On the interplay between geometry and nonequilibrium thermodynamics

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My field:

Stochastic Thermodynamics of Nonequilibrium Systems

- Based on stochastic and diffusion equations (Langevin, Kramers, Fokker-Planck, Master etc.)
- ...and on sound definitions of heat, work, entropy...
- It gives a rigorous formulation of thermodynamics.
- It studies fluctuations, rare events, optimal protocols.
- It is feasible of application to small systems and devices.

My core business:

Metabolic networks as complex thermodynamic machines

2a.png

My side interest:

To draw connections between geometry and thermodynamics

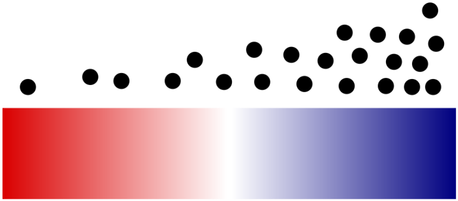
1) Constrained Brownian motion
as a model of diffusion in temperature gradients
(i.e. the diffusion matrix as a metric)

2) The "gauge" connection of nonequilibrium thermodynamics
and its underlying probabilistic symmetry
(i.e. the drift as a gauge connection)

Volume I, Part 1, Chapter 1:
Diffusion in temperature gradients

Landauer:

> *"Pebbles in a driveway accumulate on the side. In the driveway they are agitated (hot region). They are left undisturbed on the side (cold region)."*



Imagine to make small partitions. At equilibrium:

$$p_h \bar{v}_h = p_c \bar{v}_c$$

Equipartition:

$$\bar{v}^2 = k_B T$$

Then:

$$p(x) \sim \frac{1}{\sqrt{T(x)}}$$

We want to formulate a theory of diffusion in temperature gradients that realizes Landauer's intuition.

Reminder: underdamped

Langevin equation with inertia, no space dependence, unit mass:

$$\begin{aligned} \dot{x}_t &= v_t \\ \dot{v}_t &= -f(x_t) - \gamma v_t + \sqrt{2D}\,\zeta_t \end{aligned}$$

with white noise

$$\langle \zeta_t \zeta_{t'} \rangle = \delta(t - t')$$

The diffusion coefficient, the damping coefficient and the temperature are related by the Einstein relation

$$D = \gamma k_B T \qquad k_B = 1 \text{ in the following}$$

The joint PDF of (x, v) evolves with the Kramers generator

$$\partial_t P(x, v, t) = \mathcal{L}_{KR} P(x, v, t) = \dots$$

(x_t, v_t) is a Markov process, x_t is not!

Reminder: overdamped

The damping coeff. γ regulates the time scales of the system. Rescaling time and **overdamping** $\dot{v} \approx 0$ one obtains

$$\dot{x}_s = -f(x_s) + \sqrt{2D}\,\zeta_s$$

Now, x_t is a Markov process. Its PDF evolves with the Fokker-Planck generator:

$$\mathcal{L}_{FP}\, p(x) = -\partial_x \overbrace{[f\, p - D\, \partial_x p]}^{j}$$

Equilibrium vs. nonequilibrium (overdamped)

Steady state $\mathcal{L}p^* = 0$ is **equilibrium** when

$$j^* = 0 \quad \Longrightarrow \quad f = \partial_x \log p^* .$$

Otherwise it's **nonequilibrium**. In 1D nonequilibrium implies j^* uniform (on a circle, on an infinite line). Topological effect.

Equilibrium = Detailed balance = Time reversal

$$w(x' \leftarrow x)p^*(x) = w(x \leftarrow x')p^*(x')$$

where the transition rate is defined by

$$w(x' \leftarrow x) = \mathcal{L}_{FP}\, \delta(x - x')$$

Equilibrium vs. nonequilibrium (underdamped)

The situation is trickier. Recently Ge proposed a criterion. Letting

$$\ddot{x}_t = F(x_t, \dot{x}_t) + \sqrt{2D(x_t)}\,\zeta_t$$

from time reversal symmetry

$$W(x', v' \leftarrow x, v)P^*(x, v) = W(x, -v \leftarrow x', -v')P^*(x', -v')$$

one obtains

something . . .

Temperature gradients

We consider a Langevin-type equation with inertia and **state dependent temperature**

$$\begin{aligned}\dot{x}_t &= v_t \\ \dot{v}_t &= -f(x_t) - \gamma v_t + \;???\; + \sqrt{2\gamma T(x_t)}\,\zeta_t\end{aligned}$$

$??? = 0$ leads to a mainstream theory by Van Kampen, see later. I propose an alternative theory.

A desirable property: **Local equipartition**

$$\mathbb{E}(v^2|x) = \left\langle v^2 \right\rangle_x = T(x) \qquad \text{at eq. steady state}$$

Required by internal consistency when the system is the thermometer. What is “temperature” otherwise?

Assumption: Local Thermal Equilibrium

We then require that, *if* the boundary conditions allows for a time-reversible (equilibrium, detailed balanced) steady state, then

$$P^*(v|x) = \exp - \left[\frac{v^2}{2T(x)} + \psi(x) \right]$$

is the steady state (invariant measure).

You don't like this *a posteriori* assumption?

Me neither, I would prefer microscopic derivations, but this is how the whole field was born, from Einstein *assuming* the Maxwell-Boltzmann distribution and the linear damping term, and deriving the Einstein relation.

It can then be proven that our equation reads

$$\dot{v}_t = f(x_t) - \gamma v_t + v_t^2 \, \partial \ln \sqrt{T(x_t)} + \sqrt{2\gamma T(x_t)} \, \zeta_t$$

with force

$$f(x) = \partial T(x) - T(x) \partial \psi(x).$$

and corresponding Kramers generator

$$\frac{\partial P}{\partial t} + v \, \frac{\partial P}{\partial x} + \left(f + \frac{\partial T}{\partial x} \frac{\partial}{\partial v} \frac{v^2}{2T} \right) P = \gamma \frac{\partial}{\partial v} \left(T \frac{\partial P}{\partial v} + vP \right)$$

(It can nicely be written in terms of a Liouvillian and a dissipator with respect to properly defined Hamiltonian and momenta...)

Overdamping limit

One proceeds by an expansion in Hermite polynomials. Basically:

$$P(x, v, s) \approx p(x, s) \frac{e^{-\frac{v^2}{T(x)}}}{\sqrt{T(x)}} + O(\gamma^{-1})$$

The space- marginal obeys the diffusion eq. in Stratonovich form

$$\partial_t p = -\partial \left[f\, p - \sqrt{T}\, \partial \left(\sqrt{T} p \right) \right]$$

corresponding to the first-order SDE

$$\dot{x}_t = f(x_t) + \sqrt{2T(x_t)} \circ \zeta_t$$

.

The equilibrium steady state reads

$$p^*(x) \propto \frac{1}{\sqrt{T(x)}} \exp \int^x \frac{\delta W}{T}, \qquad \delta W = f(x) \circ dx$$

When no external forces, the steady state is Landauer's:

$$p^*(x) \propto \frac{1}{\sqrt{T(x)}}$$

Hurray!

Note: Van Kampen's model gives

$$p^*_{VK}(x) \propto \frac{1}{T(x)}$$

Equilibrium thermodynamics (underdamped)

Boltzmann's entropy (along a trajectory) as a probabilistic state function

$$S(x_t, v_t, t) = -\log P(x_t, v_t, t)$$

On average it gives the Gibbs-Shannon expression:

$$\langle S \rangle = -\int dxdv\, P(x, v, t) \log P(x, v, t)$$

Also, we can define the *heat flux*

$$\begin{aligned} \delta Q_t &:= -T(x_t) \circ dS(x_t, v_t, t) \\ &= -\overbrace{\left[\gamma v_t - \sqrt{2\gamma T(x_t)} \circ \zeta_t\right] \circ dx_t}^{Sekimoto} + dT(x_t) \end{aligned}$$

Notice that at equilibrium

$$\oint \frac{\delta Q}{T} = \oint dS = 0$$

Modified first law

One then finds the

$$\boxed{\text{Modified First Law: } \delta Q = dU - \delta W + \overbrace{(1 - U/T)\,dT}^{\text{“thermal work”}}}$$

Also, in the overdamping limit one obtains:

$$\boxed{\text{Overdamped First Law: } \delta Q = dT/2 - \delta W}$$

Non-reversible dyamics...

Let us assume that

$$\dot{v}_t = f(x_t) - \gamma v_t + v_t^2 \, \partial \ln \sqrt{T(x_t)} + \sqrt{2\gamma T(x_t)} \, \zeta_t$$

governs the local dynamics irrespective of boundary conditions. Suppose that boundary conditions (i.e. the domain of the Kramers generator) allow for nonequilibrium steady states. For example, we might have on the circle $x \in [0, 2\pi)$

$$f(x) = -x$$

and require $P(x, v, t) \in \mathcal{C}^1$ in all of the domain. Then

Equilibrium $\iff$ Local thermal equilibrium

... and nonequilibrium thermodynamics

Heat flux

$$\delta Q_t = -\left[\gamma v_t - \sqrt{2\gamma T(x_t)} \circ \zeta_t\right] \circ dx_t + dT(x_t)$$

If $P \in \mathcal{C}^1$, a signature of nonequilibrium is

$$\oint_{(x,v)} \frac{\delta Q}{T} = -\oint_x \frac{\delta W}{T} \neq 0 \quad \text{along some cycles}$$

Fluctuation theorem:

$$\frac{\mathbb{P}\left(\oint_{(x,v)} \frac{\delta Q}{T} \equiv \Sigma\right)}{\mathbb{P}\left(\oint_{(x,v)} \frac{\delta Q}{T} \equiv -\Sigma\right)} = e^{\Sigma}.$$

On average yields Clausius's characterization of irreversibility:

$$\mathbb{E} \oint_{(x,v)} \frac{\delta Q}{T} \geq 0.$$

We obtain all the classics of thermodynamics.

Extrinsic geometric analog

Brownian particle in n dimensions in uniform temperature T_0, constrained onto a curve satisfies the above eq. with

$$T(x) = T_0/t(x)^2$$

where $t(x)$ is the norm of the tangent vector to the curve.

Punchline:

> *Temperature can be interpreted as a measure of effective length: Random transitions are more probable to shorter distances, as if due to hotter temperatures.*

Generalization to n-dim

- From extrinsic to intrinsic description.
- We want to build a second order Langevin equation that is both frame and coordinate invariant.
- The unique solution is a **noisy geodesic equation**

$$\dot{v}^a + \Gamma^a_{bc} v^b v^c = -\gamma v^a + \sqrt{2\gamma T}\, e^a_i \zeta^i$$

- I thought I was the first to write it before I found out I wasn't...
- In the overdamping limit leads to Brownian motion on a manifold (in Ito convention)

$$\dot{x}^a = -g^{bc}\Gamma^a_{bc} + \sqrt{2}\, e^a_i \zeta^i$$

- From a physical point of view, if we didn't have both coordinate and frame invariance, we could obtain self-driven systems in some frames/coordinates.

Comparison of models

Table: Comparison of state-dependent diffusion theories.

Model	**Langevin equation**	**Einstein relation**	**Steady state**
Generally Covariant	$\ddot{x}^a + \Gamma^a_{bc}\dot{x}^b\dot{x}^c = -\gamma\dot{x}^a + \sqrt{2\sigma}e^a_i\zeta^i$	$\gamma = \beta\sigma$	$g \exp -\frac{\beta}{2} g_{ab} v^a v^b$
Covariant (Graham)	$\ddot{x}^a = e^i_b \partial_c e^a_i \dot{x}^b \dot{x}^c - \gamma\dot{x}^a + \sqrt{2\sigma}e^a_i\zeta^i$	$\gamma = \beta\sigma$	?
Van Kampen	$\ddot{x}^a = -\gamma\dot{x}^a + \sqrt{2\sigma}e^a_i\zeta^i$	$\gamma = \beta\sigma$	?
State Dep. Viscosity	$\ddot{x}^a = -\gamma^a_b\dot{x}^b + \sqrt{2\sigma}e^a_i\zeta^i$	$\gamma^a_b = \beta\sigma g^{ac}\delta_{cb}$	$\exp -\frac{\beta}{2}\delta_{ab} v^a v^b$
Pure posticipatory SDE	—	—	—
St. Dep. Visc. and Temp.	$\ddot{x}^a = -\gamma^a_b\,\dot{x}^b_t + \sqrt{2\sigma}e^a_i\zeta^i$	$\gamma^a_b = \beta\sigma g^{ac} h_{cb}$	?

Table: Symmetries and thermodynamic properties.

FP current	**1D S.S.**	**Gauge inv.**	**Covariance**	**D.B.**
$-g^{ab}\left(\partial_b p - p\,\partial_b \log\sqrt{g}\right)$	$\sqrt{g}$	Yes	Yes	Yes
$-g^{ab}\partial_b p - \left(\delta^{ij} e^a_i \partial_b e^b_j\right) p$	$\sqrt{g}$	No	Yes	No
g	Yes	No	No	
$-g^{ab}\partial_b p$	$const.$	Yes	No	Yes
$-g^{ab}\partial_b p + \delta^{ij}\left(e^b_j \partial_b e^a_i - e^a_i \partial_b e^b_j\right) p$	$const.$	No	No	No
$-h^{ab} g_{bc}\left[\partial^c p + \left(\frac{2}{3}\partial^c \log\sqrt{h} + \partial_d h^{dc}\right) p\right] + \frac{2}{3} h^{ab} G^{cd}\Omega_{cdb} p$	$h^{\frac{2}{3}} e^{\int \frac{g\partial h}{3h^2}}$	Yes	No	No

Comments

- This is *the* model when the system is its own thermometer.
- Modified First Law is appealing but needs interpretation and derivation on completely different grounds.
- Possible spinoffs: Stochastic control, large deviations, fluctuation theorems, Kramer rate theory, Maxwell demons.
- Time-dependent temperature and local thermal equilibrium.
- Metric-compatible connections with torsion: Could they give rise to nonequilibrium self-driving?
- Possible experiment: Shaping curved brownian paths with tweezers.

Biblio

Based on:

- MP, *Diffusion in nonuniform temperature and its geometric analog*, PRE **87**, 032126 (2013)
- MP, *Generally covariant state-dependent diffusion*, JSTAT P07005 (2013)

Volume I, Part 1, Chapter 2:
The gauge connection of NESM

Foundational-type of work

Two years ago in Parma

Fruitful discussion with A. Vulpiani after his talk
The role of chaos for the foundation of statistical mechanics

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AV The Stat. Mech. community is divided into:

- *Chaoticists*: dissipation is inbuilt in the fundamental laws
  I. Prigogine and I. Stengers (1985) *La nouvelle alliance*
- *Determinists*: dissipation emerges from determinism
  J. Bricmont (1995) *Science of Chaos or Chaos in Science?*

MP Objection: there also are

- *Informationists*: physics is only about measure and information
  E. T. Jaynes (1957) *Information Theory and Statistical Mechanics*

AV Stat. Mech. based on information makes no sense because the Gibbs-Shannon entropy

$$S(p) = -\int d\mathbf{x}\; p(\mathbf{x}) \ln p(\mathbf{x})$$

is not invariant under general coordinate transformations while thermodynamics should be.

MP Should entropy be coordinate invariant?

AV [Beating on the banister] Yes because reality is there independently of how you describe it.

AV Stat. Mech. based on information makes no sense because the Gibbs-Shannon entropy

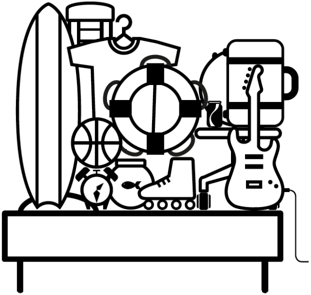
$$S(p) = -\int d\mathbf{x}\; p(\mathbf{x}) \ln p(\mathbf{x})$$

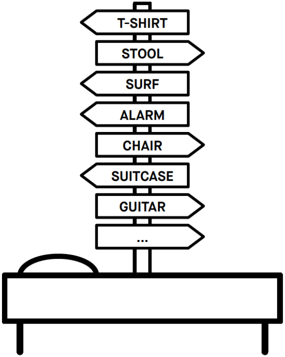
is not invariant under general coordinate transformations while thermodynamics should be. **YES**

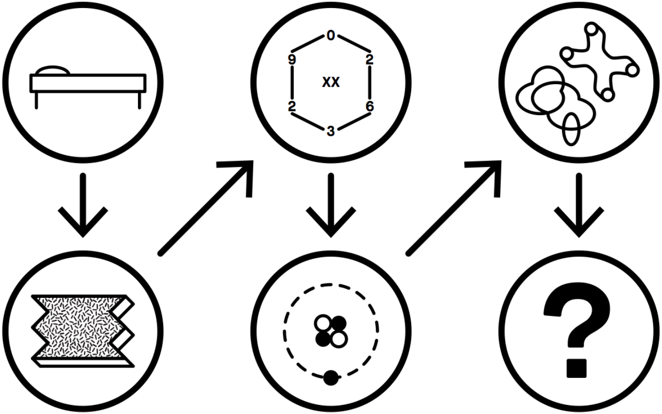
MP Should entropy be coordinate invariant? **NO**

AV [Beating on the banister] Yes because reality is there independently of how you describe it.

Subjectivity of entropy



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9
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XX
2
6
3
?

Priors

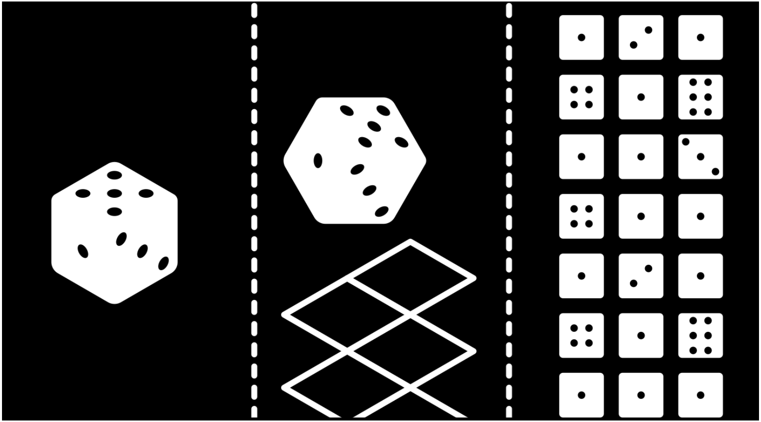
Principle of Insufficient Reason (Laplace)

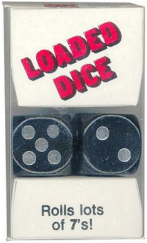
Indistinguishable states are a priori equally likely

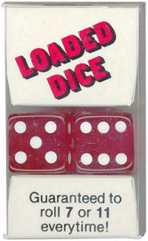
In SM, it justifies the microcanonical ensemble $p(\mathbf{x}) = \frac{1}{\mathrm{vol}\ X}$.

Frequentists: throw die $N \to \infty$ times, $\mathrm{Pr}(x) = \lim_{N\to\infty} N_x/N$.

Bayesians: $\mathrm{Pr}_{\mathrm{prior}}(x) = 1/6$ based on symmetry, then adjust assumption with experience through bayesian update.





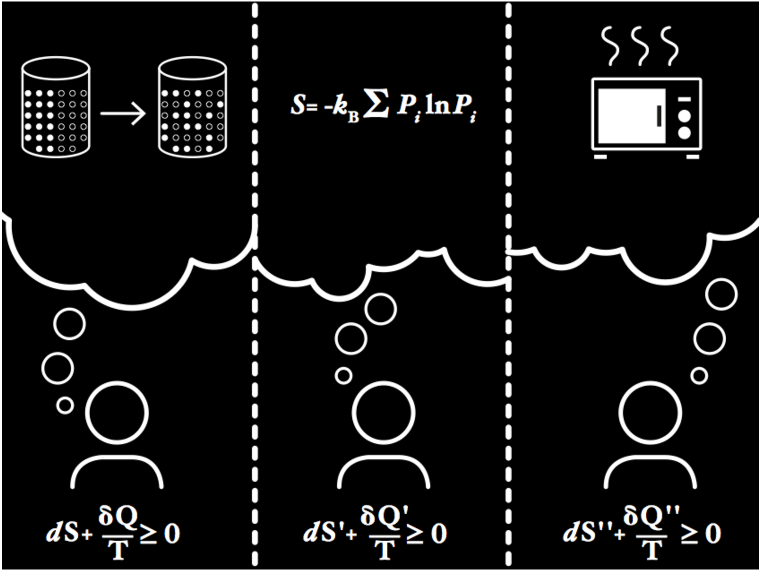


Choosing priors is discretionary.

- You can choose $p = 1/6$ and then update.
- If you know they're loaded, you might choose a different prior.

(this doesn't make all priors equally smart for practical purposes)

The hypothesis



Coordinate transformations

A riddle (from E. P. Northrop (1944) *Riddles in Mathematics*)

> *If we pick a number x between* 1 *and* 10 *at random, the probability that it is smaller than* 5 *is* $1/2$*; but if we pick x' at random between* 1 *and* 100*, the probability that it is smaller than* 25 *is* $1/4$*. How is it possible that picking a number or its square aren't equally likely?*

"At random" is a choice of prior. Laplace's principle hides here:

$$\begin{aligned} \Pr(x) &= \frac{dx}{10} \\ \Pr'(x') &= \frac{dx'}{100} = \frac{x}{5} \cdot \Pr(x) \end{aligned}$$

A change of coordinates corresponds to a change of priors

Coordinate transformation

Let $\mathbf{x} \to \mathbf{x}'(\mathbf{x})$ be invertible, orientation pres. with log jacobian

$$\varphi(\mathbf{x}) = \log\det\left(\frac{\partial \mathbf{x}'(\mathbf{x})}{\partial \mathbf{x}}\right)$$

Transformation law for the entropy

$$S(p') - S(p) = \langle \varphi \rangle.$$

Frames to move from

- *Coordinate transformation*: on the tangent bundle;
- *Prior (gauge) transformation*: on an "imitation" fiber bundle.

Open systems

Modelled via the Fokker-Planck equation:

$$\dot{p} = -\nabla \cdot \left(p\,\mathbf{A} - T\nabla p\right) = -\nabla \cdot \mathbf{J}.$$

Stochastic counterpart:

$$d\mathbf{x}_t = \mathbf{A}(\mathbf{x}_t)dt + \sqrt{T}d\mathbf{w}_t.$$

Where

- Thermodynamic force $\mathbf{A}$
- Conjugate probability current $\mathbf{J}$

Assumption: dynamics invariant of changes of priors

Gauge symmetry

Then

$$\begin{aligned} p' &= e^{-\varphi} p, \\ \mathbf{A}' &= \mathbf{A} - T \nabla \varphi. \end{aligned}$$

Gauge symmetry!

- It is local (depends on $\mathbf{x}$);
- Gauge potential: the thermodynamic force $\mathbf{A}$;
- Noncompact gauge group: $(\mathbf{R}^{+}, \times)$ (abelian, a bit trivial);
- Gauge charge: temperature T.

Second Law

We can fix the non-invariance of the (time derivative of the) entropy

$$\delta \dot{S} = \int \mathbf{J} \cdot \nabla \phi$$

by noticing that

$$-\int \mathbf{J} \cdot \mathbf{A} =: \frac{đQ}{dt}$$

has exactly the same transformation law (but for T).
Then the *entropy production*

$$\sigma := \dot{S} - \frac{1}{T}\frac{đQ}{dt}.$$

is invariant. Also:

$$\sigma \geq 0$$

Second law is independent of priors

Curvature

The main gauge-invariant quantity:

$$F_{\mu\nu} = \partial_\mu \mathbf{A}_\nu - \partial_\nu \mathbf{A}_\mu.$$

- When $F_{\mu\nu} = 0$ (flat connection) iff detailed balance
- i.e. $\mathbf{A}$ "pure gauge", it is a gradient
- At a nonequilibrium steady state

  $$\sigma = \int F_{\mu\nu} \Theta^{\mu\nu}$$

  where $\Theta^{\mu\nu}$ analogous to cycle currents.
- It serves as constraint for the MinEP principle (linear regime)

$$\left.\frac{\delta\sigma}{\delta \mathbf{J}}\right|_{\bar{F}_{\mu\nu}(\mathbf{J})} = 0 \quad \Longrightarrow \quad \nabla \cdot \mathbf{J} = 0.$$

Future inquiry

- Kirchhoff's Laws follow from Maxwells'. Could nonequilibrium gauge invariance follow from EM gauge invariance?
- Gauge invariance for Open Quantum Systems (Lindblad Eq.): non-abelian connection?
- What is the geometric nature of time reversibility in underdamped equation:

$$
\begin{aligned}
D(x)\nabla_v \log P^*(x,v) &= F(x,v) - F(x,-v) \\
D(x)v\cdot\nabla_x \log P^*(x,v) &= -\frac{1}{2}\left\{F(x,v)^2 - F(x,-v)^2 \right.\\
&\quad \left. + \left[D(x)\nabla_v\left[F(x,v)+F(x,-v)\right]\right]\right\}
\end{aligned}
$$

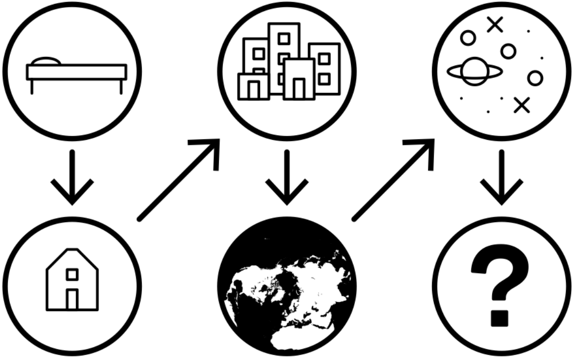
Punchlines

- Gauge symmetry under change of priors of NESM
- Thermostatics is not invariant, thermodynamics is
- Curvature is a crucial nonequilibrium invariant
- Flatness $\iff$ equilibrium

Also:

- Second Law is not "increase of entropy"
  but positive entropy production
- EP is not the production of entropy in an isolated system
- "Informationism": Observer necessary, but laws independent

Is there an "entropy of the universe"?



"All things physical are information–theoretic in origin and this is a participatory universe. Observer participancy gives rise to information; and information gives rise to physics" (J.A. Wheeler)

Based on:

- MP, *Nonequilibrium thermodynamics as a gauge theory* Eur. Phys. Lett. **97**, 30003 (2012).

- MP and F. Vedovato [1], *Of dice and men. Subjective priors, gauge invariance, and nonequilibrium thermodynamics*, Proceedings JETC2013, Brescia, Italy, July 2013.

[1] Artwork