Steepest entropy ascent principle unifies far-nonequilibrium dynamical theories

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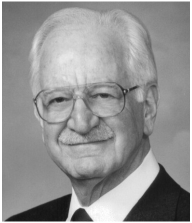
Dedication

James C. Keck
(1924-2010)

George N. Hatsopoulos
(1927–)



Elias P. Gyftopoulos
(1927-2012)

www.JamesKeckCollectedWorks.org

www.EliasGyftopoulos.org

What makes some physical principles "great"?

Mechanics

- Energy
- Momentum
- Charge
- Number of constituents (considered as indivisible)

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
  - maximal at stable equilibrium
  - exchanged via interactions
  - conserved in reversible processes
  - generated in irreversible processes

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

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

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Combined with the balance equations for energy, momentum, charge, and species, they yield the usual force$\odot$flux expression for the entropy production density:

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

$$\begin{aligned}
\underline{\boldsymbol{J}} &= \{\, r_k \;;\; \boldsymbol{J}_E \;,\; \boldsymbol{J}_{n_i} \;,\; \boldsymbol{J}_Z \;;\; \boldsymbol{J}_{mv} \,\}\\
\odot &= \{\, \times \;;\; \cdot \;,\; \cdot \;,\; \cdot \;;\; : \,\}\\
\underline{\boldsymbol{X}} &= \{\, Y_k \;;\; \nabla\frac{1}{T} \;,\; \nabla\frac{\mu_n - \mu_i}{T} \;,\; -\nabla\frac{\varphi_{\text{el}}}{T} \;;\; -\frac{1}{T}\nabla\boldsymbol{v} \,\}
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\end{aligned}$$

i.e.:

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

$\sigma = \sum_f \boldsymbol{J}_f \odot \boldsymbol{X}_f$ 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 $\boldsymbol{J}_f$ and $\boldsymbol{X}_f$, and T_o the temperature of the environment,

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

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

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

Material resistance to flux: intrinsic relation for σ

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

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

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 $\underline{J}$:

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

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Compatibility conditions:

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

Near equilibrium: 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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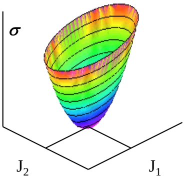
Flux picture



$$\sigma(\underline{J}) = J_f \odot X_f(\underline{J}) \approx J_f \odot R^0_{fg} \odot J_g$$

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

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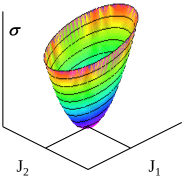

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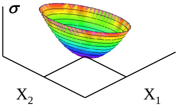

Linearize the relations $\underline{J} = \underline{J}(\underline{X}, \underline{\Gamma})$ with respect to $\underline{X}$ **near equilibrium**

$$J_f(\underline{X}) = J_f(0) + \left.\frac{\partial J_f}{\partial X_g}\right|_0 \odot X_g + \dots$$

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$$\boldsymbol{R}^0_{fg} \equiv \left.\frac{\partial \boldsymbol{X}_f}{\partial \boldsymbol{J}_g}\right|_0$$

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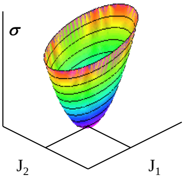
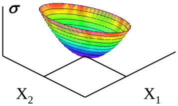


Force picture



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

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

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*Lars Onsager (1931): **additional assumptions to prove reciprocal relations**.

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.

	$\boldsymbol{X}$	Y_k	$-\frac{1}{T}\nabla \cdot \boldsymbol{v}$	$\nabla \frac{1}{T}$	$\nabla \frac{\mu_n - \mu_i}{T}$	$-\nabla \frac{\varphi_{\mathrm{el}}}{T}$	$-\frac{1}{T}(\nabla \boldsymbol{v})^{\mathrm{sym}}$
$\boldsymbol{J}$	$\odot$	$\times$	$\times$	$\cdot$	$\cdot$	$\cdot$	$:$
r_k	$\times$	$\boxtimes$	$\boxtimes$				
p	$\times$	$\boxtimes$	$\boxtimes$				
$\boldsymbol{J}_E$	$\cdot$			$\boxtimes$	$\boxtimes$	$\boxtimes$	
$\boldsymbol{J}_{n_i}$	$\cdot$			$\boxtimes$	$\boxtimes$	$\boxtimes$	
$\boldsymbol{J}_Z$	$\cdot$			$\boxtimes$	$\boxtimes$	$\boxtimes$	
$(\boldsymbol{J}_{m\boldsymbol{v}})^{\mathrm{dev}}$	$:$						$\boxtimes$

Not-too-high non-eq: nonlinear SEA force-flux relations

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**:

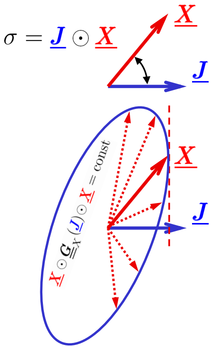
$$\max_{\underline{X}} \Big|_{\underline{J},\underline{\Gamma}} : \ \underline{J} \odot \underline{X} - \lambda_X \underline{X} \odot \underline{\underline{G}}_X \odot \underline{X}$$

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

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

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

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



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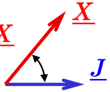

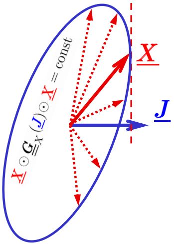

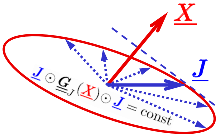

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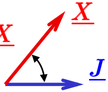

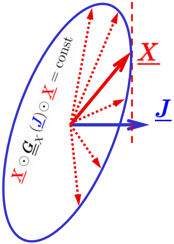

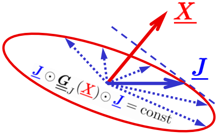

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Near eq.: $\underline{\underline{L}}(\underline{X}, \underline{\Gamma}) \to \underline{\underline{L}}_0(\underline{\Gamma})$ is nonnegative and **symmetric** since $\underline{\underline{G}}_J$ is a **metric**.

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

Onsager's variational principle, $\dot{S}_{\mathrm{gen}} - \Phi = \max$, is SEA

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

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

is equivalent to Onsager's variational principle: the spatial pattern of fluxes $\underline{\boldsymbol{J}}(x)$ selected by **Nature maximizes** $\dot{S}_{\mathrm{gen}} - \Phi$ subject to the instantaneous pattern of local-equilibrium entropic potentials $\underline{\Gamma}(x) = \{1/T(x), -\mu_1(x)/T(x), \ldots, -\mu_n(x)/T(x), -\varphi_{\mathrm{el}(x)}/T(x)\}$ and hence **for given** forces $\underline{\boldsymbol{X}}(x) = \boldsymbol{\nabla}\underline{\Gamma}(x)$, i.e.,

$$\max_{\underline{\boldsymbol{J}}(x)} \Big|_{\underline{\Gamma}(x), \underline{\boldsymbol{X}}(x) = \boldsymbol{\nabla}\underline{\Gamma}(x)} : \ \dot{S}_{\mathrm{gen}} - \Phi$$

$$\text{where: } \dot{S}_{\mathrm{gen}} = \iiint \underline{\boldsymbol{X}}(x) \odot \underline{\boldsymbol{J}}(x)\, dV \qquad \Phi = \frac{1}{2} \iiint \underline{\boldsymbol{J}}(x) \odot \underline{\underline{\boldsymbol{R}}}_0(\underline{\Gamma}(x)) \cdot \underline{\boldsymbol{J}}(x)\, dV$$

The Euler-Lagrange equations yield the linear laws

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

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

$\dot{S}_{\mathrm{gen}} = \max$	**Now equivalent to** $\dot{S}_{\mathrm{gen}} - \Phi = \max$, **since** $\Phi = \dot{S}_{\mathrm{gen}}/2$ **when** $\underline{\boldsymbol{X}} = \underline{\underline{\boldsymbol{R}}}_0 \odot \underline{\boldsymbol{J}}$

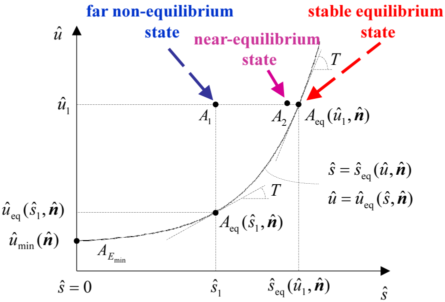
identifies which hydrodynamic pattern is stable and hence actually selected.

Far non-eq: more detailed levels of description

The **entropy of non-equilibrium states depends on many more properties** than just the conserved properties $\hat{u}$ and $\underline{\hat{n}}$

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

Different approaches differ in how the ... are filled.



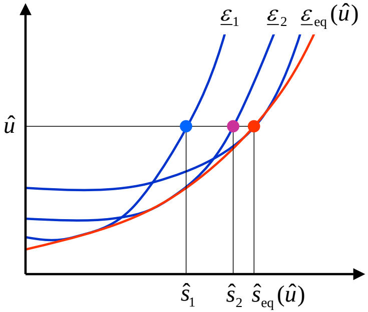
Far non-eq: RCCE Rate-Controlled Constrained Equilibrium/Quasi Equilibrium

The **entropy of non-equilibrium states depends on many more properties** than just the conserved densities $\hat{u}$ and $\hat{\underline{n}}$

$$\hat{s} = \hat{s}(\hat{u}, \hat{\underline{n}}, \underline{\varepsilon}, \underline{\alpha})$$

Here, we identify **many fast variables** $\underline{\alpha}$ and **few slow variables** $\underline{\varepsilon}$.

Keck (1978): On the time scale of the fast variables, the slow variables act as additional conserved properties. So, the state quickly relaxes to a **constrained equilibrium state** with **maximal** $\hat{s}$ **for the given instantaneous values of** $\hat{u}$, $\hat{\underline{n}}$, $\underline{\varepsilon}$.



Keck, Prog. Ener. Comb. Sci., Vol. 16, 125 (1990). www.JamesKeckCollectedWorks.org

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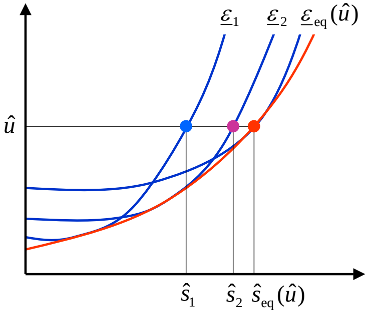

Need an equation of motion only for the **rate-controlling slow variables** ε_f's

$$\frac{d\varepsilon_f}{dt} = K_f(\hat{u}, \underline{\hat{n}}, \underline{\varepsilon}, \underline{\alpha}_{\rm ce}(\hat{u}, \underline{\hat{n}}, \underline{\varepsilon}))$$

obtained from a detailed kinetic scheme. Then, solve for $\hat{u}(t)$, $\underline{\hat{n}}(t)$ and $\underline{\varepsilon}(t)$.

Keck, Prog. Ener. Comb. Sci., Vol. 16, 125 (1990). www.JamesKeckCollectedWorks.org

Far non-eq: GENERIC steepest entropy ascent

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$$\hat{s} = \hat{s}(\hat{u}, \underline{\hat{n}}, \underline{\varepsilon}, \underline{\alpha})$$

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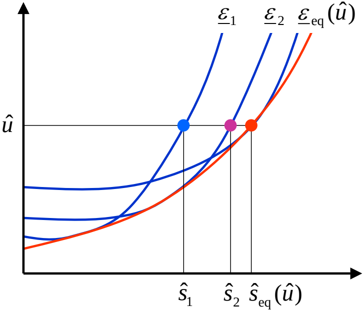
Kaufman,[1] **Morrison**,[2] and **Grmela**[3] (1984) independently propose a similar approach, that **Öttinger** and **Grmela**[1] (1997) further systematize and call GENERIC (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling).

The dissipative part of the GENERIC equation is essentially SEA.[2]



1. Kaufman, Phys. Lett. A, Vol. 100, 419 (1984).
2. Morrison, Phys. Lett. A, Vol. 100, 423 (1984).
3. Grmela, Phys. Lett. A, Vol.102, 355 (1984).

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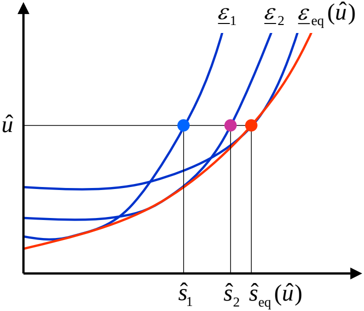


Their proposed GENERIC equation is

$$\frac{d\varepsilon_f}{dt} = G^{\mathrm{rev}}_{fg} \frac{\delta E}{\delta \varepsilon_g} + L^{\mathrm{irr}}_{fg}(\underline{\varepsilon}) \frac{\delta S}{\delta \varepsilon_g}$$

where E and S are the overall energy and entropy functionals of the state variables.

1. Kaufman, Phys. Lett. A, Vol. 100, 419 (1984).
2. Morrison, Phys. Lett. A, Vol. 100, 423 (1984).
3. Grmela, Phys. Lett. A, Vol.102, 355 (1984).

Far non-eq: kinetic theory of gases, Boltzmann eq.

The **entropy of non-equilibrium states depends on many more properties** than just the conserved densities $\hat{u}$ and $\underline{\hat{n}}$

$$\hat{s} = \hat{s}(\underline{\hat{n}}, \hat{f}_1(\boldsymbol{c}), \ldots, \hat{f}_n(\boldsymbol{c}))$$

the local state described by pdf of particles of type i with velocity between $\boldsymbol{c}$ and $\boldsymbol{c} + d\boldsymbol{c}$.

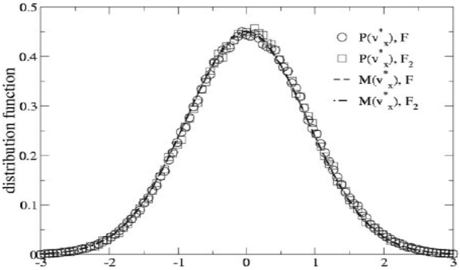
$$\hat{s} = -R \sum_i \hat{n}_i \iiint_{-\infty}^{+\infty} \hat{f}_i(\boldsymbol{c}) \ln \hat{f}_i(\boldsymbol{c})\, d\boldsymbol{c}$$

$$\hat{u} = \frac{1}{2} \sum_i M_i \hat{n}_i \iiint_{-\infty}^{+\infty} |\boldsymbol{c} - \boldsymbol{v}|^2 \hat{f}_i(\boldsymbol{c})\, d\boldsymbol{c}$$

Local equilibrium, i.e., max $\hat{s}$ for given $\hat{u}$, $\underline{\hat{n}}$, and $\boldsymbol{v}$, obtains for the Maxwellian

$$\hat{f}_i^{\mathrm{MB}}(\boldsymbol{c}) = \left[\frac{M_i}{2\pi R T}\right]^{3/2} \exp\left[-\frac{M_i}{2RT} |\boldsymbol{c} - \boldsymbol{v}|^2\right]$$

Fluxes are represented by moments of the velocity distribution



$$\boldsymbol{q}'' = \frac{1}{2} \sum_i M_i \hat{n}_i \iiint_{-\infty}^{+\infty} |\boldsymbol{c} - \boldsymbol{v}|^2 \boldsymbol{c} \hat{f}_i(\boldsymbol{c})\, d\boldsymbol{c}$$

$$\boldsymbol{J}_{m_i} = M_i \hat{n}_i \iiint_{-\infty}^{+\infty} (\boldsymbol{c} - \boldsymbol{v}) \hat{f}_i(\boldsymbol{c})\, d\boldsymbol{c}$$

$$\boldsymbol{\tau} = -\sum_i M_i \hat{n}_i \iiint_{-\infty}^{+\infty} \boldsymbol{c} \otimes \boldsymbol{c} \hat{f}_i(\boldsymbol{c})\, d\boldsymbol{c}$$

$$\boldsymbol{J}_s = -R \sum_i \hat{n}_i \iiint_{-\infty}^{+\infty} (\boldsymbol{c} - \boldsymbol{v}) \hat{f}_i(\boldsymbol{c}) \ln \hat{f}_i(\boldsymbol{c})\, d\boldsymbol{c}$$

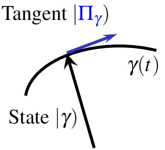
Far non-eq: states variables in various frameworks

		Framework	State Variables	Entropy density
A	IT	Information Theory	$\{p_j(\mathbf{x},t)\}$	$\hat{s} = \hat{s}(\{p_j\})$
B	RGD SSH	Rarefied Gases Dynamics Small-Scale Hydrodynamics	$f(\mathbf{c},\mathbf{x},t)$	$\hat{s} = \hat{s}(f)$
C	RET NET CK	Rational Extended Thermodynamics Non-Equilibrium Thermodynamics Chemical Kinetics	$\{\alpha_j(\mathbf{x},t)\}$	$\hat{s} = \hat{s}(\{\alpha_j\})$
D	MNET	Mesoscopic NE Thermodynamics	$P(\{\alpha_j\},\mathbf{x},t)$	$\hat{s} = \hat{s}(P(\{\alpha_j\}))$
E	QSM QT MNEQT	Quantum Statistical Mechanics Quantum Thermodynamics Mesoscopic NE QT	$\rho(\mathbf{x},t)$ $\alpha_j = \mathrm{Tr}\rho A_j$	$\hat{s} = \hat{s}(\rho)$

Focus on the dissipative part of the dynamics

	Framework	State variables	Redefine	Dynamics
A	IT	$\{p_j\}$	$\gamma = \mathrm{diag}\{\sqrt{p_j}\}$	$\dfrac{d\gamma}{dt} = \Pi_\gamma$
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	$\{\alpha_j(\mathbf{x},t)\}$	$\gamma = \mathrm{diag}\{\alpha_j\}$	$\dfrac{\partial\gamma}{\partial t} + \nabla_{\mathbf{x}}\cdot\mathbf{J}_\gamma = \Pi_\gamma$
D	MNET	$P(\{\alpha_j\},\mathbf{x},t)$	$\gamma = \sqrt{P(\{\alpha_j\},\mathbf{x},t)}$	$\dfrac{\partial\gamma}{\partial t} + \mathbf{v}\cdot\nabla_{\mathbf{x}}\gamma = \Pi_\gamma$
E	QSM QT MNEQT	ρ	$\rho = \gamma\gamma^\dagger$	$\dfrac{d\gamma}{dt} + \dfrac{i}{\hbar}H\gamma = \Pi_\gamma$

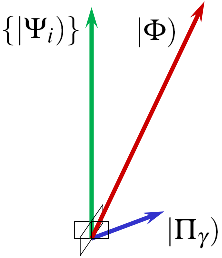
Π_γ **is the TANGENT VECTOR to the time-dependent trajectory of** γ **in state space** when time evolution is determined only by the dissipative component, i.e., as viewed from an appropriate local material frame, streaming frame, or Heisenberg picture.



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

Balance/Transport Equation for C_i — Balance/Transport Equation for S

A	$\frac{d(\gamma^2\,|\,C_i)}{dt} = \Pi_{C_i} = 0$	$-k_{\rm B}\,\frac{d(\gamma^2\,|\,\ln\gamma^2)}{dt} = \sigma$
B	$\frac{\partial(\gamma^2\,|\,C_i)}{\partial t} + \nabla_{\rm x}\cdot(\gamma^2|{\rm c}\;C_i) = \Pi_{C_i} = 0$	$-k_{\rm B}\,\frac{\partial(\gamma^2\,|\,\ln\gamma^2)}{\partial t} + k_{\rm B}\,\nabla_{\rm x}\cdot(\gamma^2|{\rm c}\;\ln\gamma^2) = \sigma$
C	$\frac{\partial C_i}{\partial t} + \nabla_{\rm x}\cdot {\rm J}_{C_i} = \Pi_{C_i} = 0$	$\frac{\partial S}{\partial t} + \nabla_{\rm x}\cdot {\rm J}_S = \sigma$
D	$\frac{\partial C_i}{\partial t} + \nabla_{\rm x}\cdot {\rm J}_{C_i} = \Pi_{C_i} = 0$	$\frac{\partial S}{\partial t} + \nabla_{\rm x}\cdot {\rm J}_S = \sigma$
E	$\frac{d(\gamma\,|\,C_i\,\gamma)}{dt} - \frac{i}{\hbar}(\gamma|[H,\,C_i]\gamma) = \Pi_{C_i} = 0$	$-k_{\rm B}\,\frac{d(\gamma|(\ln\gamma\gamma^\dagger)\,\gamma)}{dt} = \sigma$



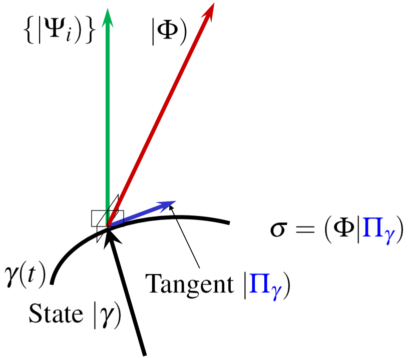
In each framework, the production terms can be written as scalar products of Π_γ with other vectors in the same space

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

Framework	Ψ_i	Φ
A, B, D	$2C_i\,\gamma$	$-2k_{\rm B}(\ln\gamma^2)\,\gamma$
C	${\rm vect}\{\Psi_{i\alpha_j}\}$	${\rm vect}\{\Phi_{\alpha_j}\}$
E	$2C_i\,\gamma$	$-2k_{\rm B}(\ln\gamma\gamma^\dagger)\,\gamma$

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

Steepest Entropy Ascent construction



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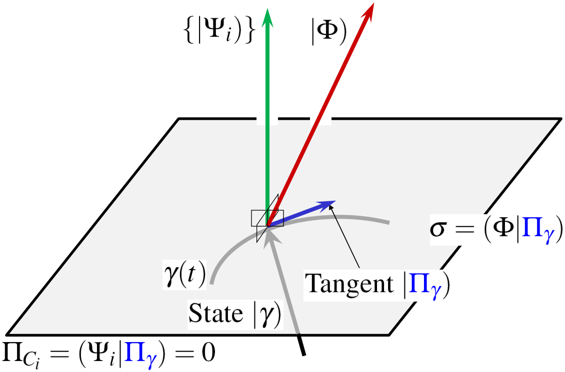

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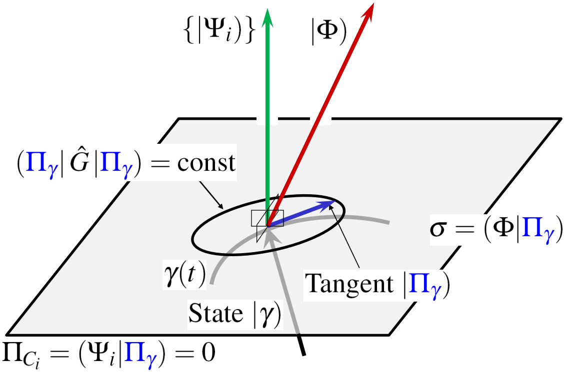

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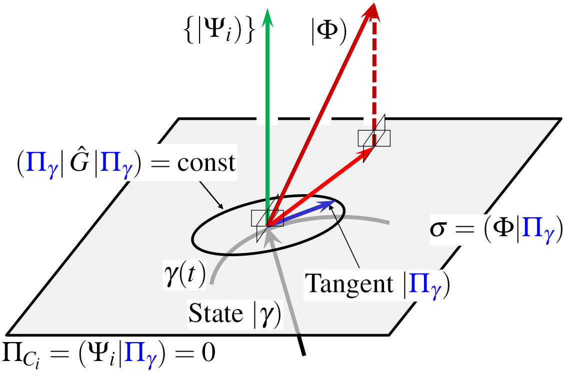

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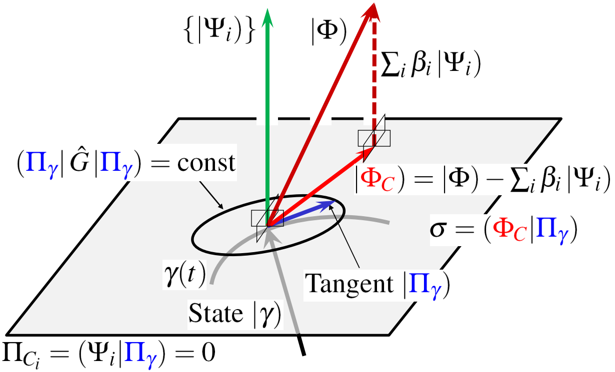

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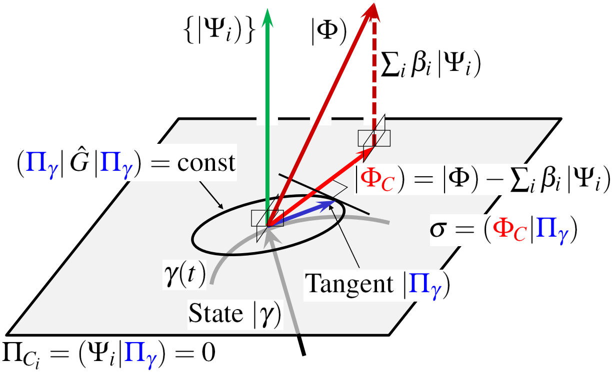

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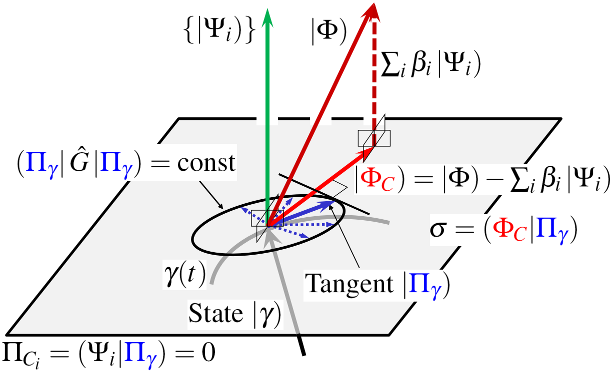

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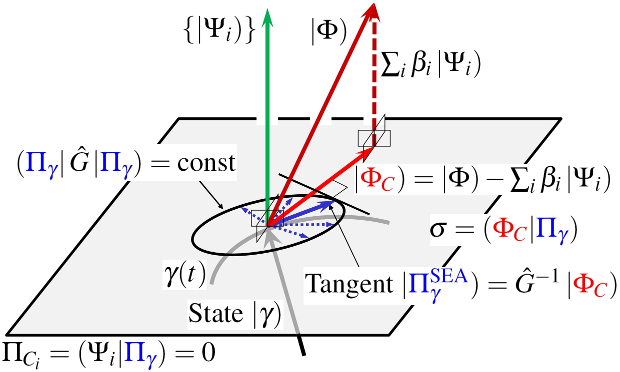


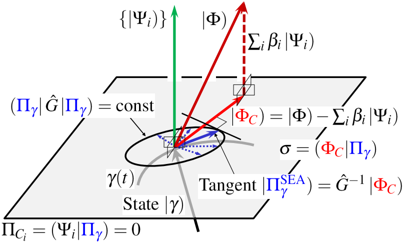
the corresponding SEA **evolution equation** is

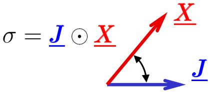
$$|\Pi_\gamma^{\mathrm{SEA}}) = \hat{G}^{-1}|\Phi - \sum_i \beta_i \Psi_i)$$

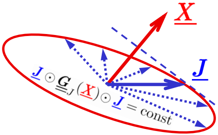
Beretta, Phys. Rev. E, Vol. 90, 042113 (2014).

Conclusions? "Great" principles from NET?

- Power of symmetry and geometry considerations
- Curie principle
- Steepest Entropy Ascent principle?
  - Near equilibrium it entails (equivalent to?) Onsager's reciprocity principle
  - 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 have been based on SEA
  - Deep connections with recent hot topics in mathematics:[a]
    - Information geometry[1]
    - Gradient flows in metric spaces[2]
    - L^2-Wasserstein metric[3] and evolution PDE's of diffusive type







1. Amari, Nagaoka, Methods of information geometry, Oxford UP, 1993.
2. Jordan, Kinderlehrer, Otto, SIAM J. Math. Anal., Vol. 29, 1 (1998).
2. Ambrosio, Gigli, Savaré, Gradient flows in metric and in the Wasserstein spaces, Birkhäuser, 2005.
3. 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 $\underline{\boldsymbol{X}} = \nabla\underline{\Gamma}$
- 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 $\underline{\boldsymbol{J}} = \boldsymbol{J}_{\hat{\underline{u}}}$
- $\underline{\Gamma} = \dfrac{\partial \hat{s}}{\partial \hat{\underline{u}}}$ and $\dfrac{\partial \underline{\Gamma}}{\partial \hat{\underline{u}}} = \dfrac{\partial^2 \hat{s}}{\partial \hat{\underline{u}} \partial \hat{\underline{u}}} \leq 0$

Then:

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

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

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

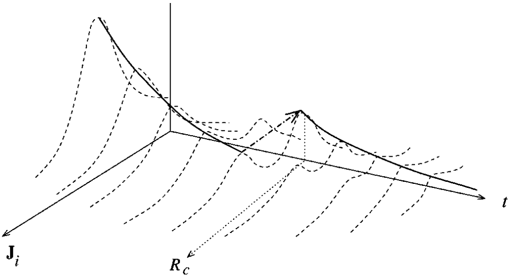
$$\iiint_V \underline{\boldsymbol{J}} \odot \frac{d\underline{\boldsymbol{X}}}{dt}\, dV = \iiint_V \underline{\boldsymbol{J}} \odot \frac{d\nabla\underline{\Gamma}}{dt}\, dV = \cancel{\iint_{\partial V} \underline{\boldsymbol{J}} \odot \frac{d\underline{\Gamma}}{dt} \cdot \boldsymbol{n}\, dA} - \iiint_V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

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

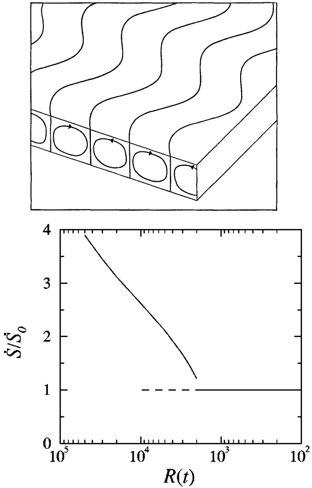
$\dot{S}_{\text{gen}}$ = max selects hydrodynamic pattern

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.

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



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

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): 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 $\quad \langle \alpha_i \dot{\alpha}_j \rangle_{p_B} = \langle \dot{\alpha}_i \alpha_j \rangle_{p_B}$

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

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

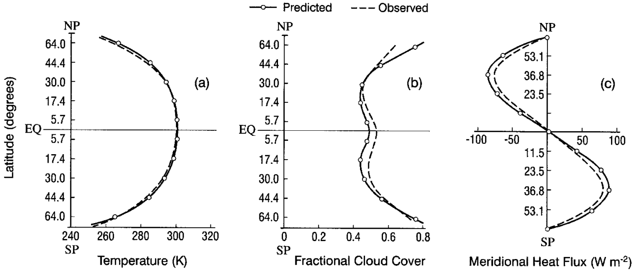
MEP principle claimed to have facets in wide range of fields and scales

For example:

- Juretic and Zupanovic (2003) model steady state **bacterial photosynthesis** and find that the MEP state has optimal yield and power efficiency, and is stable with respect to a wide range of initial values for forward rate constants.
- Shizawa and Zbib (1999) model gradient **elastoplasticity and kinematic hardening**. They introduce the plastic strain tensor and the dislocation density tensor as internal variables (effective stress and microstress are the conjugate potentials). Assuming MEP, they obtain constitutive equations of plastic deformation rate and dislocation drift rate as flow rules.
- Bejan (1996) finds applications of his **constructal theory** (*For a finite size flow system to persist in time (to live), its configuration must evolve such that it provides **easier and easier access to its currents***) in design and explaining evolution across the board, animate and inanimate, from physics to biology and social organization.
- Martyushev and Seleznev (2006) review paper.

MEP principle selects global atmospheric patterns

Paltridge (1975), Ozawa et al. (1997,2001): the global fluid system (atmosphere and ocean) seems to be in a state with the maximum rate of entropy generation by the turbulent heat transport process.



Global distributions of:
(a) mean air temperature, (b) cloud cover, (c) horizontal heat transport.
Solid line: predicted with $\dot{S}_{\rm gen} = \max$.
Dashed line: observed (Paltridge, 1975).