4.4 Relaxation time and steady state

The elastic collision of particles leading to the Maxwell speed distribution and a pressure relation as described above is one of the main processes which enforce thermodynamic equilibrium. All processes (forces) leading to thermodynamic equilibrium have to be taken into account as well when external forces are applied which (constantly) induce currents and thus hinder thermodynamic equilibrium. Two phenomena are typically discussed:

- Conditions at steady state, i.e. when all parameters do not change any more as a function of time.
- Relaxation times, i.e. time constants after which steady state, resp. thermodynamic equilibrium is reached.

In general this is discussed using the Boltzmann transport equation; here we will only discuss one simple example for particles (with radius r) moving within a liquid and being hindered in motion by viscosity η. For this example Newtons law holds:

$$F = ma + Bv = m\frac{dv}{dt} + Bv \quad . \tag{4.29}$$

$B \propto 6\pi r\eta$ is determined by the Stokes Einstein equation. The homogeneous differential equation is solved by

$$m\frac{dv}{dt} + Bv = 0 \quad \Rightarrow \quad v = Ce^{-Bt/m} \quad . \tag{4.30}$$

The inhomogeneous differential equation can be solved by variation of the constant C

$$m\frac{dC}{dt}e^{-Bt/m} - mC\frac{B}{m}e^{-Bt/m} + BCe^{-Bt/m} = F \quad , \tag{4.31}$$

leading to

$$\int dC = \frac{F}{m}\int e^{Bt/m}dt \quad \Rightarrow \quad C(t) = \frac{F}{m}\frac{m}{B}e^{Bt/m} + D = \frac{F}{B}e^{Bt/m} + D \quad . \tag{4.32}$$

Here D is an integration constant which is typically defined by the initial velocity $t \to 0 \, : \, v_0 = \frac{F}{B} + D$. Introducing a second velocity $t \to \infty \, : \, v_\infty = \frac{F}{B}$, we finally get

$$v(t) = C(t)e^{-Bt/m} = \frac{F}{B} + De^{-Bt/m} = v_0\, e^{-Bt/m} + v_\infty \left(1 - e^{-Bt/m}\right) \quad . \tag{4.33}$$

So for this example the relaxation time constant is $\tau = m/B$ and the condition at steady state $v_\infty = \frac{F}{B}$ indicates that although a constant force is applied the viscosity of the liquid implies a constant speed of the particles. Since the mobility is the proportionality factor between electrical fields (proportional to electrical forces) and the drift velocity it is quite obvious that B is inverse proportional to the mobility of the particles in the liquid.