Drazin Inverse and Steady State Thermodynamics

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Nonequilibrium steady states

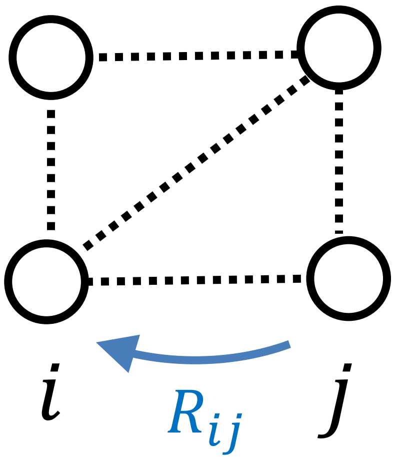
- Absence of detailed balance

→ nonequilibrium steady states (NESS)

- NESS: Continuous production of entropy

- Examples: Enzymes, molecular motors, cells, *ourselves*, climate system, …

Housekeeping heat



- Master eq.: $\frac{d\boldsymbol{p}}{dt} = R\boldsymbol{p}$
- Steady state: $R\boldsymbol{\pi} = 0$
- Housekeeping heat:

$$\delta Q_{\text{hk}}(ij) = k\,T \ln\left(\frac{R_{ij}\,\pi_j}{R_{ji}\,\pi_i}\right)$$

Ensemble property

- NESS: $\langle \delta Q_{\text{hk}} \rangle > 0$

[Oono and Paniconi (1998),
Hatano and Sasa (2001),
…]

Modified Clausius inequality

- Excess heat

$$\delta Q_{\mathrm{ex}} = \delta Q - \ \delta Q_{\mathrm{hk}}$$

- Excess entropy production

$$\Delta s_{\mathrm{ex}}^{\mathrm{univ}} \equiv -\ln \pi_{i(\tau)}^{\boldsymbol{B}} + \ln \pi_{i(0)}^{\boldsymbol{A}} + \int \frac{\delta Q_{\mathrm{ex}}}{kT}$$

- Hatano-Sasa equality

$$\left\langle \exp -\Delta s_{\mathrm{ex}}^{\mathrm{univ}} \right\rangle = 1$$

- Modified Clausius inequality

$$\left\langle \Delta s_{\mathrm{ex}}^{\mathrm{univ}} \right\rangle \equiv \Delta S_{\boldsymbol{\pi}} + \int \frac{\langle \delta Q_{\mathrm{ex}} \rangle}{T} \geq 0$$

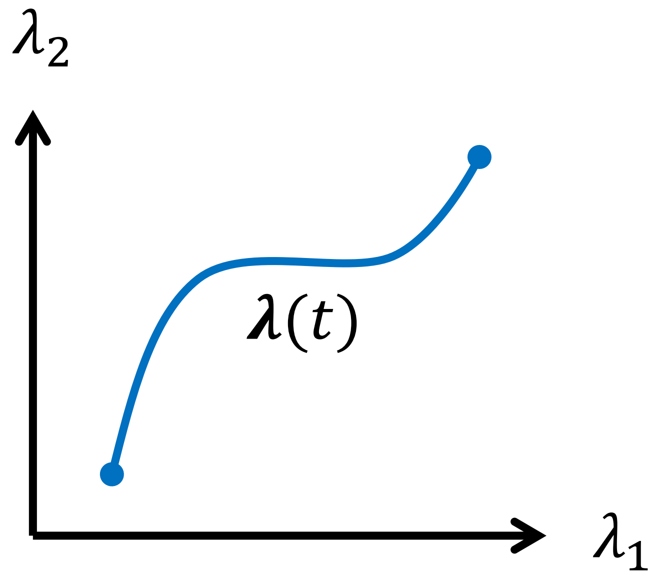
Steady state thermodynamics

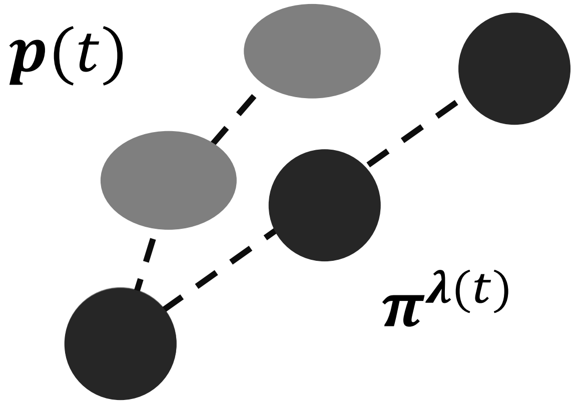
- What are the laws of "quasistatic" transitions between two NESSs?
- What happens in the semi-quasistatic limit?

Problem with conventional linear response theory

- Perturbation is assumed to be small at all times
- In a thermodynamics process, the accumulated perturbation can be large
- Instead of small perturbations, we need to consider slow perturbations

A new perturbation expansion





- For small $\dot{\boldsymbol{\lambda}}$, “lag” $\Delta\boldsymbol{p}(t) = \boldsymbol{p}(t) - \boldsymbol{\pi}^{\lambda(t)}$ is small
- Expand $\Delta\boldsymbol{p}(t)$ with respect to $\dot{\boldsymbol{\lambda}}$ (and its derivatives)

Drazin inverse

- R is singular. A generalized inverse R^+

$$R^+R = RR^+ = I - \boldsymbol{\pi}\mathbf{1}^{\mathrm{T}}, \qquad R^+\boldsymbol{\pi} = \mathbf{0}, \qquad \mathbf{1}^{\mathrm{T}}R^+ = \mathbf{0}^{\mathrm{T}}$$

- Exact expression: $R^+ = \int_0^\infty \mathrm{d}t\, e^{Rt}\left(\boldsymbol{\pi}\mathbf{1}^{\mathrm{T}} - I\right)$

- Drazin inverse (for rank 1 matrix R):

$$R^2R^D = R, \qquad R^DRR^D = R^D, \qquad RR^D = R^DR$$

Mandal and Jarzynski (2015) arXiv:1507.06269

Semi-quasistatic perturbation

- Master equation: $\frac{d\boldsymbol{p}}{dt} = R\boldsymbol{p}$
- "Lag" $\Delta\boldsymbol{p}(t) = \boldsymbol{p}(t) - \boldsymbol{\pi}^{\lambda(t)}$
- Exact equation: $\Delta\boldsymbol{p} = R^{+}\frac{d}{dt}\boldsymbol{\pi} + R^{+}\frac{d}{dt}\Delta\boldsymbol{p}$

(Iterative solution) $= R^{+}\dot{\boldsymbol{\lambda}}\,\partial_{\lambda}\boldsymbol{\pi} + R^{+}\frac{d}{dt}R^{+}\dot{\boldsymbol{\lambda}}\,\partial_{\lambda}\boldsymbol{\pi} + \cdots$

Quasistatic Leading correction

Quasistatic processes

Equilibrium

$$\Delta S^{\text{univ}} \equiv \Delta S + \int \frac{\langle \delta Q \rangle}{T} = 0$$

Clausius equality

NESS

$$\Delta S_{\text{ex}}^{\text{univ}} \equiv \Delta S_{\boldsymbol{\pi}} + \int \frac{\langle \delta Q_{\text{ex}} \rangle}{T} = 0$$

Modified Clausius equality

- $\Delta S^{\text{univ}} = \infty$

Semi-quasistatic processes

Equilibrium

$$\Delta S^{\mathrm{univ}} \approx \int dt\ \dot{\boldsymbol{\lambda}}^{\mathrm{T}} \zeta(\boldsymbol{\lambda})\, \dot{\boldsymbol{\lambda}} \geq 0$$

Equilibrium metric

NESS

$$\Delta S_{\mathrm{ex}}^{\mathrm{univ}} \approx \int dt\ \dot{\boldsymbol{\lambda}}^{\mathrm{T}} \xi(\boldsymbol{\lambda})\, \dot{\boldsymbol{\lambda}} \geq 0$$

$$\xi_{\mu\nu}(\boldsymbol{\lambda}) = -\frac{\partial \ln \boldsymbol{\pi}^{\mathrm{T}}}{\partial \lambda_\mu} R^{+} \frac{\partial \ln \boldsymbol{\pi}}{\partial \lambda_\nu}$$

An exact expression!

$$\zeta_{\mathrm{ex}} = \frac{\xi^{T} + \xi}{2}$$

Nonequilibrium metric

[Crooks (2008),
Sivak and Crooks (2012),
…]

Mandal and Jarzynski (2015) arXiv:1507.06269

Connection to thermodynamic length

Equilibrium

$$\Delta S^{\text{univ}} \approx \int dt\ \dot{\boldsymbol{\lambda}}^{\text{T}} \zeta(\boldsymbol{\lambda})\, \dot{\boldsymbol{\lambda}} \geq 0$$

NESS

$$\Delta S_{\text{ex}}^{\text{univ}} \approx \int dt\ \dot{\boldsymbol{\lambda}}^{\text{T}} \zeta_{\text{ex}}(\boldsymbol{\lambda})\, \dot{\boldsymbol{\lambda}} \geq 0$$

$$\Delta S_{\text{ex}}^{\text{univ}} \geq \frac{l_C^2}{2},$$

$$l_C = \int_C [d\boldsymbol{\lambda}^T \zeta_{\text{ex}}(\boldsymbol{\lambda}) d\boldsymbol{\lambda}]^{1/2}$$

Cauchy-Schwarz inequality

[Crooks (2008),
Sivak and Crooks (2012),
…]

[Mandal and Jarzynski (2015) arXiv:1507.06269]

A Green-Kubo formula

- Observable: $$F_\mu(t) = \frac{\partial}{\partial \lambda_\mu} \ln \pi_{s(t)}$$ State at time t

[Prost *et al.* (2009)]

- Green-Kubo: $$\zeta_{\mathrm{ex},\mu\nu}(\boldsymbol{\lambda}) = \frac{1}{2}\int_{-\infty}^{\infty} dt \left\langle F_\mu(t) F_\nu(0) \right\rangle_{\boldsymbol{\lambda}}$$

Steady state two-time correlation function

[Mandal and Jarzynski (2015) arXiv:1507.06269]

Summary

- Semi-quasistatic perturbation theory
- An exact expression of thermodynamic metric

$$\zeta_{\text{ex}} = \frac{\xi^T + \xi}{2}, \qquad \xi_{\mu\nu}(\boldsymbol{\lambda}) = -\frac{\partial \ln \boldsymbol{\pi}^{\text{T}}}{\partial \lambda_\mu} R^+ \frac{\partial \ln \boldsymbol{\pi}}{\partial \lambda_\nu}$$

- Green-Kubo expression

$$\zeta_{\text{ex},\mu\nu}(\boldsymbol{\lambda}) = \frac{1}{2}\int_{-\infty}^{\infty} dt \, \langle F_\mu(t) F_\nu(0) \rangle_{\boldsymbol{\lambda}}$$

[Mandal and Jarzynski (2015) arXiv:1507.06269]

Thank you!

Fluctuation-dissipation relation

Equilibrium

$$\langle W \rangle \approx \Delta F + \frac{\beta}{2}\sigma_W^2$$

NESS

$$\Delta S_{\mathrm{ex}}^{\mathrm{univ}} \approx \frac{1}{2}\sigma_{\Delta S_{\mathrm{ex}}^{\mathrm{univ}}}^2$$

[Hermans (1991),
Wood et al. (1991),
Speck and Seifert (2004)]

[Mandal and Jarzynski (2015) arXiv:1507.06269]