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# APPLIED MOLECULAR THEORY FOR ENGINEERS

by

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# 3. INTRODUCTION TO CLASSICAL STATISTICAL MECHANICS

## 3.1 Role of Statistical Mechanics in Materials Design

Within the hierarchy of theoretical approaches one can enlist for the first-principles design of engineering materials, statistical mechanics plays a prominent role. As shown in Figure 1.1, statistical mechanics provides a link between molecular-level information and macroscopically manifested behavior. Given the chemical constitution of a molecule or of a group of molecules in a material system, quantum mechanics can determine the potential energy as a function of the configuration, *i.e.* of the nuclear coordinates of atoms constituting the molecules; quantum mechanics can also identify stable (minimum energy) configurations of a molecule, and thus inform us about the molecule's bonded geometry (bond lengths, bond angles, torsion angles). Taking this fundamental information about molecular geometry and energetics as input, statistical mechanics proceeds to derive properties as functions of the macroscopic state of the material system formed by the molecules in question (set by variables such as temperature, pressure, composition, stress, electric field, etc.)

Properties calculable, in principle, through statistical mechanics once the potential energy hypersurface is known include thermodynamic properties, such as density, heat capacity, solubility, phase diagrams for single component and multicomponent systems, sorption isotherms, surface and interfacial tension; mechanical properties, such as elastic moduli, strength, and fracture toughness; transport and rheological properties, such as viscosity, diffusivity, and the spectrum of relaxation times governing viscoelastic response to deformation; electrical and magnetic properties, such as susceptibilities as functions of frequency; and chemical properties, such as rate constants for reaction and chemisorption and chemical equilibrium constants. Even in cases where the accurate quantitative prediction of property values is not yet possible (which one can say about the majority of materials of practical interest) one can employ statistical mechanics to arrive at useful functional forms that describe material behavior (such as equations of state describing the equilibrium *PVT* properties and constitutive equations describing the transient response to deformation of polymer melts). Even more important than this ability to capture property values or constitutive laws, however, is the fact that statistical mechanics provides a concrete picture of molecular organization and motion, and of the microscopic mechanisms underlying macroscopically manifested material behavior. This mechanistic information can help address "what if" type questions of a materials design nature. (*e.g.*, What effect will the substitution of methine hydrogens by chlorine atoms ~~groups~~ along the chains of a polymer have upon its processability and thermal stability?) The continuum engineering sciences (thermodynamics, transport phenomena, continuum mechanics and rheology, electromagnetic theory, chemical kinetics) can take as input the material properties and constitutive laws provided by statistical mechanics and proceed to predict the performance expected of a product under given application conditions, or the morphology expected to develop in a material under given processing conditions.

Such a modular scheme for product design, of course, does not exist today in the form of well-defined procedures ready to be applied automatically on a computer. Nevertheless, new bits and pieces of this scheme are being developed at a rapid pace. Advances in chemical physics are allowing the formulation of theoretical and coarse-grained simulation approaches that offer a better compromise between realism and tractability. At the same time, advances in computer hardware and algorithms expand the frontiers of what can be treated with full-scale simulation. In industrial research work aiming at the development of new and improved materials, experimental investigations are already guided and complemented by considerations based on applied molecular theory. A variety of software products have emerged, which package molecular modelling techniques in a way that facilitates application to a wide variety of systems. It is not clear whether and when a purely *ab initio* materials design approach will evolve. It is unquestionable, however, that the practicality of using applied statistical mechanics towards the solution of real-life problems is increasing ever more steeply.

*Equilibrium Statistical Mechanics* deals with systems in thermodynamic equilibrium. From a detailed description, involving on the order of $10^{23}$ microscopic variables (degrees of freedom) it passes to a thermodynamic description, involving only a handful of macroscopic thermodynamic variables. This reduction comes as a consequence of statistical laws that are discerned in the behavior of many-body systems.

*Nonequilibrium Statistical Mechanics* deals with systems off thermodynamic equilibrium and predicts the rates of approach to equilibrium from microscopic information.

Thus, it provides a molecular foundation for transport phenomena and chemical kinetics.

Statistical mechanics-based approaches can generally be distinguished into *theories* and *computer simulations.* Although statistical mechanics provides a rigorous formalism for predicting macroscopic properties from molecular-level information, an exact analytical solution of this formalism is impossible for all but the simplest molecular models (*e.g.*, monatomic ideal gas). Statistical mechanical theories introduce approximations in the molecular model employed (representation of shape, spatial arrangement, of molecules, and interactions between them), or in the mathematical formulation of the problem (*e.g.*, neglect of correlations between positions of pairs or larger groups of interacting molecules), or in both. In this way, they arrive at closed-form systems of algebraic, differential, or integral equations that can be solved analytically or numerically. When the approximations are chosen judiciously, they can provide satisfactory solutions with moderate computational effort. Molecular simulation methods, on the other hand, can be viewed as techniques for the numerical solution of the full statistical mechanical formulation, given a model for the molecular geometry and interactions. Simulations typically involve the creation of a large number of microscopic configurations for the system under study, whose characteristics are analyzed to extract mechanistic information and property values in much the same way as experimental data; hence the name *computer experiments* is often attributed to simulations. When executed correctly, simulations can provide solutions that are exact, within testable numerical error. Simulations are typically system specific, as opposed to theories, which are typically designed to address wide categories of systems. The major limitations of simulations lies in their very heavy computational requirements, which do not allow their "brute- force" application for the study of large length-scale and long time-scale phenomena in real-life materials. In many cases, this problem can be alleviated by introducing approximations, which are typically less drastic than those invoked in theories.

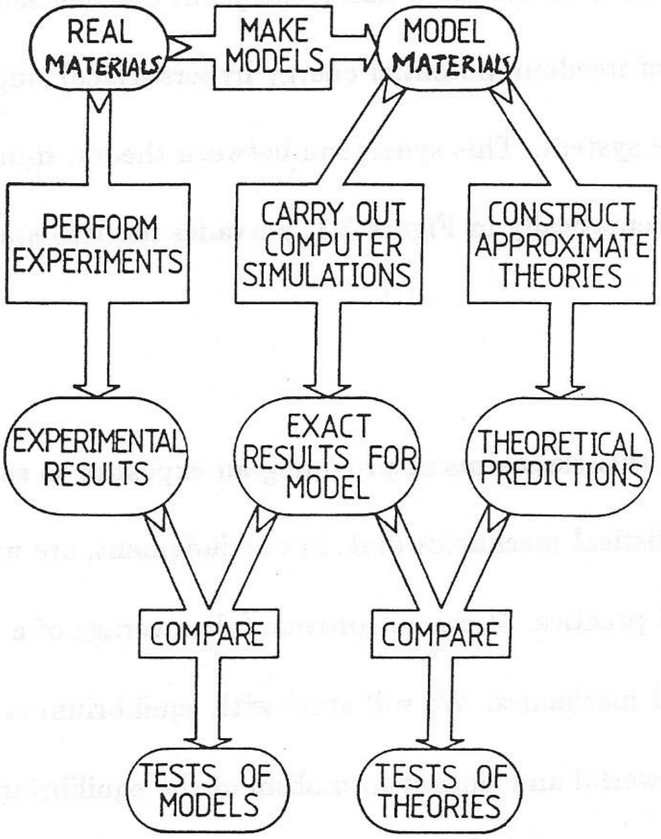

**Fig. 3.1** Connections between experiment, theory, and computer simulation [adapted from Allen and Tildesley 1987, p 5]

When applied to the same molecular model, a simulation can point out deficiencies in the approximations invoked by a theory, in much the same way as a finite element computation can be used to check a perturbation solution to a transport problem under given boundary conditions. Thus, simulations constitute excellent tests for theoretical work. Comparisons between simulation results and experimental data over the same set of macroscopic conditions, on the other hand, can point out deficiencies in the model (microscopic degrees of freedom, potential energy hypersurface) employed by the simulation to represent the system. This synergism between theory, simulation, and experiment, represented schematically in Figure 3.1, pervades modern statistical mechanics-based work.

Our discussion in this class aims at providing an exposure to some fundamental and applied aspects of statistical mechanics that, in our judgment, are useful in chemical engineering research and practice. It cannot provide full coverage of a field as rich and convoluted as is statistical mechanics. We will start with equilibrium statistical mechanics. We will outline the powerful and elegant formalism of the equilibrium ensembles and, through examples, introduce some approximations that are typically used in implementing it for fluids and solids. In the second part of our discussions we will introduce the principles underlying molecular simulations, outline how to formulate and use Monte Carlo and molecular dynamics techniques and present examples of their implementation. Next, we will examine systems that are kept away from equilibrium by the imposition of small external driving forces and discuss how time correlation functions can be used to estimate transport coefficients relating the forces with the fluxes they induce. In the latter part of the class we will briefly look at the Brownian motion description of phenomena wherein the motion of degrees of freedom is characterized by widely different time scales. We will also look at transition state theory-based techniques designed for slow dynamical processes whose rate is limited by bottlenecks in configuration space that can be overcome only infrequently.

## 3.2 From Hamiltonian Dynamics to Statistical Mechanics: Probability Distributions in Dynamical Systems

### 3.2.1 Trajectories in Phase Space

Consider a classical system with a large number of degrees of freedom (for example, $N$ molecules of a monatomic fluid in a cubic container). In quantum mechanics, a complete description of the microscopic state or "microstate" of the system is provided by the wavefunction $\Psi$, which is a function of the position coordinates of all nuclei and electrons. In classical mechanics, the state of the system is completely specified in terms of a set of *generalized coordinates* $\mathbf{q}$ and *generalized momenta* $\mathbf{p}$. For example, in the case of the monatomic fluid one can use the Cartesian position vectors of all molecules, $\mathbf{q} \equiv (q_{11}, q_{12}, q_{13},\ q_{21}, q_{22}, q_{23},\ \ldots,\ q_{N1}, q_{N2}, q_{N3}) \equiv \mathbf{r} \equiv (x_1, y_1, z_1,\ x_2, y_2, z_2,\ \ldots,\ x_N, y_N, z_N)$ , *i.e.*, a total of $3N$ components, and the molecular momenta $\mathbf{p} = (p_{11}, p_{12}, p_{13},\ p_{21}, p_{22}, p_{23},\ \ldots,\ p_{N1}, p_{N2}, p_{N3})$. In general, one can use variables other than Cartesian coordinates, *e.g.* bond lengths, bond angles and dihedral angles, to specify the configuration of systems consisting of polyatomic molecules; we will see examples of this. We will employ the symbol $\mathbf{q}$ to denote such coordinates in the most general sense, and $\mathbf{p}$ to denote the corresponding momenta. There is exactly one generalized momentum $p_j$ per generalized coordinate $q_j$, defined by [Goldstein 1980]

$$p_j = \frac{\partial \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)}{\partial \dot{q}_j} \tag{3.1}$$

where $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$ is the Lagrangian function we introduced in chapter 1, *i.e.*, the difference between kinetic and potential energies, and $\dot{q}_j$ denotes the time derivative of $q_j$. The quantities $q_j$ and $p_j$, related by Eq. (3.1), are referred to as *conjugate*. For simplicity, in the following discussion we will assume that the vector of generalized coordinates $\mathbf{q}$ has dimension $3N$, with three coordinates $\mathbf{q}_i$ corresponding to each molecule $i$.

The $3N$-dimensional set from which the generalized coordinates of the system $\mathbf{q} \equiv (\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$ take on values will be referred to as *configuration space*. The $3N$-dimensional set from which the generalized momenta $\mathbf{p} \equiv (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$ take on values will be referred to as *momentum space*. Simultaneous specification of position and momentum is permitted in the classical limit, where the restrictions imposed by the uncertainty principle become unimportant relative to the magnitude of the components of $\mathbf{p}$ and $\mathbf{q}$. The $6N$-dimensional vector $\mathbf{X} \equiv (\mathbf{p}, \mathbf{q}) \equiv (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N; \mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$ will be referred to as the *state vector* or *representative point* of the system. The $6N$-dimensional set from which $\mathbf{X}$ takes on values is the *phase space* of the system, symbolized by $\Gamma$. A point in this space represents a microstate of the entire system. The generalized coordinates $\mathbf{q}$ are also termed *configurational degrees of freedom* of the system, while the generalized momenta are sometimes called *momentum degrees of freedom.*

In the following we focus on an isolated system, which evolves in time influenced solely by interactions among its constituent particles. As time elapses, the point representative of the system moves in the $6N$- dimensional phase space, describing a trajectory. The trajectory is a one-dimensional line, each point on it corresponding to an instant in time.

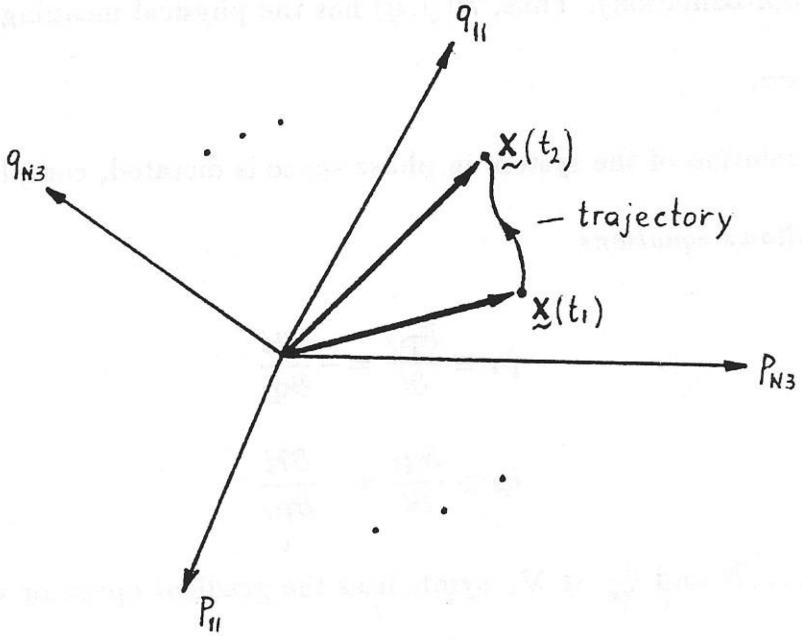

**Fig. 3.2** Schematic representation of the movement of a system point $\mathbf{X}(t)$ in a $6N$-dimensional phase space ($t_2 > t_1$).

The *Hamiltonian* $\mathcal{H}(\mathbf{X}, t) \equiv \mathcal{H}(\mathbf{p}, \mathbf{q}, t)$ is an important function of the microstate of the system. It is related to the Largrangian by

$$\mathcal{H}(\mathbf{q}, \mathbf{p}, t) = \dot{\mathbf{q}} \cdot \mathbf{p} - \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t) \tag{3.2}$$

In the example of a monatomic fluid described in terms of the Cartesian coordinates and momenta of its molecules, the Hamiltonian becomes

$$\mathcal{H}(\mathbf{p},\mathbf{r}) = \sum_i \frac{{\mathbf{p}_i}^2}{2m_i} + \mathcal{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{3.3}$$

The first term on the right hand side of Eq. (3.3) is the kinetic energy, expressed in terms of all molecular momenta. The second term is the potential energy, expressed as a function of molecular coordinates. $\mathcal{V}$ can be obtained, in principle, by solving Schrödinger's equation for all possible configurations of the nuclei $\mathbf{r}_1,\ldots,\mathbf{r}_N$ (Born-Oppenheimer approximation). Thus, $\mathcal{H}(\mathbf{p},\mathbf{q})$ has the physical meaning of the total energy of the system.

The time evolution of the system in phase space is dictated, completely deterministically, by *Hamilton's equations*

$$\dot{\mathbf{p}}_\ell \equiv \frac{\partial \mathbf{p}_\ell}{\partial t} = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}_\ell} \tag{3.4}$$

$$\dot{\mathbf{q}}_\ell \equiv \frac{\partial \mathbf{q}_\ell}{\partial t} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_\ell} \tag{3.5}$$

where $\ell = 1,2,\ldots,N$ and $\frac{\partial}{\partial \mathbf{x}} \equiv \nabla_{\mathbf{x}}$ symbolizes the gradient operator with respect to the vectorial quantity $\mathbf{x}$. In a Cartesian description, the meaning of Hamilton's equations is particularly transparent: Eq. (3.4) states that the rate of change of momentum for particle $\ell$ equals the total force on that particle, *i.e.*, this equation is a statement of Newton's second law of motion. Eq.(3.5), on the other hand, simply states that the rate of change of the position vector, *i.e.*, the velocity, equals the momentum divided by the mass.

If the Hamiltonian $\mathcal{H}$ does not depend explicitly on time (i.e., if it depends on time only through its dependence on $\mathbf{p}$ and $\mathbf{q}$, which vary with time along a trajectory,) then $\mathcal{H}$ is a constant of the motion. Such is the case for *conservative* systems, where the potential energy is a function of particle positions only:

$$\mathcal{H}(\mathbf{X}) \equiv \mathcal{H}(\mathbf{p}, \mathbf{q}) = E, \quad \text{a constant} \tag{3.6}$$

Given the microstate $\mathbf{X}(t_1)$ of the system at time $t_1$, one can uniquely determine the microstate $\mathbf{X}(t_2)$ at a later time $t_2$, where $t_2 > t_1$, by integrating Hamilton's equations of motion. Furthermore, given $\mathbf{X}(t_2)$, one can uniquely determine $\mathbf{X}(t_1)$ by integrating Hamilton's equations backwards in time. Hamiltonian dynamics, therefore, is completely *time-reversible.*

Eq. (3.6) defines a $(6N-1)$-dimensional hypersurface in phase space, on which the system must always lie if its energy is constant and equal to $E$ (if, that is, the system is isolated in thermodynamic language). We will call such a hypersurface an *energy hypersurface corresponding to energy value E.*

Hamiltonian dynamics leads to two interesting observations concerning the topology of trajectories in phase space:

**Statement 1:** Let $\mathbf{X}_A(t_1)$ and $\mathbf{X}_B(t_1)$ be the state points at time $t_1$ of two $N$-particle systems characterized by the same Hamiltonian, and let $\mathbf{X}_A(t_1) \neq \mathbf{X}_B(t_1)$. Then, the trajectories traced by the systems $A$ and $B$ in phase space will never meet at any future (or past) time.

**Proof:** Assume that the two trajectories cross at a time $t_2$, so that $\mathbf{X}_A(t_2) = \mathbf{X}_B(t_2)$. Then, by inverting the direction of time and integrating Hamilton's equations back to time $t_1$, we are led to the conclusion $\mathbf{X}_A(t_1) = \mathbf{X}_B(t_1)$, which is contrary to our hypothesis. Therefore, the trajectories of the two systems cannot meet in phase space.

**Statement 2:** The trajectory traced by a conservative system on a constant energy hypersurface as time evolves can never intersect itself. It can, however, form a closed loop.

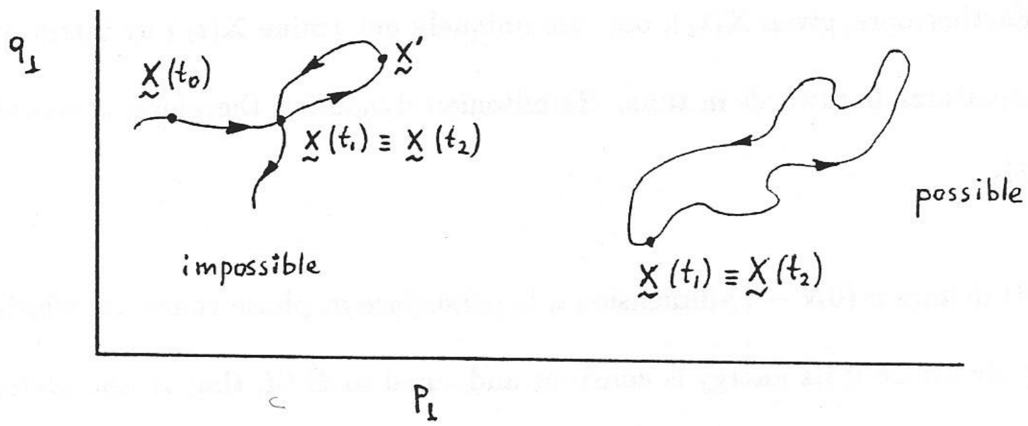

**Figure 3.3** Schematic illustration of the fact that the trajectory of an isolated system in phase space can never intersect itself.

**Proof:** Assume that the dynamical trajectory of a system evolving solely under the influence of interactions among its constituent particles crosses itself on the system's potential energy hypersurface, as shown schematically on the left-hand side of Fig. 3.3. This means that the trajectory passes through the same point in phase space, $\mathbf{X}(t_1) \equiv \mathbf{X}(t_2)$, at two different times $t_2 > t_1$. If the trajectory crosses itself without forming a single loop, we can always locate a point $\mathbf{X}(t_0)$ on it, corresponding to a time

$t_0 < t_1$ with $t_1 - t_0 < t_2 - t_1$, such that $\mathbf{X}(t_0)$ does not lie on the part of the trajectory traced between times $t_1$ and $t_2$. If, starting at $\mathbf{X}(t_1)$, we integrate the equations of motion backwards for a time interval $t_1 - t_0$, we will reach point $\mathbf{X}(t_0)$;. On the other hand, if we start at the same point $\mathbf{X}(t_2)$ and integrate the equations of motion backwards for the same time $t_1 - t_0$, we will necessarily reach a point $\mathbf{X}'$ lying on the part of the trajectory traversed between times $t_1$ and $t_2$. $\mathbf{X}(t_0)$ and $\mathbf{X}'$ must coincide, since they are arrived at by integrating Hamilton's equations for the same time interval, starting at the same phase-space point. Such a coincidence of $\mathbf{X}(t_0)$ and $\mathbf{X}'$, however, is impossible by the way we defined $\mathbf{X}(t_0)$ above. Therefore, it is not possible for the trajectory to intersect itself. On the other hand, a phase-space trajectory that forms a single closed loop is perfectly acceptable (see Fig. 3.3, right-hand side).

A corollary of the above statements is that two phase-space trajectories emanating from two distinct points in phase space either never cross each other, or are parts of the same closed-loop trajectory.

### 3.2.2 Ensembles. Ensemble Probability Density. The Liouville Equation.

When dealing with a physical system, we are typically not interested in specifying its microstate exactly. A description of the system in terms of a handful of thermodynamic variables that we can control by interacting with the system at a macroscopic level is sufficient for most applications. For example, we would describe a gas in terms of the number of moles or molecules $N$ it contains, the volume $V$ it occupies, and the total energy $E$ of its molecules, but not in terms of the positions and momenta of individual molecules. When we speak of a material system under specified macroscopic conditions, we are in fact referring not to a single microstate, but to an extremely large number of microstates, all of which are compatible with the macroscopic constraints imposed on the system. For example, when referring to the gas at given $N$, $V$, and $E$, we are in fact referring to all points on the $(6N-1)$- dimensional energy hypersurface corresponding to energy value $E$ for which all molecular coordinates lie within the confines of a three-dimensional domain of volume $V$. *Josiah Willard Gibbs* introduced this very important concept of a large collection of "replicas" of a system, all subject to the same macroscopic constraints but each existing in its own microstate, which he called an *ensemble.*

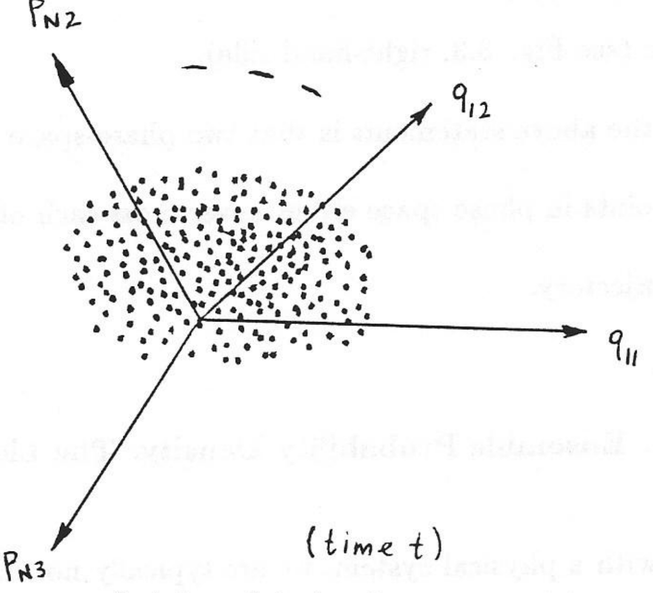

**Figure 3.4** An ensemble as a swarm of state points in phase space. The density distribution of points in the swarm is described by the probability density $\rho(\mathbf{X},t)$.

Geometrically, an ensemble corresponds to a very large set of points $\mathbf{X} \equiv (\mathbf{p},\mathbf{q})$ in phase space (see Fig.3.4). At a given time, $t$, this set of points is distributed in a certain way. We can characterize this distribution quantitatively by the *probability den-*

*sity* $\rho(\mathbf{X},t)$ of the ensemble. By definition, $\rho(\mathbf{X},t)\,d^{6N}X \equiv \rho(\mathbf{p},\mathbf{q},t)\,d^{3N}p\,d^{3N}q \equiv \rho(\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N;\,\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)\,d^3p_1d^3p_2\ldots d^3p_N\;d^3q_1d^3q_2\ldots d^3q_N$ is the probability that a state point, $\mathbf{X}$, finds itself within the volume element $d^{6N}X$, lying between $\mathbf{X}$ and $\mathbf{X}+\mathbf{dX}$, at time $t$. Note that, in the notation we are adopting here, given an $n$-dimensional vector $\mathbf{x}$, the symbol $d^nx$ stands for a differential volume element of the $n$-dimensional space from which the vector takes values, while $d\mathbf{x}$ stands for a differential $n$-dimensional vector in that space.

An ensemble is completely specified by its $\rho(\mathbf{X},t)$. The probability density obeys the normalization condition

$$\int\limits_{\Gamma}\rho(\mathbf{X},t)\,d^{6N}X \equiv \int\limits_{\Gamma}\rho(\mathbf{p},\mathbf{q},t)\,d^{3N}p\;d^{3N}q = 1 \qquad (3.7)$$

where the integration takes place over the entire phase space $\Gamma$, on which $\rho$ is defined. The probability of finding a state point of the ensemble in a small finite region $D$ of $\Gamma$-space at time $t$, is found by integrating the probability density over that region:

$$P(D,t) = \int\limits_{D}\rho(\mathbf{p},\mathbf{q},t)\,d^{3N}p\,d^{3N}q \qquad (3.8)$$

As time goes by, the swarm of points constituting the ensemble moves through phase space. This motion resembles the flow of a fluid in ordinary three- dimensional space. The question arises, how does the probability density evolve as a result of this motion? We can readily derive an equation of "continuity" for the probability density by arguments entirely analogous to those used in fluid mechanics.

Consider an arbitrary $6N$-dimensional domain or "control volume" $D$ in phase space, which is bounded by a closed $(6N-1)$-dimensional "surface" $\partial D$. We will use $\mathbf{n}(\mathbf{X})$ to denote the $6N$-dimensional unit vector that is normal to $\partial D$ at point $\mathbf{X}$, pointing toward the exterior of the domain; we will also use $d^{6N-1}X$ to denote an elementary "patch" on the $(6N-1)$-dimensional surface $\partial D$.

The systems (representative points) constituting the ensemble are neither created, nor destroyed. We can therefore write a balance of the form:

Net number of ensemble points that exit $\partial D$ per unit time =

Rate of decrease in the number of ensemble points within $D$

or

$$\oint_{\partial D} d^{6N-1}X \, \mathbf{n}\cdot\dot{\mathbf{X}} \, \rho(\mathbf{X},t) = -\frac{\partial}{\partial t}\int_{D} \rho(\mathbf{X},t)\, d^{6N}X$$

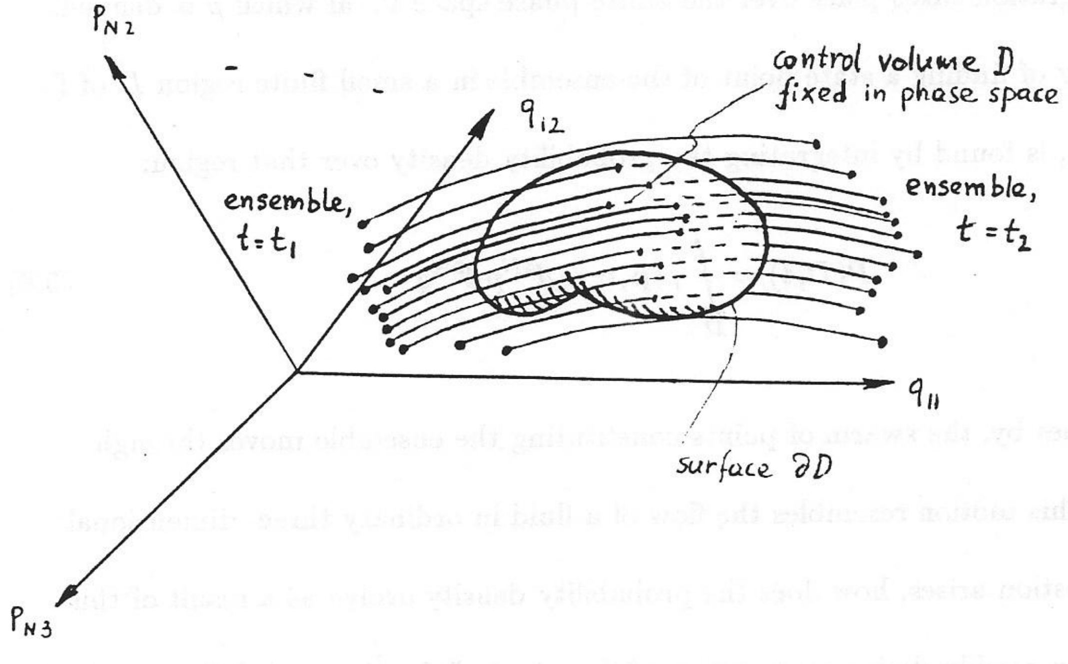

**Figure 3.5** Control volume considered in analyzing the temporal evolution of the probability density of an ensemble in phase space.

Using the divergence theorem to convert the surface integral into a volume integral in $6N$-dimensional space, we can write

$$\int_D \left[ \nabla_{\mathbf{X}} \cdot \left( \dot{\mathbf{X}}\, \rho(\mathbf{X},t) \right) + \frac{\partial}{\partial t} \rho(\mathbf{X},t) \right] \, d^{6N}X \; = \; 0$$

Since the domain $D$ is arbitrary, the integrand must vanish identically throughout phase space:

$$-\frac{\partial \rho}{\partial t} = \nabla_{\mathbf{X}} \cdot (\dot{\mathbf{X}}\, \rho) = \sum_{i=1}^{N} \left[ \frac{\partial}{\partial \mathbf{p}_i} \cdot (\dot{\mathbf{p}}_i\, \rho) + \frac{\partial}{\partial \mathbf{q}_i} \cdot (\dot{\mathbf{q}}_i\, \rho) \right] =$$

$$\sum_{i=1}^{N} \left( \frac{\partial \rho}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial \rho}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right) + \sum_{i=1}^{N} \rho \left( \frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right) \tag{3.9}$$

Note the analogy between Eq. (3.9) and the continuity equation of fluid mechanics

$$\nabla \cdot (\rho\, \mathbf{v}) + \frac{\partial \rho}{\partial t} = 0$$

where $\mathbf{v}(\mathbf{r},t)$ is the velocity. Now, $\dot{\mathbf{p}}_i$ and $\dot{\mathbf{q}}_i$ are given by Hamilton's equations (3.4) and (3.5), respectively, as a consequence of which

$$\frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i = \frac{\partial}{\partial \mathbf{q}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} = 0$$

The latter condition can also be written as

$$\nabla_{\mathbf{X}} \cdot \dot{\mathbf{X}} = 0 \tag{3.10}$$

and is a $6N$-dimensional analogue of the condition $\nabla \cdot \mathbf{v} = 0$ governing the velocity field of an incompressible fluid in fluid mechanics. We can therefore say that the swarm of points in the ensemble flows as an *incompressible fluid*, as a consequence of Hamilton's equations of motion.

Using Eq. (3.10) in Eq. (3.9), one obtains

$$\sum_{i=1}^{N}\left(\frac{\partial\rho}{\partial\mathbf{p}_i}\cdot\dot{\mathbf{p}}_i+\frac{\partial\rho}{\partial\mathbf{q}_i}\cdot\dot{\mathbf{q}}_i\right)+\frac{\partial\rho}{\partial t}=0,\ \textit{or}\ \ \dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}\rho+\frac{\partial\rho}{\partial t}=0 \tag{3.11}$$

Introducing the *total time derivative* operator

$$\frac{D}{Dt}\equiv\frac{\partial}{\partial t}+\dot{\mathbf{X}}\cdot\nabla_{\mathbf{X}}$$

we can rewrite Eq. (3.11) as

$$\frac{D\rho}{Dt}=0 \tag{3.12}$$

Eq. (3.11) tells us that, if we sit in the vicinity of a fixed point in phase space, the rate of change of the ensemble probability density at that point with time will be related to the gradient of the ensemble probability density and the phase-space "velocities" of the representative points along their trajectories. Eq. (3.12) tells us that, if we ride on a representative point, following its trajectory in Γ space, we will find the density of representative points in our neighborhood to be constant.

Employing Hamilton's equations (3.4) and (3.5) in Eq. (3.11) we obtain

$$\frac{\partial\rho}{\partial t}+\sum_{i=1}^{N}\left(\frac{\partial\mathcal{H}}{\partial\mathbf{p}_i}\cdot\frac{\partial}{\partial\mathbf{q}_i}-\frac{\partial\mathcal{H}}{\partial\mathbf{q}_i}\cdot\frac{\partial}{\partial\mathbf{p}_i}\right)\rho=0 \tag{3.13}$$

Eq. (3.13) is the *Liouville equation.* Given an ensemble of classical systems with a specified Hamiltonian, the Liouville equation completely describes the evolution of the probability density of the ensemble in phase space. The Liouville equation is often expressed in the forms:

$$\frac{\partial\rho}{\partial t}+\hat{\mathcal{H}}\rho=0 \tag{3.14}$$

or

$$i\,\frac{\partial\rho}{\partial t} = \hat{\mathcal{L}}\rho \tag{3.15}$$

where

$$\hat{\mathcal{H}} \equiv \sum_{i=1}^{N}\left(\frac{\partial\mathcal{H}}{\partial\mathbf{p}_i}\cdot\frac{\partial}{\partial\mathbf{q}_i} - \frac{\partial\mathcal{H}}{\partial\mathbf{q}_i}\cdot\frac{\partial}{\partial\mathbf{p}_i}\right)$$

is the Poisson bracket operator, and $\hat{\mathcal{L}} = -i\hat{\mathcal{H}}$ is the Liouville operator, a Hermitian operator.

The Liouville equation provides a completely *time reversible* description of the evolution of a classical dynamical system. If one reverses the direction of time, the Liouville operator changes sign and thus Eq. (3.13) retains its form. At first sight, then, the Liouville equation does not suggest an irreversible decay of the ensemble probability density distribution to a time-independent "equilibrium" distribution, as is observed in nature. The problem of how to obtain irreversible decay from the Liouville equation is a central problem of statistical physics, which we will examine briefly in the next section.

To conclude this section, let us consider again a single system evolving solely under the influence of interactions among its own degrees of freedom, its microstate tracing a trajectory in phase space as time goes by. Let $\mathcal{A}(\mathbf{p},\mathbf{q})$ be a function of the microscopic state of the system. Note that $\mathcal{A}$ depends explicitly on the generalized coordinates and momenta of all microscopic degrees of freedom, but not on time. As the system moves along its trajectory $(\mathbf{q}(t),\mathbf{p}(t))$, the value of $\mathcal{A}(\mathbf{q}(t),\,\mathbf{p}(t)) \equiv \mathcal{A}(t)$ changes. The rate of change of $\mathcal{A}$ can be found as

$$\frac{\partial\mathcal{A}}{\partial t} = \sum_{i=1}^{N}\frac{\partial\mathcal{A}}{\partial\mathbf{q}_i}\cdot\frac{\partial\mathbf{q}_i}{\partial t} + \sum_{i=1}^{N}\frac{\partial\mathcal{A}}{\partial\mathbf{p}_i}\cdot\frac{\partial\mathbf{p}_i}{\partial t}$$

Substituting the time derivatives of $\mathbf{p}_i$ and $\mathbf{q}_i$ from Hamilton's Eq. (3.4) and (3.5), respectively, we obtain

$$\frac{\partial \mathcal{A}}{\partial t} = \sum_{i=1}^{N} \frac{\partial \mathcal{A}}{\partial \mathbf{q}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} - \sum_{i=1}^{N} \frac{\partial \mathcal{A}}{\partial \mathbf{p}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{q}_i}$$

or

$$\frac{\partial \mathcal{A}}{\partial t} = \sum_{i=1}^{N} \left( \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{q}_i} - \frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) \mathcal{A} = \hat{\mathcal{H}} \mathcal{A} \tag{3.16}$$

Furthermore, invoking the definition of the Liouville operator, we can write Eq. (3.16) as

$$-i \frac{\partial \mathcal{A}}{\partial t} = \hat{\mathcal{L}} \mathcal{A} \tag{3.17}$$

The equation (3.17) describing the temporal evolution of $\mathcal{A}$ along a trajectory is formally similar to Eq. (3.15), which describes the temporal evolution of the probability density of an ensemble of systems governed by the Hamiltonian $\mathcal{H}$; the two equations differ only by a minus sign. As Eq. (3.15), Eq. (3.17) is time reversible and could be used, in principle, to predict all future and past values of any dynamical quantity $\mathcal{A}$ we are interested in if the microstate of our classical system were known completely at a given instant.

The evolution equations Eq. (3.15) and (3.17) constitute a starting point for formulating *linear response theory*; this theory relates the behavior of systems kept away from equilibrium by the imposition of small external driving forces to the dynamics of these systems under equilibrium conditions and thus forms a basis for the prediction of transport coefficients from molecular-level information [Hansen and Mc Donald 1986]. On the other hand, *projection operator* formalisms start from the full dynamical description, in terms of all degrees of freedom, that is provided by Eqs. (3.15) and (3.17), and proceed to derive descriptions cast in terms of only a few degrees of freedom; such formalisms form a basis for the theory of Brownian motion, which is highly useful in the study of a variety of physical systems. [Hansen and McDonald 1986]. An evolution equation for the probability density distribution of individual molecules in $(\mathbf{p}_i, \mathbf{q}_i)$-space (rather than of all degrees of freedom in phase space), pioneered by *Ludwig Boltzmann*, forms the basis for the kinetic theory of gases; the derivation of the Boltzmann equation bears many similarities with our derivation of Eq. (3.15) [Huang 1963]. Thus, although the immediate practical utility of Eqs. (3.15) and (3.17) is rather limited, the equations are of great conceptual value.

### 3.2.3 Ergodicity and Mixing in Phase Space

In this discussion we will restrict ourselves to ensembles of conservative systems of $N$ particles, evolving in time under the constraint of constant total energy $E$. The representative points of such an ensemble lie on a *constant energy hypersurface*, corresponding to energy $E$. Let $\Sigma(E)$ be the total "area" of this $(6N-1)$- dimensional hypersurface:

$$\Sigma(E) = \int_{E-surf.} d^{6N-1}X \tag{3.18}$$

It is our experience that an isolated system prepared under arbitrary initial conditions will evolve to a state of equilibrium, wherein its macroscopic properties are time-independent. We expect that, for an ensemble of such systems, the probability density $\rho(\mathbf{X}, t)$ will evolve towards an *equilibrium probability density* $\rho^{eq}(\mathbf{X})$. The evolution of $\rho(\mathbf{X}, t)$ will be described by the Liouville equation (3.13), and $\rho^{eq}(\mathbf{X})$ will be a *stationary* solution of the Liouville equation, characterizing an *equilibrium ensemble* under the given external constraints. The question arises, what leads to this irreversible decay of the ensemble probability density to equilibrium.

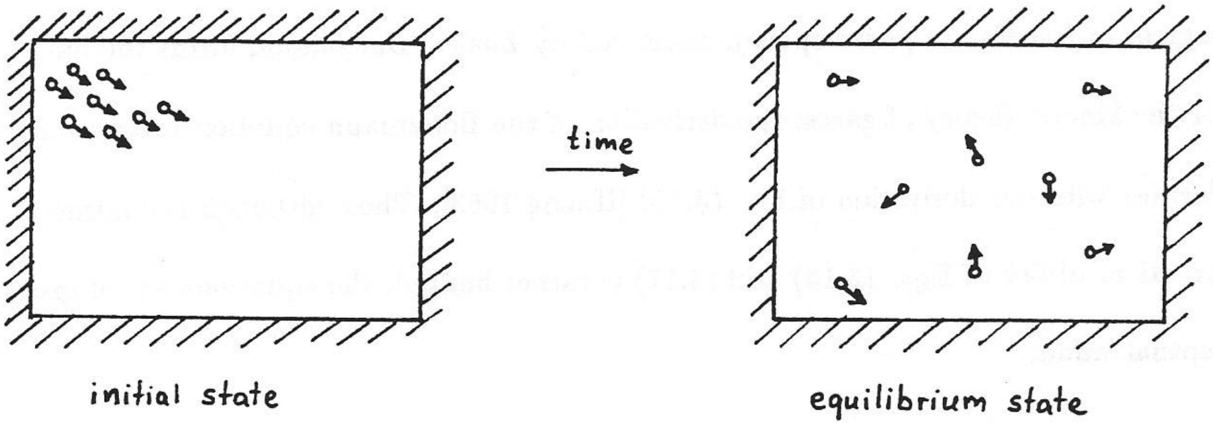

**Figure 3.6** An isolated system of $N$ interacting gas molecules in a container evolves to equilibrium.

To fix ideas, consider the simple experiment of injecting $N$ gas molecules in a small region of an initially empty rigid container (Fig. 3.6). Collisions of molecules with the container walls will be assumed perfectly elastic, but molecules can interact with each other. Under these conditions, the system of $N$ molecules is isolated. An ensemble of systems prepared in this way would be characterized by an initial probability density $\rho(\mathbf{X}, 0)$ that is highly localized in a small region of phase space (all molecules characterized by roughly the same $\mathbf{q}_i$, with $\mathbf{p}_i$ pointing in roughly the same direction). As time evolves, however, we expect that, in each system of the ensemble, collisions will make molecules spread out and explore the entire volume accessible to them and also acquire a wide distribution of momenta. The probabilty density $\rho(\mathbf{X}, t)$ will decay to an equilibrium probability density $\rho^{eq}(\mathbf{X})$ that is uniformly smeared over the entire $(6N - 1)$-dimensional energy hypersurface in the phase space of the system.

As we have pointed out, there is nothing in the Liouville equation, Eq. (3.13), that *a priori* suggests such an irreversible decay of the probability density to equilibrium. As far as the Hamiltonian equations of motion (3.4) and (3.5) are concerned, if we fed them with the phase point depicted on the right hand side of Fig. 3.6 and integrated backward in time for a time interval equal to that elapsed between the two phase points, they would give us the phase point on the left with all momenta inverted. *The origin of decay to equilibrium is not inherent in Newtonian dynamics* (or in the time-dependent Schrödinger equation, which is the quantum-mechanical analogue of Newton's second law), but is rather a consequence of the *nature of interactions*, i.e. of the form of the potential energy hypersurfaces governing physical systems. The rigorous study of the conditions under which irreversible decay to equilibrium is observed is an intriguing subject of statistical mechanics that falls outside the scope of this course. Here we confine ourselves to a qualitative discussion of two key concepts: *ergodic flow* and *mixing flow* of an ensemble of representative points in phase space.

The flow of state points on the $E$-hypersurface is defined to be *ergodic* if *almost all* points $\mathbf{X}(\mathbf{p}, \mathbf{q})$ on the hypersurface move in such a way as to pass through *every* small finite neighborhood on the $E$- hypersurface. In other words, each representative point, excluding a set of points of measure zero, follows a trajectory that, given sufficient time, will pass *arbitrarily close* to any other point on the energy hypersurface.

Fig. 3.7 depicts the flow pattern of phase-space trajectories on a constant energy hypersurface of a hypothetical system. For simplicity, the $E$-hypersurface is represented as two-dimensional. As we have seen, trajectories can never cross themselves or each other; in the figure they are represented schematically as noncrossing open lines or closed loops. We can immediately see that flow on this $E$-hypersurface is *not ergodic*: A substantial proportion of the trajectories are closed loops confined in a small region of the hypersurface. If the system is placed on such a trajectory, it will never experience the $E$-hypersurface in its entirety.

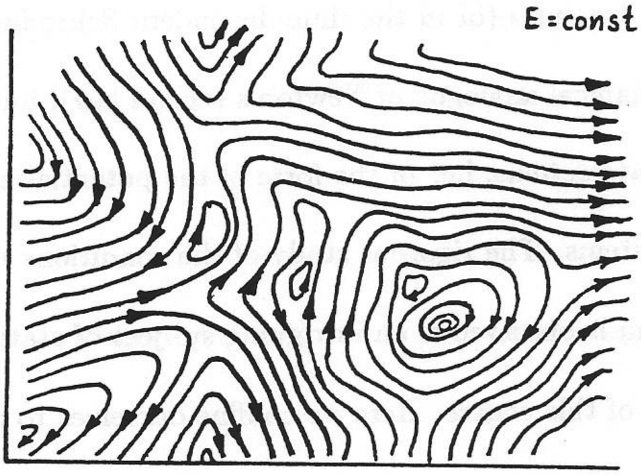

**Figure 3.7** An example of non-ergodic flow on a constant energy hypersurface in phase space.

For flow on the energy hypersurface to be ergodic, practically all lines shown in Fig. 3.7 would have to be sections of a single giant trajectory spanning the entire energy hypersurface. This *single giant trajectory* characterizing phase-space motion of an *ergodic* *system* would necessarily have the topology of a *closed loop*, which winds and folds in unimaginably intricate ways so as to visit the entire hypersurface without ever crossing itself. The time required to traverse this immensely long loop and return to exactly the same point in phase space is known as the *Poincaré cycle*. For a system of $N$ degrees of freedom, the Poincaré cycle can be shown to be on the order $e^N$ [Huang 1963]. For macroscopic systems, this is an incomprehensibly long time (compare age of the universe $= 10^{10}$ years) and has nothing to do with physics, let along engineering!

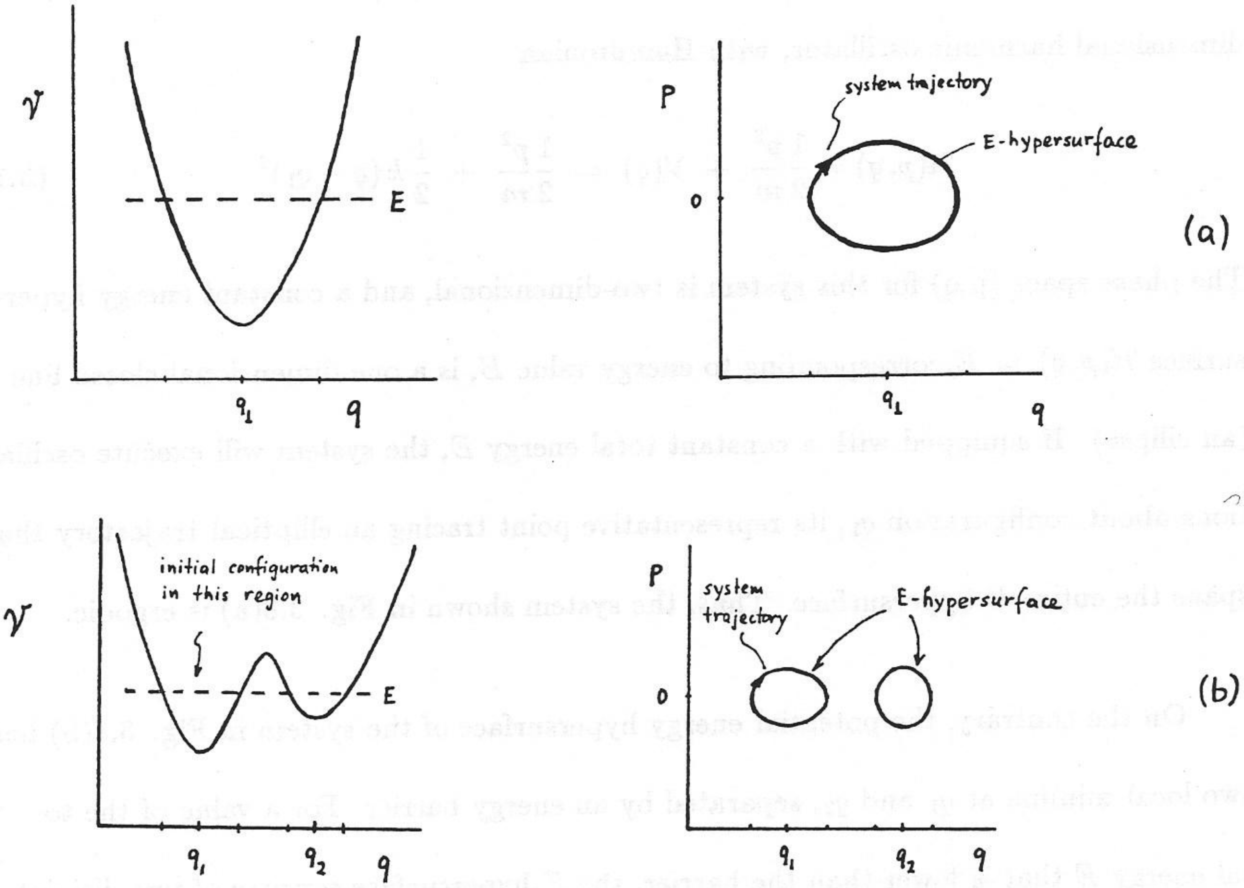

**Figure 3.8** Simple systems with one configurational degree of freedom, for the illustration of ergodic flow in phase space. Potential energy hypersurfaces are shown on the left, and phase-space plots on the right. The top system is ergodic, the bottom is non-ergodic.

It is not difficult to think of flows in phase-space that conform to Newtonian dynamics, yet are non-ergodic. Elementary examples of ergodic and non-ergodic flow are shown in Fig. 3.8 (a) and (b), respectively. In both cases the system has only one configurational degree of freedom, $q$, and one momentum degree of freedom, $p$. The diagrams on the left-hand side display the potential energy $\mathcal{V}(q)$ as a function of configuration (i.e. they are plots of the potential energy hypersurfaces in configuration space, which, in this case, are one-dimensional curves). The system of Fig. 3.8(a) is a one-dimensional harmonic oscillator, with Hamiltonian

$$\mathcal{H}(p,q) = \frac{1}{2}\frac{p^2}{m} + \mathcal{V}(q) = \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}k\,(q-q_1)^2 \tag{3.19}$$

The phase space (p,q) for this system is two-dimensional, and a constant energy hypersurface $\mathcal{H}(p,q) = E$,corresponding to energy value $E$, is a one-dimensional closed line (an ellipse). If equipped with a constant total energy $E$, the system will execute oscillations about configuration $q_1$, its representative point tracing an elliptical trajectory that spans the entire $E$-hypersurface. Thus, the system shown in Fig. 3.8(a) is ergodic.

On the contrary, the potential energy hypersurface of the system in Fig. 3.8(b) has two local minima at $q_1$ and $q_2$, separated by an energy barrier. For a value of the total energy $E$ that is lower than the barrier, the $E$-hypersurface consists of two disjoint closed curves. If the system's configuration is initially in the vicinity of $q_1$ and the total energy is $E$, then the system will execute oscillations within the potential energy well at $q_1$, its phase space trajectory evolving along the left-hand side loop of the $E$-hypersurface. The right-hand side loop of the $E$-hypersurface will not be accessed at all, however, as the barrier between the two minima is too high to be overcome at this value of $E$. For energy values lower than the potential barrier, therefore, the system of Fig. 3.8(b) is *not ergodic.* A physical example of this picture is provided by amorphous solids (glasses). The multidimensional potential energy hypersurface $\mathcal{V}(\mathbf{q})$ of these materials is thought to contain a multitude of local minima separated by barriers, many of which significantly exceed the total system energy $E$. As a result, the configuration is arrested in one of many disjoint regions that surround local minima of the potential energy $\mathcal{V}$. In liquids, on the other hand, the total energy $E$ is sufficiently high, in relation to the potential energy barriers separating local minima in $\mathcal{V}$, to allow free communication between practically all regions on the $E$-hypersurface. Glasses exhibit nonergodic, but liquids exhibit ergodic flow in configuration space.

**Ergodic Theorem** (Birkhoff, 1931) Consider an integrable function $\mathcal{A}(\mathbf{X})$ of the state point $\mathbf{X}$ of a system on an energy hypersurface corresponding to energy value $E$.
We define the *phase average* of the function $\mathcal{A}$ by

$$\langle \mathcal{A} \rangle_\Sigma \equiv \frac{\int\limits_{E-surf.} \mathcal{A}(\mathbf{X})\, d^{6N-1}X}{\int\limits_{E-surf.} d^{6N-1}X} = \frac{1}{\Sigma(E)} \int\limits_{E-surf.} \mathcal{A}(\mathbf{X})\, d^{6N-1}X \tag{3.20}$$

We also define the *time average* of the function $\mathcal{A}$ by

$$\langle \mathcal{A} \rangle_t \equiv \lim_{t \to \infty} \frac{1}{t} \int_{t_0}^{t_0+t} \mathcal{A}(\mathbf{X}(t))\, dt \tag{3.21}$$

where $\mathbf{X}(t)$ is a dynamical trajectory on the $E$-hypersurface, obtainable through integration of Hamilton's equations with given initial conditions at $t_0$.
The system is ergodic if, for all phase functions $\mathcal{A}(\mathbf{X})$, *(i)* the time average of Eq.

(3.20) exists for almost all $\mathbf{X}(t_0)$ (all but a set of measure zero); *(ii)* when it exists, the time average is equal to the phase average: $\langle \mathcal{A} \rangle_t = \langle \mathcal{A} \rangle_\Sigma$.

The physical content of the ergodic theorem is simple. For a system to be ergodic, any dynamical trajectory should unravel in time so as to practically cover the entire $E$-hypersurface. To compute an average of the phase function $\mathcal{A}$ we can either ride on a single trajectory and experience all regions of phase space as time goes by ($\langle \mathcal{A} \rangle_t$), or take a snapshot of the $E$-hypersurface at a given time and poll all representative points on it ($\langle \mathcal{A} \rangle_\Sigma$).

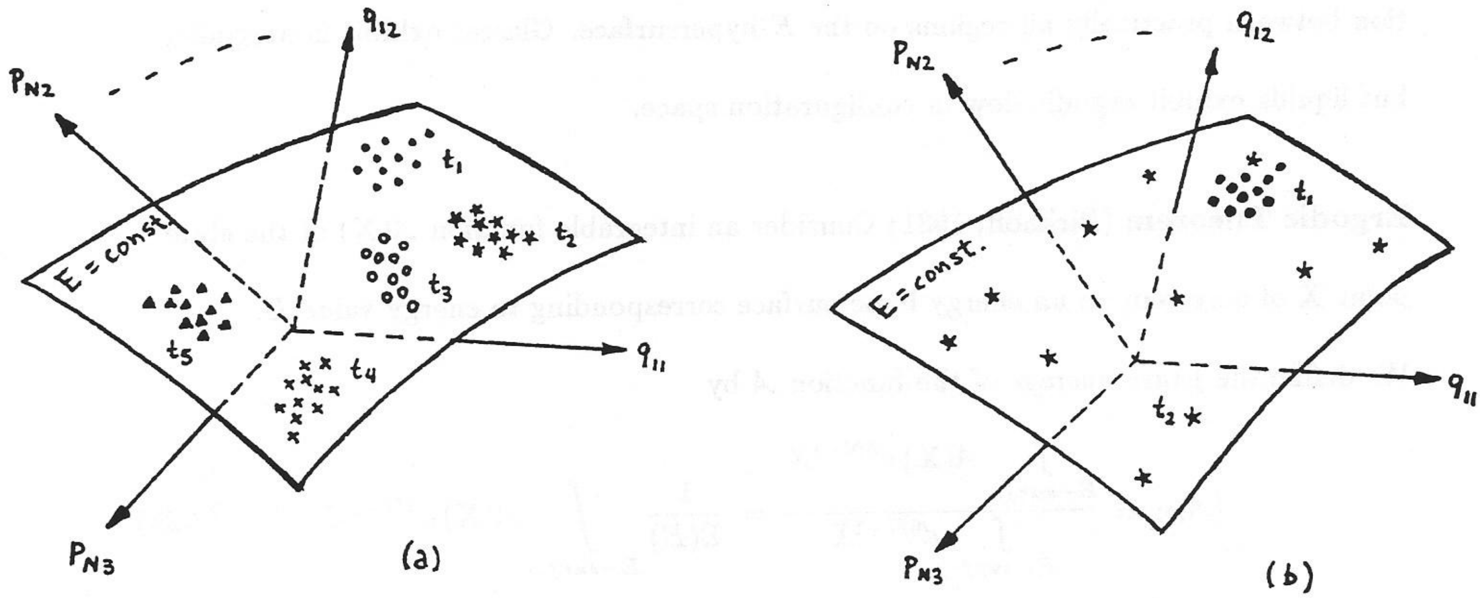

**Figure 3.9** Evolution of an ensemble of representative points on the $E$-hypersurface *(a)* for a system exhibiting ergodic but not mixing flow; *(b)* for a system exhibiting mixing flow.

Ergodic flow is not a sufficient requirement for an arbitrary ensemble probability density $\rho(\mathbf{X}, t)$ to decay to a stationary equilibrium ensemble probability density

$\rho^{eq}(\mathbf{X})$. If a system is ergodic, there is no guarantee that the swarm of representative points defining $\rho(\mathbf{X},t)$ will disperse itself on the $E$-hypersurface as time goes by. The swarm of points may maintain its integrity and wander around "in formation" on the $E$-hypersurface in such a way that, ultimately, every point visits the entire hypersurface [see Fig. 3.9($a$)]. A stronger requirement than ergodicity is needed to guarantee decay to equilibrium; this is the requirement of *mixing flow* on the $E$-hypersurface. In mixing flow, trajectories emanating from initially neighboring points on the $E$-hypersurface diverge rapidly from each other, the representative points quickly distributing themeselves over the entire hypersurface [see Fig, 3.9($b$)].

Given an ensemble of representative points on the constant energy hypersurface $\mathcal{H}(\mathbf{X}) = E$, characterized by the (in general nonstationary) probability density $\rho(\mathbf{X},t)$ and a phase function $\mathcal{A}(\mathbf{X})$, we define the *ensemble average* of $\mathcal{A}$ as

$$\langle \mathcal{A}(t) \rangle_{\rho(\mathbf{X},t)} \equiv \int_{E-surf.} \mathcal{A}(\mathbf{X})\, \rho(\mathbf{X},t)\, d^{6N-1}X \tag{3.22}$$

It is assumed here that $\rho(\mathbf{X},t)$ is normalized on the hypersurface $\mathcal{H}(\mathbf{X}) = E$. A sufficient condition for this is that $\rho(\mathbf{X},t)$ obey the normalization condition, Eq. (3.7), on the entire phase space $\Gamma$ and also be zero for all points $\mathbf{X}$ outside the hypersurface $\mathcal{H}(\mathbf{X}) = E$. If this sufficient condition is satisfied, the ensemble average of Eq. (3.22) can be defined alternatively as

$$\langle \mathcal{A}(t) \rangle_{\rho(\mathbf{X},t)} = \int_{\Gamma} \mathcal{A}(\mathbf{X})\, \rho(\mathbf{X},t)\, d^{6N}X \tag{3.23}$$

For *mixing flow* on the $E$-hypersurface, one can show that, in the limit of long times, the ensemble average of Eq. (3.22) becomes the same as the phase average of Eq. (3.20) [Reichl 1980]:

$$\langle \mathcal{A}(t)\rangle_{\rho(\mathbf{X},t)} \overset{t\to\pm\infty}{\longrightarrow} \langle \mathcal{A}\rangle_{\Sigma} \tag{3.24}$$

This suggests that, if flow on the $E$-hypersurface is mixing, the ensemble probability density $\rho(\mathbf{X},t)$ spreads out with time and ultimately evolves into the *stationary, equilibrium ensemble distribution*

$$\rho^{eq}_{NVE} = \begin{cases} \frac{1}{\Sigma(E)}, & \text{if } \mathcal{H}(\mathbf{X}) = E\ ; \\ 0, & \text{otherwise.} \end{cases} \tag{3.25}$$

Note that the equilibrium distribution of Eq. (3.25) is *uniform* on the $E$-hypersurface.

From the above discussion it follows that mixing flow is ergodic, but ergodic flow is not always mixing. Mixing flow characterizes systems with *chaotic dynamics.* The transition from stable to chaotic behavior as a function of the total energy $E$ has been studied extensively in nonlinear oscillator systems with a small number of degrees of freedom. An example is provided by the study of Henon and Heiles [Reichl 1980], who considered the phase-space trajectories of a system with two configurational degrees of freedom governed by the Hamiltonian

$$\mathcal{H} = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2) + q_1\, q_2^2 - \frac{1}{3}q_1^3 \tag{3.26}$$

Note that the quadratic term in parentheses on the right-hand side of Eq. (3.26) describes two identical one-dimensional harmonic oscillators; it is a sum of two terms of the form of Eq. (3.19) in reduced units, such that $m$ is used as the unit of mass and

$(m/k)^{\frac{1}{2}}$ is used as the unit of time. The last term of Eq. (3.26) adds nonlinearity to the first oscillator, while the next to last term constitutes a nonlinear coupling contribution to the potential energy of the two oscillators. The phase space for this system is four-dimensional, and, consequently, constant energy hypersurfaces are three-dimensional.

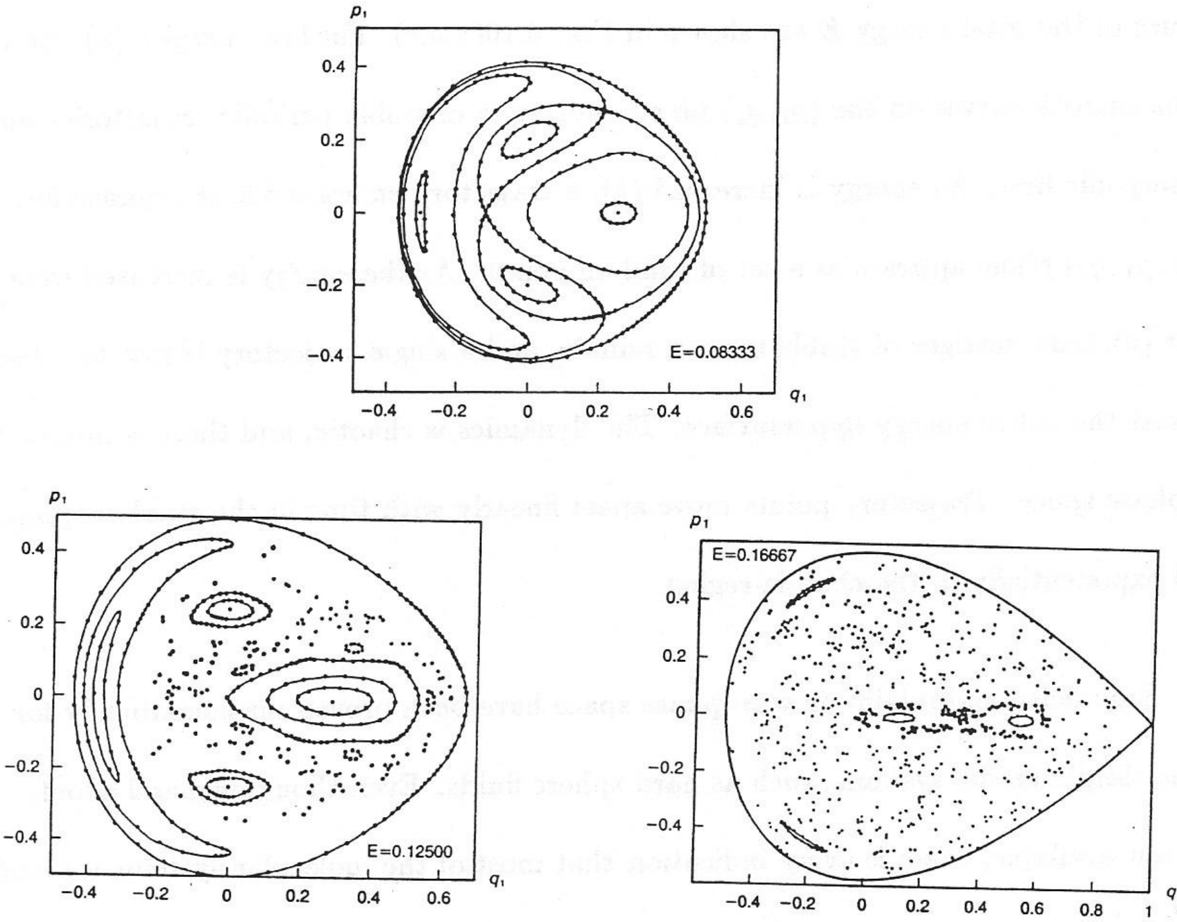

**Figure 3.10** Traces of dynamical trajectories obtained from the Henon-Heiles model, Eq. (3.26), for three different values of the total energy $E$. Points of intersection of the constant $E$ trajectories with the plane $q_2 = 0$ at which $p_2 > 0$ are shown as dots on the $(p_1, q_1)$ plots. The value of the total energy i~~d~~s indicated on each plot. With increasing energy, there is a transition to chaotic dynamics, characterized by mixing flow in phase space.

For visualizing the motion on an $E$-hypersurface it is convenient to consider the two-dimensional intersection of the $E$-hypersurface with the plane $q_2 = 0$ and register the $(p_1, q_1)$ coordinates of points at which this planar intersection is traversed by dynamical trajectories with $p_2 > 0$. $(p_1, q_1)$ plots accumulated in this way for different values of the total energy $E$ are shown in Fig. 3.10($a$,$b$,$c$). For low energies ($a$) one obtains smooth curves on the $(p_1, q_1)$ plane, indicative of stable periodic trajectories and nonergodic flow. As energy is increased ($b$), a trajectory emerges whose intersection with the $(p_1, q_1)$ plane appears as a set of random points. As the energy is increased even further ($c$), only vestiges of stable motion remain, and a single trajectory is free to wander over almost the entire energy hypersurface. The dynamics is chaotic, and there is mixing flow in phase space. Trajectory points move apart linearly with time in the stable regions, and exponentially in the chaotic region.

Ergodicity and mixing flow in phase space have been proven mathematically for some simple model systems, such as hard sphere fluids. Even though general proofs are not available, there is every indication that most of the molecular systems we deal with in nature are characterized by complex, strongly nonlinear potential energy functions, such that Hamiltonian dynamics leads to mixing flow in phase space. It is this chaotic nature of phase-space flow that is responsible for our everyday experience that an isolated system, left to evolve under the influence of its own interactions, will ultimately reach a state of thermodynamic equilibrium. As we saw in Eq. (3.25), the equilibrium probability density characterizing an ensemble of systems with given number of molecules, spatial extent, and energy is expected to be uniform over the entire constant energy hypersurface.

These considerations about ergodic and mixing flow on constant energy hypersurfaces form the basis for the postulates of equilibrium statistical mechanics, introduced axiomatically in the next chapter.

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