Kinetic Theory II [tsc9]

This module explores simple applications of kinetic theory intended as gateway to a more advanced engagement in physical kinetics – an active area of research with multifaceted approaches and a rich field of applications.

All situations considered here involve a classical ideal gas in some setting. Only one-particle distribution functions are being used.

Correlations are being neglected in this module. The most elementary correlation effects are described by non-factorizing pair distribution functions.

Gas container with tiny hole:

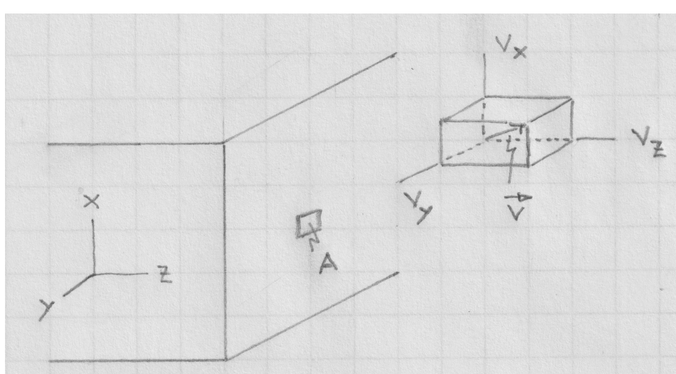
Consider a large vessel of volume V containing N atoms of a classical ideal gas in thermal equilibrium at temperature T. Its number density is uniform, $n = N/V$, and its velocity distribution is Maxwellian:

$$f_{\mathrm{MB}}(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}.$$

If the gas is allowed to leak through a tiny aperture of cross sectional area A, the rate at which particles escape and the rate at which they export energy are the following [tex62]:

$$\frac{dN}{dt} = -An\sqrt{\frac{1}{2\pi m}}(k_BT)^{1/2}, \quad \frac{dE}{dt} = An\sqrt{\frac{2}{\pi m}}(k_BT)^{3/2}.$$

Note that the rate at which particles escape decreases with increasing particle mass m, an attribute exploited in isotope separation [tex65].



The velocity distribution of particles that escape will have a higher representation of fast particles:

$$f_{\rm esc}(\mathbf{v}) = \frac{m^2 v_z}{2\pi(k_BT)^2} e^{-m(v_x^2+v_y^2+v_z^2)/2k_BT}\Theta(v_z),$$

The step function $\Theta(v_z)$ indicates the one-way stream through the hole.

As particles escape from the vessel, the particle density, $n(t)$ decrease gradually in time and approaches zero asymptotically as $t \to \infty$.

Leakage from container with heat conducting walls:

If the remaining gas is kept at constant temperature through contact with a heat bath, the density decays exponentially [tex176]:

$$n(t) = n_0 e^{-\eta_T t}, \quad \eta_T \doteq \frac{A}{V}\sqrt{\frac{k_BT}{2\pi m}}.$$

The amount of energy exported by the escaping particles is a monotonically increasing function that levels exponentially [tex176]:

$$E(t) = 2N_0 k_B T\left[1 - e^{-\eta_T t}\right], \quad N_0 \doteq n_0 V.$$

The total energy escaped, $E(\infty) = 2N_0k_BT$, is higher than the internal energy, $U_0 = \frac{3}{2}N_0k_BT$, of the gas before leakage started, which is explained by the fact that during the process the amount $\Delta Q = \frac{1}{2}N_0k_BT$ of heat flows through the walls into the remaining gas to keep it at constant temperature.

This difference is reflected in the expectation values,

$$\int d^3v\,\frac{1}{2}mv^2 f_{\rm MB}(\mathbf{v}) = \frac{3}{2}k_BT, \quad \int d^3v\,\frac{1}{2}mv^2 f_{\rm esc}(\mathbf{v}) = 2k_BT,$$

for the equilibrium distribution $f_{\rm MB}(\mathbf{v})$ inside the vessel and the distribution $f_{\rm esc}(\mathbf{v})$ of particles that have escaped.

Leakage from container with insulating walls:

Fast particles are again more likely to escape than slow particles. In this case no heat transfer through the container wall speeds up the remaining slow particles. The temperature inside the vessel drops in time [tex177]:

$$T = \frac{T_0}{\left[1 + \frac{1}{2}\sqrt{k_BT_0}\,\kappa t\right]^2}, \quad \kappa \doteq \frac{A}{6V}\sqrt{\frac{2}{\pi m}}.$$

This slows down the tail end of the leakage. The density now approaches zero in a power law [tex177]:

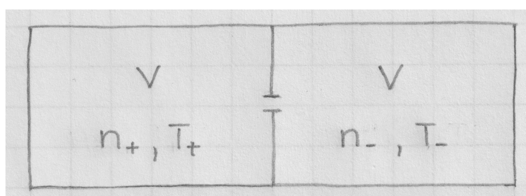
$$n(t) = \frac{n_0}{\left[1 + \frac{1}{2}\kappa\sqrt{k_B T_0}\, t\right]^6}.$$

The energy exported as a function of time saturates in a power-law as well, somewhat faster than the number of particles because the slowest particles tend to escape last [tex177]:

$$E(t) = \frac{3}{2} N_0 k_B T_0 \left[1 - \frac{1}{\left[1 + \frac{1}{2}\kappa\sqrt{k_B T_0}\, t\right]^8}\right].$$

Particle flow and energy flow between containers:

Next we consider a large vessel with insulating walls divided into two compartments of volume V and containing gases with (instantaneous) densities $n_\pm = n \pm \frac{1}{2}\Delta n$, at temperatures $T_\pm = T \pm \frac{1}{2}\Delta T$.



We set $\Delta n > 0$ and allow ΔT to be positive or negative. In [tex64] we investigate the direction of the instantaneous flow of particles and flow of energy between the two compartments through a tiny hole.

- If $\Delta T > 0$ the particle flow and energy flow are in the same direction, from high to low density and from high to low temperature.
- If $\Delta T < 0$ there are three regimes with different flow directions.

  First regime: $-\dfrac{2T}{3n} < \dfrac{\Delta T}{\Delta n} < 0.$

  The particle and energy flows are still from high to low density, but now from low to high temperature.

  Second regime: $-\dfrac{2T}{n} < \dfrac{\Delta T}{\Delta n} < -\dfrac{2T}{3n}.$

  The energy flow has reversed direction, from low to high n. The particle flow is still from high to low n.

Third regime: $\dfrac{\Delta T}{\Delta n} < -\dfrac{2T}{n}$.

Both flows have reversed direction. Particles and energy flow from high to low T, but from low to high n.

Kinematic pressure and interaction pressure:

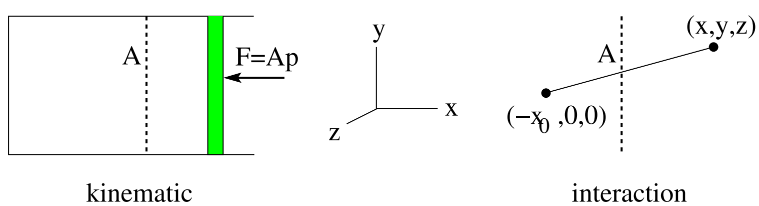
Kinematic pressure is dominant in dilute gases. Interaction pressure becomes significant in more dense gases. A different kind of pressure (discussed elsewhere) originates in quantum statistics and is manifest in fermion gases.

Kinematic pressure: pressure $p_{\rm kin}$ due to particles (present at density n) carrying net momentum P across a surface of area A in time dt [tex49]:

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

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

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



Interaction pressure: pressure $p_{\rm int}$ due to the force F inferred from an interaction potential ϕ exerted between particles across surface of area A:

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

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

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

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

Here $F > 0$ is a repulsive force and $F < 0$ an attractive force.

The total force exerted on particles at $x < 0$ by particles at $x > 0$ becomes

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

Depending on whether the force is repulsive or attractive, the interaction pressure has to be added to or subtracted from the kinematic pressure.

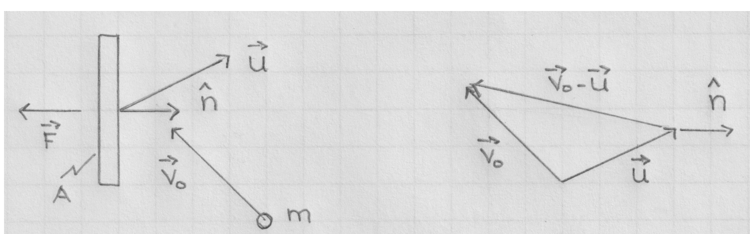
For realistic interparticle potentials with repulsive core and attractive tail, the interaction pressure is negative at low densities. The pressure reduction in the van der Waals equation of state accounts for this effect.

One quantitative application to a Gaussian interaction potential is worked out in [tex66].

Kinetic forces and mobility:

A monochromatic beam is a shower of particles with mass m, all with equal velocity $\mathbf{v}_0$. Their lateral position in the beam is randomly distributed with uniform average particle density n_0.

Situation #1:
A hard wall of area A and normal unit vector $\hat{\mathbf{n}}$ moves with velocity $\mathbf{u}$ 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):

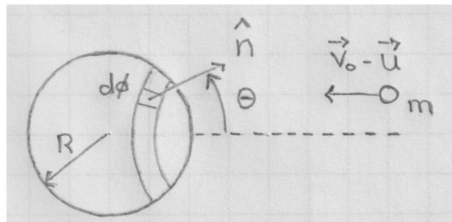
$$\frac{dN}{dt} = -n_0 A\,[\hat{\mathbf{n}}\cdot(\mathbf{v}_0 - \mathbf{u})] \quad \text{if} \quad \hat{\mathbf{n}}\cdot(\mathbf{v}_0 - \mathbf{u}) < 0.$$

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

Kinetic force: $\mathbf{F} = \dfrac{dN}{dt}\Delta\mathbf{P} = -2mn_0A\hat{\mathbf{n}}\,[\hat{\mathbf{n}}\cdot(\mathbf{v}_0 - \mathbf{u})]^2$.

This results is applicable to nearly flat infinitesimal area elements of a curved surface.

Situation #2:
Consider a heavy hard sphere of radius R moving with velocity $\mathbf{u}$ in the path of a single-velocity beam of much lighter particles (mass m, velocity $\mathbf{v}_0$, density n_0).



The kinetic force experienced by the sphere is calculated in [tex68]:

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

Situation #3:
The mobility constant μ in the equation,

$$\mathbf{u} = \mu \mathbf{F}_{\rm app},$$

relates the 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 $\mathbf{F}_{\rm app}$ is balanced by the kinetic force $\mathbf{F}$ exerted by the fluid particles on the object:

$$\mathbf{F}_{\rm app} = -\mathbf{F}.$$

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 $\mathbf{u}$ with $u \ll \langle v \rangle$) is calculated in [tex69]:

$$\mathbf{F} = -\frac{8}{3}\sqrt{2\pi m k_B T} R^2 n \, \mathbf{u}.$$

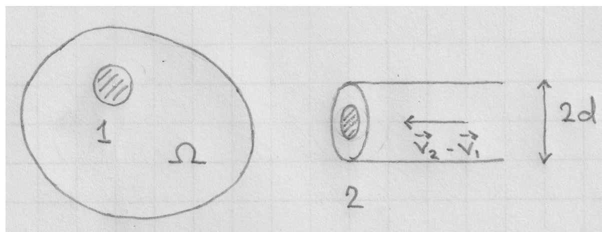
The velocities of the gas particles are characterized by the Maxwell distribution. The kinetic force is an attenuating force, proportional to the velocity of the sphere and opposite in direction.

The attenuating force increases with the density of the gas and also with the temperature of the gas. Faster particles produce larger impulse on collision than slower particles.

Collision rate and mean free path:

Here we consider a dilute gas at equilibrium. We investigate the rate at which particles collide and the distance they travel between collisions on average. All particles have mass m and diameter $d > 0$ (point particles don't collide).

We begin with two single-velocity beams of particles of densities n_1, n_2, and arbitrary velocities $\mathbf{v}_1, \mathbf{v}_2$. Both beams cross a small region of volume Ω. What is the collision rate between particles of the two beams in that region?



For the analysis we use the reference frame in which particles 1 are at rest and particles 2 move with velocity $\mathbf{v}_2 - \mathbf{v}_1$.

– Number of particles 1 and 2 in Ω: $N_1 = n_1\Omega, \quad N_2 = n_2\Omega$.
– Volume swept by one particle 2 inside Ω in time dt: $\omega_2 = \pi d^2|\mathbf{v}_2 - \mathbf{v}_1|dt$.
– Volume swept by all particles inside Ω in time dt: $\Omega_2 = N_2\omega_2$.
– Number of particles 1 inside Ω that will be hit in time dt: $dN = n_1\Omega_2$.
– Collision rate: $R_{\text{beam}} = \dfrac{dN}{dt} = n_1 n_2 \Omega \pi d^2 |\mathbf{v}_2 - \mathbf{v}_1|$.

Collision rate in classical ideal gas:
Calculating the collision rate in a gas of density n at temperature T then amounts to an integration of the beam result over the velocities $\mathbf{v}_1, \mathbf{v}_2$ weighted by the Maxwell distributions [tex70]:

$$R_{\text{gas}} = 2\Omega d^2 n^2 \sqrt{\frac{\pi k_B T}{m}}.$$

Mean free path ℓ of particle in classical ideal gas:
The mean free path can be obtained as the ratio of the total distance traveled by all particles and total number of collisions happening, all per unit time, taking into account that each collison involves two particles [tex71].

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

Exercises:

- ▷ Ideal gas atoms escaping from a container I [tex62]
- ▷ Isotope separation via diffusion [tex65]
- ▷ Ideal gas atoms escaping from a container II [tex176]
- ▷ Ideal gas atoms escaping from a container III [tex177]
- ▷ Toward thermal equilibrium via particle transfer [tex64]
- ▷ Interaction pressure produced by Gaussian interparticle potential [tex66]
- ▷ Average force of particle beam on heavy hard sphere [tex68]
- ▷ Mobility of a hard sphere in a dilute gas [tex69]
- ▷ Collision rate in a classical ideal gas [tex70]
- ▷ Mean free path of particle in classical ideal gas [tex71]
- ▷ Rate of chemical reaction in gas phase [tex67]
- ▷ Effect of escaping particles on temperature of 1D ideal gas [tex72]