

# Non-Equilibrium Thermodynamics: Foundations and Applications.

Universita degli studi di Brescia September 7-10, 2010



**fondazione**  
**cariplo**



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## Course Overview

### Lecture 1. Why non-equilibrium thermodynamics?

# Non-Equilibrium Thermodynamics: Foundations and Applications

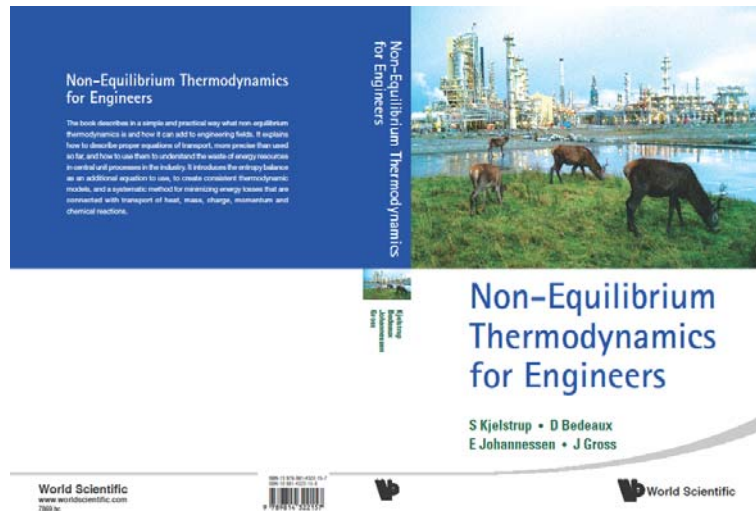
Expected background of students:

- A course in classical thermodynamics on the BSc level
- Knowledge of elementary calculus

Your expectations?



# Non-Equilibrium Thermodynamics: Foundations and Applications



Course content:

11 topics – from selected chapters of two books  
Exercises

# Non-Equilibrium Thermodynamics: Foundations and Applications

At the end of the course a student will have:

- A statement of attendance  
(2,5 CFU activity within doctoral schools)
- pdf files of the course lectures
- exercises with solutions
- lectures available on video
- colleagues in the field!
- a tool for thermodynamic analysis  
of processes



# Non-Equilibrium Thermodynamics: Foundations and Applications

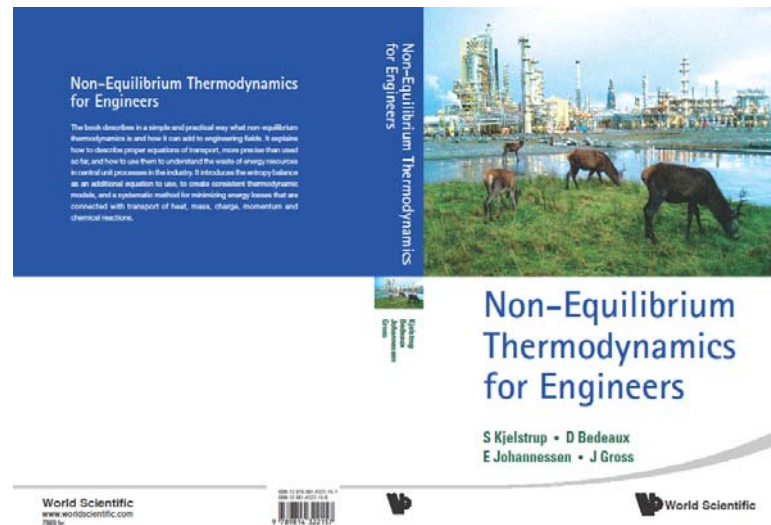
	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium thermodynamics?	Transport of heat and mass	Transport of heat and charge	Entropy production minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	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 1. Why non-Equilibrium Thermodynamics?

### Why is this field important?

Text: Chapters 1 and 2



Exercise 1

# A formulation of the second law of thermodynamics that includes time:

$$\Delta S + \Delta S_0 \geq 0$$

$$\frac{dS_{irr}}{dt} \Delta t = \Delta S + \Delta S_0$$

$$\frac{dS_{irr}}{dt} = \Omega \int_0^L \sigma(x) dx$$

$$\sigma = \sum_i J_i X_i \geq 0$$

The second law of thermodynamics

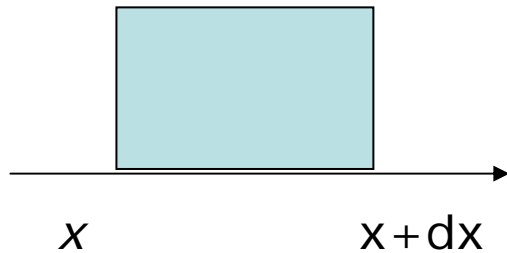


Transport direction:  $x$   
Cross-sectional area:  $\Omega$

The entropy production is a product sum of all fluxes and forces

# The entropy balance

- Entropy is not conserved in any volume element



$$\frac{\partial s}{\partial t} = -\frac{\partial}{\partial x} J_s + \sigma$$

$$\sigma = \sum_i J_i X_i \geq 0$$

- Stationary state, whole system:  $\frac{\partial s}{\partial t} = 0$

$$\frac{dS_{irr}}{dt} = (J_s^o - J_s^i) \Omega$$



# A generalisation of simple transport equations

- Empirical laws of Fourier, Fick, Ohm, Newton, Darcy...

$$J'_q = -\lambda \frac{dT}{dx} \quad J_1 = -D \frac{dc_1}{dx} \quad j = -\kappa \frac{d\phi}{dx}$$



- Non-equilibrium thermodynamics has fluxes and conjugate forces:  
Coupled flux equations

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

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

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

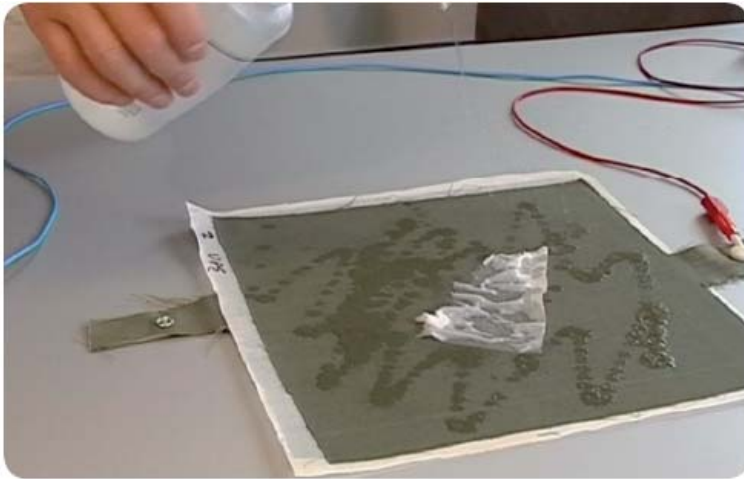
- Onsager relations

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

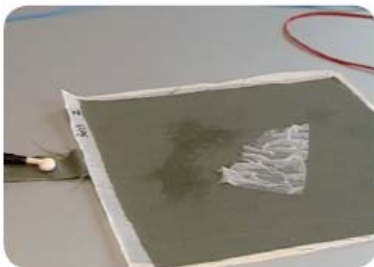
# Is coupling important?

- Water transport connected with charge transport

[http://www.osmotex.ch/en/products/textile\\_pump](http://www.osmotex.ch/en/products/textile_pump)



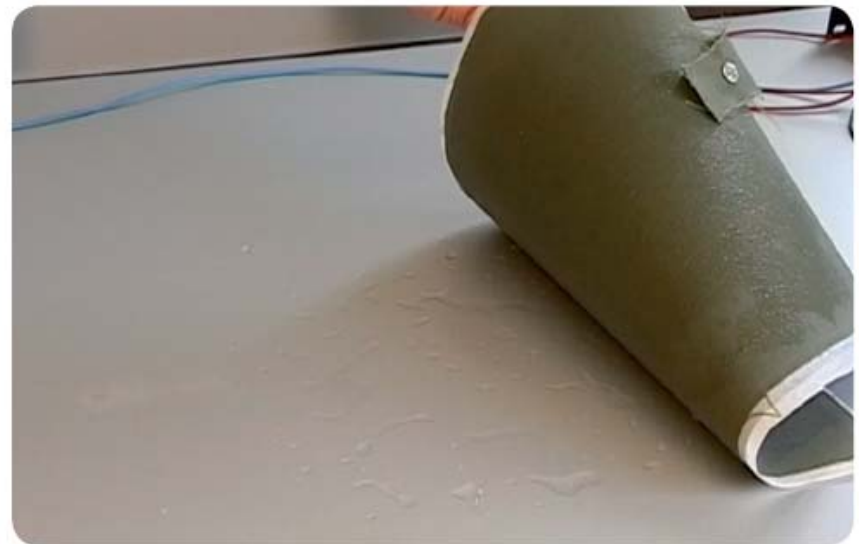
*EO-textile test-cell: A 30x30 cm piece of EO-textile with a paper tissue on top is sprayed with water.*



*This picture is shot after 17 seconds of EO pumping.*



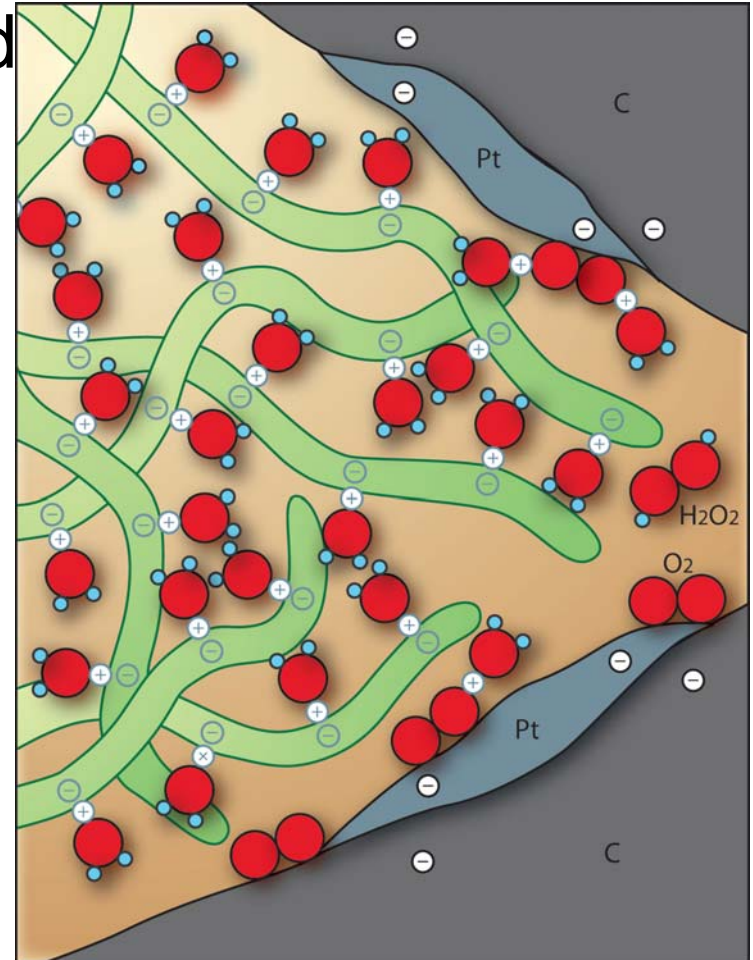
*After 28 seconds the textile surface is dry, and most of the water has been removed from the paper on top.*



*The water has been transported through the textile. In applications the water will run off. In this demonstration, the power consumption was about 5W. When dry, the power consumption falls to zero.*

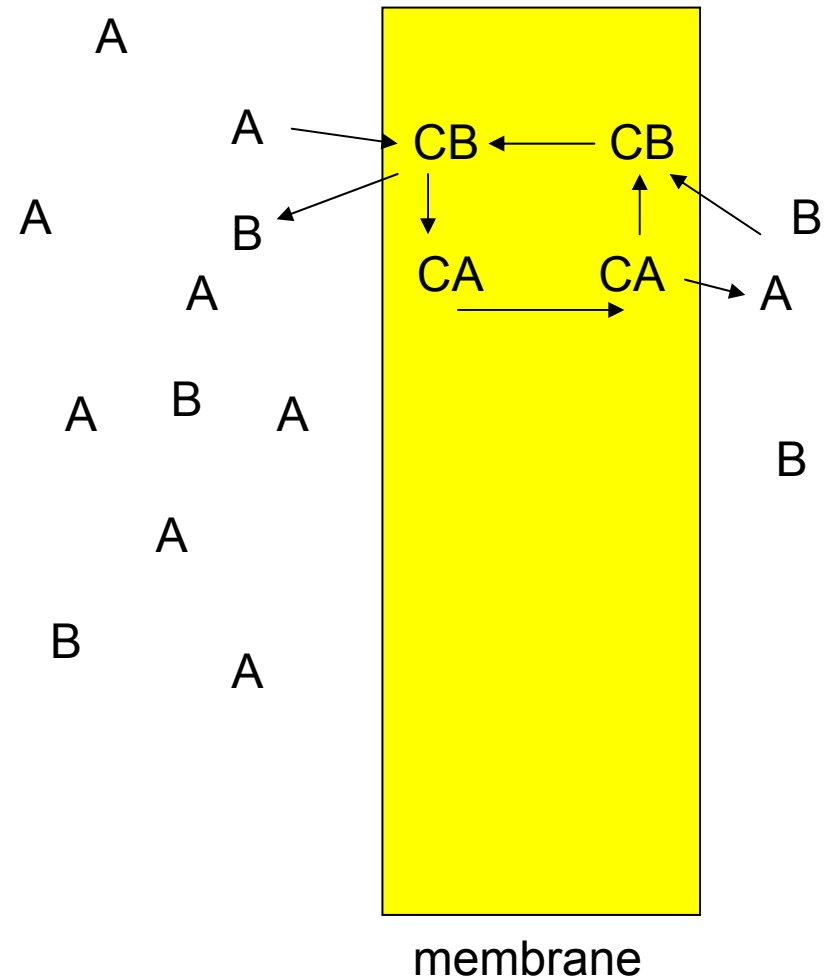
# Is coupling important?

- Water (red w/ green masses) transport is always connected with transport of ions (white) in membranes
- Heat transport can lead to mass transport and separation
- A thermocouple works, because a temperature difference triggers an electric potential difference



# Example: Coupled transports of A and B

- The large gradient in concentration of A drives A to the right
- If C moves only with A or B attached, B can be transported against its concentration gradient!



# Experiments can be well defined from flux equations

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

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

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

Example: Ohmic conductivities

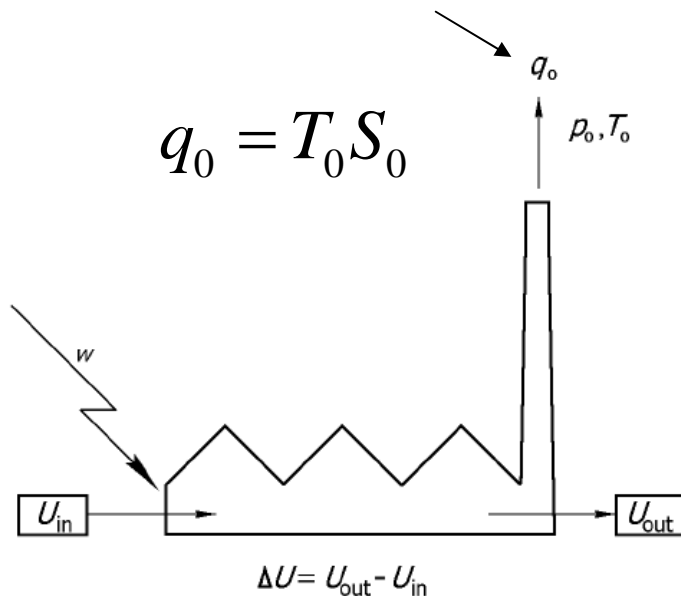
Homogeneous, isothermal conductivity:  $\left[ -\frac{j}{d\phi/dx} \right]_{dT=0, d\mu=0} = \frac{1}{T} L_{\phi\phi}$

Stationary state conductivity:  $\left[ -\frac{j}{d\phi/dx} \right]_{J'_q=0, J=0} = \frac{1}{T} \left[ L_{\phi\phi} - L_{\phi q} \frac{L_{q\phi} L_{\mu\mu} - L_{\mu\phi} L_{q\mu}}{L_{qq} L_{\mu\mu} - L_{q\mu}^2} - L_{\phi\mu} \frac{L_{qq} L_{\mu\phi} - L_{\mu q} L_{q\phi}}{L_{qq} L_{\mu\mu} - L_{q\mu}^2} \right]$

# Lost work, exergy analysis

- A process with many units

Environmental conditions



$$\Delta U = q - p_0 \Delta V + w$$

$$\Delta U = -q_0 - p_0 \Delta V + w$$

$$\Delta S + \Delta S_0 \geq 0$$

$$\frac{dS_{irr}}{dt} \Delta t = \Delta S + \Delta S_0$$

$$w = T_0 \frac{dS_{irr}}{dt} \Delta t + \Delta U + p_0 \Delta V - T_0 \Delta S$$

$$w_{ideal} = \Delta U + p_0 \Delta V - T_0 \Delta S \equiv E$$

$$w_{lost} = w - w_{ideal} = T_0 \left( \frac{dS_{irr}}{dt} \right) \Delta t$$

# Lost work from the entropy balance

of a chemical reactor

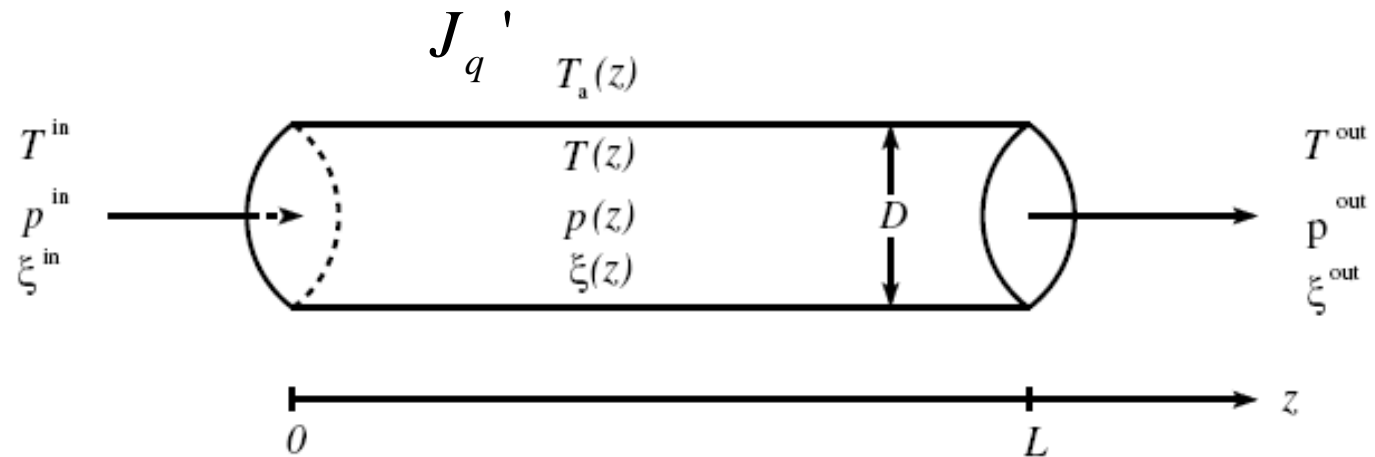


Figure 6.6: A tubular reactor.

$$\frac{dS_{irr}}{dt} = S_{out} - S_{in} - \pi D \int_L \frac{J'_q(z)}{T_a(z)} dz$$

Can also be calculated from  
fluxes and forces  
inside the reactor

# Defining the efficiency of a process

$$\text{Second law: } \eta_{II} = \frac{w}{w_{ideal}} = \frac{w_{ideal} - w_{lost}}{w_{ideal}}$$

$$\text{First law: } \eta_I = \frac{w}{q_h}$$

- The salt power plant at  $T_0, p_0$ :

$$w_{ideal} = -\Delta G, \quad w = EF \quad q = \Delta H \sim 0$$





# Summary:

## What can this theory offer?

1. A more specific formulation of the second law of thermodynamics
2. The entropy balance – also an equation of the system!
3. Transport laws in agreement with the second law
4. A possibility to test models for consistency
5. A systematic framework that also defines experiments
6. A direct calculation of the lost work
7. A better understanding of work and lost work
8. A tool that can be applied in many directions

# Exercise to lecture 1

1. What, according to your experience, are good reasons to use non-equilibrium thermodynamics?
2. In a power plant, 73 MW thermal energy is delivered at 1150 °C in the combustion chamber. The turbine produces 25 MW mechanical power. The ambient temperature is 8 °C.
  - What is the first law efficiency for the process where thermal energy is converted into mechanical energy?
  - What is the second law efficiency of the process?
  - What is the maximum attainable value for each of the efficiencies?
  - What is the expression for the lost work of the process?
  - How can we determine the lost work?
  - Give the definition of the second law efficiency in terms of the entropy production.