NANOPHYSIQUE
INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch 10. THEOREMES DE FLUCTUATIONS

James Lutsko

Lecture 11, 2020-2021

Nanosystems dehors equilibrium: theoremes de fluctuations

- Nanosystems dehors equilibre
- Theoremes de fluctuations
  - Crooks relation
  - Jarzynski relation
  - Generalized classical theorem
  - Quantum fluctuation theorem
- Des Examples
  - Microplasma
  - Protein stretching
- Steady-state fluctuation theorem

Nanosystems dehors equilibrium: theoremes de fluctuations

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Undriven & driven nonequilibrium nanosystems

Undriven nonequilibrium nanosystem:

Energy dissipation by friction at the nanoscale

6.1 nm

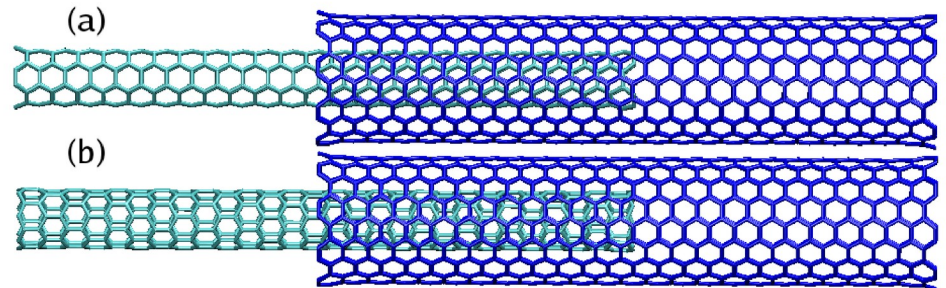Many nanosystems are most interesting when out of equilibrium

armchair-armchair DWNT:

$(4,4)@(9,9)$

$N_1 = 400$ $N_2 = 900$

(a)

zigzag-armchair DWNT:

$(7,0)@(9,9)$

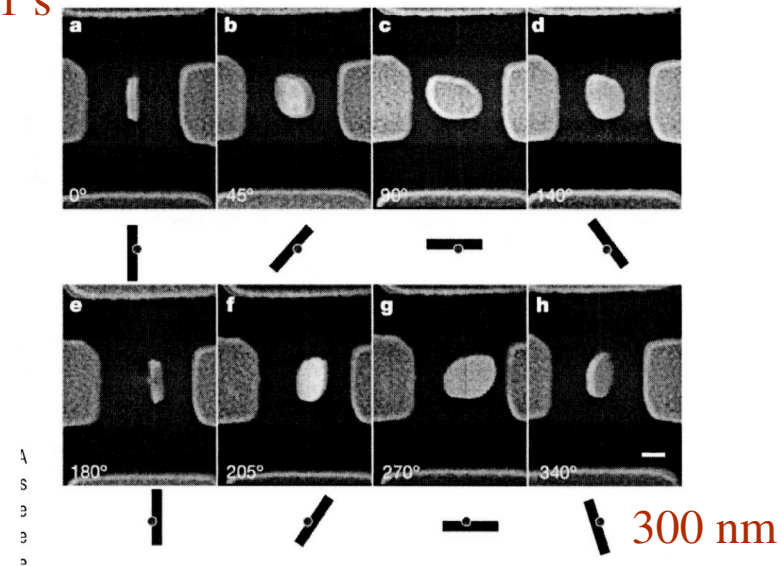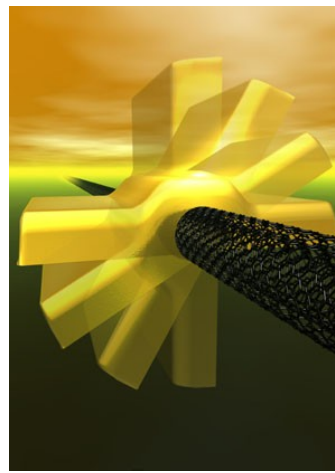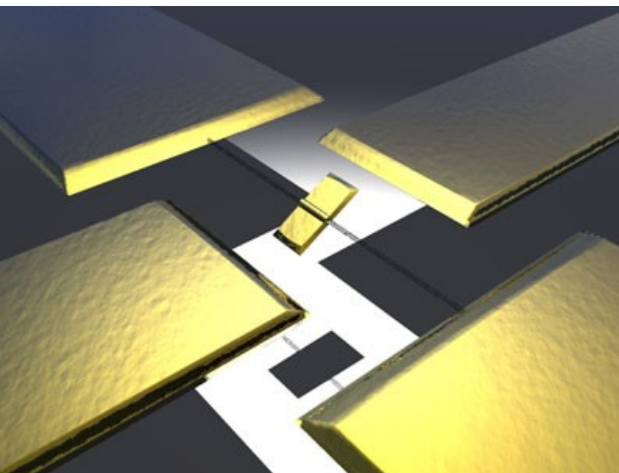$N_1 = 406$ $N_2 = 900$

(b)

J. Servantie & P. Gaspard, Phys. Rev. Lett. **91** (2003) 185503;   Phys. Rev. B **73** (2006) 125428.

Driven, out of equilibrium, transport, fluctuations

Driven nonequilibrium nanosystem: period ~ 1 s

Energy supply versus energy dissipation

300 nm

A. M. Fennimore, T. D. Yuzvinsky, Wei-Qiang Han, M. S. Fuhrer, J. Cumings & A. Zettl, Nature **424** (2003) 410.
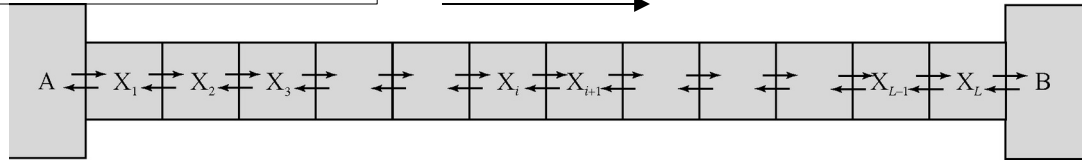
Les nanosystemes en etat stationaire de non-equilibre   Apport d'énergie
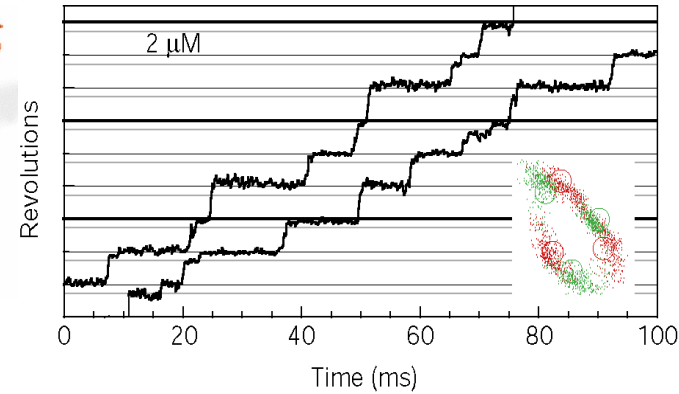
Driven, out of equilibrium, transport, fluctuations
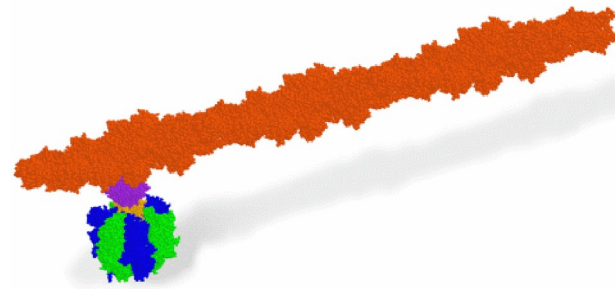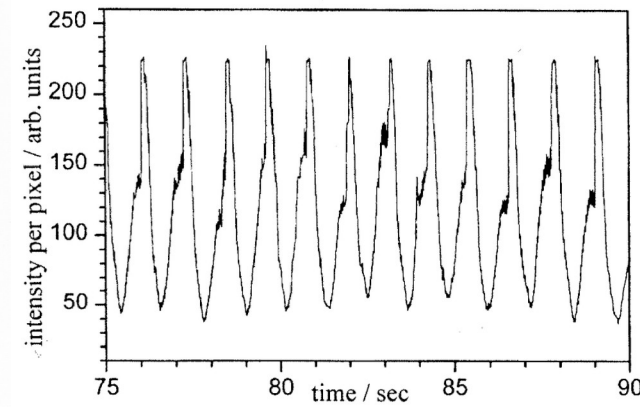
diffusion
conduction électrique

entre deux réservoirs

moteur moléculaire: F_oF_1-ATPase

K. Kinosita et al. (2001): F_1-ATPase + filament

C. Voss & N. Kruse (1996): réaction $NO_2/H_2/Pt$

diamètre 20 nm
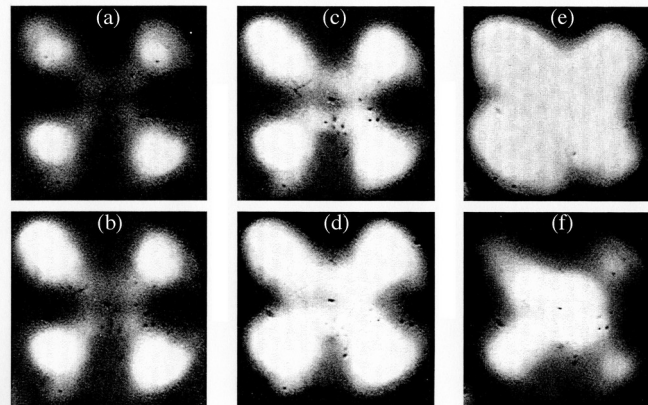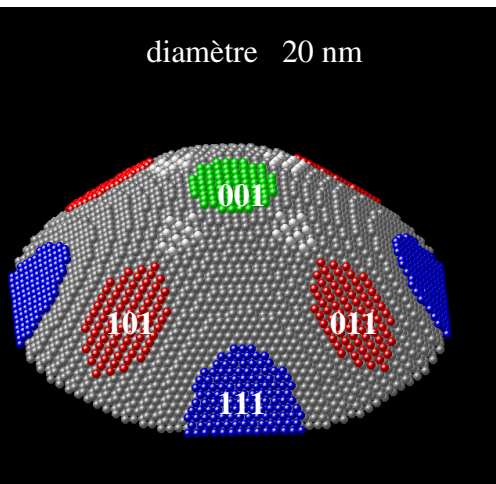
Diffusion between two reservoirs
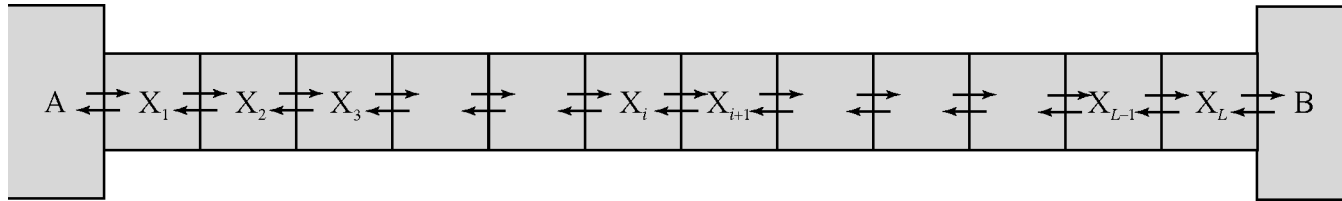
nonequilibrium steady state

time-continuous jump processes described by Pauli-type master equation

$$\frac{d}{dt}P(\omega;t)=\Sigma_{\omega'}\left[P(\omega';t)W(\omega'\rightarrow\omega)-P(\omega;t)W(\omega\rightarrow\omega')\right]$$

entropy production:

Application of macoscopic concepts (e.g. entropy production) to describe nanosystems

P. Gaspard, New J. Phys. **7** (2005) 77
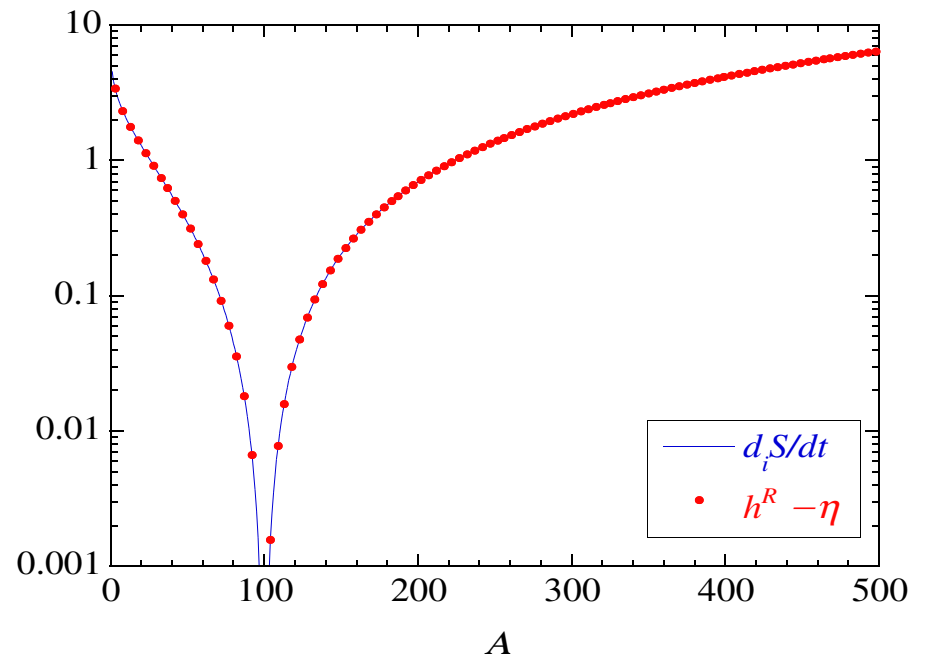
Quantum nanosystems: nanoelectronics

Driven, out of equilibrium, transport, fluctuations

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

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

GaAs-GaAlAs quantum dot   S: source $T < 1$ K
with a quantum point contact (QPC)   D: drain
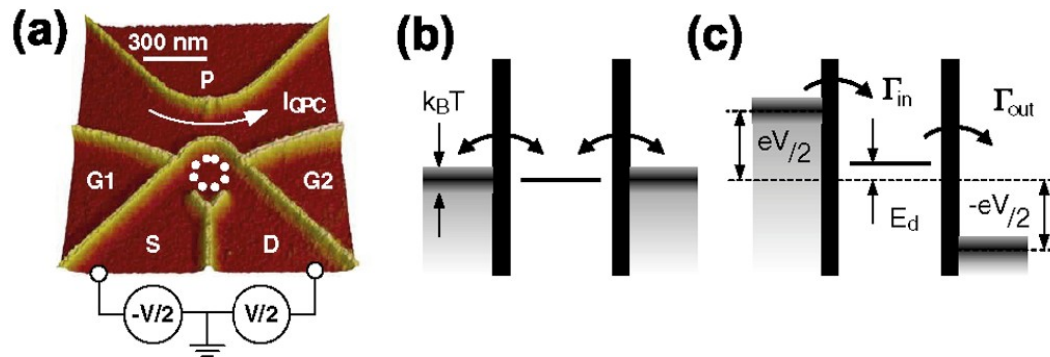
S. Gustavsson et al., Phys. Rev. Lett. **96**, 076605 (2006).
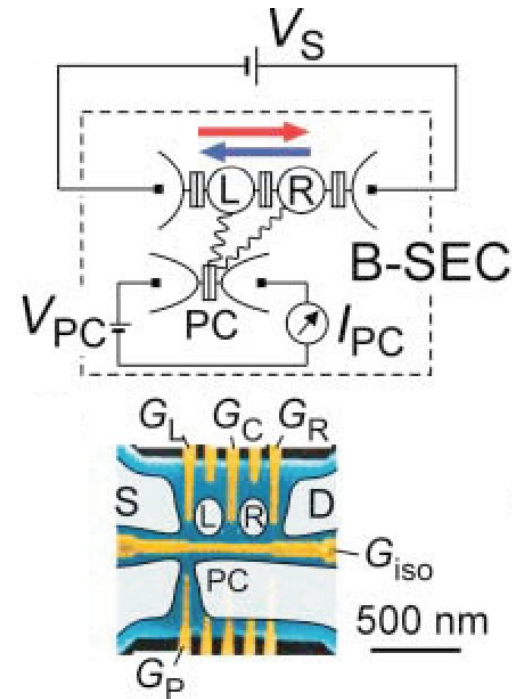
T. Fujisawa et al., Science **312**, 1634 (2006).

F$_1$-ATPase Nanomotor

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

ATP est le produit chimique qui est utilisé comme combustible.

$$F_1 = (\alpha\beta)_3\gamma$$
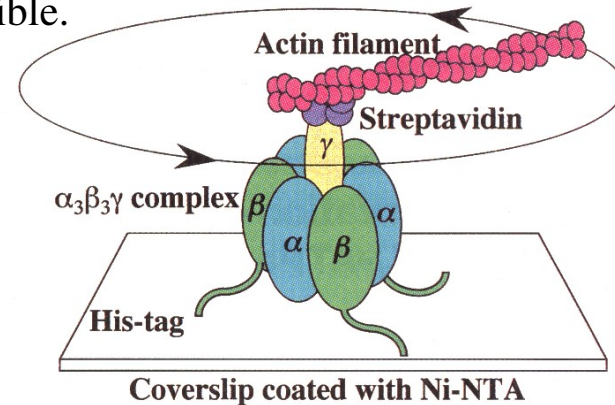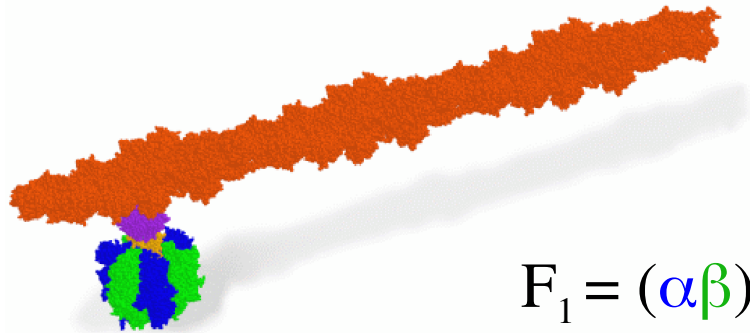
R. Yasuda, H. Noji, M. Yoshida, K. Kinosita Jr. & H. Itoh, Nature **410** (2001) 898
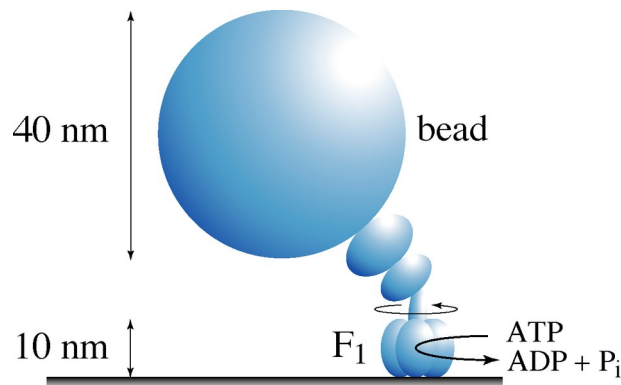
chemical fuel of the F$_1$ nanomotor:

ATP adenosine triphosphate
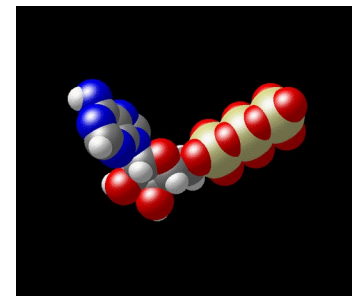
power = 10^{-18} -18^{Watt}

Driven, out of equilibrium, transport, fluctuations

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

Equilibrium

Structure in 3D space:

- no flux $\langle J_g \rangle = 0$

- no entropy production $\dfrac{d_i S}{dt} = 0$

- no energy supply needed

- equilibrium

- in contact with one reservoir

Nonequilibrium

Dynamics in 4D space-time:

- flux $\langle J_g \rangle \neq 0$

- entropy production $\dfrac{d_i S}{dt} > 0$

- energy supply required

- nonequilibrium

- in contact with several reservoirs

time
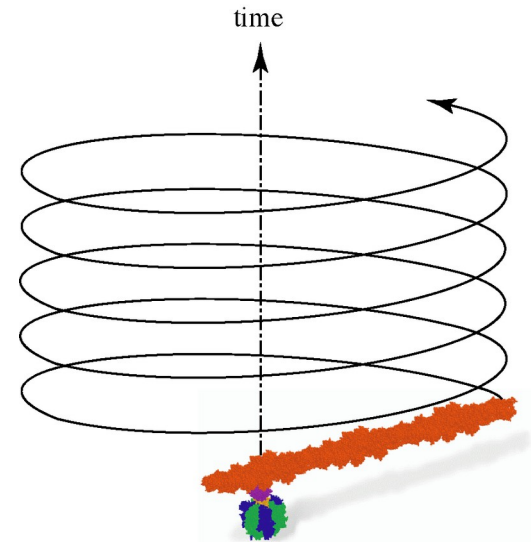
Thermodynamics of nonequilibrium processes

R. Clausius (1860):
Second law of thermodynamics: entropy S

$$\frac{dS}{dt} = \frac{dS_e}{dt} + \frac{dS_i}{dt} \text{ with } \frac{dS_i}{dt} > 0$$

$d_e S$ entropy flow

$d_i S > 0$ entropy production
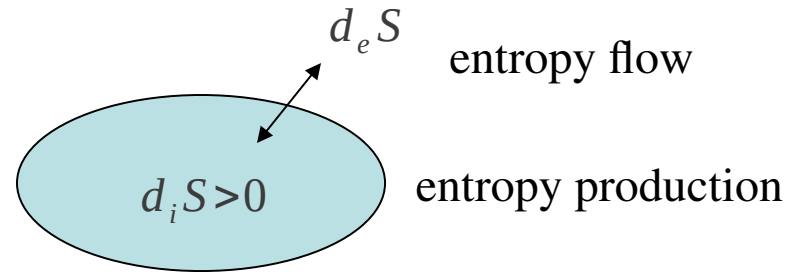
Many processes γ contribute to the entropy production:
viscosity, heat conduction, electric conduction, diffusion, chemical reactions,…

$$\frac{d_i S}{dt} = \sum_\gamma A_\gamma \langle J_\gamma \rangle$$

De Donder affinities or thermodynamic forces A_γ ⠀⠀⠀⠀ average currents or fluxes J_γ

rotary molecular motor

mechanical torque τ/T ⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀ angular velocity Ω
chemical potential difference $\Delta\mu/T$ ⠀⠀⠀⠀⠀⠀ chemical reaction rate R

$$\frac{d_i S}{dt} = \frac{\tau}{T}\Omega + \frac{\Delta\mu}{T} R > 0$$

temperature T

Systemes fluctuants hors d'equilibre

particule brownienne

dans un piège optique

et un écoulement

(2 μm)
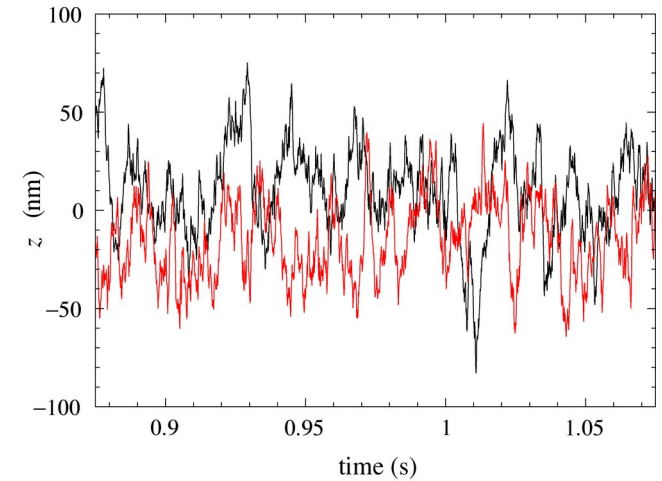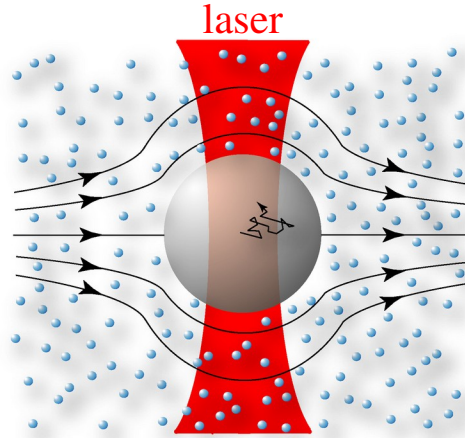
circuit électrique *RC*

(bruit thermique de Nyquist)
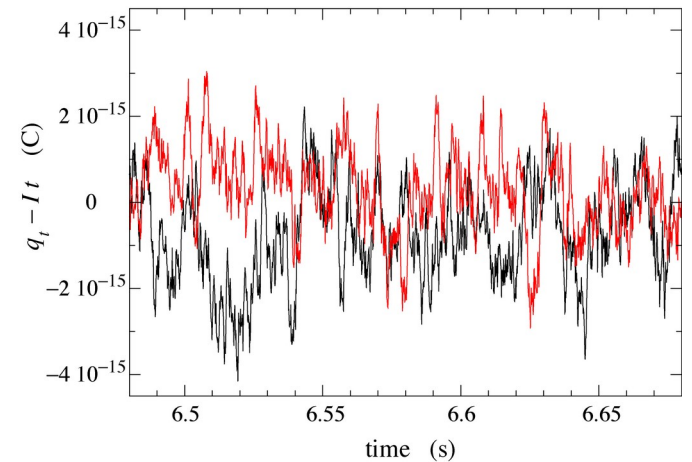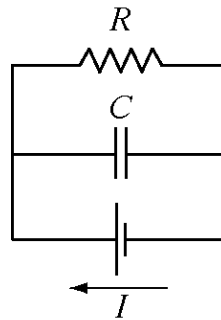
moteur moléculaire

F₁-ATPase

(Kinosita et al., 2001)
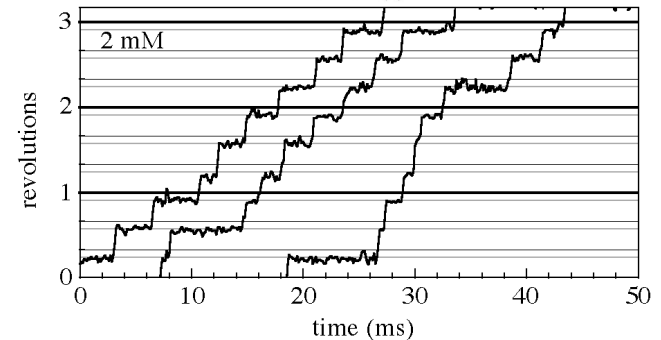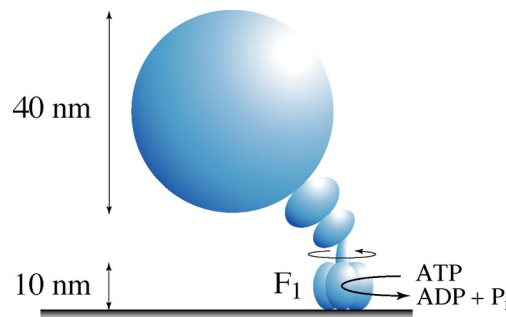
Brisure de la symetrie sous renversement du temps
$\Theta(\mathbf{r}, \mathbf{v}) = (\mathbf{r}, -\mathbf{v})$

Les équations de Newton de la mécanique sont symétriques
sous renversement du temps si l'hamiltonien H est pair en les vitesses.

L'équation de Liouville (l'equation de la mécanique statistique qui détermine
l'évolution temporelle de la densité de probabilité)ρ
est aussi symétrique sous renversement du temps .

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

La solution d'une équation peut avoir une symétrie plus basse
que l'équation elle-même (phénomène de brisure spontané de symétrie).

Les trajectoires newtoniennes T sont typiquement différentes de leur image
par renversement du temps Θ T : Θ T ≠ T

Des comportements irreversibles sont décrits en donnant aux trajectoires T
une probabilité différentes qu'à leur image par renversement du temps Θ T.

Brisure spontanée de symétrie: *modes de relaxation d'un système isolé.*

Brisure explicite de symétrie: *par les conditions aux bords dans les systèmes ouverts.*

Asymetrie temporelle dans la description statistique

non-équilibre

production d'entropie
dissipation d'énergie

(a)

vitesse **v**

réservoir 1

0

position **r**

inversion du temps

réservoir 2

trajectoires
les plus probables

**Asymétrique sous
inversion du temps**

trajectoires
remontant le temps,
moins probables
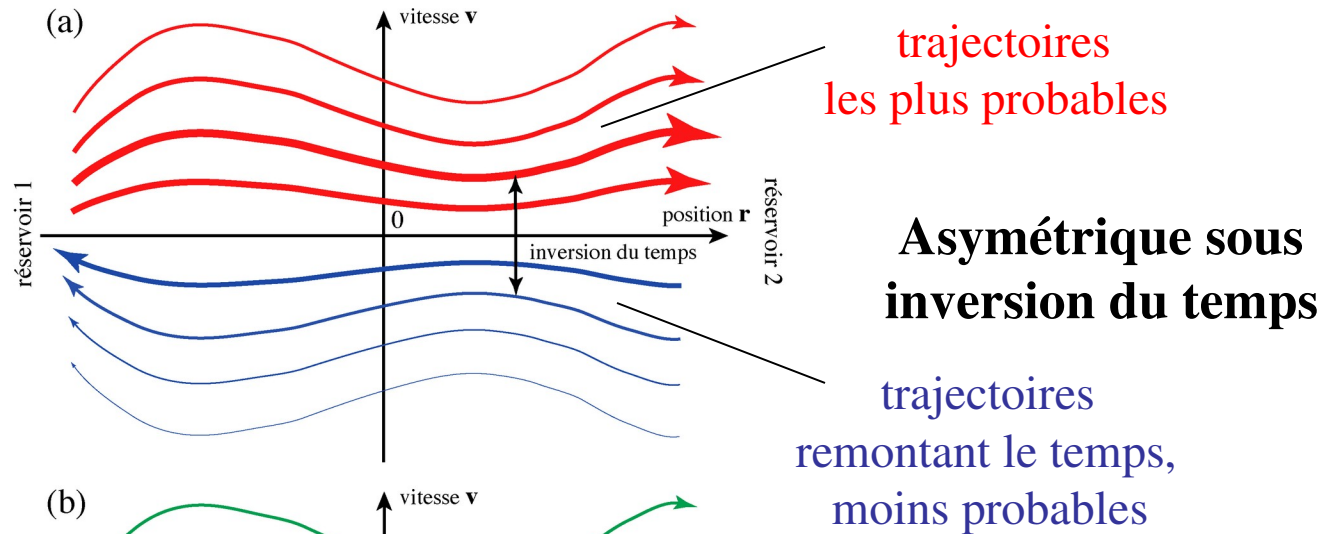
équilibre

entropie constante

(b)

vitesse **v**

0

position **r**

inversion du temps

**symétrique sous
inversion du temps**
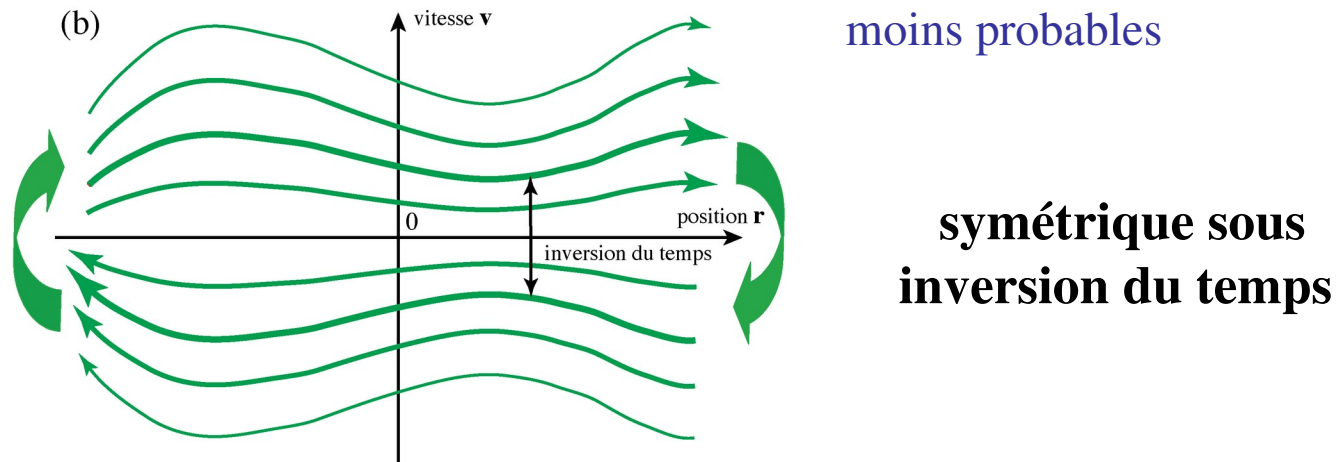
Remarque: La microréversibilité est toujours satisfaite.

Nanosystems dehors equilibrium: theoremes de fluctuations

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Dynamique microscopique Hamiltonienne

Espace des phases: $\Gamma = (\boldsymbol{q}, \boldsymbol{p}) = (\boldsymbol{q}_1, \boldsymbol{p}_1, \dots, \boldsymbol{q}_N, \boldsymbol{p}_N) \in M$, $dim\ M = 2f = 2Nd$

Fonction hamiltonienne: $H = \sum\limits_{i=1}^{N} \dfrac{p_i^2}{2\,m_i} + U(\boldsymbol{q}_1, \dots, \boldsymbol{q}_N)$

Equations d'Hamilton:

$$\dot{\boldsymbol{q}}_i = +\frac{\partial H}{\partial \boldsymbol{p}}$$

$$\dot{\boldsymbol{p}}_i = -\frac{\partial H}{\partial \boldsymbol{q}}$$

Flot d'évolution temporelle dans l'espace des phases: $\Gamma_t = F^t(\Gamma_0) \in M$

Renversement du temps: $t \to -t$ $\hat{\Theta}(\boldsymbol{q}, \boldsymbol{p}) = (\boldsymbol{q}, -\boldsymbol{p})$

Microréversibilité: $\hat{\Theta} H(\boldsymbol{q}, \boldsymbol{p}) = H(\boldsymbol{q}, -\boldsymbol{p})$

Theoreme de Liouville & équation de Liouville

Equations d'Hamilton:

$$\dot{q}_i = +\frac{\partial H}{\partial \boldsymbol{p}_i}$$

$$\dot{\boldsymbol{p}}_i = -\frac{\partial H}{\partial \boldsymbol{q}_i}$$

$$\dot{\Gamma} = J \cdot \nabla H$$

Densité de probabilité dans l'espace des phases:

$$\rho = \rho(\Gamma, t) = \rho(\boldsymbol{q}, \boldsymbol{p}, t)$$

conservation locale de la probabilité dans l'espace des phases:
équation de continuité:

$$\partial_t \rho + \nabla \cdot (\rho \dot{\Gamma}) = 0 \Leftrightarrow \partial_t \int_V \rho = -\int_{\partial V} \rho \dot{\Gamma} \cdot d\boldsymbol{S}$$

$$\nabla \cdot (\dot{\Gamma}) = \frac{\partial \dot{q}_{i,a}}{\partial q_{i,a}} + \frac{\partial \dot{p}_{i,a}}{\partial p_{i,a}}$$

$$= \frac{\partial^2 H}{\partial q_{i,a} \partial p_{i,a}} - \frac{\partial^2 H}{\partial p_{i,a} \partial q_{i,a}} = 0$$

$$\frac{d\rho}{dt} = \partial_t \rho + \dot{\Gamma} \cdot \nabla \rho = 0$$

Equation de Liouville:

$$\partial_t \rho = \{H, \rho\} \equiv \hat{L} \rho$$

opérateur liouvillien

Theoreme de Liouville & équation de Liouville

Théorème de Liouville:

La dynamique hamiltonienne preserve la densité de probabilité:

$$\rho(\Gamma, t) = \rho(\Gamma_0(\Gamma_t), t_0)$$

La dynamique hamiltonienne preserve les volumes de l'espace des phases:

$$d\Gamma(t) = d\Gamma(0)$$
$$d\boldsymbol{q}(t)\,d\boldsymbol{p}(t) = d\boldsymbol{q}(0)\,d\boldsymbol{p}(0)$$
$$d\boldsymbol{q}_1(t)\,d\boldsymbol{p}_1(t)...d\boldsymbol{q}_N(t)\,d\boldsymbol{p}_N(t) = d\boldsymbol{q}_1(0)\,d\boldsymbol{p}_1(0)...d\boldsymbol{q}_N(0)\,d\boldsymbol{p}_N(0)$$

Driven Hamiltonian Systems

Hamiltonian system:
$$H(\Gamma,\lambda)=H_S(\Gamma_S,\lambda)+H_B(\Gamma_B)+U(\Gamma_S,\Gamma_B)$$

forward process: $\lambda(t):\lambda(0)=\lambda_A\rightarrow\lambda(T)=\lambda_B$

initial state in the canonical ensemble: $\rho(\Gamma)=\dfrac{1}{Z_A}e^{-\beta H(\Gamma,\lambda_A)}\equiv\dfrac{1}{Z_A}e^{-\beta H_A(\Gamma)}$

free energy: $F_A=-k_B T\ln Z_A$

reversed process: $\lambda(t):\lambda_B\rightarrow\lambda_A$

initial state in the canonical ensemble: $\rho(\Gamma)=\dfrac{1}{Z_B}e^{-\beta H(\Gamma,\lambda_B)}\equiv\dfrac{1}{Z_B}e^{-\beta H_B(\Gamma)}$

free energy: $F_B=-k_B T\ln Z_B$

Fluctuation theorem for the nonequilibrium work

Hamiltonian system: $\quad H(\Gamma, \lambda) = H_S(\Gamma_S, \lambda) + H_B(\Gamma_B) + U(\Gamma_S, \Gamma_B)$

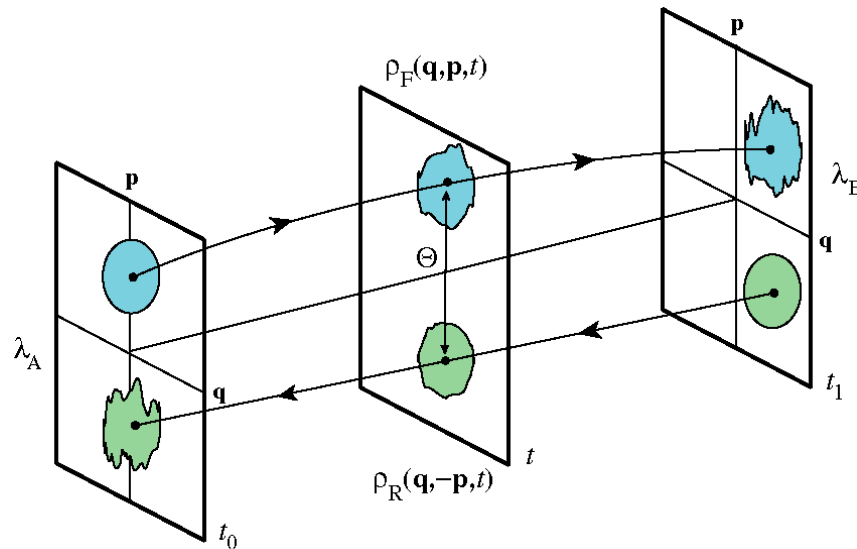forward process: $\quad \lambda(t): \lambda(0) = \lambda_A \rightarrow \lambda(T) = \lambda_B$

initial state in the canonical ensemble: $\quad \rho(\Gamma) = \dfrac{1}{Z_A} e^{-\beta H(\Gamma, \lambda_A)} \equiv \dfrac{1}{Z_A} e^{-\beta H_A(\Gamma)}$

free energy: $\quad F_A = -k_B T \ln Z_A$

work: $\quad p_F(W) \equiv \langle \delta[W - (H_B(\Gamma(T; \Gamma_0)) - H_A(\Gamma_0))] \rangle_{0,A}$

reversed process: $\quad \lambda(t): \lambda_B \rightarrow \lambda_A$

initial state in the canonical ensemble: $\quad \rho(\Gamma) = \dfrac{1}{Z_B} e^{-\beta H(\Gamma, \lambda_B)} \equiv \dfrac{1}{Z_B} e^{-\beta H_B(\Gamma)}$

free energy: $\quad F_B = -k_B T \ln Z_B$

work: $\quad p_R(W) \equiv \langle \delta[W - (H_A(\Gamma(T; \Gamma_0)) - H_B(\Gamma_0))] \rangle_{0,B}$

using microreversibility & Liouville's theorem:

Crooks fluctuation theorem (1999):
$$\Delta F = F_B - F_A$$

$$\boxed{\dfrac{p_F(W)}{p_R(-W)} = e^{\beta(W - \Delta F)} = e^{\beta W_{diss}}}$$

Nonequilibrium work fluctuation theorem : proof

probability of the work during the forward process: $\lambda(t):\lambda(0)=\lambda_A \rightarrow \lambda(T)=\lambda_B$

$$H_A(\Gamma)\equiv H(\Gamma;\lambda_A)$$
$$H_B(\Gamma)\equiv H(\Gamma;\lambda_B)$$

$$p_F(W)\equiv\langle\delta\big(W-(H_B(\Gamma(T;\Gamma_0))-H_A(\Gamma_0))\big)\rangle_{0,A}$$

$$=\frac{1}{Z_A}\int d\Gamma_0\, e^{-\beta H_A(\Gamma_0)}\delta\big(W-(H_B(\Gamma(T;\Gamma_0))-H_A(\Gamma_0))\big)$$

$$=\frac{1}{Z_A}\int d\Gamma_0\, e^{-\beta(H_B(\Gamma(T;\Gamma_0))-W)}\delta\big(W-(H_B(\Gamma(T;\Gamma_0))-H_A(\Gamma_0))\big)$$

$$=\frac{Z_B}{Z_A}\frac{1}{Z_B}\int d\Gamma\, e^{-\beta(H_B(\Gamma)-W)}\delta\big(-W-(H_A(\Gamma_0(\Gamma;-T))-H_B(\Gamma))\big) \quad \text{Liouville's theorem}$$

$$=e^{-\beta\Delta F}e^{\beta W}p_R(-W)$$

$$F_A\equiv-k_B T\ln Z_A$$
$$F_B\equiv-k_B T\ln Z_B$$
$$\Delta F\equiv F_B-F_A$$

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

Nonequilibrium work theorem

Jarzynski nonequilibrium work theorem (1997):

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

$$\beta = (k_B T)^{-1}$$

Hamiltonian system $H(\Gamma,\lambda)$
driven by a time-dependent control parameter: $\lambda(t):\lambda(0)=\lambda_A \rightarrow \lambda(T)=\lambda_B$

work performed on the system: $W \equiv H(\Gamma_T,\lambda_B) - H(\Gamma_0,\lambda_A)$

equilibrium free-energy difference: $\Delta F = -k_B T \ln(Z_B/Z_A)$

-> Clausius' thermodynamic inequality: $\langle W\rangle \geq \Delta F$

$$\langle e^x\rangle \geq e^{\langle x\rangle}$$

Proof with Crooks' fluctuation theorem:

$$\langle e^{-\beta W}\rangle = \int dW\, p_F(W)\, e^{-\beta W} = e^{-\beta\Delta F}\int dW\, p_R(-W) = e^{-\beta\Delta F}$$

dissipated work: $W_{diss} \equiv W - \Delta F$

$$\langle e^{-\beta W_{diss}}\rangle = 1$$

The isothermal-isobaric case

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

$$\beta = (k_B T)^{-1}$$

Hamiltonian system $H(\Gamma, \lambda)$
driven by a time-dependent control parameter: $\lambda(t): \lambda(0) = \lambda_A \rightarrow \lambda(T) = \lambda_B$

work performed on the system: $W \equiv H(\Gamma(T), \lambda_B) + PV_B - H(\Gamma(0), \lambda_A) - PV_A$

equilibrium free-enthalpy difference: $\Delta G \equiv -k_B T \ln(Y_B / Y_A)$

-> Clausius' thermodynamic inequality: $\langle W \rangle \geq \Delta G$

Crooks fluctuation theorem (1999):

$$\frac{p_F(W)}{p_R(-W)} = e^{\beta(W - \Delta G)} = e^{\beta W_{diss}}$$

Experimental application: stretching of biomolecules

Nonequilibrium work

System driven forward or backward by a time-dependent control: $\lambda(t): \lambda_A \to \lambda_B$
$\Gamma(t): \Gamma_0 \to \Gamma_1$

initially in the canonical equilibrium state: $\beta = (k_B T)^{-1}$

work performed on the system: $W \equiv H(\Gamma_1, \lambda_B) - H(\Gamma_0, \lambda_A)$

equilibrium free-energy difference: $\Delta F = F_B - F_A$

forward process: $\rho_F(\Gamma, t) = \rho_F(\Gamma_0, 0) = \dfrac{1}{Z_A} e^{-\beta H(\Gamma_0, \lambda_A)}$

reversed process: $\rho_R(\hat{\Theta}\Gamma, t) = \rho_R(\hat{\Theta}\Gamma_1, t_1) = \dfrac{1}{Z_B} e^{-\beta H(\hat{\Theta}\Gamma_1, \lambda_B)}$

$0 < t < t_1$

random work: $W = \Delta F + k_B T \ln \dfrac{\rho_F(\Gamma, t)}{\rho_R(\hat{\Theta}\Gamma, t)}$

average work: by Liouville's theorem & microreversibility

$$\langle W \rangle - \Delta F = k_B T \int d\Gamma \; \rho_F(\Gamma, t) \ln \frac{\rho_F(\Gamma, t)}{\rho_R(\hat{\Theta}\Gamma, t)} = k_B T \, D[\rho_F(\Gamma, t) \| \rho_R(\hat{\Theta}\Gamma, t)] > 0$$

Kullback-Leibler distance

The Kullback-Leibler distance, also called relative entropy, is always non-negative.

$$D(p\|q) \equiv \sum_i p_i \ln \frac{p_i}{q_i} > 0 \quad \text{for probability distributions:} \quad \sum_i p_i = 1 \quad \sum_i q_i = 1$$

Jensen inequality for a convex function:

$$pf(x_1) + (1-p)f(x_2) \geq f(px_1 + (1-p)x_2) \Rightarrow \sum_{i=1}^{k} p_i f(x_i) \geq f\left(\sum_{i=1}^{k} p_i x_i\right), \sum_{i=1}^{k} p_i = 1$$

Proof by induction: suppose it is true for k-1 $\quad \sum_{i=1}^{k-1} p_i' f(x_i) \geq f\left(\sum_{i=1}^{k-1} p_i' x_i\right) \quad \sum_{i=1}^{k-1} p_i' = 1$

for k
$$\sum_{i=1}^{k} p_i f(x_i) = \sum_{i=1}^{k-1} p_i f(x_i) + p_k f(x_k) = (1-p_k) \sum_{i=1}^{k-1} \frac{p_i}{1-p_k} f(x_i) + p_k f(x_k)$$

$$\geq (1-p_k) f\left(\sum_{i=1}^{k-1} \frac{p_i}{1-p_k} x_i\right) + p_k f(x_k) \geq f\left((1-p_k)\sum_{i=1}^{k-1} \frac{p_i}{1-p_k} x_i + p_k x_k\right) \geq f\left(\sum_{i=1}^{k} p_i x_i\right)$$

Now, take $\quad x_i = \frac{q_i}{p_i}, \quad f(x) = \ln x \quad\quad D(p\|q) \equiv \sum_i p_i f(x_i) \geq f\left(\sum_i p_i x_i\right) = f(1) = 0$

Corollaries

Clausius' thermodynamic inequality: $\quad W \geq \Delta F$

equilibrium free-energy difference: $\quad \Delta F = -k_B T \ln\left(Z_B / Z_A\right)$

dissipated work: $\quad W_{diss} \equiv W - \Delta F \qquad \langle W_{diss}\rangle \geq 0$

Jarzynski nonequilibrium work theorem (1997):

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

$\qquad \beta = \left(k_B T\right)^{-1}$

$$\langle e^{-\beta W_{diss}}\rangle = 1$$

(proof: exercise)

A generalization for Markovian dynamics

Markovian dynamics:

$$\Gamma(t_0) \equiv \Gamma_0 \rightarrow \Gamma(t_1) \equiv \Gamma_1 \rightarrow \Gamma_2 \ldots$$

$$P(\Gamma_{j+1}, t_{j+1}) = \int d\Gamma_j \, P(\Gamma_{j+1}, t_{j+1} | \Gamma_j, t_j) P(\Gamma_j, t_j)$$

$$P(\Gamma_0, t_0; \ldots \Gamma_N, t_N) = P(\Gamma_N, t_N | \Gamma_{N-1}, t_{N-1}) \ldots P(\Gamma_1, t_1 | \Gamma_0, t_0) P(\Gamma_0, t_0)$$

$$\langle g(\Gamma_0, t_0; \Gamma_1, t_1; \ldots, \Gamma_N, t_N) \rangle = \int d\Gamma_0 \ldots d\Gamma_N \, g(\Gamma_0, t_0; \Gamma_1, t_1; \ldots, \Gamma_N, t_N) P(\Gamma_0, t_0; \ldots \Gamma_N, t_N)$$

État stationnaire :

$$\int d\Gamma_0 \, P(\Gamma_1, t_1 | \Gamma_0, t_0; \alpha_0) P_{SS}(\Gamma_0, t_0; \alpha_0) = P_{SS}(\Gamma_1, t_1; \alpha_0)$$

$$\int d\Gamma_1 \, P(\Gamma_2, t_2 | \Gamma_1, t_1; \alpha_1) P_{SS}(\Gamma_1, t_1; \alpha_1) = P_{SS}(\Gamma_2, t_2; \alpha_1)$$

A generalization for Markovian dynamics

Notez que

$$\left\langle \frac{P_{SS}(\Gamma_N;\alpha_N)}{P_{SS}(\Gamma_N;\alpha_{N-1})} \frac{P_{SS}(\Gamma_{N-1};\alpha_{N-1})}{P_{SS}(\Gamma_{N-1};\alpha_{N-2})} \cdots \frac{P_{SS}(\Gamma_1;\alpha_1)}{P_{SS}(\Gamma_1;\alpha_0)} \right\rangle$$

$$= \int d\Gamma_0 ... d\Gamma_N \frac{P_{SS}(\Gamma_N;\alpha_N)}{P_{SS}(\Gamma_N;\alpha_{N-1})} ... P(\Gamma_2,t_2|\Gamma_1,t_1;\alpha_1) \frac{P_{SS}(\Gamma_1;\alpha_1)}{P_{SS}(\Gamma_1;\alpha_0)} P(\Gamma_1,t_1|\Gamma_0,t_0;\alpha_0) P_{SS}(\Gamma_0,t_0;\alpha_0)$$

$$= \int d\Gamma_N P_{SS}(\Gamma_N;\alpha_N) = 1$$

Définissez

$$\phi(\Gamma_j;\alpha_j) \equiv -\ln P_{SS}(\Gamma_j;\alpha_j)$$

$$\frac{P_{SS}(\Gamma_{j+1};\alpha_{j+1})}{P_{SS}(\Gamma_{j+1};\alpha_j)} = e^{\phi(\Gamma_{j+1};\alpha_{j+1}) - \phi(\Gamma_{j+1};\alpha_j)} = e^{\frac{\partial\phi(\Gamma_{j+1};\alpha_{j+1})}{\alpha_{j+1}} \dot{\alpha}_{j+1}\Delta t}$$

$$\Longrightarrow \qquad 1 = \left\langle e^{-\int_0^{t_N} \frac{\partial\phi(\Gamma(t);\alpha(t))}{\partial\alpha(t)} \dot{\alpha}(t)} \right\rangle_{SS,\alpha(0)}$$

Pour example,

$$P_{SS}(\Gamma;A) = e^{-\beta(E(\Gamma;\alpha) - F(\alpha))} \Rightarrow 1 = \left\langle e^{-\beta(E(\Gamma;\alpha(t)) - E(\Gamma;\alpha(0))) + \beta(F(\alpha(T)) - F(\alpha(0)))} \right\rangle_{SS,\alpha(0)}$$

Quantum work relation and response theory

Hamiltonienne avec champ magnétique $\quad H(t;B)$

L'operateur time reversal $\quad \hat{\Theta} H(t;B) = H(t;-B)$

Density matrice: $\quad \rho(0;B) = \dfrac{1}{Z(0;B)} e^{-\beta H(0;B)}, \quad Z(0;B) = Tr\, e^{-\beta H(0;B)} = e^{-\beta F(0;B)}$

Forward time evolution: $\quad i\hbar \dfrac{\partial}{\partial t} U_F(t;B) = H(t;B) U_F(t;B)$

Evolution of observables: $\quad A_F(t;B) = U_F(t;B)^t A\, U_F(t;B)$

$$\langle A_F(t;B)\rangle = Tr\, A(t;B)\rho(0;B)$$

Quantum work relation and response theory

Hamiltonienne avec champ magnétique $\quad H(T-t;-B)$

Backwards process: $\quad \rho(T;-B)=\dfrac{1}{Z(T;-B)}e^{-\beta H(T;-B)}, \quad Z(T;-B)=Tr\,e^{-\beta H(T;-B)}=e^{-\beta F(T;-B)}$

$$i\hbar\frac{\partial}{\partial t}U_B(t;-B)=H(T-t;-B)U_B(t;-B),\quad U(0;B)=I$$

Relation between forward and backward operators:

$$\hat{\Theta}\,U_F(T-t;B)\,U_F^t(T;B)\,\hat{\Theta}=U_R(t;-B)$$

Quantum work relation and response theory

Relation between forward and backward operators:

$$\hat{\Theta} U_F(T-t;B) U_F^t(T;B) \hat{\Theta} = U_R(t;-B)$$

Proof:

$$i\hbar \frac{\partial}{\partial t} U_F(t;B) = H(t;B) U_F(t;B)$$

$$-i\hbar \frac{\partial}{\partial t} U_F(T-t;B) = H(T-t;B) U_F(T-t;B)$$

antilinearity

$$-\hat{\Theta} i\hbar \frac{\partial}{\partial t} U_F(T-t;B) = \hat{\Theta} H(T-t;B) U_F(T-t;B)$$

$$\hat{\Theta} i = -i\hat{\Theta} \qquad i\hbar \frac{\partial}{\partial t}\left(\hat{\Theta} U_F(T-t;B)\right) = H(T-t;-B)\left(\hat{\Theta} U_F(T-t;B)\right)$$

Compare to: $\quad i\hbar \frac{\partial}{\partial t} U_B(t;-B) = H(T-t;-B) U_B(t;-B), \quad U(0;B) = I$

$$\lim_{t\to 0}\left(\hat{\Theta} U_F(T-t;B)\right) = \left(\hat{\Theta} U_F(T;B)\right) \neq I$$

Donc, mulitpliez par $\quad U_F^t(T;B)\hat{\Theta} \Rightarrow \lim_{t\to 0}\left(\hat{\Theta} U_F(T-t;B) U_F^t(T;B)\hat{\Theta}\right) = I$

Quantum work relation and response theory

Theorem:

Étant donné

Observable A avec parity $\quad \hat{\Theta} A \hat{\Theta} = \epsilon_A A, \quad \epsilon_A = \pm 1$

Fonction arbitraire $\quad \lambda(t)$

$$\left\langle e^{\int_0^T dt\, \lambda(t) A_F(t)} e^{-\beta H_F(T)} e^{\beta H(0)} \right\rangle_{F,B} = e^{-\beta \Delta F} \left\langle e^{\epsilon_A \int_0^T dt\, \lambda(T-t) A_R(t)} \right\rangle_{R,-B}$$

où $\quad H_F(T) \equiv U_F^t(T;B) H(T;B) U_F(T;B)$

Preuve:

$$\hat{\Theta} U_F(T-t;B) U_F^t(T;B) \hat{\Theta} = U_R(t;-B)$$

$$A_F(t) = U_F^t(t;B) A U_F(t;B)$$
$$= \underbrace{U_F^t(T;B) U_F(T;B)}_{=I} U_F^t(t;B) A U_F(t;B) \underbrace{U_F^t(T;B) U_F(T;B)}_{=I}$$
$$= U_F^t(T;B) \underbrace{\hat{\Theta}\hat{\Theta}}_{=I} U_F(T;B) U_F^t(t;B) \underbrace{\hat{\Theta}\hat{\Theta}}_{=I} A \underbrace{\hat{\Theta}\hat{\Theta}}_{=I} U_F(t;B) U_F^t(T;B) \underbrace{\hat{\Theta}\hat{\Theta}}_{=I} U_F(T;B)$$
$$= U_F^t(T;B) \hat{\Theta} U_R^t(T-t;B) \hat{\Theta} A \hat{\Theta} U_R(T-t;B) \hat{\Theta} U_F(T;B)$$
$$= \epsilon_A U_F^t(T;B) \hat{\Theta} U_R^t(T-t;B) A U_R(T-t;B) \hat{\Theta} U_F(T;B)$$
$$= \epsilon_A U_F^t(T;B) \hat{\Theta} A_R(T-t;B) \hat{\Theta} U_F(T;B)$$

Quantum work relation and response theory

Theorem:
$$\left\langle e^{\int_0^T dt\,\lambda(t)A_F(t)}\, e^{-\beta H_F(T)}\, e^{\beta H(0)}\right\rangle_{F,B} = e^{-\beta\Delta F}\left\langle e^{\epsilon_A \int_0^T dt\,\lambda(T-t)A_R(t)}\right\rangle_{R,-B}$$

Preuve:
$$A_F(t) = \epsilon_A\, U_F^t(T;B)\,\hat{\Theta}\,A_R(T-t;B)\,\hat{\Theta}\,U_F(T;B)$$

Donc,
$$\exp\left(\int_0^T dt\,\lambda(t)A_F(t)\right) = \exp\left(\int_0^T dt\,\lambda(t)\,\epsilon_A\,U_F^t(T;B)\,\hat{\Theta}\,A_R(T-t;B)\,\hat{\Theta}\,U_F(T;B)\right)$$
$$= U_F^t(T;B)\,\hat{\Theta}\,\exp\left(\epsilon_A\int_0^T dt\,\lambda(t)A_R(T-t;B)\right)\hat{\Theta}\,U_F(T;B)$$
$$= U_F^t(T;B)\,\hat{\Theta}\,\exp\left(\epsilon_A\int_0^T dt\,\lambda(T-t)A_R(t;B)\right)\hat{\Theta}\,U_F(T;B)$$

et
$$\left\langle e^{\int_0^T dt\,\lambda(t)A_F(t)}\,e^{-\beta H_F(T)}\,e^{\beta H(0)}\right\rangle_{F,B} = Tr\left(e^{\int_0^T dt\,\lambda(t)A_F(t)}\,e^{-\beta H_F(T)}\,e^{\beta H(0)}\frac{e^{-\beta H(0;B)}}{Z(0)}\right)$$
$$= \frac{1}{Z(0)}Tr\left(e^{\epsilon_A\int_0^T dt\,\lambda(T-t)A_R(t)}\,\hat{\Theta}\,U_F(T;B)\,e^{-\beta H_F(T)}\,U_F^t(T;B)\,\hat{\Theta}\right)$$
$$= \frac{1}{Z(0)}Tr\left(e^{\epsilon_A\int_0^T dt\,\lambda(T-t)A_R(t)}\,e^{-\beta H(T;-B)}\right)$$
$$= \frac{Z(T)}{Z(0)}\left\langle e^{\epsilon_A\int_0^T dt\,\lambda(T-t)A_R(t)}\right\rangle_{R,-B}$$

Quantum work relation and response theory

D. Andrieux and P. Gaspard, Phys. Rev. Lett. 100, 230404 (2008)

Theorem:
$$\left\langle e^{\int_0^T dt\,\lambda(t)\,A_F(t)}\,e^{-\beta H_F(T)}\,e^{\beta H(0)}\right\rangle_{F,B} = e^{-\beta\Delta F}\left\langle e^{\epsilon_A \int_0^T dt\,\lambda(T-t)\,A_R(t)}\right\rangle_{R,-B}$$

Consequnce:
$$\lambda(t)=0 \Rightarrow \left\langle e^{-\beta H_F(T)}\,e^{\beta H(0)}\right\rangle_{F,B} = e^{-\beta\Delta F} \qquad \text{Generalized Jarzynski relation.}$$

Note:
$$\left\langle e^{-\beta H_F(T)}\,e^{\beta H(0)}\right\rangle_{F,B} \neq \left\langle e^{-\beta(H_F(T)-H(0))}\right\rangle_{F,B}$$

Nanosystems dehors equilibrium: theoremes de fluctuations

- Nanosystems dehors equilibre
- Theoremes de fluctuations
  - Crooks relation
  - Jarzynski relation
  - Generalized classical theorem
  - Quantum fluctuation theorem
- Des Examples
  - Microplasma
  - Protein stretching
- Steady-state fluctuation theorem

Microplasmas : ions in an electromagnetic trap

Hamiltonian:
$$H_0 = \sum_{i=1}^{N} \left\{ \frac{1}{2m} \left[\boldsymbol{p}_i - q\,\boldsymbol{A}(\boldsymbol{q}_i) \right]^2 + q\,\Phi(\boldsymbol{q}_i) \right\} + \sum_{1 \le i < j \le N} \frac{q^2}{4\pi\,\epsilon_0\,q_{ij}}$$

vector potential:
$$\boldsymbol{A} = \frac{1}{2}\left(-By\,, Bx\,, 0 \right)$$

electric potential:
$$\Phi(\boldsymbol{q}) = V_0 \frac{2z^2 - x^2 - y^2}{r_0^2 + 2z_0^2}$$

Larmor frequency:
$$\omega_L = \frac{\omega_c}{2} = \frac{qB}{2m}$$

Hamiltonian in the Larmor rotating framework with rescaled variables:
$$H_0 = \sum_{i=1}^{N} \left[\frac{1}{2} P_i^2 + \left(\frac{1}{8} - \frac{g^2}{4} \right)\left(X_i^2 + Y_i^2 \right) + \frac{g^2}{2} Z_i^2 \right] + \sum_{1 \le i < j \le N} \frac{1}{R_{ij}}$$

trap parameter:
$$g \equiv \frac{\omega_z}{\omega_c}$$
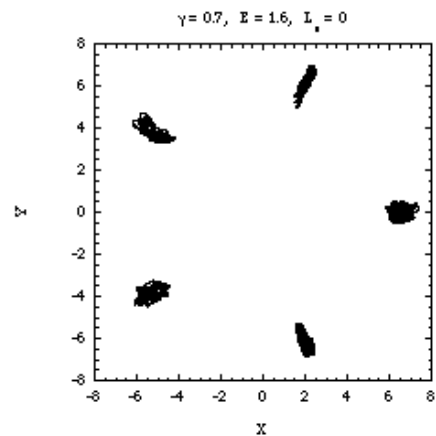
elongated trap: $|g| < \dfrac{1}{\sqrt{6}}$

spherical trap: $|g| = \dfrac{1}{\sqrt{6}}$

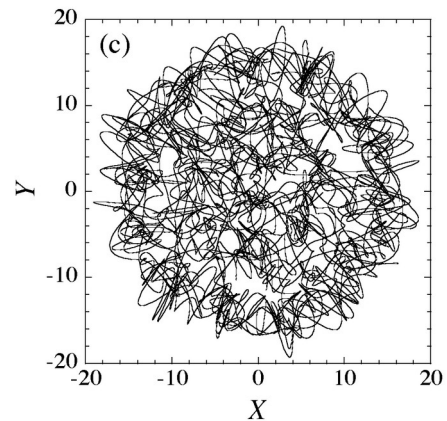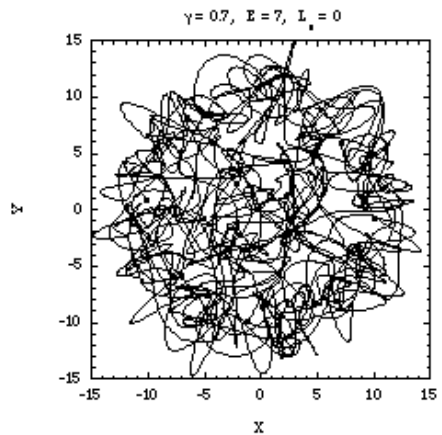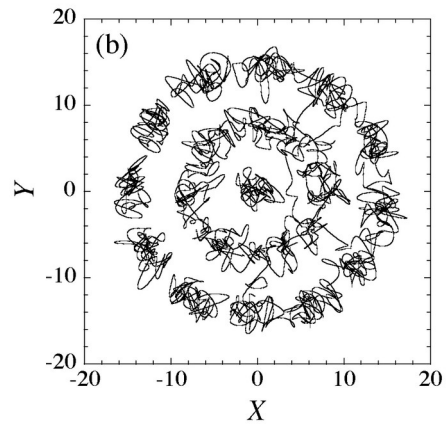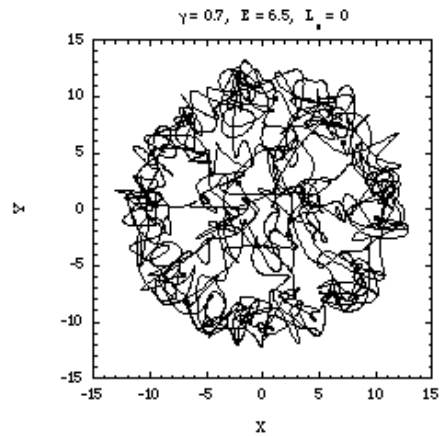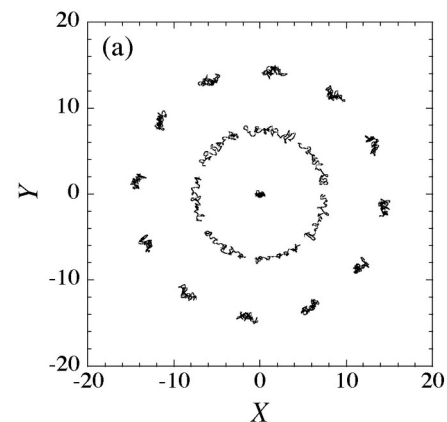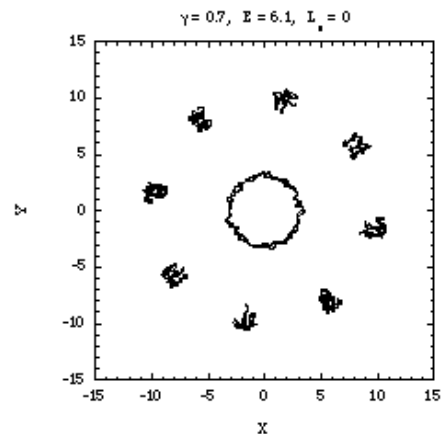flat trap: $\dfrac{1}{\sqrt{6}} < |g| < \dfrac{1}{2}$

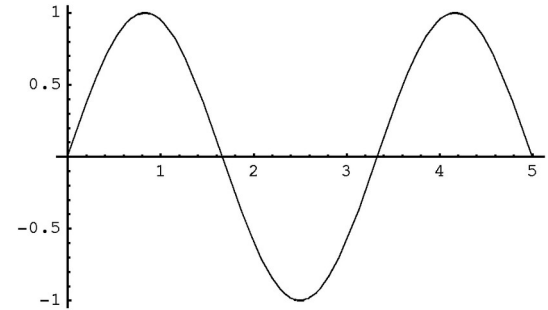# MICROPLASMAS ION TRAJECTORIES

quasi 2D trap
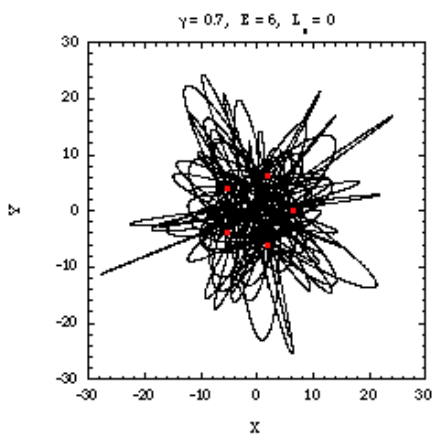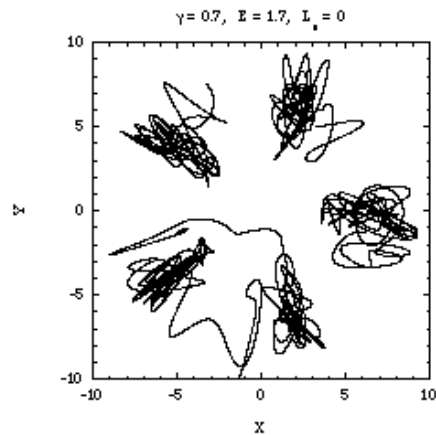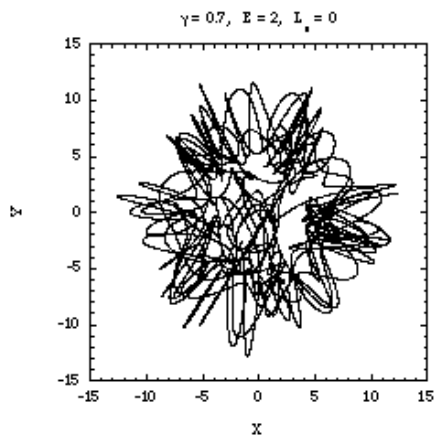
Nonequilibrium work in microplasmas

external forcing

Hamiltonian:
$$H = H_0 - A \sin \omega t \sum_{i=1}^{N} Z_i$$

time interval:
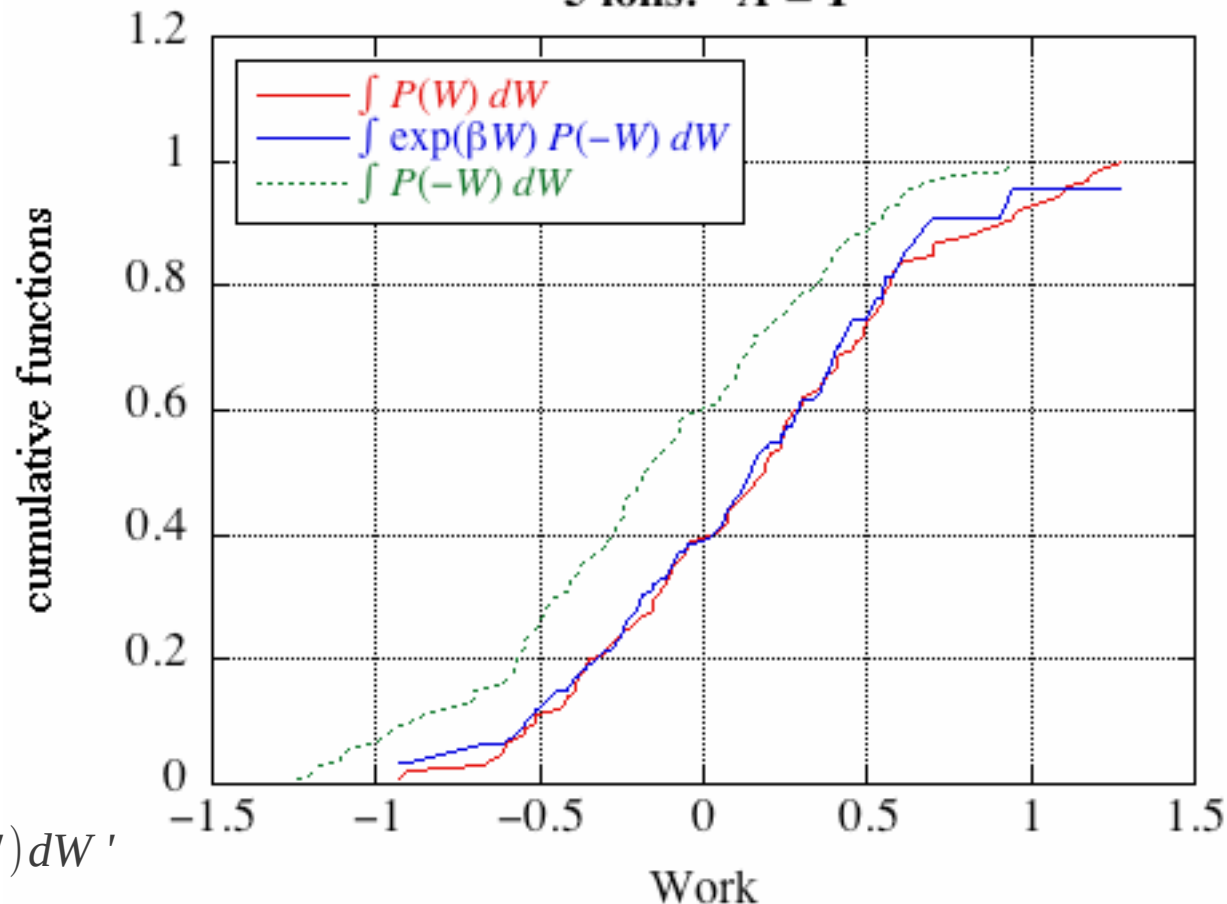$$t = 3\pi/\omega$$

$$p_F(W) = p_R(W)$$

$$\Delta F = 0$$

Nonequilibrium work
fluctuation theorem:

$$\frac{p(W)}{p(-W)} = e^{\beta W}$$

after integration:

$$\int_{-\infty}^{W} p(W')dW' = \int_{-\infty}^{W} e^{\beta W'} p(-W')dW'$$

5 ions: $A = 1$

- $\int P(W)\, dW$
- $\int \exp(\beta W)\, P(-W)\, dW$
- $\int P(-W)\, dW$

cumulative functions

Work

RNA unfolding & refolding
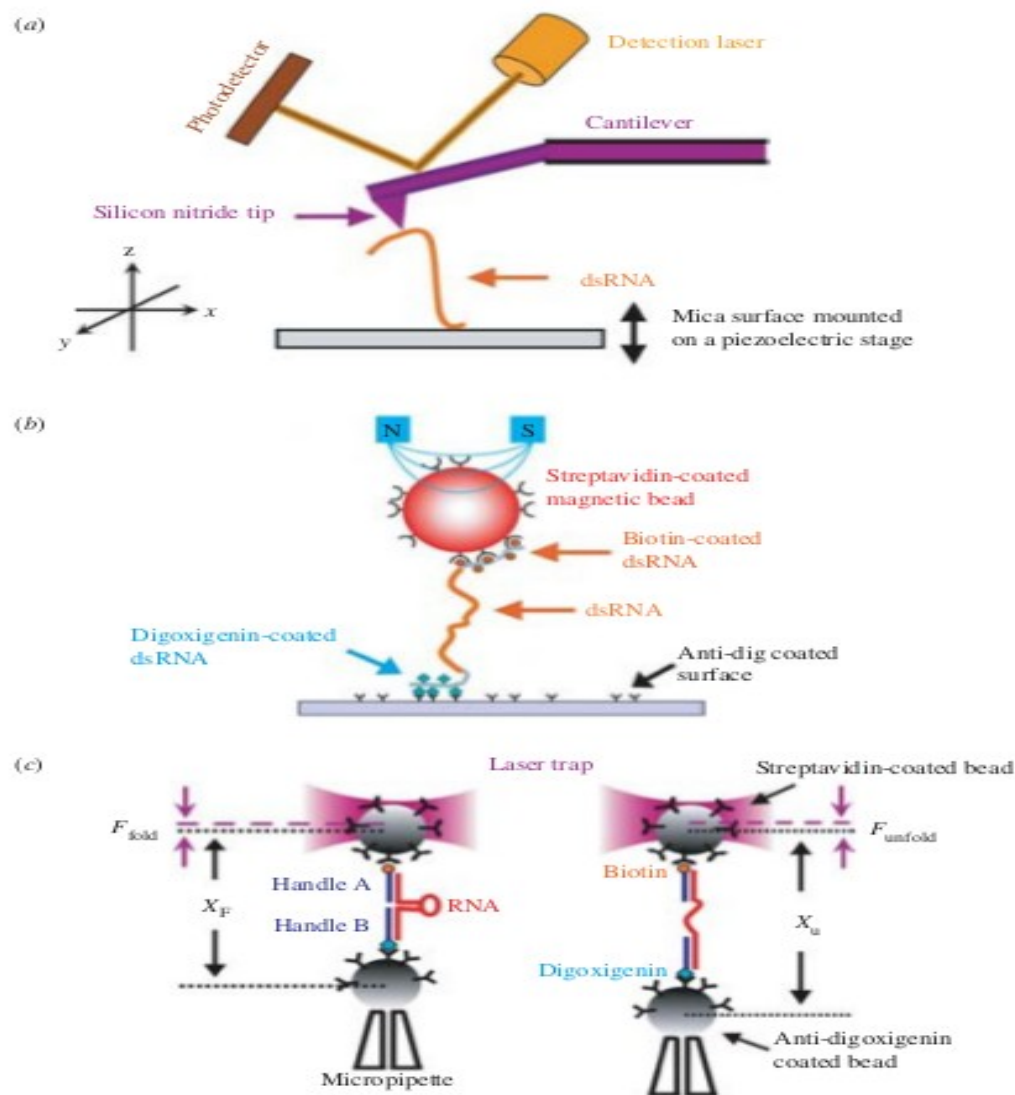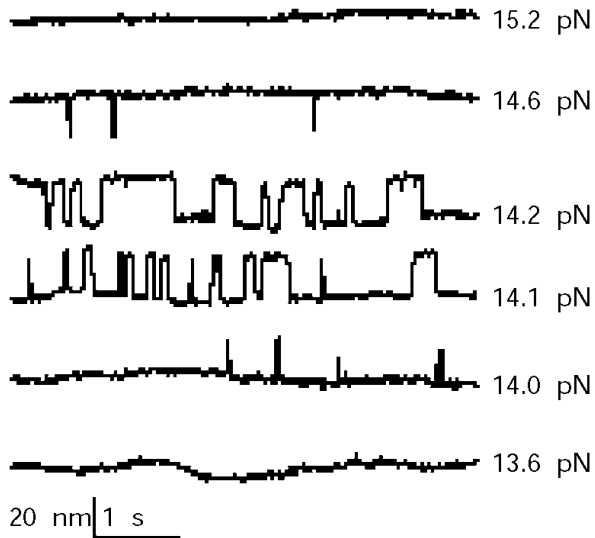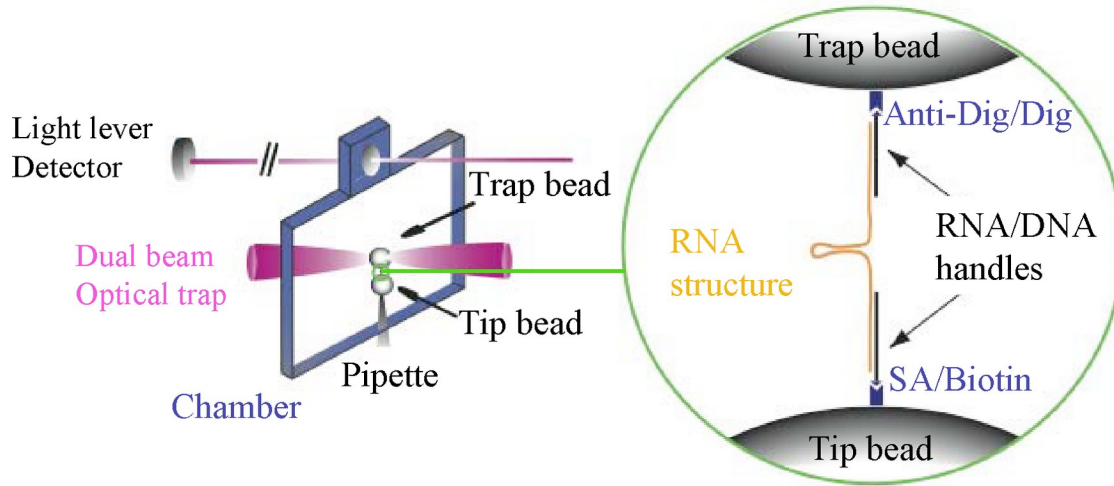
C. Bustamante, Quart. Rev. Biophys. (2006)].

Fig. 1. Experiment set-ups for mechanical studies of RNA. (*a*) Atomic force microscopy (Rief *et al.* 1997). The 'pulling' AFM consists of a cantilever, a laser detection system and a moveable surface. The silicon nitride tip of the cantilever picks up RNA molecules by 'tapping' on the surface. The position of the

RNA unfolding & refolding

D. Collin, F.Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr. & C. Bustamante,
Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies,
Nature **437** (8 September 2005) 231.

Distance between the beads versus time for different tensions
[C. Bustamante, Quart. Rev. Biophys. (2006)].
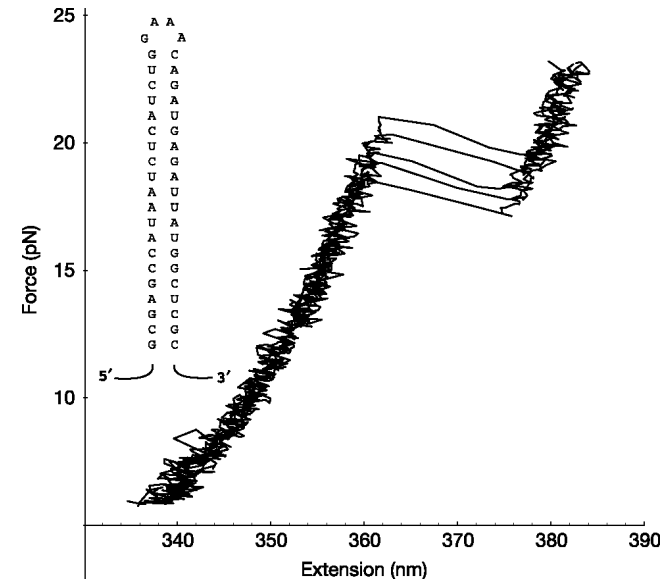
Five unfolding force-extension curves
for the RNA hairpin (loading rate of 7.5 pN s^{-1}).

rRNA

The RNA is a three-helix junction of the 16S ribosomal RNA of Escherichia coli that binds the S15 protein.
The secondary structure of this RNA plays a crucial role in the folding of the central domain
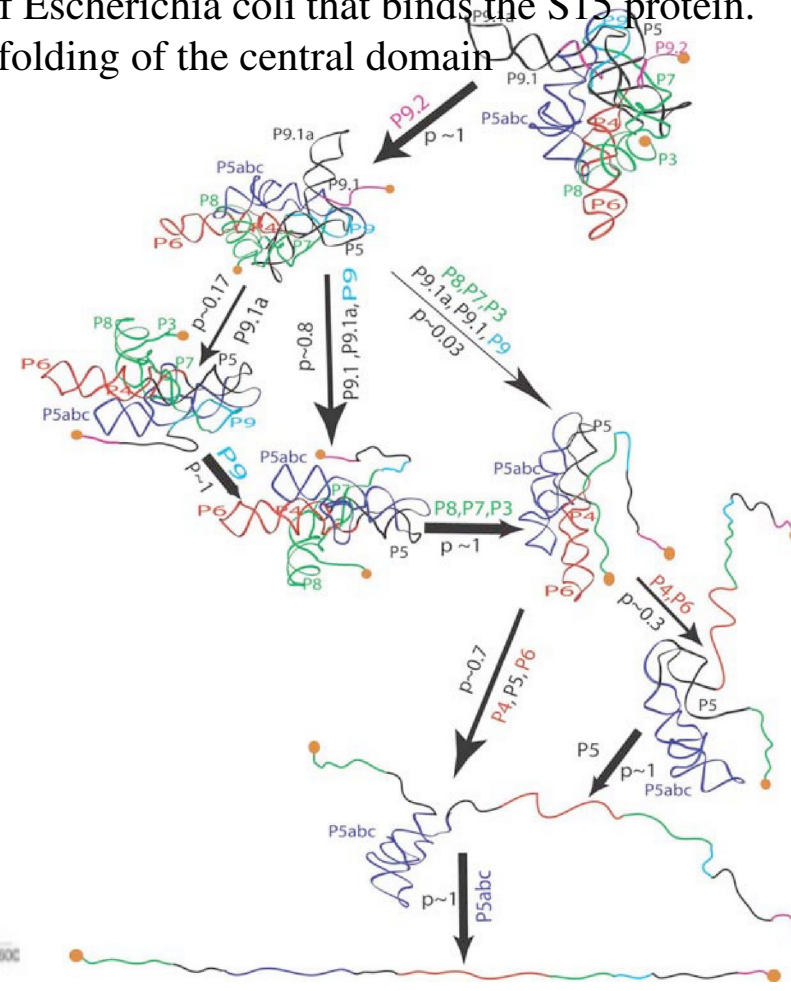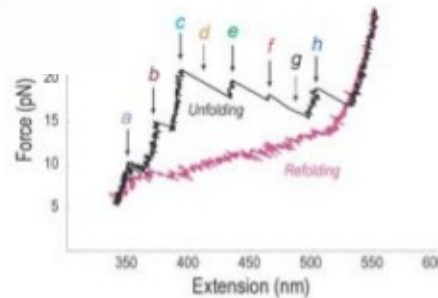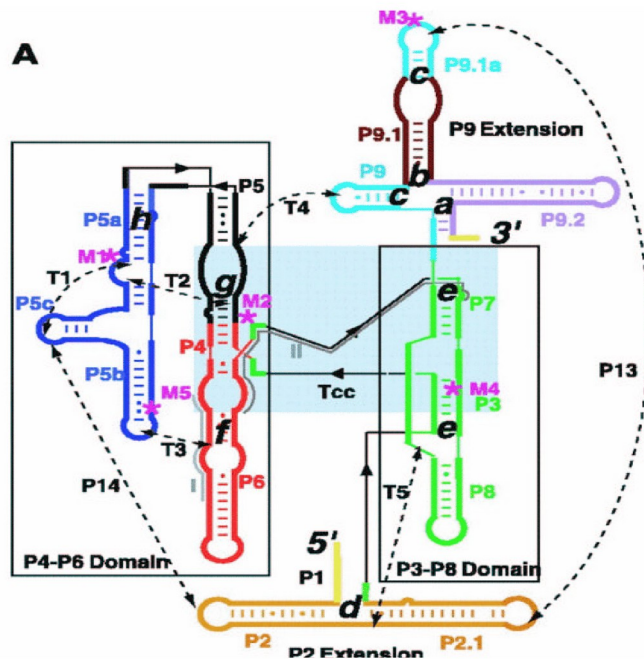
Secondary and tertiary structures of the gro
from *Tetrahymena thermophila*, a ribozyme
[C. Bustamante, Quart. Rev. Biophys. (2006)].

RNA FOLDING FREE ENERGIES

$$\frac{p_F(W)}{p_R(-W)} = e^{\beta(W - \Delta F)}$$
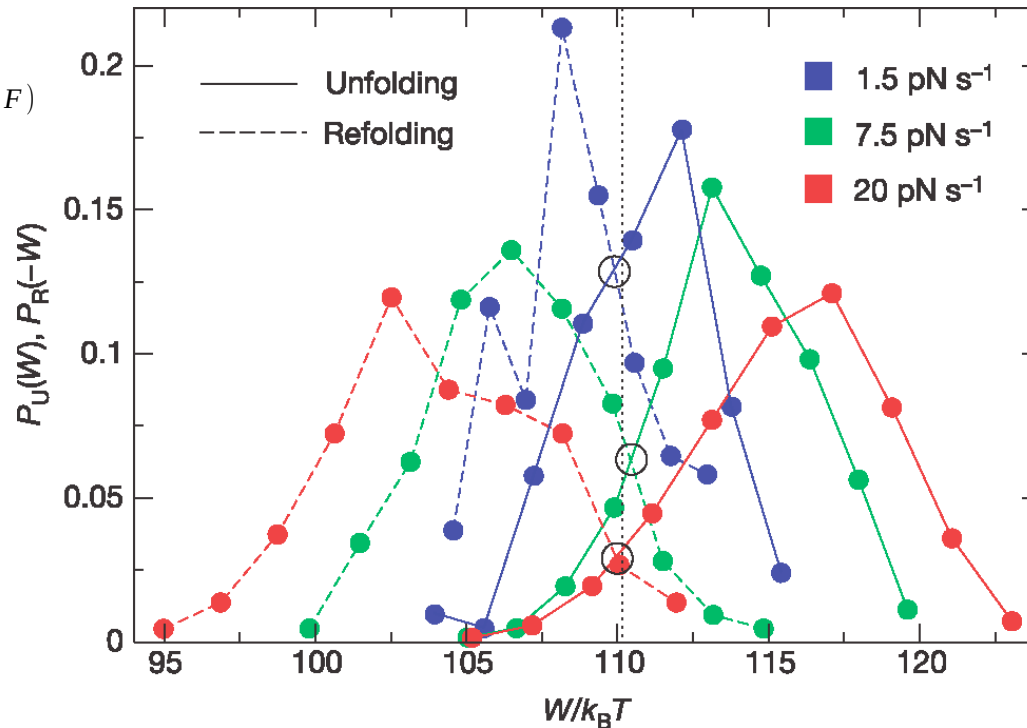
Test of the Crooks fluctuation theorem. Work distributions for RNA unfolding (continuous lines) and refolding (dashed lines). Negative work is plotted for refolding $P_R(-W)$. Statistics: 130 pulls and three molecules ($r = 1.5$ pN s^{-1}), 380 pulls and four molecules ($r = 7.5$ pN s^{-1}), 700 pulls and three molecules ($r = 20.0$ pN s^{-1}), for a total of ten separate experiments. Unfolding and refolding distributions at different speeds show a common crossing around $\Delta G = 110.3$ $k_B T$.

RNA FOLDING FREE ERGIES: WILD-TYPE & MUTANT

D. Collin, F.Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr. & C. Bustamante,
Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies,
Nature **437** (8 September 2005) 231.
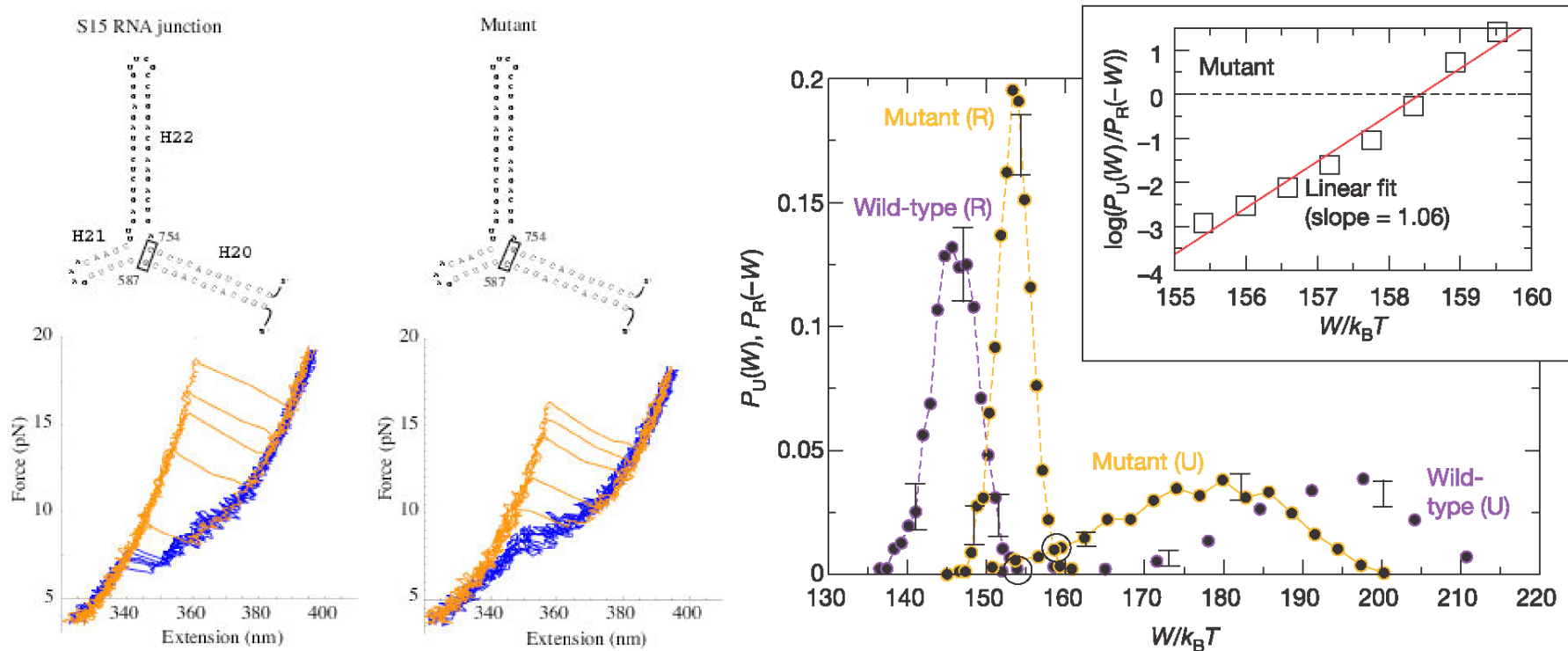
Free-energy recovery and test of the Crooks fluctuation theorem for non-Gaussian work distributions. Experiments carried out on the wild-type and mutant S15 three-helix junction without Mg2+. Unfolding (continuous lines) and refolding (dashed lines) work distributions. Statistics: 900 pulls and two molecules (wild type, purple); 1200 pulls and five molecules (mutant type, orange). Inset, test of the CFT for the mutant.
$\Delta G = 154.1\pm0.4\ k_B T$ for unfolding the wild type and $\Delta G = 157.9\pm0.2\ k_B T$ for unfolding the mutant type.

Nanosystems dehors equilibrium: theoremes de fluctuations

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Connection to the steady-state fluctuation theorem

transient driven process:

Crooks fluctuation theorem (1999):

$$\frac{p_F(W)}{p_R(-W)} = e^{\beta(W-\Delta F)} = e^{\beta W_{diss}}$$

dissipated work: $W_{diss} \equiv W - \Delta F$ $\Delta F \equiv F_B - F_A$

Jarzynski's nonequilibrium work relation (1997):

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$$ $\langle e^{-\beta W_{diss}} \rangle = 1$

transient -> stationary fluctuation theorem in the long-time limit

-> nonequilibrium steady state: fluctuating currents contributing to the dissipation

entropy production in the nonequilibrium steady state:

$$\left(\frac{d_i S}{dt} \right)_{steady\ state} = \frac{1}{T} \lim_{t \to \infty} \frac{W_{diss}(t)}{t}$$

Description in terms of a master equation

Liouville's equation of the Hamiltonian dynamics in microscopic phase space:

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

-> reduced description in terms of the coarse-grained states ω

-> master equation for the probability to visit the state ω by the time t : $P_t(\omega)$

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

$w_\rho(\omega|\omega')$ rate of the transition $\omega \xrightarrow{\rho} \omega'$ due to the elementary process $\rho = \pm 1, \ldots, \pm r$

normalization condition: $\sum_\omega P_t(\omega) = 1$

Properties of the transition rates

The transition rates are given by kinetics but their ratios can often be related to equilibrium thermodynamics:

Often, for an isothermal processes at inverse temperature $\beta = (k_B T)^{-1}$

the ratio of the transition rates of forward and backward processes $\omega \xrightarrow{+\rho} \omega', \omega \xleftarrow{-\rho} \omega'$

satisfies the condition of *local equilibrium*

$$\frac{w_{+\rho}(\omega|\omega')}{w_{-\rho}(\omega'|\omega)} = e^{\beta(X_\omega - X_{\omega'})}$$

Where for a

closed system, isothermal-isochoric ensemble, Helmholtz free energy: $X = F = E - TS$

closed system, isothermal-isobaric ensemble, Gibbs free enthalpy: $X = G = F + PV$

open system,   isothermal-isopotential-isochoric ensemble, grand potential: $X = \Omega = F - \mu N$

open system,   isothermal-isopotential-isobaric ensemble,   -   : $X = K = G - \mu N$

Nonequilibrium versus equilibrium stationary states

stationary solution of the master equation:

$$\frac{d}{dt}P_t(\omega)=\sum_{\rho,\omega'}\left[P_t(\omega')w_\rho(\omega'|\omega)-P_t(\omega)w_{-\rho}(\omega|\omega')\right]=0$$

In general, the stationary solution defines a nonequilibrium steady state $P_{st}(w)$ if nonequilibrium constraints are imposed on the system by nonvanishing affinities.

The stationary solution defines the equilibrium state $P_{st}(\omega)=P_{eq}(\omega)$ in the special case where the *detailed balance conditions* are satisfied:

$$P_{eq}(\omega')W_\rho(\omega'|\omega)=P_{eq}(\omega)W_{-\rho}(\omega|\omega')\quad\rho=\pm 1,\dots,\pm r$$

Entropy, entropy flow & entropy production

entropy at time t :
$$S_t \equiv \sum_\omega S^0(\omega) P_t(\omega) - k_B \sum_\omega P_t(\omega) \ln P_t(\omega)$$

currents:
$$J_\rho(\omega, \omega'; t) \equiv P_t(\omega') W_{+\rho}(\omega'|\omega) - P_t(\omega) W_{-\rho}(\omega|\omega')$$

affinities:
$$A_\rho(\omega, \omega'; t) \equiv k_B \ln \frac{P_t(\omega') W_{+\rho}(\omega'|\omega)}{P_t(\omega) W_{+\rho}(\omega|\omega')}$$
($=0$ in equilibrium)

time derivative of the entropy:
$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt}$$
(odd and even under time reversal)

entropy flow:
$$\frac{d_e S}{dt} = \frac{k_B}{2} \sum_{\rho, \omega, \omega'} J_\rho(\omega, \omega'; t) \left[S^0(\omega) - \frac{k_B}{2} \ln \frac{W_{+\rho}(\omega'|\omega)}{W_{-\rho}(\omega|\omega')} \right]$$

entropy production:
$$\frac{d_i S}{dt} = \frac{k_B}{2} \sum_{\rho, \omega, \omega'} \left[P_t(\omega') W(\omega'|\omega) - P_t(\omega) W(\omega|\omega') \right] \ln \frac{P_t(\omega') W_{+\rho}(\omega'|\omega)}{P_t(\omega) W_{-\rho}(\omega|\omega')}$$

$$\frac{d_i S}{dt} = \frac{1}{2} \sum_{\rho, \omega, \omega'} J_\rho(\omega, \omega'; t) A_\rho(\omega, \omega'; t) \geq 0$$

Entropy & fluctuation theorem

$$Z(t) = \ln \frac{W_{\rho_N}(\omega_N|\omega_{N-1})...W_{\rho_2}(\omega_2|\omega_1)W_{\rho_1}(\omega_1|\omega_0)}{W_{\rho_{-1}}(\omega_0|\omega_1)...W_{\rho_{-(N-1)}}(\omega_{N-2}|\omega_{N-1})W_{\rho_{-N}}(\omega_{N-1}|\omega_N)}$$

$$\underbrace{Z(t) \rightarrow \beta(X_{\omega_0} - X_{\omega_N})}_{\text{detailed balance}}$$

$$= \ln\left(\frac{P(\omega)}{P(\omega^R)}\right) - \underbrace{\ln\left(\frac{P_0(\omega_0)}{P_N(\omega_N)}\right)}_{\text{négligeable comme } t \rightarrow \infty} \approx \frac{1}{k_B}\sum_{j=1}^{N} A_{\rho_j}(\omega_{j-1}, \omega_j, t_j)$$

Generating function $\quad Q(\eta) \equiv \lim_{t \rightarrow \infty} -\frac{1}{t}\ln\langle e^{-\eta Z(t)}\rangle, \quad \frac{\langle Z(t)\rangle}{t} = \lim_{\eta \rightarrow 0}\frac{dQ}{d\eta}, \text{etc.}$

$$\langle e^{-\eta Z(t)}\rangle = \sum_{\omega(t)} P(\omega(t))\left(\frac{P(\omega^R(t))}{P(\omega(t))}\right)^{\eta}$$

$$= \sum_{\omega(t)} P(\omega^R(t))\left(\frac{P(\omega(t))}{P(\omega^R(t))}\right)^{1-\eta}$$

$$= \sum_{\omega^R(t)} P(\omega^R(t))\left(\frac{P(\omega(t))}{P(\omega^R(t))}\right)^{1-\eta}$$

$$= \sum_{\omega(t)} P(\omega(t))\left(\frac{P(\omega^R(t))}{P(\omega(t))}\right)^{1-\eta} \qquad \Longrightarrow \qquad \boxed{Q(\eta) = Q(1-\eta)}$$

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Entropy & fluctuation theorem

$$Z(t) \approx \frac{1}{k_B} \sum_{j=1}^{N} A_{\rho_j}(\omega_{j-1}, \omega_j, t_j)$$

$$\langle Z(t) \rangle \approx \int_0^t dt' \ \frac{1}{2} \frac{1}{k_B} \sum_{\rho, \omega, \omega'} J_\rho(\omega, \omega', t') A_\rho(\omega, \omega', t') = \frac{1}{k_B} \Delta_i S(t)$$

$$\frac{d_i S}{dt} = k_B \frac{1}{t} \langle Z(t) \rangle = k_B \lim_{\eta \to 0} \frac{dQ(\eta)}{d\eta}$$

$$\langle e^{-\eta Z(t)} \rangle = \sum_{\omega(t)} P(\omega(t)) \left(\frac{P(\omega^R(t))}{P(\omega(t))} \right)^{1-\eta} \to \langle e^{-Z(t)} \rangle = \sum_{\omega(t)} P(\omega(t)) = 1$$

Jarzynski:

$$\langle e^{-\beta W_{diss}} \rangle = 1$$

$$Z(t) \sim W_{diss}, \quad (t \to \infty)$$

$$\frac{d_i S}{dt} = k_B \frac{\langle W_{diss} \rangle}{t}$$

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