
Kinetic Theory and Thermodynamics

Handout 3:

Pressure and effusion

In Lecture 3 we consider dilute gases in equilibrium. We will make a couple of assumptions: first, that the molecular size is much less than the intermolecular separation, so that we assume that molecules spend most of their time whizzing around and only rarely bumping into each other; second, we will ignore any intermolecular forces. Molecules can exchange energy with each other due to collisions, but everything is in equilibrium and the gas will have a Maxwell-Boltzmann distribution. Each molecule behaves like a small system connected to a heat reservoir at temperature T , where the heat reservoir is ‘all the other molecules in the gas’.

In the lecture we derive an expression for the pressure, p , which is

$$p = \frac{1}{3}nm\langle v^2 \rangle,$$

where n is the number of molecules per unit volume and m is the molecular mass. This expression agrees with the ideal gas equation,

$$p = nk_{\text{B}}T,$$

where V is the volume, T is the temperature and k_{B} is Boltzmann’s factor.

The particle flux, Φ , is the number of molecules which strikes unit area per second and is given by

$$\Phi = \frac{1}{4}n\langle v \rangle.$$

This expression, together with the ideal gas equation, can be used to derive an alternative expression for the particle flux:

$$\Phi = \frac{p}{\sqrt{2\pi mk_{\text{B}}T}}.$$

These expressions also govern molecular effusion through a small hole.

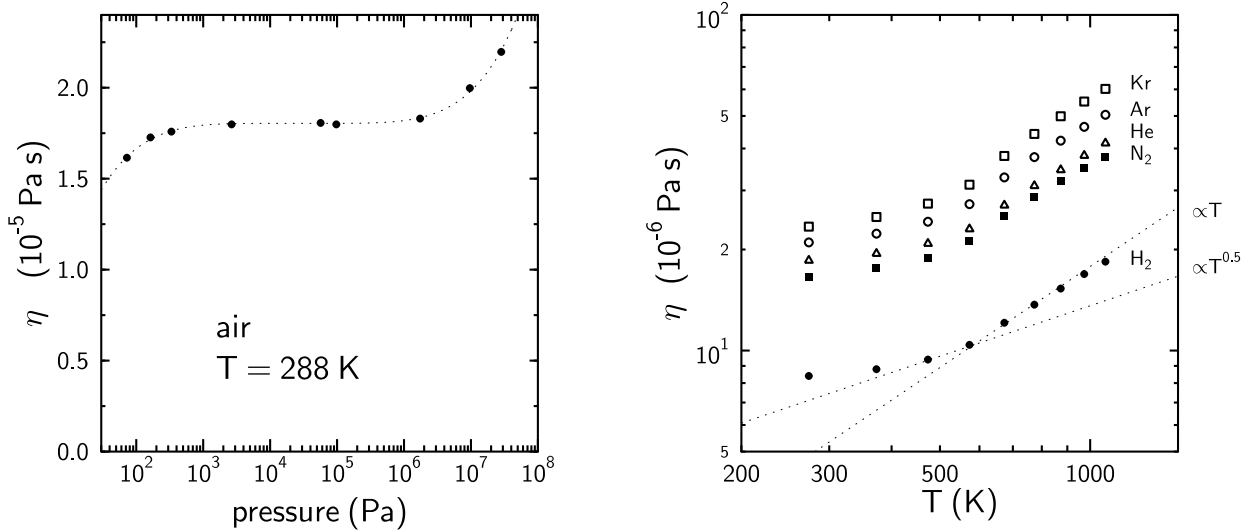
Transport properties

In Lectures 4 and 5 we use the ideas which we have described in the previous lectures to establish some results concerning transport properties. We thus consider

1. viscosity (transport of momentum),
2. thermal conductivity (transport of heat) and
3. diffusion (transport of particles).

We are therefore no longer considering equilibrium situations, though everything is still in the steady-state. The lectures will show how one can derive some simple expressions for each of the three transport properties described above. This handout can be used to illustrate how well these predictions work in practice.

Viscosity



The figure on the left shows the apparent viscosity of air as a function of pressure. It is found to be constant over a wide range of pressure. The temperature dependence of the viscosity of various gases is shown on the right, plotted from the data below.

Gas	0°C	20°C	50°C	100°C	200°C	300°C	400°C	500°C	600°C
Air	17.3	18.2	19.6	22.0	26.1	29.8	33.2	36.4	39.4
Argon	21.0	22.3	24.2	27.3	32.8	37.7	42.2	46.4	50.4
Helium	18.7	19.6	21.0	23.2	27.3	31.2	34.8	38.4	41.8
Hydrogen	8.4	8.8	9.4	10.4	12.1	13.7	15.3	16.9	18.4
Krypton	23.4	25.0	27.4	31.2	38.0	44.2	49.9	55.2	60.2
Nitrogen	16.6	17.6	18.9	21.2	25.1	28.6	31.9	34.9	37.8
Steam	9.2	9.7	10.6	12.4	16.2	20.3	24.5	28.6	32.6
Xenon	21.2	22.8	25.1	28.8	35.7	42.0	47.9	53.4	58.6

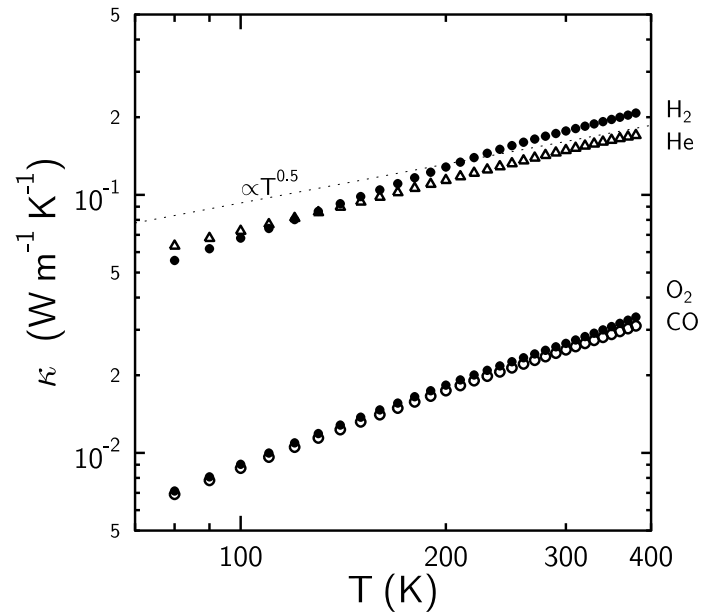
Gas (at 300 K)	2 MPa	5 MPa	10 MPa	20 MPa	30 MPa
Air	18.7	19.3	20.5	23.7	27.5
Argon	23.3	24.0	25.7	30.5	36.4
Helium	19.9	19.9	20.0	20.1	20.3
Hydrogen	8.98	9.01	9.09	9.31	9.59
Nitrogen	18.3	18.9	20.1	23.2	26.8

Viscosities in $\mu\text{Pa s}$

Thermal conductivity

The figure on the right shows the thermal conductivity (in $\text{W m}^{-1} \text{K}^{-1}$) of four gases as a function of temperature (in K) plotted on a log-log scale.

Gas	173.2 K	273.2 K	373.2 K
Argon	1.09	1.63	2.12
Air	1.58	2.41	3.17
Hydrogen	11.24	16.82	21.18
Nitrogen	1.59	2.45	3.23
Xenon	0.34	0.52	0.70



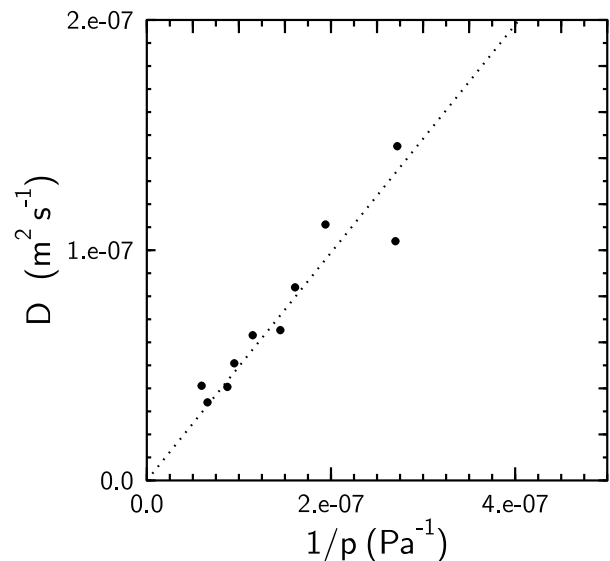
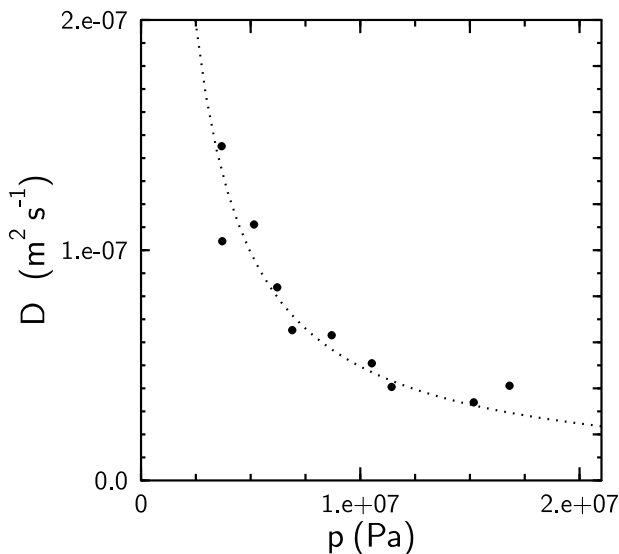
Thermal conductivities in the table above are in $10^{-2} \text{W m}^{-1} \text{K}^{-1}$

Heat capacities:

The heat capacity C relates the amount of heat something can absorb to the temperature rise that produces. A rabbit has a heat capacity, so does 3 kg of iron. But two rabbits have (approximately) double the heat capacity of one. The specific heat capacity c of something is the heat capacity per unit mass. Sometimes one can also measure the heat capacity *per unit volume* of a substance (which equals $c\rho$ where ρ is the density) or the heat capacity *per molecule* (which equals cm where m is the mass of the molecule).

Later we will write things like C_V which is the heat capacity of something at constant volume (NOT per unit volume).

Diffusion



D against p and $1/p$ for argon. (Data from T. R. Mifflin and C. O. Bennett, J. Chem. Phys. **29**, 975 (1959).)

The key results are:

(1) Viscosity, η

$$\eta = \frac{1}{3}nm\lambda\langle v \rangle$$

(2) Thermal conductivity, κ

$$\kappa = \frac{1}{3}nC\lambda\langle v \rangle$$

(where C is the heat capacity *per molecule*)

(3) Self-diffusion, D

$$D = \frac{1}{3}\lambda\langle v \rangle$$

The derivations for each one of these are fairly similar and will be covered in the lectures.

It is important to know how to use these results to predict the temperature and pressure dependences of these three quantities and under what conditions those predictions will hold. This will be discussed in the lectures.

The thermal diffusion equation

Heat flux \mathbf{J} is defined as the amount of heat passing across unit area per second. It is proportional to the gradient in the temperature, with the constant of proportionality being the thermal conductivity. Thus:

$$\mathbf{J} = -\kappa\nabla T$$

The total rate of heat flow out of a volume V , with surface S , is given by

$$\int_S \mathbf{J} \cdot d\mathbf{S} = \int_V \nabla \cdot \mathbf{J} dV$$

where the second equality follows from the divergence theorem. If heat is flowing out of the volume, then whatever is in the volume must be cooling down. If we use C as the heat capacity *per unit volume* (remember $C = c\rho$ where c is the *specific heat capacity*, defined per unit mass, and the ρ is the density), one can immediately state that the energy stored in V is $\int_V CT dV$ (plus a constant). Thus

$$\int_S \mathbf{J} \cdot d\mathbf{S} = -\frac{\partial}{\partial t} \int_V CT dV.$$

Putting all this together yields the thermal diffusion equation:

$$\nabla^2 T = \frac{C}{\kappa} \frac{\partial T}{\partial t}.$$

The one-dimensional thermal diffusion equation is then

$$\frac{\partial^2 T}{\partial x^2} = \frac{C}{\kappa} \frac{\partial T}{\partial t}.$$

This can also be written as

$$\frac{\partial^2 T}{\partial x^2} = \frac{c\rho}{\kappa} \frac{\partial T}{\partial t}.$$