

THE ROLE OF INFORMATION IN NONEQUILIBRIUM THERMODYNAMICS

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MOTIVATION

“There is only one kind of entropy, and don't let anyone tell you otherwise”

-Bill Bialek

MOTIVATION

Thermodynamic entropy is information (a Shannon entropy)

$$S \propto H[\text{micro}|\text{macro}]$$

MOTIVATION

Entropy (information) determines equilibrium state

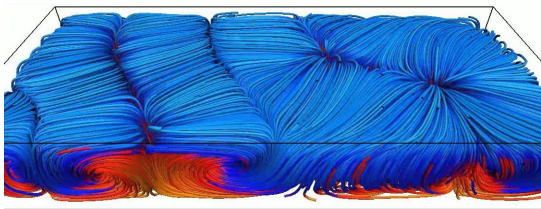
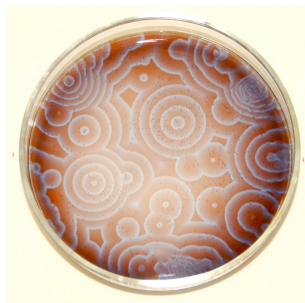
MOTIVATION

Entropy (information) determines equilibrium state

Entropy production is presumed to determine nonequilibrium steady state (myriad of proposed extremum principles)

MOTIVATION

It is thus only natural to think information of some kind will govern spontaneous pattern formation



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Equilibrium distribution one that is least biased, subject to
macroscopic constraints

ENTROPY PRODUCTION

Decompose changes of entropy as

$$dS = d_e S + d_i S$$

$d_e S$ is due to exchange of energy and matter

$d_i S \geq 0$ is the internal entropy production

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In local equilibrium field theory, entropy density $S = \int_V s \, dV$ satisfies balance equation

$$\frac{\partial \mathbf{s}}{\partial t} + \nabla \cdot \vec{J}_s = \sigma$$

where $\sigma(\vec{x}, t) \equiv \frac{d_i s}{dt}$ is the local entropy production

$$\frac{d_i S}{dt} = \int_V \sigma(\vec{x}, t) \, dV$$

LINEAR PHENOMENOLOGICAL LAWS

Table of thermodynamic forces and flows

	Force F_α	Flow (Current) J_α
Heat conduction	$\nabla \frac{1}{T}$	Energy flow \mathbf{J}_u
Diffusion	$-\nabla \frac{\mu_k}{T}$	Diffusion current \mathbf{J}_k
Electrical conduction	$\frac{-\nabla\phi}{T} = \frac{\mathbf{E}}{T}$	Ion current \mathbf{I}_k
Chemical reactions	$\frac{A_j}{T}$	Velocity of reaction $v_j = \frac{1}{V} \frac{d\xi_j}{dt}$

$$\sigma = \sum_{\alpha} F_{\alpha} J_{\alpha}$$

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Onsager Reciprocal Relations:

$$L_{ij} = L_{ji}$$

Consequence of detailed balance

LINEAR PHENOMENOLOGICAL LAWS

Some examples :

$$\text{Fourier's law : } \vec{J}_q = -\kappa \nabla T(x)$$

$$\text{Fick's law : } \vec{J}_k = -D_k \nabla n_k(x)$$

$$\text{Ohm's law : } I = \frac{V}{R}$$

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with cross-coupling: the thermoelectric effect

$$\vec{J}_q = L_{qq} \nabla \frac{1}{T} + L_{qe} \frac{\vec{E}}{T}$$

$$\vec{I}_e = L_{ee} \frac{\vec{E}}{T} + L_{eq} \nabla \frac{1}{T}$$

STEADY STATES

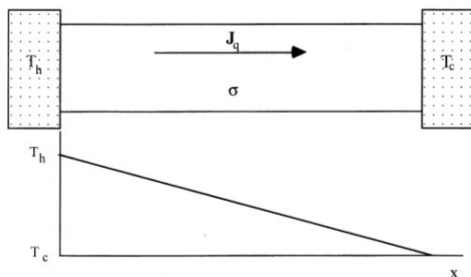
$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} = 0$$

Tendency towards equilibrium is balanced by external driving

System “discards” entropy produced by irreversible processes

STEADY STATES

An example: heat conduction



$$\sigma = \vec{J}_q \cdot \nabla \frac{1}{T}$$

$$\frac{d_i S}{dt} = \int_0^L J_q \left(\frac{\partial}{\partial x} \frac{1}{T} \right) dx = \frac{J_q}{T_c} - \frac{J_q}{T_h} > 0$$

MINIMUM ENTROPY PRODUCTION?

Use $J_q = L_{qq} \frac{\partial}{\partial x} \frac{1}{T}$

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$$\kappa \frac{\partial T}{\partial x} = \text{constant}$$

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Without the approximation, Euler-Lagrange gives

$$T \frac{\partial^2 T}{\partial x^2} = \left(\frac{\partial T}{\partial x} \right)^2$$

NONEQUILIBRIUM STATISTICAL MECHANICS

MaxEnt can be generalized to nonequilibrium settings using quantum formalism; Grandy (2008)

Density matrix is updated subject to macroscopic constraints evolving over time and space

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$$\rho_t = \frac{1}{Z_t} \exp \left[-\beta H - \int_R \lambda(\vec{x}, t) F(\vec{x}, t) d^3x dt \right]$$

$$S_t = \ln Z_t + \beta \langle H \rangle_t + \int_R \lambda(\vec{x}, t) F(\vec{x}, t) d^3x dt$$

$$\dot{S}_t = \gamma_{F(\vec{x}, t)} \left(\frac{d}{dt} \langle F(\vec{x}, t) \rangle_t - \langle \dot{F}(\vec{x}, t) \rangle_t \right)$$

$$\Rightarrow \dot{S}_{tot} = \dot{S}_t + \dot{S}_{int}$$

NONEQUILIBRIUM STATISTICAL MECHANICS

First heat conduction example:

heat current operator \vec{q} with energy density $h(\vec{x})$. Steady state density matrix given by

$$\rho_{st} = \frac{1}{Z_{st}} \exp \left[-\beta H + \int_R \vec{\mu}(\vec{x}) \cdot \vec{q}(\vec{x}) d^3x \right]$$

where $\vec{\mu}(\vec{x}) = \nabla \lambda(\vec{x})$

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in linear expansion:

$$S_{st} - S_0 \approx -\frac{1}{2} \int_R \int_R \nabla \lambda(\vec{x}) K_{qq}^0(\vec{x} - \vec{x}') \nabla' \lambda(\vec{x}') d^3x d^3x'$$

evaluation of covariance function $K_{qq}^0 = 2k_B T^2(\vec{x}) \delta(\vec{x} - \vec{x}')$ and $\lambda(\vec{x}) = \frac{1}{T(\vec{x})}$ gives thermodynamic result for entropy production

NONEQUILIBRIUM STATISTICAL MECHANICS

Second heat conduction example: relaxation to equilibrium

Start from arbitrary nonequilibrium state, evolve subject to constraint $\langle h(\vec{x}, t) \rangle_t$ that is solution to macroscopic equations of motion (Fourier's law here)

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Second heat conduction example: relaxation to equilibrium

Start from arbitrary nonequilibrium state, evolve subject to constraint $\langle h(\vec{x}, t) \rangle_t$ that is solution to macroscopic equations of motion (Fourier's law here)

$$\rho(t) = \frac{1}{Z(t)} \exp \left[- \int_V \beta(\vec{x}, t) h(\vec{x}, t) d^3x \right]$$
$$S_{int}(t) = \ln Z(t) + \int_V \beta(\vec{x}, t) \langle h(\vec{x}, t) \rangle_t d^3x$$

NONEQUILIBRIUM STATISTICAL MECHANICS

In $t \rightarrow \infty$ limit, these converge to equilibrium values

$$\rho_{eq} = \frac{1}{Z} e^{-\beta H}$$

$$S_{eq} = \ln Z + \beta \langle H \rangle_0$$

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$$\rho_{eq} = \frac{1}{Z} e^{-\beta H}$$
$$S_{eq} = \ln Z + \beta \langle H \rangle_0$$

S_{int} maximized subject with additional constraints, and thus over more restricted class of variations

$$\Rightarrow S_{int}(t) < S_{eq} \Rightarrow \dot{S}_{int} \geq 0$$

DYNAMICAL SYSTEMS PERSPECTIVE

A microscopic perspective on stochastic thermodynamics

- Altaner, Vollmer (2015)

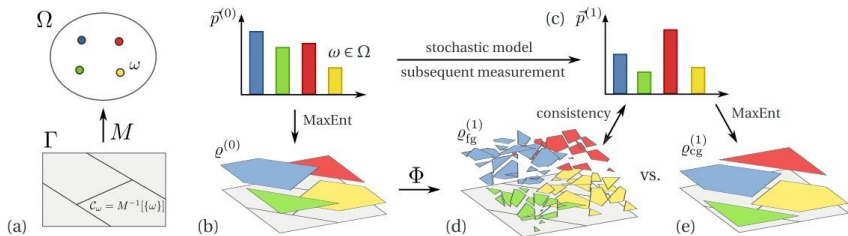


Figure 1. (a) The measurement observable M partitions phase space into disjoint cells C_ω (bottom) indexed by $\omega \in \Omega$ (top). (b) An initial phase space ensemble $\varrho^{(0)}$ is obtained from the coarse-grained ensemble $\bar{p}^{(0)}$ by a maximum entropy (MaxEnt) principle applied to each cell C_ω . (c) An iteration of a coarse-grained model or subsequent measurements on a large number of systems yield an updated coarse-grained ensemble $\bar{p}^{(1)}$. (d) The microscopic dynamics Φ propagates $\varrho^{(0)}$ to the fine-grained ensemble $\varrho_{fg}^{(1)}$. It shows an intricate structure that carries information about Φ and $\varrho^{(0)}$. (e) On the coarse-grained level, one is ignorant of the microscopic dynamics. MaxEnt yields the updated coarse-grained ensemble $\varrho_{cg}^{(1)}$.

DYNAMICAL SYSTEMS PERSPECTIVE

$$S_{\text{rel}} \equiv \mathcal{D}_{\text{KL}}[\rho_{\text{fg}}(t) || \rho_{\text{cg}}(t)]$$

Quantifies dynamical information written to unobservable degrees of freedom

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In general, $S_{\text{tot}} = S_{\text{sys}} + S_{\text{med}}$. For certain class of models :

$$\Delta S_{\text{tot}} = S_{\text{rel}}$$

and we identify S_{rel} as the thermodynamic entropy production

EP AS CORRELATION BETWEEN SYSTEM AND RESERVOIR

Esposito, Lindenberg, Van den Broeck (2009)

Consider system in contact with r finite reservoirs

$$H(t) = H_{\text{sys}}(t) + \sum_r H_r + V(t)$$

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$$H(t) = H_{\text{sys}}(t) + \sum_r H_r + V(t)$$

initially, system uncorrelated with reservoirs

$$\rho(0) = \rho_s(0) \prod_r \rho_r^{\text{eq}}$$

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Entropy of total system invariant

$$-\text{Tr}\rho(t)\ln \rho(t) = -\text{Tr}\rho(0)\ln \rho(0)$$

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Use this to find entropy change of system

$$\begin{aligned}\Delta S_{\text{sys}} &= S_{\text{sys}}(t) - S_{\text{sys}}(0) \\ &= -\text{Tr}\rho(t)\ln[\rho_s(t) \prod_r \rho_r^{\text{eq}}] + \text{Tr}\rho(t)\ln\rho(t) + \sum_r \text{Tr}[\rho_r(t) - \rho_r^{\text{eq}}]\ln\rho_r^{\text{eq}}\end{aligned}$$

EP AS CORRELATION BETWEEN SYSTEM AND RESERVOIR

has the form

$$\Delta S(t) = \Delta_e S(t) + \Delta_i S(t)$$

where

$$\Delta_e S(t) = - \sum_r \beta_r (\langle H_r \rangle_t - \langle H_r \rangle_0)$$

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Here, entropy production is DKL (correlation) between system and reservoirs

UNIFYING THEME

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This can be measured indirectly through macroscopic effects (Grandy; Altaner, Vollmer)

or directly through interaction with environment (Esposito, Lindenberg, Van den Broeck)

CROOKS RELATION

Entropy production quantifies how irreversible a process is

$$\sigma[x(t)] = \ln \frac{P[x(t)]}{\tilde{P}[\tilde{x}(t)]}$$

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DKL results consistent with this interpretation