**Boltzman Equation w/ Two-Particle Potential**

Now we’re going to back to the original many-body Boltzman equation again:



but leave off the impurity interaction, and just focus on doing a better job modeling the two-particle interaction, in manner like we did the impurity potential force in last file. So just,



First we’ll do a phenomenological approach, similar to how we did the impurity potential, and then we’ll look at how this approximation may be more rigorously derived.

**Classical Boltzman Equation for two particle potential (heuristic derivation)**

Now let’s drop any random potential and go back to.



And we want to approximate the RHS. Using the impurity stuff as inspiration, and switching to discrete space, like we did then, so that f(r,k,t) is the probability of a particle occupying a chunk of phase space Δ3rΔ3k = (2πℏ)3 centered about rk, we may say:



But now we try to be a little more sophisticated about it. Particles scatter via collisions with other particles. A particle at rk can scatter out of that state by making a collision with another particle in state rk1. Likewise, a particle at rk´ can scatter into rk by making a collision with rk1. So should be able to say:



Now apropos the middle term let’s admit that:



(I guess N should be N-1 really but whatever, and area would be the scattering cross-section area) and similarly for the other middle term. So we can write:



where e.g. P(kk1→k´k´1) is the probability that two particles in state rk and rk1 scatter into a phase space volume Δ3k´Δ3k´1 about the points (rk´, rk´1). We can combine the non-f terms into a single term, called the scattering rate W (well, going to add/subtract a few non-f terms myself).



This is the rate at which two particles in initial states **kk**1 will collide and scatter into states **k**´**k**´1. So we can write:



I’ll take a step backwards, and aver that the product f(r,k)f(r,k1) ought really be the two-particle distribution function f(r,k;r,k1). And likewise for the other guy below it. Breaking f(r,k;r,k1) into f(r,k)f(r,k1) constitutes a mean field approximation, in this context called the assumption of molecular chaos, and is where entropy and the 2nd law of thermodynamics sneaks in. But anyway, now we have for the RHS of our equation:



Filling this into our equation, we arrive at the discrete version of Boltzman’s equation:



Now let’s put the equation in terms of probability densities, and scattering rate densities. So we should have f(r,k,t) → f(r,k,t)Δ3rΔ3k, which is to say we’re changing f(r,k,t) from a discrete probability distribution to a continuous probability density. And we’re going to do the same with the scattering rate W(kk1→k´k´1). The rate of scattering from a given kk1 to the Δ3k´Δ3k´1 block surrounding k´k´1 should be proportional to volume of k´k´1 space available to scatter into. So we should be able to say W(kk1→k´k´1) → W(kk1→k´k´1)Δ3k´Δ3k´1, where the former W(kk1→k´k´1) is the discrete probability of scattering into the Δ3k´Δ3k´1 block centered about k´k´1, whereas the latter W(kk1→k´k´1) is the scattering rate *density*, one might say. Filling these in, we have:



And now we can take the continuum limit,



So this is our Boltzman equation. But we can make a simplification. For time-reversal symmetric processess, the scattering rate should be the same going forwards or backwards. This is called detailed balancing. Assuming we have such, we can simplify the RHS to:



where,



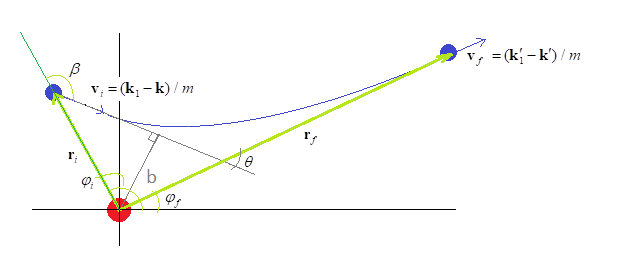
So keeping in mind our W(kk1→k´k´1) was redefined as a density, likewise P(kk1→k´k´1) is now a probability *density*, i.e., probability of scattering from kk1 → k´k´1 *per* (k-space) volume Δ3k´Δ3k´1. For most of the qualitative considerations we can stop here. But to be more quantitative, we have to put in a little more work on W. The probability (density) guy, P, is related to the differential scattering cross section converted to a probability distribution, i.e.,



where, in unfortunate notational coincidence **Ω** here is the solid angle (θ,φ) and dΩ = sin(θ)dθdφ. Pσ tells us the probability of an incoming beam with relative velocity vrel initially equal to |**k**1 – **k**|/m, say, being deflected into an angle **Ω** about its initial orientation. The magnitude of the relative velocity is unchanged, as we know from our work in Classical Mechanics collisions stuff – basically just energy conservation. And so we have the probability of the final relative velocity |**k**´1 – **k´**|/m. And so with the final **v**rel given (or at least its probability), and knowing that the center of mass momentum is unchanged thanks to no external force (or at least one which doesn’t affect things much on this time scale), we have the (probability of) the pair of momenta in the final situation. The probability (density) distribution of the final pair momenta can be written in terms of Pσ via:



where k´(Ω) and k´1(Ω) are the trajectories of the momenta after the collision. Can see this by integrating w/r to k´ and k´1 [in general, if have random variable *a*, and functions of this random variable x(a), y(a), z(a), then P(x,y,z) = ∫da P(a)δ(x-x(a))δ(y-y(a))δ(z-z(a))]. So we just need to get the final velocities in terms of the initial ones and the angle. A picture is helpful. General scattering process looks something like this (picture from Classical Mechanics folder – inverse square collisions). So particles start with initial relative position vector ri and relative velocity vector vi, and exit with relative velocity vector vf. The solid scattering angle Ω is in this picture just denoted θ, and is confined to the plane defined by **r**i×**v**i.



Recall in the classical mechanics folder we examined collisions generically using momentum and energy conservation, as well as explicitly for the hard shell interaction, and the inverse square interaction. And in all cases, we found for the final velocities of the two particles:



where **V** is the center of mas velocity, and θiv = φi – β is the angle of the original velocity vector. Translating to our **k** stuff, specializing to identical masses, and allowing for an initial setup which is azimuthally rotated about the original **v**i direction by angle φ – different kind of φ from the one in the diagram above):



where is the unit vector cos(θ0v+θ)**i** + sin(θ0v+θ)**j** rotated about the cos(θ0v)**i** + sin(θ0v)**j** direction by angle φ. For short, we could just say,



Note **i** and **j** are unit vectors in **r**i and **v**i plane. So now we have:



where we keep in mind that Ω stands for (θ, φ) basically. So now we have for W:



and our RHS simplifies to:



To facilitate doing the dΩ integral, we can orient the z axis (i.e., the θ = 0 axis) along the **k**1 – **k**k direction. Then θ0(**k**1-**k**) = 0. So we’ll have:



where,



And would be:



Altogether then, adding time arguments I forgot back into those f’s in RHS,



Pretty nasty non-linear integro-differential equation.

**Classical Boltzman Equation for two particle potential (rigorouser derivation)**

Now let’s see, roughly, how we can get this equation rigorously from the BBGKY hierarchy. So going back to the equation we derived previously:



where recall we’re now back to **Ω** = (**r**,**k**). We will presume that Fint is a short ranged force. Let’s say the range is ‘d’. Then for future reference let’s note the d**r**2 integral implicit within dΩ2 will only vary about a spherical ball of radius ‘d’ about **r**1. So I guess I’ll write:



Now to proceed we need to approximate the RHS somehow. To see how we consider the time-evolution equation for f(Ω1,Ω2,t). We worked this out in the previous RTA file:



Now we presume the external single particle forces F(r) are smoothly and slowly varying over the atomic length scale. For estimation sake, let’s say that f(Ω1,Ω2) were given by f(Ω1)f(Ω2) and f(Ω) ~ (1/V)exp(-(k2/2m + φ(r)/kT) (1/V so it’s roughly normalized). And similarly for f(Ω1,Ω2,Ω3). Then,



where R is the effective range of the internal force, and Ratom is the average radius of space available to an atom/molecule in our gas. For dilute gasses, we should have this term is very small. So we can neglect it.



where in the last line it is assumed that f(Ω1,Ω2,t) reaches some equilibrium distribution quite fast. And it is its steady state value which then feeds into the dynamics of f(Ω1,t). Then going back to the f1 integral equation, and focusing on the RHS, we can say:



where in the first line we can add the extra term b/c it’s zero by IBP. Now we’ll switch to center of mass/relative coordinates:



from which it follows:



in which case we have:



So we can write this as (denoting **Ω**, **ω** as the corresponding ‘center of mass’, and ‘relative’ variables):



We can presume that f2 doesn’t depend much on the center of mass coordinates, just relative coordinates (because correlations should be same no matter where the particles are centered in the box – it should only matter how far apart the particles are – and also no matter what the average momentum is, which should be close to zero pretty much always anyway). If so then we have:



We’ll observe that in the top line, the two **K** terms cancel. Next, recall the statement at the top of the page where we say that r2 is only varying within a ball about r1 of radius d. We do not expect the external force to vary appreciably at all within such a small radius. So we can replace F(r2) with F(r1). In that case, the force terms also cancel. And then we have:



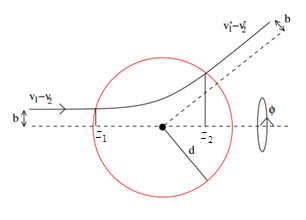
Can’t set the ∂/∂r2 part of ∂/∂r = ∂/∂r1 - ∂/∂r2 integrand term to zero via the usual IBP because of implicit restriction on range of dΩ2 integral. And can’t say ∫dΩ2f(Ω1,Ω2,t) = f(Ω1,t) because of same reason. Now we begin to introduce the scattering cross-section. To facilitate doing this we need set up an integral over the center of mass coordinates we’ve introduced. We can change variables of integration from **r**2 to **r** = **r**1 – **r**2, and so:



Now use cylindrical coordinates on the d3r integral, aligning the z direction with **k**, and we could write it as:



where dσ covers the target area transverse to the z direction. And remember that radius of circle is d, twice the radius of the particle(s), because that is the distance between the particle centers within which the force acts.



So we have (not changing the position arguments in the anti-derivative because we can presume that f doesn’t change much with z over that interval, though it does change a lot w/r to the momentum arguments):



If we do the molecular chaos assumption and factorize the two-particle distribution function, we’ll have:



and this is basically what we have above.