Notes on Thermodynamics of Thermoelectricity - Collège de France - Spring 2013

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(Dated: March 26, 2013)

I. BASIC TRANSPORT EQUATIONS

General references on this section: books by Ashcroft-Mermin,[1] Pottier,[9] Callen,[2] Lebon et al..[7]

A. Thermodynamic functions

State variables: temperature T, chemical potential μ, possibly others...

Grand-canonical partition function: $Z = \mathrm{Tr}e^{-\beta(\hat{H}-\mu\hat{N})}$

Grand-canonical potential (also called Gibbs free-energy):

$$\Omega(T,\mu) = -k_B T \ln Z = E - TS - \mu N \tag{1}$$

E: internal energy, S: entropy

Change of heat of the system, work done by the system:

$$\delta Q = TdS \ , \ \ \delta W = \mu dN \ , \ \ dE = \delta Q + \delta W = TdS + \mu dN \tag{2}$$

Hence:

$$d\Omega = dE - TdS - SdT - \mu dN - Nd\mu = -SdT - Nd\mu \tag{3}$$

so that:

$$S = -\frac{\partial \Omega}{\partial T}\Big|_\mu \ , \ \ N = -\frac{\partial \Omega}{\partial \mu}\Big|_T \tag{4}$$

The corresponding entropy and particle current densities will be denoted $\boldsymbol{j}_S$ and $\boldsymbol{j}_N$. The latter is related to the local electrical current density by $\boldsymbol{j}_e \equiv q\boldsymbol{j}_N = -e\boldsymbol{j}_N$ ($q = -e$ electron charge, $e > 0$). The heat current (from $\delta Q = TdS$) is given by $\boldsymbol{j}_Q = T\boldsymbol{j}_S$.

Generalized thermodynamic forces (Onsager): view entropy as a function of internal energy and other state variables $S = S(U, \mu, \cdots)$.

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 $\boldsymbol{E}$.

B. Linear response and thermoelectric coefficients

We define transport coefficients from linear response equations for the pairs of conjugate variables:

$$\begin{pmatrix} \boldsymbol{j}_N \\ \boldsymbol{j}_S \end{pmatrix} = - \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \Delta\mu \\ \Delta T \end{pmatrix} \tag{7}$$

which satisfy Onsager's symmetry relations (we assume here that there is no magnetic field):

$$L_{12} = L_{21} \tag{8}$$

Converting to electric and heat currents, we obtain:

$$\begin{pmatrix} \boldsymbol{j}_e \\ \boldsymbol{j}_Q \end{pmatrix} = \begin{pmatrix} q^2 L_{11} & q L_{12} \\ Tq L_{21} & T L_{22} \end{pmatrix} \begin{pmatrix} \boldsymbol{E} \\ -\boldsymbol{\nabla} T \end{pmatrix} \equiv \underline{\sigma} \begin{pmatrix} \boldsymbol{E} \\ -\boldsymbol{\nabla} T \end{pmatrix} \tag{9}$$

The different entries in the conductivity matrix $\underline{\sigma}$ are defined from the following setups:

- Electrical conductivity. $\boldsymbol{j}_e = \sigma \boldsymbol{E}$ with $\boldsymbol{\nabla} T = 0$, hence:

$$\sigma \equiv q^2 L_{11} \tag{10}$$

- Seebeck coefficient ('thermoelectric power'). We consider a system in the presence of a thermal gradient and tune the field so that no particle current flows, i.e. $q^2 L_{11} \boldsymbol{E} = q L_{12} \boldsymbol{\nabla} T$. This condition ('stopping force') defines the Seebeck coefficient (or themoelectric power):

$$\alpha \equiv \frac{E}{\nabla T}\Big|_{j_N=0} = \frac{L_{12}}{q L_{11}} \tag{11}$$

- Peltier coefficient. The Peltier effect is that fact that an electrical current flowing through a conductor is accompanied by a heat current. The corresponding heat should be distinguished from the heat dissipated by Joule effect in the conductor. Joule heating is irreversible, while the Peltier current is *reversible* and reverses sign when the direction of the current is reversed. The Peltier coefficient (or Peltier heat per unit charge Π) is defined in the absence of a temperature gradient as the ratio between the heat current and the electrical current:

$$\Pi \equiv \frac{j_Q}{j_e}\Big|_{\nabla T=0} = T \frac{L_{21}}{q L_{11}} \tag{12}$$

  Because of Onsager's symmetry: $\Pi = T\alpha$ (one of the two Kelvin relations).

- Thermal conductivity. Under the same condition of no particle current, we calculate the ratio of heat current to thermal gradient: $\boldsymbol{j}_Q = \left[T L_{22} - Tq L_{21} \frac{L_{12}}{q L_{11}} \right] (-\boldsymbol{\nabla} T) \equiv -\kappa \, \boldsymbol{\nabla} T$, hence:

$$\kappa = T \left[L_{22} - \frac{L_{21} L_{12}}{L_{11}} \right] = T \frac{\det \underline{L}}{L_{11}} \tag{13}$$

- $\det \underline{\sigma} = \sigma\kappa$.

Rewriting of the conductivity matrix

$$\begin{pmatrix} \boldsymbol{j}_e \\ \boldsymbol{j}_Q \end{pmatrix} = \underline{\sigma} \begin{pmatrix} \boldsymbol{E} \\ -\boldsymbol{\nabla} T \end{pmatrix} \ , \ \underline{\sigma} = \begin{pmatrix} \sigma & \alpha\sigma \\ T\alpha\sigma & \kappa(1+\overline{z}) \end{pmatrix} \tag{14}$$

where we have defined the *dimensionless figure of merit* by:

$$\overline{z} \equiv Z.T \equiv T \frac{\alpha^2 \sigma}{\kappa} \tag{15}$$

Onsager coefficients in terms of conductivities:

$$L_{11} = \sigma/q^2 \ , \ \ L_{12} = L_{21} = \alpha\sigma/q \ , \ \ L_{22} = \frac{\kappa}{T}(1 + \overline{z}) \tag{16}$$

As we shall see later, $\overline{z}$ plays a key role in setting the thermoelectric *efficiency* of energy conversion. Alternatively, a convenient measure of the ratio of reversible vs. irreversible (dissipative) processes[6] is the coupling constant g ($-1 \leq g \leq +1$ since $\det L > 0$):

$$g \equiv \frac{L_{12}}{\sqrt{L_{11}L_{22}}} \ , \ g^2 = \frac{\overline{z}}{1 + \overline{z}} \tag{17}$$

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 $O(1)$.

II. ENTROPY (HEAT) CURRENT AND PRODUCTION RATE

Useful references: Goupil et al.,[5] Snyder et al.,[10] Van den Broeck[11]

A. Currents

Because of $\delta Q = TdS$, the heat and entropy currents are related by:

$$\boldsymbol{j}_Q = T\,\boldsymbol{j}_S \tag{19}$$

In terms of the gradients:

$$\boldsymbol{j}_S = \alpha\sigma\boldsymbol{E} - \frac{\kappa}{T}(1 + \overline{z})\boldsymbol{\nabla}T \tag{20}$$

Using instead the electrical current density and thermal gradient as variables and the relation $\boldsymbol{j}_e = \sigma\boldsymbol{E} - \alpha\sigma\boldsymbol{\nabla}T$, we can eliminate $\boldsymbol{E}$ and obtain:

$$\boldsymbol{j}_S = \alpha\boldsymbol{j}_e - \frac{\kappa}{T}\boldsymbol{\nabla}T \ , \ \ \boldsymbol{j}_Q = \alpha T\boldsymbol{j}_e - \kappa\boldsymbol{\nabla}T \tag{21}$$

The second term is just Fourier law and reflects the irreversible heat current due to the thermal gradient (heat diffusion). In contrast, the first term corresponds to entropy carried along by the moving charge carriers, and is reversed when reversing the sign of the particle current. One can say that the Seebeck coefficient measures the flow of entropy per unit charge.

Since efficient energy conversion requires to minimize the irreversible process viz. reversible processes (ie that heat is as much as possible associated with reversible current flow rather than dissipation), it is clear that we'll need to have α as large as possible and κ as small as possible.

Since (first principle) the internal energy is given by: $du = Tds + \mu dn$, the energy current reads:

$$\boldsymbol{j}_u = T\boldsymbol{j}_s + \mu\boldsymbol{j}_n \tag{22}$$

B. Irreversible heat and entropy production rate

Reminder: given an observable Φ, associated volumic density $\phi(\boldsymbol{r}, t)$ (i.e $\Phi_V = \int_V d^3 r \phi$ in a volume V), and associated current density $\boldsymbol{j}_\phi$ (i.e. the amount flowing out of volume V per unit time is $-d\Phi/dt = \int_S d^2 r \boldsymbol{j}_\phi$, we can write:

$$\frac{\partial \phi}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_\phi = \frac{\partial \phi}{\partial t}|_{prod} \tag{23}$$

in which the r.h.s is the local production rate of this quantity. For a conserved quantity, the rhs vanishes.

We apply this to the entropy using $ds = \frac{1}{T} du - \frac{\mu}{T} dn$ and the conservation of particle number and internal energy:

$$\frac{\partial u}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_u = 0 \ , \ \ \frac{\partial n}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_n = 0 \tag{24}$$

Hence:

$$\frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \frac{\mu}{T} \frac{\partial n}{\partial t} \tag{25}$$

$$= -\frac{1}{T} \boldsymbol{\nabla} \cdot \boldsymbol{j}_u + \frac{\mu}{T} \boldsymbol{\nabla} \cdot \boldsymbol{j}_n \tag{26}$$

$$= -\boldsymbol{\nabla} \left[\frac{1}{T} \boldsymbol{j}_u - \frac{\mu}{T} \boldsymbol{j}_n \right] + \boldsymbol{j}_u \cdot \boldsymbol{\nabla} \frac{1}{T} + \boldsymbol{j}_n \cdot \boldsymbol{\nabla} \left(-\frac{\mu}{T} \right) \tag{27}$$

Finally:

$$T \left[\frac{\partial s}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_s \right] = \boldsymbol{j}_s \cdot (-\boldsymbol{\nabla} T) + \boldsymbol{j}_n \cdot (-\boldsymbol{\nabla} \mu) \tag{28}$$

The rhs is T times the net local entropy production rate, ie the net heat production rate. It should correspond to *irreversible processes*, as will be verified below.

We also recognize that it is the sum of the power due to the electric field ($\boldsymbol{j}_n \cdot (-\boldsymbol{\nabla} \mu) = \boldsymbol{j}_e \cdot \boldsymbol{E}$) and the power corresponding to entropy (heat) flow. Below we shall define an efficiency (relative to Carnot) as:

$$\eta_r \equiv \frac{-\boldsymbol{j}_n \cdot \boldsymbol{\nabla} \mu}{\boldsymbol{j}_s \cdot \boldsymbol{\nabla} T} = \frac{\boldsymbol{j}_e \cdot \boldsymbol{E}}{\boldsymbol{j}_s \cdot \boldsymbol{\nabla} T} \tag{29}$$

Obviously, $\eta_r = +1$ corresponds to a reversible adiabatic process in which there is no entropy production, i.e. a Carnot process.

Finally, we can use the linear response equations $\boldsymbol{J} = \underline{L} \boldsymbol{G}$ with $\boldsymbol{G} \equiv \begin{pmatrix} -\boldsymbol{\nabla} \mu \\ -\boldsymbol{\nabla} T \end{pmatrix}$ to obtain:

$$\frac{\partial s}{\partial t}|_{prod} \equiv \frac{\partial s}{\partial s} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_s = \frac{1}{T} \boldsymbol{G} \cdot \underline{L} \boldsymbol{G} \tag{30}$$

Since the entropy production rate must be non-negative from the second principle, we see that $\underline{L}$ *must be a positive semi-definite matrix*. For a 2×2 matrix, this amounts to:

$$L_{11} \geq 0 \ , \ \ L_{22} \geq 0 \ , \ \ \det \underline{L} \geq 0 \tag{31}$$

If instead we wish to use the current and thermal gradient as basic variables, we can use $-L_{11} \boldsymbol{\nabla} \mu = \boldsymbol{j}_n + L_{12} \boldsymbol{\nabla} T$ and obtain after simple algebra:

$$\frac{\partial Q}{\partial t}|_{irr} \equiv \left[\frac{\partial s}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_s \right] = \rho \boldsymbol{j}_e^2 + \frac{\kappa}{T} (\boldsymbol{\nabla} T)^2 \tag{32}$$

with $\rho = 1/\sigma$ the electrical resitivity. First term is Joule heating, second is heat lost by thermal resistance. Both correspond to purely irreversible (dissipative) processes, as expected. Note that the thermoelectric power does not enter here. We also see that to minimize dissipative losses for a given current and thermal gradient, we need a large electrical conductivity and low thermal conductivity.

Note: The compensation of reversible terms requires $L_{12} = L_{21}$, which provides an intuitive justification of Onsager's relations.
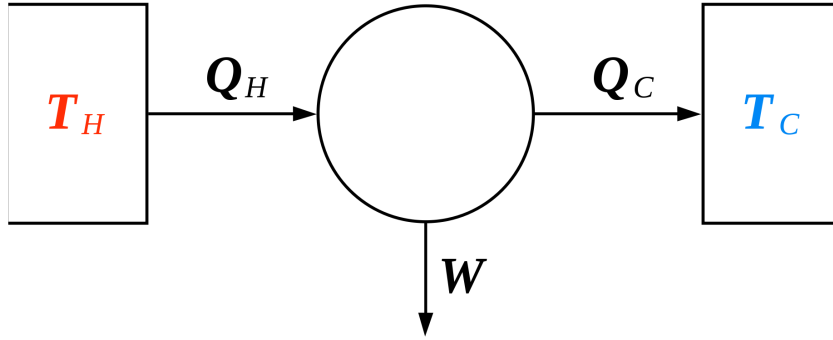
FIG. 1: Basic principle of a simple engine. Heat is provided by a hot source and rejected to a cold environment. Work $W = Q_H - Q_C$ is produced. (After Wikipedia). If the entire operation is reversible, we have a Carnot engine.

C. Total rate of entropy (heat) change, Kelvin effect

We can finally estimate the *total* rate of change of entropy (heat), both irreversible and reversible, using $T\dot{s} = \dot{Q}_{irr} - T\boldsymbol{\nabla} \cdot \boldsymbol{j}_s$. We calculate $\boldsymbol{\nabla} \cdot \boldsymbol{j}_s$:

$$\boldsymbol{\nabla} \cdot \boldsymbol{j}_s = \boldsymbol{\nabla}(\alpha \boldsymbol{j}_e) - \boldsymbol{\nabla}\left[\frac{\kappa}{T}\boldsymbol{\nabla}T\right] \tag{33}$$

$$= \boldsymbol{j}_e \cdot \boldsymbol{\nabla}\alpha - \frac{\kappa}{T}\nabla^2 T - \frac{1}{T}\boldsymbol{\nabla}T \cdot \boldsymbol{\nabla}\kappa + \frac{\kappa}{T^2}(\boldsymbol{\nabla}T)^2 \tag{34}$$

where we have used the conservation law $\boldsymbol{\nabla} \cdot \boldsymbol{j}_e = 0$. Finally:

$$\dot{Q} = T\dot{s} = \rho j_e^2 - T\boldsymbol{j}_e \cdot \boldsymbol{\nabla}\alpha + \kappa \nabla^2 T + \boldsymbol{\nabla}T \cdot \boldsymbol{\nabla}\kappa \tag{35}$$

Under the following assumptions (cf. Ashcroft-Mermin):

- α and κ depend mostly on T, weak dependence on μ (?)
- Uniform temperature gradient, so that $\nabla^2 T \simeq 0$

we finally obtain:

$$\dot{Q} \approx \rho \boldsymbol{j}_e^2 + \frac{\partial \kappa}{\partial T}(\boldsymbol{\nabla}T)^2 - T\frac{\partial \alpha}{\partial T}\boldsymbol{j}_e \cdot \boldsymbol{\nabla}T \tag{36}$$

The last term corresponds to a *reversible effect*: it changes sign upon reversing the current at fixed temperature gradient. Heat production or consumption is associated to this reversible process. It comes in addition to the irreversible Joule heating which is always dissipated to the environment. This effect was first discussed by William Thomson (Lord Kelvin). The coefficient $T\partial \alpha/\partial T$ is called the Thomson coefficient. It can be measured by reversing the sign of the current at constant temperature gradient, to cancel the other terms.

III. EFFICIENCY OF ENERGY CONVERSION

A. Reminder: the Carnot engine

The general principle of a heat engine is recalled on Fig. 1. Heat Q_H is produced by a hot source and converted partly into work W and partly into heat (loss) Q_C rejected to the cold environment. The first principle of thermodynamics
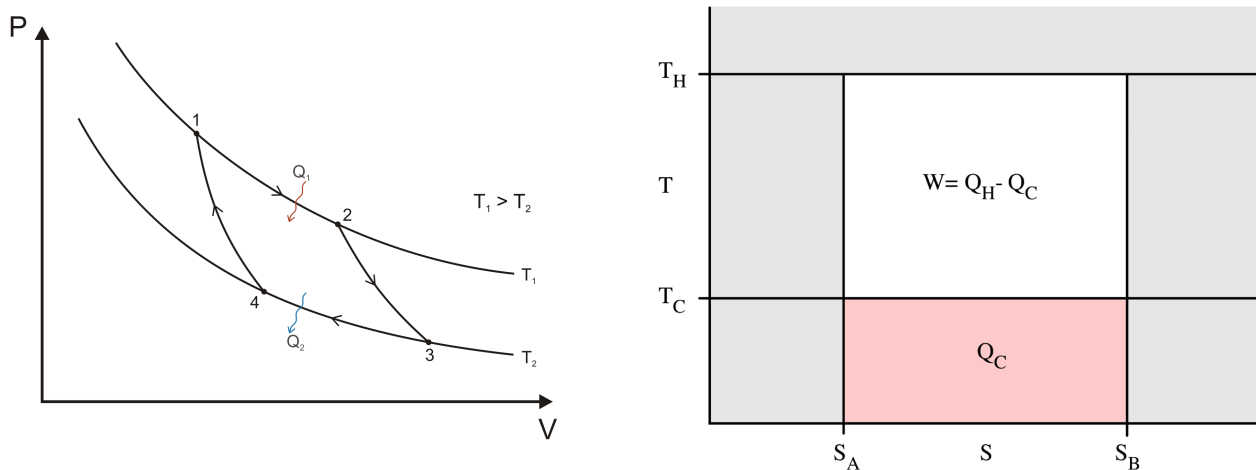
FIG. 2: Carnot cycle: (pressure,volume) and (entropy,temperature) representations. (After Wikipedia).

(conservation of internal energy) implies that:

$$Q_H = W + Q_C \tag{37}$$

Assuming that the hot source remains at constant temperature, the entropy provided by the hot source to the engine is Q_H/T_H. Similarly, the entropy released by the engine to the cold reservoir is Q_C/T_C. Hence, the total entropy change of the engine is:

$$\Delta S_{\text{eng}} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} \tag{38}$$

The efficiency of the engine is the ratio of the work done by the heat provided:

$$\eta \equiv \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} \tag{39}$$

Carnot (*Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*, 1824) was the first to realize that maximum efficiency is attained for a *reversible engine* in which $\Delta S_{\text{eng}} = 0$. From (38) this implies that the maximum possible efficiency of a heat engine is:

$$\eta_C = 1 - \frac{T_C}{T_H} \tag{40}$$

Note that it depends *only* on the temperatures of teh cold and hot sources. Hence, given T_C, it is advantageous to have an engine functioning at the highest possible temperatures. Importantly however, it should be noted that reversibility implies that the process is infinitely slow (quasi-static) and hence that *a Carnot engine delivers zero power* !

The schematic functioning of a Carnot engine over a full cycle of operation is depicted in Fig. 2 in (p, V) and (S, T) variables.

The fact that the reversible Carnot engine provides the maximum possible efficiency is illustrated/demonstrated on Fig. 3. By virtue of the second principle of thermodynamics, the temperature of the engine during one cycle can never exceed T_H (otherwise it cannot extract heat from the hot source and never go below T_C (otherwise it cannot reject heat to the cold source). Hence, the problem is to maximize $(Q_H - Q_C)/Q_C$ given these constraints and it is clear geometrically that the Carnot cycle is the answer.
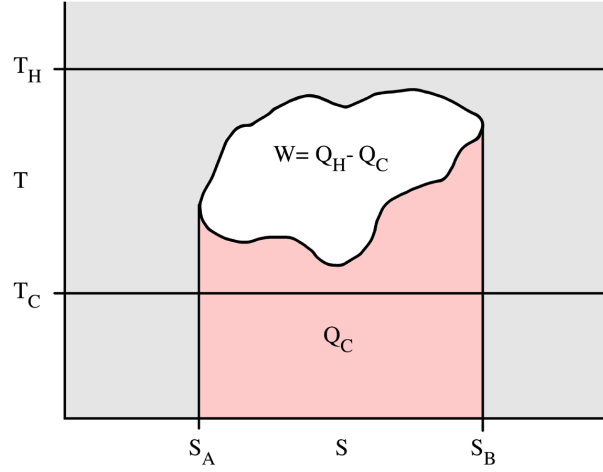
FIG. 3: Non-Carnot cycle: maximizing efficiency means maximizing the ratio of the white area to the total one subject to the constraints from the second principle of thermodynamics that the operating temperature remains between T_C and T_H.
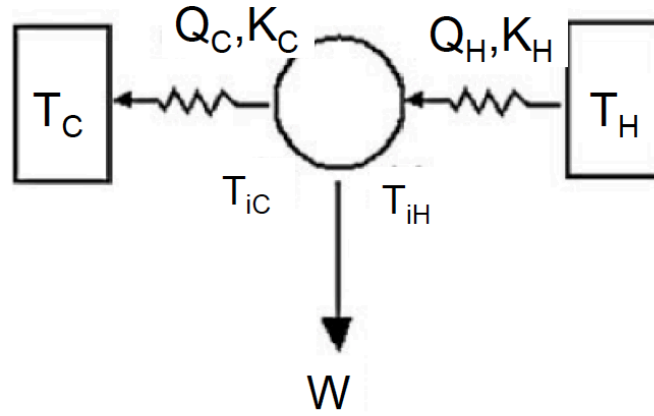

FIG. 4: An 'endoreversible' engine. The engine itself operates in a reversible manner between internal temperatures T_{iH} and T_{iC}. It is coupled to the heat reservoirs by finite thermal conductances $K_{H,C}$ and hence heat transfer between the engine and the reservoirs is irreversible.

B. Efficiency at maximum power: Chambadal-Novikov (-Curzon-Ahlborn), endoreversible engines

In order to go beyond Carnot's ideal efficiency analysis (corresponding to zero power output...), Paul Chambadal[3] and I. I. Novikov,[8] concerned with the efficiency of nuclear power plants, established in 1957 the efficiency at maximum power output of an 'endoreversible' engine (Fig. 4). This can be considered as the starting point of the field of so-called *finite-time thermodynamics*. The Chambadal-Novikov result has been rediscovered by Curzon and Ahlborn[4] in 1975. The presentation below follows Callen[2] and Lebon et al..[7]

Denoting by $K_{C,H}$ the thermal conductance coupling the engine to the heat reservoirs, the heat flow rates per unit time are given by:

$$\dot{Q}_H = K_H \left(T_H - T_{iH}\right) \ , \ \dot{Q}_C = K_H \left(T_{iC} - T_C\right) \tag{41}$$

Hence, assuming constant operating temperatures, the time corresponding to heat injection Q_H and heat rejection Q_C are:

$$t_H = \frac{Q_H}{K_H(T_H - T_{iH})} \quad , \quad t_H = \frac{Q_C}{K_C(T_{iC} - T_C)} \tag{42}$$

Hence, a total time of operation:

$$t = \frac{Q_H}{K_H(T_H - T_{iH})} + \frac{Q_C}{K_C(T_{iC} - T_C)} \quad , \quad P = \frac{W}{t} \tag{43}$$

We now use:

- The first-principle, stating that: $W = Q_H - Q_C$

- The endoreversibility of the engine itself, stating that the engine functions in a reversible manner and hence has Carnot efficiency: $Q_H/T_{iH} = Q_C/T_{iC}$ and $\eta = W/Q_H = 1 - T_{iC}/T_{iH}$

Introducing the variables $x_h \equiv T_{iH}/T_H$ (≤ 1) and $x_c \equiv T_{iC}/T_C$ (≥ 1), we can replace W, Q_H and Q_C to obtain the power and efficiency in the form:

$$P = \frac{x_h T_H - x_c T_C}{\frac{x_h}{K_H(1-x_h)} + \frac{x_c}{K_C(x_c-1)}} \quad , \quad \eta = 1 - \frac{T_C}{T_H}\frac{x_c}{x_h} \tag{44}$$

One can now extremalize the power with respect to x_c, x_h and obtain the following result for the efficiency at maximum power (Chambadal-Novikov efficiency):

$$\eta(P_{\max}) = 1 - \sqrt{\frac{T_C}{T_H}} \tag{45}$$

Remarkably, this expression *only depends on the ratio T_C/T_H, and not on the thermal conductances.* It is apparently a (much) more realistic estimate of the efficiency of actual engines (cf. Curzon-Ahlborn's article). Note that the CN-efficiency is half the Carnot efficiency in teh limit of an infinitesimal temperature gradient $T_H - T_C \ll T_C, T_H$.

The maximum power output is found to be:

$$P_{\max} = \frac{K_H K_C}{(\sqrt{K_H} + \sqrt{K_C})^2}\left[\sqrt{T_H} - \sqrt{T_C}\right]^2 \tag{46}$$

and:

$$T_{iH} = \sqrt{T^* T_H} \quad , \quad T_{iC} = \sqrt{T^* T_C} \quad , \quad \sqrt{T^*} \equiv \frac{\sqrt{K_H T_H} + \sqrt{K_C T_C}}{\sqrt{K_H} + \sqrt{K_C}} \tag{47}$$

C. Efficiency of thermoelectric energy conversion: general analysis, local form

Here, we shall investigate the efficiency defined above:

$$\eta_r \equiv \frac{-\boldsymbol{j}_n \cdot \boldsymbol{\nabla}\mu}{\boldsymbol{j}_s \cdot \boldsymbol{\nabla}T} = \frac{\boldsymbol{j}_e \cdot \boldsymbol{E}}{\boldsymbol{j}_s \cdot \boldsymbol{\nabla}T} \tag{48}$$

Let us recall that this is a relative efficiency with respect to a reversible Carnot process (which would then correspond to $\eta_r = 1$), and that it is a local definition, for infinitesimal gradients.

The idea is to study η_r as a function of the ratio between conjugate forces $\nabla\mu/\nabla T$. We shall actually consider the dimensionless parameter:
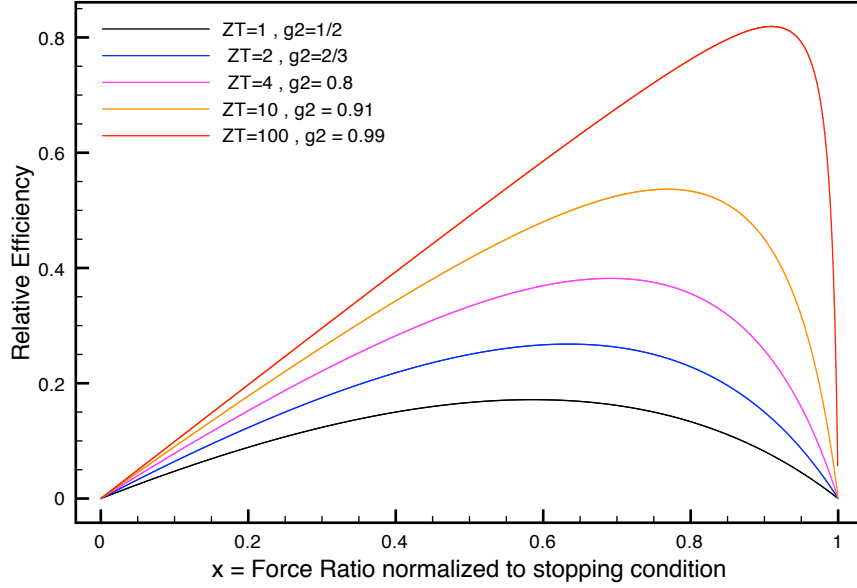
$$x \equiv \frac{E}{\alpha \nabla T} \tag{49}$$

FIG. 5: Relative efficiency vs. dimensionless force ratio, for different values of the dimensionless figure of merit (coupling)

This can be viewed as the force ratio normalized to the 'stopping' value at which current flow vanishes (i.e. the Seebeck value): $x = E/E_{stop}$.

Using:

$$\begin{pmatrix} \boldsymbol{j}_e \\ \boldsymbol{j}_s \end{pmatrix} = \begin{pmatrix} \sigma & \alpha\sigma \\ \alpha\sigma & \frac{\kappa}{T}(1+\overline{z}) \end{pmatrix} \begin{pmatrix} \boldsymbol{E} \\ -\boldsymbol{\nabla}T \end{pmatrix} \tag{50}$$

we obtain:

$$\alpha \frac{j_e}{j_s} = \frac{x-1}{x-(1+\overline{z})/\overline{z}} \tag{51}$$

and hence (using the dimensionless coupling g introduced above):

$$\eta_r = \frac{x(x-1)}{x-(1+\overline{z})/\overline{z}} = \frac{x(x-1)}{x-1/g^2} \quad , \quad g^2 \equiv \frac{\overline{z}}{1+\overline{z}} \tag{52}$$

This is plotted in Fig. 5

Differentiating, we can obtain the value of the force ratio $x = x_{max} \geq 1/2$ which maximizes the efficiency, and corresponding value of η_r:

$$\eta_r^{max} = \frac{\sqrt{\overline{z}+1}-1}{\sqrt{\overline{z}+1}+1} = \frac{1-\sqrt{1-g^2}}{1+\sqrt{1+g^2}} \quad , \quad x_{max} = \frac{1}{\overline{z}}\left[\overline{z}+1-\sqrt{\overline{z}+1}\right] = \frac{1-\sqrt{1-g^2}}{g^2} \tag{53}$$

We can also calculate the electrical power (sign convention: such that $p > 0$ - clarify):

$$p = -\boldsymbol{j}_e \cdot \boldsymbol{E} = -\sigma\boldsymbol{E}^2 + \alpha\sigma\boldsymbol{E} \cdot \boldsymbol{\nabla}T = \overline{z}\frac{\kappa}{T}(\nabla T)^2\, x(1-x) \tag{54}$$

Hence, we see that the maximum power is always reached for $x = 1/2$, half of the stopping (Seebeck) field. The maximum power is:

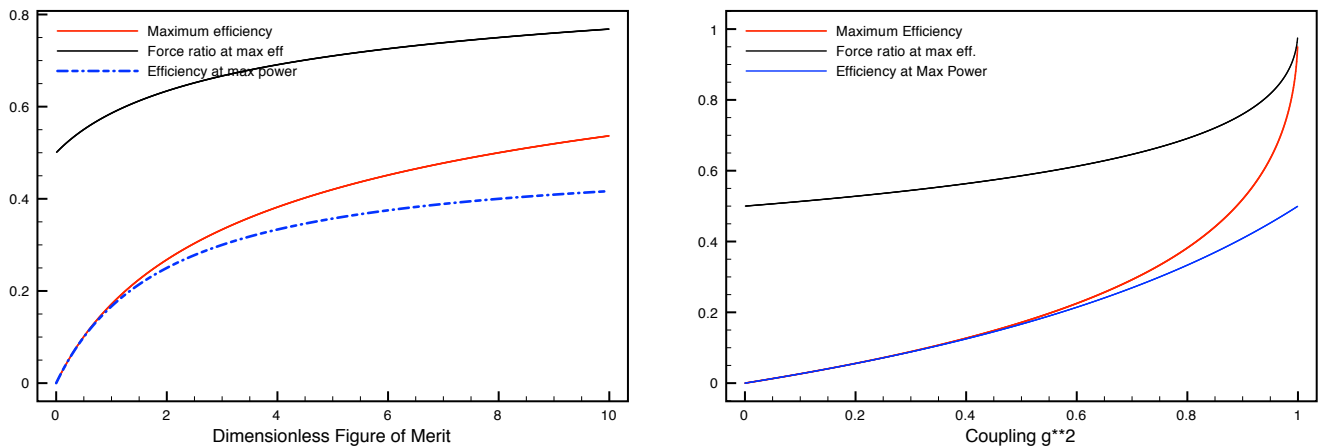$$p_{max} = \frac{\overline{z}}{4}\frac{\kappa}{T}(\nabla T)^2 = \frac{\alpha^2\sigma}{4}(\nabla T)^2 \tag{55}$$

FIG. 6: Maximum efficiency and efficiency at maximum power as a function of (Left) the dimensionless figure of merit in the range $\overline{z} \leq 10$ and (Right) the coupling $g^2 = \overline{z}/(\overline{z}+1)$ in the full range.

We see that it is directly set by the combination $\alpha^2 \sigma$, named for this reason *'power factor'* in the field of thermoelectrics. The corresponding efficiency at maximum power is:

$$\eta_r(p_{max}) = \frac{\overline{z}}{2(2+\overline{z})} = \frac{g^2}{2(2-g^2)} \tag{56}$$

We observe that it tends to exactly *half of the Carnot efficiency* in the endoreversible limit $\overline{z} \to \infty$ ($g^2 \to 1$). This precisely corresponds to the Chambadal-Novikov-Curzon-Ahlborn result, in the limit of infinitesimal gradients, since $1 - \sqrt{T_c/T_h} \sim \eta_C/2$ with $\eta_C = 1 - T_c/T_h \sim \Delta T/T_c$ in this limit.

Finally, we can also eliminate the force ratio, and establish an efficiency vs. power plot. We define the power normalized to its maximum value:

$$\overline{p} \equiv \frac{p}{p_{max}} = 4x(1-x) \tag{57}$$

and invert:

$$x = \frac{1}{2}\left[1 \pm \sqrt{1-\overline{p}}\right] \tag{58}$$

with the upper (+) sign for $x \geq 1/2$ and the lower (−) one for $x \leq 1/2$. Inserting this into the expression of η_r, we obtain two branches:

$$\eta_r = \frac{\overline{p}}{2 + 4/\overline{z} \pm 2\sqrt{1-\overline{p}}} \quad , \quad (+ : x \leq 1/2 \ , \ - : x \geq 1/2) \tag{59}$$

D.   Generality

The analysis of the previous section is completely general[11] and applies to any energy-transformation process, with $x = (X_1/X_2)/(X_1/X_2)_{stop}$ the normalized ratio of forces and $g^2 = L_{12}^2/L_{11}L_{22}$. Applications to biophysics (e.g. ADP/ATP conversion) or climate science can be found in the literature (see e.g. [7,11] for references).

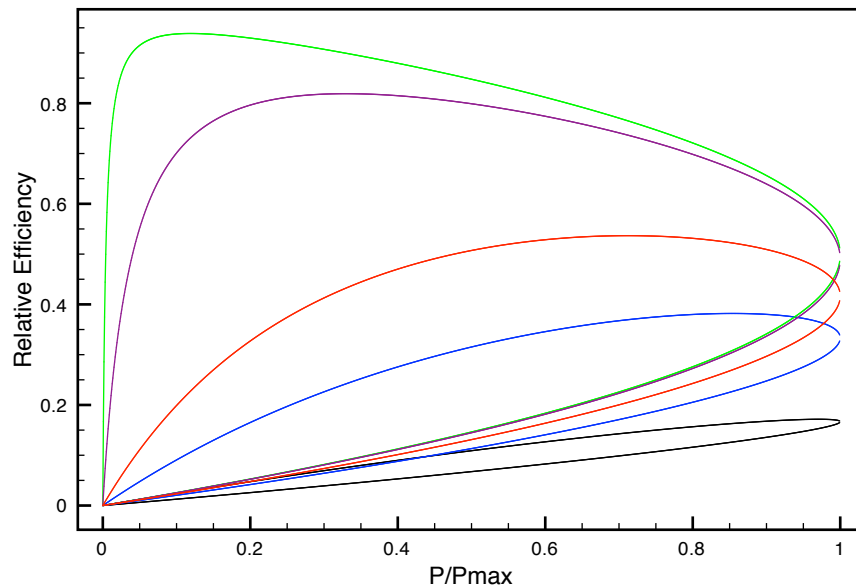[1] N. W. Ashcroft and N. D. Mermin, *Solid-state physics*, Saunders, 1976.

FIG. 7: Relative efficiency vs. power normalized to its maximum value, for (bottom to top): $\bar{z} = 1, 4, 10, 100, 1000$. 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.

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