This month’s and the next two month’s blogs mostly follow Chapter 12 in *Fundamentals of Statistical and Thermal Physics* by Frederick Reif with some occasional input from (and comment on) other resources. The primary aim of this post is to show how a very simplistic theory can put the mean free path to use in non-equilibrium situations to make a connection between macroscopically observing bulk transport and the underlying microscopic mechanical motions.

The three cases we will look at are the macroscopic effects of: 1) self-diffusion, which involves the transport of mass, 2) fluid viscosity, which involves the transport of momentum, and 3) heat conduction, which involves the transport of energy. This order follows the common order used in continuum mechanics for following bulk effect and the corresponding equations in that context are: 1) mass continuity, 2) Cauchy momentum equation, and 3) energy equation.

It is important to stress, that each of these computations is done without regard to the velocity distributions beyond what has already been employed to calculate the mean speed ${\bar V}$ and the mean free path $\lambda$. Thus, the results that are obtained need to consumed with some care. The functional dependence of the macroscopic terms on the underlying mechanical analogs is expected to be correct by the overall numerical factor will likely be off by up to a factor of 3 or 4. This situation is very similar to those discussed in previous blogs concerning which of the statistically significant speeds (most probable, mean, or RMS) should be used in any computation.

This blog will focus on self-diffusion as the model problem since the other two (viscosity and thermal) follow in much the same way.

Self Diffusion

In Reif’s treatment of self-diffusion, he considers a substance consisting of similar molecules where some subset of them is tagged so that they are observationally distinguishable but (though he doesn’t quite say this) their distinguishability doesn’t affect their mechanical motion. The mechanism he proffers is that they emit some sort of nuclear radiation that, ostensibly, doesn’t change the mass, but a fluorescence, for example by Raman spectroscopy, might have been a better choice. Regardless, it seems that he is trying to avoid the situation in which the mass concentration $\rho\_m$ varies by constructing a scenario in which only the number concentration $n$ does, ostensibly to avoid bulk motion due to macroscopic flows (i.e., the pressure is uniform).

Once the molecules have been tagged, he constructs a scenario in which the number density is uniform in the $x$ and $y$ at any fixed value of $z$ but which varies as $z$ does. As a result, the number density depends on position and time so that $n = n(z,t)$. There is now a corresponding number density flux ${\vec J} = J\_z(z,t) {\hat z}$ in the $z$-direction. Macroscopically, we assume that since $J\_z$ is non-zero when there are differences in the number density, then a linear relationship of the form

\[ J\_z = - D \frac{\partial n}{\partial z} \; , \]

will be adequate provided the gradients are small in some sense. This relationship is a specific example of Fick’s law

\[ {\vec J} = - D \nabla n \; \]

and $D$ is the self-diffusion constant. Support for so naming $D$ comes from the fact that if we take the divergence of both side of Fick’s law and the use number continuity equation

\[ \frac{\partial n}{\partial t} + \nabla \cdot {\vec J} = 0 \; \]

to eliminate $\nabla \cdot {\vec J}$ we get

\[ -\frac{\partial n}{\partial t} = -D \nabla^2 n \; , \]

which is the classical diffusion equation. This classical form, which is well-known, depends on the assumption that $D$ has no spatial dependence; an assumption that is usually stated but not justified. The elementary transport theory that Reif presents gives a rationale for this assumption and a mechanism to explore for when and how it might break down.

Now consider any plane whose normal is parallel to ${\hat z}$ in between the boundaries with the least and the most concentration of the tagged molecules

\*\*image 1\*\*

Reif argues that $1/6$ of the particles are heading in any of the 6 cardinal direction of $\pm {\hat x}$, $\pm {\hat y}$, and $\pm {\hat z}$. The forward and reverse number density fluxes, relative to crossing the plane in the +$z$-direction, are given by

\[ {vec J}\_{forward} = \frac{1}{6} n(z-\lambda) {\bar V} {\hat z} \; \]

and

\[ {\vec J}\_{reverse} = -\frac{1}{6} n(z + \lambda) {\bar V}{\hat z} \; .\]

Note that the mean free path comes in by linking the flux crossing the plane with the number density at a point $z \pm \lambda$ away from which represents that flux originates. In other words, the molecules that are crossing the plane at $z$ are carrying information from a region one mean free path away, since they will, on average, have suffered no collisions (i.e., interactions) in their travels from that region.

The $z$-component of the number density flux is then

\[ J\_z(z) {\hat z} = {\vec J}\_{forward} + {\vec J}\_{reverse} \; \]

or

\[ J\_z(z) = \frac{1}{6} {\bar V} \left[ n(z-\lambda) – n(z + \lambda) \right] = -\frac{1}{3} \lambda {\bar V} \frac{\partial n}{\partial z} \; .\]

Comparing the macroscopic expression arising from Fick’s law to this one we arrive at

\[ D = \frac{1}{3} \lambda {\bar V} \; .\]

It is interesting to note that in both Kittel’s and Kromer’s book *Thermal Physics* and in Ashley Carter’s *Classical and Statistical Thermodynamics* one finds more complicated arguments about averaging over directions and distances to get the leading numerical factor of $1/3$ in the above relation. I find each of the arguments personally difficult to follow; particularly problematic is that there is a strong linkage between the mean speed, the direction of motion, and the mean free path that leads to a ‘double average’ that ends up resulting in the same wrong numerical factor out front. As discussed above, the value of $1/3$ can be expected to be good only to a factors on the order of unity. Reif’s presentation, which simply asserts an intuitive $1/6$ for each of the $6$ cardinal direction, seems far more understandable and concise.

Last month’s blog presented the prototype ‘algorithm’ for relating macroscopic transport properties (e.g., the diffusion coefficient) to their microscopic mechanical attributes (e.g., the mean free path). This post extends the analysis by giving an elementary expression for relating viscosity and heat conduction to the mean free path, mean speed, and related molecular terms.

Viscosity

Viscosity as a macroscopic physical phenomenon has been discussed in previous blogs ([here](http://underthehood.blogwyrm.com/?p=1323) and [here](http://underthehood.blogwyrm.com/?p=1345)) and so only short summary will be provided here. The basic idea is that flow is often fixed or stagnant on a one surface while moving on another. This is the [essential point that Prandtl realized in his concept of boundary layer flow](http://underthehood.blogwyrm.com/?p=1313). The prototypical example is the flow is shown in the figure below where some fluid is forced to flow in the $x$-direction between two plates, separated by a distance $w$ in the $y$-direction, by moving the top plate with a velocity ${\vec u} = U {\hat x}$ with respect to the bottom plate which remains fixed.

\*\*image\*\*

The $x$-component of the fluid’s velocity $u\_x$ varies as a function of $y$ and the usual definition of the stress in the problem relates it to the velocity gradient

\[ d\_{xy} = \mu \frac{\partial u\_x(y)}{\partial y} \; . \]

The physical meaning of the stress is that $d\_{xy}$ is the amount of momentum $p\_x$ in the $x$-direction transported across any plane in the $y$-direction, which we will call $p\_{xy} = - d\_{xy}$ (with an appropriate change in sign to account for difference between a force acting on the fluid and the reaction of the fluid itself).

Again, using the Reif’s argument $1/6$ of the molecules will be crossing some plane $y=Y$ in the upward direction and $1/6$ of them will crossing downward. Assuming the molecular mass as $M$ and the number density as $n$, the difference in momentum is

\[ p\_{xy} = \frac{1}{6} M n {\bar V} \left[ u\_x(y - \lambda) - u\_x(y + \lambda) \right] = - \frac{1}{3} M n \frac{\partial u\_x}{\partial y} \lambda \; . \]

Comparing the two expressions gives the viscosity in terms of the microscopic parameters as

\[ \mu = \frac{1}{3} M n \{\bar V} \lambda = M n D \; . \]

As with all these types of results, this one should be taken with a grain of salt regarding the numeric factor. Other authors also get this $1/3$ but they do so using quite different ways of ‘averaging’ across the populations. Nonetheless, the functional dependence of the viscosity on the microscopic parameters is correct and, in this case, the analysis of this dependence leads to some interesting conclusions.

The first thing to note is that Reif expresses the mean free path generally as

\[ \lambda = \frac{1}{\sqrt{2} \sigma n } \; , \]

where $\sigma$ is the generic cross-section, which takes the value $\pi d^2$ for hard sphere collisions giving the expression derived earlier. This generalization will prove useful in a bit but first let’s look at using this formula for the mean free path explicitly for viscosity. Putting these together gives an expression for the viscosity

\[ \mu = \frac{1}{3 \sqrt{2} \sigma} M \{\bar V} \; \]

that may be quite surprising. The amount of viscosity delivered by a gas is independent of density, at least over a wide range of values for the physical parameters that enter into this theory. The limitations occur in the limits of a very small mean free path, in which the gas molecules are nearly always colliding with each other, or when the mean free path is larger than the physical size of the experiment. Kittel and Kroemer, in their book Thermal Physics, cite a quote from Robert Boyle in 1660 as reading

“Experiment 26 … We observ’d also that when the Receiver was full of Air, the included Pendulum continu’d its Recursions about fifteen minutes (or a quarter of an hour) before it left off swinging; and that after the exsuction of the Air, the Vibration of the same Pendulum (being fresh put into motion) appear’d not (by a minutes Watch) to last sensibly longer. So that the event of this experiment being other than we expected, scarce afforded us any other satisfaction, than that of our not having omitted to try it.”

Before pressing on with more physics, it is worth noting that there are two satisfying things about the above quote. The first is that Boyle was scrupulous enough to report the null result of performing this experiment; a sentiment that bucks the trend of modern science where only ‘breakthroughs’ are reported. Second, it is refreshing to hear the ‘snark’ that Boyle conveys on his own behalf.

Finally, Reif presents how the viscosity changes as a function of temperature. There is an obvious dependence of speed through the explicit appearance of ${\bar V} \propto T^{1/2}$ in calculating the viscosity. And, if the collision process were accurately modeled in terms of hard spheres this would be all there was to the dependence. However, the scattering cross section is, generically, a function of speed since the underlying forces (i.e., Coulomb scattering) have a stronger influence on the particle when it is moving slowly. This is where the relaxation of the hard sphere scattering assumption becomes relevant as the scattering cross section becomes a function of speed, which, in turn, is a function of temperature in the general case. Thus, in the general case

\[ \mu = \mu \left( {\bar V}(T), \sigma ( {\bar V}(T)) \; \]

leading to an overall dependance that Reif cites going as

\[ \mu \propto T^{0.7} \; . \]

An interesting implication of this functional dependence (with or without the extra, implicit temperature dependence coming through the effective cross section) is that the viscosity of a gas increases with increasing temperature, which is the exact opposite effect as is active in the vast majorities of liquids.