Quasi-linear versus potential-based formulations of force-flux relations and the GENERIC for irreversible processes: comparisons and examples

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Where innovation starts

irreversible dynamics

- relations between forces and fluxes (e.g. …)

$$\boldsymbol{f} \quad \leftrightarrow \quad \boldsymbol{j}(\boldsymbol{f})$$

- (quasi-)linear relations [1,2]
  - perturbation theory
  - fluctuation-dissipation theorem

- dissipation potential [3]

$$\boldsymbol{j}(\boldsymbol{f}) = \boldsymbol{L}(\boldsymbol{f}) \cdot \boldsymbol{f}$$

$$\boldsymbol{j}(\boldsymbol{f}) = \frac{\partial \phi(\boldsymbol{f})}{\partial \boldsymbol{f}}$$

[1] de Groot, Mazur, 1962. Non-equilibrium Thermodynamics.
[2] Lifshitz, Pitaevskii, 1981. Physical Kinetics. Vol. 10, Landau and Lifshitz Series on Theoretical Physics.
[3] Šilhavý, 1997. The Mechanics and Thermodynamics of Continuous Media.

motivation

- **Fluid mechanics (hydrodyn.; fluctuating hydrodyn.)**
  - transport processes (thermal, diffusion, electric, thermophoretic, …)
  - relativistic hydrodynamics (special and general relativity)
- **Kinetic theory of gases**
- **Suspensions**
  - two-phase flow, LCPs
  - crystallization (flow-induced)
- **Solid mechanics**
  - elasticity, viscoplasticity, anisotropic yielding
  - damage mechanics
  - dislocation reactions
- **Complex fluids with structural variables (tensor, distr. fct.)**
  - dumbbell
  - reptation
  - pompom, XPP
- **Modeling**
  - coarse graining, multi-scale simulations
  - mean-field approximations


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comparison

- entropy production (2nd law) $\pi = \boldsymbol{j} \cdot \boldsymbol{f} \geq 0$

- quasi-linear relations $\boldsymbol{j}(\boldsymbol{f}) = \boldsymbol{L}(\boldsymbol{f}) \cdot \boldsymbol{f}$

  - $\boldsymbol{L}_{\mathsf{skw}}$ is irrelevant

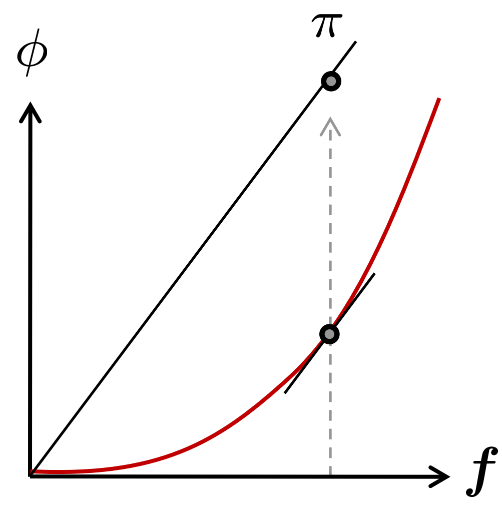
  - $\boldsymbol{L}_{\mathsf{sym}} \geq \mathbf{0}$

comparison

- entropy production (2nd law) $\pi = \boldsymbol{j} \cdot \boldsymbol{f} \geq 0$

- dissipation potential $\boldsymbol{j}(\boldsymbol{f}) = \phi_{,\boldsymbol{f}}$

$$\pi = \phi_{,\boldsymbol{f}} \cdot \boldsymbol{f} \geq 0$$



  - positivity and convexity

$$\pi = \phi_{,\boldsymbol{f}} \cdot \boldsymbol{f} \geq \phi \geq 0$$

$\phi_{,\boldsymbol{f}} := \partial \phi(\boldsymbol{f}) / \partial \boldsymbol{f}$

close to equilibrium: linear response

- entropy production (2nd law) $\pi = \boldsymbol{j} \cdot \boldsymbol{f} \geq 0$

- linear relation $\boldsymbol{j}(\boldsymbol{f}) = \boldsymbol{L} \cdot \boldsymbol{f}$
- dissipation potential $\boldsymbol{j}(\boldsymbol{f}) = \phi_{,\boldsymbol{f}}$

$$\phi = \frac{1}{2}\boldsymbol{f} \cdot \left[\phi_{,\boldsymbol{f},\boldsymbol{f}}\right]_{\boldsymbol{0}} \cdot \boldsymbol{f}$$

$$\Downarrow$$

$$\boldsymbol{j} = \underbrace{\left[\phi_{,\boldsymbol{f},\boldsymbol{f}}\right]_{\boldsymbol{0}}}_{\boldsymbol{L}_{\text{sym}}} \cdot \boldsymbol{f}$$

$$\phi = \frac{1}{2}\boldsymbol{f} \cdot \boldsymbol{L} \cdot \boldsymbol{f}$$

$$\Downarrow$$

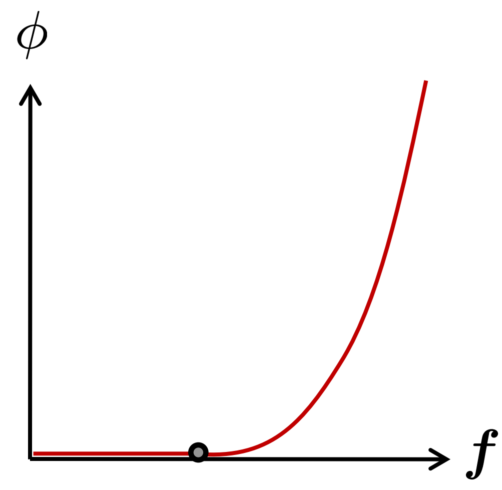
$$\boldsymbol{j} = \boldsymbol{L}_{\text{sym}} \cdot \boldsymbol{f}$$

general

- $j(f) = \phi_{,f} \quad \overset{?}{\to} \quad j(f) = L \cdot f$

- construction of $L_{\text{sym}} \geq 0$

$$L_{\text{sym}} \geq \frac{1}{\pi}\, \phi_{,f} \otimes \phi_{,f}$$



- close to equilibrium $\pi \to 0$: ✓
- general: $\pi \geq \phi \geq 0$

$$j = 0$$

$$\lim_{j \to 0} \pi$$

✓

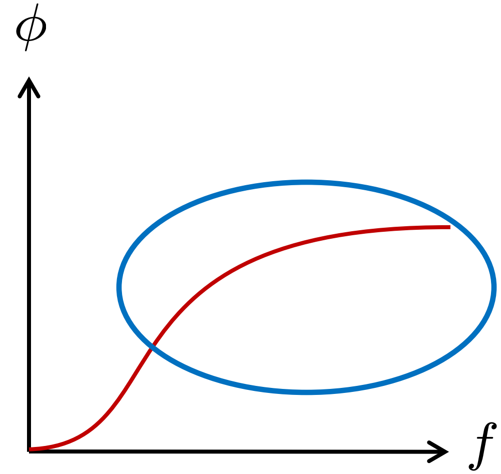
general

- $j(f) = L \cdot f \quad \overset{?}{\rightarrow} \quad j(f) = \phi_{,f}$

- counter example (1): conflict with convexity

$$L(f) = \exp\left(-f^2/2\right) \geq 0$$

$$\phi = 1 - \exp\left(-f^2/2\right) \geq 0$$



general

- $\boldsymbol{j}(\boldsymbol{f}) = \boldsymbol{L} \cdot \boldsymbol{f} \quad \stackrel{?}{\rightarrow} \quad \boldsymbol{j}(\boldsymbol{f}) = \phi_{,\boldsymbol{f}}$

- counter example (2): non-dissipative irreversible dynamics

$$\boldsymbol{j}_{\text{skw}} = \boldsymbol{L}_{\text{skw}} \cdot \boldsymbol{f} \quad \rightarrow \quad \pi_{\text{skw}} = 0 \quad \rightarrow \quad \phi_{\text{skw}} = 0$$

- slip (Schowalter derivative) [1,2,3]

$$D_t \boldsymbol{c} = \boldsymbol{\kappa} \cdot \boldsymbol{c} + \boldsymbol{c} \cdot \boldsymbol{\kappa}^T - \frac{\xi}{2}(\boldsymbol{c} \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{c})$$

$$\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^T$$
$$\dot{\boldsymbol{\gamma}} = \boldsymbol{\kappa} + \boldsymbol{\kappa}^T$$

[1] Wapperom, Hulsen, J. Rheol. 42, 999, 1998.
[2] Dressler et al., Rheol. Acta 38, 117, 1999.
[3] Öttinger, Beyond Equilibrium Thermodynamics, 2005.

general

- $\boldsymbol{j}(\boldsymbol{f}) = \boldsymbol{L} \cdot \boldsymbol{f} \quad \overset{?}{\longrightarrow} \quad \boldsymbol{j}(\boldsymbol{f}) = \phi_{,\boldsymbol{f}}$

- counter example (3) [condition] $\boldsymbol{j}_{,\boldsymbol{f}} = \left[\boldsymbol{j}_{,\boldsymbol{f}}\right]^T$

$$L_{\mu\nu} + L_{\mu\rho,\nu}\, f_\rho = L_{\nu\mu} + L_{\nu\rho,\mu}\, f_\rho$$

$$\Downarrow$$

$$[L_{\mathsf{sym}}]_{\mu\rho,\nu}\; f_\rho = [L_{\mathsf{sym}}]_{\nu\rho,\mu}\; f_\rho$$

[1] Wapperom, Hulsen, J. Rheol. 42, 999, 1998.
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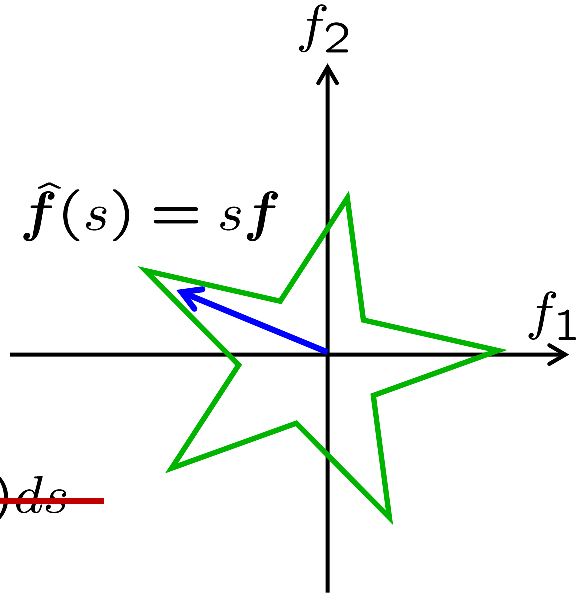
more elegant procedure

- generalization of Helmholtz theorem

$$\boldsymbol{j}(\boldsymbol{f}) = p(\boldsymbol{f})_{,\boldsymbol{f}} + \boldsymbol{s}(\boldsymbol{f})$$

with $$p(\boldsymbol{f}) = \int_0^1 \boldsymbol{j}(\hat{\boldsymbol{f}}(s)) \cdot \boldsymbol{f} \, ds$$

~~$$\boldsymbol{s}(\boldsymbol{f}) = -\int_0^1 2\,\mathrm{skw}\left\{\boldsymbol{j}(\hat{\boldsymbol{f}}(s))_{,\hat{\boldsymbol{f}}(s)}\right\} \cdot \hat{\boldsymbol{f}}(s) ds$$~~



if $\boldsymbol{j}_{,\boldsymbol{f}}$ is symmetric;
especially: $\boldsymbol{j} = \phi_{,\boldsymbol{f}}$

- one can show

$$\boldsymbol{f} \cdot \boldsymbol{s}(\boldsymbol{f}) = 0$$

$$\pi = p(\boldsymbol{f})_{,\boldsymbol{f}} \cdot \boldsymbol{f}$$

[1] Edelen, 1973
[2] Edelen, 1986
[3] Šilhavý, 1997, Ch. 12.

more elegant procedure

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- quasi-linear relation

$$\boldsymbol{j} = \boldsymbol{L}_{\mathsf{sym}} \cdot \boldsymbol{f} \longrightarrow p(\boldsymbol{f})$$

$$+\boldsymbol{L}_{\mathsf{skw}} \cdot \boldsymbol{f} \xrightarrow{(1)} \boldsymbol{s}(\boldsymbol{f})$$

(2): $\boldsymbol{L}_{\mathsf{sym}} \cdot \boldsymbol{f} \longrightarrow \boldsymbol{s}(\boldsymbol{f})$

(2) $(\boldsymbol{j}_{\mathsf{sym}})_{,\boldsymbol{f}}$ sym.

[1] Edelen, 1973
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GENERIC

G	eneral
E	quation for the
N	on-
E	quilibrium
R	eversible-
I	rreversible
C	oupling

$$\underbrace{}_{}\frac{\partial \boldsymbol{x}}{\partial t} = \overbrace{\boldsymbol{L} \cdot \frac{\delta E}{\delta \boldsymbol{x}}}^{\text{reversible}} + \overbrace{\boldsymbol{M} \cdot \frac{\delta S}{\delta \boldsymbol{x}}}^{\text{irreversible}}$$

Poisson operator

$\boldsymbol{L}^T = -\boldsymbol{L}$

$\boldsymbol{L} \cdot (\delta S / \delta \boldsymbol{x}) = \boldsymbol{0}$

$\boldsymbol{L}$ Jacobi id.

friction matrix

$\boldsymbol{M}^T = \boldsymbol{M}$

$\boldsymbol{M} \cdot (\delta E / \delta \boldsymbol{x}) = \boldsymbol{0}$

$\boldsymbol{M} \geq \boldsymbol{0}$

Grmela, Öttinger, PRE 56 (1997), 6620. Öttinger, Grmela, PRE 56 (1997), 6633.
Öttinger, Beyond Equilibrium Thermodynamics, 2005.

GENERIC

- quasi-linear form

$$\frac{\partial \boldsymbol{x}}{\partial t} = \boldsymbol{L} \cdot \frac{\delta E}{\delta \boldsymbol{x}} + \underline{\boldsymbol{M} \cdot \frac{\delta S}{\delta \boldsymbol{x}}}$$

- dissipation-potential representation

$$\frac{\partial \boldsymbol{x}}{\partial t} = \boldsymbol{L} \cdot \frac{\delta E}{\delta \boldsymbol{x}} + \underline{\frac{\delta \Phi}{\delta(\delta S / \delta \boldsymbol{x})}}$$

Grmela, Öttinger, PRE 56 (1997), 6620. Öttinger, Grmela, PRE 56 (1997), 6633.
Öttinger, Beyond Equilibrium Thermodynamics, 2005.

GENERIC

- mapping between GENERIC and force-flux relations

relation between force and entropy derivative
with $\boldsymbol{C}$ independent of $\delta S/\delta \boldsymbol{x}$

$$\boldsymbol{f} = \boldsymbol{C}^T \cdot \frac{\delta S}{\delta \boldsymbol{x}}$$

entropy production:

$$\dot{S} = \int \pi = \int \boldsymbol{j} \cdot \boldsymbol{f} = \int \dot{\boldsymbol{x}}|_{\text{irr}} \cdot \frac{\delta S}{\delta \boldsymbol{x}} \quad \rightarrow \quad \dot{\boldsymbol{x}}|_{\text{irr}} = \boldsymbol{C} \cdot \boldsymbol{j}$$

quasi-linear form:

$$\boldsymbol{j} = \boldsymbol{L} \cdot \boldsymbol{f} \quad \rightarrow \quad \dot{\boldsymbol{x}}|_{\text{irr}} = \underbrace{\boldsymbol{C} \cdot \boldsymbol{L} \cdot \boldsymbol{C}^T}_{\boldsymbol{M}} \cdot \frac{\delta S}{\delta \boldsymbol{x}}$$

Edwards, 1998.
Öttinger, Beyond Equilibrium Thermodynamics, 2005.

GENERIC

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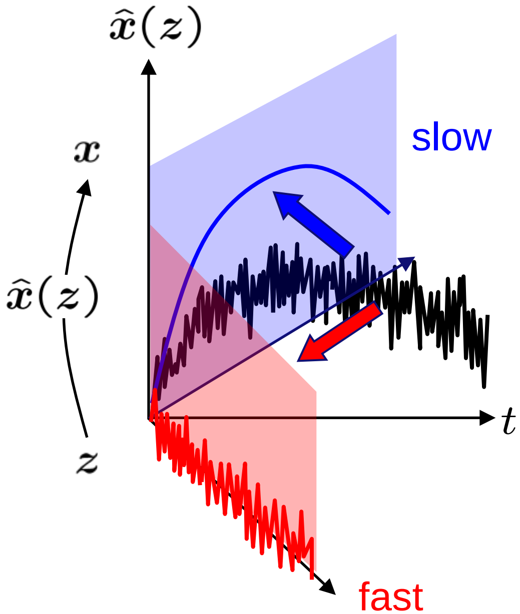
dissipation-potential form:

$$\boldsymbol{j} = \phi_{,\boldsymbol{f}} \quad \rightarrow \quad \dot{\boldsymbol{x}}|_{\mathsf{irr}} = \frac{\delta \Phi}{\delta(\delta S/\delta \boldsymbol{x})}$$

Edwards, 1998.
Öttinger, Beyond Equilibrium Thermodynamics, 2005.

coarse graining: projection operators

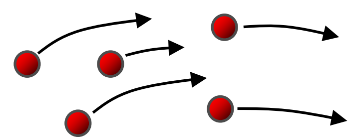


separation of
time scales

reversible

$$L(x) = \ldots$$

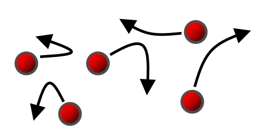
(N. B. Wecando)



irreversible

fluctuations

$$M(x) = \frac{1}{k_{\mathrm{B}}} \int_0^{\tau} \left\langle \dot{\hat{x}}^{\mathrm{f}}(t)\, \dot{\hat{x}}^{\mathrm{f}}(0) \right\rangle_x dt$$



Öttinger, PRE, 1998.
Öttinger, Beyond Equilibrium Thermodynamics, 2005.

example 1: heat conduction

- forces and fluxes $\boldsymbol{j} = \boldsymbol{q}$

$$\boldsymbol{f} = \nabla(1/T)$$

$$\boldsymbol{L} = T^2 \boldsymbol{K}$$

- possible potential-representation

1. $\boldsymbol{L} = \boldsymbol{L}^T$
2. $\boldsymbol{L} \geq \boldsymbol{0}$
3. $L_{\mu\rho,\nu} \, f_\rho = L_{\nu\rho,\mu} \, f_\rho$

example 2: chemical reaction(s)

- forces and fluxes $J = \dot{\xi}$

$$F = -\frac{1}{kT}\sum_{i=1}^{n} \nu_i \mu_i$$

$$L = R\left[\exp(F) - 1\right]/F$$

$$\begin{aligned} \dot{T} &= \theta\dot{\xi} \\ \dot{N}_1 &= \nu_1\dot{\xi} \\ &\cdots \\ \dot{N}_n &= \nu_n\dot{\xi} \end{aligned}$$

- possible potential-representation

1. here: $P = R\left[\exp(F) - 1 - F\right]$
2. Grmela (2010) $\tilde{P} = \tilde{R}\left[\exp(F/2) + \exp(-F/2) - 2\right]$

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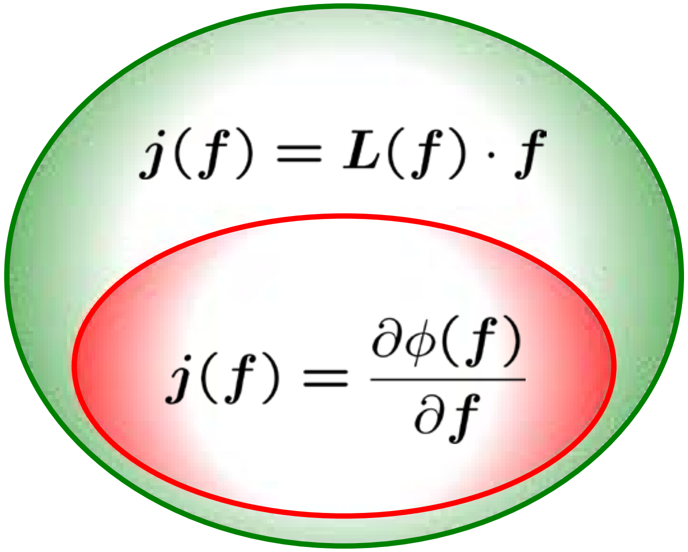
summary

- relations between forces and fluxes (e.g. …)

$$f \qquad \leftrightarrow \qquad j(f)$$

- (quasi-)linear relations [1,2]
  - perturbation theory
  - fluctuation-dissipation theorem

- dissipation potential [3]



Hütter, Svendsen, manuscript submitted to Contin. Mech. Thermodyn., 2012.