and its consequences

Joseph Liouville

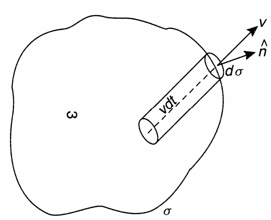
Born,24 March 1809 in Saint-Omer,France
Died,8 Sept 1882 in Paris,France

Liouvill theorem

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho(q,p;t),H] = 0$$

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

$$\frac{\partial}{\partial t}\int_{\omega} \rho \, d\omega \equiv \text{آهنگ افزایش نقاط نماینده در حجم}$$



where $d\omega \equiv (d^{3N}q \, d^{3N}p)$

On the other hand, the net rate at which the representative points "flow" out of ω (across the bounding surface a) is given by

$$\int_{\sigma} \rho(\boldsymbol{v}\cdot\hat{\boldsymbol{n}})\,d\sigma$$ **آهنگ خروج نقاط نماینده از حجم**

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

By the divergence theorem, it can be written as

$$\int_{\sigma} \rho(\boldsymbol{v}\cdot\hat{\boldsymbol{n}})\,d\sigma = \int_{\omega} \operatorname{div}(\rho\boldsymbol{v})\,d\omega$$

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

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

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

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

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

$$\vec{v} = \left(\dot{x},\dot{y},\dot{z}\right)$$

$$\vec{\nabla}.\vec{v} = \left(\hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z}\right).\left(v_x\hat{x} + v_y\hat{y} + v_z\hat{z}\right) =$$

$$= \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

$$\vec{v} = \left(\dot{x},\dot{y},\dot{z},\dot{p}_x,\dot{p}_y,\dot{p}_z\right)$$

$$\vec{\nabla}.\vec{v} = \left(\hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z} + \hat{p}_x\frac{\partial}{\partial p_x} + \hat{p}_y\frac{\partial}{\partial p_y} + \hat{p}_z\frac{\partial}{\partial p_z}\right).\left(\dot{x}\hat{x} + \dot{y}\hat{y} + \dot{z}\hat{z} + \dot{p}_x\hat{p}_x + \dot{p}_y\hat{p}_y + \dot{p}_z\hat{p}_z\right) =$$

$$= \frac{\partial\dot{x}}{\partial x} + \frac{\partial\dot{y}}{\partial y} + \frac{\partial\dot{z}}{\partial z} + \frac{\partial\dot{p}_x}{\partial p_x} + \frac{\partial\dot{p}_y}{\partial p_y} + \frac{\partial\dot{p}_z}{\partial p_z}$$

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

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

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

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

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

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

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

$$\begin{cases} \dot{q}_i = \dfrac{\partial H}{\partial p_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{cases} \Longrightarrow \frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} =$$

$$= \frac{\partial^2 H}{\partial p_i \partial q_i} = \frac{\partial}{\partial q_i}\frac{\partial H}{\partial p_i}$$

$$= -\frac{\partial \dot{p}_i}{\partial q_i}$$

$$\boxed{\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial q_i} = 0}$$

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

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

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

$$d\rho = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}dq_i + \frac{\partial \rho}{\partial p_i}dp_i\right)$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial \rho}{\partial p_i}\frac{dp_i}{dt}\right) =$$

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

$$= \frac{\partial \rho}{\partial t} + \vec{\nabla}.(\rho\vec{v}) = 0$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \vec{\nabla}.(\rho\vec{v}) = 0$$

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

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right) = 0$$

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

$$\langle A \rangle_t = \int \Psi^*(x,t) A \Psi(x,t) dx$$

$$\frac{d\langle A \rangle_t}{dt} = \int \Psi^*(x,t)\frac{\partial A}{\partial t}\Psi(x,t)dx + \int \frac{\partial \Psi^*(x,t)}{\partial t} A\Psi(x,t)dx + \int \Psi^*(x,t) A \frac{\partial \Psi(x,t)}{\partial t}dx$$

$$= \left\langle \frac{\partial A}{\partial t} \right\rangle_t + \int \left(\frac{1}{i\hbar}H\Psi\right)^* A\Psi dx + \int \Psi^* A\left(\frac{1}{i\hbar}H\Psi\right)dx$$

$$= \left\langle \frac{\partial A}{\partial t} \right\rangle_t + \frac{i}{\hbar}\int \Psi^* H A \Psi dx - \frac{i}{\hbar}\int \Psi^* A H \Psi dx =$$

$$= \left\langle \frac{\partial A}{\partial t} \right\rangle_t + \frac{i}{\hbar}\langle [H, A] \rangle_t$$

$$\frac{d\langle A \rangle_t}{dt} = \left\langle \frac{\partial A}{\partial t} \right\rangle_t + \frac{i}{\hbar}\langle [H, A] \rangle_t$$

$$\frac{d\langle x \rangle}{dt} = \frac{i}{\hbar}\langle [H, x] \rangle = \frac{i}{\hbar}\left\langle \left[\frac{p^2}{2m} + V(x), x\right] \right\rangle$$

$$[p^2, x] = p[p, x] + [p, x]p = \frac{2\hbar}{i}p$$

$$[V(x), x] = 0$$

$$\frac{d}{dt}\langle x \rangle = \left\langle \frac{p}{m} \right\rangle$$