Nonequilibrium entropy and the second law of thermodynamics

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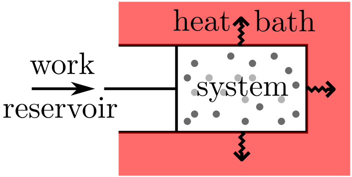
"Entropy." — "Entropy?" — "Yeah, entropy. Boris explained it. It's why you can't get the toothpaste back in the tube."

Outline

- nonequilibrium thermodynamics: phenomenology
- thermodynamic entropy out of equilibrium
- entropy production as change in thermodynamic entropy

The Nonequilibrium Second Law (Clausius, 1865)



Today

For ease of presentation only **one heat bath**.

the concept of entropy production:

(S = *thermodynamic* entropy!)

$$
\begin{aligned}
0 &\leq \Delta S_{\text{universe}} \\
&= \Delta S_S + \Delta S_{\text{env}} \quad \text{(weak coupling)} \\
&= \Delta S_S - \int \frac{\bar{d}Q}{T} \quad \text{(ideal bath)} \\
&= \Delta S_S - \frac{Q}{T_0} \quad \text{(weakly perturbed bath, } T_0 = \text{initial temp.)}
\end{aligned}
$$

Quantum-Classical Dictionary

	quantum	classical
$\mathcal{H}$	Hilbert space	phase space Γ
ρ	density matrix	phase space distribution
H	Hamiltonian	Hamiltonian
$\partial_t \rho$	$= -\frac{i}{\hbar}[H, \rho]$	$= \{H, \rho\}$
$\mathrm{tr}\{\dots\}$	trace operation	phase space integral $\int d\Gamma \dots$
$S_{\mathrm{vN}}(\rho)$	$= -\mathrm{tr}\{\rho \ln \rho\}$	$= -\int d\Gamma \rho(\Gamma) \ln[\rho(\Gamma)/h^{Nd}]$
Π_x	projector with outcome x	characteristic function for a set x: $\Pi_x(\Gamma) = 1$ if $\Gamma \in x$, otherwise 0
V_x	rank $\mathrm{tr}\{\Pi_x\}$	volume $\int d\Gamma \Pi_x(\Gamma)/h^{Nd}$

(today $k_B \equiv 1$)

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Proposal 1

$$S = S_{\mathsf{vN}}(\rho) = -\mathsf{tr}\{\rho \ln \rho\}$$

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Problem

$$\frac{d}{dt} S_{\mathrm{vN}}[\rho(t)] = 0.$$

Proposal 2

$$S = S_{\mathrm{Boltzmann}}(x) = \ln V_x$$

x – some macroscopic constraint(s)

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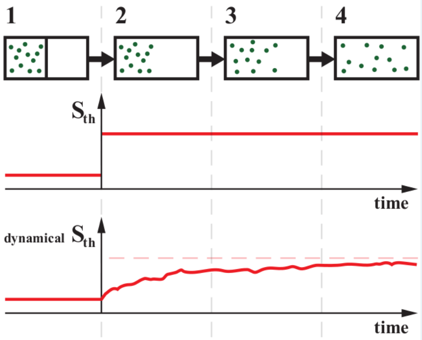
Problem (Šafránek, Deutsch & Aguirre, arXiv 1905.03841)

- little dynamical information
- typically zero for small systems ($V_x = \text{tr}\{\Pi_x\} = 1$)



Proposal 3

Observational entropy

$$S = S_{\mathrm{obs}}^{X}(\rho) = \sum_{x} p_x(-\ln p_x + \ln V_x)$$

with $X = \sum_x x\Pi_x$ some (typically coarse-grained) observable, $p_x = \mathrm{tr}\{\Pi_x \rho\}$, and $V_x = \mathrm{tr}\{\Pi_x\}$.

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History

- first introduced by von Neumann (or Wigner?) in Z. Phys. **57**, 30 (1929)
- closely related: "coarse-grained entropy" for classical systems see, e.g., the Ehrenfests, *Begriffliche Grundlagen der statistischen Auffassung in der Mechanik* (1911), Wehrl, Rev. Mod. Phys. **50**, 221 (1978); goes back to an idea of Gibbs.
- recently revived by Šafránek, Deutsch & Aguirre, Phys. Rev. A **99**, 010101 (2019)

Properties of Observational Entropy (1/2)

Šafránek, Deutsch & Aguirre, PRA 99, 012103 (2019)

(1) boundedness

$$S_{\mathrm{vN}}(\rho) \leq S^{X}_{\mathrm{obs}}(\rho) \leq \ln \dim \mathcal{H}$$

(2) extensivity

If $X = X_1 \otimes \cdots \otimes X_n$ and $\rho = \rho_1 \otimes \cdots \otimes \rho_n$, then

$$S^{X}_{\mathrm{obs}}(\rho) = \sum_{i=1}^{n} S^{X_i}_{\mathrm{obs}}(\rho_i).$$

(3) equivalence

$$S^{X}_{\mathrm{obs}}(\rho) = S_{\mathrm{vN}}(\rho) \quad \Leftrightarrow \quad \rho = \sum_{x} p_x \omega(x) \quad (p_x \text{ arbitrary})$$

with $\omega(x) \equiv \Pi_x / V_x$ (generalized microcanonical ensemble).

Properties of Observational Entropy (2/2)

Strasberg & Winter, arXiv 2002.08817

Now consider dynamics

Change of $S_{\text{obs}}^{X_t}[\rho(t)]$ with $X = X_t$, initial time $t = 0$.

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(4) "second law" (see also Gibbs, Lorentz, Wehrl, Zubarev, ...)

If $S_{\text{obs}}^{X_0}[\rho(0)] = S_{\text{vN}}[\rho(0)]$, then $\Delta S_{\text{obs}}^{X_t}(t) \geq 0$.

(5) fluctuation thm. see also Schmidt, Gemmer, Z Naturforsch A 75 265, 2020

If $S_{\text{obs}}^{X_0}[\rho(0)] = S_{\text{vN}}[\rho(0)]$, then

$$\left\langle e^{-\Delta s_{\text{obs}}^{X_t}(t)} \right\rangle = \sum_{x_t, x_0} p(x_t, x_0) e^{-\Delta s_{\text{obs}}^{X_t}(t)} = 1,$$

where

$$p(x_t, x_0) = \text{tr}\{\Pi_{x_t} U(t) \Pi_{x_0} \rho(0) \Pi_{x_0} U(t)^\dagger\},$$

$$\Delta s_{\text{obs}}^{X_t}(t) = s_{\text{obs}}^{X_t}(t) - s_{\text{obs}}^{X_0}(0) = -\ln \frac{p_{x_t}}{V_{x_t}} + \ln \frac{p_{x_0}}{V_{x_0}}.$$

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Energy measurements

spectral decomposition: $H|E_i\rangle = E_i|E_i\rangle$

coarse-grained projector: $\Pi_E = \Pi_{E,\delta} = \sum_{E_i \in [E, E+\delta)} |E_i\rangle\langle E_i|$

measured observable: $X = \sum_E E\Pi_E \xrightarrow[\delta \to 0]{} H$

observational entropy: $S_{\text{obs}}^E(\rho) = \sum_E p_E(-\ln p_E + \ln V_E)$

equilibrium states: $\Omega = \left\{ \sum_E p_E \omega(E) \middle| \, p_E \text{ arbitrary} \right\}$

(note: δ is a free parameter in theory, assumed to be chosen small enough, left implicit in the notation)

Heat and work in isolated systems

$$\partial_t \rho(t) = -\frac{i}{\hbar}[H(\lambda_t), \rho(t)],\ \rho(0) \in \Omega(\lambda_0)$$

standard definition of work

$$\Delta U(t) = \mathrm{tr}\{H(\lambda_t)\rho(t) - H(\lambda_0)\rho(0)\} \equiv W_{\mathrm{tot}}(t)\ (\geq 0)$$

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$$W_{\mathrm{rec}}(t) \equiv \Delta U(t) - \int_0^t T_s^* dS_{\mathrm{obs}}^E \left[\frac{e^{-H(\lambda_s)/T_s^*}}{Z(\lambda_s)}\right]$$

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Theorem (reversible process)

$$W_{\mathrm{rec}}(t) = W_{\mathrm{tot}}(t) \quad \Leftrightarrow \quad \Delta S_{\mathrm{obs}}^{E_t}(t) = 0 \quad \Leftrightarrow \quad \rho(t) \in \Omega(\lambda_t)$$

otherwise $Q_{\mathrm{rem}}(t) \equiv \Delta U(t) - W_{\mathrm{rec}}(t) > 0$

Entropy production in open systems

$$H_{SB}(\lambda_t) = H_S(\lambda_t) + V_{SB} + H_B,\ \rho_{SB}(0) \in \rho_S(0) \otimes \Omega_B$$

- chosen observable: $X_t = S_t \otimes E_B$

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- Clausius inequality with $\int_0^t \dot{Q}_{\mathrm{rem}}^B(s)ds = \Delta E_B(t)$:

$$\Delta S_{\mathrm{obs}}^{S_t}(t) + \int_0^t \frac{\dot{Q}_{\mathrm{rem}}^B(s)}{T_s^*} \geq \Delta S_{\mathrm{obs}}^{S_t,E_B}(t) \geq 0$$

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- depending on the level of control of $H_S(\lambda_t)$:

$$Q_{\text{rem}}(t) = \left\{ \begin{array}{l} W_{\text{tot}} - \Delta F_S^{\text{eq}} \\ W_{\text{tot}} - \Delta F_S^{\text{noneq}} \end{array} \right\} \geq 0.$$

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Summary (Strasberg & Winter, arXiv 2002.08817)

see also Strasberg, arXiv 1906.09933

Observational entropy...

- ...seems to be a good candidate for thermodynamic entropy out of equilibrium **(compare also with Šafránek, Deutsch & Aguirre)**
- ...provides a *consistent* derivation of the second law for open systems **("the thermodynamic entropy of the universe never decreases!")**
- ...provides an extremely flexible tool **(one or multiple bath, beyond Gibbs states, including a large class of correlated states, etc.)**

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