THERMOELECTRICITE: CONCEPTS, MATERIAUX ET ENJEUX ENERGETIQUES

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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
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):

\[ s = -\frac{\partial \Omega}{\partial T}|_\mu \quad , \quad n = -\frac{\partial \Omega}{\partial \mu}|_T \]

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 (2\textsuperscript{nd} principle of thermo.) implies that $L$ is a positive semi-definite matrix (see later).

This amounts to:

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

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

$$\bar{\mu}(r) = \mu(r) + q V(r), \quad \bar{V}(r) = V(r) + \frac{1}{q} \mu(r)$$

(5)

$\bar{\mu}$ is called the *electrochemical potential*. In any experiment, only the total voltage drop arising from $\bar{V}(r)$ can be measured, not separately $\nabla V$ and $\nabla \mu$. The energy we need to give to the system to add one particle is $\mu$, the electrostatic energy to add one extra charge $q$ is $q \bar{V}$. Hence, it is actually convenient to forget about the scalar potential $V(r)$, and consider only $\bar{\mu}(r)$. 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 $\mu$. The measured electric field can be obtained as:

$$\mathbf{E} \equiv -\nabla \bar{V}(r) = -\frac{1}{q} \nabla \bar{\mu} = \frac{1}{e} \nabla \mu = -\nabla V - \frac{1}{q} \nabla \mu$$

(6)

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

In practice, electric field: $$\vec{E} = \frac{1}{e} \nabla \mu$$
Electrical and heat currents:

\[ \vec{j}_e = q \vec{j}_n \quad (q = -e) \]

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:
\[ j_n = 0 \Rightarrow j_Q = \kappa(-\nabla T) \]

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

(no particle current)
Seebeck and Peltier coefficients:

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

   \[ j_e = 0 \Rightarrow \vec{E} = \alpha \vec{\nabla}T \quad , \quad \alpha \equiv \frac{L_{12}}{qL_{11}} \]

2. **Peltier effect**: electrical current induces heat current

   \[ \nabla T = 0 \Rightarrow j_Q = \Pi j_e \quad , \quad \Pi \equiv T \frac{L_{21}}{qL_{11}} \]

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 \( \mu \))
Conductivity matrix:

\[
\begin{pmatrix}
  j_e \\
  j_Q
\end{pmatrix} = \sigma \begin{pmatrix}
  E \\
  -\nabla T
\end{pmatrix}, \quad \sigma = \begin{pmatrix}
  \sigma & \alpha \sigma \\
  T \alpha \sigma & \kappa (1 + \bar{z})
\end{pmatrix}
\]

Dimensionless figure of merit:

\[
\bar{z} \equiv T \frac{\alpha^2 \sigma}{\kappa}
\]

Note: \[\text{det}\sigma = \sigma \kappa\]
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 $[j_X] = [X]/[\text{time}[\text{length}]]^2$. Hence:

- Conductivity $\sigma$ has dimension $\Omega^{-1} m^{-1}$. A good metal has a resistivity of order $1 \mu\Omega \text{cm}$, diamond has $10^{20} \mu\Omega \text{cm}$

- Seebeck has dimension $\text{Field \cdot Length/\text{Temperature}} = \text{Energy/\text{Temperature}}$, hence the unit of $k_B/e$. We note that:

$$\frac{k_B}{e} = 86.3 \mu V K^{-1}$$  \hspace{1cm} (18)

- Thermal conductivity has dimension $\text{Energy}/[\text{Length}^2 \times \text{Time}] \times [\text{Length/\text{Temperature}}] = [\text{Power}]/[\text{Length} \times \text{Temperature}]$. 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 $\kappa$ of order $10^{-2} - 10^{-3}$. Glass is $O(1)$. 
Conductivité thermique : ordre de grandeur à T = 300 K

Matériaux cristallins ou amorphes

Métaux purs

Pu (5.2)

Pt (72)

Al (237)

Ag (436)

Semi-conducteurs (faible et large gap)

Bi₂Te₃ (2.0)

Ge (60)

Si (150)

Diamant (2000)

Alliages métalliques

S (0.27)

Verre

Glace

Oxydes

Solides non métalliques

Mousses

Fibres

Isolants

Huiles

H₂O (0.61)

H₂ (0.18)

Liquides

O₂ (0.03)

Gaz

Conductivité thermique (W/mK)

From: B. Lenoir, GDR Thermoelectricité summer school 2012
Effet Seebeck : ordre de grandeur à 300 K

From: B.Lenoir, GDR Thermoelectricite summer school 2012
Coupling constant characterizing energy conversion:

\[ g \equiv \frac{L_{12}}{\sqrt{L_{11}L_{22}}} , \quad g^2 = \frac{\bar{z}}{1 + \bar{z}} \]

\[ \det L \geq 0 \implies -1 \leq g \leq +1 \]
Entropy and heat production rates

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

\[
\frac{\partial s}{\partial t}_{prod} \equiv \frac{\partial s}{\partial s} + \nabla \cdot \mathbf{j}_s = \frac{1}{T} \mathbf{G} \cdot \mathbf{L} \mathbf{G}
\]

\[
\mathbf{G} \equiv \left( \begin{array}{c} -\nabla \mu \\ -\nabla T \end{array} \right)
\]

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

\[
\dot{Q} \approx \rho j_e^2 + \frac{\partial \kappa}{\partial T} (\nabla T)^2 - T \frac{\partial \alpha}{\partial T} j_e \cdot \nabla T
\]

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

\[\frac{\partial \alpha}{\partial T} \quad \text{: Thomson coefficient}\]
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:

- **$T_H$**
- **$Q_H$**
- **$Q_C$**
- **$T_C$**
- **$W$**
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 2$^{nd}$ 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 Polytechnique 1753-1823

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

\[ \eta(P_{\text{max}}) = 1 - \sqrt{\frac{T_C}{T_H}} \]

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

Chambadal-Novikov efficiency
TABLE I. Observed performance of real heat engines.

<table>
<thead>
<tr>
<th>Power source</th>
<th>$T_2$ (°C)</th>
<th>$T_1$ (°C)</th>
<th>$\eta$  (Carnot)</th>
<th>$\eta'$ (Eq. 14)</th>
<th>$\eta$ (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Thurrock (U.K.) Coal Fired Steam Plant</td>
<td>$\sim25$</td>
<td>565</td>
<td>64.1%</td>
<td>40%</td>
<td>36%</td>
</tr>
<tr>
<td>CANDU (Canada) PHW Nuclear Reactor</td>
<td>$\sim25$</td>
<td>300</td>
<td>48.0</td>
<td>28%</td>
<td>30%</td>
</tr>
<tr>
<td>Larderello (Italy) Geothermal Steam Plant</td>
<td>80</td>
<td>250</td>
<td>32.3%</td>
<td>17.5%</td>
<td>16%</td>
</tr>
</tbody>
</table>
$x = \text{Force Ratio normalized to stopping condition}$

$ZT=1, g2=1/2$
$ZT=2, g2=2/3$
$ZT=4, g2=0.8$
$ZT=10, g2 = 0.91$
$ZT=100, g2 = 0.99$
Dimensionless Figure of Merit

- Maximum efficiency
- Force ratio at max eff
- Efficiency at max power
FIG. 4: 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.