Physics 127b: Statistical Mechanics

Kinetic Theory

Kinetic theory is the simplest approach that describes the dynamics of enormous numbers of particles. Often it is the only one where we can make progress in actually calculating numbers such as viscosity or electrical conductivity! It describes nearly ideal gases: usually the interactions are only taken into account in the *collisions* (to be defined below) that lead to the approach to equilibrium, and *not* in the properties of that equilibrium (such as the equation of state, compressibility etc.). In some cases (e.g. Fermi liquid theory) it is useful to take other effects of the interactions into account in a mean field sort of way.

An "ideal gas" is a good approximation for a system consisting of a low density of particles *or quasiparticles* (thermal excitations from a quantum ground state). In the latter case the density of quasiparticles is always low at low enough temperatures, and so kinetic theory is useful. Since we are often interested in low temperature properties of a quantum system, this application makes kinetic theory much more interesting. So kinetic theory is useful in:

- classical gases;
- the interstellar medium (particles and phonons);
- plasmas;
- quantum systems at low temperatures (e.g. phonons and rotons in a Bose superfluid; phonons in solids; particle-hole excitations from a Fermi sea…);

—a surprisingly large variety of interesting systems.

We will phrase the argument in terms of the classical gas.

The simplification

The full description of a many particle system involves the phase space distribution $\rho(\vec{x}_1, \vec{x}_2 \ldots \vec{x}_N; \vec{p}_1, \vec{p}_2 \ldots \vec{p}_N; t) d^{3N}q d^{3N}p$ giving the probability (fraction of members of the ensemble) of finding the system with particle 1 at a position between $\vec{x}_1$ to $\vec{x}_1 + d\vec{x}_1$ with momentum between $\vec{p}_1$ to $\vec{p}_1 + d\vec{p}_1$, particle 2 ….—a very complicated and complete description.

Kinetic theory works with the *one-particle distribution* $f(\vec{x}, \vec{p}, t) d^3x d^3p$ giving the average number of particles in volume d^3x about $\vec{x}$ and with momentum in a range d^3p about $\vec{p}$. It is normalized to the total number of particles N

$$\int\int d^3x\, d^3p\, f(\vec{x}, \vec{p}, t) = N. \tag{1}$$

It is related to the full description by integrating over $N - 1$ particles:

$$f(\vec{x}, \vec{p}, t) \sim N \int \ldots \int \rho(\vec{x}, \vec{x}_2 \ldots \vec{x}_N; \vec{p}, \vec{p}_2 \ldots \vec{p}_N; t) d^3x_2 \ldots d^3x_N d^3p_2 \ldots d^3p_N \tag{2}$$

where the $\sim$ derives from the complicated normalization choice for ρ—if ρ were normalized so that the integral over all $\vec{x}_i$ and $\vec{p}_i$ were unity, the $\sim$ would be replaced by an equality. Any *single particle* quantity can be calculated from f, but obviously a great deal of information is thrown away in getting to f, and not everything can be calculated in terms of it. For example, the average interaction energy from pairwise particle interactions cannot be exactly calculated from f, since this involves two particle correlations. But we are dealing with nearly ideal gases, so this is OK!

In a classical context we often prefer to deal with the velocity rather than momentum. We can use a distribution $f(\vec{x}, \vec{v}, t)$ (a different function obviously—I should use f_p and f_v—but they only differ by a factor of m^3 and I'll be sloppy in the notation, using f for whichever one we are currently using.)

Elementary results

I presume you have seen the elementary kinetic theory results for the equilibrium gas. If the following are not familiar, you can look in *Fundamentals of Statistical and Thermal Physics §7.9-13* by *Reif*. Another good reference on Kinetic Theory is the first chapter of *Physical Kinetics* by *Landau and Lifshitz*.

In a spatially uniform region and in equilibrium the distribution is the *Maxwell distribution*

$$f(\vec{x}, \vec{v}, t) \to f(\vec{v}) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T}, \tag{3}$$

with $n = N/V$ the number of molecules per volume. (Check the normalization.) Other distributions easily follow. For one component of the velocity the distribution is

$$\begin{aligned} g(v_x) &= \int\int dv_y dv_z f(\vec{v}) &(4)\\ &= n\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_B T}, &(5)\end{aligned}$$

and for the speed the average number of particles with speed between v and $v + dv$ is $4\pi v^2 f(v) dv$. This function has a maximum at $v = \sqrt{2}\sqrt{k_B T/m}$, and averages $\overline{v} = \sqrt{8/\pi}\sqrt{k_B T/m}$ and $\overline{v^2} = 3k_B T/m$.

It is easy to calculate simple results for the ideal gas by appropriate integrals over $f(\vec{v})$. For example the number of molecules hitting unit area of surface per unit time (or the rate at which molecules exit through a hole small compared to the mean free path so that bulk flow is not established known as *effusion*) is $\frac{1}{4} n\bar{v}$, and the pressure is $\frac{1}{3} nm\overline{v^2}$.

Boltzmann Equation

For an ideal gas each particle evolves independently under its own Hamiltonian and so the evolution of f is given by a Liouville equation

$$\frac{df}{dt} = 0 \tag{6}$$

where the total derivative along a phase space trajectory $\vec{x}(t)$, $\vec{p}(t)$ is taken, i.e.

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{x}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} = 0 \tag{7}$$

writing $\vec{v} = \vec{p}/m$ for $d\vec{x}/dt$ and $d\vec{p}/dt = \vec{F}$ with $\vec{F}$ the force from any applied potential. (The result for $f(\vec{x}, \vec{v}, t)$ is readily derived.) This is known as the *Vlasov equation* or the *collisionless Boltzmann equation*.

We now take weak interactions into account by adding a "collision term" to the right hand side

$$\frac{df}{dt} = \left.\frac{df}{dt}\right|_{coll}. \tag{8}$$

Of course, without specifying $df/dt|_{coll}$ this is an empty statement. The secret of the full *Boltzmann equation* is deriving this term, and then its consequences on the evolution of f.

Since f is a truncation of the full phase space distribution, and we know (in principle!) how this evolves under the full Hamiltonian including interactions, we can derive an equation for f, and then the "collision term" appears as everything that does not fit on the left hand side of Eq. (8)! The following is meant to be a brief sketch of this, and certainly not a complete derivation. Again *Physical Kinetics* is a good reference for a more complete treatment.

Let's consider *normalized* N particle distributions (i.e. the normalized version of ρ) $f^{(N)}(\vec{x}_1 \dots \vec{x}_N; \vec{p}_1 \dots \vec{p}_N)$ such that

$$\int \dots \int f^{(N)} d^{3N}x d^{3N}p = 1 \tag{9}$$

and reduced distributions $f^{(1)}(\vec{x}_1, \vec{p}_1)$, $f^{(2)}(\vec{x}_1, \vec{x}_2; \vec{p}_1, \vec{p}_2)$ etc. are then

$$f^{(1)} = \int \dots \int f^{(N)} d\tau_2 \dots d\tau_N \tag{10}$$

$$f^{(2)} = \int \dots \int f^{(N)} d\tau_3 \dots d\tau_N \tag{11}$$

$$\vdots \tag{12}$$

(denoting $\vec{x}_1$, $\vec{p}_1$ by τ_1 and the phase space volume element $d^3x_1 d^3p_1$ by $d\tau_1$ etc.). Our f is just $Nf^{(1)}$.

Then it is not too hard to show that

$$\frac{\partial f^{(1)}(\tau_1)}{\partial t} + \vec{v}_1 \cdot \frac{\partial f^{(1)}(\tau_1)}{\partial \vec{x}_1} + \vec{F}(\vec{x}_1) \cdot \frac{\partial f^{(1)}(\tau_1)}{\partial \vec{p}_1} = \tag{13}$$

$$N \int \frac{\partial u_{12}(\vec{x}_1, \vec{x}_2)}{\partial x_1} \cdot \frac{\partial f^{(2)}(\tau_1, \tau_2)}{\partial \vec{p}_1} \tag{14}$$

where u_{12} is the pair interaction potential. Note that the term on the right hand side is very similar to the force term on the left hand side, but involves two particle correlations and so depends on $f^{(2)}$.

We could imagine deriving an equation for $\partial f^{(2)}/\partial t$, and then the two equations would solve the problem. Unfortunately, it is becomes apparent that the equation for $f^{(2)}$ will involve $f^{(3)}$ etc., and we develop an infinite *hierarchy* of equations. (This is typically the case where we try to solve a many body problem by looking at equations for low order correlation functions—there is no free lunch!)

We "derive" the Boltzmann equation by *approximating* the right hand side with terms *only depending on* $f^{(1)}$. There are two essential pieces of physics in the approximation. Firstly, it is assumed that only two particles are ever interacting together (i.e. three body interactions are neglected beyond the product of pairwise interactions). Secondly the effect of the correlations on a short time scale *induced* by the collisions are ignored in subsequent collisions—the approximation of *molecular chaos*. In a dense system we might worry that two particles that have just collided may rapidly collide again due to the particles "rattling around" in a cage of neighbors. In a dilute gas this does not seem likely, so the assumption seems very reasonable. However this approximation has a profound effect: the original Liouville equation satisfies the time reversal invariance of the original equations, whereas the Boltzmann equation does not. This of course is vital if we are going to study the relaxation towards equilibrium and dissipative processes. It is usually the case that the transition from reversible to irreversible dynamics appears through "sleight of hand" rather than careful, systematic derivation.

The Relaxation Time Approximation

We will first study the effect of collisions in a simple approximation: we suppose that collisions relax the distribution back to the equilibrium distribution or a *local equilibrium* distribution exponentially with a single time constant τ

$$\left.\frac{df}{dt}\right|_{coll} \simeq -\frac{f-f_0}{\tau}. \tag{15}$$

Here f_0 is often the global equilibrium distribution. However since the collisions conserve certain quantities—maybe energy, momentum, particle number etc.—these are not changed and f_0 may describe the local equilibrium at fixed values of these conserved quantities. The quantities conserved depend on the application: in scattering off fixed impurities energy and number are conserved, but not momentum; in binary collisions in a gas energy, momentum and number are all conserved. The local equilibrium distribution will be characterized by the appropriate conjugate fields (temperature for conserved energy etc.) that may not be the global equilibrium value.

Consider the simple example of a charged gas in a constant, uniform electrical field scattering off fixed impurities—the problem of electrical resistance.

The Boltzmann equation is

$$\frac{q\vec{E}}{m}\cdot\frac{\partial f}{\partial\vec{v}} = -\frac{f-f_0}{\tau} \tag{16}$$

since the other terms on the right hand side are zero in steady state and for a spatially uniform situation. (Both these conditions can easily be relaxed, e.g. to consider the transient in a spatially varying field, or the response to a time varying field.) The distribution f_0 here is just the equilibrium one. For small electric fields, f will be close to f_0, and we can use this substitution on the right hand side, i.e. for $f = f_0 + f_1$ with $f_1$small

$$f_1 \simeq -\frac{\tau q}{m}\vec{E}\cdot\frac{\partial f_0}{\partial\vec{v}} = -\frac{\tau q}{m}\vec{E}\cdot\hat{v}\frac{\partial f_0}{\partial v} \tag{17}$$

where $\hat{v}$ is the unit vector along $\vec{v}$,and the second expression results since f_0 is spherically symmetric. Now the electric current is easily calculated

$$\vec{j} = \overleftrightarrow{\sigma}\cdot\vec{E} = \int q\vec{v}f(\vec{v}) = \int q\vec{v}f_1(\vec{v}) \tag{18}$$

(since f_0 yields zero current). This gives the conductivity tensor

$$\sigma_{ij} = \frac{\tau q^2}{m}\int v\left(-\frac{\partial f_0}{\partial v}\right)\hat{v}_i\hat{v}_j d^3v. \tag{19}$$

This is readily calculated for f_0 the Maxwell distribution or for a f_0 the Fermi-Dirac distribution for the gas of electron quasiparticles in a low temperature (compared to the Fermi energy!) metal. In either case the integral is just $n\delta_{ij}$ with n the particle density, giving a diagonal conductivity

$$\sigma = nq^2\tau/m. \tag{20}$$