We begin with a slight detour into classical dynamics to understand the physical content of the Boltzmann equation and how it can be reconciled with the microscopic equations of motion. Recall that the Hamiltonian $H = T + V$ of a classical system (here $T$ is the kinetic energy and $V$ the potential energy) generates the equations of motion for the position and momentum $(p, q)$ for each of $N$ particles through Hamilton’s equations:

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}. \quad (1)$$

A simple example is the motion of a single particle in a quadratic potential, the harmonic oscillator:

$$H = \frac{p^2}{2m} + \frac{kq^2}{2}, \quad \dot{p} = -kq, \quad \dot{q} = \frac{p}{m}. \quad (2)$$

The trajectories in the phase plane $(q, p)$ are ellipses of constant energy, around which the particles move clockwise.

It is pretty straightforward to show that the volume element in phase space, $dp \wedge dq$, is preserved by the Hamiltonian flow. Consider the evolution of a region that starts as a rectangle at time $t$ with corners $(p_i, q_i), (p_i, q_i + dq_i), (p_i + dp_i, q_i + dq_i), (p + dp_i, dq_i)$. At time $t + dt$, the corners have evolved under Hamilton’s equations.

The first corner evolves to $(p_i - dt \frac{\partial H}{\partial q_i}, q_i + dt \frac{\partial H}{\partial p_i}) \equiv (p'_i, p'_j)$. The second corner evolves to $(p'_i + dp_i - dt \frac{\partial \partial H}{\partial p_i, \partial q_i}, q'_i + dq_i + dt \frac{\partial \partial H}{\partial q_i, \partial p_i})$. The rectangle becomes a parallelogram to leading order in $dt$, and the fourth corner evolves to $(p'_i - dt dq_i \frac{\partial H}{\partial q_i, \partial q_i}, q'_i + dq_i + dt dq_i \frac{\partial H}{\partial q_i, \partial p_i})$. The change in volume to order $dt$ is now

$$dV = dt \sum_i dp_i dq_i \left( \frac{\partial}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i} \frac{\partial H}{\partial q_i} \right) + O(dt^2) \Rightarrow \frac{dV}{dt} = 0. \quad (3)$$

The above geometric argument is formalized in Liouville’s theorem for the distribution function $g(p_1, \ldots, p_N, q_1, \ldots, q_N)$ on the phase space of $N$ particles,

$$\frac{dg}{dt} = \frac{\partial g}{\partial t} + \sum_{i=1}^{Nd} \left( \dot{q}_i \frac{\partial g}{\partial q_i} + \dot{p}_i \frac{\partial g}{\partial p_i} \right) = 0. \quad (4)$$

Proof: Systems are locally conserved (never appear or disappear), so for any phase space volume $V$ the change in the integral of $g$ satisfies

$$-\int_V \frac{\partial g}{\partial t} dV = \int_{\partial V} n \cdot v g dS. \quad (5)$$
Here $\partial V$ is a bounding surface for $V$ in $2dN$-dimensional phase space and $\nabla$ is the $2d$-dimensional gradient. The phase space velocity vector (not the normal velocity) $v$ is $2d$-dimensional, with components

$$v = (\dot{p}_1, \ldots, \dot{p}_d, \dot{q}_1, \ldots, \dot{q}_N)$$  \hspace{1cm} (6)

This can be transformed into an integral of the divergence over $V$,

$$- \int_V \frac{\partial g}{\partial t} \, dV = \int_V \nabla \cdot (vg) \, dV.$$  \hspace{1cm} (7)

Since this holds for any volume,

$$- \frac{\partial g}{\partial t} = \sum_{i=1}^{Nd} \left[ \frac{\partial}{\partial p_i} (\dot{p}_i g) + \frac{\partial}{\partial q_i} (\dot{q}_i g) \right]$$

$$= \sum_{i=1}^{Nd} \left[ \frac{\partial}{\partial p_i} (-\frac{\partial H}{\partial q_i} g) + \frac{\partial}{\partial q_i} (\frac{\partial H}{\partial p_i} g) \right].$$  \hspace{1cm} (8)

Now we note that the second derivatives of $H$ cancel since partial derivatives commute, leaving

$$\frac{\partial g}{\partial t} + \sum_{i=1}^{Nd} \left[ p_i \frac{\partial g}{\partial p_i} + q_i \frac{\partial g}{\partial q_i} \right] = 0,$$  \hspace{1cm} (9)

which proves the theorem.

Comment I: this theorem justifies the intuitive argument given before that $df/dt = 0$ for single-particle distribution functions $f(p, q)$ in the absence of collisions, as Liouville’s theorem can be rewritten for a single particle as

$$\frac{\partial f}{\partial t} + \frac{p}{m} \cdot \nabla_x f + \mathbf{F} \cdot \nabla_p f = 0.$$  \hspace{1cm} (10)

Comment II: Note that generalizations of (4) hold for other conserved quantities, such as energy and momentum, that “travel with” the system in phase space. We will use this fact repeatedly below.

Comment III: It should be clarified that the conservation of volume in phase space is much more than just conservation of probability (5). Liouville’s theorem implies, for instance, that a distribution function $f$ which starts at value $a$ for volume $V_1$ and value $0$ for the rest of phase space will **always** have value $a$ for a volume of the same size as $V_1$, and value $0$ elsewhere. Conservation of probability would imply only that the integral of $f$ would be $V_1 a$.

At first glance this seems difficult to reconcile with the Boltzmann equation, which will be shown below to predict flow to an equilibrium configuration. Before resolving the paradox, let’s work out one surprising consequence of Liouville’s theorem. Consider a region $\omega$ of phase space at time $0$ and its image at time $t$. The image must have the same volume as the original region. Now advance to time $2t$; the image at time $2t$ must still have the same volume, and so on. If phase space is of finite volume, as for a spatially bounded system of particles with finite energy (so that momentum is bounded), then eventually two of these images must overlap, which means that some point of phase space must, when mapped under time evolution by some time $nt$, return very nearly to itself (“to an arbitrarily small neighborhood” of the initial point).
We can actually make this statement much stronger. Let $\Omega_0$ be the union of all the images of $\omega$ for $t \geq 0$, and let $\Omega_\tau$ be the union of all the images of $\omega$ for $t \geq \tau$. Clearly $\Omega_\tau \subseteq \Omega_0$. But think of $\Omega_0$ itself as a set of initial points. Then evolving $\Omega_0$ to time $\tau$ clearly yields $\Omega_\tau$, which with Liouville’s theorem implies that $\Omega_0$ and $\Omega_\tau$ have the same volume. A set which is contained in another set of the same volume must differ from the larger set by a set of volume 0, so “almost every” point of $\Omega_0$ is also in $\Omega_\tau$. In particular, almost every point of $\omega$ is also in $\Omega_\tau$ (assuming $\omega$ is of nonzero volume). So almost every point of $\omega$ recurs at some time $t \geq \tau$.

The above statement of the “Poincare recurrence theorem” means, returning to our example of particles that are initially confined to one half of a box, that eventually the particles will all return to that half of the box. How can this be reconciled with the increase of entropy in the Boltzmann equation? Until the 1950s or so, the answer given was simply that the Poincare recurrence time is astronomically long (which is true), and that the Boltzmann equation is simply an approximate description valid for short times. But why does it work so well?

To understand why, consider the image of an initial rectangular region of phase space. For the harmonic oscillator, the shape of this image never becomes very complicated, and for an integral number of periods of the oscillator, the image takes exactly its original shape. The harmonic oscillator is, however, atypical in that it is “integrable”. A consequence of integrability is that nearby trajectories do not separate rapidly with increasing times.

However, many problems are now known to be chaotic: nearby trajectories diverge exponentially rapidly with increasing times. As a result, after a long time the image of the initial region must be a very complicated shape. The specific area of dynamical systems dealing with area-preserving maps is often referred to as “Hamiltonian chaos” because of its importance for Hamiltonian evolution of classical physical systems.

The validity of the predictions of the Boltzmann equation is related to the idea of “coarse-graining” in chaotic systems: as time goes by, the size over which features in phase space average out becomes smaller and smaller. Put another way, if we have only some finite precision in our resolution of phase space, or can only measure 1-particle distributions rather than all of the distributions, then eventually statistical averages such as those contained in the Boltzmann equation will become valid (in practice quite rapidly). An example of how an area-preserving map for 2 particles leads to an apparent increase of entropy for the 1-particle distribution is assigned as a problem.

Showing that this chaotic process really happens in a given problem is quite difficult and mostly required the advent of computers. An example of a chaotic system is the “Sinai billiard”: a billiard ball moves in the plane in a shape made by cutting a quarter circle off from one corner of a rectangle. A distribution of noninteracting billiard balls starting at nearly the same point in phase space will appear to diffuse as a result, even though Liouville’s theorem still holds.

Liouville’s theorem will be the basis for the BBGKY hierarchy to be derived below, which can be thought of as justification and improvement of Boltzmann’s equation. Let’s detour for a moment to find what one-particle distributions $f$ are preserved by the Boltzmann equation. The collision term derived in Lecture II for a monatomic gas at one spatial point $r$ is

$$C(f) = \int w(f_1 f_2 - f_1 f_2) dp_2 dp_1 dp_2.$$

(11)
momenta with \[ \mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}'_1 + \mathbf{p}'_2, \] (12)
we have \( f_1 f_2 = f'_1 f'_2, \) or
\[ \log f(\mathbf{p}_1) + \log f(\mathbf{p}_2) = \log f(\mathbf{p}'_1) + \log f(\mathbf{p}'_2). \] (13)
The algebra we went through in proving the \( H \) theorem shows that this is actually a necessary condition to obtain \( dS/dt = 0 \), assuming that \( w \) is nonzero. Now (13) will hold as long as \( \log f \) is a sum of quantities which are conserved in the collision process. The conservation of momentum and energy in collisions forces some constraints on the collision term \( C(f) \): we have
\[ \int C(f) \, d\mathbf{p}_1 = \int C(f) \, dp_{1i} \, dp_1 = \int C(f) \frac{p_{1i}^2}{2m} \, dp_1 = 0. \] (14)
Assuming that the only conserved quantities are energy, momentum, and particle number, then we take
\[ \log f(\mathbf{p}) = c_0 + c_1 \cdot \mathbf{p} + c_2 \mathbf{p}^2 = c_2 (\mathbf{p} - \mathbf{p}_0)^2 + C. \] (15)
Here \( \mathbf{p}_0 = -c_1/2c_2 \) and \( C = c_0 - c_1^2/4c_2 \).

Now we can start to recognize the familiar Maxwellian distribution of velocities in a gas. The integral over all momenta should give the local number density, so
\[ \left( \frac{\pi}{c_2} \right)^{d/2} e^C = n(r), \] (16)
which determines \( e^C = n(r)(c_2/2\pi)^{d/2} \). The local momentum density is \( n(r)\mathbf{p}_0 \), and the local energy density is
\[ n(r) \int \frac{p^2}{2m} f(\mathbf{p}) \, d\mathbf{p} = n(r) \left( \frac{p_0^2}{2m} + \frac{d}{4c_2m} \right). \] (17)
It remains to derive \( c_2 \), which is best done by constructing the equation of state (cf. Huang). Taking a shortcut and invoking the answer from an undergraduate course or equipartition, we know the mean energy for a gas at rest is \( dkT/2 \), so \( c_2 = (2mKT)^{-1} \). Finally, the equilibrium distribution given by the collision term is
\[ f_0(\mathbf{p}, \mathbf{r}) = \frac{n(r)e^{-(\mathbf{p} - \mathbf{p}_0)^2/2mkT}}{(2\pi mkT)^{d/2}}. \] (18)

There are still at this point multiple possibilities for equilibrium: it could be that at every point the collision integral vanishes because the distribution is Maxwellian, but the local mean energy and velocity vary. It remains to show that any gradient in local density, momentum, or energy will lead to a current directed so as to eliminate the gradient. Such gradients can survive for quite a long time relative to the collisional time scale, and are best studied using the Navier-Stokes equation to be derived below.
The Liouville equation can be used to derive a more general set of equations than the Boltzmann equation. Suppose we have a problem of $N$ particles moving in the Hamiltonian (switching back to variables $(r,p)$)

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} U_i + \sum_{i<j}^{N} v_{ij}$$

$$U_i = U(r_i), \quad v_{ij} = v(|r_i - r_j|). \quad (19)$$

Then Liouville’s equation becomes (where $F = -\nabla U$, $K_{ij} = -\nabla r_i v_{ij}$)

$$\frac{\partial g}{\partial t} = \sum_{i=1}^{N} \left[ -F_i - \sum_{j=1, j \neq i}^{N} K_{ij} \right] \cdot \nabla p_i g - \frac{p_i}{m} \cdot \nabla r_i g \quad (20)$$

Here $g$ is the distribution function in $N$-particle phase space.

Liouville’s theorem can be restated as

$$\left[ \frac{\partial}{\partial t} + h_N(r_1, p_1, \ldots, r_N, p_N) \right] g = 0, \quad (21)$$

where the differential operator $h_N$ is defined as

$$h_N(r_1, p_1, \ldots, r_N, p_N) = \sum_{i=1}^{N} \left[ \frac{p_i}{m} \cdot \nabla r_i + F_i \cdot \nabla p_i \right]$$

$$+ \frac{1}{2} \sum_{i,j=1}^{N} K_{ij} \cdot (\nabla p_i - \nabla p_j). \quad (22)$$

Now define the single-particle distribution function as, with $z = (r,p)$ and $g$ normalized to 1,

$$f_1(t, p, r) \equiv \langle \sum_{i=1}^{N} \delta(p - p_i) \delta(r - r_i) \rangle = N \int g(z_1, \ldots, z_N) \, dz_2 \ldots dz_N. \quad (23)$$

The factor of $N$ appears naturally since $g$ is symmetric under permutations of the $z_i$. To obtain an equation for the evolution of $f_1$, we integrate out all but one coordinate in the Liouville equation (21). In general, to find the evolution equation of $f_n$ it is useful to write

$$h_N = h_n + h_{N-n} + \sum_{i=1}^{n} \sum_{j=n+1}^{N} K_{ij} \cdot (\nabla p_i - \nabla p_j) \quad (24)$$

where we have suppressed the coordinate dependence. In the next lecture we will show that the combinatorial factors cancel appropriately and yield

$$\left( \frac{\partial}{\partial t} + h_n \right) f_n(z_1, \ldots, z_n) = -\sum_{i=1}^{n} \int dz_{s+1} K_{i,s+1} \cdot \nabla p_i f_{s+1}(z_1, \ldots, z_{s+1}). \quad (25)$$

The set of these equations for all values of $n$ is referred to as the BBGKY hierarchy (Bogoliubov-Born-Green-Kirkwood-Yvon).