MICROREVERSIBILITY AND TIME ASYMMETRY IN NONEQUILIBRIUM STATISTICAL MECHANICS AND THERMODYNAMICS

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- **INTRODUCTION: TIME-REVERSAL SYMMETRY BREAKING**
- **FLUCTUATION THEOREM FOR CURRENTS & NONLINEAR RESPONSE**
- **THEOREM OF NONEQUILIBRIUM TEMPORAL ORDERING**
- **CONCLUSIONS**

ICTS Program on Non-Equilibrium Statistical Physics,

Indian Institute of Technology, Kanpur

NESP2010 Ilya Prigogine Lecture, 30 January 2010

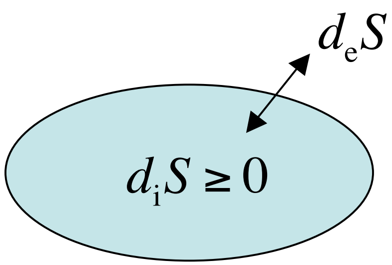
ILYA PRIGOGINE (1917-2003)

Second law of thermodynamics:

Open system:

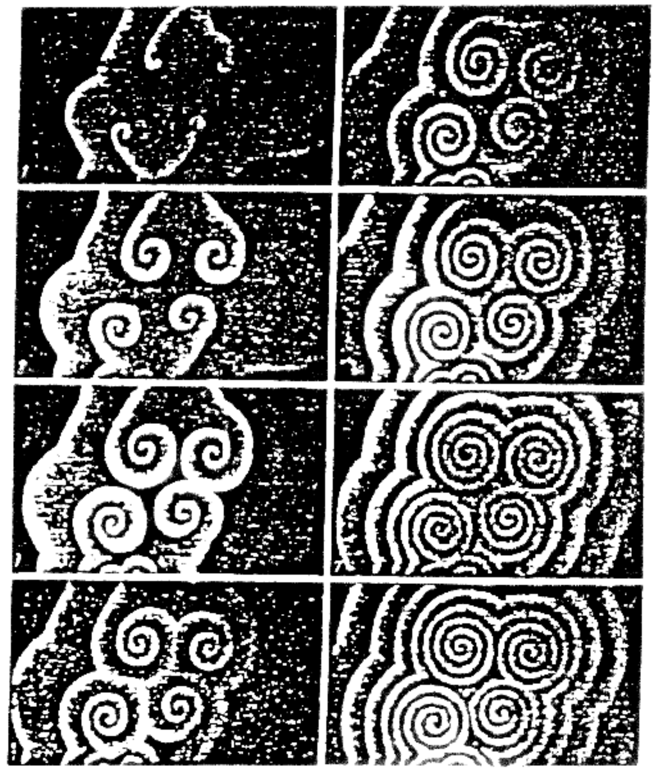
$$dS = d_e S + d_i S$$

entropy flow

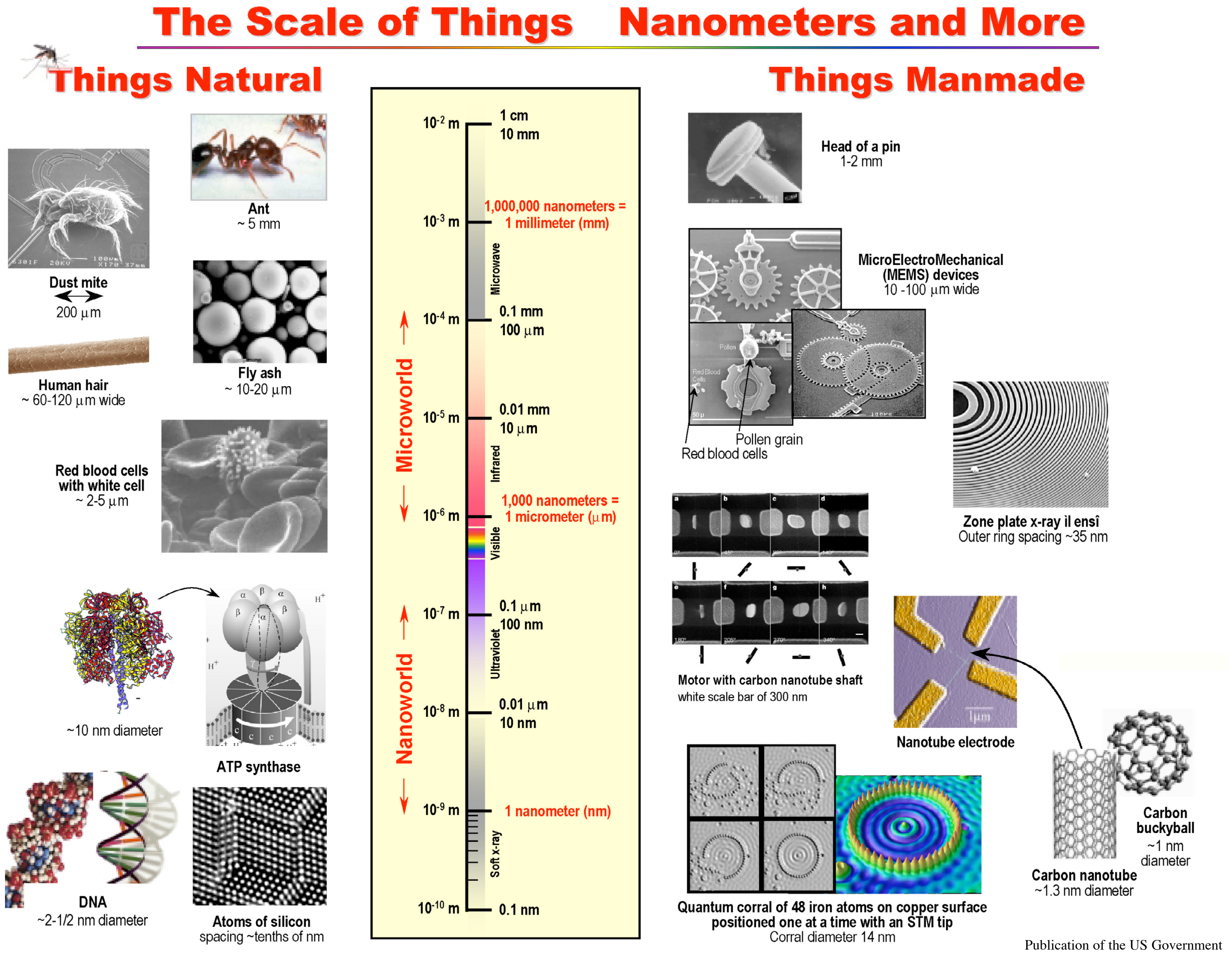


entropy production

spiral waves in the BZ reaction



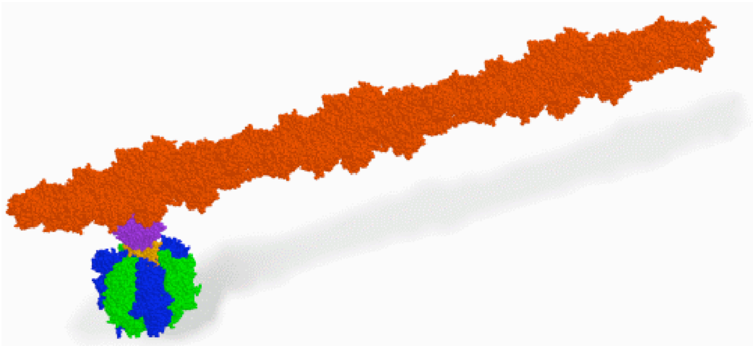
Nobel Prize in Chemistry (1977)
for his contributions to non-equilibrium thermodynamics,
particularly the theory of dissipative structures.



The Scale of Things Nanometers and More
Things Natural
Things Manmade
Dust mite
200 μm
Ant
~ 5 mm
Human hair
~ 60-120 μm wide
Fly ash
~ 10-20 μm
Red blood cells
with white cell
~ 2-5 μm
~10 nm diameter
ATP synthase
DNA
~2-1/2 nm diameter
Atoms of silicon
spacing ~tenths of nm
10^-2 m
1 cm
10 mm
10^-3 m
1,000,000 nanometers =
1 millimeter (mm)
Microwave
10^-4 m
0.1 mm
100 μm
Microworld
10^-5 m
0.01 mm
10 μm
Infrared
10^-6 m
1,000 nanometers =
1 micrometer (μm)
Visible
10^-7 m
0.1 μm
100 nm
Ultraviolet
Nanoworld
10^-8 m
0.01 μm
10 nm
10^-9 m
1 nanometer (nm)
Soft x-ray
10^-10 m
0.1 nm
Head of a pin
1-2 mm
MicroElectroMechanical
(MEMS) devices
10 -100 μm wide
Pollen grain
Red blood cells
Zone plate x-ray il ensî
Outer ring spacing ~35 nm
Motor with carbon nanotube shaft
white scale bar of 300 nm
Nanotube electrode
Carbon
buckyball
~1 nm
diameter
Carbon nanotube
~1.3 nm diameter
Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm
Publication of the US Government

F_1-ATPase NANOMOTOR

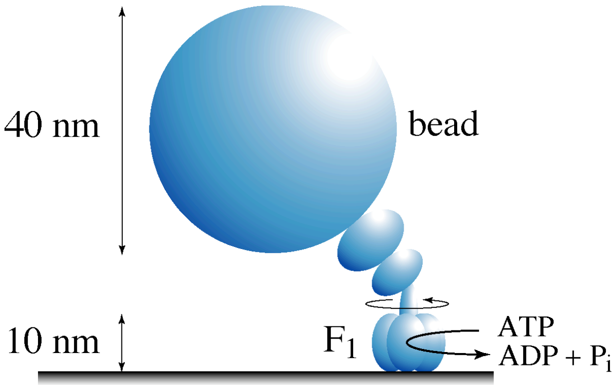
H. Noji, R. Yasuda, M. Yoshida, & K. Kinosita Jr., Nature **386** (1997) 299



(Courtesy Professor K. Kinosita Jr.)

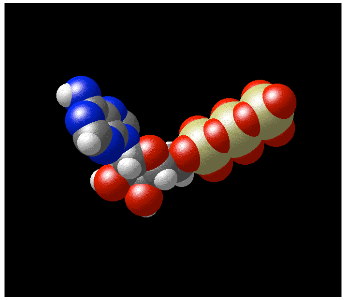
protein: $F_1 = (\alpha\beta)_3\gamma$

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



chemical fuel of the F_1 nanomotor:

ATP adenosine triphosphate



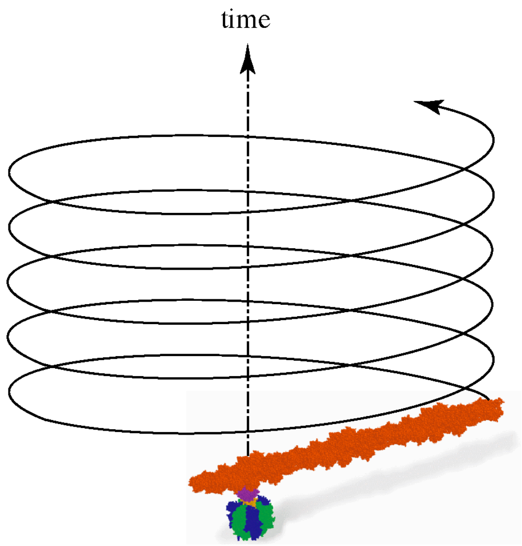
power = 10^{-18} Watt

OUT-OF-EQUILIBRIUM NANOSYSTEMS

Nanosystems sustaining fluxes of matter or energy, dissipating energy supply

Examples:
- electronic nanocircuits
- heterogeneous catalysis at the nanoscale
- molecular motors
- ribosome
- RNA polymerase: information processing

Structure in 3D space:	***Dynamics in 4D space-time:***
• no flux $\langle J_\gamma \rangle = 0$	• flux $\langle J_\gamma \rangle \neq 0$
• no entropy production $\frac{d_i S}{dt} = 0$	• entropy production $\frac{d_i S}{dt} > 0$
• no energy supply needed	• energy supply required
• equilibrium	• nonequilibrium
• in contact with one reservoir	• in contact with several reservoirs

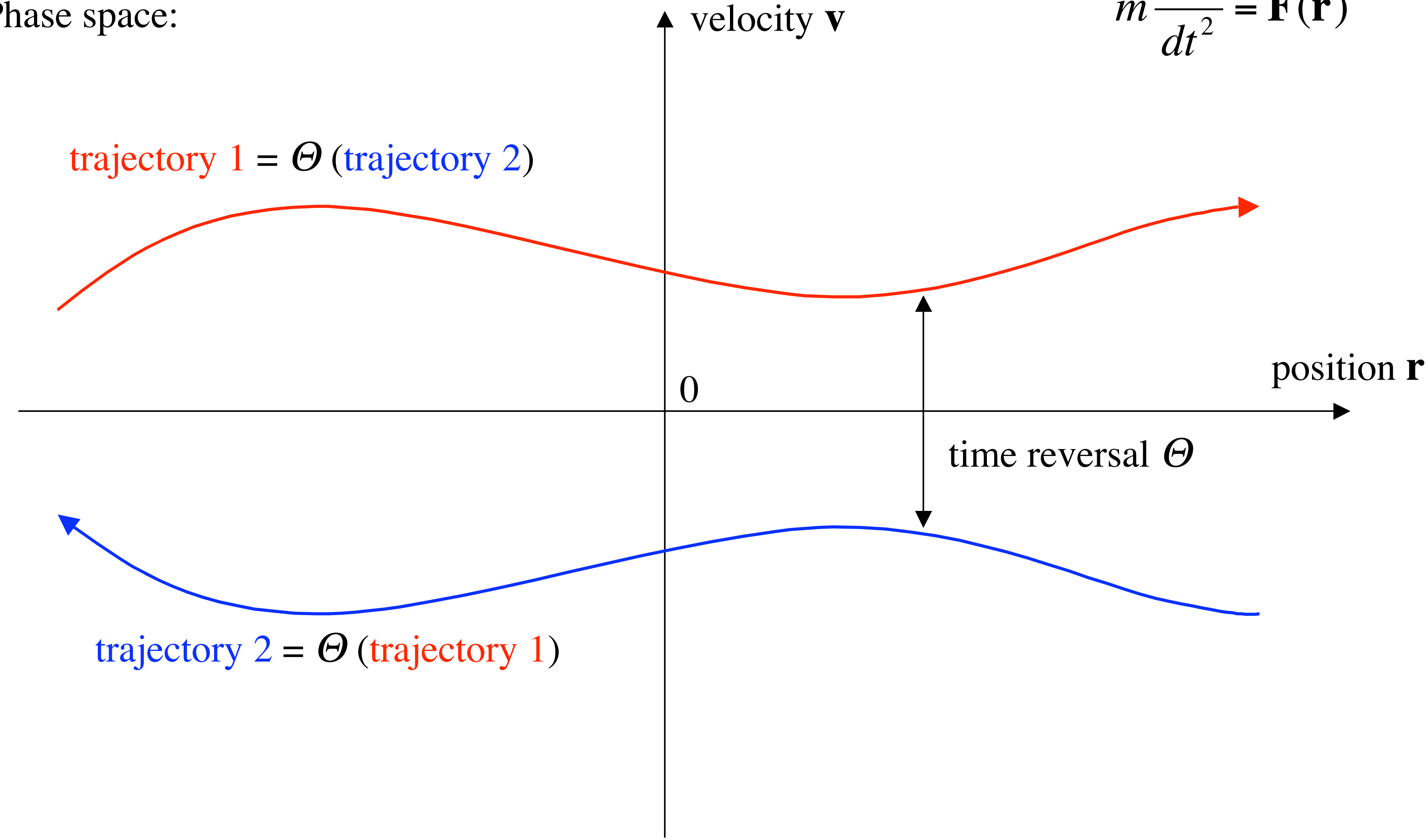


MICRODYNAMICS: TIME-REVERSAL SYMMETRY $\Theta(\mathbf{r},\mathbf{v}) = (\mathbf{r},-\mathbf{v})$

Newton's equation of mechanics is time-reversal symmetric.

$$m\frac{d^2\mathbf{r}}{dt^2} = \mathbf{F}(\mathbf{r})$$

Phase space:

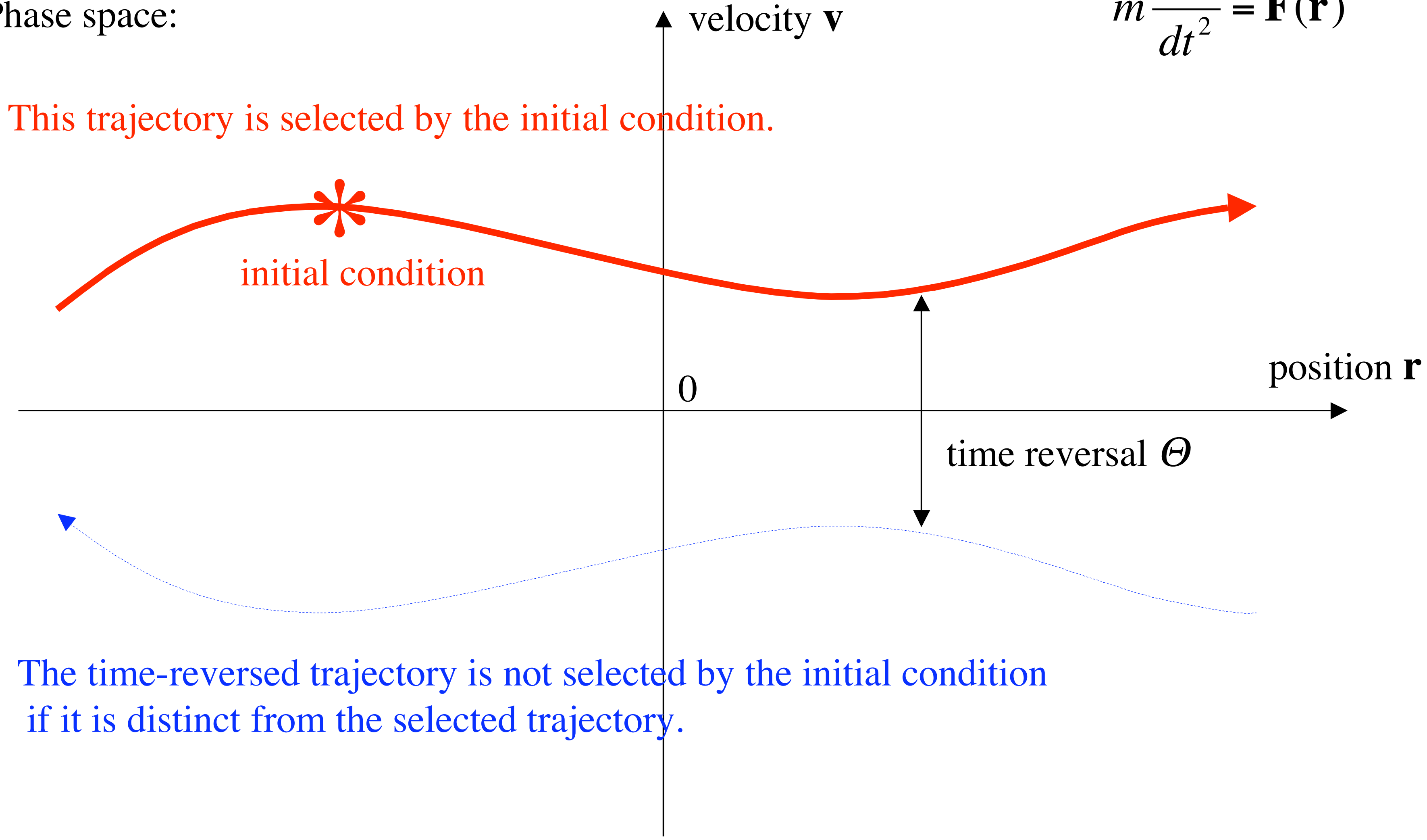


BREAKING OF TIME-REVERSAL SYMMETRY

Selecting the initial condition typically breaks the time-reversal symmetry.

Phase space:

$$m\frac{d^2\mathbf{r}}{dt^2} = \mathbf{F}(\mathbf{r})$$

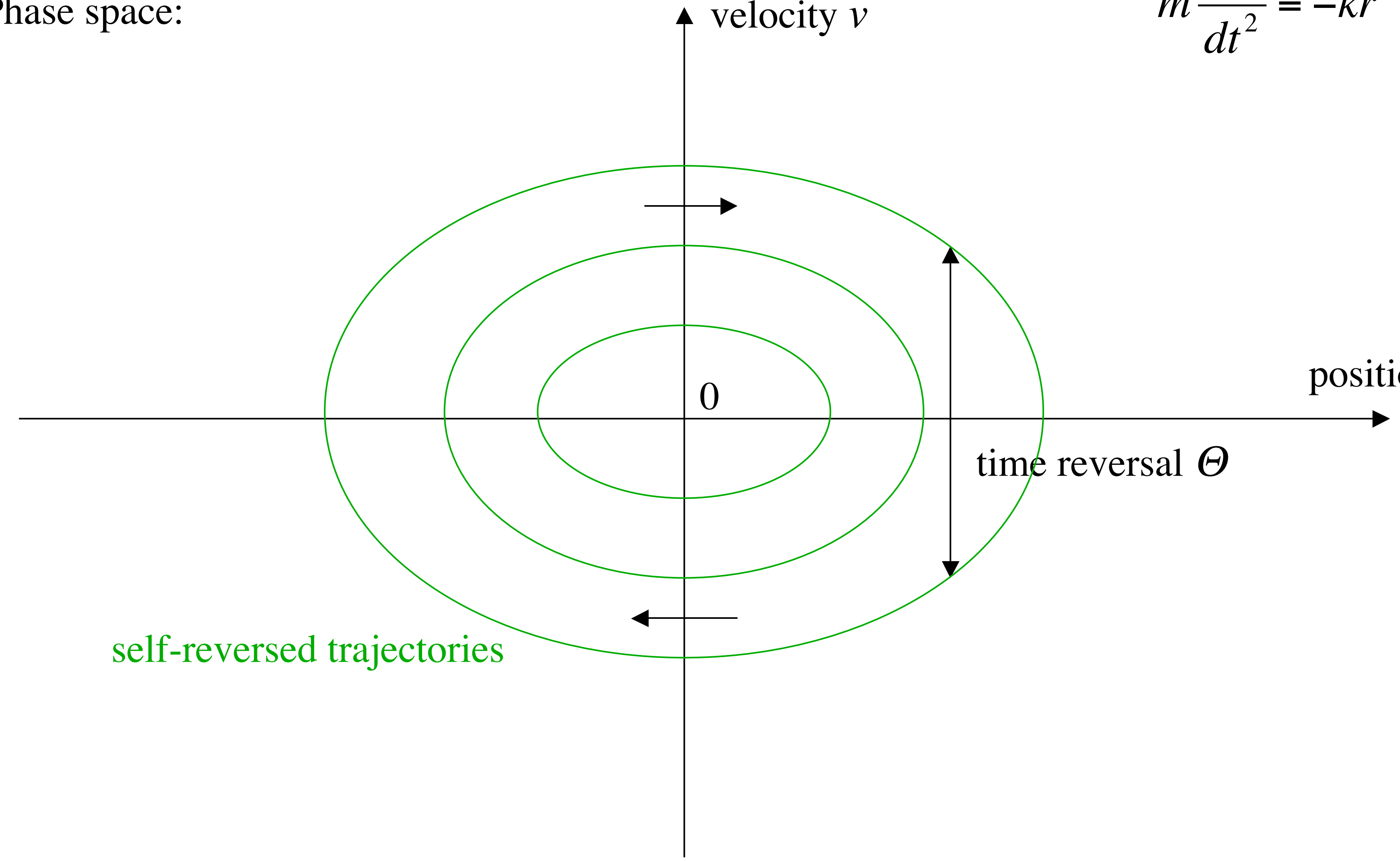


HARMONIC OSCILLATOR

All the trajectories are time-reversal symmetric in the harmonic oscillator.

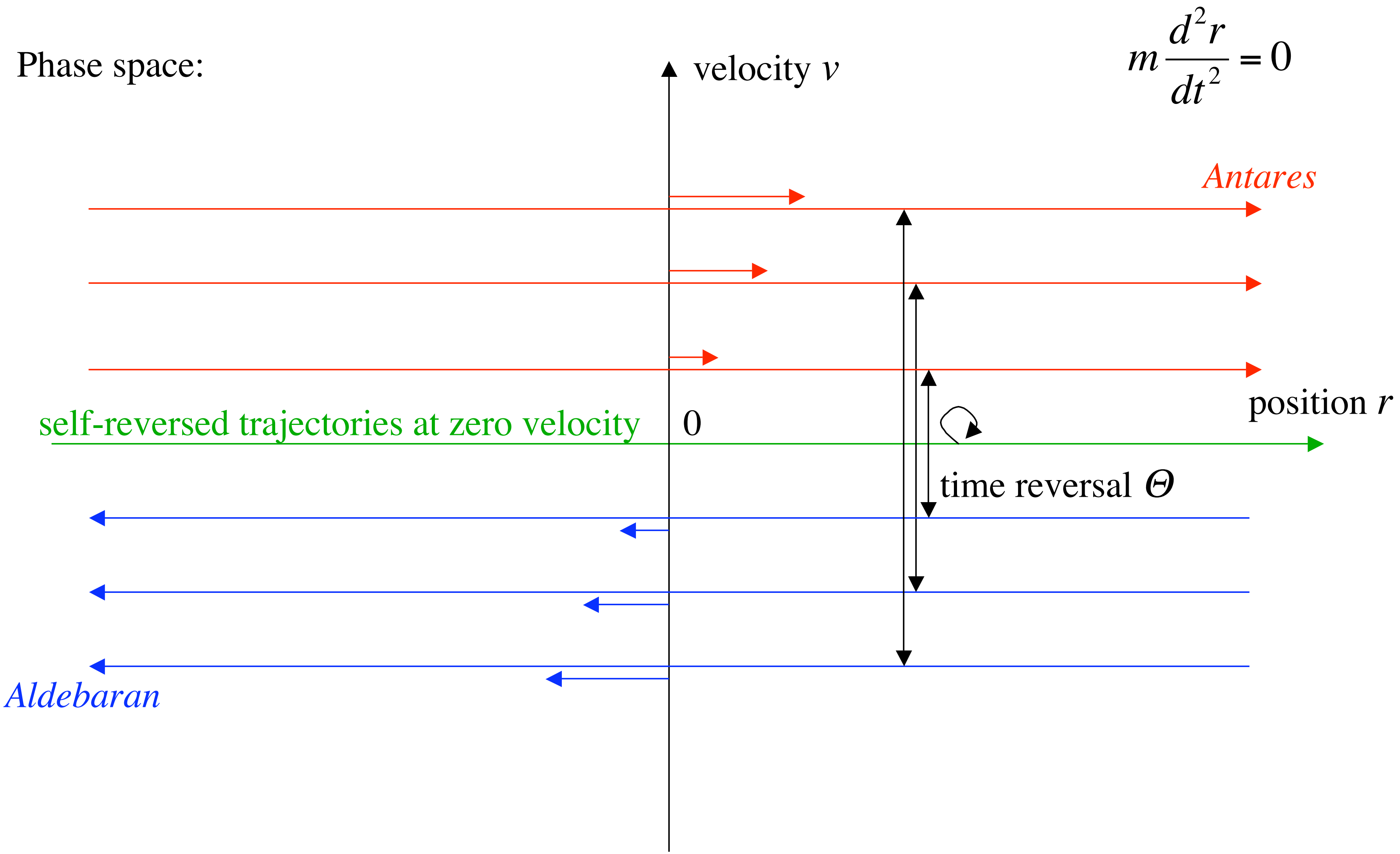
$$m\frac{d^2r}{dt^2} = -kr$$

Phase space:



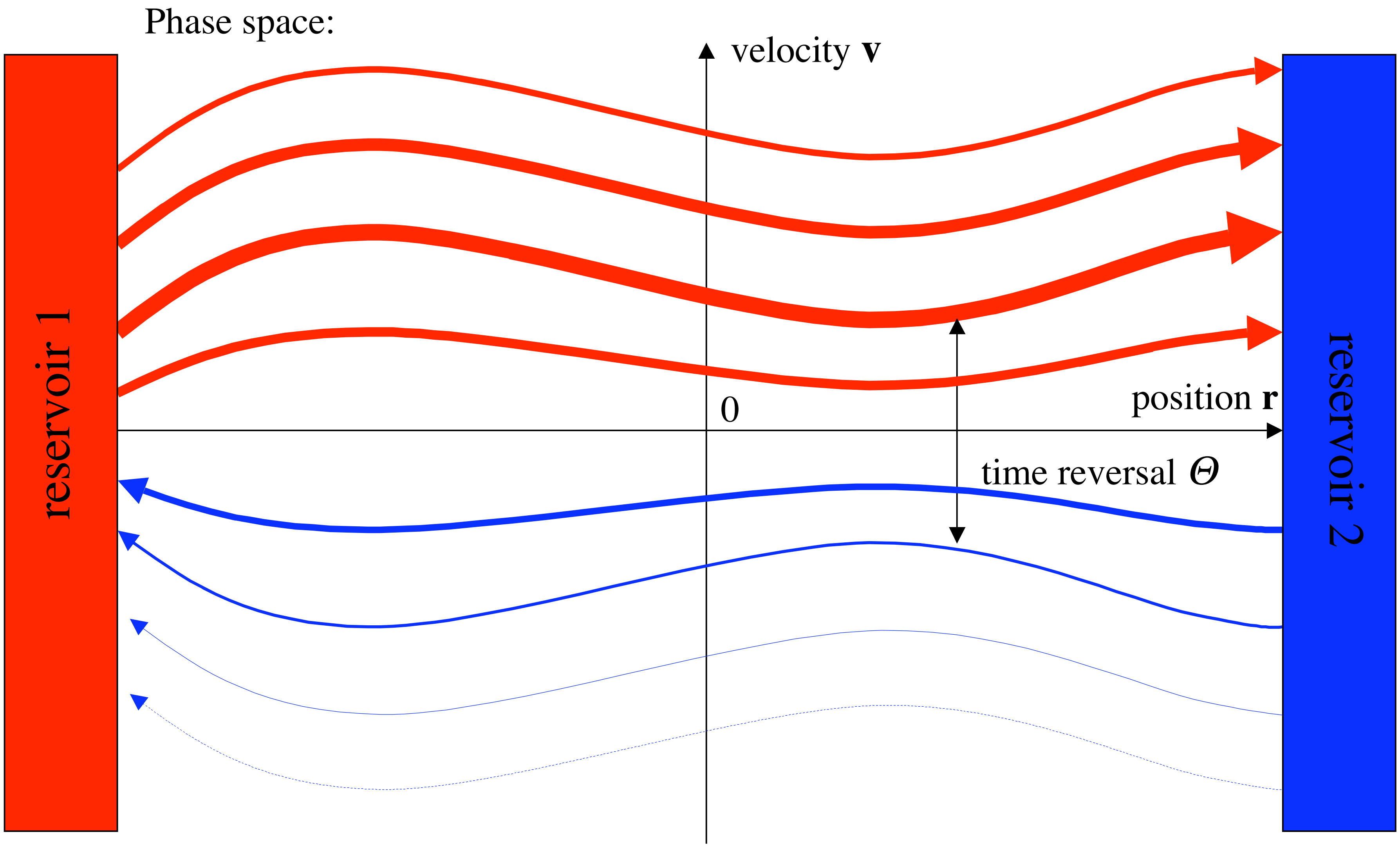
FREE PARTICLE

Almost all of the trajectories are distinct from their time reversal.



BREAKING OF TIME-REVERSAL SYMMETRY IN NONEQUILIBRIUM STEADY STATES

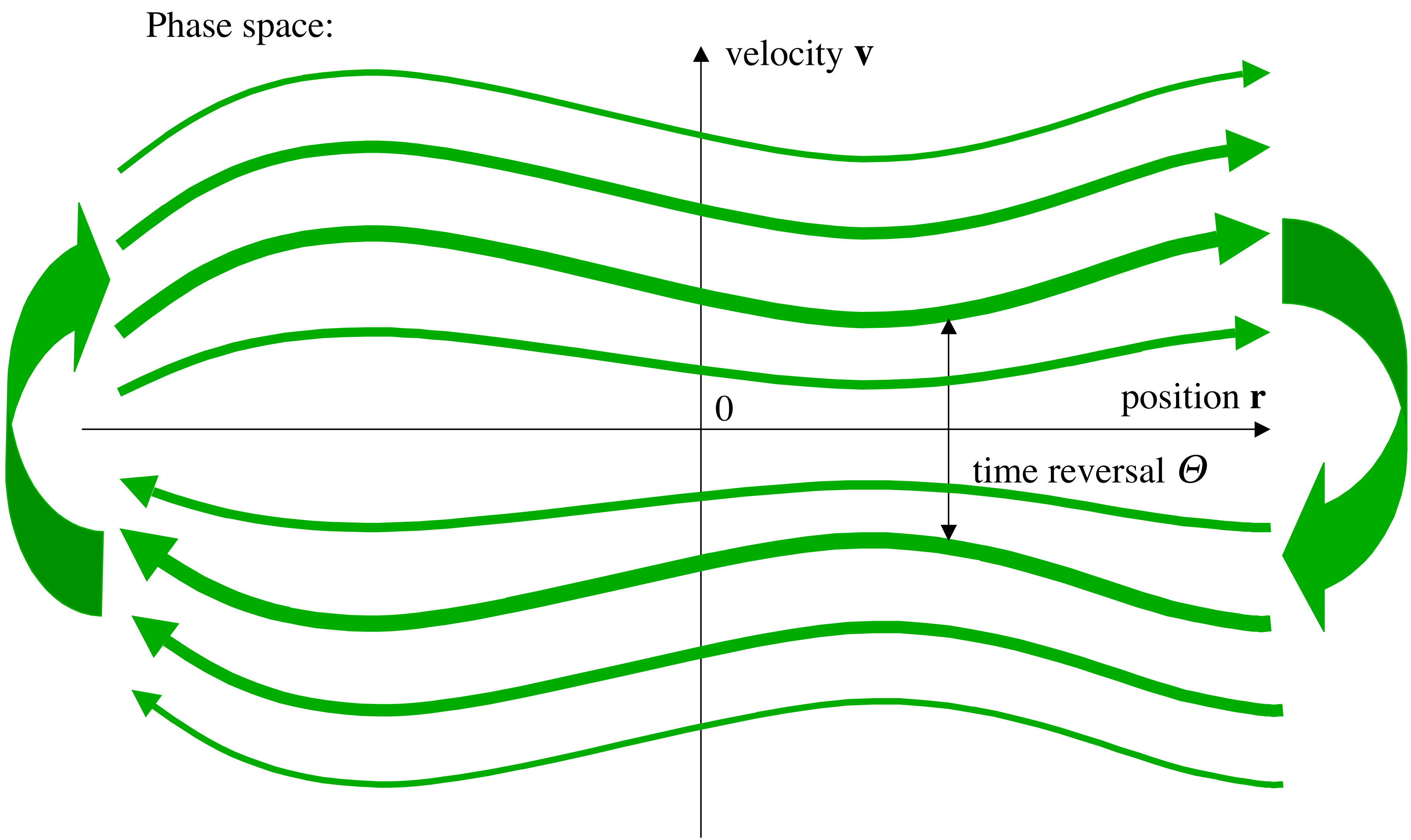
weighting each trajectory with a probability



Nonequilibrium stationary probability distribution: ***directionality***

DETAILED BALANCING AT EQUILIBRIUM

The time-reversal symmetry, e.g. detailed balancing, is restored at equilibrium.



Equilibrium stationary probability distribution: ***no directionality***

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 $\mathcal{T}$ are different from their time-reversal image $\Theta\,\mathcal{T}$:

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

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

Stationary probability distribution: (random event $\mathcal{A}$)

equilibrium: $P_{\rm eq}(\Theta\,\mathcal{A}) = P_{\rm eq}(\mathcal{A})$ (detailed balancing)

nonequilibrium: $P_{\rm neq}(\Theta\,\mathcal{A}) \neq P_{\rm neq}(\mathcal{A})$

STEADY-STATE FLUCTUATION THEOREM FOR CURRENTS

fluctuating currents: $J_\gamma = \frac{1}{t}\int_0^t j_\gamma(t')\,dt'$

ex: • electric currents in a nanoscopic conductor
• rates of chemical reactions
• velocity of a molecular motor

De Donder affinities or thermodynamic forces: $A_\gamma = \frac{\Delta G_\gamma}{T} = \frac{G_\gamma - G_\gamma^{\rm eq}}{T}$ (free energy sources)

Stationary probability distribution P :

• No directionality at equilibrium $A_\gamma = 0$
• Directionality out of equilibrium $A_\gamma \neq 0$

$$\frac{P\{+J_\gamma\}}{P\{-J_\gamma\}} \approx {\rm e}^{\frac{t}{k_{\rm B}}\sum_\gamma A_\gamma J_\gamma}$$

time interval:

$t \to +\infty$

valid far from equilibrium as well as close to equilibrium

thermodynamic entropy production: $\left.\frac{d_{\rm i}S}{dt}\right|_{\rm st} = \sum_{\gamma=1}^{c} A_\gamma \langle J_\gamma \rangle \geq 0$

D. Andrieux & P. Gaspard, *Fluctuation theorem and Onsager reciprocity relations*, J. Chem. Phys. **121** (2004) 6167.

D. Andrieux & P. Gaspard, *Fluctuation theorem for currents and Schnakenberg network theory*, J. Stat. Phys. **127** (2007) 107.

GENERATING FUNCTION OF THE CURRENTS: FULL COUNTING STATISTICS

fluctuation theorem for the currents:

with the probability distribution P

$$\frac{P\{+J_\gamma\}}{P\{-J_\gamma\}} \approx \mathrm{e}^{\frac{t}{k_B}\sum_\gamma A_\gamma J_\gamma}$$

generating function:

$$Q(\{\lambda_\gamma, A_\gamma\}) = \lim_{t\to\infty} -\frac{1}{t}\ln\left\langle \exp\left[-\sum_\gamma \lambda_\gamma \int_0^t j_\gamma(t')\,dt'\right]\right\rangle_{\text{noneq.}}$$

fluctuation theorem for the currents bis:

$$Q(\{\lambda_\gamma, A_\gamma\}) = Q(\{A_\gamma - \lambda_\gamma, A_\gamma\})$$

average currents: $$J_\alpha = \left.\frac{\partial Q}{\partial \lambda_\alpha}\right|_{\lambda_\alpha = 0} = \sum_\beta L_{\alpha,\beta} A_\beta + \frac{1}{2}\sum_{\beta,\gamma} M_{\alpha,\beta\gamma} A_\beta A_\gamma + \frac{1}{6}\sum_{\beta,\gamma,\delta} N_{\alpha,\beta\gamma\delta} A_\beta A_\gamma A_\delta + \cdots$$

LINEAR & NONLINEAR RESPONSE THEORY

linear response coefficients

Green-Kubo formulas: 2nd cumulants

$$L_{\alpha,\beta} = -\frac{1}{2}\frac{\partial^2 Q}{\partial\lambda_\alpha\partial\lambda_\beta}\left(\{0,0\}\right) = \frac{1}{2}\int_{-\infty}^{+\infty}\left\langle\left[j_\alpha(t)-\langle j_\alpha\rangle\right]\left[j_\beta(0)-\langle j_\beta\rangle\right]\right\rangle dt$$

Onsager reciprocity relations: $L_{\alpha,\beta} = L_{\beta,\alpha}$ is totally symmetric

nonlinear response coefficients at 2nd order

2nd responses of currents: $M_{\alpha,\beta\gamma} \equiv \frac{\partial^3 Q}{\partial\lambda_\alpha\partial A_\beta\partial A_\gamma}\left(\{0,0\}\right)$

1st responses of 2nd cumulants: $R_{\alpha\beta,\gamma} \equiv -\frac{\partial^3 Q}{\partial\lambda_\alpha\partial\lambda_\beta\partial A_\gamma}\left(\{0,0\}\right)$

= 1st responses of diffusivities: $R_{\alpha\beta,\gamma} = \frac{\partial}{\partial A_\gamma}\int_{-\infty}^{+\infty}\left\langle\left[j_\alpha(t)-\langle j_\alpha\rangle\right]\left[j_\beta(0)-\langle j_\beta\rangle\right]\right\rangle_{\text{noneq.}} dt\Big|_{\mathbf{A}=0}$

2nd responses of currents =
1st responses of 2nd cumulants:

$$\boxed{M_{\alpha,\beta\gamma} = \tfrac{1}{2}\left(R_{\alpha\beta,\gamma} + R_{\alpha\gamma,\beta}\right)}$$

D. Andrieux & P. Gaspard, J. Chem. Phys. **121** (2004) 6167; J. Stat. Mech. (2006) P01011.

NONLINEAR RESPONSE THEORY (cont'd)

fluctuation theorem for the currents: $$Q(\{\lambda_\gamma, A_\gamma\}) = Q(\{A_\gamma - \lambda_\gamma, A_\gamma\})$$

average current: $$J_\alpha = \left.\frac{\partial Q}{\partial \lambda_\alpha}\right|_{\lambda_\alpha=0} = \sum_\beta L_{\alpha,\beta} A_\beta + \frac{1}{2}\sum_{\beta,\gamma} M_{\alpha,\beta\gamma} A_\beta A_\gamma + \frac{1}{6}\sum_{\beta,\gamma,\delta} N_{\alpha,\beta\gamma\delta} A_\beta A_\gamma A_\delta + \cdots$$

nonlinear response coefficients at 3rd order

3rd responses of currents: $$N_{\alpha,\beta\gamma\delta} \equiv \frac{\partial^4 Q}{\partial\lambda_\alpha \partial A_\beta \partial A_\gamma \partial A_\delta}(\{0,0\})$$

2nd responses of 2nd cumulants: $$T_{\alpha\beta,\gamma\delta} \equiv -\frac{\partial^4 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial A_\gamma \partial A_\delta}(\{0,0\})$$

1st responses of 3rd cumulants = 4th cumulants:

$$S_{\alpha\beta\gamma,\delta} \equiv \frac{\partial^4 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial A_\delta}(\{0,0\}) = -\frac{1}{2}\frac{\partial^4 Q}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(\{0,0\})$$

relations at 3nd order: $$N_{\alpha,\beta\gamma\delta} = \tfrac{1}{2}\left(T_{\alpha\beta,\gamma\delta} + T_{\alpha\gamma,\beta\delta} + T_{\alpha\delta,\beta\gamma} - S_{\alpha\beta\gamma,\delta}\right)$$

D. Andrieux & P. Gaspard, J. Stat. Mech. (2007) P02006.

QUANTUM NANOSYSTEMS

de Broglie quantum wavelength: $\lambda = h/(mv)$

electrons are much lighter than nuclei -> quantum effects are important in electronics

S. Gustavsson et al., *Counting Statistics of Single Electron Transport in a Quantum Dot*, Phys. Rev. Lett. **96**, 076605 (2006).

$T = 350$ mK

current fluctuations in a GaAs-GaAlAs quantum dot (QD): real-time detection with a quantum point contact (QPC)

$V_{\mathrm{QD}} = 1.2$ mV $\quad I_{\mathrm{QD}} = 127$ aA

$V_{\mathrm{QPC}} = 0.5$ mV $\quad I_{\mathrm{QPC}} = 4.5$ nA

limit of a large bias voltage: $\left| \pm eV/2 - \varepsilon \right| >> k_{\mathrm{B}} T$

bidirectionality not observed

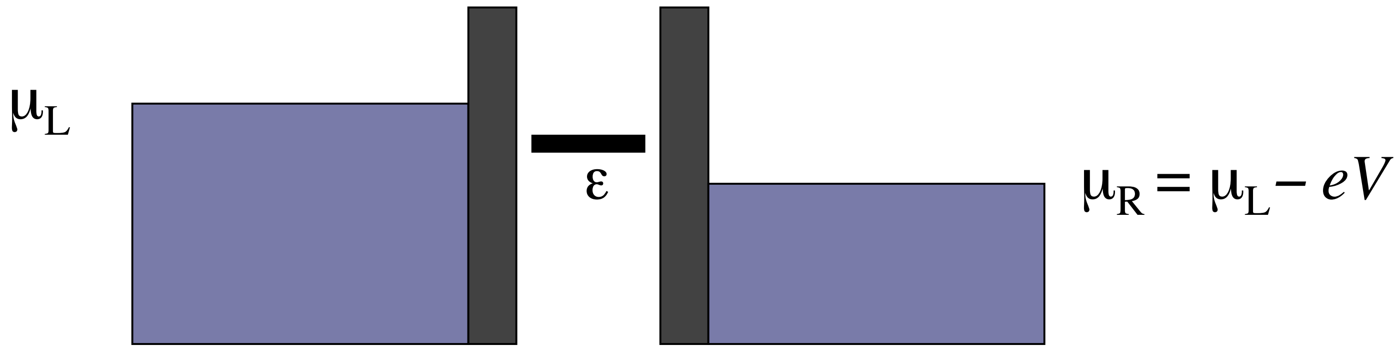
T. Fujisawa et al., *Bidirectional Counting of Single Electrons*, Science **312**, 1634 (2006).

current fluctuations in a AlGaAs/GaAs double quantum dot: real-time detection with a quantum point contact

bidirectionality observed

FULL COUNTING STATISTICS OF FERMIONS

- L. S. Levitov & G. B. Lesovik, *Charge distribution in quantum shot noise*, JETP Lett. **58**, 230 (1993)
- D. A. Bagrets and Yu. V. Nazarov, *Full counting statisticsof charge transfer in Coulomb blockade systems*, Phys. Rev. B **67**, 085316 (2003).
- J. Tobiska & Yu. V. Nazarov, *Inelastic interaction corrections and universal relations for full counting statistics in a quantum contact*, Phys. Rev. B **72**, 235328 (2005).
- D. Andrieux & P. Gaspard, *Fluctuation theorem for transport in mesoscopic systems*, J. Stat. Mech. P01011 (2006).
- U. Harbola, M. Esposito, and S. Mukamel, *Quantum master equation for electron transport through quantum dots and single molecules*, Phys. Rev. B **74**, 235309 (2006).
- M. Esposito, U. Harbola, and S. Mukamel, *Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems*, Rev. Mod. Phys. **81**, 1665 (2009).



charging rate from side ρ: $\alpha_\rho = W_\rho(0|1) = \Gamma_\rho f_\rho$

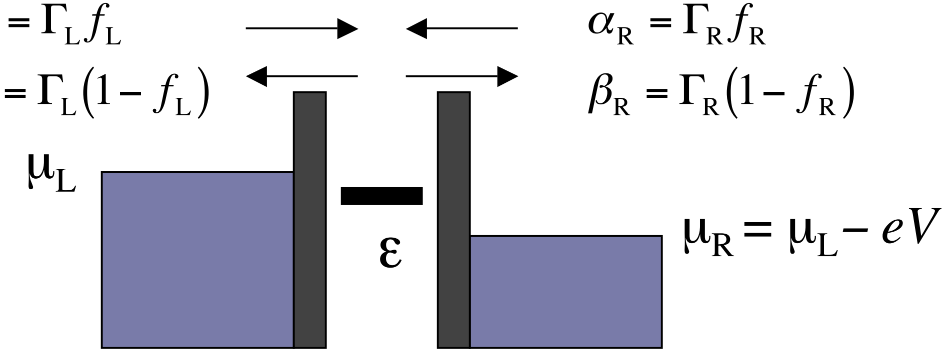
discharging rate from side ρ: $\beta_\rho = W_\rho(1|0) = \Gamma_\rho(1 - f_\rho)$

Fermi-Dirac distributions: $f_\rho = \dfrac{1}{1 + e^{(\varepsilon-\mu_\rho)/(k_B T)}}$ $\rho = L,R$

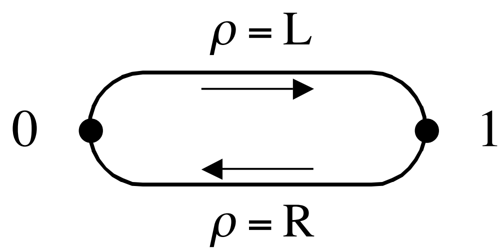
FLUCTUATION THEOREM FOR FERMION TRANSPORT

$\alpha_{\mathrm{L}} = \Gamma_{\mathrm{L}} f_{\mathrm{L}}$ $\qquad$ $\alpha_{\mathrm{R}} = \Gamma_{\mathrm{R}} f_{\mathrm{R}}$

$\beta_{\mathrm{L}} = \Gamma_{\mathrm{L}}(1 - f_{\mathrm{L}})$ $\qquad$ $\beta_{\mathrm{R}} = \Gamma_{\mathrm{R}}(1 - f_{\mathrm{R}})$



graph:



affinity or thermodynamic force defined over the cycle: $\dfrac{\alpha_{\mathrm{L}}\beta_{\mathrm{R}}}{\alpha_{\mathrm{R}}\beta_{\mathrm{L}}} = \mathrm{e}^{\beta(\mu_{\mathrm{L}} - \mu_{\mathrm{R}})} = \mathrm{e}^{\beta eV} \equiv \mathrm{e}^{A}$

Pauli master equation: $$\frac{d\mathbf{P}}{dt} = \begin{bmatrix} -\alpha_{\mathrm{L}} - \alpha_{\mathrm{R}} & \beta_{\mathrm{L}} + \beta_{\mathrm{R}} \\ \alpha_{\mathrm{L}} + \alpha_{\mathrm{R}} & -\beta_{\mathrm{L}} - \beta_{\mathrm{R}} \end{bmatrix} \cdot \mathbf{P}$$

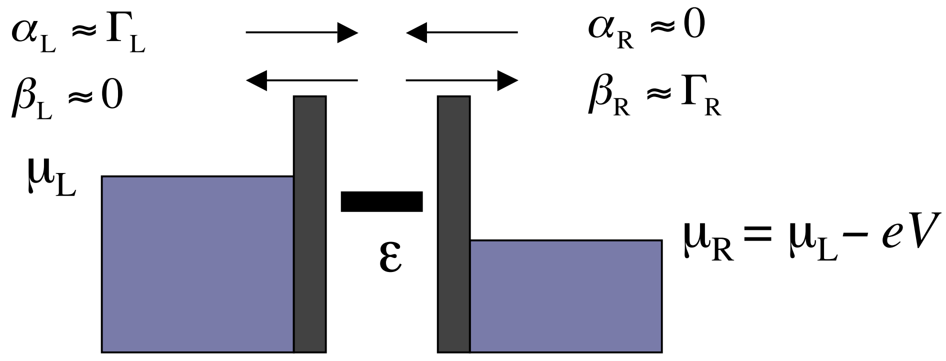
eigenvalue equation: $$\begin{bmatrix} -\alpha_{\mathrm{L}} - \alpha_{\mathrm{R}} & \beta_{\mathrm{L}}\mathrm{e}^{\lambda} + \beta_{\mathrm{R}} \\ \alpha_{\mathrm{L}}\mathrm{e}^{-\lambda} + \alpha_{\mathrm{R}} & -\beta_{\mathrm{L}} - \beta_{\mathrm{R}} \end{bmatrix} \cdot \mathbf{F} = -Q\mathbf{F}$$

generating function:

$$Q(\lambda) = \frac{1}{2}\left[\alpha_{\mathrm{L}} + \alpha_{\mathrm{R}} + \beta_{\mathrm{L}} + \beta_{\mathrm{R}} - \sqrt{(\alpha_{\mathrm{L}} + \alpha_{\mathrm{R}} - \beta_{\mathrm{L}} - \beta_{\mathrm{R}})^2 + 4(\alpha_{\mathrm{L}}\mathrm{e}^{-\lambda} + \alpha_{\mathrm{R}})(\beta_{\mathrm{L}}\mathrm{e}^{\lambda} + \beta_{\mathrm{R}})}\right]$$

fluctuation theorem: $Q(\lambda) = Q(A - \lambda)$ $\qquad$ $\dfrac{P(k,t)}{P(-k,t)} \approx \exp(\beta eVk)$ $\qquad$ $t \to \infty$

FULL COUNTING STATISTICS OF FERMIONS: LARGE BIAS VOLTAGE



$\rho = L,R$

$$f_\rho = \frac{1}{1 + e^{(\varepsilon - \mu_\rho)/(k_B T)}}$$

limit of a large bias voltage: $\left| \pm eV/2 - \varepsilon \right| >> k_B T$

Fermi-Dirac distributions: $f_L \approx 1 \qquad f_R \approx 0$

fully irreversible limit: infinite nonequilibrium driving force: $\dfrac{\alpha_L \beta_R}{\alpha_R \beta_L} = e^A \to \infty$

fluctuation theorem: $\dfrac{P(k,t)}{P(-k,t)} \approx \infty$

generating function:

$$Q(\lambda) \approx \frac{1}{2}\left[\Gamma_L + \Gamma_R - \sqrt{(\Gamma_L - \Gamma_R)^2 + 4\Gamma_L \Gamma_R e^{-\lambda}}\right]$$

QUANTUM FLUCTUATION THEOREM WITH A MAGNETIC FIELD B

D. Andrieux, P. Gaspard, T. Monnai & S. Tasaki,
The fluctuation theorem for currents in open quantum systems,
New J. Phys. **11** (2009) 043014; *Erratum* 109802

affinities or thermodynamic forces:

$$A_0 \equiv \beta_1 - \beta_2$$

$$A_\alpha \equiv -\beta_1 \mu_{1\alpha} + \beta_2 \mu_{2\alpha} \qquad \text{for } \alpha = 1,2,\ldots,c$$

quantum steady-state fluctuation theorem for currents:

$$Q\left(\left\{\lambda_\gamma, A_\gamma\right\}; B\right) = Q\left(\left\{A_\gamma - \lambda_\gamma, \lambda_\gamma\right\}; -B\right)$$

linear response coefficients

Casimir-Onsager reciprocity relations: $L_{\alpha,\beta}(B) = L_{\beta,\alpha}(-B)$

nonlinear response coefficients: magnetic-field asymmetry

$$\frac{\partial^3 Q}{\partial\lambda_\alpha \partial A_\beta \partial A_\gamma}(\mathbf{0},\mathbf{0};B) = -\frac{\partial^3 Q}{\partial\lambda_\alpha \partial A_\beta \partial A_\gamma}(\mathbf{0},\mathbf{0};-B)$$

$$R_{\alpha\beta,\gamma}(B) = R_{\alpha\beta,\gamma}(-B) + \frac{\partial^3 Q}{\partial\lambda_\alpha \partial A_\beta \partial A_\gamma}(\mathbf{0},\mathbf{0};B)$$

$$M_{\alpha,\beta\gamma}(B) + M_{\alpha,\beta\gamma}(-B) = R_{\alpha\beta,\gamma}(-B) + R_{\alpha\gamma,\beta}(-B) + \frac{\partial^3 Q}{\partial\lambda_\alpha \partial A_\beta \partial A_\gamma}(\mathbf{0},\mathbf{0};B)$$

FLUCTUATION THEOREM FOR BOSON TRANSPORT

- U. Harbola, M. Esposito, and S. Mukamel., *Statistics and fluctuation theorem for boson and fermion transport through mesoscopic junctions*, Phys. Rev. B **76**, 085408 (2007).
- M. Esposito, U. Harbola, and S. Mukamel., *Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems*, Rev. Mod. Phys. **81**, 1665 (2009).

A single oscillator mode between two heat baths at different temperatures

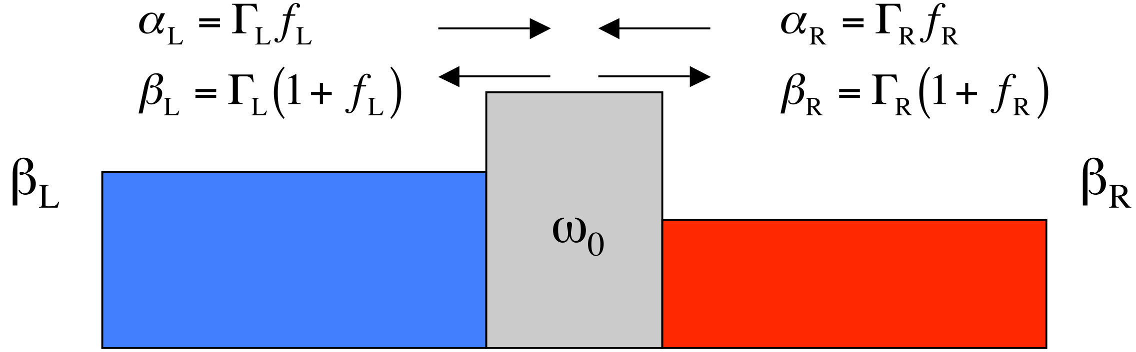
Bose-Einstein distributions:

$$f_\rho = \frac{1}{e^{\beta_\rho \hbar\omega_0} - 1}$$

$$\rho = \mathrm{L,R}$$

$$\alpha_\mathrm{L} = \Gamma_\mathrm{L} f_\mathrm{L} \qquad \alpha_\mathrm{R} = \Gamma_\mathrm{R} f_\mathrm{R}$$

$$\beta_\mathrm{L} = \Gamma_\mathrm{L}(1+f_\mathrm{L}) \qquad \beta_\mathrm{R} = \Gamma_\mathrm{R}(1+f_\mathrm{R})$$



affinity or thermodynamic force:

$$\frac{\alpha_\mathrm{L}\beta_\mathrm{R}}{\alpha_\mathrm{R}\beta_\mathrm{L}} = e^{-\hbar\omega_0(\beta_\mathrm{L}-\beta_\mathrm{R})} \equiv e^{A}$$

master equation:

$$\frac{dP(N,t)}{dt} = (\beta_\mathrm{L}+\beta_\mathrm{R})(N+1)P(N+1,t) - (\beta_\mathrm{L}+\beta_\mathrm{R})NP(N,t) + (\alpha_\mathrm{L}+\alpha_\mathrm{R})NP(N-1,t) - (\alpha_\mathrm{L}+\alpha_\mathrm{R})(N+1)P(N,t)$$

eigenvalue equation:

$$-Q(\lambda)F(N,t) = \left(\beta_\mathrm{L}e^{\lambda}+\beta_\mathrm{R}\right)(N+1)F(N+1,t) - (\beta_\mathrm{L}+\beta_\mathrm{R})NF(N,t) + (\alpha_\mathrm{L}+\alpha_\mathrm{R})NF(N-1,t) - \left(\alpha_\mathrm{L}e^{-\lambda}+\alpha_\mathrm{R}\right)(N+1)F(N,t)$$

fluctuation theorem: $Q(\lambda) = Q(A-\lambda)$ $\quad \frac{P(k,t)}{P(-k,t)} \approx \exp\left[-\hbar\omega_0(\beta_\mathrm{L}-\beta_\mathrm{R})k\right] \quad t \to \infty$

STATISTICS OF PATHS / HISTORIES

Coarse-graining: cell ω in the phase space
stroboscopic observation of the trajectory with sampling time Δt : $\Gamma(n\Delta t;\boldsymbol{r}_0,\boldsymbol{p}_0)$ in cell ω_n
path or history: $\boldsymbol{\omega} = \omega_0\omega_1\omega_2\ldots\omega_{n-1}$

If $\boldsymbol{\omega} = \omega_0\omega_1\omega_2\ldots\omega_{n-1}$ is a possible path, then $\boldsymbol{\omega}^{\mathrm{R}} = \omega_{n-1}\ldots\omega_2\omega_1\omega_0$ is also a possible path.
But, again, $\boldsymbol{\omega} \neq \boldsymbol{\omega}^{\mathrm{R}}$.

Stationary probability distribution as solution of Liouville equation:

$$P(\omega_0\omega_1\omega_2\ldots\omega_{n-1}) = \lim_{t\to\infty}\int d\Gamma\; p(\Gamma,t)\; I_{\omega_0\cap\Phi^{-\Delta t}(\omega_1)\ldots\cap\Phi^{-(n-1)\Delta t}(\omega_{n-1})}(\Gamma)$$

Statistical description: **probability of a path or history**:
equilibrium steady state: $P_{\mathrm{eq}}(\omega_0\omega_1\omega_2\ldots\omega_{n-1}) = P_{\mathrm{eq}}(\omega_{n-1}\ldots\omega_2\omega_1\omega_0)$ (detailed balancing)
nonequilibrium steady state: $P_{\mathrm{neq}}(\omega_0\omega_1\omega_2\ldots\omega_{n-1}) \neq P_{\mathrm{neq}}(\omega_{n-1}\ldots\omega_2\omega_1\omega_0)$

In a nonequilibrium steady state, $\boldsymbol{\omega}$ and $\boldsymbol{\omega}^{\mathrm{R}}$ have different probability weights:
breaking of the time-reversal symmetry by the nonequilibrium probability distribution.

TEMPORAL DISORDER

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 (coin tossing Bernoulli process: $h = \log 2$)

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

the probability of the time-reversed path decays as

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

temporal disorder per unit time: (dynamical randomness)

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

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

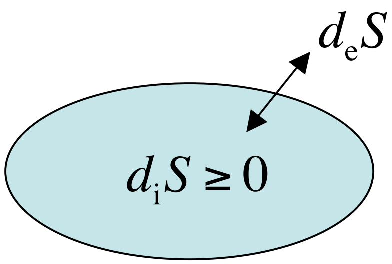
$$h^{\mathrm{R}} = \lim_{n\to\infty} (-1/n\Delta t) \sum_{\boldsymbol{\omega}} P(\boldsymbol{\omega}) \ln P(\boldsymbol{\omega}^{\mathrm{R}})$$

The time-reversed temporal disorder per unit time characterizes

the dynamical randomness of the time-reversed paths.

THERMODYNAMIC ENTROPY PRODUCTION

Open system interacting with its environment:



Second law of thermodynamics: entropy S

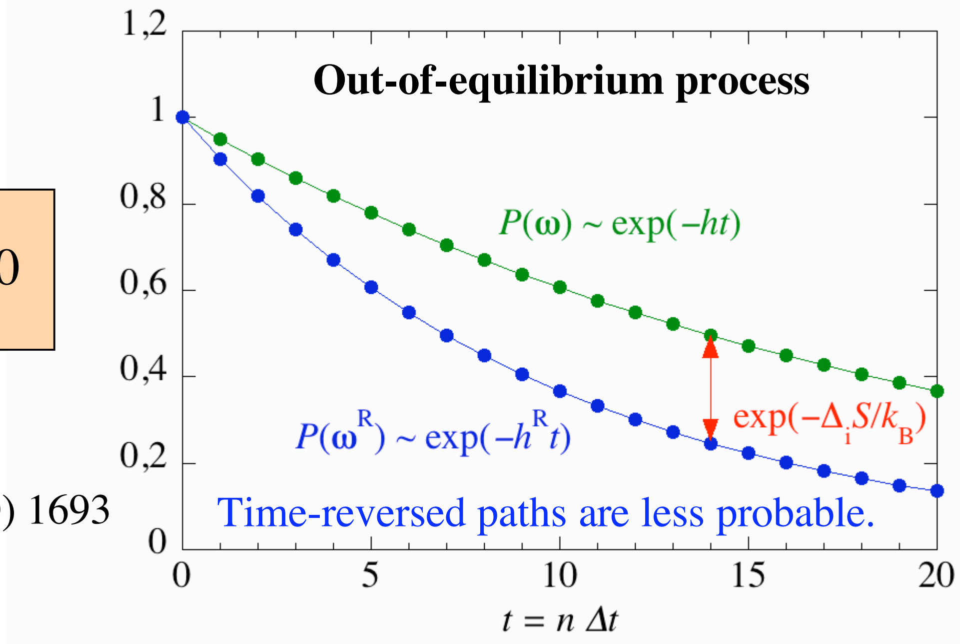
$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \quad \text{with} \quad \frac{d_i S}{dt} \geq 0$$

Entropy production:

$$\frac{1}{k_B}\frac{d_i S}{dt} = h^R - h \geq 0$$

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

P. Gaspard and G. Nicolis, Phys. Rev. Lett. **65** (1990) 1693



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

thermodynamic entropy production = time asymmetry of temporal disorder

OUT-OF-EQUILIBRIUM DIRECTIONALITY

thermodynamic entropy production = temporal disorder h^{R} of time-reversed paths
– temporal disorder h of typical paths
= time asymmetry in temporal disorder
= *measure of the breaking of the time-reversal symmetry in the probability distribution*

Theorem of nonequilibrium 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.

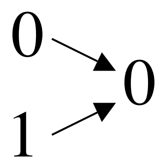
There is thus no contradiction with Boltzmann's interpretation of the second law.

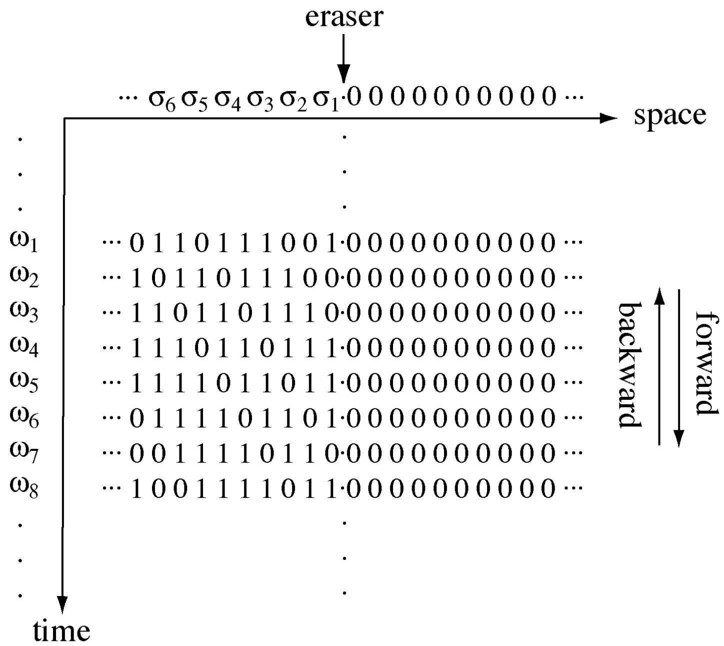
Nonequilibrium processes can generate dynamical order and information.

Remark: This dynamical order is a key feature of biological phenomena.

DEDUCTION OF LANDAUER'S PRINCIPLE

Erasing information in the memory of a computer
is irreversible and dissipates energy.





thermodynamic entropy production per erased bit: $\Delta_{\rm i} S = k_{\rm B}\left(h^{\rm R} - h\right) = k_{\rm B} D$

Shannon disorder per bit: $D \equiv \lim_{l\to\infty} -\frac{1}{l} \sum_{\sigma_1\sigma_2\ldots\sigma_l} \mu(\sigma_1\sigma_2\ldots\sigma_l)\, \ln\, \mu(\sigma_1\sigma_2\ldots\sigma_l)$

Landauer's case of a random binary sequence: $\Delta_{\rm i} S = k_{\rm B}\left(h^{\rm R} - h\right) = k_{\rm B} \ln 2$

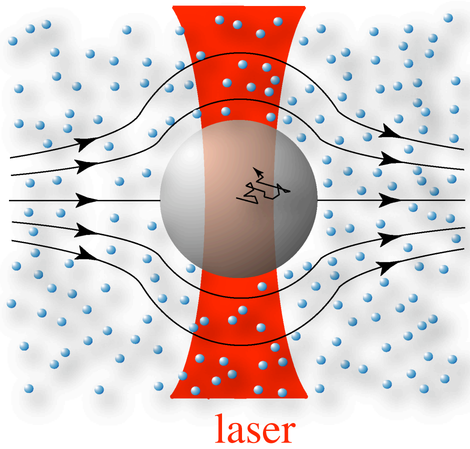
D. Andrieux & P. Gaspard, *Dynamical randomness, information, and Landauer's principle,* EuroPhysics Letters **81** (2008) 28004

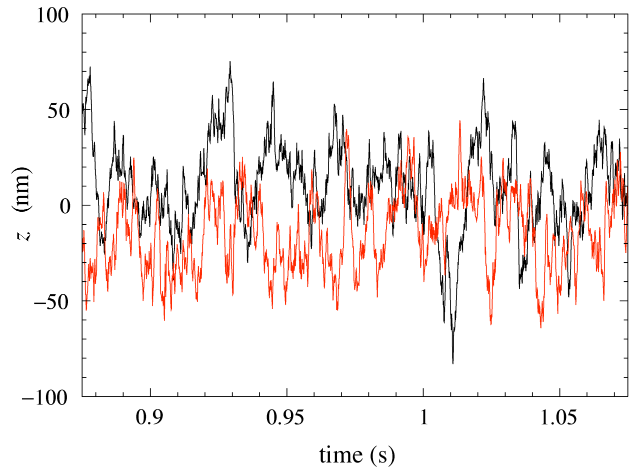
OUT-OF-EQUILIBRIUM FLUCTUATING SYSTEMS

Energy supply

Brownian particle in an optical trap and a flow

(Ciliberto et al., 2008)



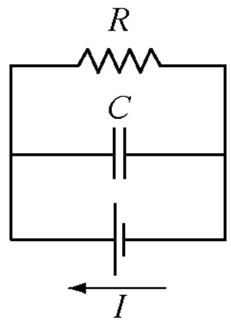


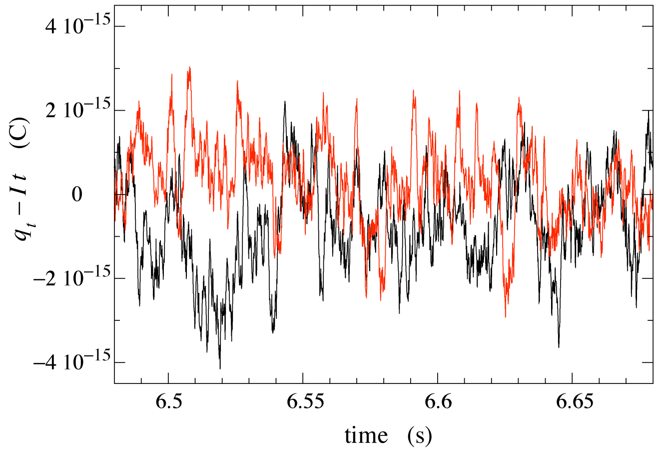
D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, J. Stat. Mech. (2008) P01002

RC electric circuit

(Nyquist thermal noise)

(Ciliberto et al., 2008)

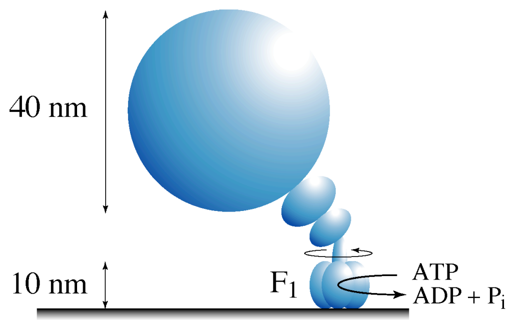


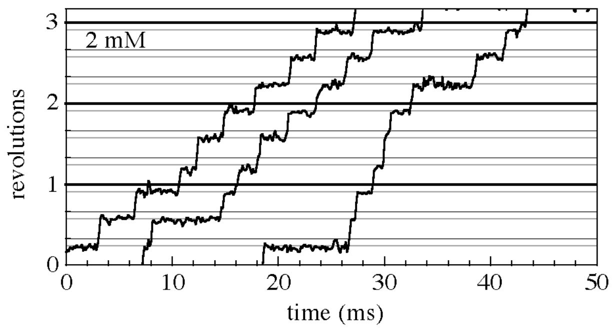


D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, J. Stat. Mech. (2008) P01002

Molecular motor F_1-ATPase

(Kinosita et al., 2001)





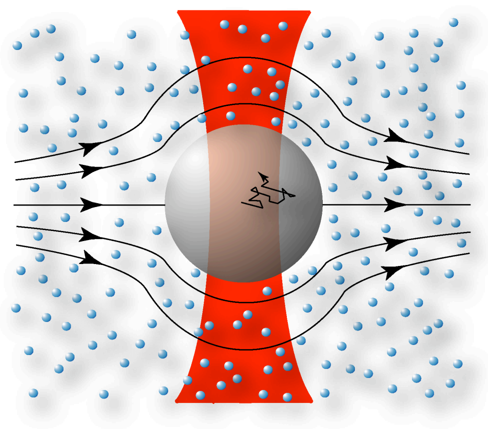
R. Yasuda, H. Noji, M. Yoshida, K. Kinosita Jr. & H. Itoh, Nature **410** (2001) 898

BROWNIAN PARTICLE OUT OF EQUILIBRIUM

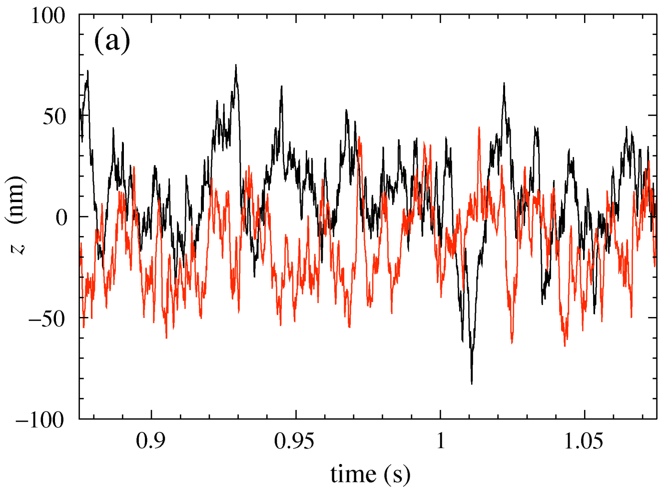
D. Andrieux, P. Gaspard, S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan, J. Stat. Mech. (2008) P01002

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

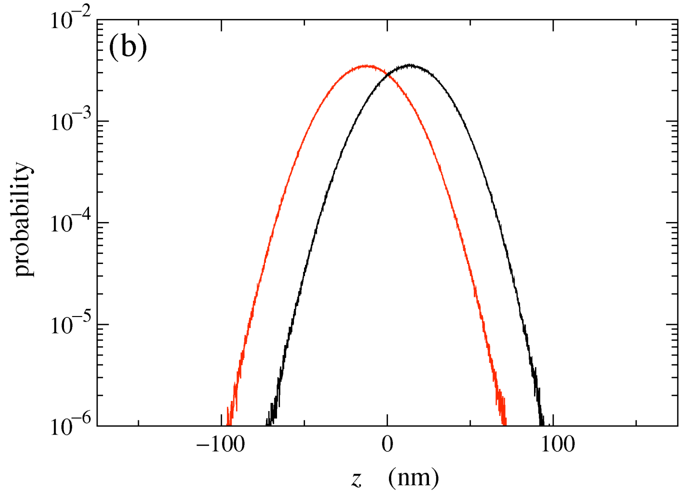
laser



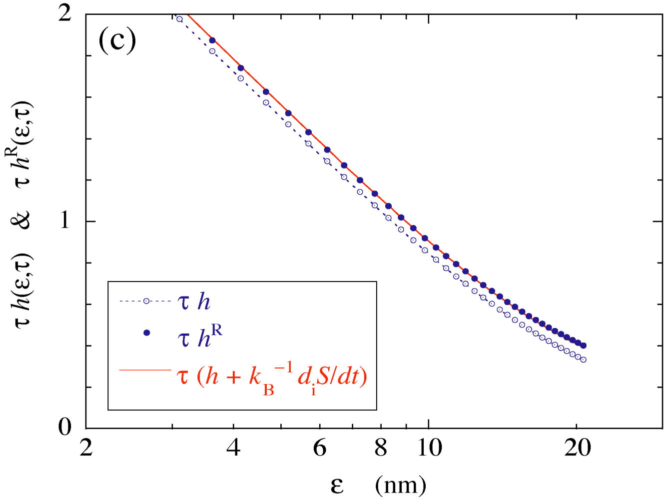
trajectories for u and $-u$



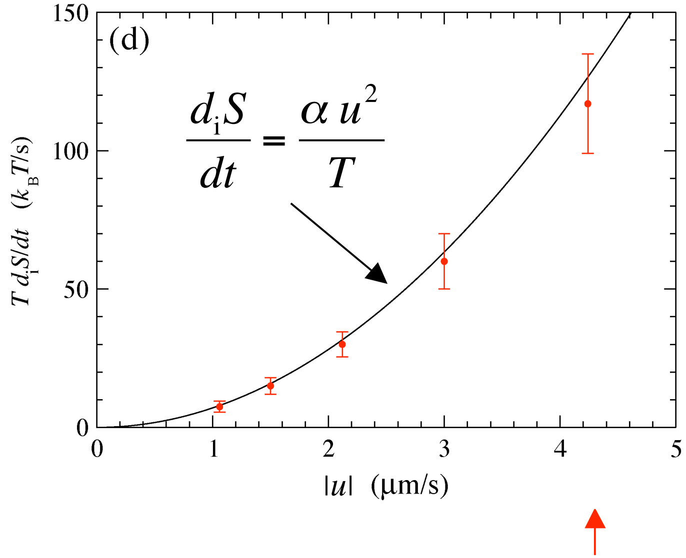
probability distributions of position



Temporal disorders of typical and reversed trajectories



Their difference is the thermodynamic production entropy

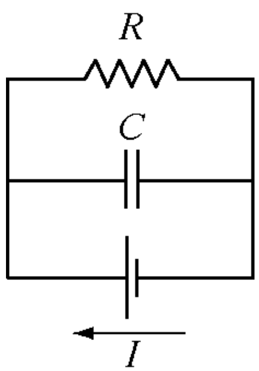


Irreversibility is observed down to the nanoscale.

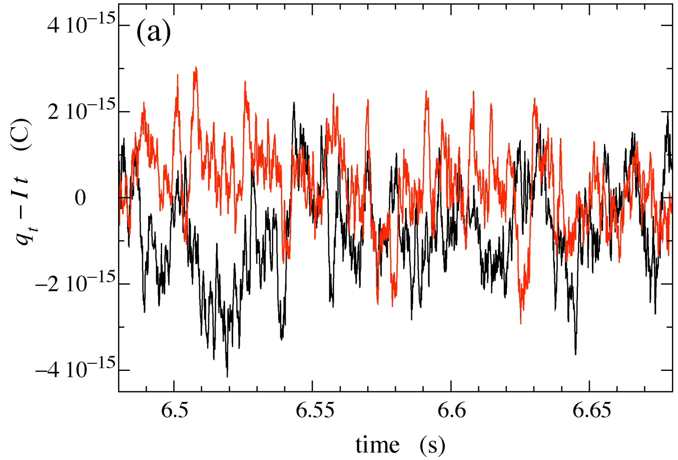
RC ELECTRIC CIRCUIT OUT OF EQUILIBRIUM

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

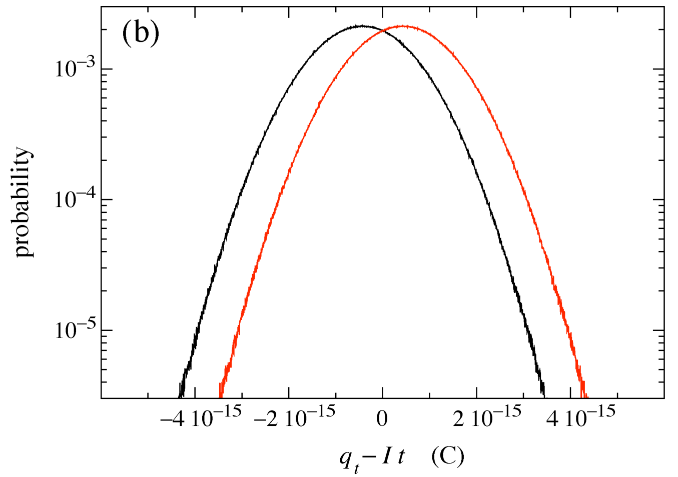
$R = 9.22\ \mathrm{M\Omega}$ $\quad C = 278\ \mathrm{pF}$ $\quad \tau_R = RC = 2.56\ \mathrm{ms}$



paths for I and $-I$

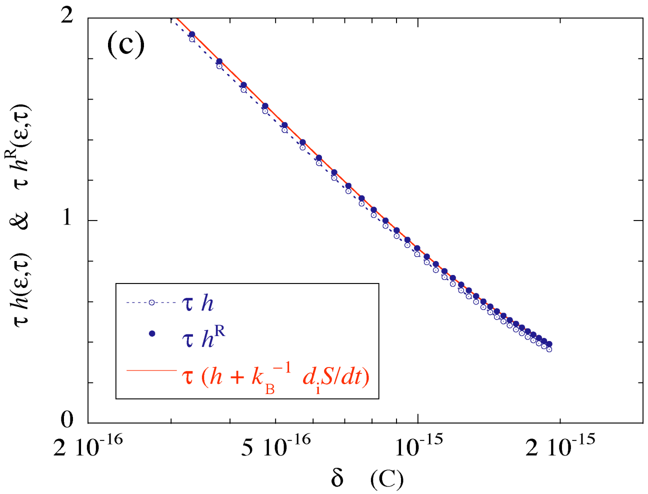


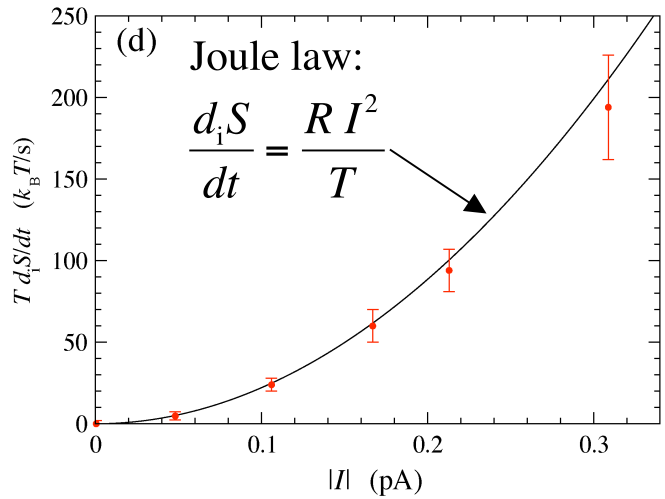
probability distributions of charges



Temporal disorders of typical and reversed trajectories

Their difference is the thermodynamic entropy production.

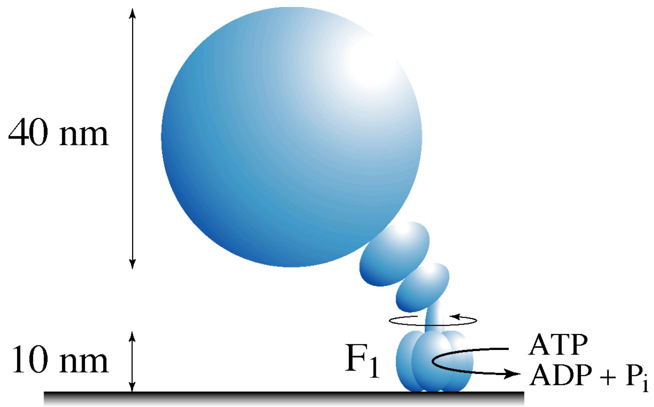


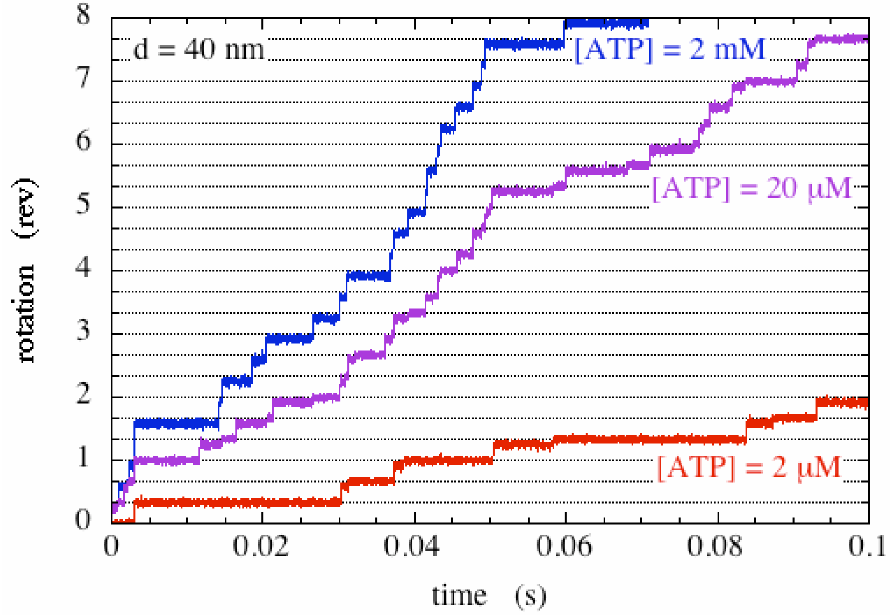


Irreversibility is observed down to fluctuations of several thousands of electrons.

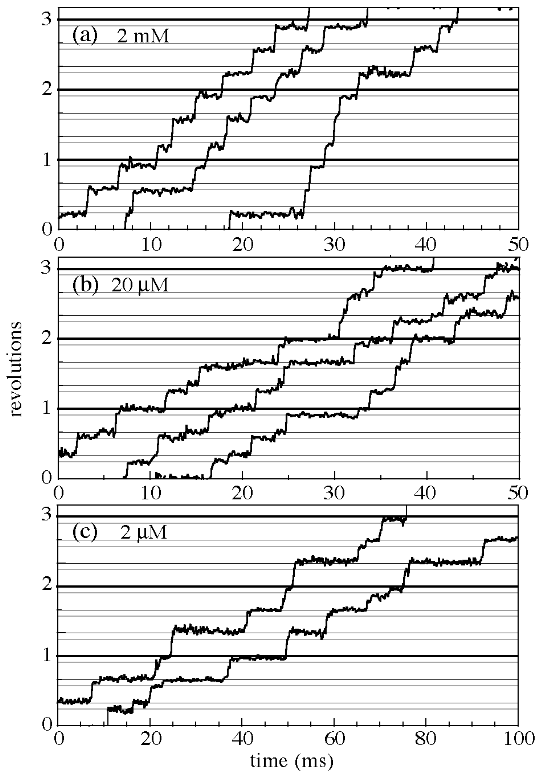
OUT-OF-EQUILIBRIUM TRAJECTORIES OF THE MOLECULAR MOTOR

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





Random trajectories simulated by a model:
P. Gaspard & E. Gerritsma, J. Theor. Biol. **247** (2007) 672



Random trajectories observed in experiments:
R. Yasuda, H. Noji, M. Yoshida, K. Kinosita Jr. & H. Itoh, Nature **410** (2001) 898

at equilibrium:
…212132131223132…
random

out of equilibrium:
…123123123123123…
regular: directionality

CONCLUSIONS

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

Statistical thermodynamics for nonequilibrium nanosystems:

- Fluctuation theorem for currents in steady states
- Fluctuation theorem for quantum systems
- Extensions of Onsager-Casimir reciprocity relations to nonlinear response

Thermodynamic entropy production:

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

thermodynamic arrow of time

= time asymmetry in temporal disorder

Theorem of nonequilibrium temporal ordering as a corollary of the second law:

Directionality and lowering of randomness in the motion.

The farther from equilibrium, the lower the temporal disorder.

Thermodynamic arrow of time down to the nanoscale

Explanation of directionality in nonequilibrium systems