

2.43 ADVANCED THERMODYNAMICS

Spring Term 2024

LECTURE 25

Room 3-442

Friday, May 10, 11:00am - 1:00pm

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Room 3-351d

Onsager nonequilibrium cross effects and the Curie symmetry principle

Each flux may be a function of all the forces, $\underline{J}_i = \underline{J}_i(\{\underline{X}_k\})$, 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	$-\frac{1}{T}\underline{\nabla} \cdot \underline{v}_m$	$-\frac{1}{T^2}\underline{\nabla}T$	$-\frac{1}{T}\underline{\nabla}\mu_{i,T}$	$-\frac{1}{T}\underline{\nabla}\varphi$	$\frac{1}{T}(\underline{\nabla}\underline{v}_m + \underline{\nabla}\underline{v}_m^T)'$
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.

Relation between **independent diffusive fluxes in heat&diffusion** interactions

- Recall the local simple-system equilibrium assumption,

$$E = U(S, V, \mathbf{n}) + \frac{1}{2}mv_m^2 + mgz + q\varphi - \frac{1}{2}m\omega^2r^2 \quad m = V\sum_i c_i M_i \quad q = V\sum_i c_i z_i F$$

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

where the last equality defines the **partial energy** $e_i = u_i + \mu_i^{\text{tot}} - \mu_i$ 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

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

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

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

- 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: $\mu_i = h_i - T s_i$, $\underline{J}_q = F \sum_i z_i \underline{J}_{n_i}$, $\mu_i^{\text{tot}} = \mu_i / M_i$.
- So, the relation for **heat&diffusion interactions** may be written in several equivalent forms

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

$$\begin{aligned} \underline{J}_E^{\text{nw}} &= \underline{q}'' + \sum_{i=1}^{r-1} (h_i - h_r) \underline{J}_{n_i} + \varphi \underline{J}_q \\ \underline{J}_S &= \frac{\underline{q}''}{T} + \sum_{i=1}^{r-1} (s_i - s_r) \underline{J}_{n_i} \end{aligned}$$

σ 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

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

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

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

- 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:

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

- 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)

$$\underline{J}_{ij} = \frac{c_i c_j}{c} \left[\frac{\underline{J}_{n_i}}{c_i} - \frac{\underline{J}_{n_j}}{c_j} \right] = -\underline{J}_{ji}$$

$$\underline{X}_{ij} = -\frac{1}{T} \underline{\nabla} (\mu_i - \mu_j)|_T = -\underline{X}_{ji}$$

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

$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} + \frac{1}{2} \sum_{ij} \underline{J}_{ij} \cdot \underline{X}_{ij} - \frac{1}{T} \underline{I}'' \cdot \underline{\nabla} \varphi$$

$$\underline{J}_{n_i} = \frac{1}{M} \sum_j M_j \underline{J}_{ij} \quad \text{from } \underline{J}_m = \sum_i M_i \underline{J}_{n_i} = 0$$

Cross effects between vectorial fluxes and forces

$$\sigma = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \frac{1}{2} \sum_{ij} J_{ij} \cdot \underline{X}_{ij} + \sum_k r_k Y_k + \Phi/T$$

$$\underline{J}_{ij} = \frac{c_i c_j}{c} \left[\frac{J_{ni}}{c_i} - \frac{J_{nj}}{c_j} \right] = -\underline{J}_{ji}$$

$$\underline{X}_{ij} = -\frac{1}{T} \underline{\nabla} (\mu_i - \mu_j)|_T = -\underline{X}_{ji}$$

So, for no viscous dissipation ($\Phi = 0$), no chemical reactions ($r_k = 0$) or chemical equilibrium ($Y_k = 0$), and only three components

$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \underline{J}_{12} \cdot \underline{X}_{12} + \underline{J}_{13} \cdot \underline{X}_{13} + \underline{J}_{23} \cdot \underline{X}_{23}$$

Assume linear force-flux relations

$$\underline{q}'' = L_{QQ} \underline{\nabla} \frac{1}{T} - L_{QP} \frac{1}{Tc} \underline{\nabla} p - L_{QZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Q12} \underline{X}_{12} + L_{Q13} \underline{X}_{13} + L_{Q23} \underline{X}_{23}$$

$$\underline{J}_n = L_{PQ} \underline{\nabla} \frac{1}{T} - L_{PP} \frac{1}{Tc} \underline{\nabla} p - L_{PZ} \frac{1}{T} \underline{\nabla} \varphi + L_{P12} \underline{X}_{12} + L_{P13} \underline{X}_{13} + L_{P23} \underline{X}_{23}$$

$$\underline{J}_q = L_{ZQ} \underline{\nabla} \frac{1}{T} - L_{ZP} \frac{1}{Tc} \underline{\nabla} p - L_{ZZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Z12} \underline{X}_{12} + L_{Z13} \underline{X}_{13} + L_{Z23} \underline{X}_{23}$$

$$\underline{J}_{12} = L_{12Q} \underline{\nabla} \frac{1}{T} - L_{12P} \frac{1}{Tc} \underline{\nabla} p - L_{12Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1212} \underline{X}_{12} + L_{1213} \underline{X}_{13} + L_{1223} \underline{X}_{23}$$

$$\underline{J}_{13} = L_{13Q} \underline{\nabla} \frac{1}{T} - L_{13P} \frac{1}{Tc} \underline{\nabla} p - L_{13Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1312} \underline{X}_{12} + L_{1313} \underline{X}_{13} + L_{1323} \underline{X}_{23}$$

$$\underline{J}_{23} = L_{23Q} \underline{\nabla} \frac{1}{T} - L_{23P} \frac{1}{Tc} \underline{\nabla} p - L_{23Z} \frac{1}{T} \underline{\nabla} \varphi + L_{2312} \underline{X}_{12} + L_{2313} \underline{X}_{13} + L_{2323} \underline{X}_{23}$$

Thermoelectric effects

$$\sigma = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \frac{1}{2} \sum_{ij} J_{ij} \cdot \underline{X}_{ij} + \sum_k r_k Y_k + \Phi/T$$

$$\underline{J}_{ij} = \frac{c_i c_j}{c} \left[\frac{J_{ni}}{c_i} - \frac{J_{nj}}{c_j} \right] = -\underline{J}_{ji}$$

$$\underline{X}_{ij} = -\frac{1}{T} \underline{\nabla} (\mu_i - \mu_j)|_T = -\underline{X}_{ji}$$

So, for no viscous dissipation ($\Phi = 0$), no chemical reactions ($r_k = 0$) or chemical equilibrium ($Y_k = 0$), and only three components

$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} I'' \cdot \underline{\nabla} \varphi + \underline{J}_{12} \cdot \underline{X}_{12} + \underline{J}_{13} \cdot \underline{X}_{13} + \underline{J}_{23} \cdot \underline{X}_{23}$$

Assume linear force-flux relations

$$\underline{q}'' = L_{QQ} \underline{\nabla} \frac{1}{T} - L_{QP} \frac{1}{Tc} \underline{\nabla} p - L_{QZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Q12} \underline{X}_{12} + L_{Q13} \underline{X}_{13} + L_{Q23} \underline{X}_{23}$$

$$\underline{J}_n = L_{PQ} \underline{\nabla} \frac{1}{T} - L_{PP} \frac{1}{Tc} \underline{\nabla} p - L_{PZ} \frac{1}{T} \underline{\nabla} \varphi + L_{P12} \underline{X}_{12} + L_{P13} \underline{X}_{13} + L_{P23} \underline{X}_{23}$$

$$\underline{J}_q = L_{ZQ} \underline{\nabla} \frac{1}{T} - L_{ZP} \frac{1}{Tc} \underline{\nabla} p - L_{ZZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Z12} \underline{X}_{12} + L_{Z13} \underline{X}_{13} + L_{Z23} \underline{X}_{23}$$

$$\underline{J}_{12} = L_{12Q} \underline{\nabla} \frac{1}{T} - L_{12P} \frac{1}{Tc} \underline{\nabla} p - L_{12Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1212} \underline{X}_{12} + L_{1213} \underline{X}_{13} + L_{1223} \underline{X}_{23}$$

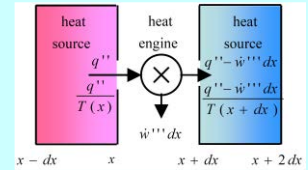
$$\underline{J}_{13} = L_{13Q} \underline{\nabla} \frac{1}{T} - L_{13P} \frac{1}{Tc} \underline{\nabla} p - L_{13Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1312} \underline{X}_{12} + L_{1313} \underline{X}_{13} + L_{1323} \underline{X}_{23}$$

$$\underline{J}_{23} = L_{23Q} \underline{\nabla} \frac{1}{T} - L_{23P} \frac{1}{Tc} \underline{\nabla} p - L_{23Z} \frac{1}{T} \underline{\nabla} \varphi + L_{2312} \underline{X}_{12} + L_{2313} \underline{X}_{13} + L_{2323} \underline{X}_{23}$$

Second law efficiency of the thermoelectric generator

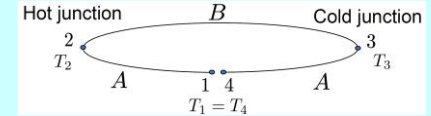
Recall we defined the local maximum work obtainable from a temperature gradient. When we add the electrical work obtainable from the Seebeck effect, we have

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



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

$$\dot{W}_{\text{el}} = \int \dot{w}_{\text{el}}''' \text{ad}l \quad \text{with} \quad \dot{w}_{\text{el}}''' = \dot{w}_{\text{rev}}''' - T\sigma$$



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

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

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

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

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

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

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

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

Thermo-osmosis of pure substances in porous media

$$\sigma = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \frac{1}{2} \sum_{ij} J_{ij} \cdot \underline{X}_{ij} + \sum_k r_k Y_k + \Phi/T$$

$$\underline{J}_{ij} = \frac{c_i c_j}{c} \left[\frac{J_{ni}}{c_i} - \frac{J_{nj}}{c_j} \right] = -\underline{J}_{ji}$$

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So, for no viscous dissipation ($\Phi = 0$), no chemical reactions ($r_k = 0$) or chemical equilibrium ($Y_k = 0$), and only three components

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Assume linear force-flux relations

$$\underline{q}'' = L_{QQ} \underline{\nabla} \frac{1}{T} - L_{QP} \frac{1}{Tc} \underline{\nabla} p - L_{QZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Q12} \underline{X}_{12} + L_{Q13} \underline{X}_{13} + L_{Q23} \underline{X}_{23}$$

$$\underline{J}_n = L_{PQ} \underline{\nabla} \frac{1}{T} - L_{PP} \frac{1}{Tc} \underline{\nabla} p - L_{PZ} \frac{1}{T} \underline{\nabla} \varphi + L_{P12} \underline{X}_{12} + L_{P13} \underline{X}_{13} + L_{P23} \underline{X}_{23}$$

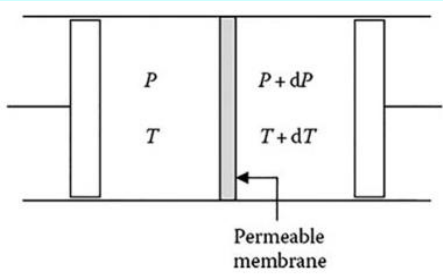
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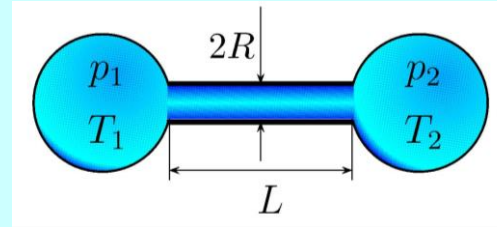
$$\underline{J}_{23} = L_{23Q} \underline{\nabla} \frac{1}{T} - L_{23P} \frac{1}{Tc} \underline{\nabla} p - L_{23Z} \frac{1}{T} \underline{\nabla} \varphi + L_{2312} \underline{X}_{12} + L_{2313} \underline{X}_{13} + L_{2323} \underline{X}_{23}$$

Thermo-osmosis of pure substances in porous media



Thermo-osmotic effect is a flow against the hydrostatic pressure, driven by a temperature gradient.

Mechano-caloric effect is a heat flux driven by a pressure gradient.



$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p \quad \text{and assume linear flux-force relations}$$

$$\underline{q}'' = L_{QQ} \underline{\nabla} \frac{1}{T} - L_{QP} \frac{1}{Tc} \underline{\nabla} p$$

$$\underline{J}_n = L_{PQ} \underline{\nabla} \frac{1}{T} - L_{PP} \frac{1}{Tc} \underline{\nabla} p$$

Rewrite in terms of more familiar variables, $v = 1/c$

$$\underline{q}'' = -k \underline{\nabla} T + \chi \underline{\nabla} p$$

$$\frac{J_n}{c} = \pi \underline{\nabla} T - \frac{\kappa}{\eta} \underline{\nabla} p$$

$\chi =$ mechano-caloric coefficient

$\pi =$ thermo-osmotic permeability

Important: Onsager symmetry

$$L_{PQ} = L_{QP} \text{ implies } \chi = T\pi$$

where we defined:

$$k = \frac{L_{QQ}}{T^2}$$

$$\frac{\kappa}{\eta} = \frac{L_{PP}}{Tc^2} \quad \kappa = \text{Darcy permeability}$$

$$\eta = \text{shear viscosity}$$

$$\pi = -\frac{L_{PQ}}{T^2c}$$

$$\chi = -\frac{L_{QP}}{Tc}$$

Nonequilibrium in heat, mass, and charge transfer

Thermo-diffusion effects

Interdiffusion of two constituents at uniform T and p

$$\sigma = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \frac{1}{2} \sum_{ij} J_{ij} \cdot \underline{X}_{ij} + \sum_k r_k Y_k + \Phi/T$$

$$\underline{J}_{ij} = \frac{c_i c_j}{c} \left[\frac{J_{ni}}{c_i} - \frac{J_{nj}}{c_j} \right] = -\underline{J}_{ji}$$

$$\underline{X}_{ij} = -\frac{1}{T} \underline{\nabla} (\mu_i - \mu_j)|_T = -\underline{X}_{ji}$$

So, for no viscous dissipation ($\Phi = 0$), no chemical reactions ($r_k = 0$) or chemical equilibrium ($Y_k = 0$), and only three components

$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + J_{12} \cdot \underline{X}_{12} + J_{13} \cdot \underline{X}_{13} + J_{23} \cdot \underline{X}_{23}$$

Assume linear force-flux relations

$$\begin{aligned} \underline{q}'' &= L_{QQ} \underline{\nabla} \frac{1}{T} - L_{QP} \frac{1}{Tc} \underline{\nabla} p - L_{QZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Q12} \underline{X}_{12} + L_{Q13} \underline{X}_{13} + L_{Q23} \underline{X}_{23} \\ J_n &= L_{PQ} \underline{\nabla} \frac{1}{T} - L_{PP} \frac{1}{Tc} \underline{\nabla} p - L_{PZ} \frac{1}{T} \underline{\nabla} \varphi + L_{P12} \underline{X}_{12} + L_{P13} \underline{X}_{13} + L_{P23} \underline{X}_{23} \\ J_q &= L_{ZQ} \underline{\nabla} \frac{1}{T} - L_{ZP} \frac{1}{Tc} \underline{\nabla} p - L_{ZZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Z12} \underline{X}_{12} + L_{Z13} \underline{X}_{13} + L_{Z23} \underline{X}_{23} \\ J_{12} &= L_{12Q} \underline{\nabla} \frac{1}{T} - L_{12P} \frac{1}{Tc} \underline{\nabla} p - L_{12Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1212} \underline{X}_{12} + L_{1213} \underline{X}_{13} + L_{1223} \underline{X}_{23} \\ J_{13} &= L_{13Q} \underline{\nabla} \frac{1}{T} - L_{13P} \frac{1}{Tc} \underline{\nabla} p - L_{13Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1312} \underline{X}_{12} + L_{1313} \underline{X}_{13} + L_{1323} \underline{X}_{23} \\ J_{23} &= L_{23Q} \underline{\nabla} \frac{1}{T} - L_{23P} \frac{1}{Tc} \underline{\nabla} p - L_{23Z} \frac{1}{T} \underline{\nabla} \varphi + L_{2312} \underline{X}_{12} + L_{2313} \underline{X}_{13} + L_{2323} \underline{X}_{23} \end{aligned}$$

Interdiffusion of two constituents at uniform T and p

$$\begin{aligned}\sigma &= \underline{J}_{n_1} \cdot \underline{\nabla} \lambda_1 + \underline{J}_{n_2} \cdot \underline{\nabla} \lambda_2 \\ &= -\frac{1}{T} \underline{J}_{n_1} \cdot \underline{\nabla} \mu_1 - \frac{1}{T} \underline{J}_{n_2} \cdot \underline{\nabla} \mu_2\end{aligned}$$

Using the Gibbs-Duhem relation

$$0 = -\rho s \underline{\nabla} T + \underline{\nabla} p - \sum_i c_i \underline{\nabla} \mu_i,$$

for $\underline{\nabla} T = 0$ and $\underline{\nabla} p = 0$, we have

$$0 = c_1 \underline{\nabla} \mu_1|_{T,p} + c_2 \underline{\nabla} \mu_2|_{T,p}$$

$$\underline{\nabla} \mu_2|_{T,p} = -\frac{c_1}{c_2} \underline{\nabla} \mu_1|_{T,p} \quad c_i = n_i/V$$

$$\underline{\nabla} \mu_1|_{T,p} = \frac{c_2}{c_1 + c_2} \underline{\nabla} (\mu_1 - \mu_2)|_{T,p}$$

Substituting we may write σ as

$$\begin{aligned}\sigma &= -\frac{1}{T} \left[\underline{J}_{n_1} - \frac{c_1}{c_2} \underline{J}_{n_2} \right] \cdot \underline{\nabla} \mu_1|_{T,p} \\ &= \underbrace{\frac{c_1 c_2}{c_1 + c_2} \left[\frac{\underline{J}_{n_1}}{c_1} - \frac{\underline{J}_{n_2}}{c_2} \right]}_{\underline{J}_{12} = -\underline{J}_{21}} \cdot \underbrace{\left[-\frac{\underline{\nabla} (\mu_1 - \mu_2)|_{T,p}}{T} \right]}_{\underline{X}_{12} = -\underline{X}_{21}}\end{aligned}$$

where \underline{J}_{12} and \underline{X}_{12} are the **flux of particles 1 relative to 2** and the **conjugated force**.

Note that: $\underline{X}_{12} = \frac{c}{c_2} \underline{X}_1 = -\frac{c}{c_1} \underline{X}_2$

Assume linear force-flux law

$$\underline{J}_{12} = L_{12} \underline{X}_{12} = \frac{1}{R} \frac{c_1 c_2}{c} D_{12}^{\text{MS}} \underline{X}_{12}$$

where we call D_{12}^{MS} the **Maxwell-Stefan coefficient of diffusion of 1 relative to 2**.

Now recall that $\underline{J}_m = \sum_i M_i \underline{J}_{n_i} = 0$ implies

$$\begin{aligned}M_1 \underline{J}_{n_1} + M_2 \underline{J}_{n_2} = 0 &\Rightarrow \underline{J}_{n_2} = -M_1 \underline{J}_{n_1} / M \\ \Rightarrow \underline{J}_{12} = \frac{M}{M_2} \underline{J}_{n_1} = -\frac{M}{M_1} \underline{J}_{n_2} &\Rightarrow\end{aligned}$$

$$\underline{J}_{n_1} = \frac{M_2}{M} \underline{J}_{12} = \frac{M_2 c_1 c_2}{M R c} D_{12}^{\text{MS}} \underline{X}_{12} = \frac{M_2 c_1}{M R} D_{12}^{\text{MS}} \underline{X}_1$$

From $y_i = n_i/n$, $dn_i = n_i (d \ln y_i + d \ln n)$, $\sum_j \mu_{i,j} n_i = \sum_j \mu_{j,i} n_i = 0$, $d\mu_i|_T = v_i dp + \sum_j \mu_{i,j} dn_j$, obtain $\sum_j (\partial \mu_i / \partial \ln n_j)_{T,p,n'_j} = 0$

$$d\mu_i|_{T,p} = \sum_j (\partial \mu_i / \partial \ln n_j)_{T,p,n'_j} d \ln y_j$$

$$\underline{X}_1 = -\frac{1}{T} \underline{\nabla} \mu_i|_{T,p} = -\frac{1}{T y_1 y_2} \left[\frac{\partial \mu_1}{\partial \ln n_1} \right]_{T,p,n_2} \underline{\nabla} y_1$$

$$\underline{J}_{n_1} = - \underbrace{\frac{M_2 D_{12}^{\text{MS}}}{y_1 y_2 M} \left[\frac{\partial \mu_1 / RT}{\partial \ln n_1} \right]_{T,p,n_2}}_{D_1^{\text{F}}} c_1 \underline{\nabla} y_1$$

$D_1^{\text{F}} = \text{Fick diffusion coefficient}$

Thermophoresis: interdiffusion of two constituents at uniform p

$$\sigma = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \frac{1}{2} \sum_{ij} J_{ij} \cdot \underline{X}_{ij} + \sum_k r_k Y_k + \Phi/T$$

$$\underline{J}_{ij} = \frac{c_i c_j}{c} \left[\frac{J_{ni}}{c_i} - \frac{J_{nj}}{c_j} \right] = -\underline{J}_{ji}$$

$$\underline{X}_{ij} = -\frac{1}{T} \underline{\nabla} (\mu_i - \mu_j)|_T = -\underline{X}_{ji}$$

So, for no viscous dissipation ($\Phi = 0$), no chemical reactions ($r_k = 0$) or chemical equilibrium ($Y_k = 0$), and only three components

$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J'' \cdot \underline{\nabla} \varphi + \underline{J}_{12} \cdot \underline{X}_{12} + \underline{J}_{13} \cdot \underline{X}_{13} + \underline{J}_{23} \cdot \underline{X}_{23}$$

Assume linear force-flux relations

$$\underline{q}'' = L_{QQ} \underline{\nabla} \frac{1}{T} - L_{QP} \frac{1}{Tc} \underline{\nabla} p - L_{QZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Q12} \underline{X}_{12} + L_{Q13} \underline{X}_{13} + L_{Q23} \underline{X}_{23}$$

$$\underline{J}_n = L_{PQ} \underline{\nabla} \frac{1}{T} - L_{PP} \frac{1}{Tc} \underline{\nabla} p - L_{PZ} \frac{1}{T} \underline{\nabla} \varphi + L_{P12} \underline{X}_{12} + L_{P13} \underline{X}_{13} + L_{P23} \underline{X}_{23}$$

$$\underline{J}_q = L_{ZQ} \underline{\nabla} \frac{1}{T} - L_{ZP} \frac{1}{Tc} \underline{\nabla} p - L_{ZZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Z12} \underline{X}_{12} + L_{Z13} \underline{X}_{13} + L_{Z23} \underline{X}_{23}$$

$$\underline{J}_{12} = L_{12Q} \underline{\nabla} \frac{1}{T} - L_{12P} \frac{1}{Tc} \underline{\nabla} p - L_{12Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1212} \underline{X}_{12} + L_{1213} \underline{X}_{13} + L_{1223} \underline{X}_{23}$$

$$\underline{J}_{13} = L_{13Q} \underline{\nabla} \frac{1}{T} - L_{13P} \frac{1}{Tc} \underline{\nabla} p - L_{13Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1312} \underline{X}_{12} + L_{1313} \underline{X}_{13} + L_{1323} \underline{X}_{23}$$

$$\underline{J}_{23} = L_{23Q} \underline{\nabla} \frac{1}{T} - L_{23P} \frac{1}{Tc} \underline{\nabla} p - L_{23Z} \frac{1}{T} \underline{\nabla} \varphi + L_{2312} \underline{X}_{12} + L_{2313} \underline{X}_{13} + L_{2323} \underline{X}_{23}$$

Thermophoresis: interdiffusion of two constituents at uniform p

$$\sigma = \underline{J}_E \cdot \underline{\nabla} \tau + \underline{J}_{n_1} \cdot \underline{\nabla} \lambda_1 + \underline{J}_{n_2} \cdot \underline{\nabla} \lambda_2 = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \underline{J}_{12} \cdot \underline{\nabla} (\mu_1 - \mu_2)|_T$$

$$\underline{J}_{12} = \frac{c_1 c_2}{c_1 + c_2} \left[\frac{\underline{J}_{n_1}}{c_1} - \frac{\underline{J}_{n_2}}{c_2} \right] \quad \underline{\nabla} (\mu_1 - \mu_2)|_T = \frac{\partial (\mu_1 - \mu_2)}{\partial \ln c_1} \frac{\underline{\nabla} c_1}{c_1}$$

Assume linear force-flux relations

$$\underline{q}'' = -L_{QQ} \frac{1}{T^2} \underline{\nabla} T - L_{Q12} \frac{1}{T} \underline{\nabla} (\mu_1 - \mu_2)|_T$$

$$\underline{J}_{12} = -L_{12Q} \frac{1}{T^2} \underline{\nabla} T - L_{1212} \frac{1}{T} \underline{\nabla} (\mu_1 - \mu_2)|_T$$

Rewrite in terms of familiar variables as

$$\underline{q}'' = -k \underline{\nabla} T - c_1 (1 - c_1) D_T T \frac{\partial (\mu_1 - \mu_2)}{\partial c_1} \underline{\nabla} c_1$$

$$\underline{J}_{12} = -c_1 (1 - c_1) D_T \underline{\nabla} T - D_{12} \underline{\nabla} c_1$$

where we used $L_{Q12} = L_{12Q}$ and defined:

$$k = \frac{L_{QQ}}{T^2}$$

$$D_T = \frac{L_{Q12}}{c_1 (1 - c_1) T^2} = \text{thermo-diffusion coefficient}$$

$$D_{12} = \frac{L_{1212}}{T} \left[\frac{\partial (\mu_2 - \mu_1)}{\partial c_1} \right]_{T,p} = \text{Fick interdiffusion coefficient}$$

Thermophoresis: interdiffusion of two constituents at uniform p

$$\sigma = \underline{J}_E \cdot \underline{\nabla} \tau + \underline{J}_{n_1} \cdot \underline{\nabla} \lambda_1 + \underline{J}_{n_2} \cdot \underline{\nabla} \lambda_2 = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \underline{J}_{12} \cdot \underline{\nabla} (\mu_1 - \mu_2)|_T$$

$$\underline{J}_{12} = \frac{c_1 c_2}{c_1 + c_2} \left[\frac{\underline{J}_{n_1}}{c_1} - \frac{\underline{J}_{n_2}}{c_2} \right] \quad \underline{\nabla} (\mu_1 - \mu_2)|_T = \frac{\partial (\mu_1 - \mu_2)}{\partial \ln c_1} \frac{\underline{\nabla} c_1}{c_1}$$

Assume linear force-flux relations

$$\underline{q}'' = -L_{QQ} \frac{1}{T^2} \underline{\nabla} T - L_{Q12} \frac{1}{T} \underline{\nabla} (\mu_1 - \mu_2)|_T$$

$$\underline{J}_{12} = -L_{12Q} \frac{1}{T^2} \underline{\nabla} T - L_{1212} \frac{1}{T} \underline{\nabla} (\mu_1 - \mu_2)|_T$$

Rewrite in terms of familiar variables as

$$\underline{q}'' = -k \underline{\nabla} T - c_1 (1 - c_1) D_T T \frac{\partial (\mu_1 - \mu_2)}{\partial c_1} \underline{\nabla} c_1$$

$$\underline{J}_{12} = -c_1 (1 - c_1) D_T \underline{\nabla} T - D_{12} \underline{\nabla} c_1$$

where we used $L_{Q12} = L_{12Q}$ and defined:

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$$D_{12} = \frac{L_{1212}}{T} \left[\frac{\partial (\mu_2 - \mu_1)}{\partial c_1} \right]_{T,p} = \text{Fick interdiffusion coefficient}$$

Get from with

$$\underline{q}'' \quad \underline{\nabla} T \quad \underline{\nabla} c_1 = 0 \quad (\text{Fourier})$$

$$\underline{J}_{12} \quad \underline{\nabla} c_1 \quad \underline{\nabla} T = 0 \quad (\text{Fick})$$

$$\underline{J}_{12} \quad \underline{\nabla} T \quad \underline{\nabla} c_1 = 0 \quad (\text{Soret})$$

$$\underline{q}'' \quad \underline{\nabla} c_1 \quad \underline{\nabla} T = 0 \quad (\text{Dufour})$$

$$\underline{q}'' \quad \underline{\nabla} T \quad \underline{J}_{12} = 0 \quad (\text{reduced } \underline{q}'', \sigma)$$

$$\underline{\nabla} T \quad \underline{q}'' \quad \underline{J}_{12} = 0 \quad (\text{higher } \underline{\nabla} T, \sigma)$$

$$\underline{J}_{12} \quad \underline{\nabla} c_1 \quad \underline{q}'' = 0 \quad (\text{reduced } \underline{J}_{12}, \sigma)$$

$$\underline{\nabla} c_1 \quad \underline{J}_{12} \quad \underline{q}'' = 0 \quad (\text{higher } \underline{\nabla} c_1, \sigma)$$

Reciprocity $L_{Q12} = L_{12Q}$ implies that only three of the above effects need to be measured.

With respect to when $\underline{\nabla} c_1 = 0$, if $\underline{\nabla} c_1$ is allowed to build up ($\underline{J}_{12} = 0$):

- For **prescribed** $\underline{\nabla} T$, we find **smaller** \underline{q}'' and **smaller** σ .

- For **prescribed** \underline{q}'' , we find **larger** $\underline{\nabla} T$ and **larger** σ .

Thermophoresis: interdiffusion of two constituents at uniform p

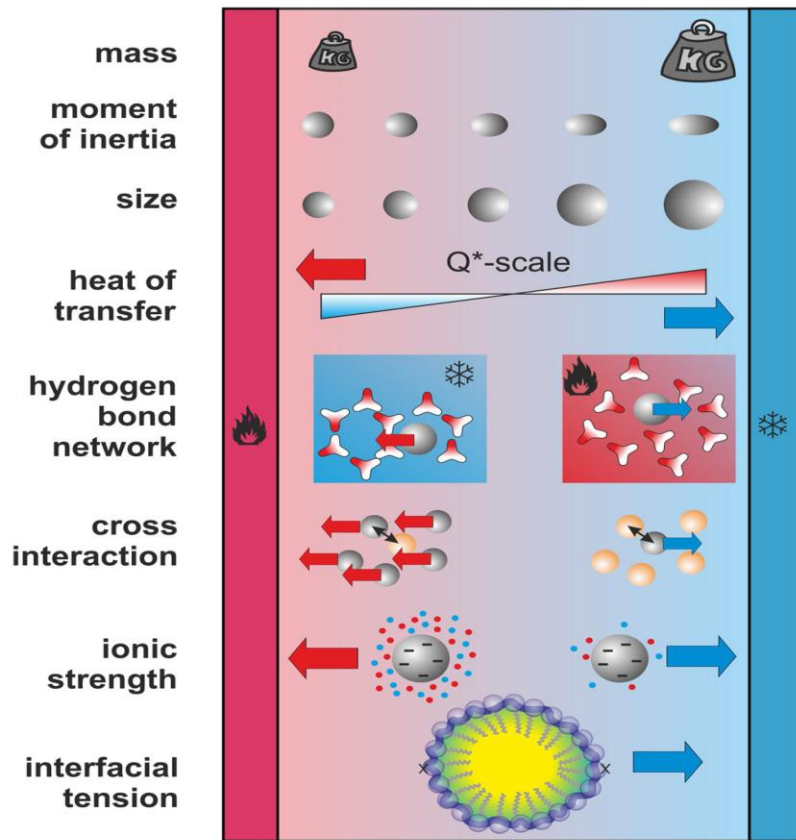


Figure 3. Sketch of a roadmap to identify the direction of the thermophoretic motion. Only general trends are identified, which do not hold for all but the majority of liquid systems. For instance *mass*, *moment of inertia* and *size* often govern the behaviour of gaseous systems and are considered in the kinetic theory of gases. *Hydrogen bonds* and *cross interactions* are especially important for systems containing water. Charge effects or the *ionic strength* dependence are discussed for salt solutions and colloidal mixtures. Finally, the importance of the *heat of transfer*-scale, Q^* -scale, will be demonstrated for low molecular mixtures. Further details are in the text.

Figure 3 from D. Neither and S. Wiegand. "Thermophoresis of biological and biocompatible compounds in aqueous solution." *Journal of Physics: Condensed Matter* 31, 503003 (2019).

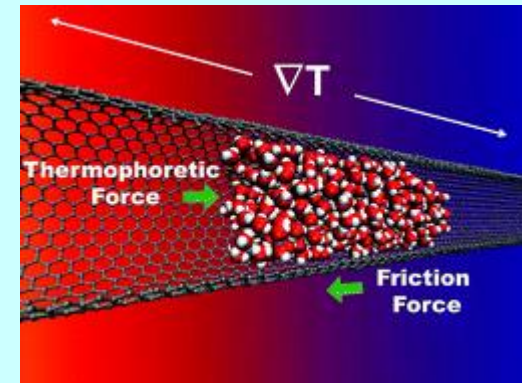
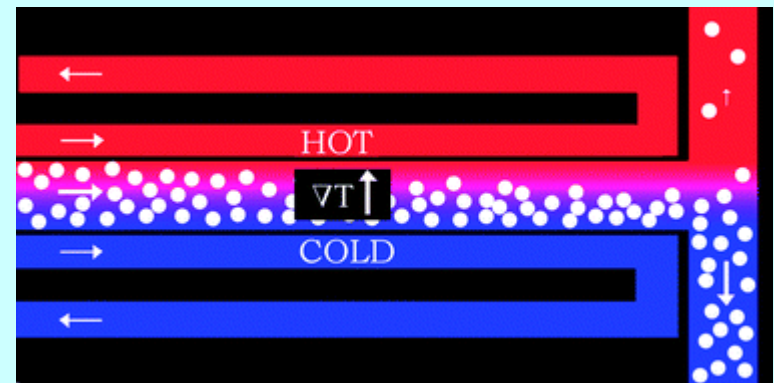
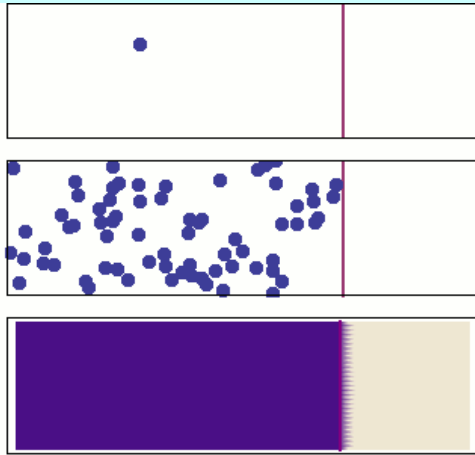


Figure 1 from E. Oyarzua, J.H. Walther, Ha.A. Zambrano, *Physical Chemistry Chemical Physics* 20, 3672 (2018).



Form R. Piazza, "Thermophoresis: moving particles with thermal gradients." *Soft Matter* 4, 1740 (2008).

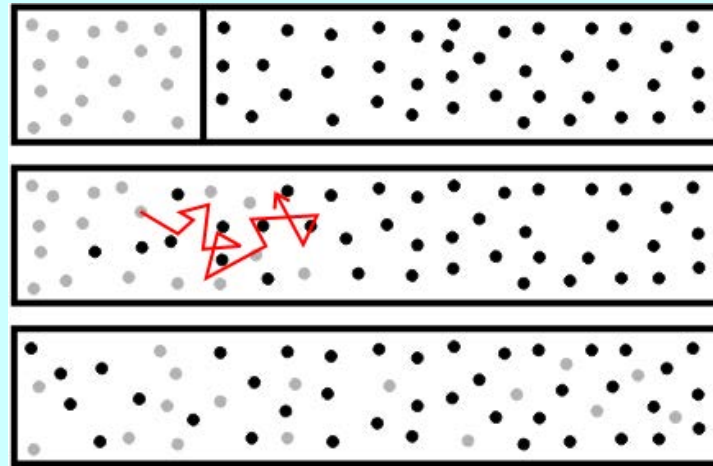
Other mechanisms for molecular transport in a pore/capillary



Sbyrnes321 from [Wikipedia](#)



Runningamok19 from [Wikipedia](#)



Jkrieger from [Wikipedia](#)

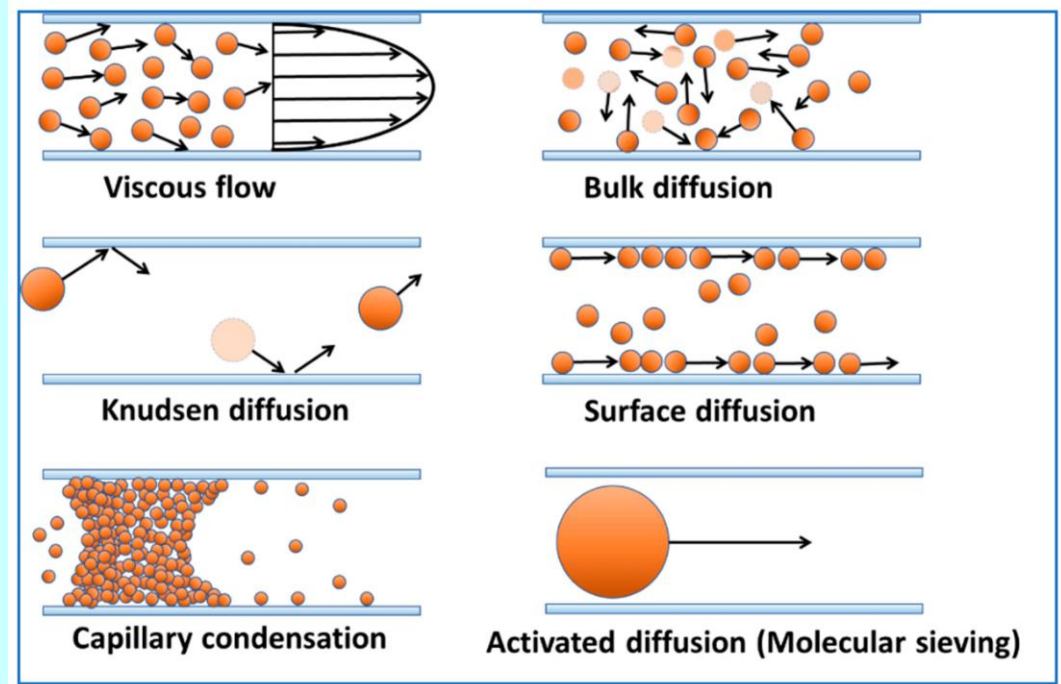


Figure 3 from R.R. Ratnakar and B. Dindoruk, Processes 10, 1194 (2022).

Active matter is particles that deploy nonequilibrium to self-propel

self-propulsion of a non-spherical particle or a Janus particle induced by local spinodal decomposition

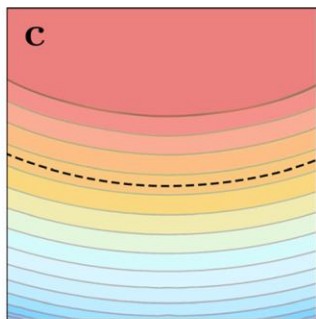
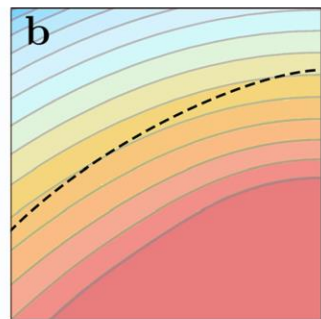
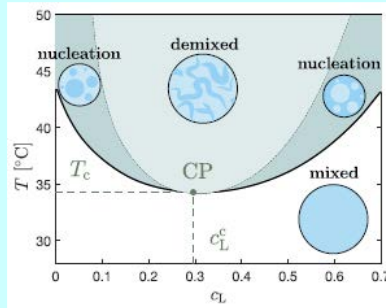
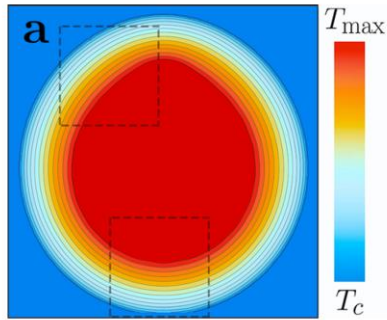


Fig. 4 Isothermals around a non-spherical particle. **a** Composition profile $\phi(\mathbf{r})$ in the vicinity of an axisymmetric particle with a surface temperature above the critical value T_c of water-2,6-lutidine. ϕ is constant at the isothermal surface and decreases with distance; the dark blue area indicates the range where $T \leq T_c$ and where the composition takes the bulk value ϕ_c . The gray lines in the critical droplet ($T \geq T_c$) indicate iso-composition surfaces. **b** The curvature of the top of the particle is larger than that of its bottom; as a consequence, ϕ varies more rapidly close to the top and the iso-composition lines are denser. The dashed line, at a constant distance from the particle surface, crosses iso-composition lines; thus there is a composition gradient $\nabla_{\parallel}\phi$ parallel to the surface, which induces a diffusio-osmotic creep velocity and results in self-propulsion of the particle. Our detailed analysis relates the particle velocity to the Fourier series of the particle shape $R(\theta)$. **c** Instead, the bottom of the particle is almost spherical with roughly constant curvature and zero creep velocity.

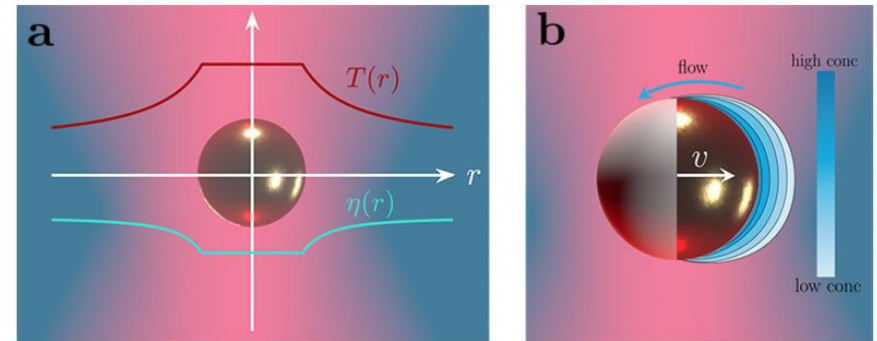


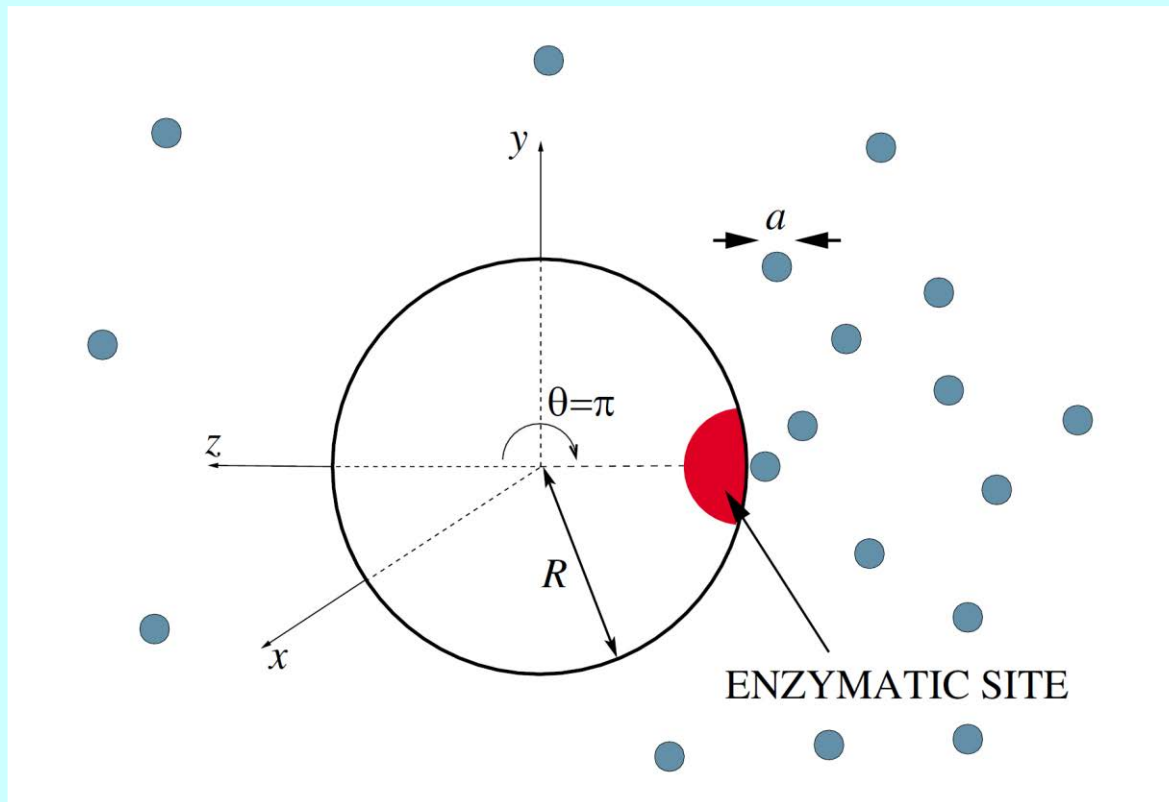
Figure 2.2: Importance of shape asymmetry for self-propulsion. **a** A spherical particle under illumination of a laser beam creates a temperature profile $T(r)$ that is constant at the particle's surface and decreases with $1/r$ radially outwards. Similarly, the viscosity $\eta(r)$ of the surrounding fluid changes. As the temperature profile is radially symmetric, the particle's effective temperature is increased leading to hot Brownian motion but no net movement. For a Janus particle in **b**, where only one hemisphere is coated with an absorbing material, a local concentration gradient can be induced through phase separation of a critical mixture. The resulting creep flow on the particle's surface produces linear motion of the particle with velocity v in the opposite direction.

Figures from Falko Schmidt, "Active Matter in a Critical State. From passive building blocks to active molecules, engines and active droplets." PhD Thesis 2021, University of Gothenburg

From F. Schmidt et al. *Nature communications* 12, 1902 (2021).

Molecular motors deploy nonequilibrium

Molecular motors are machines that convert chemical energy to mechanical work. Here a colloidal particle with an enzymatic site that lowers the activation energy of an otherwise nonequilibrium mixture of reactants. The products of the reaction cause concentration gradients which activate diffusiophoretic mechanisms



R. Golestanian, T.B. Liverpool, and A. Ajdari. "Propulsion of a molecular machine by asymmetric distribution of reaction products." *Physical review letters* 94, 220801 (2005).

Thermophoresis in solutions of electrolytes and charged particles

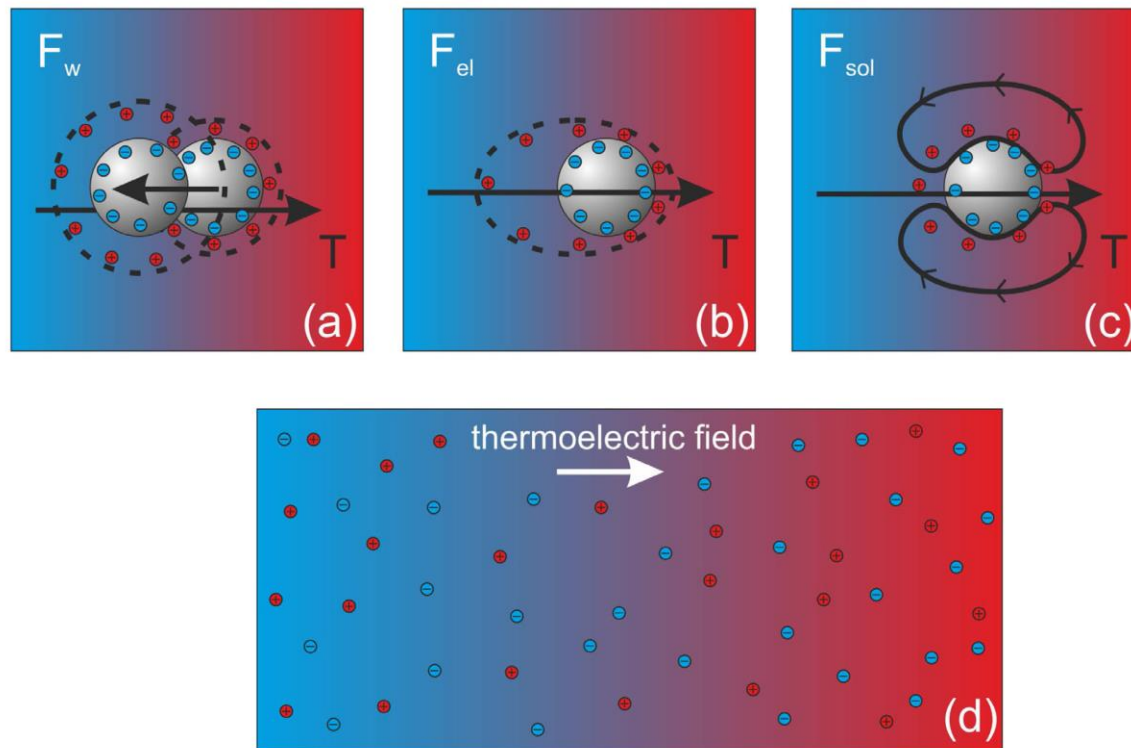


Figure 4. (a)–(c) Sketch of the three forces acting on a charged colloidal sphere in a temperature gradient according to Dhont and Briels [99]. (a) The internal force F_w due to the change of the double-layer structure on displacement of the sphere. The dashed lines indicate the extent of the unperturbed double layer at ambient temperature, that is, the temperature at the origin of the colloidal sphere. (b) The electric force F_{el} that is due to the non-spherically symmetric double-layer structure. The dashed line indicates the asymmetry of the double layer. (c) The solvent-friction force F_{sol} is due to the solvent flow that is induced by electric body forces arising from the asymmetry of the double-layer structure. The lines indicate solvent flow lines. (d) Illustration of thermoelectric field arising from a thermal gradient in a binary electrolyte solution.

From D. Niether, and S. Wiegand. *Journal of Physics: Condensed Matter* 31, 503003 (2019).

Now you are (almost) ready to model electrochemical systems!

$$\sigma = -\frac{1}{T^2} \underline{q}'' \cdot \underline{\nabla} T - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \frac{1}{2} \sum_{ij} J_{ij} \cdot \underline{X}_{ij} + \sum_k r_k Y_k + \Phi/T$$

$$\underline{J}_{ij} = \frac{c_i c_j}{c} \left[\frac{J_{ni}}{c_i} - \frac{J_{nj}}{c_j} \right] = -\underline{J}_{ji}$$

$$\underline{X}_{ij} = -\frac{1}{T} \underline{\nabla} (\mu_i - \mu_j)|_T = -\underline{X}_{ji}$$

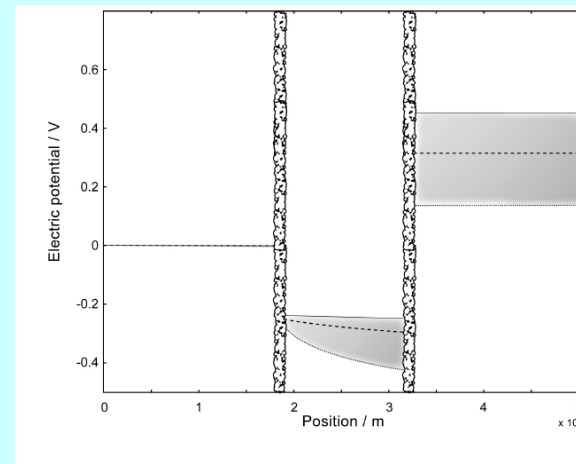
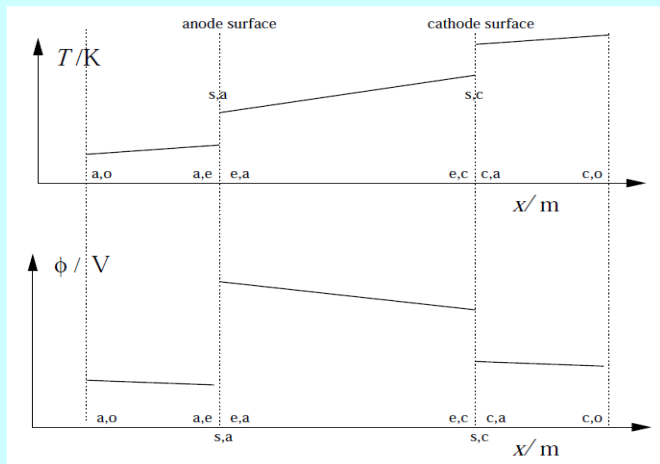
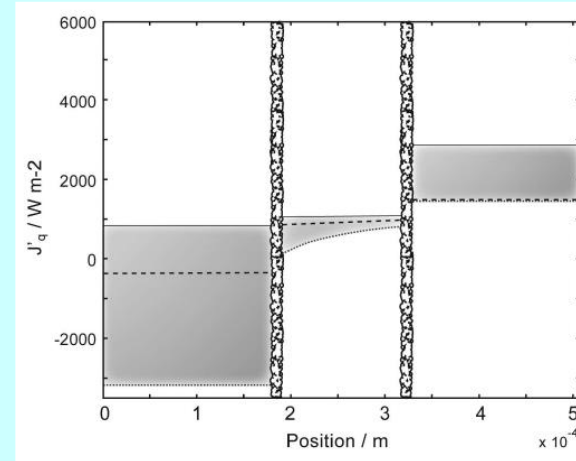
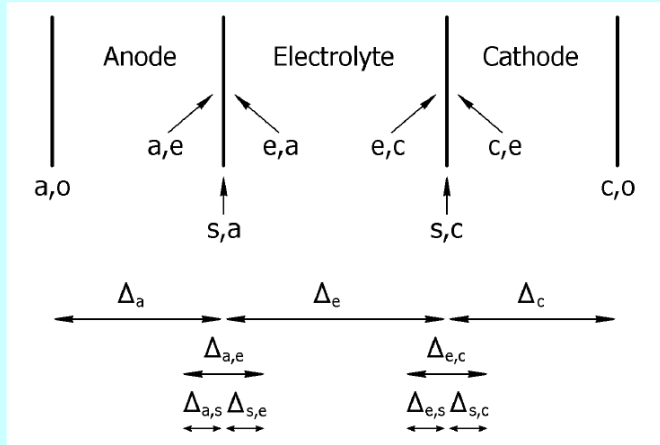
So, for no viscous dissipation ($\Phi = 0$), no chemical reactions ($r_k = 0$) or chemical equilibrium ($Y_k = 0$), and only three components

$$\sigma = \underline{q}'' \cdot \underline{\nabla} \frac{1}{T} - \frac{1}{T} \frac{J_n}{c} \cdot \underline{\nabla} p - \frac{1}{T} J_q \cdot \underline{\nabla} \varphi + \underline{J}_{12} \cdot \underline{X}_{12} + \underline{J}_{13} \cdot \underline{X}_{13} + \underline{J}_{23} \cdot \underline{X}_{23}$$

Assume linear force-flux relations

$$\begin{aligned} \underline{q}'' &= L_{QQ} \underline{\nabla} \frac{1}{T} - L_{QP} \frac{1}{Tc} \underline{\nabla} p - L_{QZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Q12} \underline{X}_{12} + L_{Q13} \underline{X}_{13} + L_{Q23} \underline{X}_{23} \\ \underline{J}_n &= L_{PQ} \underline{\nabla} \frac{1}{T} - L_{PP} \frac{1}{Tc} \underline{\nabla} p - L_{PZ} \frac{1}{T} \underline{\nabla} \varphi + L_{P12} \underline{X}_{12} + L_{P13} \underline{X}_{13} + L_{P23} \underline{X}_{23} \\ \underline{J}_q &= L_{ZQ} \underline{\nabla} \frac{1}{T} - L_{ZP} \frac{1}{Tc} \underline{\nabla} p - L_{ZZ} \frac{1}{T} \underline{\nabla} \varphi + L_{Z12} \underline{X}_{12} + L_{Z13} \underline{X}_{13} + L_{Z23} \underline{X}_{23} \\ \underline{J}_{12} &= L_{12Q} \underline{\nabla} \frac{1}{T} - L_{12P} \frac{1}{Tc} \underline{\nabla} p - L_{12Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1212} \underline{X}_{12} + L_{1213} \underline{X}_{13} + L_{1223} \underline{X}_{23} \\ \underline{J}_{13} &= L_{13Q} \underline{\nabla} \frac{1}{T} - L_{13P} \frac{1}{Tc} \underline{\nabla} p - L_{13Z} \frac{1}{T} \underline{\nabla} \varphi + L_{1312} \underline{X}_{12} + L_{1313} \underline{X}_{13} + L_{1323} \underline{X}_{23} \\ \underline{J}_{23} &= L_{23Q} \underline{\nabla} \frac{1}{T} - L_{23P} \frac{1}{Tc} \underline{\nabla} p - L_{23Z} \frac{1}{T} \underline{\nabla} \varphi + L_{2312} \underline{X}_{12} + L_{2313} \underline{X}_{13} + L_{2323} \underline{X}_{23} \end{aligned}$$

Modeling electrochemical systems



Figures 13.1, 13.2, 19.4, 19.5 from S. Kjelstrup, D. Bedeaux: **Non-equilibrium Thermodynamics for Heterogeneous Systems**, Advances in Statistical Mechanics, Vol. 16 (World Scientific, Singapore 2008).

S. Kjelstrup and D. Bedeaux, **Thermodynamics of Electrochemical Systems**. In: Breitkopf, C., Swider-Lyons, K. (eds) Springer Handbook of Electrochemical Energy. (Springer Handbooks. Springer, Berlin, Heidelberg 2017), pp. 69-93.

D. Bedeaux, **Nonequilibrium thermodynamics and statistical physics of surfaces**. Advances in Chemical Physics 64, 47-109 (1986).

Nonequilibrium beyond the linear regime

More on far-nonequilibrium models

Far non-eq: states depend on many variables

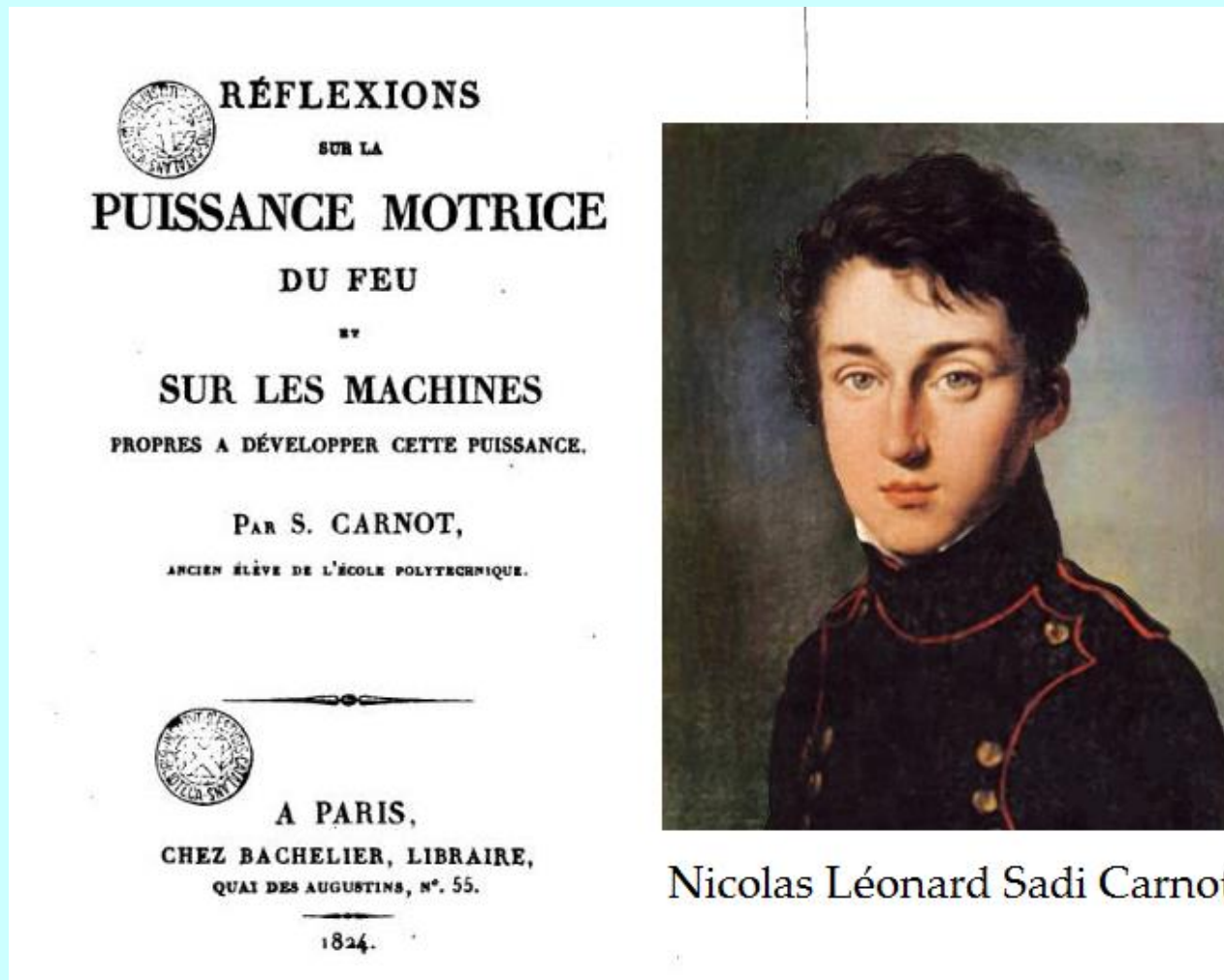
		Framework	State	Entropy
A	IT	Information Theory	$\{p_j(\mathbf{x}, t)\}$	$\hat{s} = -k_B \sum_j p_j \ln p_j$
	SM	Statistical Mechanics		
B	RGD	Rarefied Gases Dynamics	$f(\mathbf{c}, \mathbf{x}, t)$	$\hat{s} = -k_B \iiint f \ln f d\mathbf{c}$
	SSH	Small-Scale Hydrodynamics		
C	RET	Rational Extended Thermodynamics	$\{y_j(\mathbf{x}, t)\}$	$\hat{s} = \hat{s}(\{y_j\})$
	NET	Non-Equilibrium Thermodynamics		
	CK	Chemical Kinetics		
D	MNET	Mesoscopic NE Thermodynamics	$P(\{y_j\}, \mathbf{x}, t)$	$\hat{s} = \hat{s}(P(\{y_j\}))$
E	QSM	Quantum Statistical Mechanics	$\rho(\mathbf{x}, t)$ $\hat{a} = \text{Tr} \rho A$	$\hat{s} = -k_B \text{Tr} \rho \ln \rho$
	QT	Quantum Thermodynamics		
	MNEQT	Mesoscopic NE QT		
F	QSM	Cahn-Hilliard models	$\{y_j(\mathbf{x}, t)\}$	$\hat{s} = \hat{s}(\{y_i\}, \{\nabla y_j \cdot \nabla y_k\})$
	QT	Diffuse Interface methods		
	MNEQT	Non-local NE models		

More on far-nonequilibrium models

Various statistical and numerical simulation methods:

- Boltzmann equation
- Chapman-Enskog approximation
- Grad 13-moment regularized approximations
- Fokker-Planck equation
- Langevin stochastic equation
- Molecular Dynamics
- Kinetic Monte Carlo
- Dissipative Particle Dynamics
- Coarse-Grained Molecular Dynamics
- Ab-Initio Molecular Dynamics
- Probabilistic Cellular Automata
- ...
- ...
- ...

In 2024 Thermodynamics turned 200 years old!



Nicolas Léonard Sadi Carnot

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- Every two years. Next deadline February 1, 2025.
- For PhD defenses held between Jan.1, 2023 and Dec.31, 2024.
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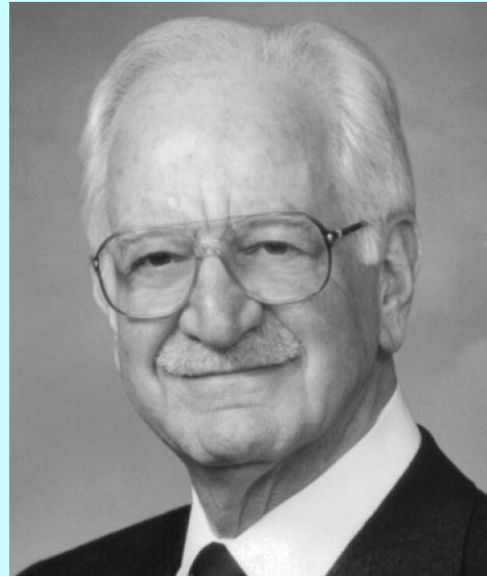
Thank you for attending (or viewing) these lectures!

I dedicate them in memory of my mentors

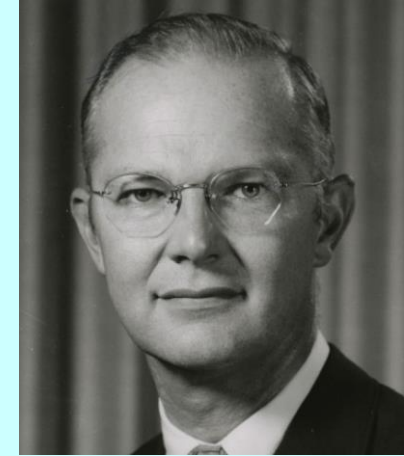


**Mario Silvestri
(1919-1994)**

**with gratitude for having inspired
my journey into this captivating field**



**Elias P. Gyftopoulos
(1927-2012)**



**James C. Keck
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**James L. Park
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