Physics 212: Statistical mechanics II  
Lecture II

The most famous example of how entropy increases in a real system is the dilute classical gas. The first assumption we will make is that
\[
\lambda = na^3 \ll 1, \tag{1}
\]
or that the "gaseousness parameter" is small. Here \( n \) is the density of particles per unit volume and \( a \) is the range of the interparticle interaction: \( \lambda \) is just the number of particles within an interaction range of a fixed particle. For hard spheres, \( a \) is just the sphere radius. For Van der Waals-type forces between neutral atoms or molecules, the interaction potential falls off sufficiently rapidly (usually \( V(r) \sim r^{-6} \)) that our approximations are still well justified.

One reason why plasma physics is difficult is that there the interparticle potential is given by the rather strong Coulomb force, \( V(r) \propto r^{-1} \), so that the physics is quite complicated and the Debye screening must be taken into account.

The second assumption is that the particles lack internal rotational or vibrational structure. At room temperatures, this is a reasonable assumption for the vibrational levels of many gases. Rotations may be quite low energy, but in practice molecules often rotate so fast (i.e., the rotational levels are at such low energy) that they are simply averaged over on the intercollision time scale.

Now we need a model for how the particles in the gas collide. Let \( \Gamma_1, \Gamma_1', \Gamma_2, \) and \( \Gamma_2' \) be the momentum variables of two incoming and two outgoing particles from a collision: \( \Gamma = (p) \). We write \( \Gamma \) instead of \( p \) so that the formulas can be generalized to cases where internal angular momenta, for example, are conserved in collisions as well as normal momenta; then \( \Gamma = (p, L, \ldots) \). We consider collisions that take \( \Gamma_1, \Gamma_2 \) to \( \Gamma_1', \Gamma_2' \). Then define \( w(\Gamma_1', \Gamma_2'; \Gamma_1, \Gamma_2) \) so that the rate per unit spatial volume at which pairs of particles from \( \Gamma_1, \Gamma_2 \) get transferred via collisions to \( \Gamma_1', \Gamma_2' \)

\[
R = (f(t, r, \Gamma_1) d\Gamma_1)(f(t, r, \Gamma_2) d\Gamma_2) w(\Gamma_1', \Gamma_2'; \Gamma_1, \Gamma_2)(d\Gamma_1' d\Gamma_2'). \tag{2}
\]

In the above we ignored the position variables in \( w \) and are assuming that the collision process is translation invariant. There will be a bit more said about the assumptions which go into the definition of \( f \) below.

The picture is that we are obtaining the collision function \( w \) from some microscopic physics like quantum mechanics. That physics will probably be time-reversal invariant, in which case

\[
w(\Gamma_1, \Gamma_2; \Gamma_1', \Gamma_2') = w((\Gamma_1')^T, (\Gamma_2')^T; (\Gamma_1)^T, (\Gamma_2)^T). \tag{3}
\]

For the monatomic gas to be considered below, which has no additional angular momentum or other internal variables so \( \Gamma^T = (-p) \) and also has parity invariance, (3) becomes just

\[
w(\Gamma_1, \Gamma_2; \Gamma_1', \Gamma_2') = w(-\Gamma_1', -\Gamma_2'; -\Gamma_1, -\Gamma_2) = w(\Gamma_1', \Gamma_2'; \Gamma_1, \Gamma_2). \tag{4}
\]

In order to understand the meaning of \( w \) in more familiar terms, note that in three dimensions \( f d\Gamma \) has units of \( 1/\text{volume} \), so \( w d\Gamma_1' d\Gamma_2' \) must have units of volume/time. Now

\[
\frac{w(\Gamma_1, \Gamma_1'; \Gamma_2, \Gamma_2')}{v_1 - v_2} d\Gamma_1' d\Gamma_2' = d\sigma. \tag{5}
\]
The left side is a quantity with dimensions of area, and is equal to the differential cross section to send particles into the momentum ranges \((dΓ′_1, dΓ′_2)\), which you may be familiar with in single-particle scattering. Classically, this is just the target area in the relative coordinate system of the two particles.

Consider the time evolution of a gas of particles with no collisions or external forces. Each particle moves with constant velocity, and the distribution function along phase space paths is constant:

\[
\frac{df}{dt} = \partial_t f + \mathbf{v} \cdot \nabla_x f = 0.
\]  

The “convective” derivative above follows the distribution function along the paths of a particle. For an example, consider one particle moving on a line. If at \(t = 0\) there is a \(\delta\)-function for the one-particle distribution function to be at position \(x_0\) with momentum \(p_0\),

\[
f(t = 0, x, p) = \delta(x - x_0)\delta(p - p_0),
\]
then after a time \(t\) the new distribution function is

\[
f(t, x, p) = \delta(x - (x_0 + pt/m))\delta(p - p_0),
\]

which is easily shown to satisfy (6).

When the particles are not moving freely but under the action of an external one-body force, (6) becomes just

\[
\frac{df}{dt} = \partial_t f + \mathbf{v} \cdot \nabla_x f + \mathbf{F} \cdot \nabla_p f = 0.
\]

Here \(\mathbf{F}\) comes from some force law that acts on each particle independently. Such forces will still not increase the entropy: the distribution function \(f\) is still convected along particle trajectories, even though the particle trajectories are more complicated. There is no approach to equilibrium yet.

Now let’s get rid of the one-body potential for brevity and add a two-body collision term:

\[
\frac{df}{dt} = \partial_t f + \mathbf{v} \cdot \nabla_x f = C(f).
\]

What is \(C(f)\)? Well, the variation it induces in \(f(t, x, p)\) will contain two parts. The first part will be losses because of particles which are scattered from \(p\) to some other momentum \(p'\). The second part will be gains because of particles which are scattered to \(p\) from some other momentum \(p'\).

From our definition of \(w\) above, we know that the total number of collisions per time in a volume \(dV\) that take particles out of a momentum range \(dp_1\) is

\[
dV d\mathbf{p}_1 \int w(\mathbf{p}'_1, \mathbf{p}'_2; \mathbf{p}_1, \mathbf{p}_2) f(t, r, \mathbf{p}_1) f(t, r, \mathbf{p}_2) \, d\mathbf{p}_2 \, d\mathbf{p}'_1 \, d\mathbf{p}'_2.
\]

Likewise, assuming I have the indices and signs in the right place, the rate of collisions that bring particles into the momentum range \(dp_1\) is

\[
dV d\mathbf{p}_1 \int w(\mathbf{p}_1, \mathbf{p}_2; \mathbf{p}'_1, \mathbf{p}'_2) f(t, r, \mathbf{p}_1') f(t, r, \mathbf{p}_2') \, d\mathbf{p}_2 \, d\mathbf{p}_1' \, d\mathbf{p}'_2.
\]
To save space, henceforth write
\[ w = w(p_1', p_2'; p_1, p_2), \quad w' = w(p_1, p_2; p_1', p_2'). \] (13)

For the simple monatomic gas, \( w = w' \) from (4), but postpone using that for now.

Now we can write out the collision term as
\[ C(f) = \int (w' f_1' f_2' - w f_1 f_2) \, dp_2 \, dp_1' \, dp_2'. \] (14)

Here for brevity \( f_1 \equiv f(t, r, p_1) \) and so forth for \( p_2, p_1', p_2' \). Later we will discuss the collision term in an explicit case.

For the monatomic gas, we can use \( w = w' \) so
\[ C(f) = \int w' (f_1' f_2' - f_1 f_2) \, dp_2 \, dp_1' \, dp_2'. \] (15)

It is a nontrivial exercise to derive (15) from (14) without time-reversal invariance, so that \( w = w' \) no longer holds.

Finally, pulling everything together, we obtain
\[ \partial_t f_1 + v \cdot \nabla x f_1 = \int w' (f_1' f_2' - f_1 f_2) \, dp_2 \, dp_1' \, dp_2'. \] (16)

This is the celebrated Boltzmann equation, derived in 1872 (!).

Now let’s look at a rather fundamental prediction of this equation. The entropy for a one-particle distribution function \( f \) is, as shown below,
\[ S = -\int f \log f \, d^d x \, d^d p. \] (17)

Boltzmann actually used a definition differing by a constant and a sign: his \( H = N - S \), which you may see in some textbooks. Assume for simplicity a monatomic gas, so that \( w = w' \), although this assumption is not fundamental. Our goal is to show that the Boltzmann equation predicts
\[ \frac{dS}{dt} \geq 0, \] (18)
or that entropy cannot decrease.

Let me pause to justify the entropy definition (17) of a probability distribution. We will show that \( S = -\sum_i p_i \log p_i \) for a discrete distribution of probabilities \( p_i \); then (17) is simply the generalization to a continuous distribution of probabilities. Consider, as in the previous lecture, a large number \( N \) of identical systems which can be in any of \( k \) different states. Let \( \nu_i \) be the number of systems in state \( i \), with
\[ \sum_i \nu_i = N. \] (19)

The number of “microstates” of the \( N \) systems which correspond to a given set \( (\nu_1, \ldots, \nu_k) \) is
\[ P \equiv \frac{N!}{\nu_1! \nu_2! \cdots \nu_k!}. \] (20)
The fundamental assumption here is that every microstate is equally likely. Now using Stirling’s approximation
\[ \log P = N(\log N - 1) - \sum_i \nu_i(\log \nu_i - 1). \] (21)

In using Stirling’s approximation we are assuming that \( N \) is large but not that \( k \) is large: \( k \) may be as small as 2, as for a coin flip, and the above is still valid. To be more precise, we are assuming that \( N \) is so large that any configurations in which one of the \( \nu_i \) is small are very rare. Then Stirling’s approximation is justified not just for \( N! \) but also for \( \nu_i! \). We can immediately cancel two terms because the sum of the \( \nu_i \) is just \( N \). Doing so and introducing the probabilities \( p_i \equiv \nu_i/N \) gives
\[ \log P = N \log N - \sum_i N p_i \log(Np_i) = N(\log N - \sum_i p_i(\log N + \log p_i)). \] (22)

Once again two terms can be cancelled via the sum condition (19). Finally, the entropy for one system is defined to be
\[ S \equiv \frac{\log P}{N} = -\sum_i p_i \log p_i, \] (23)

the promised formula. The only subtleties in the generalization of this to continuous functions \( f \) arises for singular functions like the \( \delta \)-function. For nonsingular functions on phase space, just divide phase space into a large number of small boxes \( dV \) and interpret \( f dV/N \) as the probability that a given particle is in \( dV \) to use the above.

The time derivative of the entropy is then
\[ \frac{dS}{dt} = \int \partial_t(f \log f) \, dx \, dp = -\int (1 + \log f) \partial_t f \, dx \, dp. \] (24)

The only change in the entropy occurs from the collisional term, not the convective terms (mathematical verification of this fact is left to the reader). So the entropy is now
\[ \frac{dS}{dt} = -\int (1 + \log f_1)C(f_1) \, dp_1 \, dx = -\int (1 + \log f_1)(w(f'_1 f'_2 - f_1 f_2) \, dp_2 \, dp'_1 \, dp'_2) \, dp_1 \, dx. \] (25)

Now imagine shuffling the variables \( p_1 \leftrightarrow p_2, \, p'_1 \leftrightarrow p'_2 \) on the right-hand-side, without changing its value, and adding that to the above. Then
\[ 2\frac{dS}{dt} = -\int (2 + \log f_1 f_2)w(f'_1 f'_2 - f_1 f_2) \, dp_2 \, dp'_1 \, dp'_2 \, dp_1 \, dx. \] (26)

Now do another shuffle, of incoming and outgoing momenta (i.e. primed and unprimed variables) and add the result to the above:
\[ 4\frac{dS}{dt} = -\int (2 + \log f_1 f_2)w(f'_1 f'_2 - f_1 f_2) \, dp_2 \, dp'_1 \, dp'_2 \, dp_1 \, dx \]
\[-\int (2 + \log f_1 f_2) w(f_1 f_2 - f'_1 f'_2) dp_2 dp'_1 dp'_2 dp_1 dx.\] (27)

Canceling terms in the above leaves simply
\[\frac{dS}{dt} = \frac{1}{4} \int w(\log f_1 f_2 - \log f'_1 f'_2) (f_1 f_2 - f'_1 f'_2) dp_1 dp_2 dp'_1 dp'_2 dx.\] (28)

The last step is just showing that \((\log f_1 f_2 - \log f'_1 f'_2) (f_1 f_2 - f'_1 f'_2)\) cannot be negative. This is a function of two variables \(x = f_1 f_2\) and \(y = f'_1 f'_2\), which simplifies to \(g(x, y) = (x - y) \log(x/y)\). All the \(f\) functions are probability distributions and hence nonnegative, so \(x\) and \(y\) are nonnegative and \(g(x, y) = y(x/y - 1) \log(x/y)\) will be nonnegative if \(g'(x/y) = (x/y - 1) \log(x/y)\) is nonnegative.

Now write \(u = x/y\), so \(g'(u) = (u - 1) \log u\). Finally, the function \((u - 1) \log u\) is always nonnegative for positive \(u\), as the two parts \(u - 1\) and \(\log u\) always have the same sign.

What property was assumed about the two-particle distribution function in the form of \(w\) in order to obtain the Boltzmann equation, which is closed? Answer: that it was a product distribution, i.e., particle momenta were independent except for collisions:
\[F(t, r, p_1, r, p_2) = f(t, r, p_1) f(t, r, p_2).\] (29)

This is sometimes known as the “assumption of molecular chaos.” The first part of the next lecture will show how to relax this assumption and obtain the BBGKY hierarchy of evolution equations. Another question to be addressed in the next lecture is how the above is consistent with what we know about the deterministic evolution of Hamiltonian systems.