Thermoelectric systems under various boundary conditions

ICTP Conference on Modern Concepts and New Materials for Thermoelectricity

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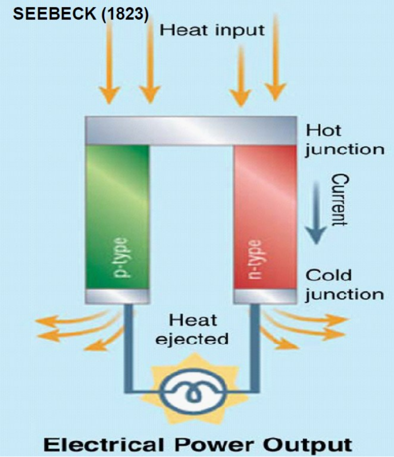
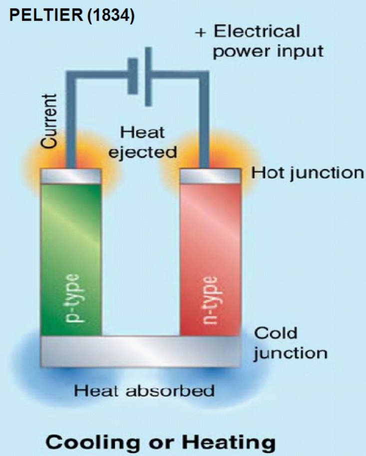
Outline

- Brief history
- Energy conversion
- Boundaries
- Entropy per carrier
- Thermostatic of the electron gas
- Onsager-Callen in a nutshell
- Thermoelectricity: beyond solid-state physics
- Mesoscopic Thermoelectricity: Landauer-Buttiker
- A fluid in a machine: boundaries again

Thermoelectricity



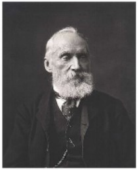


History

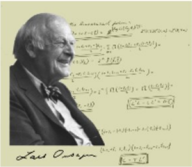
Alessandro Volta
18 February 1745 – 5 March 1827)

Thomas Johann Seebeck
(9 April 1770 - 10 December 1831)

Jean Charles Athanase Peltier
(February 22, 1785- October 27, 1845)



William Thomson, 1st Baron Kelvin
26 June 1824 - 17 December 1907

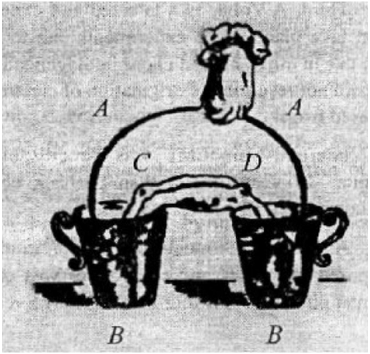


Lars Onsager
27 November , 1903 -- October 5, 1976

Herbert B. Callen
1 July 1919 – 22 March 1993

A. F. Ioffe
1880 – 1960

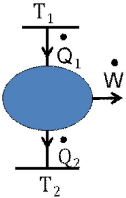
Seebeck and Volta

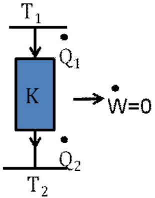


- 1794 — 1795: Letter to professor Antonio Maria Vassalli (accademia delle scienze di torino)

"... 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".

A fluid and a machine



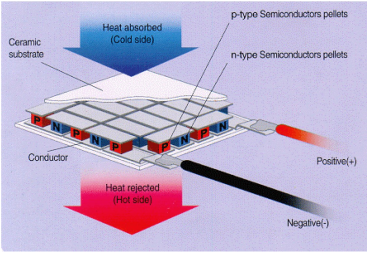


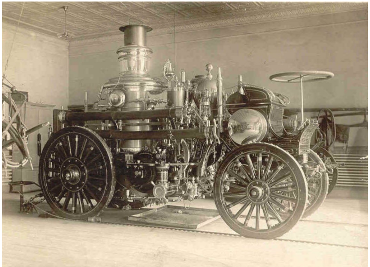
- $P = \dot{W} = \dot{Q}_1 - \dot{Q}_2$
- Reversible case : $\dot{S}_1 = \dot{S}_2 = \frac{\dot{Q}_1}{T_1} = \frac{\dot{Q}_2}{T_2} \Rightarrow \dot{W} = \dot{Q}_1 \left(1 - \frac{T_2}{T_1}\right)$.
- Irreversible case: $\dot{Q}_1 = \dot{Q}_2 \Rightarrow \dot{W} = \dot{Q}_1 - \dot{Q}_2 = 0$.
- Real system: Non conservation of heat and entropies.

$\Rightarrow$ **Good thermodynamic system = perfect transport of the entropy (no scattering, Strong coupling limit)**
$\Rightarrow$ **A good working fluid is a fluid that carries a huge amount of entropy. (cf phase transition required)**

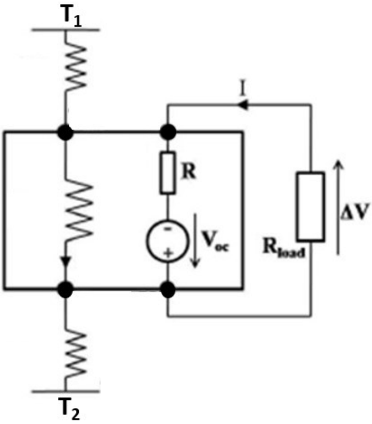
Corresponding thermodynamics

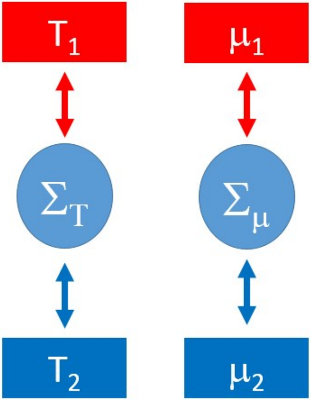
Classical gas	$P_{partial}$	T
Fermi gas	$\mu(T)$	T



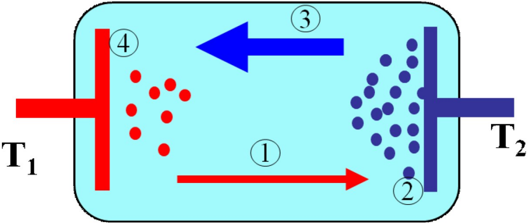


Boundaries





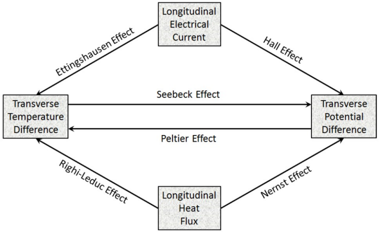
Basic Thermoelectric Cell



- $\Delta T = T_1 - T_2$.
- $dU = TdS + \mu dN + VedN = TdS + \widetilde{\mu}dN$
- $\Delta\widetilde{\mu} = f(\Delta T)$
- Seebeck coefficient: $\alpha = -\left(\frac{\Delta V}{\Delta T}\right)_{I=0} = \frac{1}{e}\left(\frac{\Delta\widetilde{\mu}}{\Delta T}\right)_{I=0}$
- Ideal processes: Isothermal for 2 et 4, and Isentropic for 1 and 3.
- $\Rightarrow$**The goal is clearly to optimize the transport of the entropy**

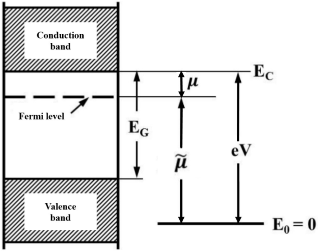
Zoology of the effects[1]

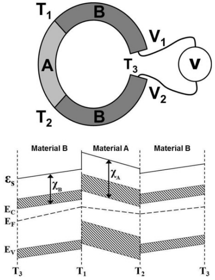
Name of the coefficient	Symbol	Definition	Conditions
Electrical conductivity	ϱ	$\frac{E_x}{j_x}$	$j_y = j_z = 0, \quad \nabla T = 0$
Thermal conductivity	κ	$-\dot{q}_x / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \quad \frac{\mathrm{d}T}{\mathrm{d}y} = \frac{\mathrm{d}T}{\mathrm{d}z} = 0$
Seebeck coefficient	α	$E_x / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \quad \frac{\mathrm{d}T}{\mathrm{d}y} = \frac{\mathrm{d}T}{\mathrm{d}z} = 0$
Peltier coefficient	Π	$\frac{\dot{q}_x}{j_x}$	$j_y = j_z = 0, \quad \nabla T = 0$
Hall coefficient	R_{H}	$\frac{E_y}{j_x B_z}$	$j_y = j_z = 0, \quad \nabla T = 0$
Nernst coefficient	$\mathcal{N}$	$\frac{E_y}{B_z} / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \quad \frac{\mathrm{d}T}{\mathrm{d}y} = \frac{\mathrm{d}T}{\mathrm{d}z} = 0$
Ettingshausen coefficient	P_{E}	$\frac{1}{j_x B_z} \frac{\mathrm{d}T}{\mathrm{d}y}$	$j_y = j_z = 0, \quad \nabla T = 0$
Righi-Leduc coefficient	S_{RL}	$\frac{1}{B_z} \frac{\mathrm{d}T}{\mathrm{d}y} / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \quad \frac{\mathrm{d}T}{\mathrm{d}z} = 0$



[1] Continuum Theory and modeling of Thermoelectric Elements, Edited by C. Goupil, Wiley 2016

Electrochemical potential



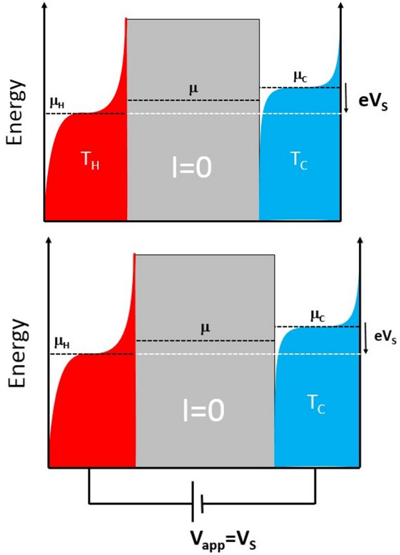


$$\tilde{\mu} = \mu + eV$$

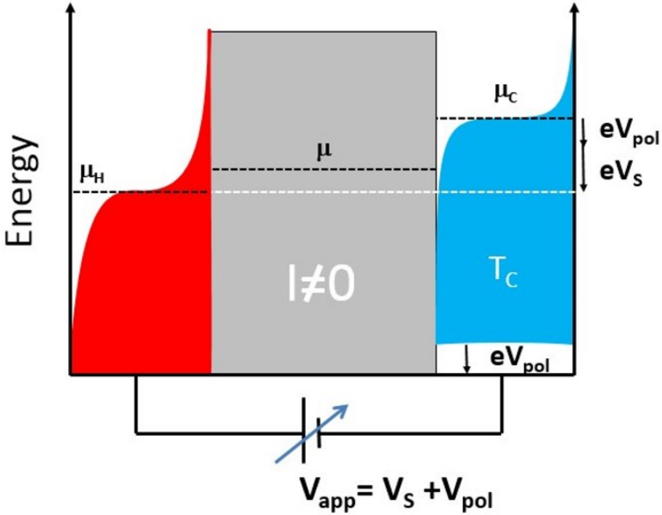
- μ : Chemical potential. (Fermi energy measured from the bottom of BC)
- Electrochemical[2] driving force: $\nabla\tilde{\mu}$
- Not important for metals but VERY important fro semiconductors or liquids!
- Insulating Gate polarization for motion of the Fermi level inside the Gap.

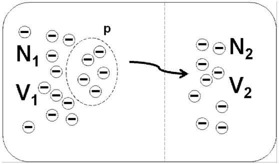
[2]see Apertet et al. (EPJ 2016)

Thermal Biasing: open circuit



Thermal Biasing: active load, non zero current





$$dS = k \ln\left(\frac{\Omega'}{\Omega}\right) = kp \ln\left(\frac{c_1}{c_2}\right)$$

$$S_N = k \ln\left(\frac{c_1}{c_2}\right)$$

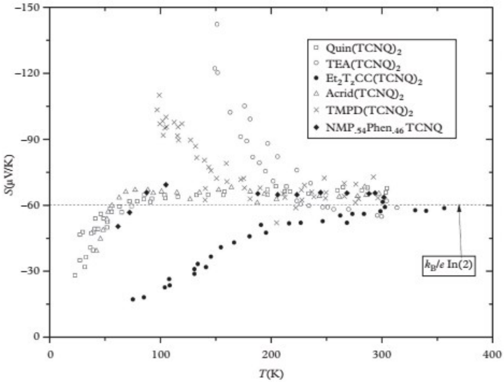
$\Rightarrow$Entropy per carrier, $\left(\frac{\partial S}{\partial N}\right)_T = -\left(\frac{\partial \widetilde{\mu}}{\partial T}\right)_N$

If hopping process then[3] $S_N = k \ln\left(\frac{c}{1-c}\right)$

[3] See Chaikin P. M. and Beni G. (1976) in: Kamran Behnia, Fundamentals of Thermoelectricity, (Oxford 2015).

[4] See presentation by V. P. Gusynin

Example: Organic Thermoelectricity[5]

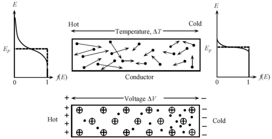


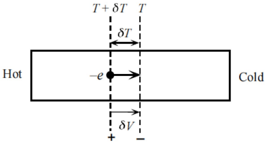
$$\alpha = \frac{S_N}{e} = -\frac{k}{e}\ln 2 \approx -59.8\mu V$$

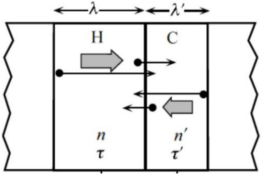
[5]Chaikin P. M., Kwak J. F., and Epstein A. J., Phys. Rev. Lett. 42, 117182 (1979). H. Conwell E. M. (1978), Phys. Rev. B 18, 18181823

Seebeck for metal

Sommerfeld expansion: $E_{F0} = \mu$: $E_F(T) = \frac{3}{5} E_{F0}(T) \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{E_{F0}} \right)^2 \right]$







$$e\delta V = E_{moy}(T + \delta T) - E_{moy}(T) \approx \frac{\pi^2 k^2 T}{2E_{F0}} \delta T$$

$$\alpha = -\frac{\delta V}{\delta T} = -\frac{\pi^2 k^2 T}{2eE_{F0}}$$

$$J = J_{H \to C} - J_{C \to H} = \frac{1}{2} \left[\frac{n_H \lambda_H}{\tau_H} - \frac{n_C \lambda_C}{\tau_C} \right]$$

- Mott et Jones correction: $\alpha \approx -\frac{\pi^2 k^2 T}{3eE_{F0}} \xi$

Coupling matrix

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

- Symetry due to Maxwell relation: $\left(\frac{\partial S}{\partial \widetilde{\mu}}\right)_T = \left(\frac{\partial N}{\partial T}\right)_{\widetilde{\mu}}$

$$\beta = \frac{1}{N}\left(\frac{\partial N}{\partial T}\right)_{\widetilde{\mu}}$$

$$\chi_T = \frac{1}{N}\left(\frac{\partial N}{\partial \widetilde{\mu}}\right)_T$$

$$C_{\widetilde{\mu}} = C_N + \frac{\beta^2 T}{\chi_T} = C_N\left(1 + \frac{\beta^2}{\chi_T C_N} T\right)$$

$$\begin{pmatrix} dN \\ dS \end{pmatrix} = N \begin{pmatrix} \chi_T & \beta \\ \beta & \frac{C_{\widetilde{\mu}}}{T} \end{pmatrix} \begin{pmatrix} d\widetilde{\mu} \\ dT \end{pmatrix}$$

State Equation and coupling terms

- Internal energy[6]: $U = \frac{3}{2}NkT$
- State equation: $N = 2V\left(\frac{2\pi m_c^* k_B}{h^2}\right)^{\frac{3}{2}} T^{3/2} \exp\frac{\mu}{kT}$
- $\beta = \frac{\alpha e}{N}\left(\frac{\partial N}{\partial \widetilde{\mu}}\right)_T = S_N \frac{1}{N}\left(\frac{\partial N}{\partial \widetilde{\mu}}\right)_T = S_N \chi_T$
  - $\left(\frac{\partial N}{\partial \widetilde{\mu}}\right)_T = \frac{N}{kT}$ and $\left(\frac{\partial N}{\partial T}\right)_{\widetilde{\mu}} = \frac{N}{T}\left(\frac{3}{2} - \frac{\mu}{kT}\right)$
  - $\left(\frac{\partial \mu}{\partial T}\right)_N = \frac{\mu}{T} - \frac{3}{2}k = -S_N \Rightarrow \alpha = \frac{S_N}{e} = \frac{k}{e}\left(\frac{\mu}{kT} - \frac{3}{2}\right)$
  - $\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_N + \frac{\left(\frac{\partial N}{\partial T}\right)_{\widetilde{\mu}}^2}{\left(\frac{\partial N}{\partial \widetilde{\mu}}\right)_T} = \frac{N}{kT}k^2\left[\frac{3}{2} + \left(\frac{3}{2} - \frac{\mu}{kT}\right)^2\right]$

So,

$$\begin{pmatrix} dN \\ dS \end{pmatrix} = \frac{N}{kT}\begin{pmatrix} 1 & k\left(\frac{3}{2} - \frac{\mu}{kT}\right) \\ k\left(\frac{3}{2} - \frac{\mu}{kT}\right) & k^2\left(\frac{3}{2} + \left(\frac{3}{2} - \frac{\mu}{kT}\right)^2\right) \end{pmatrix}\begin{pmatrix} d\widetilde{\mu} \\ dT \end{pmatrix}$$

[6] See also D. K. C. MacDonald, Thermoelectricity, An introduction to the principles. (Dover 1962)

Onsager in a nutshell

$$\mathbf{F}_N = \nabla(-\frac{\widetilde{\mu}}{T})$$

$$\mathbf{F}_E = \nabla(\frac{1}{T})$$

so,

$$\begin{pmatrix} \mathbf{J}_N \\ \mathbf{J}_E \end{pmatrix} = \begin{pmatrix} L_{NN} & L_{NE} \\ L_{EN} & L_{EE} \end{pmatrix} \begin{pmatrix} \nabla(-\frac{\widetilde{\mu}}{T}) \\ \nabla(\frac{1}{T}) \end{pmatrix}$$

$$\mathbf{J}_U = \mathbf{J}_Q + \widetilde{\mu}\mathbf{J}_N$$

$$\begin{pmatrix} \mathbf{J}_N \\ \mathbf{J}_Q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} -\frac{1}{T}\nabla(\widetilde{\mu}) \\ \nabla(\frac{1}{T}) \end{pmatrix}$$

with $L_{12} = L_{21}$
$L_{11} = L_{NN}$
$L_{12} = L_{NE} - \mu L_{NN}$
$L_{22} = L_{EE} - 2\mu L_{EN} + \mu^2 L_{NN}$

Thermoelectricity in a nutshell

- Isothermal electrical conduction (Ohm's law): $\sigma_T = \frac{e^2}{T} L_{11}$
- Thermal conductivity (Fourier's law): $\kappa_J = \frac{1}{T^2}\left[\frac{L_{11}L_{22} - L_{21}L_{12}}{L_{11}}\right]$
- Thermal convection :$\kappa_E = \frac{L_{22}}{T^2}$
- Seebeck coefficient: $\alpha = \frac{1}{eT}\frac{L_{12}}{L_{11}}$
- Figure of Merit: $ZT = \frac{\alpha^2 \sigma_T}{\kappa_J} T$

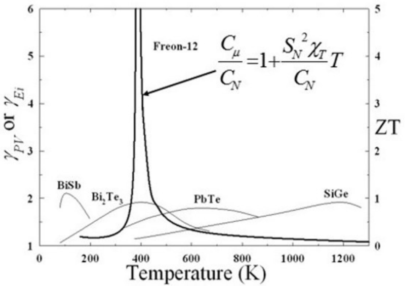
$$\kappa_E = \kappa_J \left[1 + \frac{\alpha^2 \sigma_T}{\kappa_J} T\right]$$

And[7]

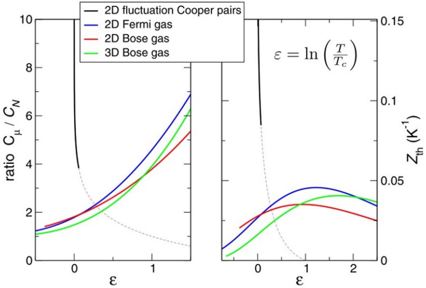
$$C_\mu = C_N \left[1 + \frac{\beta^2}{\chi_T C_N} T\right]$$

[7] See Cronin B. Vining. The thermoelectric process, Materials Research Society Symposium 32, pages 3–13. Mater. Res. Soc., 1997.

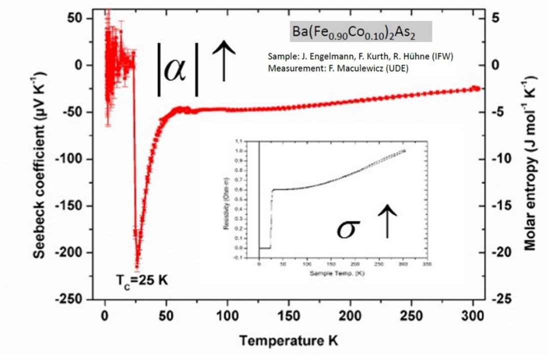
Electronic phase transition

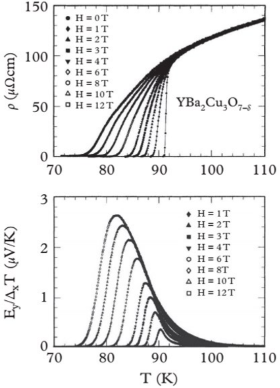


Cronin B. Vining. The thermoelectric process
MRS Symposium 32, pages 3-13 (1997)



H. Ouerdane et al. , Phys. Rev. B 91, 100501(R) (2015)



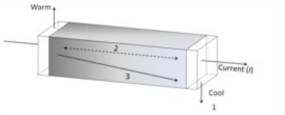


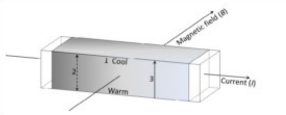
Ri H.-C., Gross R., Gollnik F., Beck A., and Huebener R. P. (1994). Phys. Rev. B 50, 3312–3330. (after Behnia, Kamran. Fundamentals of Thermoelectricity (2015 Oxford)

Observed for both Seebeck and Nernst signals.

[8] See presentation by A. Glatz

ZTs[9]





Thermoelectric figure of merit			**Thermomagnetic figure of merit**	
$Z_{\mathrm{TE}} = \frac{\alpha^2}{\varrho\,\kappa}$			$Z_{\mathrm{TM}} = \frac{\mathcal{N}^2\,B^2}{\varrho_{\mathrm{L}}\,\kappa_{\mathrm{T}}}$	
Effect	Requirements	No.	Effect	Requirements
Thermoelectric cooling (Peltier effect)	Large Seebeck coefficient (α)	1	Thermomagnetic cooling (Ettingshausen effect)	Large thermo-magnetic coefficients ($\mathcal{N}$) Large magnetic field (B)
Joule heating	Low resistivity (ϱ)	2	Joule heating	Low longitudinal resistivity (ϱ_{L})
Heat conduction	Low thermal conductivity (κ)	3	Heat conduction	Low transverse thermal conductivity (κ_{T})

9 Continuum Theory and modeling of Thermoelectric Elements, Edited by C. Goupil, Wiley 2016

Wiedemann-Franz law

$$\frac{\kappa_J}{T\sigma_T} = \frac{\frac{L_{11}L_{22}-L_{12}^2}{T^2L_{11}}}{e^2L_{11}} = \frac{L_{22}}{e^2L_{11}T^2}\left[1-\frac{L_{12}^2}{L_{11}L_{22}}\right] = \frac{L_{22}}{e^2L_{11}T^2}\left[1-\frac{L_{12}}{L_{22}}TS_N\right]$$

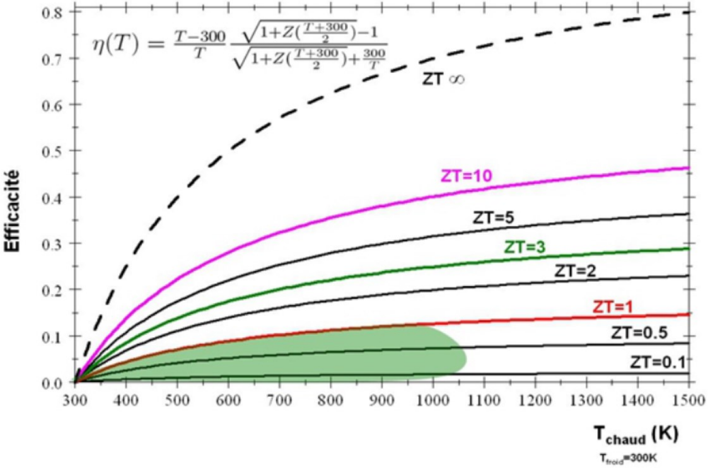
- If $\frac{L_{12}}{L_{22}}TS_N$ small then,

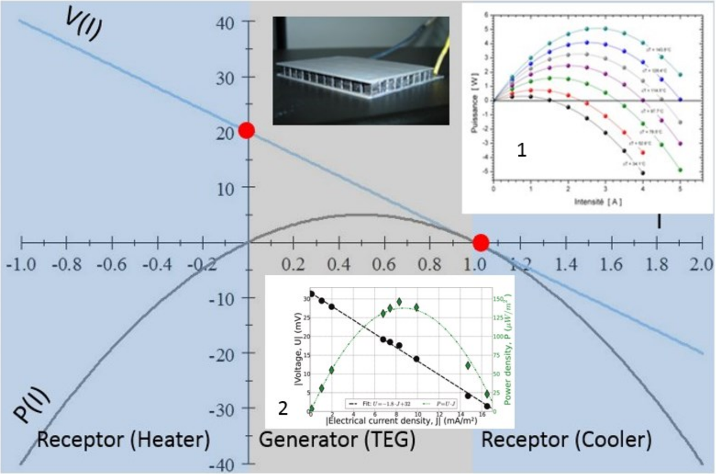
$$\frac{\kappa_J}{T\sigma_T} \approx L_0 = \frac{\kappa_E}{T\sigma_T}$$

- Note that this correspond to a zero figure of merit!
- Lorentz factor: $L_0 = \frac{L_{22}}{e^2L_{11}T^2} = \frac{\kappa_E}{\sigma_T}T$
- Metal approximation: $L_0 = \frac{\pi^2k^2}{3e^2} = 2,45.10^{-8}(V/K)^2$
- Lorentz gas[10] approximation: $L_0 \approx \left(\frac{5}{2}+s\right)\frac{k^2}{e^2}$

[10] $\tau(E) \propto E^s$

Efficiency of of thermogenerator



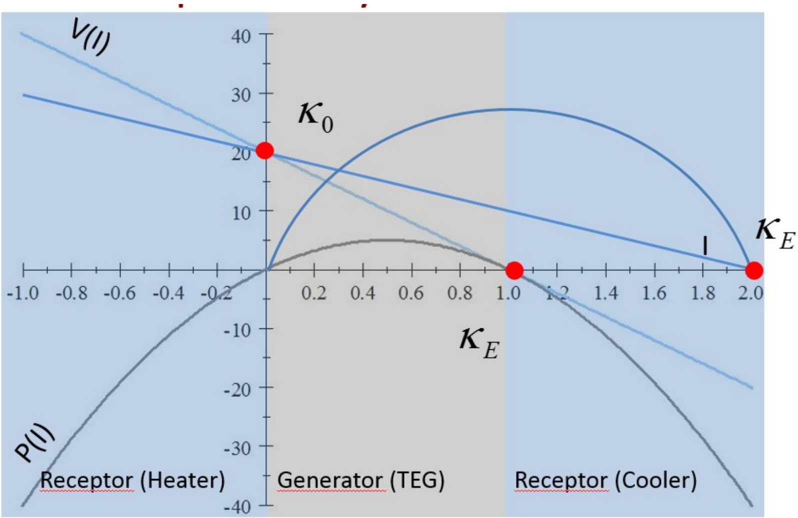


1) Goupil et al., Renault-Valeo Renoter project, 2012

2) Salez et al., Phys. Chem. Chem. Phys., 2017, 19,9409

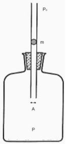
$$\kappa_E = \kappa_J \left[1 + ZT\right]$$

Power and ZT



$$\kappa_E = \kappa_J \left[1 + ZT\right]$$

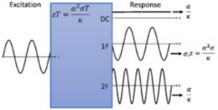
Impedance spectroscopy [11]

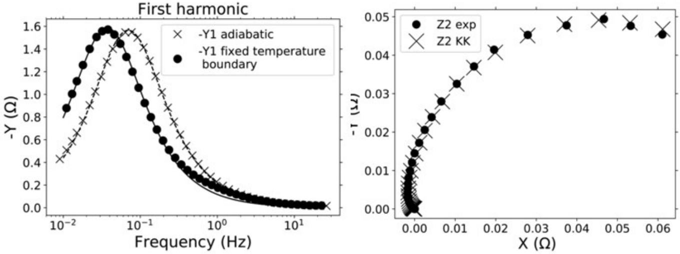
Historical Ruchardt experiment:  $\omega = \sqrt{\frac{\gamma P A^2}{mV}}$

Non-linear impedance spectroscopy for complete thermoelectric characterization: Beyond the zT estimation

Journal of Applied Physics 124, 235106 (2018); https://doi.org/10.1063/1.5063419

E. Thiébaut, F. Pesty, C. Goupil, G. Guegan, and P. Lecoeur





[11] see presentation by J. Garcia Canadas

Kinetic Integrals

- Electrical current: $J = \int_0^\infty e v_\mathrm{e}(E)\left[f(E) - f_0(E)\right] g(E)\mathrm{d}E$
- Total energy: $J_E = \int_0^\infty \epsilon v(E)\left[f(E) - f_0(E)\right] g(E)\mathrm{d}E$
- Heat: $J_Q = J_E - \frac{E_\mathrm{F}}{e} J = \int_0^\infty (E - E_\mathrm{F}) v(E)\left[f(E) - f_0(E)\right] g(E)\mathrm{d}E$

$$f(E) - f_0(E) = \tau(E)v(E)\frac{\partial f_0}{\partial E}\left[\nabla\widetilde{\mu} + \frac{E - \widetilde{\mu}}{T}\nabla T\right]$$

- $L_{11} = T\int_0^\infty \Sigma(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E$
- $L_{12} = L_{21} = T\int_0^\infty (E - E_\mathrm{F})\Sigma(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E$
- $L_{22} = T\int_0^\infty (E - E_\mathrm{F})^2\Sigma(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E$
- $\Sigma(E) = \tau(E)v^2(E)(E)$.

General expressions

$$\int_0^{\infty} (E - E_{\mathrm{F}})^n \Sigma(E) \left(-\frac{\partial f_0}{\partial E}\right) \mathrm{d}E \equiv K_n$$

$$\begin{aligned}
\sigma_T &= \frac{e^2 L_{11}}{T} = e^2 K_0 \\
S_N &= \frac{1}{T}\,\frac{L_{12}}{L_{11}} = \frac{1}{T}\,\frac{K_1}{K_0} \\
\alpha &= \frac{S_N}{e} = \frac{1}{eT}\,\frac{K_1}{K_0} \\
\kappa_J &= \frac{Det\,[\mathcal{L}]}{T^2 L_{11}} = \frac{1}{T}\,\left(K_2 - \frac{K_1^2}{K_0}\right) \\
\kappa_E &= \frac{L_{22}}{T^2} = \frac{K_2}{T}
\end{aligned} \tag{1}$$

Simple metals

- $\sigma_T = e^2 K_0 = e^2 \Sigma(E_F) = e^2 \frac{n}{m^*} \tau$
- $\alpha = \frac{1}{eT} \frac{K_1}{K_0} = \frac{\pi^2 k^2 T}{3e} \left[\frac{1}{\Sigma(E)} \frac{d}{dE} \Sigma(E) \right]_{E=E_F} = \frac{\pi^2 k^2 T}{3e} \frac{d \ln(\Sigma(E))}{dE} |_{E=E_F} = \frac{\pi^2 k^2 T}{2eE_F}$
- $\kappa_E = \frac{K_2}{T} = \frac{\pi^2 k^2 T}{3} \Sigma(E_F) = \frac{\pi^2 k^2 T}{3e^2} \sigma_T$
- $\kappa_J = \frac{K_2}{T} \left[1 - \frac{K_1^2}{K_2 K_0} \right] = \kappa_{E=0} \left[1 - \frac{\pi^2 k^2 T^2}{3} \left(\frac{d \ln(\Sigma(E))}{dE} |_{E=E_F} \right)^2 \right]$
- $ZT = \frac{1}{\left[1 - \frac{\pi^2 k^2 T^2}{3} \left(\frac{d \ln(\Sigma(E))}{dE} |_{E=E_F} \right)^2 \right]} - 1$
- The metal case gives $E_F >> kT$ so α becomes negligible.

Semiconductors: Lorentz gas

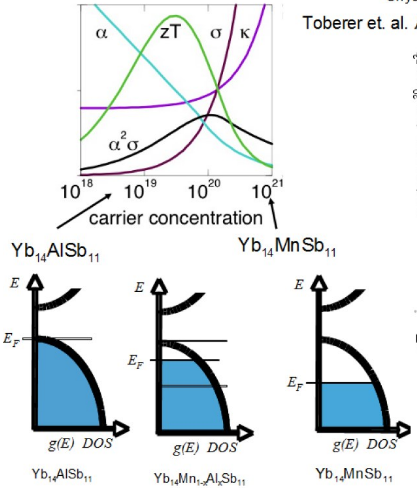
Firstly proposed by Lorentz for the metals, which is not adequate, but suitable for non-degenerated semiconductors with scattering by impurities.

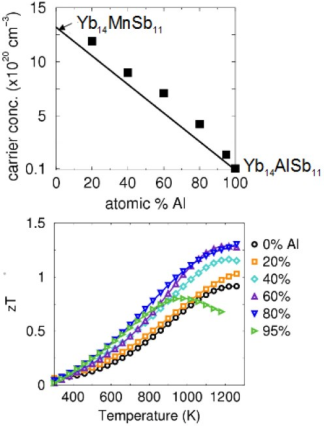
- $\sigma_T = \frac{e^2 n\tau_0}{m}$
- $\alpha = \frac{1}{eT}\frac{L_{12}}{eL_{11}} = \frac{5}{2e}k - \frac{\mu}{eT}$
- $\kappa_E = \frac{L_{22}}{T^2} = \frac{n\tau_0}{mT}\left[\frac{35}{4}k^2T^2 - 5\mu kT + \mu^2\right]$
- $\kappa_J = \frac{L_{22}}{T^2}\left[1 - \frac{L_{12}^2}{L_{11}L_{22}}\right] = \frac{5}{2}\frac{n\tau_0}{m}k^2T$

Example of optimization: DOS engineering in Zintl phase

Snyder, *Nature Materials* **7**, 105 (2008)

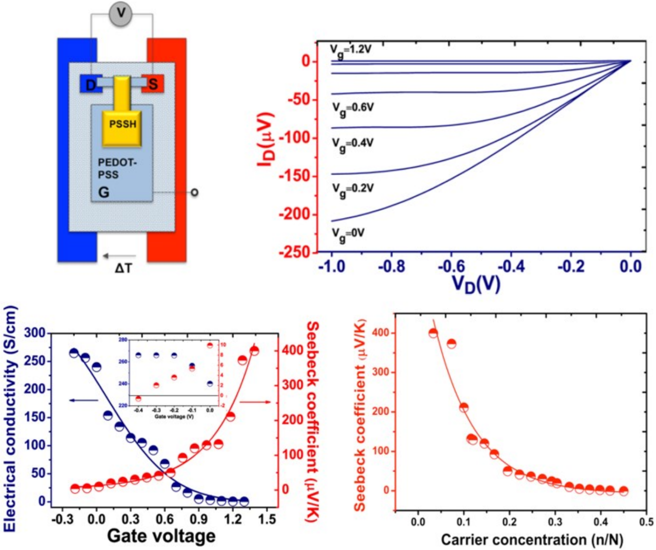
Toberer et. al. ***Adv. Functional Mater.***, (2008)





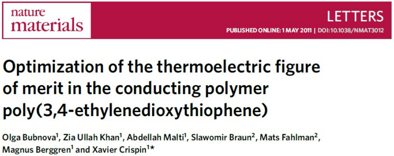
Next generation RTG

Tuning the Thermoelectric Properties: Organic example[12]



[12] O. Bubnova, M. Berggren, and Xavier Crispin, J. Am. Chem. Soc., 2012, 134 (40)

Organic thermoelectricity[13]

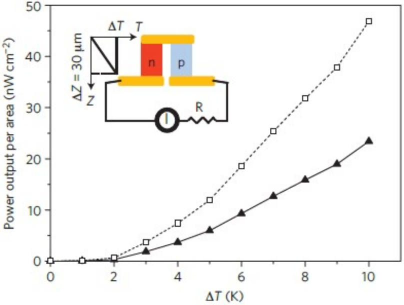


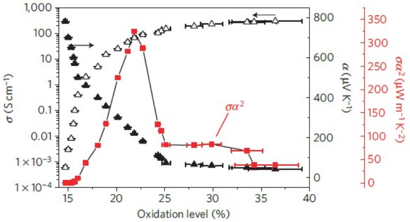
nature materials | LETTERS

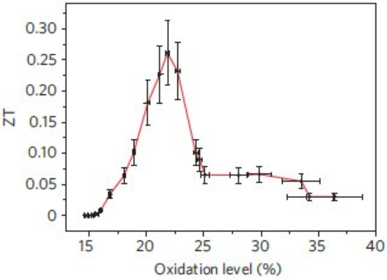
PUBLISHED ONLINE: 1 MAY 2011 | DOI:10.1038/NMAT3012

Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene)

Olga Bubnova[1], Zia Ullah Khan[1], Abdellah Malti[1], Slawomir Braun[2], Mats Fahlman[2], Magnus Berggren[1] and Xavier Crispin[1*]

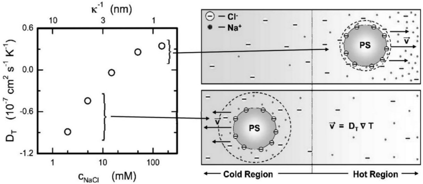




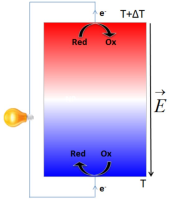


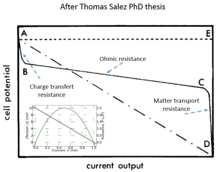
[13] See the presentations by X. Crispin,

Ionic liquids[14] and colloids[15]



S. A. Putnam and David G. Cahill, Langmuir, 2005, 21 (12), pp 5317–5323





- $\mathbf{J}_i = -D_i \left(\nabla n_i + \frac{n_i}{kT} \left[\frac{Q_i}{T} \nabla T - q_i \mathbf{E}_0 \right] \right)$
- $S_{Ni} = \frac{Q_i}{T} = 2k\alpha_i$ and $\alpha = \sum_i \alpha_i \frac{n_i}{n_0}$
- Stationary state: $\frac{\nabla n_0}{n_0} = -\alpha \frac{\nabla T}{T}$
- Then, $\mathbf{E}_0 = -\frac{\nabla \tilde{\mu}}{e} = \gamma \frac{kT}{e} \frac{\nabla n_0}{n_0} = -\alpha\gamma \frac{k}{e} \nabla T \Longrightarrow S_N = \frac{2}{\gamma} \frac{\nabla \tilde{\mu}}{\nabla T}$

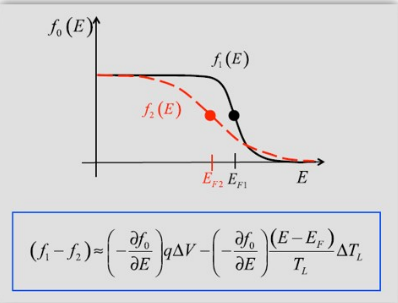
[14] after Alois Würger 2010 Rep. Prog. Phys. 73 126601

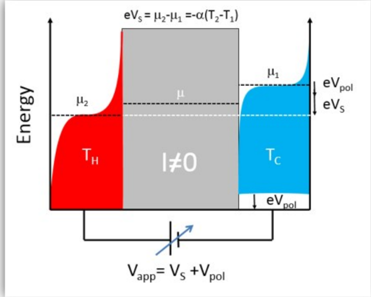
[15] See the presentations by A. Würger, S. Wiegand, R. Perzynski, H. Keppner, V. Shikin, M. Bobrowski, K. Battacharya and M. Vasilakaki

Mesoscopic thermoelectricity [16]

(Molemkamp 1990, Van Houten 1992) (after Lundstrom et al)

$$\boxed{I = \frac{2e}{h}\int T(E)M(E)\left(f_C - f_H\right)}$$

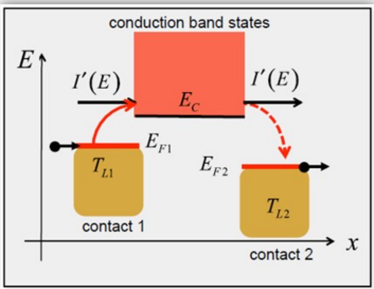


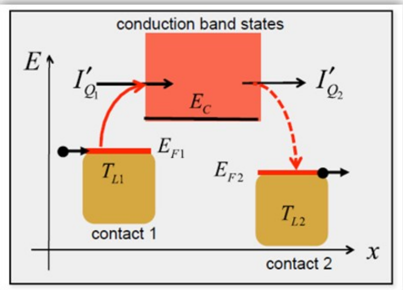


[16] see presentations by M. Kiselev, P. Gehring and J. Pekola

Mesoscopic thermoelectricity: levels

(after Lundstrom et al)





$$I = \frac{2e}{h}\int T(E)M(E)(f_1 - f_2)dE$$

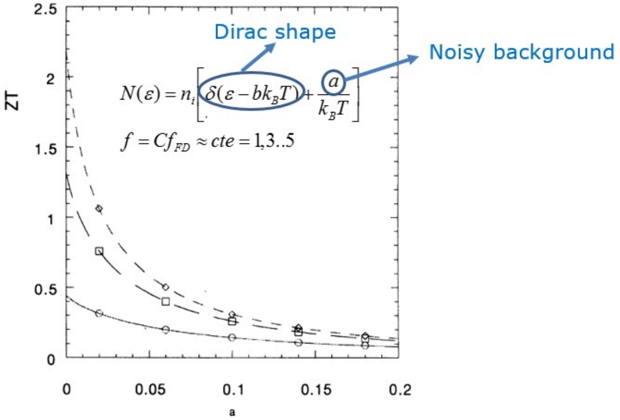
$$I_Q = \frac{2e}{h}\int (E-\mu_F)T(E)M(E)(f_1 - f_2)dE$$

The best thermoelectric: a channel question

The best thermoelectric

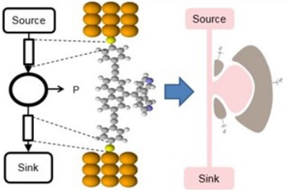
G. D. MAHAN*† AND J. O. SOFO‡

Proc. Natl. Acad. Sci. USA
Vol. 93, pp. 7436–7439, July 1996
Applied Physical Sciences

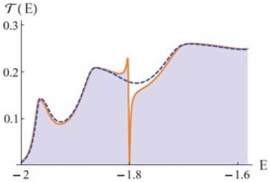


Engineering of the channel

A, Abbout, H. Ouerdane, and C. Goupil
Physical Review B vol. 87, 155410(2013)

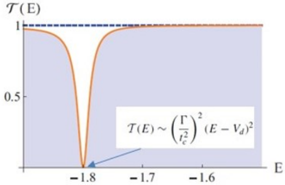


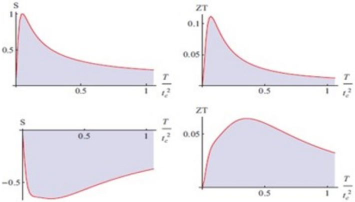
Hypothesys:
1. Monomode channel
2. Balistic channel $T(E) = 1$ in absence of cavity
3. Asymmetry of the coupling induced by phonons



Divergence of α : $T(E) \propto \sigma$

$$\alpha = -\frac{\pi^2 k^2 T}{3e}\left(\frac{\partial \ln(\sigma)}{\partial E}\right)_{E=E_F}$$





Low dimensions: [17]

ADVANCED MATERIALS

DOI: 10.1002/adma.200600527

New Directions for Low-Dimensional Thermoelectric Materials**

By *Mildred S. Dresselhaus,* Gang Chen, Ming Y. Tang, Ronggui Yang, Hohyun Lee, Dezhi Wang, Zhifeng Ren, Jean-Pierre Fleurial,* and *Pawan Gogna*

2007

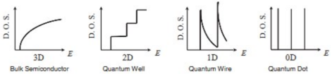
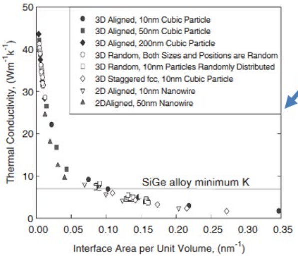


Figure 1. Electronic density of states for a) a bulk 3D crystalline semiconductor, b) a 2D quantum well, c) a 1D nanowire or nanotube, and d) a 0D quantum dot. Materials systems with low dimensionality also exhibit physical phenomena, other than a high density of electronic states (DOS), that may be useful for enhancing thermoelectric performance (see text).



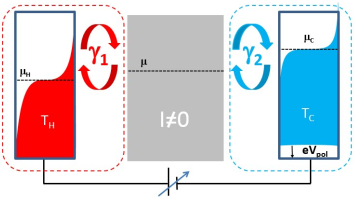
- Increase the power factor $\alpha^2 s$
- Decrease κ_{Lat}
- Separate the mean free path of phonons and electrons.
- Electron Energy filtering cf $(E-\mu_F)$
- Engineering of the DOS.

$$S = \frac{\pi^2 k_B}{3} k_B T \left(\frac{d\left[\ln \sigma(E)\right]}{dE} \right)_{E=E_F}$$

[17] See the presentation by B Fauqué

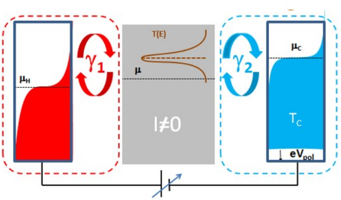
Mesoscopic thermoelecticity: only a channel question?

- One thermodynamic fluid, one ZT?
- One engine?
- Two heat exchangers?
- Two reservoirs?
- Strong coupling, or leakage coupling possible?



$$I = \frac{2e}{h}\frac{\gamma_1\gamma_2}{\gamma_1+\gamma_2}(f_H - f_C)$$

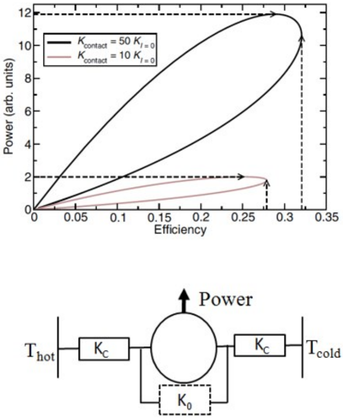
Ok if one isolated level



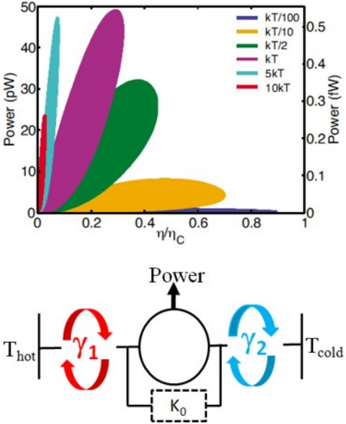
$$I = \frac{2e}{h}\int (f_H - f_C)\,T(E)dE \qquad T(E) = \frac{\left(\frac{\Gamma}{2}\right)^2}{(E-E_0)^2 + \left(\frac{\Gamma}{2}\right)^2}$$

$$I_Q = \frac{2}{h}\int (E-\mu_H)(f_H - f_C)\,T(E)dE \qquad \Gamma = \gamma_1 + \gamma_2$$

Macro versus Meso: The boundary conditions question



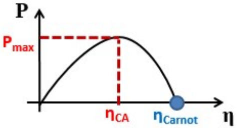
Y Apertet et al. EPL 97 (2012)



N. Nakpathomkun et al. PRB 82 (2010)

A fluid in a machine: boundary conditions: Curzon-Ahlborn

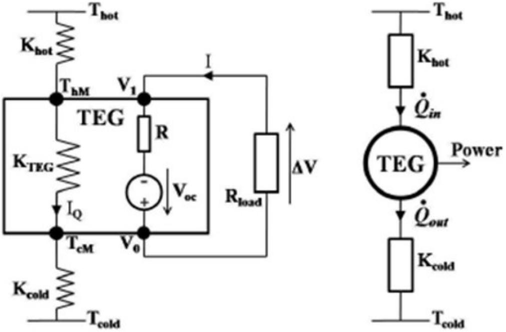
$$\eta_C = \frac{W}{Q_{in}} = 1 - \frac{T_{cold}}{T_{hot}}$$



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

- **J. Yvon,** The saclay Reactor: Two Years of Experience in the Use of a Compresed 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)

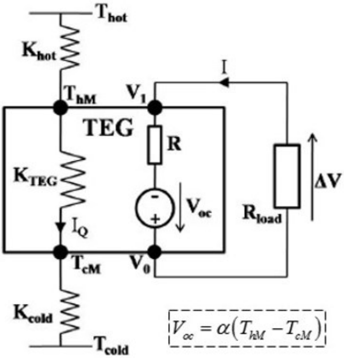
Boundary conditions: Beyond endoreversible



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

Boundary conditions: Onsager approach

Y.Apertet, H. Ouerdane, O. Glavatskaya, C.Goupil, and Ph. Lecoeur, EPL 97 (2012)
H. Ouerdane, Y.Apertet, C.Goupil, and Ph. Lecoeur, Eur. Phys. J. Special Topics224, 839–864 (2015)



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

Force-Flux :

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

$$I_Q = \underbrace{\alpha T . I}_{\text{Convection}} + \underbrace{K_0 .(T_{hM} - T_{cM})}_{\text{Conduction}}$$

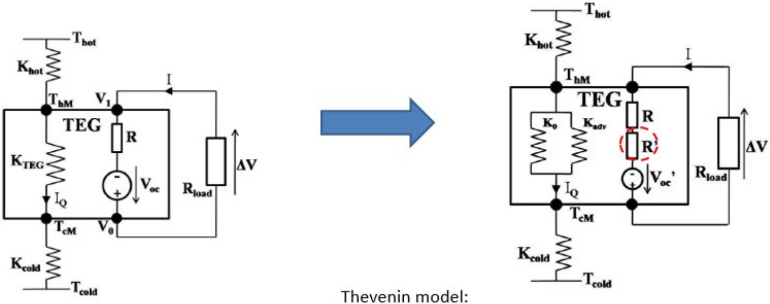
$$I_Q = \underbrace{\left(\frac{\alpha^2 T}{\underbrace{R + R_{load}}_{K_{adv}}} + K_0 \right)}_{K_{TEG}} (T_{hM} - T_{cM})$$

Effective thermal conductance !

Convection

Conduction

Boundary conditions: Feedback effect



Thevenin model:

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

Is a function of R_{load}!

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

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

Y. Apertet, et al. EPL 97 (2012)

Boundary conditions: Impedance matching

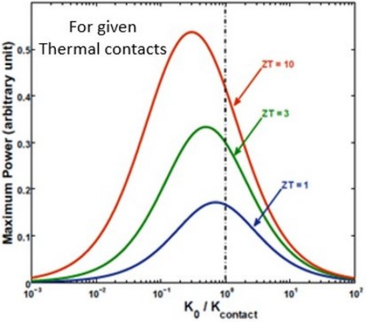
Electrical matching

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

Thermal matching

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

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



See also:
M. Freunek et al., J. Elec. Mat. **38** (2009)
K. Yazawa et A. Shakouri, JAP **111** (2012)

Importance of the thermal matching!

Y. Apertet, et al. EPL 97 (2012)

Boundary conditions: Universality of the Efficiency at Max Power

PRL **95**, 190602 (2005) PHYSICAL REVIEW LETTERS week ending 4 NOVEMBER 2005

Thermodynamic Efficiency at Maximum Power

C. Van den Broeck

Hasselt University, B-3590 Diepenbeek, Belgium

(Received 14 July 2005; published 2 November 2005)

We show by general arguments from linear irreversible thermodynamics that for a heat engine, operating between reservoirs at temperatures T_0 and T_1, $T_0 \geq T_1$, the efficiency at maximum power is bounded from above by $1 - \sqrt{T_1/T_0}$.

EPL, **81** (2008) 20003 www.epljournal.org

doi: 10.1209/0295-5075/81/20003

Efficiency at maximum power: An analytically solvable model for stochastic heat engines

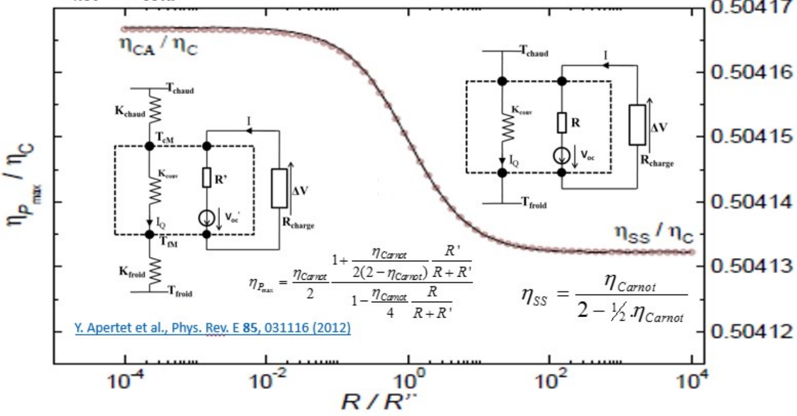
$$\boxed{\eta_{SS} = \frac{\eta_{Carnot}}{2 - \gamma\eta_{Carnot}}} \qquad 0 \leq \gamma \leq 1$$

T. Schmiedl and U. Seifert

II. Institut für Theoretische Physik, Universität Stuttgart - 70550 Stuttgart, Germany

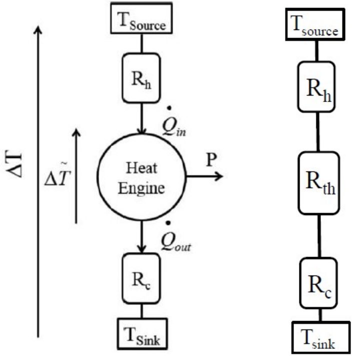
From endoreversible to exoreversible

$K_{hot} = K_{cold}$



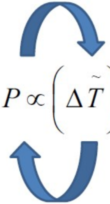
Closed-loop: basics

General system: non endoreversible



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

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



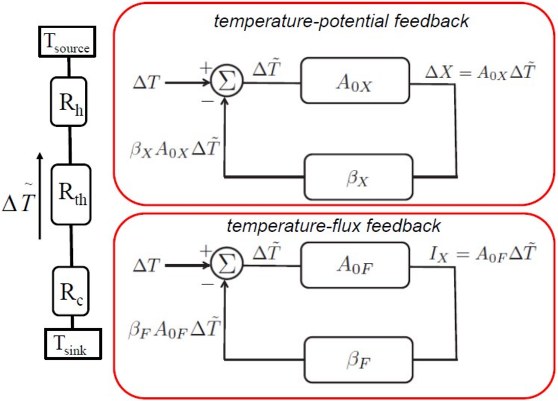
$$P \propto \left(\Delta \tilde{T}\right)^2$$

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

C. Goupil et al.
PHYSICAL REVIEW E **94**, 032136 (2016)

Closed-loop

Feedback effects



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

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

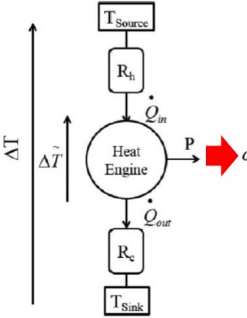
$$\frac{\Delta\tilde{T}}{\Delta T} = \frac{1}{1 + A_0\beta}$$

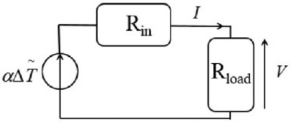
$$\boxed{A_{CL} = \frac{A_0}{1 + A_0\beta}}$$

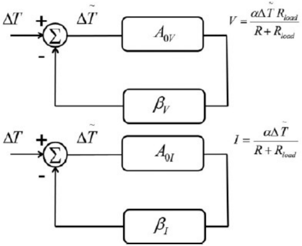
$$\boxed{A_0\beta = \frac{R_h + R_c}{R_{th}}}$$

Closed-loop: Application to Thermoelectricity

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



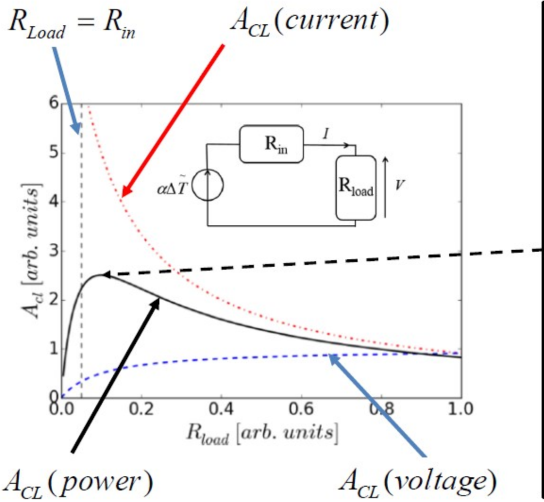




$$A_{0V} = A_{0I}\,R_{\text{load}} = \alpha\,\frac{R_{\text{load}}}{R_{\text{in}} + R_{\text{load}}},$$

$$\beta_V = \frac{\beta_I}{R_{\text{load}}} = \frac{R_\theta}{A_{0V}\,R_{\text{th}}} = \frac{R_\theta}{R_{\text{th}}}\,\frac{R_{\text{in}} + R_{\text{load}}}{\alpha\,R_{\text{load}}}.$$

Closed-loop: Feedback resistance



The maximal power is not obtained for

$R_{Load}=R_{in}$

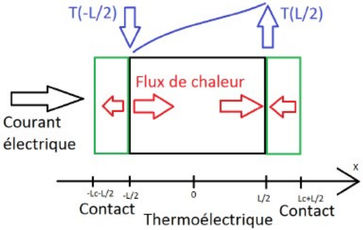
But for

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

Feedback

Y. Apertet et al. Physical Review B vol. 85, 033201 (2012)
Y. Apertet et al. Europhysics Letters vol. 97, 28001 (2012)

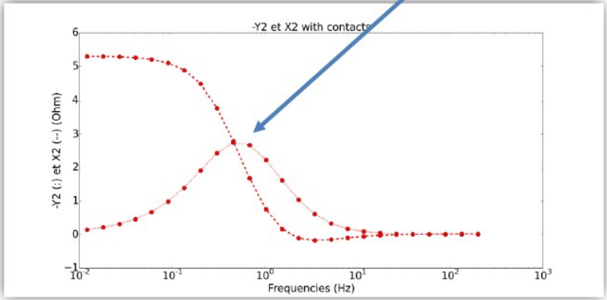
Closed-loop: Feedback Impedance



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

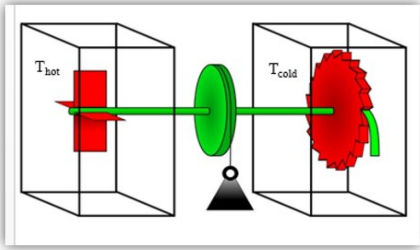
$$C_{TE} = \frac{C_\Sigma}{\alpha^2 T}$$

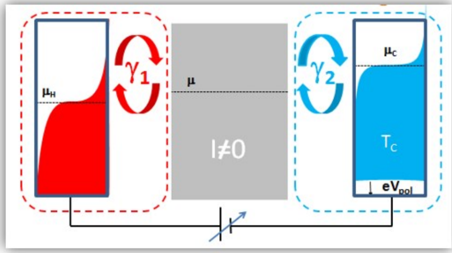
$$\tau_{TE} = R_{TE} C_{TE}$$ → T-µ time constant



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

Thermal ratchet: principle





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

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 »

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

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

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

Strong coupling configuration

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

Thermoelectric ratchet

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

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

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

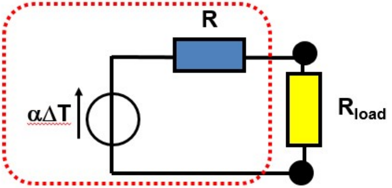
$$I_{Q_{cold}} = \alpha T_{cold} I + K\Delta T + (1-\gamma) R I^2$$

dissipative resistance

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

$$P = \left[\alpha \Delta T - \boxed{R} I\right] I$$

Entropy per tooth

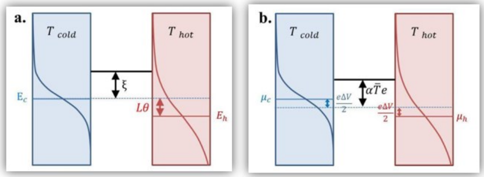


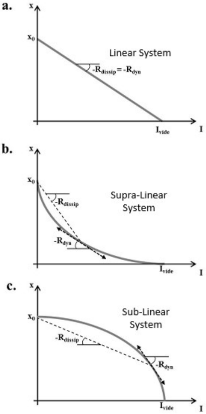
Apertet et al. PRE 2014

Thermal ratchet: beyond the linear output impedance[18]

Maximum power : $$x_{MP} = x_0 \frac{R_{dyn}}{R_{dyn} + R_{dissip}}$$

Efficiency at maximum power : $$\eta_{MP} = \frac{\eta_C}{\frac{R_{dissip}}{R_{dyn}}(1-\gamma\eta_C)+1}$$





[18] Apertet et al, PRE vol. 90, 012113 (2014)

Thank you!

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