Recent results in nonequilibrium statistical mechanics

On the Origin and the Use of Fluctuation Relations for the Entropy

TO SHOW :

1. that the ENTROPY PRODUCTION can be usefully given as the SOURCE TERM of TIME-SYMMETRY BREAKING in the action of the space-time distribution for reduced variables;

2. that a number of relevant (in)equalities, FLUCTUATION RELATIONS, can be derived from this algorithm.

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ABSTRACT:
The development of thermodynamics and statistical mechanics has been strongly influenced and steered by questions on the working and the efficiency of heat engines. When machines get smaller, as is the case for molecular motors, new challenges appear that ask for investigating fluctuations of entropy and its production. Last decade has witnessed serious progress in that direction with establishing generalized fluctuation-dissipation relations and symmetries under time-reversal. I will review some of these results and give a unified approach enabling to make connections with a variety of experimental situations. Special emphasis will be put on the case of kinesin and its motility.

GENERAL CONTEXT

(Possible) Intersections between (non)equilibrium statistical physics and biology include

- microscopic foundation of chemical thermodynamics
- appearance of order and self-organization
- models of large amounts of locally interacting particles
- treatment of open systems, maintained currents, entropy production, energy balances,...

WHAT IS NEW?

concentrate on one aspect:

FLUCTUATIONS OF
ENTROPY PRODUCTION

having relevance to

- efficiency calculations
- randomness calculations
- equilibrium free energy measurements

WHAT IS ENTROPY?

1. Thermodynamic entropy: Carnot $\rightarrow$ Kelvin $\rightarrow$ Clausius $\Rightarrow$ operational definition of entropy for interconnected equilibrium states.

$$dS = \frac{1}{T}(dE + p\,dV - \sum \mu_i dN_i)$$

SECOND LAW:

$$S(\text{final}) - S(\text{initial}) \geq 0$$

2. Microscopic entropy: Boltzmann $\rightarrow$ Planck $\rightarrow$ Einstein $\Rightarrow$ nonequilibrium entropy.

$$S = k_B \log W$$

H-THEOREM:

$$S(x_t) \geq S(x_s), \quad t \geq s$$

TO REMEMBER

- scales: micro $\rightarrow$ macro.

An entropy difference $S' - S$ of about 0.1 millicalorie at room temperature corresponds to a phase volume ratio of

$$\frac{W}{W'} = \exp -(S' - S)/k_B = e^{-10^{20}}$$

Any visible change in the entropy per particle (as measured in units of k_B) corresponds to a ratio of phase volumes that is exponential in the number of particles.

At the other extreme: total heat exchanges of the order of $k_B T$ are subject to important fluctuations.

- determining factors.

$\sim$ conservation laws, addition rules, symmetries.

$\sim$ autonomous equations.

$\sim$ reservoirs with specified intensive variables.

WHAT IS ENTROPY PRODUCTION?

For open driven system: entropy production = the total change of entropy in the "universe" BUT we can view it...

FROM THE SUBSYSTEM

work, heat, entropy production become path-dependent functions
depending on the whole history of the subsystem.

TOTAL ENTROPY CHANGE = CHANGE OF ENTROPY IN THE SUBSYSTEM

PLUS

CHANGE OF ENTROPY IN THE ENVIRONMENT/RESERVOIRS

BASIC RESULT:

RELATION WITH TIME-REVERSAL

that the ENTROPY PRODUCTION (both for closed and for open systems be it in the transient regime or in the steady state regime) can be usefully given as the SOURCE TERM of TIME-SYMMETRY BREAKING in the action of the space-time distribution for reduced variables.

For theoretical and mathematical description, see e.g.

references:

C. Maes: Fluctuation relations and positivity of the entropy production in irreversible dynamical systems, Nonlinearity 17, 1305 - 1316 (2004).
C. Maes and E. Verbitskiy: Large Deviations and a Fluctuation Symmetry for Chaotic Homeomorphisms, Commun. Math. Phys. 233, 137-151 (2003).
C. Maes and K. Netocny: Time-reversal and Entropy, J. Stat. Phys. 110, 269-310 (2003).
C. Maes: On the origin and the use of fluctuation relations for the entropy, Séminaire Poincaré, 6 décembre 2003.

For examples, see next.

EXAMPLE 1: Channel for ion transport driven by concentration difference at the ends; *mesoscopic model*.

Suppose that ions enter from the left reservoir with intensity λ_{i}^1 and leave to the left reservoir with intensity λ_{o}^1. Similarly at the right with intensities λ_{i}^1, respectively λ_{o}^1.

We calculate the ratio between probabilities for a trajectory ω and its time-reversed trajectory $\Theta\omega$:
whenever in ω a particle enters the channel (from the left), in $\Theta\omega$ a particle leaves the channel (to the left). With J_1 the ion-current into the left reservoir and J_2 the ion-current into the right reservoir,

$$\log \frac{\mathrm{Prob}[\omega]}{\mathrm{Prob}[\Theta\omega]} = -J_1 \log \frac{\lambda_{\mathrm{i}}^1}{\lambda_{\mathrm{o}}^1} - J_2 \log \frac{\lambda_{\mathrm{i}}^2}{\lambda_{\mathrm{o}}^2}$$

In terms of chemical potential μ_1, respectively μ_2 at ambient temperature T,

$$k_B \log \frac{\mathrm{Prob}[\omega]}{\mathrm{Prob}[\Theta\omega]} = -J_1 \frac{\mu_1}{T} - J_2 \frac{\mu_2}{T}$$

which is the total change of entropy in the reservoirs.

EXAMPLE 2: Particle in optical trap

$$H_t(p,q) = \frac{p^2}{2m} + \frac{\kappa}{2}(q - a(t))^2$$

with $a(t)$ the time-dependent position of a trap. Force exerted on the particle is

$$F_t(q) = -\kappa(q - a(t))$$

in isothermal medium at inverse temperature β.

For example, theoretically described by

$$\dot{q}_t = v_t$$

$$m\dot{v}_t = -\kappa(q_t - a(t)) - \gamma v_t + \zeta_t, \quad \langle \zeta_t \zeta_s \rangle = 2k_B T \gamma \delta(t-s)$$

Compute again

$$\log \frac{P(\omega)}{P(\Theta\omega)}$$

to find it equal to

$$= -\kappa \int_0^\tau dt\, \dot{a}(t)(q_t - a(t))$$

the total work done on the system:

$$= \kappa \frac{(a(\tau) - q_\tau)^2 - (a(0) - q_0)^2}{2}$$

$$-\kappa \int_0^\tau dt\, v_t\, (q_t - a(t))$$

which equals the entropy production up to a total time-difference.

BASIC CONSEQUENCE:

SYMMETRY OF ENTROPY PRODUCTION

Argument: with $\Theta\omega$ the time-reversed trajectory,

$$\langle f\Theta\rangle = \sum_\omega f(\Theta\omega) P(\omega)$$

$$\langle f\Theta\rangle = \sum_\omega f(\omega) \frac{P(\Theta\omega)}{P(\omega)} P(\omega)$$

$$\langle f\Theta\rangle = \sum_\omega f(\omega) e^{-R(\omega)} P(\omega)$$

and in particular

$$\langle f(-R)\rangle = \langle f(R) e^{-R}\rangle$$

which is the so called steady state fluctuation symmetry, asymptotically valid for the entropy production averaged over large times.

Specific consequences:

1. irreversible work — equilibrium free energy relations, so called Jarzynski relation:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$$

is obtained by taking $f \equiv 1$.

2. symmetry in fluctuations:

$$\frac{P(R = r)}{P(R = -r)} = e^{r}$$

EXAMPLE 3: A Markov Model for Kinesin

C. Maes and M.H. van Wieren, J. Stat. Phys. **112**, 329–355 (2003).

Abstract:
We investigate the validity of a Markov approach for the motility of kinesin. We show in detail how the various mechanochemical states and reaction rates that were explored experimentally, may be used to create a Markov-chain model. We compare the performance of this model to motility data and we find global similarities in the load and ATP-concentration dependency of speed and average distance travelled. We also discuss the relation between the experimentally found stalling behavior and thermodynamic expectations. Finally, the Markov chain modelling provides a way to calculate the mean entropy production and the (power) efficiency.

THERMODYNAMIC SCHEME OF CHEMICAL MOTOR:

First law (per particle):

$$W + Q + e_2 - e_1 = 0$$

For the (total) entropy production in the steady state, we must add the changes of entropy in all the reservoirs:

Second law

$$Q + (\mu_1 - e_1) - (\mu_2 - e_2) \geq 0$$

$\Rightarrow$ maximal work per particle that can be done by our molecular motor is always bounded as

$$W \leq \mu_1 - \mu_2$$

If $Q \geq 0$ (heat released to the environment), then also

$$W \leq e_1 - e_2$$

STATISTICAL MECHANICAL SCHEME OF CHEMICAL MOTOR:
via CONSTRUCTION of Markov process on mechano-chemical states....
allowing the calculation of the variable entropy current and entropy production.

The mean entropy production rate is

$$J[\frac{\Delta\mu}{T} - F\frac{\lambda}{T}]$$

where J is the mean current, F is load, λ is mean distance travelled per power stroke, $\Delta\mu$ is difference in chemical potential ($\hookrightarrow$ ATP-concentration).
BUT THERE ARE FLUCTUATIONS...