2.43 ADVANCED THERMODYNAMICS

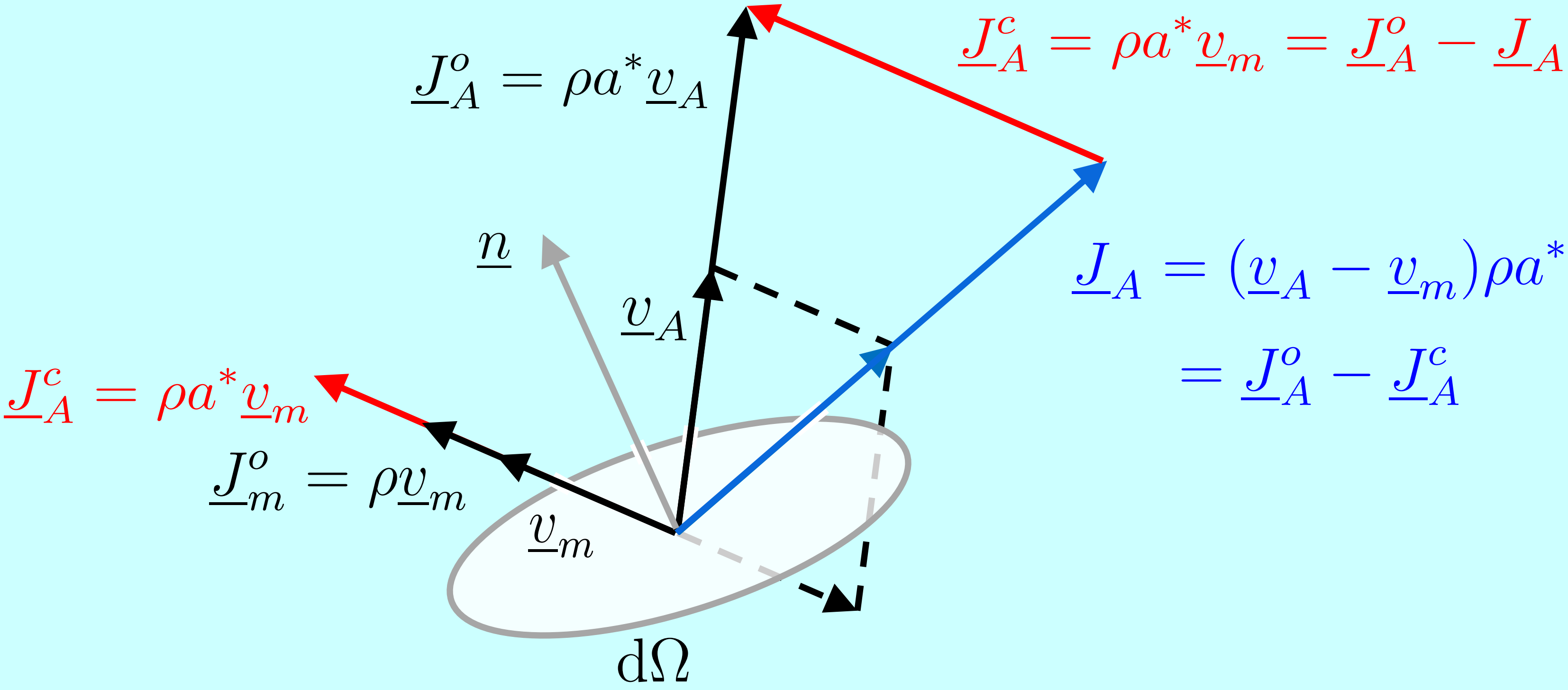
Spring Term 2024
LECTURE 23

Room 3-442
Tuesday, April 30, 2:30pm - 4:30pm

Instructor: Gian Paolo Beretta
beretta@mit.edu
Room 3-351d

Ingredients of the general balance equations for the extensive properties of a continuum:

Diffusive and convective fluxes in terms of transport velocities



Amount $\delta A^{\underline{n}\rightarrow}$ of property A that crosses an infinitesimal planar surface of area $\mathrm{d}\Omega$ in the direction of the unit normal $\underline{n}$ during the time interval between t and $t + \mathrm{d}t$

$$\delta A^{\underline{n}\rightarrow} = (\underline{v}_A \cdot \underline{n})\rho a^* \,\mathrm{d}\Omega\,\mathrm{d}t = (\underline{J}^o_A \cdot \underline{n})\,\mathrm{d}\Omega\,\mathrm{d}t$$

"Heat&diffusion" mode of interaction between adjacent elements

The energy, entropy, and mole fluxes are related by

$$\underline{J}_S = \tau\,\underline{J}_E + \textstyle\sum_i \lambda_i^{\rm tot}\,\underline{J}_{n_i} \qquad \text{recall:} \quad \tau = \frac{1}{T} \ \text{and}\ \lambda_i^{\rm tot} = -\frac{\mu_i^{\rm tot}}{T}$$

and, therefore, the divergences of the fluxes are related by

$$\underline{\nabla}\cdot\underline{J}_S = \underline{\nabla}\tau\cdot\underline{J}_E + \tau\underline{\nabla}\cdot\underline{J}_E + \textstyle\sum_i \underline{\nabla}\lambda_i^{\rm tot}\cdot\underline{J}_{n_i} + \textstyle\sum_i \lambda_i^{\rm tot}\underline{\nabla}\cdot\underline{J}_{n_i}$$

The mass specific energy of the fluid element at $(\boldsymbol{x}, t)$ may be written as

$$\begin{aligned} e^* &= u^*(\rho s^*, \underline{c}) + \tfrac{1}{2}v_m^2 + gz + \rho_q\varphi/\rho \\ \rho e^* &= \rho\, u^*(\rho s^*, \underline{c}) + \textstyle\sum_i c_i\left(\tfrac{1}{2}M_i v_m^2 + M_i g z + z_i F\varphi\right) \end{aligned}$$

where $u^* = u^*(\rho s^*, \underline{c})$ is the stable-equilibrium simple-system fundamental relation expressing the specific energy for a surrogate fluid element with the same entropy density and molar densities but viewed from a reference frame moving with the barycentric velocity $\underline{v}_m$ and with the chemical reactions and the gravitational and electrostatic fields turned off. Recalling that the natural variables of the chemical potential μ_i are $T, p, \boldsymbol{y}$, the total potentials, therefore, are

$$\mu_i^{\rm tot} = \mu_i(T, p, \boldsymbol{y}) + \tfrac{1}{2}M_i v_m^2 + M_i g z + z_i F\varphi$$

which results when E is assumed to be a function of S, V, $\underline{n}$, $\frac{1}{2}v_m^2$, gz, and φ, and the total potential is defined as

$$\mu_i^{\rm tot} = \left(\frac{\partial E}{\partial n_i}\right)_{S, V, \underline{n}', v_m, z, \varphi} = \left(\frac{\partial(\rho e^*)}{\partial c_i}\right)_{s, \underline{c}', v_m, z, \varphi}$$

where the second equality follows from observing that $(\mathrm{d}E)_V = V\,\mathrm{d}(\rho e^*)$, $(\mathrm{d}S)_V = V\,\mathrm{d}(\rho s^*)$, and $(\mathrm{d}n_i)_V = V\,\mathrm{d}c_i$.

General balance equations for an extensive property of a continuum

The **local balance equations** for energy, entropy, number of moles, and momentum (equation of motion) are (for future reference we write each of them in the **two equivalent forms** :

$$\frac{\partial \rho e^*}{\partial t} + \underline{\nabla}\cdot\underline{J}^o_E = \rho\frac{De^*}{Dt} + \underline{\nabla}\cdot\underline{J}_E = 0$$

$$\frac{\partial \rho s^*}{\partial t} + \underline{\nabla}\cdot\underline{J}^o_S = \rho\frac{Ds^*}{Dt} + \underline{\nabla}\cdot\underline{J}_S = \sigma$$

$$\frac{\partial c_i}{\partial t} + \underline{\nabla}\cdot\underline{J}^o_{n_i} = \frac{Dc_i}{Dt} - \frac{c_i}{\rho}\frac{D\rho}{Dt} + \underline{\nabla}\cdot\underline{J}_{n_i} = \sum_k \nu_{ik} r_k$$

$$\frac{\partial \rho \underline{v}_m}{\partial t} + \underline{\nabla}\cdot\underline{J}^o_{\underline{v}_m} = \rho\frac{D\underline{v}_m}{Dt} - \underline{\nabla}\cdot\underline{\underline{\tau}} = -\rho\underline{\nabla}\varphi_g - \rho_q\underline{\nabla}\varphi$$

Here $\rho_q = F\sum_i c_i z_i$ is the charge density, $\underline{g} = -\underline{\nabla}\varphi_g$ the gravitational acceleration ($\rho\underline{g}$ is the net gravitational force density), $\underline{E} = -\underline{\nabla}\varphi$ the electrostatic field ($q\underline{E}$ is the net electrostatic force density) and, recall, $\underline{\underline{\tau}} = -\underline{\underline{P}} = -\underline{J}_{\underline{v}_m}$ is the stress tensor.

Considering that each chemical reaction conserves mass and charge, $\sum_i M_i\nu_{ik} = 0$ and $\sum_i z_i\nu_{ik} = 0$, from the above balance equation we may obtain the balance equations for components masses, overall mass, volume, overall charge, kinetic energy, and gravitational and electrostatic potential energy, respectively,

$$\frac{\partial \rho_i}{\partial t} + \underline{\nabla}\cdot\underline{J}^o_{m_i} = \rho\frac{Dx_i}{Dt} + \underline{\nabla}\cdot\underline{J}_{m_i} = M_i\sum_k \nu_{ik} r_k$$

$$\frac{\partial \rho}{\partial t} + \underline{\nabla}\cdot(\rho\underline{v}_m) = \frac{D\rho}{Dt} + \rho\underline{\nabla}\cdot\underline{v}_m = 0 \qquad \rho\frac{Dv}{Dt} = -\frac{1}{\rho}\frac{D\rho}{Dt} = \underline{\nabla}\cdot\underline{v}_m$$

$$\rho\frac{D(\frac{1}{2}v_m^2)}{Dt} = \underline{\nabla}\cdot(\underline{\underline{\tau}}\cdot\underline{v}_m) - \underline{\underline{\tau}} : \underline{\nabla}\,\underline{v}_m - \rho\underline{v}_m\cdot\underline{\nabla}\varphi_g - \rho_q\underline{v}_m\cdot\underline{\nabla}\varphi$$

$$\rho\frac{D(\varphi_g)}{Dt} = \rho\underline{v}_m\cdot\underline{\nabla}\varphi_g \qquad \rho\frac{D(\rho_q\varphi/\rho)}{Dt} = \rho_q\underline{v}_m\cdot\underline{\nabla}\varphi$$

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

Also recall that here $r_k = r_k(\underline{x}, t)$ denotes the local rate of change of the k-th reaction coordinate ε_k per unit volume (some authors use the symbol r_k to the denote $\dot{\varepsilon}_k$ per unit mass, and the symbol ν_{ik} to denote $M_i\nu_{ik}$, so that for them the local rate of production/consumption of component i, in mass per unit of volume, due to the k-th chemical reaction is $\nu_{ik} r_k$, whereas here it is $M_i\nu_{ik} r_k$).

Nonequilibrium in heat, mass, and charge transfer

the extrinsic relation for the entropy production density in terms of fluxes and forces

General “entropic form” of the expression for σ

- Assume local simple-system equilibrium, with $e^* = u^*(\rho s^*, \boldsymbol{c}) + \frac{1}{2}v_m^2 + \varphi_g + \rho_q\varphi/\rho$

$$\rho e^* = \rho u^*(\rho s^*, \boldsymbol{c}) + \textstyle\sum_i c_i \left(\frac{1}{2}M_i v_m^2 + M_i\varphi_g + z_i F\varphi\right)$$

$$\mu_i^{\rm tot} = \mu_i + \tfrac{1}{2}M_i v_m^2 + M_i\varphi_g + z_i F\varphi \qquad \lambda^{\rm tot} = -\mu^{\rm tot}/T \qquad \tau = 1/T$$

- Assume that Euler relation + Gibbs relation, $\mathrm{d}(\rho s^*) = \tau\,\mathrm{d}(\rho u^*) + \sum_i \lambda_i^{\rm tot}\,\mathrm{d}c_i$, for each fluid parcel, following its motion, therefore

$$\frac{D\rho s^*}{Dt} = \tau\,\frac{D\rho u^*}{Dt} + \sum_i \lambda_i^{\rm tot}\,\frac{Dc_i}{Dt} \qquad \text{recall also that} \quad Y_k = \sum_i \lambda_i^{\rm tot}\nu_{ik}$$

- Assume "heat&diffusion" mode of interaction for the non-work interactions between adjacent elements of the continuum, i.e.:

$$\underline{J}_S = \tau\,\underline{J}_E^{\rm nw} + \sum_i \lambda_i^{\rm tot}\,\underline{J}_{n_i} \qquad \text{and} \quad \underline{J}_E = \underline{J}_E^{\rm nw} + \underline{J}_E^{\rm w} \quad \text{with} \quad \underline{J}_E^{\rm w} = -\underline{\underline{\tau}}\cdot\underline{v}_m$$

where $\underline{J}_E^{\rm w}$ is the energy flux due to work interactions between fluid elements. Therefore,

$$\underline{\nabla}\cdot\underline{J}_S = \underline{\nabla}\tau\cdot\underline{J}_E^{\rm nw} + \tau\underline{\nabla}\cdot\underline{J}_E + \tau\underline{\nabla}\cdot(\underline{\underline{\tau}}\cdot\underline{v}_m) + \sum_i \underline{\nabla}\lambda_i^{\rm tot}\cdot\underline{J}_{n_i} + \sum_i \lambda_i^{\rm tot}\underline{\nabla}\cdot\underline{J}_{n_i}$$

- Combining all the above with the balance equations in the previous slide, yields:

$$\sigma = \underline{J}_E^{\rm nw}\cdot\underline{\nabla}\tau + \sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\lambda_i^{\rm tot} + \sum_k Y_k r_k + \frac{1}{T}\,\underline{\underline{\tau}} : \underline{\nabla}\,\underline{v}_m + \frac{p}{T}\,\underline{\nabla}\cdot\underline{v}_m$$

σ in terms of the **measurable heat flux q''** in the absence of charge carriers

$$\sigma = \dot{s}'''_{\rm irr} = \underline{J}_E^{\rm nw}\cdot\underline{\nabla}\tau + \sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\lambda_i + \sum_k Y_k r_k + \frac{1}{T}\underline{\underline{\tau}} : \underline{\nabla}\,\underline{v}_m + \frac{p}{T}\underline{\nabla}\cdot\underline{v}_m$$

Recall (heat&diffusion for the non-work interactions): $\underline{J}_E^{\rm nw} = \underline{q}'' + \sum_i h_i \underline{J}_{n_i}$

$$\sigma = (\underline{q}'' + \textstyle\sum_i h_i \underline{J}_{n_i})\cdot\underline{\nabla}\tau - \textstyle\sum_i \underline{J}_{n_i}\cdot\underline{\nabla}(\mu_i\tau) + \textstyle\sum_k Y_k r_k + \frac{1}{T}\underline{\underline{\tau}} : \underline{\nabla}\,\underline{v}_m + \frac{p}{T}\underline{\nabla}\cdot\underline{v}_m$$

Note that $h_i\,\underline{\nabla}\tau - \underline{\nabla}(\mu_i\tau) = -\tau\,\underline{\nabla}\mu_i|_T$ (from $\mu_i = h_i - Ts_i$ and $\mathrm{d}\mu_i = -s_i\,\mathrm{d}T + \mathrm{d}\mu_i|_T$)

$$\sigma = \underline{q}''\cdot\underline{\nabla}\tau - \tau\textstyle\sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\mu_i|_T + \textstyle\sum_k Y_k r_k + \frac{1}{T}\underline{\underline{\tau}}' : \underline{\nabla}\,\underline{v}_m - \frac{1}{T}p_m\,\underline{\nabla}\cdot\underline{v}_m + \frac{p}{T}\underline{\nabla}\cdot\underline{v}_m$$

$$\sigma = -\frac{1}{T^2}\underline{q}''\cdot\underline{\nabla}T - \frac{1}{T}\sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\mu_i|_T + \sum_k Y_k r_k + \frac{1}{T}\Phi$$

where in the last steps we also defined:

- $\Phi = \frac{1}{3}(p - p_m)\underline{\nabla}\cdot\underline{v}_m + \frac{1}{2}\underline{\underline{\tau}}' : (\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\rm T})'$ is the so-called **dissipation function** (local rate of dissipation of mechanical energy that gets transformed into thermal energy).
- $p_m = -\mathrm{Tr}(\underline{\underline{\tau}})/3$ and $\underline{\underline{\tau}}'$ is the **deviatoric component of the local stress tensor**, such that $\underline{\underline{\tau}} = -p_m\underline{\underline{\delta}} + \underline{\underline{\tau}}'$. Recall, $\underline{\underline{\tau}} = -\underline{J}_{m\underline{v}_m}$ is the negative of the momentum flux with respect to the baricentric flow velocity (decomposed in its isotropic and deviatoric components).
- $\frac{1}{2}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\rm T})' = \frac{1}{2}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\rm T}) - \frac{1}{3}(\underline{\nabla}\cdot\underline{v}_m)\,\underline{\underline{\delta}}$ is the **deviatoric component of the symmetric part of the local strain rate tensor**.

σ in terms of the measurable heat flux q'' and the current density I''

$$\sigma = \dot{s}'''_{\rm irr} = \underline{J}_E^{\rm nw}\cdot\underline{\nabla}\tau + \sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\lambda_i^{\rm tot} + \sum_k r_k Y_k + \Phi/T$$

Recall (heat&diffusion with charge):

$$\underline{J}_E^{\rm nw} = \underline{q}'' + \sum_i h_i \underline{J}_{n_i} + \varphi\, \underline{J}_q$$

where

$$\underline{J}_q = F\sum_i z_i \underline{J}_{n_i}$$

is the **diffusion flux of charge**.

$$\sigma = (\underline{q}'' + \sum_i h_i\underline{J}_{n_i} + \varphi\underline{J}_q)\cdot\underline{\nabla}\tau - \sum_i \underline{J}_{n_i}\cdot\underline{\nabla}(\mu_i^{\rm tot}\tau) + \sum_k r_k Y_k + \Phi/T$$

Using $\underline{\nabla}\lambda_i = -\underline{\nabla}(\mu_i\tau) = -h_i\,\underline{\nabla}\tau - \tau\,\underline{\nabla}\mu_i|_T$ and $\mu_i^{\rm tot} = \mu_i + z_i F\varphi$ yields

$$\sigma = \underline{q}''\cdot\underline{\nabla}\tau - \tau\sum_i\underline{J}_{n_i}\cdot\underline{\nabla}\mu_i|_T - \tau\,\underline{J}_q\cdot\underline{\nabla}\varphi + \sum_k r_k Y_k + \Phi/T$$

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

where $\underline{I}'' = \underline{J}_q^o = \underline{J}_q + \rho_q\,\underline{v}_m = F\sum_i z_i\underline{J}^o_{n_i}$ is the **current density** and

$\rho_q = F\sum_i z_i c_i$ is the **charge density**.

σ in terms of q'', I'' and Φ: an "extrinsic relation"

”Extrinsic” because:

- it follows from general balance equations and local equilibrium assumptions only, and
- it holds for all materials, independently of their particular properties.

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

Rewrite in order of increasing tensorial character

$$\begin{aligned}
\sigma = {} & \overbrace{\sum_k r_k Y_k}^{\text{scalars}} - \overbrace{\frac{1}{3}\frac{1}{T}(p_m - p)\underline{\nabla}\cdot\underline{v}}^{\text{scalars}} \\
& - \overbrace{\frac{1}{T^2}\underline{q}''\cdot\underline{\nabla}T}^{\text{vectors}} - \overbrace{\frac{1}{T}\sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\mu_i|_T}^{\text{vectors}} - \overbrace{\frac{1}{T}(\underline{I}'' - \rho_q\,\underline{v}_m)\cdot\underline{\nabla}\varphi}^{\text{vectors}} \\
& + \overbrace{\frac{1}{T}\underline{\underline{\tau}}' : \frac{1}{2}(\underline{\nabla}\,\underline{v} + \underline{\nabla}\,\underline{v}^{\mathrm{T}})'}^{\text{tensors}}
\end{aligned}$$

$T_o\,\sigma$ is the rate of exergy dissipation per unit volume

$$\begin{aligned}\sigma = {} & \overbrace{\sum_k r_k Y_k}^{\text{scalars}} - \frac{1}{T}\overbrace{\frac{1}{3}(p_m - p)\underline{\nabla} \cdot \underline{v}_m}^{\text{scalars}} \\ & - \frac{1}{T^2}\overbrace{\underline{q}'' \cdot \underline{\nabla} T}^{\text{vectors}} - \frac{1}{T}\overbrace{\sum_i \underline{J}_{n_i} \cdot \underline{\nabla}\mu_i|_T}^{\text{vectors}} - \frac{1}{T}\overbrace{(\underline{I}'' - \rho_q \underline{v}_m) \cdot \underline{\nabla}\varphi}^{\text{vectors}} \\ & + \frac{1}{T}\overbrace{\underline{\underline{\tau}}' : \frac{1}{2}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\mathrm{T}})'}^{\text{tensors}}\end{aligned}$$

$T_0\sigma$ represents the rate of exergy dissipation per unit volume (exergy with respect to a reservoir at temperature T_0) when we drive:

a chemical reaction rate in the direction of decreasing affinity;

a heat flux down a temperature gradient;

a diffusion flux down a chemical potential gradient;

a capillary flow down a pressure gradient;

an electric current down a voltage drop;

a momentum flux down a velocity gradient.

Force-Flux shorthand notation

$$\sigma = \overbrace{\sum_k r_k Y_k}^{\text{scalars}} - \frac{1}{T}\overbrace{\frac{1}{3}(p_m - p)\underline{\nabla}\cdot\underline{v}_m}^{\text{scalars}}$$

$$- \frac{1}{T^2}\overbrace{\underline{q}''\cdot\underline{\nabla}T}^{\text{vectors}} - \frac{1}{T}\overbrace{\sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\mu_i|_T}^{\text{vectors}} - \frac{1}{T}\overbrace{(\underline{I}'' - \rho_q\underline{v}_m)\cdot\underline{\nabla}\varphi}^{\text{vectors}}$$

$$+ \frac{1}{T}\overbrace{\underline{\underline{\tau}}' : \frac{1}{2}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\mathrm{T}})'}^{\text{tensors}}$$

Often, for shorthand, this is rewritten formally as

$$\sigma = \sum\nolimits_f \boldsymbol{J}_f \odot \boldsymbol{X}_f$$

where we define the supervectors $\boldsymbol{J}_f$ and $\boldsymbol{X}_f$, and the superdot product $\odot$ as follows

$$\begin{array}{lcllllllllllll}
\underline{\boldsymbol{J}} & = & \{ & r_k & ; & (p_m - p) & ; & \underline{q}'' & ; & \underline{J}_{n_i} & ; & (\underline{I}'' - \rho_q\underline{v}_m) & ; & \underline{\underline{\tau}}' \quad \} \\
\odot & = & \{ & \times & ; & \times & ; & \cdot & ; & \cdot & ; & \cdot & ; & : \quad \} \\
\underline{\boldsymbol{X}} & = & \{ & Y_k & ; & \underline{\nabla}\cdot\underline{v}_m & ; & -\frac{1}{T^2}\underline{\nabla}T & ; & \frac{1}{T}\underline{\nabla}\mu_i|_T & ; & -\frac{1}{T}\underline{\nabla}\varphi & ; & \frac{1}{T}\frac{1}{2}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\mathrm{T}})' \quad \}
\end{array}$$

Nonequilibrium in heat, mass, and charge transfer

linear relations between forces and fluxes

cross effects and Onsager reiprocal relations

Curie principle

Material resistance to flux and forces: “intrinsic” relations for σ

Off equilibrium each material in its own way tries to restore equilibrium:

- **it resists to imposed fluxes $\underline{\boldsymbol{J}}$ by building up forces $\underline{\boldsymbol{X}}$**

The flux→force **constitutive relation** characterizes the non-equilibrium behavior of the material:

$$\underline{\boldsymbol{X}} = \underline{\boldsymbol{X}}(\underline{\boldsymbol{J}}, \underline{\Gamma})$$

In this picture, σ is a function of $\underline{\boldsymbol{J}}$:

$$\sigma = \sum_f \boldsymbol{J}_f \odot \boldsymbol{X}_f(\underline{\boldsymbol{J}}, \underline{\Gamma}) = \sigma(\underline{\boldsymbol{J}}, \underline{\Gamma})$$

- **it resists to imposed forces $\underline{\boldsymbol{X}}$ by building up fluxes $\underline{\boldsymbol{J}}$**

The force→flux **constitutive relation** characterizes the non-equilibrium behavior of the material:

$$\underline{\boldsymbol{J}} = \underline{\boldsymbol{J}}(\underline{\boldsymbol{X}}, \underline{\Gamma})$$

In this picture, σ is a function of $\underline{\boldsymbol{X}}$:

$$\sigma = \sum_f \boldsymbol{J}_f(\underline{\boldsymbol{X}}, \underline{\Gamma}) \odot \boldsymbol{X}_f = \sigma(\underline{\boldsymbol{X}}, \underline{\Gamma})$$

Compatibility conditions:

- $\sigma(0, \underline{\Gamma}) = 0$ at equilibrium ($\underline{\boldsymbol{J}}_{\rm eq} = 0$ and $\underline{\boldsymbol{X}}_{\rm eq} = 0$)
- $\sigma \geq 0$ off equilibrium
- Onsager reciprocity near equilibrium
- Curie principle for isotropic conditions
- near-equilibrium force-flux constitutive relations may depend on the local equilibrium potentials; hence, the dependence on $\{\underline{\Gamma} = \{1/T, -\mu_1/T, \dots, -\mu_n/T, -\varphi/T\}$

Direct laws (neglecting cross effects)

$\sigma = \sum_k r_k Y_k$	see chemical kinetics	
$-\frac{1}{3}\frac{1}{T}(p_m - p)\underline{\nabla}\cdot\underline{v}_m$	$p_m - p = -\eta_{\substack{\text{bulk}\\ \text{viscosity}}}\,\underline{\nabla}\cdot\underline{v}_m$	Lamb law[‡] for Newtonian fluid 1879
$-\frac{1}{T^2}\underline{q}''\cdot\underline{\nabla}T$	$\underline{q}'' = -k_{\substack{\text{thermal}\\ \text{conductivity}}}\,\underline{\nabla}T$	Fourier law for isotropic material 1822
$-\frac{1}{T}\sum_i \underline{J}_{n_i}\cdot\underline{\nabla}\mu_i\vert_T$	$\underline{J}_{n_i} = -\frac{c_i}{RT}D_{i,\text{diffusivity}}\underline{\nabla}\mu_i\vert_T$	Fick law for isotropic material 1855
$-\frac{1}{T}\underline{J}_q\cdot\underline{\nabla}\varphi$	$\underline{J}_q = -\frac{1}{\rho_{\substack{\text{electrical}\\ \text{resistivity}}}}\underline{\nabla}\varphi$	Ohm law of conduction 1827
$\frac{1}{T}\underline{\underline{\tau}}' : \frac{1}{2}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\mathrm{T}})'$	$\underline{\underline{\tau}}' = \eta_{\substack{\text{shear}\\ \text{viscosity}}}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\mathrm{T}})'$	Navier law[†] for Newtonian fluid 1821

† + ‡ yield: $\underline{\underline{\tau}} = -p\,\underline{\underline{\delta}} + \eta_{\substack{\text{shear}\\ \text{viscosity}}}(\underline{\nabla}\,\underline{v}_m + \underline{\nabla}\,\underline{v}_m^{\mathrm{T}}) + (\eta_{\substack{\text{bulk}\\ \text{viscosity}}} - \frac{2}{3}\eta_{\substack{\text{shear}\\ \text{viscosity}}})(\underline{\nabla}\cdot\underline{v}_m)\,\underline{\underline{\delta}}$

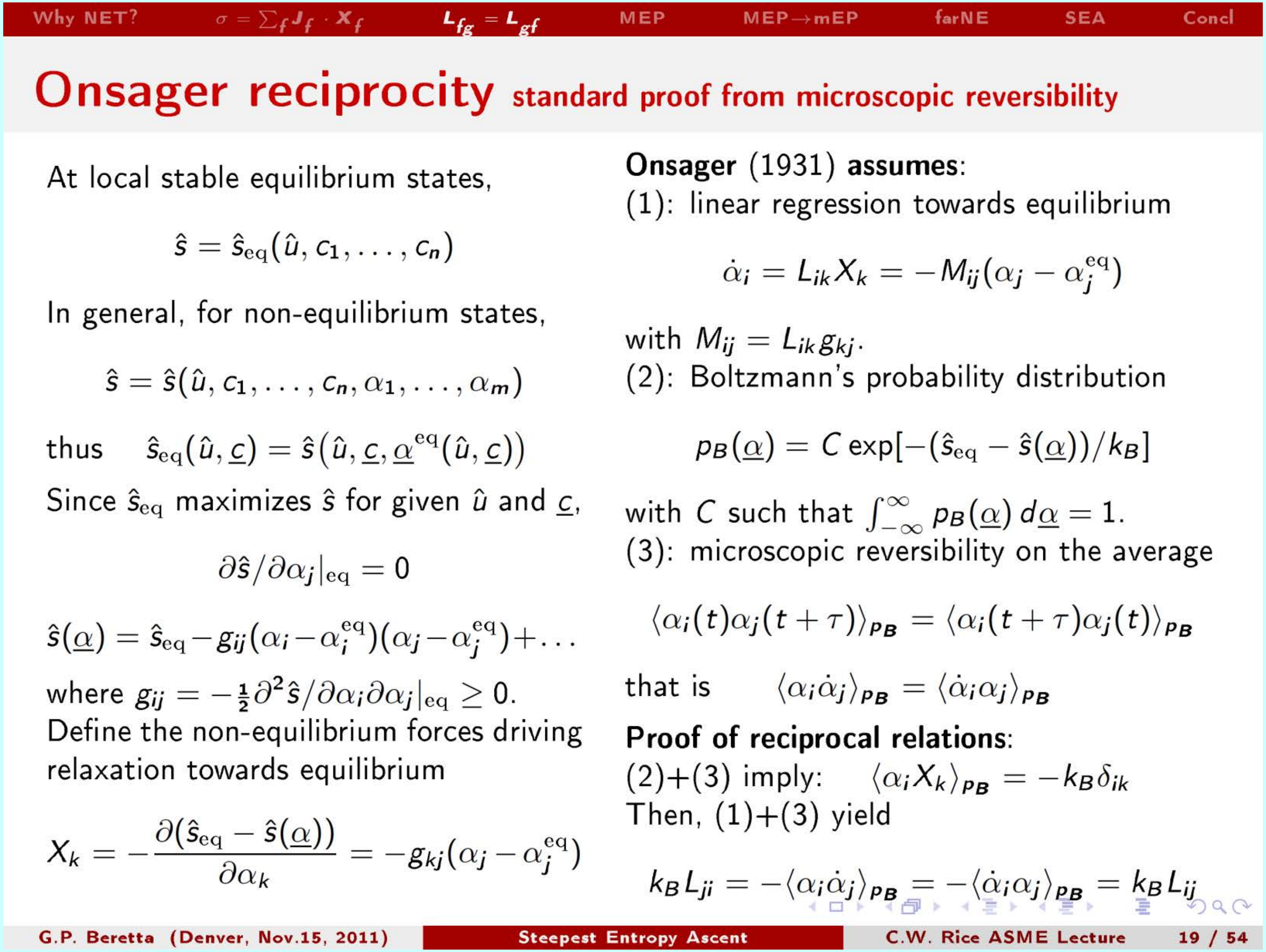
Onsager nonequilibrium cross effects and the Curie symmetry principle

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.

sketch of Onsager's original proof



Why NET? $\sigma = \sum_f J_f \cdot X_f$ $L_{fg} = L_{gf}$ MEP MEP→mEP farNE SEA Concl

Onsager reciprocity standard proof from microscopic reversibility

At local stable equilibrium states,

$$\hat{s} = \hat{s}_{\rm eq}(\hat{u}, c_1, \ldots, c_n)$$

In general, for non-equilibrium states,

$$\hat{s} = \hat{s}(\hat{u}, c_1, \ldots, c_n, \alpha_1, \ldots, \alpha_m)$$

thus $\hat{s}_{\rm eq}(\hat{u}, \underline{c}) = \hat{s}(\hat{u}, \underline{c}, \underline{\alpha}^{\rm eq}(\hat{u}, \underline{c}))$

Since $\hat{s}_{\rm eq}$ maximizes $\hat{s}$ for given $\hat{u}$ and $\underline{c}$,

$$\partial\hat{s}/\partial\alpha_j|_{\rm eq} = 0$$

$$\hat{s}(\underline{\alpha}) = \hat{s}_{\rm eq} - g_{ij}(\alpha_i - \alpha_i^{\rm eq})(\alpha_j - \alpha_j^{\rm eq}) + \ldots$$

where $g_{ij} = -\frac{1}{2}\partial^2\hat{s}/\partial\alpha_i\partial\alpha_j|_{\rm eq} \geq 0$.
Define the non-equilibrium forces driving relaxation towards equilibrium

$$X_k = -\frac{\partial(\hat{s}_{\rm eq} - \hat{s}(\underline{\alpha}))}{\partial\alpha_k} = -g_{kj}(\alpha_j - \alpha_j^{\rm eq})$$

Onsager (1931) **assumes**:
(1): linear regression towards equilibrium

$$\dot{\alpha}_i = L_{ik}X_k = -M_{ij}(\alpha_j - \alpha_j^{\rm eq})$$

with $M_{ij} = L_{ik}g_{kj}$.
(2): Boltzmann's probability distribution

$$p_B(\underline{\alpha}) = C \exp[-(\hat{s}_{\rm eq} - \hat{s}(\underline{\alpha}))/k_B]$$

with C such that $\int_{-\infty}^{\infty} p_B(\underline{\alpha})\, d\underline{\alpha} = 1$.
(3): microscopic reversibility on the average

$$\langle\alpha_i(t)\alpha_j(t+\tau)\rangle_{p_B} = \langle\alpha_i(t+\tau)\alpha_j(t)\rangle_{p_B}$$

that is $\langle\alpha_i\dot{\alpha}_j\rangle_{p_B} = \langle\dot{\alpha}_i\alpha_j\rangle_{p_B}$

Proof of reciprocal relations:
(2)+(3) imply: $\langle\alpha_i X_k\rangle_{p_B} = -k_B\delta_{ik}$
Then, (1)+(3) yield

$$k_B L_{ji} = -\langle\alpha_i\dot{\alpha}_j\rangle_{p_B} = -\langle\dot{\alpha}_i\alpha_j\rangle_{p_B} = k_B L_{ij}$$

G.P. Beretta (Denver, Nov.15, 2011) Steepest Entropy Ascent C.W. Rice ASME Lecture 19 / 54

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

Orthogonality relations yield Onsager relations in the linear regime as a consequence of the

principle of maximum entropy production rate (Ziegler, 1958)

Given the **constraint** $\sigma = \sum_i \boldsymbol{J}_i \odot \boldsymbol{X}_i$, which is required by the balance equations, assume linear relations between fluxes and forces, $\boldsymbol{J}_i = \sum_j \underline{\underline{\boldsymbol{L}}}_{ij} \odot \boldsymbol{X}_j$, so that

$$\sigma = \sum_i \sum_j \boldsymbol{X}_i \odot \underline{\underline{\boldsymbol{L}}}_{ij} \odot \boldsymbol{X}_j \qquad \text{and} \qquad \frac{\partial \sigma}{\partial \boldsymbol{X}_i} = \sum_j \boldsymbol{X}_j \odot \underline{\underline{\boldsymbol{L}}}_{ji} + \sum_j \underline{\underline{\boldsymbol{L}}}_{ij} \odot \boldsymbol{X}_j$$

Assume σ is maximal subject to the constraint. Using the method of Lagrange multipliers,

maximize σ subject to $\sigma - \sum_i \boldsymbol{J}_i \odot \boldsymbol{X}_i = 0$, i.e., maximize $\mathcal{L} = \sigma - \lambda \left(\sigma - \sum_i \boldsymbol{J}_i \odot \boldsymbol{X}_i \right)$

$$0 = \left(\frac{\partial \mathcal{L}}{\partial \boldsymbol{X}_i} \right)_{\boldsymbol{J}} = (1-\lambda) \frac{\partial \sigma}{\partial \boldsymbol{X}_i} + \lambda \boldsymbol{J}_i \quad \Rightarrow \quad \boldsymbol{J}_i = \frac{\lambda - 1}{\lambda} \frac{\partial \sigma}{\partial \boldsymbol{X}_i} \quad (1)$$

Ziegler orthogonality

Substitute this back into the constraint, to determine the Lagrange multiplier:

$$\sigma = \frac{\lambda-1}{\lambda} \sum_i \boldsymbol{X}_i \odot \frac{\partial \sigma}{\partial \boldsymbol{X}_i} = \frac{\lambda-1}{\lambda} \sum_i \sum_j \boldsymbol{X}_i \odot \left(\underline{\underline{\boldsymbol{L}}}_{ij} + \underline{\underline{\boldsymbol{L}}}_{ji} \right) \odot \boldsymbol{X}_j = \frac{\lambda-1}{\lambda} 2\sigma$$

Therefore we must have $2(\lambda-1)/\lambda = 1$ implies $\lambda = 2$ and we may rewrite Eq.(1) as follows

$$\boldsymbol{J}_i = \frac{1}{2} \frac{\partial \sigma}{\partial \boldsymbol{X}_i} \quad \text{or} \quad \sum_j \underline{\underline{\boldsymbol{L}}}_{ij} \odot \boldsymbol{X}_j = \frac{1}{2} \sum_j \left(\underline{\underline{\boldsymbol{L}}}_{ij} + \underline{\underline{\boldsymbol{L}}}_{ji} \right) \odot \boldsymbol{X}_j$$

that is, $2\sum_j \underline{\underline{\boldsymbol{L}}}_{ij} \odot \boldsymbol{X}_j - \sum_j \underline{\underline{\boldsymbol{L}}}_{ij} \odot \boldsymbol{X}_j - \sum_j \underline{\underline{\boldsymbol{L}}}_{ji} \odot \boldsymbol{X}_j = 0$ or $\sum_j \left(\underline{\underline{\boldsymbol{L}}}_{ij} - \underline{\underline{\boldsymbol{L}}}_{ji} \right) \odot \boldsymbol{X}_j = 0$

This holds for all possible combinations of values of the $\boldsymbol{X}_j$'s only if $\underline{\underline{\boldsymbol{L}}}_{ij} = \underline{\underline{\boldsymbol{L}}}_{ji}$, i.e., if the matrix is symmetric.

Orthogonality relations in the nonlinear regime as a consequence of the principle of maximum entropy production rate (Ziegler, 1958)

Given the **constraint** $\sigma = \sum_i \underline{\boldsymbol{J}}_i \odot \underline{\boldsymbol{X}}_i$, which is required by the balance equations, assume nonlinear relations between fluxes and forces, $\underline{\boldsymbol{J}}_i = \underline{\boldsymbol{J}}_i(\{\underline{\boldsymbol{X}}_k\})$, so that

$$\sigma = \sum_j \underline{\boldsymbol{X}}_j \odot \underline{\boldsymbol{J}}_j(\{\underline{\boldsymbol{X}}_k\}) \qquad \text{and} \qquad \frac{\partial \sigma}{\partial \underline{\boldsymbol{X}}_i} = \underline{\boldsymbol{J}}_i + \sum_j \underline{\boldsymbol{X}}_j \odot \frac{\partial \underline{\boldsymbol{J}}_j}{\partial \underline{\boldsymbol{X}}_i}$$

Assume σ is maximal subject to the constraint. Using the method of Lagrange multipliers,

maximize σ subject to $\sigma - \sum_i \underline{\boldsymbol{J}}_i \odot \underline{\boldsymbol{X}}_i = 0$, i.e., maximize $\mathcal{L} = \sigma - \lambda \left(\sigma - \sum_i \underline{\boldsymbol{J}}_i \odot \underline{\boldsymbol{X}}_i\right)$

$$0 = \left(\frac{\partial \mathcal{L}}{\partial \underline{\boldsymbol{X}}_i}\right)_{\underline{\boldsymbol{J}}} = (1-\lambda)\frac{\partial \sigma}{\partial \underline{\boldsymbol{X}}_i} + \lambda \underline{\boldsymbol{J}}_i \quad \Rightarrow \quad \underline{\boldsymbol{J}}_i = (\lambda - 1)\sum_j \underline{\boldsymbol{X}}_j \odot \frac{\partial \underline{\boldsymbol{J}}_j}{\partial \underline{\boldsymbol{X}}_i} \quad (1)$$

Ziegler orthogonality

Substitute this back into the constraint, to determine the Lagrange multiplier:

$$\sum_\ell \underline{\boldsymbol{X}}_\ell \odot \underline{\boldsymbol{J}}_\ell = (\lambda - 1)\sum_j \sum_\ell \underline{\boldsymbol{X}}_j \odot \frac{\partial \underline{\boldsymbol{J}}_j}{\partial \underline{\boldsymbol{X}}_\ell} \odot \underline{\boldsymbol{X}}_\ell \quad \Rightarrow \quad \lambda(\{\underline{\boldsymbol{X}}_k\}) = 1 + \frac{\sum_\ell \underline{\boldsymbol{X}}_\ell \odot \underline{\boldsymbol{J}}_\ell(\{\underline{\boldsymbol{X}}_k\})}{\sum_j \sum_\ell \underline{\boldsymbol{X}}_j \odot \frac{\partial \underline{\boldsymbol{J}}_j}{\partial \underline{\boldsymbol{X}}_\ell}(\{\underline{\boldsymbol{X}}_k\}) \odot \underline{\boldsymbol{X}}_\ell}$$

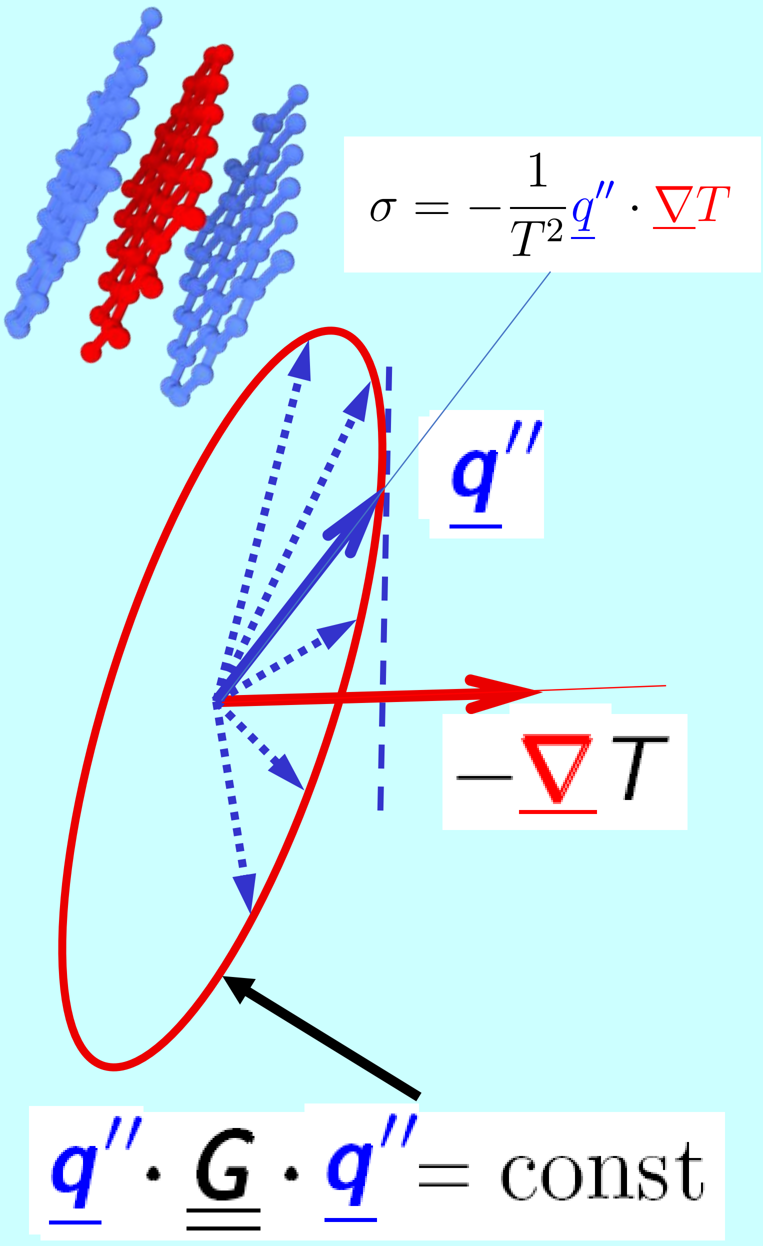
Therefore, the nonlinear relations $\underline{\boldsymbol{J}}_i = \underline{\boldsymbol{J}}_i(\{\underline{\boldsymbol{X}}_k\})$ must satisfy the orthogonality condition

$$\underline{\boldsymbol{J}}_i = \frac{\sum_\ell \underline{\boldsymbol{X}}_\ell \odot \underline{\boldsymbol{J}}_\ell(\{\underline{\boldsymbol{X}}_k\})}{\sum_j \sum_\ell \underline{\boldsymbol{X}}_j \odot \frac{\partial \underline{\boldsymbol{J}}_j}{\partial \underline{\boldsymbol{X}}_\ell}(\{\underline{\boldsymbol{X}}_k\}) \odot \underline{\boldsymbol{X}}_\ell} \sum_j \underline{\boldsymbol{X}}_j \odot \frac{\partial \underline{\boldsymbol{J}}_j}{\partial \underline{\boldsymbol{X}}_i}(\{\underline{\boldsymbol{X}}_j\})$$

This holds for all possible combinations of values of the $\underline{\boldsymbol{X}}_j$'s.

For example, for the linear relation $\underline{\boldsymbol{J}}_i = \sum_j \underline{\underline{\boldsymbol{L}}}_{ij} \odot \underline{\boldsymbol{X}}_j$ it reduces to the condition $\underline{\boldsymbol{J}}_i = \sum_j \underline{\underline{\boldsymbol{L}}}_{ji} \odot \underline{\boldsymbol{X}}_j$ which we already know requires $\underline{\underline{\boldsymbol{L}}}_{ji} = \underline{\underline{\boldsymbol{L}}}_{ij}$.

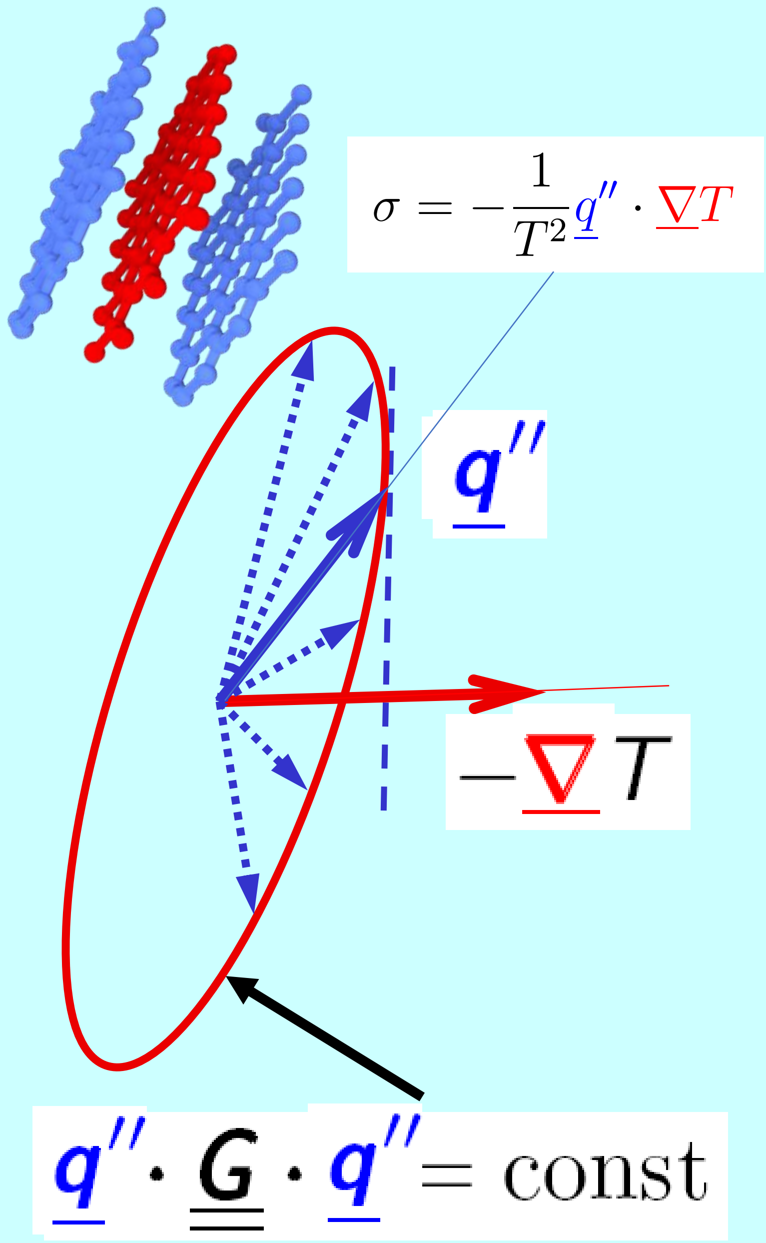
Material resistance to flux and forces: steepest entropy ascent



When an external action keeps a fluid or solid element away from equilibrium, its entropy is lower than the maximum value allowed by the values of the conserved quantities and the symmetries of the problem. The material reacts by exhibiting a spontaneous tendency to return to equilibrium: if the system constraints allow simultaneous flows of multiple conserved quantities (energy, chemical species with or without electric charge, ...) the different flows and gradients collaborate in searching for the direction (in state space) of **steepest entropy ascent with respect to a local metric $\underline{\underline{G}}$** that represents how the combined mechanisms that govern its internal dynamics resist to the evolution of the state towards certain directions (in state space) more than others. This metric thus determines the local direction of evolution. The collaboration of different flows and gradients give rise to coupling phenomena. If the state is not far from equilibrium, the connections between flows and gradients can be linearized, and the symmetry of $\underline{\underline{G}}$ (any metric is symmetric) implies the Onsager reciprocity principle.

G.P. Beretta, "The fourth law of thermodynamics: steepest entropy ascent."
Phil. Trans. Royal Society A 378: 20190168 (2020).

Material resistance to flux and forces: steepest entropy ascent



$$\sigma = -\frac{1}{T^2}\underline{q}''\cdot\underline{\nabla}T$$

$$\underline{q}''$$

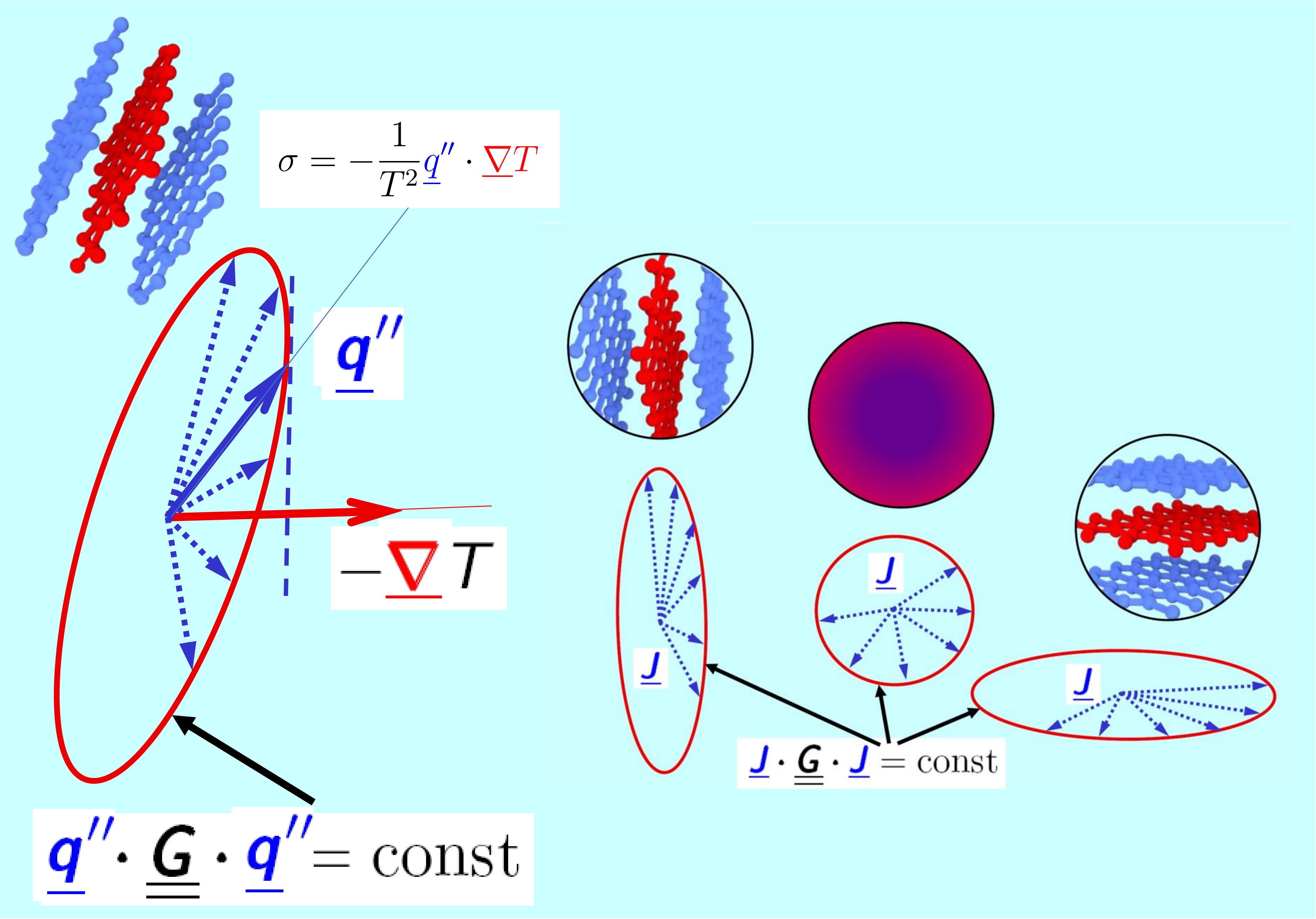
$$-\underline{\nabla}T$$

$$\underline{q}''\cdot\underline{\underline{G}}\cdot\underline{q}'' = \text{const}$$

Because of the anisotropy, the material offers less resistance to heat flux along the highly conductive principal direction than in any other less conductive directions. This is represented by the red ellipse, which represents the locus of the tips of all the heat flux vectors $\underline{q}''$ to which the material offers the same dissipation rate, defined by the quadratic form $\underline{q}''\cdot\underline{\underline{G}}\cdot\underline{q}''$ where the tensor $\underline{\underline{G}}$ is a local state property, the thermal resistivity tensor of the material.

The local entropy production rate per unit volume σ is given by the scalar product of the temperature gradient, the vector $-\underline{\nabla}T$, and the heat flux vector $\underline{q}''$. The fourth law here says that the material will choose, among all the possible equally-dissipative heat-flux directions, the one that maximizes the local entropy production rate. The figure shows that among all possible directions, it is the solid blue vector $\underline{q}''$ that maximizes its orthogonal projection onto the red vector $-\underline{\nabla}T$. Near equilibrium this is the geometrical version of Onsager's linear theory of irreversible thermodynamics, and the fact that $\underline{\underline{G}}$ is a metric (any metric is symmetric) implies automatically the Onsager reciprocity principle with no need of further assumptions. It can even be extended further from equilibrium, at least as far as the local equilibrium approximation keeps giving reasonable values of the local properties.

Material resistance to flux and forces: steepest entropy ascent

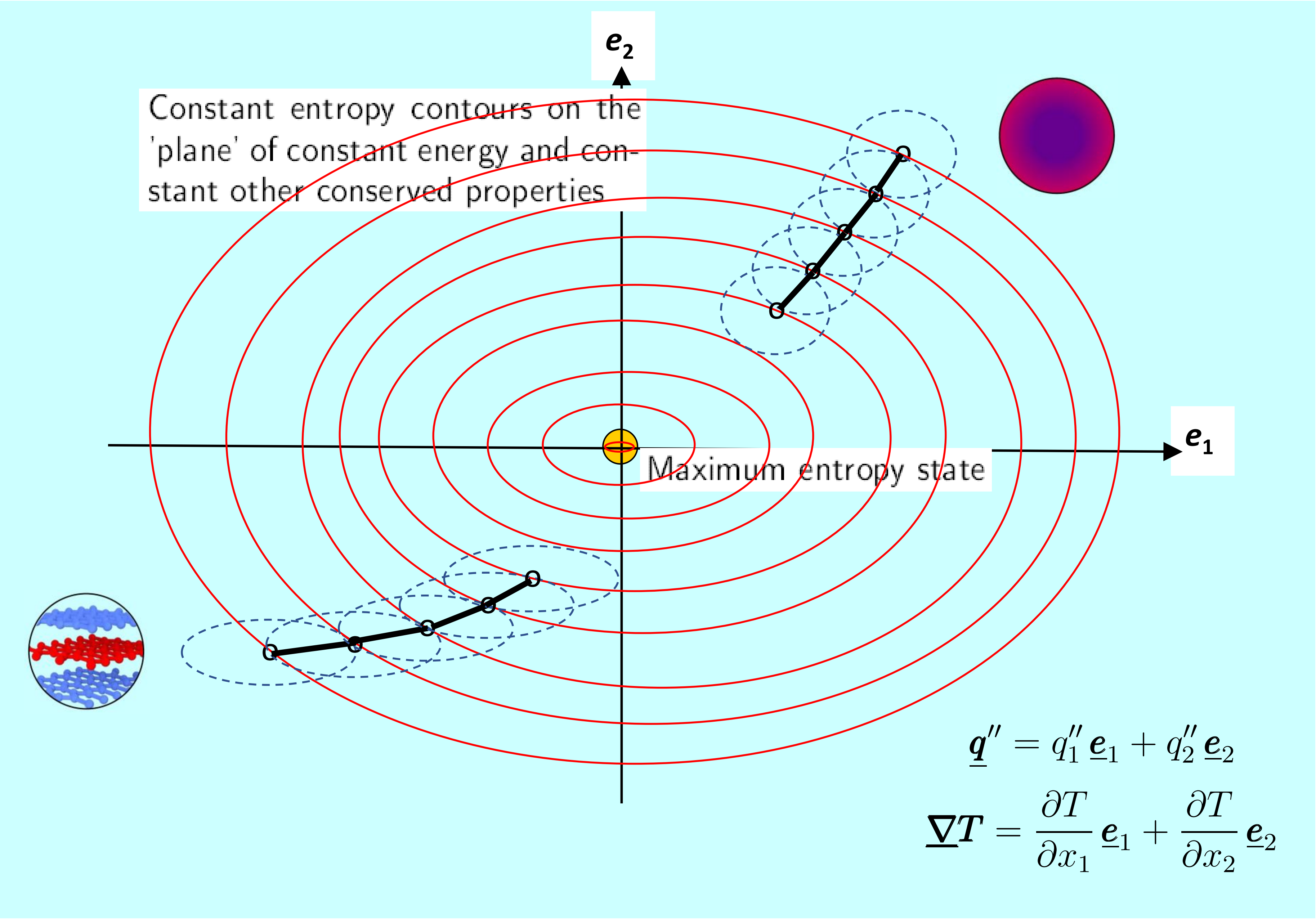


$$\sigma = -\frac{1}{T^2}\underline{q}''\cdot\underline{\nabla}T$$

$$\underline{J}\cdot\underline{\underline{G}}\cdot\underline{J} = \text{const}$$

$$\underline{q}''\cdot\underline{\underline{G}}\cdot\underline{q}'' = \text{const}$$

Material resistance to flux and forces: steepest entropy ascent



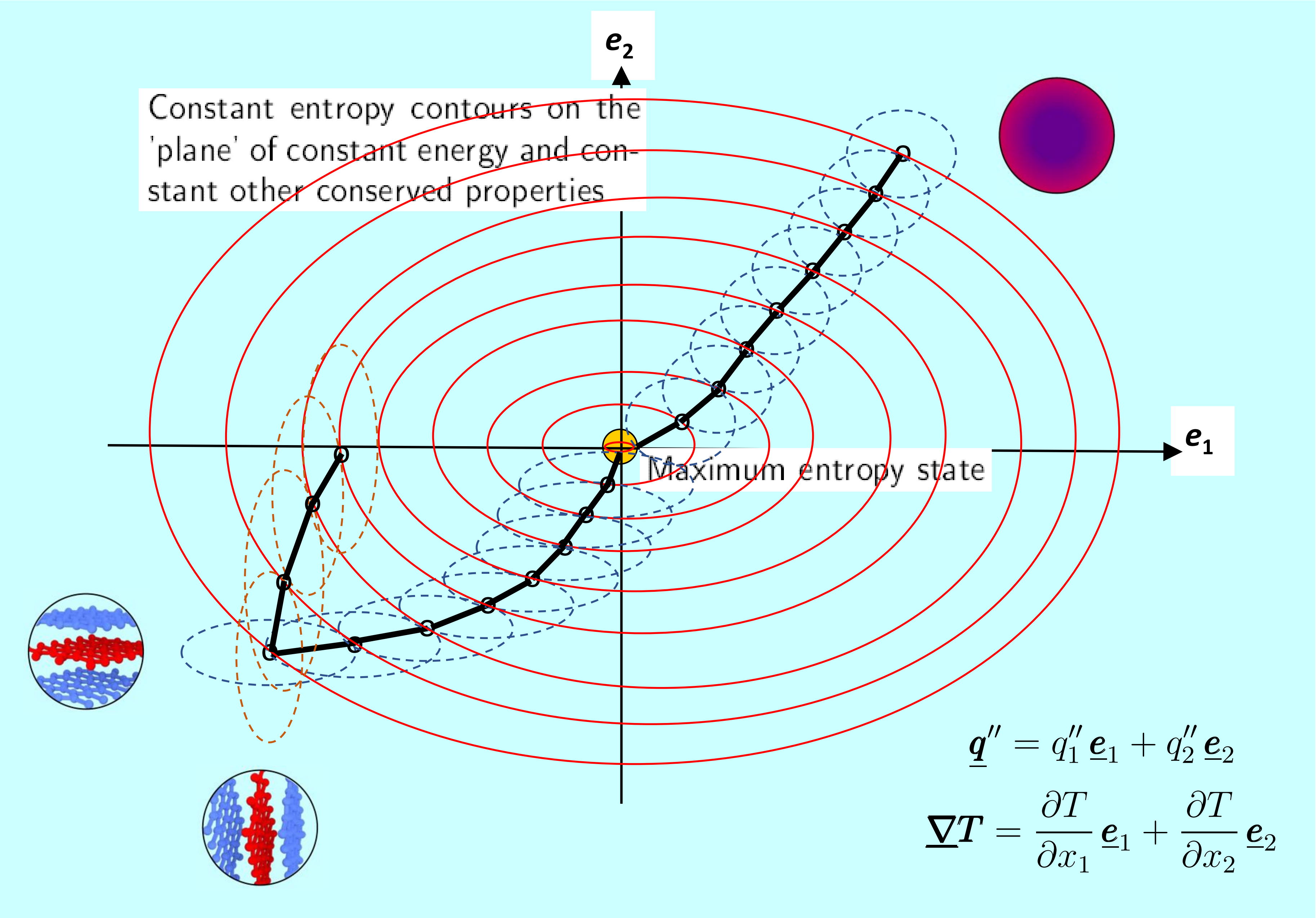
Constant entropy contours on the 'plane' of constant energy and constant other conserved properties

Maximum entropy state

$$\underline{\boldsymbol{q}}'' = q_1'' \, \underline{\boldsymbol{e}}_1 + q_2'' \, \underline{\boldsymbol{e}}_2$$

$$\underline{\boldsymbol{\nabla}} \boldsymbol{T} = \frac{\partial T}{\partial x_1} \underline{\boldsymbol{e}}_1 + \frac{\partial T}{\partial x_2} \underline{\boldsymbol{e}}_2$$

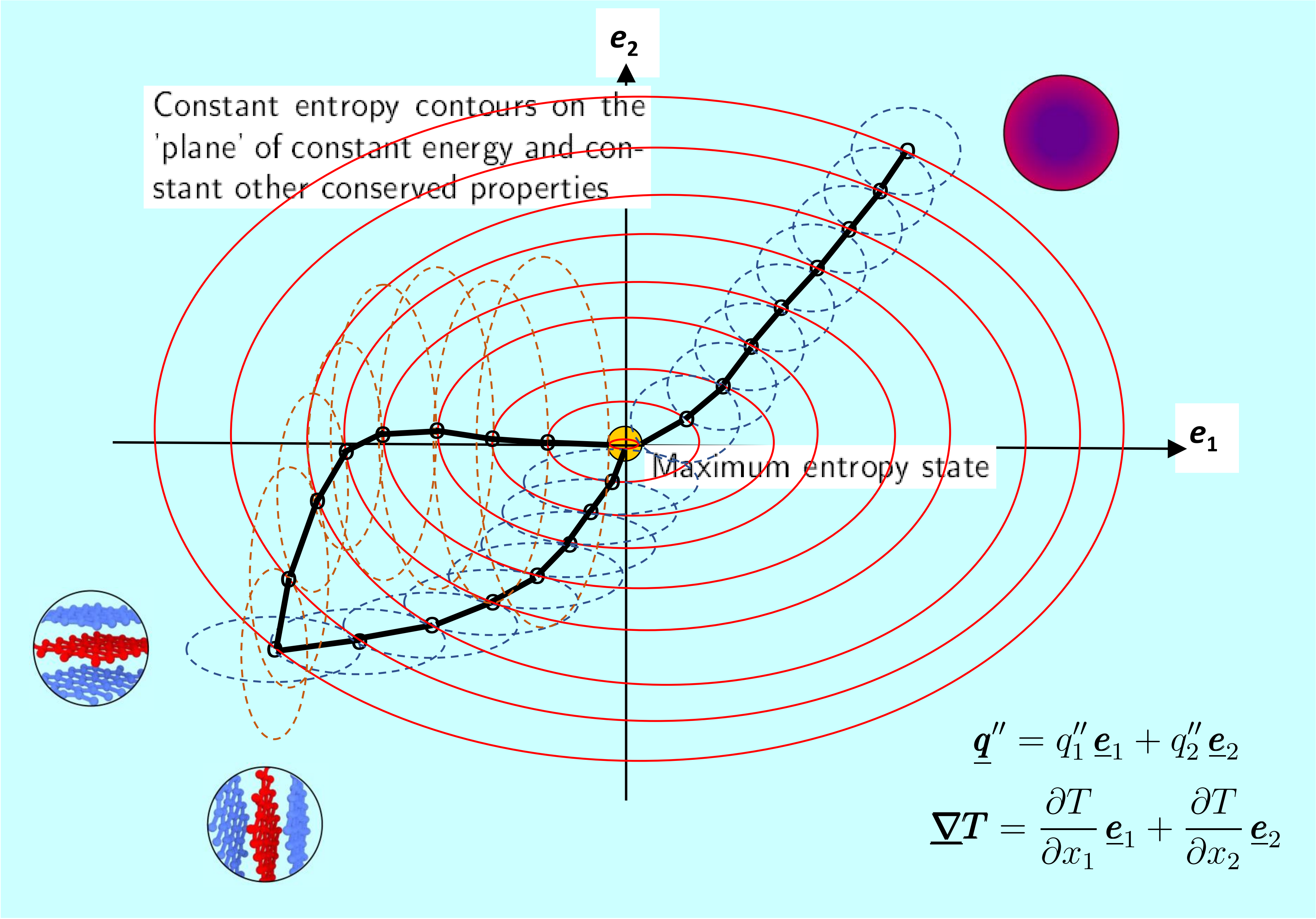
Material resistance to flux and forces: steepest entropy ascent



$$\underline{\boldsymbol{q}}'' = q_1''\,\underline{\boldsymbol{e}}_1 + q_2''\,\underline{\boldsymbol{e}}_2$$

$$\underline{\boldsymbol{\nabla T}} = \frac{\partial T}{\partial x_1}\underline{\boldsymbol{e}}_1 + \frac{\partial T}{\partial x_2}\underline{\boldsymbol{e}}_2$$

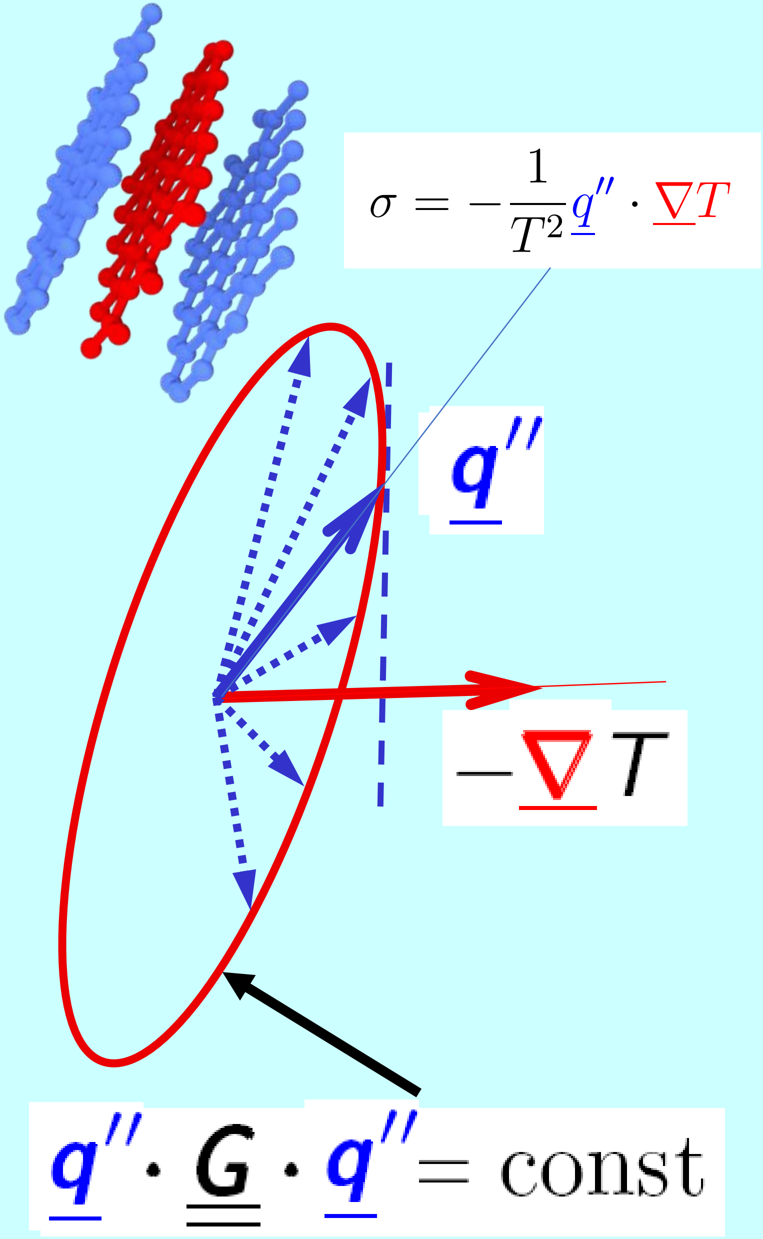
Material resistance to flux and forces: steepest entropy ascent



$$\underline{\boldsymbol{q}}'' = q_1''\,\underline{\boldsymbol{e}}_1 + q_2''\,\underline{\boldsymbol{e}}_2$$

$$\underline{\boldsymbol{\nabla} \boldsymbol{T}} = \frac{\partial T}{\partial x_1}\,\underline{\boldsymbol{e}}_1 + \frac{\partial T}{\partial x_2}\,\underline{\boldsymbol{e}}_2$$

We may call **Fourth Law** the statement of existence of metric $\underline{\underline{G}}$



$$\sigma = -\frac{1}{T^2}\underline{q}'' \cdot \underline{\nabla} T$$

$\underline{q}''$

$-\underline{\nabla} T$

$$\underline{q}'' \cdot \underline{\underline{G}} \cdot \underline{q}'' = \mathrm{const}$$

The Fourth Law is a statement of existence of the nonequilibrium metric $\underline{\underline{G}}$, a property defined for every state of the system (remember the first lectures: the words system and state are loaded words!). This statement parallels that of the First Law and the Second Law, which for any (well-defined) system are essentially statements of existence of the properties energy and entropy, respectively.

G.P. Beretta, "The fourth law of thermodynamics: steepest entropy ascent." *Phil. Trans. Royal Society A* 378: 20190168 (2020).

"Not near but not too far" from SES (so that the assumed local equilibrium Gibbs relation still holds):

force-flux relations from SEA (steepest entropy ascent)

Flux picture constitutive relation:

$$\boxed{\underline{\boldsymbol{X}} = \underline{\boldsymbol{X}}(\underline{\boldsymbol{J}},\underline{\Gamma})}$$

SEA principle: given $\underline{\boldsymbol{J}}$ and $\underline{\Gamma}$ there is **metric** $\underline{\underline{\boldsymbol{G}}}_X(\underline{\boldsymbol{J}},\underline{\Gamma})$ that makes the direction of $\underline{\boldsymbol{X}}$ be that of **steepest entropy ascent**:

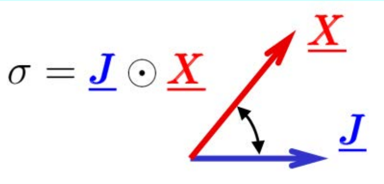
$$\max_{\underline{\boldsymbol{X}}}\Big|_{\underline{\boldsymbol{J}},\underline{\Gamma}} :\ \underline{\boldsymbol{J}}\odot\underline{\boldsymbol{X}} - \lambda_X\, \underline{\boldsymbol{X}}\odot\underline{\underline{\boldsymbol{G}}}_X\odot\underline{\boldsymbol{X}}$$

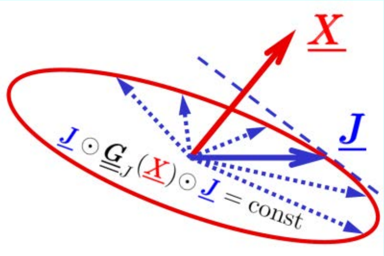
$$(\partial/\partial\underline{\boldsymbol{X}})_{\underline{\boldsymbol{J}},\underline{\Gamma}} = 0 \ \Rightarrow\ \underline{\boldsymbol{J}} - 2\lambda_X\,\underline{\underline{\boldsymbol{G}}}_X\odot\underline{\boldsymbol{X}} = 0$$

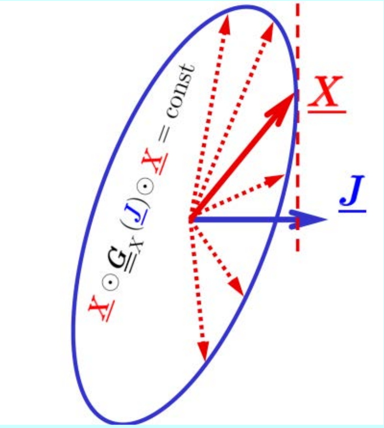
$$\underline{\underline{\boldsymbol{R}}} \equiv \underline{\underline{\boldsymbol{G}}}_X(\underline{\boldsymbol{J}},\underline{\Gamma})^{-1}/2\lambda_X(\underline{\boldsymbol{J}},\underline{\Gamma})$$

$$\underline{\boldsymbol{X}} = \underline{\underline{\boldsymbol{R}}}(\underline{\boldsymbol{J}},\underline{\Gamma})\odot\underline{\boldsymbol{J}}$$

Near eq.: $\underline{\underline{\boldsymbol{R}}}(\underline{\boldsymbol{J}},\underline{\Gamma}) \to \underline{\underline{\boldsymbol{R}}}_0(\underline{\Gamma})$ is nonnegative and **symmetric** since $\underline{\underline{\boldsymbol{G}}}_X$ is a **metric**.







Force picture constitutive relation:

$$\boxed{\underline{\boldsymbol{J}} = \underline{\boldsymbol{J}}(\underline{\boldsymbol{X}},\underline{\Gamma})}$$

SEA principle: given $\underline{\boldsymbol{X}}$ and $\underline{\Gamma}$ there is **metric** $\underline{\underline{\boldsymbol{G}}}_J(\underline{\boldsymbol{X}},\underline{\Gamma})$ that makes the direction of $\underline{\boldsymbol{J}}$ be that of **steepest entropy ascent**:

$$\max_{\underline{\boldsymbol{J}}}\Big|_{\underline{\boldsymbol{X}},\underline{\Gamma}} :\ \underline{\boldsymbol{X}}\odot\underline{\boldsymbol{J}} - \lambda_J\, \underline{\boldsymbol{J}}\odot\underline{\underline{\boldsymbol{G}}}_J\odot\underline{\boldsymbol{J}}$$

$$(\partial/\partial\underline{\boldsymbol{J}})_{\underline{\boldsymbol{X}},\underline{\Gamma}} = 0 \ \Rightarrow\ \underline{\boldsymbol{X}} - 2\lambda_J\,\underline{\underline{\boldsymbol{G}}}_J\odot\underline{\boldsymbol{J}} = 0$$

$$\underline{\underline{\boldsymbol{L}}} \equiv \underline{\underline{\boldsymbol{G}}}_J(\underline{\boldsymbol{X}},\underline{\Gamma})^{-1}/2\lambda_J(\underline{\boldsymbol{X}},\underline{\Gamma})$$

$$\underline{\boldsymbol{J}} = \underline{\underline{\boldsymbol{L}}}(\underline{\boldsymbol{X}},\underline{\Gamma})\odot\underline{\boldsymbol{X}}$$

Near eq.: $\underline{\underline{\boldsymbol{L}}}(\underline{\boldsymbol{X}},\underline{\Gamma}) \to \underline{\underline{\boldsymbol{L}}}_0(\underline{\Gamma})$ is nonnegative and **symmetric** since $\underline{\underline{\boldsymbol{G}}}_J$ is a **metric**.

Note: $\lambda_X = 1/2$ makes $\underline{\underline{\boldsymbol{G}}}_X = \underline{\underline{\boldsymbol{L}}}_0$.

$$\underline{\underline{\boldsymbol{R}}}_0^{-1} = \underline{\underline{\boldsymbol{L}}}_0$$

Note: $\lambda_J = 1/2$ makes $\underline{\underline{\boldsymbol{G}}}_J = \underline{\underline{\boldsymbol{R}}}_0$.

The Fourth Law: existence for every state of a local nonequilibrium dissipative metric G

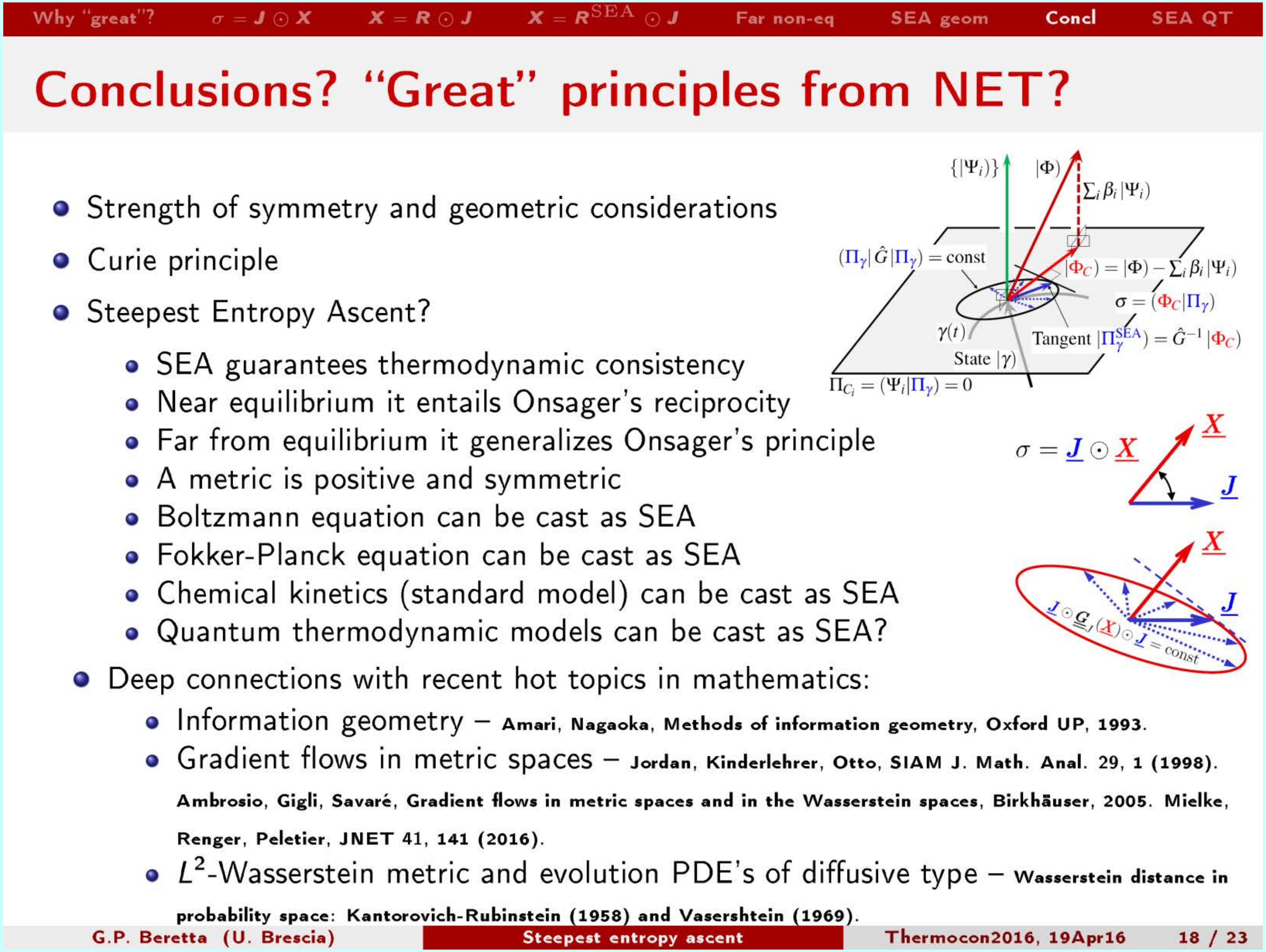
As documented in [1], forty years of nonequilibrium theories — apparently diverse, often independently, and still mostly unaware of the interconnections — incorporate the model of dissipative dynamics in ways that are all essentially equivalent to the principle of **local steepest entropy ascent**. In particular, without claiming completeness:

- variational principles (>1931: Onsager, several authors: see e.g. review [2])
- maximum entropy production principle (1958: Ziegler; 1972: Edelen)
- nonlinear SEA equation of motion for quantum thermodynamics (1981: Beretta)
- steepest entropy ascent (>1984: Beretta, Gyftopoulos, Park, Hatsopoulos)
- metriplectic formalism (>1984: Morrison, Kaufman, Grmela)
- least action in chemical kinetics (1987: Sieniutycz)
- Onsager's principle: a unifying bio-theme (>1989: Morel, Fleck [3])
- law of maximum entropy production, LMEP (>1989: Swenson)
- constructal law (>1996: Bejan)
- GENERIC† (>1997: Grmela, Öttinger)
- gradient flows (>1998: Jordan, Kinderlehrer, Otto, Mielke)
- quantum evolution with max ent production (2001: Gheorghiu-Svirschevski)
- maximum entropy production principle, MEPP (2003: Dewar, Martyushev)
- large deviation theory (>2004: Evans, Touchette, Peletier)
- fourth law of termodynamics and LMEP (>2006: Morel, Fleck, Swenson [4])
- applications of SEA to transport phenomena (>2014: von Spakovsky, see e.g. [5])

[1] G.P. Beretta, Phil.Trans.Roy.Soc.A 378, 20190168 (2020). [2] P. Ván and R. Kovács, Phil.Trans.Roy.Soc.A 378, 20190178 (2020).
[3] R.E. Morel, G. Fleck, J.Theor.Biology 136, 171 (1989).
[4] R. Swenson, Chemistry 18, 333 (2009); R. Swenson, Phil.Trans.Roy.Soc.A 381, 20220277 (2023).
[5] G. Li, M.R. von Spakovsky, C. Hin, Phys.Rev.B 97, 024308 (2018); G. Li, M.R. von Spakovsky, Phys.Rev.E 98, 042113 (2018).

† For the proof of equivalence of SEA and GENERIC see A. Montefusco, F. Consonni, G.P. Beretta, Phys.Rev.E 91, 042138 (2015).

More on Steepest Entropy Ascent

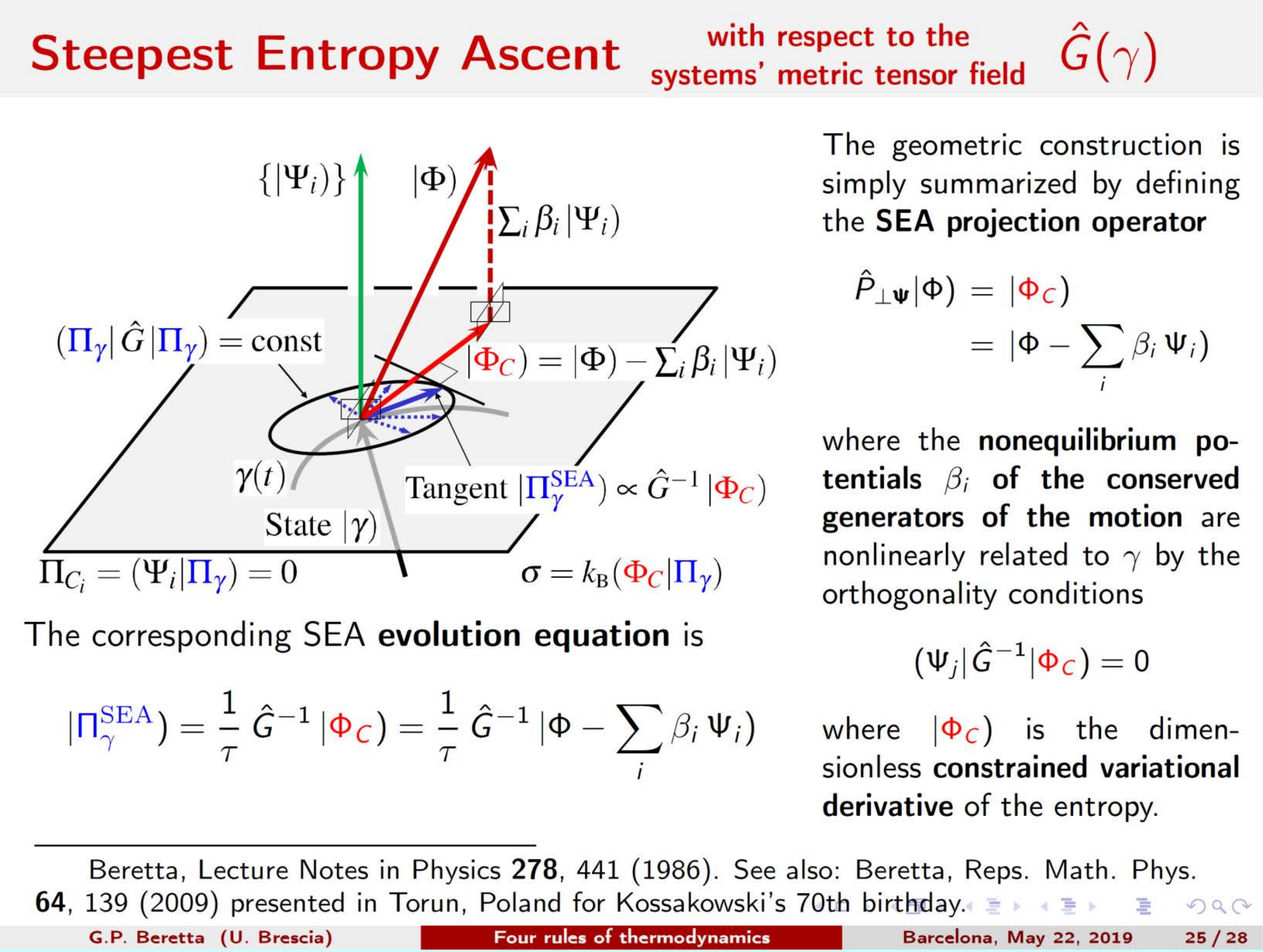


Conclusions? "Great" principles from NET?

- Strength of symmetry and geometric considerations
- Curie principle
- Steepest Entropy Ascent?
  - SEA guarantees thermodynamic consistency
  - Near equilibrium it entails Onsager's reciprocity
  - Far from equilibrium it generalizes Onsager's principle
  - A metric is positive and symmetric
  - Boltzmann equation can be cast as SEA
  - Fokker-Planck equation can be cast as SEA
  - Chemical kinetics (standard model) can be cast as SEA
  - Quantum thermodynamic models can be cast as SEA?
- Deep connections with recent hot topics in mathematics:
  - Information geometry – **Amari, Nagaoka, Methods of information geometry, Oxford UP, 1993.**
  - Gradient flows in metric spaces – **Jordan, Kinderlehrer, Otto, SIAM J. Math. Anal. 29, 1 (1998). Ambrosio, Gigli, Savaré, Gradient flows in metric spaces and in the Wasserstein spaces, Birkhäuser, 2005. Mielke, Renger, Peletier, JNET 41, 141 (2016).**
  - L^2-Wasserstein metric and evolution PDE's of diffusive type – **Wasserstein distance in probability space: Kantorovich-Rubinstein (1958) and Vasershtein (1969).**

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

More on Steepest Entropy Ascent



Steepest Entropy Ascent with respect to the systems' metric tensor field $\hat{G}(\gamma)$

The geometric construction is simply summarized by defining the **SEA projection operator**

$$\hat{P}_{\perp\Psi}|\Phi) = |\Phi_C) = |\Phi - \sum_i \beta_i \Psi_i)$$

where the **nonequilibrium potentials** β_i **of the conserved generators of the motion** are nonlinearly related to γ by the orthogonality conditions

$$(\Psi_j|\hat{G}^{-1}|\Phi_C) = 0$$

where $|\Phi_C)$ is the dimensionless **constrained variational derivative** of the entropy.

The corresponding SEA **evolution equation** is

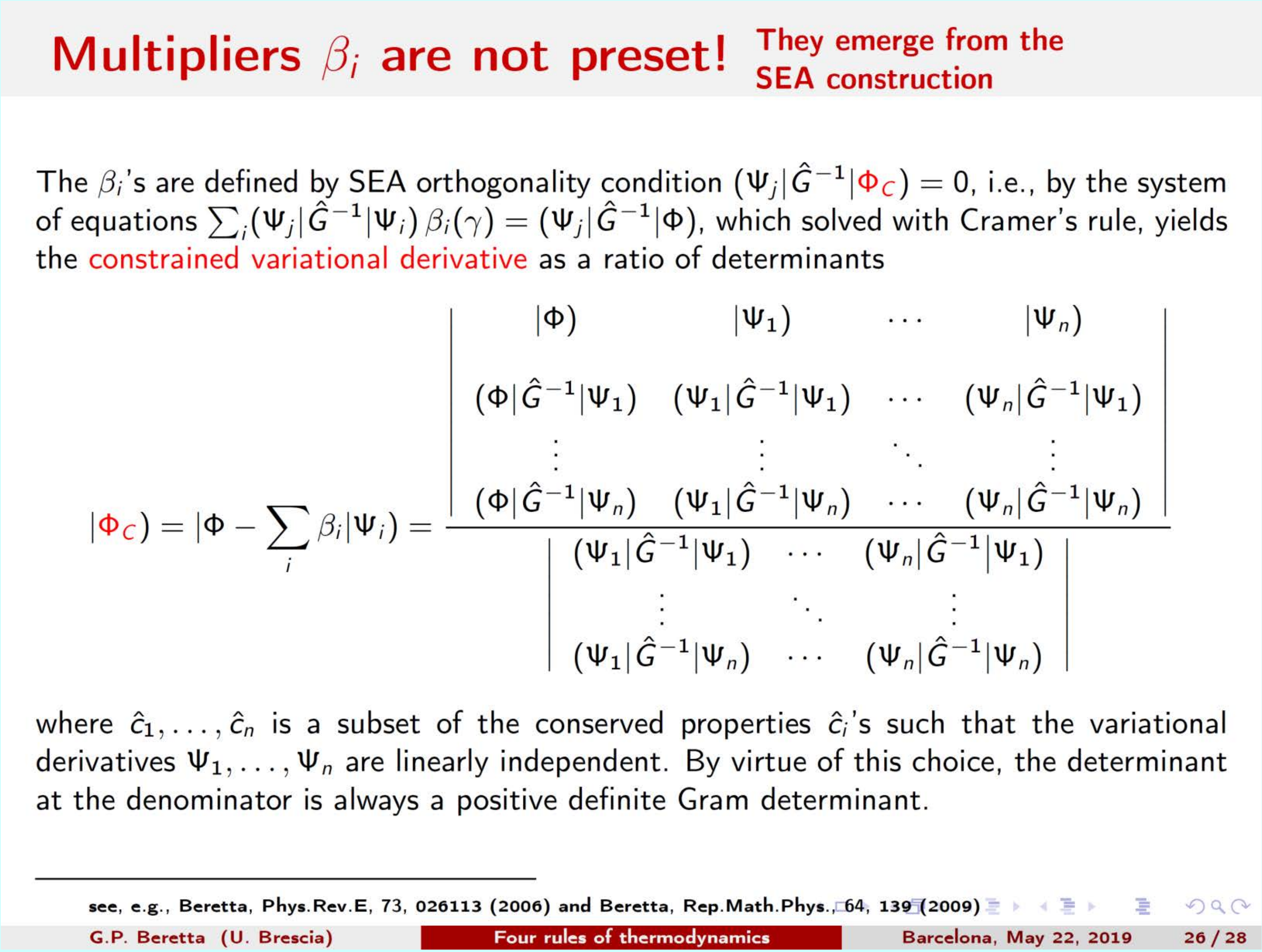
$$|\Pi_\gamma^{\text{SEA}}) = \frac{1}{\tau}\,\hat{G}^{-1}|\Phi_C) = \frac{1}{\tau}\,\hat{G}^{-1}|\Phi - \sum_i \beta_i \Psi_i)$$

Beretta, Lecture Notes in Physics **278**, 441 (1986). See also: Beretta, Reps. Math. Phys. **64**, 139 (2009) presented in Torun, Poland for Kossakowski's 70th birthday.

G.P. Beretta (U. Brescia) Four rules of thermodynamics Barcelona, May 22, 2019 25 / 28

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

More on Steepest Entropy Ascent



Multipliers β_i are not preset! They emerge from the SEA construction

The β_i's are defined by SEA orthogonality condition $(\Psi_j|\hat{G}^{-1}|\Phi_C) = 0$, i.e., by the system of equations $\sum_i (\Psi_j|\hat{G}^{-1}|\Psi_i)\,\beta_i(\gamma) = (\Psi_j|\hat{G}^{-1}|\Phi)$, which solved with Cramer's rule, yields the constrained variational derivative as a ratio of determinants

$$|\Phi_C) = |\Phi - \sum_i \beta_i |\Psi_i) = \frac{\begin{vmatrix} |\Phi) & |\Psi_1) & \cdots & |\Psi_n) \\ (\Phi|\hat{G}^{-1}|\Psi_1) & (\Psi_1|\hat{G}^{-1}|\Psi_1) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_1) \\ \vdots & \vdots & \ddots & \vdots \\ (\Phi|\hat{G}^{-1}|\Psi_n) & (\Psi_1|\hat{G}^{-1}|\Psi_n) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_n) \end{vmatrix}}{\begin{vmatrix} (\Psi_1|\hat{G}^{-1}|\Psi_1) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_1) \\ \vdots & \ddots & \vdots \\ (\Psi_1|\hat{G}^{-1}|\Psi_n) & \cdots & (\Psi_n|\hat{G}^{-1}|\Psi_n) \end{vmatrix}}$$

where $\hat{c}_1, \ldots, \hat{c}_n$ is a subset of the conserved properties $\hat{c}_i$'s such that the variational derivatives $\Psi_1, \ldots, \Psi_n$ are linearly independent. By virtue of this choice, the determinant at the denominator is always a positive definite Gram determinant.

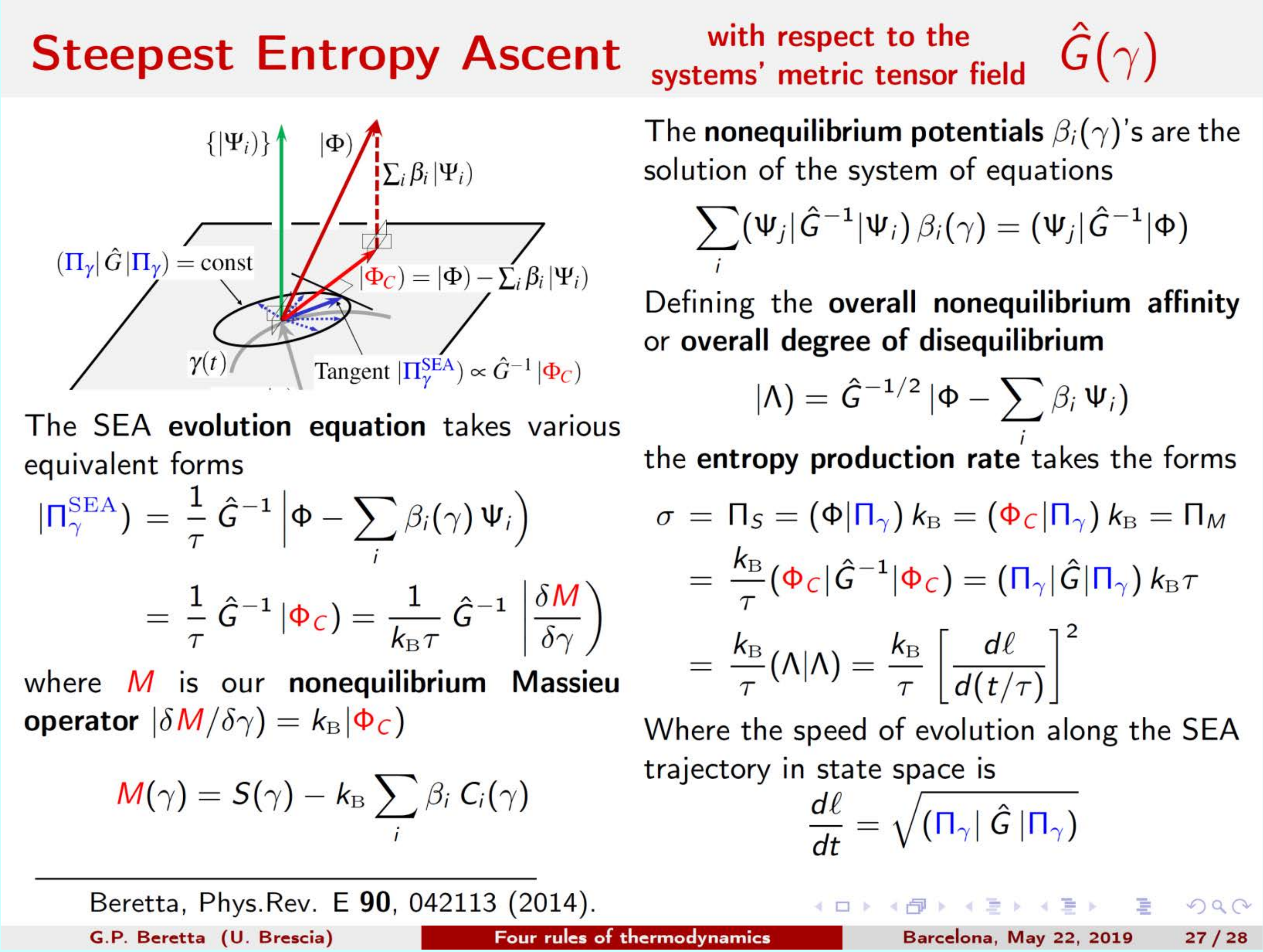
---

see, e.g., Beretta, Phys.Rev.E, 73, 026113 (2006) and Beretta, Rep.Math.Phys., 64, 139 (2009)

G.P. Beretta (U. Brescia) | Four rules of thermodynamics | Barcelona, May 22, 2019 | 26 / 28

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

More on Steepest Entropy Ascent



Steepest Entropy Ascent with respect to the systems' metric tensor field $\hat{G}(\gamma)$

The SEA **evolution equation** takes various equivalent forms

$$|\Pi_\gamma^{\text{SEA}}) = \frac{1}{\tau}\,\hat{G}^{-1}\left|\Phi - \sum_i \beta_i(\gamma)\,\Psi_i\right)$$

$$= \frac{1}{\tau}\,\hat{G}^{-1}\,|\Phi_C) = \frac{1}{k_{\text{B}}\tau}\,\hat{G}^{-1}\left|\frac{\delta M}{\delta\gamma}\right)$$

where M is our **nonequilibrium Massieu operator** $|\delta M/\delta\gamma) = k_{\text{B}}|\Phi_C)$

$$M(\gamma) = S(\gamma) - k_{\text{B}}\sum_i \beta_i\, C_i(\gamma)$$

The **nonequilibrium potentials** $\beta_i(\gamma)$'s are the solution of the system of equations

$$\sum_i (\Psi_j|\hat{G}^{-1}|\Psi_i)\,\beta_i(\gamma) = (\Psi_j|\hat{G}^{-1}|\Phi)$$

Defining the **overall nonequilibrium affinity** or **overall degree of disequilibrium**

$$|\Lambda) = \hat{G}^{-1/2}\,\left|\Phi - \sum_i \beta_i\,\Psi_i\right)$$

the **entropy production rate** takes the forms

$$\sigma = \Pi_S = (\Phi|\Pi_\gamma)\,k_{\text{B}} = (\Phi_C|\Pi_\gamma)\,k_{\text{B}} = \Pi_M$$

$$= \frac{k_{\text{B}}}{\tau}(\Phi_C|\hat{G}^{-1}|\Phi_C) = (\Pi_\gamma|\hat{G}|\Pi_\gamma)\,k_{\text{B}}\tau$$

$$= \frac{k_{\text{B}}}{\tau}(\Lambda|\Lambda) = \frac{k_{\text{B}}}{\tau}\left[\frac{d\ell}{d(t/\tau)}\right]^2$$

Where the speed of evolution along the SEA trajectory in state space is

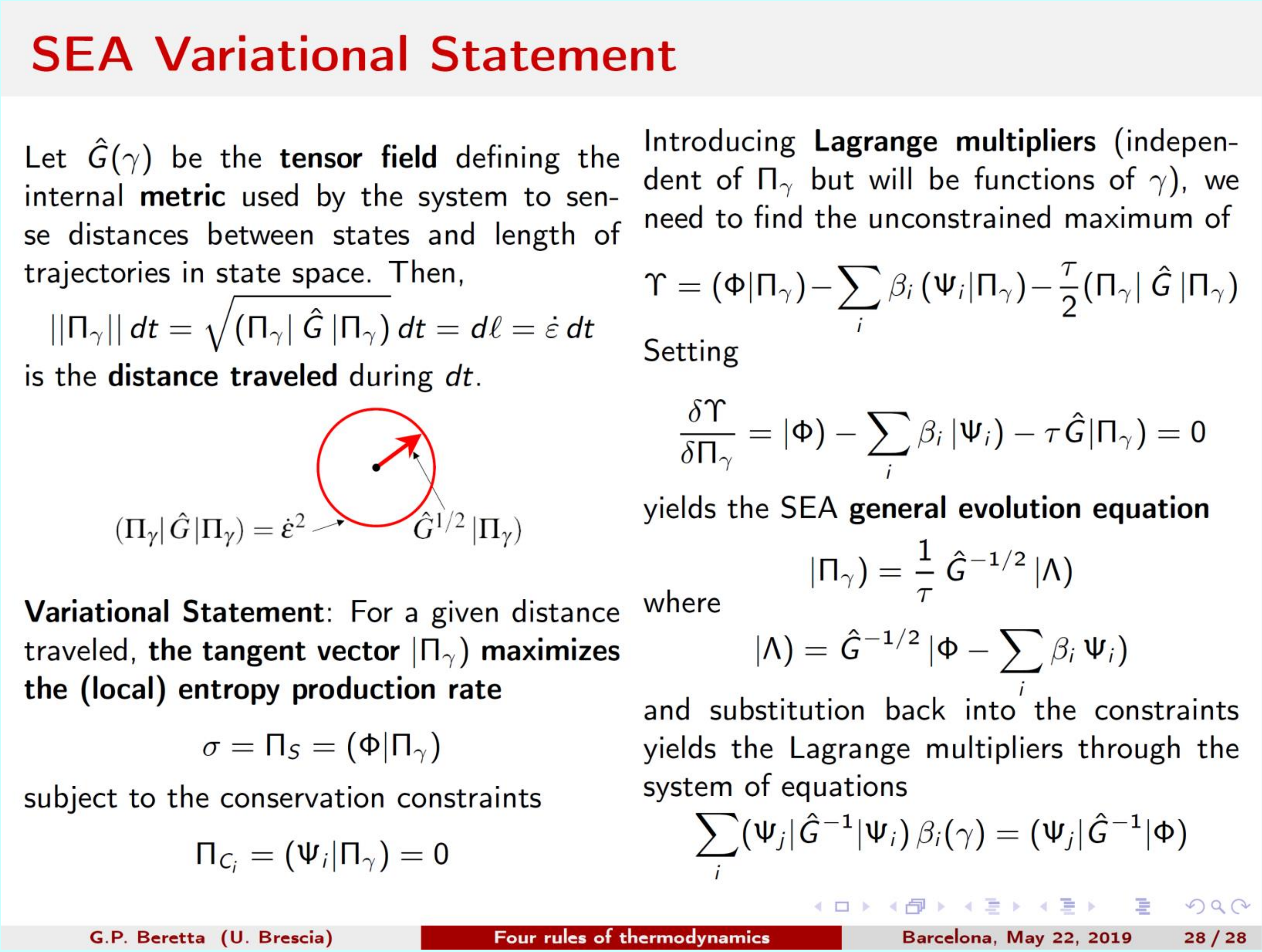
$$\frac{d\ell}{dt} = \sqrt{(\Pi_\gamma|\,\hat{G}\,|\Pi_\gamma)}$$

Beretta, Phys.Rev. E **90**, 042113 (2014).

G.P. Beretta (U. Brescia) Four rules of thermodynamics Barcelona, May 22, 2019 27 / 28

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

More on Steepest Entropy Ascent



SEA Variational Statement

Let $\hat{G}(\gamma)$ be the **tensor field** defining the internal **metric** used by the system to sense distances between states and length of trajectories in state space. Then,

$$||\Pi_\gamma||\,dt = \sqrt{(\Pi_\gamma|\,\hat{G}\,|\Pi_\gamma)}\,dt = d\ell = \dot{\varepsilon}\,dt$$

is the **distance traveled** during dt.

$(\Pi_\gamma|\,\hat{G}\,|\Pi_\gamma) = \dot{\varepsilon}^2$

$\hat{G}^{1/2}\,|\Pi_\gamma)$

Variational Statement: For a given distance traveled, **the tangent vector $|\Pi_\gamma)$ maximizes the (local) entropy production rate**

$$\sigma = \Pi_S = (\Phi|\Pi_\gamma)$$

subject to the conservation constraints

$$\Pi_{C_i} = (\Psi_i|\Pi_\gamma) = 0$$

Introducing **Lagrange multipliers** (independent of Π_γ but will be functions of γ), we need to find the unconstrained maximum of

$$\Upsilon = (\Phi|\Pi_\gamma) - \sum_i \beta_i\,(\Psi_i|\Pi_\gamma) - \frac{\tau}{2}(\Pi_\gamma|\,\hat{G}\,|\Pi_\gamma)$$

Setting

$$\frac{\delta\Upsilon}{\delta\Pi_\gamma} = |\Phi) - \sum_i \beta_i\,|\Psi_i) - \tau\hat{G}|\Pi_\gamma) = 0$$

yields the SEA **general evolution equation**

$$|\Pi_\gamma) = \frac{1}{\tau}\,\hat{G}^{-1/2}\,|\Lambda)$$

where

$$|\Lambda) = \hat{G}^{-1/2}\,|\Phi - \sum_i \beta_i\,\Psi_i)$$

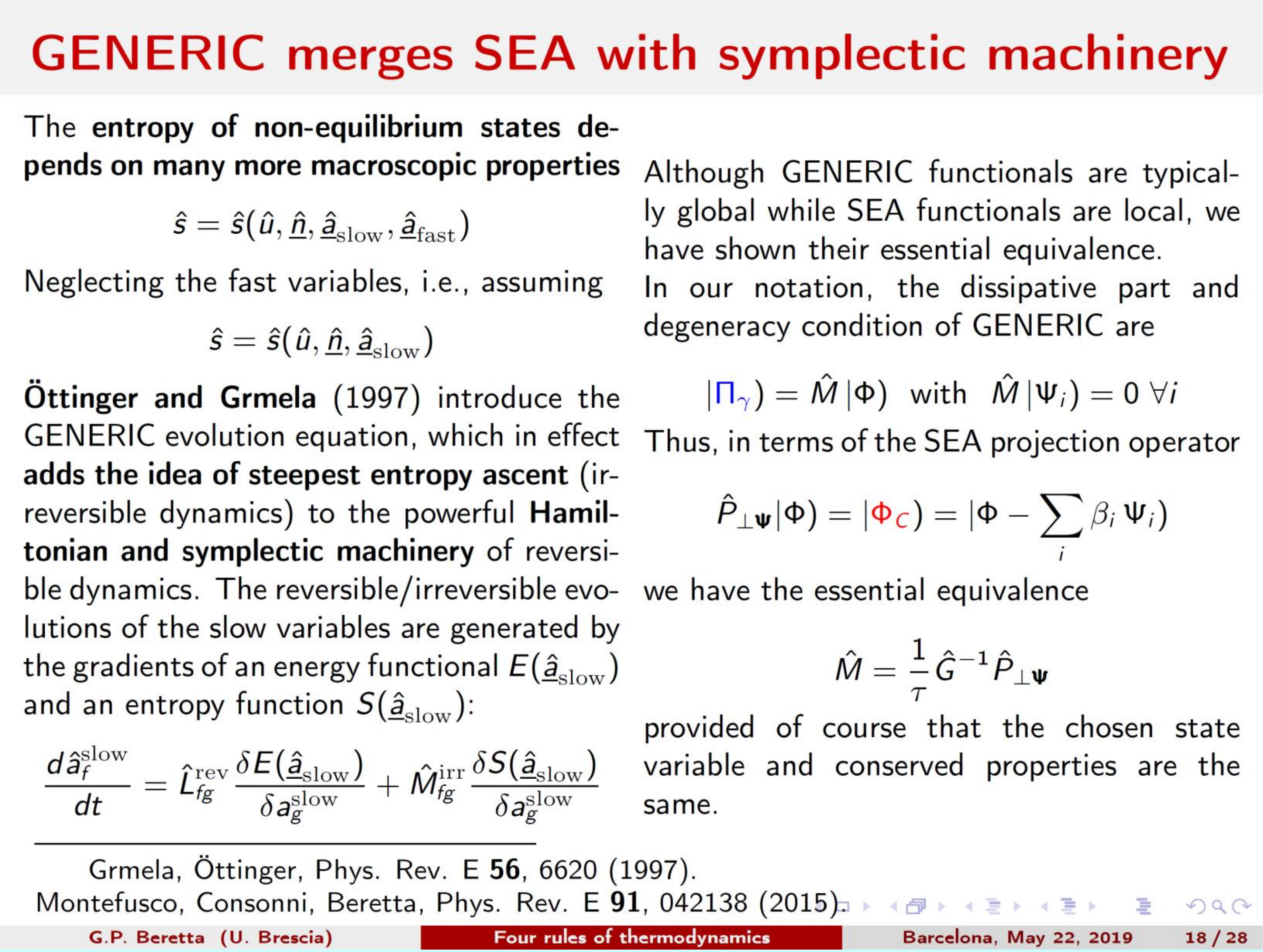
and substitution back into the constraints yields the Lagrange multipliers through the system of equations

$$\sum_i (\Psi_j|\hat{G}^{-1}|\Psi_i)\,\beta_i(\gamma) = (\Psi_j|\hat{G}^{-1}|\Phi)$$

G.P. Beretta (U. Brescia) Four rules of thermodynamics Barcelona, May 22, 2019 28 / 28

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

More on Steepest Entropy Ascent



GENERIC merges SEA with symplectic machinery

The **entropy of non-equilibrium states depends on many more macroscopic properties**

$$\hat{s} = \hat{s}(\hat{u}, \underline{\hat{n}}, \underline{\hat{a}}_{\rm slow}, \underline{\hat{a}}_{\rm fast})$$

Neglecting the fast variables, i.e., assuming

$$\hat{s} = \hat{s}(\hat{u}, \underline{\hat{n}}, \underline{\hat{a}}_{\rm slow})$$

Öttinger and Grmela (1997) introduce the GENERIC evolution equation, which in effect **adds the idea of steepest entropy ascent** (irreversible dynamics) to the powerful **Hamiltonian and symplectic machinery** of reversible dynamics. The reversible/irreversible evolutions of the slow variables are generated by the gradients of an energy functional $E(\underline{\hat{a}}_{\rm slow})$ and an entropy function $S(\underline{\hat{a}}_{\rm slow})$:

$$\frac{d\hat{a}_f^{\rm slow}}{dt} = \hat{L}_{fg}^{\rm rev}\frac{\delta E(\underline{\hat{a}}_{\rm slow})}{\delta a_g^{\rm slow}} + \hat{M}_{fg}^{\rm irr}\frac{\delta S(\underline{\hat{a}}_{\rm slow})}{\delta a_g^{\rm slow}}$$

Although GENERIC functionals are typically global while SEA functionals are local, we have shown their essential equivalence.
In our notation, the dissipative part and degeneracy condition of GENERIC are

$$|\Pi_\gamma) = \hat{M}\,|\Phi) \quad \text{with} \quad \hat{M}\,|\Psi_i) = 0\ \forall i$$

Thus, in terms of the SEA projection operator

$$\hat{P}_{\perp\boldsymbol{\Psi}}|\Phi) = |\Phi_C) = |\Phi - \sum_i \beta_i\,\Psi_i)$$

we have the essential equivalence

$$\hat{M} = \frac{1}{\tau}\hat{G}^{-1}\hat{P}_{\perp\boldsymbol{\Psi}}$$

provided of course that the chosen state variable and conserved properties are the same.

Grmela, Öttinger, Phys. Rev. E **56**, 6620 (1997).
Montefusco, Consonni, Beretta, Phys. Rev. E **91**, 042138 (2015).

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

More on Steepest Entropy Ascent

Gradient flows are SEA-like dynamical systems

Let the states γ be points of a Riemannian manifold $(\mathcal{M},\hat{G})$ and assume S a (dimensionless) functional on $\mathcal{M}$. The gradient flow of S on $(\mathcal{M},\hat{G})$ is a dynamical system in $\mathcal{M}$ given by the differential equation (in dimensionless time)

$$\left|\tau\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right) = \left|\mathrm{grad}S_{|\gamma}\right)$$

The metric tensor $\hat{G}$ is an essential element of the notion. It converts the differential DS of S, which is a cotangent vector field, into the gradient of S, which is a tangent vector field: for all vector fields v on $\mathcal{M}$

$$(\mathrm{diff}\,S|v) = \hat{G}(\mathrm{grad}S, v)$$

Therefore, for all vector fields v along γ

$$(\mathrm{diff}\,S_{|\gamma}|v) = \hat{G}_{|\gamma}(\mathrm{grad}S_{|\gamma}, v) = \hat{G}\left(\tau\frac{\mathrm{d}\gamma}{\mathrm{d}t}, v\right)$$

The rate of change of the entropy is

$$k_{\mathrm{B}}\frac{\mathrm{d}S(\gamma)}{\mathrm{d}t} = \left(\mathrm{diff}\,S_{|\gamma}\left|\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right.\right)k_{\mathrm{B}} = \hat{G}_{\gamma}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}t},\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right)k_{\mathrm{B}}\tau$$

to be compared with the SEA

$$\sigma = \left(\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right|\hat{G}_{\gamma}\left|\frac{\mathrm{d}\gamma}{\mathrm{d}t}\right)k_{\mathrm{B}}\tau$$

The main differences between SEA, the dissipative part of GENERIC, and gradient flow formulations stem from the technical nature of the bilinear forms adopted to define gradients.

Jordan, Kinderlehrer, Otto, SIAM J. Math. Analysis **29**, 1 (1998). Otto, Comm. Par. Diff. Eqs. **26**, 101 (2001). Mielke, Nonlinearity **24**, 1329 (2011). Sieniutycz, Chem. Eng. Sci. **42**, 2697 (1987).

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

A related, but more general nonequilibrium law of nature, that so far escaped a formal mathematical formulation:

Bejan's "constructal law" of design and evolution in Nature

(**Bejan**, 1996): "For a finite-size flow system to persist in time (to live) it must evolve such that it provides greater and greater access to the currents that flow through it."

(**Bejan and Lorente**, 2004): "The constructal law is the statement proclaiming the existence and the time direction of the **evolution of configuration**. It is far more general than 'maximum entropy production'. It is not a statement of optimality (min, max), end design or destiny. No flow system is destined to end up in a certain configuration at long times."

"In 1996, the constructal law was formulated and proposed to expand thermodynamics in a fundamental way (...) to recognize that there is a universal phenomenon not covered by the first law and the second law. That phenomenon is the **generation of configuration**, or the generation of 'design' in nature. All thermodynamic systems in nature are flow systems (i.e. live, non-equilibrium systems), and they all have configuration. If they do not have it, then they acquire it, in time. The generation of configuration is ubiquitous, like other phenomena covered by other 'laws' in physics. Biological systems are configured. Geophysical systems are configured. Engineering and societal systems are configured. The configuration phenomenon unites the animate with the inanimate."

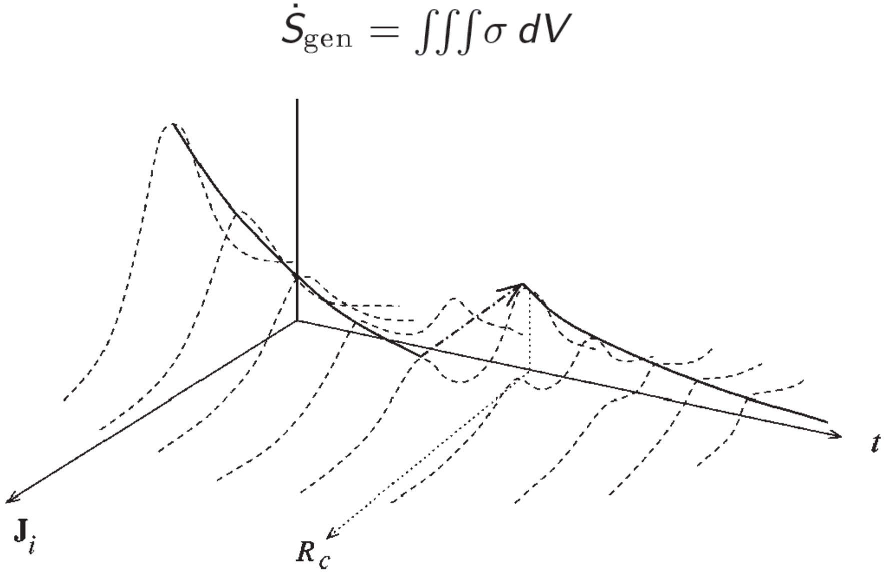
Bejan claims "that this universal phenomenon is covered by the constructal law. This law accounts for a natural tendency in time (from existing flow configurations, to easier flowing configurations). This tendency is distinct from the natural tendency summarized as the second law."

Text excerpts from Adrian Bejan and Sylvie Lorente, The constructal law of design and evolution in nature, Philos. Trans. R. Soc. Lond. B, 365, 1335 (2010)

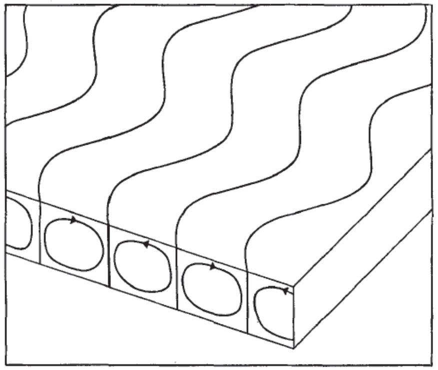
While the state evolves towards the steady state with minimum global EP (or the SES)

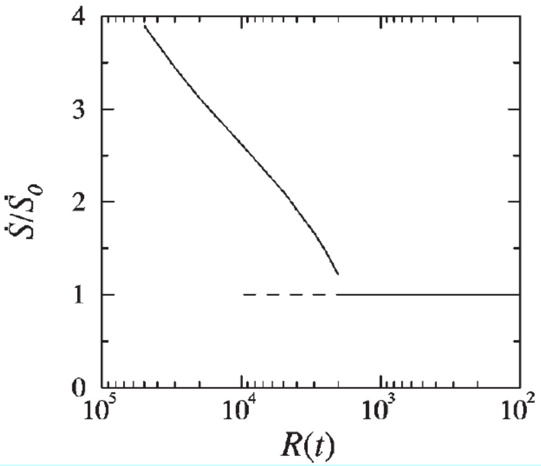
maximal local EP selects the hydrodynamic pattern

Rayleigh-Benard 2D rolls in horizontal layer of fluid heated from below as a function of Rayleigh number R (Woo, 2002). A slow decrease in R is allowed with time.



Woo, Phys. Rev. E, Vol. 66, 066104 (2002).





While the state evolves towards the steady state with minimum global EP (or the SES)

maximal local EP selects the most efficient flow pattern

Flow in a porous medium heated from below:

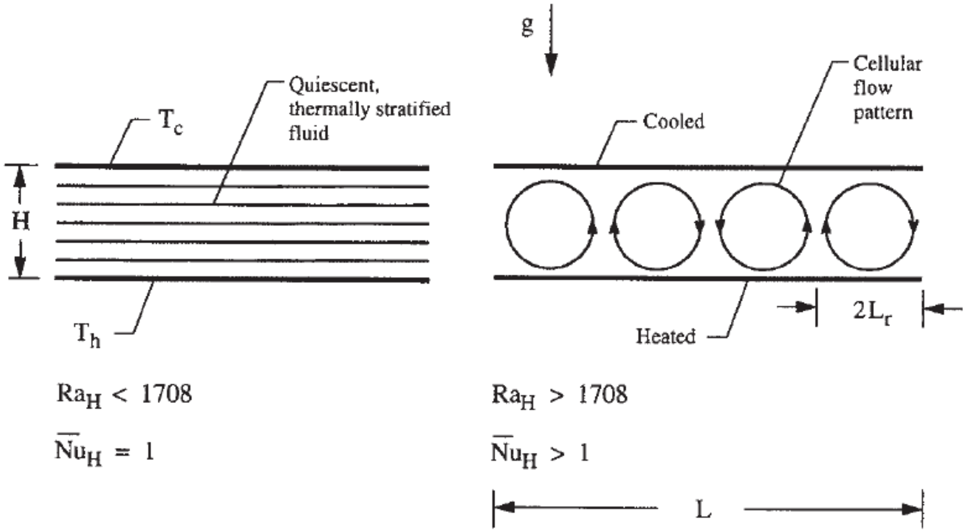


Figure 4. Horizontal layer saturated with fluid and heated from below.

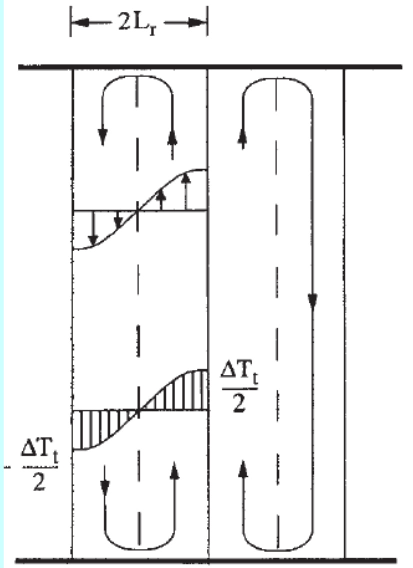


Figure 5. The extreme in which the flow consists of many vertical and slender counterflows.

Figures from: A. Bejan, Int. J. Energy Res., 27, 859 (2003).

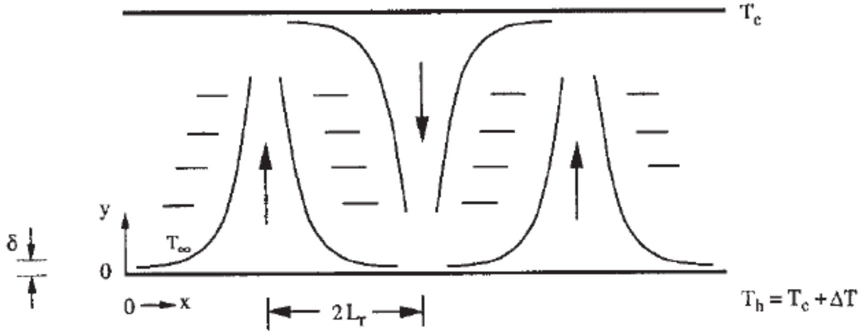


Figure 7. The extreme in which the flow consists of a few isolated plumes.

This slide was not discussed in class. It was added a posteriori as useful reference in response to a student's request.

Maximal local EP (SEA) implies minimum global EP at steady state

Glansdorff and Prigogine (1954) noted that assuming the following broad set of conditions:

- stationary boundary conditions, $d\underline{\Gamma}/dt|_{\Omega} = 0$
- no convection and no reactions, so that $\underline{\boldsymbol{X}} = \nabla\underline{\Gamma}$
- linear regime, $\underline{\boldsymbol{J}} = \underline{\underline{\boldsymbol{L}}} \odot \underline{\boldsymbol{X}}$, $\sigma = \underline{\boldsymbol{X}} \odot \underline{\underline{\boldsymbol{L}}} \odot \underline{\boldsymbol{X}}$
- constant Onsager conductivities, $d\underline{\underline{\boldsymbol{L}}}/dt = 0$
- $\hat{s} = \hat{s}(\hat{u})$ with all $\hat{u}$ conserved
- $\dfrac{d\hat{\underline{u}}}{dt} = -\boldsymbol{\nabla}\cdot\underline{\boldsymbol{J}}$ with $\underline{\boldsymbol{J}} = \underline{J}_{\hat{\underline{u}}}$
- $\underline{\Gamma} = \dfrac{\partial \hat{s}}{\partial \hat{\underline{u}}}$ and $\dfrac{\partial \underline{\Gamma}}{\partial \hat{\underline{u}}} = \dfrac{\partial^2 \hat{s}}{\partial \hat{\underline{u}}\partial \hat{\underline{u}}} \le 0$

Then*:

$$\frac{d\dot{S}_{\text{gen}}}{dt} = \iiint \frac{d\sigma}{dt}\,dV = 2\iiint \underline{\boldsymbol{J}} \odot \frac{d\underline{\boldsymbol{X}}}{dt}\,dV = 2\iiint \frac{d\hat{\underline{u}}}{dt} \odot \frac{\partial^2 \hat{s}}{\partial \hat{\underline{u}}\partial \hat{\underline{u}}} \odot \frac{d\hat{\underline{u}}}{dt}\,dV \le 0$$

This means that the free fluxes and forces adjust until the system reaches the stable **stationary (steady) state with minimum** $\dot{S}_{\text{gen}}$ for the imposed fluxes and forces.

If instead no fluxes nor forces are imposed, i.e., the systems is isolated, than the initial fluxes and forces adjust until they vanish and the system reaches SES.

For variable conductivities, $d\underline{\underline{\boldsymbol{L}}}/dt \neq 0$, the theorem loses validity.

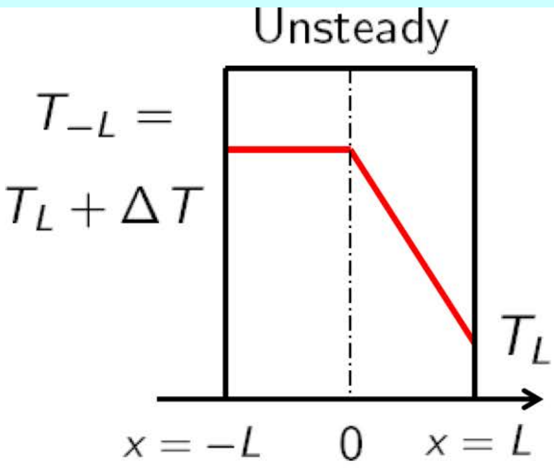
* Proof:

$$\frac{d\dot{S}_{\text{gen}}}{dt} = \iiint \frac{d\sigma}{dt}\,dV = \iiint \frac{d}{dt}\underline{\boldsymbol{X}} \odot \underline{\underline{\boldsymbol{L}}} \odot \underline{\boldsymbol{X}}\,dV = 2\iiint \underline{\boldsymbol{J}} \odot \frac{d\underline{\boldsymbol{X}}}{dt}\,dV + \cancel{\iiint \underline{\boldsymbol{X}} \odot \frac{d\underline{\underline{\boldsymbol{L}}}}{dt} \odot \underline{\boldsymbol{X}}\,dV}$$

$$\iiint_V \underline{\boldsymbol{J}} \odot \frac{d\underline{\boldsymbol{X}}}{dt}\,dV = \iiint_V \underline{\boldsymbol{J}} \odot \frac{d\nabla\underline{\Gamma}}{dt}\,dV = \cancel{\iint_{\partial V} \underline{\boldsymbol{J}} \odot \frac{d\underline{\Gamma}}{dt}\cdot\boldsymbol{n}\,dA} - \iiint_V \frac{d\underline{\Gamma}}{dt} \odot \nabla\cdot\underline{\boldsymbol{J}}\,dV$$

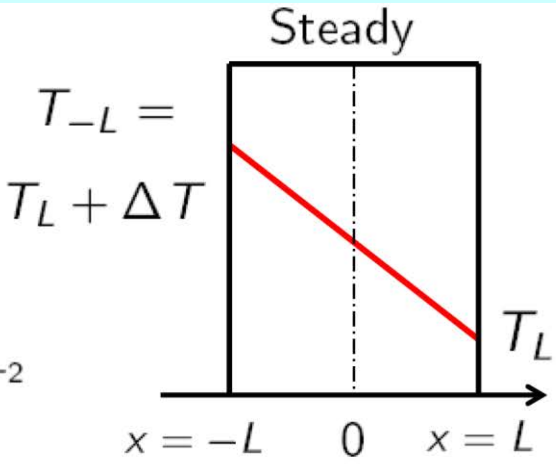
$$-\iiint \frac{d\underline{\Gamma}}{dt}\odot\nabla\cdot\underline{\boldsymbol{J}}\,dV = \iiint \frac{d\underline{\Gamma}}{dt}\odot\frac{d\hat{\underline{u}}}{dt}\,dV = \iiint \frac{d\hat{\underline{u}}}{dt}\odot\frac{\partial\underline{\Gamma}}{\partial\hat{\underline{u}}}\odot\frac{d\hat{\underline{u}}}{dt}\,dV = \iiint \frac{d\hat{\underline{u}}}{dt}\odot\frac{\partial^2\hat{s}}{\partial\hat{\underline{u}}\partial\hat{\underline{u}}}\odot\frac{d\hat{\underline{u}}}{dt}\,dV \le 0$$

Maximal local EP (SEA) implies minimum global EP at steady state

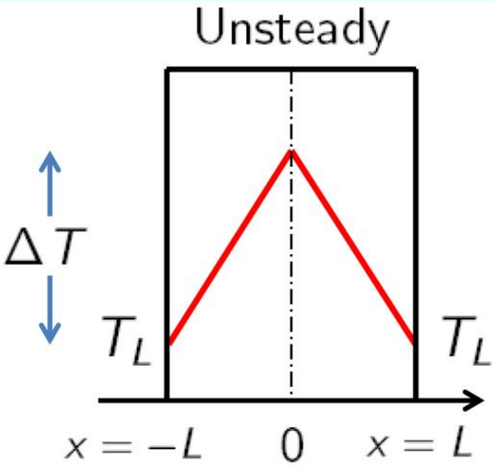


$q''_x = -k\, dT/dx$

$\sigma = (dT/dx)^2 k/T^2$

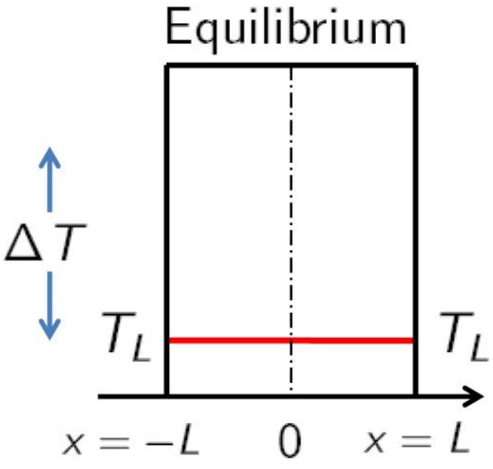


$\dot{S}_{\text{gen}} = A\int_{-L}^{L} \sigma\, dx = (\Delta T)^2 kA/L$ ⇒ $\dot{S}_{\text{gen}} = (\Delta T)^2 kA/2L$ (minimum)



$q''_x = -k\, dT/dx$

$\sigma = (dT/dx)^2 k/T^2$



$\dot{S}_{\text{gen}} = 2(\Delta T)^2 kA/L$ ⇒ $\dot{S}_{\text{gen}} = 0$ (minimum)

Image Credits

Slide 35:

Text excerpts about constructal law courtesy of National Library of Medicine.

Slide 36:

Figure showing Rayleigh-Benard 2D rolls in horizontal layer © American Physical Society. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

Slide 37:

Figure 4, Figure 5, and Figure 7 © John Wiley & Sons, Inc. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

2.43 Advanced Thermodynamics
Spring 2024