4.7 General fluxes and forces

In the last section we discussed the 3D version of a flux of particles. Now we will generalize this for the flux of any species/property Γ. The current density of such flux is

$$\vec{j}_\Gamma = \frac{1}{A}\frac{d\Gamma}{dt} = -D\vec{\nabla}\Gamma = L\vec{X} \quad , \tag{4.60}$$

- L can be taken as a phenomenological coefficient.
- $\vec{X}$ is a thermodynamic force driving the current density $\vec{j}_\Gamma$.
- Due to the "principle of correspondence" each of these forces corresponds to its flux so that the product $\vec{j}_\Gamma \vec{X}$ gives the entropy production (in [J / Ks])

$$\frac{dS}{dt} = \vec{j}_\Gamma \vec{X} \geq 0 \quad , \tag{4.61}$$

  The most relevant and typical pairs of fluxes and forces are summarized in the following table

	Heat transfer	Expansion	Diffusion	Chemical reaction	Electrical current
X	$\Delta(1/T)$	$\Delta(p/T)$	$-\Delta(\mu_k/T)$	A_r/T	U/T
j	$\frac{\partial Q}{\partial t}$	$\frac{\partial V}{\partial t}$	$\frac{\partial n_k}{\partial t}$	$\frac{\partial \xi}{\partial t} = v$	$\frac{\partial q}{\partial t} = I$

  For the diffusion of many (real) systems not Δc (as for ideal systems) but $\Delta\mu$ represents the driving force. $A_r = \frac{dG}{d\xi}$ is the chemical affinity

- Eq. (4.60) is the starting point for the linear irreversible thermodynamics. Due to the linear approximation it is only a good approximation for irreversible changes close to equilibrium.
- Extension 1: $\vec{j}$ and $\vec{X}$ do not need to be parallel, e.g. for the transport in anisotropic crystals; so in general L is a tensor.
- Extension 2: Coupling of different forces and fluxes, e.g. diffusion driven by concentration and temperature gradient; so in general L is a high dimensional tensor coupling all forces to all fluxes:

$$\begin{aligned} j_1 &= L_{11}X_1 + L_{12}X_2 + \ldots + L_{1n}X_n \\ j_2 &= L_{21}X_1 + L_{22}X_2 + \ldots + L_{2n}X_n \\ \vdots &= \quad \vdots \qquad\quad \vdots \qquad\quad \vdots \\ j_n &= L_{n1}X_1 + L_{n2}X_2 + \ldots + L_{nn}X_n \end{aligned} \tag{4.62}$$

  Due to the Onsager theorem the tensor L of the phenomenological coefficients is always symmetric, i.e.

$$L_{ij} = L_{ji} \tag{4.63}$$