Non-Equilibrium Thermodynamics: Foundations and Applications.

Lecture 10: Entropy production minimization. Theory

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Non-Equilibrium Thermodynamics: Foundations and Applications

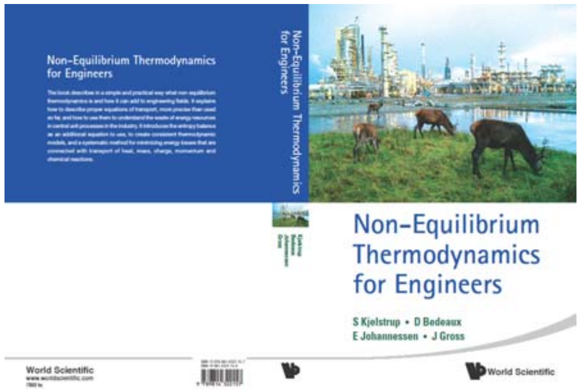
	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium ther-modynamics?	Transport of heat and mass	Transport of heat and charge	Entropy produc-tion minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion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

Non-Equilibrium Thermodynamics: Foundations and Applications

10. Entropy production minimization theory

”How do we find the optimal operation of a process unit?”

Chapter 9



Process units, examples

- Heat exchangers
- Distillation columns
- Chemical reactors
- …..

Several units in a whole process (flowsheet).

First: The method.
Expansion of ideal gas and heat exchange

A work producing process

- The maximum available work output

$$w = w_{\max} - w_{lost}$$

- The lost work $w_{lost} = T_0(dS_{irr} / dt) > 0$

$$dS_{irr} / dt = \int \sigma dV$$

Optimal means:
minimum *total* entropy production given a fixed demand on the process

Mathematical methods for constrained optimisation

Euler Lagrange optimisation:

$$L = \frac{dS_{irr}}{dt} + \sum_i \lambda_i P_i$$

Constraint examples:

$$P = P_1$$

$$T_a = T_0$$

- Uses the objective function directly

Control theory

$$H = \sigma(z,t) + \sum_i \lambda_i (z,t) f_i$$

Energy balance $f_T = \frac{dT}{dz} = ...$

Momentum balance $f_p = \frac{dp}{dz} = ...$

Mass balance $f_\xi = \frac{d\xi}{dz} = ...$

Extra conditions, i.e. $p_{ext} = const.$

- Uses the a local formulation of the optimisation problem
- Defines control variables and state variables
- Mathematically robust
- An autonomous Hamiltonian is constant along the path

Pontryagin

Optimal isothermal expansion of an ideal gas:

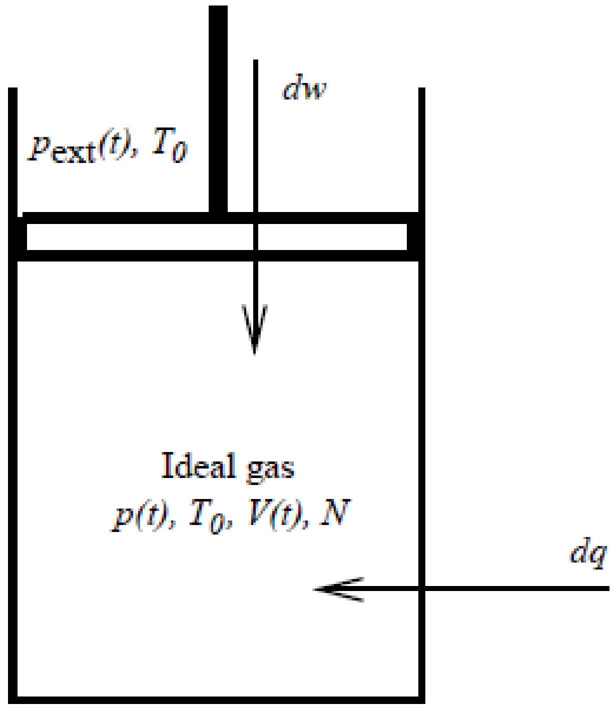


Figure 9.1: A container filled with N mol of an ideal gas with pressure $p(t)$, temperature T_0, and volume $V(t)$. The heat dq is added to the gas and work dw is done in a small time interval dt. The container is equipped with a piston. The gas expands isothermally against an external pressure $p_{\text{ext}}(t)$. The temperature of the environment is T_0.

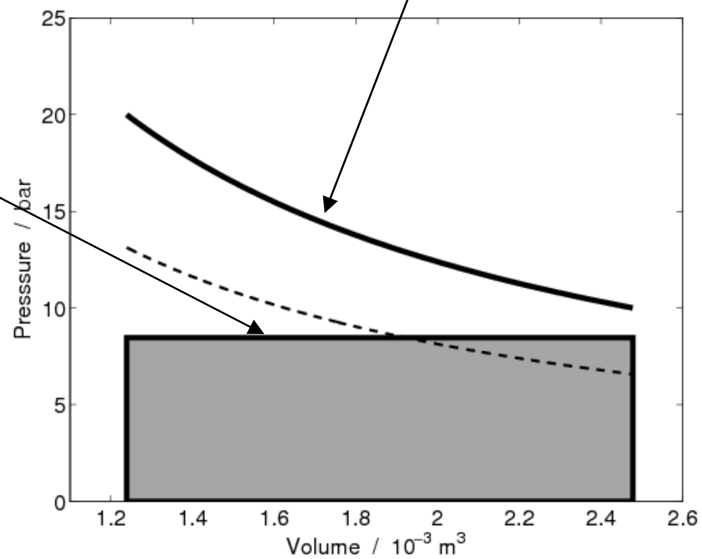
Optimal isothermal expansion

- Find the external pressures in a K-step process that gives minimum *total* entropy production, when the volume of the system changes from V_1 to V_2

N moles of ideal gas in a piston, K=1

$$w_{max} = NRT_0 \ln \frac{p_2}{p_1}$$

$$w = -\int_{V_1}^{V_2} p_{ext} dV = -p_{ext} \int_{p_1}^{p_2} NRT_0 d\left(\frac{1}{p}\right) = -NRT_0 \left(\frac{1}{p_2} - \frac{1}{p_1}\right)$$



$$w_{lost} = w - w_{max} = -NRT_0 \left[p_{ext} \left(\frac{1}{p_2} - \frac{1}{p_1}\right) + \ln \frac{p_2}{p_1} \right]$$

Assume that the piston moves according to:

$$\frac{dp(t)}{dt} = -\frac{f}{NRT_0} \left(p_{ext}(t) - p(t) \right)$$

f is related to the friction between piston and wall

Total entropy production for a K-step process

Prefer to sum over process duration

Control variable

$$\frac{dS_{\text{irr}}}{dt} = \sum_{i=1}^{K} \int_{t_{1,i}}^{t_{2,i}} \frac{1}{T_0} \left(p_{\text{ext},i} - p(t)\right) \left(-\frac{dV(t)}{dt}\right) dt$$

$$= -N\,R \left[\sum_{i=1}^{K} p_{\text{ext},i} \left(\frac{1}{p_{2,i}} - \frac{1}{p_{1,i}} \right) + \ln \frac{p_2}{p_1} \right]$$

Control theory uses the local entropy production:

$$\sigma(t) = \frac{1}{T_0} \left(p_{\text{ext}}(t) - p(t)\right) \left(-\frac{dV(t)}{dt}\right)$$

$$= \frac{1}{T_0} \frac{f}{p(t)^2} \left[p_{\text{ext}}(t) - p(t)\right]^2$$

The Hamiltonian becomes:

Constraint

$$\mathcal{H} = \frac{1}{T_0} \frac{f}{p(t)^2} \left(p_{\text{ext}}(t) - p(t)\right)^2 + \lambda(t) \frac{f}{N\,R\,T_0} \left(p_{\text{ext}}(t) - p(t)\right)$$

The Hamiltonian is autonomous (depends only implicitly on time) and is therefore constant !

$$\mathcal{H} = \frac{1}{T_0}\,\frac{f}{p(t)^2}\,\left(p_{\text{ext}}(t) - p(t)\right)^2 + \lambda(t)\,\frac{f}{N\,R\,T_0}\,\left(p_{\text{ext}}(t) - p(t)\right)$$

$$\frac{dp(t)}{dt} = \frac{\partial \mathcal{H}}{\partial \lambda} = \frac{f}{NRT_0}\left(p_{\text{ext}}(t) - p(t)\right) \qquad (9.12)$$

$$\frac{d\lambda(t)}{dt} = -\frac{\partial \mathcal{H}}{\partial p} = 2\,\frac{1}{T_0}\,\frac{f}{p(t)^2}\,\left(p_{\text{ext}}(t) - p(t)\right)\,\frac{p_{\text{ext}}(t)}{p(t)} + \lambda(t)\,\frac{f}{NRT_0} \qquad (9.13)$$

Solve for Lagrange multiplier from: $\frac{\partial \mathcal{H}}{\partial p_{\text{ext}}} = 2\,\frac{1}{T_0}\,\frac{f}{p(t)^2}\,\left(p(t)_{\text{ext}} - p(t)\right) + \lambda(t)\,\frac{f}{N\,R\,T_0} = 0$

By introducing the result in the Hamiltonian, we find

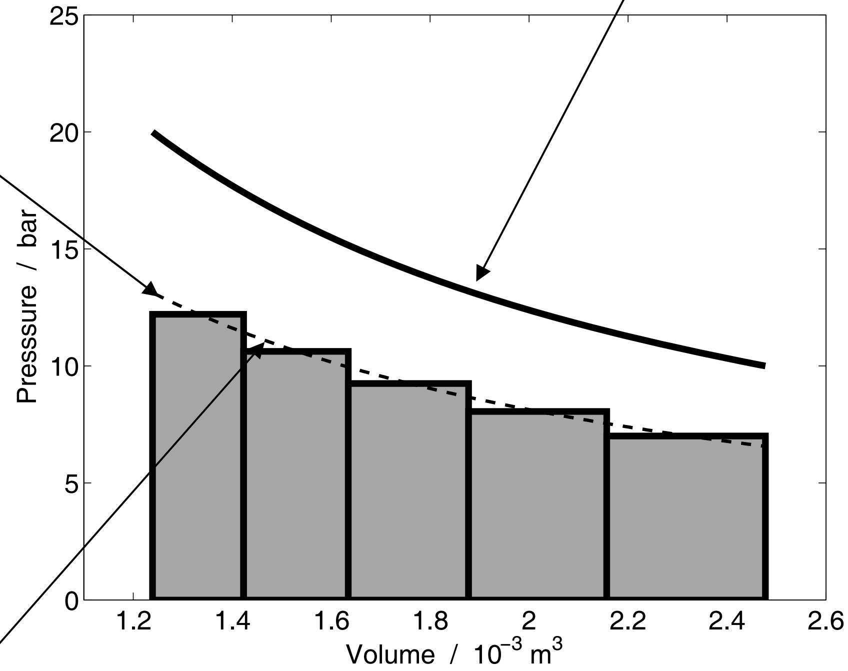
$$\mathcal{H}^{\min} = \frac{1}{T_0}\,\frac{f}{p(t)^2}\,\left(p_{\text{ext}}(t) - p(t)\right)^2 - 2\,\frac{1}{T_0}\,\frac{f}{p(t)^2}\,\left(p_{\text{ext}}(t) - p(t)\right)^2$$

The Hamiltonian reduces to the entropy production which then also is constant along the path! **Equipartition of entropy production**

The optimal path

The pressure variation giving minimum lost work

Max. work



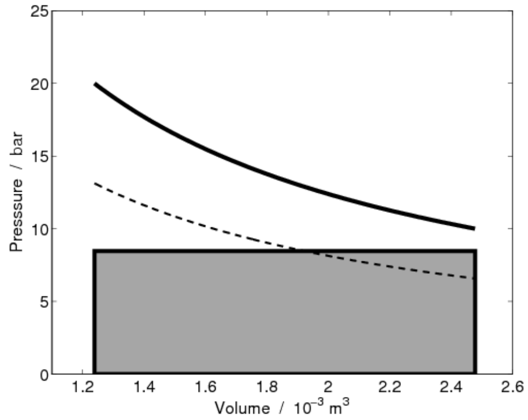
Solution:

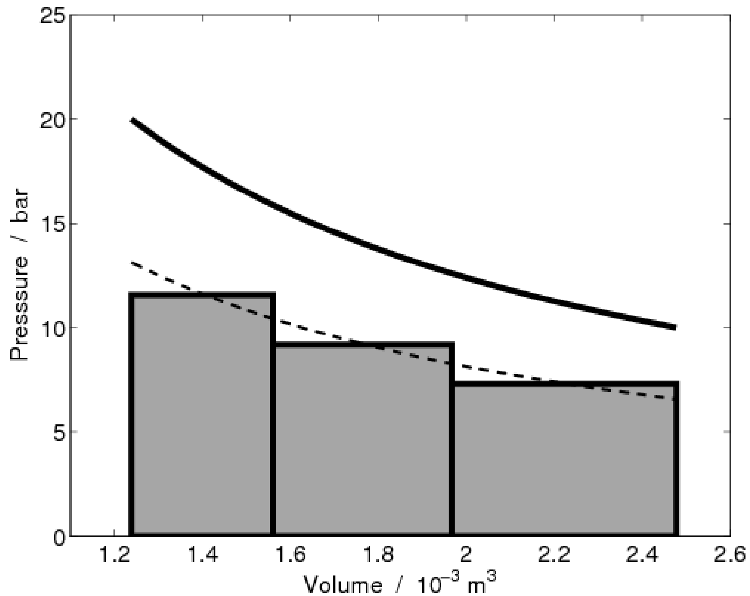
$$p_{ext} = p_1 \left(1 + \frac{NRT_0}{f\theta} \ln \frac{p_2}{p_1}\right)\left(\frac{p_2}{p_1}\right)^{t/\theta}$$

$$p(t) = p_1 \left(\frac{p_2}{p_1}\right)^{t/\theta}$$

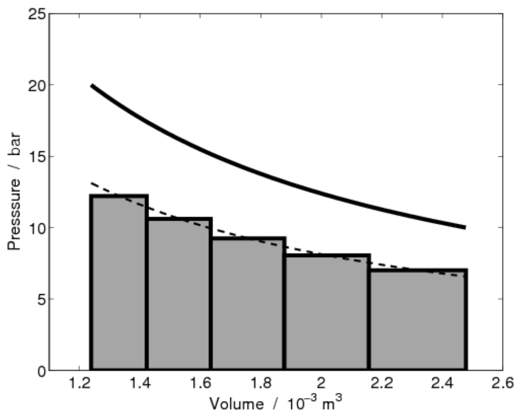
The entropy production is constant along the optimal path!

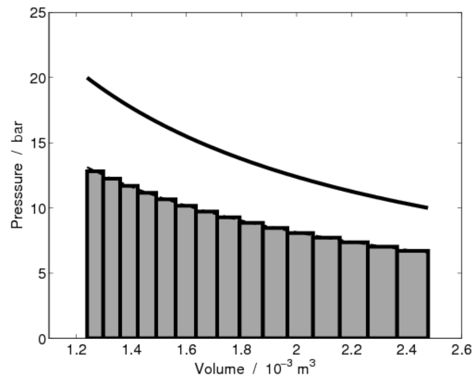
1, 3, 5 and 15 step expansion results



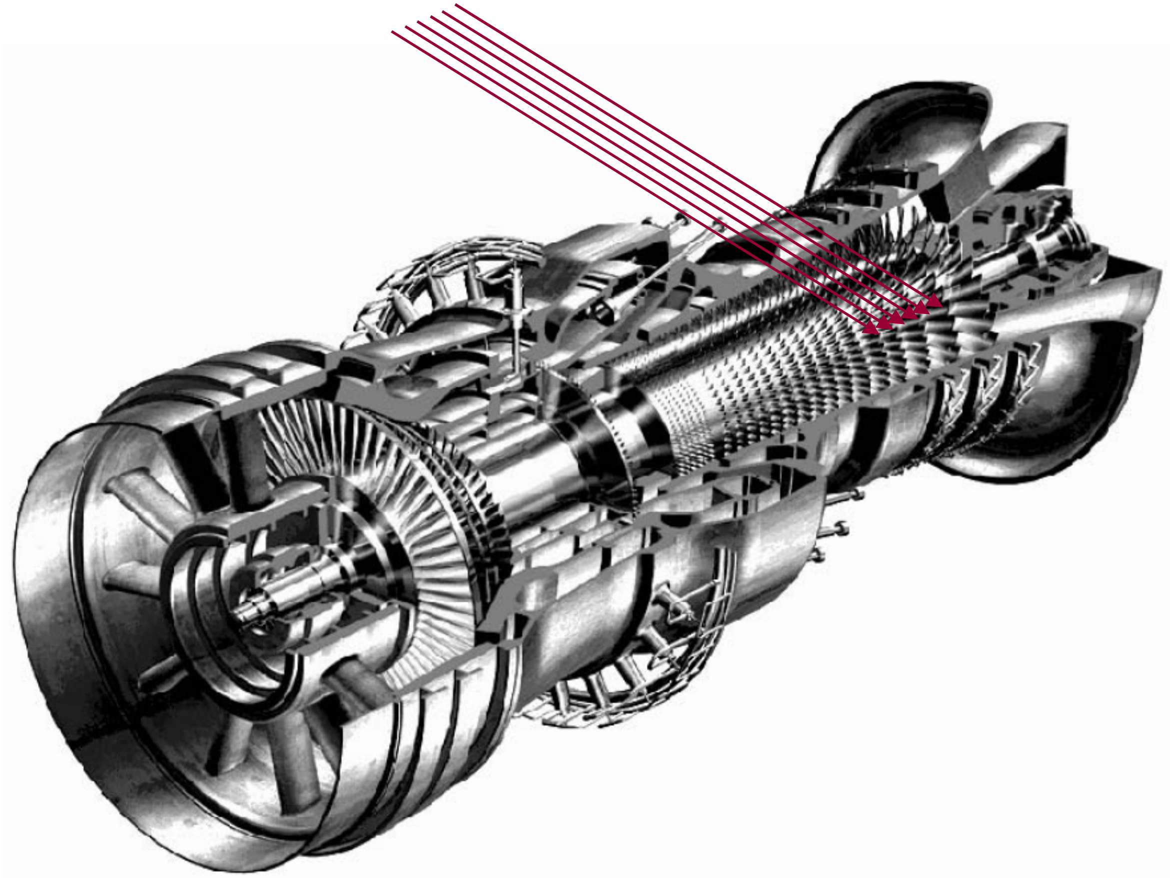


N = 1 mol *T* = 298 K *p*1 = 20 bar *p*2 = 10 bar
f = 500 m3 Pa/s
Θ = 10 s



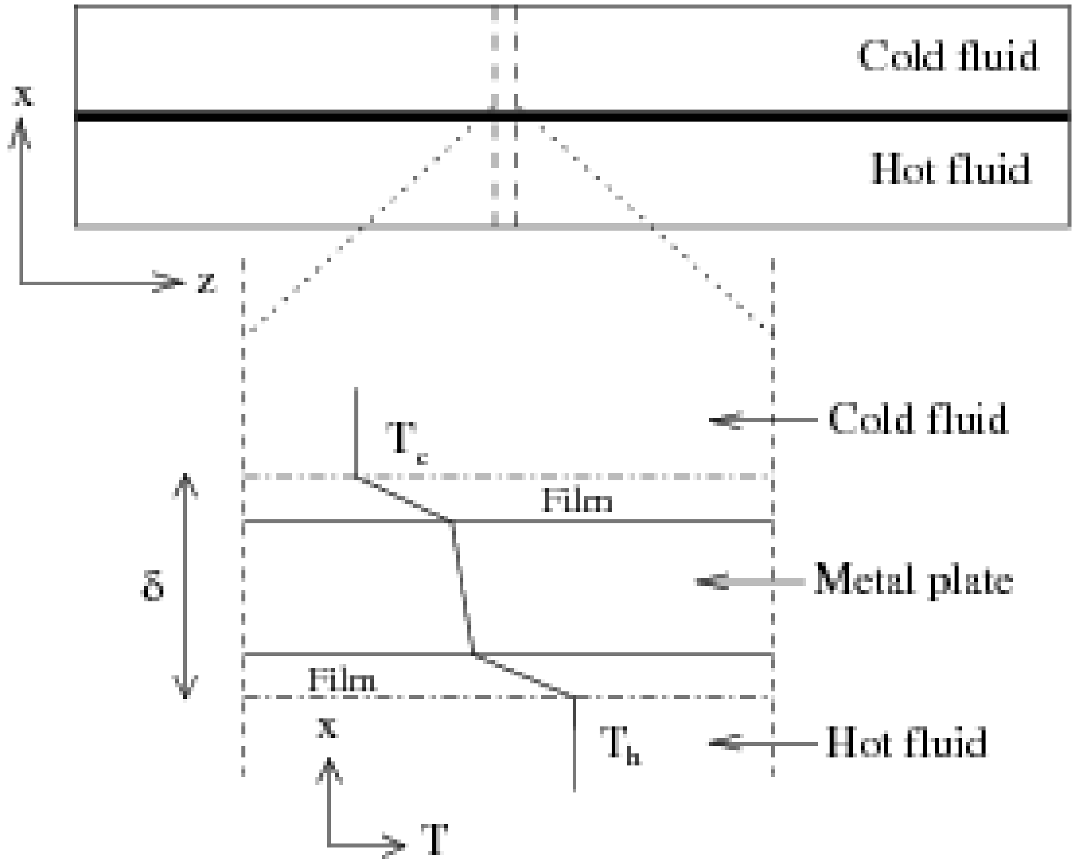


Continuous Expansion of Gases in a Turbine



„Multistage“ gas turbine – a realization of the K-step expansion case?

Optimal heat exchange



Optimal heat exchange

- **Find the temperature profile *$T_h(z)$* that gives minimum entropy production, when a given amount of heat is transferred from the hot fluid**

Constraint

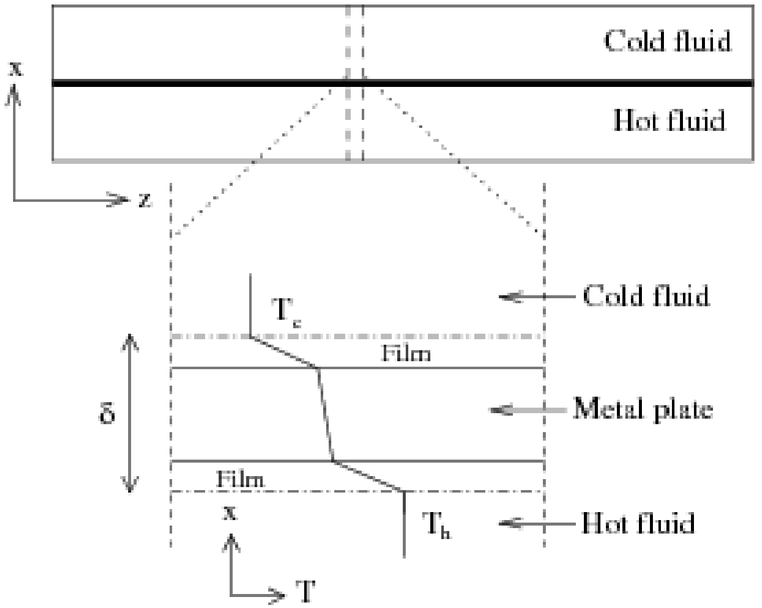
Fixed heat transferred, with fixed:

$$T_{h,in} \text{ and } T_{h,out}$$

Energy balance gives local constraint:

$$FC_p dT_h(z) = J_q^{'}(z)\Delta y dz$$

$$\frac{dT_h(z)}{dz} = \frac{J_q^{'}(z)\Delta y}{FC_p}$$

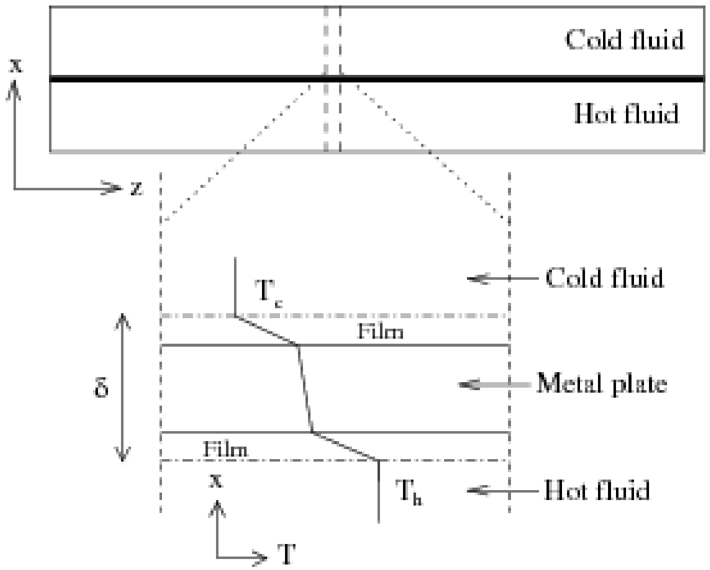


The entropy production of heat exchange

$$\sigma(x,z) = J_q^{'}(x,z)\frac{d}{dx}\left(\frac{1}{T(x,z)}\right)$$

$$J_q^{'}(x,z) = J_q^{'}(z)$$

$$\sigma(z) = \Delta y\int_0^{\delta}\sigma(x,z)dx = \Delta y J_q^{'}(z)\left[\frac{1}{T_h(z)} - \frac{1}{T_c(z)}\right]$$



$$J_q^{'} = l_{qq}\Delta\left(\frac{1}{T}\right)$$

$$\frac{dS_{irr}}{dt} = \Delta y\int_0^L \sigma(z)dz = \Delta y\int_0^L \left(l_{qq}\right)^{-1}\left[J_q^{'}\right]^2 dz$$

Hamiltonian: $$\mathcal{H} = \Delta y \, l_{qq}\left(T_h(z)\right) \left[\Delta\left(\frac{1}{T}\right)\right]^2 + \lambda(z)\,\frac{\Delta y \, J_q'(z)}{F\,C_p\left(T_h(z)\right)} = \text{constant}$$

- 3 differential eqs.

$$\frac{dT_h(z)}{dz} = \frac{\partial\mathcal{H}}{\partial\lambda} \qquad \frac{d\lambda(z)}{dz} = -\frac{\partial\mathcal{H}}{\partial T_h}$$

$$\frac{\partial\mathcal{H}}{\partial T_c} = \Delta y \, l_{qq}\left(T_h(z)\right) \left[2\,\Delta\left(\frac{1}{T}\right) + \frac{\lambda(z)}{F\,C_p\left(T_h(z)\right)}\right] \frac{1}{T_c(x)^2} = 0$$

- Solve the last one for λ, introduce result in Hamiltonian

- Result:

$$\mathcal{H} = \Delta y \, l_{qq}\left(T_h(z)\right) \left[\Delta\left(\frac{1}{T}\right)\right]^2 - 2\,\Delta y \, J_q'(z)\,\Delta\left(\frac{1}{T}\right)$$

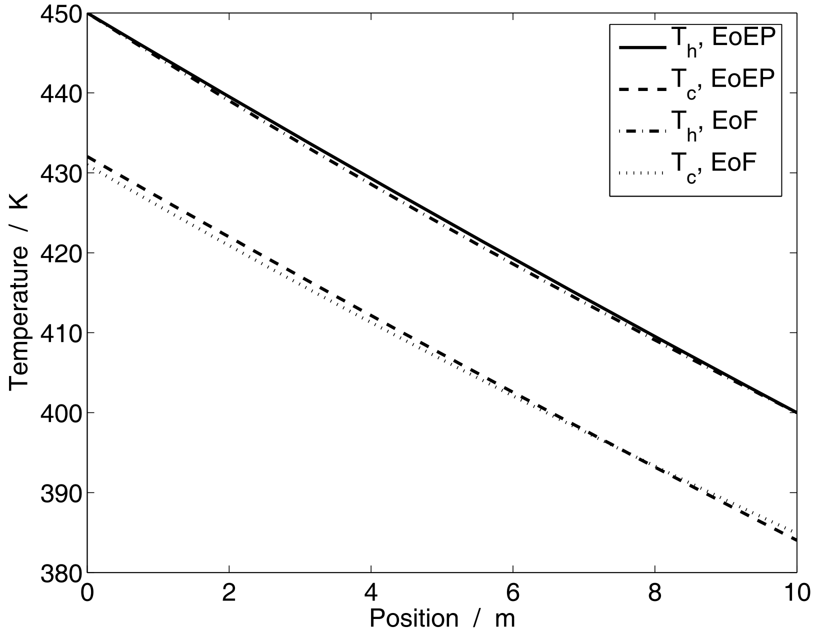
$$= -\,\sigma(z) = \text{constant}$$

Optimal heat exchange: Results

The local and total entropy production for heat exchange

$$\sigma_{\mathrm{EoEP}} = \frac{1}{\Delta y\, U}\left[\frac{F\, C_p}{L}\ \ln\left(\frac{T_{h,\mathrm{out}}}{T_{h,\mathrm{in}}}\right)\right]^2$$

$$\left(\frac{dS_{\mathrm{irr}}}{dt}\right)_{\mathrm{EoEP}} = \frac{1}{\Delta y\, L\, U}\left[F\, C_p\ \ln\left(\frac{T_{h,\mathrm{out}}}{T_{h,\mathrm{in}}}\right)\right]^2$$



- Exact solution: Constant entropy production (EoEP)
- Approximate solution: Constant thermal force (EoF)

$$\Delta\left(\frac{1}{T}\right)_{\mathrm{EoEP}} = \frac{F\, C_p}{\Delta y\, U}\ \frac{1}{T_h(z)^2}\ \frac{dT_h(z)}{dz} = \frac{F\, C_p}{\Delta y\, U\, L}\ \ln\left(\frac{T_{h,\mathrm{out}}}{T_{h,\mathrm{in}}}\right)\ \frac{1}{T_h(z)}$$

Why do we minimize the entropy production?

- We can obtain a realistic target for the efficiency of a process unit
- We can compare processes when we use the yardstick that measures lost work
- We can find typical behaviour (i.e. equipartition): thumb rules

Summary:

1. Energy efficient design means to take the entropy production into account!
2. The path of *minimum* total entropy production can be found for operation of certain process units, given certain boundary conditions
3. Use control theory to find it!
4. The operating path has constant local entropy production in simple cases (expansion of ideal gas, heat exchange)
5. Constant driving force is a good approximation to a state with constant local entropy production in heat exchange