Thermodynamic interpretation of dynamical fluctuation functionals

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Shellyfest, 8 October 2007

nonequilibrium statistical mechanics

1. clarifying status of entropy production principles;

2. about a canonical structure of nonequilibrium fluctuations: What matters beyond the linear regime? (Time-symmetric fluctuations!)

CLOSE-TO-EQUILIBRIUM QUESTIONS

What is the meaning and validity of entropy production principles?

(Related question: What is the meaning and validity of MacLennan-Zubarev ensembles?)

ENTROPY PRODUCTION PRINCIPLES, how and why true?

FACT: it often happens, but not always, that extremizers of the entropy production functional coincide with stationary or most typical values in a nonequilibrium process close-to-equilibrium.

Example: minimum entropy production principle $\sim$ Prigogine, which in the context of Markov processes amounts to verifying that the stationary measure is to first order around equilibrium a minimum of the entropy production functional.

Where does the minimum entropy production principle come from?

$(X_t)_{t\geq 0}$ = stationary ergodic Markov process, with invariant measure ρ.

Consider the time-averages

$$p_T(x) = \frac{1}{T} \int_0^T \chi[X_t = x] \, dt$$

the fraction (in large time T) to observe the state x.

Then,

$$\boldsymbol{P}[p_T \simeq \mu] \simeq e^{-TI(\mu)}$$

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where $I(\mu)$ is the Donsker-Varadhan functional (1975) that depends on the transition intensities of the Markov process.

We ask what of the physics that goes in the Markov process, is visible in the fluctuation functional $I(\mu)$.
(Thinking about statistical foundation of variational principles in thermodynamics.)

E.g. how does $I(\mu)$ look close-to-equilibrium?

Close-to-equilibrium here means two things: for $\epsilon \ll 1$

1. dynamics is very weakly driven out of equilibrium with driving forces of order ϵ.

2. fluctuation functional is evaluated for statistics that are very close (order ϵ) to the equilibrium statistics.

The steady-state probability that

$$p_T = \frac{1}{T} \int_0^T \chi[X_t = \cdot]\, dt \simeq \mu$$

that the occupation statistics is given by the law μ obeys a fluctuation formula

$$\boldsymbol{P}[p_T \simeq \mu] \simeq e^{-T I(\mu)}$$

and we evaluate the fluctuation functional

$$I^\epsilon(\mu^\epsilon)$$

up to second order in perturbation around equilibrium.

The answer is given in terms of the following functional:

For probability μ, define

$$\sigma(\mu) = \lim_{T \downarrow 0} \frac{1}{T} S[\boldsymbol{P}_\mu^T \,|\, \boldsymbol{P}_{\mu_T}^T \Theta] = \lim_{T \downarrow 0} \frac{1}{T} \boldsymbol{E}_\mu^T \left[\log \frac{\mathrm{d}\boldsymbol{P}_\mu^T}{\mathrm{d}\boldsymbol{P}_{\mu_T}^T \Theta} \right]$$

The process $\boldsymbol{P}_\mu^T$ starts from probability measure μ and runs for a time T; the process $\boldsymbol{P}_{\mu_T}^T \Theta$ is its time-reversal. The logarithmic ratio $\sigma(\mu)$ measures the amount of instantaneous time-reversal breaking.

We (= Karel Netočný) find:

$$I^{\epsilon}(\mu^{\epsilon}) = \frac{1}{4}[\sigma^{\epsilon}(\mu^{\epsilon}) - \sigma^{\epsilon}(\rho^{\epsilon})] + o(\epsilon^2)$$

where ϵ measures the distance from equilibrium (detailed balance).

$$I^\epsilon(\mu^\epsilon) = \frac{1}{4}[\sigma^\epsilon(\mu^\epsilon) - \sigma^\epsilon(\rho^\epsilon)] + o(\epsilon^2)$$

(Mathematical proof is published in

C. Maes and K. Netočný: Minimum entropy production principle from a dynamical fluctuation law: J. Math. Phys. **48**, 053306 (2007).J. Math. Phys. 2007.)

interpretation of $\sigma(\mu)$...?

Acknowledgment: We thank S. Goldstein for insisting on clarifying the connections with the Boltzmann entropy...

C. Maes and K. Netočný: Time-reversal and Entropy, J. Stat. Phys. **110**, 269–310 (2003).

Abstract: ... The main result identifies under general conditions the statistical mechanical entropy production as the source term of time-reversal breaking in the path space measure for the evolution of reduced variables. This provides a general algorithm for computing the entropy production and to understand in a unified way a number of useful (in)equalities...

In other words: $\sigma(\mu)$ is the INSTANTANEOUS ENTROPY PRODUCTION RATE.

And so:

ENTROPY PRODUCTION AS RATE FUNCTION.

For probability μ,

$$\sigma(\mu) = \lim_{T \downarrow 0} \frac{1}{T} S[\boldsymbol{P}_\mu^T \,|\, \boldsymbol{P}_{\mu_T}^T \Theta] = \lim_{T \downarrow 0} \frac{1}{T} \boldsymbol{E}_\mu^T \Big[\log \frac{\mathrm{d}\boldsymbol{P}_\mu^T}{\mathrm{d}\boldsymbol{P}_{\mu_T}^T \Theta} \Big]$$

is the instantaneous entropy production rate when in μ.

The steady-state probability that

$$p_T = \frac{1}{T}\int_0^T \chi[X_t = \cdot]\, dt \simeq \mu$$

that the occupation statistics is given by the law μ obeys a fluctuation formula

$$\boldsymbol{P}[p_T \simeq \mu] \simeq e^{-T I(\mu)}$$

related to the entropy production functional as

$$I(\mu) \propto \sigma(\mu) - \sigma(\rho) + \ldots.$$

up to second order in perturbation around equilibrium.

More precisely,

$$I^\epsilon(\mu^\epsilon) = \frac{1}{4}[\sigma^\epsilon(\mu^\epsilon) - \sigma^\epsilon(\rho^\epsilon)] + o(\epsilon^2)$$

where ϵ measures the distance from equilibrium (detailed balance).

Corollary: the minimum entropy production principle (to lowest order around equilibrium, the stationary measure is characterized by minimal entropy production) can be understood from a more general variational principle AT LEAST WHEN THE VARIABLES ARE EVEN UNDER TIME-REVERSAL....

EXPLAINING the counter example in R. Landauer, Stability and entropy production in electrical circuits: J.Stat.Phys. **13**:1–16 (1975). RL in series: Kirchhoff's second law for the current J

$$RJ + L\frac{\mathrm{d}J}{\mathrm{d}t} = E$$

with entropy production rate equal to $\beta R J^2$.

Clearly, the stationary current $J^* = E/R$ does not minimize that entropy production. But it does minimize the fluctuation functional

$$I(J) = \frac{\beta R}{4}\Big(J - \frac{E}{R}\Big)^2$$

for the dynamics (inserting Johnson-Nyquist noise)

$$\mathrm{d}J_t = \frac{E - RJ_t}{L}\,\mathrm{d}t + \sqrt{\frac{2R}{\beta L^2}}\,\mathrm{d}B_t$$

Fluctuation functional $I(J)$ for the empirical current $\int_0^T J_t \, \mathrm{d}t \, /T$:

$$I(J) = \frac{\beta R}{4}\Big(J - \frac{E}{R}\Big)^2$$

As generally true, the minimum of $I(J)$ over J is given by the correct stationary value.
However, that $I(J)$ clearly differs from the physical entropy production $\beta R J^2$.

Reason: while we can find the most probable current $J^* = E/R$ by minimizing $I(J)$, it does not correspond to a minimization of the entropy production, even in the linear irreversible regime BECAUSE current is ODD under time-reversal.

More examples are found in S. Bruers, C. Maes and K. Netočný: On the validity of entropy production principles for linear electrical circuits: J. Stat. Phys. (2007).

For odd observables the above argument proposes a different functional that replaces the entropy production, leading finally to the MAXIMUM entropy production principle, we must MAXIMIZE $\sigma(J)$ subject to the condition that all dissipated power equals the entropy production, as in the stationary state.

see S. Bruers, C. Maes and K. Netočný: On the validity of entropy production principles for linear electrical circuits: J. Stat. Phys. (2007) for details.

RELATED QUESTION:

What is the meaning of the MacLennan-Zubarev ensembles ?

According to MacLennan, Zubarev..., the stationary distribution close to equilibrium can be written in the form

$$\rho = \frac{1}{Z}\, e^{-\beta U + \phi}$$

with a nonequilibrium correction ϕ that is claimed to be directly related to the entropy production or dissipation in a driven system.

People have even argued that this is *logical* from the point of view of some nonequilibrium maximum entropy principle.

What is the meaning of the MacLennan-Zubarev ensembles ?

$$\rho = \frac{1}{Z}\, e^{-\beta U + \phi}$$

with ϕ *entropy production...?*

In fact, FOR PHYSICAL REASONS, the answer is more subtle.
(Mathematics is also not so terribly easy here...)

from the HOMEPAGE of Shelly Goldstein:

No attempt will be made here to explain what mathematical physics is about. There is no general agreement even among the experts. Moreover, this field of research is regarded as somewhat dubious by many physicists. However, the following words of Maxwell are right on target:

The first processes, therefore, in the effectual studies of the sciences, must be ones of simplification and reduction of the results of previous investigations to a form in which the mind can grasp them.

J.C. MAXWELL, On Faraday's lines of force cf. recent preprint by Komatsu and Nakagawa, arXiv cond-mat/0708.3158. Another application of the fluctuation symmetry for the entropy production

$$\rho_T(x) = \rho_o(x) \, \langle \exp(-S) \rangle_x$$

can be asymptotically expanded in a parameter ϵ = strength of the driving.

A rephrasing of McLennan's proposal saying that the nonequilibrium linear order correction to the equilibrium measure is just the entropy production appears not correct as such; the rigorous meaning is in the sense that one has to take the linear component of the irreversible part of the entropy flux, which turns out to have a transient character and gets in fact cancelled in mean by the other contributions (energy fluxes) to the total entropy production (which is itself of order ϵ^2).

Next ...

to the theory of large deviations for nonequilibrium purposes:

CHARACTERIZATION OF A CANONICAL STRUCTURE IN THE LARGE DEVIATION FUNCTIONALS

on and beyond entropy production.

Context of fluctuating hydrodynamics for lattice gases, interacting particle systems, Onsager-Machlup theory,...

Consider

$$(X_t)_{t\geq 0} = \text{stationary ergodic Markov process},$$

MAIN QUESTION:

What is the probability to see a deviating density and/or current profile?

Is there anything systematic?

Possible differences with existing work by e.g. Bodineau, Derrida and Bertini, De Sole, Gabrielli, Jona-Lasinio, Landim are:

- no emphasis on diffusion-approximation or on hydrodynamic rescaling;

- emphasis on (thermodynamic) canonical structure with novel concept of traffic;

- attempt to direct calculation (not via generating function, Bethe-Ansatz,...) but on a more fine-grained level of description.

Above: OCCUPATION statistics looks at residence times, time-averages

$$p_T(x) = \frac{1}{T}\int_0^T \chi[X_t = x]\, dt$$

the fraction (in large time T) to observe the state x.

$$\boldsymbol{P}[p_T \simeq \mu] \simeq e^{-TI(\mu)}$$

We have seen

ENTROPY PRODUCTION AS RATE FUNCTION.

in the sense: the occupation statistics obeys a fluctuation formula

$$\boldsymbol{P}[p_T \simeq \mu] \simeq e^{-TI(\mu)}$$

related to the entropy production functional as

$$I(\mu) \propto \sigma(\mu) - \sigma(\rho) + ...$$

up to second order in perturbation around equilibrium.

... but that is strange.

JOINT occupations and currents:

obey an exponential fluctuation law with functional $I(\mu, j)$

$$\boldsymbol{P}[p_T \simeq \mu, J_T \sim j] \simeq e^{-TI(\mu,j)}$$

result is about canonical structure of $I(\mu, j)$

For a linear response theory , mostly only the entropy production matters, cf. Green-Kubo, MacLennan-Zubarev, Prigogine,...

Beyond linear order, the fluctuations of **time-symmetric** observables get coupled with those that are anti-symmetric

We suggest two (classes of) canonical variables: current and traffic.

Many details are in:

C. Maes., K. Netočný, B.Wynants: arXiv cond-mat/0709/4327

C.Maes, K. Netočný and B. Wynants: arXiv cond-mat/0708.0489

C. Maes and K. Netočný: arXiv cond-mat/0705.2344

METHOD and IDEA

- Take collection A of all trajectories ω that realize
fraction of time spent in state x is $\mu(x)$, and
fraction of (signed) jumps between states x and y is $j(x,y)$

- Find new (modified) process P^* so that

$$P^*[A] = 1, \qquad P[\omega] = P^*[\omega]\, e^{-T\, I(\mu,j)}$$

Then,

$$P[A] \simeq e^{-T\, I(\mu,j)}$$

OBSERVE

that we take a rather FINE-GRAINED description with respect to observations of *total current, occupation in some domains,...*

If a MORE COARSE-GRAINED statistics is wanted (such as TOTAL current over all bonds, over all particles,...), then we need to take a further contraction, i.e., a further mimimization of the fluctuation functional $I(\mu, j)$,

which could be highly non-trivial and very model-dependent.

The fluctuation functional $I(\mu, j)$ is canonical in the following sense.

Write the transition rates

$$\lambda(x,y) \equiv \lambda_F(x,y) = \lambda_0(x,y)\, e^{\frac{1}{2}F(x,y)}$$

with driving $F(x,y) = -F(y,x)$ and so that the rates $\lambda_0(x,y)$ correspond to a reference equilibrium (= detailed balanced) dynamics.

To characterize the fluctuation functional $I(\mu, j)$ (without conditions of close-to-equilibrium), we introduce quantities related to the time-symmetric sector, and quantities related to the time-antisymmetric sector.

The question is not only to see if and how the entropy production introduces time-antisymmetric terms in the fluctuation functional, but also to see how the time-symmetric terms are affected by the driving.

Introduce the "Hamiltonian"

$$H(\mu, F) = 2\sum_{x,y} \mu(x)[\lambda_F(x,y) - \lambda_0(x,y)]$$

which is excess traffic.

traffic = dynamical activity =

$$\mu(x)\lambda(x,y) + \mu(y)\lambda(y,x)$$

$H(\mu, F)$ is a potential function for the (expected transient) currents

$$\delta H(\mu, F) = \frac{1}{2}\sum_{x,y} j_{\mu,F}(x,y)\delta F(x,y)$$

Take Legendre transform of H,

$$G(\mu, j) = \sup_F \Big[\frac{1}{2}\sum_{x,y} F(x,y)j(x,y) - H(\mu, F)\Big]$$

Associated canonical equations

$$\frac{\partial H}{\partial F(x,y)} = j(x,y)\,, \qquad \frac{\partial G}{\partial j(x,y)} = F(x,y)$$

Fluctuation functional $I(\mu, j) =$ obtains the following general form:

$$I(\mu, j) = \frac{1}{2}[G(\mu, j) + H(\mu, F) - \dot{S}(F, j)]$$

where $\dot{S}(F, j) = \frac{1}{2}\sum_{x,y} F(x, y)j(x, y)$ is the total entropy current into all reservoirs.

Since the functional $G(\mu, j)$ directly specifies the equilibrium fluctuations as $I_{\text{eq}}(\mu, j) = G(\mu, j)/2$, we get in an explicit form the nonequilibrium correction with respect to that equilibrium reference.

Another way of writing:

$$I(\mu, j) = \frac{1}{4}\sum_{x,y}\Delta(x,y)j(x,y) - \frac{1}{2}\sum_{x,y}[t^*_\mu(x,y) - t_\mu(x,y)]$$

wich is excess entropy production plus excess traffic:

$\Delta(x,y)$ = excess driving, and traffic

$$t_\mu(x,y) = \mu(x)\lambda(x,y) + \mu(y)\lambda(y,x)$$

$$t^*_\mu(x,y) = \mu(x)\lambda(x,y)e^{\Delta(x,y)/2} + \mu(y)\lambda(y,x)e^{-\Delta(x,y)/2}$$

EXAMPLE:

Random walker moving on ring, totally asymmetric, at rate 1. Then, to make current j, we get the excess driving as $\log j$. The traffic is equal to the magnitude of the current.

Hence, fluctuation functional for the current is

$$I(j) = j \log j - j + 1$$

Examples with just few particles in the system, and with infinite stationary reservoirs are the easiest, cf. like in quantum dots,...for direct computation.

About *small fluctuations.*

For steady state arbitrarily far from equilibrium – the structure of small deviations through the rescaled functional $I(\mu, j) = \epsilon^2 I^{(2)}(v, \mathrm{j})$ with $\mu = \rho(1 + \epsilon v), j = \bar{j} + \epsilon \mathrm{j}$.

The driving F is kept fixed and both the density and current are expanded around the stationary values ρ respectively $\bar{j}$.

In the stationary regime, the rate function for the joint distribution of time-averaged occupations and currents is

$$I^{(2)}(v,\mathrm{j};F) = \frac{1}{2}\sum_{(xy)}\Big[\frac{1}{2\bar{\tau}}\mathrm{j}^2 + \frac{\bar{\tau}}{2}(\nabla^- v)^2 - \frac{\bar{j}}{\bar{\tau}}\mathrm{j}\nabla^+ v + \frac{\bar{j}^2}{2\bar{\tau}}(\nabla^+ v)^2\Big](x,y)$$

which demonstrates

(1) that the occupation-current coupling is proportional to the stationary current and indeed vanishes only close to equilibrium when moreover $\bar{j} = O(\epsilon)$;
(2) the steady traffic $\bar{\tau}$ plays the role of a variance in the fluctuation law.

Conclusions

- dynamical fluctuation theory explains entropy production principles;

- there exists a canonical structure in the joint fluctuations of currents and occupations;

- the (new) notion of traffic complements that of entropy production beyond close-to-equilibrium, to summarize the effect of the driving on the time-symmetric observables.

...and next time, there will be more examples...

Papers can be downloaded from

`http://itf.fys.kuleuven.be/~christ/`

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