

Non-Equilibrium Thermodynamics: Foundations and Applications.

Lecture 3: Flux equations and Onsager relations

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<http://www.chem.ntnu.no/nonequilibrium-thermodynamics/>

Non-Equilibrium Thermodynamics: Foundations and Applications

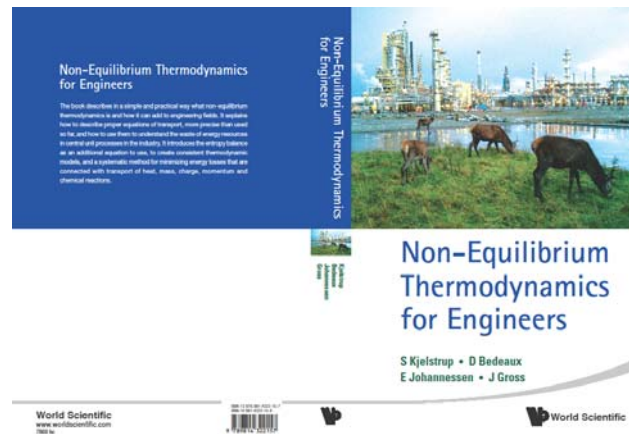
	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium thermodynamics?	Transport of heat and mass	Transport of heat and charge	Entropy production minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	Transport of mass and charge	Entropy production minimization. Examples.
16:00-17:00	Flux equations and Onsager relations	Power from regular and thermal osmosis	Modeling the polymer electrolyte fuel cell	

Non-Equilibrium Thermodynamics: Foundations and Applications

Lecture 3: Flux equations and Onsager relations

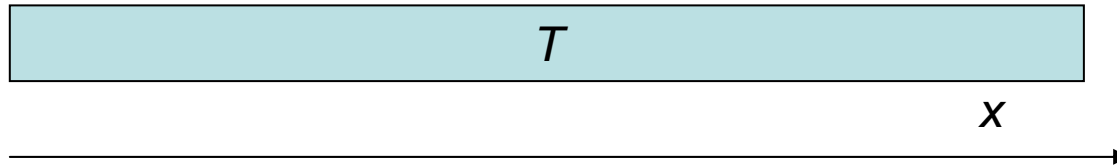
”What is coupling and why it is important”

Text: Chapter 4.1



Exercise 3

Electric conductor



$$\sigma = j \left[-\frac{1}{T} \frac{\partial \phi}{\partial x} \right]$$

$$\text{Ohms law: } j = -\kappa \frac{\partial \phi}{\partial x}$$

$$\kappa = \frac{1}{r}$$

Resistivity

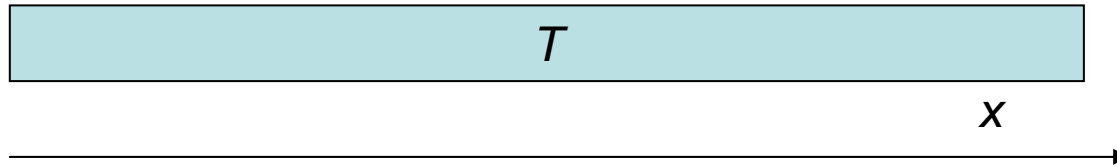
$$\sigma = \frac{1}{T} r j^2$$

$$\text{Joule heat: } r j^2 = \sigma T$$



After some time a gradient in T develops!

We have *coupled* transport of heat and charge



$$\sigma = j \left[-\frac{1}{T} \frac{\partial \phi}{\partial x} \right] + J_q \frac{\partial}{\partial} \left(\frac{1}{T} \right)$$



- *Each flux is a linear combination of each force!*

$$j = L_{\phi\phi} \left[-\frac{1}{T} \frac{\partial \phi}{\partial x} \right] + L_{q\phi} \frac{\partial}{\partial} \left(\frac{1}{T} \right)$$

$$J_q = L_{q\phi} \left[-\frac{1}{T} \frac{\partial \phi}{\partial x} \right] + L_{qq} \frac{\partial}{\partial} \left(\frac{1}{T} \right)$$



The three basic postulates of non-equilibrium thermodynamics

1. The entropy production *can be written as* a product sum of conjugate flux-force pairs (there is local eq.)

$$\sigma = J'_q \frac{\partial}{\partial x} \left(\frac{1}{T} \right) + j \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right) + \sum J_j \left[-\frac{1}{T} \frac{\partial \mu_{j,T}}{\partial x} \right] + r \left(-\frac{\Delta G}{T} \right)$$

2. Each flux is a linear homogeneous function of all forces of the same *tensorial* order:

$$J'_q = L_{qq} \frac{\partial}{\partial x} \left(\frac{1}{T} \right) + L_{q\mu} \left[-\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right] + L_{q\phi} \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right)$$

$$J = L_{\mu q} \frac{\partial}{\partial x} \left(\frac{1}{T} \right) + L_{\mu\mu} \left[-\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right] + L_{\mu\phi} \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right)$$

$$j = L_{\phi q} \frac{\partial}{\partial x} \left(\frac{1}{T} \right) + L_{\phi\mu} \left[-\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right] + L_{\phi\phi} \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right)$$

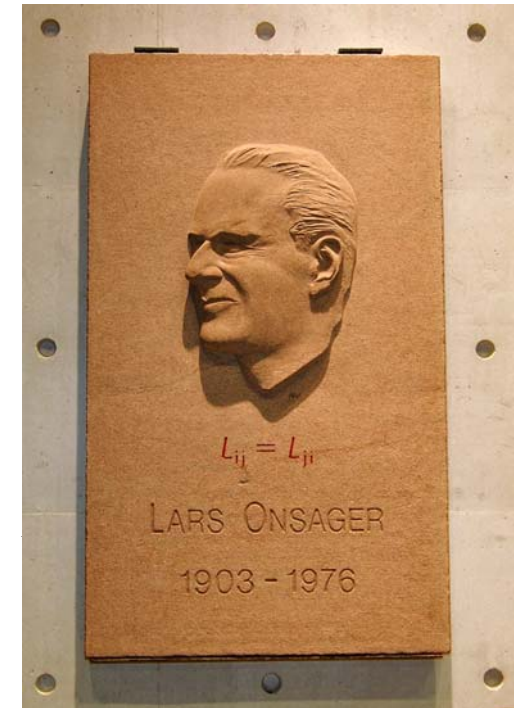
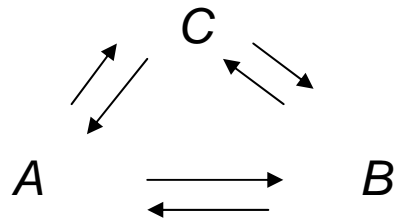
$$r = l \left(-\frac{\Delta G}{T} \right)$$

3. Onsager relations are valid with independent fluxes and forces

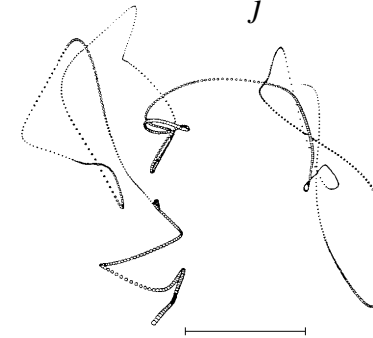
$$L_{q\mu} = L_{\mu q} \quad L_{q\phi} = L_{\phi q} \quad L_{\phi\mu} = L_{\mu\phi}$$

Onsager's proof

- Fluctuations around equilibrium are described by the Boltzmann entropy
- Microscopic reversibility
- Relaxation of fluctuations to equilibrium can be described with the macroscopic laws;
- The system is sufficiently aged
- Independent variables are used in the description

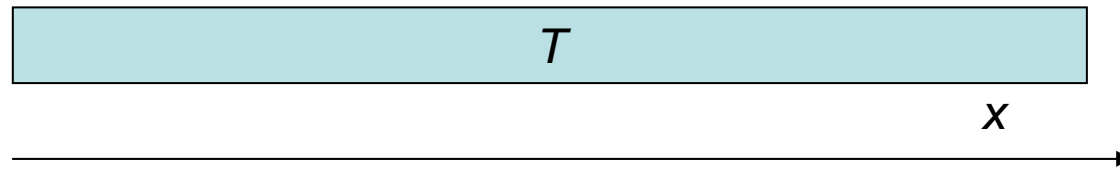


$$\alpha_i(t + \tau) = \alpha_i(t) + \tau \sum_j L_{ij} X_j$$



The time a particle needs to diffuse across its own diameter: 10^{-6} s

Coupled transports in general



$$\sigma = J_1 X_1 + J_2 X_2 + J_3 X_3 \dots$$

➔ Each flux is a linear homogeneous function of each force!

$$J_1 = L_{11} X_1 + L_{12} X_2$$

$$J_2 = L_{21} X_1 + L_{22} X_2$$

L_{ij} 's do not depend on J_i or X_i

$$J'_q = -\lambda \frac{dT}{dx} = L_{qq} \frac{d}{dx} \frac{1}{T} = -\frac{L_{qq}}{T^2} \frac{dT}{dx}$$

The coefficients can be functions of state variables!

Why is coupling important?

Given two fluxes and two forces:

$$J_1 = L_{11}X_1 + L_{12}X_2$$

$$J_2 = L_{21}X_1 + L_{22}X_2$$

We eliminate the second force:

$$X_2 = -(L_{21} / L_{22})X_1 + J_2 / L_{22}$$

And use it to express the entropy production:

$$\sigma = J_1X_1 + J_2X_2$$

$$= (L_{11} - L_{12}L_{21} / L_{22})X_1^2 + \frac{L_{12}}{L_{22}}J_2X_1 - \frac{L_{21}}{L_{22}}J_2X_1 + J_2^2 / L_{22}$$

$$= (L_{11} - L_{12}L_{21} / L_{22})X_1^2 + J_2^2 / L_{22}$$

Two terms cancel because the Onsager relations apply!

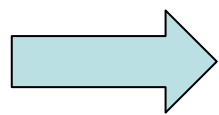
Lost work in the absence of coupling

- Heat transport along the x-axis. Cross-sectional area: Ω
- The total entropy production and the Carnot efficiency

$$\frac{dS_{irr}}{dt} = \Omega \int_L \sigma(x) dx = \Omega \int_L J'_q \frac{\partial}{\partial x} \left[\frac{1}{T} \right] dx$$

Stationary state:

$$\begin{aligned} \frac{dS_{irr}}{dt} &= \Omega J'_q \int_L \frac{\partial}{\partial x} \left[\frac{1}{T} \right] dx = \Omega J'_q \int_{T_h}^{T_c} \frac{\partial}{\partial T} \left[\frac{1}{T} \right] dT \\ &= \Omega \frac{dQ}{dt} \left[\frac{1}{T_c} - \frac{1}{T_h} \right] = \Omega \frac{\eta_I}{T_c} \frac{dQ}{dt} \quad \eta_I = \frac{T_h - T_c}{T_h} \end{aligned}$$

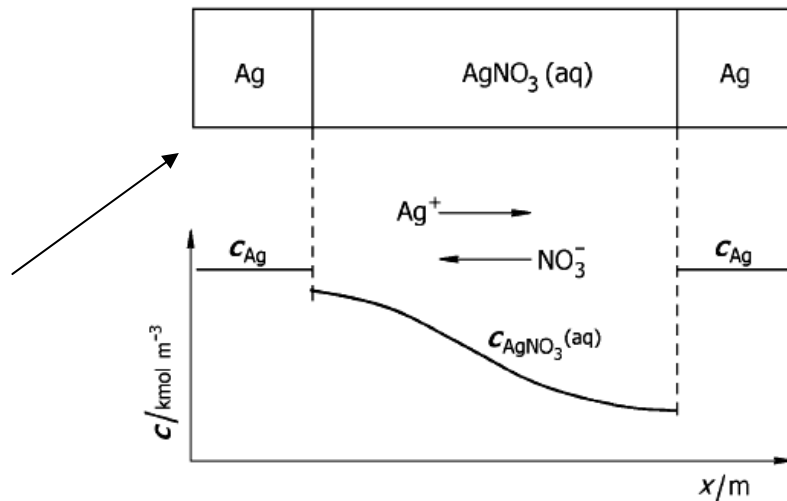


The lost work is identical to work that can be obtained in a Carnot machine (which is reversible).

$$W_{lost} = \eta_I \Omega \frac{T_0}{T_c} \frac{dQ}{dt}$$

Lost work and coupling

- The energy available for work in this concentration cell lies in the concentration gradient of the salt.
- Diffusion will after some time make the system homogeneous
- *The loss can be prevented by introducing net charge transfer via electrodes: Lecture 8*



*Two electrodes of silver
in a non-uniform
solution of silver nitrate*

$$J = L_{\mu\mu} \left[-\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right] + L_{\mu\phi} \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right)$$

$$j = L_{\phi\mu} \left[-\frac{1}{T} \frac{\partial \mu_{1,T}}{\partial x} \right] + L_{\phi\phi} \left(-\frac{1}{T} \frac{\partial \phi}{\partial x} \right)$$

Summary

1. Fluxes are linear, homogeneous functions of the forces
2. The coefficients on the diagonal, the main coefficients, lead to dissipation
3. The remaining coefficients, the coupling coefficients can be associated with work (reversible processes).
4. The coefficients are functions of state variables
5. Empirical transport coefficients can be related to the Onsager coefficients. Onsager coefficients possess a beneficial symmetry.



*We can take advantage of the symmetry,
and do the easiest measurement !*

Exercise to Lecture 3

- 1 a) Write general flux equations for transport of two components.
Express J_1 as a function of X_1 and J_2 .
 - b) Why must L_{11} and L_{22} always be positive?
 - c) What does it mean that $L_{12} = 0$?
 - d) Under what conditions do we have $L_{11} L_{22} - (L_{12})^2 = 0$?
-
2. Two aqueous solutions of equal volume are separated by a cation-selective membrane. Initially the left hand-side solution contains 0.1 kmol m^{-3} KCl and 0.1 kmol m^{-3} HCl, while the right hand-side solution contains 0.1 kmol m^{-3} .
 - a) Give the directions of diffusion for K^+ and H^+ .
 - b) Give the driving forces for diffusion of H^+ and K^+
 - c) Give the concentrations when diffusion stops.
Assume that no water transfer takes place.