THE THERMODYNAMIC ARROW OF TIME AT THE NANOSCALE

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- **INTRODUCTION: TEMPORAL DISORDER & CHAOS THEORY**
- **ENTROPY PRODUCTION & TIME ASYMMETRY OF TEMPORAL DISORDER**
- **MOLECULAR MOTORS & COPOLYMERIZATIONS**
- **CONCLUSIONS**

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Indian Institute of Technology Madras, Chennai, India, 9-10 November 2008

TEMPORAL DISORDER alias DYNAMICAL RANDOMNESS

In random processes, the probability of a typical path sampled at scale ε decays as

$$P(\omega) = P(\omega_0\, \omega_1\, \omega_2\, \ldots\, \omega_{n-1}) \sim \exp(-h\, \Delta t\, n)$$

The temporal disorder (dynamical randomness) is characterized by the entropy per unit time:

$$h(\varepsilon) = \lim_{n\to\infty} (-1/n\Delta t) \sum_{\omega} P(\omega) \ln P(\omega)$$

Origin in a closed system with a microscopic Newtonian dynamics: microscopic chaos
Kolmogorov-Sinai entropy per unit time:

$$h_{\mathrm{KS}} = \mathrm{Sup}_{\varepsilon}\, h(\varepsilon)$$

Gas of hard spheres of diameter σ and mass *m* at temperature *T* and density *n*:
Pesin's identity: (Dorfman & van Beijeren)

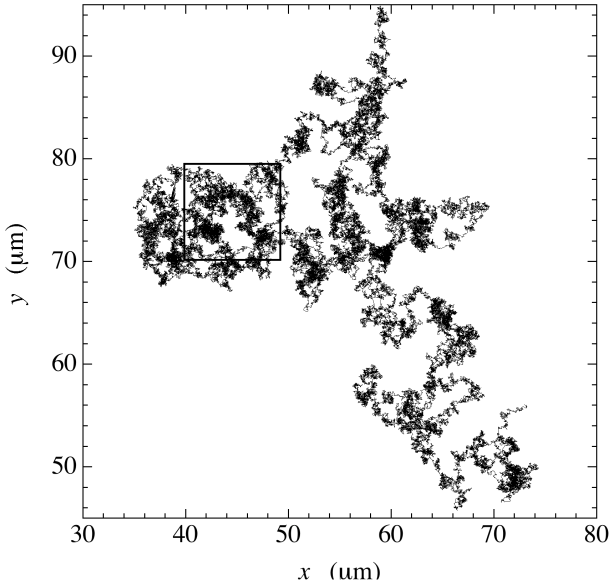
$$h_{\mathrm{KS}} = \sum_{\lambda_i > 0} \lambda_i = 4\, n^2 \sigma^2 \sqrt{\frac{\pi k_{\mathrm{B}} T}{m}} \ln \frac{3.9}{\pi n \sigma^3}$$

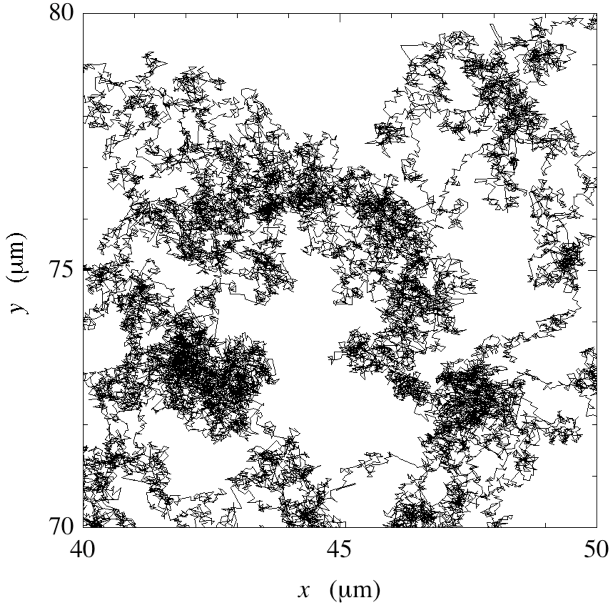
Equilibrium Brownian motion of diffusion coefficient *D*:
entropy per unit time at spatial scale ε

$$h(\varepsilon) \propto \frac{D}{\varepsilon^2}$$

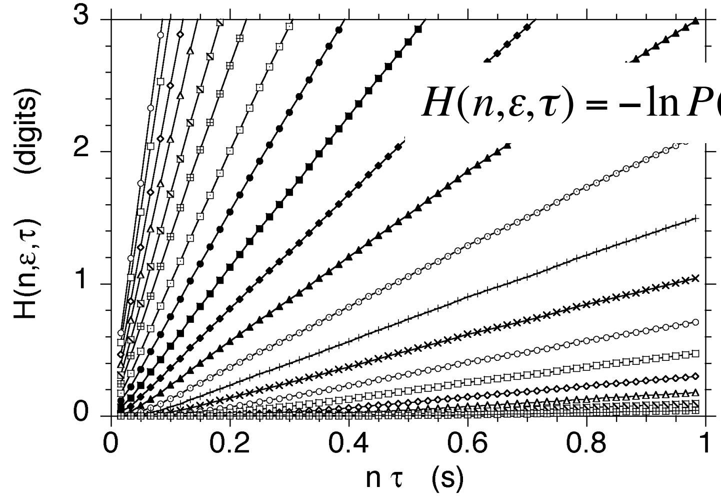
TEMPORAL DISORDER OF BROWNIAN MOTION

thermodynamic equilibrium





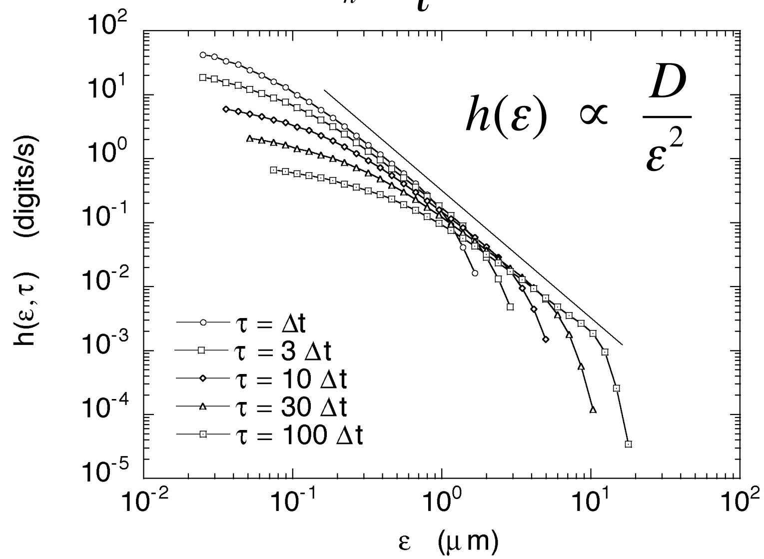
entropy H at spatial scale ε and sampling time τ



$$H(n,\varepsilon,\tau) = -\ln P(\omega_0 \omega_1 \dots \omega_{n-1})$$

entropy per unit time h at spatial scale ε

$$h(\varepsilon,\tau) = \lim_{n\to\infty} \frac{1}{\tau}\left[H(n+1,\varepsilon,\tau) - H(n,\varepsilon,\tau)\right]$$



$$h(\varepsilon) \propto \frac{D}{\varepsilon^2}$$

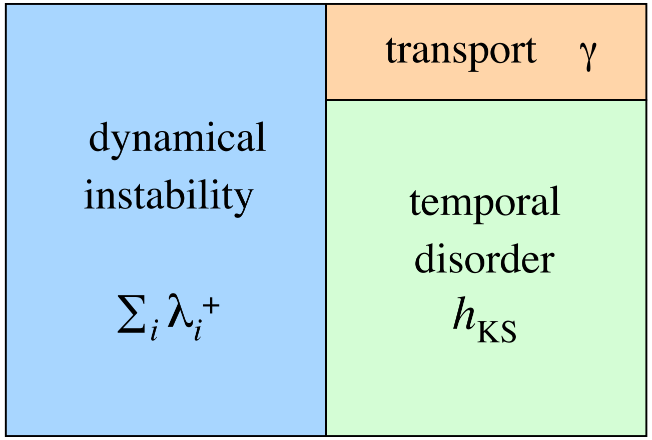
P. Gaspard, M. E. Briggs, M. K. Francis, J. V. Sengers, R. W. Gammon, J. R. Dorfman, & R. V. Calabrese, Nature **394** (1998) 865.

ESCAPE-RATE THEORY:
CHAOS-TRANSPORT RELATIONSHIP

Combining transport theory with dynamical systems theory,
we obtain a relationship giving the transport coefficient α in terms of the Lyapunov exponents λ_i and the Kolmogorov-Sinai entropy per unit time $h_{\rm KS}$:

$$\alpha = \lim_{L,V\to\infty} \left(\frac{L}{\pi}\right)^2 \left(\sum_{\lambda_i>0} \lambda_i - h_{\rm KS}\right)_L$$

large-deviation dynamical relationship



Out of equilibrium, the system has a lower temporal disorder (dynamical randomness)
than possible by its dynamical instability.

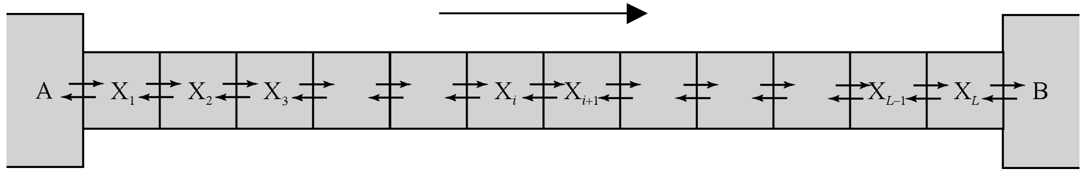
P. Gaspard & G. Nicolis, Phys. Rev. Lett. **65** (1990) 1693; J. R. Dorfman & P. Gaspard, Phys. Rev. E **51** (1995) 28

NONEQUILIBRIUM SYSTEMS MANIFEST DYNAMICAL ORDER

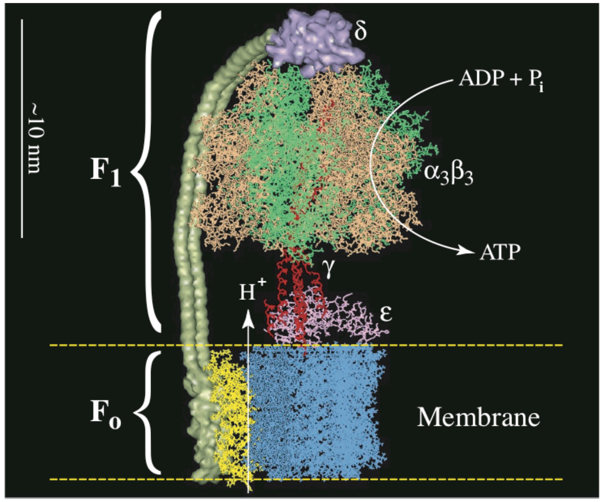
Energy supply

diffusion
electric conduction

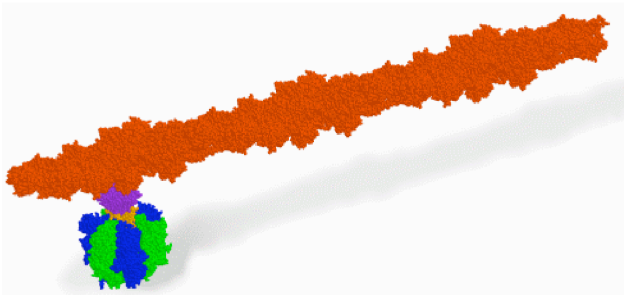
between two reservoirs

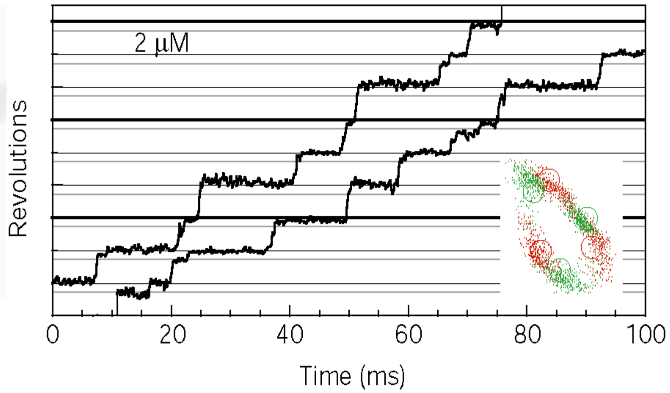


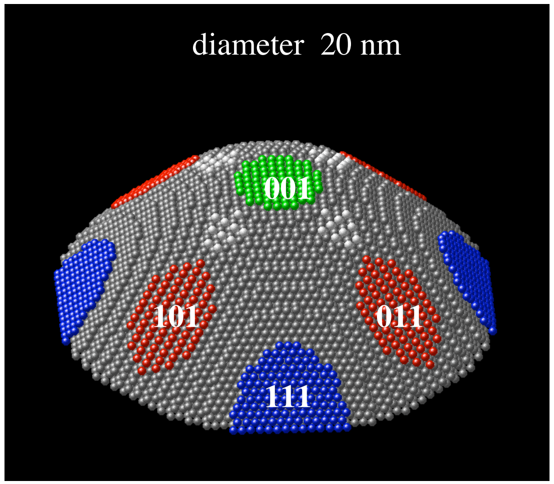
molecular motor: F_oF_1-ATPase



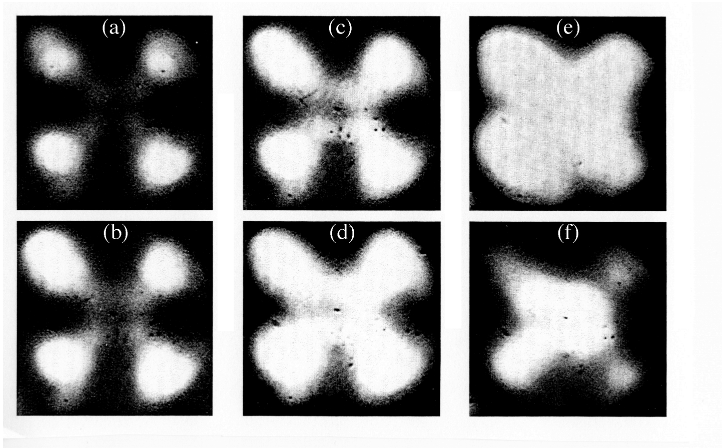
K. Kinosita and coworkers (2001): F_1-ATPase + filament/bead

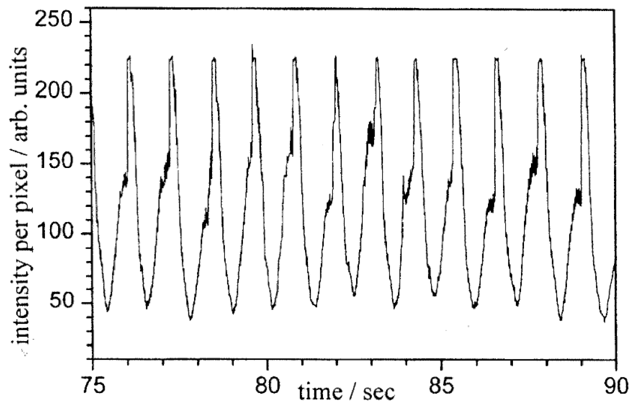






C. Voss and N. Kruse (1996): $NO_2/H_2/Pt$ catalytic reaction





BREAKING OF TIME-REVERSAL SYMMETRY $\Theta(\mathbf{r},\mathbf{v}) = (\mathbf{r},-\mathbf{v})$

Newton's equation of mechanics is time-reversal symmetric
if the Hamiltonian H is even in the momenta.

Liouville equation of statistical mechanics,
ruling the time evolution of the probability density p
is also time-reversal symmetric.

$$\frac{\partial p}{\partial t} = \{H, p\} = \hat{L}p$$

The solution of an equation may have a lower symmetry than the equation itself
(spontaneous symmetry breaking).

Typical Newtonian trajectories $\boldsymbol{T}$ are different from their time-reversal image $\Theta\,\boldsymbol{T}$:

$$\Theta\,\boldsymbol{T} \neq \boldsymbol{T}$$

Irreversible behavior is obtained by weighting differently
the trajectories $\boldsymbol{T}$ and their time-reversal image $\Theta\,\boldsymbol{T}$ with a probability measure.

<u>Spontaneous symmetry breaking</u>: *relaxation modes of an autonomous system*

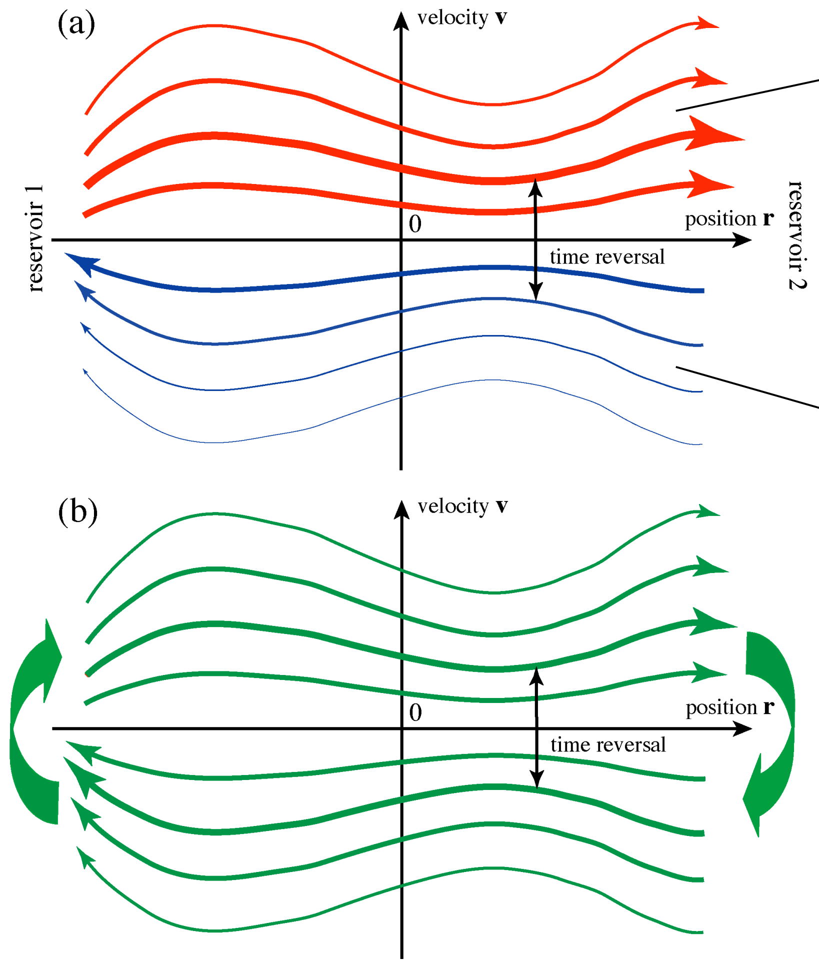
<u>Explicit symmetry breaking</u>: *nonequilibrium steady state by the boundary conditions*

P. Gaspard, Physica A **369** (2006) 201-246.

2nd LAW OF THERMODYNAMICS AND TIME ASYMMETRY IN THE STATISTICAL DESCRIPTION

nonequilibrium

entropy production
energy dissipation



most probable trajectories

Asymmetry under time reversal

less probable reversed trajectories

equilibrium

constant entropy

Symmetry under time reversal

Thanks to the fluctuations, the reversed trajectories are observables, even if their probability is small.

Remark: Microreversibility is always satisfied.

TEMPORAL DISORDER OF TIME-REVERSED PATHS

nonequilibrium steady state: $P\,(\omega_0\,\omega_1\omega_2 \ldots \omega_{n-1}) \neq P\,(\omega_{n-1} \ldots \omega_2\,\omega_1\,\omega_0)$

If the probability of a typical path decays as

$$P(\boldsymbol{\omega}) = P(\omega_0\,\omega_1\,\omega_2\,\ldots\,\omega_{n-1}) \sim \exp(\,-h\,\Delta t\,n\,)$$

the probability of the time-reversed path decays as

$$P(\boldsymbol{\omega}^{\mathrm{R}}) = P(\omega_{n-1}\,\ldots\,\omega_2\,\omega_1\,\omega_0) \sim \exp(\,-h^{\mathrm{R}}\,\Delta t\,n\,) \qquad \text{with } h^{\mathrm{R}} \neq h$$

entropy per unit time: temporal disorder (dynamical randomness)

$$h = \lim_{n\to\infty} (-1/n\Delta t) \sum_{\boldsymbol{\omega}} P(\boldsymbol{\omega}) \ln P(\boldsymbol{\omega})$$

time-reversed entropy per unit time: P. Gaspard, J. Stat. Phys. **117** (2004) 599

$$h^{\mathrm{R}} = \lim_{n\to\infty} (-1/n\Delta t) \sum_{\boldsymbol{\omega}} P(\boldsymbol{\omega}) \ln P(\boldsymbol{\omega}^{\mathrm{R}})$$

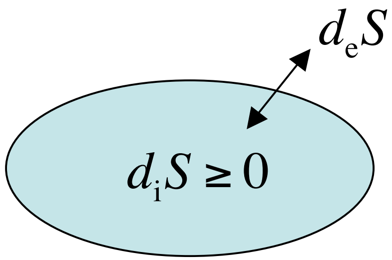
The time-reversed entropy per unit time characterizes

the temporal disorder (dynamical randomness) of the time-reversed paths.

THERMODYNAMIC ENTROPY PRODUCTION

Second law of thermodynamics: entropy S

$$\frac{dS}{dt} = \frac{d_{\mathrm{e}}S}{dt} + \frac{d_{\mathrm{i}}S}{dt} \qquad \text{with} \qquad \frac{d_{\mathrm{i}}S}{dt} \geq 0$$



entropy flow

entropy production

Entropy production:

$$\frac{1}{k_{\mathrm{B}}} \frac{d_{\mathrm{i}}S}{dt} = h^{\mathrm{R}} - h \geq 0$$

P. Gaspard, J. Stat. Phys. **117** (2004) 599

$$\frac{P(\underline{\omega})}{P(\underline{\omega}^{\mathrm{R}})} = \frac{P(\omega_0\omega_1\omega_2 \dots \omega_{n-1})}{P(\omega_{n-1} \dots \omega_2\omega_1\omega_0)} \approx \mathrm{e}^{n\Delta t\left(h^{\mathrm{R}} - h\right)} = \mathrm{e}^{\frac{n\Delta t}{k_{\mathrm{B}}} \frac{d_{\mathrm{i}}S}{dt}}$$

Property: $h^{\mathrm{R}} \geq h$

$$\frac{1}{k_{\mathrm{B}}} \frac{d_{\mathrm{i}}S}{dt} = \lim_{n \to \infty} \frac{1}{n\Delta t} \sum_{\underline{\omega}} P(\underline{\omega}) \ln \frac{P(\underline{\omega})}{P(\underline{\omega}^{\mathrm{R}})} \geq 0 \qquad \text{(relative entropy)}$$

equality iff $P(\omega) = P(\omega^{\mathrm{R}})$ (detailed balance) which holds at equilibrium.

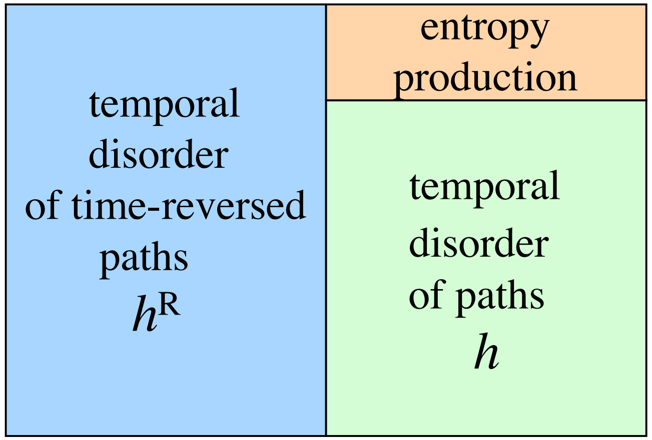
C. Maes and K. Netocny, J. Stat. Phys. **110** (2003) 269

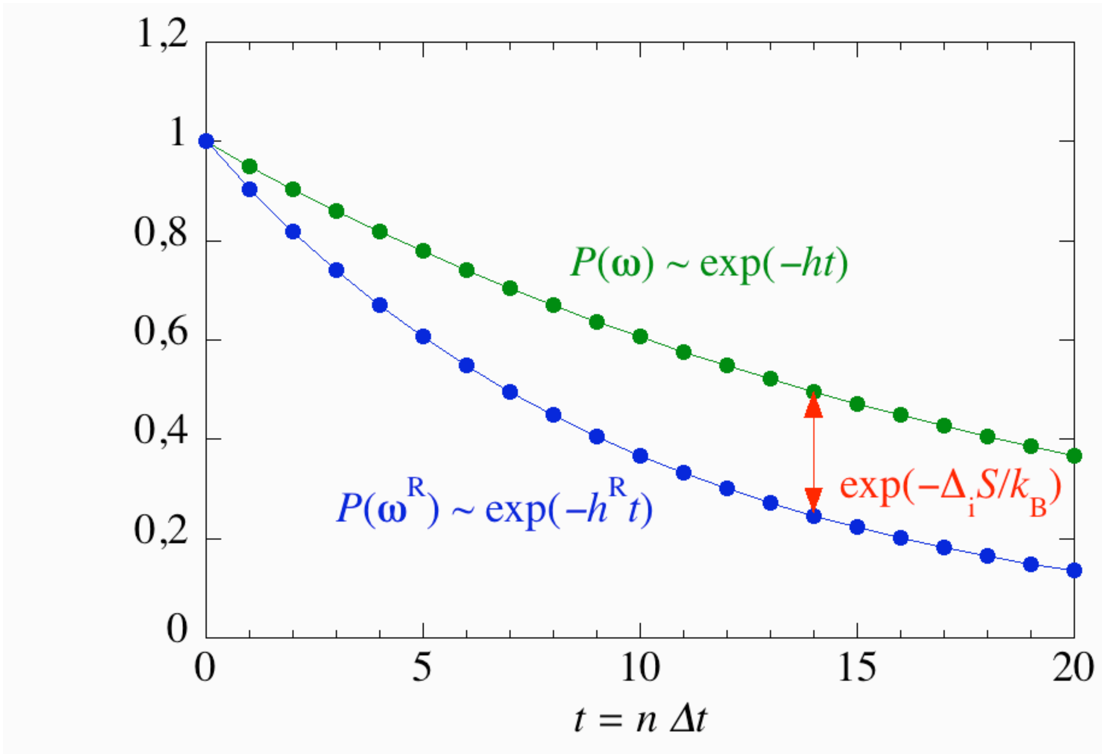
TIME ASYMMETRY IN TEMPORAL DISORDER

nonequilibrium steady state:

thermodynamic entropy production:

$$\frac{1}{k_{\mathrm{B}}}\frac{d_{\mathrm{i}}S}{dt} = h^{\mathrm{R}} - h \geq 0$$





P. Gaspard, J. Stat. Phys. **117** (2004) 599

If the probability of a typical path decays as

$$P(\underline{\omega}) = P(\omega_0\omega_1\omega_2\ldots\,\omega_{n-1}) \approx \exp\left(-n\,\Delta t\;h\right)$$

the probability of the corresponding time-reversed path decays faster as

$$P(\underline{\omega}^{\mathrm{R}}) = P(\omega_{n-1}\ldots\,\omega_2\omega_1\omega_0) \approx \exp\left(-n\,\Delta t\;h^{\mathrm{R}}\right) = \exp\left(-n\,\Delta t\;h\right)\,\exp\left(-n\,\Delta t\;\frac{d_{\mathrm{i}}S}{dt}\right)$$

The thermodynamic entropy production is due to a time asymmetry in temporal disorder.

OUT-OF-EQUILIBRIUM TEMPORAL ORDERING

thermodynamic entropy production = temporal disorder h^{R} of time-reversed paths
– temporal disorder h of typical paths
= time asymmetry in temporal disorder

Theorem of temporal ordering as a corollary of the second law:
In nonequilibrium steady states, the typical paths are more ordered **in time** *than the corresponding time-reversed paths, in the sense that* $h < h^{\mathrm{R}}$.

Temporal ordering is possible out of equilibrium at the expense of the increase of phase-space disorder.

There is thus no contradiction with Boltzmann's interpretation of the second law.

It shows in a quantitative way that nonequilibrium processes can generate dynamical order and information.

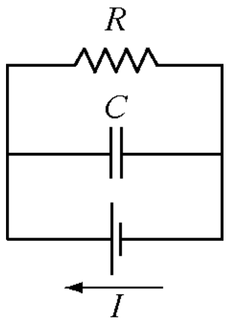
Remark: This is a key feature of biological phenomena.

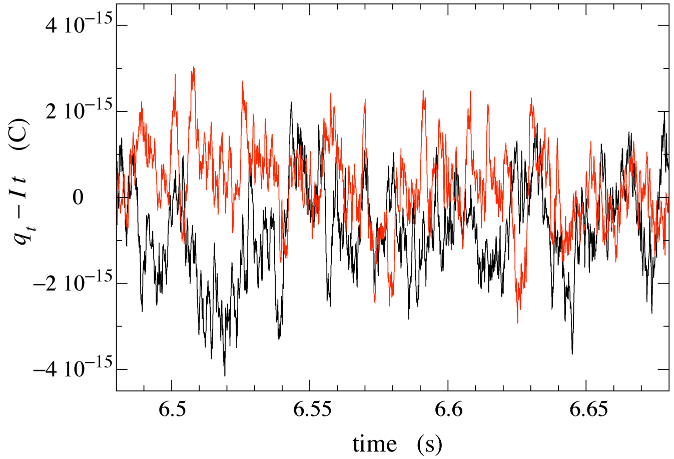
OUT-OF-EQUILIBRIUM FLUCTUATING SYSTEMS

RC **electric circuit**

(Nyquist thermal noise)

(Ciliberto et al.)



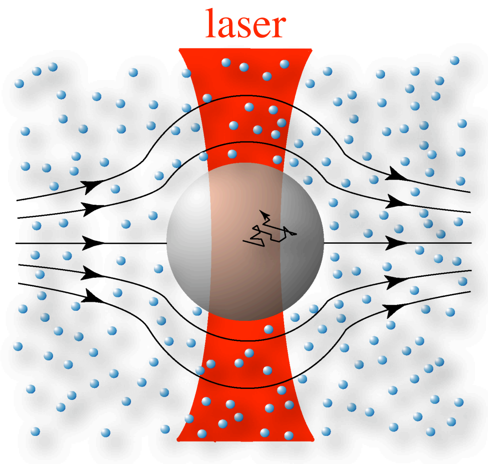


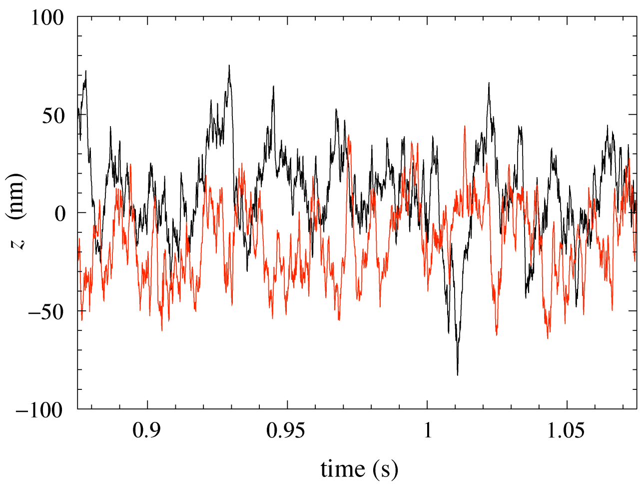
Brownian particle

in an optical trap

and a flow

(Ciliberto et al.)

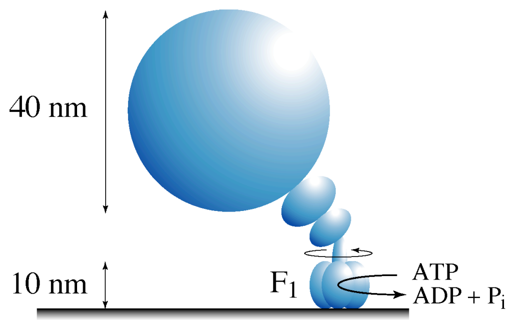


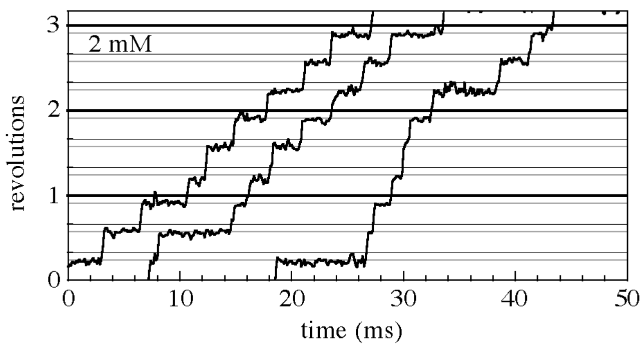


Molecular motor

F_1-ATPase

(Kinosita et al., 2001)





DRIVEN BROWNIAN MOTION

Polystyrene particle of 2 μm diameter
in a 20% glycerol-water solution at temperature 298 K, driven by an optical tweezer.

relaxation time: $\tau_R = \alpha / k = 3.05\ 10^{-3}\,\text{s}$

trap stiffness: $k = 9.62\ 10^{-6}\ \text{kg s}^{-2}$

trap velocity: $u = \pm\ 4.24\ \mu\text{m/s}$

friction α

driving force: $F = -k(x - ut)$

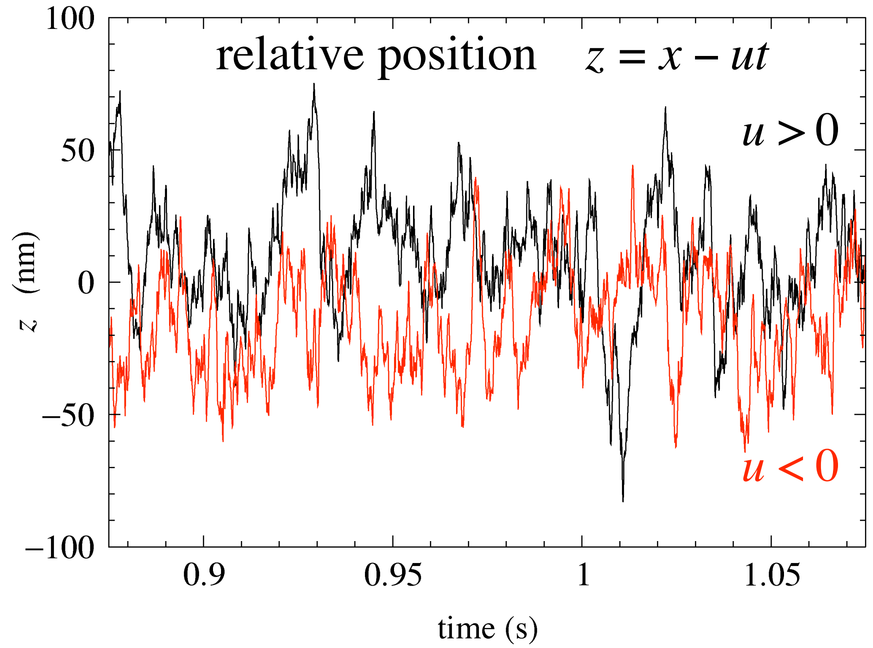
Langevin equation: $\dfrac{dx}{dt} = -\dfrac{x-ut}{\tau_R} + \sqrt{\dfrac{2k_\mathrm{B}T}{\alpha}}\,\xi_t$

position x

white noise ξ_t

dissipated heat: $Q_t = -k\int_0^t \dot{x}_{t'}\ (x_{t'} - ut')\ dt'$

mean dissipated heat: $\langle Q_t \rangle = \alpha\, u^2 t$



D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, Phys. Rev. Lett. **98** (2007) 150601

PATH PROBABILITIES OF NONEQUILIBRIUM FLUCTUATIONS

comoving frame of reference: $z \equiv x - ut$ $\qquad \dfrac{dz}{dt} = -\dfrac{z}{\tau_R} - u + \sqrt{\dfrac{2}{\alpha\beta}}\,\xi_t$ $\qquad \beta \equiv \dfrac{1}{k_{\mathrm{B}} T}$

stationary probability density: $$p_{\mathrm{st}}(z) = \sqrt{\frac{\beta k}{2\pi}} \exp\left[-\frac{\beta k}{2}(z + u\tau_R)^2\right]$$

path probability: $$P_{\mathrm{sign}\,u}\left[z_t \middle| z_0\right] \propto \exp\left[-\frac{\alpha\beta}{4}\int_0^t dt'\left(\dot{z}_{t'} + k z_{t'} + u\right)^2\right]$$

ratio of probabilities for u>0 and u<0:

$$\ln \frac{P_+\left[z_t \middle| z_0\right]}{P_-\left[z_t^{\mathrm{R}} \middle| z_0^{\mathrm{R}}\right]} = -\frac{\beta k}{2}\left(z_t^2 - z_0^2\right) - \beta k\, u \int_0^t z_{t'}\, dt' = \beta Q_t$$

heat generated by dissipation: $Q_t = W_t - \Delta V_t$

thermodynamic entropy production: $$\frac{d_{\mathrm{i}}S}{dt} = \lim_{t\to\infty}\frac{1}{t}\frac{\langle Q_t\rangle}{T} = \lim_{t\to\infty}\frac{k_{\mathrm{B}}}{t}\int Dz_t\; P_+\left[z_t\right]\,\ln\frac{P_+\left[z_t\right]}{P_-\left[z_t^{\mathrm{R}}\right]}$$

D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, Phys. Rev. Lett. **98** (2007) 150601

RELATIONSHIP TO TEMPORAL DISORDER

path: $\mathbf{Z}_m = \left[z(m\tau),\ldots,z(m\tau + n\tau - \tau)\right]$

path probability: $P_+\left[\mathbf{Z}_m\right] = P\left[\left|z(m\tau) - z(j\tau)\right| < \varepsilon,\ldots,\left|z(m\tau + n\tau - \tau) - z(j\tau + n\tau - \tau)\right| < \varepsilon\right]$

algorithm of time series analysis by Grassberger & Procaccia (1980's)

(ε,τ)-entropy: $$H(\varepsilon,\tau,n) = -\frac{1}{M}\sum_{m=1}^{M}\ln P_+\left[\mathbf{Z}_m\right]$$

time-reversed (ε,τ)-entropy: $$H^{\mathrm{R}}(\varepsilon,\tau,n) = -\frac{1}{M}\sum_{m=1}^{M}\ln P_-\left[\mathbf{Z}_m^{\mathrm{R}}\right]$$

(ε,τ)-entropy per unit time: $$h(\varepsilon,\tau) = \lim_{n\to\infty}\frac{1}{\tau}\left[H(\varepsilon,\tau,n+1) - H(\varepsilon,\tau,n)\right]$$

time-reversed (ε,τ)-entropy per unit time: $$h^{\mathrm{R}}(\varepsilon,\tau) = \lim_{n\to\infty}\frac{1}{\tau}\left[H^{\mathrm{R}}(\varepsilon,\tau,n+1) - H^{\mathrm{R}}(\varepsilon,\tau,n)\right]$$

thermodynamic entropy production: $$\frac{d_{\mathrm{i}}S}{dt} = k_{\mathrm{B}}\lim_{\varepsilon,\tau\to 0}\left[h^{\mathrm{R}}(\varepsilon,\tau) - h(\varepsilon,\tau)\right]$$

D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, Phys. Rev. Lett. **98** (2007) 150601

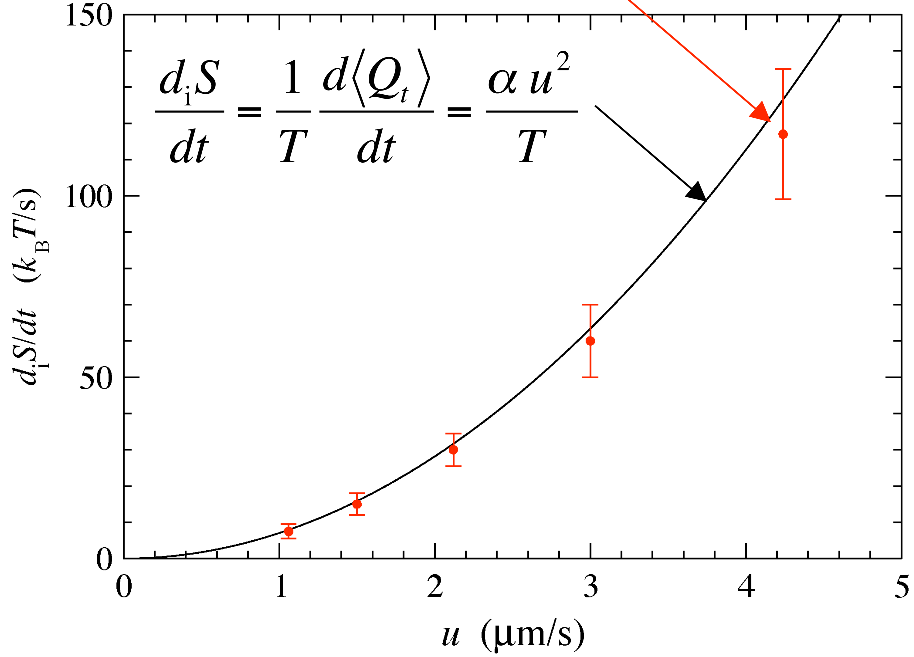
DRIVEN BROWNIAN MOTION

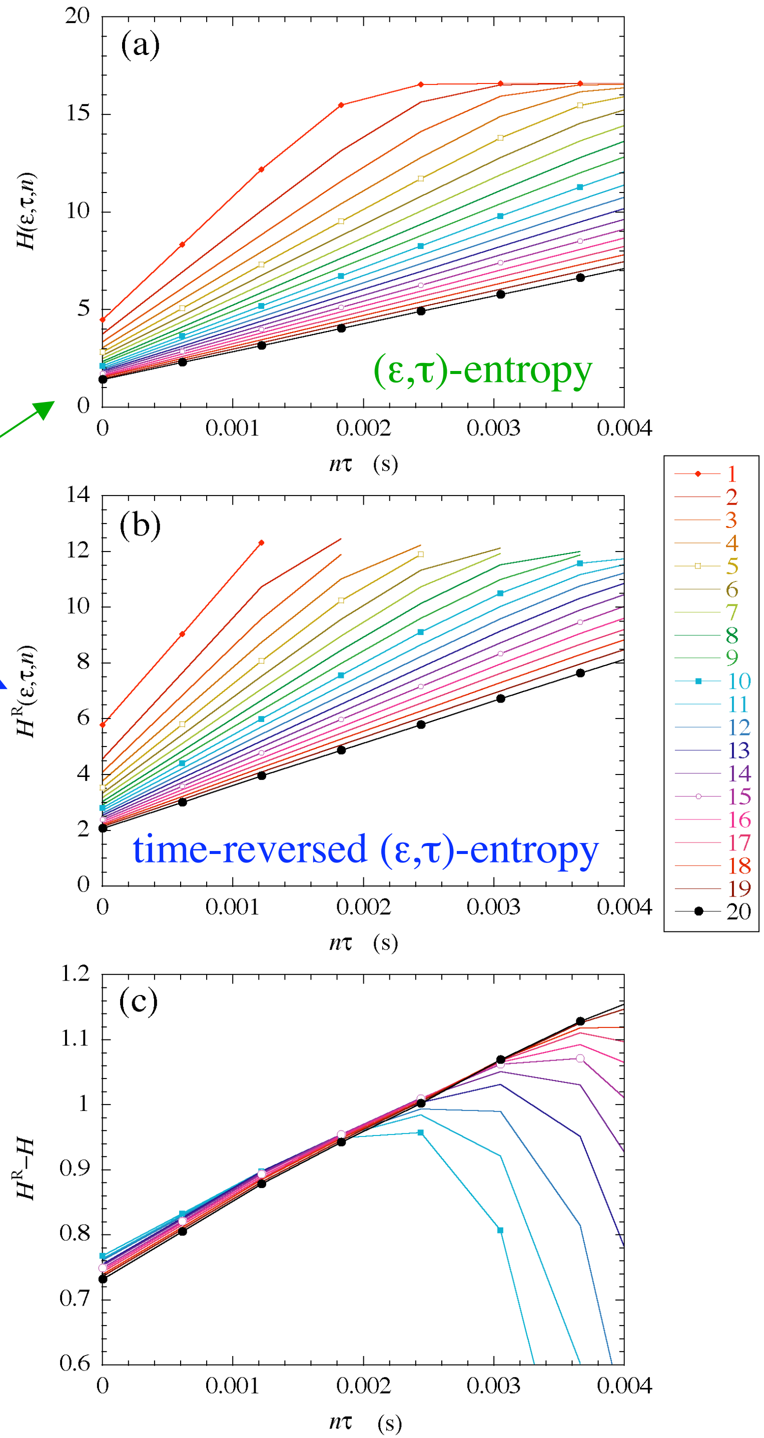
time series: $2\ 10^7$ sampling frequency: 8192 Hz

resolution: $\varepsilon = k\ 0.558$ nm $\quad k = 1 - 20$

thermodynamic entropy production:

$$\frac{d_i S}{dt} = k_B \lim_{\varepsilon,\tau\to\infty} \left[h^R(\varepsilon,\tau) - h(\varepsilon,\tau) \right]$$





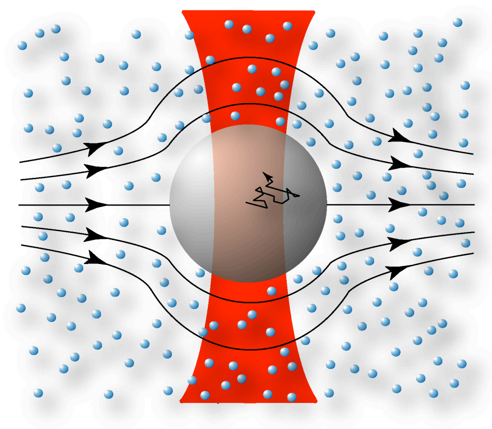
D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, Phys. Rev. Lett. **98** (2007) 150601

BROWNIAN PARTICLE OUT OF EQUILIBRIUM

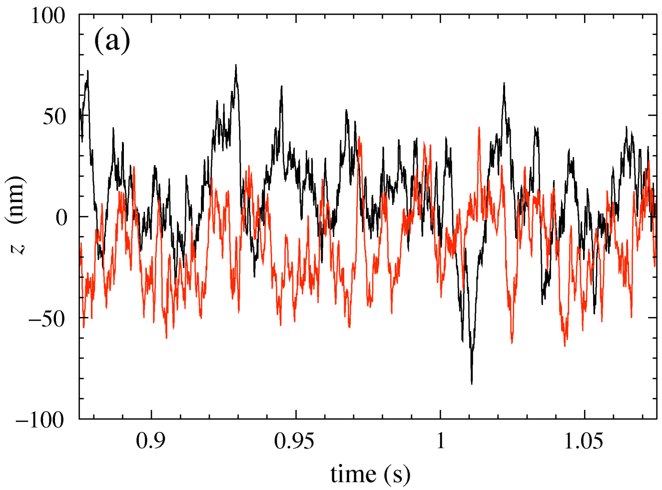
D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, J. Stat. Mech. (2008) P01002

particle of 2 μm diameter in an optical trap and a flow of speed u

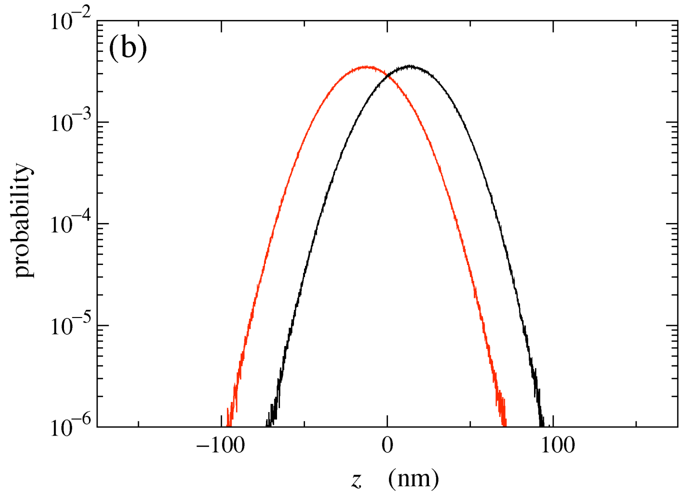
laser



trajectories for u and $-u$

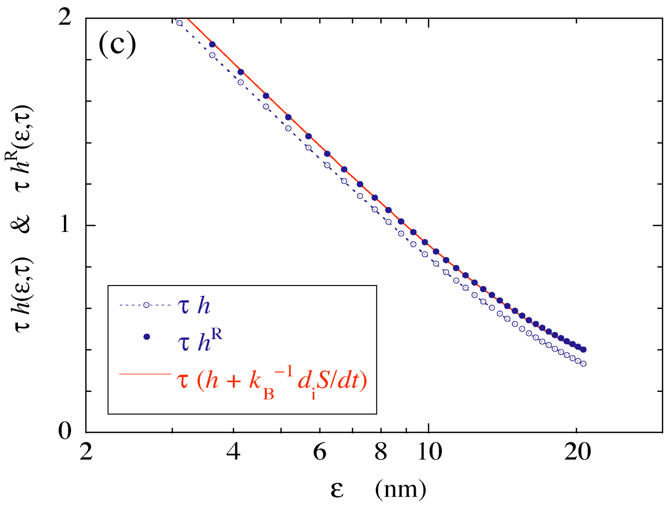


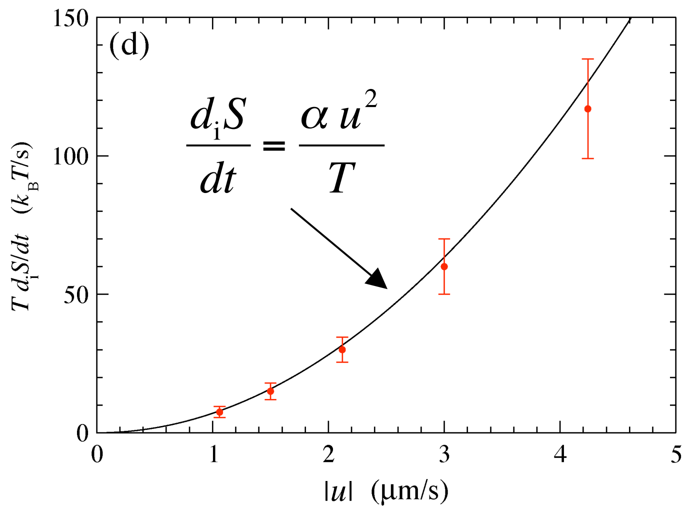
probability distributions of position



Temporal disorders
of typical and reversed
trajectories

Their difference
is the production
of thermodynamic entropy



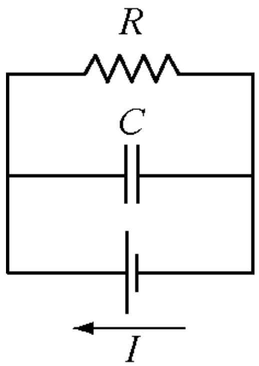


Irreversibility is observed down to the nanoscale.

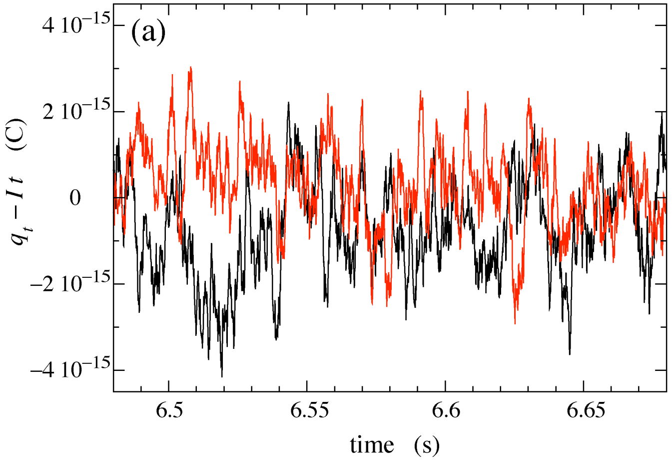
RC ELECTRIC CIRCUIT OUT OF EQUILIBRIUM

D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, J. Stat. Mech. (2008) P01002

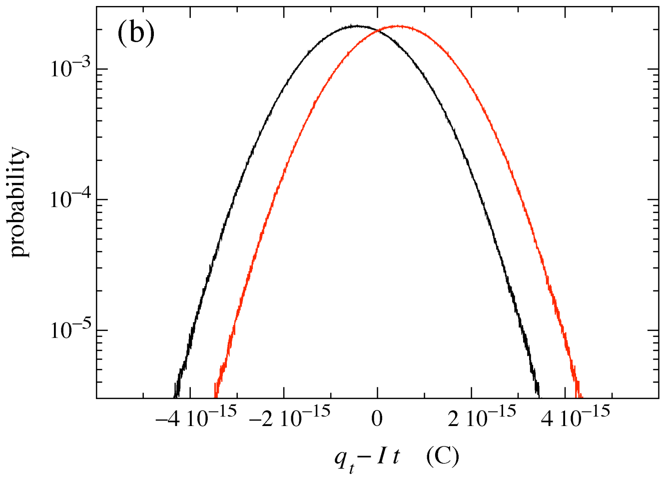
$R = 9.22\ \text{M}\Omega$ $\qquad C = 278\ \text{pF}$ $\qquad \tau_R = RC = 2.56\ \text{ms}$



paths for I and $-I$



probability distributions of charges



Temporal disorders
of typical and reversed
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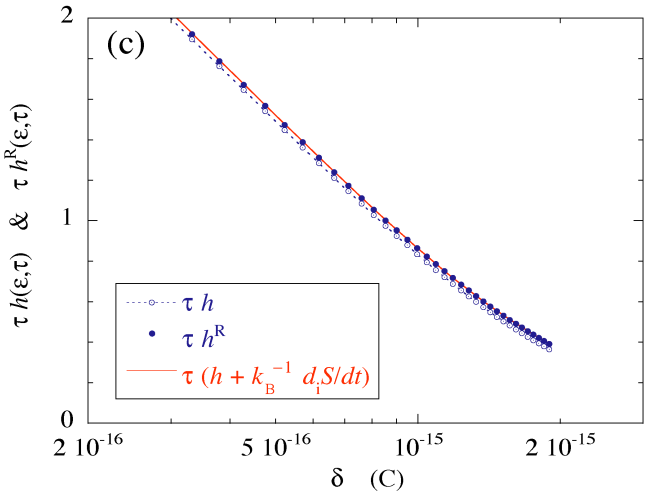
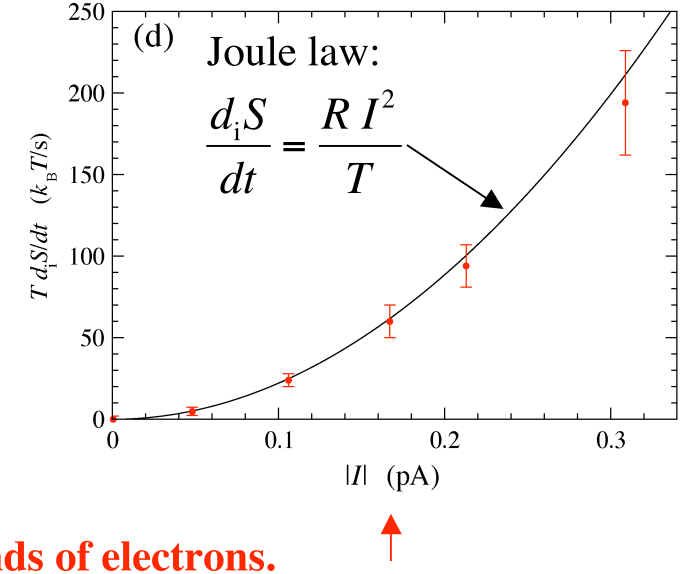
Their difference
is the production
of thermodynamic entropy





Irreversibility is observed down to fluctuations of several thousands of electrons.

COMPARISON WITH THE FLUCTUATION THEOREM

fluctuating heat dissipation over a time interval t : $\qquad \zeta \approx \dfrac{Q_t}{tT}$

decay rate of the probability of such a fluctuation:

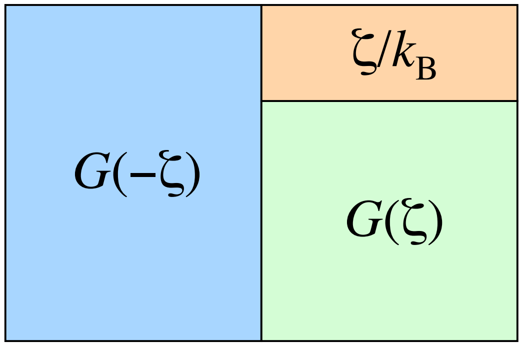
$$G(\zeta) = \lim_{t\to\infty} \; -\frac{1}{t}\ln \mathrm{Prob}\left\{\zeta < \frac{Q_t}{tT} < \zeta + d\zeta\right\}$$

Fluctuation theorem: $\qquad \zeta = k_{\mathrm{B}}\left[G(-\zeta) - G(\zeta)\right] \qquad \text{for} \quad -\langle\zeta\rangle < \zeta < \langle\zeta\rangle$

thermodynamic entropy production = mean value of ζ : $\qquad \left.\dfrac{d_{\mathrm{i}}S}{dt}\right|_{\mathrm{st}} = \langle\zeta\rangle \geq 0$

$$G(\langle\zeta\rangle) = 0$$

$$\langle\zeta\rangle = k_{\mathrm{B}}G(-\langle\zeta\rangle)$$



$$\left.\frac{d_{\mathrm{i}}S}{dt}\right|_{\mathrm{st}} = \langle\zeta\rangle = k_{\mathrm{B}}\left[h^{\mathrm{R}}(\varepsilon,\tau) - h(\varepsilon,\tau)\right]$$

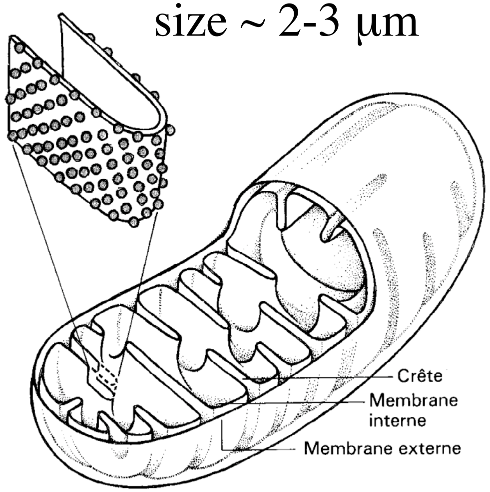
$$h^{\mathrm{R}}(\varepsilon,\tau) \geq G(-\langle\zeta\rangle)$$

ε can go down to the nanoscale

MOLECULAR MOTORS IN MITOCHONDRIA

size ~ 2-3 μm

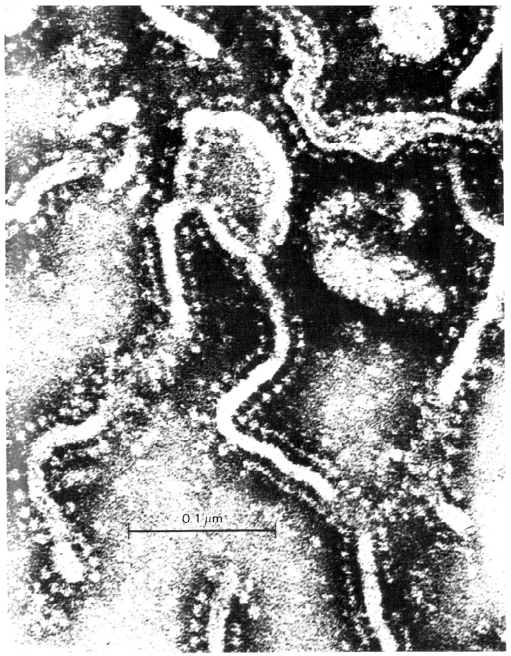
Energy plant of cells: synthesis of ATP



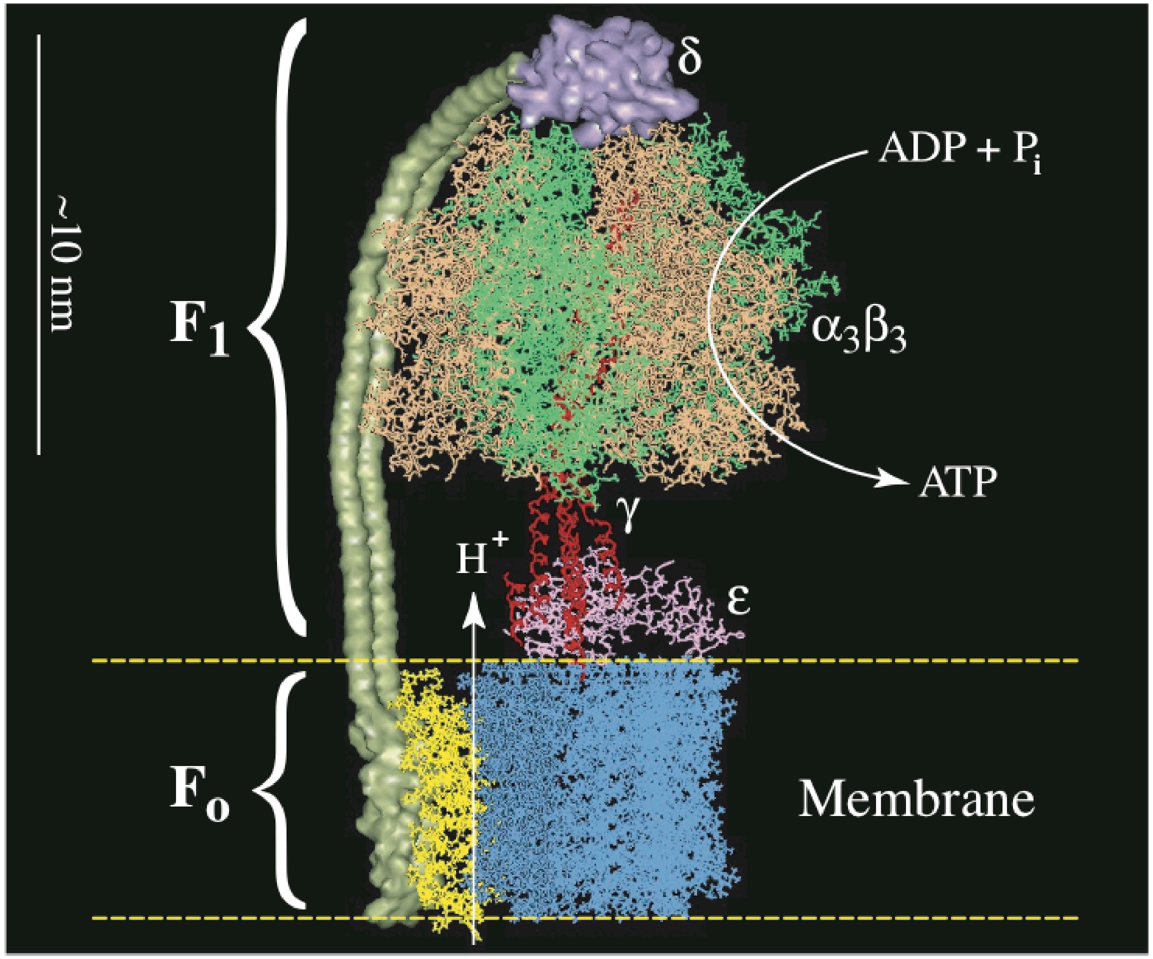
Internal membrane with:

F_o = proton turbine

F_1 = synthesis of ATP (23500 atoms)

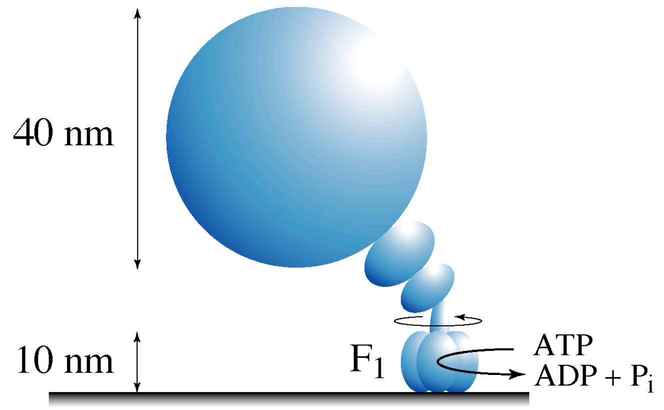


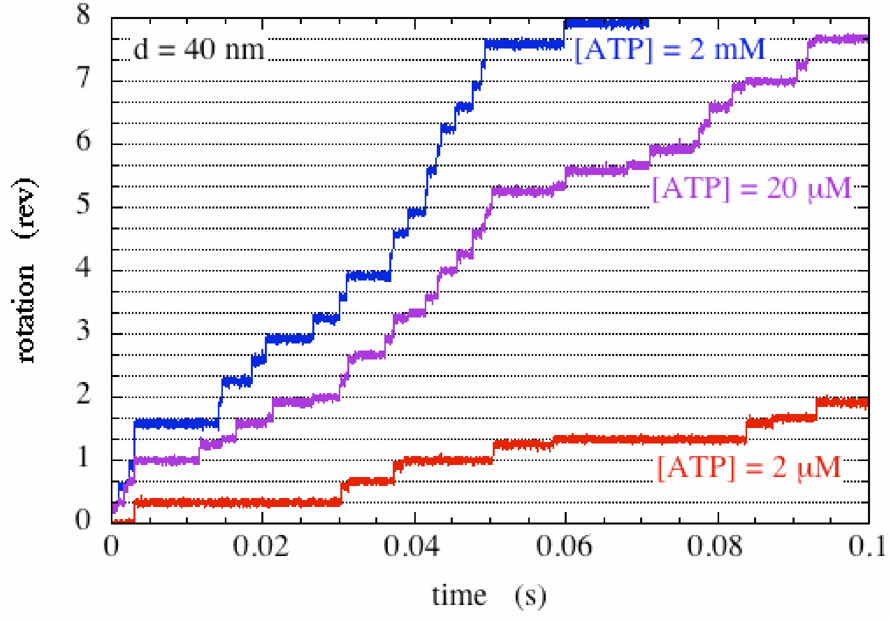
Chr. de Duve, *Une visite guidée de la cellule vivante* (De Boeck Université, Bruxelles, 1987).



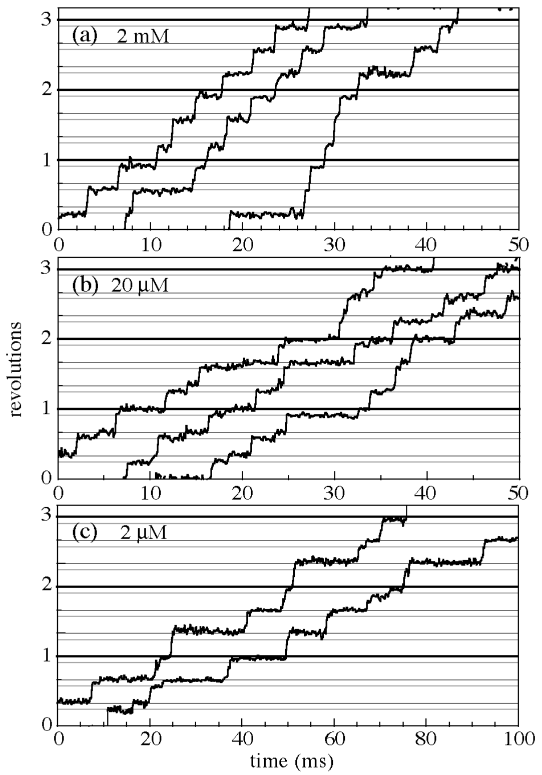
OUT-OF-EQUILIBRIUM TRAJECTORIES OF THE MOLECULAR MOTOR

Power of
the motor:
10^{-18} Watt





Random trajectories
simulated by the model



Random trajectories
observed in experiments

R. Yasuda, H. Noji, M. Yoshida,
K. Kinosita Jr. & H. Itoh,
Nature **410** (2001) 898

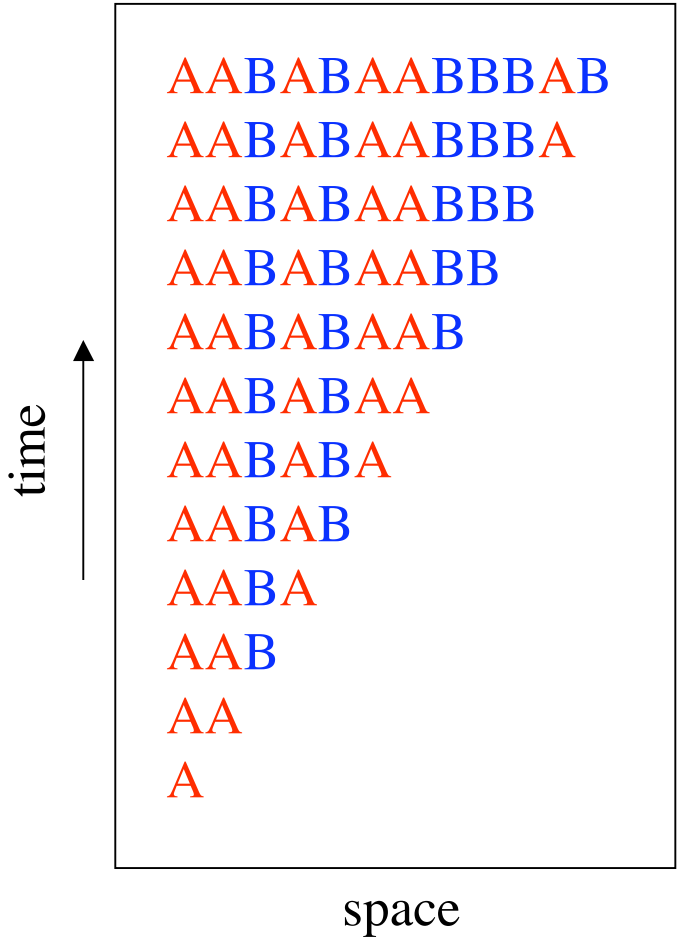
at equilibrium:
…21213213122313 2…
(random)

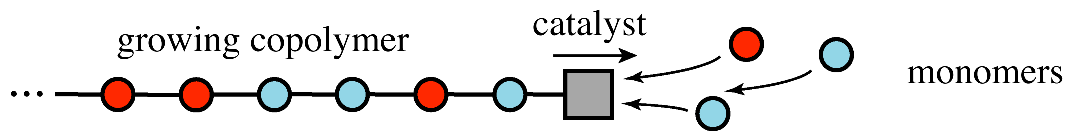
out of equilibrium:
…123123123123123…
(more regular)

COPOLYMERIZATION PROCESSES

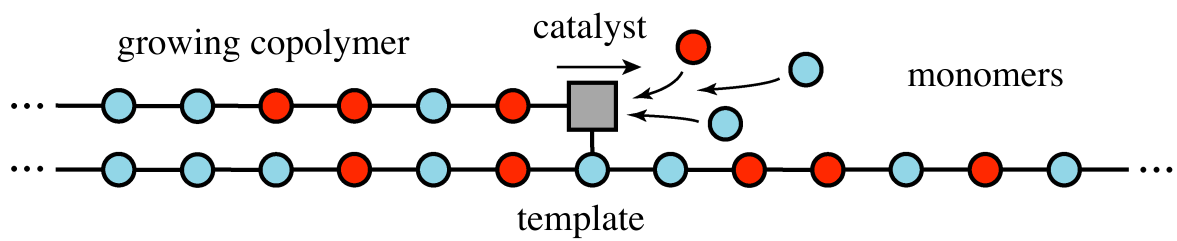
out-of-equilibrium temporal ordering + spatial support of information
= information generation or processing

spatial support of information = random copolymer (covalent bonds)
= Schrödinger aperiodic crystal





free copolymerization: random copolymers
ex: styrene-butadiene rubber
atactic polypropylene



copolymerization on a template:
ex: DNA replication
DNA-mRNA transcription
mRNA-protein translation

D. Andrieux & P. Gaspard, *Nonequilibrium generation of information in copolymerization processes*
Proc. Natl. Acad. Sci. U.S.A. **105** (2008) 9516

STATISTICAL THERMODYNAMICS OF COPOLYMERIZATION PROCESSES

growth of a single copolymer ω: $$\frac{d}{dt}P_t(\omega) = \sum_{\omega'}\left[P_t(\omega')W(\omega'|\omega) - P_t(\omega)W(\omega|\omega')\right]$$

entropy of the copolymer in its environment: $$S_t \equiv \sum_{\omega} S(\omega)\, P_t(\omega) - k_{\mathrm{B}} \sum_{\omega} P_t(\omega)\, \ln P_t(\omega)$$

The growth proceeds in a regime described by a stationary statistical distribution $\mu_l(\omega|\alpha)$:

$$P_t(\omega) = p_t(l)\ \mu_l(\omega|\alpha)$$ with the statistical distribution of lengths $p_t(l)$

entropy production: $$\frac{d_{\mathrm{i}}S}{dt} = v\, A \geq 0$$ average growth velocity: $$v = \frac{d\langle l \rangle_t}{dt}$$

affinity or thermodynamic force: $$A = \varepsilon + D(\text{polymer}|\text{template})$$
$$= \varepsilon + D(\text{polymer}) - I(\text{polymer},\text{template})$$

D = disorder = Shannon entropy of $\mu_l(\omega|\alpha)$ I = mutual information of $\mu_l(\omega|\alpha)$

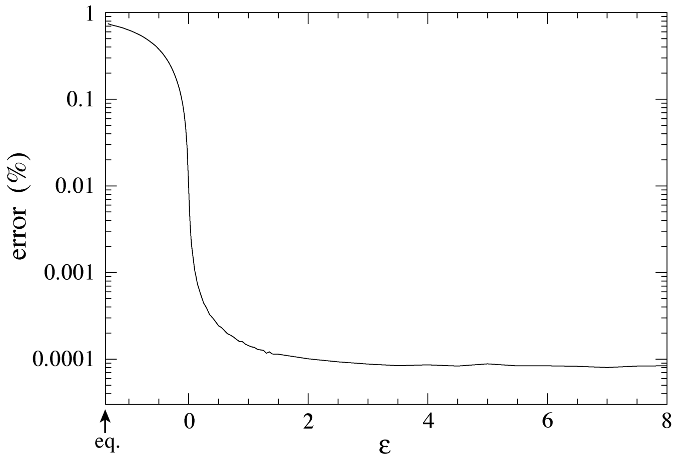
driving force: $$\varepsilon = -\frac{g}{T}$$ Gibbs free energy per monomer: $$g = \lim_{l\to\infty}\frac{1}{l}\sum_{\omega}\mu_l(\omega|\alpha)G(\omega)$$

D. Andrieux & P. Gaspard, *Nonequilibrium generation of information in copolymerization processes*
Proc. Natl. Acad. Sci. U.S.A. **105** (2008) 9516

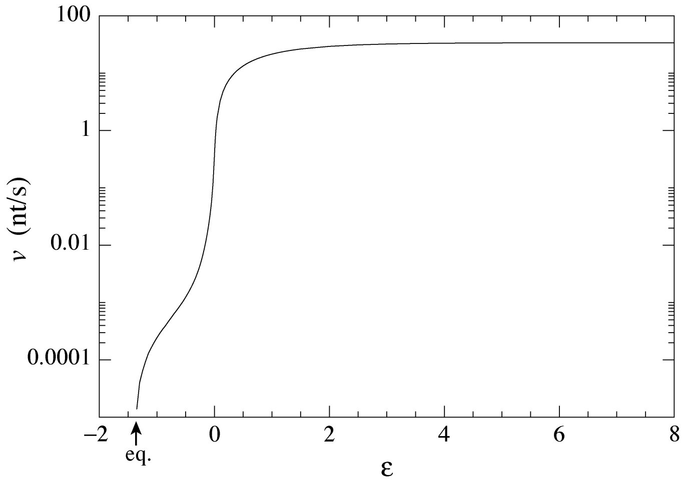
COPOLYMERIZATION PROCESSES: DNA REPLICATION

DNA polymerase Pol γ replicating human mitochondrial DNA (A, C, G, T)

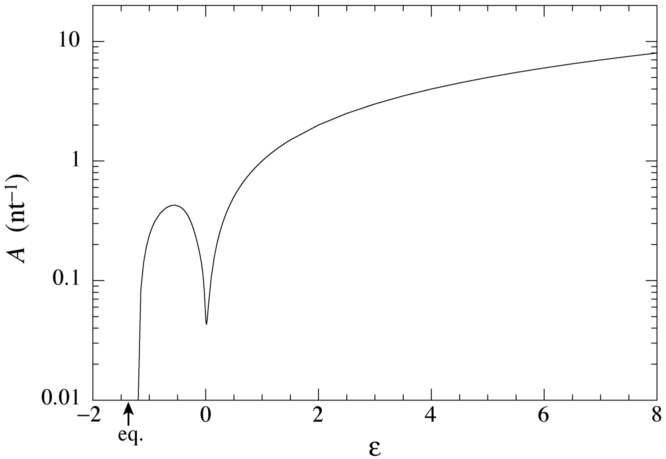
percentage of errors in replicating



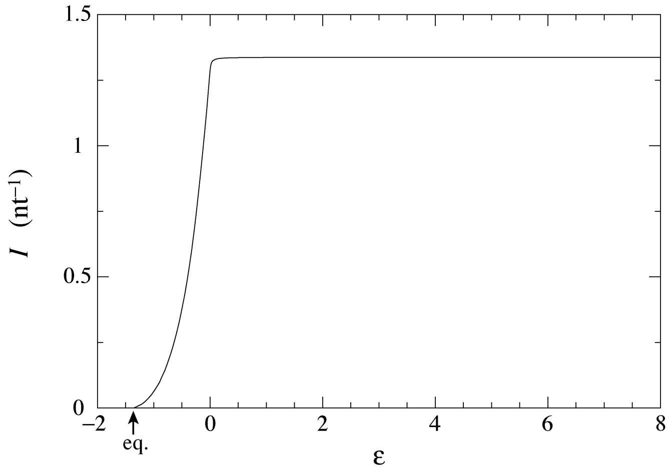
velocity of replication



affinity per nucleotide $A = \varepsilon + D(\omega|\alpha)$



mutual information $I(\omega,\alpha) = D(\omega) - D(\omega|\alpha)$



D. Andrieux & P. Gaspard, *Nonequilibrium generation of information in copolymerization processes*
Proc. Natl. Acad. Sci. U.S.A. **105** (2008) 9516

CONCLUSIONS

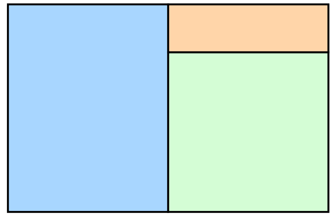
Breaking of time-reversal symmetry in the statistical description of nonequilibrium systems

<u>Entropy production and temporal disorder:</u>

$$\frac{1}{k_{\mathrm{B}}}\frac{d_{\mathrm{i}}S}{dt} = h^{\mathrm{R}} - h \geq 0$$

thermodynamic arrow of time

= time asymmetry in temporal disorder



<u>Out-of-equilibrium temporal ordering as a corollary of the second law:</u>
In nonequilibrium steady states, the typical paths are more ordered **in time** *than the corresponding time-reversed paths.*

Thermodynamic arrow of time down to the nanoscale

Statistical thermodynamics of nonequilibrium nanosystems:
molecular motors & copolymerization processes

Perspectives to understand the origins of dynamical order in biology:
biological systems as physico-chemical systems
with a built-in thermodynamic arrow of time