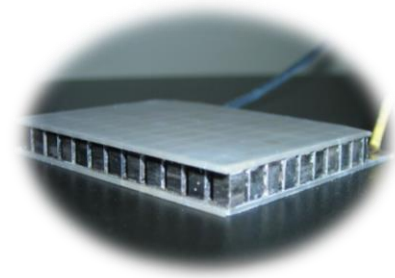


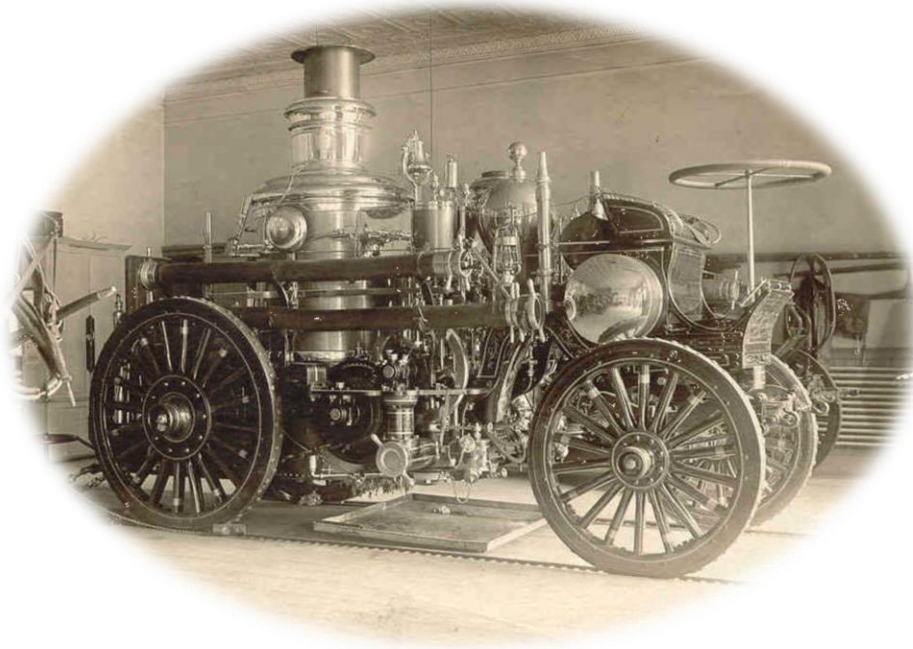
$$(P, T) \Leftrightarrow (\mu, T)$$



From thermoelectricity to finite time thermodynamics: a closed loop approach to thermodynamics

C. Goupil, H. Ouerdane, E. Herbert, Y. D'Angelo and Ph. Lecoœur

Fluid and engine



Un corps solide, une barre métallique, par exemple, alternativement chauffée et refroidie, augmente et diminue de longueur, et peut mouvoir des corps fixés à ses extrémités. Un liquide alternativement chauffé et refroidi augmente et diminue de volume et peut vaincre des obstacles plus ou moins grands opposés à sa dilatation.

RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE,

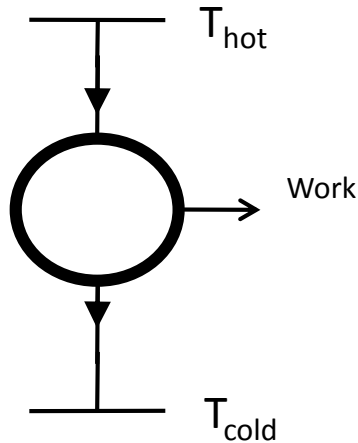
PAR S. CARNOT,

ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

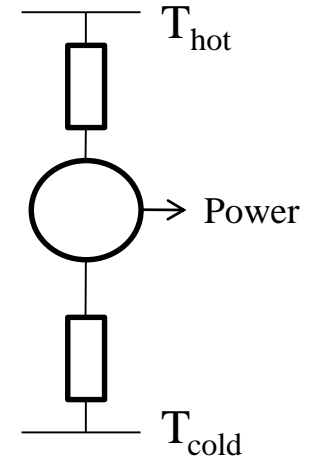
A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, N°. 55.

1824.

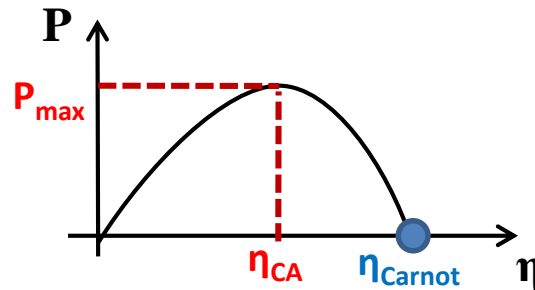
Endoreversible: OYCNCNA



Finite Time
Thermodynamics
FTT



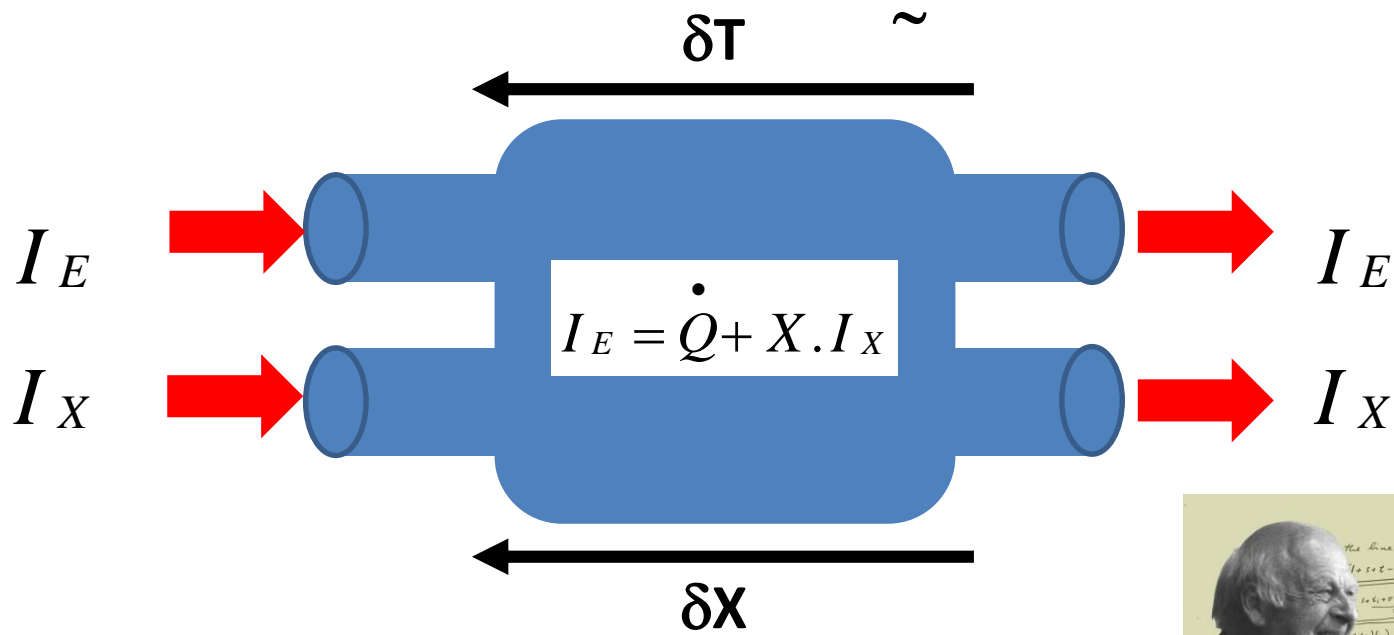
$$\eta_C = \frac{W}{Q_{in}} = 1 - \frac{T_{cold}}{T_{hot}}$$



$$\eta_{CA} = \frac{\dot{W}}{\dot{Q}_{in}} = 1 - \sqrt{\frac{T_{cold}}{T_{hot}}}$$

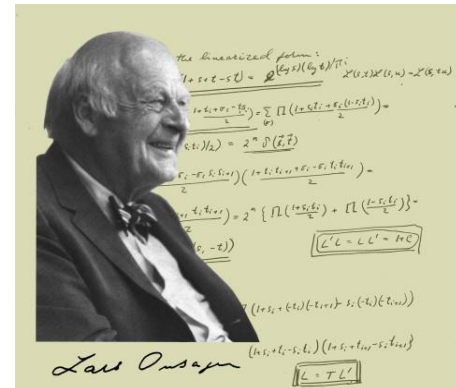
- **H. T. Odum & R. C. Pinkerton**, TIME'S SPEED REGULATOR: THE OPTIMUM EFFICIENCY FOR MAXIMUM POWER OUTPUT IN PHYSICAL AND BIOLOGICAL SYSTEMS, American Scientist, Vol. 43, No. 2 (APRIL 1955), pp. 331-343
- **J. Yvon**, The saclay Reactor: Two Years of Experience in the Use of a Compressed gas as a Heat Transfer Agent, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy (1955)
- **P. Chambadal** *Les centrales nucléaires*. Armand Colin, Paris, France, 4 1-58, (1957)
- **I.I. Novikov**, Efficiency of an Atomic Power Generation Installation, Atomic Energy 3 (1957)
- **F.L. Curzon & B. Ahlborn**, Efficiency of a Carnot Engine at Maximum Power Output, Am. J. Phys. 43 (1975)

Non endoreversible: Onsager (1931)



$$\begin{pmatrix} I_X \\ I_E \end{pmatrix} = \begin{pmatrix} L_{NN} & L_{NE} \\ L_{EN} & L_{EE} \end{pmatrix} \begin{pmatrix} \delta \left(-\frac{X}{T} \right) \\ \delta \left(\frac{1}{T} \right) \end{pmatrix}$$

$$\begin{bmatrix} dN \\ dS \end{bmatrix} = \begin{bmatrix} \left(\frac{\partial N}{\partial \mu} \right)_T & \left(\frac{\partial N}{\partial T} \right)_\mu \\ \left(\frac{\partial S}{\partial \mu} \right)_T & \left(\frac{\partial S}{\partial T} \right)_\mu \end{bmatrix} \begin{bmatrix} d\mu \\ dT \end{bmatrix}$$



Lars Onsager 27 November , 1903 -- October 5, 1976

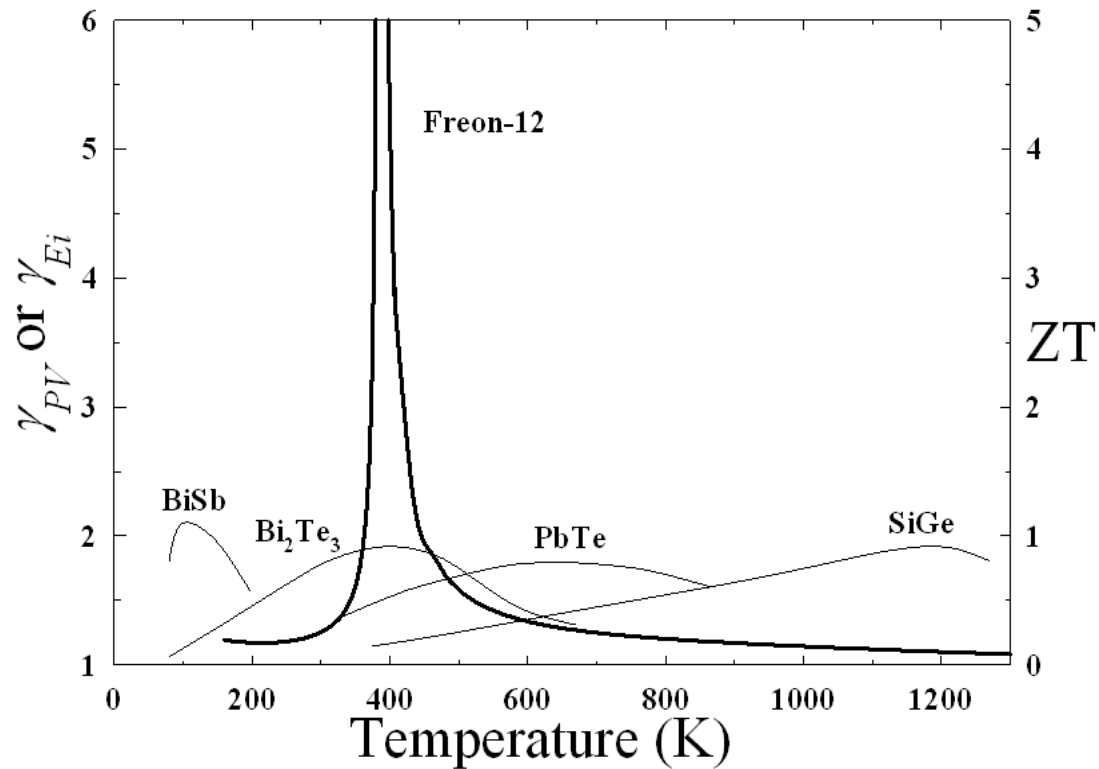
- Two currents (energy & matter)
- Two conductivities. (viscosities)
- One coupling coefficient

Thermodynamic fluid

$$\frac{\kappa_E}{\kappa_0} = 1 + \frac{\alpha^2 \sigma_T}{\kappa_0} T$$

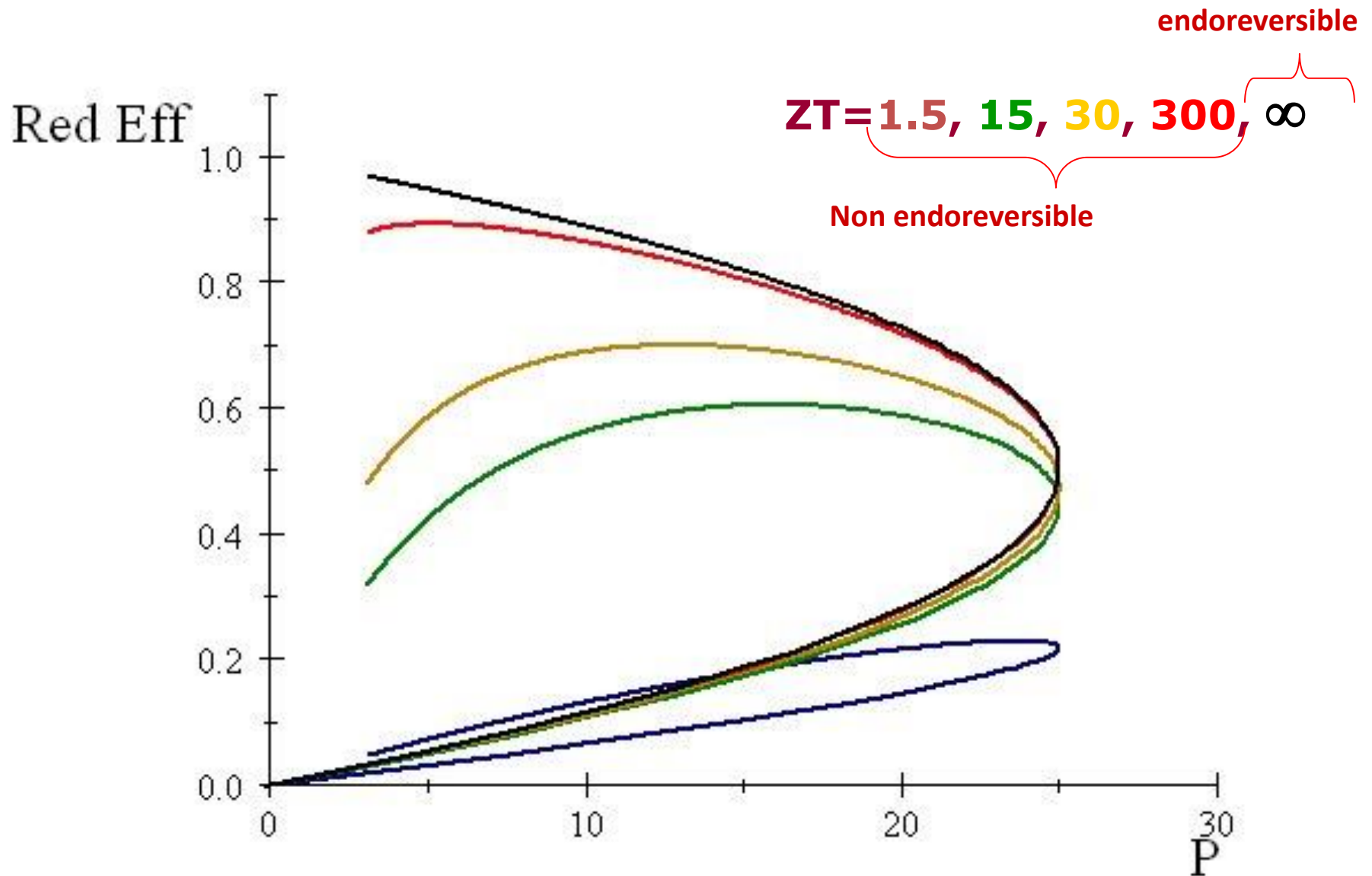
$$\frac{\sigma_Q}{\sigma_T} = 1 + \frac{\alpha^2 \sigma_T}{\kappa_0} T$$

$$\frac{C_\mu}{C_N} = 1 + \frac{S_N^2 \chi_T}{C_N} T$$



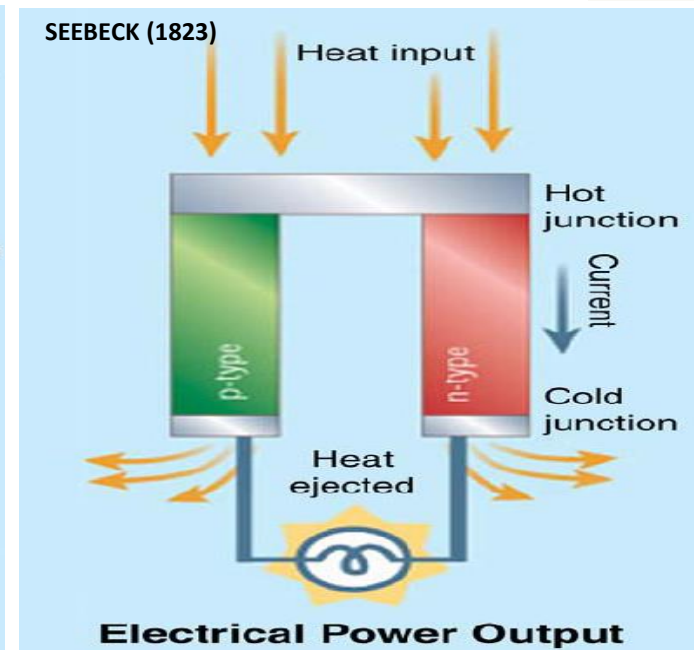
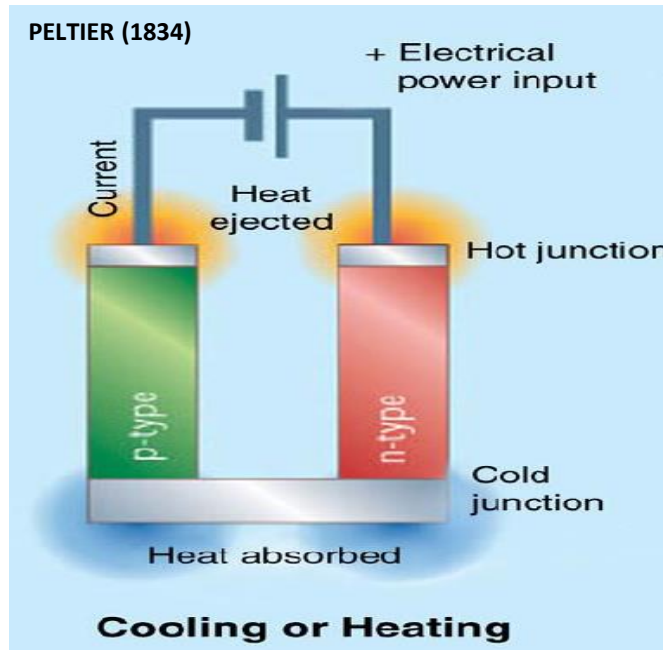
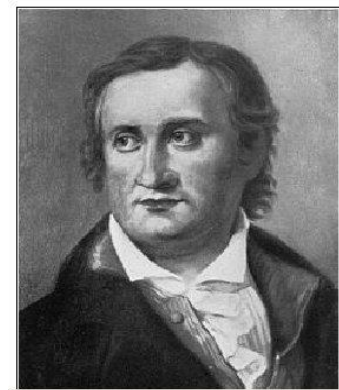
Vining 1997

Efficiency or Power



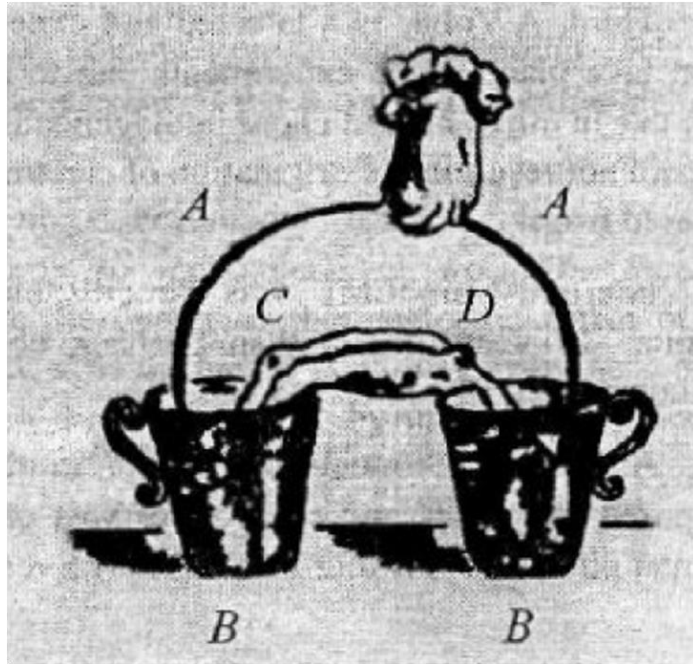


Thermoelectricity



“Coupling Ohm’s law and Fourier’s law”

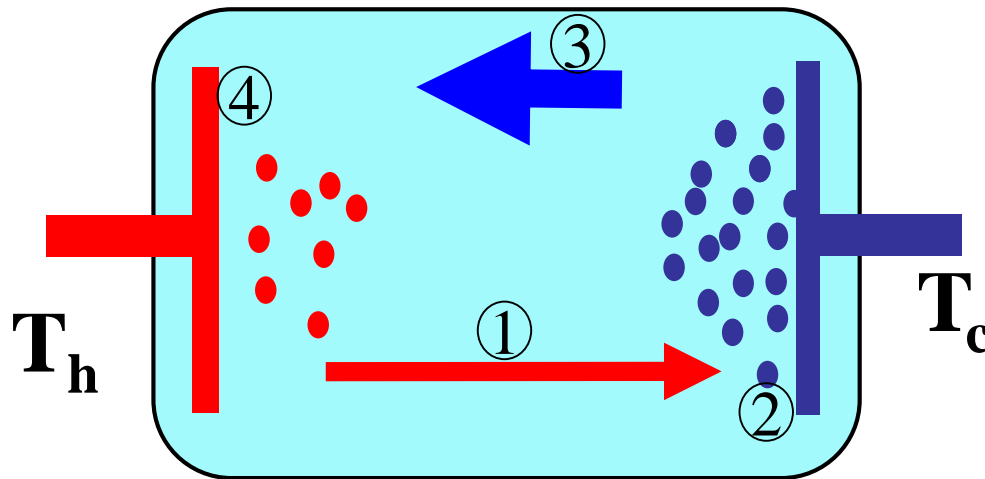
The Volta Story



Alessandro Volta
18 February 1745 – 5 March 1827)

1794 --- 1795: Letter to professor Antonio Maria Vassalli (accademia delle scienze di torino) "... I immersed for a mere 30 seconds the end of such arc into boiling water, removed it and allowing no time for it to cool down, resumed the experiment with two glasses of cold water. It was then that the frog in the water started contracting, and it happened even two, three, four times on repeating the experiment till one end of the iron previously immersed into hot water did not cool down".

Thermal & Electrical coupling.



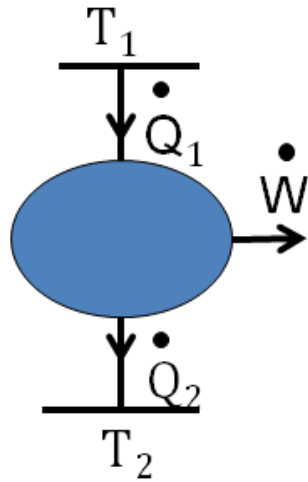
- 1: Adiabatic.
- 2: Isothermal.
- 3: Adiabatic.
- 4: Isothermal.

- Reversible adiabatic transport of the carriers. (isentropic)
- The convective part contribute to the entropy transport...
- ... but not the conductive part .(leak)
- => Reduce the conductive part and increase the convective part .
- The electrical conductivity should be large.
- => Yes but by increasing mobility only.

What is a good TE system?

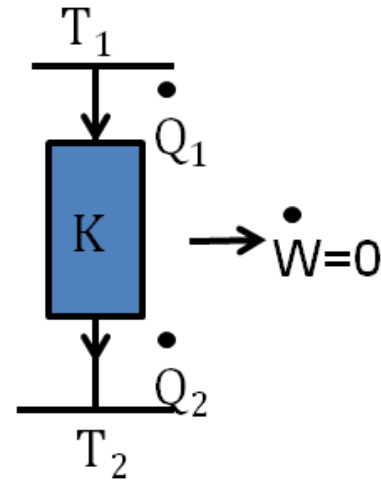
$$P = \dot{W} = \dot{Q}_1 - \dot{Q}_2$$

Fully reversible

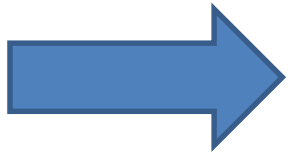


$$\dot{S}_1 = \dot{S}_2 = \frac{\dot{Q}_1}{T_1} = \frac{\dot{Q}_2}{T_2} \Rightarrow \dot{W} = \dot{Q}_1 \left(1 - \frac{T_2}{T_1}\right)$$

Fully irreversible

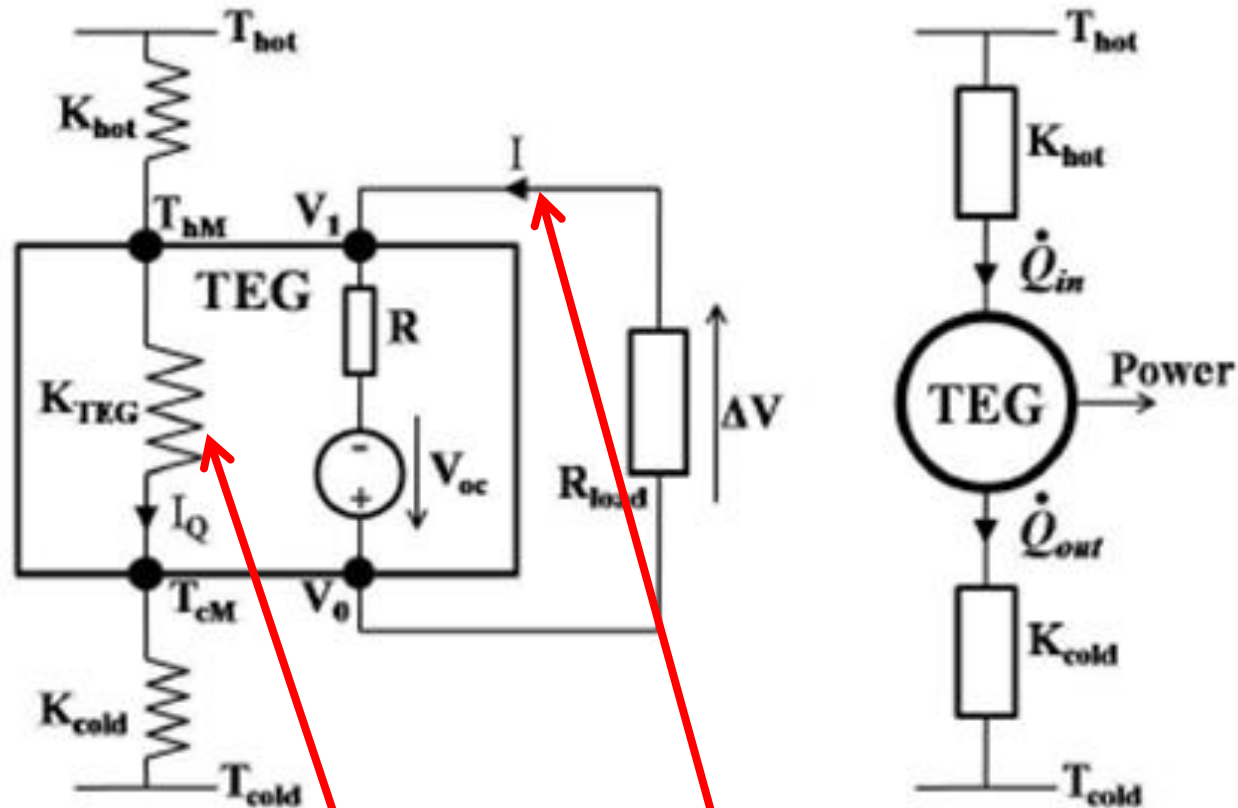


$$\dot{Q}_1 = \dot{Q}_2 \Rightarrow \dot{W} = \dot{Q}_1 - \dot{Q}_2 = 0$$



The perfect engine : when entropy becomes conservative.

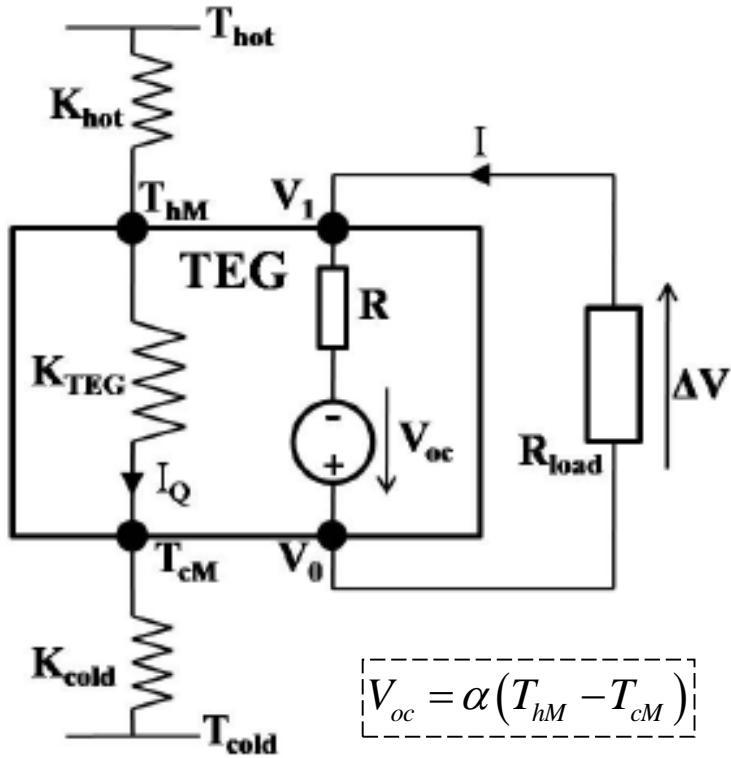
Nodal model: presentation



$$\frac{K_E}{K_0} = 1 + \frac{\alpha^2 \sigma_T}{K_0} T$$

$$K_{TEG}(I) = K_0 \left[1 + \frac{I}{I_{CC}} ZT \right]$$

Nodal model: Onsager description



Force-Flux :

$$\begin{bmatrix} I \\ I_Q \end{bmatrix} = \begin{bmatrix} \frac{1}{R} & \frac{\alpha}{R} \\ \frac{\alpha T}{R} & \frac{\alpha^2 T}{R} + K_0 \end{bmatrix} \cdot \begin{bmatrix} \Delta V \\ T_{hM} - T_{cM} \end{bmatrix}$$

$$I_Q = \underbrace{\alpha T \cdot I}_{\text{advection}} + \underbrace{K_0 \cdot (T_{hM} - T_{cM})}_{\text{conduction}}$$

$$I_Q = \underbrace{\left(\frac{\alpha^2 T}{R + R_{load}} + K_0 \right)}_{K_{TEG}} (T_{hM} - T_{cM})$$

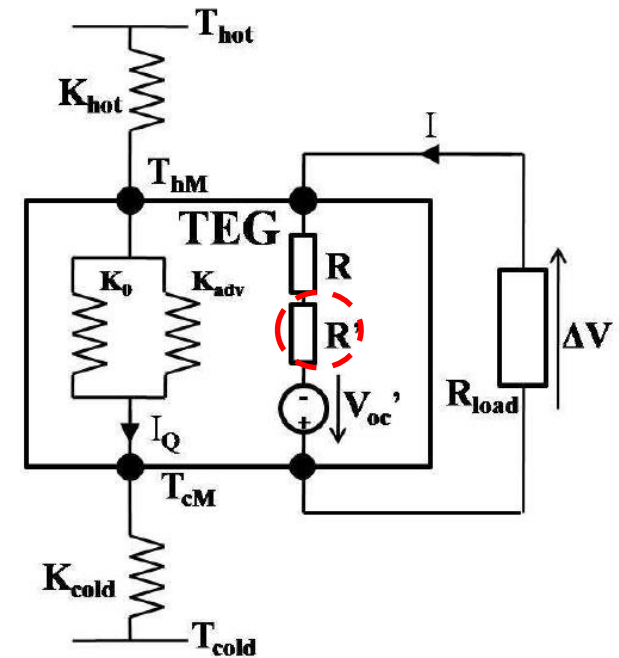
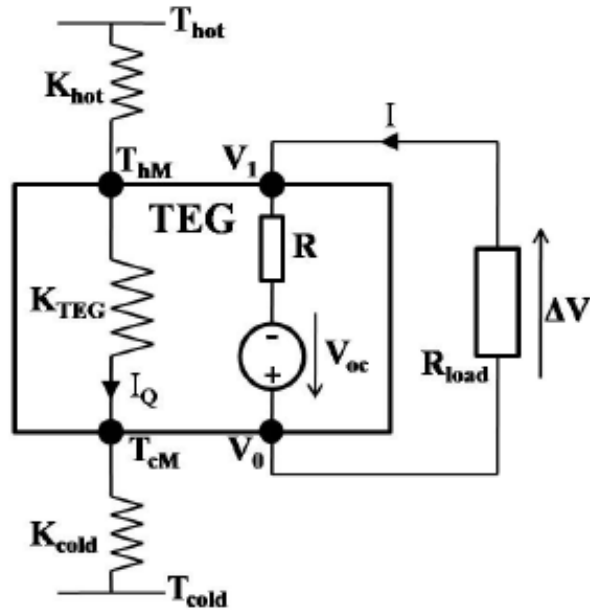
$\underbrace{\frac{\alpha^2 T}{R + R_{load}}}_{K_{adv}}$
 K_0

Effective thermal
conductance !

advection

Conduction

Nodal model: resulting picture



Thevenin model:

Is a function
of R_{load} !

$$V_{oc} = \alpha (T_{hM} - T_{cM})$$

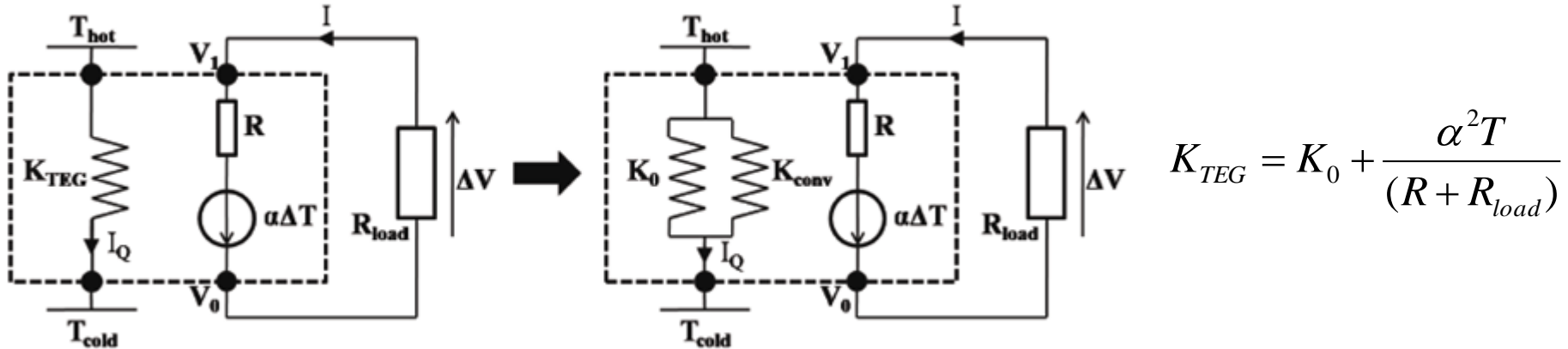
$$V_{oc} = \underbrace{\alpha \Delta T \frac{K_{contact}}{K_{contact} + K_0}}_{V_{oc}'} - I \underbrace{\frac{\alpha^2 T}{K_{contact} + K_0}}_{R'}$$

$$K_{TEG}(I) = K_0 \left[1 + \frac{I}{I_{CC}} ZT \right]$$

[Y. Apertet, et al. EPL 97 \(2012\)](#)

- The feedback comes from K_c
- No R_{TE} if the coupling is perfect, $K_c \Rightarrow \infty$

Thermoelectric Prandtl number



$$\sigma_P = \frac{\text{Kinematic viscosity}}{\text{Thermal diffusivity}} \equiv \frac{\text{momentum diffusion}}{\text{heat diffusion}}$$

Influence of the fluid velocity profile on the temperatures profile.

$$\sigma_{P_{TE}} = \frac{K_{conv} \Delta T}{K_0 \Delta T} = \frac{\alpha^2 T}{K_0 (R + R_{load})} = \frac{ZT}{1 + \frac{R_{load}}{R}}$$

Then

The thermoelectric Prandtl number is controlled by the electrical load !
(Electrical feedback on the dissipative properties, including thermal)

So

The Prandtl number is maximal in short_circuit (or more...).

But

The maximal power is obtained for half this value :

$$\sigma_{P_{TE}(R=R_{load})} = \frac{ZT}{2}$$

Impedance matching

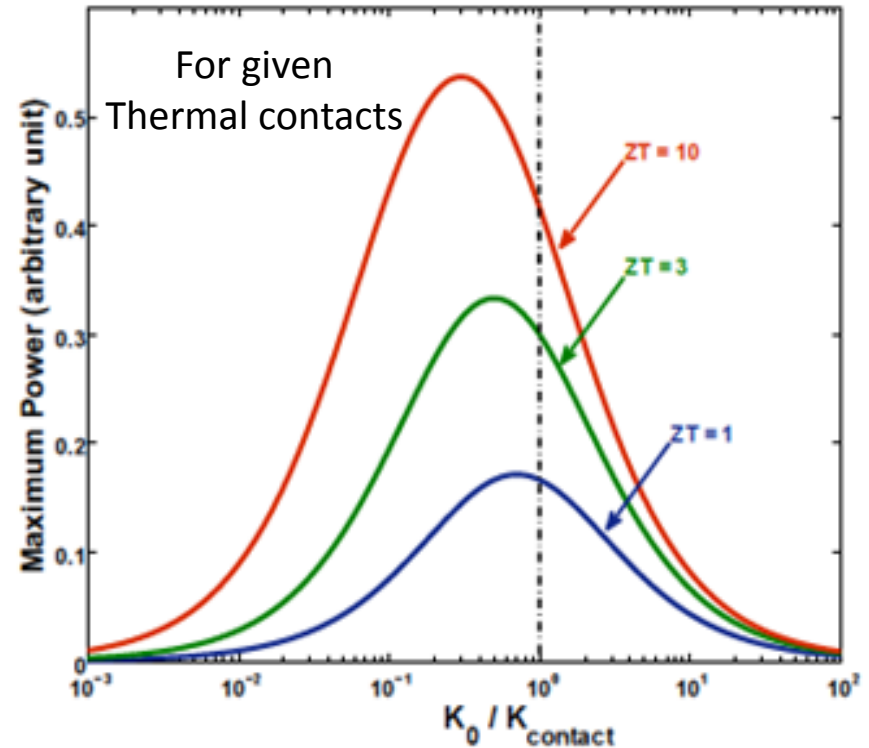
Electric adaptation

$$R_{\text{load}} = R_{\text{TEG}}$$

Thermal adaptation

$$K_{\text{contact}} = K_{\text{TEG}}.$$

$$\begin{cases} K_{\text{contact}} / K_0 = \sqrt{ZT + 1} \\ R_{\text{load}} / R = \sqrt{ZT + 1} \end{cases}$$



See also:

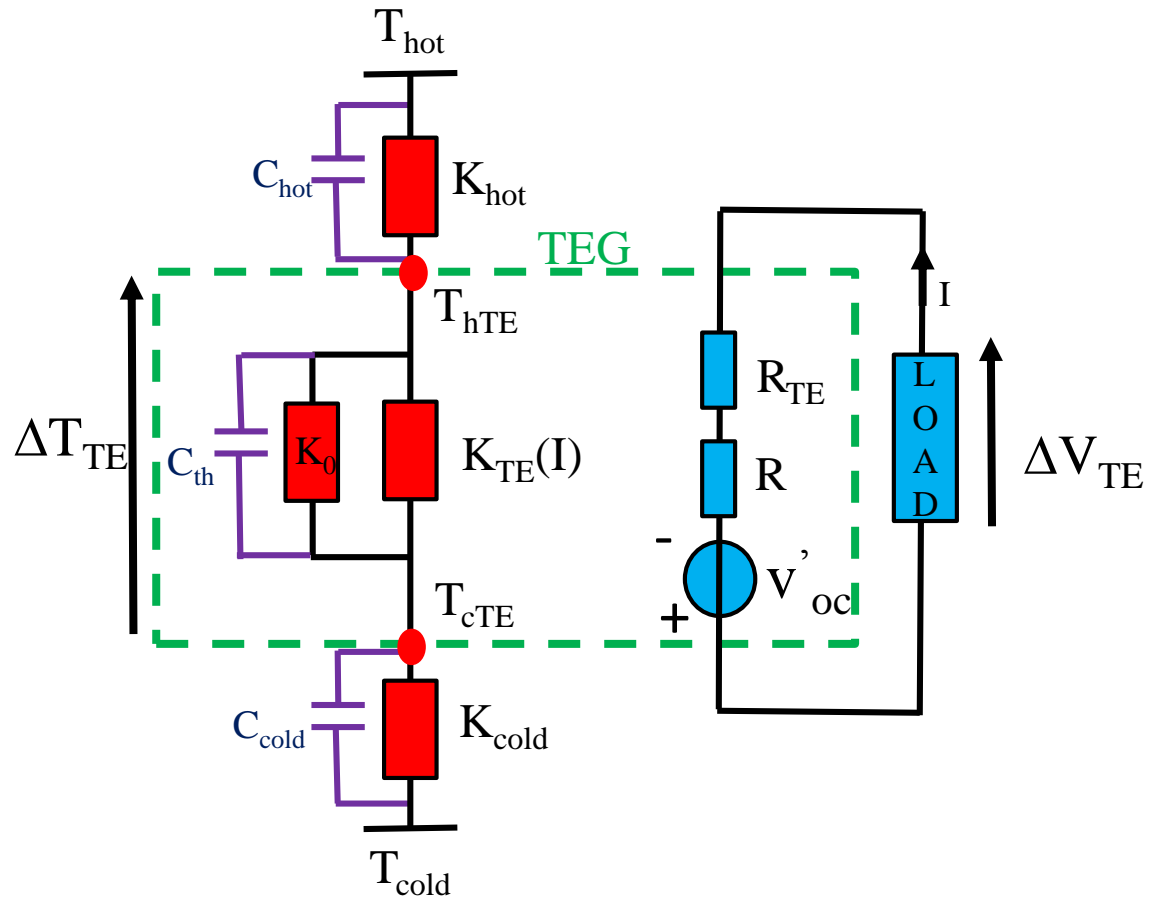
[M. Freunek et al., J. Elec. Mat. **38** \(2009\)](#)

[K. Yazawa et A. Shakouri, JAP **111** \(2012\)](#)

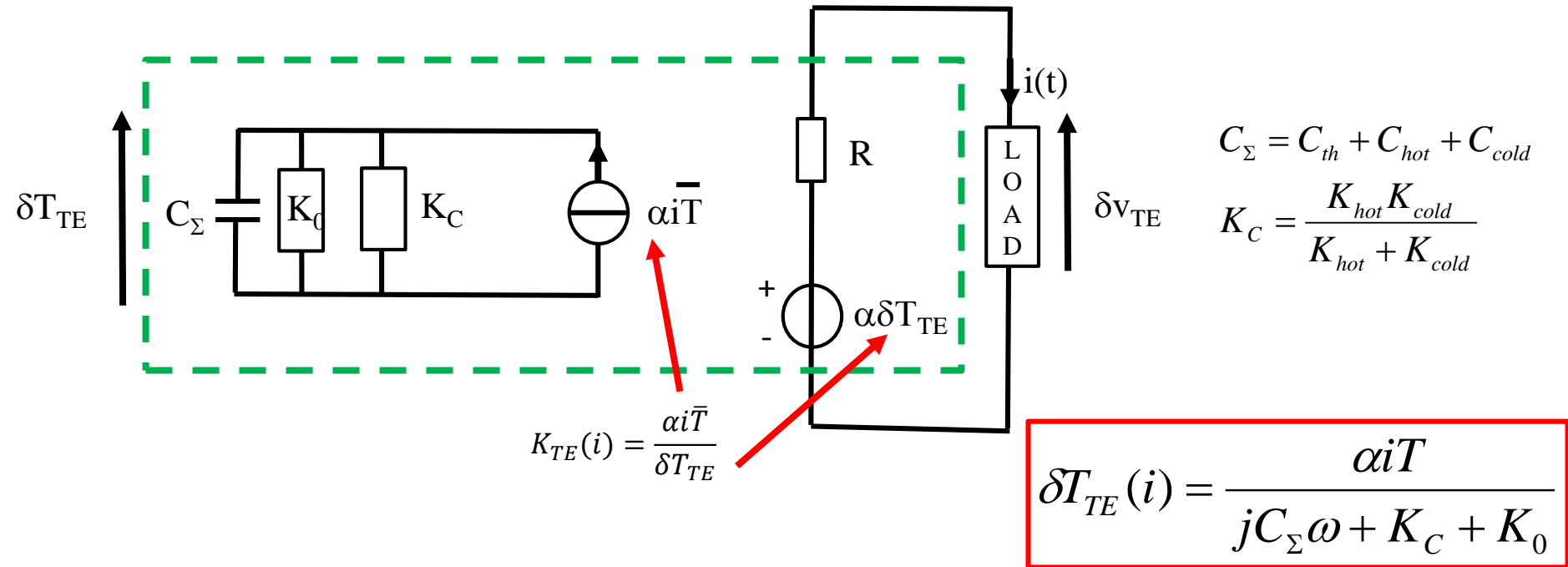
The thermal adaptation is fundamental
for correct working conditions!

[Y. Apertet, et al. EPL **97** \(2012\)](#)

1st order harmonic response



Small signal analysis



Small signal analysis

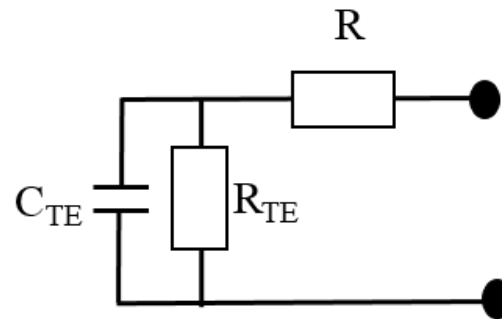
$$\alpha \delta T_{TE} = \frac{\alpha^2 i T}{j C_{Th} \omega + K_c + K_0} = \frac{i}{\frac{j C_{Th} \omega}{\alpha^2 T} + \frac{1}{R_{TE}}}$$

$$\frac{\alpha \delta T_{TE}}{i} = \frac{R_{TE}}{1 + j \omega \frac{C_{Th}}{\alpha^2 T} R_{TE}}$$

Total output impedance

$$Z(j\omega) = R + \frac{R_{TE}}{1 + j\omega\tau_{TE}}$$

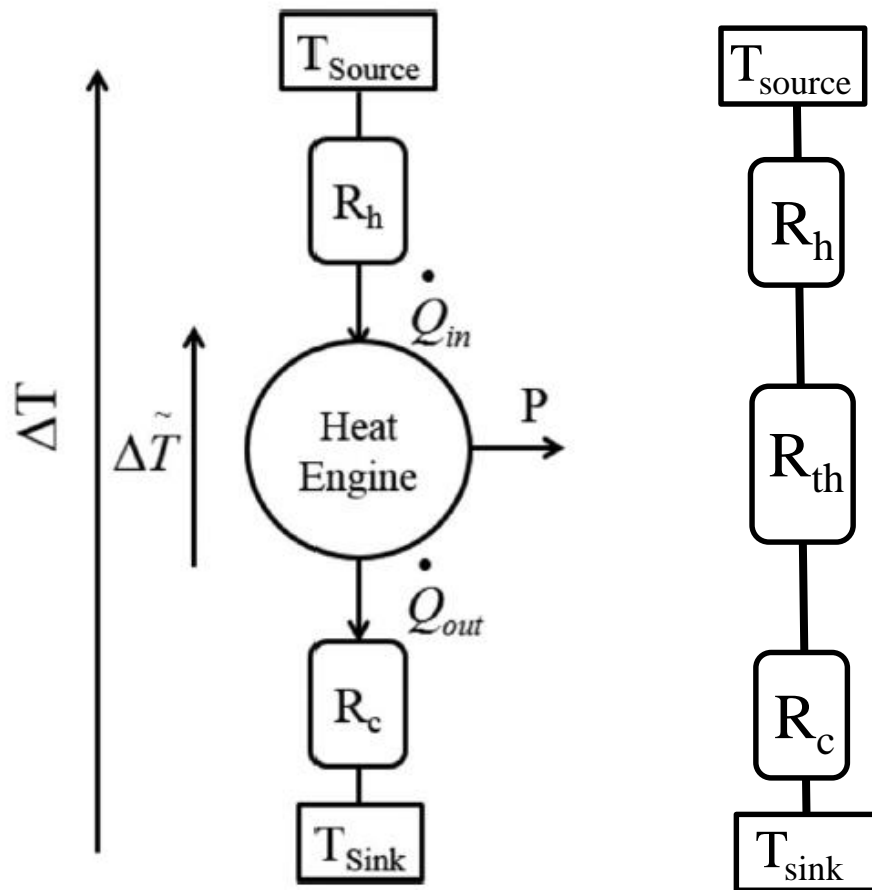
$$\left\{ \begin{array}{l} R_{TE} = \frac{\alpha^2 T}{K_c + K_0} \\ C_{TE} = \frac{C_\Sigma}{\alpha^2 T} \\ \tau_{TE} = R_{TE} C_{TE} \end{array} \right.$$



Maximal output power if impedance matching => Better @ non zero frequency?

Generalization: Closed loop

General system: non endoreversible



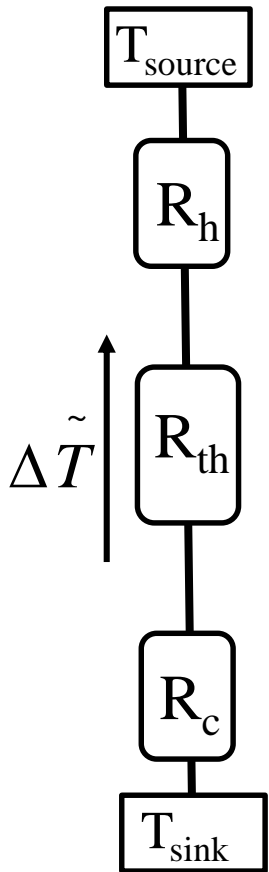
$$P \propto \left(\Delta \tilde{T} \right)^2$$

The system is mainly driven by its thermal boundary conditions which defines the feedback factors.

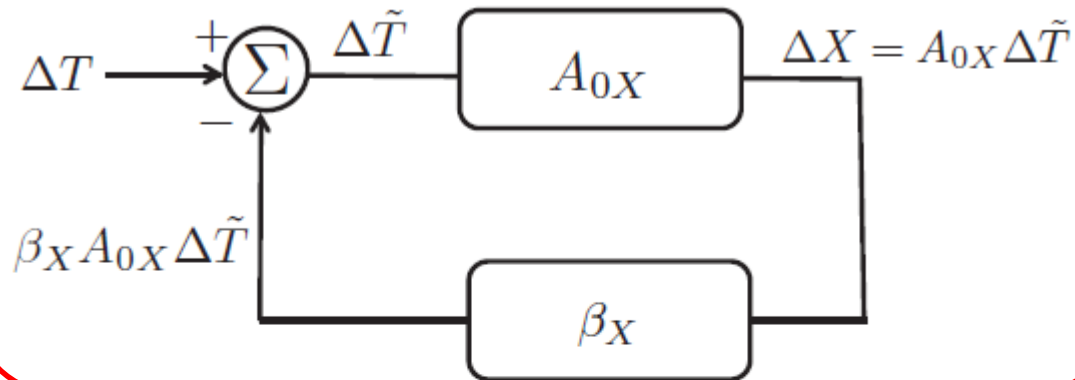
$$R_{th} = \frac{\Delta \tilde{T}}{\dot{Q}_{Avg}}$$

$$\Delta \tilde{T} = \Delta T R_{th} / (\tilde{R}_{th} + R_{\theta})$$

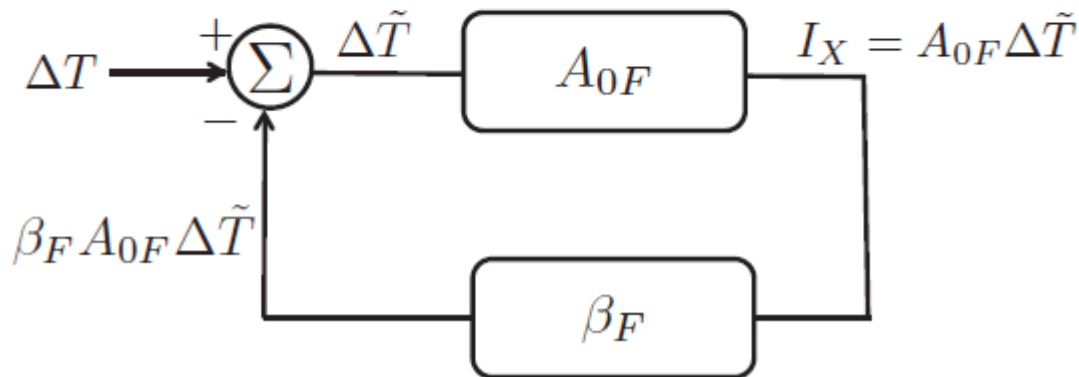
Feedback effects



temperature-potential feedback



temperature-flux feedback



$$A_{0X} = \Delta X / \Delta \tilde{T}.$$

$$A_{0F} = I_X / \Delta \tilde{T}.$$

$$\frac{\Delta \tilde{T}}{\Delta T} = \frac{1}{1 + A_0 \beta}$$

$$A_{CL} = \frac{A_0}{1 + A_0 \beta}$$

$$A_0 \beta = \frac{R_h + R_c}{R_{th}}$$

Working modes

Power $\Rightarrow P = \Delta X I_X = A_{0X} A_{0F} (\Delta \tilde{T})^2 = A_{0X} A_{0F} \left(\frac{\Delta T}{1 + A_0 \beta} \right)^2$

Efficiency $\Rightarrow \eta = \frac{P}{\dot{Q}_{\text{in}}} = \frac{A_{0X} A_{0F} \Delta T}{R_{\text{th}}} \left(\frac{1}{1 + A_0 \beta} \right)^3$

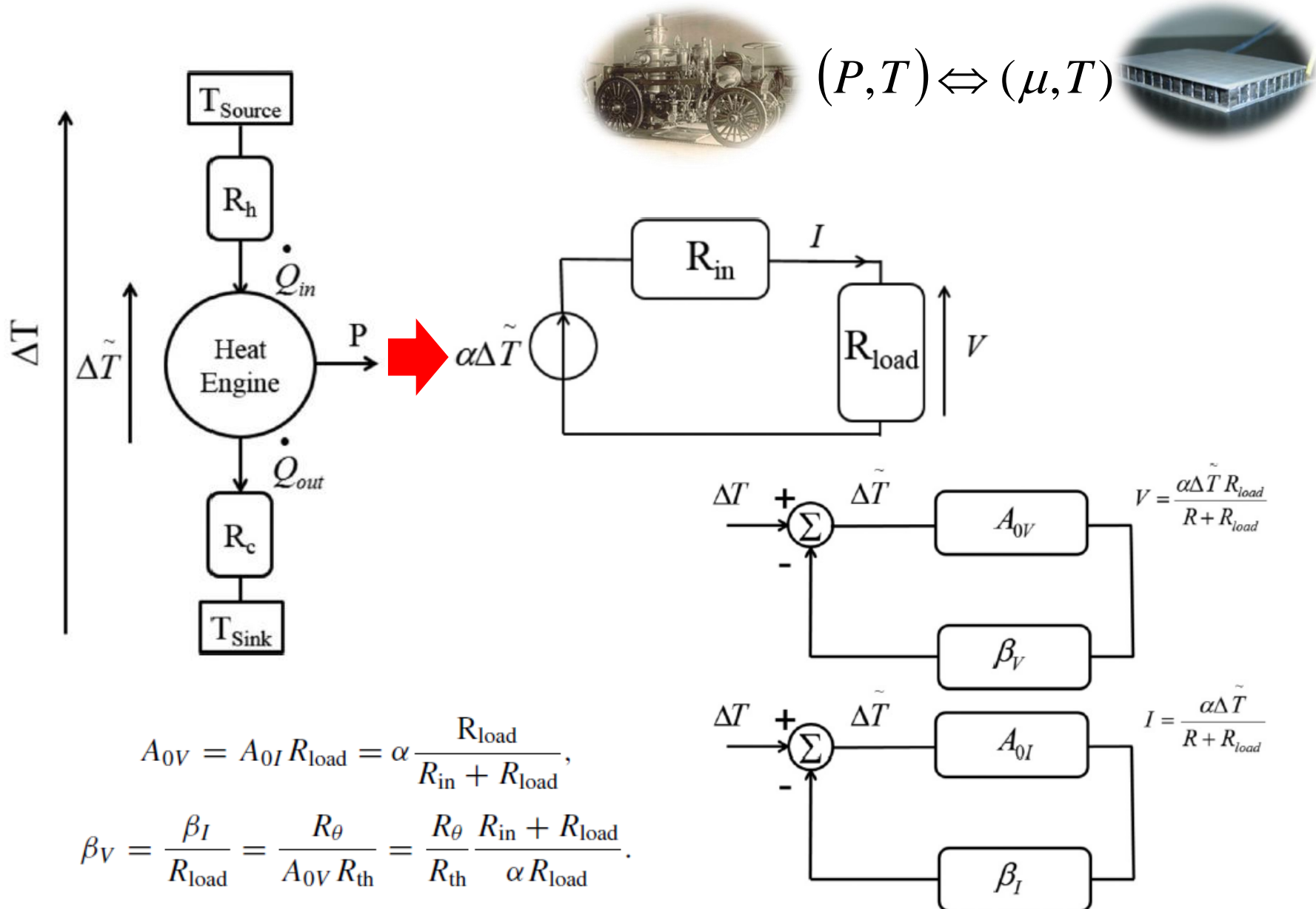
Conversion, feedback, and gain	A_{0X}	A_{0F}	β_X	β_F	A_{cl}
Zero load	A_{0X}^*	0	$\frac{R_\theta}{\alpha R_{\text{th}}}$	∞	$\frac{A_{0X}^*}{1 + \frac{R_\theta}{R_{\text{th}}}}$
Blocking load	0	$\frac{\alpha}{\beta_F^*} \frac{R_\theta}{R_{\text{th}}}$	∞	β_F^*	0

$$A_{CL} = \frac{A_0}{1 + A_0 \beta}$$

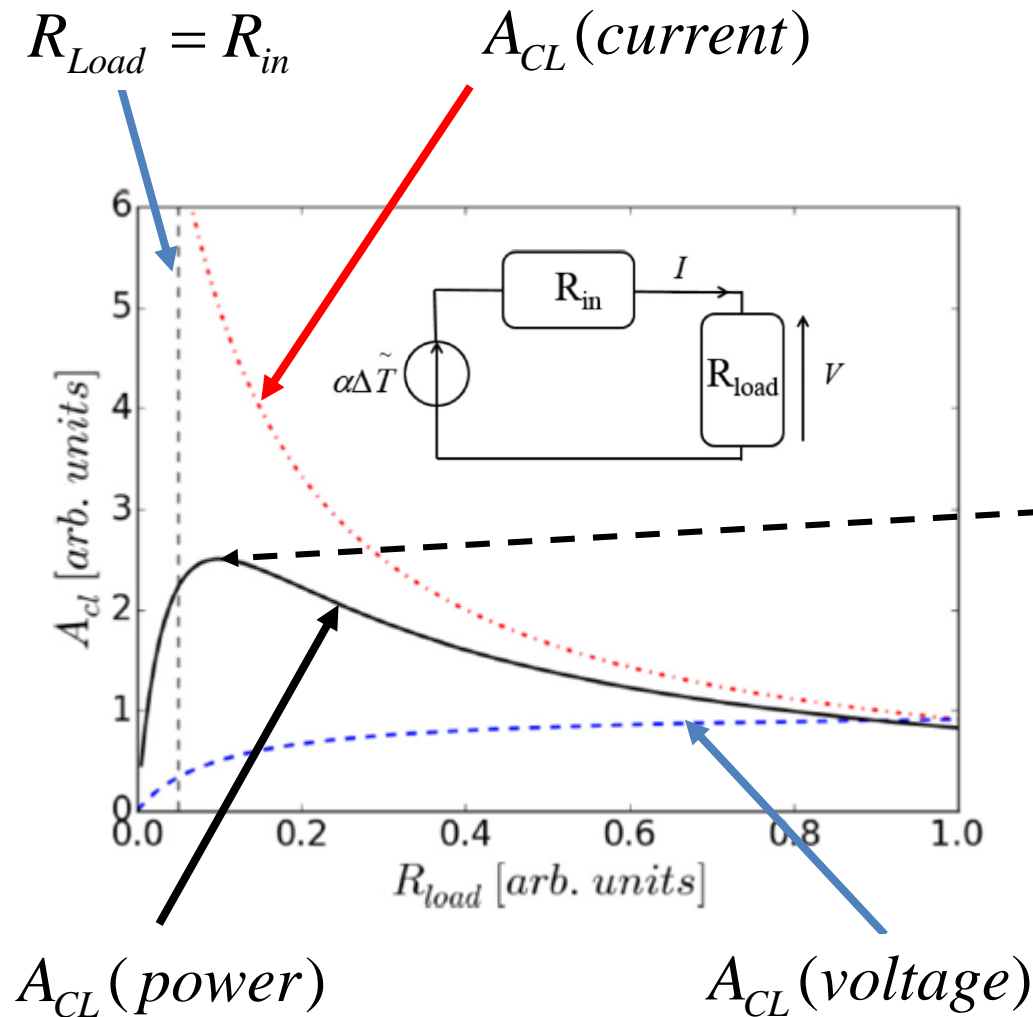


Possible oscillations of the system!

Application: Thermoelectricity



Application: Thermoelectricity



The maximal power is not obtained for

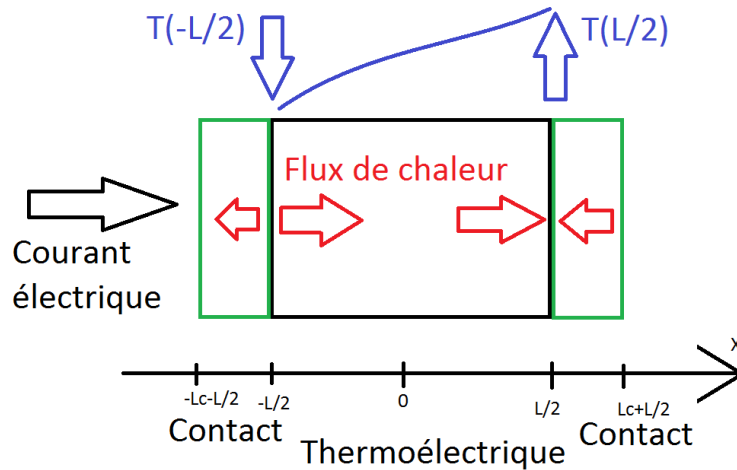
$$R_{Load} = R_{in}$$

But for

$$R_{load} = R_{in} + R_{TE}$$

Feedback

Experimental: Thermoelectricity

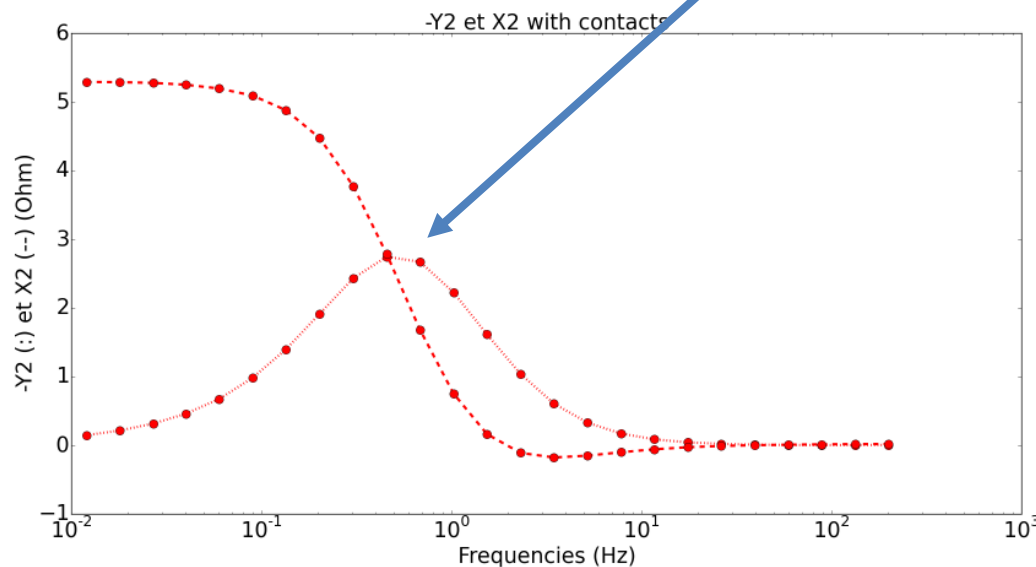


$$R_{TE} = \frac{\alpha^2 T}{K_C + K_0}$$

Extra dissipation

$$C_{TE} = \frac{C_\Sigma}{\alpha^2 T}$$

$$\tau_{TE} = R_{TE} C_{TE} \rightarrow T-\mu \text{ time constant}$$

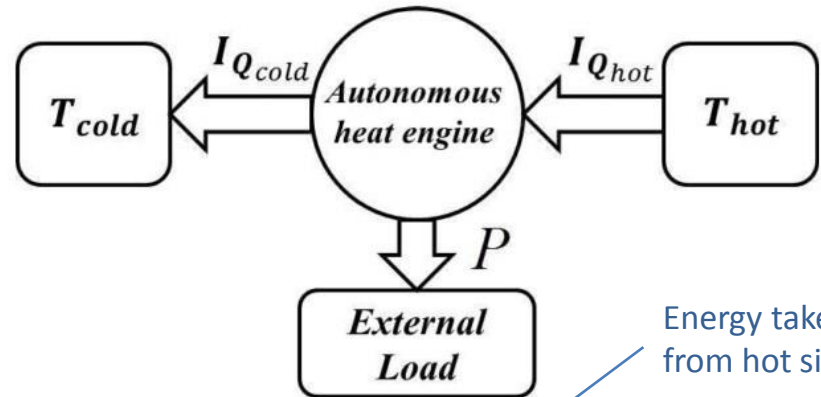
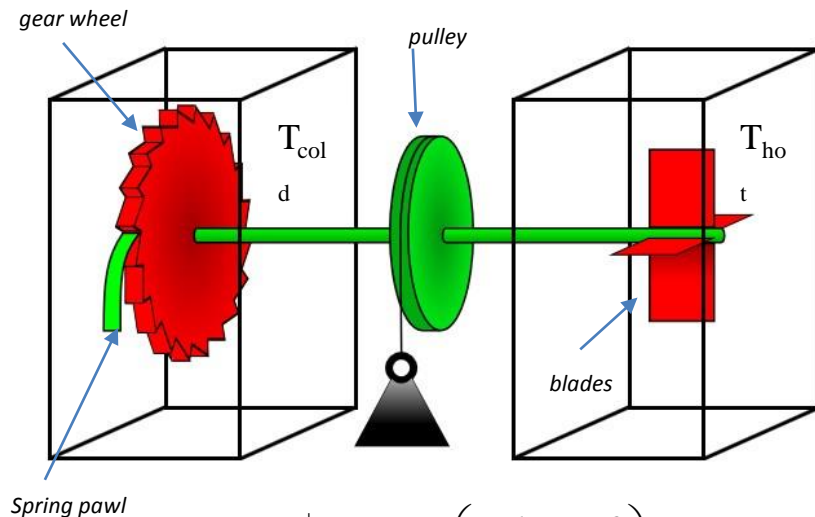


Experimental evidence of the Thermal to Electrochemical potential feedback coupling. (Etienne Thiebaut's PhD)

Ratchet approach

Feynman ratchet model

R.P. Feynman, R.B. Leighton, and M. Sands,
The Feynman Lectures on Physics I
Addison-Wesley, Reading, (1963), Chap. 46.



$$\dot{N}^+ = \nu \exp\left(-\frac{\xi + L\theta}{k_B T_{hot}}\right)$$

torque

$$\dot{N}^- = \nu \exp\left(-\frac{\xi}{k_B T_{cold}}\right)$$

spring energy

escape frequency

$$\dot{N}_{eff} = \dot{N}^+ - \dot{N}^-$$

effective « current »

$$I_{Q_{hot}} = (\xi + L\theta) \dot{N}_{eff}$$

$$I_{Q_{cold}} = \xi \dot{N}_{eff}$$

$$P = I_{Q_{hot}} - I_{Q_{cold}} = L\theta \dot{N}_{eff}$$

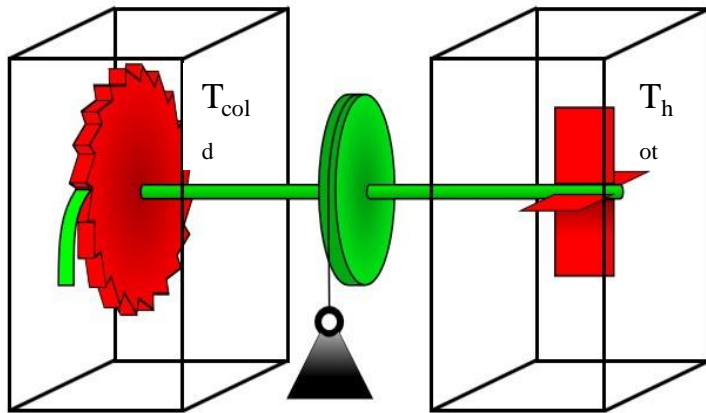
Energy taken from hot side

Energy delivered to the cold side

Strong coupling configuration

Velasco et al. J. Phys. D: Appl. Phys. 34 (2001) 1000–1006

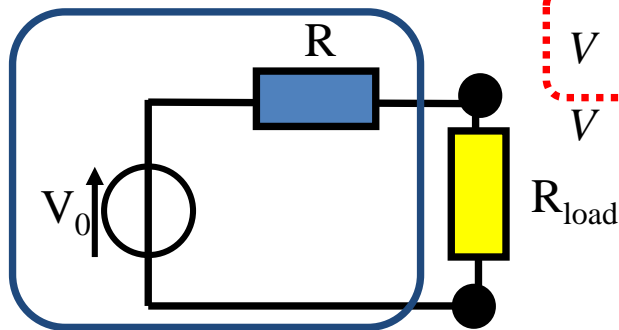
Linearization & thermoelectric model



$$\dot{N}^+ = v \left(1 - \frac{\xi + L\theta}{k_B T_{hot}} \right)$$

$$\dot{N}^- = v \left(1 - \frac{\xi}{k_B T_{cold}} \right)$$

$$\dot{N}_{eff} = \frac{v}{k_B T_{hot}} \left(\frac{\xi \Delta T}{T_{cold}} + L\theta \right) = \frac{v}{k_B T_{hot}} [L_0 \theta - L\theta]$$



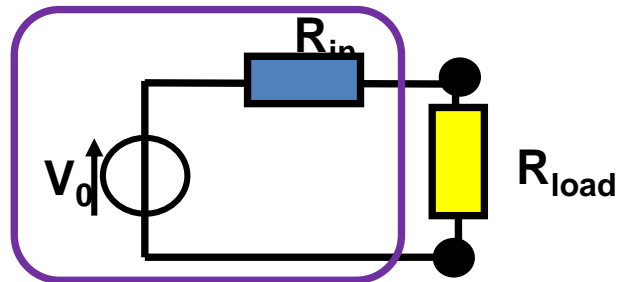
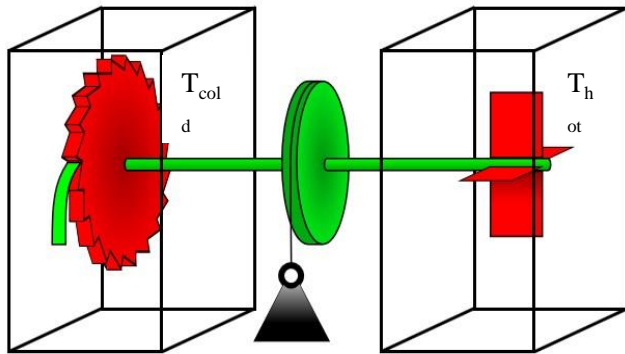
$$V = \alpha \Delta T - R I \iff L\theta = L_0 \theta - \frac{k_B T_{hot}}{v} \dot{N}_{eff}$$

$$V = R_{load} I$$

$$L_0 \theta = \frac{\xi \Delta T}{T_{cold}} : \text{stopping force (open voltage)}$$

$$L\theta = 0 : (\text{short circuit})$$

Power budget



$$I_{Q_{hot}} = (\xi + L\theta) \dot{N}_{eff} = \left(\frac{\xi}{T_{cold}} \right) T_{hot} \dot{N}_{eff} - \frac{k_B T_{hot}}{\nu} \dot{N}_{eff}^2$$

$$I_{Q_{cold}} = \left(\frac{\xi}{T_{cold}} \right) T_{cold} \dot{N}_{eff}$$

« entropy per tooth »
(Seebeck like: α_{FR})

$$I_{Q_{hot}} = \alpha T_{hot} I + K \Delta T - \frac{1}{2} R I^2$$

$$I_{Q_{cold}} = \alpha T_{cold} I + K \Delta T + \frac{1}{2} R I^2$$

dissipative
resistance

$$P = \left[\left(\frac{\xi}{T_{cold}} \right) \Delta T - \frac{k_B T_{hot}}{\nu} \dot{N}_{eff} \right] \dot{N}_{eff}$$

$$P = [\alpha \Delta T - R I] I$$

Apertet et al. PRE 2014

Extension to non-linear model

$$I_{Q_{hot}} = (\xi + L\theta) \dot{N}_{eff} = \alpha_{FR} T_{hot} \dot{N}_{eff} - [L_0\theta - L\theta] \dot{N}_{eff}$$

$$I_{Q_{cold}} = \left(\frac{\xi}{T_{cold}} \right) T_{cold} \dot{N}_{eff} = \alpha_{FR} T_{cold} \dot{N}_{eff}$$

$$P = L\theta \dot{N}_{eff} = \alpha_{FR} \Delta T \dot{N}_{eff} - \frac{[L_0\theta - L\theta] \dot{N}_{eff}^2}{\dot{N}_{eff}}$$

$$R_{dissip} = \frac{L_0\theta - L\theta}{\dot{N}_{eff}} = \frac{L_0\theta}{\dot{N}_{eff}} - R_{load}$$

$$R_{dyn} = \frac{k_B T_{hot}}{v}$$

In the non linear case the dissipative resistance and the linear resistance do not coincide.

Non-linear model & efficiency

Parameters :

- x : Force
- I : Flux

- $R_{\text{dyn}} = - \frac{dx}{dI}$
- $R_{\text{dissip}} = \frac{x_0 - x}{I}$
- γ : coefficient de répartition de la chaleur dissipée

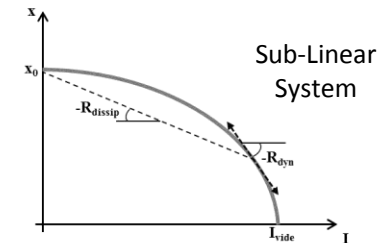
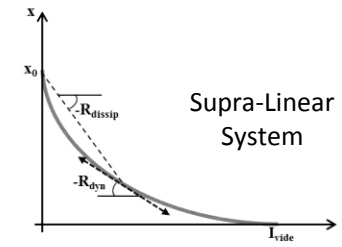
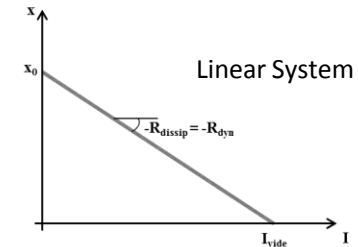
In a non linear system these parameters are functions of the working point!

Maximum power :

$$x_{\text{MP}} = x_0 \frac{R_{\text{dyn}}}{R_{\text{dyn}} + R_{\text{dissip}}}$$

Efficiency at maximum power :

$$\eta_{\text{MP}} = \frac{\eta_C}{\frac{R_{\text{dissip}}}{R_{\text{dyn}}} (1 - \gamma \eta_C) + 1}$$



Special thanks to

- Henni Ouerdane
- Yann Apertet
- Eric Herbert
- Yves d'Angelo
- Etienne Thiebaut
- Philippe Lecoœur



<http://www.dyco.fr>