Kinetic Theory.
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In the simplest model, the equilibrium distribution of gas particle velocities is this: all particles move with the same speed, “c”. The equipartition theorem requires: \( mc^2/2 \approx 3kT/2 \). One-sixth of them move in each of 6 directions: up, down, left, right, forward, and backward.

In a more accurate model, \( f(v) \) represents the relative probability of a particle having a particular velocity (not speed), \( v \).

In a calculation of transport of quantity, “X”, we first identify all of the particles that carry “X”. We figure out how many particles with a particular velocity, \( v \), will hit the target area, \( A \), in a short time, \( \Delta t \), then we sum over velocities. The sum is weighted by how much “X” each particle carries with it.

**Calculation of Pressure for an Ideal Gas.**

![Diagram](image)

We calculate the pressure, \( P \), that a gas exerts on an area, \( A \), of the wall of its container by calculating the net momentum transfer to the area in short time \( \Delta t \), then dividing by \( A\Delta t \). In the simplest model, there are six allowed particle velocities, but only the one perpendicular to “A” describes particles that will hit the area. The number of particles to hit “A” in time \( \Delta t \) is \( 1/6^{th} \) of the number of particles in a volume \( Ac\Delta t \), which is \( nAc\Delta t/6 \). Since particles bounce off the wall, the momentum transport per particle is: \( 2mc \), not just \( mc \). Thus:

\[
P = \text{momentum transfer/}A\Delta t = (n/6)c\times2mc = 2n/3 \times mc^2/2 = nkT,
\]

which is the ideal gas law for pressure. If our gas had multiple components, then the same calculation would apply to each component, and pressures would add.

If we choose the \( z \) axis to be perpendicular to the area, the more accurate expression involves an integral over all velocities rather than a sum over 6 directions:

\[
P = n \times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(v) dv_y f(v) dv_z \times 2mv_z / \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y f(v).
\]
Note limits on the integral over $v_z$ in the numerator: particles don’t hit the area unless their z velocity is positive. $f(v)$ is the relative probability of a particle having a velocity, $v$, so the denominator is needed to insure proper normalization. In spherical coordinates, $v_z = v \cos \theta$, so we have:

$$
P = n \times \int_{\theta = 0}^{\pi} \cos^2 \theta \int_{v_z = -1}^{1} v^2 \exp(-mv^2/2kT) \frac{1}{\int_{\theta = 0}^{\pi} \int_{v_z = -1}^{1} v^2 \exp(-mv^2/2kT)}.
$$

Note that the limits on the integral over $\cos \theta$ in the numerator ensure that $v_z > 0$. After integration over $\cos \theta$ and rearranging, we have:

$$
P = \frac{2n}{3} \times \int_{v_z = 0}^{\infty} v^2 \exp(-mv^2/2kT) \frac{mv^2/2}{\int_{v_z = 0}^{\infty} v^2 \exp(-mv^2/2kT)}.
$$

The ratio of integrals over $v$ is the thermal average of the kinetic energy, $mv^2/2$, which is $3kT/2$. The final result is:

$$
P = nkT,
$$

as we found in the simpler model above.

*From KK appendix A: \( \int_{0}^{\infty} dx x^4 \exp(-x^2) = 3/2 \times \frac{1}{2} \times \sqrt{\pi}; \int_{0}^{\infty} dx x^2 \exp(-x^2) = \frac{1}{2} \times \sqrt{\pi}. \)
Calculation of flux of particles through a hole smaller than a mean-free-path: Effusion.

In the simplest model, where particles have the same speed $c$ and only 6 directions of motion, the particle flux is:

$$J_n = nc/6,$$

where $n$ is the density of particles. We assume that the loss of particles through the hole does not affect the distribution of velocities of particles still in the box.

In the more accurate model, the expression for the flux is the same as for the pressure problem, above, except that there’s no factor of $2mv_z$:

$$J_n = n \times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(v) v_z \frac{v}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(v)}.$$

Changing to spherical coordinates in the integrals, the integral over $\phi$ cancels out, and we find:

$$J_n = n \times \frac{1}{4} \int_{0}^{\infty} \int_{0}^{\infty} v^2 \exp(-mv^2/2kT) \frac{v}{\int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} v^2 \exp(-mv^2/2kT)}.$$

The integrals over $\cos \theta$ give the factor of $1/4$. The ratio of integrals over $v$ is just the thermal average speed, $<v>$. The final result is:

$$J_n = n <v>/4.$$

This result is not much different from the result, $J_n = nc/6$, of the simpler calculation. The calculation shows that “c” is the average speed, not the rms speed or some other typical speed.
Flux of Particles Due to a Gradient in Particle Density: Diffusion.

This problem is like the problem of particle flux through a hole, but we have to take the difference between flux upward and flux downward in order to get the net flux. The “hole” is an imaginary construct. In the simplest model, with one speed and 6 directions of motion, the net particle flux upward is:

\[ J_n = \frac{n_{\text{below}} c}{6} - \frac{n_{\text{above}} c}{6}, \]

where \( n_{\text{below}} \) and \( n_{\text{above}} \) are the density of particles below and above the imaginary “hole”. We have assumed that temperature is the same everywhere, so \( c \) is the same. A typical particle that crosses the hole comes from a region of space that is one mean-free-path below or above the hole. Thus, \( n_{\text{below}} - n_{\text{above}} \approx -\frac{dn}{dz} \times 2\ell \), and:

\[ J_n \approx -\frac{dn}{dz} \times \frac{\ell c}{3}. \]

The particle flux is proportional to \( -\frac{dn}{dz} \), and the constant of proportionality is: \( D = \frac{\ell c}{3} \).

In the more accurate model, the effective density, \( n(z) \), depends on where the particles come from. Particles passing through the hole move a distance of one mean free path, \( \ell \). Particles with velocity \( v \) at an angle \( \theta \) relative to the +z axis come from a \( z \) position: \( z = -\ell \cos \theta \), where the density of particles is: \( n(0) + \frac{dn}{dz} \times (-\ell \cos \theta) \). We need to subtract the downward flux from the upward flux to get the net flux:

\[
J_n = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(v) v_z [n(0) + \frac{dn}{dz} \times (-\ell \cos \theta)] + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(v) v_z [n(0) + \frac{dn}{dz} \times (-\ell \cos \theta)] / \int \int \int f(v).
\]

Note that the factor of “\( v_z \)” in both integrands makes the first integral, the upward flux, “positive”, while the second integral, the downward flux, is “negative”. Indeed, if the density of particles were uniform, then the integrals would exactly cancel, i.e., the net integral of \( f(v)v_zn(0) \) vanishes. The remaining integrals can be added, resulting in one integral over \( \theta \) from 0 to \( \pi \) and an integral from \( v = 0 \) to \( \infty \). Changing to spherical coordinates in the integrals, we find:

\[
J_n = (-\frac{dn}{dz}) \ell \times \int d(cos \theta) \cos^2 \theta \int dv \ v^3 \exp(-mv^2/2kT) / \int d(cos \theta) \int dv \ v^2 \exp(-mv^2/2kT).
\]

The ratio of \( \theta \) integrals is 1/3, and the ratio of \( v \) integrals is the average speed, \( <v> \). Thus:

\[ J_n = \ell \frac{<v>}{3} \times (-\frac{dn}{dz}). \]

Again, the particle flux is proportional to the gradient in concentration, \( -\frac{dn}{dz} \), and the diffusion constant is the constant of proportionality: \( D = \ell \frac{<v>}{3} \).
Calculation of Electrical Conductivity.

We assume that we have a neutral system, with equal densities $n$ of particles with charges $+q$ and $-q$. Their masses are $m^+$ and $m^-$. In the presence of a uniform dc electric field, $E_z$, charged particles accelerate and gain momentum. The average time between collisions is the “collision time”, $\tau_C$. Particles lose their extra momentum after this time, on average. The average “extra” momentum for each particle is force integrated over time: $qE_z\tau_C$, so the average extra velocity is: $\Delta v_z = qE_z\tau_C/m$, regardless of the initial velocity of the particle. The general expression for electric current density is: $J_z = nq\langle v_z \rangle$, so here we have:

$$J_q,z = (nq^2\tau_C/m^+ + nq^2\tau_C/m^-)E_z.$$  

Remember that both species of charge carry current in the same direction, even though the particles accelerate in opposite directions. The net conductivity is:

$$\sigma = nq^2\tau_C/m^+ + nq^2\tau_C/m^-.$$  

In metals, the electrons carry the dc current, while the ions are stuck in the crystal lattice. Ions can respond to ac fields, however, especially when the frequency coincides with a particular phonon frequency.

Calculation of Viscosity.

We want to calculate the flux of x-momentum, $mv_x$, in the z direction. We consider flux across the plane at a given $z$. The net flux is nonzero when the flow velocity, $\langle v_x \rangle(z)$, varies along the z direction due to an externally applied shear. Note: $\langle v_x \rangle(z)$ means that the local flow rate is a function of $z$; this is not a multiplication of a velocity with $z$.

The rate at which particles move upward through the plane at “z” is: $n(z)c/6$. The average x-momentum carried by a particle is: $m\langle v_x \rangle(z-\ell)$. Hence the upward flux of x-momentum is: $n(z-\ell)c/6 \times m\langle v_x \rangle(z-\ell)$. The downward flux of x-momentum is: $n(z+\ell)c/6 \times m\langle v_x \rangle(z+\ell)$. If the density is the same above and below the plane, then the net flux of x-momentum in the z direction is:

$$J_{Px,z} = nc/6 \times 2\ell \times m[-d\langle v_x \rangle/dz] = (nc\ell m/3)[-d\langle v_x \rangle/dz].$$  

The flux is proportional to $-d\langle v_x \rangle/dz$, and the constant of proportionality is the viscosity: $\eta = nm\ell c/3$. A more careful calculation finds the same result:

$$\eta = nc\ell m/3.$$  

The mean-free-path, $\ell$, is inversely proportional to $n$: $\ell = 1/n\sigma$, where $\sigma \approx \pi d^2$ is the cross section for scattering and $d =$ particle diameter. Thus, $\eta$ is independent of $n$. It depends on temperature through the speed, $c \propto \sqrt{T}$.
Calculation of Thermal Conductivity.

This is the hardest transport coefficient to calculate (correctly). Specifically, we consider a tube of gas connecting a hot reservoir with a cold reservoir. In steady state, there is no net flow of particles anywhere in the tube. The temperature of the gas decreases linearly with distance from the hot to cold reservoir, i.e., there is a constant temperature gradient. The density of particles increases as you go from hot to cold.

We will do the simplest calculation, only. Consider an area, \( A \), transverse to the temperature gradient. The temperature of the gas at \( A \) is \( T \). The flux of energy from the hot side is the flux of particles multiplied by the average energy per particle, \( u \). For a monatomic gas, \( u = \frac{3kT}{2} \); for diatomic gas in classical limit for rotations, \( u = \frac{5kT}{2} \), etc. The typical temperature, \( T_L \), of a hot particle (on the Left hand side of the figure above) is the temperature 1 mean free path to the left of the area: \( T_L = T - \ell \frac{dT}{dx} \). Similar ideas hold for the flux from the cold side, so the net flow of energy to the right is:

\[
J_u = n_L c_L u_L / 6 - n_R c_R u_R / 6.
\]

The net flow of particles is:

\[
J_n = n_L c_L / 6 - n_R c_R / 6 = 0.
\]

Thus, the product \( nc \) is constant throughout the tube of gas. Using this result, we have a flux of energy:

\[
J_u = -(nc\ell/3)du/dx = (nc\ell/3)(du/dT)(-dT/dx).
\]

Now, \( ndu/dT \) is the heat capacity per unit volume, \( C_V \). Thus, we find heat flow is proportional to \(-dT/dx\):

\[
J_u = C_V c\ell/3 \times (-dT/dx),
\]

where the thermal conductivity is: \( K = C_V c\ell/3 \). Since heat capacity is proportional to density, \( n \), while mean free path is inversely proportional to \( n \), \( K \) is independent of gas density.