5.62 Physical Chemistry II
Spring 2008

Kinetic Theory of Gases:
Mean Free Path and Transport

The mean free path λ. The mean free path is the average distance a particle traverses before it experiences a collision. In Lecture #31 we determined the average collision frequency for a particle, Z. The mean time between collisions is simply Z^{-1}. If the mean speed of a particle is $\bar{v}$ then the mean free path is

$$\lambda = \frac{\bar{v}}{Z}.$$

As a result, for like particles we find the mean free path equal to:

$$\lambda = \frac{1}{\sqrt{2}\rho\pi d^2}.$$

This is an important and interesting result. For a dilute hard sphere gas, the mean free path depends only on density; it is independent of temperature. However, if the particles had an attractive or repulsive potential between them, the mean free path would depend on T.

Typical values at 300K for O_2 $d = 0.361$ nm $\pi d^2 = 41 \text{Å}^2$

	Z	Z_{TOT}/V	λ
1 bar	6.2×10^9 coll s^{-1}	7.6×10^{34} coll m^{-3}s^{-1}	7.1×10^{-8} m (10^{-6} in)
10^{-6} bar	6.2×10^3 coll s^{-1}	7.6×10^{22} coll m^{-3}s^{-1}	7.1×10^{-2} m (3 in)

Why is Z proportional to ρ and Z_{TOT} to ρ^2 ?

The effusion picture described in Lecture #31 assumed that no collisions occur when molecules pass through a hole of area A and thickness d. This means that it is necessary to assume that $d \ll \lambda$. If this is condition is not satisfied, the description of gas escaping from the vessel must include collisions and transport phenomena.

The probability of a particle traveling a distance r before experiencing a collision is

p(r) r	$p(r) = \lambda e^{-\lambda r}$ $0 < r < \infty$ Is this probability distribution normalized? What are $\bar{r}$ and $\overline{r^2}$?
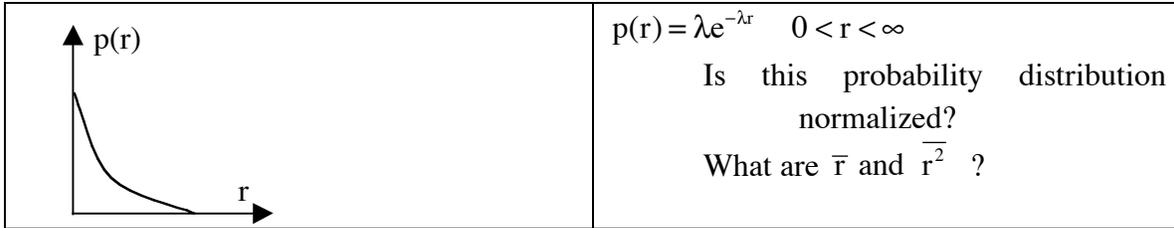
<u>Variation of the mean free path with density and temperature</u>. The expression we have derived for the m.f.p. is valid only for hard spheres at very low density. How does the m.f.p. behave under more general conditions?

The simple expression predicts that the m.f.p. goes to zero at infinite density. However we should instead expect that the m.f.p. goes to zero at a critical density ρ_c which corresponds to the volume per particle:

$$\rho_c = \frac{1}{v_c} = \frac{3}{4\pi d^3}$$

so a more general prediction of the behavior of the m.f.p. with density might be:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2}\left[\frac{1}{\rho} - \frac{1}{\rho_c}\right].$$

If the particles attract or repel each other, there will also be an effect on the m.f.p. Qualitatively, we expect that if the potential is repulsive between the particles, the frequency of collisions will decrease and the m.f.p. will increase. If the potential is attractive, we expect that the frequency of collisions will increase and the m.f.p. will decrease. Both of these effects will be more pronounced at lower temperatures when the forces between the particles results in a larger fractional change in the velocity ($\Delta v/\bar{v}$) of the particles, because $\bar{v} \propto \sqrt{T}$.

<u>The mean free path and collisions</u>. In dilute gases the m.f.p. is an important quantity because it gives the microscopic distance scale over which collisions will influence the transfer of physical quantities such as mass, momentum, and energy between colliding partners.
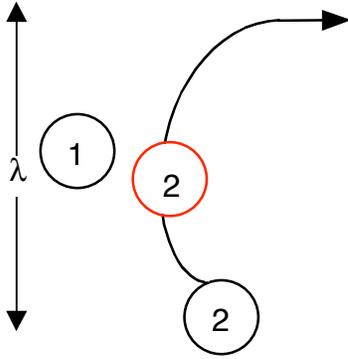
This pair-collision picture lies at the heart of the elementary kinetic theory of transport. Elementary kinetic theory describes the main transport processes in a unified way and provides molecular expressions for the transport coefficients.

Transport equations. These are equations that describe non-equilibrium phenomena – the flow of a physical quantity in response to perturbation of the local thermodynamic variable. When the perturbation from equilibrium is "small," the transport equations have the form:

Flux	Transport coefficient	Gradient of thermodynamic variable
mass	Diffusion coefficient.	Concentration
momentum	Shear viscosity	Velocity
heat	Thermal conductivity	Temperature

The fluxes are all defined as *the physical quantity transported per unit area per unit time.*

We consider the simple physical situation of the gradient in the "z" direction and because the gas is isotropic, the flux in the "z" direction. The flux (denoted by j with a right superscript that specifies the physical quantity transported and a right subscript that specifies the direction of flow) flows in the direction opposite to the gradient in order to re-establish equilibrium. Thus, transport equation are often referred to as "relaxation equations."

Transport equations. The transport equations describe the movement of physical quantities on a macroscopic scale. For diffusion (transport of mass),

$$j_z^m(z,t) = -D\frac{\partial \rho(z,t)}{\partial z}.$$

Here D is the diffusion coefficient and the superscript "m" on the flux denotes mass. Since the units of $j_z^m(z,t)$ are mass/area-time, and the units of ρ are mass/volume, the units of D must be area/time, usually cm^2/sec.

<u>For heat conduction</u> (transport of energy):

$$j_z^e(z,t) = -\kappa \frac{\partial T(z,t)}{\partial z}$$

where κ is the thermal conductivity, T is the temperature, and the superscript "e" on the flux denotes energy. The units of κ are energy/ length-sec-degree.

<u>For viscosity</u> (transport of momentum). The situation is more complicated. The prototype physical situation is gas (or a fluid) located between two plates. The bottom plate is stationary and the top plate is pulled with a certain force.
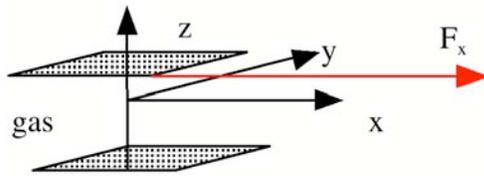
The force in the x direction F_x per unit area of the plate, will cause the x-component of velocity to vary with z, $v_x(z)$.

The transport equation is:

$$F_x = -\eta \frac{dv_x(z,t)}{dz}.$$

Note that force/unit area has the same units as momentum per unit time per unit area, so F_x is a momentum flux. The units of the viscosity coefficient, η, are mass/ length-sec.

<u>Kinetic theory has two tasks</u>. The first is to explain why the transport equations have the particular form of a flux proportional to a spatial gradient of a local thermodynamic quantity. The second task is to obtain a molecular expression for each transport coefficient (e.g. D, κ, η).

In the simple form of kinetic theory this is accomplished by considering the <u>microscopic</u> process of collisions in the gas. The analysis is based on some important approximations, but it leads to useful results: the form of the transport equations is explained and approximate values for the transport coefficients are obtained.

Once the microscopic analysis justifies the form of the transport equations, it becomes possible to obtain a set of <u>conservation equations</u> that are valid on a macroscopic scale. If a flux of a certain quantity Y has the form

$$\vec{j}^y = -L\vec{\nabla}Y$$

then, choosing a fixed volume element, conservation of Y (flux of Y entering the volume element must be equal to the flux of Y leaving the volume element) leads to the result:

$$\frac{\partial Y}{\partial t} = -\vec{\nabla} \cdot \vec{j}^y = \vec{\nabla} \cdot L\vec{\nabla}Y = L\nabla^2 Y.$$

Typical values of transport coefficients for dilute gases at 272 °K

Gas	Self diffusion coefficient D cm²/sec	Thermal conductivity κ 10^5 cal cm^{-1} sec^{-1} K^{-1}	Shear viscosity η 10^5 g cm^{-1} sec
Argon	0.156	3.94	20.99
CO_2	0.181	3.49	13.66
CH_4	0.206	7.21	10.30

W. Kauzmann, "Kinetic Theory of Gases," W. A. Benjamin, New York, 1966, page 209.