Stochastic Thermodynamics and Thermodynamics of Information

Lecture I: Motivation, Basics

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Motivations

- What is Stochastic Thermodynamics (ST) and why are we interested in it?
- What systems are of interest to ST?
- What is the relation between ST, and Statistical Mechanics on one side and Thermodynamics on the other side?
- What is Information Thermodynamics and what is its relation to ST?

***Stochastic Thermodynamics** is a thermodynamic theory for mesoscopic, non-equilibrium physical systems interacting with equilibrium thermal (and/or chemical) reservoirs*

Stochastic Thermodynamics

Thermodynamic: ST aims at drawing a correspondence between a mesoscopic stochastic dynamics and macroscopic thermodynamics

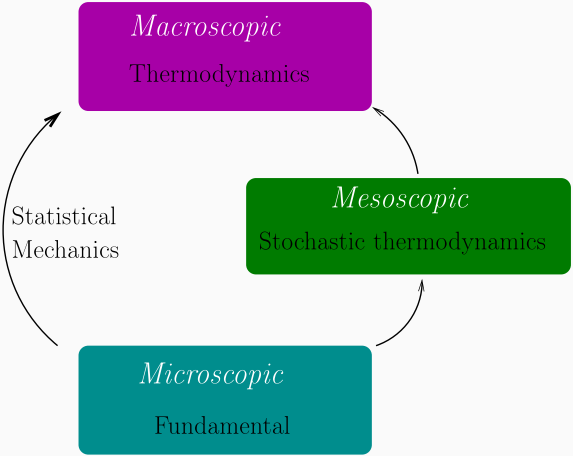
Mesoscopic: ST deals with physical systems with typical energy $\sim k_{\mathrm{B}}T$: colloidal particles, macromolecules, etc.

Non-equilibrium: One typically considers either manipulated systems, or systems kept in steady states out of equilibrium

Interacting: Systems evolve according to a stochastic dynamics resulting from interactions with one (or more) thermal reservoirs, which are represented by random noise

Equilibrium reservoirs: Thermal reservoirs relax very fast, so that they can effectively be considered always at equilibrium. This separation of timescales is key to the simplicity of stochastic thermodynamics

Stochastic Thermodynamics



Thermodynamics of Information and ST

- Maxwell's demon thought experiment showed how entropy is related to the lack of knowledge on the system
- Maxwell, Boltzmann, Gibbs emphasized the link between thermodynamical entropy and disorder of a physical systems
- Szilárd's demon showed how information on a system can be put to advantage to apparently "violate" the 2nd law
- Information on a system must be taken into account in the entropy balance: The corresponding entropies are $\sim k_{\mathrm{B}}$ per DoF
- For mesoscopic systems $\Delta E \sim k_{\mathrm{B}}T$, $\Delta S \sim k_{\mathrm{B}}$, information is thermodynamically relevant

Stochastic dynamics

- Non-equilibrium systems require a dynamical description
- The systems are mesoscopic: Dynamics is stochastic (non-deterministic)
- Stochastic dynamics is constrained by equilibrium statistical mechanics requirements
- Energy and entropy balance is evaluated on the reservoirs (ordinary thermodynamics)
- The resulting identities do not explicitly involve the dynamics

Disclaimer: I shall only consider classical systems

Plan of the Course

1. Stochastic Thermodynamics: What is it and why is it useful?
2. Prerequisites: Thermodynamics, Statistical Mechanics, Stochastic Dynamics, Information Theory
3. Basic concepts of Stochastic Thermodynamics (ST): Mesoscopic systems, Work and Heat in ST, Fluctuating entropy
4. Fluctuation relations and their uses
5. Thermodynamic of Information: Entropy and Information balance, Thermodynamic and computational reversibility, Speed-accuracy tradeoffs
6. Experimental results
7. Ramification: Work extraction and population dynamics, Statistical physics of adaptation, Historical (retrospective) fitness
8. Conclusions and outlook

Principles of Thermodynamics

First principle: $\Delta E = Q + W$

- E: Internal energy (function of state)
- W: "mechanical" work (*controlled* energy exchange)
- Q: "heat" (*uncontrolled* energy exchange)
- W and Q are functions of the *process*, not of the state

Second principle: There is a function of state $S(X)$ such that $\Delta S \geq 0$ for adiabatically isolated systems

- $\Delta S = Q^{\mathrm{rev}}/T$
- $\Delta S = \Delta_{\mathrm{i}} S + \Delta_{\mathrm{e}} S$, $\Delta_{\mathrm{i}} S \geq 0$

Reservoirs

Reservoirs are *thermodynamic equilibrium systems*

Energy vs. Entropy change in a reservoir:

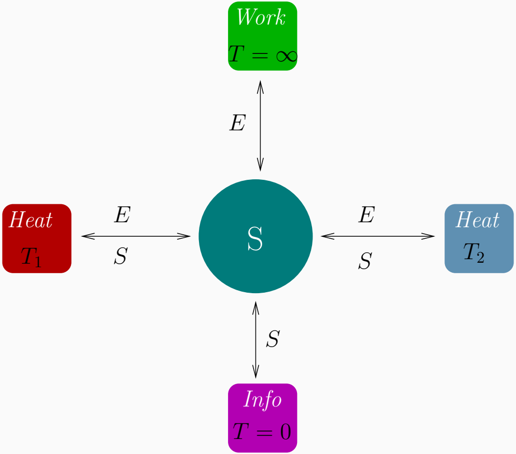
$$\Delta E = T\,\Delta S$$

Thermal reservoirs: $\Delta S = \Delta E / T$

Work reservoirs: $\Delta E \neq 0$, $\Delta S = 0$, $\Rightarrow T = \infty$

Information reservoirs: $\Delta E = 0$, $\Delta S \neq 0$, $\Rightarrow T = 0$

Reservoirs



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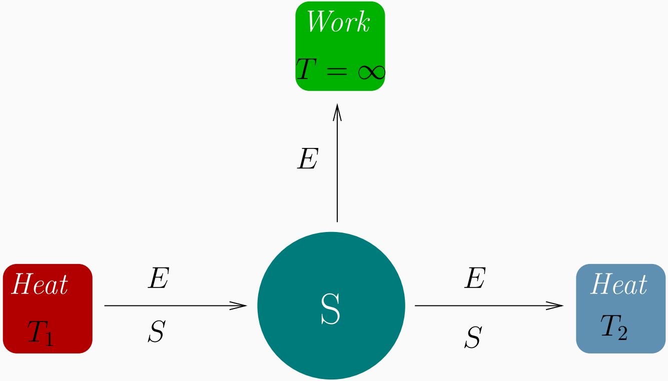
Carnot's Engine



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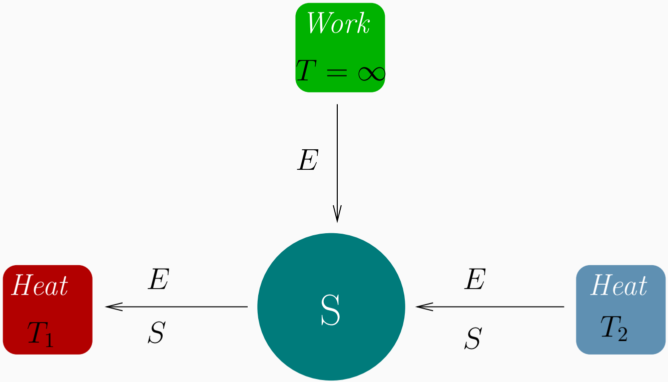
Refrigerator



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Statistical mechanics of equilibrium

- Equilibrium states are described by *ensembles*
- Canonical ensemble:

$$p_x^{\mathrm{eq}} = \mathrm{e}^{(F-E_x)/k_{\mathrm{B}}T} \qquad F = -k_{\mathrm{B}}T \log \sum_x \mathrm{e}^{-E_x/k_{\mathrm{B}}T}$$

- Entropy of an equilibrium ensemble (Gibbs' formula)

$$S = -k_{\mathrm{B}} \sum_x p_x^{\mathrm{eq}} \log p_x^{\mathrm{eq}}$$

- Helmholtz' free energy

$$F = \langle E \rangle_{p^{\mathrm{eq}}} - TS, \qquad \langle E \rangle_{p^{\mathrm{eq}}} = \sum_x p_x^{\mathrm{eq}} E_x$$

Stochastic dynamics

- System states x, energy E_x
- Transitions $x' \longrightarrow x$: rate $R_{xx'}$ (due to coupling with reservoir (r) at temperature T)
- **Master equation** for the occupation probability $p_x(t)$:

$$\frac{\mathrm{d}p_x}{\mathrm{d}t} = \sum_{x'\,(\neq x)}{}' \left[\underbrace{R_{xx'}p_{x'}}_{\text{inflow}} - \underbrace{R_{x'x}p_x}_{\text{outflow}} \right]$$

- Connection to equilibrium: We require the **detailed-balance condition:** (DB)

$$\frac{R_{xx'}}{R_{x'x}} = \frac{p_x^{\mathrm{eq}}}{p_{x'}^{\mathrm{eq}}} = \mathrm{e}^{(E_{x'} - E_x)/k_{\mathrm{B}}T}$$

- DB expresses *microscopic reversibility*: $J^{\mathrm{eq}}_{x \longrightarrow x'} = J^{\mathrm{eq}}_{x' \longrightarrow x}$
- Starting from an arbitrary $p_x(t{=}0)$ one has $p_x(t) \to p_x^{\mathrm{eq}}$

Shannon entropy

Shannon's entropy is a measure of the information content of a probability distribution function (pdf)

$$H(p) = -\sum_x p_x \log p_x$$

Properties:

- $H(p) \geq 0$
- $H(p) = 0 \Leftrightarrow p_x = \delta_{xx_0},\ \exists x_0$
- $H(p_X p_Y) = H(p_X) + H(p_Y)$
- If $X = \{1, \ldots, r\}$, $H(p_X) \leq \log r$

Gibbs' formula reads

$$S = k_{\mathrm{B}} H(p^{\mathrm{eq}})$$

Relative entropy

The **relative entropy** (or **Kullback-Leibler divergence**) of two pdf's p and q is a measure of their difference

$$D_{\mathrm{KL}}(p\|q) = \sum_x p_x \log \frac{p_x}{q_x}$$

Properties:

- $D_{\mathrm{KL}}(p\|q) \geq 0$
- $D_{\mathrm{KL}}(p\|q) \neq D_{\mathrm{KL}}(q\|p)$
- $D_{\mathrm{KL}}(p\|q) = 0 \Leftrightarrow p_x = q_x, \forall x$

Relative entropy and equilibrium

$\mathcal{S}$ described by a pdf p, in contact with a reservoir at temperature T:

- Average energy $\langle E\rangle_p = \sum_x p_x E_x$
- Shannon entropy $H(p) = -\sum_x p_x \log p_x$
- Relative entropy wrt the equilibrium distribution:

$$D_{\mathrm{KL}}(p\|p^{\mathrm{eq}}) = \sum_x p_x \log \frac{p_x}{p_x^{\mathrm{eq}}} = \frac{-F^{\mathrm{eq}} + \langle E\rangle_p}{k_{\mathrm{B}}T} - H(p)$$
$$= \frac{1}{k_{\mathrm{B}}T}\left(\underbrace{\langle E\rangle_p - k_{\mathrm{B}}TH(p)}_{\mathcal{F}^{\mathrm{non-eq}}} - F^{\mathrm{eq}}\right)$$

- Consequences:
    - Minimum obtains for $p = p^{\mathrm{eq}}$
    - If $\langle E\rangle_p = \langle E\rangle_{p^{\mathrm{eq}}}$, $k_{\mathrm{B}}H(p) \leq S$

Relative entropy and the approach to equilibrium

- Let $\mathcal{S}$ obey a Master Equation with rates $R = (R_{ij})$ satisfying detailed balance (DB) at temperature T
- Given $p(t) = (p_x(t))$, evaluate

$$\mathcal{D} = \frac{\mathrm{d}}{\mathrm{d}t} D_{\mathrm{KL}}(p \| p^{\mathrm{eq}})$$

- We have

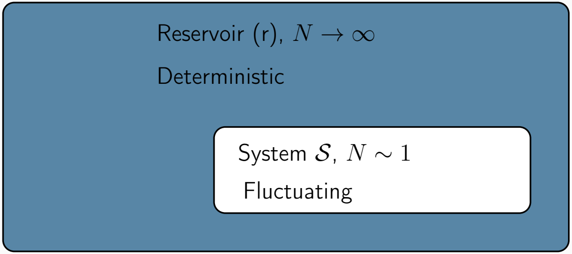
$$\mathcal{D} = \sum_x \frac{\mathrm{d}p_x}{\mathrm{d}t} \log \frac{p_x}{p_x^{\mathrm{eq}}} = \sum_x \left[{\sum_{x'\,(\neq x)}}' (R_{xx'} p_{x'} - R_{x'x} p_x) \log \frac{p_x}{p_x^{\mathrm{eq}}} \right]$$

$$= {\sum_{x<x'}}' (R_{xx'} p_{x'} - R_{x'x} p_x) \left(\log \frac{p_x}{p_x^{\mathrm{eq}}} - \log \frac{p_{x'}}{p_{x'}^{\mathrm{eq}}} \right)$$

$$= {\sum_{x<x'}}' R_{xx'} p_{x'}^{\mathrm{eq}} \left(\frac{p_{x'}}{p_{x'}^{\mathrm{eq}}} - \frac{p_x}{p_x^{\mathrm{eq}}} \right) \left(\log \frac{p_x}{p_x^{\mathrm{eq}}} - \log \frac{p_{x'}}{p_{x'}^{\mathrm{eq}}} \right) \leq 0$$

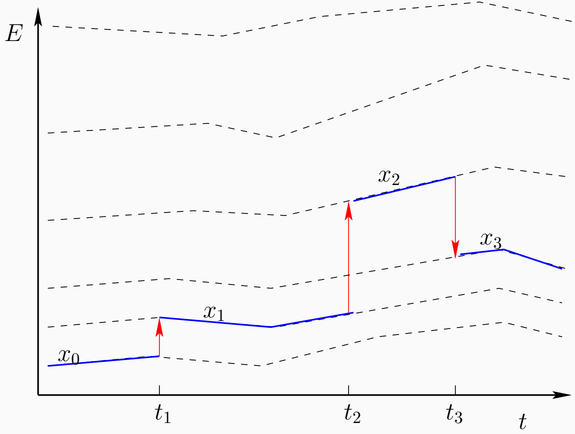
- $\Rightarrow p^{\mathrm{eq}}$ is the only stable fixed point

Mesoscopic systems



- Reservoir dynamics: *very fast*
- The system is manipulated via a parameter λ
- Details of the reservoir-system interaction are hidden under the carpet

Manipulated system: DB is satisfied with $E_x = E_x(\lambda(t)), \forall t$



Trajectory: $\boldsymbol{x} = ((x_0, t_0), (x_1, t_1), \ldots, (x_n, t_n), t_{\mathrm{f}})$

Manipulated system: DB is satisfied with $E_x = E_x(\lambda(t))$, $\forall t$

- $E_x = E_x(\lambda)$, $\lambda = \lambda(t)$ ("protocol")
- $R_{x'x} = R_{x'x}(\lambda)$ satisfying the DB
- Change of energy for the system:

$$E_{x_\mathrm{f}}(t_\mathrm{f}) - E_{x_0}(t_0) = \underbrace{\sum_{k=1}^{n} \left(E_{x_k}(t_k) - E_{x_{k-1}}(t_k)\right)}_{\text{heat}=\mathcal{Q}} + \underbrace{\sum_{k=1}^{n+1} \int_{t_{k-1}}^{t_k} \mathrm{d}t \; \dot{\lambda}(t) \; \left.\frac{\partial E_{x_{k-1}}}{\partial \lambda}\right|_{\lambda(t)}}_{\text{work}=\mathcal{W}}$$

- Stochastic 1st law: $\Delta E = \mathcal{Q} + \mathcal{W}$

2nd Law in Stochastic Thermodynamics

- From DB:

$$\frac{R_{xx'}}{R_{x'x}} = \mathrm{e}^{-(E_x - E_{x'})/k_\mathrm{B}T} = \mathrm{e}^{-\mathcal{Q}_{xx'}/k_\mathrm{B}T} = \mathrm{e}^{\Delta S^{(\mathrm{r})}_{xx'}/k_\mathrm{B}}$$

- Protocol $\boldsymbol{\lambda} = (\lambda(t))$, $R = (R_{xx'}(\lambda(t)))$
- Probability of a trajectory $\boldsymbol{x} = ((x_0, t_0), (x_1, t_1), \ldots, (x_n, t_n), t_\mathrm{f})$:

$$\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x}) = \mathrm{e}^{-\int_{t_n}^{t_\mathrm{f}} \mathrm{d}t\, \gamma_{x_n}(t)} \underbrace{R_{x_n x_{n-1}}(\lambda(t_n))\,\mathrm{d}t_n}_{\text{jump}} \underbrace{\mathrm{e}^{-\int_{t_{n-1}}^{t_n} \mathrm{d}t'''\, \gamma_{x_{n-1}}(t''')}}_{\text{dwell}} \cdots$$

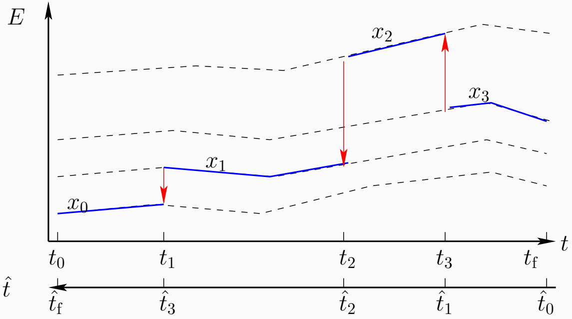
$$\times\, \mathrm{e}^{-\int_{t_1}^{t_2} \mathrm{d}t''\, \gamma_{x_1}(t'')} R_{x_1 x_0}(\lambda(t_1))\,\mathrm{d}t_1\, \mathrm{e}^{-\int_{t_0}^{t_1} \mathrm{d}t'\, \gamma_{x_0}(t')} p_{x_0}(t_0)$$

$$\gamma_x(t) = {\sum_{x'\,(\neq x)}}' R_{x'x}(\lambda(t)) \qquad \text{escape rate}$$

2nd Law in Stochastic Thermodynamics

Time inversion:

- Reverse path $\hat{\boldsymbol{x}}$: $\hat{x}(t) = x(\hat{t})$, $\hat{t} = t_0 + (t_\mathrm{f} - t)$
- Reverse protocol $\hat{\boldsymbol{\lambda}}$: $\hat{\lambda}(t) = \lambda(\hat{t})$



- Probability of the reverse trajectory $\hat{\boldsymbol{x}}$ with the reverse protocol $\hat{\boldsymbol{\lambda}}$:

$$\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}}) = \mathrm{e}^{-\int_{\hat{t}_n}^{\hat{t}_\mathrm{f}} \mathrm{d}t\, \hat{\gamma}_{\hat{x}_n}(t)} \cdots R_{\hat{x}_1 \hat{x}_0}(\hat{\lambda}(\hat{t_1}))\, \mathrm{d}t_1 \mathrm{e}^{-\int_{\hat{t}_0}^{\hat{t}_1} \mathrm{d}t'\, \hat{\gamma}_{\hat{x}_0}(t')} p_{\hat{x}_0}(\hat{t}_0)$$

2nd Law in Stochastic Thermodynamics

- Ratio $\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})/\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})$: "dwell factors" cancel out

$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})} = \prod_{k=1}^{n} \frac{R_{x_{k+1}x_k}(\lambda(t_k))}{R_{x_k x_{k+1}}(\lambda(t_k))} \cdot \frac{p_{x_0}(t_0)}{p_{x_\mathrm{f}}(t_\mathrm{f})}$$

$$= \exp\left[-\frac{1}{k_\mathrm{B}T}\sum_{k=1}^{n} \mathcal{Q}_{x_{k+1}x_k} - \log p_{x_\mathrm{f}}(t_\mathrm{f}) + \log p_{x_0}(t_0)\right]$$

- Conditioning on the starting and final states, we obtain *Crooks' relation*:

$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x}|x_0)}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}}|\hat{x}_0{=}x_\mathrm{f})} = \exp\left(-\frac{1}{k_\mathrm{B}T}\sum_{k=1}^{n} \mathcal{Q}_{x_{k+1}x_k}\right) = \mathrm{e}^{\Delta S^{(\mathrm{r})}(\boldsymbol{x})/k_\mathrm{B}}$$

2nd Law in Stochastic Thermodynamics

- Define the *fluctuating entropy*:

$$s = -k_{\mathrm{B}} \log p_x$$

- Detailed fluctuation theorem (Seifert, 2005):

$$\frac{\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})}{\mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})} = \mathrm{e}^{(\Delta S^{(\mathrm{r})}(\boldsymbol{x}) + \Delta s)/k_{\mathrm{B}}} = \mathrm{e}^{\Delta_i S(\boldsymbol{x})/k_{\mathrm{B}}}$$

- Integral fluctuation theorem: From

$$\mathcal{P}_{\boldsymbol{\lambda}}(\boldsymbol{x})\, \mathrm{e}^{-\Delta_i S(\boldsymbol{x})/k_{\mathrm{B}}} = \mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}})$$

  we obtain

$$\left\langle \mathrm{e}^{-\Delta_i S/k_{\mathrm{B}}} \right\rangle = \int \mathcal{D}\hat{\boldsymbol{x}}\, \mathcal{P}_{\hat{\boldsymbol{\lambda}}}(\hat{\boldsymbol{x}}) = 1$$

- By Jensen's inequality $\left\langle \mathrm{e}^{f} \right\rangle \geq \mathrm{e}^{\langle f \rangle}$:

$$\langle \Delta_{\mathrm{i}} S \rangle \geq 0$$

Summary

- There is some order even out of equilibrium...
- Fluctuation relations exhibit properties of microscopic reversibility in a fluctuating environment
- We have focused on manipulated systems (obeying DB at all times)

Next lecture:

- Uses and subtleties of the fluctuation relations
- Systems violating DB (non-equilibrium steady states)

Thank you!

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