Non-Equilibrium Thermodynamics for Engineers

Lecture 2:

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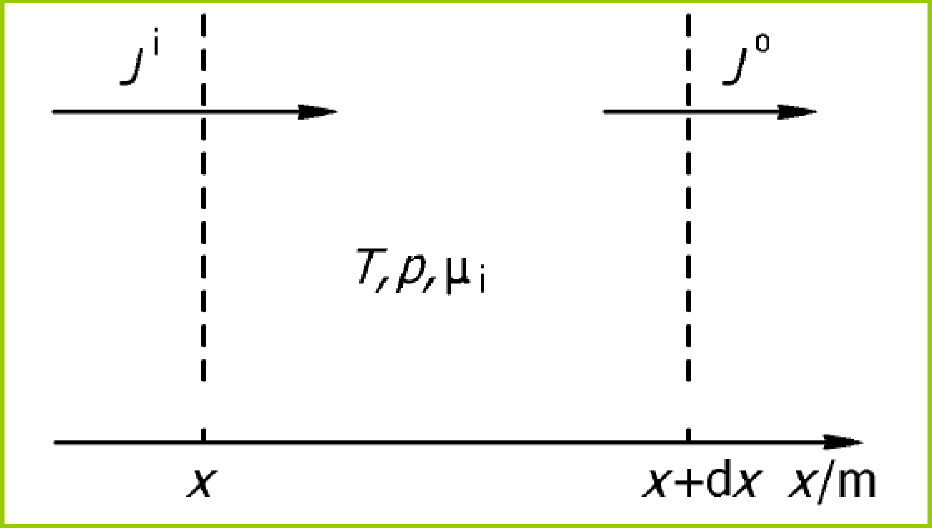
Finding the entropy production

We always combine:

1. Gibbs equation
2. The first law
3. The mass balances



The volume element at rest

Gibbs equation for an open system

$$dU = TdS - pdV + \sum_{j=1}^{n} \mu_j dN_j$$

We need a local formulation, so we introduce *U=uV, S= sV, N_j = c_j V*

$$Vdu + udV = T(Vds + sdV) - pdV + \sum \mu_j (c_j dV + Vdc_j)$$

$$V(du - Tds - \sum \mu_j dc_j) = (u - TS + p + \sum \mu_j c_j) dV$$

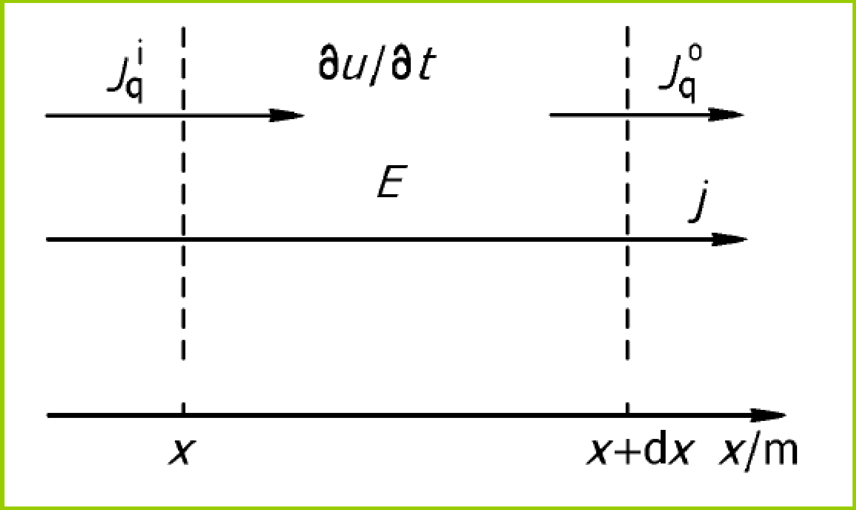
$$U = TS - pV + \sum \mu_j N_j \qquad \text{x} \frac{1}{V}$$

$$u = Ts - p + \sum \mu_j c_j$$

$$du = Tds + \sum \mu_j dc_j$$

$$\frac{ds}{dt} = \frac{1}{T}du - \frac{1}{T}\sum \mu_j \frac{dc_j}{dt}$$

The first law
of a system with transport of heat, mass and charge*



$$\frac{\partial u}{\partial t} = -\frac{\partial}{\partial x} J_q + Ej$$

The total heat flux is the sum of the measurable heat flux and latent heat transported

$$J_q = J'_q + \sum_{j=1}^{n} H_j J_j$$

The measured emf and the gradient in electric potential

$$E = -\frac{\partial \phi}{\partial x}$$

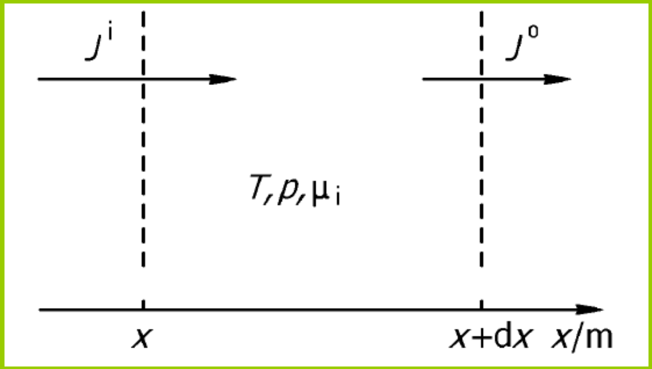
***The system is in mechanical equilibrium**

Mass conservation

- The reaction rate *r* and the reaction Gibbs energy

$$\Delta_r G = \sum_j \nu_j \mu_j$$

$$\frac{\partial c_j}{\partial t} = -\frac{\partial}{\partial x} J_j \pm \nu_j r \quad \text{for} \quad j = 1, \ldots, n$$



- No charge accumulation

$$\frac{\partial z}{\partial t} = -\frac{\partial}{\partial x} j = 0$$

Deriving the entropy production

$$\frac{\partial s}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} - \frac{1}{T}\sum \mu_j \frac{\partial c_j}{\partial t} =$$

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

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

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

4 conjugate flux-force pairs

$$\sigma = J_q \frac{\partial}{\partial x}\left(\frac{1}{T}\right) + j\left[-\frac{1}{T}\frac{\partial \phi}{\partial x}\right] + \sum J_j\left[-\frac{\partial}{\partial x}\frac{\mu_j}{T}\right] + r\left[-\frac{\Delta G}{T}\right]$$

$$J_s = \frac{1}{T}\left[J_q - \mu_j J_j\right]$$

Entropy flux

A practical problem:

- The total heat flux cannot be measured

$$J_q = J'_q + \sum_{j=1}^{n} H_j J_j$$

- We would like to replace the total heat flux by the measurable heat flux as a variable

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

- In order to combine terms better we need the derivative of

$$\mu_j / T$$

Mathematics for state functions

The differential of the chemical potential

$$dG = -SdT + Vdp + \sum \mu_i dN_i$$

$$d\mu_j = -S_j dT + V_j dp + \sum \left(\frac{\partial \mu_i}{\partial N_j} \right)_{p,T,N_i} dN_i$$

$$d\mu_j = -S_j dT + V_j dp + d\mu_j^c$$

gives the expression we introduce
in the entropy production:

$$d\left[\frac{\mu_j}{T}\right] = \frac{1}{T}\left(d\mu_{j,T} + \frac{d\mu_j}{dT} dT \right) + \mu_j d\left[\frac{1}{T}\right]$$

$$= \frac{1}{T}\left(d\mu_{j,T} - S_j dT \right) + \mu_j d\left[\frac{1}{T}\right]$$

with $d\mu_{j,T} = V_j dp + d\mu_j^c = d\mu_j + S_j dT$

$$\sigma = \left[J_q^{'} + \sum J_j H_j \right] \frac{\partial}{\partial x}\left(\frac{1}{T}\right) - j\frac{1}{T}\frac{\partial \phi}{\partial x} - \sum J_j \frac{\partial}{\partial x}\frac{\mu_j}{T} + \quad .....$$

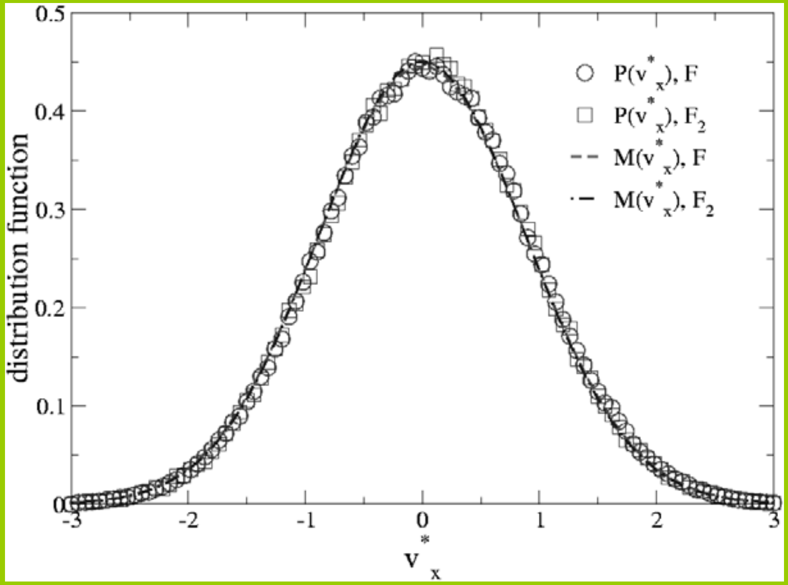
$$= \left[J_q^{'} + \sum J_j H_j \right] \frac{\partial}{\partial x}\left(\frac{1}{T}\right) - j\frac{1}{T}\frac{\partial \phi}{\partial x} - \sum J_j \left[\frac{1}{T}\left(\frac{\partial}{\partial x}\mu_{j,T} - S_j \frac{\partial}{\partial x} T \right) + \mu_j \frac{\partial}{\partial x}\left[\frac{1}{T}\right] \right] + ...$$

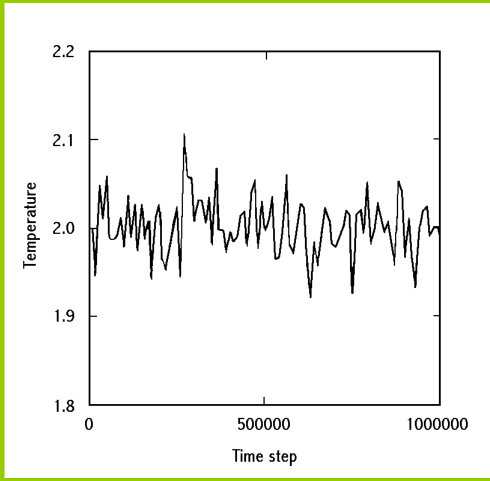
$$= J_q^{'} \frac{\partial}{\partial x}\left(\frac{1}{T}\right) + j\left(-\frac{1}{T}\frac{\partial \phi}{\partial x} \right) + \sum J_j \left[-\frac{1}{T}\frac{\partial \mu_{j,T}}{\partial x} \right] + ...$$

This form can be related to experiements

Validity of basic assumptions in non-equilibrium thermodynamics

- **We have assumed local equilibrium in any volume element**
- **Molecular velocity distributions are then nearly Maxwellian as in this example where fluorine atom reacts to the molecule**

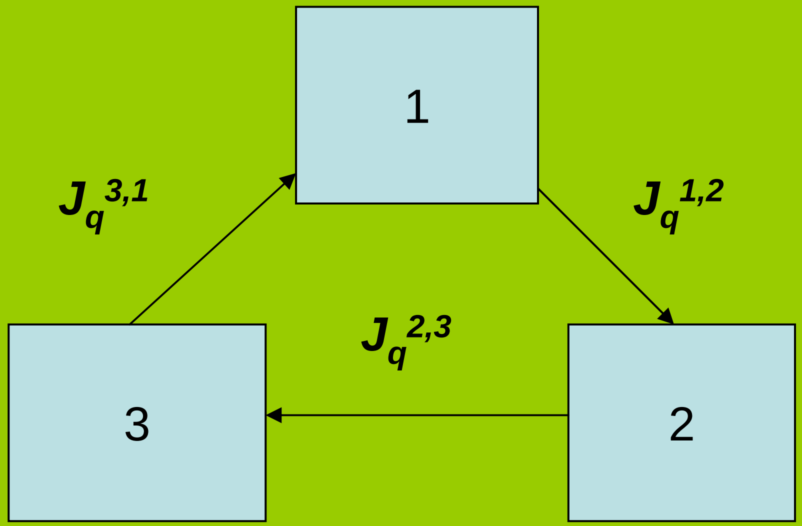




Temperature (and concentration) fluctuations can be large

Why we must use the entropy production to define dissipation

Consider an Example of three reservoirs with heat transport



The total entropy production is:

$$\frac{dS_{irr}}{dt} = \frac{1}{T_1}\frac{dU_1}{dt} + \frac{1}{T_2}\frac{dU_2}{dt} + \frac{1}{T_3}\frac{dU_3}{dt}$$

$$= J_q^{1,2}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] + J_q^{2,3}\left[\frac{1}{T_3} - \frac{1}{T_2}\right] + J_q^{3,1}\left[\frac{1}{T_1} - \frac{1}{T_3}\right] \neq 0$$

The dissipation function gives zero losses!

$$\psi = T_1\frac{dS_1}{dt} + T_2\frac{dS_2}{dt} + T_3\frac{dS_3}{dt} = 0$$

Summary

- **The entropy production gives the conjugate flux-force pairs.**
- **The value of the entropy production is independent of the frame of reference**
- **A change in flux leads to a change in a force**
- **Two equivalent forms of the entropy production have been derived. Other forms can be found, i.e. using the entropy flux as a variable**

$$J_s = \frac{1}{T}\left(J_q - \sum_{j=1}^{n} \mu_j J_j\right) = \frac{1}{T}\left(J_q' + \sum_{j=1}^{n} S_j J_j\right)$$

- **The form to use depends on the application of interest**