Steepest entropy ascent in nonequilibrium quantum dynamics

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What makes some physical principles "great"?

Mechanics

- Mass
- Energy
- Momentum
- Charge

- Angular momentum
- Number of constituents considered as indivisible in the model
- Other quantum invariants

are:

- properties of all states
- exchanged via interactions
- conserved in all processes

Thermodynamics

- Second Law: among all states with identical values of all conserved properties, one and only one is stable equilibrium

- Entropy is:
  - a property of all states
  - exchanged via interactions
  - conserved in reversible processes
  - generated in irreversible processes
  - maximal at stable equilibrium

Any "great" principles from NET?

Usual NET **assumptions** for **near-equilibrium** models:

- Continuum (fields)
- Local (or nonlocal) equilibrium relations
- Heat&Diffusion fluxes within the continuum

- $e = u(s, c_i) + \text{specific kinetic and potential energies} + \text{nonlocal energies such as } \frac{1}{2}\nabla c_i \cdot \nabla c_j$
- $\mu_{i\rm tot} = \mu_i + \text{partial molar kinetic and potential energies} + \text{nonlocal terms}$
- $d(\rho u) = T\, d(\rho s) + \sum_i \mu_{{\rm tot},i}\, dc_i \qquad Y_k = -\frac{1}{T}\sum_i \nu_{ik}\mu_i$ (affinity)
- $\boldsymbol{J}_E = T\, \boldsymbol{J}_S + \sum_i \mu_{{\rm tot},i}\, \boldsymbol{J}_{n_i} \qquad \boldsymbol{J}_Z = \sum_i z_i \boldsymbol{J}_{n_i}$ (charge flux)

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Combined with the **balance equations** (for energy, momentum, charge, species, etc.) they yield the usual **force⊙flux expression** for the **entropy production density**:

$$\sigma = \sum_f \boldsymbol{J}_f \odot \boldsymbol{X}_f$$

$$\underline{\boldsymbol{J}} = \{\, r_k \,;\, \boldsymbol{J}_E \,,\, \boldsymbol{J}_{n_i} \,,\, \boldsymbol{J}_Z \,;\, \boldsymbol{J}_{m\boldsymbol{v}} \,\}$$

$$\odot = \{\, \times \,;\, \cdot \,,\, \cdot \,,\, \cdot \,;\, : \,\}$$

$$\underline{\boldsymbol{X}} = \{\, Y_k \,;\, \nabla\frac{1}{T} \,,\, \nabla\frac{\mu_n - \mu_i}{T} \,,\, -\nabla\frac{\varphi_{\mathrm{el}}}{T} \,;\, -\frac{1}{T}\nabla\boldsymbol{v} \,\}$$

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i.e.:

$$\sigma = \sum_k r_k Y_k + \boldsymbol{J}_E \cdot \nabla\frac{1}{T} + \sum_{i=1}^{n-1} \boldsymbol{J}_{n_i} \cdot \nabla\frac{\mu_n - \mu_i}{T} - \boldsymbol{J}_Z \cdot \nabla\frac{\varphi_{\rm el}}{T} - \frac{1}{T}\boldsymbol{J}_{m\boldsymbol{v}} : \nabla\boldsymbol{v}$$

$\sigma = \sum_f J_f \odot X_f$ is an extrinsic relation

Extrinsic because:

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

For given J_f and X_f, and T_o the temperature of the environment,

$$T_o \sigma = T_o \sum_f J_f \odot X_f$$

represents the **rate of exergy dissipation** per unit volume when we drive:

- a chemical reaction rate down a decreasing Gibbs free energy;
- a heat flux down a decreasing temperature;
- a diffusion flux down a decreasing chemical potential;
- an electric current down a decreasing voltage;
- a capillary flow down a decreasing pressure;
- a momentum flux down a decreasing strain;

Material resistance to flux: intrinsic relation for σ

Off equilibrium, local material properties depend on the local equilibrium potentials

$$\underline{\Gamma} = \{1/T, -\mu_1/T, \ldots, -\mu_n/T, -\varphi_{\rm el}/T\}$$

and determine how strongly **the material tries to restore equilibrium**:

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

The flux→force constitutive relation characterizes the material:

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

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

$$\sigma = \sum_f J_f \odot X_f(\underline{J}, \underline{\Gamma}) = \sigma(\underline{J}, \underline{\Gamma})$$

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Compatibility conditions:

- $\sigma(0, \underline{\Gamma}) = 0$ at equilibrium (where $\underline{J}_{\rm eq} = 0$ and $\underline{X}_{\rm eq} = 0$)
- $\sigma \geq 0$ off equilibrium
- Curie principle for isotropic conditions
- Onsager reciprocity near equilibrium

Near equilibrium: Pierre Curie's "great" principle

Pierre Curie (1894): **the symmetry of the cause is preserved in its effects**. Therefore, in isotropic conditions, fluxes and forces of different tensorial character do not couple.

	X	Y_k	$-\frac{1}{T}\nabla\cdot \boldsymbol{v}$	$\nabla\frac{1}{T}$	$\nabla\frac{\mu_n-\mu_i}{T}$	$-\nabla\frac{\varphi_{\mathrm{el}}}{T}$	$-\frac{1}{T}(\nabla\boldsymbol{v})^{\mathrm{sym}}$
J	$\odot$	$\times$	$\times$	$\cdot$	$\cdot$	$\cdot$	$:$
r_k	$\times$	⊠	⊠				
$\mathrm{Tr}(J_{m\boldsymbol{v}})$	$\times$	⊠	⊠				
J_E	$\cdot$			⊠	⊠	⊠	
J_{n_i}	$\cdot$			⊠	⊠	⊠	
J_Z	$\cdot$			⊠	⊠	⊠	
$(J_{m\boldsymbol{v}})^{\mathrm{dev}}$	$:$						⊠

Near-eq linear regime: Onsager's "great" principle

Linearize the relations $\underline{X} = \underline{X}(\underline{J}, \underline{\Gamma})$
with respect to $\underline{J}$ **near equilibrium**

$$X_f(\underline{J}) = X_f(0) + \left.\frac{\partial X_f}{\partial J_g}\right|_0 \odot J_g + \dots$$

$$R^0_{fg} \equiv \left.\frac{\partial X_f}{\partial J_g}\right|_0$$

$$X_f \approx R^0_{fg}(\underline{\Gamma}) \odot J_g$$

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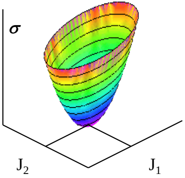
- Second Law: $R^0_{fg} \geq 0$
- Curie: $R^0_{fg} = 0$ for X_f and J_g of different tensorial order.
- Reciprocity*: $R^0_{fg} = R^0_{gf}$

Flux picture



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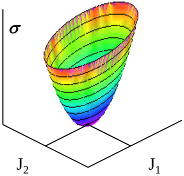
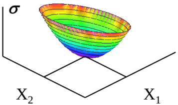


Force picture



$$\underline{\underline{R}}_0^{-1} = \underline{\underline{L}}_0 \geq 0$$

Linearize the relations $\underline{J} = \underline{J}(\underline{X}, \underline{\Gamma})$ with respect to $\underline{X}$ **near equilibrium**

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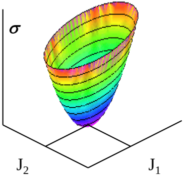

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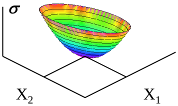

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*Lars Onsager (1931) proves **reciprocity** based on **additional assumptions** (see slide 19):

(1) linear regression of deviations from equilibrium,
(2) Einstein-Boltzmann distribution of deviations,
(3) microscopic reversibility on the average.

Near eq: Steepest entropy ascent implies reciprocity

Flux picture constitutive relation:

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

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

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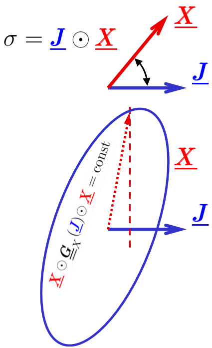
$$\underline{X} = \underline{\underline{R}}(\underline{J}, \underline{\Gamma}) \odot \underline{J}$$

$\underline{\underline{R}}(\underline{J}, \underline{\Gamma})$ is positive and **symmetric** because $\underline{\underline{G}}_X$ is a **metric**.



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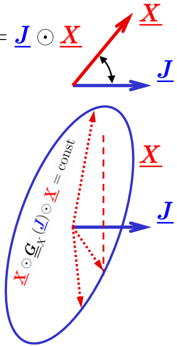

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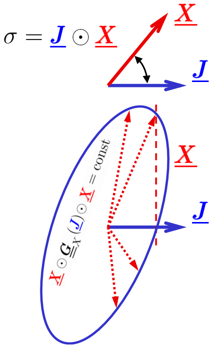

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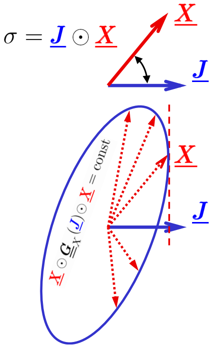

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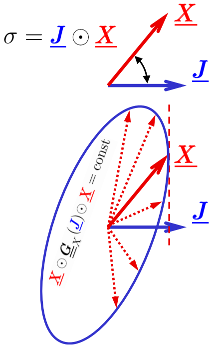

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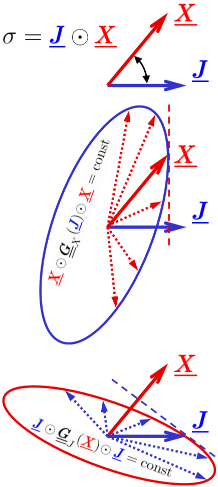

Force picture constitutive relation:

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

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$\underline{\underline{L}}(\underline{X}, \Gamma)$ is positive and **symmetric** because $\underline{\underline{G}}_J$ is a **metric**.

Near eq: Steepest entropy ascent implies reciprocity

Flux picture constitutive relation:

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

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

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

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

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

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

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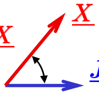
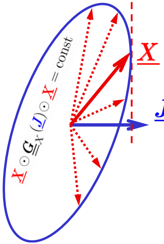
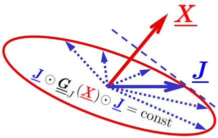
Near eq.: $\underline{\underline{R}}(\underline{J},\Gamma) \to \underline{\underline{R}}_0(\Gamma)$

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







$$\Rightarrow \quad \underline{\underline{R}}_0^{-1} = \underline{\underline{L}}_0 \quad \Leftarrow$$

Force picture constitutive relation:

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

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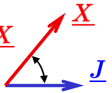

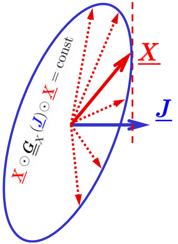

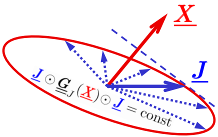

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Onsager's variational principle, $\dot S_{\rm gen} - \Phi_{\rm diss} = $ max, is SEA

Near equilibrium, the SEA principle in the flux picture, with $\lambda_J = 1/2$ and $\underline{\underline{G}}_J = \underline{\underline{R}}_0$

$$\max_{\underline{J}} \Big|_{\underline{X},\underline{\Gamma}} : \; \underline{X} \odot \underline{J} - \frac{1}{2} \underline{J} \odot \underline{\underline{R}}_0 \odot \underline{J}$$

is equivalent to Onsager's variational principle: the spatial pattern of fluxes $\underline{J}(x)$ selected by **Nature maximizes** $\dot S_{\rm gen} - \Phi_{\rm diss}$ subject to the instantaneous pattern of local-equilibrium entropic potentials $\underline{\Gamma}(x) = \{1/T(x), -\mu_1(x)/T(x), \ldots, -\mu_n(x)/T(x), -\varphi_{\rm el(x)}/T(x)\}$ and hence **for given** forces obeying $\underline{X}(x) = \nabla \underline{\Gamma}(x)$ (i.e., no convection and no reaction),

$$\max_{\underline{J}(x)} \Big|_{\underline{\Gamma}(x), \underline{X}(x) = \nabla \underline{\Gamma}(x)} : \; \dot S_{\rm gen} - \Phi_{\rm diss}$$

$$\text{where: } \dot S_{\rm gen} = \iiint \underline{X}(x) \odot \underline{J}(x)\, dV \qquad \Phi_{\rm diss} = \frac{1}{2} \iiint \underline{J}(x) \odot \underline{\underline{R}}_0(\underline{\Gamma}(x)) \cdot \underline{J}(x)\, dV$$

The Euler-Lagrange equations yield the linear laws

$$\underline{J}(x) = \underline{\underline{L}}_0(\underline{\Gamma}(x)) \odot \underline{X}(x) \qquad \text{where } \underline{\underline{L}}_0(\underline{\Gamma}(x)) = \underline{\underline{R}}_0(\underline{\Gamma}(x))^{-1}$$

The convective nonlinearity of the conservation laws may lead to instabilities and multiple solutions (e.g., conduction vs convective rolls, laminar vs turbulent flow, phase inversion, change of hydrodynamic pattern). In such cases, the principle

$\dot S_{\rm gen} = $ **max** — **Now equivalent to** $\dot S_{\rm gen} - \Phi_{\rm diss} = $ **max, since** $\Phi_{\rm diss} = \dot S_{\rm gen}/2$ **when** $\underline{X} = \underline{\underline{R}}_0 \odot \underline{J}$

identifies which hydrodynamic pattern is stable and hence actually selected.

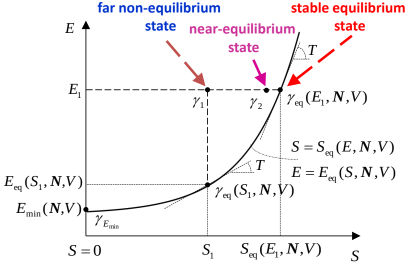
Far non-eq: more detailed levels of description

The **entropy of non-equilibrium states** is well defined, but **depends on possibly many more properties** than just the conserved properties.

$$S = S[\gamma] \quad E = E[\gamma] \quad N_i = N_i[\gamma] \quad \ldots$$

Where γ denotes the full set of state variables or fields in the chosen framework of description (square brackets denote functionals).

Representation of nonequilibrium states on E vs S graph (see Gyftopoulos, Beretta, Thermodynamics, Dover 2005.)



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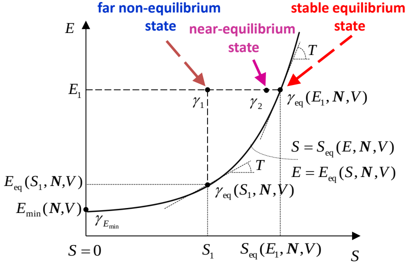

If states depend on time only, $\gamma = \gamma(t)$:

$$\frac{dS}{dt} = \Pi_S, \quad \frac{dE}{dt} = \Pi_E, \quad \cdots$$

If states are continuum fields, $\gamma = \gamma(\boldsymbol{x}, t)$:

$$\frac{\partial S}{\partial t} + \nabla \cdot \mathbf{J}_S^o = \Pi_S, \quad \frac{\partial E}{\partial t} + \nabla \cdot \mathbf{J}_E^o = \Pi_E, \quad \dots$$

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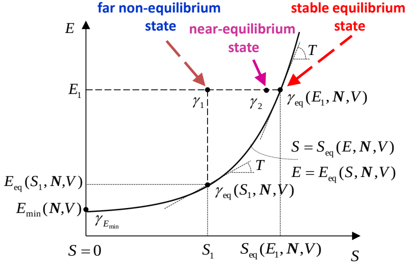

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where, in either case,

$$\Pi_S = \left(\frac{\delta S}{\delta \gamma} \middle| \Pi_\gamma\right) \geq 0, \quad \Pi_E = \left(\frac{\delta E}{\delta \gamma} \middle| \Pi_\gamma\right) = 0, \ldots$$

$$S = \rho s,\ E = \rho e, \ldots$$
$$\mathbf{J}_S^o = \mathbf{J}_S + \rho s \mathbf{v},$$
$$\mathbf{J}_E^o = \mathbf{J}_E + \rho e \mathbf{v}, \ldots$$

Far non-eq: more detailed levels of description

The **entropy of non-equilibrium states** is well defined, but **depends on possibly many more properties** than just the conserved properties.

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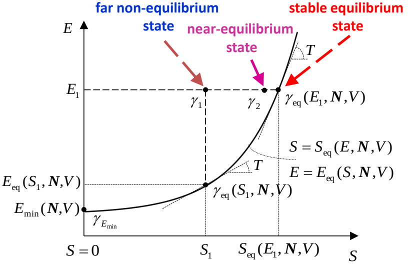

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here with $\dfrac{d\gamma}{dt} + \mathcal{R}_\gamma = \boldsymbol{\Pi_\gamma}$

and here with $\dfrac{\partial \gamma}{\partial t} + \nabla \cdot \mathbf{J}_\gamma^o = \boldsymbol{\Pi_\gamma}$

Far non-eq: state variables in various frameworks

	Frameworks	State Variables γ
RGD	Rarefied Gases Dynamics	$f(\mathbf{c}, \mathbf{x}, t)$
SSH	Small-Scale Hydrodynamics	
RET	Rational Extended Thermodynamics	$\{\alpha_j(\mathbf{x}, t)\}$
NET	Non-Equilibrium Thermodynamics	
CK	Chemical Kinetics	
MNET	Mesoscopic NE Thermodynamics	$P(\{\alpha_j\}, \mathbf{x}, t)$
SM	Statistical Models	$\{p_j(t)\}$
IT	Information Theory	
QSM	Quantum Statistical Mechanics	$\rho(t)$ density operator
QT	Quantum Thermodynamics	
MNEQT	Mesoscopic NE QT	$\alpha_j = \mathrm{Tr}\rho\, A_j$

Far non-eq: state variables in various frameworks

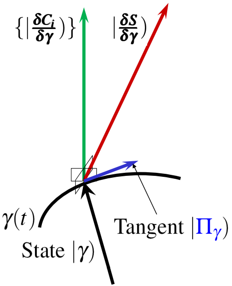
Dynamical law

Either of the form:

$$\frac{\partial \gamma}{\partial t} + \nabla \cdot \mathbf{J}^o_\gamma = \boldsymbol{\Pi}_\gamma$$

or of the form:

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



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QSM	Quantum Statistical Mechanics	$\rho(t)$ density
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MNEQT	Mesoscopic NE QT	$\alpha_j = \mathrm{Tr}\rho A_j$

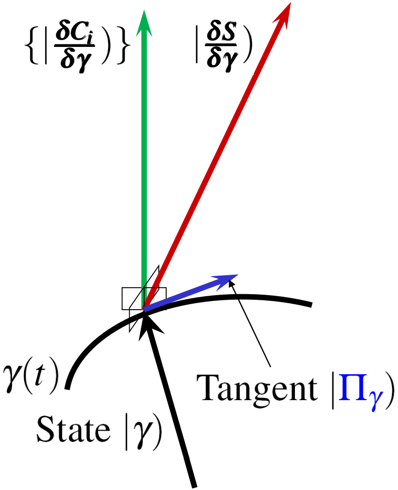
In each framework, **the production terms** in the balance or evolution equations for entropy and conserved properties C_i (such as E, N_i, etc) **are scalar products**

$$\Pi_S = \left(\frac{\delta S}{\delta \gamma}\middle|\boldsymbol{\Pi}_\gamma\right) \geq 0 \qquad \Pi_{C_i} = \left(\frac{\delta C_i}{\delta \gamma}\middle|\boldsymbol{\Pi}_\gamma\right) = 0$$

where $\boldsymbol{\Pi}_\gamma$ is the **tangent vector to the trajectory** $\gamma(t)$ **in state space**

More precisely, it is its component due to the dissipative part of the evolution equation.

Steepest Entropy Ascent construction



Beretta, Phys.Rev.E, 90, 042113 (2014). See also Montefusco, Consonni, Beretta, Phys.Rev.E, 91, 042138 (2015)

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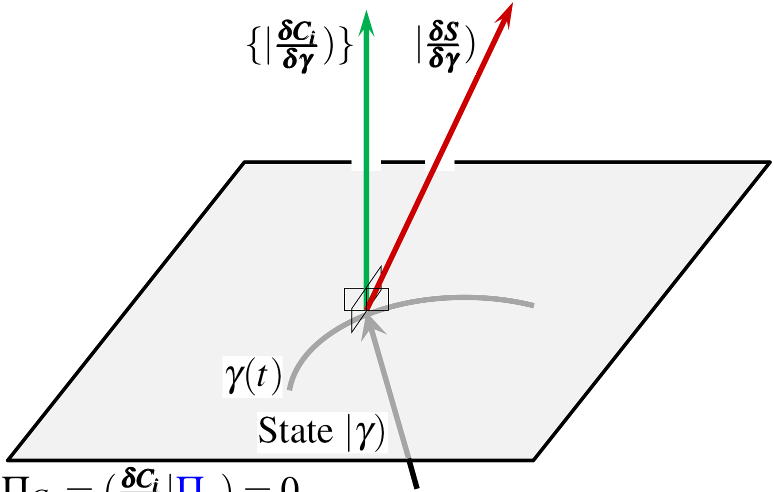

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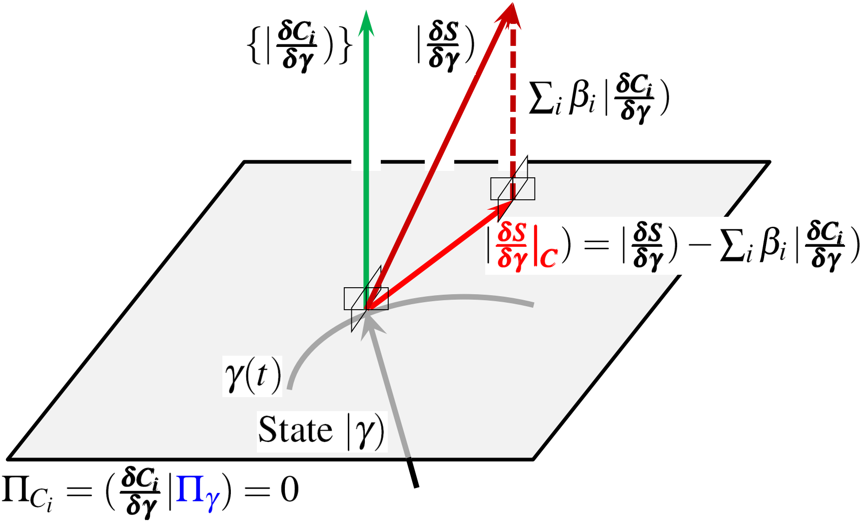

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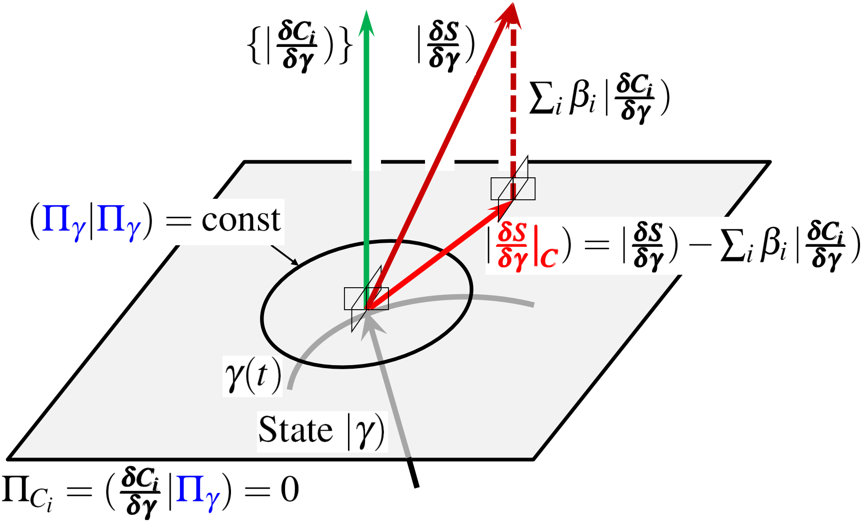

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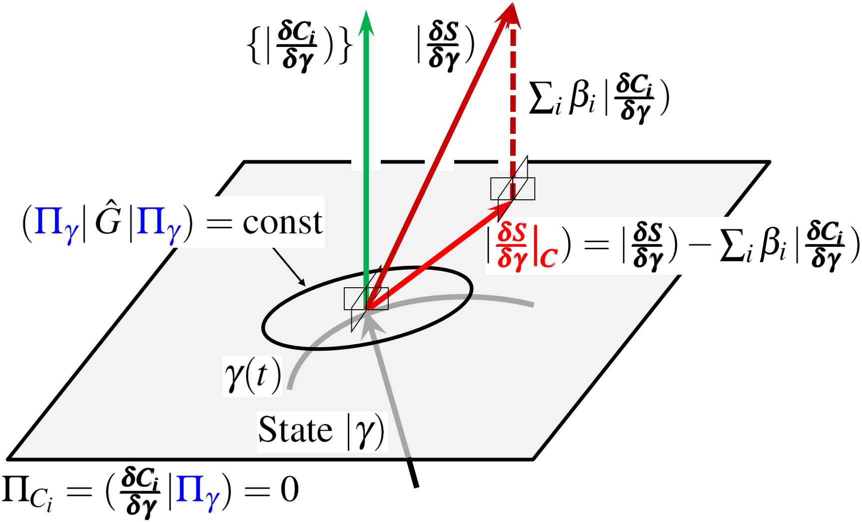

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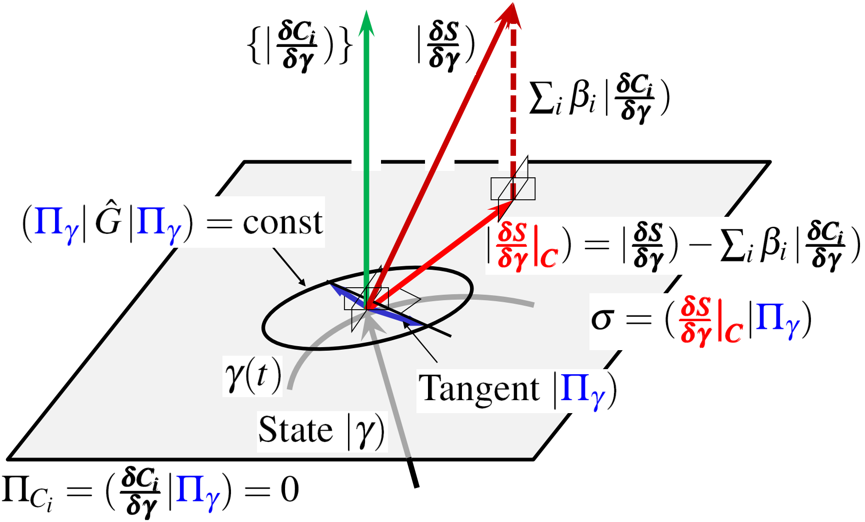

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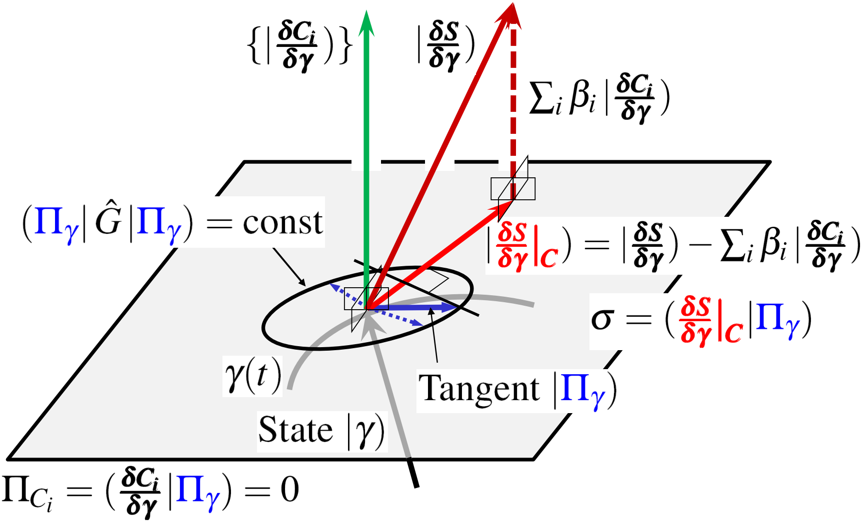

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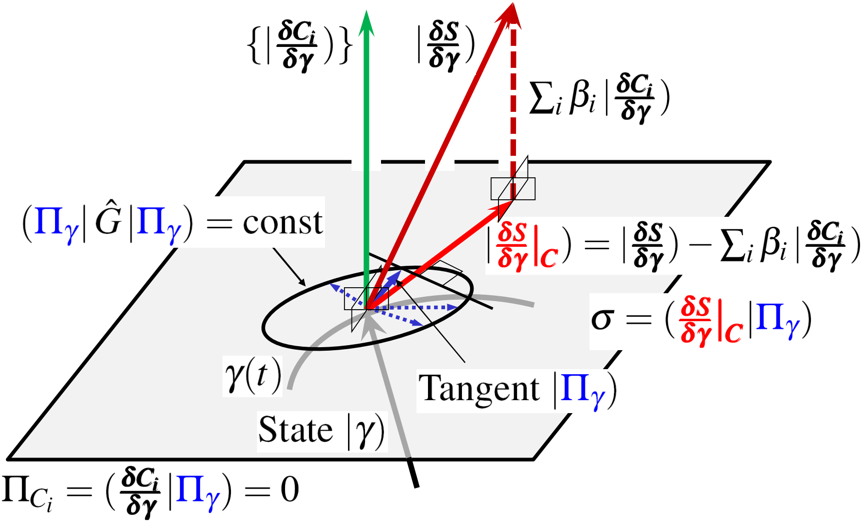

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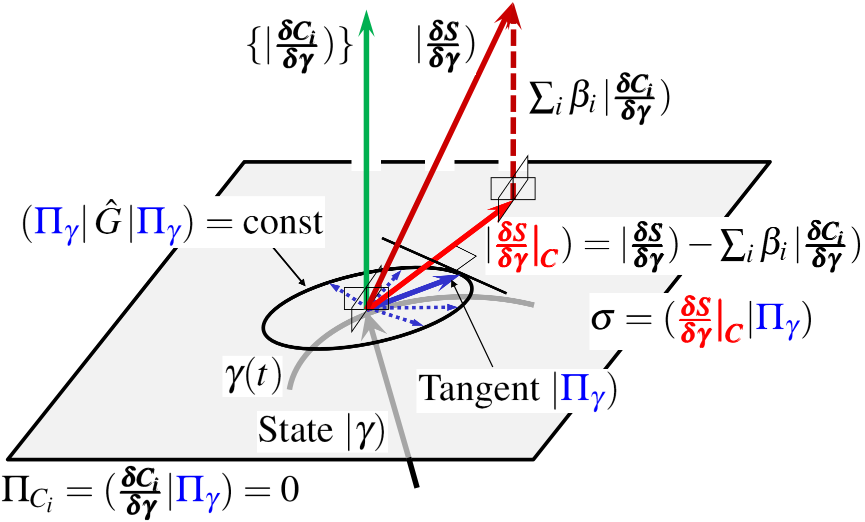

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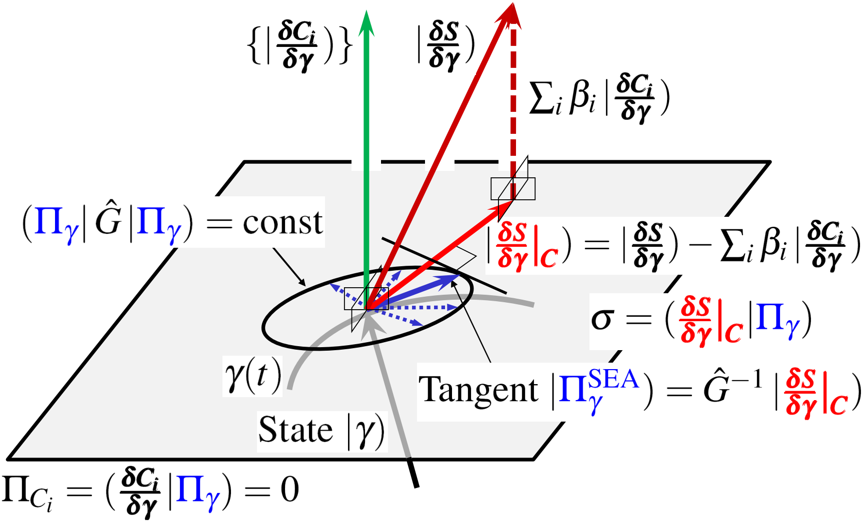

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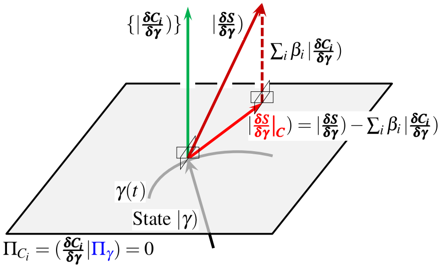
Multipliers β_i define the constrained variational derivative



Defined by orthogonality

$$\left(\frac{\delta S}{\delta\gamma}\Big|_C \Big| \frac{\delta C_j}{\delta\gamma}\right) = 0 \ \forall j$$

i.e., by the system of equations

$$\sum_i \left(\frac{\delta C_i}{\delta\gamma}\Big|\frac{\delta C_j}{\delta\gamma}\right)\beta_i = \left(\frac{\delta S}{\delta\gamma}\Big|\frac{\delta C_j}{\delta\gamma}\right) \ \forall j$$

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

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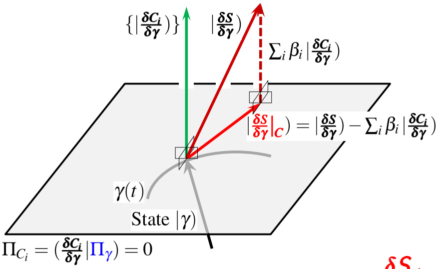

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Solving the system with Cramer's rule, the constrained variational derivative may be written as a ratio of determinants

$$\frac{\delta S}{\delta\gamma}\Big|_C = \frac{\begin{vmatrix} \frac{\delta S}{\delta\gamma} & \frac{\delta C_1}{\delta\gamma} & \cdots & \frac{\delta C_n}{\delta\gamma} \\ \left(\frac{\delta S}{\delta\gamma}\Big|\frac{\delta C_1}{\delta\gamma}\right) & \left(\frac{\delta C_1}{\delta\gamma}\Big|\frac{\delta C_1}{\delta\gamma}\right) & \cdots & \left(\frac{\delta C_n}{\delta\gamma}\Big|\frac{\delta C_1}{\delta\gamma}\right) \\ \vdots & \vdots & \ddots & \vdots \\ \left(\frac{\delta S}{\delta\gamma}\Big|\frac{\delta C_n}{\delta\gamma}\right) & \left(\frac{\delta C_1}{\delta\gamma}\Big|\frac{\delta C_n}{\delta\gamma}\right) & \cdots & \left(\frac{\delta C_n}{\delta\gamma}\Big|\frac{\delta C_n}{\delta\gamma}\right) \end{vmatrix}}{\begin{vmatrix} \left(\frac{\delta C_1}{\delta\gamma}\Big|\frac{\delta C_1}{\delta\gamma}\right) & \cdots & \left(\frac{\delta C_n}{\delta\gamma}\Big|\frac{\delta C_1}{\delta\gamma}\right) \\ \vdots & \ddots & \vdots \\ \left(\frac{\delta C_1}{\delta\gamma}\Big|\frac{\delta C_n}{\delta\gamma}\right) & \cdots & \left(\frac{\delta C_n}{\delta\gamma}\Big|\frac{\delta C_n}{\delta\gamma}\right) \end{vmatrix}}$$

where $C_1, \ldots, C_n$ is a subset of the C_i's such that the variational derivatives $\frac{\delta C_1}{\delta\gamma}, \ldots, \frac{\delta C_n}{\delta\gamma}$ are linearly independent. By virtue of this choice, the determinant at the denominator is a positive definite Gram determinant.

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

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Given the density operator ρ, assume

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With respect to the scalar product

$$(A|B) = \tfrac{1}{2}\mathrm{Tr}(A^\dagger B + B^\dagger A)$$

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

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

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

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

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

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

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

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

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 $\hat{G}_\gamma$:

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

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

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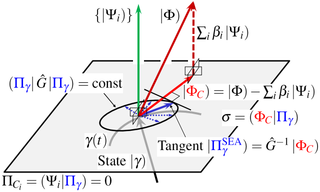
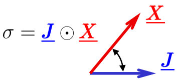
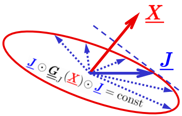
Conclusions? "Great" principles from NET?



- 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 should also 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.**
  - L^2-Wasserstein metric and evolution PDE's of diffusive type – **Wasserstein distance in probability space: Kantorovich-Rubinstein (1958) and Vasershtein (1969).**

If: steady state, no convection, no reactions, linear regime, constant conductivities
Then: local MEP (SEA) implies min global EP

Glansdorff-Prigogine (1954) noted that assuming

- stationary boundary conditions, $d\underline{\Gamma}/dt|_\Omega = 0$
- no convection and no reactions, so that $\underline{X} = \nabla\underline{\Gamma}$
- linear regime, $\underline{J} = \underline{\underline{L}} \odot \underline{X}$, $\sigma = \underline{X} \odot \underline{\underline{L}} \odot \underline{X}$
- constant Onsager conductivities, $d\underline{\underline{L}}/dt = 0$

- $\hat{s} = \hat{s}(\hat{u})$ with all $\hat{u}$ conserved
- $\dfrac{d\underline{\hat{u}}}{dt} = -\nabla \cdot \underline{J}$ with $\underline{J} = J_{\underline{\hat{u}}}$
- $\underline{\Gamma} = \dfrac{\partial \hat{s}}{\partial \underline{\hat{u}}}$ and $\dfrac{\partial \underline{\Gamma}}{\partial \underline{\hat{u}}} = \dfrac{\partial^2 \hat{s}}{\partial \underline{\hat{u}} \partial \underline{\hat{u}}} \leq 0$

Then:

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

i.e., the free fluxes and forces adjust until the system reaches a stable **stationary state with minimum** $\dot{S}_{\mathrm{gen}}$. For variable conductivities, $d\underline{\underline{L}}/dt \neq 0$, the theorem loses validity.

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

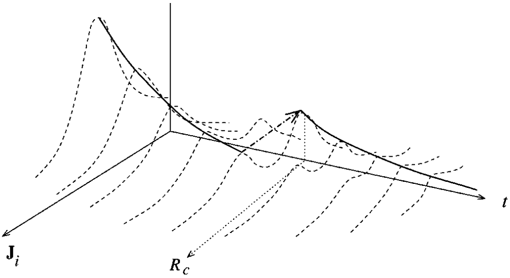
$$\iiint_V \underline{J} \odot \frac{d\underline{X}}{dt}\, dV = \iiint_V \underline{J} \odot \frac{d\nabla\underline{\Gamma}}{dt}\, dV = \cancel{\iint_{\partial V} \underline{J} \odot \frac{d\underline{\Gamma}}{dt} \cdot \boldsymbol{n}\, dA} - \iiint_V \frac{d\underline{\Gamma}}{dt} \odot \nabla \cdot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

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

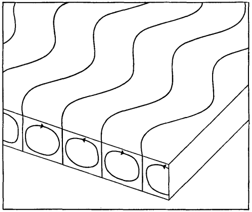
$\dot{S}_{\rm gen} =$ max selects hydrodynamic pattern

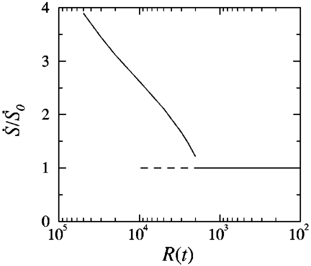
Rayleigh-Benard 2D rolls in horizontal layer of fluid heated from below as a function of Rayleigh number R (Woo, 2002). A slow decrease in R is allowed with time.

$$\dot{S}_{\rm gen} = \iiint \sigma \, dV$$



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





Onsager reciprocity from microscopic reversibility (standard proof)

At local stable equilibrium states,

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

In general, for non-equilibrium states,

$$\hat{s} = \hat{s}(\hat{u}, \underline{\hat{n}}, \alpha_1, \dots, \alpha_m)$$

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

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

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

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

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): Einstein-Boltzmann 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

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

Steepest entropy ascent before GENERIC and quantum thermodynamics before today's quantum thermodynamics

Most of these references are available from www.quantumthermodynamics.org:

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Uniting mechanics and statistics

An adventurous scheme which seeks to incorporate thermodynamics into the quantum laws of motion may end arguments about the arrow of time — but only if it works.

THE logical relationship between the laws of mechanics and those of thermodynamics deserves more attention than it usually receives. Thermodynamics and statistical mechanics are ways of describing the behaviour of macroscopic systems made from components whose behaviour is determined by the laws of mechanics, classically those of Newton (as amended), but otherwise the equations of motion of quantum mechanics. Where the first law of thermodynamics is concerned, there is no difficulty. In both classical and quantum mechanics, total energy is a constant of the motion and is thus always conserved, at least in a closed system.

The difficulty arises chiefly with the second law of thermodynamics, and not only because there is such a variety of ways in which this principle can be defined. But now a group of three theoreticians has put forward an intriguing way in which the laws of quantum mechanics may be modified so as to incorporate the second law from what appears to be the outset (Beretta, G. P., Gyptopoulos, E. P. & Park, J. L., *Il Nuovo Cimento B* **87**, 77–97; 1985). Whether the modification proposed is sufficient, only time will tell, but the objective seems well worth the trouble Beretta *et al.* have taken.

The difficulty is well illustrated by the way in which some kind of correspondence is established between the mechanical behaviour of a system and its thermodynamic properties. For more than a century, people have been brooding on the paradox that while the laws of classical (and, for that matter, quantum) mechanics are symmetrical with respect to time inversion, the second law selects from all possible trajectories of motion only those corresponding to a continual increase of the entropy. The arrow of time is conjured like a rabbit from a hat.

The definition of entropy in terms of the mechanical properties of the constituents of a system is similarly clouded. The classical model is Boltzmann's *H*-theorem (1872), which shows that the rate of change with time of a certain mathematical construct from the probability distribution of single particles in phase space will always be zero or negative. So Boltzmann argued, his quantity *H* is admirably suited to be the negative of what is known in thermodynamics as entropy. This is argument by analogy, but none the worse for that — if it works.

Since Boltzmann's time, there has accumulated a rich literature on the implied paradox of the conflict between the irreversibility of macroscopic processes and the reversibility (in time) of the laws of mechanics and thus of microscopic processes. Indeed, the argument was begun by Loschmidt in 1976, but now even elementary text-books of thermodynamics reckon to give some kind of account of it.

The standard explanation is that the apparent paradox is not a paradox at all, but a confusion about timescales. Any measure of entropy, that derived from Boltzmann's *H* or otherwise, will fluctuate (and so decrease as well as increase on a short timescale), which is not inconsistent with the notion that the average value of the entropy should increase steadily over long periods of time (or remain unchanged when the system is in equilibrium).

Much the same is said of the recurrence paradox, based on the observation due to Poincaré that the point in phase space (momentum as well as position) representing the state of a classical system will return to more or less the same place after a sufficient length of time. On the face of things, that means that non-equilibrium states of a system will repeatedly recur. The standard resolution of that paradox is the observation that, for any realistic system, the interval of time between recurrences will be huge, much greater than, say, the age of the Universe. Again there is nothing wrong with these arguments, but they are far from being rigorous.

So why not take the bull by the horns, and build irreversibility into the laws of mechanics? That is the point from which Beretta *et al.* start. Properly, they acknowledge that they are not the first to tread this path. They work with quantum statistical mechanics, where the formalism is easier. They start from the equation of motion for the operator representing the state of a physical system, say **m**, which is, in operator language, $d\mathbf{m}/dt = -i/\hbar[\mathbf{H},\mathbf{m}]$, where t is time, **H** the Hamiltonian operator of the system and i and $\hbar$ the square route of minus once and Planck's constant (divided by 2π) respectively. The quantity in square brackets is the commutator of its two components, **mH**−**Hm**.

The natural way to proceed is to assume that this equation is modified in such a way that the right-hand side is some other function of the state operator **m** than in the standard form. The objective is to find a form of the function which is compatible both with what is known of the evolution of thermodynamic systems and, perhaps more important, the dynamics of real microscopic systems. Beretta *et al.* have convinced themselves that the function they are seeking cannot be a linear function of **m**. What they propose is the addition to the right-hand side of the quantum equation of motion of a particular function of **m** which, by including both the square root and the logarithm of the state operator of the system, is non-linear enough to satisfy anybody's taste.

Almost magically, the system has some of the obviously necessary properties. For example, for a system in a pure quantum state, say that represented by a solution of Schrodinger's equation, the extra terms vanish and the simple form of the equation of motion applies. Similarly, constants of the motion in the new system are also constants of the motion determined by the simpler equation of motion.

What can be said about the entropy? In reality, the state operator **m** is the equivalent of what is called the density matrix in quantum statistical mechanics, which is why Beretta *et al.* define entropy in terms of the operator **mlogm**, where the logarithm is the natural logarithm of the operator **m**. Specifically, the entropy of the negative of the trace of this operator multiplied by Boltzmann's constant; the authors are able to show that is increases (or does not increase) in the course of time.

So is this a demonstration that the laws of mechanics and of thermodynamics can indeed be combined? Not quite. For one thing, there are various mathematical problems that make some of the steps in the argument conjectural. Worse still, some of the operator functions in the formalism are sometimes undefined. But the system does have the merit of hanging together — the paper now published extends to composite systems the treatment of one-component systems published a year ago.

None of this implies that the arguments about the reconciliation between microscopic reversibility and macroscopic irreversibility will now be stilled. Indeed, while for as long as the present justification of the basis of statistical mechanics holds water, there will be many who say that what Beretta *et al.* have done is strictly unnecessary. But this is a field in which the proof of the pudding is in the eating.

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