The Fourth Law of Thermodynamics:

every nonequilibrium state is characterized by a metric in state space with respect to which its spontaneous attraction towards stable equilibrium is along the path of steepest entropy ascent

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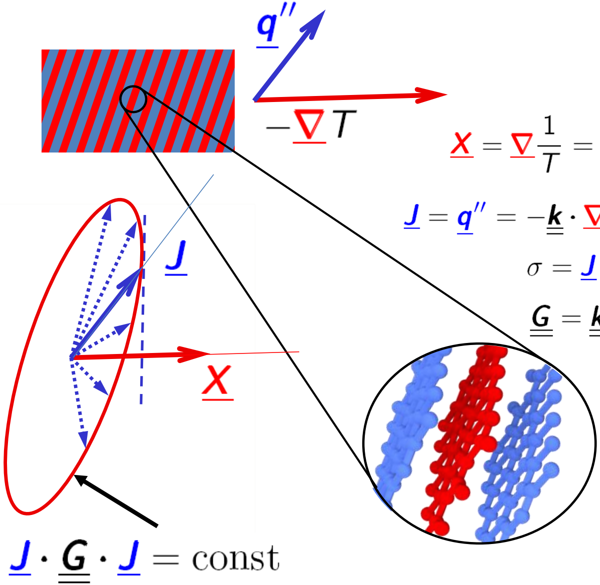
Fourier law in nanostructured anisotropic media



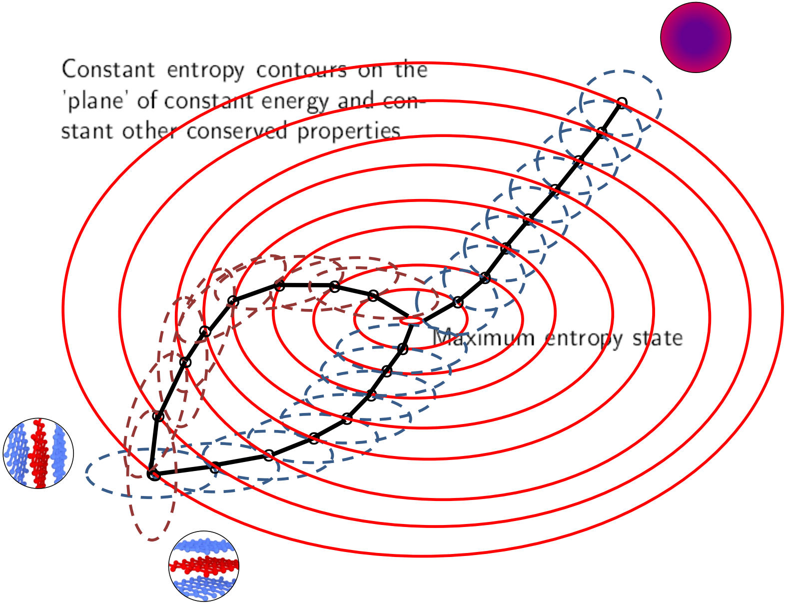
$$\underline{X} = \underline{\nabla} \frac{1}{T} = \underline{\nabla} \left(\frac{\partial S}{\partial E} \right)$$

$$\underline{J} = \underline{q''} = -\underline{\underline{k}} \cdot \underline{\nabla} T = T^2 \underline{\underline{k}} \cdot \underline{X}$$

$$\sigma = \underline{J} \cdot \underline{X}$$

$$\underline{\underline{G}} = \underline{\underline{k}}^{-1}$$

Steepest Entropy Ascent with respect to a Metric

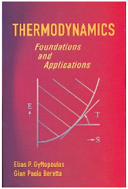


Entropy defined for non-equilibrium states

Hatsopoulos, Gyftopoulos, Found.Phys. **6**, 15, 127, 439, 561 (1976).

Beretta, J.Math.Phys. **25**, 1507 (1984).

Gyftopoulos, Beretta, Thermodynamics. Foundations and Applications, Macmillan 1991, reprint Dover 2005.



See also (>1998):
Lieb, Yngvason, Proc.R.Soc.A **470**, 192 (2014) and refs. therein.

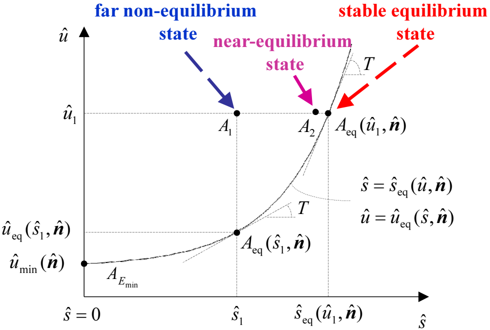
Zanchini, Beretta, Entropy **16**, 1547 (2014) and refs. therein.

Energy vs Entropy diagram

for a fluid or solid element of a continuum:

$\hat{u} = \rho u$, energy density
$\hat{s} = \rho s$, entropy density
$\hat{\boldsymbol{n}} = \hat{n}_1, \dots, \hat{n}_n$, concentrations

Project all states with given $\hat{\boldsymbol{n}}$ onto the $\hat{u}$ vs $\hat{s}$ plane:



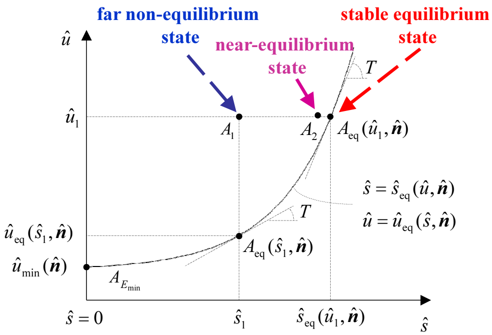
Non-equilibrium states require more independent variables

From the **second law** follows:
$\rightarrow$ **maximum entropy principle:**
among all the states with given values of the energy density, $\hat{u}$, and the concentrations, $\underline{\hat{n}}$, the stable equilibrium states has maximal entropy density

$$\hat{s}_{\rm ne} < \hat{s}_{\rm eq}$$

$\rightarrow$ **fundamental relation for the stable equilibrium states:**

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



$\rightarrow$ **a non-equilibrium fundamental relation** requires **more independent variables**:

$$\hat{s} = \hat{s}_{\rm ne}(\gamma) \quad \hat{u} = \hat{u}_{\rm ne}(\gamma) \quad \underline{\hat{n}} = \underline{\hat{n}}_{\rm ne}(\gamma) \qquad \text{with} \qquad \hat{s}_{\rm ne}(\gamma_{\rm eq}) = \hat{s}_{\rm eq}(\hat{u}_{\rm ne}(\gamma_{\rm eq}), \underline{\hat{n}}_{\rm ne}(\gamma_{\rm eq}))$$

the values $\gamma_{\rm eq} = \gamma_{\rm eq}(\hat{u}, \underline{\hat{n}})$ at stable equilibrium are fixed by the values of $\hat{u}$ and $\underline{\hat{n}}$.
The variables γ characterize the different approaches/models/levels of description/theories.

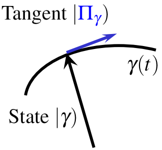
states depend on many variables

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

Reformulate in terms of square-root-probabilities

Framework		State	Redefine	Dynamics
A	IT SM	$\{p_j\}$	$\gamma = \mathrm{diag}\{\sqrt{p_j}\}$	$\dfrac{d\gamma}{dt} = \Pi_\gamma$
B	RGD SSH	$f(\mathbf{c}, \mathbf{x}, t)$	$\gamma = \sqrt{f}$	$\dfrac{\partial\gamma}{\partial t} + \mathbf{c}\cdot\nabla_{\mathbf{x}}\gamma + \mathbf{a}\cdot\nabla_{\mathbf{c}}\gamma = \Pi_\gamma$
C	RET NET CK	$\{y_j(\mathbf{x}, t)\}$	$\gamma = \mathrm{diag}\{y_j\}$ dimensionless	$\dfrac{\partial\gamma}{\partial t} + \nabla_{\mathbf{x}}\cdot\mathbf{J}_\gamma = \Pi_\gamma$
D	MNET	$P(\{y_j\}, \mathbf{x}, t)$	$\gamma = \sqrt{P(\{y_j\}, \mathbf{x}, t)}$	$\dfrac{\partial\gamma}{\partial t} + \mathbf{v}\cdot\nabla_{\mathbf{x}}\gamma = \Pi_\gamma$
E	QSM QT MNEQT	ρ	$\rho = \gamma\gamma^\dagger$	$\dfrac{d\gamma}{dt} + \dfrac{i}{\hbar}H\gamma = \Pi_\gamma$

In each framework, Π_γ may be viewed as the TANGENT VECTOR to the time-dependent trajectory of γ in state space as viewed from an appropriate local material frame, streaming frame, or Heisenberg picture.



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

Quantum description of a QuDit (when $[H, \rho] = 0$)

For a D level system, we take

- $\gamma = \sum_{n=1}^{D} \sqrt{p_n} P_n$

The density operator is

- $\rho = \sum_{n=1}^{D} p_n P_n$

and for the special class of states with $[H, \rho] = 0$, the Hamiltonian operator is

- $H = \sum_{n=1}^{D} e_n P_n$

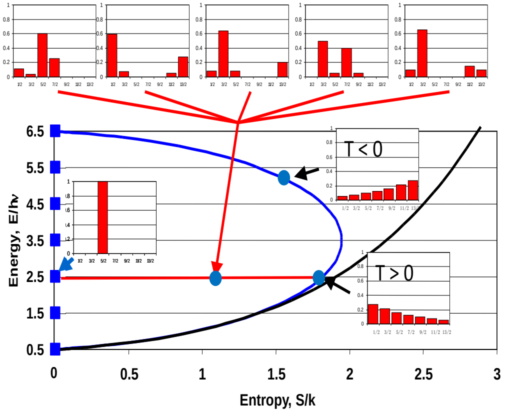
the energy

- $E = \sum_{n=1}^{D} p_n g_n e_n$

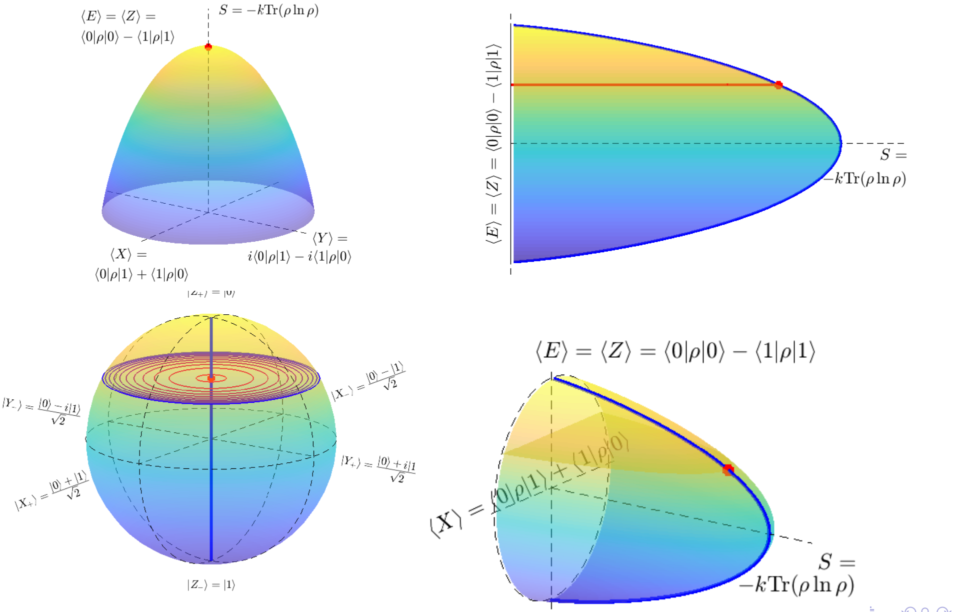
the entropy,

- $S = -k_\mathrm{B} \sum_{n=1}^{D} p_n g_n \ln p_n$

- p_n represents the degree of involvement of energy level e_n in sharing the energy load of the system
- $p_n e_n / E$ fraction of energy carried by level e_n
- S measures the overall degree of sharing



Quantum description (pictorial) of a single Qubit



Different laws of evolution, but same structure

They can all be written in the same **general form**:

$$\frac{d\gamma}{dt} = \mathcal{R}_\gamma + \boldsymbol{\Pi_\gamma}$$

as a result we have the BALANCE EQUATIONS:

- the term $\mathcal{R}_\gamma$ accounts for reversible dynamics, inertia, convective and diffusive transport between adjacent elements of the continuum
- the term $\boldsymbol{\Pi_\gamma}$ is responsible for entropy generation, while it conserves all constants of the motion

$$\hat{u} = \hat{u}_{\rm ne}(\gamma) \quad \rightarrow \quad \frac{\mathrm{d}\hat{u}}{\mathrm{d}t} = (\frac{\delta \hat{u}_{\rm ne}}{\delta\gamma}|R_\gamma) \qquad (\frac{\delta \hat{u}_{\rm ne}}{\delta\gamma}|\boldsymbol{\Pi_\gamma}) = 0$$

$$\hat{\boldsymbol{n}} = \hat{\boldsymbol{n}}_{\rm ne}(\gamma) \quad \rightarrow \quad \frac{\mathrm{d}\hat{\boldsymbol{n}}}{\mathrm{d}t} = (\frac{\delta \hat{\boldsymbol{n}}_{\rm ne}}{\delta\gamma}|R_\gamma) \qquad (\frac{\delta \hat{\boldsymbol{n}}_{\rm ne}}{\delta\gamma}|\boldsymbol{\Pi_\gamma}) = 0$$

$$\hat{s} = \hat{s}_{\rm ne}(\gamma) \quad \rightarrow \quad \frac{\mathrm{d}\hat{s}}{\mathrm{d}t} = (\frac{\delta \hat{s}_{\rm ne}}{\delta\gamma}|R_\gamma) + (\frac{\delta \hat{s}_{\rm ne}}{\delta\gamma}|\boldsymbol{\Pi_\gamma}) \qquad \sigma = (\frac{\delta \hat{s}_{\rm ne}}{\delta\gamma}|\boldsymbol{\Pi_\gamma}) \geq 0$$

Moreover, there exists a **metric** G with which the system "perceives" the distance between neighbouring states, $d(\gamma,\gamma+\mathrm{d}\gamma)^2 = (\mathrm{d}\gamma|G|\mathrm{d}\gamma)$ with respect to which the term $\boldsymbol{\Pi_\gamma}$ has the **direction of steepest entropy ascent** compatible with the conservation laws:

$$|\boldsymbol{\Pi_\gamma}) = G^{-1}|\frac{\delta \hat{s}_{\rm ne}}{\delta\gamma} - \beta_u \frac{\delta \hat{u}_{\rm ne}}{\delta\gamma} - \boldsymbol{\beta}_n \cdot \frac{\delta \hat{\boldsymbol{n}}_{\rm ne}}{\delta\gamma})$$

SEA Quantum Thermodynamics version 1984 assumed $\hat{G}_\gamma = \hat{I}$

$$\rho = \gamma^\dagger \gamma \;\Rightarrow\; \dot\rho = \dot\gamma^\dagger \gamma + \gamma^\dagger \dot\gamma$$

$$\frac{d\gamma}{dt} - \frac{i}{\hbar}\gamma H = \boldsymbol{\Pi_\gamma} \;\Rightarrow$$

$$\frac{d\rho}{dt} + \frac{i}{\hbar}[H,\rho] = \boldsymbol{\Pi_\gamma^\dagger}\gamma + \gamma^\dagger \boldsymbol{\Pi_\gamma}$$

$$S = -k\mathrm{Tr}\rho\ln\rho, \quad E = \mathrm{Tr}\rho H$$

$$\Delta H = H - E\, I$$

$$\Delta S = -k\ln\rho - S\, I$$

$$\langle\Delta H\Delta H\rangle = \mathrm{Tr}\rho(\Delta H)^2 = \mathrm{Tr}\rho H^2 - E^2$$

$$\langle\Delta S\Delta H\rangle = \mathrm{Tr}\rho\Delta S\Delta H = -k\mathrm{Tr}\rho H\ln\rho - E\, S$$

$$\dot S = \left(2\gamma\Delta M_\rho \middle| \hat{G}_\gamma^{-1} \middle| 2\gamma\Delta M_\rho\right)$$

As stable equilibrium is approached

$$\rho_{\mathrm{eq}}(E) \Rightarrow \frac{\exp(-H/kT(E))}{\mathrm{Tr}\exp(-H/kT(E))} \quad :$$

SEA dynamics with respect to metric $\hat{G}_\gamma$:

$$|\boldsymbol{\Pi_\gamma}) = \hat{G}_\gamma^{-1}\left|\frac{\delta\hat{s}_{\mathrm{ne}}}{\delta\gamma}\Big|_C\right)$$

$$\frac{\delta\hat{s}_{\mathrm{ne}}}{\delta\gamma}\Big|_C = -2k\frac{\begin{vmatrix}\gamma\ln\rho & \gamma & \gamma H\\ \mathrm{Tr}\rho\ln\rho & 1 & \mathrm{Tr}\rho H\\ \mathrm{Tr}\rho H\ln\rho & \mathrm{Tr}\rho H & \mathrm{Tr}\rho H^2\end{vmatrix}}{\begin{vmatrix}1 & \mathrm{Tr}\rho H\\ \mathrm{Tr}\rho H & \mathrm{Tr}\rho H^2\end{vmatrix}}$$

$$= 2\gamma\Delta S - \frac{1}{\theta_H(\rho)}\gamma\Delta H = 2\gamma\Delta M_\rho$$

where $\theta_H(\rho) = \dfrac{\langle\Delta H\Delta H\rangle}{\langle\Delta S\Delta H\rangle}$ nonequilibrium dynamical temperature

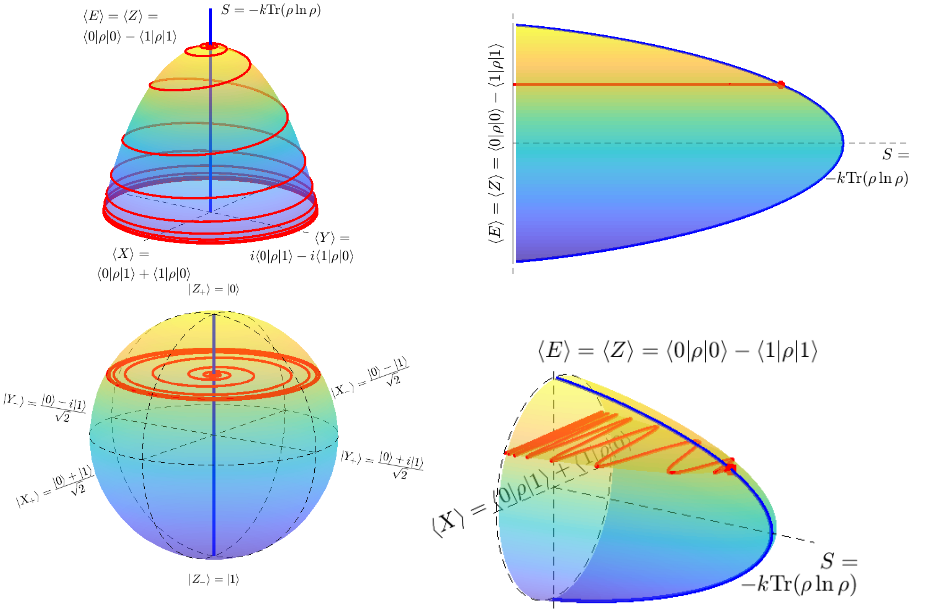
and $M_\rho = -k\ln\rho - \dfrac{H}{\theta_H(\rho)}$ nonequilibrium Massieu operator

$$\mathrm{Tr}\rho M_\rho \Rightarrow S_{\mathrm{eq}}(E) - \frac{E}{T(E)}$$

$$\theta_H(\rho) \Rightarrow T(E) \qquad 2\gamma\Delta M_\rho \Rightarrow 0$$

See Refs. [12–23] and [27–32] in Montefusco et al, Phys.Rev.E, 91, 042138 (2015) and Beretta, Rep.Math.Phys., 64, 139 (2009)

Steepest Entropy Ascent for a single Qubit



The principle of local steepest entropy ascent is a 1984 precursor of several modern theories of non-equilibrium dynamics

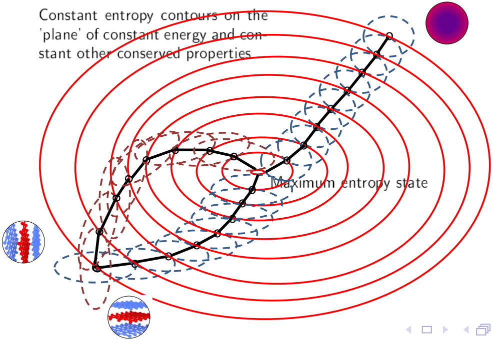
- Ziegler's attempts to generalize Onsager's principle (1958)
- equation of motion for quantum thermodynamics (1981: Beretta)
- steepest entropy ascent (1984: Beretta, Gyftopoulos, Park, Hatsopoulos)
- metriplectic formalism (1984: Morrison, Kaufman, Grmela)
- least action in chemical kinetics (1987: Sieniutycz)
- 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)
- SEAQT (>2014: von Spakovsky)

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

The fourth law: steepest entropy ascent

Every non-equilibrium state of a system or local subsystem for which entropy is well defined must be equipped with a METRIC IN STATE SPACE with respect to which the irreversible component of its time evolution is in the direction of steepest entropy ascent compatible with the conservation constraints.

Beretta, Phil.Trans.R.Soc.A **378**, 20190168 (2020)



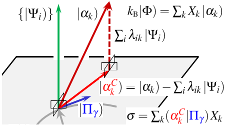
Far non-eq: SEA+CE approximation $\Rightarrow$ Onsager relations

extended to the far non-equilibrium

Assume each state γ maximizes the entropy $S(\gamma)$ subject to fixed values of a set of rate controlling slow variables $A_k(\gamma) = \mathrm{Tr} A_k \gamma\gamma^\dagger$. Introducing Lagrange multipliers X_k/k_B (**affinity or force** conjugated to $\langle A_k\rangle$) we have

$$|\Phi) = \frac{1}{k_\mathrm{B}} \sum_k X_k\, |\boldsymbol{\alpha}_k)$$

$$\text{where } |\boldsymbol{\alpha}_k) = \frac{\delta S(\gamma)}{\delta\gamma} \text{ and } X_k = \frac{\partial S(\gamma)}{\partial \langle A_k\rangle(\gamma)}$$



Then the SEA equation takes the form

$$|\Pi_\gamma^\mathrm{SEA}) = \frac{1}{\tau k_\mathrm{B}} \sum_k X_k\, \hat{G}^{-1}\, |\boldsymbol{\alpha}_k^C)$$

where

$$|\boldsymbol{\alpha}_k^C) = |\boldsymbol{\alpha}_k - \sum_i \lambda_{ik}\, \Psi_i)$$

the **partial nonequilibrium potentials** λ_{ik} are the solution of the orthogonality conditions

$$\sum_i (\Psi_j|\hat{G}^{-1}|\Psi_i)\,\lambda_{ik} = (\Psi_j|\hat{G}^{-1}|\boldsymbol{\alpha}_k)$$

and $|\Phi_C) = \sum_k X_k\, |\boldsymbol{\alpha}_k^C)$. By defining the **nonequilibrium Onsager conductivities**:

$$L_{jk} = \frac{1}{k_\mathrm{B}\tau}(\boldsymbol{\alpha}_j^C|\hat{G}^{-1}|\boldsymbol{\alpha}_k^C) = L_{kj}$$

the **entropy production rate** becomes a quadratic form in the **forces**

$$\sigma = \frac{k_\mathrm{B}}{\tau}(\Lambda|\Lambda) = \sum_{j,k} X_j\, L_{jk}\, X_k = \sum_j X_j J_j$$

and the **fluxes** J_j, i.e., the **dissipative production rates of the RCCE variables**, are linearly related to the forces

$$J_j \equiv \Pi_{A_j} = (\boldsymbol{\alpha}_j|\Pi_\gamma) = \sum_k L_{jk}\, X_k$$

Beretta, Found.Phys. **17** 365 (1987). Beretta, Phil.Trans.R.Soc.A **378**, 20190168 (2020)