Non-Equilibrium Thermodynamics: Foundations and Applications.

Lecture 7: Transport of heat and charge

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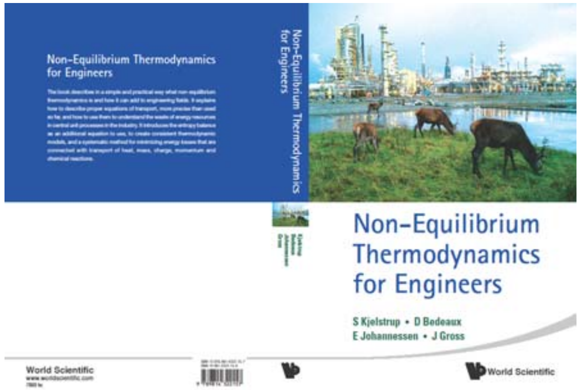
Non-Equilibrium Thermodynamics: Foundations and Applications

	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	

7. Transport of heat and charge

Chapter 4.5

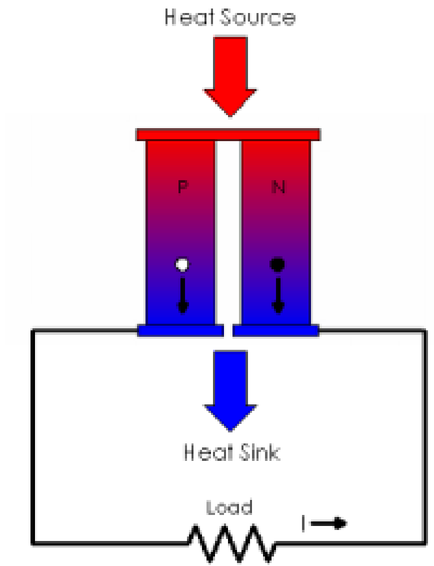


Chapter 9

Exercise

Your working procedure

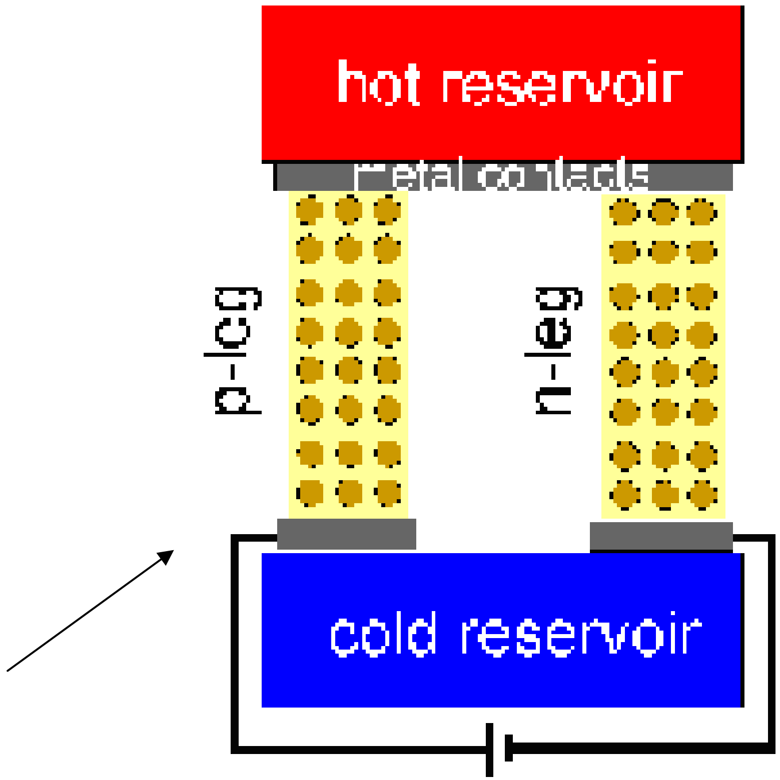
1. The entropy production
2. The fluxes
3. The coefficients
4. Electric work from thermal energy in an electrochemical cell
5. Adding work to provide cooling



BiTe (Bi_2Te_3)
can be used around 400 ^{o}C

Thermocouple: Pt/Pt 10%Rh

Potential work is lost by entropy production



Two semiconductors In a temperature gradient

- The energy available for work in the thermoelectric converted cell has its origin in the temperature gradient.
- Heat conduction will after some time make the system homogeneous, if heat reservoirs are not maintained

The entropy production in the thermoelectric converter

The electric potential difference due to dT over a distance d*x*

$$\sigma = J_q \left(\frac{d}{dx} \frac{1}{T} \right) + j \left(- \frac{1}{T} \frac{d\phi}{dx} \right)$$

Heat flux in J/s m²

Electric current density does also not depend on the frame of reference

The coupled flux equations

$$J_1 = L_{qq}\frac{\partial}{\partial x}\left(\frac{1}{T}\right) - L_{q\phi}\frac{1}{T}\frac{\partial \phi}{\partial x}$$

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

Relations to Fourier's law

$$\left(J_q\right)_{dc=0} = -\lambda\frac{\partial T}{\partial x} = L_{qq}\frac{\partial}{\partial x}\left(\frac{1}{T}\right) = -\frac{L_{qq}}{T^2}\frac{\partial T}{\partial x}$$

$$\lambda(\bar{T}) = -\left(\frac{J_q}{\Delta T / \Delta x}\right)_{dc=0} = L_{qq}\frac{1}{\bar{T}^2}$$

and Ohm's law:

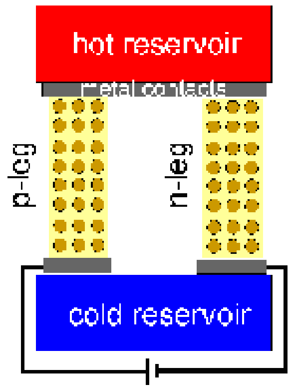
$$\left(j\right)_{dT=0} = -L_{\phi\phi}\frac{1}{T}\frac{\partial \phi}{\partial x}$$

$$\frac{L_{\phi\phi}}{T} = -\left(\frac{j}{\Delta\phi / \Delta x}\right)_{dT=0}$$

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

Onsager relations are now linking the Peltier and Seebeck effects

The heat flux



- Conduction and charge transfer are superimposed:

$$J_1 = L_{qq} \frac{\partial}{\partial x}\left(\frac{1}{T}\right) - L_{q\phi} \frac{1}{T}\frac{\partial \phi}{\partial x}$$

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

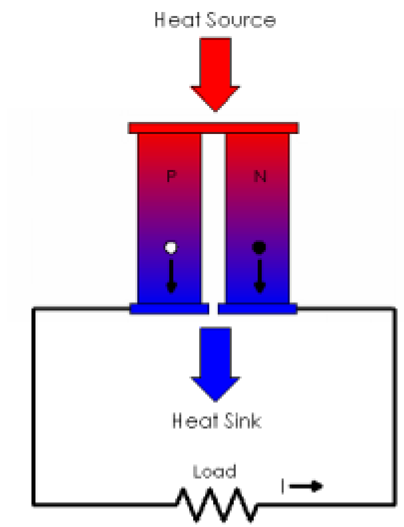
$$J_q = -\frac{1}{T^2}\left(L_{qq} - \frac{L_{q\phi}L_{\phi q}}{L_{\phi\phi}}\right)\frac{\partial T}{\partial x} + \frac{L_{q\phi}}{L_{\phi\phi}}\, j$$

Stationary state thermal conductivity
< than thermal conductivity of
Homogeneous conductor

Coupling means heat transport
with the electric current

Defines the Peltier heat!

The Peltier heat



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

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

Defining the Peltier heat:

$$\pi = \left[\frac{J_q}{j}\right]_{dT=0} = \frac{L_{q\phi}}{L_{\phi\phi}}$$

Useful work from the temperature gradient

The electric work in V (for one faraday transferred):

$$\Delta\phi = \int_L \frac{\partial \phi}{\partial x}dx = -\int_L \left[\frac{\pi}{T}\frac{\partial T}{\partial x} - \frac{T}{L_{\phi\phi}}j\right]dx$$

We used the Onsager relation!

Ohmic potential drop across dx

The Seebeck coefficient

$$\Delta\phi = \int_L \frac{\partial \phi}{\partial x} dx = -\int_L \left[\frac{\pi}{T} \frac{\partial T}{\partial x} - \frac{T}{L_{\phi\phi}} j \right] dx$$

Useful work from the temperature gradient

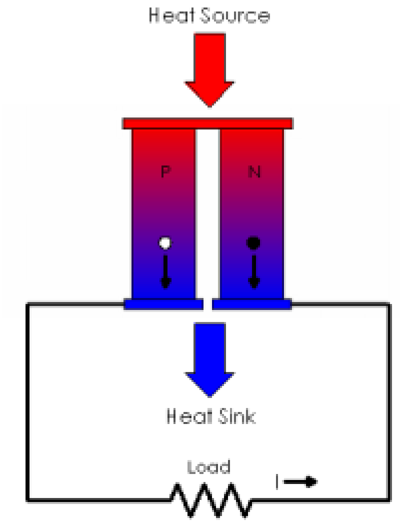
The Seebeck coefficient and the Peltier coefficient are related (Onsager relations)

$$\left(\frac{\Delta\phi}{\Delta T} \right)_{j=0} = -\left(\frac{\pi}{T} \right)_{dT=0}$$

Thermoelectric potential – for a semiconductor is a few mikrovolt per degree temperature difference

Seebeck coefficient: Relatively more easy to measure!

Reversible heat transport in a conductor



$$J_q = -\frac{1}{T^2}\left(L_{qq} - \frac{L_{q\phi}L_{\phi q}}{L_{\phi\phi}}\right)\frac{\partial T}{\partial x} + \frac{L_{q\phi}}{L_{\phi\phi}}\, j$$

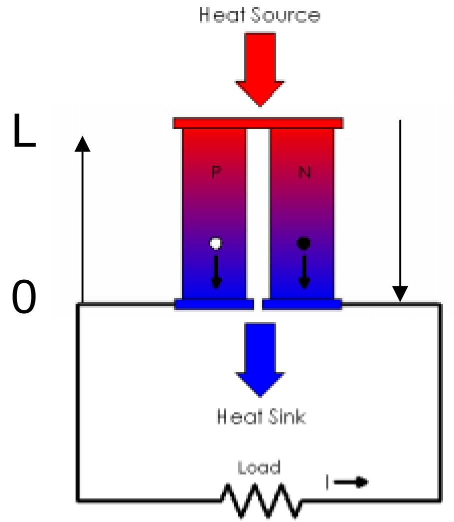
Heat carried with charge

Peltier heat

$$\left(\frac{J_q}{j}\right)_{dT=0} = \frac{L_{q\phi}}{L_{\phi\phi}} = \frac{\pi}{F} = \frac{1}{F}TS^*$$

Defines the transported entropy:
Different for electrons, holes and ions!

Thermoelectric power of a unit cell



$$\Delta\phi_{converter} = \int_0^L \left(\frac{\partial \phi_p}{\partial x}\right) dx + \int_L^0 \left(\frac{\partial \phi_n}{\partial x}\right) dx = \int_0^L \left(\frac{\partial \phi_p}{\partial x}\right) dx - \int_0^L \left(\frac{\partial \phi_n}{\partial x}\right) dx$$

$$= -\int_0^L (S_p^* \frac{1}{F} \frac{\partial T}{\partial x} - r_p j) dx - \int_L^0 (S_n^* \frac{1}{F} \frac{\partial T}{\partial x} - r_n j) dx$$

$$= -\frac{1}{F}\left(S_p^* - S_n^*\right) \Delta T + (r_p + r_n) j \Delta x$$

$$\left[\frac{\Delta\phi_{converter}}{\Delta T}\right]_{j=0} = -\frac{1}{F}\left(S_p^* - S_n^*\right)$$

Seebeck coefficient of a unit cell.
Several units make one module.
Larger effects in electrochemical cells?

Are thermoelectric converters useful?

$$\pi = \left[\frac{J_q}{j}\right]_{dT=0} = \frac{L_{q\phi}}{L_{\phi\phi}} = TS^*$$

The electric work from transported entropies

$$\left[\frac{\Delta\phi_{converter}}{\Delta T}\right]_{j=0} = -\frac{1}{F}\left(S_p^* - S_n^*\right)$$

An Icelandic company
is developing thermoelectric
applications for harnessing
geothermal power.

A converter with no moving parts.
The thermocouple

Cooling by thermoelectricity

- Thermoelectric coolers make use of the Peltier effect to transport heat, applying an electric current. The junction of materials cools down

Summary

- The transports of heat and charge have been described by the fluxes and forces defined by the entropy production
- The origin of electric work in systems with transport of heat and charge is the coupling coefficent, or the Peltier heat (transported entropy)
- This coupling coefficient is not large in semiconductors
- We have studied simple thermoelectric converters. Reversible heat transport may be important in industry as well as in biology

Exercise for Lecture 7

1. The temperature difference available in a casting are of a silicon producer is 300 K. What is the electric potential obtainable from a thermoelectric module with Seebeck coefficient 3.82 10^{-3} V/K? The module electric resistance is 1.8 ohm. How many modules are needed to run a fan which requires 5.9 W at 0.1 A?
2. What is the heat flux obtainable from one module, passing an electric current through the junction of 0.1 A at isothermal conditions?