

Transport

When a system is not in equilibrium, various transport processes may occur. By a “transport process” is meant the transfer of energy, charge, particles, etc. by the physical motion of particles. In some cases, wave phenomena may be important in transport processes such as heat conduction in an electrical insulator. The fact that the material is an insulator means that the electrons are not free to move. The conduction of heat occurs by atoms passing energy from one to the next. So there is no net flow of atoms, but there is a flow of heat energy. This is similar to what happens with sound waves. Of course, sound waves can be thought of as phonons. . . . In the case of electric current, charge is transported by the physical movement of particles. In an electrical conductor, heat is transported by the “wavelike” action described earlier and also by the flow of electrons.

We will consider systems which are only mildly out of equilibrium. Usually these systems will be in a *steady state* in which nothing varies with time. Of course, this is an idealization—if we consider heat conduction by a system connecting two thermal reservoirs, then the reservoirs are assumed to be so large that the removal of heat energy from one reservoir and its addition to the other makes negligible change in the reservoirs.

If the system is only slightly out of equilibrium, it usually happens that a flow will be set up in such a direction that it would restore equilibrium. For example, consider a rod connecting two thermal reservoirs at different temperatures. Heat energy flows through the rod from the high temperature reservoir to the low temperature reservoir. This is the direction required to move closer to equilibrium. Note that since we’re discussing a non-equilibrium situation, the system tries to maximize or minimize the appropriate thermodynamic function (to get to equilibrium). In this case, we have reservoirs in thermal contact (through the rod). No work can be done and no particles can be exchanged. So the appropriate thing to do is to try and maximize the entropy. Sure enough, energy leaving a high temperature reservoir removes some entropy from that reservoir, but when that same energy is deposited in the low temperature reservoir, more entropy is added than was removed from the high temperature reservoir. So the system is creating entropy which is what you do if you want to maximize it! In other situations, the flow might be such that it would minimize the free energy.

Since we are speaking of a flow in response to a non-equilibrium situation, it seems reasonable that the “strength” of the flow should be proportional to the departure from equilibrium, at least for small departures from equilibrium. In other words, we’re going to assume that the flow can be expanded in a Taylor series in whatever measures the departure from equilibrium. The constant term must be zero (no flow at equilibrium) so the first term must be the linear term. We’ll assume that the linear term is non-zero and departures from equilibrium are small enough that we only need consider the linear term.

How do we measure a flow? An electric current density is an example. Recall that the electric current density is a vector which has the dimensions of charge per unit area

per unit time. In general, we'll consider the *flux density* which is a vector with units of whatever is being transported per unit area per unit time. The direction of the vector gives the direction in which the whatever is being transported. The magnitude gives the net amount of whatever that crosses a unit area perpendicular to the direction of the vector in a unit time. In the case of electric current density, negative charges moving with some velocity in some direction produce the same current as positive charges moving with the same velocity in the opposite direction. The current or flux density is always the **net** current or flux density. Sometimes we want the current or flux crossing a surface. This has units of whatever per unit time. It is found by integrating the current density or flux density times the unit normal over the surface,

$$I = \int_{\text{surface}} \mathbf{J} \cdot \mathbf{n} dA ,$$

where I is the current or flux, \mathbf{J} is the current density or flux density, \mathbf{n} is the unit normal to the surface pointing from the negative side to the positive side of the surface, and dA is the differential area element on the surface.

Food for thought: suppose the quantity being transported is itself a vector. How would you describe the flux density?

How do we measure a departure from equilibrium? In general, any non-uniformities in a system indicate non-equilibrium. For example, temperature variations, variations in particle concentrations, or variations in electric potential might indicate a non-equilibrium situation. But there's more to it than just a variation; there is also the scale of the variation. A 10,000 Volt potential difference between two electrodes in air is not a big deal if the electrodes are separated by several meters. Rather dramatic effects occur if they're separated by only a millimeter—probably more than the linear term is needed to describe the resulting transport! In other words, how rapidly the non-uniformity varies with position is the important quantity for determining the transport.

The upshot of all this hand waving is that a transport process is described by

$$\mathbf{J} = (\text{Constant}) \times [\nabla(\text{Scalar Field})] .$$

Some transport laws are the following: Ohm's law relating electric current density, \mathbf{J}_q to the electric field or the gradient of the electric potential where the coefficient is the conductivity, σ (not the entropy nor the cross section, here),

$$\mathbf{J}_q = \sigma \mathbf{E} = -\sigma \nabla \Phi .$$

The negative sign indicates that (positive) charge flows from high to low potential. For particle diffusion there is Fick's law relating the particle flux density, \mathbf{J}_n , to the concentration. The proportionality constant is called the diffusivity, D ,

$$\mathbf{J}_n = -D \nabla n .$$

Again, the negative sign indicates that particles diffuse from high to low concentrations. Note that diffusivity has dimensions of area per unit time or length times velocity. Fourier's law describes heat conduction. It relates the flow of energy (heat), \mathbf{J}_u to the temperature gradient. The proportionality constant is the thermal conductivity, K ,

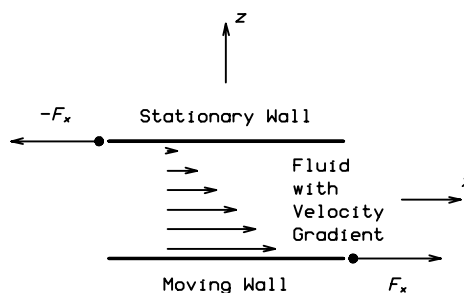
$$\mathbf{J}_u = -K\nabla\tau .$$

Guess what the negative sign means! In these units, K has the dimensions of one over a length times a time. In conventional units, K has the dimensions of energy per Kelvin per length per time.

K&K also discuss viscosity as a transport process. It is a transport process, but it's the transport of momentum—a vector! As K&K discuss viscosity, they refer to the transport of x -momentum in the z -direction. This is a force in the x -direction exerted by something at small z on something at large z and vice versa. Ordinary pressure is a transport of (say) x -momentum in the x -direction; a force in the x direction exerted by something at small x on something at large x and vice versa. Ordinary pressure might be thought of as a “straight ahead” force. The force due to z -transport of x -momentum may be thought of as a “sideways” force. Of course, that's too vernacular a term, so it's actually called a shear force. The diagram shows the standard example of viscosity. A fluid occupies the space between two parallel plates or walls. One plate is kept stationary and the other has a constant velocity in the x direction. The velocity is small enough that the fluid flows smoothly (laminar, not turbulent, flow). In the steady state, there will be a gradient in the velocity of the fluid as indicated in the diagram. Fluid elements in neighboring layers exert a drag force on each other. Fluid in contact with the walls exerts drag forces on the walls. These forces are in the x direction, but they are transmitted in the z direction. Also, it should be fairly clear that the force on a wall must be proportional to the area of the wall. The intensive quantity is force per unit area, like a pressure. Force is momentum per unit time, so we have momentum per unit area per unit time which is a momentum flux density. The faster the plates move relative to each other for a given thickness of fluid, the larger the drag force, so the gradient we need is the z -derivative of the x -component of the velocity. In other words

$$\frac{F_x}{A_z} = J_{p_x,z} = -\eta \frac{dv_x}{dz} .$$

The subscripts on J indicate it's the x -momentum flux density in the z direction. The proportionality constant, η is called the viscosity. Its dimensions are mass per length per time. The cgs unit of viscosity is the poise, 1 poise = 1 g cm⁻¹ s⁻¹.



Transport Coefficients

The constants that occur in the transport equations must depend on the microscopic processes which are going on in the system. In particular, if the system is a gas, then they must depend on the collision rate, the typical velocity and the mean free path. For example, if we consider diffusion, then if gas atoms were point particles, diffusion would occur at the typical average speed of the gas molecules. Instead, diffusion is much slower because particles are bigger than points and they collide and have their velocities randomized after roughly a mean free path. What we are going to do now is obtain order of magnitude expressions for these constants in terms of microscopic parameters. The discussion will be at the same level as the simple derivation of the mean free path. We will miss out on factors of order unity, but we will determine the overall dependencies on microscopic parameters.

Diffusivity

As a first example, we will work out an expression for the diffusivity of molecules in a gas (or solute molecules in a dilute solution). Let's suppose there is a concentration gradient in the z -direction. Imagine sitting at a point in the gas and watching the molecules go by. If dn/dz is positive then when you see molecules coming from the $+z$ direction, they've come from a place where the concentration was higher. Molecules coming at you from the $-z$ direction came from a place where the concentration was lower. Molecules coming at you from anywhere in the xy -plane have come from places with the same concentration. Molecules from other directions have come from intermediate concentrations. How far away have the molecules come from? Assumption: on average, they came from one mean free path away and have the concentration at that location. What is the flux density of such molecules. Assumption: it's just the concentration we've just mentioned times the average velocity. So if we look in direction (θ, ϕ) , the concentration carried by the molecules coming from that direction is

$$n(\mathbf{r}_0 + \delta\mathbf{r}) = n(\mathbf{r}_0) + \frac{dn}{dz}\delta r_z = n(\mathbf{r}_0) + \ell \cos\theta \frac{dn}{dz},$$

where \mathbf{r}_0 is the position under discussion and $\delta\mathbf{r}$ is a vector of length ℓ in direction (θ, ϕ) . As mentioned, to get the flux density, we multiply by the average velocity. But this gives the flux density in the direction opposite to (θ, ϕ) . We want the z -component of the flux density (the other components average to zero by symmetry), so we need to multiply by a $\cos\theta$. Also, we need a minus sign to account for the fact it's opposite to (θ, ϕ) . Altogether, the z -component of flux density carried by molecules coming from (θ, ϕ) is

$$J_z(\theta, \phi) = -\bar{c} \cos\theta \left(n(\mathbf{r}_0) + \ell \cos\theta \frac{dn}{dz} \right).$$

Now, we need to average J_z over all θ and ϕ . That is, average over the surface of a sphere. The first term averages to 0. The second term involves the average of $\cos^2 \theta$ over the surface of a sphere. It's useful to remember that this is $1/3$. (But easy to work out if you forget.) Finally, we have

$$J_z = -\frac{1}{3}\bar{c}\ell\frac{dn}{dz},$$

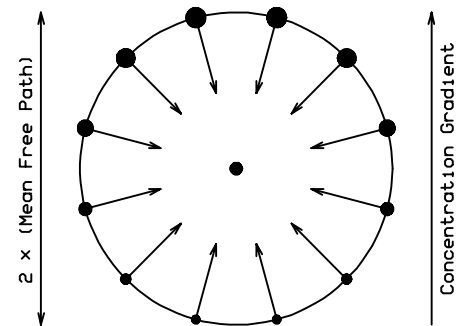
from which we deduce that the diffusivity is

$$D \approx \frac{1}{3}\bar{c}\ell,$$

where the approximation sign reflects the approximate nature of our treatment. This also means it doesn't much matter whether you use the mean free path expression with or without the $\sqrt{2}$ factor!

A Bit More on the Diffusivity

When we obtained our expression for the diffusivity, we did an integral over a sphere of radius one mean free path. The sphere is shown in the diagram. We used one mean free path, because, on average, a particle passing through the center of the sphere had its last collision one mean free path away. And, on average, it reflects the concentration, temperature, whatever, at the point where it had its last collision. The arrows in the diagram show the velocity vectors (on average—the average velocity, \bar{c}) of particles leaving the sphere and heading toward the center. The size of the dots is meant to indicate the concentration. There are more particles per unit volume at the “top” of the sphere than at the “bottom”, so more particles go by in the downward than the upward direction. The integral we did, which gave the result $D = \bar{c}\ell/3$, was just a formal treatment of this picture.



Thermal Conductivity

To get an expression for the thermal conductivity, we can use the same approach, but modified in details, that we used for the diffusivity. Recall that the transport law is

$$\mathbf{J}_u = -K\nabla\tau ,$$

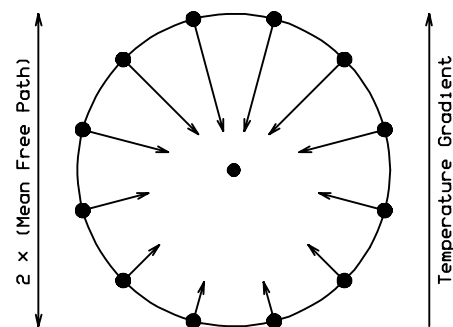
where \mathbf{J}_u is the energy flux density, τ is the temperature, K is the thermal conductivity which we want to evaluate by looking at what’s going on at the molecular level. As a first approach, we consider a point in an ideal gas in which there is a temperature gradient, go one mean free path away, look at the energy density, calculate the flux density of the energy from that direction, and then integrate over a sphere to get the average flux density of the energy. There is just one small problem. The energy density in an ideal gas must be constant!

Why is that? There is a temperature gradient, but if the gas is at rest, with no external forces applied, there cannot be a pressure gradient. The ideal gas law is $p = n\tau$ and for a monatomic ideal gas, the energy density is $(3/2)n\tau$ which must be constant if p is constant. For other ideal gases, the $3/2$ factor will be different, but it will still be true that the energy density is constant as long as the pressure is constant. This is the source of the following amusing paradox. You get up in the morning. It’s cold. You turn up the heat. Pretty soon you’re nice and warm. Where is the energy consumed by the furnace as the air in your room was heated? It’s not in the room where you are—it’s all outside! In any case, let’s represent the energy density, energy per unit volume by

$$u = \hat{C}_V\tau ,$$

where \hat{C}_V is the heat capacity at constant volume per unit volume for the gas under consideration. For a monatomic ideal gas, $\hat{C}_V = 3n/2$. If there is a temperature gradient, but the pressure is constant, then \hat{C}_V has a gradient opposite to the temperature.

If the energy density is constant, then how can there be a flow of energy? The temperature varies, so the average velocity varies. The flux density varies because the energy is transported faster in high temperature regions than in low temperature regions. This is indicated in the figure where the dots represent energy density, not a function of position, and the arrows show the mean speed which is larger at the larger temperatures, so energy from the high temperature region (“top”) of the sphere arrives faster than energy from the low temperature region. The z component of the energy flux density coming from one mean free path away from the center of the sphere in the direction (θ, ϕ) is



$$J_{u,z}(\theta, \phi) = -u\bar{c}(\ell, \theta, \phi) \cos\theta ,$$

Now,

$$\bar{c}(\ell, \theta, \phi) = \bar{c}(0) + \ell \cos \theta \frac{d\bar{c}}{dz}.$$

Remember that $\bar{c} \propto \sqrt{\tau}$, so

$$\frac{d\bar{c}}{\bar{c}} = \frac{1}{2} \frac{d\tau}{\tau}.$$

We plug this into our expression for the flux density and we have

$$J_{u,z}(\theta, \phi) = -u \cos \theta \left(\bar{c}(0) + \ell \cos \theta \frac{d\tau}{dz} \frac{\bar{c}}{2\tau} \right).$$

Now we average over the surface of the sphere. The term containing $\bar{c}(0)$ gives 0 and the other term yields

$$J_{u,z} = -u\ell \frac{\bar{c}}{6\tau} \frac{d\tau}{dz} = -\frac{1}{6} \hat{C}_V \bar{c} \ell \frac{d\tau}{dz}.$$

We conclude

$$K \approx \frac{1}{6} \hat{C}_V \bar{c} \ell \approx \frac{1}{2} \hat{C}_V D.$$

Again, the approximation signs are there so we don't take the factors out in front too seriously, because our treatment is very simplified.

In fact, you will notice that we have an overall factor of 1/2 compared to K&K (who also provide a simplified treatment). I believe our factor of 1/2 comes from the proper treatment of the velocity gradient in terms of the temperature gradient. However, there are a lot of things we have left out! In fact doing the integrals correctly is a bit messy, but let me just mention one thing that makes changes to what we've done. The velocity appears in the energy, that which is to be transported, and in the speed of the transport. So we really need to average the energy times the velocity with the Maxwell probability distribution. This increases the average over what we have. It's similar to the change in the speed distribution of particles coming out of small hole in an oven that we worked out in an early homework assignment. I believe this effect changes the factor out in front to 2/3 instead of 1/2. (For monatomic molecules—it affects diatomic molecules differently because not all the energy is translational kinetic energy.)

In any case, the main physical terms are in our expression. Ignoring the overall factors, we have

$$K \propto \hat{C}_V \bar{c} \ell \propto n \sqrt{\frac{\tau}{m}} \frac{1}{nd^2} \propto \sqrt{\frac{\tau}{m}} \frac{1}{d^2}.$$

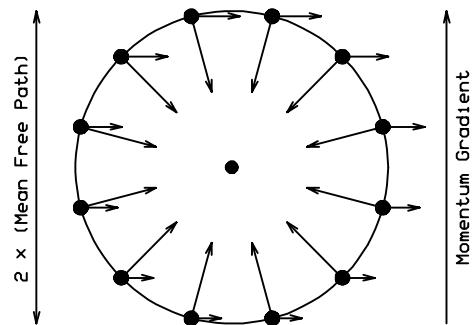
This tells us that other things being equal, light, small molecules have higher thermal conductivities than heavy or big molecules. Table 14.3 of K&K shows this to be the case. For example, the conductivity of ^4He is about six times that of N_2 . The other possibly surprising thing about this expression is that the only macroscopic parameter it depends on is the temperature. It does not matter how dense a gas is, it conducts heat at the

same rate. A low density gas doesn't have as many molecules to conduct heat as a high density gas, and so you might have expected that a low density gas wouldn't be as effective. However, the low density means that the molecules can go farther between collisions and "starting over." There are fewer molecules, but each one can do a better job.

Of course, this breaks down when the density is so high that the gas is about to become a liquid or when the density is so low that we are in the regime where the mean free path is on the scale of macroscopic dimensions.

Viscosity

We apply the same method as before to relate the viscosity to microscopic parameters. The figure shows momentum in the x direction with a gradient in the z direction. Rightward pointing arrows are the momentum vectors and radial arrows are the transport velocity vectors. It's important to remember that the momentum vectors represent a bulk motion of the gas. In other words, the velocity probability distribution has its center shifted away from zero, $\exp(-m(v_x - v_{x0})^2/2\tau)$ rather than $\exp(-mv_x^2/2\tau)$. The transport velocity vectors are random velocities and we're just picking the radial ones to calculate the flow at the center of the sphere.



The transport law is

$$J_{p_x,z} = -\eta \frac{dv_x}{dz},$$

where v_x is the bulk velocity of the gas. If $\rho = mn$ is the mass density then the x -momentum flux density z -component of the gas at (ℓ, θ, ϕ) which is flowing in a radial direction is

$$J_{p_x,z}(\ell, \theta, \phi) = -\rho(\ell, \theta, \phi)v_x(\ell, \theta, \phi)\bar{c}(\ell, \theta, \phi) \cos \theta.$$

We assume the density and the average velocity are constant, so

$$J_{p_x,z}(\ell, \theta, \phi) = -\rho\bar{c} \cos \theta \left(v_x(0) + \ell \cos \theta \frac{dv_x}{dz} \right).$$

Now we average over the sphere. The term containing $v_x(0)$ gives zero and we are left with

$$J_{p_x,z} = -\frac{1}{3}\rho\bar{c}\ell \frac{dv_x}{dz}.$$

We conclude

$$\eta \approx \frac{1}{3}\rho\bar{c}\ell \approx \rho D.$$

Again, our treatment is very simplified. We've ignored the fact that the x component of the transport velocity must be averaged with the x -component of momentum using the Boltzmann factor. I believe that if this is taken into account, it multiplies the results by 4/5.

But again, we've got all the important terms in our expression. Ignoring all the numerical factors,

$$\eta \propto mn \sqrt{\frac{\tau}{m}} \frac{1}{nd^2} \propto \sqrt{m\tau} \frac{1}{d^2}.$$

Small or heavy molecules have a higher viscosity than large or light molecules. Again, the only macroscopic parameter the viscosity depends on is the temperature. In particular, there is (surprisingly?) no dependence on pressure or density. Partially evacuating an experimental apparatus will not reduce "air drag" unless the vacuum is good enough that the mean free path becomes bigger than the size of the apparatus!

Caveat: we are talking about the air drag for viscous flow, where the drag is caused by the viscous forces. This is low speed, laminar flow. A more usual case for macroscopic objects moving through air is inertial drag caused by having to move the air "out of the way." This provides a force proportional to ρv^2 .

If we form the ratio of the thermal conductivity to the viscosity we have

$$\frac{K}{\eta} = \frac{1}{2} \frac{\hat{C}_V}{\rho},$$

or

$$\frac{K\rho}{\eta\hat{C}_V} = \text{Constant— independent of gas.}$$

Table 14.3 of K&K with experimentally determined values shows this to be approximately correct. Good! However, our constant is 1/2 (5/6 if the corrections mentioned above are included), while the table has values around 1.9 – 2.5. Not so good! To do a better job we need to pay more attention to all the details of the probabilities and be sure that we compute all the averages correctly. Also note in table 14.3 that the values for monatomic gases are somewhat higher than for diatomic gases. This goes in the direction mentioned in passing above.