where $\mathbf{J}(\mathbf{p}^N, \mathbf{q}^N; \mathbf{R}) = \sum_{i=1}^{N} (\mathbf{p}_i/m)\delta(\mathbf{q}_i - \mathbf{R})$ is the particle current phase function. Equation (3) is a balance equation which reflects the conservation of particle number on the microscopic level.

It is interesting to note that the probability density, $\rho(\mathbf{X}^N, t)$, is often interpreted in terms of an "ensemble" of systems. This was the view originally taken by W. Gibbs. Let us consider an ensemble of η identical systems (η very large). If we look at each system at a given time, it will be represented by a point in the $6N$-dimensional phase space. The distribution of points representing our ensemble of systems will be proportional to $\rho(\mathbf{X}^N, t)$. That is, the density of system points in phase space will be given by $\eta\rho(\mathbf{X}^N, t)$.

6.C. ERGODIC THEORY AND THE FOUNDATIONS OF STATISTICAL MECHANICS [6–13]

The subject of ergodic theory was primarily the domain of mathematicians until the advent of modern computers. However, in recent years it has become an even more important subject of research because of its importance in such diverse fields as celestial mechanics (stability of the solar system) and chemistry (stability of isolated excited molecules) and because it asks questions which lie at the very foundations of statistical mechanics.

As we shall see, the flow of probability in phase space is of a very special type. There are absolutely no diffusion processes present. Historically, two types of probability flow have been important in understanding the behaviour of phase space, namely, ergodic flow and mixing flow. For systems with ergodic flow, we obtain a unique stationary probability density (a constant on the energy surface) which characterizes systems with a fixed energy at equilibrium. However, a system with ergodic flow cannot necessarily reach this equilibrium state if it does not start out there. For decay to equilibrium, we must have at least the additional property of mixing. Mixing systems are ergodic (the converse is not always true, however) and can exhibit random behavior. In addition, reduced distribution functions can be defined which decay to an equilibrium state. We give examples of mixing flow in the special topics Section (S6.D).

Ergodic and mixing behavior for real systems is difficult to establish in general. It has been done only for a few model systems. However, there is a large class of conservative systems, the anharmonic oscillators, which are of great importance in mechanics, chemistry, and the theory of solids. These systems are neither ergodic nor mixing but exhibit behavior reminiscent of both in local regions of their phase space. They have been studied extensively with computers in recent years and give great insight into the behavior of flows in phase space and the possible mechanism behind the irreversibility we observe in nature. We briefly discuss such systems in the special topics in Section (S6.E).

Let us now define ergodic flow. Consider a Hamiltonian system with $3N$ degrees of freedom with Hamiltonian $H(\mathbf{p}^N, \mathbf{q}^N) = E$. If we relabel the momentum coordinates so $p_1 = p_{x,1}$, $p_2 = p_{y,1}$, $p_3 = p_{z,1}$, $p_4 = p_{x,2}, \ldots$, $p_{3N} = p_{z,N}$ (with similar relabeling for the position coordinates), then Hamilton's equations can be written

$$\begin{aligned}\frac{dq_1}{(\partial H/\partial p_1)} &= \cdots = \frac{dq_{3N}}{(\partial H/\partial p_{3N})} = \cdots = -\frac{dp_1}{(\partial H/\partial q_1)} = \cdots \\ &= -\frac{dq_{3N}}{(\partial H/\partial q_{3N})} = dt.\end{aligned} \tag{6.33}$$

Equation (6.33) provides us with $6N - 1$ equations between phase space coordinates which, when solved, give us $6N - 1$ constants, or integrals, of the motion,

$$f_i(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N}) = C_i, \tag{6.34}$$

where $i = 1, 2, \ldots, 6N - 1$ and C_i is a constant. However, these integrals of the motion can be divided into two kinds: isolating and nonisolating. Isolating integrals define a whole surface in the phase space and are important in ergodic theory, while nonisolating integrals do not define a surface and are unimportant [6, 14]. One of the main problems of ergodic theory is to determine how many isolating integrals a given system has. An example of an isolating integral is the total energy, $H(\mathbf{p}^N, \mathbf{q}^N) = E$. For N particles in a box, it is the only isolating integral (at least for hard spheres).

Let us consider a system for which the only isolating integral of the motion is the total energy and assume that the system has total energy, E. Then trajectories in Γ space (the $6N$-dimensional phase space) which have energy, E, will be restricted to the energy surface, S_E. The energy surface, S_E, is a $(6N - 1)$-dimensional "surface" in phase space which exists because of the global integral of the motion, $H(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N}) = E$. The flow of state points on the energy surface is defined to be *ergodic* if almost all points, $\mathbf{X}(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N})$, on the surface move in such a way that they pass through every small finite neighborhood, R_E, on the energy surface. Or, in other words, each point samples small neighborhoods over the entire surface during the course of its motion (a given point, $\mathbf{X}(p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N})$ cannot pass through every point on the surface, because a line which cannot intersect itself cannot fill a surface of two or more dimensions). Note that not all points need sample the surface, only "almost all." We can exclude a set of measure zero from this requirement.

A criterion for determining if a system is ergodic was established by Birkhoff [15] and is called the *ergodic theorem*. Let us consider an integrable phase function $f(\mathbf{X}^N)$ of the state point $\mathbf{X}^N$. We may define a phase average of the function $f(\mathbf{X}^N)$ on the energy surface by the equation

$$\langle f \rangle_S = \frac{1}{\sum(E)} \int_{S_E} f(\mathbf{X}^N) dS_E = \frac{1}{\sum(E)} \int_\Gamma \delta(H^N(\mathbf{X}^N) - E) f(\mathbf{X}^N) d\mathbf{X}^N, \quad (6.35)$$

where dS_E is an area element of the energy surface which is invariant (does not change size) during the evolution of the system and $\sum(E)$ is the area of the energy surface and is defined as

$$\sum(E) = \int_{S_E} dS_E = \int_\Gamma \delta(H^N(\mathbf{X}^N) - E) d\mathbf{X}^N \quad (6.36)$$

(we are using the notation of Section 6.B). We may define a time average of the function $f(\mathbf{X}^N)$ by the equation

$$\langle f \rangle_T = \lim_{T\to\infty} \frac{1}{T} \int_{t_0}^{t_0+T} f(\mathbf{X}^N(t)) dt \quad (6.37)$$

for all trajectories for which the time average exists. Birkhoff showed that the time average in Eq. (6.37) exists for all integrable phase functions of physical interest (that is, for smooth functions).

It terms of averages, the *ergodic theorem* may be stated as follows: *A system is ergodic if for all phase functions, $f(\mathbf{X}^N)$: (i) the time average, $\langle f \rangle_T$, exists for almost all $\mathbf{X}^N$ (all but a set of measure zero), and (ii) when it exists it is equal to the phase average, $\langle f \rangle_T = \langle f \rangle_S$.*

To find the form of the invariant area element, dS_E, let us first write an expression for the volume of phase space, $\Omega(E)$, with energy less than E—that is, the region of phase space for which $0 < H^N(X^N) < E$. We shall assume that the phase space can be divided into layers, each with different energy, and that the layers can be arranged in the order of increasing energy. (This is possible for all systems that we will consider.) The volume, $\Omega(E)$, can then be written

$$\Omega(E) = \int_{0<H^N(\mathbf{X}^N)<E} d\mathbf{X}^N = \int_{0<H^N(\mathbf{X}^N)<E} dA_H dn_H, \quad (6.38)$$

where dA_H is an area element on a surface of constant energy and dn_H is normal to that surface. Since $\nabla_{\mathbf{X}} H^N$ is a vector perpendicular to the surface $H^N(\mathbf{X}^N)$ =constant, we can write $dH^N = |\nabla_{\mathbf{X}} H^N| dn_H$ and the volume becomes

$$\Omega(E) = \int_0^E dH^N \sum(H^N), \quad (6.39)$$

where

$$\sum(H^N) = \int_{S_H} \frac{dA_H}{|\nabla_{\mathbf{X}} H^N|} \quad (6.40)$$

is a function of H^N and is an invariant measure of the surface area for a given value of H^N. If we take the derivative of $\Omega(E)$, we find

$$\frac{d\Omega(E)}{dE} = \sum(E) = \int_{S_E} \frac{dA_E}{|\nabla_{\mathbf{X}} H^N|_{H=E}}. \tag{6.41}$$

The area, $\sum(E)$, is called the *structure function*. By the same argument, if we wish to take the average value of a function $f(\mathbf{X}^N)$ over the surface, we can write

$$\langle f \rangle_S = \frac{1}{\sum(E)} \int_{S_E} f(\mathbf{X}^N) \frac{dA_E}{|\nabla_{\mathbf{X}} H^N|_{H^N=E}} = \frac{1}{\sum(E)} \frac{d}{dE} \int_{0<H^N(\mathbf{X}^N)<E} f(\mathbf{X}^N) d\mathbf{X}^N. \tag{6.42}$$

Thus, the differential

$$dS_E = \frac{dA_E}{|\nabla_{\mathbf{X}} H^N|_{H^N=E}} \tag{6.43}$$

is the invariant surface area element.

■ **EXERCISE 6.3.** Compute the structure function for a gas of N noninteracting particles in a box of volume V. Assume that the system has a total energy E.

Answer: The Hamiltonian for the gas is

$$H^N = \sum_{i=1}^{3N} \frac{p_i^2}{2m} = E. \tag{1}$$

The volume of phase space with energy less than E is

$$\Omega(E) = \int_V d\mathbf{q}_1 \cdots \int_V d\mathbf{q}_N \int d\mathbf{p}_1 \cdots \int d\mathbf{p}_N \quad \text{for} \quad \mathbf{p}_1^2 + \cdots + \mathbf{p}_N^2 \leq 2mE. \tag{2}$$

This can be written $\Omega(E) = V^N \Omega_p$, where

$$\Omega_p = \int d\mathbf{p}_1 \cdots \int d\mathbf{p}_N \Theta(R^2 - \mathbf{p}_1^2 - \cdots - \mathbf{p}_N^2). \tag{3}$$

is the volume enclosed in momentum space and $R^2 = 2mE$. The volume in momentum space, Ω_p, has the form $\Omega_p = A_{3N} R^{3N}$. Let us find A_{3N}. This can be done by a trick. First do the integral

$$\int_{-\infty}^{\infty} dp_{1,x} \cdots \int_{-\infty}^{\infty} dp_{3N,z} \exp[-(p_{1,x}^2 + \cdots + p_{3N,z}^2)] = \left(\int_{-\infty}^{\infty} dp e^{-p^2} \right)^{3N} = \pi^{3N/2}. \tag{4}$$

Next note that $(d\Omega_p/dE) = \int d\mathbf{p}_1 \cdots \int d\,\mathbf{p}_N \delta(R^2 - \mathbf{p}_1^2 - \cdots - \mathbf{p}_N^2)$ so that

$$\int_0^\infty dR \frac{d\Omega_p}{dR} e^{-R^2} = \int_{-\infty}^{\infty} dp_{1,x} \cdots \int_{-\infty}^{\infty} dp_{3N,z} \exp[-(p_{1,x}^2 + \cdots + p_{3N,z}^2)]$$
$$= 3NA_{3N} \int_0^\infty dR R^{3N-1} e^{-R^2} = \frac{3}{2} NA_{3N} \Gamma\left(\frac{3}{2}N\right), \tag{5}$$

where $\Gamma(x)$ is the gamma function. If we equate Eq. (4) to Eq. (5), we find

$$A_{3N} = \frac{2\pi^{3N/2}}{3N\Gamma(3N/2)}. \tag{6}$$

Thus, the volume of the region of phase space with energy less than E is

$$\Omega(E) = \frac{2V^N \pi^{3N/2} R^{3N}}{3N\Gamma(3N/2)} = \frac{V^N (2\pi m E)^{3N/2}}{\Gamma(3N/2+1)}, \tag{7}$$

The structure function, $\sum(E)$, equals $(d\Omega(E)/dE)$.

If a system is ergodic, the fraction of time that its state, $X^N(\mathbf{p}^N, \mathbf{q}^N)$, spends in a given region R_E of the energy surface will be equal to the fraction of the surface S_E occupied by R_E. Let us consider a function $\phi(R_E)$ such that $\phi(R_E) = 1$ when X^N is in R_E and $\phi(R_E) = 0$ otherwise. Then it is easy to see that, for an ergodic system,

$$\lim_{T\to\infty} \frac{\tau_{R_E}}{T} = \frac{\sum(R_E)}{\sum(E)}, \tag{6.44}$$

where τ_{R_E} is the time the trajectory spends in R_E and $\sum(R_E)$ is the area occupied by R_E.

A system can exhibit ergodic flow on the energy surface only if there are no other isolating integrals of the motion which prevent trajectories from moving freely on the energy surface. If no other isolating integrals exist, the system is said to be metrically transitive (trajectories move freely on the energy surface). If a system is ergodic, it will spend equal times in equal areas of the energy surface. If we perform measurements to decide where on the surface the system point is, we should find that result. We can also ask for the probability of finding the system in a given region R_E of the energy surface. Since we have nothing to distinguish one region from another, the best choice we can make is to assume that the probability $P(R_E)$ of finding the system in R_E is equal to the fraction of the energy surface occupied by

R_E. Thus,

$$P(R_E) = \frac{1}{\sum(E)} \int_{R_E} dS_E = \frac{\sum(R_E)}{\sum(E)}. \tag{6.45}$$

From Eq. (6.45) it is a simple matter to write down a normalized probability density for the energy surface, namely,

$$\rho(\mathbf{X}^N, S_E) = \frac{1}{\sum(E)}. \tag{6.46}$$

Equation (6.46) is called the *fundamental distribution law* by Khintchine and called the *microcanonical ensemble* by Gibbs. Since it is a function only of the energy, it is a stationary state of the Liouville equation (6.27). It says that all states on the energy surface are equally probable. Equation (6.46) forms the foundation upon which all of equilibrium and most of nonequilibrium statistical mechanics are built. Its importance cannot be overemphasized. In Exercise 6.2, we give a simple example of ergodic flow.

In this section, we have discussed ergodic theory for classical systems. However, it is also possible to formulate analogous definitions for quantum systems. In fact, the criterion is rather sample. A quantum system is ergodic if and only if the system has a nondegenerate energy spectrum [16]. This means, of course, that there are no other observables which commute with the Hamiltonian.

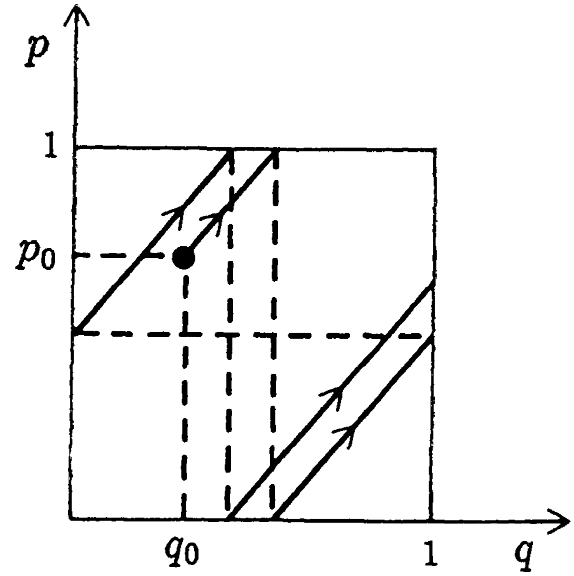
■ **EXERCISE 6.4.** Consider a dynamical flow on the two-dimensional unit square, $0 \leq p \leq 1$ and $0 \leq q \leq 1$, given by the equations of motion, $(dp/dt) = \alpha$ and $(dq/dt) = 1$. Assume that the system has periodic boundary conditions. (a) Show that this flow is ergodic. (b) If the initial probability density at time, $t = 0$, is $\rho(p, q, 0)$, compute the probability density at time, t.

Answer:

(a) The equations of motion are easily solved to give

$$p(t) = p_0 + \alpha t \quad \text{and} \quad q(t) = q_0 + t, \tag{1}$$

where p_0 and q_0 are the initial momentum and position, respectively. If we eliminate the time t, we obtain the phase space trajectory, $p = p_0 + \alpha(q - q_0)$, on the square surface. If α is a rational number, $\alpha = (m/n)$ (m and n integers), then the trajectory will be periodic and repeat itself after a period, n. If α is irrational, the trajectory will be dense on the unit square (but will not fill it)). A trajectory is shown in the accompanying figure.



When α is irrational, the system is ergodic. Let us show this explicitly. Since the phase space is periodic, any integrable function, $f(p, q)$, can be expanded in a Fourier series,

$$f(p,q) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} A_{m,n} e^{2\pi i(mq+np)}. \tag{2}$$

We wish to show that the time average and the phase average of the function, $f(p, q)$, are equal for α irrational. The time average is given by

$$\begin{aligned} \langle f \rangle &= \lim_{T\to\infty} \frac{1}{T} \int_{t_0}^{t_0+T} dt \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} A_{m,n} e^{2\pi i[m(q_0+t)+n(p_0+\alpha t)]} \\ &= A_{0,0} + \lim_{T\to\infty} \frac{1}{T} \sum_{m=-\infty}^{\infty}{}' \sum_{n=-\infty}^{\infty}{}' A_{m,n} e^{2\pi i[m(q_0+t_0)+n(p_0+\alpha t_0)]} \\ &\quad \times \left(\frac{e^{2\pi i(m+n)T} - 1}{2\pi i(m+\alpha n)} \right). \end{aligned} \tag{3}$$

The primes on the summations indicate that the values $m = 0$ and $n = 0$ are excluded from the summation. For irrational values of α, the denominator can never equal zero. Therefore

$$\langle f \rangle_T = A_{0,0}. \tag{4}$$

Similarly, we can show that

$$\langle f \rangle_s = \int_0^1 \int_0^1 dp dq \, f(p,q) = A_{0,0}. \tag{5}$$

Hence, the system is ergodic (note that $dpdq = dp_0 dq_0$, so area is preserved).

(b) The probability density satisfies periodic boundary conditions, so we can write

$$\rho(p,q,t) = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \rho_{m,n}(t) e^{2\pi imq} e^{2\pi inp}. \tag{6}$$

It is easy to show that $\rho_{m,n}(t) = \rho_{m,n}(0)e^{2\pi i(m+\alpha n)t}$. Next note that $\int_0^1 dq e^{2\pi imq} = \delta_{m,0}$ and $\sum_{m=-\infty}^{\infty} e^{2\pi imq} = \delta(q)$. Using these relations, we find

$$\rho(p,q,t) = \rho(p+\alpha t, q+t, 0). \tag{7}$$

From Eq. (7) we see that ergodicity is not sufficient to cause a system which initially has a nonstationary distribution (localized on the energy surface) to approach a stationary state (spread throughout the energy surface). The probability density in Eq. (7) does not change shape with time, but simply wanders intact through the phase space. In order to approach a stationary state the system must be 'mixing'. Conditions for mixing flow are discussed in special topics Section S6.D.

6.D. THE QUANTUM PROBABILITY DENSITY OPERATOR

For quantum systems, the phase space coordinates do not commute so we cannot introduce a probability density function directly on the phase space. Because of the noncommutivity of phase space coordinates, we cannot simultaneously know the values of all the phase space coordinates. Instead we will introduce a *probability density operator* or *density operator* as it is commonly called. The density operator contains all possible information about the state of the quantum system. If we wish we can use it to construct the Wigner distribution, which is a function that reduces to the classical probability density in the limit where Planck's constant goes to zero.

The probability density operator $\hat{\rho}(t)$ (we shall call it the density operator), contains all possible information about the state of the quantum system. It is a positive definite Hermitian operator. Given that we know the density operator, $\hat{\rho}(t)$, for a system, we can use it to obtain the expectation value of any observable $\hat{O}$ at time t. The expectation value is defined as

$$\langle O(t) \rangle = \mathrm{Tr}\, \hat{O}\hat{\rho}(t), \tag{6.47}$$

where Tr denotes the trace. The density operator is normalized so that

$$\mathrm{Tr}\, \hat{\rho}(t) = 1. \tag{6.48}$$

In Eqs. (6.47) and (6.48), the trace can be evaluated using any convenient complete set of states. For example, we could use the eigenstates of the operator, $\hat{O}$, or any other Hermitian operator, $\hat{A}$, which may or may not commute with $\hat{O}$. We will let $\{|o_i\rangle\}$ and $\{|a_i\rangle\}$ denote the complete orthonormal sets of eigenstates of the operators, $\hat{O}$ and $\hat{A}$, respectively, and let $\{o_i\}$ and $\{a_i\}$ be the corresponding sets of eigenvalues ($\hat{O}|o_i\rangle = o_i|o_i\rangle$ and $\hat{A}|a_i\rangle = a_i|a_i\rangle$). For simplicity we use Dirac notation (cf. Appendix B). The trace can be evaluated in either of these basis. Thus, we can write

$$\langle O(t)\rangle = \sum_i o_i\langle o_i|\hat{\rho}(t)|o_i\rangle = \sum_i\sum_j\langle a_i|\hat{O}|a_j\rangle\langle a_j|\hat{\rho}(t)|a_i\rangle, \tag{6.49}$$

where $o_i = \langle o_i|\hat{O}|o_i\rangle$ and we have used the completeness relation, $\sum_i |a_i\rangle\langle a_i| = \hat{1}$, where $\hat{1}$ is the unit operator. The diagonal matrix element, $\langle o_i|\hat{\rho}(t)|o_i\rangle(\langle a_i|\hat{\rho}(t)|a_i\rangle)$, gives the probability to find the system in the state $|o_i\rangle(|a_i\rangle)$, at time t. The set of numbers, $\langle a_j|\hat{\rho}(t)|a_i\rangle$, forms a matrix representation of the density operator (called the *density matrix*) with respect to the basis states, $\{|a_i\rangle\}$. The density matrix is a positive definite Hermitian matrix. The off-diagonal matrix element, $\langle a_j|\hat{\rho}(t)|a_i\rangle$ for $i \neq j$, cannot be interpreted as a probability.

The introduction of a density operator allows a more general description of a quantum system than does the Schrödinger equation. As we shall see, it can also be used to describe the equilibrium and near equilibrium states of a many-body system. To see this it is useful to distinguish between "pure states" and "mixed states." Consider a quantum system in the state $|\psi(t)\rangle$ which evolves according to the Schrödinger equation,

$$i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle, \tag{6.50}$$

where $\hat{H}$ is the Hamiltonian operator, and $\hbar$ is Planck's constant. The density operator which describes this "pure state" is simply

$$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|. \tag{6.51}$$

A "mixed state" is an incoherent mixture of states $|\psi_i(t)\rangle$:

$$\hat{\rho}(t) = \sum_i p_i|\psi_i(t)\rangle\langle\psi_i(t)|, \tag{6.52}$$

where p_i is the probability to be in the state $|\psi_i(t)\rangle$, and the states $|\psi_i(t)\rangle$ each satisfy the Schrödinger equation. Equilibrium and near-equilibrium states of many-body systems are of this type.

Using the Schrödinger equation, the equation of motion of the density operator is easily found to be

$$i\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{1}{\hbar}[\hat{H},\hat{\rho}(t)] = \hat{L}\hat{\rho}(t), \tag{6.53}$$

where $[\hat{H},\hat{\rho}(t)]$ is the commutator of the Hamiltonian, $\hat{H}$, with $\hat{\rho}(t)$, and the operator $\hat{L} \equiv \frac{1}{\hbar}[\hat{H}]$, is proportional to the commutator of $\hat{H}$ with everything on its right. The operator $\hat{L}$ is the quantum version of the *Liouville operator* and is a Hermitian operator. Equation (6.53) is called the *Liouville equation* and gives the evolution of the *state* of the system (in the Schrödinger picture). If the density operator is known at time $t = 0$, then its value at time t is given by

$$\hat{\rho}(t) = e^{-i\hat{L}t}\hat{\rho}(0) = e^{-(i/\hbar)\hat{H}t}\hat{\rho}(0)e^{+(i/\hbar)\hat{H}t} \tag{6.54}$$

If we substitute Eq. (6.54) into Eq. (6.47) and use the invariance of the trace under cyclic rotation of operators, then Eq. (6.47) takes the form

$$\langle O(t)\rangle = \mathrm{Tr}\,\hat{O}(t)\hat{\rho}(0), \tag{6.55}$$

where

$$\hat{O}(t) = e^{+(i/\hbar)\hat{H}t}\hat{O}(0)e^{-(i/\hbar)\hat{H}t}. \tag{6.56}$$

Thus the operator, $\hat{O}$, obeys a different equation of motion,

$$-i\frac{\partial\hat{O}(t)}{\partial t} = \frac{1}{\hbar}[\hat{H},\hat{O}(t)] = \hat{L}\hat{O}(t), \tag{6.57}$$

which is different from that of the density matrix. Equation (6.57) gives the evolution of the system in the "Heisenberg" picture.

It is often convenient to expand the density operator in terms of a complete orthonormal set of eigenstates $\{|E_i\rangle\}$ of the Hamiltonian, $\hat{H}$, where E_i is the eigenvalue corresponding to eigenstate $|E_i\rangle$. If we note the completeness relation $\sum_i |E_i\rangle\langle E_i| = \hat{1}$, then Eq. (6.54) takes the form

$$\hat{\rho}(t) = \sum_i\sum_j \langle E_i|\hat{\rho}(0)|E_j\rangle e^{-(i/\hbar)(E_i-E_j)t}|E_i\rangle\langle E_j|. \tag{6.58}$$

From Eq. (6.58), we see that a stationary state, $\hat{\rho}_s$, occurs when all off-diagonal matrix elements $\langle E_i|\hat{\rho}(0)|E_j\rangle$ with $i \neq j$, of $\hat{\rho}(0)$ vanish of $E_i \neq E_j$. Thus, for a state with no degenerate energy levels, the stationary state, $\hat{\rho}_s$, must be diagonal in the energy basis. This can only happen if $\hat{\rho}_s$ is a function of the

Hamiltonian,

$$\hat{\rho}_s = f(\hat{H}). \tag{6.59}$$

For a system with degenerate energy levels, one may still diagonalize both $\hat{\rho}$ and $\hat{H}$ simultaniously by introducing additional invariants of the motion, $\hat{I}$ which commute with each other and with $\hat{H}$. Thus, in general, a stationary state will be a function of all mutually commuting operators, $\hat{H}, \hat{I}_1, \ldots, \hat{I}_n$,

$$\hat{\rho}_s = f(\hat{H}, \hat{I}_1, \ldots, \hat{I}_n). \tag{6.60}$$

For systems which approach thermodynamic equilibrium, the stationary state may be an equilibrium state.

■ **EXERCISE 6.5.** Consider a harmonic oscillator with Hamiltonian, $\hat{H} = (1/2m)(\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2)$. Assume that at time $t = 0$ the oscillator is a state described by the density operator, $\hat{\rho}(0) = \hbar\sqrt{ab}(e^{-a\hat{x}^2}e^{-b\hat{p}^2} + e^{-b\hat{p}^2}e^{-a\hat{x}^2})$, where a and b are constants with the dimensions of inverse length squared and inverse momentum squared, respectively. (a) Compute the probability to find the particle in the interval $x \to x + dx$ at time $t = 0$. (b) Write the Liouville equation in the position basis. (c) Compute the probability to find the particle in the interval $x \to x + dx$ at time t.

Answer:

(a) The probability to find the particle in the interval $x \to x + dx$ at time $t = 0$ is $\langle x|\hat{\rho}(0)|x\rangle dx$, where $|x\rangle$ is an eigenstate of the position operator $\hat{x}$. We will use the notation $\rho_{x',x}(0) \equiv \langle x'|\hat{\rho}(0)|x\rangle$. Then

$$\begin{aligned}\rho_{x',x}(0) &= \hbar\sqrt{ab}(e^{-ax'^2} + e^{-ax^2})\langle x'|e^{-b\hat{p}^2}|x\rangle \\ &= \frac{\sqrt{ab}}{2\pi}(e^{ax'^2} + e^{-ax^2})\int_{-\infty}^{\infty} dpe^{-bp^2}e^{i(p/\hbar)(x'-x)} \\ &= \frac{1}{2}\sqrt{\frac{a}{\pi}}(e^{-ax'^2} + e^{-ax^2})\exp\left(-\frac{(x'-x)^2}{4b\hbar^2}\right),\end{aligned} \tag{1}$$

where we have used the completeness relation, $\int_{-\infty}^{\infty} dp|p\rangle\langle p| = \hat{1}$, for momentum eigenstates and the conventions of Appendix B. The probability to find the particle in the interval $x \to x + dx$ is $\rho_{x,x}(0)dx$, where

$$\rho_{x,x}(0) = \sqrt{\frac{a}{\pi}}\, e^{-ax^2}. \tag{2}$$

(b) The Liouville equation in the position basis is

$$
\begin{aligned}
i\hbar\frac{\partial\rho_{x',x}(t)}{\partial t} &= \frac{1}{2m}\int_{-\infty}^{\infty} dx''(\langle x'|\hat{p}^2|x''\rangle\rho_{x'',x}(t) - \rho_{x',x''}(t)\langle x''|\hat{p}^2|x\rangle) \\
&\quad + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t) \\
&= \frac{1}{4m\pi\hbar}\int_{-\infty}^{\infty} dp\int_{-\infty}^{\infty} dx''p^2(e^{i(p/\hbar)(x'-x'')}\rho_{x'',x}(t) \\
&\quad - \rho_{x',x''}(t)e^{i(p/\hbar)(x''-x)}) + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t) \\
&= \frac{-\hbar}{4m\pi}\int_{-\infty}^{\infty} dp\int_{-\infty}^{\infty} dx''\left(\left(\frac{\partial^2}{\partial x''^2}e^{i(p/\hbar)(x'-x'')}\right)\rho_{x'',x}(t)\right. \\
&\quad \left. - \rho_{x',x''}(t)\left(\frac{\partial^2}{\partial x''^2}e^{i(p/\hbar)(x''-x)}\right)\right) \\
&\quad + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t).
\end{aligned} \tag{3}
$$

If we now assume that $\rho_{x',x}(t) \to 0$ as $x' \to \infty$ or $x \to \infty$, then we can integrate by parts in Eq. (3) and obtain

$$
i\hbar\frac{\partial\rho_{x',x}(t)}{\partial t} = \frac{\hbar^2}{2m}\left(\frac{\partial^2\rho_{x',x}(t)}{\partial x'^2} - \frac{\partial^2\rho_{x',x}(t)}{\partial x^2}\right) + \frac{1}{2}m\omega^2(x'^2 - x^2)\rho_{x',x}(t). \tag{4}
$$

(c) To find $\rho_{x,x}(t)$, let us first solve the Liouville equation in the basis of eigenstates of the Hamiltonian, $\hat{H} = (1/2m)\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2$. From Exercise 5.8, we see that the Hamiltonian has eigenvalues $E_n = \hbar\omega(n + \frac{1}{2})$ and eigenstates $|n\rangle$, $(\hat{H}|n\rangle = E_n|n\rangle)$, which in the position basis are

$$
\langle x|n\rangle = \sqrt{\frac{1}{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{H}_n\left(\sqrt{\frac{m\omega}{\hbar}}\,x\right)e^{m\omega x^2/2\hbar}, \tag{5}
$$

where $\mathrm{H}_n(\sqrt{(m\omega/\hbar)}x)$ is a Hermite polynomial. The Liouville equation in the basis of eigenstates $|n\rangle$ is

$$
i\hbar\frac{\partial\rho_{n',n}(t)}{\partial t} = \hbar\omega(n' - n)\rho_{n',n}(t), \tag{6}
$$

where $\rho_{n',n}(t) = \langle n'|\hat{\rho}(t)|n\rangle$. The solution to Eq. (6) is

$$
\rho_{n',n}(t) = e^{-i\omega(n'-n)t}\rho_{n',n}(0). \tag{7}
$$

Let us now note that $\rho_{n',n}(0) = \int_{-\infty}^{\infty} dx'_0 \int_{-\infty}^{\infty} dx_0 \langle n'|x'_0\rangle \rho_{x'_0,x_0}(0)\langle x_0|n\rangle$. Then the density matrix, $\rho_{x',x}(t)$, can be written

$$\rho_{x',x}(t) = \sum_{n'=0}^{\infty}\sum_{n=0}^{\infty}\int_{-\infty}^{\infty} dx'_0 \times \int_{-\infty}^{\infty} dx_0 \langle x'|n'\rangle\langle n|x\rangle\langle x_0|n\rangle\langle n'|x'_0\rangle e^{-i\omega(n'-n)t}\rho_{x'_0,x_0}(0). \tag{8}$$

If we use the initial condition in part (a), the probability density, $\rho_{x,x}(t)$, can be written

$$\rho_{x,x}(t) = \frac{1}{2}\sqrt{\frac{a}{\pi}}\sum_{n'=0}^{\infty}\sum_{n=0}^{\infty}\int_{-\infty}^{\infty} dx'_0 \times \int_{-\infty}^{\infty} dx_0 \langle x|n'\rangle\langle n|x\rangle\langle x_0|n\rangle\langle n'|x'_0\rangle e^{-i\omega(n'-n)t} \times (e^{-ax_0'^2} + e^{-ax_0^2})\exp\left(-\frac{(x'_0 - x_0)^2}{4b\hbar^2}\right). \tag{9}$$

Let us now use Eq. (5) and note the identity in Eq. (10) of Exercise 5.8. With this we can write

$$\sum_{n=0}^{\infty}\langle x_0|n\rangle\langle n|x\rangle e^{+in\omega t} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\sqrt{f(t)}e^{m\omega(x^2+x_0^2)/2\hbar} \times \exp\left(-\frac{m\omega}{\hbar}f(t)(x^2 + x_0^2 - 2x_0xe^{i\omega t})\right), \tag{10}$$

where $f(t) = ie^{-i\omega t}/2\sin(\omega t)$. If we use Eq. (10) to perform the summations in Eq. (9), then we are left integrals over x'_0 and x_0 which can be performed explicitly. After considerable algebra, we find

$$\rho_{x,x}(t) = \sqrt{\frac{a}{\pi}}\,\mathrm{Re}\left[\frac{1}{\sqrt{B(t)}}e^{-ax^2/B(t)}\right], \tag{11}$$

where Re denotes the real part and

$$B(t) = \cos^2(\omega t) + \frac{a}{bm^2\omega^2}\sin^2(\omega t) + i\frac{2a\hbar}{m\omega}\cos(\omega t)\sin(\omega t). \tag{12}$$

■ **EXERCISE 6.6.** An ensemble of silver atoms (each with spin $\frac{1}{2}$) is prepared so that 60% of the atoms are in the $S_z = +\frac{\hbar}{2}$ eigenstate of $\hat{S}_z$ and 40% of the atoms are in the $S_x = -\frac{\hbar}{2}$ eigenstate of $\hat{S}_x$ ($\hat{S}_x$ and $\hat{S}_z$ are the x and z components of the spin angular momentum operator). (a) Compute the density matrix at time $t = 0$ in the basis of eigenstates of $\hat{S}_z$. (b) Assume that the silver atoms sit in a magnetic field, $\mathbf{B} = B_0\hat{\mathbf{y}}$, and have a magnetic Hamiltonian, $\hat{H} = \mu\mathbf{S}\cdot\mathbf{B}$, where μ is the magnetic moment of a silver atom. Compute the density matrix at time t (in the basis of eigenstates of $\hat{S}_z$). (c) Compute $\langle S_z(t)\rangle$ at time $t = 0$ and at time t.

Answer:

(a) Let $|i_\pm\rangle$ denote the eigenstates of $\hat{S}_k(k = x, y, z)$ with eigenvalues $\pm(\hbar/2)$ so $(\hat{S}_k|k_\pm\rangle = \pm(\hbar/2)|k_\pm\rangle)$. The density operator at time $t = 0$ is the mixed state

$$\hat{\rho}(0) = \frac{6}{10}|z_+\rangle\langle z_+| + \frac{4}{10}|x_-\rangle\langle x_-|. \tag{1}$$

Now note that the matrix representation of the components $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ in the basis of eigenstates of $\hat{S}_z$ are

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{2}$$

The eigenstates of $\hat{S}_x$ and $\hat{S}_y$, in the basis of eigenstates of $\hat{S}_z$ are

$$\begin{pmatrix} \langle z_+|x_\pm\rangle \\ \langle z_-|x_\pm\rangle \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \langle z_+|y_\pm\rangle \\ \langle z_-|y_\pm\rangle \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm i \end{pmatrix}, \tag{3}$$

respectively. The eigenstates of $\hat{S}_z$ in the basis of eigenstates of $\hat{S}_z$ are

$$\begin{pmatrix} \langle z_+|z_+\rangle \\ \langle z_-|z_+\rangle \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \langle z_+|z_-\rangle \\ \langle z_-|z_-\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{4}$$

Using these results we find the initial density matrix in the $|z_\pm\rangle$ basis,

$$\rho(0) = \begin{pmatrix} \frac{4}{5} & -\frac{1}{5} \\ -\frac{1}{5} & \frac{1}{5} \end{pmatrix}. \tag{5}$$

(b) The Hamiltonian is $\hat{H} = \frac{1}{2}\mu\hbar B_0(|y_+\rangle\langle y_+| - |y_-\rangle\langle y_-|)$ (this is its spectral decomposition). If we let $\rho_{y++} \equiv \langle y_+|\hat{\rho}|y_+\rangle$, then the Liouville equation for various matrix elements of the density matrix in basis $|y_\pm\rangle$ is given by

$$i\frac{\partial\rho_{y++}(t)}{\partial t} = 0, \quad i\frac{\partial\rho_{y+-}(t)}{\partial t} = \mu B_0\rho_{y+-}(t), \quad i\frac{\partial\rho_{y-+}(t)}{\partial t} = -\mu B_0\rho_{y-+}(t) \quad \text{and} \quad i\frac{\partial\rho_{y--}(t)}{\partial t} = 0, \tag{6}$$

Now note that the initial density matrix in the basis $|y_\pm\rangle$ is given by

$$\rho(0) = \begin{pmatrix} \frac{1}{2} & \frac{3+2i}{10} \\ \frac{3-2i}{10} & \frac{1}{2} \end{pmatrix}. \tag{7}$$

Using Eq. (7), we can solve Eqs. (6) and write the density matrix at time t in the basis $|y_\pm\rangle$. We find

$$\rho(t) = \begin{pmatrix} \frac{1}{2} & \frac{3+2i}{10} e^{-i\mu B_0 t} \\ \frac{3-2i}{10} e^{+i\mu B_0 t} & \frac{1}{2} \end{pmatrix}. \tag{8}$$

We now can transform Eq. (8) to the basis $|z_\pm\rangle$ to obtain

$$\rho(t)=\begin{pmatrix} \frac{1}{2}+\frac{3}{10}\cos(\mu B_0 t)+\frac{1}{5}\sin(\mu B_0 t) & \frac{3}{10}\sin(\mu B_0 t)-\frac{1}{5}\cos(\mu B_0 t) \\ \frac{3}{10}\sin(\mu B_0 t)-\frac{1}{5}\cos(\mu B_0 t) & \frac{1}{2}-\frac{3}{10}\cos(\mu B_0 t)-\frac{1}{5}\sin(\mu B_0 t) \end{pmatrix}. \tag{9}$$

(c) The average z-component of spin angular momentum at time, $t = 0$ is

$$\langle S_z(0)\rangle = \mathrm{Tr}\,\hat{S}_z\hat{\rho}(0) = \frac{\hbar}{2}\mathrm{Tr}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \frac{4}{5} & -\frac{1}{5} \\ -\frac{1}{5} & \frac{1}{5} \end{pmatrix} = \frac{3}{10}\hbar. \tag{10}$$

The average z component of spin angular momentum at time t is

$$\langle S_z(t)\rangle = \frac{3}{10}\hbar\cos(\mu B_0 t) + \frac{1}{5}\hbar\sin(\mu B_0 t). \tag{11}$$

▶ SPECIAL TOPICS

▶ S6.A. Reduced Probability Densities and the BBGKY Hierarchy [2, 5, 17]

The N-particle probability density, $\rho(\mathbf{X}^N, t)$, contains much more information than we would ever need or want. Most quantities we measure experimentally can be expressed in terms of one-body or two-body phase functions. One-body phase functions are usually written in the form

$$O^N_{(1)}(\mathbf{X}^N) = \sum_{i=1}^{N} O(\mathbf{X}_i), \tag{6.61}$$

and two-body phase functions are written in the form

$$O^N_{(2)}(\mathbf{X}^N) = \sum_{i<j}^{N(N-1)/2} O(\mathbf{X}_i, \mathbf{X}_j), \tag{6.62}$$

An example of a one-body phase function is the kinetic energy, $\sum_{i=1}^N p_i^2/2m$, of an N-particle system. An example of a two-body phase function is the potential energy, $\sum_{i<j}^{N(N-1)/2} V(|\mathbf{q}_i - \mathbf{q}_j|)$, of an N-particle system. To find the expectation value of a one-body phase function, we only need to know the one-body reduced probability density. Similarly, to find the expectation value of a two-body phase function, we only need to know the two-body reduced probability density.

The one-body reduced probability density is given by

$$\rho_1(\mathbf{X}_1, t) = \int \cdots \int d\mathbf{X}_2 \cdots d\mathbf{X}_N \, \rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t), \tag{6.63}$$

where $\rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t) \equiv \rho(\mathbf{X}^N, t)$. The s-body reduced probability density is given by

$$\rho_s(\mathbf{X}_1, \ldots, \mathbf{X}_s, t) = \int \cdots \int d\mathbf{X}_{s+1} \ldots d\mathbf{X}_N \, \rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t). \tag{6.64}$$

If the probability density, $\rho(\mathbf{X}_1, \ldots, \mathbf{X}_N, t)$, is known at time t, then the expectation value of the one-body phase function at time t is given by

$$\langle O_{(1)}(t) \rangle = \sum_{i=1}^N \int \cdots \int d\mathbf{X}_1 \ldots d\mathbf{X}_N \, O(\mathbf{X}_i) \rho(\mathbf{X}^N, t) = N \int d\mathbf{X}_1 O(\mathbf{X}_1, t) \rho_1(\mathbf{X}_1, t). \tag{6.65}$$

Similarly, the expectation value of the two-body phase function at time t is

$$\begin{aligned} \langle O_{(2)}(t) \rangle &= \sum_{i<j}^{N(N-1)/2} \int \cdots \int d\mathbf{X}_1 \ldots d\mathbf{X}_N \, O(\mathbf{X}_i, \mathbf{X}_j) \rho(\mathbf{X}^N, t) \\ &= \frac{N(N-1)}{2} \int\int d\mathbf{X}_1 d\mathbf{X}_2 O(\mathbf{X}_1, \mathbf{X}_2, t) \rho_2(\mathbf{X}_1, \mathbf{X}_2, t). \end{aligned} \tag{6.66}$$

In Eqs. (6.65) and (6.66), we have assumed that the probability density is symmetric under interchange of particle labels if the Hamiltonian is symmetric.

The equation of motion of $\rho_s(\mathbf{X}_1, \ldots, \mathbf{X}_s, t)$ can be obtained from the Liouville equation. It is convenient to first introduce another quantity,

$F_s(\mathbf{X}_1, \dots, \mathbf{X}_s, t)$, defined as

$$F_s(\mathbf{X}_1, \dots, \mathbf{X}_s, t) \equiv V^s \int \cdots \int d\mathbf{X}_{s+1} \dots d\mathbf{X}_N \, \rho(X_1, \dots, \mathbf{X}_N, t), \tag{6.67}$$

and

$$F_N(\mathbf{X}_1, \dots, \mathbf{X}_N, t) \equiv V^N \rho(\mathbf{X}_1, \dots, \mathbf{X}_N, t). \tag{6.68}$$

Let us assume that the evolution of the system is governed by a Hamiltonian of the form

$$H^N(\mathbf{X}^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j}^{N(N-1)/2} \phi(|\mathbf{q}_i - \mathbf{q}_j|), \tag{6.69}$$

where $\phi(|\mathbf{q}_i - \mathbf{q}_j|)$ is a two-body spherically symmetric interaction potential between particles i and j. The Liouville operator is

$$\hat{L}^N = -i \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{q}_i} + i \sum_{i<j}^{N(N-1)/2} \hat{\Theta}_{ij}, \tag{6.70}$$

where

$$\hat{\Theta}_{ij} = \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} + \frac{\partial \phi_{ij}}{\partial \mathbf{q}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j} \tag{6.71}$$

and $\phi_{ij} = \phi(|\mathbf{q}_i - \mathbf{q}_j|)$. If we integrate the Liouville equation, (6.27), over $\mathbf{X}_{s+1}, \dots, \mathbf{X}_N$ and multiply by V^s, we obtain

$$\begin{aligned} \frac{\partial F_s}{\partial t} + i\hat{L}^s F_s =& V^s \int \cdots \int d\mathbf{X}_{s+1} \cdots d\mathbf{X}_N \\ & \times \left\{ -\sum_{i=s+1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{q}_i} + \sum_{i \le s; s+1 \le j \le N} \hat{\Theta}_{ij} + \sum_{s+1 \le k < l} \hat{\Theta}_{kl} \right\} \\ & \times \rho^N(\mathbf{X}_1, \dots, \mathbf{X}_N, t). \end{aligned} \tag{6.72}$$

If we assume that $\rho(\mathbf{X}_1, \dots, \mathbf{X}_N, t) \to 0$ for large values of $\mathbf{X}_i$, then the first and third terms on the right-hand side of Eqs. (6.72) go to zero. One can see this by using Gauss's theorem and changing the volume integration to surface integration. For a large system the contribution from $\rho(\mathbf{X}_1, \dots, \mathbf{X}_N, t)$ on the surface goes to zero. The second term on the right-hand side can be written in the form

$$V^s\int\cdots\int d\mathbf{X}_{s+1}\cdots d\mathbf{X}_N \sum_{i\le s;s+i\le j\le N} \hat{\Theta}_{ij}\rho^N(\mathbf{X}_1,\ldots,\mathbf{X}_N,t)$$
$$= V^s(N-s)\sum_{i=1}^{s}\int d\mathbf{X}_{s+1}\hat{\Theta}_{i,s+1}\int\cdots\int d\mathbf{X}_{s+2}\cdots d\mathbf{X}_N\rho^N(\mathbf{X}_1,\ldots,\mathbf{X}_N,t)$$
$$= \frac{(N-s)}{V}\sum_{i=1}^{s}\int d\mathbf{X}_{s+1}\hat{\Theta}_{i,s+1}F_{s+1}(\mathbf{X}_1,\ldots,\mathbf{X}_{s+1},t).$$

Equation (6.72) then becomes

$$\frac{\partial F_s}{\partial t}+i\hat{L}^sF_s = \frac{(N-s)}{V}\sum_{i=1}^{s}\int d\mathbf{X}_{s+1}\hat{\Theta}_{i,s+1}F_{s+1}(\mathbf{X}_1,\ldots,\mathbf{X}_{s+1},t). \tag{6.73}$$

For a fixed values of s we may take the limit $N\to\infty, V\to\infty$, such that $v\equiv V/N$ remains constant (this is called the thermodynamic limit) and Eq. (6.73) becomes

$$\frac{\partial F_s}{\partial t}+i\hat{L}^sF_s = \frac{1}{v}\sum_{i=1}^{s}\int d\mathbf{X}_{s+1}\hat{\Theta}_{i,s+1}F_{s+1}(\mathbf{X}_1,\ldots,\mathbf{X}_{s+1},t). \tag{6.74}$$

Equation (6.74) gives a hierarchy of equations of motion for the reduced probability densities $F_s(\mathbf{X}_1,\ldots,\mathbf{X}_N,t)$. It is called the BBGKY hierarchy after authors Bogoliubov [17], Born and Green [18], Kirkwood [19], and Yvon [20]. The most useful equations in the hierarchy are those for $F_1(\mathbf{X}_1,t)$ and $F_2(\mathbf{X}_1,\mathbf{X}_2,t)$:

$$\frac{\partial F_1}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial F_1}{\partial \mathbf{q}_1} = \frac{1}{v}\int d\mathbf{X}_2\hat{\Theta}_{12}F_2(\mathbf{X}_1,\mathbf{X}_2,t) \tag{6.75}$$

and

$$\frac{\partial F_2}{\partial t}+\left(\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial \mathbf{q}_1}+\frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial \mathbf{q}_2}-\hat{\Theta}_{12}\right)F_2 = \frac{1}{v}\int d\mathbf{X}_3(\hat{\Theta}_{13}+\hat{\Theta}_{23})F_3(\mathbf{X}_1,\mathbf{X}_2,\mathbf{X}_3,t). \tag{6.76}$$

Notice that the equation of motion of F_1 depends on F_2, the equation of motion for F_2 depends on F_3, and so on. This makes the equations of the hierarchy impossible to solve unless some way can be found to truncate it. For example, if we could find some way to write $F_2(\mathbf{X}_1,\mathbf{X}_2,t)$ in terms of $F_1(\mathbf{X}_1,t)$ and $F_1(\mathbf{X}_2,t)$, then we could in principle solve Eq. (6.75) for the reduced probability density $F_1(\mathbf{X}_1,t)$. Equation (6.75) is called the *kinetic equation.*

▶ S6.B. Reduced Density Matrices and the Wigner Distribution [16, 21–25]

For quantum mechanical system, the phase space coordinates of particles do not commute, and therefore it is impossible to specify simultaneously the position and momentum of the particles. As a result, it is also not possible to define a distribution function on the phase space which can be interpreted as a probability density. However, Wigner [16] was first to show that it is possible to introduce a function which formally analogous to the classical probability density and which reduces to it in the classical limit.

Before we introduce the Wigner function, it is useful to introduce the idea of one- and two-body reduced density matrices. In quantum mechanics, as in classical mechanics, we generally deal with one-body operators,

$$\hat{O}^N_{(1)} = \sum_{i=1}^{N} \hat{O}(\hat{\mathbf{p}}_i, \hat{\mathbf{q}}_i), \tag{6.77}$$

such as the N-body kinetic energy operator, and we also deal with two-body operators,

$$\hat{O}^N_{(2)} = \sum_{i<j}^{N(N-1)/2} \hat{O}(\hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j, \hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j), \tag{6.78}$$

such as the interaction potential. The trace of a one-body operator, in the position basis, can be written

$$\begin{aligned}
\langle O_{(1)}(t)\rangle &= \mathrm{Tr}\, \hat{O}^N_{(1)}\hat{\rho}(t) \\
&= \sum_{i=1}^{N} \int dx_1 \cdots \int dx_N \int dx'_1 \cdots \int dx'_N \langle x_1, \ldots, x_N | \hat{O}_i | x'_1, \ldots, x'_N\rangle \\
&\quad \times \langle x'_1, \ldots, x'_N | \hat{\rho}(t) | x_1, \ldots, x_N\rangle \\
&= N \int dx_1 \cdots \int dx_N \int dx'_1 \langle x_1 | \hat{O}_1 | x'_1\rangle \langle x'_1, x_2, \ldots, x_N | \hat{\rho}(t) | x_1, \ldots, x_N\rangle \\
&\equiv \int dx_1 \int dx'_1 \langle x_1 | \hat{O}_1 | x'_1\rangle \langle x'_1 | \hat{\rho}_{(1)}(t) | x_1\rangle,
\end{aligned} \tag{6.79}$$

where $\hat{O}_i = \hat{O}(\hat{\mathbf{p}}_i, \hat{\mathbf{q}}_i)$ and

$$\langle x'_1 | \hat{\rho}_{(1)}(t) | x_1\rangle = N \int dx_2 \cdots \int dx_N \langle x'_1, x_2, \ldots, x_N | \hat{\rho}(t) | x_1, \ldots, x_N\rangle \tag{6.80}$$

is the one-body reduced density matrix. (We use the notation of Appendix B.)

The two-body reduced density matrix is defined in an analogous manner. The trace of a two-body operator in the position basis can be written

$$
\begin{aligned}
\langle O_{(2)}(t)\rangle &= \mathrm{Tr}\,\hat{O}^N_{(2)}\hat{\rho}(t) \\
&= \sum_{i<j}^{N(N-1)/2} \int dx_1 \cdots \int dx_N \int dx'_1 \cdots \int dx'_N \langle x_1,\ldots,x_N|\hat{O}_{i,j}|x'_1,\ldots,x'_N\rangle \\
&\quad \times \langle x'_1,\ldots,x'_N|\hat{\rho}(t)|x_1,\ldots,x_N\rangle \\
&= \frac{N(N-1)}{2}\int dx_1 \cdots \int dx_N \int dx'_1 \int dx'_2 \langle x_1,x_2|\hat{O}_{1,2}|x'_1,x'_2\rangle \\
&\quad \times \langle x'_1,x'_2,x_3,\ldots,x_N|\hat{\rho}(t)|x_1,\ldots,x_N\rangle \\
&\equiv \frac{1}{2}\int dx_1 \int dx_2 \int dx'_1 \int dx'_2 \langle x_1,x_2|\hat{O}_{1,2}|x'_1,x'_2\rangle \langle x'_1,x'_2|\hat{\rho}_{(2)}(t)|x_1,x_2\rangle,
\end{aligned}
\tag{6.81}
$$

where $\hat{O}_{i,j} = \hat{O}(\hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j, \hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j)$ and

$$
\begin{aligned}
\langle x'_1,x'_2|\hat{\rho}_{(2)}(t)|x_1,x_2\rangle = N(N-1)\int dx_3 \cdots \int dx_N \\
\times \langle x'_1,x'_2,x_3,\ldots,x_N|\hat{\rho}(t)|x_1,\ldots,x_N\rangle
\end{aligned}
\tag{6.82}
$$

is the two-body reduced density matrix.

We can now introduce the one- and two-particle reduced Wigner functions. The one-particle reduced Wigner function is defined as

$$
f_1(\mathbf{k},\mathbf{R},t) \equiv \int d\,\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \left\langle \mathbf{R} + \frac{\mathbf{r}}{2} |\hat{\rho}_{(1)}(t)| \mathbf{R} - \frac{\mathbf{r}}{2} \right\rangle,
\tag{6.83}
$$

and the two-particle reduced Wigner function is defined as

$$
\begin{aligned}
f_2(\mathbf{k}_1,\mathbf{k}_2,\mathbf{R}_1,\mathbf{R}_2;t) = \int\int d\,\mathbf{r}_1 d\,\mathbf{r}_2 e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\cdot\mathbf{k}_2\mathbf{r}_2} \\
\times \left\langle \mathbf{R}_1 + \frac{\mathbf{r}_1}{2}; \mathbf{R}_2 + \frac{\mathbf{r}_2}{2} |\rho_{(2)}(t)| \mathbf{R}_1 - \frac{\mathbf{r}_1}{2}, \mathbf{R}_2 - \frac{\mathbf{r}_2}{2} \right\rangle.
\end{aligned}
\tag{6.84}
$$

Higher-order Wigner functions can be defined in a similar manner.

In analogy to the classical distribution function, the one-particle Wigner function obeys the relations

$$
\int \frac{d\,\mathbf{k}}{(2\pi)^3} f_1(\mathbf{k},\mathbf{R},t) = \langle \mathbf{R}|\hat{\rho}_{(1)}(t)|\mathbf{R}\rangle = n(\mathbf{R},t),
\tag{6.85}
$$

where $n(\mathbf{R},t)$ is the average number of particles at point $\mathbf{R}$ and time, t, and

$$\int d\mathbf{R} f_1(\mathbf{k},\mathbf{R},t) = \langle \mathbf{k}|\hat{\rho}_{(1)}(t)|\mathbf{k}\rangle = n(\mathbf{k},t), \tag{6.86}$$

and $n(\mathbf{k},t)$ is the average number of particles with wavevector, $\mathbf{k}$, at time t. The Wigner function can be used to take phase space averages in the same way as the classical distribution functions. For example, the average current is defined as

$$\langle \mathbf{j}(\mathbf{R},t)\rangle = \int \frac{d\mathbf{k}}{(2\pi)^3}\hbar\mathbf{k} f_1(\mathbf{k},\mathbf{R},t), \tag{6.87}$$

where $\hbar$ is Planck's constant. However, the Wigner function can become negative and therefore cannot always be interpreted as a probability density.

We can derive the equation of motion for $f_1(\mathbf{k},\mathbf{R},t)$ in the following way. For a system with a Hamiltonian

$$\hat{H} = \sum_{i=1}^{N}\frac{\hbar^2 k_i^2}{2m} + \sum_{i<j}^{N(N-1)/2} V(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j), \tag{6.88}$$

the equation of motion for the one-particle reduced density matrix is

$$\begin{aligned}\frac{\partial}{\partial t}\langle \mathbf{r}_1|\hat{\rho}_{(1)}(t)|\mathbf{r}_2\rangle = &-\frac{i\hbar}{2m}(\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2})\cdot(\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}_2})\langle \mathbf{r}_1|\hat{\rho}_{(1)}(t)|\mathbf{r}_2\rangle \\ &-\frac{i}{\hbar}\int d\mathbf{r}'[V(\mathbf{r}_2-\mathbf{r}') - V(\mathbf{r}_1-\mathbf{r}')]\langle \mathbf{r}_1,\mathbf{r}'|\hat{\rho}_{(2)}(t)|\mathbf{r}_2,\mathbf{r}'\rangle,\end{aligned} \tag{6.89}$$

where $V(\mathbf{r}_1 - \mathbf{r}_2) = \langle \mathbf{r}_1,\mathbf{r}_2|V(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j)|\mathbf{r}_1,\mathbf{r}_2\rangle$.

Let us now change to relative and center-of-mass coordinates, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, respectively. We then multiply by $e^{i\mathbf{k}\cdot\mathbf{r}}$ and integrate over $d\mathbf{r}$ and find

$$\begin{aligned}&\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial}{\partial t}\left\langle \mathbf{R}+\frac{\mathbf{r}}{2}|\hat{\rho}_{(1))}(t)|\mathbf{R}-\frac{\mathbf{r}}{2}\right\rangle \\ &\quad= -\frac{i\hbar}{m}\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}}\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{r}}\left\langle \mathbf{R}+\frac{\mathbf{r}}{2}|\hat{\rho}_{(1)}(t)|\mathbf{R}-\frac{\mathbf{r}}{2}\right\rangle \\ &\quad\quad -\frac{i}{\hbar}\int d\mathbf{r}'\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}}\left[V\left(\mathbf{R}-\frac{\mathbf{r}}{2}-\mathbf{r}'\right) - V\left(\mathbf{R}+\frac{\mathbf{r}}{2}-\mathbf{r}'\right)\right] \\ &\quad\quad \times\left\langle \mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{r}'|\hat{\rho}_{(2)}(t)|\mathbf{R}-\frac{\mathbf{r}}{2},\mathbf{r}'\right\rangle.\end{aligned} \tag{6.90}$$

In Eq. (6.90) we can integrate the first term on the right by parts to remove the derivative with respect to $\mathbf{r}$. We can also introduce dummy variables into the second term on the right and make use of definitions in Eqs. (6.83) and (6.84) to obtain

$$\begin{aligned}\frac{\partial}{\partial t} f_1(\mathbf{k},\mathbf{R},t) = &-\frac{\hbar}{m}\mathbf{k}\cdot\nabla_{\mathbf{R}} f_1(\mathbf{k},\mathbf{R},t) \\ &-\frac{i}{\hbar}\int\frac{d\mathbf{k}'}{(2\pi)^3}\int d\mathbf{r}'\left[V\left(\mathbf{R}-\mathbf{r}'-\frac{1}{2i}\frac{\partial}{\partial\mathbf{k}}\right)-V\left(\mathbf{R}-\mathbf{r}'+\frac{1}{2i}\frac{\partial}{\partial\mathbf{k}}\right)\right] \\ &\times f_2(\mathbf{k},\mathbf{R};\mathbf{k}',\mathbf{r}';t).\end{aligned} \tag{6.91}$$

Equation (6.91) is the quantum kinetic equation for the one-particle reduced Wigner function. If we rewrite it in terms of momenta $\mathbf{p}=\hbar\mathbf{k}$ and $\mathbf{p}'=\hbar\mathbf{k}'$, it takes the form

$$\begin{aligned}&\frac{\partial}{\partial t} f_1'(\mathbf{p},\mathbf{R},t)+\frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{R}} f_1'(\mathbf{p},\mathbf{R},t) \\ &\quad=-\frac{i}{\hbar}\int\frac{d\mathbf{p}}{(2\pi)^3}\int d\mathbf{r}'\left[V\left(\mathbf{R}-\mathbf{r}'-\frac{\hbar}{2i}\frac{\partial}{\partial\mathbf{p}}\right)-V\left(\mathbf{R}-\mathbf{r}'+\frac{\hbar}{2i}\frac{\partial}{\partial\mathbf{p}}\right)\right] \\ &\quad\times f_2'(\mathbf{p},\mathbf{R};\mathbf{p}',\mathbf{r}';t),\end{aligned} \tag{6.92}$$

where

$$f_n'(\mathbf{p}_1,\mathbf{r}_1;\ldots;\mathbf{p}_n,\mathbf{r}_n)=\frac{1}{\hbar^{3n}}f_n\left(\frac{1}{\hbar}\mathbf{p}_1,\mathbf{r}_1;\ldots;\frac{1}{\hbar}\mathbf{p}_n,\mathbf{r}_n\right). \tag{6.93}$$

We can now expand the potential on the right-hand side in powers of $\hbar$ and take the limit $\hbar\to 0$. We then retrieve the classical kinetic equation.

The Wigner function can be used to take the average value of a large class of ordinary functions of momentum and position but in some cases it will give the wrong answer. The average value of any quantity which is only a function of position or only a function of momentum can always be taken (this is easily seen from Eqs. (6.85) and (6.86)). However, only those functions which involve both position and momentum can be used for which the Weyl correspondence between the quantum and classical version of the operators holds. To see this, let us consider the classical function $O(\mathbf{p},\mathbf{q})$ of phase space variables $\mathbf{p}$ and $\mathbf{q}$. We can find the quantum version of this function as follows. We first introduce its Fourier transform, $\tilde{O}(\boldsymbol{\sigma},\boldsymbol{\eta})$, with the equation

$$O(\mathbf{p},\mathbf{q})=\int\int d\boldsymbol{\sigma}\,d\boldsymbol{\eta}\,\tilde{O}(\boldsymbol{\sigma},\boldsymbol{\eta})e^{i(\boldsymbol{\sigma}\cdot\mathbf{p}+\boldsymbol{\eta}\cdot\mathbf{q})}. \tag{6.94}$$

Matrix elements of the quantum operator corresponding to $O(\mathbf{p}, \mathbf{q})$ can be obtained from the Fourier transform, $\tilde{O}(\boldsymbol{\sigma}, \boldsymbol{\eta})$, via the equation

$$\langle \mathbf{r}'|\hat{O}|\mathbf{r}''\rangle = \int\int d\boldsymbol{\sigma} d\boldsymbol{\eta}\, \tilde{O}(\boldsymbol{\sigma}, \boldsymbol{\eta})\langle \mathbf{r}'|e^{i(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}} - \boldsymbol{\eta}\cdot\hat{\mathbf{q}})}|\mathbf{r}''\rangle, \tag{6.95}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{q}}$ are momentum and position operators. If the classical function $O(\mathbf{p}, \mathbf{q})$ and matrix elements of the corresponding operator $\hat{O}$ are related by the above procedure, then the expectation value of $\hat{O}$ is given by

$$\langle O(t)\rangle = \int\int d\mathbf{p} d\mathbf{r} O(\mathbf{p}, \mathbf{r}) f_1'(\mathbf{p}, \mathbf{r}, t). \tag{6.96}$$

There are some cases for which the Weyl procedure does not give the correct correspondence between classical and quantum operators (such as the commutator $[\hat{\mathbf{p}}, \hat{\mathbf{r}}]_-$, the square of the Hamiltonian $\hat{H}^2$, the square of the angular momentum $\mathbf{L}^2$, etc.) and the Wigner function gives the wrong result. Then it is necessary to introduce more general quantum phase space distributions which may in general be complex functions [25].

■ **EXERCISE 6.7.** Compute the Wigner function for a system with a density operator, $\hat{\rho} = \hbar\sqrt{ab}(e^{-a\hat{x}^2}e^{-b\hat{p}^2} + e^{-b\hat{p}^2}e^{-a\hat{x}^2})$.

Answer: First compute the matrix element of the density operator in the position basis,

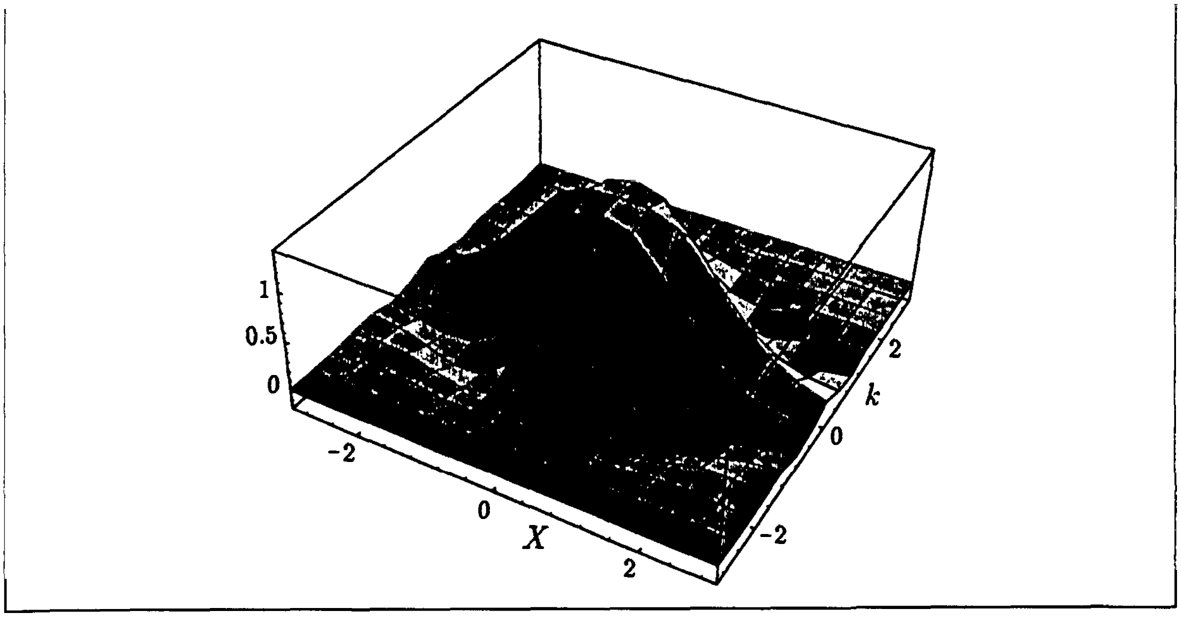
$$\langle x_1|\hat{\rho}|x_2\rangle = \frac{1}{2}\sqrt{\frac{a}{\pi}}(e^{-ax_1^2} + e^{-ax_2^2})\exp\left(-\frac{(x_1 - x_2)^2}{4b\hbar^2}\right). \tag{1}$$

Now let $x_1 = X + (x/2)$ and $x_1 - (x/2)$. The Wigner function is then given by (after some algebra)

$$f(k, X) = \int_{-\infty}^{\infty} dx e^{ikx}\left\langle X + \frac{x}{2}|\hat{\rho}|X - \frac{x}{2}\right\rangle$$

$$= \sqrt{\frac{4ab\hbar^2}{1 + ab\hbar^2}}\exp\left(\frac{-aX^2}{1 + ab\hbar^2}\right)\exp\left(\frac{-bk^2\hbar^2}{1 + ab\hbar^2}\right)\cos\left(\frac{2ab\hbar^2 kX}{1 + ab\hbar^2}\right). \tag{2}$$

A plot of the Wigner function is shown here for $a = 1$ and $b\hbar^2 = 2$. Note that there are some regions where it becomes negative, indicating that it is not a probability density.



▶ S6.C. Microscopic Balance Equations [26]

For quantum systems with short-ranged interactions and long-wavelength inhomogeneities, we can derive microscopic balance equations for the particle density, momentum density, and energy density in a manner analogous to the derivation for classical systems. We first note, however, that the position and momentum operators satisfy the commutation relations,

$$[\hat{\mathbf{p}}_i, \hat{\mathbf{p}}_j]_- = 0, \qquad [\hat{\mathbf{q}}_i, \hat{\mathbf{q}}_j]_- = 0, \quad \text{and} \quad [\hat{\mathbf{q}}_i, \hat{\mathbf{p}}_j]_- = i\hbar\delta_{ij}. \tag{6.97}$$

The commutator of the momentum operator $\hat{\mathbf{p}}_i$ with an arbitrary function of coordinate operators is

$$[\hat{\mathbf{p}}_i, F(\hat{\mathbf{q}}_1, \ldots, \hat{\mathbf{q}}_N)]_- = -i\hbar\frac{\partial F}{\partial \hat{\mathbf{q}}_i}, \tag{6.98}$$

while the commutator of $\hat{\mathbf{q}}_i$ with an arbitrary function of momenta $G(\hat{\mathbf{p}}_1, \ldots, \hat{\mathbf{p}}_N)$ is

$$[\hat{\mathbf{q}}_i, G(\hat{\mathbf{p}}_1, \ldots, \hat{\mathbf{p}}_N)]_- = i\hbar\frac{\partial G}{\partial \hat{\mathbf{p}}_i}. \tag{6.99}$$

Let us assume that the dynamics of the system is governed by a Hamiltonian of the form

$$\hat{H}^N = \sum_{i=1}^{N}\frac{|\hat{\mathbf{p}}_i|^2}{2m} + \sum_{i<j}^{(1/2)N(N-1)} V(|\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j|). \tag{6.100}$$

Then from Eq. (6.57) the equation of motion for the operator $\hat{\mathbf{q}}_i$ is

$$\frac{\partial \hat{\mathbf{q}}_i}{\partial t} = \frac{i}{\hbar}[\hat{H}, \hat{\mathbf{q}}_i]_- = \frac{\hat{\mathbf{p}}_i}{m}. \tag{6.101}$$

The equation of motion of $\hat{\mathbf{p}}_i$ is given by

$$\frac{\partial \hat{\mathbf{p}}_i}{\partial t} = -\sum_{l \neq i}\left[\frac{\partial V(|\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_l|)}{\partial \hat{\mathbf{q}}_i}\right] = \sum_{l \neq i} \hat{\mathbf{F}}_{il}. \tag{6.102}$$

These equations have the same form as the classical equations.

For quantum systems, the microscopic expressions for the densities must be Hermitian in order to be observable. Thus, we must have symmetrized expressions for operators which involve both momentum and position. Using Eq. (6.57) and the above equations, we can show that the balance equation for the particle number density is given by

$$\frac{\partial}{\partial t}\hat{n}(\hat{\mathbf{q}}^N; \mathbf{R}) = -\nabla_{\mathbf{R}} \cdot \hat{\mathbf{J}}^n(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}), \tag{6.103}$$

where the particle density is defined as

$$\hat{n}(\hat{\mathbf{q}}^N; \mathbf{R}) = \sum_{i=1}^{N} \delta(\hat{\mathbf{q}}_i - \mathbf{R}) \tag{6.104}$$

and the particle current density is defined as

$$\hat{\mathbf{J}}^n(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = \frac{1}{2}\sum_{i=1}^{N}\left[\frac{\hat{\mathbf{p}}_i}{m}\delta(\hat{\mathbf{q}}_i - \mathbf{R}) + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\frac{\hat{\mathbf{p}}_i}{m}\right]. \tag{6.105}$$

As usual, we let $\hat{\mathbf{p}}^N$ denote the set of momenta $\hat{\mathbf{p}}^N = (\hat{\mathbf{p}}_1, \ldots, \hat{\mathbf{p}}_N)$ and we let $\hat{\mathbf{q}}^N$ denote the set of positions $\hat{\mathbf{q}}^N = (\hat{\mathbf{q}}_1, \ldots, \hat{\mathbf{q}}_N)$.

The balance equation for the momentum density takes the form

$$m\frac{\partial}{\partial t}\hat{\mathbf{J}}^n(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = -\nabla_{\mathbf{R}} \cdot \hat{\mathbf{J}}^p(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}), \tag{6.106}$$

where the momentum current tensor, $\hat{\mathbf{J}}^p(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R})$, is defined as

$$\begin{aligned}
\hat{\mathbf{J}}^p(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = &\frac{1}{4m}\sum_{i=1}^{N}[\hat{\mathbf{p}}_i\hat{\mathbf{p}}_i\delta(\hat{\mathbf{q}}_i - \mathbf{R}) + (\hat{\mathbf{p}}_i\delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i)^T \\
&+ \hat{\mathbf{p}}_i\delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i\hat{\mathbf{p}}_i] \\
&+ \frac{1}{2}\sum_{i \neq l}^{N}\sum^{N}(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_l) \cdot \mathbf{F}_{il}\delta(\mathbf{q}_i - \mathbf{R}).
\end{aligned} \tag{6.107}$$

In Eqs. (6.106) and (6.107) the notation

$$\nabla_{\mathbf{R}} \cdot (\hat{\mathbf{p}}_i \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i)^T \equiv \hat{\mathbf{p}}_i \nabla_{\mathbf{R}} \cdot \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{\mathbf{p}}_i \tag{6.108}$$

has been used.

Finally, the balance equation for the energy density can be written

$$\frac{\partial}{\partial t}\hat{h}(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) = -\nabla_{\mathbf{R}} \cdot \hat{\mathbf{J}}^h(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}), \tag{6.109}$$

where the energy density is defined as

$$\hat{h}(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) \equiv \frac{1}{2}\sum_{i=1}^{N} [\hat{h}_i \delta(\hat{\mathbf{q}}_i - \mathbf{R}) + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{h}_i] \tag{6.110}$$

with

$$\hat{h}_i = \frac{|\hat{\mathbf{p}}_i|^2}{2m} + \frac{1}{2}\sum_{j \neq i} V(|\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j|) \tag{6.111}$$

and the energy current density is defined as

$$\begin{aligned}\hat{\mathbf{J}}^h(\hat{\mathbf{p}}^N, \hat{\mathbf{q}}^N; \mathbf{R}) \equiv & \frac{1}{4}\sum_{i=1}^{N}\Bigg[\hat{h}_i \frac{\hat{\mathbf{p}}_i}{m}\delta(\hat{\mathbf{q}}_i - \mathbf{R}) + \hat{h}_i \delta(\hat{\mathbf{q}}_i - \mathbf{R})\frac{\hat{\mathbf{p}}_i}{m} \\ & + \frac{\hat{\mathbf{p}}_i}{m}\delta(\hat{\mathbf{q}}_i - \mathbf{R})\hat{h}_i + \delta(\hat{\mathbf{q}}_i - \mathbf{R})\frac{\hat{\mathbf{p}}_i}{m}\hat{h}_i\Bigg] \\ & + \frac{1}{4}\sum^{N}\sum^{N}_{i \neq j}\Bigg[\frac{(\hat{\mathbf{p}}_i + \hat{\mathbf{p}}_j)}{m} \cdot \hat{\mathbf{F}}_{ij}(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j)\delta(\hat{\mathbf{q}}_i - \mathbf{R}) \\ & + \delta(\hat{\mathbf{q}}_i - \mathbf{R})(\hat{\mathbf{q}}_i - \hat{\mathbf{q}}_j)\hat{\mathbf{F}}_{ij} \cdot \frac{(\hat{\mathbf{p}}_i + \hat{\mathbf{p}}_j)}{m}\Bigg].\end{aligned} \tag{6.112}$$

To obtain Eq. (6.112), one must use the fact that the center-of-mass coordinates commute with the relative coordinates.

▶ S6.D. Mixing Flow [7–9]

Ergodicity is not a sufficient condition on a dynamical flow to ensure that a probability distribution that initially is localized on an energy surface will spread, in a course grained manner, throughout the energy surface. Spreading throughout the energy surface is the type of behavior that we need for a

Newtonian system to approach a state that might be used as an equilibrium state. A type of flow that does have this feature, and therefore might exhibit irreversibility in a course-grained sense (because of the unstable nature of its dynamics!) is *mixing flow*. Mixing flow is chaotic and causes any initial probability distribution to spread throughout the energy surface. *Mixing flow is ergodic, but ergodic flows are not always mixing* (the exceptions, however, are rare).

A system is mixing if, for all square integrable functions, $f(\mathbf{X}^N)$ and $g(\mathbf{X}^N)$, on the energy surface, S_E, we obtain

$$\lim_{t\to\pm\infty} \frac{1}{\sum(E)} \int_{S_E} f(\mathbf{X}^N) g(\mathbf{X}^N(t)) dS_E = \frac{\int_{S_E} f(\mathbf{X}^N) dS_E \int_{S_E} g(\mathbf{X}^N) dS_E}{(\sum(E))^2}, \qquad (6.113)$$

where $\sum(E)$ is the structure function defined in Section 6.C.

Equation (6.113) ensures that the average value of a dynamical function $f(\mathbf{X}^N)$ will approach a stationary value in the limit $t \to \pm\infty$. Let $g(\mathbf{X}^N) = \rho(\mathbf{X}^N)$, where $\rho(\mathbf{X}^N)$ is a nonstationary probability density. Then

$$\langle f(t) \rangle = \int_{S_E} f(\mathbf{X}^N) \rho(\mathbf{X}^N(t)) dS_E \underset{t\to\pm\infty}{\longrightarrow} \frac{1}{\sum(E)} \int_{S_E} f(\mathbf{X}^N) dS_E. \qquad (6.114)$$

Thus, $f(t)$ approaches an average with respect to the stationary state $\rho_s = [\sum(E)]^{-1}$.

It is important to emphasize that mixing gives a coarse-grained and not a fine-grained approach to a stationary state. The average of the probability density becomes uniform, but the probability density itself cannot because of Eq. (6.24). The probability density does not change in a neighborhood of a moving phase point, but it can change at a given point in space. We can visualize this if we consider a beaker containing oil and water. We add the oil and water carefully so that they are initially separated, and we assume that they cannot diffuse into one another. We then stir them together (Fig. 6.2). The local density and the total volume of the oil remain constant, but the oil will get stretched into filaments throughout the water. Therefore, on the average, the density of the oil will become uniform throughout the beaker. If we are careful enough, we can also stir the oil back into its original shape. Therefore, while we get an approach to uniformity, the whole process can be reversed. However, as we shall see, mixing does lead to the appearance of random behavior in deterministic systems and coarse-grained irreversibility.

The meaning of Eq. (6.113) may therefore be summarized as follows. Let A and B be two finite arbitrary regions on the surface S_E. Let us assume that all phase points initially lie in A. If the system is mixing, and we let it evolve in time, the fraction of points which lie in A or B in the limit $t \to \pm\infty$ will equal the fraction of area S_E occupied by A or B, respectively.

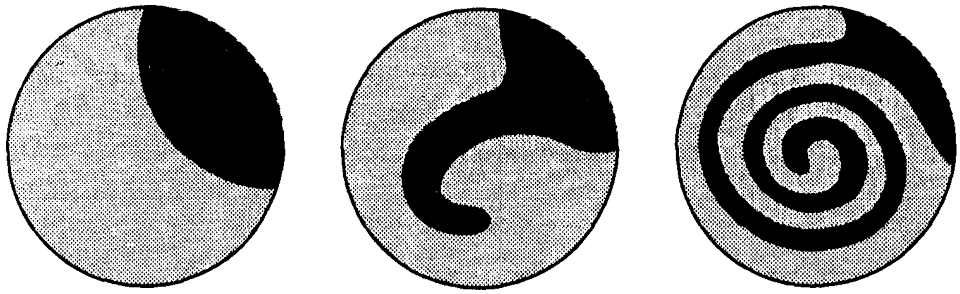


Fig. 6.2. Stirring oil and water together leads to uniformity, *on the average.*

An example of a discrete dynamical system which is mixing is the Baker's map. The dynamics evolves on a unit square, $0 \leq p \leq 1$ and $0 \leq q \leq 1$. The state points evolve in discrete time steps and change value in a discontinuous manner. The dynamical evolution is governed by an "alphabet" with two letters, 0 and 1, and the set, $\{S\}$, of all possible infinite sequences of letters. Each infinite sequence has the form $S = (\ldots, S_{-2}, S_{-1}, S_0, S_1, S_2 \ldots)$, where $S_k = (0 \text{ or } 1)$ and $k = (0, \pm 1, \pm 2, \ldots)$, and corresponds to a state point in the two-dimensional phase space. Each sequence maps onto the unit square according to the rules,

$$p = \sum_{k=0}^{-\infty} S_k 2^{k-1} = \frac{S_0}{2} + \frac{S_{-1}}{4} + \frac{S_{-2}}{8} + \cdots \quad \text{and}$$
$$q = \sum_{k=1}^{\infty} S_k 2^{-k} = \frac{S_1}{2} + \frac{S_2}{4} + \frac{S_3}{8} + \cdots . \tag{6.115}$$

Thus, if all $S_k = 0$, then $p = q = 0$, and if all $S_k = 1$, then $p = q = 1$ since $\sum_{k=1}^{\infty} (\frac{1}{2})^k = 1$. All other cases also lie on the unit square, $0 \leq p \leq 1$ and $0 \leq q \leq 1$.

The dynamics is introduced into the phase space by means of the Bernoulli shift, U, which is defined so that $US_k = S_{k+1}$. That is, the operator, U, acting on a sequence, S, shifts each element to the right one place. The shift acting on the sequence, S, is equivalent to the following transformation (the Baker's transformation) on the unit square:

$$U(p, q) = \begin{cases} (2p, \frac{1}{2}q), & 0 \leq p \leq \frac{1}{2} \\ (2p - 1, \frac{1}{2}q + \frac{1}{2}), & \frac{1}{2} \leq p \leq 1. \end{cases} \tag{6.116}$$

The inverse transformations is

$$U^{-1}(p, q) = \begin{cases} (\frac{1}{2}p, 2q), & 0 \leq q \leq \frac{1}{2} \\ (\frac{1}{2}p + \frac{1}{2}, 2q - 1), & \frac{1}{2} \leq q \leq 1. \end{cases} \tag{6.117}$$

The Jacobian of the transformation is equal to one. Therefore, the mapping, U, is area-preserving. Let us now look at how the probability density evolves under the action of the shift, U. Let $\rho_0(p,q)$ be the initial probability density and let us assume that it is continuous and smooth. After we allow U to act n times, we obtain

$$\rho_n(p,q) = U^n \rho_0(p,q) = \rho_0(U^{-n}p, U^{-n}q). \tag{6.118}$$

More explicitly,

$$\rho_{n+1}(p,q) = \begin{cases} \rho_n(\frac{1}{2}p, 2q), & 0 \le q \le \frac{1}{2} \\ \rho_n(\frac{1}{2}p + \frac{1}{2}, 2q-1), & \frac{1}{2} \le q \le 1 \end{cases} \tag{6.119}$$

The time evolution operator, U, is an example of a Frobenius–Perron operator [27] and [28].

The effect of the Baker's transformation is to stretch an initial area element into filaments throughout the unit square, much as a baker does in kneading dough. Note that whenever $S_0 = 0$ the point corresponding to the sequence, S, will lie to the left of $p = \frac{1}{2}$ and when $S_0 = 1$ it will lie to the right of $p = \frac{1}{2}$. Therefore, points corresponding to sequences with 0 and 1 distributed at random in the positions, S_k, will be shifted to the right or left of $p = \frac{1}{2}$ by U at random. If initially the probability density is $\rho_0(p,q) = 0$ for $0 \le p \le \frac{1}{2}$ and $0 \le q \le 1$ and $\rho(p,q) = 2$ for $\frac{1}{2} \le p \le 1$ and $0 \le q \le 1$, then the probability density at times $n = 1, 2, 3$, are shown in Fig. 6.3.

As we have seen above, there is an element of randomness in the position of a point in the p direction. Let us look at the reduced probability density, $\phi(p)$, in the p direction. The quantity $\phi_n(p)dp$ is the probability of finding a point in the interval $p \to dp$ at 'time' n. It is defined as $\phi_n \equiv \int_0^1 dq \rho_n(p,q)$. Using Eq. (6.119), $\phi_{n+1}(p)$ becomes

$$\phi_{n+1}(p) = \frac{1}{2}\phi_n\left(\frac{p}{2}\right) + \frac{1}{2}\phi_n\left(\frac{p}{2} + \frac{1}{2}\right). \tag{6.120}$$

The reduced probability evolves in a Markovian manner. We can show that $\lim_{n\to\infty}\phi_n(p) = 1$ and, therefore, that the reduced or coarse-grained probability

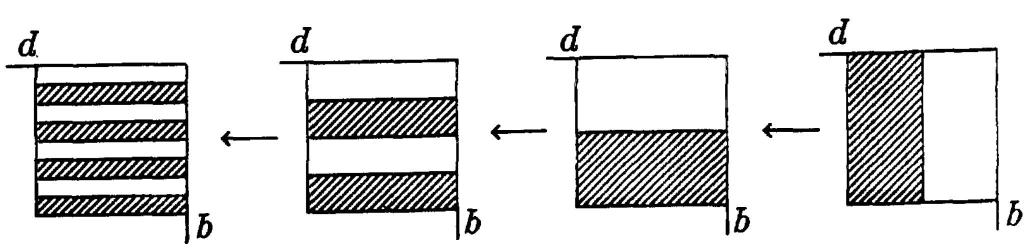


Fig. 6.3. Evolution of an initial probability under the action of the Baker's map.

density approaches a constant. If we iterate Eq. (6.120), we obtain

$$\phi_n(p) = \frac{1}{2^n}\sum_{k=0}^{2^n-1}\phi_0\left(\frac{p}{2^n}+\frac{k}{2^n}\right). \tag{6.121}$$

For a continuous and smooth function, $\phi_0(p)$, we obtain

$$\lim_{n\to\infty}\phi_n(p) = \lim_{n\to\infty}\int_0^{1-1/2^n} dy\,\phi_0\left(\frac{p}{2^n}+y\right) = \int_0^1 dy\phi_0(y) = 1, \tag{6.122}$$

where we have let $y = k2^{-n}$. Notice that for $n \to -\infty, \phi_n(p)$ will *not* approach a constant. However, a reduced probability density, defined in terms of the variable q, does. Therefore, the Baker's transformation exhibits irreversibility in a course-grained sense.

■ **EXERCISE 6.8.** Compute the trace of the Baker map, $\hat{U}^n$.

Answer: Let us denote $\hat{U}^n(p,q) = (p^n(p,q), q^n(p,q))$, where $p^n(p,q)$ and $q^n(p,q)$ are functions of p and q. The trace of U^n can be written

$$\mathrm{Tr}\,\hat{U}^{\,n} = \int_0^1 dp\int_0^1 dp\delta(p - p^n(p,q))\delta(q - q^n(p,q)). \tag{1}$$

Before we evaluate Eq. (1), let us note the following property of the Dirac delta function. Let us consider a function, $f(x)$, which has zeros at points $x_{0,k}$ (where $k = 1, 2, \ldots, M$), so that $f(x_{0,k}) = 0$. Then

$$\delta(f(x)) \equiv \sum_{k=1}^{M}\frac{\delta(x - x_{0,k})}{|f'(x_{0,k})|}, \tag{2}$$

where $f'(x) = (df/dx)$.

We now can evaluate the trace of $\hat{U}^n$. Notice that the delta functions will give contributions when $p^n = p$ and $q^n = q$. That is, for all 2^n nth-order periodic *points* of the map, $\hat{U}^n$. First note that $(dp_n/dp_0) = 2^n$ and $(dq_n/dq_0) = (1/2^n)$. Thus,

$$\begin{aligned}\mathrm{Tr}\,\hat{U}^n &= \sum_{\textit{Period n points}}\left|\frac{dp_n}{dp_0} - 1\right|^{-1}\left|\frac{dq_n}{dq_0} - 1\right|^{-1} = 2^n(2^n-1)^{-1}\left(1-\frac{1}{2^n}\right)^{-1} \\ &= \left(1-\frac{1}{2^n}\right)^{-2} = \sum_{m=0}^{\infty}(m+1)\left(\frac{1}{2^m}\right)^n \end{aligned} \tag{3}$$

(cf. Ref. 28). The trace of U^n is equal to the sum of the eigenvalues of U^n.

▶ S6.E. Anharmonic Oscillator Systems [4]

The study of anharmonic oscillator systems has long been important in statistical mechanics in connection with the theory of heat transport in solids [29]. One would like to know the mechanism of heat conduction. If heat is added to a harmonic lattice and divided unequally between the normal modes, there is no way for the system to reach equilibrium because the normal modes do not interact. However, if slight anharmonicities exist in the lattice, it was expected that equipartition of energy would occur and that the system would thus reach equilibrium.

In 1955, Fermi, Pasta, and Ulam [30] conducted a computer experiment intending to show this. They studied a system of 64 oscillators with cubic and broken linear coupling. They found that when energy was added to a few of the lower modes there was no tendency for the energy to spread to the other modes. This behavior is quite different from what one would expect if the anharmonic oscillator system were an ergodic system. Then one expects the system to reach a stationary state in which all states with the same energy would be equally probable, and one expects to see energy sharing among the modes.

The type of behavior that Fermi, Pasta, and Ulam observed is now fairly well understood in terms of a theorem due to Kolmogorov [31], Arnold [32], and Moser [33] (commonly called the KAM theorem). The theorem states that for a system with weak anharmonic coupling (which satisfies the conditions of the KAM theorem), most of the energy surface will be composed of invariant tori and the system will exhibit behavior in many respects similar to that of an unperturbed harmonic oscillator system. The energy surface will not be metrically transitive. As the coupling is increased, however, the invariant regions of phase space break down and at some point one expects to see a sharp transition to chaotic behavior and something similar to equipartition of energy between the modes. (True equipartition requires ergodicity, and it is not clear that anharmonic oscillator systems are ergodic above the transition energy.)

There is now a variety of nonlinear oscillator systems which have been studied and which exhibit a transition from stable to chaotic behavior as certain parameters are changed [4]. Henon and Heiles [34] studied the bounded motion of orbits for a system with two degrees of freedom governed by the Hamiltonian

$$H = \tfrac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2) + q_1 q_2^2 - \tfrac{1}{3}q_1^3. \tag{6.123}$$

The trajectories move in a four-dimensional phase space but are restricted to a three-dimensional surface because the total energy is a constant of the motion. It is possible to study a two-dimensional cross section of the three-dimensional energy surface. For example, we can consider the surface $q_2 = 0$ and look at a trajectory each time it passes through the surface with positive velocity $p_2 > 0$. It is then possible to plot successive points of the trajectory $(q_2 = 0, p_2 > 0)$ in the p_1, q_1 plane. If the only constant of motion is the total energy, E, then the points should be free to wander through the region of the p_1, q_1 plane

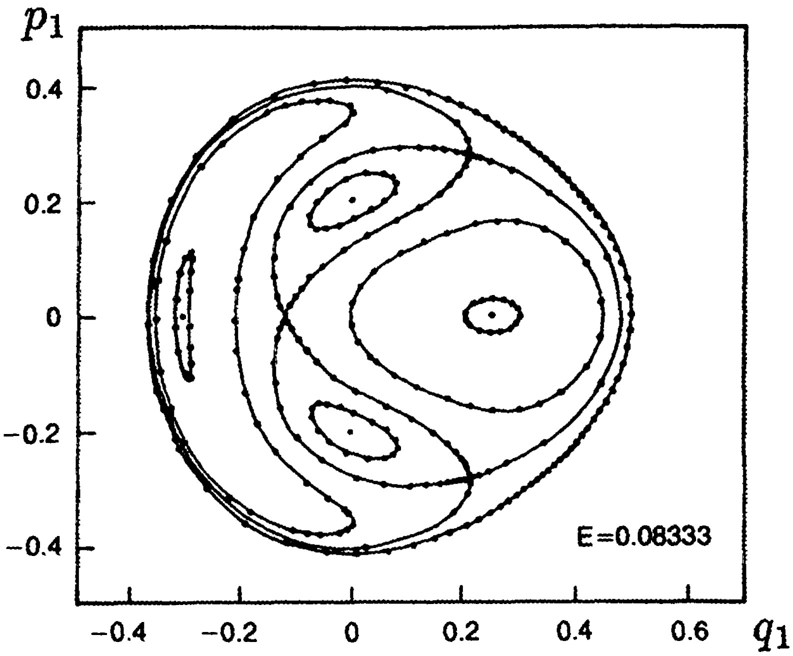


Fig. 6.4. Henon–Heiles result for $E = 0.08333$. (Based on Ref 34.)

corresponding to the energy surface. The motion we see will appear to be quite similar to ergodic motion. If there is an additional constant of the motion, the points will lie on a smooth curve in the p_1, q_1 plane.

Henon and Heiles studied trajectories whose motion was governed by Eq. (6.123) for a variety of energies. The results are sketched in Fig. 6.4. For an energy, $E = 0.08333$, they found only smooth curves, indicating that to computer accuracy there was an additional constant of the motion. Each closed curve in Fig. 6.4 corresponds to one trajectory. The three points of intersection of lines are hyperbolic fixed points, and the four points surrounded by curves are elliptic fixed points [4]. However, at an energy $E = 0.12500$, the picture begins to break down (cf. Fig. 6.5). Each closed curve in Fig. 6.5 corresponds to one trajectory. The five islands correspond to one trajectory, and the random dots outside the closed curve correspond to one trajectory. At an energy of $E = 0.16667$, almost no stable motion remains (cf. Fig. 6.6). A single trajectory is free to wander over almost the entire energy surface. In a very small energy range the system has undergone a transition from stable to chaotic behavior. Additional studies of the Henon–Helies system [35, 36] have shown that trajectory points move apart linearly in the stable regions, whereas they move apart exponentially in the chaotic regions.

The change from stable to chaotic behavior sets in rather abruptly. This has been understood in terms of an overlapping of resonances in the system. The Hamiltonian for a general anharmonic system with two degrees of freedom can be written in terms of action angle variables in the form

$$H = H_0(J_1, J_2) + \lambda V(J_1, J_2, \phi_1, \phi_2) \qquad (6.124)$$

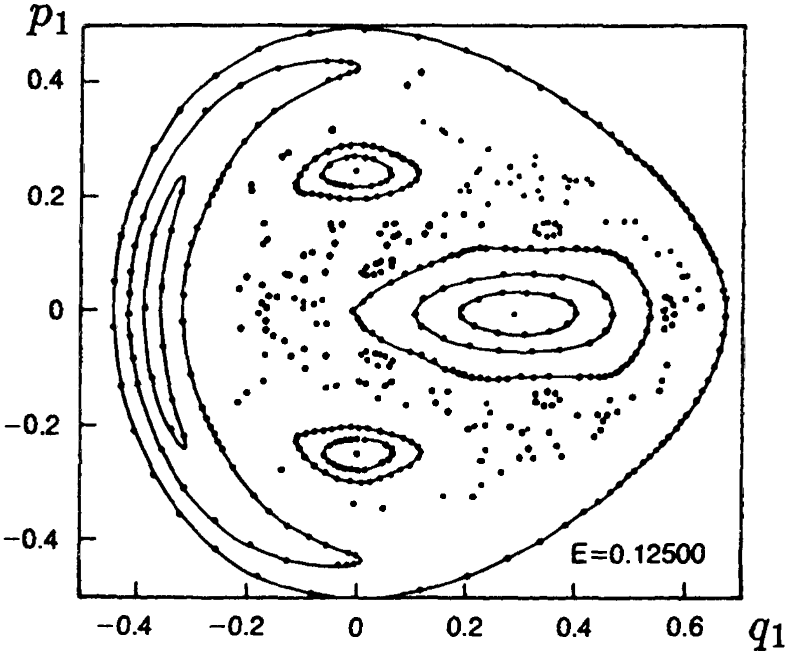


Fig. 6.5. Henon–Heiles result for $E = 0.12500$. (Based on Ref 34.)

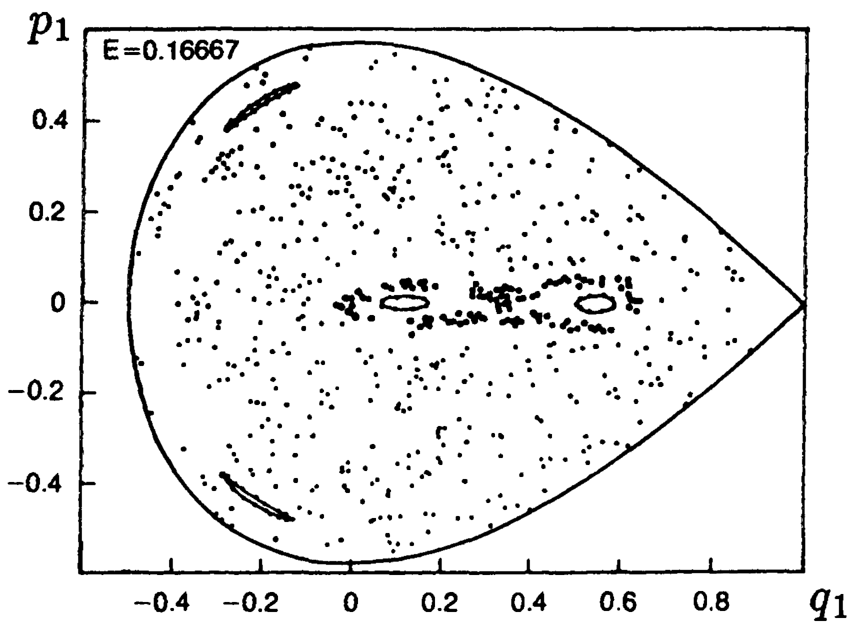


Fig. 6.6. Henon–Heiles result for $E = 0.16667$. (Based on Ref 34.)

by means of the transformation

$$p_i = -(2m\omega J_i)^{1/2}\sin\phi_i \quad \text{and} \quad q_i = \left(\frac{2J_i}{m\omega}\right)^{1/2}\cos\phi_i.$$

The function $H_0(J_1, J_2)$ has a polynomial dependence on the action variables J_1 and J_2 (not merely a linear dependence as would be the case for a harmonic system) and no angle dependence, while $V(J_1, J_2, \phi_1, \phi_2)$ depends on both action and angle variables and is a periodic function of the angles. When $\lambda = 0$ the action variables will be constants of the motion, and the angles ϕ_1 and ϕ_2 will change in time according to the equations

$$\phi_i = \omega_i(J_1, J_2)t + \phi_{i,0} \tag{6.125}$$

for $(i = 1, 2)$ where

$$\omega_i(J_1, J_2) = \frac{\partial H_0}{\partial J_i}. \tag{6.126}$$

For the anharmonic case, the frequencies $\omega_i(J_1, J_2)$ will be continuous because they depend on the action variables, even for two degrees of freedom. This continuous dependence on the action variables is quite different from a harmonic oscillator system where the frequencies, ω_i, are constant.

For systems which satisfy the conditions of the KAM theorem (namely, small λ and nonzero Hessian, det $|\partial^2 H_0/\partial_{J_i}\partial_{J_j}| \neq 0$ for $(i,j) = 1$ and 2), only a very small region of phase space, the resonance regions, will exhibit chaotic behavior. The rest of the phase space will correspond to stable motion. If one tries to construct new action variables $\mathscr{J}_i$ which are constants of the motion when $\lambda \neq 0$ but small, one finds that this can be done for most of the phase space, except for the resonance zones. In the resonance zones, perturbation expansions for $\mathscr{J}_i$ diverge. Let us construct a perturbation expansion [37] for the action variables $\mathscr{J}_i$ to lowest order in λ. Let us consider a Hamiltonian of the form

$$H = H_0(J_1, J_2) + \lambda \sum_{n_1, n_2} V_{n_1,n_2}(J_1, J_2)\cos(n_1\phi_1 + n_2\phi_2) \tag{6.127}$$

and let us introduce the generator

$$F(\mathscr{J}_1, \mathscr{J}_2, \phi_1, \phi_2) = \mathscr{J}_1\phi_1 + \mathscr{J}_2\phi_2 + \sum_{n_1, n_2} B_{n_1,n_2}\sin(n_1\phi_1 + n_2\phi_2) \tag{6.128}$$

of a canonical transformation from variables J_i, ϕ_i to variables $\mathscr{J}_i$, Φ_i, such that the variables $\mathscr{J}_i$ are constants of the motion. Then

$$J_i = \frac{\partial F}{\partial \phi_i} = \mathscr{J}_i + \sum_{n_1,n_2} n_i B_{n_1,n_2}\cos(n_1\phi_1 + n_2\phi_2) \tag{6.129}$$

for $i = 1, 2$ and

$$\Phi_i = \frac{\partial F}{\partial \mathscr{J}_i} \tag{6.130}$$

for $i = 1, 2$. If we substitute Eq. (6.129) into Eq. (6.127) and keep terms to lowest order in λ (this requires a Taylor series expansion of H_0), we obtain

$$H = H_0(\mathscr{J}_1, \mathscr{J}_2) + \sum_{n_1, n_2} \{(n_1\omega_1 + n_2\omega_2)B_{n_1,n_2} + \lambda V_{n_1,n_2}\} \cos(n_1\phi_1 + n_2\phi_2). \tag{6.131}$$

To lowest order in λ, $\mathscr{J}_1$ and $\mathscr{J}_2$ will be constants of motion if we choose

$$B_{n_1,n_2} = \frac{-\lambda V_{n_1,n_2}}{(n_1\omega_1 + n_2\omega_2)}. \tag{6.132}$$

Then

$$H = H_0(\mathscr{J}_1 \mathscr{J}_2) + O(\lambda^2) \tag{6.133}$$

and

$$\mathscr{J}_1 = J_1 + \sum_{n_1,n_2} \frac{\lambda V_{n_1,n_2}}{(n_1\omega_1 + n_2\omega_2)} \cos(n_1\phi_1 + n_2\phi_2) + O(\lambda^2) \tag{6.134}$$

Note, however, that since ω_1 and ω_2 are functions of J_1 and J_2, there are values of J_1 and J_2 for which the denominator $(n_1\omega_1 + n_2\omega_2)$ can be zero, and the perturbation expansion becomes meaningless. Indeed, as long as

$$|n_1\omega_1 + n_2\omega_2| \leq \lambda V_{n_1,n_2}, \tag{6.135}$$

the perturbation expansion will diverge and $\mathscr{J}_i$ is not a well-behaved invariant. This region of phase space is called the resonance zone and $(n_1\omega_1 + n_2\omega_2) = 0$ is the resonance condition. It is in the resonance zones that one observes chaotic behavior.

If the regions of phase space which contain resonances, and a small region around each resonance, are excluded from the expansion for $\mathscr{J}_1$, then one can have a well-behaved expression for $\mathscr{J}_1$. Thus, one can exclude regions which satisfy the condition

$$[n_1\omega_1(J_1, J_2) + n_2\omega_2(J_1, J_2)] \ll \lambda V_{n_1,n_2}.$$

For smooth potentials, V_{n_1,n_2} decreases rapidly for increasing n_1 and n_2. Thus for increasing n_1 and n_2, ever smaller regions of the phase space are excluded.

Kolmogorov, Arnold, and Moser proved that as $\lambda \to 0$ the amount of excluded phase space approaches zero. The idea behind their proof is easily seen in terms of a simple example [38]. Consider the unit line (a line of length one). It contains an infinite number of rational fractions, but they form a set of measure zero on the line. If we exclude a region

$$\left(\frac{m}{n}-\frac{\varepsilon}{n^3}\right) \leq \frac{m}{n} \leq \left(\frac{m}{n}-\frac{\varepsilon}{n^3}\right)$$

around each rational fraction, the total length of the unit line that is excluded is

$$\sum_{n=1}^{\infty}\sum_{m=1}^{n}\left(\frac{2\varepsilon}{n^3}\right) = 2\varepsilon\sum_{n=1}^{\infty}\frac{1}{n^2} = \frac{\varepsilon\pi^2}{3}\underset{\varepsilon\to 0}{\longrightarrow} 0.$$

Thus, for small λ, we can exclude the resonance regions in the expansion of $\mathscr{J}_1$ and still have a large part of the phase space in which $\mathscr{J}_1$ is well-defined and invariant tori can exist.

Walker and Ford [37] give a simple exactly soluble example of the type of distortion that a periodic potential can create in phase space. It is worth repeating here. They consider a Hamiltonian of the type

$$H = H_0(J_1, J_2) + \lambda J_1 J_2 \cos(2\phi_1 - 2\phi_2) = E, \tag{6.136}$$

where

$$H_0(J_1, J_2) = J_1 + J_2 - J_1^2 - 3J_1J_2 + J_2^2. \tag{6.137}$$

For this model, there are two constants of the motion, namely, the total energy $H = E$ and

$$I = J_1 + J_2. \tag{6.138}$$

Therefore, we do not expect to see any chaotic behavior for this system. However, the unperturbed phase space will still be distorted when $\lambda \neq 0$. The frequencies ω_i for this model are given by

$$\omega_1 = \frac{\partial H_0}{\partial J_1} = 1 - 2J_1 - 3J_2 \tag{6.139}$$

and

$$\omega_2 = \frac{\partial H_0}{\partial J_2} = 1 - 3J_1 + 2J_2. \tag{6.140}$$

If we want the frequencies to remain positive, we must choose $0 \leq J_1 \leq \frac{5}{13}$ and $0 \leq J_2 \leq \frac{1}{13}$ and, therefore, $E \leq \frac{3}{13}$.

Let us plot trajectories for the Walker–Ford case $(q_2 = 0, p_2 > 0)$ (note that $q_i = (2J_i)^{1/2}\cos\phi_i$ and $p_i = -(2J_i)^{1/2}\sin\phi_i$). We find that for $\lambda = 0$ the trajectories trace out concentric circles in the p_1, q_1 plane. When the

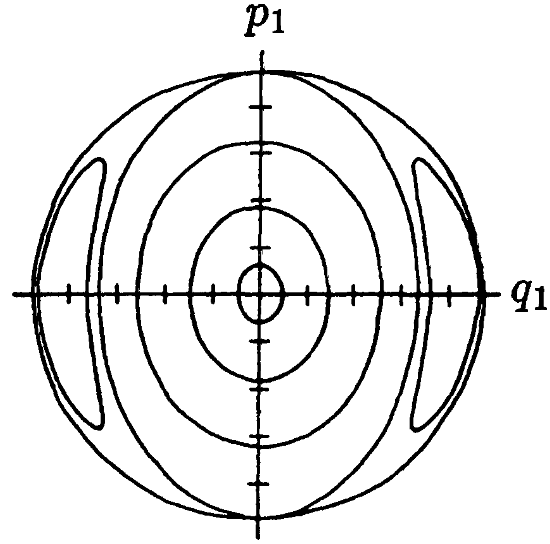


Fig. 6.7. Cross–section of the energy surface for the Hamiltonian, $H = J_1 + J_2 - J_1^2 - 3J_1J_2 + J_2^2 + \lambda J_1J_2\cos(2\phi_1 - 2\phi_2) = E$. There is no chaotic behavior. (Based on Ref. 37.)

perturbation is turned on ($\lambda \neq 0$), the phase space becomes highly distorted. If we set $\phi_2 = \frac{3}{2}\pi$ (this means $q_2 = 0, p_2 > 0$) and substitute Eq. (6.138) into Eq. (6.136), we obtain the following equation for the perturbed level curves:

$$(3 + \lambda\cos 2\phi_1)J_1^2 - (5I + \lambda I\cos 2\phi_1)J_1 + I + I^2 - E = 0. \tag{6.141}$$

They are sketched in Fig. 6.7. Most of the phase space is only slightly distorted from the unperturbed case. However, there is a region which is highly distorted and in which two elliptic fixed points (surrounded by orbits) and two hyperbolic fixed points appear [4]. The fixed points occur for values of J_i and ϕ_i such that $\dot{J}_1 + \dot{J}_2 = (\dot{\phi}_1 - \dot{\phi}_2) = 0$. If we use the fact that $\dot{J}_i = -\partial H/\partial\phi_i$ and $\dot{\phi}_i = \partial H/\partial J_i$ and condition $\phi_2 = 3\pi/2$, we find that the hyperbolic orbits occur when

$$J_1 = \frac{(5-\lambda)}{(1-\lambda)}J_2 \quad \text{and} \quad (\phi_1 - \phi_2) = 0 \quad \text{and} \quad \pi, \tag{6.142}$$

while the elliptic orbits occur for

$$J_1 = \frac{(5+\lambda)}{(1+\lambda)}J_2, \qquad (\phi_1 - \phi_2) = \frac{\pi}{2} \quad \text{and} \quad \frac{3\pi}{2}. \tag{6.143}$$

The first-order resonance condition for this model [cf. Eq. (6.135)] is $2\omega_1 - 2\omega_2 = 0$ or, from Eqs. (6.139) and (6.140), $J_1 = 5J_2$. Therefore, from Eqs. (6.142) and (6.143) we see that the distorted region of phase space lies in the resonance zone.

In general, for a Hamiltonian of the form

$$H = H_0(J_1, J_2) + \lambda V(J_1, J_2)\cos(n_1\phi_1 + n_2\phi_2) \qquad (6.144)$$

there will be no chaotic behavior because there is always an extra constant of motion,

$$I = n_2 J_1 - n_1 J_2. \qquad (6.145)$$

However, when the Hamiltonian is of the more general form given in Eq. (6.127), the extra constant of motion is destroyed and the resonance zones become more complicated and begin to overlap. When this occurs one begins to see chaotic behavior.

Walker and Ford study the example

$$H = H_0(J_1, J_2) + \lambda_1 J_1 J_2 \cos(2\phi_1 - 2\phi_2) + \lambda_2 J_1 J_2^{3/2} \cos(2\phi_1 - 3\phi_2), \quad (6.146)$$

where an extra cosine term has been added to Eq. (6.136). For this model there is no longer an extra constant of motion. There are two primary resonances which grow as λ_1 and λ_2 are increased. In Fig. 6.8, we sketch their results. For low energies there is no chaotic behavior (to computer accuracy). However, as the resonance zones grow and begin to overlap, the trajectories in the regions of overlap become unstable and begin to exhibit chaotic behavior. In Fig. 6.8 the dots correspond to a single trajectory.

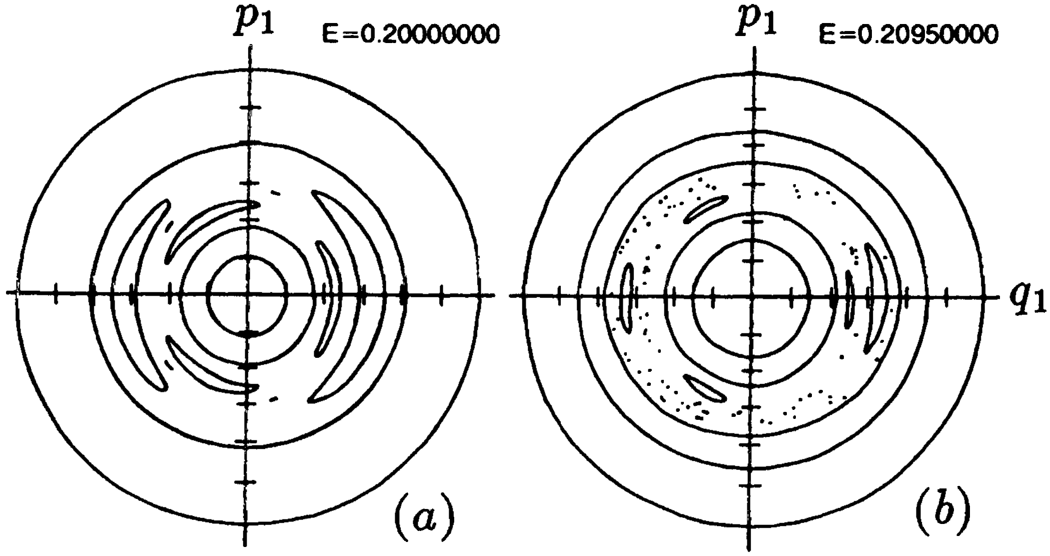


Fig. 6.8. Cross section of the energy surface for the Hamiltonian, $H = J_1 + J_2 - J_1^2 - 3J_1J_2 + J_2^2 + \lambda_1 J_1 J_2 \cos(2\phi_1 - 2\phi_2) + \lambda_2 J_1 J_2 \cos(2\phi_1 - 3\phi_2) = E$. (a) Phase space trajectories below the energy of primary resonance overlap. (b) Phase space trajectories above the energy of primary resonance overlap. When primary resonances overlap, large-scale chaos occurs in their neighborhood. (Based on Ref. 37.)

Thus, from these simple examples we see that the chaotic, or ergodiclike, behavior of phase space for the anharmonic oscillator system appears to be caused by the overlapping of resonances. If the energy surface is filled with resonance zones, as is often the case, then we expect chaotic behavior to set in at very low energy.

Anharmonic oscillator systems are a rather special type of system and their ergodicity has never been established, for obvious reasons. A completely different type of system is a system of hard spheres. For systems of hard spheres, ergodicity and mixing behavior have been established [39]. A proof that systems with Lennard-Jones types of potential are ergodic has never been given. However, when the number of degrees of freedom becomes large, the "regular" regions of the phase space appear to become relatively less important than the chaotic regions and statistical mechanics, which is built on the assumption that ergodicity appears to work perfectly for those systems.

The chaotic behavior illustrated in this section is indicative of unstable flow in phase space. Orbits in the chaotic region which initially neighbor one another move apart exponentially and may move to completely different parts of the energy surface. If we start with an ensemble of orbits in some region of phase space and assign a probability distribution to them, the probability distribution will spread on the energy surface, and we will become less certain about the actual state of the system. Systems with unstable flow have the potential of exhibiting decay to thermodynamic equilibrium: An initially localized probability distribution can spread and, in a coarse-grained sense, can fill the energy surface.

▶ S6.F. Newtonian Dynamics and Irreversibility [40, 41]

The instability and chaos that we have described in the baker map, Eq. (6.116), and that we have illustrated in the Henon–Heiles system appears to be a source of the irreversibility seen in nature. One of the great paradoxes of physics is the fact that Newton's equations are reversible, but much of nature evolves in an irreversible manner: Nature appears to have an "arrow of time." There is a new field of statistical physics which finally is resolving this paradox [40–44]. The resolution of the paradox is most easily seen in the spectral properties of chaotic maps such as the baker map. Individual trajectories in chaotic systems move apart exponentially and become impossible to compute even after a fairly short time. However, in such systems, smooth initial probability distributions generally relax to a smooth final distribution after some time. There are now several "reversible" chaotic maps for which a spectral decomposition can be obtained in terms of the decay rates and their associated eigenstates [28, 42, 43]. The decay rates are related to the Lyopounov exponents for the underlying chaos, and determine the physically observable decay properties of such systems. The spectral theory of these systems can be formulated outside of Hilbert space.

Considerable progress has also been made in understanding the emergence of irreversible behavior in unstable Hamiltonian systems, at least for the case when the dynamical phase space contains dense sets of resonances. For such systems a spectral theory can also be formulated outside the Hilbert space [45–46]. We don't have space to say more about this beautiful new area of statistical physics, but the cited references should give interested readers a fairly readable entrance to the field. Ref. 41 gives a historial overview.

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PROBLEMS

Problem 6.1. Consider a system of N uncoupled harmonic oscillators with Hamiltonian, $H = \sum_{i=1}^{N}(p_i^2/2m_i + k_i q_i^2/2)$. Assume that the system initially has a probability density $\rho(\mathbf{p}^N, \mathbf{q}^N, 0) = \prod_{i=1}^{N} \delta(p_i - p_{i0})\delta(q_i - q_{i0})$. Compute the probability density $\rho(\mathbf{p}^N, \mathbf{q}^N, t)$ at time t, where $\mathbf{p}^N = (p_1, \ldots, p_N)$ and $\mathbf{q}^N = (q_1, \ldots, q_N)$.

Problem 6.2. Consider a particle which bounces vertically in a gravitational field, as discussed in Exercise 6.1. Assume an initial probability distribution, $\rho(p,z,0) = \frac{10}{9}\delta(z)\Theta(1.0-p)\Theta(p-0.1)$($\Theta(x)$ is the Heaviside function; $\Theta(x)=1$ for $x>0$ and $\Theta(x)=0$ for $x<0$). What is $\rho'(J,\theta,0)$? Sketch $\rho(p,z,t)$ and $\rho'(J,\theta,t)$ for $t=0.4$, mass $m=1$, and gravitational acceleration $g=1$.

Problem 6.3. Consider a particle with mass $m=1$ moving in an infinite square well potential, $V(x)=0$ for $-1<x<1$ and $V(x)=\infty$ otherwise. Assume that initially the particle lies at $x=-1$ with momentum, $p=p_0$ for $0.1 \le p_0 \le 1.0$ in the positive x direction. (a) Find the solution of the Liouville equation in action-angle space at time t. (b) At what time does the initial distribution of points begin to break apart in (p,x) space?

Problem 6.4. For a noninteracting gas of N particles in a cubic box of volume $V=L^3$, where L is the length of the side of box, find the solution, $\rho(\mathbf{p}^{3N},\mathbf{q}^{3N},t)$, of the Liouville equation at time t, where $\mathbf{p}^{3N}=(\mathbf{p}_1,\ldots,\mathbf{p}_N)$ and $\mathbf{q}^{3N}=(\mathbf{q}_1,\ldots,\mathbf{q}_N)$ with $\mathbf{p}_i=(p_{ix},p_{iy},p_{iz})$ and $\mathbf{q}_i=(q_{ix},q_{iy},q_{iz})$. Assume periodic boundary conditions, and assume that the probability density at time $t=0$ is given by

$$\rho(\mathbf{p}^{3N}\cdot\mathbf{q}^{3N},0)=\left(\frac{\sqrt{\pi}}{2L}\right)^{3N}\prod_{i=1}^{N}\prod_{\alpha=x,y,z}e^{-p_{i\alpha}^2}\sin\left(\frac{\pi q_{i\alpha}}{L}\right)\quad \text{for}\quad 0\le q_{i\alpha}\le L.$$

Problem 6.5. Consider a system with one degree of freedom whose dynamics is governed by a Hamiltonian of the form $H(p,q)=\frac{1}{2}p^2+\frac{1}{4}q^4=E$, where E is the total energy. Assume that initially $\rho(p,q,0)=(1/\sqrt{\pi})\delta(p)e^{-q^2}$. Solve the Liouville equation for $\rho(p,q,t)$. (*Hint*: It is useful to first transform to action-angle variables. The solution involves elliptic functions.)

Problem 6.6. A two-level system has a Hamiltonian matrix

$$\begin{pmatrix} H_{1,1} & H_{1,2} \\ H_{2,1} & H_{2,2}\end{pmatrix}=\begin{pmatrix} 3 & 4i \\ -4i & -3\end{pmatrix},$$

where, for example, $H_{1,2}\equiv\langle 1|\hat{H}|2\rangle$. The density matrix at time $t=0$ is

$$\begin{pmatrix} \rho_{1,1}(0) & \rho_{1,2}(0) \\ \rho_{2,1}(0) & \rho_{2,2}(0)\end{pmatrix}=\begin{pmatrix} 1 & 0 \\ 0 & 0\end{pmatrix}.$$

(a) Find the density matrix

$$\begin{pmatrix} \rho_{1,1}(t) & \rho_{1,2}(t) \\ \rho_{2,1}(t) & \rho_{2,2}(t)\end{pmatrix}$$

at time t. (b) What is the probability to be in the state $|1\rangle$ at time $t=0$? At time t? For simplicity, assume that $\hbar=1$.

Problem 6.7. An atom with spin 1 has a Hamiltonian $\hat{H}=AS_z^2+B(\hat{S}_x^2-\hat{S}_y^2)$, where $\hat{S}_x,\hat{S}_y$, and $\hat{S}_z$ are the x,y, and z components of the spin angular momentum operator. In the basis of eigenstates of the operator, $\hat{S}_z$, these three operators have the matrix representations

$$\hat{S}_z=\hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1\end{pmatrix},\quad \hat{S}_x=\frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0\end{pmatrix},\quad\text{and}\quad \hat{S}_y=\frac{\hbar}{i\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0\end{pmatrix}.$$

(a) Write the density matrix (in the basis of eigenstates of $\hat{S}_z$) at time $t = 0$ for two different cases: (i) The atom is initially in an eigenstate of $\hat{S}_z$ with eigenvalue $+\hbar$; (ii) the atom is initially in an eigenstate of $\hat{S}_x$ with eigenvalue $+\hbar$. (b) Compute the density matrix (in the basis of eigenstates of $\hat{S}_z$) at time t for each of the two cases in (a). (c) Compute the average z component of spin at time t for the two cases in (a).

Problem 6.8. Consider a harmonic oscillator with Hamiltonian $\hat{H} = (1/2m)\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2$. Assume that at time $t = 0$ the oscillator is in an eigenstate of the momentum operator, $\hat{\rho}(0) = |p_0\rangle\langle p_0|$. (a) Write the Liouville equation in the momentum basis. (b) Compute the density matrix $\langle p'|\hat{\rho}(t)\rangle|p\rangle$, at time t.

Problem S6.1. Locate all period-3 points of the Baker map in the (p, q) plane.