``Enseigner la recherche en train de se faire''

COLLÈGE DE FRANCE
1530

Chaire de
Physique de la Matière Condensée

THERMOELECTRICITE: CONCEPTS, MATERIAUX ET ENJEUX ENERGETIQUES

Antoine Georges

Cycle 2012-2013

Second lecture – March 27, 2013

- **Transport coefficients, linear response**
- **Thermodynamics of energy conversion and application to thermoelectrics** [mostly on blackboard, detailed notes available on website]:

- Entropy current and entropy production rate
- Efficiency of energy conversion:
- Reminders on Carnot engines
- Endoreversible engines and Chambadal-Novikov efficiency
- The efficiency vs. Power diagram

Séminaire – 27 mars 2013

Kamran BEHNIA, ESPCI-LPEM, Paris

La thermoélectricité comme sonde sensible de la structure électronique des solides

Excerpt from abstract:

Nous allons passer en revue quelques cas de l'emploi de cette sonde sensible, mais encore mal comprise, de l'organisation des électrons dans les solides. Dans les systèmes fortement corrélés, les effets thermoélectriques documentent la naissance des électrons lourds à basse température et leur vie tumultueuse sous champ magnétique. Dans les métaux dilués, l'effet Nernst présentent des oscillations quantiques géantes sous fort champ magnétique. Le profil de ces oscillations dépend de la dimensionnalité du système comme en témoigne le contraste entre le graphite et le graphène. Cette sensibilité rend l'effet Nernst un excellent outil de fermiologie. Elle a notamment permis d'établir la structure de la plus petite surface de Fermi qui traverse une instabilité supraconductrice.

Transport equations:
Linear response
and thermoelectric coefficients

Transport equations (linear response) :

Grand-canonical potential (per unit volume):

$$\Omega(T,\mu) = -k_B T \ln Z_G$$

Particle-number and Entropy (densities):

$$s = -\frac{\partial \Omega}{\partial T}\Big|_\mu \;\;,\;\; n = -\frac{\partial \Omega}{\partial \mu}\Big|_T$$

Particle and entropy currents: linear response

$$j_n = -L_{11}\nabla\mu - L_{12}\nabla T$$
$$j_s = -L_{21}\nabla\mu - L_{22}\nabla T$$

Positivity of entropy production (2nd principle of thermo.) implies that L is a positive semi-definite matrix (see later).

This amounts to:

$$L_{11} \geq 0 \quad , \quad L_{22} \geq 0 \quad , \quad \det L \geq 0$$

Onsager's reciprocity relation (in the absence of an applied magnetic field):

$$L_{12} = L_{21}$$

Chemical potential: in fact `electrochemical' potential'

Note: electrochemical potential. Consider a system with a local electrostatic potential, conjugate to the local charge density $n_q(\boldsymbol{r})$ and a local chemical potential, conjugate to the local particle density $n(\boldsymbol{r})$. For carriers of charge q ($= -e$ the electron charge with $e > 0$), we have $n_q(\boldsymbol{r}) = qn(\boldsymbol{r})$. The scalar potential $V(\boldsymbol{r})$ and chemical potential $\mu(\boldsymbol{r})$ thus cannot be independently observed, and only the following combinations are relevant:

$$\overline{\mu}(\boldsymbol{r}) = \mu(\boldsymbol{r}) + qV(\boldsymbol{r}) \ , \ \ \overline{V}(\boldsymbol{r}) = V(\boldsymbol{r}) + \frac{1}{q}\mu(\boldsymbol{r}) \tag{5}$$

$\overline{\mu}$ is called the *electrochemical potential.* In any experiment, only the total voltage drop arising from $\overline{V}(\boldsymbol{r})$ can be measured, not separately $\boldsymbol{\nabla} V$ and $\boldsymbol{\nabla}\mu$. The energy we need to give to the system to add one particle is μ, the electrostatic energy to add one extra charge q is qV. Hence, it is actually convenient to forget about the scalar potential $V(\boldsymbol{r})$, and consider only $\overline{\mu}(\boldsymbol{r})$. This is what is done in these notes: the 'chemical potential' is actually the electrochemical potential *but the bar is dropped everywhere for simplicity* and it is simply denoted μ. The measured electric field can be obtained as:

$$\mathcal{E} \equiv -\boldsymbol{\nabla}\overline{V}(\boldsymbol{r}) = -\frac{1}{q}\boldsymbol{\nabla}\overline{\mu} = \frac{1}{e}\boldsymbol{\nabla}\overline{\mu} = -\boldsymbol{\nabla}V - \frac{1}{q}\boldsymbol{\nabla}\mu \tag{6}$$

In the following all overbars are dropped and the electric field is simply called $\boldsymbol{E}$.

In practice, electric field: $\vec{E} = \dfrac{1}{e}\vec{\nabla}\mu$

Electrical and heat currents:

$$\vec{j}_e = q\vec{j}_n \ (q = -e)$$

Heat : $\delta Q = T\,ds \Rightarrow j_Q = T\,j_s$

$$\vec{j}_e \ = \ q^2 L_{11}\vec{E} - q\,L_{12}\nabla T$$

$$\vec{j}_Q = T j_s \ = \ Tq\,L_{21}\vec{E} - T\,L_{22}\nabla T$$

Electrical conductivity: $\nabla T = 0 \Rightarrow \sigma = q^2 L_{11}$

Thermal conductivity:
(no particle current)

$$j_n = 0 \Rightarrow j_Q = \kappa(-\nabla T)$$

$$\kappa = T\left[L_{22} - \frac{L_{12}L_{21}}{L_{11}}\right]$$

Seebeck and Peltier coefficients:

1. Seebeck effect: thermal gradient induces a voltage drop between the two ends of a conductor

$$j_e = 0 \Rightarrow \vec{E} = \alpha \vec{\nabla} T \ , \quad \alpha \equiv \frac{L_{12}}{q L_{11}}$$

2. Peltier effect: electrical current induces heat current

$$\nabla T = 0 \Rightarrow j_Q = \Pi \, j_e \ , \quad \Pi \equiv T \frac{L_{21}}{q L_{11}}$$

Kelvin's relation (consequence of Onsager): $\Pi = T \alpha$

The Seebeck coefficient measures the entropy per charge flow:

$$j_s = \alpha \, j_e - \frac{\kappa}{T} \nabla T$$

(eliminating μ)

Conductivity matrix:

$$\begin{pmatrix} \boldsymbol{j}_e \\ \boldsymbol{j}_Q \end{pmatrix} = \underline{\sigma} \begin{pmatrix} \boldsymbol{E} \\ -\boldsymbol{\nabla} T \end{pmatrix} \quad , \quad \underline{\sigma} = \begin{pmatrix} \sigma & \alpha\sigma \\ T\alpha\sigma & \kappa(1+\overline{z}) \end{pmatrix}$$

Dimensionless figure of merit:

$$\boxed{\overline{z} \equiv T\frac{\alpha^2\sigma}{\kappa}}$$

Note: $\det \underline{\sigma} = \sigma\kappa$

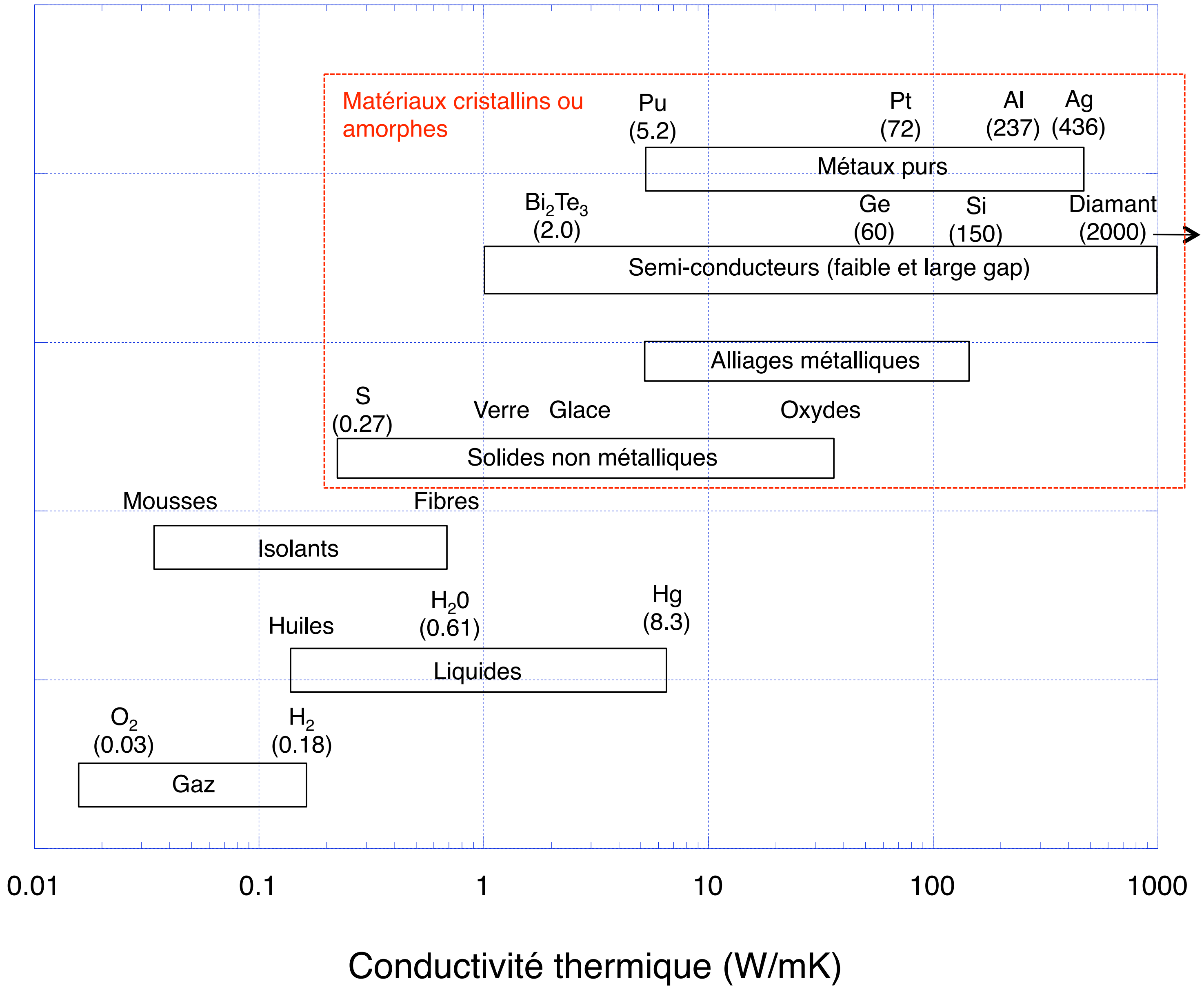
Dimensions. The current density j_X associated with a quantity X is such that $dX/dt = I_X = \int d^2l j_X$ is given by the flux traversed by j_X, hence $[j_X] = [X]/[time][length]^2$. Hence:

- Conductivity σ has dimension $\Omega^{-1}m^{-1}$. A good metal has a resistivity of order $1\mu\Omega$cm, diamond has $10^{20}\mu\Omega$cm
- Seebeck has dimension $Field.Length/Temperature = Energy/Temperature$, hence the unit of k_B/e. We note that:

$$\boxed{\frac{k_B}{e} = 86.3\mu V K^{-1}} \tag{18}$$

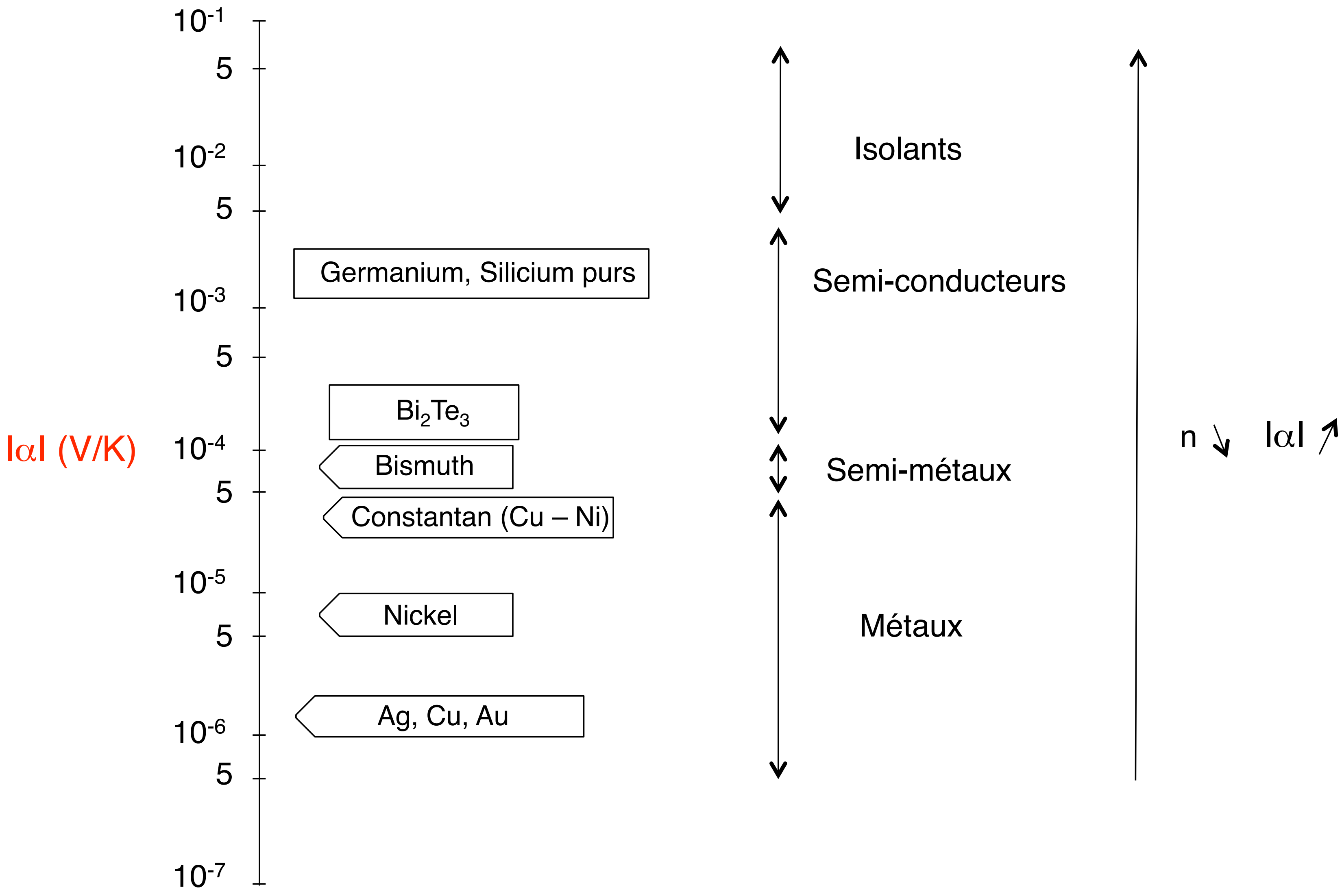
- Thermal conductivity has dimension $Energy/[Length^2 \times Time] \times [Length/Temperature] = [Power]/[Length \times Temperature]$. Unit is hence $W.m^{-1}K^{-1}$. Diamond, one of the best thermal conductors has $\kappa \sim 10^3 W.m^{-1}K^{-1}$ while silicon aerogels, excellent thermal insulators, have κ of order $10^{-2} - 10^{-3}$. Glass is $O(1)$.

Conductivité thermique : ordre de grandeur à T = 300 K



From: B.Lenoir, GDR Thermoelectricite summer school 2012

Effet Seebeck : ordre de grandeur à 300 K



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Coupling constant characterizing energy conversion :

$$g \equiv \frac{L_{12}}{\sqrt{L_{11} L_{22}}} \;,\; g^2 = \frac{\overline{z}}{1+\overline{z}}$$

$$\det \underline{L} \geq 0 \quad \Rightarrow \quad -1 \leq g \leq +1$$

Entropy and heat production rates

$$T\left[\frac{\partial s}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}_s\right] = \boldsymbol{j}_s\cdot(-\boldsymbol{\nabla}T) + \boldsymbol{j}_n\cdot(-\boldsymbol{\nabla}\mu)$$

$$\frac{\partial s}{\partial t}|_{prod} \equiv \frac{\partial s}{\partial s} + \boldsymbol{\nabla}\cdot\boldsymbol{j}_s = \frac{1}{T}\boldsymbol{G}\cdot\underline{L}\boldsymbol{G}$$

$$\boldsymbol{G} \equiv \begin{pmatrix} -\boldsymbol{\nabla}\mu \\ -\boldsymbol{\nabla}T \end{pmatrix}$$

$$\frac{\partial Q}{\partial t}|_{irr} \equiv \left[\frac{\partial s}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}_s\right] = \rho\boldsymbol{j}_e^2 + \frac{\kappa}{T}(\boldsymbol{\nabla}T)^2$$

The Kelvin effect

$$\dot{Q} \approx \rho \boldsymbol{j}_e^2 + \frac{\partial \kappa}{\partial T}(\boldsymbol{\nabla} T)^2 - T\frac{\partial \alpha}{\partial T}\boldsymbol{j}_e \cdot \boldsymbol{\nabla} T$$

Heat: rate of heat change contains a REVERSIBLE term
In addition to the irreversible Joule heating.
Heat production or absorption depending on sign of current

$\partial \alpha / \partial T$: Thomson coefficient

EFFICIENCY OF ENERGY CONVERSION

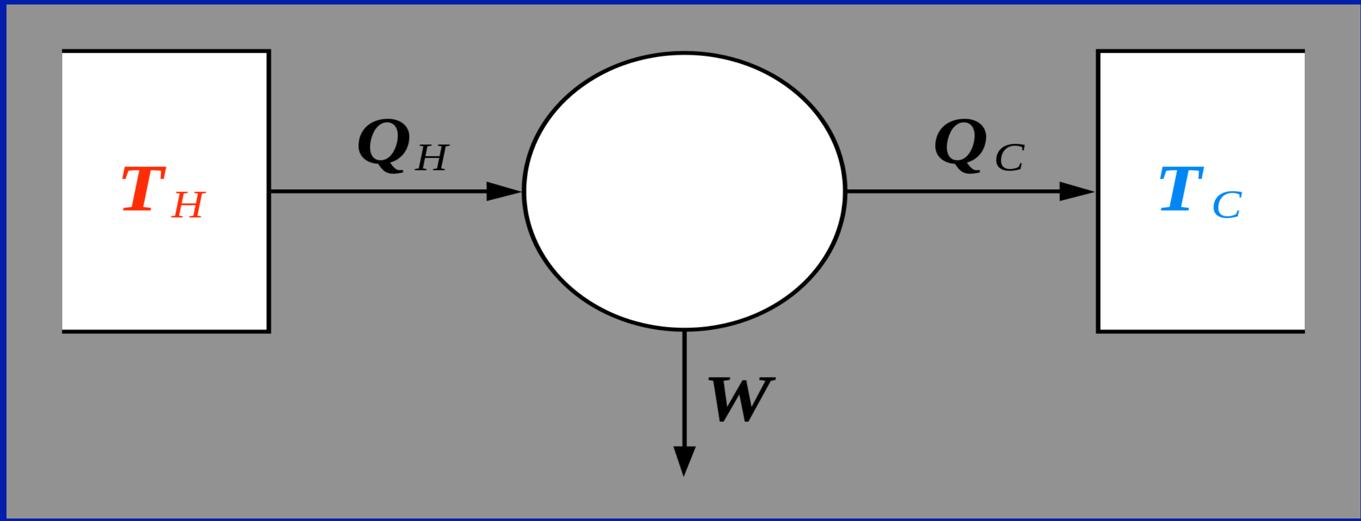
- General considerations and application to Thermoelectrics -

Maximum theoretical efficiency: the Carnot reversible engine

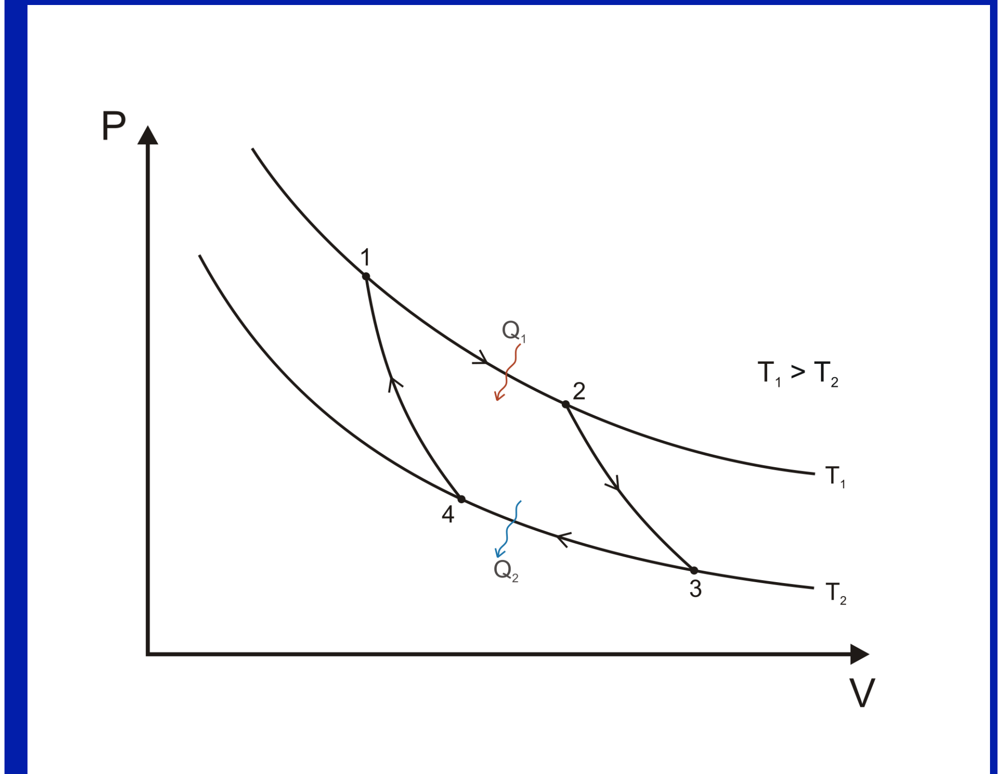
Carnot efficiency:

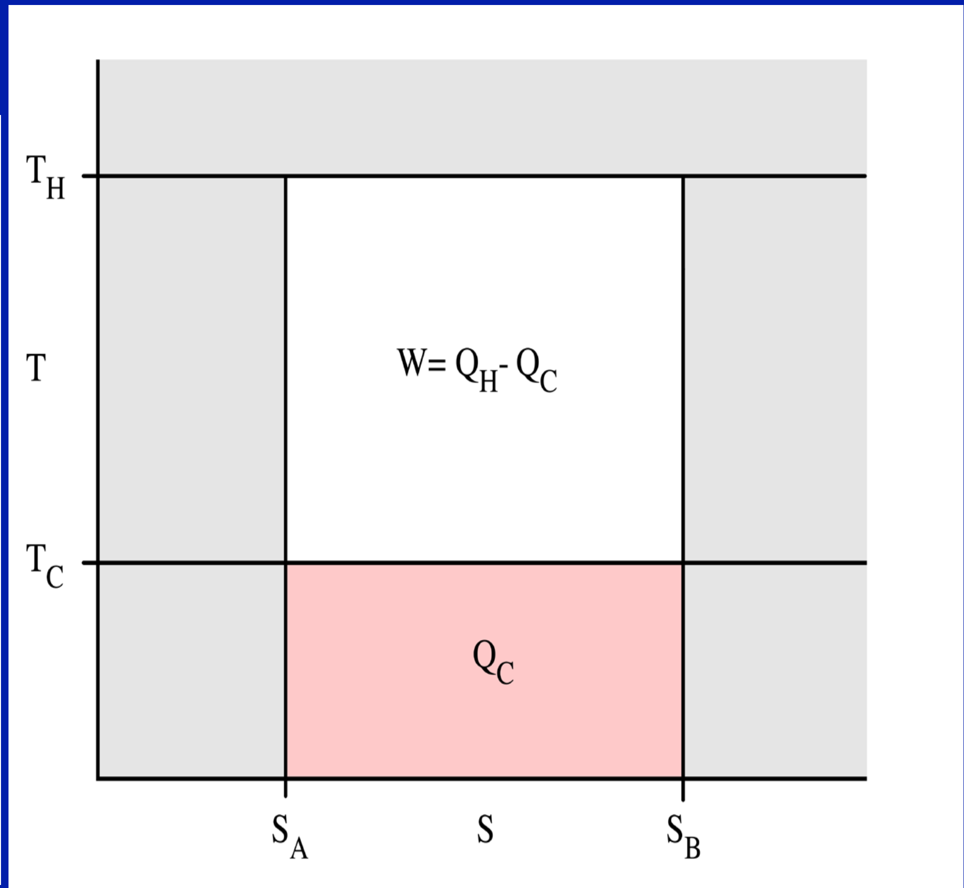
$$\eta_C = 1 - \frac{T_C}{T_H}$$

Since it corresponds to a reversible,
quasi-static and hence infinitely slow process,
a Carnot engine delivers ZERO POWER !

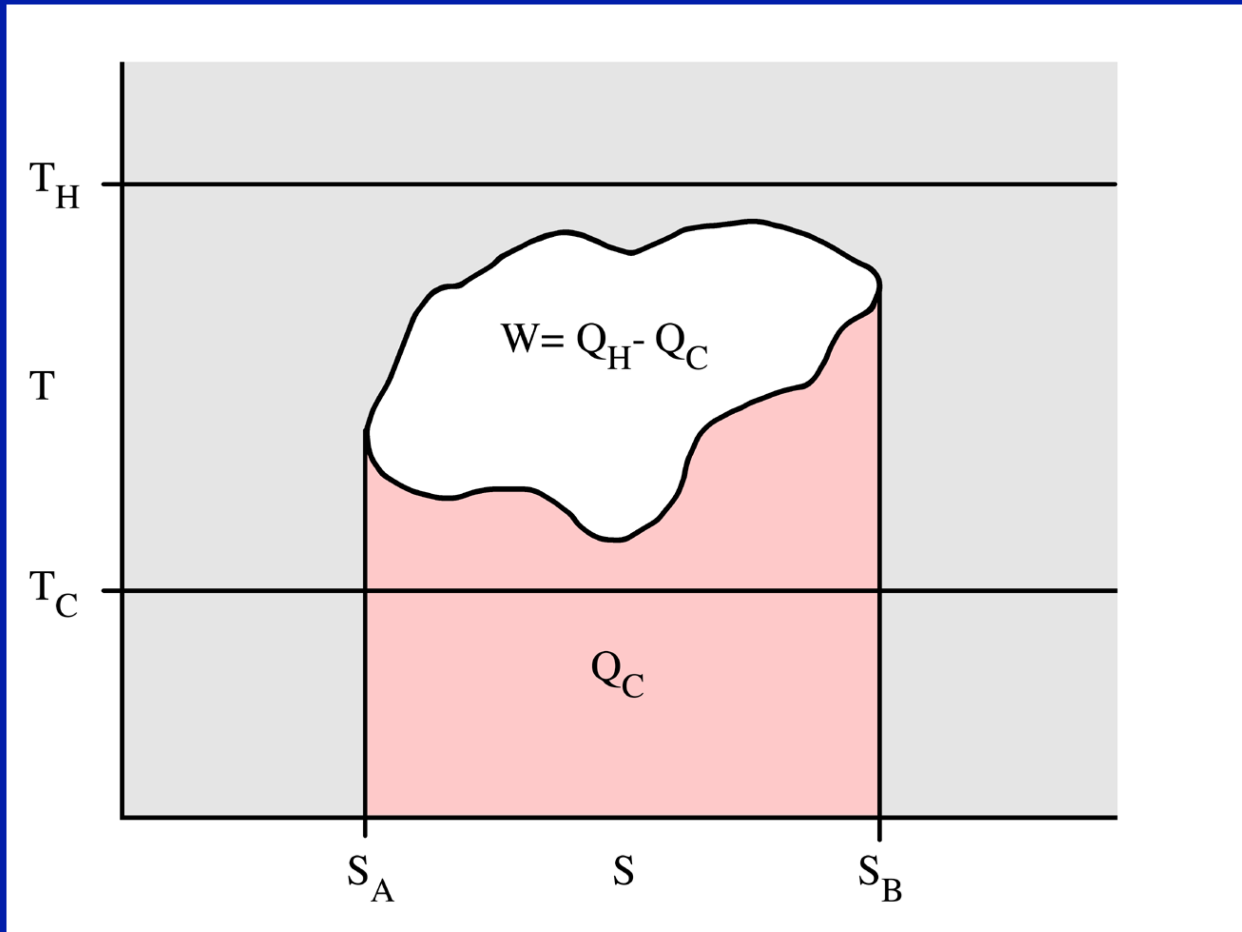


Carnot cycle :





A Carnot cycle maximizes efficiency… but delivers zero power !



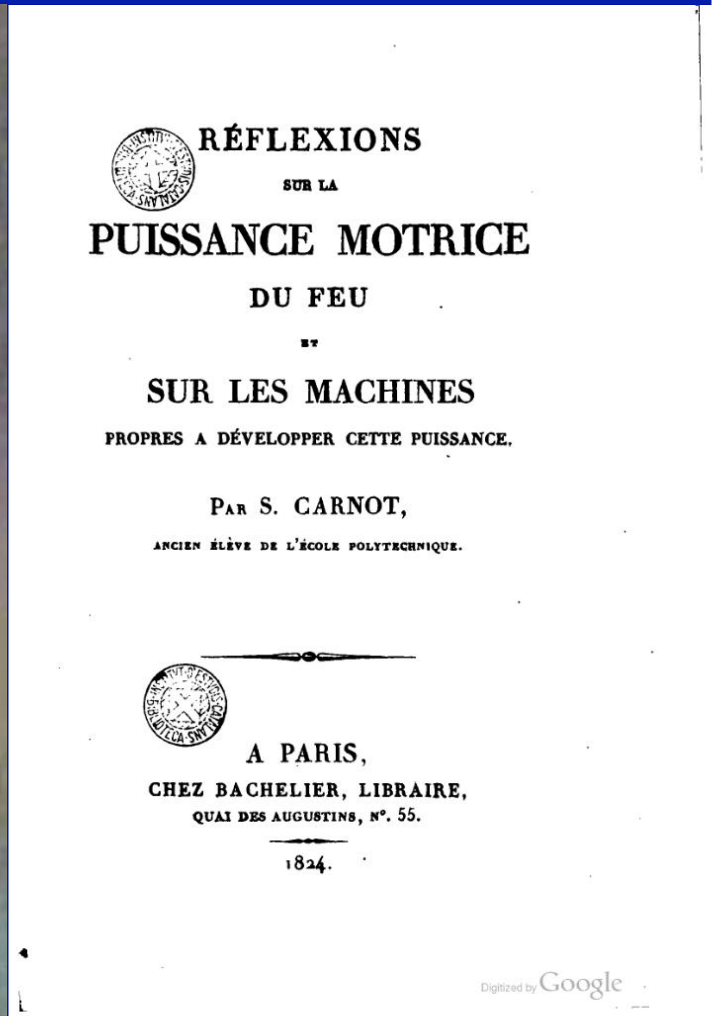
A general cycle (non-Carnot): Carnot maximizes the ratio of the white to total area, subject to the constraints of the 2nd principle.

Sadi Carnot (1796-1832)

- Officer and Physicist/Engineer -

[Not to be confused with President Sadi Carnot (1837- 1894)]
Both are descendents of Lazare Carnot, great revolutionary, statesman,
also a mathematician and physicist,
and one of the founders of Ecole Polytechnique1753-1823

Sadi Carnot, then a student at Ecole Polytechnique (painting by Louis Leoplod Boilly [Wikipedia])



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.

Efficiency at maximum power of an `endoreversible' engine: the Chambadal-Novikov (Curzon-Ahlborn) efficiency

$$\eta_{CN} = 1 - \sqrt{\frac{T_C}{T_H}}$$

Efficiency at maximum power,

according to:

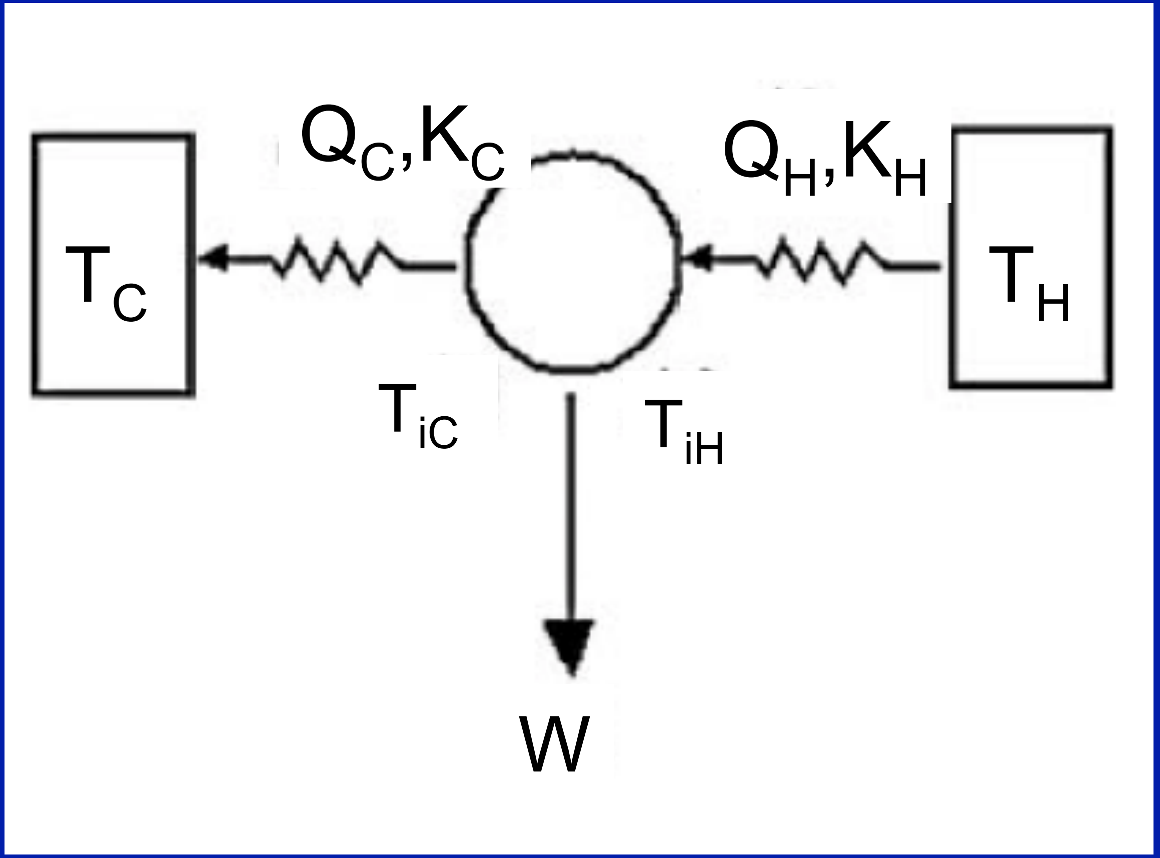
Chambadal-Novikov

(Curzon-Ahlborn),

Endoreversible engines,

« Finite-Time Thermodynamics »

An endoreversible engine



$$\boxed{\eta(P_{\max}) = 1 - \sqrt{\frac{T_C}{T_H}}}$$

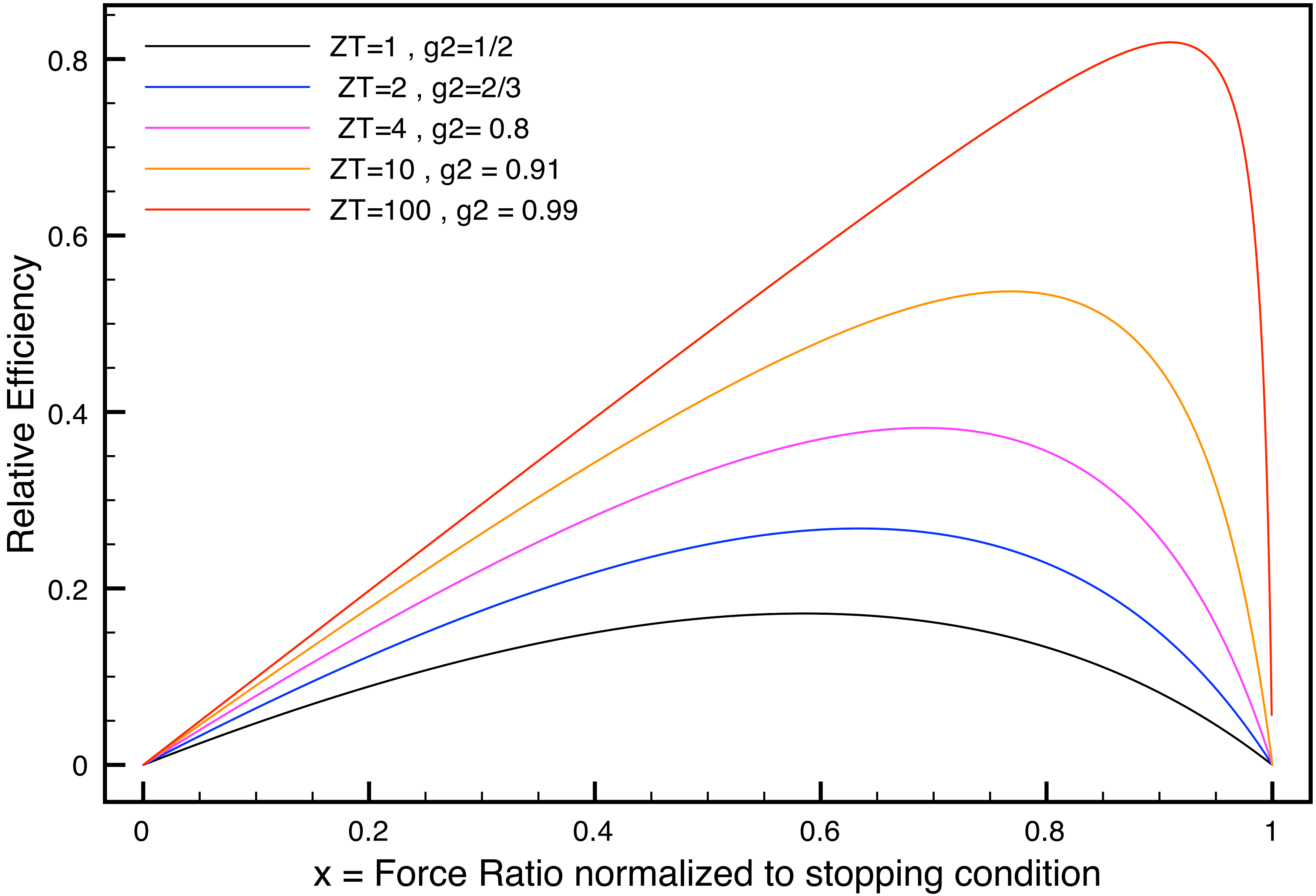
Chambadal-Novikov efficiency

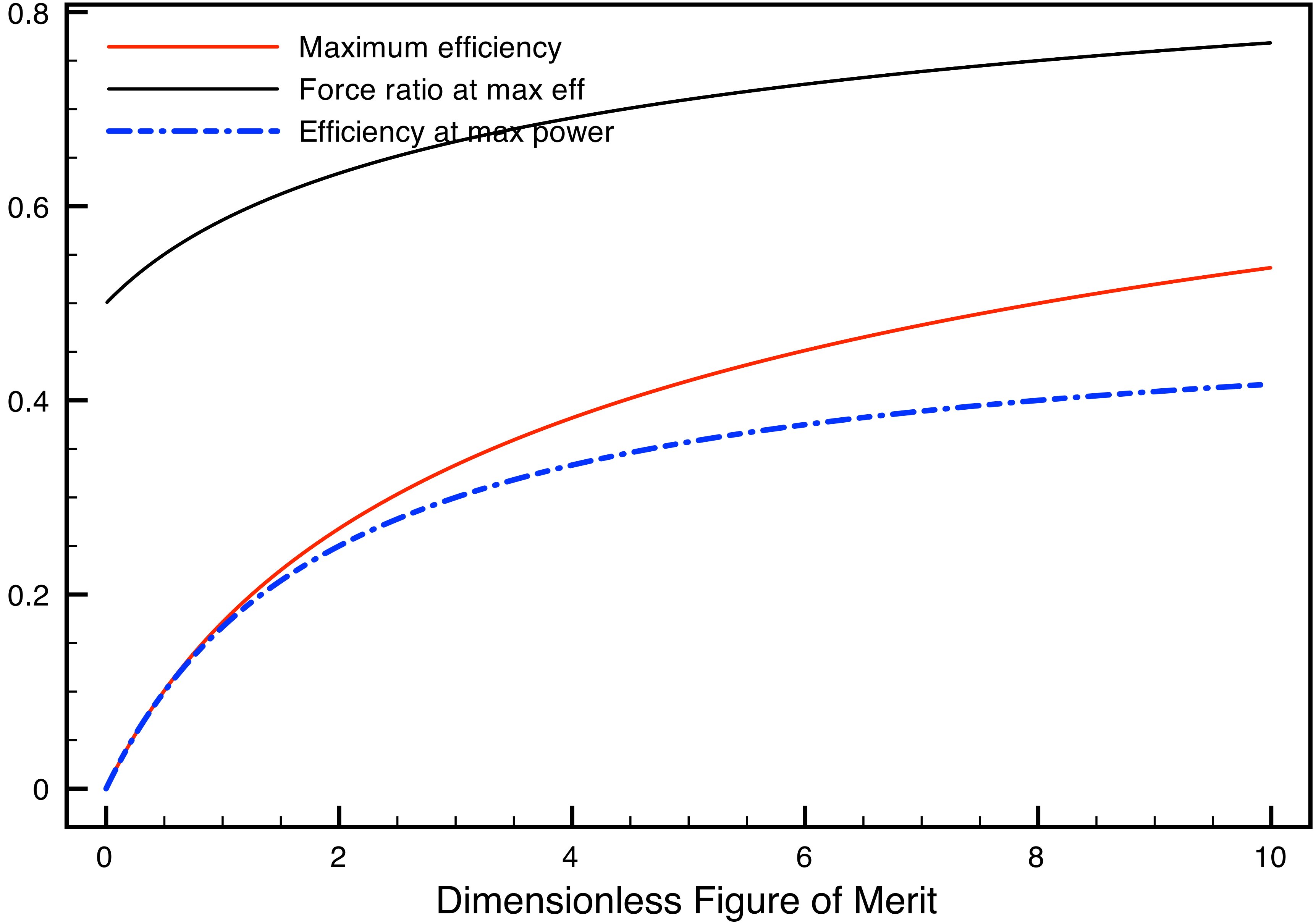
$$P_{\max} = \frac{K_H K_C}{(\sqrt{K_H} + \sqrt{K_C})^2} \left[\sqrt{T_H} - \sqrt{T_C}\right]^2$$

F. L. Curzon and B. Ahlborn

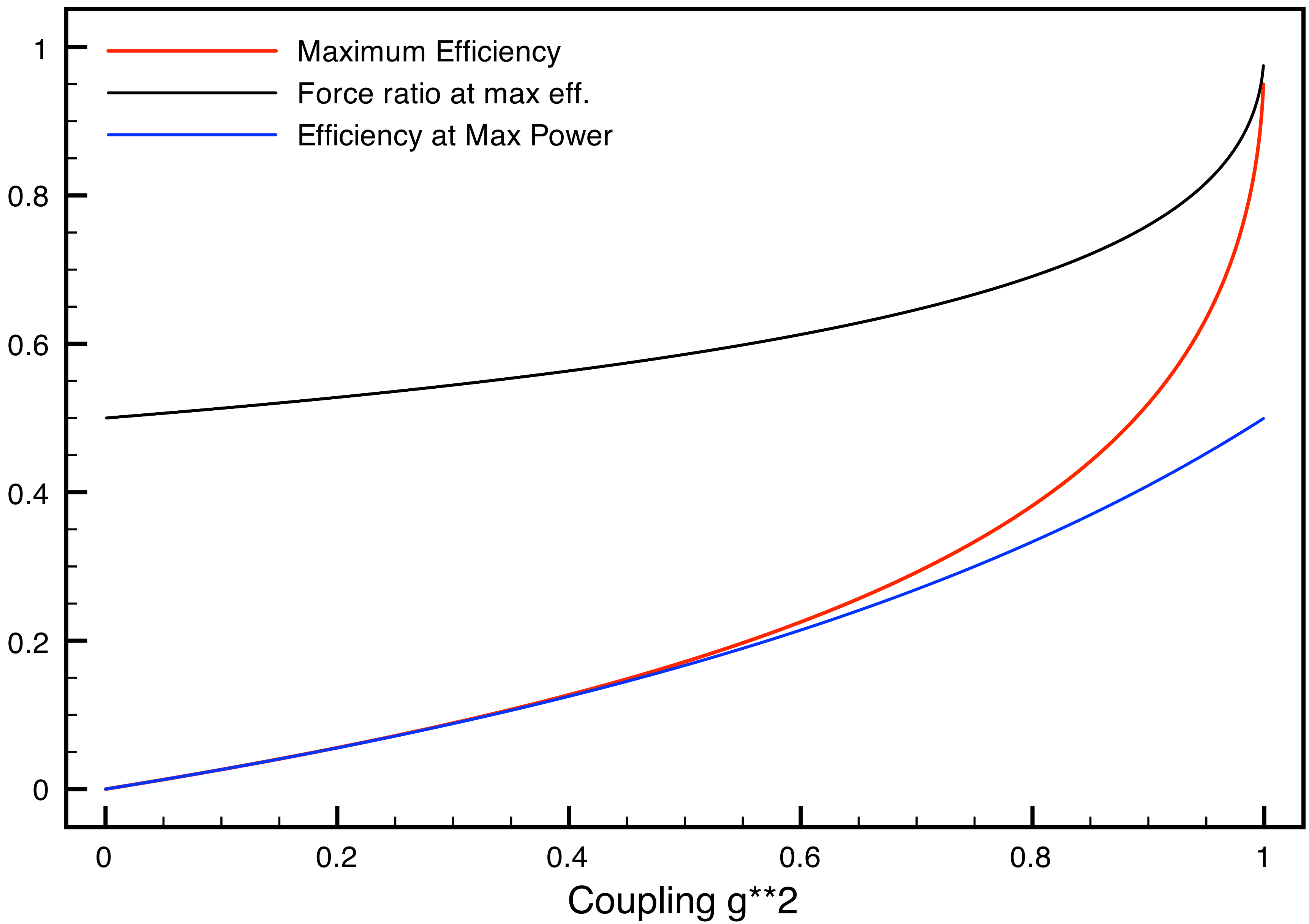
TABLE I. Observed performance of real heat engines.

Power source	T_2 (°C)	T_1 (°C)	η (Carnot)	η' (Eq. 14)	η (observed)
West Thurrock (U.K.)[2] Coal Fired Steam Plant	~25	565	64.1%	40%	36%
CANDU (Canada)[4] PHW Nuclear Reactor	~25	300	48.0	28%	30%
Larderello (Italy)[5] Geothermal Steam Plant	80	250	32.3%	17.5%	16%


ZT=1 , g2=1/2
ZT=2 , g2=2/3
ZT=4 , g2= 0.8
ZT=10 , g2 = 0.91
ZT=100 , g2 = 0.99
Relative Efficiency
0
0.2
0.4
0.6
0.8
0
0.2
0.4
0.6
0.8
1
x = Force Ratio normalized to stopping condition



Maximum efficiency
Force ratio at max eff
Efficiency at max power
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
Dimensionless Figure of Merit



Maximum Efficiency
Force ratio at max eff.
Efficiency at Max Power
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
Coupling g**2

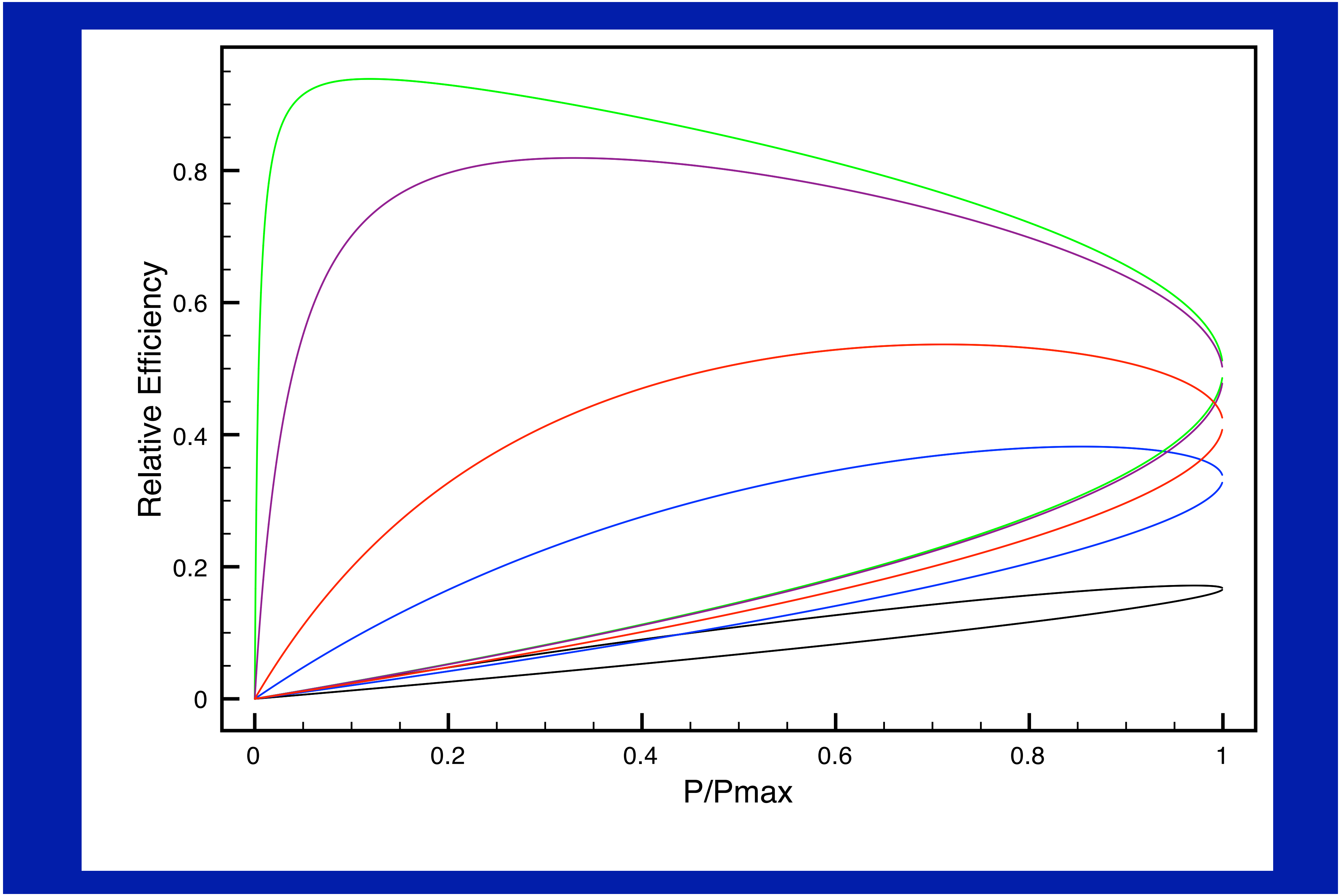


FIG. 4: Relative efficiency vs. power normalized to its maximum value, for (bottom to top): $\overline{z} = 1, 4, 10, 100, 1000$. The upper (resp. lower) branches correspond to a force ratio $x \geq 1/2$ (resp. $x \leq 1/2$). Maximum efficiency is realized on the upper branch.