2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 24

Room 3-442
Tuesday, May 7, 2:30pm - 4:30pm

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Onsager nonequilibrium cross effects and the Curie symmetry principle

Each flux may be a function of all the forces, $\underline{\boldsymbol{J}}_i = \underline{\boldsymbol{J}}_i(\{\underline{\boldsymbol{X}}_k\})$, however, (Pierre Curie,1894): **the symmetry of the cause is preserved in its effects**. Therefore, e.g., **in isotropic conditions**, fluxes and forces of different tensorial character cannot couple.

	Force	Y_k	$-\frac{1}{T}\underline{\nabla}\cdot\underline{v}_m$	$-\frac{1}{T^2}\underline{\nabla}T$	$-\frac{1}{T}\underline{\nabla}\mu_{i,T}$	$-\frac{1}{T}\underline{\nabla}\varphi$	$\frac{1}{T}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\mathrm{T}})'$
Flux	$\odot$	$\times$	$\times$	$\cdot$	$\cdot$	$\cdot$	$:$
r_k	$\times$	chemical kinetics	$\boxtimes$				
$p_m - p$	$\times$	$\boxtimes$	Lamb 1879				
$\underline{q}''$	$\cdot$			Fourier 1822	Dufour 1872	Peltier 1834	
$\underline{J}_{n_i}$	$\cdot$			Soret 1879	Fick 1855	Reuss 1807	
$\underline{J}_q$	$\cdot$			Seebeck[1] 1821	Quincke 1859	Ohm 1827	
$\underline{\underline{\tau}}'$	$:$						Navier 1821

1 : First discovered by Volta (1787) and later rediscovered by Seebeck.

Only a fraction of J_E is q'' in a "heat&diffusion" interaction

If constituents carry electric charge $\quad \mu_i \to \mu_{i,\text{tot}} = \mu_i + z_i F \varphi$

$$\mathbf{J}_E = T\mathbf{J}_S + \sum_i \mu_i \mathbf{J}_{n_i} \to \mathbf{J}_E = T\mathbf{J}_S + \sum_i \mu_{i,\text{tot}} \mathbf{J}_{n_i} = T\mathbf{J}_S + \sum_i \mu_i \mathbf{J}_{n_i} + \varphi \mathbf{I}''$$

Use $\mu_i = h_i - T s_i$ and (*) $\quad \mathbf{I}'' = F \sum_i z_i \mathbf{J}_{n_i}$

rewrite as $\mathbf{q}'' = \mathbf{J}_E - \sum_i h_i \mathbf{J}_{n_i} - \varphi \mathbf{I}'' = T\left(\mathbf{J}_S - \sum_i s_i \mathbf{J}_{n_i}\right)$

Therefore

$$\mathbf{J}_E = \mathbf{q}'' + \sum_i h_i \mathbf{J}_{n_i} + \varphi \mathbf{I}''$$

$$\mathbf{J}_S = \frac{\mathbf{q}''}{T} + \sum_i s_i \mathbf{J}_{n_i}$$

(*) Partial charge flux due to the diffusion of component i: $\quad \mathbf{I}_i'' = z_i F \mathbf{J}_{n_i}$

(*) Total charge flux (current density):

$$\mathbf{I}'' = \sum_i \mathbf{I}_i'' = \sum_i z_i F \mathbf{J}_{n_i}$$

Relation between independent diffusive fluxes in heat&diffusion interactions

- Recall the local simple-system equilibrium assumption,

$$E = U(S,V,\boldsymbol{n}) + \tfrac{1}{2}mv_m^2 + mgz + q\varphi - \tfrac{1}{2}m\omega^2\mathrm{r}^2 \qquad m = V\textstyle\sum_i c_i M_i \qquad q = V\textstyle\sum_i c_i z_i F$$

$$\mu_i^{\rm tot} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,\boldsymbol{n}_i',v_m,z,\varphi,\omega,\mathrm{r}} = \mu_i + \tfrac{1}{2}M_i v_m^2 + M_i g z + z_i F\,\varphi - \tfrac{1}{2}M_i\omega^2\mathrm{r}^2 = \mu_i + e_i - u_i$$

where the last equality defines the **partial energy** $e_i = u_i + \mu_i^{\rm tot} - \mu_i$ and is justified by recalling the general relation $U = \sum_i n_i u_i = V\sum_i c_i u_i$ and rewriting the energy as

$$E = \rho e^* V = V\textstyle\sum_i c_i\left(u_i + \tfrac{1}{2}M_i v_m^2 + M_i\varphi_g + z_i F\,\varphi - \tfrac{1}{2}M_i\omega^2\mathrm{r}^2\right) = \sum_i c_i e_i = \sum_i c_i(u_i + \mu_i^{\rm tot} - \mu_i)$$

with $e_i^* = e_i/M_i$, $u_i^* = u_i/M_i$ the relation $e_i - u_i = \tfrac{1}{2}M_i v_m^2 + M_i g z + z_i F\,\varphi - \tfrac{1}{2}M_i\omega^2\mathrm{r}^2$ becomes

$$e_i^* - u_i^* = \tfrac{1}{2}v_m^2 + gz + z_i F\,\varphi/M_i - \tfrac{1}{2}\omega^2\mathrm{r}^2 \quad\Rightarrow\quad (e_i^* - u_i^*) - (e_r^* - u_r^*) = (z_i/M_i - z_r/M_r)F\,\varphi$$

- Recall, $\underline{J}_{m_i} = M_i \underline{J}_{n_i}$, $\underline{J}_m = \sum_i M_i \underline{J}_{n_i} = \sum_i \underline{J}_{m_i} = 0$ so the fluxes are not all independent and we can write $\underline{J}_{m_r} = -\sum_{i=1}^{r-1}\underline{J}_{m_i}$. Also recall: $\mu_i = h_i - T\,s_i$, $\underline{J}_q = F\sum_i z_i \underline{J}_{n_i}$, $\mu_i^{*\rm tot} = \mu_i^{\rm tot}/M_i$.
- So, the relation **for heat&diffusion interactions** may be written in several equivalent forms

$$\begin{aligned}
\underline{J}_E^{\rm nw} &= T\,\underline{J}_S + \textstyle\sum_i \mu_i^{\rm tot}\,\underline{J}_{n_i} = T\,\underline{J}_S + \sum_i \mu_i^{*\rm tot}\,\underline{J}_{m_i}\\
&= T\,\underline{J}_S + \textstyle\sum_{i=1}^{r-1}(\mu_i^{*\rm tot} - \mu_r^{*\rm tot})\,\underline{J}_{m_i}\\
&= T\,\underline{J}_S + \textstyle\sum_{i=1}^{r-1}(\mu_i^* - \mu_r^*)\,\underline{J}_{m_i} + \varphi\underline{J}_q\\
&= T\left[\underline{J}_S - \textstyle\sum_{i=1}^{r-1}(s_i^* - s_r^*)\,\underline{J}_{m_i}\right] + \sum_{i=1}^{r-1}(h_i^* - h_r^*)\,\underline{J}_{m_i} + \varphi\underline{J}_q\\
&= \underbrace{T\left[\underline{J}_S - \textstyle\sum_{i=1}^{r-1}(s_i - s_r)\,\underline{J}_{n_i}\right]}_{\underline{q}''} + \sum_{i=1}^{r-1}(h_i - h_r)\,\underline{J}_{n_i} + \varphi\underline{J}_q
\end{aligned}$$

$\underline{q}''$ (definition of **measurable heat flux**)

$$\underline{J}_E^{\rm nw} = \underline{q}'' + \textstyle\sum_{i=1}^{r-1}(h_i - h_r)\,\underline{J}_{n_i} + \varphi\underline{J}_q$$

$$\underline{J}_S = \frac{\underline{q}''}{T} + \textstyle\sum_{i=1}^{r-1}(s_i - s_r)\,\underline{J}_{n_i}$$

Electromagnetic radiation: a carrier of energy and entropy

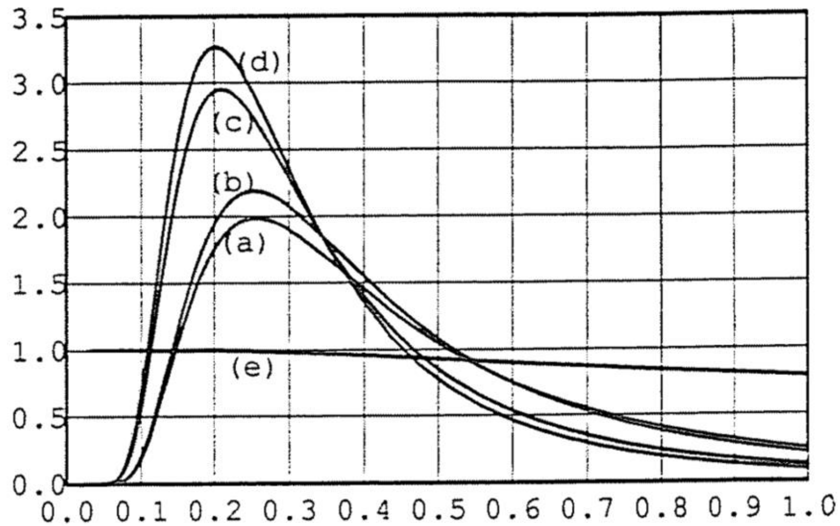

Fig. 3 Graphs as functions of $y = \lambda kT/hc$. The area under each of the curves (*a*), (*b*), (*c*), and (*d*) is unity. The maxima occur respectively at (*a*) $y = 0.201405$, (*b*) $y = 0.208713$. (*c*) $y = 0.252417$, and (*d*) $y = 0.255057$.

$$\frac{hc}{kT}\frac{u_\lambda}{u} = \frac{15}{\pi^4}\frac{1/y^5}{e^{1/y}-1} \quad (a)$$

$$\frac{hc}{kT}\frac{s_\lambda}{s} = \frac{45}{4\pi^4}\frac{1}{y^4}\left(\frac{1/y}{e^{1/y}-1} + \ln\frac{1}{1-e^{-1/y}}\right) \quad (b)$$

$$\frac{hc}{kT}\frac{p_\lambda}{p} = \frac{45}{\pi^4}\frac{1}{y^4}\ln\frac{1}{1-e^{-1/y}} \quad (c)$$

$$\frac{hc}{kT}\frac{n_\lambda}{n} = \frac{1}{2\zeta(3)}\frac{1/y^4}{e^{1/y}-1} \quad (d)$$

$$\frac{p_\lambda}{n_\lambda kT} = (e^{1/y}-1)\ln\frac{1}{1-e^{-1/y}} \quad (e)$$

$$J_u^{A\to B} = \sigma(T_A^4 - T_B^4)$$

$$J_s^{A\to B} = \frac{4}{3}\sigma(T_A^3 - T_B^3)$$

$$J_n^{A\to B} = \frac{30\zeta(3)}{\pi^4 k}\sigma(T_A^3 - T_A^3) = \frac{1}{0.27766\,k}J_S^{A\to B}$$

$$J_{u_\nu}^{A\to B} = \frac{2\pi h\nu^3}{c^2}\left[\frac{1}{\exp(h\nu/kT_A)-1} - \frac{1}{\exp(h\nu/kT_B)-1}\right]$$

$$J_{s_\nu}^{A\to B} = \frac{2\pi k\nu^2}{c^2}\left[\frac{h\nu/kT_A}{\exp(h\nu/kT_A)-1} - \frac{h\nu/kT_B}{\exp(h\nu/kT_B)-1} + \ln\frac{1-\exp(-h\nu/kT_B)}{1-\exp(-h\nu/kT_A)}\right]$$

$$J_{n_\nu}^{A\to B} = \frac{2\pi\nu^2}{c^2}\left[\frac{1}{\exp(h\nu/kT_A)-1} - \frac{1}{\exp(h\nu/kT_B)-1}\right] = \frac{J_{u_\nu}^{A\to B}}{h\nu}$$

$\sigma = ca/4 = 2\pi^5 k^4/15h^3c^2 = 5.67083\times10^{-8}$ W/m^{2}K^4

$30\zeta(3)\sigma/\pi^4 k = 1.52057\times10^{15}$ 1/m^{2}sK^3

G.P. Beretta and E.P. Gyftopoulos, Electromagnetic Radiation: A Carrier of Energy and Entropy, Journal of Energy Resources Technology, Vol. 137, 021005 (2015).

$\boldsymbol{\sigma}$ in terms of relative diffusive fluxes and forces

$$\sigma = -\frac{1}{T^2}\underline{q}''\cdot\underline{\nabla}T - \frac{1}{T}\sum_{i=1}^r \underline{J}_{n_i}\cdot\underline{\nabla}\mu_i|_T - \frac{1}{T}(\underline{I}''-\rho_q\,\underline{v}_m)\cdot\underline{\nabla}\varphi + \sum_k r_k Y_k + \Phi/T$$

Rewrite the second term as follows

$$\frac{1}{T}\sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\mu_i|_T = \frac{1}{T}\sum_i \frac{\underline{J}_{n_j}}{c}\cdot\underline{\nabla}p + \frac{1}{T}\sum_i\sum_j \frac{c_i c_j}{c}\frac{\underline{J}_{n_i}}{c_i}\cdot\underline{\nabla}(\mu_i-\mu_j)|_T$$

$$= \frac{1}{T}\frac{\underline{J}_n}{c}\cdot\underline{\nabla}p + \frac{1}{2T}\sum_{ij}\frac{c_i c_j}{c}\left[\frac{\underline{J}_{n_i}}{c_i} - \frac{\underline{J}_{n_j}}{c_j}\right]\cdot\underline{\nabla}(\mu_i-\mu_j)|_T$$

$$= \frac{1}{T}\frac{\underline{J}_n}{c}\cdot\underline{\nabla}p + \frac{1}{2T}\sum_{ij}\underline{J}_{ij}\cdot\underline{\nabla}(\mu_i-\mu_j)|_T = \frac{1}{T}\frac{\underline{J}_n}{c}\cdot\underline{\nabla}p - \frac{1}{2}\sum_{ij}\underline{J}_{ij}\cdot\underline{X}_{ij}$$

- In the first step we used the relation $\underline{\nabla}\mu_i|_T = \frac{1}{c}\underline{\nabla}p + \sum_j \frac{c_j}{c}\underline{\nabla}(\mu_i-\mu_j)|_T$ which follows from the Gibbs-Duhem relation $\underline{\nabla}p = \sum_{i=1}^r c_i\,\underline{\nabla}\mu_i|_T$ by noting that given a relation $\underline{b} = \sum_j c_j \underline{Z}_j$ with $c = \sum_j c_j$ it is easy to verify that $c\underline{Z}_i = \underline{b} + \sum_j(\underline{Z}_i - \underline{Z}_j)c_j$.
- In the second step we used the following (easy to verify) identity:

$$\sum_i\sum_j a_i a_j \underline{V}_i\cdot(\underline{Z}_i-\underline{Z}_j) = \tfrac{1}{2}\sum_i\sum_j a_i a_j(\underline{V}_i-\underline{V}_j)\cdot(\underline{Z}_i-\underline{Z}_j)$$

- In the third step we defined the **diffusive flux of i particles relative to j particles** and in the fourth step its **conjugate diffusive force** (degree of disequilibrium)

$$\underline{J}_{ij} = \frac{c_i c_j}{c}\left[\frac{\underline{J}_{n_i}}{c_i} - \frac{\underline{J}_{n_j}}{c_j}\right] = -\underline{J}_{ji} \qquad\qquad \underline{X}_{ij} = -\frac{1}{T}\underline{\nabla}(\mu_i-\mu_j)|_T = -\underline{X}_{ji}$$

So, **for no flow ($\underline{v}_m = 0$, $\Phi = 0$), uniform pressure ($\underline{\nabla}p = 0$), and no chemical reactions**

$$\boxed{\sigma = \underline{q}''\cdot\underline{\nabla}\frac{1}{T} + \frac{1}{2}\sum_{ij}\underline{J}_{ij}\cdot\underline{X}_{ij} - \frac{1}{T}\underline{I}''\cdot\underline{\nabla}\varphi} \qquad \underline{J}_{n_i} = \frac{1}{M}\sum_j M_j \underline{J}_{ij} \quad \text{from } \underline{J}_m = \sum_i M_i J_{n_i} = 0$$

Nonequilibrium in heat, mass, and charge transfer

Thermo-electric effects

Thermoelectric effects in solid conductors

$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} - \frac{1}{T} \underline{I}'' \cdot \underline{\nabla} \varphi = \underline{q}'' \cdot \underline{\nabla} \tau + \underline{I}'' \cdot (-\tau \underline{\nabla} \varphi)$$

- Assume linear force-flux relations

$$\begin{cases} \underline{q}'' = \underline{\underline{L}}_{11} \cdot \underline{\nabla} \tau + \underline{\underline{L}}_{12} \cdot (-\tau \underline{\nabla} \varphi) \\ \underline{I}'' = \underline{\underline{L}}_{21} \cdot \underline{\nabla} \tau + \underline{\underline{L}}_{22} \cdot (-\tau \underline{\nabla} \varphi) \end{cases}$$

Thermoelectric effects in solid conductors

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$$\begin{cases} -\underline{\nabla}\varphi = \dfrac{\underline{\underline{L}}_{22}^{-1}}{\tau} \cdot (\underline{I}'' - \underline{\underline{L}}_{21} \cdot \underline{\nabla}\tau) = \dfrac{1}{T}\underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21} \cdot \underline{\nabla}T + T\underline{\underline{L}}_{22}^{-1} \cdot \underline{I}'' \\ \underline{q}'' = -\dfrac{1}{T^2}(\underline{\underline{L}}_{11} - \underline{\underline{L}}_{21} \cdot \underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21}) \cdot \underline{\nabla}T + \underline{\underline{L}}_{12} \cdot \underline{\underline{L}}_{22}^{-1} \cdot \underline{I}'' \end{cases}$$

Thermoelectric effects in solid conductors

$$\sigma = \underline{q}'' \cdot \underline{\nabla}\frac{1}{T} - \frac{1}{T}\underline{I}'' \cdot \underline{\nabla}\varphi = \underline{q}'' \cdot \underline{\nabla}\tau + \underline{I}'' \cdot (-\tau\underline{\nabla}\varphi)$$

- Assume linear force-flux relations

$$\begin{cases} \underline{q}'' = \underline{\underline{L}}_{11} \cdot \underline{\nabla}\tau + \underline{\underline{L}}_{12} \cdot (-\tau\underline{\nabla}\varphi) \\ \underline{I}'' = \underline{\underline{L}}_{21} \cdot \underline{\nabla}\tau + \underline{\underline{L}}_{22} \cdot (-\tau\underline{\nabla}\varphi) \end{cases}$$

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$$\begin{cases} -\underline{\nabla}\varphi = \underline{\underline{\varepsilon}} \cdot \underline{\nabla}T + \underline{\underline{r}} \cdot \underline{I}'' \\ \underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla}T + \underline{\underline{\Pi}} \cdot \underline{I}'' \end{cases}$$

$$\underline{\underline{\varepsilon}} = \frac{1}{T}\underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21} \qquad \underline{\underline{r}} = T\underline{\underline{L}}_{22}^{-1}$$

$$\underline{\underline{k}} = \frac{1}{T^2}(\underline{\underline{L}}_{11} - \underline{\underline{L}}_{21} \cdot \underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21}) \qquad \underline{\underline{\Pi}} = \underline{\underline{L}}_{12} \cdot \underline{\underline{L}}_{22}^{-1}$$

Thermoelectric effects in solid conductors

$$\sigma = \underline{q}'' \cdot \underline{\nabla}\frac{1}{T} - \frac{1}{T}\underline{I}'' \cdot \underline{\nabla}\varphi = \underline{q}'' \cdot \underline{\nabla}\tau + \underline{I}'' \cdot (-\tau\underline{\nabla}\varphi)$$

- Assume linear force-flux relations

$$\begin{cases} \underline{q}'' = \underline{\underline{L}}_{11} \cdot \underline{\nabla}\tau + \underline{\underline{L}}_{12} \cdot (-\tau\underline{\nabla}\varphi) & = -\dfrac{\underline{\underline{L}}_{11}}{T^2} \cdot \underline{\nabla}T - \dfrac{\underline{\underline{L}}_{12}}{T} \cdot \underline{\nabla}\varphi \\ \underline{I}'' = \underline{\underline{L}}_{21} \cdot \underline{\nabla}\tau + \underline{\underline{L}}_{22} \cdot (-\tau\underline{\nabla}\varphi) & = -\dfrac{\underline{\underline{L}}_{21}}{T^2} \cdot \underline{\nabla}T - \dfrac{\underline{\underline{L}}_{22}}{T} \cdot \underline{\nabla}\varphi \end{cases}$$

$$\begin{cases} -\underline{\nabla}\varphi = \dfrac{\underline{\underline{L}}_{22}^{-1}}{\tau} \cdot (\underline{I}'' - \underline{\underline{L}}_{21} \cdot \underline{\nabla}\tau) = \dfrac{1}{T}\underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21} \cdot \underline{\nabla}T + T\underline{\underline{L}}_{22}^{-1} \cdot \underline{I}'' \\ \underline{q}'' = -\dfrac{1}{T^2}(\underline{\underline{L}}_{11} - \underline{\underline{L}}_{12} \cdot \underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21}) \cdot \underline{\nabla}T + \underline{\underline{L}}_{12} \cdot \underline{\underline{L}}_{22}^{-1} \cdot \underline{I}'' \end{cases}$$

$$\begin{cases} -\underline{\nabla}\varphi = \underline{\underline{\varepsilon}} \cdot \underline{\nabla}T + \underline{\underline{r}} \cdot \underline{I}'' \\ \underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla}T + \underline{\underline{\Pi}} \cdot \underline{I}'' \end{cases}$$

$$\underline{\underline{\varepsilon}} = \frac{1}{T}\underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21} \qquad \underline{\underline{r}} = T\underline{\underline{L}}_{22}^{-1}$$

$$\underline{\underline{k}} = \frac{1}{T^2}(\underline{\underline{L}}_{11} - \underline{\underline{L}}_{12} \cdot \underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{21}) \qquad \underline{\underline{\Pi}} = \underline{\underline{L}}_{12} \cdot \underline{\underline{L}}_{22}^{-1}$$

Onsager reciprocity implies

$$\underline{\underline{L}} = \begin{Bmatrix} \underline{\underline{L}}_{11} & \underline{\underline{L}}_{12} \\ \underline{\underline{L}}_{21} & \underline{\underline{L}}_{22} \end{Bmatrix} = \underline{\underline{L}}^{\mathrm{T}}$$

$$\underline{\underline{L}}_{ij} = \underline{\underline{L}}_{ji}^{\mathrm{T}} \quad \text{and} \quad \underline{\underline{L}}_{12} = \underline{\underline{L}}_{21}$$

$$\Rightarrow \quad \underline{\underline{\Pi}}^{\mathrm{T}} = (\underline{\underline{L}}_{12} \cdot \underline{\underline{L}}_{22}^{-1})^{\mathrm{T}} = (\underline{\underline{L}}_{22}^{-1})^{\mathrm{T}} \cdot \underline{\underline{L}}_{12}^{\mathrm{T}} = \underline{\underline{L}}_{22}^{-1} \cdot \underline{\underline{L}}_{12} = T\,\underline{\underline{\varepsilon}}$$

$$\underline{\underline{k}}^{\mathrm{T}} = \frac{1}{T^2}(\underline{\underline{L}}_{11}^{\mathrm{T}} - \underline{\underline{L}}_{21}^{\mathrm{T}} \cdot (\underline{\underline{L}}_{22}^{-1})^{\mathrm{T}} \cdot \underline{\underline{L}}_{12}^{\mathrm{T}}) = \underline{\underline{k}} \quad \text{and} \quad \underline{\underline{r}}^{\mathrm{T}} = \underline{\underline{r}}$$

Of course, for an isotropic material, $\underline{\underline{L}}_{ij} = L_{ij}\underline{\underline{\delta}}$ and

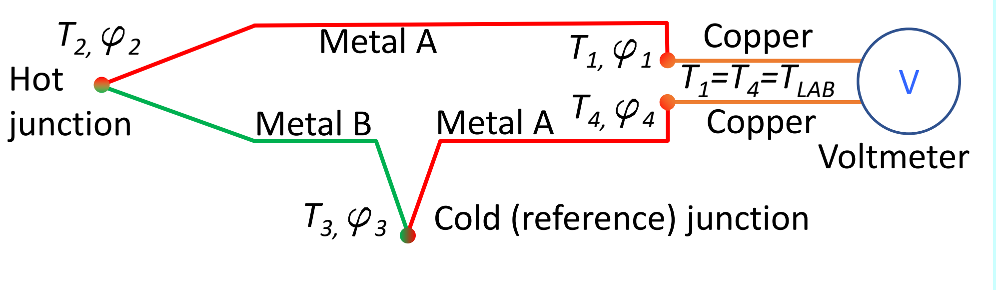
$$\underline{\underline{k}} = k\underline{\underline{\delta}} \quad \underline{\underline{r}} = r\underline{\underline{\delta}} \quad \underline{\underline{\Pi}} = \Pi\underline{\underline{\delta}} \quad \underline{\underline{\varepsilon}} = \varepsilon\underline{\underline{\delta}} \quad \Pi = T\varepsilon$$

$$\sigma = \frac{1}{T^2}\underline{\nabla}T \cdot \underline{\underline{k}} \cdot \underline{\nabla}T + \frac{1}{T}\underline{I}'' \cdot \underline{\underline{r}} \cdot \underline{I}'' = \frac{1}{T^2}(\underline{q}'' - \underline{\underline{\Pi}} \cdot \underline{I}'') \cdot \underline{\underline{k}}^{-1} \cdot (\underline{q}'' - \underline{\underline{\Pi}} \cdot \underline{I}'') + \frac{1}{T}\underline{I}'' \cdot \underline{\underline{r}} \cdot \underline{I}''$$

Seeebeck effect and the thermocouple

$$\begin{cases} \underline{q}'' = \underline{\underline{L}}_{11} \cdot \underline{\nabla\tau} + \underline{\underline{L}}_{12} \cdot (-\tau\underline{\nabla\varphi}) \\ \underline{I}'' = \underline{\underline{L}}_{21} \cdot \underline{\nabla\tau} + \underline{\underline{L}}_{22} \cdot (-\tau\underline{\nabla\varphi}) \end{cases}$$

$$\begin{cases} -\underline{\nabla\varphi} = \underline{\underline{\varepsilon}} \cdot \underline{\nabla T} + \underline{\underline{r}} \cdot \underline{I}'' \\ \underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla T} + \underline{\underline{\Pi}} \cdot \underline{I}'' \end{cases}$$



Assuming $\underline{I}'' = 0$ we project the vector equation

$$-\underline{\nabla\varphi} = \varepsilon\underline{\nabla T}$$

along the local infinitesimal vector $\mathrm{d}\ell$ tangent to the wire axis. Note that $\underline{\nabla\varphi} \cdot \mathrm{d}\underline{\ell} = \mathrm{d}\varphi$ and $\underline{\nabla T} \cdot \mathrm{d}\underline{\ell} = \mathrm{d}T$, so that integrating from positions a and b of a wire we have $\int_a^b \underline{\nabla\varphi} \cdot \mathrm{d}\underline{\ell} = \varphi_b - \varphi_a$ and, assuming ε is a function of temperature, $\int_a^b \varepsilon\underline{\nabla T} \cdot \mathrm{d}\underline{\ell} = \int_a^b \varepsilon(T')\,\mathrm{d}T'$. Doing this between the junctions

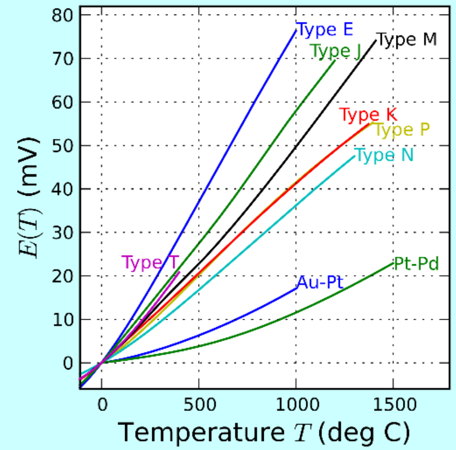
$$-(\varphi_2 - \varphi_1) = \int_1^2 \varepsilon_A(T')\,\mathrm{d}T'$$
$$-(\varphi_3 - \varphi_2) = \int_2^3 \varepsilon_B(T')\,\mathrm{d}T'$$
$$-(\varphi_4 - \varphi_3) = \int_3^4 \varepsilon_A(T')\,\mathrm{d}T'$$

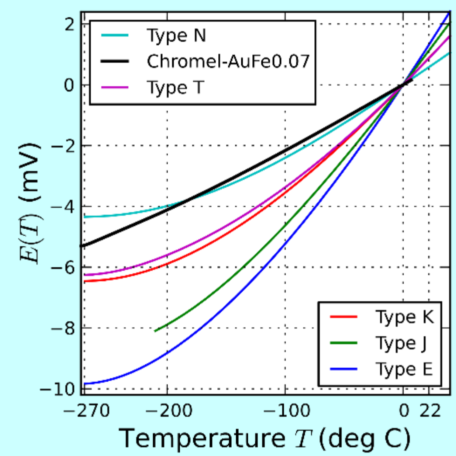
and adding these equations, yields the electromotive force that can be measured by the voltmeter between the junctions at $T_1 = T_4$

$$-(\varphi_4 - \varphi_1) = \int_3^2 [\varepsilon_A(T') - \varepsilon_B(T')]\,\mathrm{d}T' = E(T_2) - E(T_3)$$

where we define the **characteristic function of the thermocouple pair**

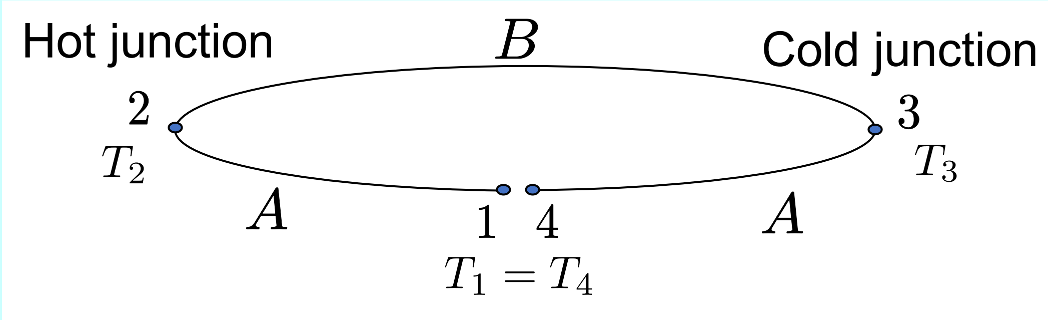
$$E(T) = \int_{T_{\rm ref}}^{T} [\varepsilon_A(T') - \varepsilon_B(T')]\,\mathrm{d}T'$$





Figures by Nanite from Wikipedia

Seebeck effect and the thermoelectric generator



If a load is connected to terminals 1 and 4, the EMF induces a current I, hence in the thermocouple wires there is a voltage drop $R_e I$, so the voltage difference at the load terminals is: $\Delta V = -(\varphi_4 - \varphi_1) - R_{\rm el} I = (\overline{\varepsilon}_A - \overline{\varepsilon}_B)(T_2 - T_3) - R_{\rm el} I$.

The electrical power generated is

$$\dot{W}_{\rm el} = \Delta V\, I = (\overline{\varepsilon}_A - \overline{\varepsilon}_B)(T_2 - T_3) I - R_{\rm el} I^2$$

it is maximum for $2R_{\rm el} I = (\overline{\varepsilon}_A - \overline{\varepsilon}_B)(T_2 - T_3)$

$$\dot{W}_{\rm el,max} = (\overline{\varepsilon}_A - \overline{\varepsilon}_B)^2 (T_2 - T_3)^2 / 4R_{\rm el}$$

The thermal power consumed is

$$\dot{Q} = (T_2 - T_3)/R_{\rm th} + (\overline{\Pi}_A - \overline{\Pi}_B) I$$

and at maximum power is

$$= (T_2 - T_3)\left[\frac{1}{R_{\rm th}} + \frac{(\overline{\Pi}_A - \overline{\Pi}_B)(\overline{\varepsilon}_A - \overline{\varepsilon}_B)}{2R_{\rm el}}\right]$$

$R_{\rm el} =$ Overall electric resistance [Ohm]

$$R_{\rm el} = \frac{r_A\,\ell_A}{a_A} + \frac{r_B\,\ell_B}{a_B}$$

$r =$ electrical resistivity [Ohm m]

$\ell =$ wire length [m]

$a =$ wire cross-section area [m^2]

$R_{\rm th} =$ Overall thermal resistance [W/K]

$$\frac{1}{R_{\rm th}} = \frac{k_A\,a_A}{\ell_A} + \frac{k_B\,a_B}{\ell_B}$$

$k =$ thermal conductivity [W/m K]

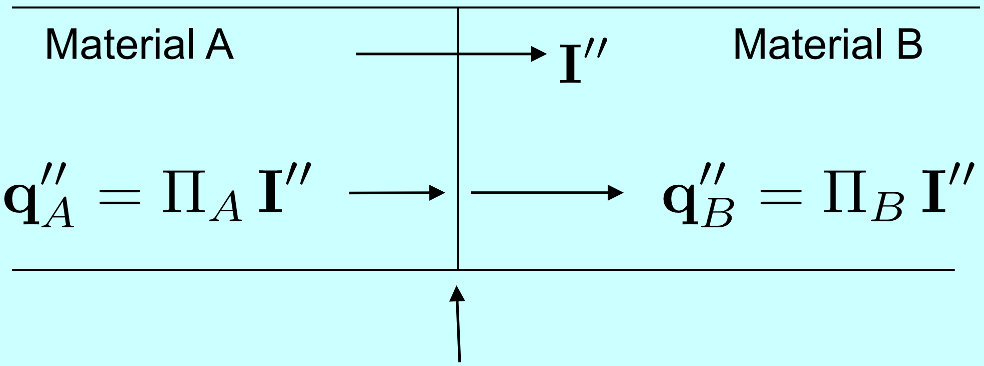
$\ell =$ wire length [m]

$a =$ wire cross-section area [m^2]

Peltier effect

$$\begin{cases} \underline{q}'' = \underline{\underline{L}}_{11} \cdot \underline{\nabla \tau} + \underline{\underline{L}}_{12} \cdot (-\tau \underline{\nabla \varphi}) \\ \underline{I}'' = \underline{\underline{L}}_{21} \cdot \underline{\nabla \tau} + \underline{\underline{L}}_{22} \cdot (-\tau \underline{\nabla \varphi}) \end{cases}$$

$$\begin{cases} -\underline{\nabla}\varphi = \underline{\underline{\varepsilon}} \cdot \underline{\nabla} T + \underline{\underline{r}} \cdot \underline{I}'' \\ \underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla} T + \underline{\underline{\Pi}} \cdot \underline{I}'' \end{cases}$$



Assuming that $\nabla T = 0$

$$\mathbf{q}''_B - \mathbf{q}''_A = (\Pi_B - \Pi_A)\, \mathbf{I}''$$

If the current flows from the material with lower Π to the material with higher Π, $\Pi_A > \Pi_B$ (or $\Pi_B > \Pi_A$), the junction where current flows at uniform temperature has to be heated (or cooled) to be kept at uniform temperature. If the current flows in the direction in which the junction tends to cool, we have a refrigerating effect.

For example, for Cu at 300 K

$\varepsilon = 1.5\,\mu\mathrm{V/K}$ and $k = 385\,\mathrm{W/K\,m}$, so

$$\left.\frac{q''_x}{I''_x}\right|_{dT/dx=0} = \Pi = \varepsilon T = 1.5\,\mu\mathrm{V/K}\,300\,\mathrm{K} = 0.45\,\frac{\mathrm{mW/mm^2}}{\mathrm{A/mm^2}}$$

$$\left.\frac{dT}{dx}\right|_{q''_x=0} = \frac{\varepsilon T}{k} I''_x = \frac{1.5\,\mu\mathrm{V/K}\,300\,\mathrm{K}}{385\,\mathrm{W/K\,m}} = 1.2\,\frac{\mathrm{K/m}}{\mathrm{A/mm^2}}$$

Thermocouple, thermoelectric generator, and Peltier cell

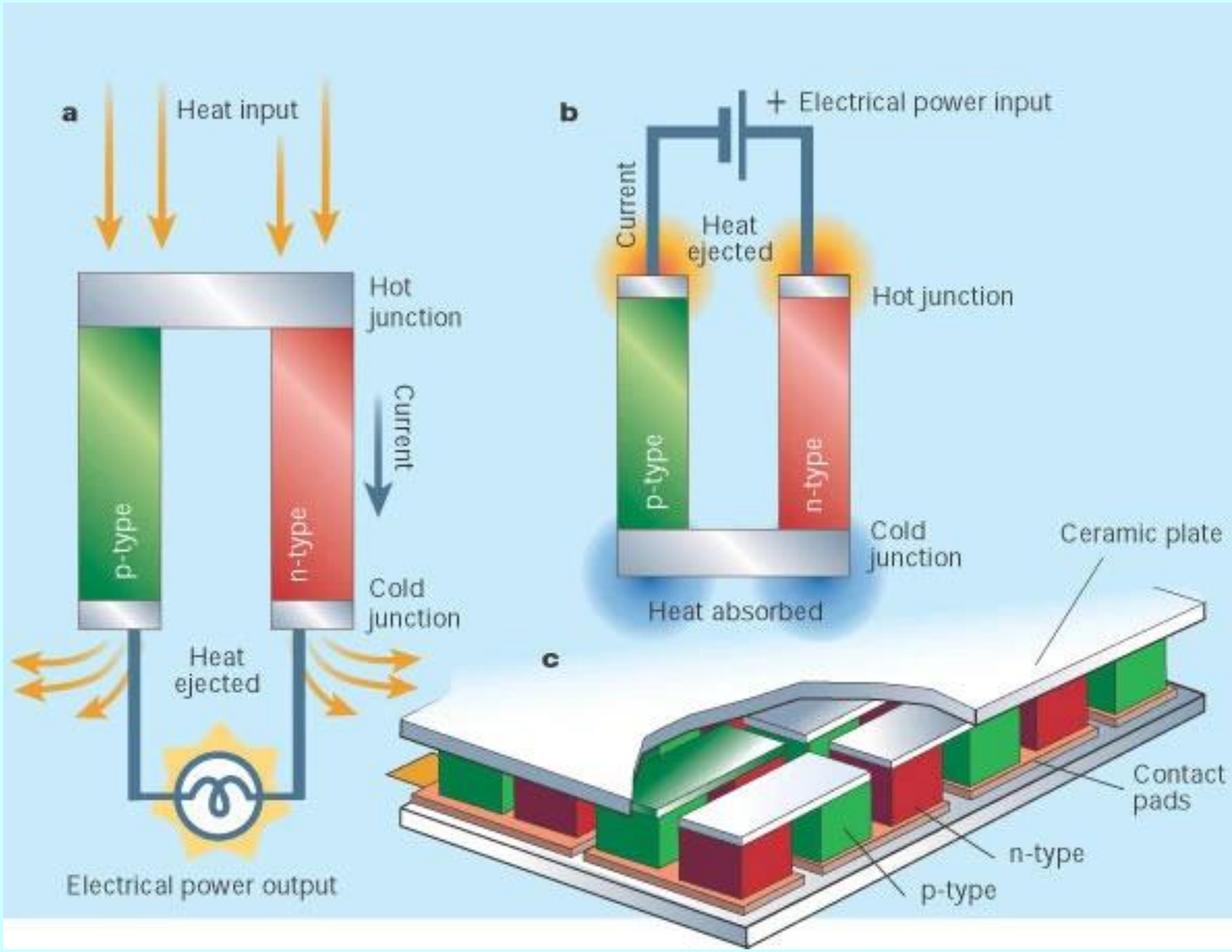
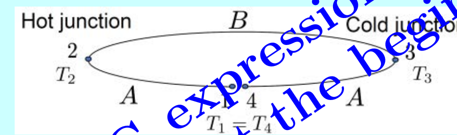


Figure 1 from C.B. Vining, Nature 413, 577 (2001).

Second law efficiency of the thermoelectric generator

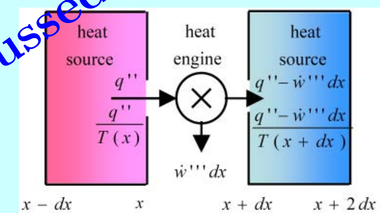
Note that the electrical power of the thermoelectric generator can be written as

$$\dot W_{\rm el} = \int \dot w'''_{\rm el}\, a d\ell \quad \text{with} \quad \dot w'''_{\rm el} = -\underline{\nabla}\varphi \cdot \underline{I}''$$



Recall that we defined the local maximum work obtainable from a temperature gradient

$$\dot w'''_{\rm rev} = T \underline{q}'' \cdot \underline{\nabla}\frac{1}{T} = -\underline{q}'' \cdot \frac{\underline{\nabla}T}{T}$$



Now, substitute the thermo-electricity relations and recall that $\Pi = T\varepsilon$

$$\begin{cases} -\underline{\nabla}\varphi = \varepsilon \underline{\nabla}T + r\underline{I}'' \\ \underline{q}'' = -k\underline{\nabla}T + \Pi \underline{I}'' \end{cases}$$

$$\dot w'''_{\rm el} = \varepsilon \underline{I}'' \cdot \underline{\nabla}T + r\underline{I}'' \cdot \underline{I}'' \quad \text{which takes the maximal value}$$

$$\dot w'''_{\rm el,max} = \frac{\varepsilon^2}{2r}\underline{\nabla}T \cdot \underline{\nabla}T \quad \text{at} \quad \underline{I}'' = -\frac{\varepsilon}{2r}\underline{\nabla}T \quad \text{where}$$

$$\underline{q}'' = -\left(k + \frac{\varepsilon\Pi}{2r}\right)\underline{\nabla}T \quad \text{and} \quad \dot w'''_{\rm rev} = \left(k + \frac{\varepsilon\Pi}{2r}\right)\frac{1}{T}\underline{\nabla}T \cdot \underline{\nabla}T$$

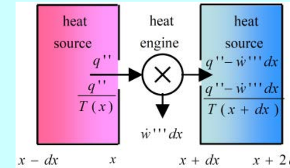
$$\Rightarrow \quad \eta_{\rm II}\big|_{\rm @maxW} = \frac{\dot w'''_{\rm el,max}}{\dot w'''_{\rm rev}} = \frac{1}{1 + 2/\mathcal{Z}} \quad \text{where} \quad \mathcal{Z} = \frac{\varepsilon^2 T}{rk}$$

$\mathcal{Z}$ is dimensionless, traditionally considered a figure of merit of a thermoelectric material and more often denoted by zT or ZT.

This slide was used in Lecture 24 but starts from the WRONG expression of $\dot w'''_{\rm el}$. Please ignore it and replace it with the next slide, also discussed at the beginning of Lecture 25.

Second law efficiency of the thermoelectric generator

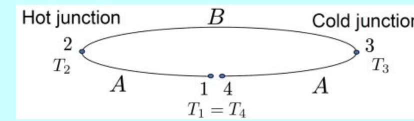
Recall we defined the local maximum work obtainable from a temperature gradient. When we add the electrical work obtainable from the Seebeck effect, we have



$$\dot{w}'''_{\rm rev} = -\underline{q}'' \cdot \frac{\underline{\nabla} T}{T} - \underline{I}'' \cdot \underline{\underline{\varepsilon}} \cdot \underline{\nabla} T$$

Note that the electrical power of the thermoelectric generator can be written as

$$\dot{W}_{\rm el} = \int \dot{w}'''_{\rm el}\, a d\ell \quad \text{with} \quad \dot{w}'''_{\rm el} = \dot{w}'''_{\rm rev} - T\,\sigma$$



Now, use the thermo-electricity relations, recalling that $\underline{\underline{r}}^{\rm T} = \underline{\underline{r}}$, $\underline{\underline{k}}^{\rm T} = \underline{\underline{k}}$, and $\underline{\underline{\Pi}}^{\rm T} = T\underline{\underline{\varepsilon}}$,

$$\sigma = \frac{1}{T^2}\underline{\nabla} T \cdot \underline{\underline{k}} \cdot \underline{\nabla} T + \frac{1}{T}\underline{I}'' \cdot \underline{\underline{r}} \cdot \underline{I}'' \quad \text{and} \quad \begin{cases} -\underline{\nabla}\varphi = \underline{\underline{\varepsilon}} \cdot \underline{\nabla} T + \underline{\underline{r}} \cdot \underline{I}'' \\ \underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla} T + \underline{\underline{\Pi}} \cdot \underline{I}'' \end{cases}$$

to obtain $\dot{w}'''_{\rm el} = 2\underline{I}'' \cdot \underline{\underline{\varepsilon}} \cdot \underline{\nabla} T - \underline{I}'' \cdot \underline{\underline{r}} \cdot \underline{I}''$. At $\underline{I}''|_{\rm @maxW} = -\underline{\nabla} T \cdot \underline{\underline{\varepsilon}}^{\rm T} \cdot \underline{\underline{r}}^{-1} = -\underline{\underline{r}}^{-1} \cdot \underline{\underline{\varepsilon}} \cdot \underline{\nabla} T$ we have

$$\dot{w}'''_{\rm el,max} = \underline{\nabla} T \cdot \underline{\underline{\varepsilon}}^{\rm T} \cdot \underline{\underline{r}}^{-1} \cdot \underline{\underline{\varepsilon}} \cdot \underline{\nabla} T = \frac{1}{T}\underline{\nabla} T \cdot \underline{\underline{k}} \cdot \underline{\underline{\mathcal{Z}}} \cdot \underline{\nabla} T \quad \text{where} \quad \underline{\underline{\mathcal{Z}}} = T\underline{\underline{k}}^{-1} \cdot \underline{\underline{\varepsilon}}^{\rm T} \cdot \underline{\underline{r}}^{-1} \cdot \underline{\underline{\varepsilon}} \xrightarrow[\text{material}]{\text{isotropic}} \mathcal{Z} = \frac{\varepsilon^2 T}{r\,k}$$

At this maximum power condition, we have $\underline{q}''|_{\rm @maxW} = -\underline{\underline{k}} \cdot \left[\underline{\underline{\delta}} + \underline{\underline{\mathcal{Z}}}\right] \cdot \underline{\nabla} T$

$$\dot{w}'''_{\rm rev}|_{\rm @maxW} = \frac{1}{T}\underline{\nabla} T \cdot \underline{\underline{k}} \cdot \left[\underline{\underline{\delta}} + 2\underline{\underline{\mathcal{Z}}}\right] \cdot \underline{\nabla} T \qquad \sigma|_{\rm @maxW} = \frac{1}{T^2}\underline{\nabla} T \cdot \underline{\underline{k}} \cdot \left[\underline{\underline{\delta}} + \underline{\underline{\mathcal{Z}}}\right] \cdot \underline{\nabla} T$$

$$\Rightarrow \quad \eta_{\rm II}|_{\rm @maxW} = \frac{\dot{w}'''_{\rm el,max}}{\dot{w}'''_{\rm rev}|_{\rm @maxW}} = 1 - \frac{T\sigma|_{\rm @maxW}}{\dot{w}'''_{\rm rev}|_{\rm @maxW}} = \frac{\underline{\nabla} T \cdot \underline{\underline{k}} \cdot \underline{\underline{\mathcal{Z}}} \cdot \underline{\nabla} T}{\underline{\nabla} T \cdot \underline{\underline{k}} \cdot [\underline{\underline{\delta}} + 2\underline{\underline{\mathcal{Z}}}] \cdot \underline{\nabla} T} \xrightarrow[\text{material}]{\text{isotropic}} \frac{\mathcal{Z}}{1 + 2\mathcal{Z}}$$

$\underline{\underline{\mathcal{Z}}}$ is a dimensionless tensor, that can be used as a figure of merit for developing **nano-structured (anisotropic) thermoelectric materials**.

Thomson heating/cooling effect vs Joule heating

Balance equation for the internal energy u^*

$$\rho\frac{Du^*}{Dt} = \rho\frac{De^*}{Dt} - \rho\frac{D(e^*-u^*)}{Dt} = -\underline{\nabla}\cdot\underline{J}_E - \underline{\nabla}\cdot(\underline{\underline{\tau}}\cdot\underline{v}_m) + \underline{\underline{\tau}}:\underline{\nabla}\,\underline{v}_m$$

$$\underline{J}_E = \underline{J}_E^{\rm nw} + \underline{J}_E^{\rm w} \text{ with } \underline{J}_E^{\rm nw} = \underline{q}'' + \varphi\underline{J}_q \text{ and } \underline{J}_E^{\rm w} = -\underline{\underline{\tau}}\cdot\underline{v}_m$$

$$\rho\frac{Du^*}{Dt} = -\underline{\nabla}\cdot\underline{J}_E^{\rm nw} + \underline{\underline{\tau}}:\underline{\nabla}\,\underline{v}_m = -\underline{\nabla}\cdot\underline{q}'' - \underline{\nabla}\cdot(\varphi\underline{J}_q) + \underline{\underline{\tau}}:\underline{\nabla}\,\underline{v}_m$$

$$-\underline{\nabla}\cdot\underline{q}'' = -\underline{\nabla}\cdot(-k\underline{\nabla}T + \underline{\underline{\Pi}}\cdot\underline{J}_q) = \underline{\nabla}\cdot(k\underline{\nabla}T) - \Pi\underline{\nabla}\cdot\underline{J}_q - \underline{J}_q\cdot\underline{\nabla}\Pi$$

$$-\underline{\nabla}\cdot(\varphi\underline{J}_q) = -\varphi\underline{\nabla}\cdot\underline{J}_q - \underline{J}_q\cdot\underline{\nabla}\varphi = -\varphi\underline{\nabla}\cdot\underline{J}_q + \underline{J}_q\cdot(\varepsilon\underline{\nabla}T + r\underline{J}_q)$$

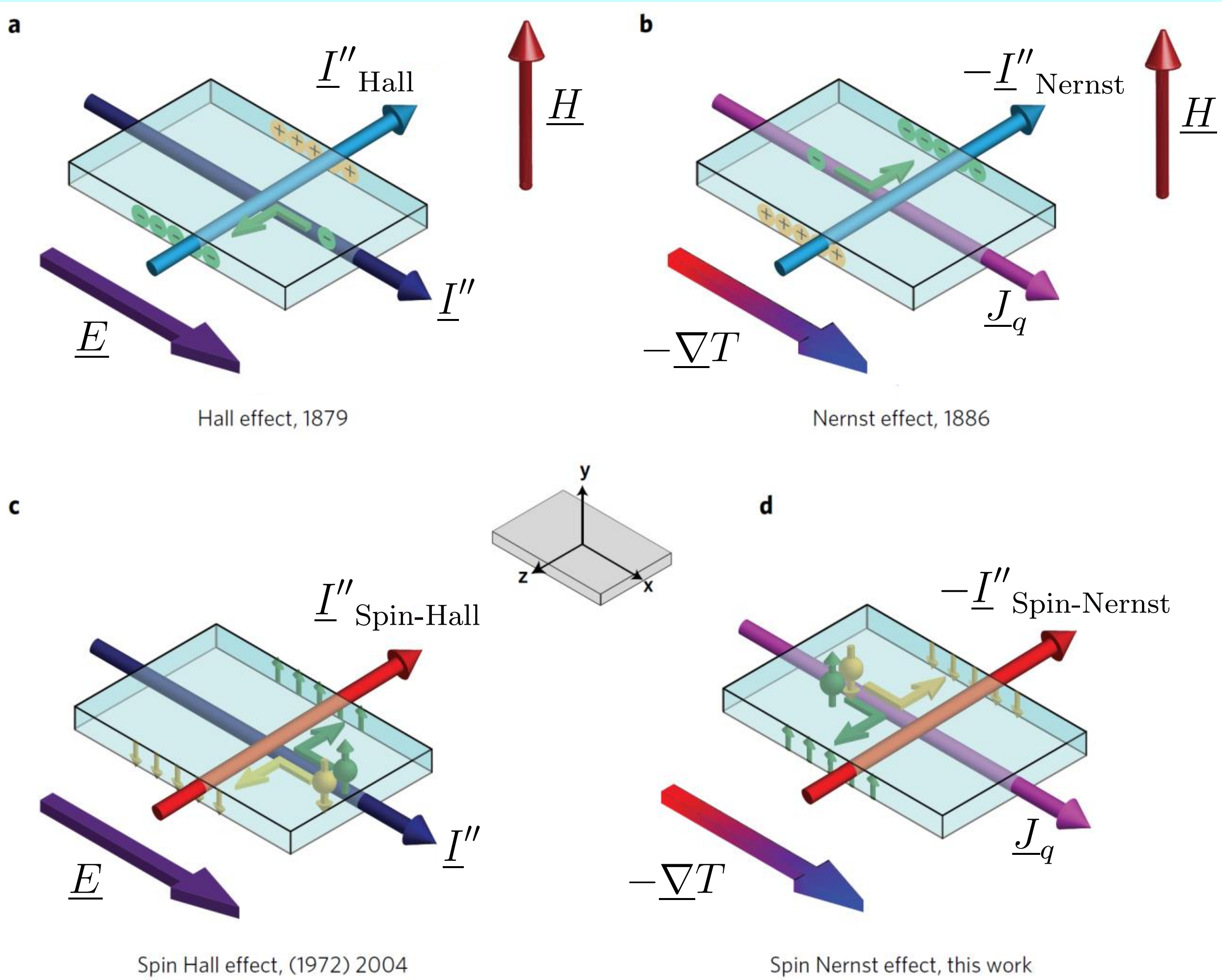
use $\underline{\nabla}\cdot\underline{J}_q = 0$ (from charge conservation) and $\underline{\nabla}\Pi = \dfrac{\partial\Pi}{\partial T}\underline{\nabla}T$

define $\Upsilon = \dfrac{\partial\Pi}{\partial T} - \varepsilon = \dfrac{\partial\Pi}{\partial T} - \dfrac{\Pi}{T} = T\dfrac{\partial\varepsilon}{\partial T}$ **Thomson coefficient**

$$\underbrace{\rho\frac{Du^*}{Dt}}_{\substack{\text{material}\\\text{deriva-}\\\text{tive of } u^*}} = \underbrace{\underline{\nabla}\cdot(k\underline{\nabla}T)}_{\substack{\text{Fourier}\\\text{thermal}\\\text{diffusion}}} + \underbrace{r\underline{J}_q\cdot\underline{J}_q}_{\substack{\text{Joule}\\\text{effect}\\(>0)}} + \underbrace{\underline{\underline{\tau}}:\underline{\nabla}\,\underline{v}_m}_{\substack{\text{viscous}\\\text{dissipation}\\(>0)}} - \underbrace{\Upsilon\underline{J}_q\cdot\underline{\nabla}T}_{\substack{\textbf{Thomson}\\\textbf{effect}\\(>0\text{ or }<0)}}$$

The Thomson effect adds a source term to the Joule effect, but can be both positive and negative, that is, either a ‘generation’ or a ‘consumption’ of thermal energy. It represents the direct ‘reversible’ conversion of thermal into electric energy and viceversa.

Cross effects in charge and spin current transport



a: In the Hall effect, a transverse charge current density $\underline{I}''_{\mathrm{Hall}}$ arises when a magnetic field $\underline{H}$ and a charge current density $\underline{I}''$ are applied normal to each other.

b: The Nernst effect is the thermal analogue of the Hall effect.

c: In the spin Hall effect, a transverse spin current density $\underline{I}''_{\mathrm{Spin\text{-}Hall}}$ perpendicular to the charge current density $\underline{I}''$ is generated due to spin–orbit coupling.

d: A transverse spin current density $\underline{I}''_{\mathrm{Spin\text{-}Nernst}}$ is also generated by a longitudinal temperature gradient.

Adapted from figure 1 of S. Meyer et al., Nature Materials 16, 977 (2017)

Spin-Seebeck effect

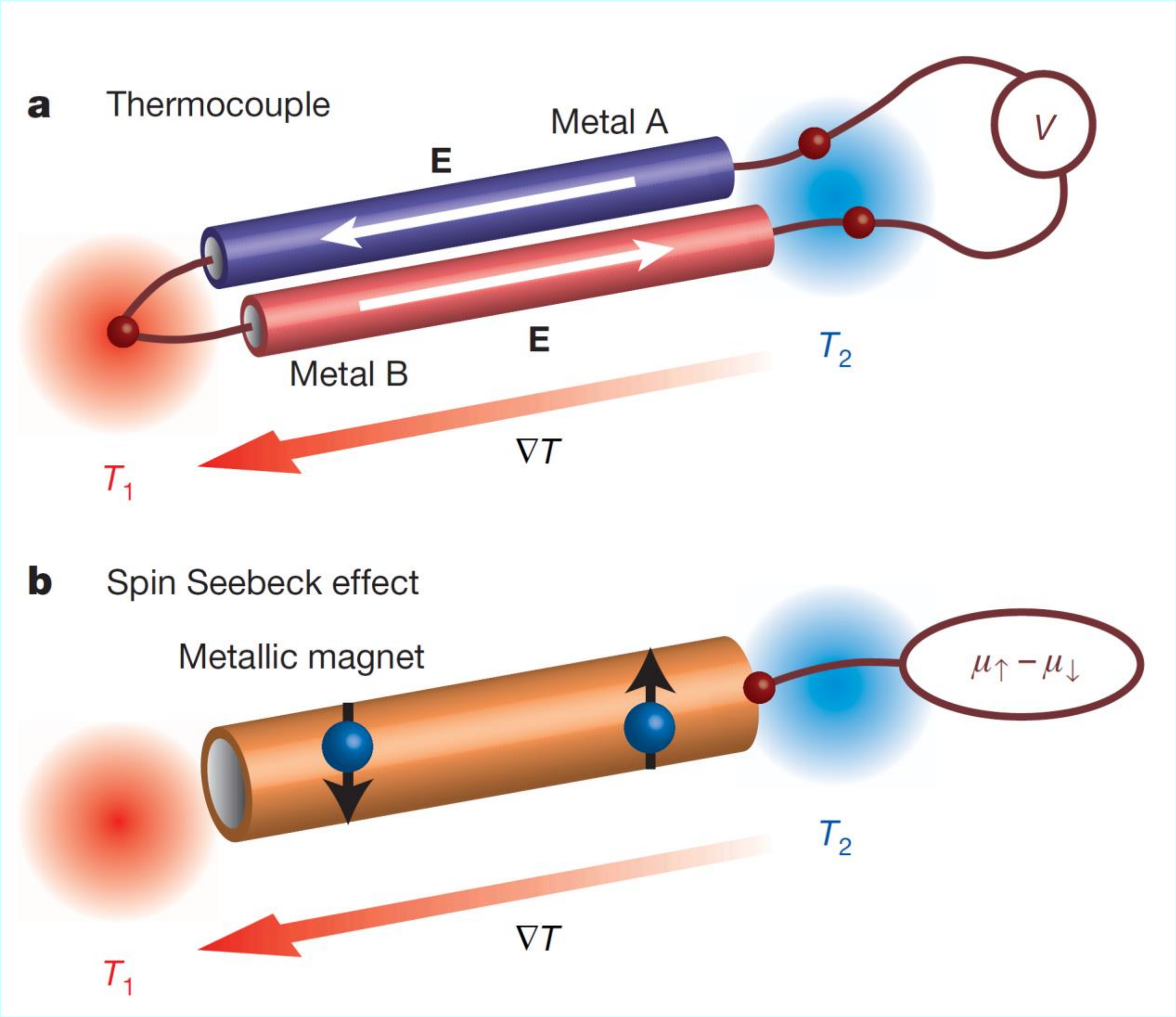


Figure 1 from K. Uchida et al., Nature 455, 778 (2008)

a: A thermocouple is composed of two conductors (metals A and B) connected together. They have different Seebeck coefficients, and therefore, the voltage V between the output terminals is proportional to the temperature gradient $\nabla T = (T_1 - T_2)/L$ between the ends of the couple. **b**: In a metallic magnet, the spin-up ($\uparrow$) and spin-down ($\downarrow$) conduction electrons have different Seebeck coefficients. When a temperature gradient is applied, a spin-voltage (difference $\mu_\uparrow - \mu_\downarrow$ in the electrochemical potentials of spin-up and spin-down electrons) proportional to the temperature difference appears.

Image Credits

Slide 5:

Slide 12:

- Image showing thermocouple reference functions for nickel-alloy types E, J, K, M, N, and T is in the public domain.
- Image showing thermocouple characteristics at low temperatures is in the public domain.

Slide 15:

Slide 19:

Slide 20: