High Vacuum Statistical Mechanics

As we’ve mentioned, when the pressure is less than about a millionth of an atmosphere at room temperature, the mean free path becomes long enough that it’s comparable to the size of laboratory apparatus. As the gas becomes even more rarified, it becomes a better and better approximation to completely ignore the interactions between gas molecules and to consider only the interactions between the molecules and the walls of the container.

The flux density of particles crossing a unit area perpendicular to the $x$ direction and headed in the positive $x$ direction is

$$J_{n,x} = n \left( \frac{m}{2\pi \tau} \right)^{3/2} \int_{0}^{+\infty} v_x \, dv_x \, e^{-mv_x^2/2\tau} \int_{-\infty}^{+\infty} dv_y \, e^{-mv_y^2/2\tau} \int_{-\infty}^{+\infty} dv_z \, e^{-mv_z^2/2\tau} ,$$

$$= n \left( \frac{m}{2\pi \tau} \right)^{1/2} \int_{0}^{+\infty} v_x \, dv_x \, e^{-mv_x^2/2\tau} ,$$

$$= n \sqrt{\frac{\tau}{2\pi m}} ,$$

$$= \frac{1}{4} n \bar{c} .$$

If there is a hole of area $A$ in a vacuum system (with a good vacuum on the outside, too), the flux of particles leaving through the hole is

$$\Phi = \frac{1}{4} A n \bar{c} = n S , \quad S = \frac{1}{4} A \bar{c} .$$

$S$ is called the conductance of the hole. It’s just the volume of gas which flows through the hole per unit time. Of course, the gas isn’t very dense, so this may not be much mass!

We can write the particle flux as

$$\Phi = \frac{p}{\tau} S = \frac{Q}{\tau} , \quad Q = p S .$$

$Q$ is called the throughput. It has the dimensions of a pressure times a volume per unit time. An interesting point about the throughput is that, numerically, it gives the volume per second that flows through a hole at unit pressure.
In general, there will be a flux of particles passing through a hole from both sides. The net flux passing through the hole from side 1 to side 2 is

$$\Phi_{\text{net}} = \frac{1}{4} A (n_1 \bar{c}_1 - n_2 \bar{c}_2) = \frac{1}{4} A \left( \frac{p_1 \bar{c}_1}{\tau_1} - \frac{p_2 \bar{c}_2}{\tau_2} \right).$$

Suppose we want there to be no net flux (by the way, we assume the gas on either side of the hole is the same kind of gas; the same molecular mass). Then

$$\frac{p_1 \bar{c}_1}{\tau_1} = \frac{p_2 \bar{c}_2}{\tau_2},$$

or

$$\frac{p_1}{p_2} = \frac{\tau_1}{\tau_2} \left/ \frac{\bar{c}_1}{\bar{c}_2} \right. = \sqrt{\frac{\tau_1}{\tau_2}},$$

and there can be a net flux of molecules even when the pressures are the same! The net flow is from the cold side to the hot side. In order to have zero net flux when there is a temperature difference, the pressure on the hot side must be higher than the pressure on the cold side!

Since the energy of a molecule is proportional to the temperature, the net energy flux is

$$P_{\text{net}} \propto p_1 \sqrt{\tau_1} - p_2 \sqrt{\tau_2}.$$ 

Even when the pressures are equal and the net flow of particles is from cold to hot, the net flow of energy is from hot to cold!

An interesting calculation involves the flow through a tube under high vacuum conditions. There must be a pressure difference from one end of the tube to the other to account for the “friction” between the molecules and the walls of the tube. We suppose the gas particles are flowing through the tube with mean speed (parallel to the tube) $\langle u \rangle$. The tube has diameter $d$, input opening cross section $A = \pi d^2 / 4$, length $L$, and the concentration of molecules in the tube is $n$. We suppose that on average, when a molecule hits the wall of the tube, it has a velocity parallel to the direction of flow equal to the average velocity, $\langle u \rangle$. When it recoils from its collision with the wall of the tube, on the average, it has zero velocity parallel to the tube. In other words, each collision with the wall transfers momentum $P = m \langle u \rangle$ and scatters the molecule isotropically. This is analogous to the assumption that a molecule is thermalized at its last scattering which occurred one mean free path away. This is the assumption we made when considering transport in gases. The rate at which molecules strike the tube is $n \bar{c} \pi L d / 4$, so the net longitudinal force on the tube is

$$F = \frac{\pi}{4} m \langle u \rangle n \bar{c} L d = \Delta p A,$$

where the pressure difference times the area of the opening is “external force.” We solve for the average velocity and then the net flux of molecules through the tube,

$$\langle u \rangle = \frac{\Delta p d}{mn \bar{c} L},$$
\[ \Phi_{net} = n\langle u \rangle A = \frac{\Delta p Ad}{m\bar{c}L} = \frac{\Delta p S}{\tau}, \]

where

\[ S = \frac{Ad\tau}{m\bar{c}L} = \frac{1}{4} A\bar{c} \left( \frac{\pi d}{2L} \right), \]

is the conductance of the tube. We see that the conductance is the same as the conductance of a hole with the same opening area as the tube multiplied by the ratio of the diameter to the length. This just says that the longer the tube, the more likely it is that a molecule will collide with the walls of the tube and the harder it is for a molecules to get through. Of course, the above treatment breaks down for a short tube because it gives a bigger conductance than a simple hole. This is because the assumption that most molecules hit the wall breaks down for a short tube. K&K point out that the factor of \( \pi/2 \) in parentheses should be replaced by \( 4/3 \) if a more careful averaging is done. Oh well...

Vacuum pumps have a characteristic “speed” which is the volume per unit time pumped at the input pressure of the tube. Note that this is the same definition as that of the conductance of a hole or tube. Conductance is also referred to as speed. If a pump is in series with a tube the reciprocals of the speeds add to give the reciprocal effective speed. So speed (conductance) is inverse resistance and in this respect, the conductance and resistance we’ve been talking about are like electrical conductivity and resistivity. To see this suppose the system is isothermal and suppose the pressure at the intake end of the tube is \( p_1 \) and the pressure at the output of the tube which is the input of the pump is \( p_2 \). Then the net flux is (analogous to electric current)

\[ \Phi_{net} = \frac{p_1}{\tau} S_{\text{eff}} = \frac{p_1 - p_2}{\tau} S_{\text{tube}} = \frac{p_2}{\tau} S_{\text{pump}}, \]

from which we deduce

\[ \frac{1}{S_{\text{eff}}} = \frac{1}{S_{\text{tube}}} + \frac{1}{S_{\text{pump}}}. \]

Also note that \( p/\tau \) is analogous to the electric potential. (Although we might be pushing this a little too far, since there’s a \( \sqrt{\tau} \) in the speeds which comes from \( \bar{c} \).)

If we start out with a volume \( V \) of ideal gas at temperature \( \tau \), containing \( N \) molecules, then \( p = N\tau/V \). If this is attached to a pumping system with effective speed \( S \), the rate at which the pressure decreases is

\[ \frac{dp}{dt} = \frac{\tau}{V} \frac{dN}{dt} = -\frac{\tau}{V} \frac{pS}{\tau} = -\frac{S}{\tau} p, \]

which has the solution

\[ p = p_0 e^{-t/t_0}, \quad t_0 = \frac{V}{S}. \]

Note that we assumed the system is isothermal. In actual practice, the pressure goes down rapidly (roughly like the above solution) at first, but then reductions occur much more
slowly. Molecules adsorbed on the surfaces of the vacuum apparatus de-adsorb and must be pumped out. Also, molecules trapped in the interiors of porous materials can outgas and keep the pressure from dropping as rapidly as one would expect.

Diffusion Equations

All of our transport equations had the generic form of a gradient of a quantity times a constant yielded a flux density of a related quantity. For example, consider heat conduction and temperature,

\[ J_u = -K \nabla \tau . \]

When we discussed transport we assumed a steady state. However, the main requirement for the above transport equation to be valid is that the system be not too far from equilibrium so that we need only consider a linear relation between flux density and driving force.

Suppose we consider the divergence of \( J_u \). What is the physical meaning of \( \nabla \cdot J_u \)? To find out, we’ll integrate over a volume \( V \) bounded by a surface \( S \) and use the divergence theorem,

\[ \int_V \nabla \cdot J_u \, dV = \oint_S J_u \cdot n \, dA , \]

where \( n \) is the outward pointing unit normal to the surface \( S \) and \( dA \) is an element of area on the surface. Recall that the magnitude of \( J_u \) is the energy per unit time that flows across a unit area perpendicular to \( J_u \). The integral above is the amount of energy that leaves the volume \( V \) by passing through the surface \( S \). Assuming that any change in energy inside \( S \) must be the result of energy passing through the boundaries of \( S \), we have

\[ \int_V \nabla \cdot J_u \, dV = - \frac{d}{dt} \int_V u \, dV , \]

where \( u \) is the energy density. If we assume \( S \) is a fixed surface, then we can move the time derivative inside the integral where it must become a partial derivative. We have

\[ \int_V \left( \nabla \cdot J_u + \frac{\partial u}{\partial t} \right) \, dV = 0 . \]

This must be true for any volume, so the integrand must be zero and we have

\[ \nabla \cdot J_u + \frac{\partial u}{\partial t} = 0 . \]

This is called a continuity equation. It simply says that the change in energy in a volume is due to energy passing through the boundaries of the volume. It can also be called an
energy conservation equation. It’s exactly analogous to the charge conservation equation in E&M; just replace $J_u$ with $J_q$ (electric current density) and $u$ with $\rho$ (charge density).

Now we consider the time rate of change of $u$ in more detail. In our previous discussion, we took $u = \dot{C}_V \tau$, where $\dot{C}_V$ is the heat capacity per unit volume at constant volume. This was motivated by considering an ideal gas. We will assume that volume changes can be ignored, and then we have

$$du = \dot{C} \, d\tau,$$

which is valid for systems other than an ideal gas provided $\dot{C}$ can be treated as independent of temperature. Then the continuity equation becomes

$$\nabla \cdot J_u + \dot{C} \frac{\partial \tau}{\partial t} = 0.$$

Finally we substitute from the transport equation to eliminate $J_u$ and we have

$$\nabla^2 \tau - \frac{1}{D_\tau} \frac{\partial \tau}{\partial t} = 0,$$

$$D_\tau = K \frac{\dot{C}}{C}.$$

The constant $D_\tau$ is the “diffusivity” of the temperature or internal energy (since $du = \dot{C} \, d\tau$). The equation we’ve just derived, which has a second space derivative minus a constant times a first time derivative, is called a diffusion equation. You will notice it looks a little like the Schroedinger equation, except it’s entirely real. This changes the character of the solutions from oscillations (for Schroedinger) to “spreading out” (for diffusion). It also looks a little like a wave equation except a wave equation has a second time derivative. Again, this changes the solutions from oscillations to diffusion.

The diffusion equation, like Schroedinger’s equation and the wave equation, is one of the ubiquitous partial differential equations of physics. In the homework you are asked to derive the diffusion equation for particle diffusion.

Note that the diffusivity has the dimensions of a speed times a length, or length squared divided by time. For a gas, the order of magnitude is the the average velocity times the mean free path. For an insulating solid, one might guess it’s the speed of sound times the mean distance between molecules. For a metallic solid, it’s more complicated as energy is transported by electrons but stored in lattice vibrations.

The diffusion equation occurs with a magnetic field in a conducting medium. Starting from Ampere’s law (Gaussian units), we have

$$\nabla \times B = \frac{1}{c} \frac{\partial E}{\partial t} + \frac{4\pi}{c} J.$$

In a conducting medium, $J = \sigma E$ where $\sigma$ is the conductivity. Insert this in place of the current density and take the curl of Ampere’s law.

$$\nabla \times (\nabla \times B) = \frac{1}{c} \frac{\partial \nabla \times E}{\partial t} + \frac{4\pi \sigma}{c} \nabla \times E.$$
We expand the double curl with a vector identity,

\[ \nabla \times (\nabla \times B) = \nabla (\nabla \cdot B) - \nabla^2 B = -\nabla^2 B , \]

where we eliminated the first term since there is a Maxwell equation which says \( \nabla \cdot B = 0 \). Substitute for \( E \) from Faraday’s law,

\[ \nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t} , \]

to get

\[ -\nabla^2 B = -\frac{1}{c^2} \frac{\partial^2 B}{\partial t^2} - \frac{4\pi \sigma}{c^2} \frac{\partial B}{\partial t} . \]

If the conductivity is larger than the characteristic frequency associated with the time variation of \( B \), in other words, for a good conductor, we can ignore the term with the second time derivative compared to the first and we have

\[ \nabla^2 B - \frac{1}{D_B} \frac{\partial B}{\partial t} = 0, \quad D_B = \frac{c^2}{4\pi \sigma} . \]

Sample Solution of the Diffusion Equation: Equilibrating Bar

In the next few sections we’ll discuss some solutions of the diffusion equation. The first thing to notice is that it’s a linear, homogeneous equation. This means that any solution can be multiplied by a constant and this yields another solution. Also, the sum of any two solutions is a solution.

In general, the solution must be determined in conjunction with the boundary conditions: specifications of the desired solution at a given time from which the solution can be integrated forward (it’s a first time derivative). It is often a good idea to expand the solution as a sum of simple solutions such as plane waves. The plane waves can be evaluated at \( t = 0 \) and adjusted to fit the boundary conditions. Then the diffusion equation is used to determine the time dependence of each wave.

As an example, suppose we have a bar which has been used to conduct heat between a hot reservoir and a cold reservoir. If the bar has come to a steady state, and if it has a uniform cross section, there will be a linear temperature gradient along the bar. Suppose the reservoirs are removed and the bar is isolated from the rest of the world. What happens? Heat flows from the hot end of the bar to the cold end until the bar reaches a uniform temperature distribution. What happens in detail? To answer that, we have to solve the diffusion equation with the initial condition that there is a uniform temperature gradient in the bar.
We let $x$, $0 < x < L$, represent the coordinate along the bar, with $L$ being the length of the bar. At $t = 0$, when the reservoirs are removed, we can take the temperature in the bar to be

$$\tau(x, 0) = \frac{1}{2} \Delta \tau (1 - 2x/L),$$

where $\Delta \tau$ is the temperature difference from one end to the next. This makes the mean temperature 0. Actually, we can add a constant to this temperature without affecting the problem, so the mean temperature can be the mean temperature of the two reservoirs. Since this is a one-dimensional problem, $\nabla^2 = d^2/dx^2$ and we have $\nabla^2 \tau = 0$ which says $d\tau/dt = 0$ which says that the bar just sits there with the linear temperature gradient. We know this can’t be right, but where did we go wrong? In fact, it’s right when the bar is between the two reservoirs and a steady state has been reached. But in this situation, heat is entering the bar at the hot end and leaving the bar at the cold end. Once we remove the bar from the reservoirs, we need to look for solutions with $J_x(x = 0) = 0$ and $J_x(x = L) = 0$. Since $J \propto \nabla \tau$, we need solutions with $d\tau/dx = 0$ at the ends of the bar. Our boundary conditions are that at $t = 0$ the bar has a linear temperature gradient as above, and for all time $t > 0$, $d\tau/dx = 0$ at the ends of the bar.

These may seem like incompatible conditions. The problem is the abrupt change of slope at the ends of the bar. We will see that what happens in our solution is that the heat flow in the bar when it’s removed from the reservoirs causes an “infinitely” fast flattening of the slope at the ends so there is no heat flow into or out of the ends. (In real life, it’s not possible to remove the bar from the reservoir abruptly, so it’s not necessary to have this infinitely fast change!)

Suppose we consider a solution of the form $\sin(kx)f(t)$, where $k$ is a constant (the wave number) and $f(t)$ is a yet to be determined function of time. If we plug this into the diffusion equation, we have

$$-k^2 \sin(kx)f(t) - \frac{1}{D} \sin(kx) \frac{\partial f(t)}{\partial t},$$

which has the solution for $f(t)$,

$$f(t) = f_0 e^{-Dk^2 t}.$$

Similarly,

$$\tau(x, t) = \cos(kx)e^{-Dk^2 t},$$

is also a solution of the diffusion equation. An arbitrary sum of these solutions is also a solution. So, our plan is to evaluate the solutions at $t = 0$, find a sum which matches the boundary conditions, and then add the time dependence to the sum to get the solution for times greater than $t > 0$. The solutions above don’t necessarily satisfy the boundary condition having to do with the gradient of $\tau$ at the ends of the bar. In particular, we can’t
use the \( \sin(kx) \) functions at all, because they give \( d\tau/dx \propto \cos(kx) \) which is non-zero at \( x = 0 \). So we can only use the \( \cos(kx) \) functions which automatically satisfy the boundary condition at \( x = 0 \). At \( x = L \), we have \( d\tau/dx \propto \sin(kL) \). This will be zero if \( kL = n\pi \) where \( n \) is an integer.

So, our general solution which satisfies the boundary conditions at the ends of the bar is

\[
\tau(x, t) = \sum_{n=1}^{\infty} A_n \cos(k_n x) e^{-Dk_n^2 t}, \quad k_n = \frac{n\pi}{L},
\]

where \( A_n \) are constants to be adjusted to make the solution have the correct linear dependence at \( t = 0 \). In other words, we are writing the linear temperature gradient as a Fourier series. To determine the coefficients \( A_n \), we multiply by \( \cos(k_m x) \) and integrate from 0 to \( L \). We get 0 for \( n \neq m \). For \( n = m \), we have

\[
\int_0^L A_m \cos(k_m x) \cos(k_m x) \, dx = A_m L/2.
\]

We do the same thing with the desired linear dependence. Note that when \( n \) is even the cosine functions are symmetric about the center of the bar. The temperature gradient is odd about the center of the bar, so there will be no even terms in the sum. For the odd terms, the coefficients are

\[
A_n L/2 = \int_0^L \frac{1}{2} \Delta\tau (1 - 2x/L) \cos(n\pi x/L) \, dx,
\]

\[
= \frac{\Delta\tau L}{2n\pi} (1 - 2x/L) \sin(n\pi x/L) \bigg|_0^L + \frac{\Delta\tau L}{2n\pi} \frac{2}{L} \int_0^L \sin(n\pi x/L) \, dx,
\]

\[
= 0 - 0 - \frac{\Delta\tau L}{n^2\pi^2} \cos(n\pi x/L) \bigg|_0^L,
\]

\[
= \frac{2\Delta\tau L}{n^2\pi^2}, \quad \text{remember } n \text{ is odd}
\]

Which gives

\[
A_n = \frac{4\Delta\tau}{n^2\pi^2},
\]

and our solution for \( t > 0 \) is

\[
\tau(x, t) = \sum_{n=1,3,5,...} \frac{4\Delta\tau}{n^2\pi^2} \cos(k_n x) e^{-Dk_n^2 t}, \quad k_n = \frac{n\pi}{L}.
\]

Some comments are in order. Each mode decays like \( \exp(-t/t_n) \) where the decay time is

\[
t_n = \frac{L^2}{Dn^2\pi^2},
\]
so short wavelength (large $k_n$) modes decay very fast compared to the $n = 1$ mode. The decay time is inversely proportional to the square of the wavenumber. It is the very short wavelengths that are necessary to produce the discontinuity in slope at the ends of the bar. The discontinuity decays very rapidly (infinitely rapidly if we go all the way to $n = \infty$!).

The figure shows the temperature as a function of position in the bar for several times including $t = 0$, and $t = (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1)t_1$ where $t_1 = L^2/D\pi^2$ is the decay time of the longest mode. The plotted functions include the Fourier terms $n = 1, 3, 5, 7, 9, 11, 13, 15$. The function for $t = 0$ has some small wiggles at the ends. This is because it’s missing the high frequency ($n > 15$) components. By the time the $n = 1$ component has experienced one decay time, the next slowest decaying term, $n = 3$, has experienced 9 decay times. In other words the temperature profile becomes indistinguishable from a half cycle of a cosine very quickly!