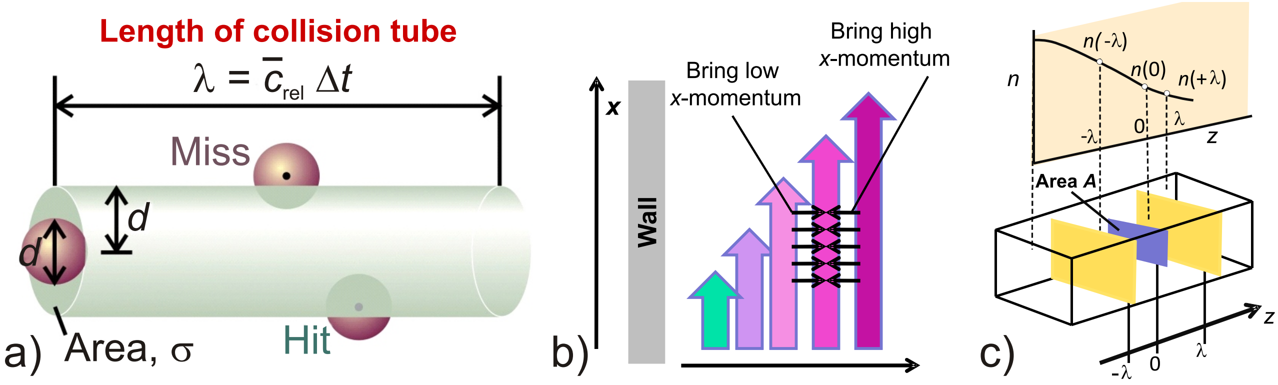

Figure 4.3: a) Geometry of the collision tube. b) Momentum distribution close to a wall allowing for the definition of viscosity. c) General model for describing transport phenomena.

4.5 Simple collision theory and transport model

Scattering is the essential concept to understand transport phenomena in vapors, liquids, and solids. Without scattering all particles would keep their velocity even without any external force which of course is experimentally only found under vacuum condition. Typically moving particles with a density n are scattered by (non moving) particles (defects) with a density N. One possible fundamental error being related to scattering is the expectation that a mean free path λ between two scattering events of the moving particles is related to the mean distance between defects. This would in 3D imply that $\lambda \propto N^{1/3}$ which is in contradiction to the experimental finding $\lambda \propto N$. The correct modeling needs for the concept of a collision/scattering cross section σ. This concept has first been introduced and can most easily be understood for a perfect gas where the moving particles and the scatter centers are the same gas molecules. On the one hand the perfect gas allows for a very easy and illustrative understanding of the collision cross section area, on the other hand that both scattering partners are moving implies an additional complexity to the problem. So in what follows we will discuss both examples in parallel.
As illustrated in Fig. 4.3 a) the starting point of the discussion of scattering of gas molecules is a frozen state model, i.e. all particles except one are assumed to stay fix while one particle is moving down the collision tube. Just geometrically a collision cross section σ is defined:

$$\sigma = \pi\,(r_1 + r_2)^2 \approx \pi\,(2r_1)^2 = \pi d^2 \quad \text{for} \quad r_1 \approx r_2 \quad . \tag{4.34}$$

For classical particles (gas molecules) the size of the diameter d of a collision tube is quite easy to understand and well determined, but e.g. for electrons within a metal "colliding" with defects the electron scattering cross section is more a fitting parameter quantifying the relevance of defects as scattering centers.
Introducing the volume of the collision tube V_{ct} and using the particle density n^* the mean free path λ is calculated by

$$\lambda\sigma = V_{ct} = \frac{1}{n^*} \quad \text{i.e.} \quad \lambda = \frac{1}{\sigma\, n^*} \quad . \tag{4.35}$$

Introducing the average time between two collisions Δt and the average relative speed between particles $\bar{c}_{rel}$ we get $\Delta t = \lambda/\bar{c}_{rel}$ which allows us to calculate the number of collisions inside the collision tube per time by

$$z = \frac{1}{\Delta t} = \frac{V_{ct} n^*}{\Delta t} = \frac{\sigma \bar{c}_{rel} \Delta t n^*}{\Delta t} = \sigma \bar{c}_{rel} n^* \quad . \tag{4.36}$$

- For e.g. electrons and typical defects $\bar{c}_{rel} = \bar{c}$ is just the average speed of the electrons which can be calculated using various models, $n^* = N$ is the defect density, and σ a parameter depending on the type of defects and the type of metal.
- For a perfect gases $n^* = p/kT$ and $\bar{c}_{rel} = \sqrt{2}\bar{c}$ (According to Eq. (4.23) the factor $\sqrt{2}$ shows up from a non trivial averaging procedure and will not be discussed here in more detail), so

$$z = \frac{\sqrt{2} p\, \sigma\, \bar{c}}{kT} \quad , \tag{4.37}$$

which e.g. for N_2 at 300 K and 1 bar ($M = 28\,g/mol$) leads to

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} \approx 476\, m/s \quad ; \quad z \approx 7 \times 10^9 s^{-1} \quad , \tag{4.38}$$

so the time between two collisions is $1/z = 1.4 \times 10^{-10}s$.
The mean free path λ, i.e. the average distance that particles can travel between two collisions, is

$$\lambda = \bar{c}\frac{1}{z} = \frac{1}{\sqrt{2}\sigma n^*} = \frac{kT}{\sqrt{2}p\sigma} \quad , \tag{4.39}$$

which for the example of N_2 above results in $\lambda \approx 68\,nm$.

Each moving particle transports several other properties like it's charge, energy, momentum, or mass. Having thermodynamic equilibrium on average for each particle moving in one direction one particle is found moving in the opposite direction, so no net transport exists. Introducing forces/reservoirs which continuously sustain gradients in certain properties net transport will occur; thus we leave the regime of thermodynamic equilibrium and discuss kinetics.
The following model is quite general. We will discuss the transport of the property Γ by moving particles with a density n^* and a velocity v which by collision transfer Γ to other particles. Such collisions will on average occur when particles have traveled a mean free path λ. As the only relevant simplification we assume that the lateral changes in the parameter Γ, n^*, and v are of linear order on the length scale of λ, i.e. a Taylor expansion up to linear order is suitable to calculate net transport of Γ. Schematically this conditions are shown in Fig. 4.3 c), and Fig. 4.3 b) illustrates the situation used for describing viscosity, i.e. Γ being the momentum in x direction with gradients in z direction.
Let us discuss the situation at an arbitrary position z_1. From the right side a particle flow will collide at position z_1 coming on average from $z_1 + \lambda$, i.e.

$$\frac{1}{6}n^*(z_1+\lambda)v(z_1+\lambda) \approx \frac{1}{6}\left[n(z_1) + \lambda\frac{dn}{dz}\right]\left[v(z_1) + \lambda\frac{dv}{dz}\right] \quad . \tag{4.40}$$

Correspondingly from the left side we find

$$\frac{1}{6}n^*(z_1-\lambda)v(z_1-\lambda) \approx \frac{1}{6}\left[n(z_1) - \lambda\frac{dn}{dz}\right]\left[v(z_1) - \lambda\frac{dv}{dz}\right] \quad . \tag{4.41}$$

We will use the above relations to find the corresponding microscopic descriptions for transport of matter (diffusion), energy (heat transport), and momentum (viscosity)

$$j_{diff} = -D\frac{dn}{dz} \quad j_{heat} = -\kappa\frac{dT}{dz} \quad j_{viscosity} = -\eta\frac{dv_x}{dz} \quad . \tag{4.42}$$

Just for simplicity we restrict the notation to 1 D and will later (easily) translate to a 3D notation.
The difference between both particle flows in Eq. (4.40) and Eq. (4.41) is already one of the fundamental transport mechanisms. Having $v = const. = \bar{c}$ (i.e. $T = const.$) we find

$$-\frac{1}{3}\lambda\bar{c}\frac{dn}{dx} := -D\frac{dn}{dx} = j_{diff} \quad , \text{i.e.} \quad D = \frac{1}{3}\lambda\bar{c} \quad . \tag{4.43}$$

For viscosity n and v and the variation of v_x in z direction is illustrated in Fig. 4.3. Only the transported momentum in x direction differs along the z-direction:
From right:

$$-\frac{1}{6}n^*vm\left[v_x + \lambda\frac{dv_x}{dz}\right] \quad . \tag{4.44}$$

From left:

$$+\frac{1}{6}n^*vm\left[v_x - \lambda\frac{dv_x}{dz}\right] \quad , \tag{4.45}$$

leading to the difference

$$-\frac{1}{3}n^*vm\lambda\frac{dv_x}{dz} \quad , \text{i.e.} \quad \eta = \frac{1}{3}n^*mv\lambda \quad . \tag{4.46}$$

- For *gases* the viscosity is independent of the pressure since according to Eq. (4.39) the product $\lambda n^* = const.$. Since $v \propto T$ the viscosity of gases increases with increasing temperature.
- In contrast for *liquids* the viscosity decreases with increasing temperature, following a law $\eta = Ae^{b/T}$. This can be explained by a necessary activation energy for a sliding of molecule layers against each other.

Having temperature gradients within gases each particle transports heat energy $\frac{1}{2}m\overline{v^2} = \frac{f}{2}kT$. The heat currents are

From right:

$$\frac{1}{6}n^*(z_1+\lambda)\left(\overline{v}+\lambda\frac{dv}{dz}\right)\frac{f}{2}kT(z_1+\lambda) \quad . \tag{4.47}$$

From left:

$$-\frac{1}{6}n^*(z_1-\lambda)\left(\overline{v}-\lambda\frac{dv}{dz}\right)\frac{f}{2}kT(z_1-\lambda) \quad . \tag{4.48}$$

Since p is constant (i.e. isobaric condition), according to the ideal gas equation we find $const. = p = kTN/V = kTn^*$, so only the change in velocity is relevant leading to the difference

$$-\frac{1}{3}n^*\frac{f}{2}kT\lambda\frac{d\overline{v}}{dz} \quad . \tag{4.49}$$

Since $T \propto \overline{v}^2$ we get

$$\frac{1}{\overline{v}}\frac{d\overline{v}}{dz} = \frac{1}{2}\frac{1}{T}\frac{dT}{dz} \quad , \tag{4.50}$$

finally leading to a heat current

$$j = -\frac{1}{3}n^*\frac{f}{2}k\overline{v}\lambda\frac{dT}{dz} \quad \text{, i.e.} \quad \kappa = \frac{f}{6}n^*k\overline{v}\lambda \tag{4.51}$$