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Thermodynamical formalism for stationary states of Markov chains

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A too ambitious title ?

I will introduce the notion of record of transitions, and
make the link with recent work of Carati,
and recent work about the fluctuation theorem.

At the end I will discuss thermodynamics of a one-parameter model.

J Naudts, E Van der Straeten, *Transition records of stationary Markov chains,* arXiv:cond-mat/0607485.

Contents

1 Intro

Current interest in
- stationary non-equilibrium states
- non-Gibbsian states

Markovian dynamics

- start from dynamical system
- partition phase space into cells
- describe dynamics by transition probabilities.

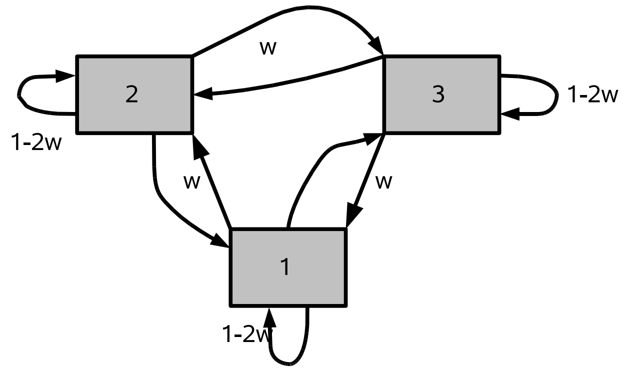
Thermodynamics out of equilibrium

stationary states, non-equilibrium

characterised by (energy) currents

results depend on path in thermodynamic parameter space

2 Markov chains



EXAMPLE A 3-state system

$$w(x,y) = \begin{pmatrix} 1-2w & w & w \\ w & 1-2w & w \\ w & w & 1-2w \end{pmatrix}$$ transition probabilities

$$p(x) = \frac{1}{3}\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$ stationary probability distribution

satisfies $\sum_x p(x)w(x,y) = p(y)$ (stationarity condition)

$p(x)$ satisfies also $p(x)w(x,y) = p(y)w(y,x)$ (detailed balance condition)

- detailed balance $\equiv$ equilibrium (minus stability)

- detailed balance implies stationarity:

$$\sum_x p(x)w(x,y) = \sum_x p(y)w(y,x) = p(y)$$

- interest in non-equilibrium stationary states

EXAMPLE

$$w(x,y) = \begin{pmatrix} 1-2w & w(1+\zeta) & w(1-\zeta) \\ w(1-\zeta) & 1-2w & w(1+\zeta) \\ w(1+\zeta) & w(1-\zeta) & 1-2w \end{pmatrix}$$

Now, $p(x)$ is still stationary, but detailed balance is not satisfied.

3 Distribution of transition records

Exercise

path 1 1 3 3 2 3 3 1 has probability

$p(1)w(1,1)w(1,3)w(3,3)^2w(3,2)w(2,3)w(3,1)$

same probability as 1 3 3 2 3 3 1 1 or 1 1 3 2 3 3 3 1 or ...

transition	record
$1 \to 1$	1
$1 \to 2$	0
$1 \to 3$	1
$2 \to 1$	0
$2 \to 2$	0
$2 \to 3$	1
$3 \to 1$	1
$3 \to 2$	1
$3 \to 3$	2

probability of all paths starting in $x = 1$ and having transition record $k = (1, 0, 1, 0, 0, 1, 1, 1, 2)$, is of form $d_x(k) = c_n(x, k) \prod_{y,z} w(y, z)^{k_{y,z}}$

$c_n(x, k)$ is the number of equivalent paths of length n

record of visits is (3,1,4) — used by Carati

A. Carati, Thermodynamics and time averages, Physica A348, 110-120 (2005).

"Record of transitions" is more general than "Record of visits" because $\sum_y k_{x,y}$ is number of visits to state x
(neglecting the last state of the path)

The distribution $d_x(k)$ always belongs to the exponential family
(Boltzmann-Gibbs distribution)

$$d_x(k) = c_n(x, k) \exp(-\Psi_\theta(k))$$

with $\Psi_\theta(k) = -\sum_{x,y} k_{x,y} \ln w(x, y)$ (the entropy variable)

Consequence: $w(u, u)\langle k_{u,v}\rangle_x = \langle k_{u,u}\rangle_x w(u, v)$

This means that $\langle k_{u,v}\rangle_x$, the average number of transitions from u to v, is proportional to $w(u, v)$, the probability to go from u to v.

EXAMPLE

Let $p(x)$ be an arbitrary probability distribution

for example $p(x) = \frac{1}{Z}\exp_q(-\beta H(x))$

with deformed exponential $\exp_q$ and Hamiltonian $H(x)$

Detailed balance is satisfied with $w(x,y) = p(y)$, independent of x.

The distribution $d_x(k)$ is exponential with

$$\Psi_\theta(k) = -\sum_y \left(\sum_x k_{x,y}\right) \ln p(y)$$

$$= n \ln Z - \frac{1}{1-q}\sum_y \left(\sum_x k_{x,y}\right) \ln\left(1 - \beta(1-q)H(y)\right)$$

Only the distribution of visit records is needed!

4 Linear production of dynamical entropy

DYNAMIC STABILITY REQUIREMENT:

Because $d_x(k)$ is exponential, it satisfies the Maximum Entropy Principle for the Boltzmann-Gibbs entropy.

We have no choice of entropy!

Probability of a path $\gamma = (x_0, x_1, \cdots, x_n)$ of given length $n+1$ is $p(x_0)w(\gamma)$ with $w(\gamma) = w(x_0, x_1)w(x_1, x_2)\cdots w(x_{n-1}, x_n)$.

The dynamic entropy is $$S_\theta^{(n)} = -k_B \sum_\gamma p(\gamma_i) w(\gamma) \ln w(\gamma).$$

Notation $\gamma_i \equiv x_0$.

Result of calculation: $S_\theta^{(n)} = \sum_x p(x)\langle\Psi_\theta\rangle_x$ with $\langle\Psi_\theta\rangle_x = \sum_k d_x(k)\Psi_\theta(k)$.

The dynamic entropy is the average of the entropy variable.

THEOREM If p is stationary then $S_\theta^{(n)} = n \sum_x p(x) I_x$

with $I_x = -k_B \sum_y w(x,y) \ln w(x,y)$.

Dynamic entropy increases lineraly with every step of the Markov chain.

Proof ...

Example

If $w(x,y) = p(y)$ then $I_x = -k_B \sum_y p(y) \ln p(y) \equiv S(p)$.
In this case the dynamic entropy is n times the static B-G entropy.
In general is $S_\theta^{(n)} \leq nS(p)$.

5 Fluctuation theorem

- discovered in 1993 by Evans, Cohen and Morriss

D.J. Evans, E.G.D. Cohen, G.P. Morriss, *Probability of second law violations in shearing steady states,*

Phys. Rev. Lett. **71**, 2401-2404 (1993).

- "The probability of observing an entropy production opposite to that dictated by the second law of thermodynamics decreases exponentially with time." cfr Wikipedia

Inverted path of Markov chain: $(x_0, x_1, \cdots x_n)$ inverted is $(x_n, x_{n-1}, \cdots x_0)$.

Given initial state $x = x_0$ and transition record k, let $y = x_n$ denote the final state and $\overline{k}$ the transition record of the inverted path.

Let $$W_x(k) = \ln \frac{d_x(k)}{d_y(\overline{k})}$$ entropy production variable,

(called action variable by Lebowitz and Spohn)

J. Lebowitz, H. Spohn, J. Stat. Phys. **95**, 333 (1999)

Note that $W_x(k) = -\Psi_\theta(k) + \Psi_\theta(\overline{k})$.

FLUCTUATION THEOREM $$\frac{\text{Prob}(W_x(k) = K)}{\text{Prob}(W_x(k) = -K)} = e^K. \quad (*)$$

Proof: 4 lines ...

The probability distribution of the action variable $W_x(k)$ has symmetry (*).

EXAMPLE

$$q(K) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(K-K_0)^2/2\sigma^2} \text{ satisfies } \frac{q(K)}{q(-K)} = e^K$$
when $\sigma = 1/\sqrt{2}\pi$ and $K_0 = 1/4\pi$.

Experimental verification ... and verification by computer simulations

NOTE The fluctuation theorem holds for more general systems than Markov chains!

D.J. Evans, E.G.D. Cohen, G.P. Morriss, *Probability of second law violations in shearing steady states,*
Phys. Rev. Lett. **71**, 2401-2404 (1993).

S. Ciliberto, C. Laroche, *An experimental test of the Gallavotti-Cohen fluctuation theorem*
Journal de physique IV, **8**, 215-219 (1998).

G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles, D.J. Evans, *Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales,*
Phys. Rev. Lett. **89**, 050601 (2002).

D.M. Carberry, J.C. Reid, G.M. Wang, E.M. Sevick, D.J. Searles, D.J. Evans, *Fluctuations and Irreversibility: An Experimental Demonstration of a Second-Law-Like Theorem Using a Colloidal Particle Held in an Optical Trap,*
Phys. Rev. Lett. **92**, 140601 (2004).

...

NOTE Other fluctuation theorems exist, for example that of Crooks

G.E. Crooks, *Entropy production fluctuation theorem and the nonequilibrium work relation for free-energy differences*,
Phys. Rev. E**60**, 2721-2726 (1999).

The thermodynamic entropy production is the average of the entropy production variable $W_x(k)$.

$$\sum_x p(x)\langle W_x\rangle_x = \overline{S}_\theta^{(n)} - S_\theta^{(n)} \geq 0.$$

THEOREM If p is stationary then $\overline{S}_\theta^{(n)} - S_\theta^{(n)} = n\Delta S$

with $\Delta S = \frac{1}{2}\sum_{x,y}\left(p(x)w(x,y) - p(y)w(y,x)\right)\ln\frac{p(x)w(x,y)}{p(y)w(y,x)}$.

P. Gaspard, *Time-Reversed Dynamical Entropy and Irreversibility in Markovian Random Processes,*

J. Stat. Phys. **117**, 599-615 (2004).

The entropy production is zero
when the detailed balance condition holds.

6 A one-parameter model

The model is determined by a symmetric matrix $a_{x,y}$ indexed by the states x, y of the Markov chain. Fix one parameter $\xi > 0$.

Example of Glauber dynamics $\quad a_{x,y} = \max\{H(x), H(y)\}$ with Hamiltonian $H(x)$ In this case is $\xi = \beta$, the inverse temperature.

Introduce a partition function $\Xi(\xi) = \sum_{x,y} e^{-\xi a_{x,y}}$.

Then $p(x)$ and $w(x, y)$ are given by

$$p(x) = \frac{1}{\Xi(\xi)} \sum_{y} e^{-\xi a_{x,y}} \quad \text{and} \quad w(x, y) = \frac{1}{\Xi(\xi)p(x)} e^{-\xi a_{x,y}}.$$

Detailed balance is satisfied $\quad (p(x)w(x,y) = \dfrac{1}{\Xi(\xi)} e^{-\xi a_{x,y}}$ is symmetric).

$\ln \Xi(\xi)$ is a Massieu function - it satisfies

$$\frac{\mathrm{d}}{\mathrm{d}\xi} \ln \Xi(\xi) = -\sum_{x,y} p(x)w(x,y)a_{x,y} \equiv -\langle a \rangle.$$

and $$\ln \Xi(\xi) = S(p) + \frac{1}{n} S_\theta^{(n)} - \xi \langle a \rangle.$$

Compare with

$$\frac{\mathrm{d}}{\mathrm{d}\beta} \ln Z(\beta) = -\sum_{x} p(x)H(x) \equiv -\langle H \rangle$$

and $$\ln Z(\beta) = S(p) - \beta \langle H \rangle.$$

CONCLUSION This model extends thermostatistics to path-depending 'Hamiltonians' $a_{x,y}$.

7 Two-parameter extension

Notation Add an index 0 to quantities of the 1-parameter model

Let be given an anti-symmetric matrix $\epsilon_{x,y}$ and
a solution r_y of the eigenvalue equation $$\sum_y w_0(x,y)\epsilon_{x,y}r_y = 0 \quad (*).$$

Given ζ, let $w(x,y) = w_0(x,y)(1+\zeta b_{x,y})$ with $b_{x,y} = r_x \epsilon_{x,y} r_y$.

> $|\zeta|$ should not be too large so that $w(x,y) \geq 0$ holds.
> $\sum_y w(x,y) = 1$ follows using (*).

CALCULATION $p_0(x)$ is the stationary state independent of ζ

CALCULATION $\langle \epsilon \rangle = \zeta \sum_{x,y} p_0(x) w_0(x,y) r_x \epsilon^2_{x,y} r_y = \zeta \langle b\epsilon \rangle_0$.

Linear response theory is exact in this model!

FURTHER CALCULATIONS

Dynamic entropy variable $\Psi_\theta(k) = \Psi_\theta^0(k) - \sum_{x,y} k_{x,y} \ln(1 + \zeta b_{x,y})$.

Distribution of transition records $d_x(k) = d_x^0(k) \prod_{x,y} (1 + \zeta b_{x,y})^{k_{x,y}}$.

NOTE $\langle \epsilon \rangle = \zeta \langle b\epsilon \rangle_0$ and $\langle a \rangle = \langle a \rangle_0$

(using $\langle ab \rangle_0 = 0$ and the fact that ab is antisymmetric)

Hence, in general is $\frac{\partial}{\partial \xi}\langle \epsilon \rangle \neq \frac{\partial}{\partial \zeta}\langle a \rangle$. This implies the non-existence of a Massieu function $\Phi(\xi, \zeta)$ such that $\frac{\partial \Phi}{\partial \xi} = -\langle a \rangle$ and $\frac{\partial \Phi}{\partial \zeta} = -\langle \epsilon \rangle$.

EXERCISE Consider the 3-state model with

$$w_0(x,y) = \begin{pmatrix} 1-2w & w & w \\ w & 1-2w & w \\ w & w & 1-2w \end{pmatrix} \text{ and } \quad p_0(x) = \frac{1}{3}\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

Let $\epsilon = \begin{pmatrix} 0 & 1 & -1 \\ -1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix}$ and $r = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$. ($|\zeta| < 1$ is needed)

Show that $\langle \epsilon \rangle = 2w\zeta$ and $\Delta S = 2\zeta w \ln \dfrac{1+\zeta}{1-\zeta}$

8 Summary

- It is easy to derive the fluctuation theorem in the context of Markov chains
- The distribution of transition records is a natural tool
- In the Markov case it belongs automatically to the exponential family
- A related concept is the record of visits, used by Carati
- In the stationary case, the entropy production increases linearly in the number of steps
- The one-parameter model generalizes thermostatistics to path-dependent generators
- Still open is the problem of formulating thermodynamics for stationary non-equilibrium states.