**Brownian Motion**

So we looked at diffusion in the context of a some entropic force – like a chemical potential gradient, or thermal gradient, or external force – driving the transport of particles from one spot to another. In these circumstances we had been implicitly presuming that the collisions of the particles with impurities, or whatever, were substantial enough that the changes in momentum undergone during a collision were large in comparison to the momentum imparted by the external force, or gradient. This meant that the system would tend to quickly relax to equilibrium, locally, and we can presume the behavior of the particles was just a sort of small deviation from local equilibrium. But we may be interested in scenarios where the momentum fluctuations induced by collisions with the substrate (or whatever) are *small* in comparison to that gained by the external force, or chemical potential gradient. One typical example is Brownian motion: basically a dilute heavy solute dissolved in some lighter solvent (like spritz of perfume in the air). In this case, the solute particles would be only slightly affected by the collisions with the solvent particles because they’re so light (and the solute particles would only rarely collide with themslves so we can neglect that too). And so whatever momentum the solute gains from, say, diffusing, will be large in comparison to the fluctuations in momentum brought about via collisions. Thus the equilibration process brought about by the collisions would be slow, and unlikely to establish local equilibrium. And so the local equilibrium presumption upon which we have based our analysis would have to be modified. According to the analysis of one guy I read, we can still use the local equilibrium formalism, as long as we now extend our concept of ‘local’, to include (**r**,**v**), instead of just **r**. Basically we consider the density, energy, entropy, etc., as functions in phase space, rather than just position space.

**Translational Diffusion**

So basically we consider s(u(**r**),n(**r**)) → s(u(**r**,**v**),n(**r**,**v**)). Note we’re still not treating average v as a state variable, just like we didn’t when we analyzed this problem before (but when we could consider collisions to be effective in engendering equilibration). FWIW, n(**r**,**v**) would basically be N×f(**r**,**v**), where f(**r**,**v**) is the single particle distribution function in Statistical Mechanics. I don’t know the justification for this, physically. But going through the motions, we may write the balance equations as follows, generalizing flux equations through space (see the continuum transport file):



(and recall in the continuum transport file we argued that to requisite order accuracy it was legitimate to take **π** → p**1**, well, at least if also isotropic medium) to flux equations through phase space:



where superscripts r, v mean components in those ‘directions’ in phase space. And the currents presumably also depend on **r** and **v**. But otherwise, not sure what the expression for these currents would look like. Seems we could straight-forwardly generalize the **v** appearing in the currents from a **v** in position space to a **v** in phase space. Not sure what we’d do with **j**q, though, for instance. Presuming as before that Tds = du – μdn, we have:



(carry out derivative in second line and it reproduces first line, and in last line I guess we’ll simplify to constant T) Now use: Ts = u + p – μn → Ts**v** = u**v** + p**v** – μn**v** → T(s**v** + **j**q/T) = u**v** + p**v** + **j**q – μn**v** → T**j**s = **j**ε - μ**j** . And we’re left with:



(we found the analogous result in the continuum transport file) So then we’d do the usual Onsager ansatz:



So the L’s are now 3×3 matrices. And this time, we don’t have **L**21 = **L**12. Positive definiteness of entropy production at position r in real space (regardless of v) requires rather that **L**12 = -**L**21, due to time reversal symmetry. Hmmm. Don’t know. Don’t care. We can impose some additional requirements on these **L**’s. The flux through position space would formally be given by:



but also given by, according to our statistical arguments at the beginning of the folder, or at least those in the Stat Mech folder:



Equating these two,



To make progress at this point we have to postulate a form for the velocity-dependent chemical potential. An ideal gas’s chemical potential is:



At constant T, this is basically,



We may improvise to generalize this to:



Then we have:



In order for this to be true for any n(**r**,**v**), we need **L**11 = 0, **L**12 = -n/m (proportional to identity tensor). For then,



where we say that the ∂n/∂**v** integral gives zero as n(**r**,**v**) ought to indeed be zero when |**v**| → ∞. Finally, we’ll phenomenologically identify **L**22 with n/mτ (proportional to unit tensor), where τ is the velocity relaxation time. Can take this as simply a definition for now. So now we have:



which is weird because **L**11 was non-zero in the normal local-equilibrium treatments. But okay. Now the Onsager relations come to:



Filling these back into the density balance equation…



Rearranging equation,



If change variables from **v** to **p** = m**v**, then we’d have:



which is:



This is the Fokker-Plank equation. This is precisely the result we’ll get when we use statistical mechanics to analyze the problem, specifically when we use the Langevin model. Might make a few observations, going back to the currents,



Now say our gas has equilibrated in velocity space, i.e., that it velocity distribution has assumed

Maxwellian form. This happens even during diffusion, and pretty fast, on the order of the time constant τ (see the stat mech files on this), even while the gas has not reached equilibrium in position space (because it keeps spreading out of course). Then j(v) must be zero. And so,



Plugging this into the position space current expression, and integrating both sides w/r to v, we’d have:



So we can identify the diffusion constant as:



Further, if we plug this into our diffusion equation now,



Integrating both sides w/r to v we get the RHS to vanish because n(r,v) → 0 as |v| → ∞. And so we have:



But then filling in our result for this current above, we get:



where D is that given above. This is the Einstein diffusion equation. We’ll derive this equation through microscopic means in the stat mech folder. But this approach shows that it can be derived from the microscopic Langevin approach by making the approximation that the momentum part of the distribution function is in perpetual equilibrium. Interesting that we can continue to fruitfully push the concept of entropy so far beyond equilibrium. Oh those n’s and j’s should have t’s in their arguments too.

**‘Angular’ Diffusion in a force field**

Let’s now consider the case of dipoles in an electric field. We may consider ε(s,n,ψ) → ε(s(θ),n(θ),ψ(θ)) where n(θ) is the density of dipoles at angle θ, and ψ(θ) is some force (electric) field. In that case we may write: ε(s,n,ψ) = ε0(s,n) – nqψ, where q = P (the dipole moment), and ψ = Ecosθ. It seems a little odd to consider dipoles not necessarily contiguous as a group. But so we do. The balances are:



where j is the current of dipoles transitioning from θ to θ + dθ. Working out the entropy equation,



not sure if we should identify the first term as js or what. More likely, it seems that js = 0 on physical grounds, and we’re setting the overall ∂/∂θ term to zero for usual reasons. Either way, then



And therefore



where I’ve assumed a form of the chemical potential analogous to the ideal one. And so then we have:



which is Debye’s equation.