Emergence of Molecular Order in Nonequilibrium Systems and the Physics of Information

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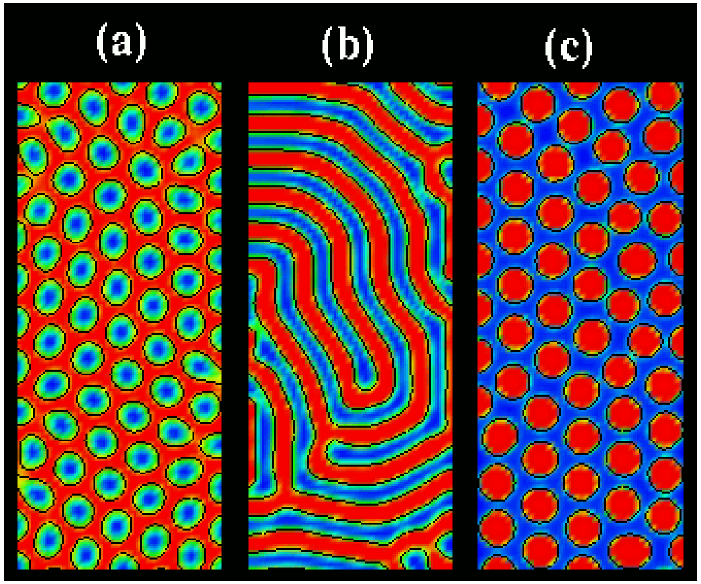
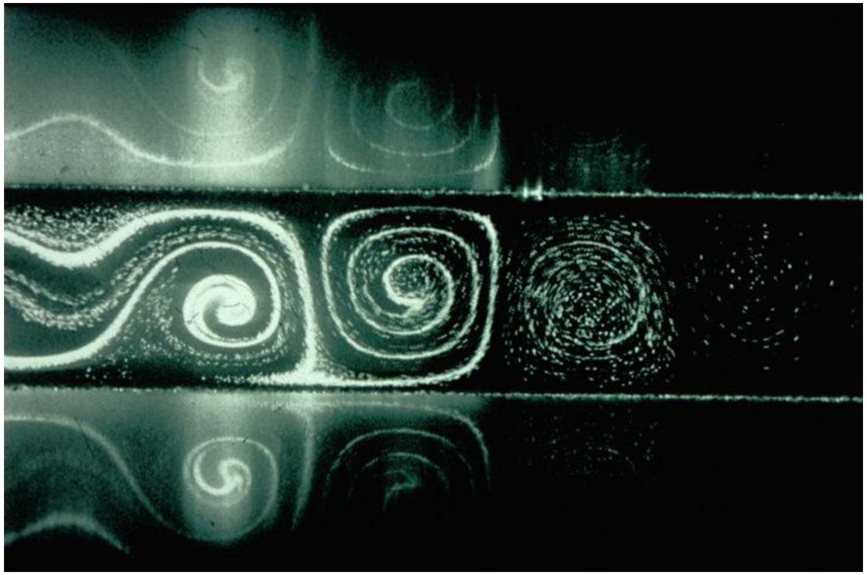
Collective order is developed through unstable fluctuations and far-from-equilibrium successive bifurcations (Nicolis and Prigogine 1977)

Turing patterns

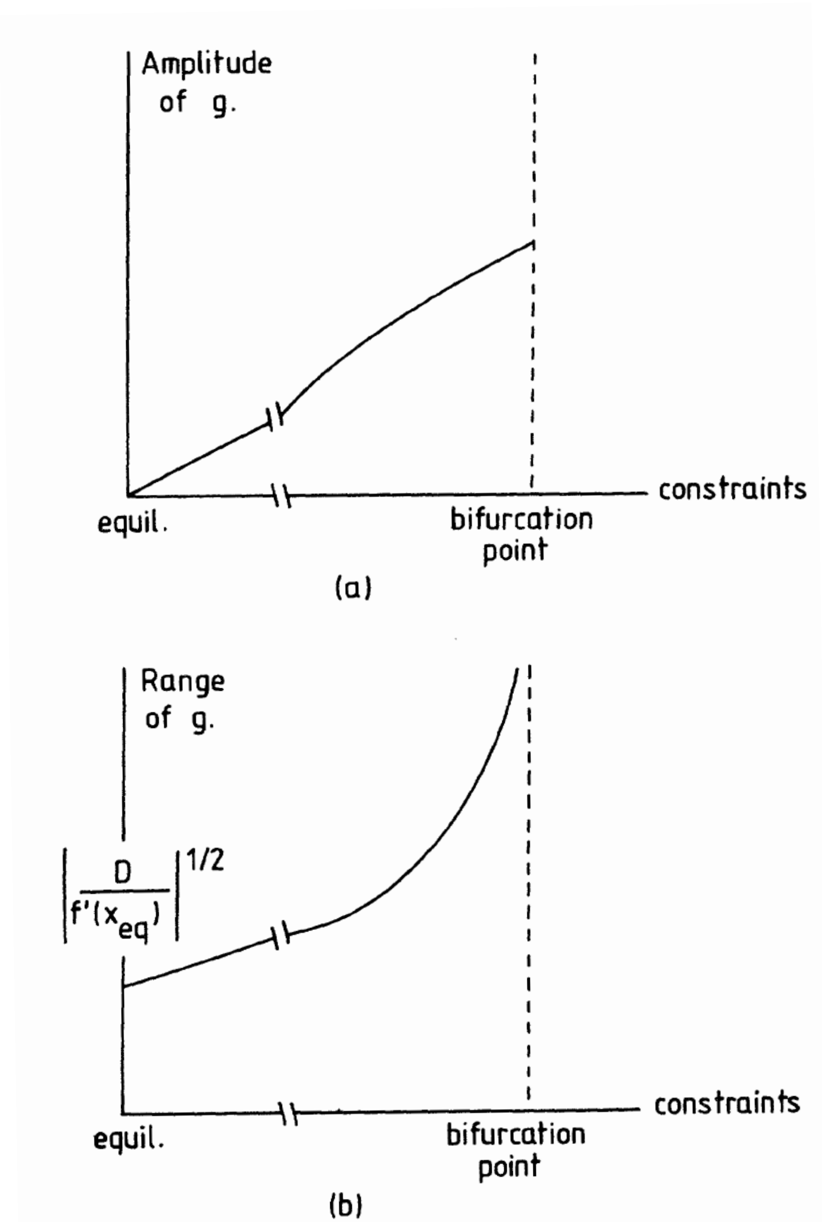


Rayleigh-Bénard convection rolls



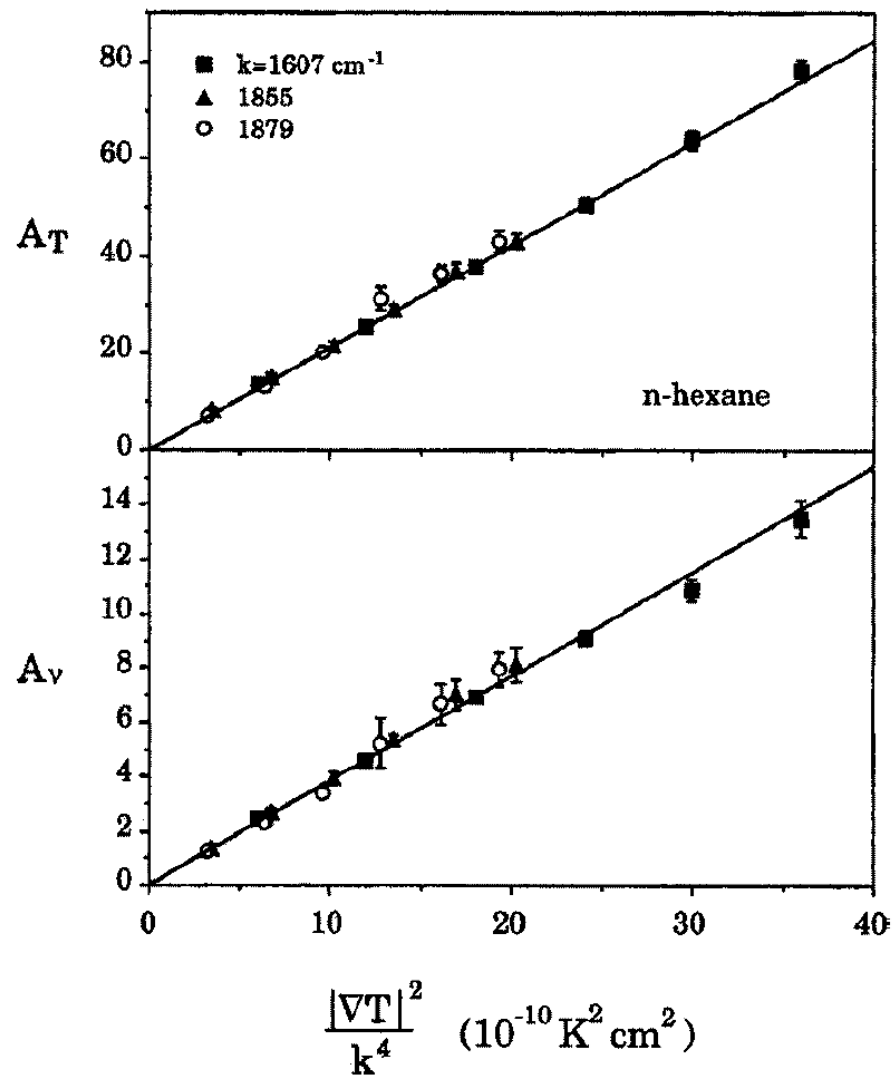
Macroscopic self-organization (non-equilibrium or dissipative structures)

Nonequilibrium states present long-range correlations



Nicolis and Mansour 1984

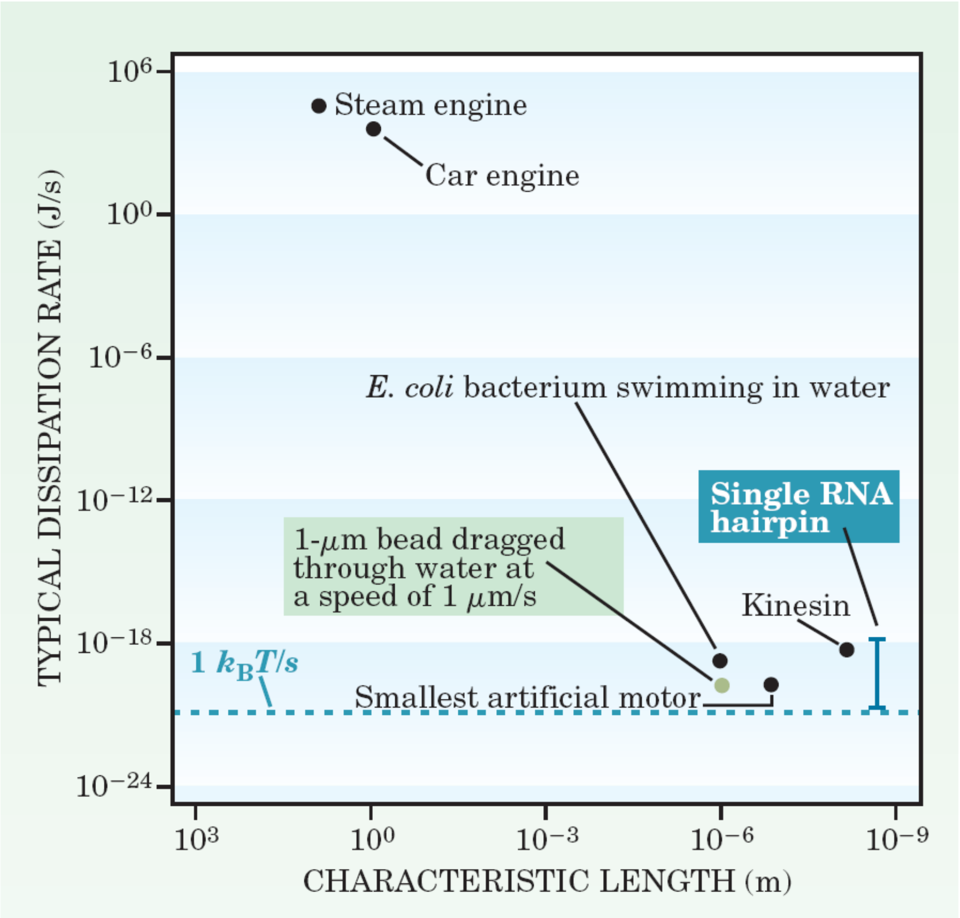
Li et al. 1994



Nonequilibrium & noisy dymanics at the nanoscale

- Molecular motors:
  kinesin, myosin, RNA polymerase, ...
- Electronic circuits:
  q-dots, single-electron transistors, ...
- Chemical networks:
  catalysis, microfluidic, ...
- Nanomachines, ...

length ~ nm - μm
energy ~ kT
$N << N_{Avogadro}$



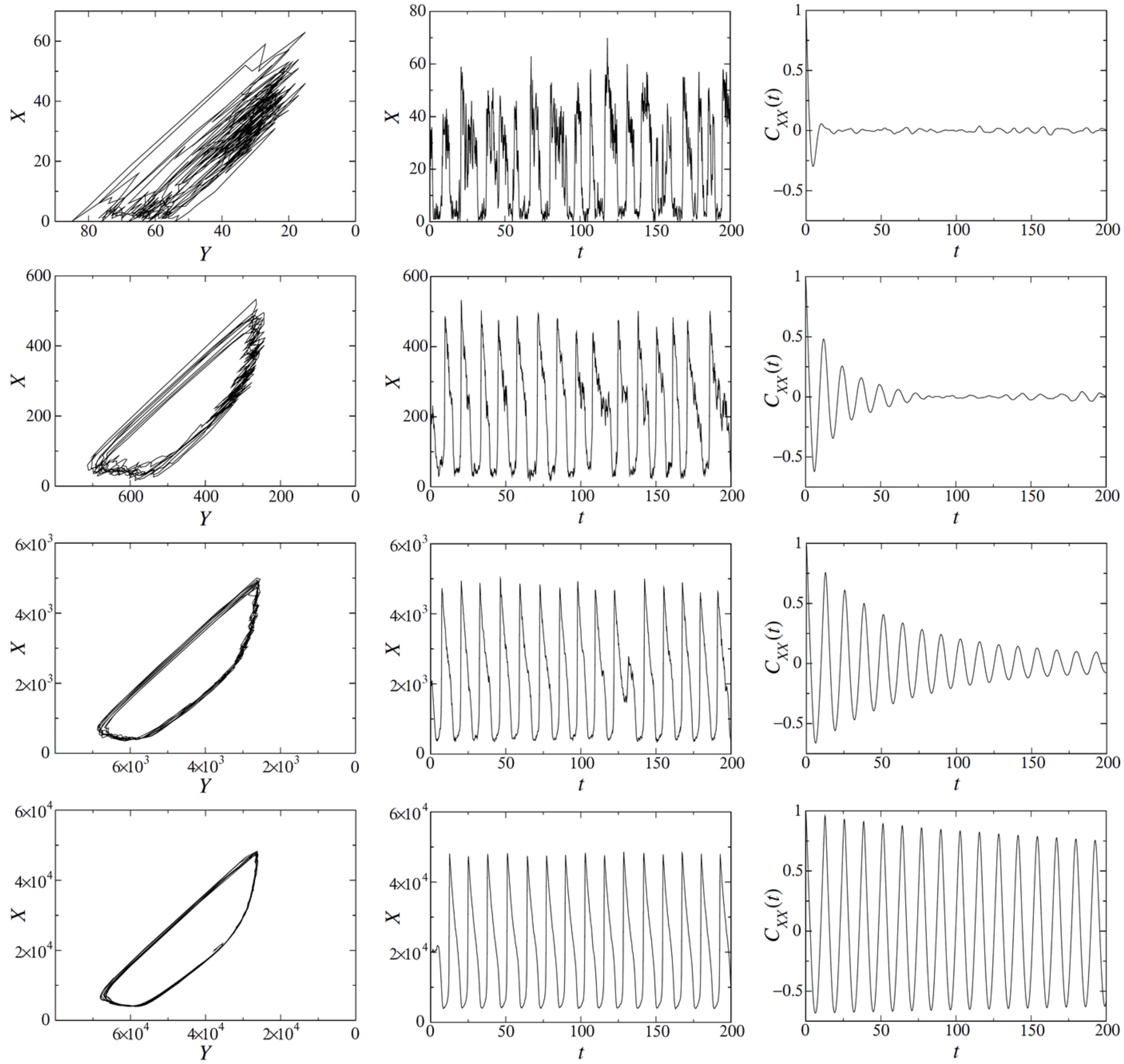
Bustamante et al., Physics Today 2005

$$\mathrm{A} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{X}$$

$$\mathrm{B} + \mathrm{X} \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} \mathrm{Y} + \mathrm{C}$$

$$2\mathrm{X} + \mathrm{Y} \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} 3\mathrm{X}$$

Brusselator oscillating chemical network



phase space

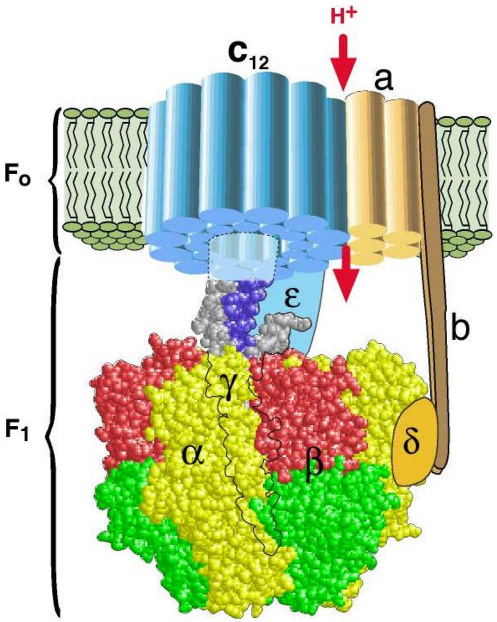
X(t)

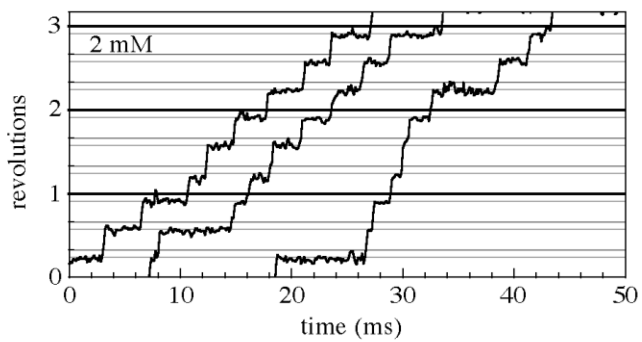
correlation function

From the macro to the microscopic scale

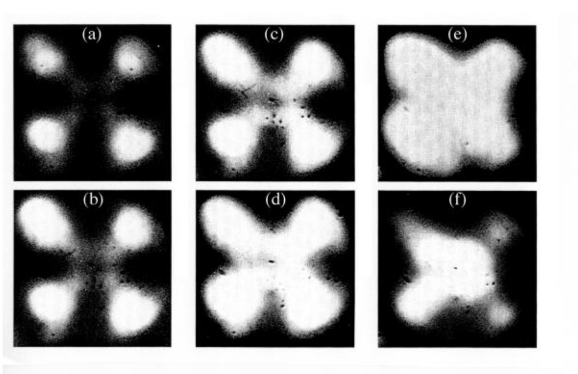
Andrieux and Gaspard, JCP 2008

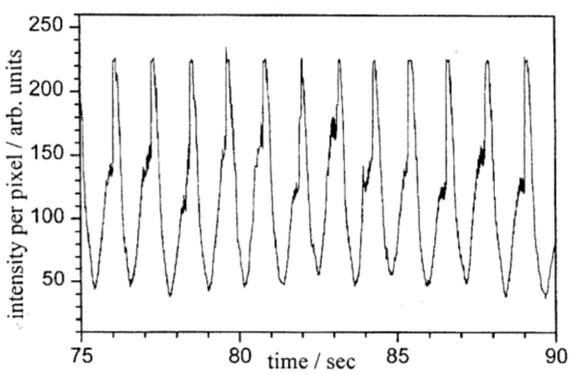
Nonequilibrium systems manifest a dynamical order



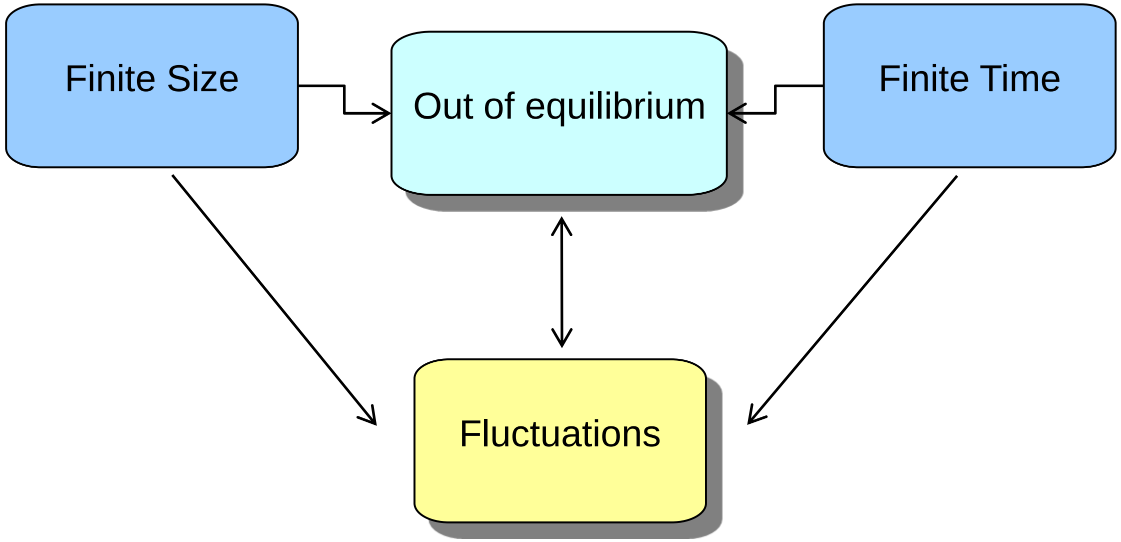


Kinosita and coworkers (2001):
F1-ATPase + actin filament





Voss and Kruse (1996):
NO2/H2/Pt catalytic reaction



How does self-organization emerge at the nanoscale?

1. **Dissipation and dynamical ordering**

2. **Thermodynamics of information processing**

   Copolymerizations, DNA replication, ...

Origin of dynamical order?

Out of equilibrium

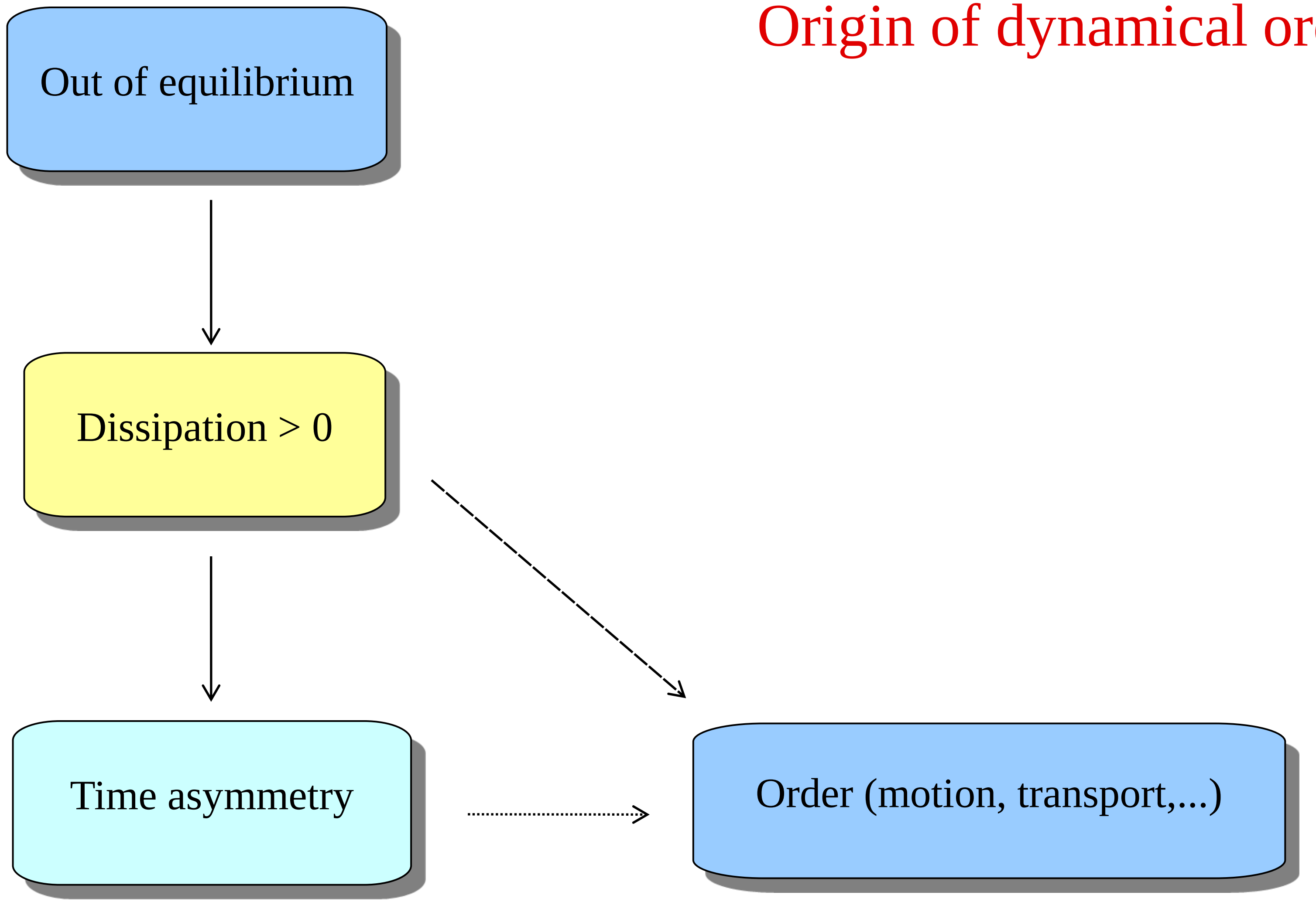
↓

Dissipation > 0

↘

Order (motion, transport,...)

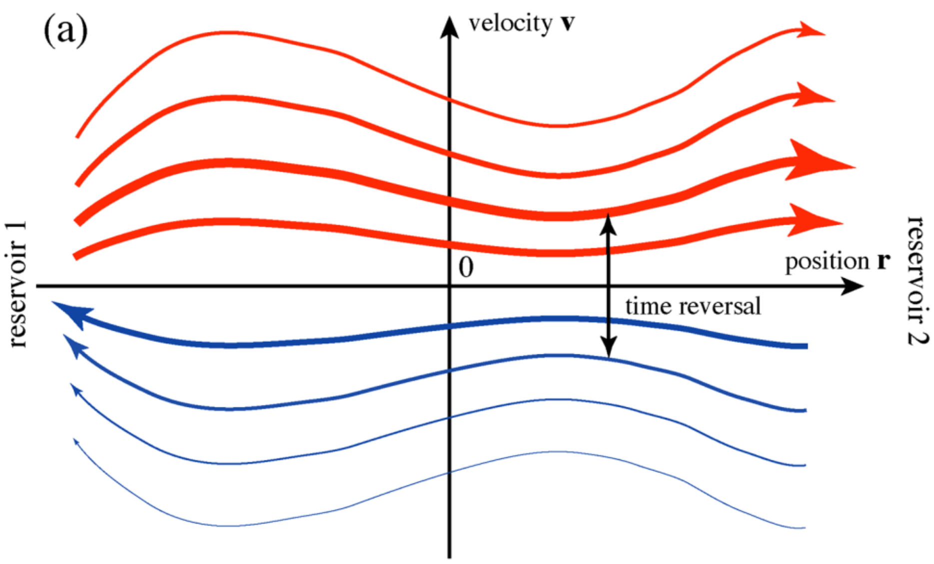
Origin of dynamical order?



Spontaneous symmetry breaking in phase space

Equations of motion are symmetric under time-reversal (micro-reversibility),

but their solutions are not:



$\underline{\omega}$

$\neq$

$\underline{\omega}^{R}$

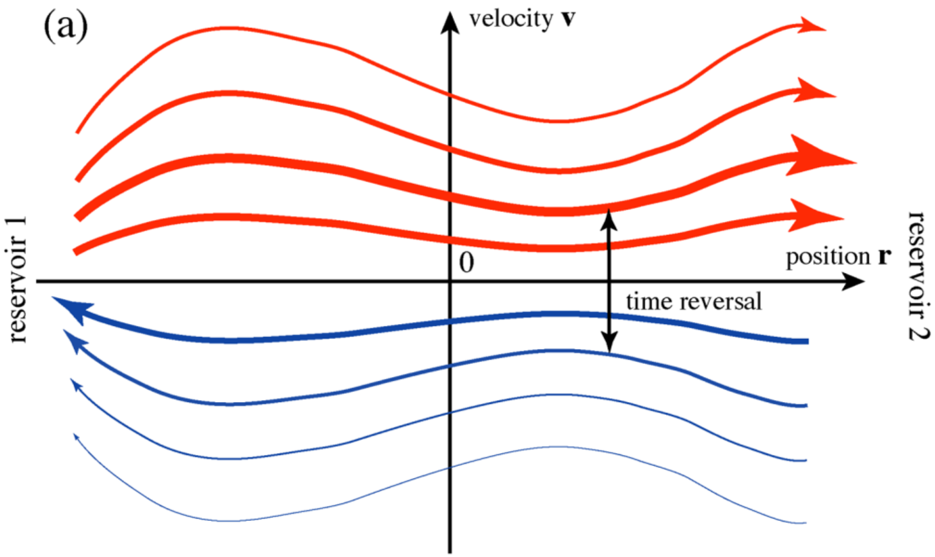
Spontaneous symmetry breaking in phase space

Equations of motion are symmetric under time-reversal (micro-reversibility),

but their solutions are not:

Equilibrium: $P(\underline{\omega}) = P(\underline{\omega}^{R})$

Out of equilibrium: $P(\underline{\omega}) \neq P(\underline{\omega}^{R})$



$\underline{\omega}$

$\neq$

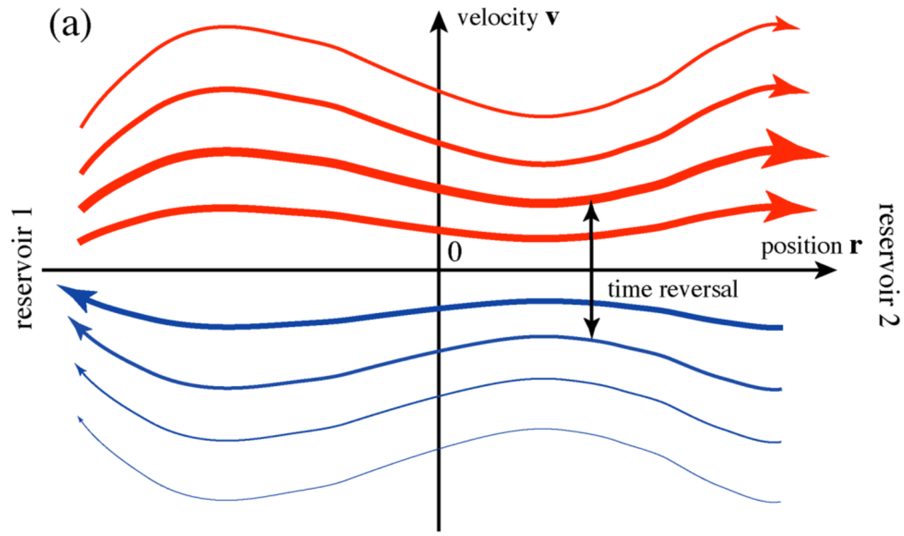
$\underline{\omega}^{R}$

Can we relate irreversibility to the microscopic dynamics?

Dynamical randomness

Equilibrium: $P(\underline{\omega}) = P(\underline{\omega}^{R})$

Out of equilibrium: $P(\underline{\omega}) \neq P(\underline{\omega}^{R})$



$\underline{\omega}$

$\neq$

$\underline{\omega}^{R}$

The probability of a typical path decays as

$$P(\underline{\omega}) = P(\omega_0\ \omega_1\omega_2\ \ldots\ \omega_n) \sim \exp(\ -n\ h\ )$$

h = *Kolmogorov-Sinai entropy* is a measure of dynamical randomness (predictability)

The probability of the time-reversed path decays as

$$P(\underline{\omega}^{R}) = P(\omega_n\ \ldots\ \omega_2\ \omega_1\ \omega_0\ ) \sim \exp(\ -n\ h^{R}\ )$$

h^{R} = temporal disorder of the time-reversed paths

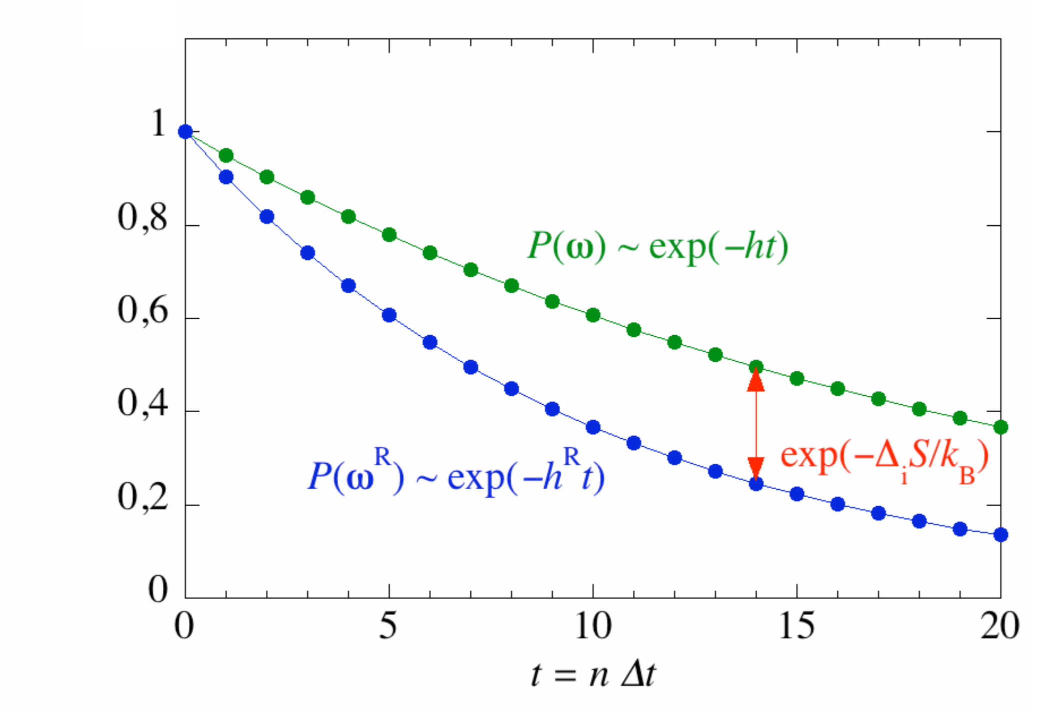
Gaspard 2004

Dissipation and out-of-equilibrium temporal ordering

The typical paths are more ordered ***in time*** than the corresponding time-reversed paths:

$h^R = h$ equilibrium

$h^R \geq h$ nonequilibrium



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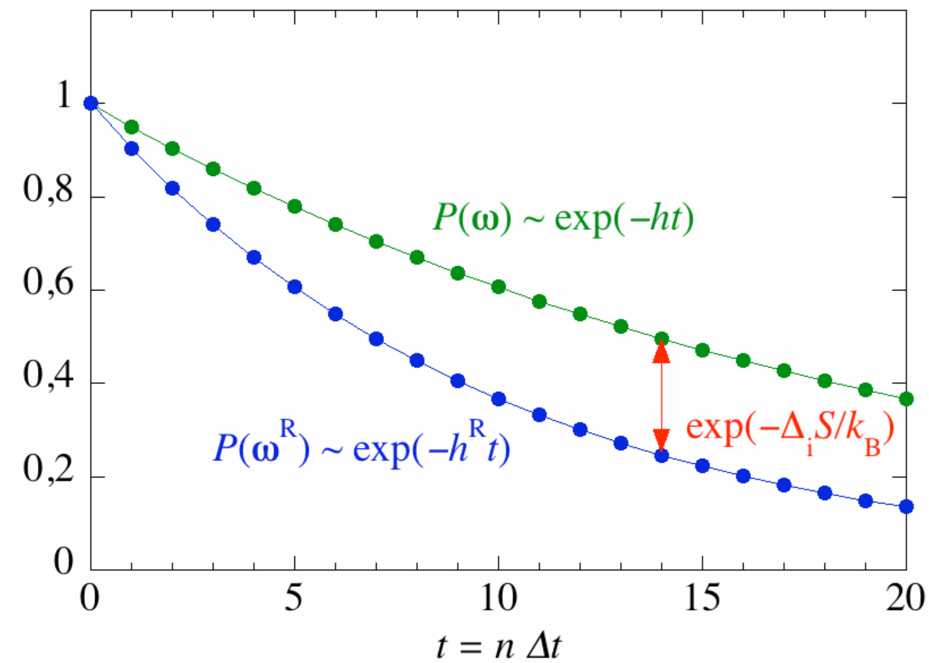


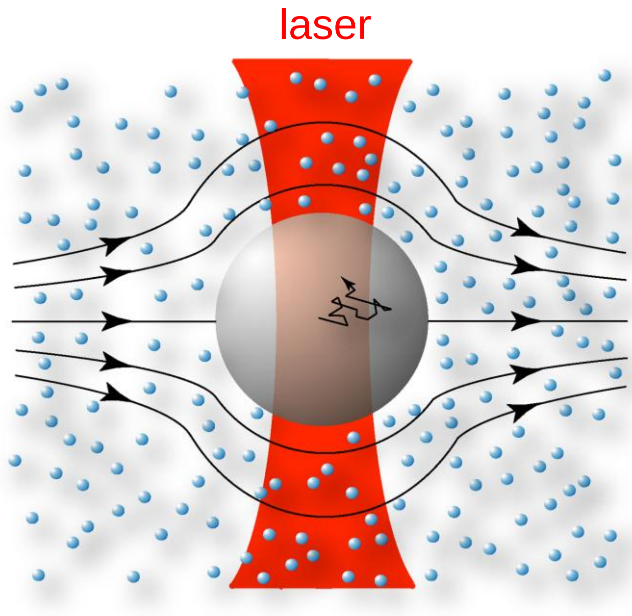
The thermodynamic entropy production is expressed as

$$\Delta_i S = h^R - h$$

= temporal disorder of time reversed paths – temporal disorder of typical paths
= time asymmetry in the temporal disorder

⇒ Nonequilibrium processes can generate dynamical order and information

2 mm diameter polystyrene particle in a 20% glycerol-water solution trapped by optical tweezers and driven by a moving fluid



driving force $F = -k\,(x-ut)$

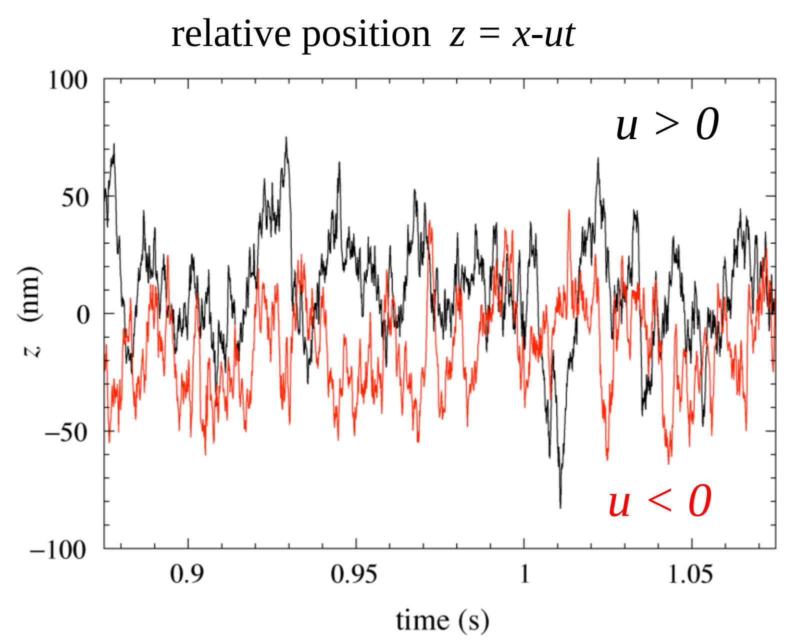
friction α

relaxation time $\tau = 3$ ms

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

fluid velocity $u = \pm\ 4.24$ µm/s

resolution $\varepsilon = k \times 0.558$ nm (k=11-20)

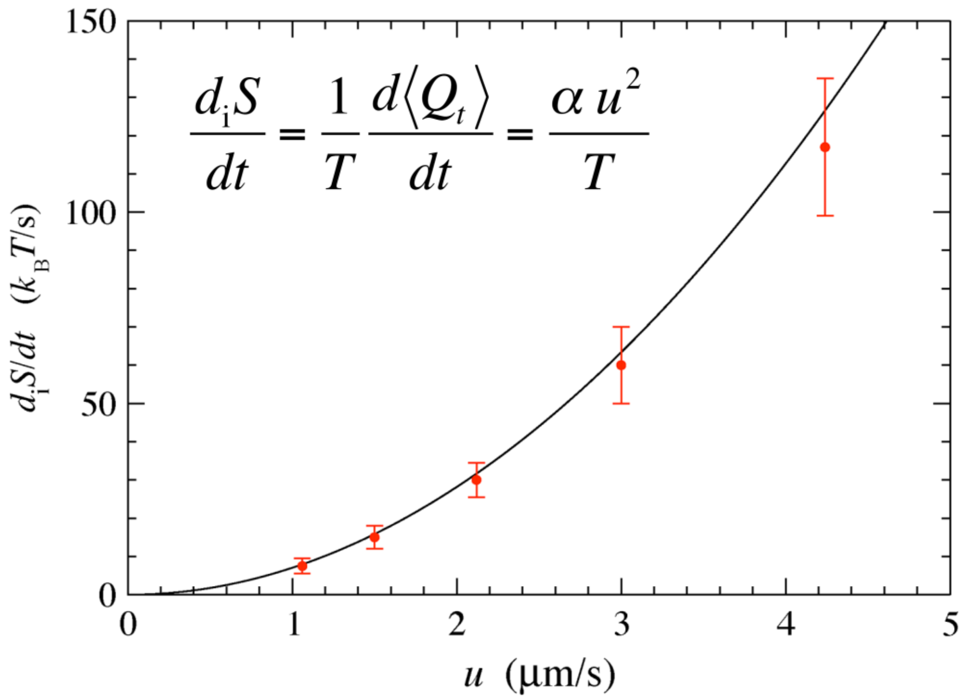


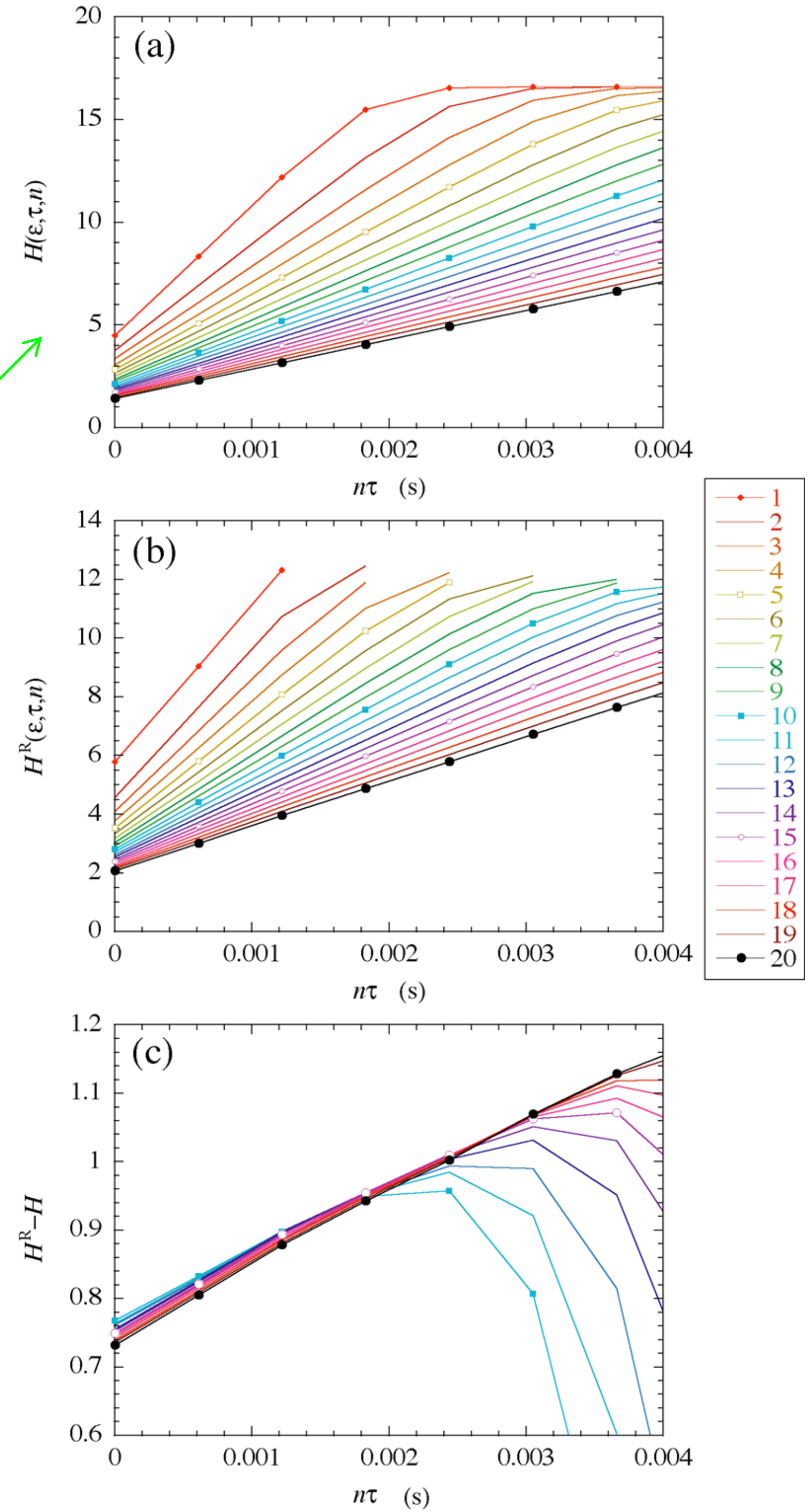
Langevin equation $$\frac{dx}{dt} = -\frac{x-ut}{\tau_R} + \sqrt{\frac{2k_B T}{\alpha}}\xi_t$$

Driven Brownian motion

Entropy production and (ε,τ)-entropies per unit time down to the nanoscale

$$\frac{d_i\mathcal{S}}{dt} = \lim_{\varepsilon\to 0}\lim_{\tau\to 0}\ k_{\mathrm{B}}\left[h^{\mathrm{R}}(\varepsilon,\tau) - h(\varepsilon,\tau)\right]$$





Path probabilities and dissipation

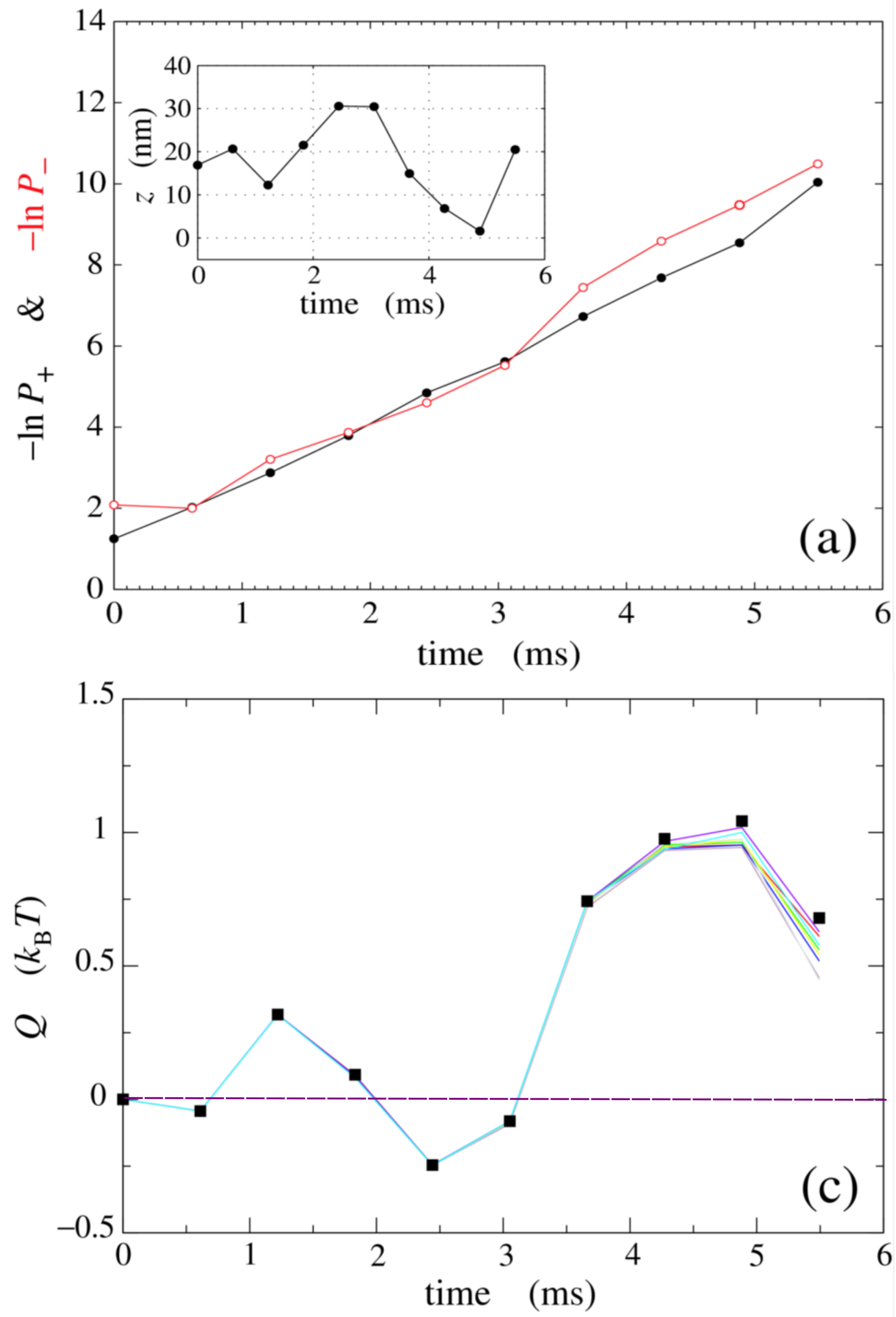
Probabilities ($\pm u$) for a random path:

Heat dissipated along the random path:

$$\ln \frac{P_+[z_t|z_0]}{P_-[z_t^{\mathrm{R}}|z_0^{\mathrm{R}}]} = \frac{Q_t}{k_{\mathrm{B}}T}$$

with

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



Andrieux et al., JSM 2008

Erasure of (correlated) random bits and Landauer's principle

Consider the erasure process of a sequence of random bits with Shannon entropy D

$\Rightarrow$ Minimal dissipation is $D\, k_B T$ per bit.

Zurek 1989, Andrieux and Gaspard 2008

Erasure of (correlated) random bits and Landauer's principle

Consider the erasure process of a sequence of random bits with Shannon entropy D

- Erasure process generates no information: $h = 0$
- In reversed time, information is generated at rate $h^{R} = D \; k_{B}T$
- Erasure process dissipates $h^{R} - h = D \, k_{B}T$ per bit.

Based on dynamical randomness and model independent

$\Rightarrow$ Minimal dissipation is $D \, k_{B}T$ per bit.

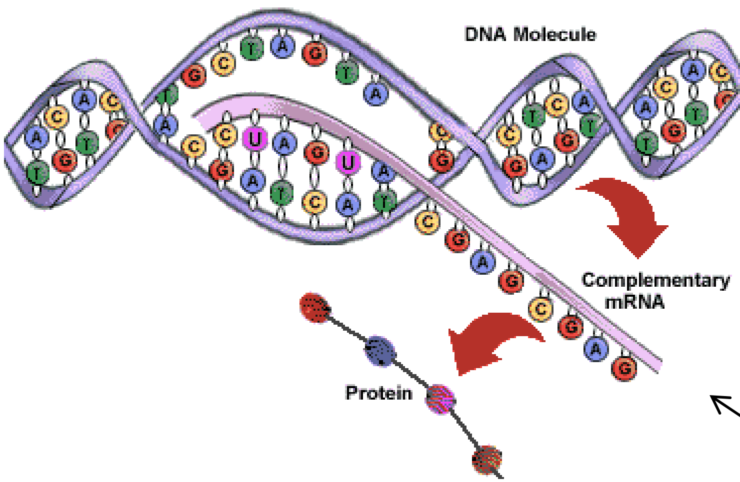
Zurek 1989, Andrieux and Gaspard 2008

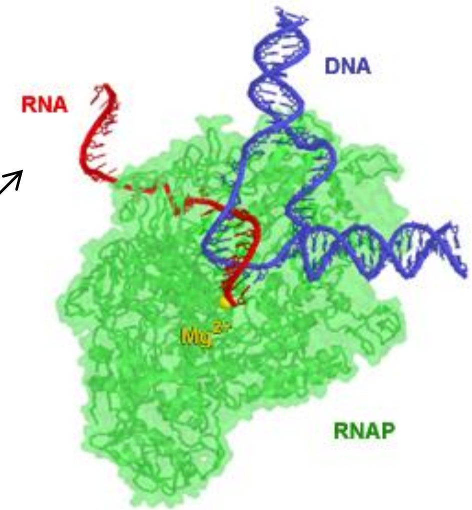
Information generation in polymerization processes

Genetic information is encoded in DNA structure

DNA transcription

RNA Polymerase



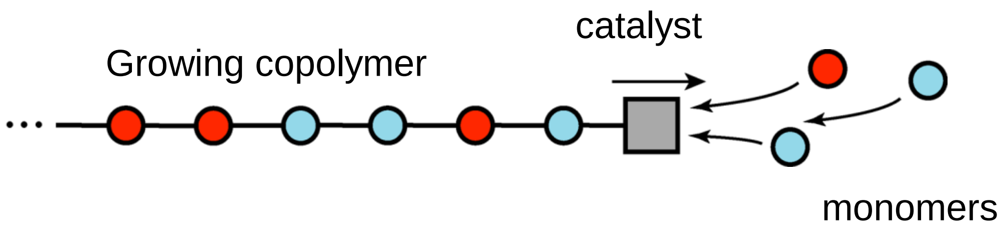


Errors due to thermal & chemical fluctuations

Accuracy of transcription & replication?

How is information generated?

Single polymer synthesis model



$$\text{Polymer} + \text{A} \underset{k_{-A}}{\overset{k_{+A}}{\rightleftharpoons}} \text{Polymer-A}$$

$$\text{Polymer} + \text{B} \underset{k_{-B}}{\overset{k_{+B}}{\rightleftharpoons}} \text{Polymer-B}$$

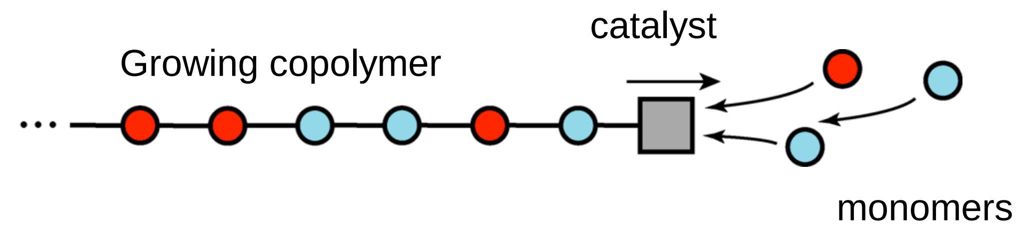
time ↑

AABAABAA
AABAABAAB
AABAABAA
AABAABA
AABAAB
AABAA
AABA
AABAB
AABA
AAB
AA
A

→ space

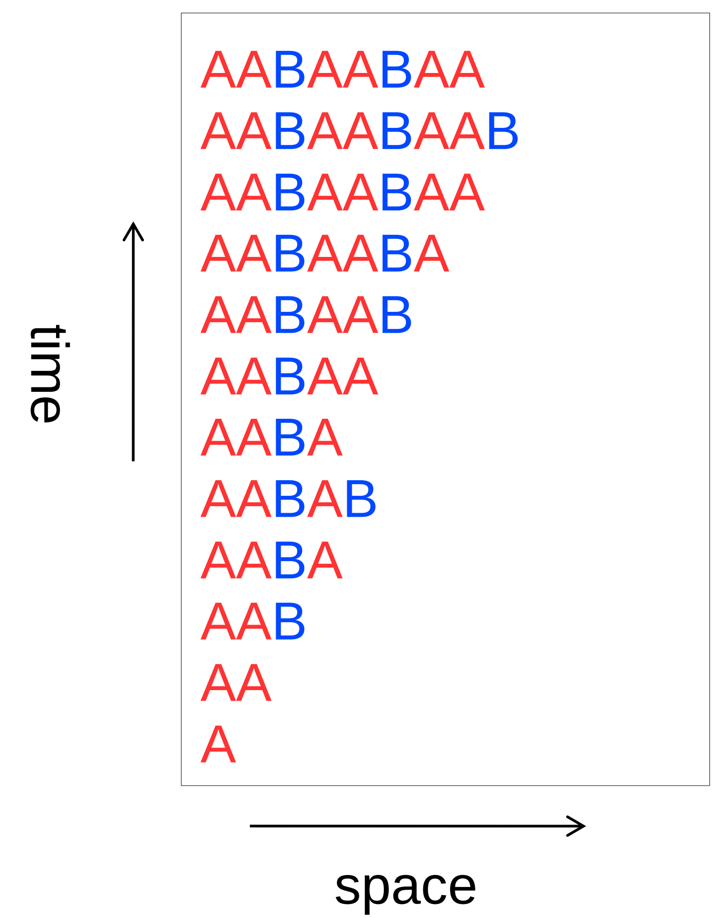
<u>examples</u>: styrene-butadiene rubber
atactic polypropylene

Single polymer synthesis model



$$\text{Polymer} + \text{A} \xrightleftharpoons[k_{-A}]{k_{+A}} \text{Polymer-A}$$

$$\text{Polymer} + \text{B} \xrightleftharpoons[k_{-B}]{k_{+B}} \text{Polymer-B}$$



Master equation dynamics:

$$\frac{d}{dt}P_t(\omega) = \sum_{\omega'}\left[P_t(\omega')W(\omega'|\omega) - P_t(\omega)W(\omega|\omega')\right]$$

where ω is a given sequence of the chain.

What governs the polymer growth?

driving force (free energy difference):

$$\log\,(k_{+A}\,[A]\;/\;k_{-A}) = \log\,(k_{+B}\,[B]\;/\;k_{-B}) = \varepsilon$$

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driving force (free energy difference):

$$\log (k_{+A}\,[A] \,/\, k_{-A}) = \log (k_{+B}\,[B] \,/\, k_{-B}) = \varepsilon$$

$\rightarrow$ fixed selectivity: $k_{+A}\,[A] \,/ k_{+B}\,[B] = k_{-A}/k_{-B}$

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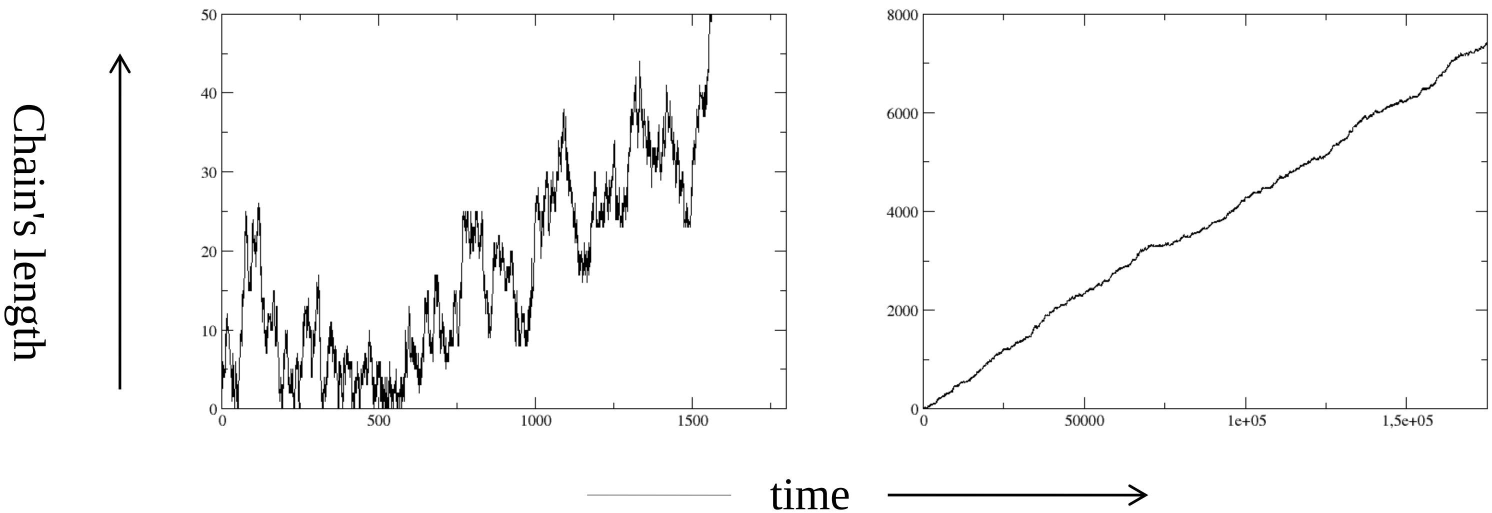
$\rightarrow$ fixed selectivity: $k_{+A}[A] / k_{+B}[B] = k_{-A}/k_{-B}$

Thermodynamic equilibrium is *not* realized at zero driving force:

Steady growth at $\varepsilon = 0$ or $k_{+A}[A] = k_{-A}$ and $k_{+B}[B] = k_{-B}$



Thermodynamics of polymerization

The thermodynamic force (dissipation per step) is

$$\boxed{A = \varepsilon}$$

driving force

A = 0 : equilibrium
A > 0 : polymer grows

Thermodynamics of polymerization

The thermodynamic force (dissipation per step) is

$$\boxed{A = \varepsilon + D(\text{polymer})}$$

driving force — disorder

A = 0 : equilibrium
A > 0 : polymer grows

Shannon entropy: $0 \leq D = \lim_{n \to \infty} -(1/n)\, p_n(\omega) \ln p_n(\omega) \leq \ln 2$

Thermodynamics of polymerization

The thermodynamic force (dissipation per step) is

$$\boxed{A = \varepsilon + D(\text{polymer})}$$

driving force disorder

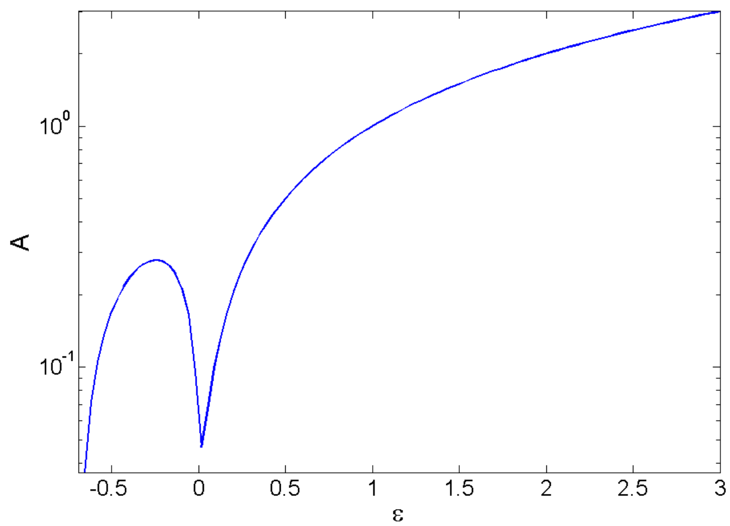
A = 0 : equilibrium
A > 0 : polymer grows

Shannon entropy: $0 \leq D = \lim_{n \to \infty} -(1/n)\, p_n(\omega) \ln p_n(\omega) \leq \ln 2$

- Randomness in the sequence acts as a positive driving force
- Thermodynamic equilibrium at negative driving force: $\varepsilon_{eq} < 0$
- Affinity is not fixed by the external conditions (concentrations, ...) but emerges from the *internal* dynamics

Error-Dissipation Tradeoff

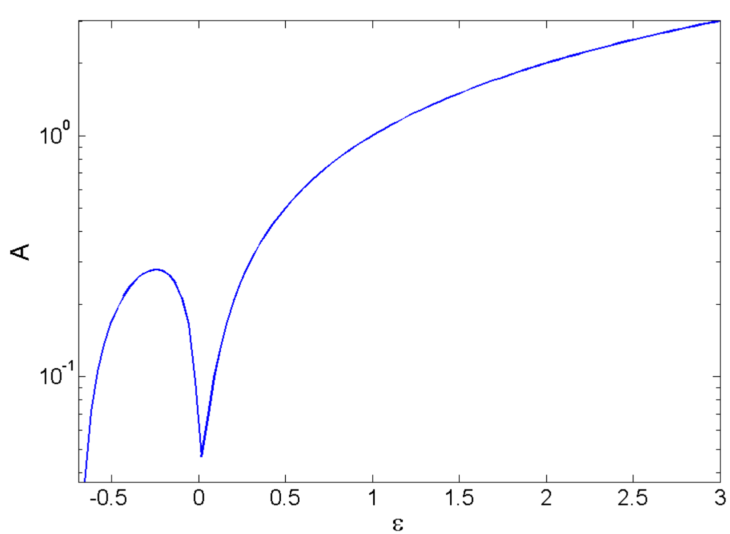
affinity per nucleotide $A = \varepsilon + D(\varepsilon)$



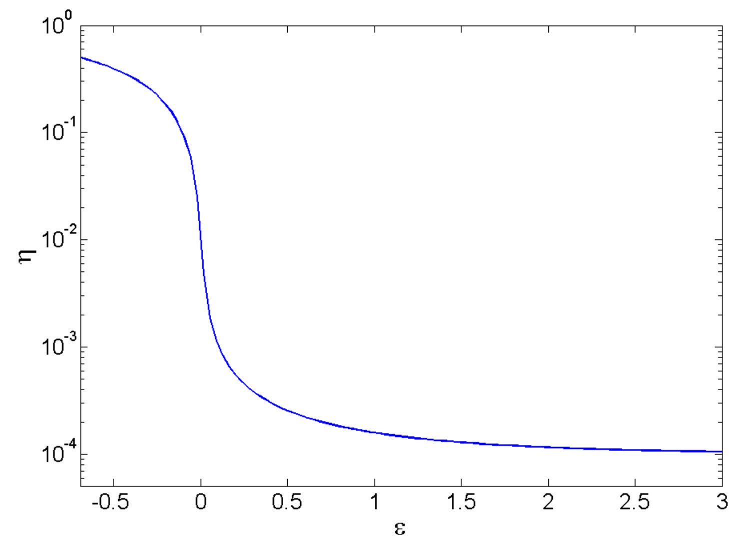
- A single copolymer may grow by an **entropic effect** ($-\ln 2 < \varepsilon < 0$) coming from the randomness D in the monomer sequence

Error-Dissipation Tradeoff

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



percentage of errors (= [A]/[B])



- A single copolymer may grow by an **entropic effect** ($-\ln 2 < \varepsilon < 0$) coming from the randomness D in the monomer sequence
- Error rate diminishes away from equilibrium even **with fixed selectivity**

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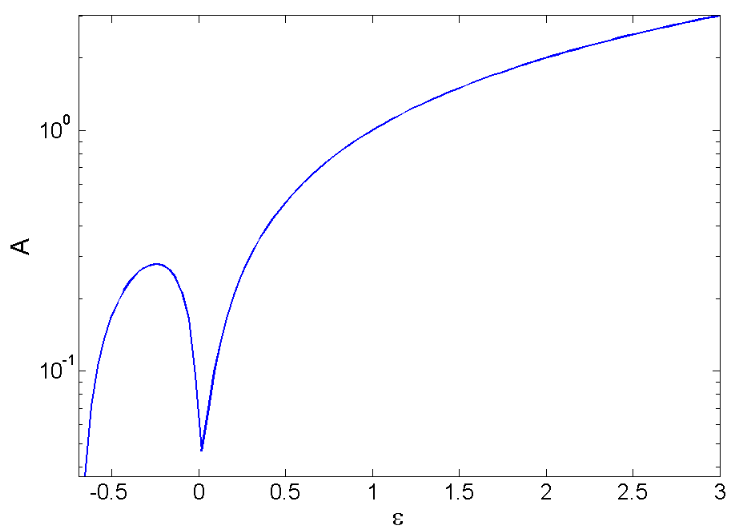

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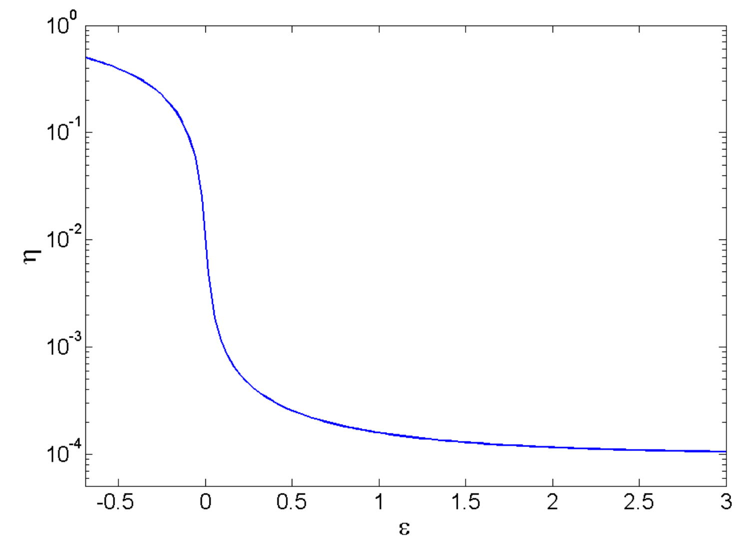
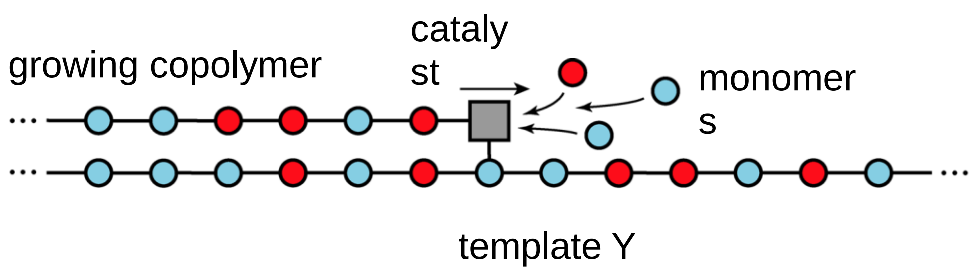


- A single copolymer may grow by an **entropic effect** ($-\ln 2 < \varepsilon < 0$) coming from the randomness D in the monomer sequence
- Error rate diminishes away from equilibrium even **with fixed selectivity**
- $\varepsilon < -\ln 2 \leftrightarrow$ **Landauer**'s principle

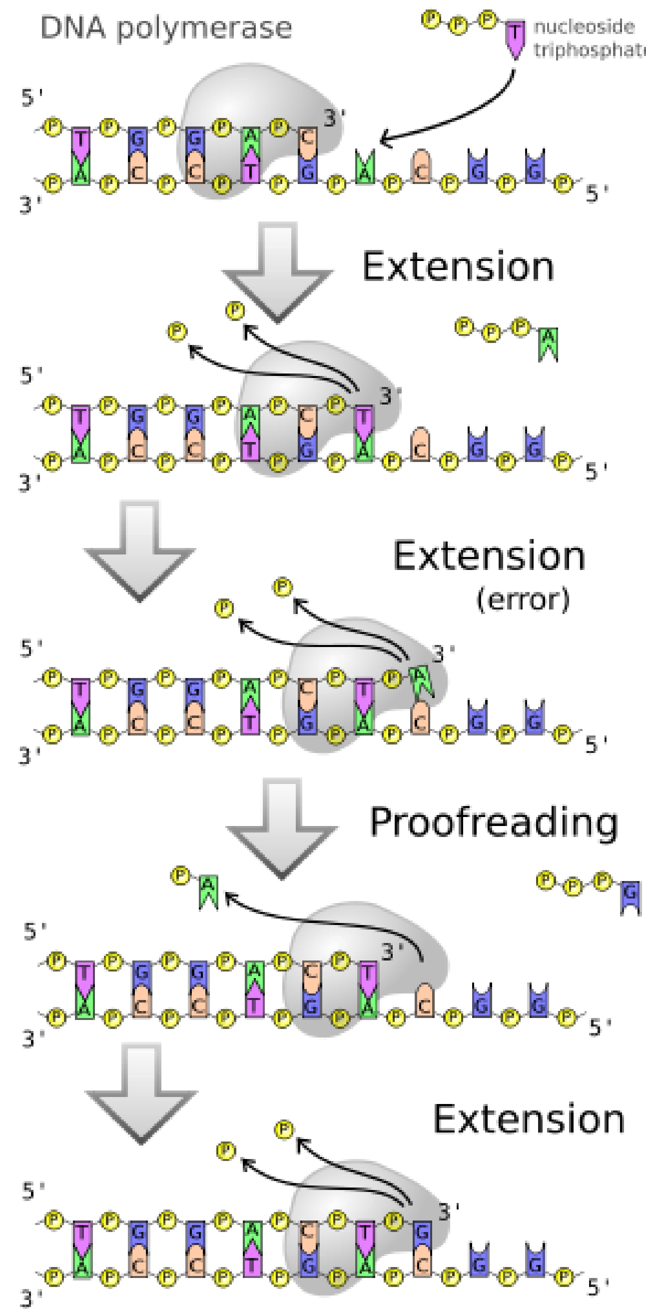
Thermodynamics of copying information

Polymerization reactions depend on the template:



$$\text{Polymer} + \text{X} \underset{k_{-X|Y}}{\overset{k_{+X|Y}}{\rightleftharpoons}} \text{Polymer-X}$$

<u>examples</u>: DNA replication
DNA-mRNA transcription
mRNA-protein translation



Speed-Error-Dissipation-Information Tradeoff

The thermodynamic force or dissipation per step is

$$\boxed{A = \varepsilon + D(\text{polymer}) - I\ (\text{polymer, template})}$$

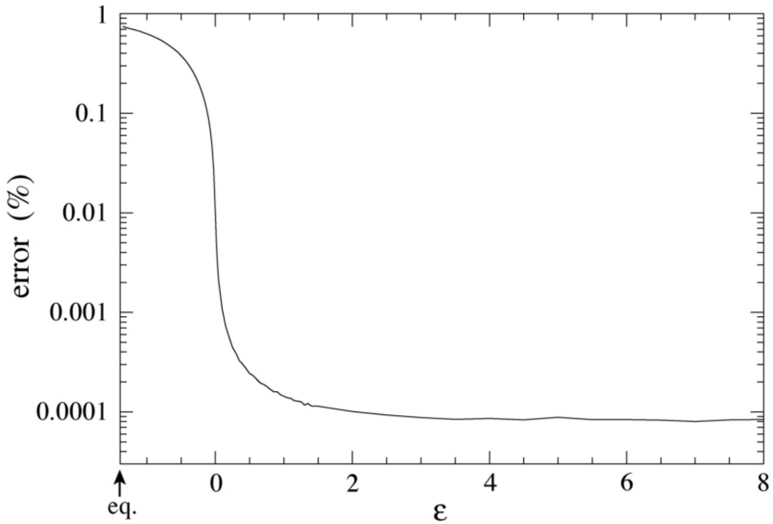
driving force disorder mutual information

- D and I are information theoretic quantities that characterize information transmission in communication channels
- Disorder and information act as positive thermodynamic forces (D-I > 0)
- Thermodynamic cost of copying information

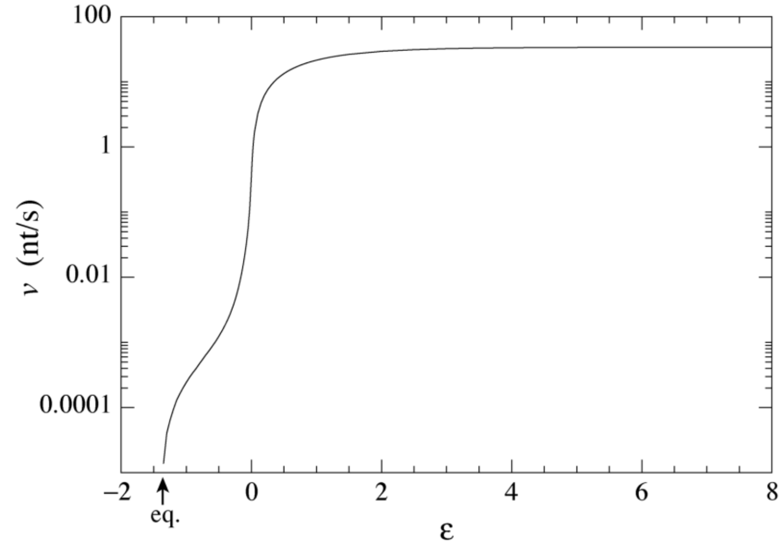
Andrieux and Gaspard 2008

Fidelity in DNA replication is controlled by dissipation

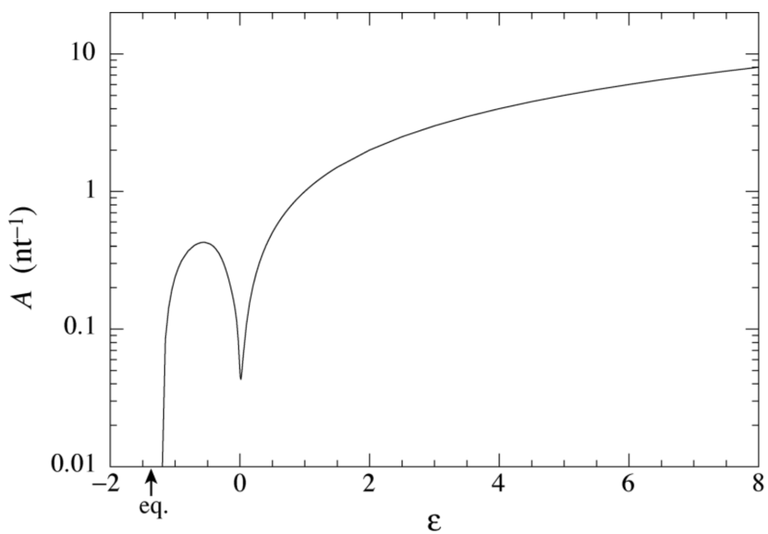
percentage of errors



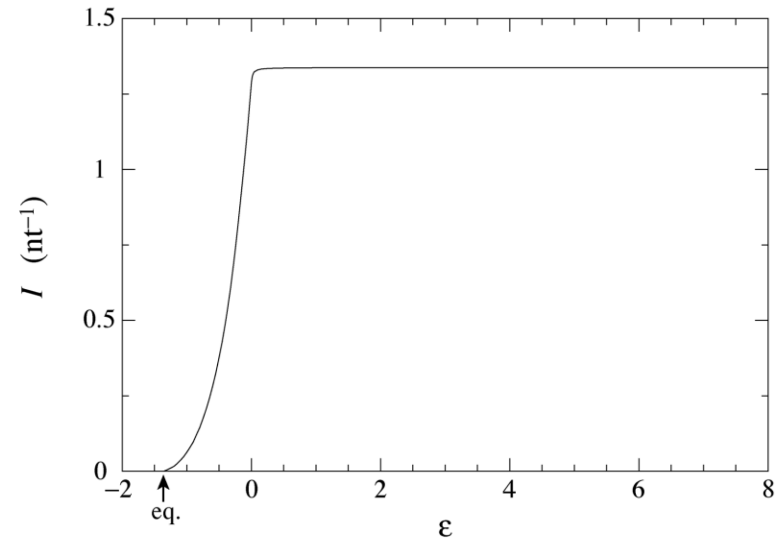
velocity of replication



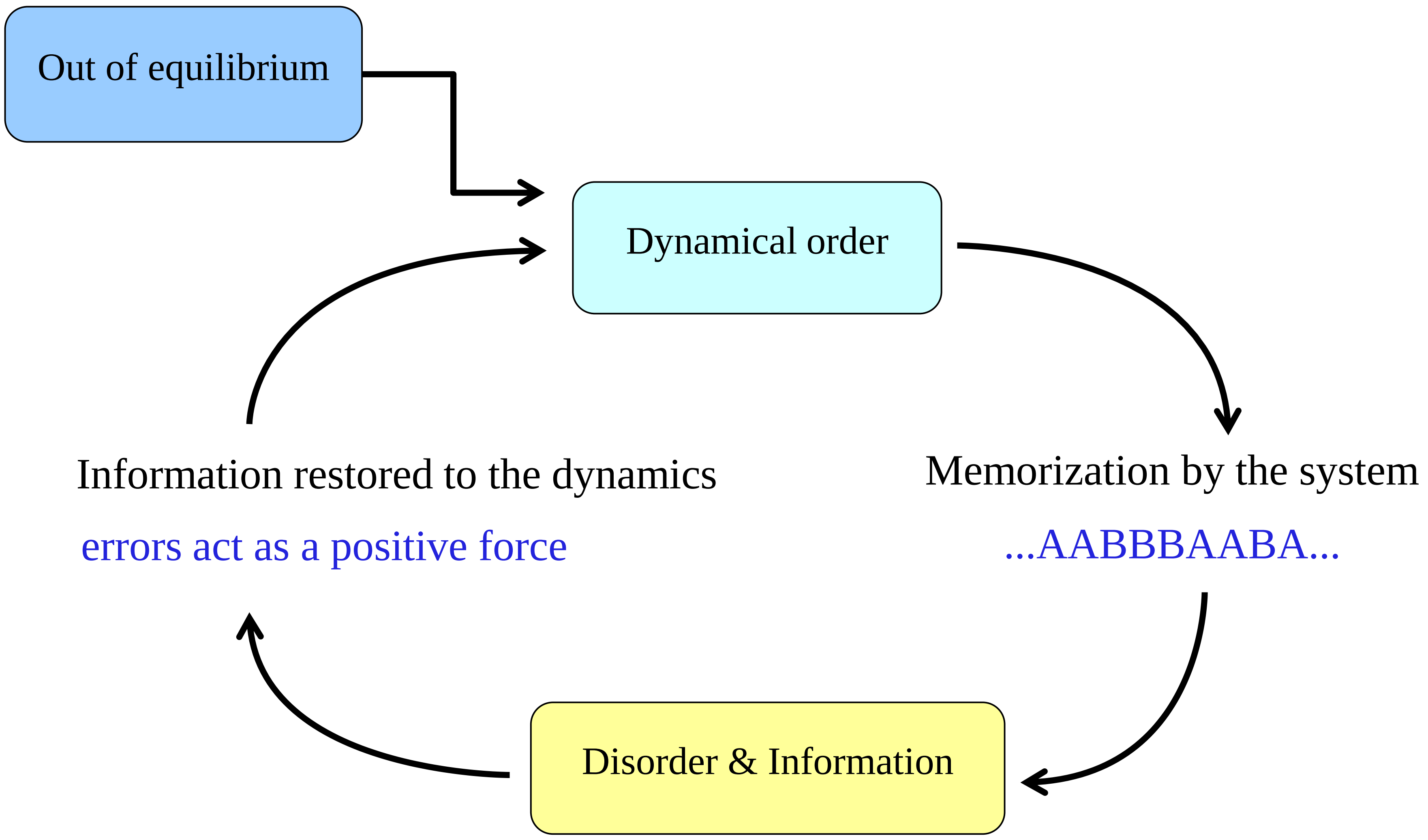
affinity per nucleotide $A = \varepsilon + D - I$



mutual information I(X,Y)

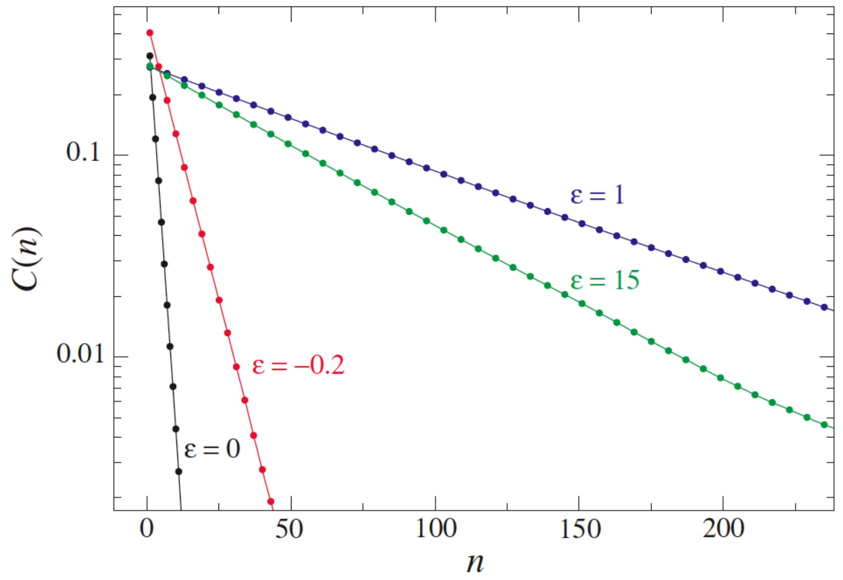


Self-sustained nonequilibrium organization



Dissipation-information tradeoff in correlated processes

Spatial correlations increase out of equilibrium:

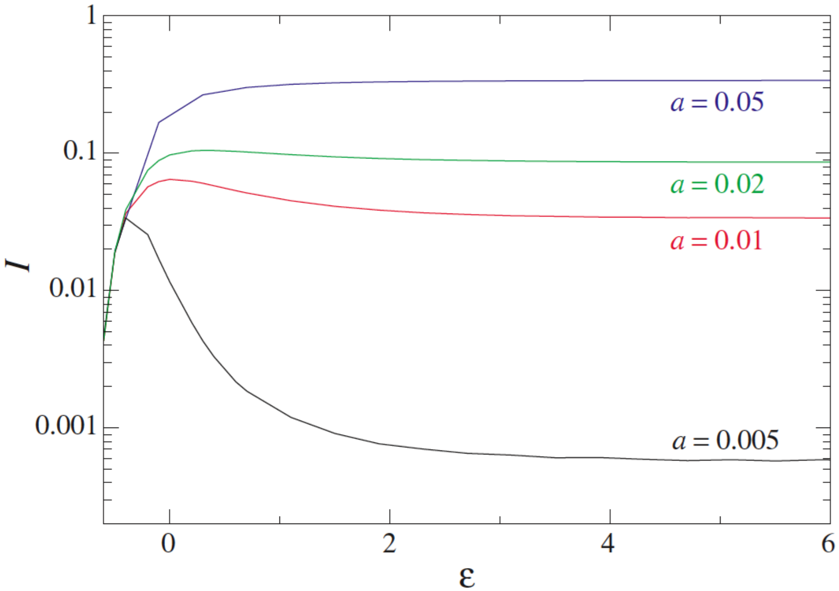


First-neighbor interaction:

$$\omega m + n \underset{k_{-mn}}{\overset{k_{+mn}}{\rightleftharpoons}} \omega mn$$

Mutual information is not always

maximal in the totally irreversible case:



Andrieux and Gaspard 2009

Summary

Nonequilibrium self-organization and molecular order

Irreversibility & temporal order

The typical paths are more ordered **in time** than the time-reversed ones $h^{\mathrm{R}} \geq h$

Irreversibility measures the time asymmetry in dynamical randomness $\Delta_i S = h^{\mathrm{R}} - h$

Thermodynamic arrow of time revealed down to the nanoscale in driven Brownian motion

Nonequilibrium information processing

Landauer principle $D\, k_B T$ per bit

Constructive role of nonequilibrium fluctuations: DNA replication,...

Disorder and information as thermodynamics forces $A = \varepsilon + D - I$

Mechanism for nonequilibrium self-organization ($\neq$ nonlinearities, ratchet effect, ...)

Acknowledgments

Collaborators

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