Lecture 7

Reap: Liouville eqn $\rightarrow$ BGKY

$n = 1$: $x = 0$

$$\left[ \frac{\partial}{\partial t} + \frac{1}{m} \cdot \frac{\partial}{\partial \vec{r}} \right] f(\vec{r}, \vec{p}, t) = \left( \frac{\partial f}{\partial \vec{r}} \right)_c$$

$$= -\left[ \partial' (dp^{'}) E(\vec{r} - \vec{r}') \cdot \frac{\partial}{\partial \vec{p}} f^{(2)}(\vec{r}', \vec{p}', \vec{r}'', \vec{p}'') \right]$$

Vlasov approx: $f^{(2)} \approx f \cdot f$ doesn't work for short-ranged hard potentials. "Collisions!"

Need Boltzmann's approach.
form. Imagine that the atoms/molecules are point-like and collide elastically. We consider the case of no external force, \( \mathbf{F} = 0 \), and imagine that the atoms only interact on contact (i.e. like hard spheres). Then

\[ E_i = \frac{1}{2m_i} \mathbf{p}_i^2 \]

is the total energy of atom \( i \) between collisions.

Consider the types of scattering events that give rise to a probability flux into or out of an infinitesimal cell volume about \((r, \mathbf{p})\), i.e. contributions to \( \partial f(r, \mathbf{p})/\partial t \).

The flux into \((r, \mathbf{p})\) can be estimated as, accounting for energy and momentum conservation in the collision:
\[ J^{(+)}(C, E, t) \sim \left( \frac{d}{d^3m} \right) \frac{d}{dp_1} \frac{d}{dp_2} \frac{d}{dp_3} \delta(E + p_1 - p_2 - p_3) \delta(E - E_1 - E_2 - E_3) \cdot f(C, p_2, t) f(C, p_3, t) \]

where the prefactor is needed for dimensional considerations; \( d \) is the particle diameter.

Let
\[ R = \left( \frac{d}{d^3m} \right) \delta(E + p_1 - p_2 - p_3) \delta(E - E_1 - E_2 - E_3) \]

then
\[ f_2 = f(C, p_2, t) \]

\[ J^{(+)}(C, E, t) \sim \int dp_2 \int dp_3 R f_2 f_3 \]

Similarly, the flux out \( \overrightarrow{E}(C, E) \) is:
\[ J^{(-)}(C, E, t) \sim \int dp_1 \int dp_2 \int dp_3 R f f_1 \]

where \( R \) is the same, since we know that \( J^{(+)} = J^{(-)} \) at equilibrium. Hence
\[ * * \]
\[ \left[ \frac{\partial f(C, p, t)}{\partial t} \right] \sim \int dp_1 \int dp_2 \int dp_3 R (f_2 f_3 - f f_1) \]

This approximation leads to the so-called "Boltzmann Eqn" for \( f \):
\[ \frac{\partial f}{\partial t} + \frac{1}{m} \mathbf{p} \cdot \frac{\partial f}{\partial \mathbf{r}} = \int dp_x dp_y dp_z R \left( f_{\text{eq}} - f \right) \]

A few comments:

1) The Boltzmann eqn is the starting point for non-\textit{eq} studies of dilute gases. It is nonlinear and must be solved numerically.

2) A more rigorous expression is given in McQuarrie's text for continuous pair potentials \( \psi(r) \) that incorporate the kinematics of two particles interacting at a distance.

\[ \frac{\partial f}{\partial t} + \frac{1}{m} \mathbf{p} \cdot \nabla f = \int dp_x dp_y dp_z R \left( f_{\text{eq}} - f \right) \]

\section{Collisions, Viscosity, Heat, and Sound}

Our analysis of Boltzmann's eqn will be limited to studying the linearized approach to equilibrium. In particular, we write

\[ f(\mathbf{r}, \mathbf{p}, t) = f_{\text{eq}}(\mathbf{p}) \left[ 1 + \frac{1}{2} (\mathbf{p}, t) \right] e^{i \mathbf{k} \cdot \mathbf{r}} \]

and treat the second term as a small perturbation from equilibrium. We follow the discussion in Ma's text and consider plane wave disturbances in \( \mathbf{r} \). Specifically,
Let's choose $k = k^2$, so $e^{ik\cdot r} = e^{ikr}$.

Our goal is to study how small amplitude ($\psi \ll 1$) wave-like disturbances from equilibrium relax in time.

A substitution into the BE leads to

$$(4) \quad \frac{\partial^2}{\partial t^2} \psi(p,t) = -K \psi$$

where $K$ is a linear operator acting on $\psi$ and defined by:

$$K \psi = \frac{i}{m} k p \cdot \psi(p,t)$$

$$+ \int dp_1 dp_2 dp_3 \left( \phi^*(p_1) \mathcal{R} (\psi^* \psi_2 - \psi_2^* \psi) \right)$$

Eqn (4) has a solution of the form

$$\psi(p,t) = \sum_n c_n e^{-\gamma_n t} \phi_n(p)$$

where $\gamma_n$, $\phi_n$ are the eigenvalues/eigenvectors of $K$:

$$K \phi_n(p) = \gamma_n \phi_n(p) \quad \left( n = 0, 1, 2, \ldots \right)$$

and $c_n$ are constant coefficients.

It proves convenient to expand the $\gamma_n$ and $\phi_n$ as expansions for small $k$, i.e. long-wavelength disturbances.
We write
\[ V_n = V_n^{(0)} + k V_n^{(1)} + k^2 V_n^{(2)} + \ldots \]
\[ \phi_n^{(k)}(p) = \phi_n^{(0)}(p) + k \phi_n^{(1)}(p) + \ldots \]

To \( O(k^0) \):
\[ K^{(0)} \phi_n^{(0)} = V_n^{(0)} \phi_n^{(0)} \]
where \( K^{(0)} \) contains just the integral operator in \( K \). It is possible to prove that

1. \( V_n^{(0)} \geq 0 \) for all \( n \).

2. There are 5 eigenfunctions with \( V_n^{(0)} = 0 \). These are known as "conserved modes", since long-wavelength excitations of these modes don't decay in time. They are:

   "mass" \( \phi_n^{(0)}(p) = 1 \)

   "momentum" \( \phi_\alpha^{(0)}(p) = p_\alpha / (2 \pi \hbar) \), \( \alpha = 1, 2, 3 \)

   "energy" \( \phi_4^{(0)}(p) = (E - \langle E \rangle) / \langle (E - \langle E \rangle)^2 \rangle^{1/2} \)

   \[ \uparrow \]

   \[ \frac{p^2}{2m} \]

We have normalized these \( k = 0 \) eigenvalues. The relevant inner product is:
\[(g, h) = \int dp \, f_n(p) \, p \, h(p) = \langle gh \rangle\]

where the last expression is just the ensemble average. The eigenfunctions are orthonormal in the sense that

\[(\phi_n^{(0)}, \phi_m^{(0)}) = \delta_{n,m} \quad (\phi_n^{(0)}, \phi_n^{(0)}) = \delta_{n,m} \quad (\phi_n^{(0)})^2 = \delta_{n,m}\]

Next, we consider higher order terms in the \(\hbar\) expansion. To carry out the perturbation analysis, it is helpful to note that this is a situation where the ground state eigenvalues are degenerate. Such a situation arises frequently in QM, at \(\mathcal{O}(\hbar)\):

1. The 3 "groundstate" eigenfunctions
   \[\phi_0^{(0)} \text{ (mass)}, \phi_3^{(0)} \text{ (longitudinal} (z) \text{ momentum}), \text{ and } \phi_4^{(0)} \text{ (energy)} \] are mixed (linearly combined) to create two new "sound" modes. They have eigenvalues
   \[\gamma_{\pm}^{(1)} = \pm i \, C \quad ; \quad i = \sqrt{-1}\]
   where
   \[C = \left(5k_B^2 T\right)^{1/2} \quad \text{"Sound Velocity"}\]
2. The eigenvalues of the other 3 linearly independent modes remain zero to $O(k)$.

At $O(k^2)$:

1. Mass, longitudinal momentum, and energy remain linearly combined into two sound modes.

2. The two transverse momentum modes $\phi_1^{(0)}, \phi_2^{(0)}$ remain unmixed with other modes to $O(k^2)$.

3. A heat conduction mode appears that is a linear combination of the energy mode $\phi_3^{(0)}$ and the mass mode $\phi_0^{(0)}$.

4. The eigenvalues are

\[ \sqrt{\tau} = \pm i c k + D_5 k^2 \text{ "sound"} \]

\[ \tau_t = D_t k^2 \text{ "transverse momentum"} \]

\[ \tau_e = D_e k^2 \text{ "heat"} \]

where

\[ D_5 \sim D_t \sim D_e \sim \bar{v}_{\text{rms}} \lambda \sim \left( \frac{h T}{m} \right)^{1/2} \frac{1}{d^2 \rho} \]
and all have the units of diffusion coefficients.

\( \Phi \) The sound modes are disturbances of the form

\[ f(x, \xi, t) \sim \exp(ik_xt) \phi(k_x, \xi) e^{-D_\xi k^2 t} \]

which are waves traveling in the direction of \( x \) with velocities \( c = \frac{v_{rms}}{\sqrt{2}} \). The waves are damped with an attenuation factor \( e^{-D_\xi k^2 t} \). Because \( D_\xi \propto \rho^{-1} \), the waves are strongly damped in a dilute gas. This is because sound propagation requires collisions!

\( \Phi \) The two modes with eigenvalues \( \nu_\xi \) correspond to diffusive momentum transport in the two directions perpendicular to \( x \). This is simply viscous flow and \( D_\xi = \frac{\nu_{visc}}{\rho} \) is the kinematic shear viscosity.

\( \Phi \) The heat conduction mode is of the form

\[ f(x, \xi, t) \sim \exp(ik_xt) \phi(k_x, \xi) e^{-D_\xi k^2 t} \]

where \( D_e \equiv k_t / (\rho c_p) \) is the thermal diffusivity, \( k_t \) is the thermal conductivity, and \( c_p \) is the constant heat capacity.
To summarize:

1) The Boltzmann equation, which is an approximate closure approximation for dilute gases, predicts diffusive transport of heat, mass, and momentum, consistent with macroscopic linear hydrodynamics.

2) We see again that collisions produce diffusive behavior, as well as the collective propagation of sound waves!

3) Numerical solutions of the BE can provide interesting results well beyond the scope of our linear analysis of the approach to equilibrium.

4) An interesting feature of the BE, is that it predicts diffusive, irreversible transport behavior. It can be shown that the quantity

\[ S(t) = - \int d\mathbf{p} f(c, \mathbf{p}, t) \ln f(c, \mathbf{p}, t) \]

is always increasing in time, \( \frac{dS}{dt} \geq 0 \), with a maximum \( \frac{dS}{dt} = 0 \).