Towards statistical mechanics

Phase space volumes are conserved by Hamiltonian dynamics

We can use many nearby initial conditions to define a region in phase space with some \( (2N) \)-dimensional volume. Under the dynamical evolution from each of these initial conditions this region (defined by \( \{q_k(t)\}, \{p_k(t)\} \)) will evolve. For Hamiltonian dynamics the \textit{volume is conserved}.

This is illustrated by the following sketch and argument for a 2-dimensional phase space:

Under evolution for a small time \( \delta t \) the area \( \Delta A(t) = \Delta q \Delta p \) evolves into an area

\[
\Delta A(t + \delta t) \simeq \Delta q \left( 1 + \frac{\partial \dot{q}}{\partial q} \delta t \right) \Delta p \left( 1 + \frac{\partial \dot{p}}{\partial p} \delta t \right) = \Delta q \Delta p \left[ 1 + \left( \frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} \right) \delta t + O(\delta t^2) \right]
\]

(The area is still approximately the \( q \)-width times the \( p \)-height, since the distortion of the rectangle is small—angles of order \( \delta t \) away from right-angles. The \( q \)-width changes because \( \dot{q} \) is a function of \( q \), etc. The dependence of \( \dot{q} \) on \( p \) and \( \dot{p} \) on \( q \) just gives the small rotations of the sides that do not affect the area to \( O(\delta t) \).)

This gives

\[
\frac{d\Delta A}{dt} = (\vec{\nabla}_{\text{ph}} \cdot \vec{v}_{\text{ph}}) \Delta A
\]

We can define the “velocity” of a point \((q, p)\) in a 2-dimensional phase space (with unit vectors \((\hat{q}, \hat{p})\), as well as the phase space “gradient”:

\[
\vec{v}_{\text{ph}} \equiv \dot{q} \hat{q} + \dot{p} \hat{p}, \quad \text{and} \quad \vec{\nabla}_{\text{ph}} \equiv \frac{\partial}{\partial q} + \frac{\partial}{\partial p}.
\]

The divergence of the phase space velocity is zero for Hamiltonian dynamics:

\[
\vec{\nabla}_{\text{ph}} \cdot \vec{v}_{\text{ph}} = \frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} = \frac{\partial}{\partial q} \frac{\partial H}{\partial p} + \frac{\partial}{\partial p} \left( - \frac{\partial H}{\partial q} \right) = 0.
\]

The same argument would work in general \( 2N \)-dimensional phase space with

\[
\vec{v}_{\text{ph}} \cdot \vec{v}_{\text{ph}} = \sum_{k=1}^{N} \left( \frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} \right),
\]
again zero for Hamiltonian dynamics. Thus, \((\Delta A)/dt = 0\); phase space volumes are conserved under Hamiltonian dynamics. Hand and Finch Appendix 5A presents a more mathematical proof of this result.

**Liouville’s theorem**

In statistical mechanics, where we are dealing with typically \(10^{23}\) interacting particles, we can’t hope to follow the precise dynamics of each particle. Instead we introduce the phase space density \(\rho\{\{q_k\}, \{p_k\}, t\}\) which is the probability density of finding the system near phase space point \((\{q_k\}, \{p_k\})\). Precisely, the probability of finding the system with phase space coordinates in the range \(q_1\) to \(q_1 + dq_1\), \(q_2\) to \(q_2 + dq_2\), \ldots \(p_N\) to \(p_N + dp_N\) is \(\rho(\{q_k\}, \{p_k\}, t) dq_1 dq_2 \ldots dp_N\). Probability is defined in terms of an ensemble: a collection of a large number \(N_E\) copies of the system. The probability of something is then the fraction of members of the ensemble with that something.

Liouville’s theorem states that the phase space density is constant evolving along the flow

\[
\frac{d\rho}{dt} = \sum_k \frac{\partial \rho}{\partial q_k} \frac{dq_k}{dt} + \sum_k \frac{\partial \rho}{\partial p_k} \frac{dp_k}{dt} + \frac{\partial \rho}{\partial t} = \vec{v}_{ph} \cdot \vec{\nabla}_{ph} \rho + \frac{\partial \rho}{\partial t} = 0, \tag{6}
\]

with \(d/dt\) the total derivative coming from the time dependence of \(\{q_k\}\) and \(\{p_k\}\) (the motion of the phase space point at velocity \(\vec{v}_{ph}\) through a spatially varying \(\rho\)), as well as any explicit time dependence \(\partial \rho / \partial t\).

This follows directly from the fact that volumes in phase space are conserved, and that the volumes are defined by a fixed set of members of the ensemble. We can also proceed more formally:

**Conservation of probability:** probability of finding the system in some phase space volume only changes by the flow of probability into the volume

\[
\frac{\partial}{\partial t} \int_V \rho dV = - \int_S (\rho \vec{v}_{ph}) \cdot d\vec{S} \tag{7}
\]

where \(S\) is the surface enclosing the phase space volume \(V\). The divergence theorem gives

\[
\int_V \left[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}_{ph}) \right] dV = 0. \tag{8}
\]

Since this is true for any volume we must have

\[
\frac{\partial \rho}{\partial t} + \vec{v}_{ph} \cdot \vec{\nabla} \rho + \rho \vec{v}_{ph} \cdot \vec{v}_{ph} = 0. \tag{9}
\]

known as the continuity equation (here for the probability density). Expanding the derivative

\[
\frac{\partial \rho}{\partial t} + \vec{v}_{ph} \cdot \vec{\nabla} \rho + \rho \vec{v}_{ph} \cdot \vec{v}_{ph} = 0. \tag{10}
\]

So far we have only used the fact that probability is conserved (its integral is 1, a constant).

**Hamiltonian dynamics:** Now we put in Hamiltonian dynamics so that \(\vec{v}_{ph} = 0\). This gives Eqn. 6 above, Liouville’s theorem.
**Connection with statistical mechanics**

This is not really part of the present class, but is to connect with a statistical mechanics class, e.g. Ph127.

We associate equilibrium in statistical mechanics ("thermodynamic equilibrium") with a phase space density that is time independent at each point in phase space

\[
\frac{\partial \rho}{\partial t} = 0. \tag{11}
\]

Together with Liouville's theorem this gives

\[
\vec{v}_{ph} \cdot \nabla \rho = 0 \tag{12}
\]

i.e. the density does not change moving along a phase-space trajectory. Now if we assume *ergodicity*, that a single phase space trajectory visits the vicinity of each *accessible* point in phase space (that is, each point consistent with the conserved energy and any other conserved quantities) we argue that \( \rho \) is the same at every (accessible) point of phase space. This is the statement of *equal probability* for every accessible state that is the fundamental starting point of statistical mechanics.

The assumption of ergodicity is a big assumption, and most "toy" Hamiltonian systems we deal with (e.g. a collection of simple harmonic oscillators) are not ergodic. Some simple chaotic Hamiltonian systems can be shown to be ergodic; many are not. Whether typical physical systems we deal with in statistical mechanics/thermodynamics are ergodic (or are sufficiently ergodic for the argument to be valid), and whether the whole discussion is even relevant to the equal probability assumption, is still a matter of study. The systems of interest in statistical mechanics may never be entirely isolated from the rest of the universe as we have assumed, for example, and the equal probabilities might arise from small perturbations to the systems.
Towards quantum mechanics

Schrödinger’s equation

The pioneers of quantum mechanics were well versed in classical mechanics, and the Hamiltonian approach provided a fruitful path towards guessing how to formulate quantum mechanics. In quantum mechanics a single particle is described by a complex wave function \( \Psi(\vec{r}) \) such that the probability of finding the particle at \( \vec{r} \) is \( |\Psi(\vec{r})|^2 \). The possible energies and wave functions are determined by solving the equation

\[
\hat{H}(\vec{r}, -i\hbar\vec{\nabla})\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{13}
\]

where the operator \( \hat{H}(\vec{r}, -i\hbar\vec{\nabla}) \) is given by taking the classical Hamiltonian \( H(\vec{r}, \vec{p}) \) and making the replacement \( \vec{p} \to -i\hbar\vec{\nabla} \). For example

\[
p^2 \to (-i\hbar\vec{\nabla})^2 = -\hbar^2 \nabla^2, \tag{14}
\]

so that for the particle in a potential \( V(\vec{r}) \) Schrödinger’s equation is

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}) + V(\vec{r})\Psi(\vec{r}) = E\Psi(\vec{r}). \tag{15}
\]

The one-dimensional version often encountered first in a quantum mechanics class is

\[
-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x). \tag{16}
\]

Mathematics then shows that for a particle in a potential \( V(\vec{r}) \) there are bound states with a discrete set of possible energies \( E_n < 0 \) (assuming \( V(\vec{r} \to \infty) = 0 \)) and also a continuum set of energies \( E_n > 0 \) for unbound states, with corresponding wave functions \( \Psi_n(\vec{r}) \) (localized to the region of the potential well for the bound states, extending to infinity as plane waves for the unbound states). The \( E_n \) are the eigenvalues and the \( \Psi_n(\vec{r}) \) the eigenvectors of the differential equation eigenvalue problem formed by Eq. (15) and the boundary conditions (e.g. that the wave function remains finite at infinity).

As a more complicated example consider a particle of mass \( m \) and charge \( q \) in an electromagnetic field. As discussed in the notes to Lecture 2, the Lagrangian (in the Newtonian limit) is

\[
L = \frac{1}{2}mv^2 - q\Phi(\vec{r}, t) + q\vec{v} \cdot \vec{A}(\vec{r}, t), \tag{17}
\]

with \( \phi, \vec{A} \) the scalar and vector potentials. The canonical momentum conjugate to \( \vec{r} \) is

\[
\vec{p} = \frac{\partial L}{\partial \vec{v}} = m\vec{v} + q\vec{A}. \tag{18}
\]

Note that the momentum is no longer \( m\vec{v} \). The Hamiltonian is

\[
H = \vec{p} \cdot \vec{v} - L = \frac{1}{2}mv^2 + q\Phi(\vec{r}, t), \tag{19}
\]

and the magnetic potential drops out – perhaps not too surprising since the magnetic field does no work on the charge. Now expressed in terms of the momentum we have

\[
H(\vec{r}, \vec{p}) = \frac{[\vec{p} - q\vec{A}(\vec{r}, t)]^2}{2m} + q\Phi(\vec{r}, t). \tag{20}
\]

The quantum problem is given by \( \vec{p} \to -i\hbar\vec{\nabla} \) as before.
Time dependence

In classical mechanics we can ask for the time dependence of physical quantities such as the angular momentum \( \vec{L} = \sum_i \vec{r}_i \times \vec{p}_i \) that depend on the positions and momenta. Let’s look at such a physical “observable” \( O(\{q_k\}, \{p_k\}, t) \) that depends on the coordinates and the conjugate momenta, and maybe time. The full time dependence of the observable as the particles move under Hamiltonian dynamics is

\[
\frac{dO}{dt} = \sum_{k=1}^{N} \left( \frac{\partial O}{\partial q_k} \dot{q}_k + \frac{\partial O}{\partial p_k} \dot{p}_k \right) + \frac{\partial O}{\partial t}.
\]  

\( (21) \)

I now introduce the general notation of a Poisson bracket:

Definition For functions \( A(\{q_k\}, \{p_k\}, t) \), \( B(\{q_k\}, \{p_k\}, t) \), the Poisson bracket is defined as

\[
[A, B]_{q,p} = \sum_{k=1}^{N} \left( \frac{\partial A}{\partial q_k} \frac{\partial B}{\partial p_k} - \frac{\partial A}{\partial p_k} \frac{\partial B}{\partial q_k} \right).
\]  

\( (22) \)

Using the Hamilton equations of motion for \( \dot{q}_k, \dot{p}_k \) in Eq. \( (21) \) gives

\[
\frac{dO}{dt} = [O, H]_{q,p} + \frac{\partial O}{\partial t}.
\]  

\( (23) \)

In particular, if \( \partial O/\partial t = 0 \) and \( [O, H]_{q,p} = 0 \), \( O \) is a constant of the motion.

In quantum mechanics the same physical observable is represented by an operator \( \hat{O} \), and the possible values of the observable that can be measured are given by the eigenvalues \( o \) of the equation \( \hat{O}\Psi = o\Psi \) (thus the operator corresponding to the energy is the Hamiltonian). The position operator is just \( \hat{r} \) and the momentum operator is \( -i\hbar \hat{\nabla} \) (strictly, I am evaluating these operators in a particular representation, the position representation). Typically these operators do not commute: operating on a wave function first with \( \hat{B} \) and then \( \hat{A} \) is not the same as operating in the reverse order \( \hat{A}\hat{B}\Psi \neq \hat{B}\hat{A}\Psi \). (Try for yourself: operate with \( x \) and \( p_x = -i\hbar \partial / \partial x \) on some function \( f(x) \) in both orders.) The difference is called the commutator \( [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \).

The time dependence in quantum mechanics can be represented in a number of ways (referred to as the Schrödinger picture, the Heisenberg picture, or the Interaction picture). In the Schrödinger picture, the time dependence is in the wavefunction, not the operators (except for any explicit time dependence in the operators, due, eg, to a time-varying external potential). We then take the expectation value of an operator in a quantum state \( \psi(t) \), \( \langle \hat{O} \rangle(t) = \langle \psi|\hat{O}|\psi \rangle(t) \). Its evolution in time is given by Ehrenfest’s theorem:

\[
\frac{d \langle \hat{O} \rangle}{dt} = -\frac{i}{\hbar} <\hat{O}, \hat{H}> + \langle \frac{\partial \hat{O}}{\partial t} \rangle,
\]  

\( (24) \)

which is analogous to the classical result with the Poisson bracket replaced by \( -i/\hbar \) times the commutator.