4.6 Non stationary condition

In this section we will discuss time dependencies, e.g. how long it takes to reach steady state or thermodynamic equilibrium. For this we will allow the concentration c to change at any point. Such local concentration changes are induced by lateral current flow and/or local sources or drains. First we discuss changes of the local concentration c as a function of time just induced by local current densities. This is illustrated in Fig. 4.4 a) for the change of concentration c in a (tiny) volume Al induced by a difference of current flowing into and out of this volume in x direction, i.e. in a 1D model. The number of particles entering the volume at position x per time dt is

$$dn^{in} = j(x)Adt \quad . \tag{4.52}$$

Correspondingly the number of particles leaving the volume at position $x+l$ per time dt is

$$dn^{out} = j(x+l)Adt \quad . \tag{4.53}$$

Thus the change of concentration in the volume Al per time dt is

$$\frac{dc}{dt} = \frac{dn^{in} - dn^{out}}{Aldt} = \frac{j(x) - j(x+l)}{l} = \frac{j(x) - \left[j(x) + l\frac{dj}{dx}\right]}{l} = -\frac{dj}{dx} \quad . \tag{4.54}$$

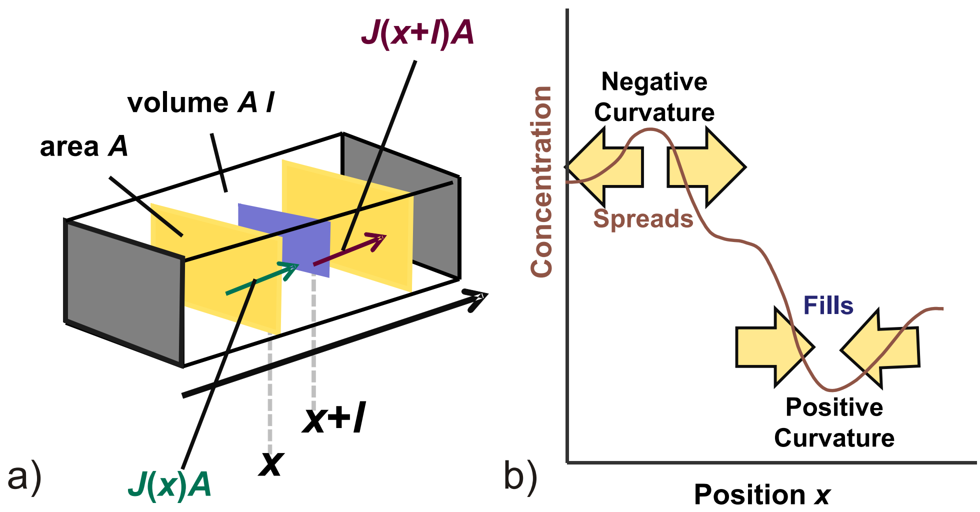

Figure 4.4: a) General model for describing continuity in transport phenomena. b) Diffusion generally levels out concentration gradients.

Here we just used that for small l the linear order of the Taylor expansion is enough to describe the changes of $j(x+l)$. Eq. (4.54) is the continuity equation in 1D. Combining it with the equation for diffusion current (cf. Eq. (4.42)) we get the one dimensional diffusion equation

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \quad . \tag{4.55}$$

As illustrated in Fig. 4.4 b) diffusion reduces curvatures ("Nature abhors a wrinkle"):

- Negative curvature: decrease of $c(t)$.
- Positive curvature: increase of $c(t)$.
- In steady state, i.e. stationary condition, we have

$$\frac{dc}{dt} = 0 \quad \Rightarrow \quad \frac{dc}{dx} = const. \quad . \tag{4.56}$$

- Without sources and drains at the surface we find $\frac{dc}{dx} = 0$ which describes thermodynamic equilibrium.

The generalization of the 1D version of the continuity equation Eq. (4.54) is straight forward since in general the gradients in y and z direction can contribute to the change of the local concentration as well, leading to

$$\frac{dc}{dt} = -\frac{dj_x}{dx} - \frac{dj_y}{dy} - \frac{dj_z}{dz} = -\vec{\nabla}\vec{j} = -\operatorname{div}\vec{j} \quad , \tag{4.57}$$

which is the continuity equation in 3D.
Taking the 3D version of the diffusion equation as introduced in Eq. (4.42)

$$\vec{j} = -D\vec{\nabla}c = -D \operatorname{grad} c \quad , \tag{4.58}$$

and combining it with Eq. (4.57) we get the diffusion equation

$$\frac{dc}{dt} = D\vec{\nabla}\vec{\nabla}c = D \operatorname{div} \operatorname{grad} c = D\Delta c \quad . \tag{4.59}$$