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# 08. Kinetic Theory II

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### [tex62] Ideal gas atoms escaping from a container

A dilute gas is confined to a large vessel in thermal equilibrium at temperature T.

(a) Find the rate at which gas atoms escape into the vacuum through a tiny hole of area A in the wall of the vessel.

(b) If the wall with the hole is perpendicular to the z-axis, find the distribution  $f_z(v_z)$  for the gas atoms escaping through the hole.

#### [tex64] Toward thermal equilibrium via particle transfer

A vessel with insulating walls is divided into two compartments by an internal wall that is also insulating but has a small hole of area A. The two compartments contain dilute gases of slightly different densities,  $n_{\pm} = n \pm \frac{1}{2}dn$ , at slightly different temperatures,  $T_{\pm} = T \pm \frac{1}{2}dT$ .

(a) Show that the rates at which particles and energy are transferred through the hole are (in leading orders of dn and  $dT$ ):

$$
\frac{dN}{dt} = \frac{A}{\sqrt{2\pi m}} \left[ \sqrt{k_B T} dn + \frac{1}{2} \frac{n}{\sqrt{k_B T}} d(k_B T) \right], \quad \frac{dE}{dt} = \frac{A\sqrt{2}}{\sqrt{\pi m}} \left[ (k_B T)^{3/2} dn + \frac{3}{2} n \sqrt{k_B T} d(k_B T) \right].
$$

(b) If the compartment with the higher particle density is at the lower temperature it is possible to create situations where either the particle flow or the energy flow is zero. Find the values of  $dn/dT$  in terms of n and T for which we have either  $dN/dt = 0$  or  $dE/dt = 0$ .

### [tex65] Isotope separation via diffusion

A vessel is divided into two compartments by a thin wall with many holes. The chamber on the left contains a dilute gas mixture of two isotopes (masses  $m_A, m_B$ ; particle densities  $n_A, n_B$ ) of some atom. As the gas diffuses into the chamber on the right, it is evacuated immediately by a pump into the left chamber of an identical vessel.

(a) Find the ratio of the numbers of type B and type A particles that are pumped out of the first vessel.

(b) Consider a battery of 20 vessels and pumps connected in series. If  $n_A = n_B$  in the left chamber of the first vessel and if  $m_A/m_B = 0.8$ , find  $n'_A/n'_B$  of the gas when it is pumped into a container by the last pump.



## Kinematic pressure and interaction pressure  $_{[tln42]}$

The kinematic pressure is dominant in gases and the interaction pressure is dominant in liquids.

Kinematic pressure due to particles carrying net momentum across a surface:

Impulse equals momentum transfer:  $F dt = Ap_{kin}dt = P_{in} - P_{out}$ .

$$
P_{in} = \int_{v_x>0} d^3v f(\vec{v}) (mv_x) n |Av_x dt|, \quad P_{out} = \int_{v_x<0} d^3v f(\vec{v}) (mv_x) n |Av_x dt|.
$$

$$
\Rightarrow p_{kin} = nm \int d^3v f(\vec{v}) v_x^2 = \frac{1}{3} nm \langle v^2 \rangle.
$$

Interaction pressure due to interparticle force exerted across surface:

Consider a central-force potential  $\phi(r)$ .

Potential energy of particle at position  $(-x_0, 0, 0)$  due to the presence of all particles at  $x > 0$ :

$$
U(-x_0) = n \int_0^{\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz \, \phi \left( \sqrt{(x+x_0)^2 + y^2 + z^2} \right).
$$

Force on particle at  $x = -x_0$ :  $F(x_0) = -U'(-x_0)$ .

Here  $F > 0$  means repulsive and  $F < 0$  means attractive.

Total force exerted on particles at  $x < 0$  by particles at  $x > 0$ :

$$
F_{tot} = nA \int_0^\infty dx_0 F(x_0) \quad \Rightarrow \quad p_{int} = \frac{F_{tot}}{A}.
$$

Note: For realistic interparticle potentials with repulsive core and attractive tail, the interaction pressure is negative at low densities. This is effectively taken into account by the van der Waals equation of state.



### [tex66] Interaction pressure produced by Gaussian interparticle potential

Consider a dilute gas of density  $n$ , where the particles interact via a Gaussian central-force potential,  $\phi(r) = \phi_0 e^{-r^2/a^2}$ , with  $\phi_0 = 1 \text{eV} = 1.6 \times 10^{-19} \text{J}$ ,  $a = 2 \times 10^{-10} \text{m}$ .

(a) Calculate the interaction pressure  $p_{int}$  under the assumption that the particles are distributed randomly in space. Express the result as a function of  $\phi_0$ , n, a.

(b) Compare the interaction pressure  $p_{int}$  with the kinetic pressure  $p_{kin}$  for a dilute gas at  $T = 293K$ and  $n = 2.7 \times 10^{25} \text{m}^{-3}$ .

# Kinetic forces and mobility  $_{[tln43]}$

Consider a *single-velocity beam*: a shower of particles with mass  $m$ , all with velocity  $\vec{v}_0$ , distributed randomly in space with particle density  $n_0$ .

**Situation**  $\#1$ : A hard wall of area A and normal unit vector  $\vec{n}$  moves with velocity  $\vec{u}$  through the path of the single-velocity beam. Find the kinetic force experienced by the wall.



Rate of collisions (viewed from the rest frame of the wall):

$$
\frac{dN}{dt} = -n_0 A \left[ \vec{n} \cdot (\vec{v}_0 - \vec{u}) \right] \quad \text{if} \quad \vec{n} \cdot (\vec{v}_0 - \vec{u}) < 0.
$$

Momentum transfer per collision:  $\Delta \vec{P} = 2m\vec{n} [\vec{n} \cdot (\vec{v}_0 - \vec{u})]$ .

Kinetic force:  $\vec{F} = \frac{dN}{dt} \Delta \vec{P} = -2mn_0 A \vec{n} [\vec{n} \cdot (\vec{v_0} - \vec{u})]^2$ .

**Situation**  $\#2$ **:** Consider a heavy hard sphere of radius R moving with velocity  $\vec{u}$  in the path of a single-velocity beam of light particles (mass m, velocity  $\vec{v}_0$ , density  $n_0$ ). The kinetic force experienced by the sphere is calculated in exercise [tex68]:

$$
\vec{F} = \pi m n_0 R^2 |\vec{v}_0 - \vec{u}| (\vec{v}_0 - \vec{u}).
$$

**Situation #3:** The mobility constant  $\mu$  in the equation  $\vec{u} = \mu \vec{F}_{app}$  relates the steady state velocity  $\vec{u}$  of an object moving through a fluid to the external force applied to the object. In steady-state motion, the external force is balanced by the kinetic force  $\vec{F}$  exerted by the fluid particles on the object:  $\vec{F}_{app} = -\vec{F}$ . The kinetic force exerted by a dilute gas (density *n*, particle mass m, temperature  $T$ ) on a slowly moving heavy hard sphere (radius  $R$ , velocity  $\vec{u}$  with  $u \ll \langle v \rangle$  is calculated in exercise [tex69]:

$$
\vec{F} = -\frac{8}{3}\sqrt{2\pi mk_B T}R^2 n\vec{u}.
$$

## [tex68] Average force of particle beam on heavy hard sphere

Consider a heavy hard sphere of radius  $R$  moving with velocity  $\bf{u}$  in the path of a single-velocity beam of light particles (mass m, velocity  $\mathbf{v}_0$ , density  $n_0$ ). Show that the average force exerted by the beam on the sphere is

$$
\mathbf{F} = \pi mn_0 R^2 |\mathbf{v}_0 - \mathbf{u}| (\mathbf{v}_0 - \mathbf{u}).
$$

### [tex69] Mobility of a hard sphere in a dilute gas

The mobility constant  $\mu$  in the equation  $\mathbf{u} = \mu \mathbf{F}_{app}$  relates the steady state velocity  $\mathbf{u}$  of an object moving through a fluid to the external force applied to the object. In steady-state motion, the external force is balanced by the average force F exerted by the fluid particles on the object:  $\mathbf{F}_{app} = -\mathbf{F}.$ 

Show that the average force exerted by a dilute gas (density n, particle mass  $m$ , temperature T) on a slowly moving heavy hard sphere (radius R, velocity **u** with  $u \ll \langle v \rangle$ ) is

$$
\mathbf{F} = -\frac{8}{3}\sqrt{2\pi mk_BT}R^2n\mathbf{u}.
$$

## Collision rate and mean free path  $_{[tln44]}$

Consider two single-velocity beams of hard spheres with diameter  $d$ , mass  $m$ , particle densities  $n_1, n_2$ , and velocities  $\vec{v}_1, \vec{v}_2$ .

Find the collision rate of particles in a region of volume  $\Omega$  at the intersection of the two beams.



View from rest frame of beam 1.

Number of particles in  $\Omega$ :  $N_1 = n_1 \Omega$ ,  $N_2 = n_2 \Omega$ .

Volume swept by one particle 2 inside  $\Omega$  in time dt:  $\omega_2 = \pi d^2 |\vec{v}_2 - \vec{v}_1| dt$ .

Volume swept by all particles inside  $\Omega$ :  $\Omega_2 = N_2 \omega_2$ .

Number of particles 1 inside  $\Omega$  that will be hit in time dt:  $dN = n_1 \Omega_2 dt$ .

Collision rate: 
$$
R_{coll} = \frac{dN}{dt} = n_1 n_2 \Omega \pi d^2 |\vec{v}_2 - \vec{v}_1|.
$$

### Collision rate in classical ideal gas:

From the above result, the rate of particle collisions within a region  $\Omega$  of a classical ideal gas with density n in thermal equilibrium at temperature  $T$  is then calculated in exercise [tex70]:

$$
R = 2\Omega d^2 n^2 \sqrt{\pi k_B T/m}.
$$

#### Mean free path of particle in classical ideal gas:

From the collision rate of particles in a classical ideal gas, the the mean free path (average distance travelled between collisons) is then calculated in exercise [tex71]:

$$
\ell = \frac{1}{\sqrt{2}\pi d^2 n}.
$$

### [tex70] Collision rate in classical ideal gas

Given the collision rate  $R_{coll} = \Omega n_1 n_2 \pi d^2 |\mathbf{v}_2 - \mathbf{v}_1|$  in a region of volume  $\Omega$  in the path of two single-velocity beams of particles (diameter d, mass m, velocities  $\mathbf{v}_1, \mathbf{v}_2$ , densities  $n_1, n_2$ ), show that the collision rate within a region  $\Omega$  of a classical ideal gas with density n in thermal equilibrium at temperature  ${\cal T}$  is

$$
R = 2\Omega d^2 n^2 \sqrt{\pi k_B T / m}.
$$

## [tex71] Mean free path of particle in classical ideal gas

Given that the collision rate of particles (diameter d, mass  $m$ ) in a region of volume  $\Omega$  of a classical ideal gas with density n in thermal equilibrium at temperature T is  $R = 2\Omega d^2 n^2 \sqrt{\pi k_B T/m}$  as demonstrated in [tex70]. show that the average distance traveled by a particle between collisions (mean free path) is

$$
\ell = \frac{1}{\sqrt{2}\pi d^2 n}.
$$

## [tex67] Rate of chemical reaction  $A + A \rightarrow A_2$  in gas phase

The rate at which a chemical reaction of the type  $A + A \rightarrow A_2$  takes place in a dilute gas is  $R = \alpha N_R$ , where  $\alpha$  is a constant and  $N_R$  is the density of pairs of atoms with a center-of-mass kinetic energy  $K_{cm}$  in excess of some value  $\epsilon_0$ . Here  $K_{cm}$  is defined as the kinetic energy of the two particles in a reference frame that moves with the center-of-mass velocity. Show that

$$
R = \frac{2\alpha n^2}{\sqrt{\pi}} \int_{x_0}^{\infty} dx \, x^2 e^{-x^2}, \quad x_0 = \sqrt{\epsilon_0 / k_B T},
$$

where  $n$  is the particle density.

#### [tex72] Effect of escaping particles on temperature of 1D ideal gas

A classical ideal gas (particle mass m, particle density n, temperature T, energy density  $u =$  $\frac{1}{2}nk_BT$ ) is contained in the region  $0 < x < L$ . The particles can only move in  $\pm x$ -direction. We assume that the velocities satisfy a 1D Maxwell distribution at all times. All particles that hit the wall at  $x = 0$  are reflected elastically. The wall at  $x = L$  allows any particle that hits it to pass through with a probability  $\epsilon_0 \ll 1$ , independent of the particle's energy. Otherwise the particle is reflected elastically.

(a) Calculate the rate at which the system loses particles and energy. Express the rates in the form  $dn/dt = f_n(n,T)$  and  $du/dt = f_u(n,T)$ .

(b) The slowly varying particle density  $n(t)$  and energy density  $u(t)$  cause a slowly varying temperature  $T(t)$  of the remaining gas. Derive from the results of (a) a differential equation for the function  $T(t)$  and solve it.