NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch 7. THEOREMES DE FLUCTUATIONS

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Lecture 8, 2019-2020

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

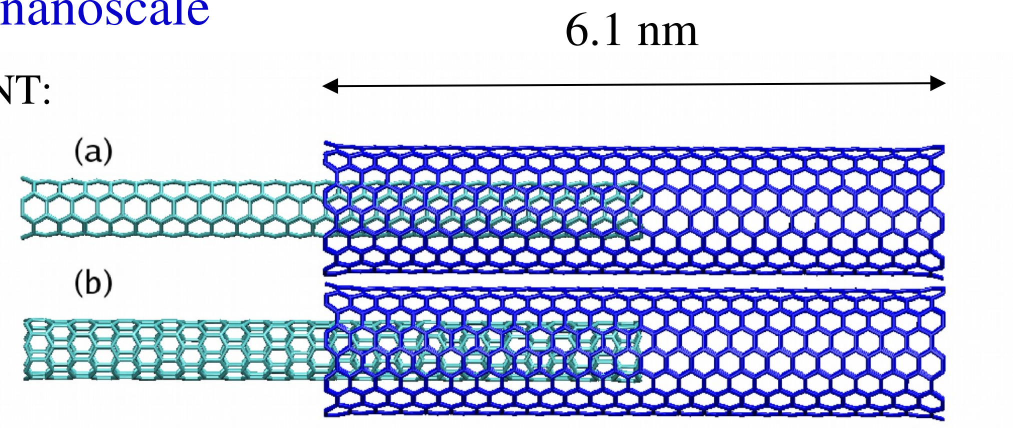
Undriven nonequilibrium nanosystem:

Energy dissipation by friction at the nanoscale

Many nanosystems are most interesting when out of equilibrium

armchair-armchair DWNT:
(4,4)@(9,9)
$N_1 = 400$ $N_2 = 900$

zigzag-armchair DWNT:
(7,0)@(9,9)
$N_1 = 406$ $N_2 = 900$



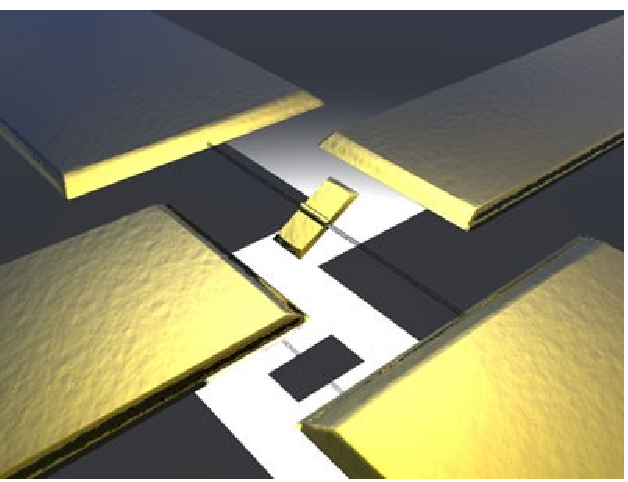
J. Servantie & P. Gaspard, Phys. Rev. Lett. **91** (2003) 185503; Phys. Rev. B **73** (2006) 125428.

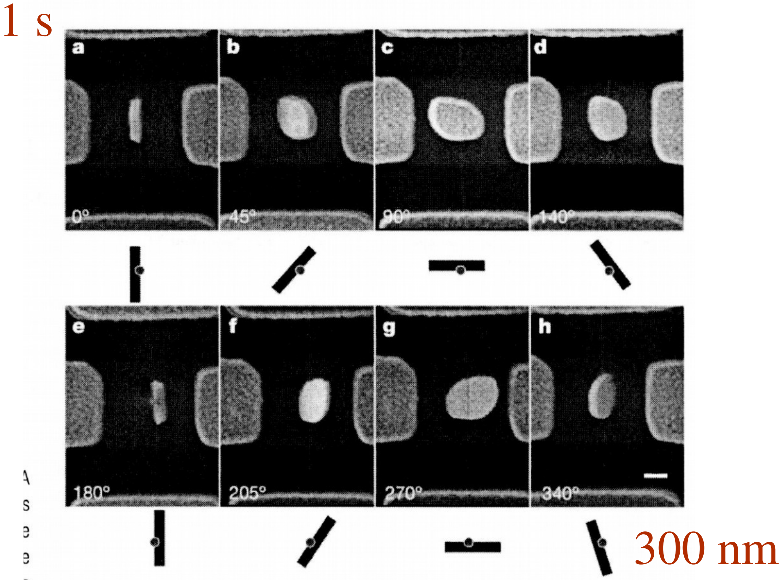
Driven, out of equilibrium, transport, fluctuations

Driven nonequilibrium nanosystem:

Energy supply versus energy dissipation

period ~ 1 s





A. M. Fennimore, T. D. Yuzvinsky, Wei-Qiang Han, M. S. Fuhrer, J. Cumings & A. Zettl, Nature **424** (2003) 410.

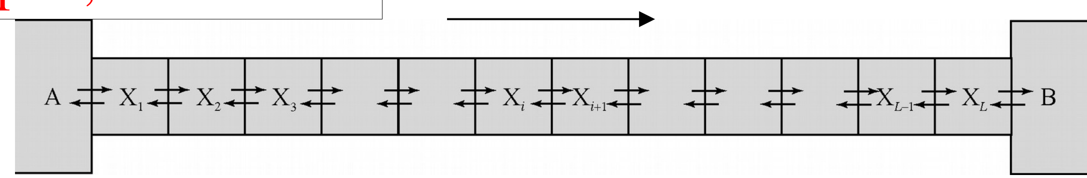
Les nanosystemes en etat stationaire de non-equilibre

Apport d'énergie

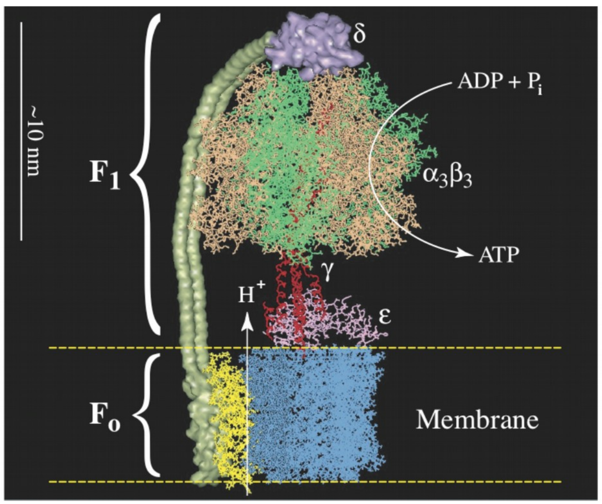
Driven, out of equilibrium, transport, fluctuations

diffusion
conduction électrique

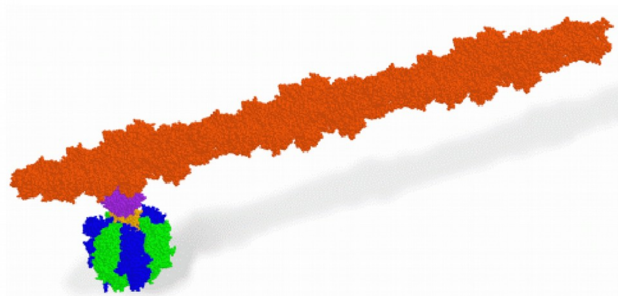
entre deux réservoirs

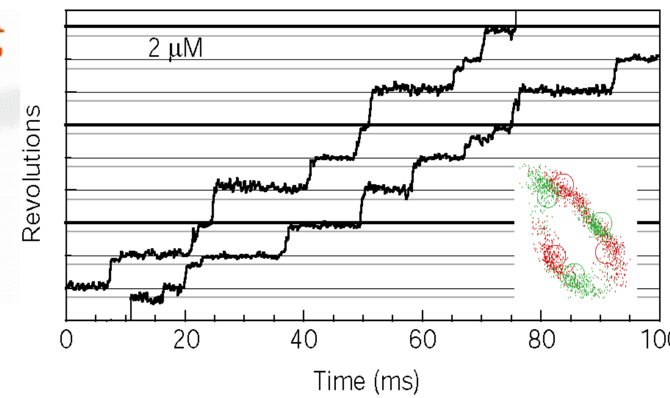


moteur moléculaire: F_oF_1-ATPase

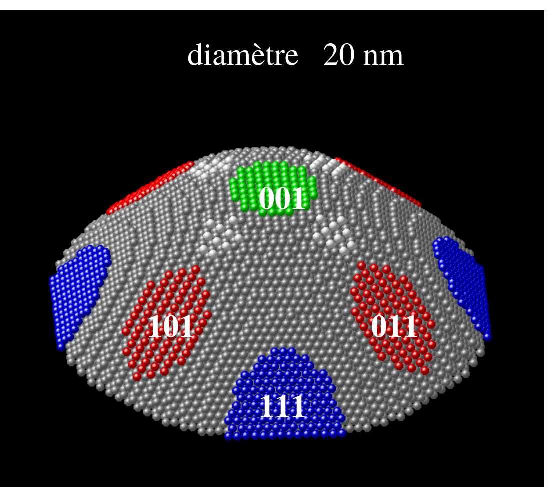


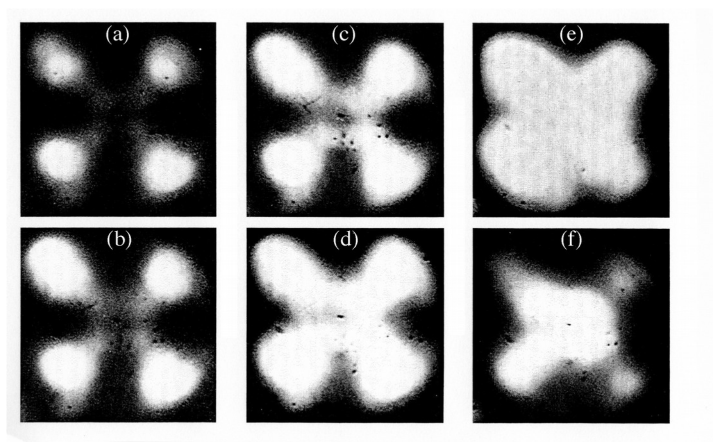
K. Kinosita et al. (2001): F_1-ATPase + filament

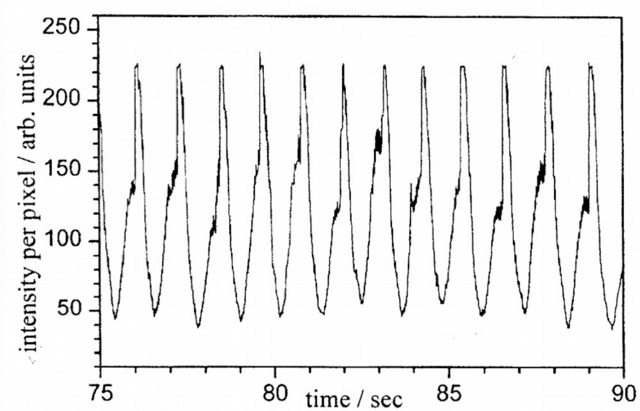




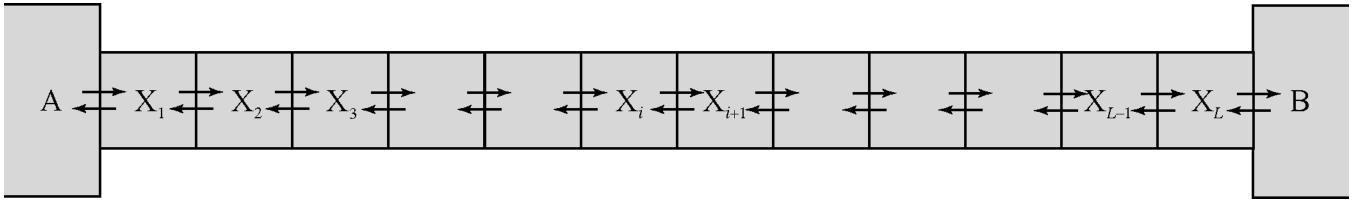
C. Voss & N. Kruse (1996): réaction $NO_2/H_2/Pt$







Diffusion between two reservoirs



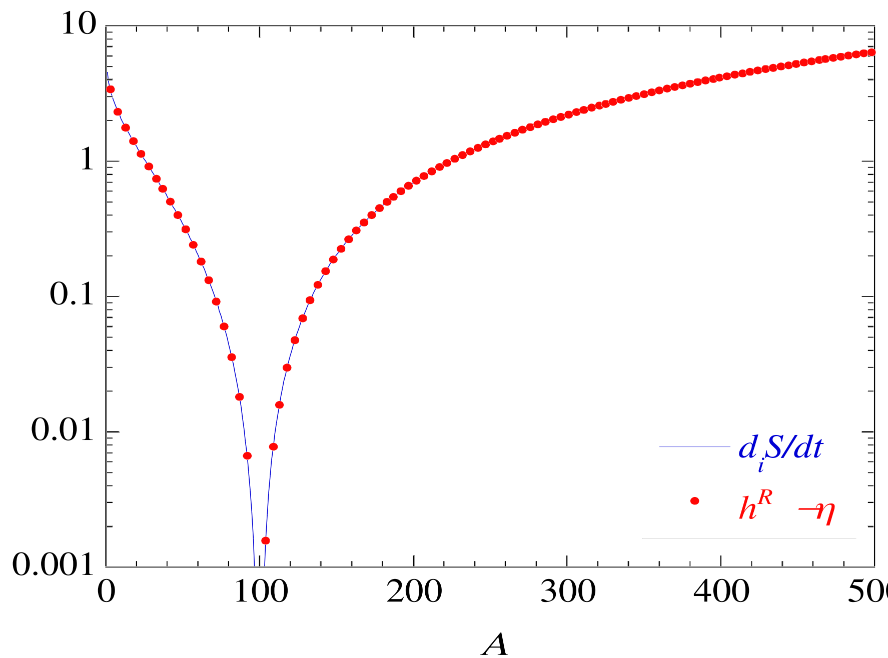
nonequilibrium steady state

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

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

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

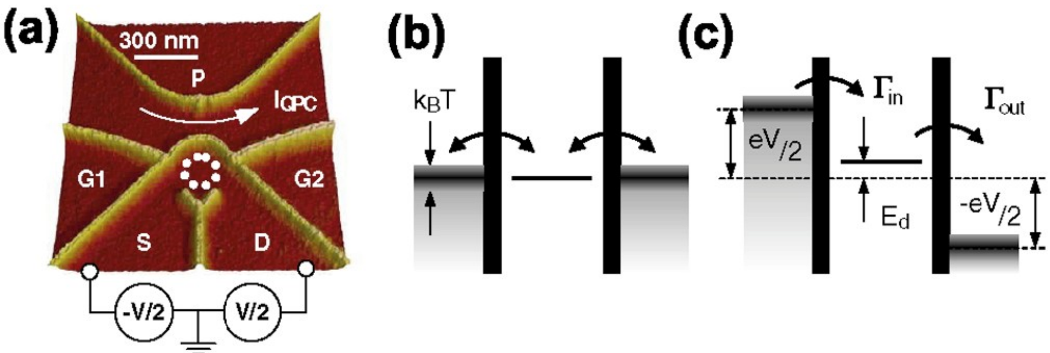
de Broglie quantum wavelength: $\lambda = h/(mv)$

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

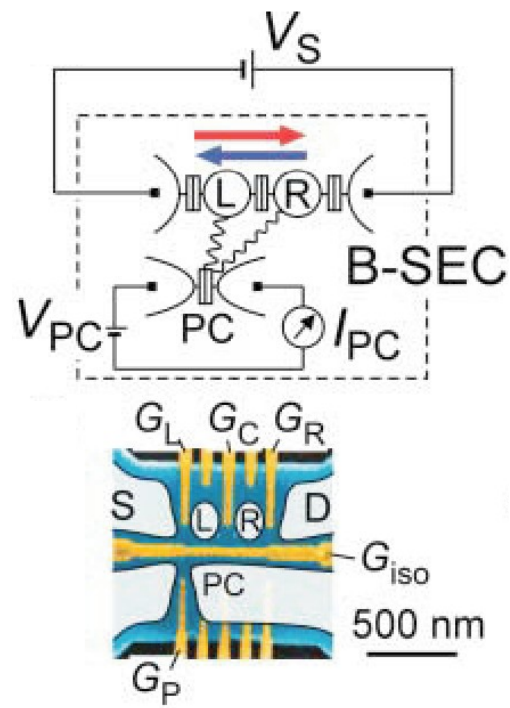
GaAs-GaAlAs quantum dot
with a quantum point contact (QPC)

S: source
D: drain

$T < 1$ K



S. Gustavsson et al., Phys. Rev. Lett. **96**, 076605 (2006).

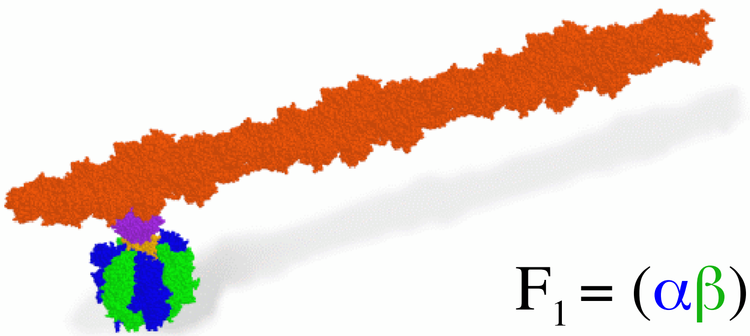


T. Fujisawa et al., Science **312**, 1634 (2006).

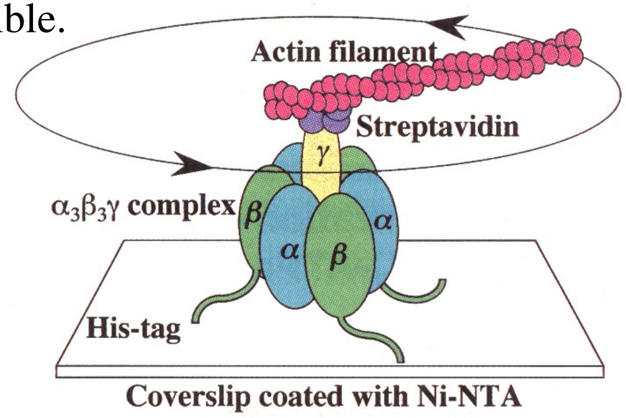
F_1-ATPase NANOMOTOR

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

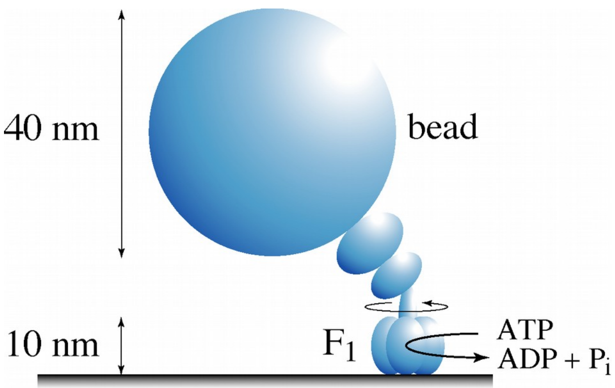
ATP est le produit chimique qui est utilisé comme combustible.



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

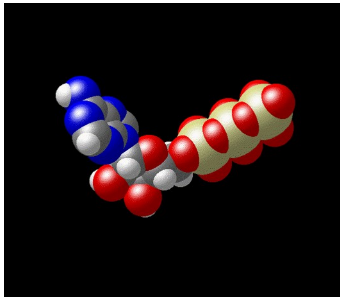


R. Yasuda, H. Noji, M. Yoshida, K. Kinosita Jr. & H. Itoh, Nature **410** (2001) 898



chemical fuel of the F_1 nanomotor:

ATP adenosine triphosphate



power = 10^{-18} -18$^{\mathrm{Watt}}$

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

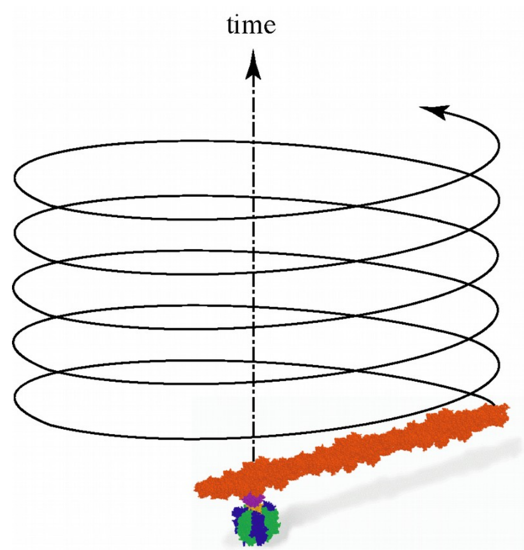
Structure in 3D space:

- no flux $\langle J_g \rangle = 0$
- no entropy production $\frac{d_i S}{dt} = 0$
- no energy supply needed
- equilibrium
- in contact with one reservoir

Nonequilibrium

Dynamics in 4D space-time:

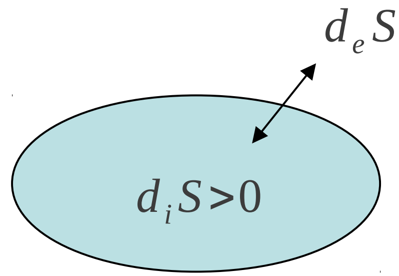
- flux $\langle J_g \rangle \neq 0$
- entropy production $\frac{d_i S}{dt} > 0$
- energy supply required
- nonequilibrium
- in contact with several reservoirs



THERMODYNAMICS OF NONEQUILIBRIUM PROCESSES

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

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



entropy flow

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
chemical potential difference $\Delta\mu/T$

angular velocity Ω
chemical reaction rate R

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

temperature T

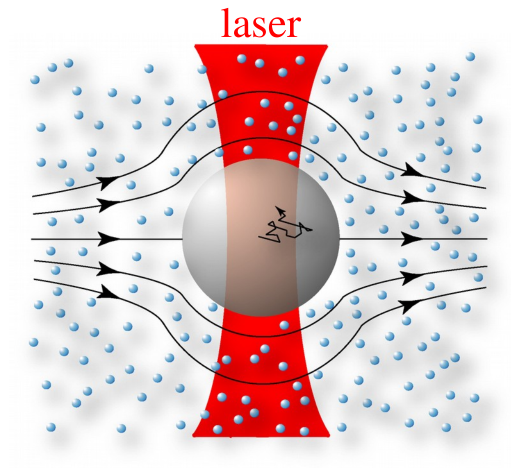
Systemes fluctuants hors d'equilibre

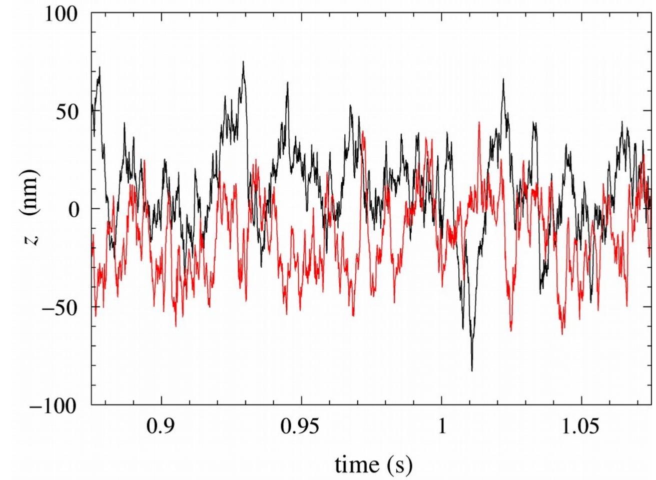
particule brownienne

dans un piège optique

et un écoulement

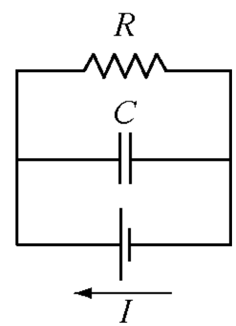
(2 μm)

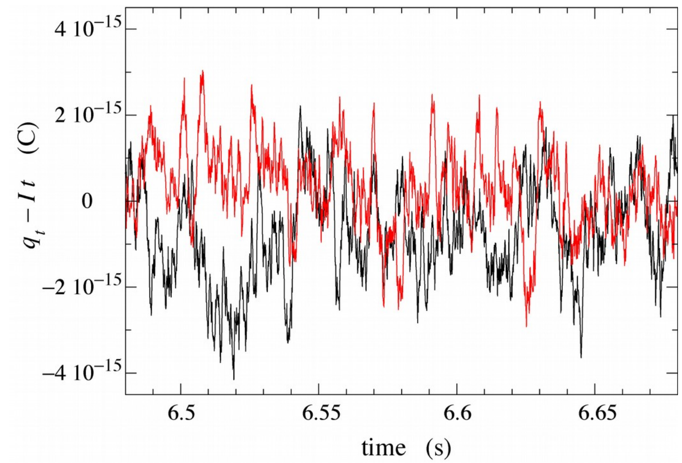




circuit électrique *RC*

(bruit thermique de Nyquist)

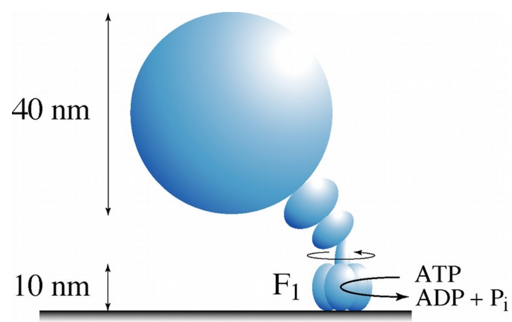


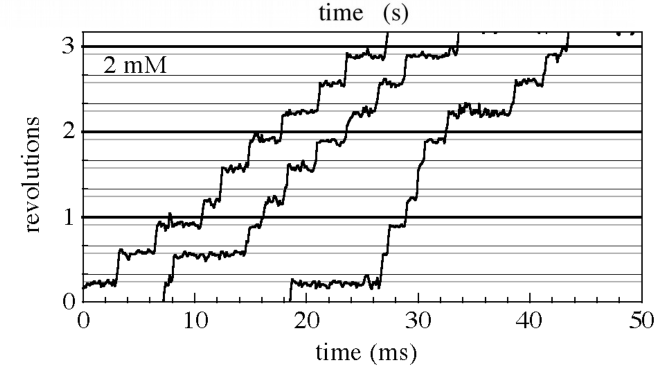


moteur moléculaire

F_1-ATPase

(Kinosita et al., 2001)





Brisure de la symetrie sous renversement du temps

Θ(r,v) = (r,-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 $\neq$ 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.*

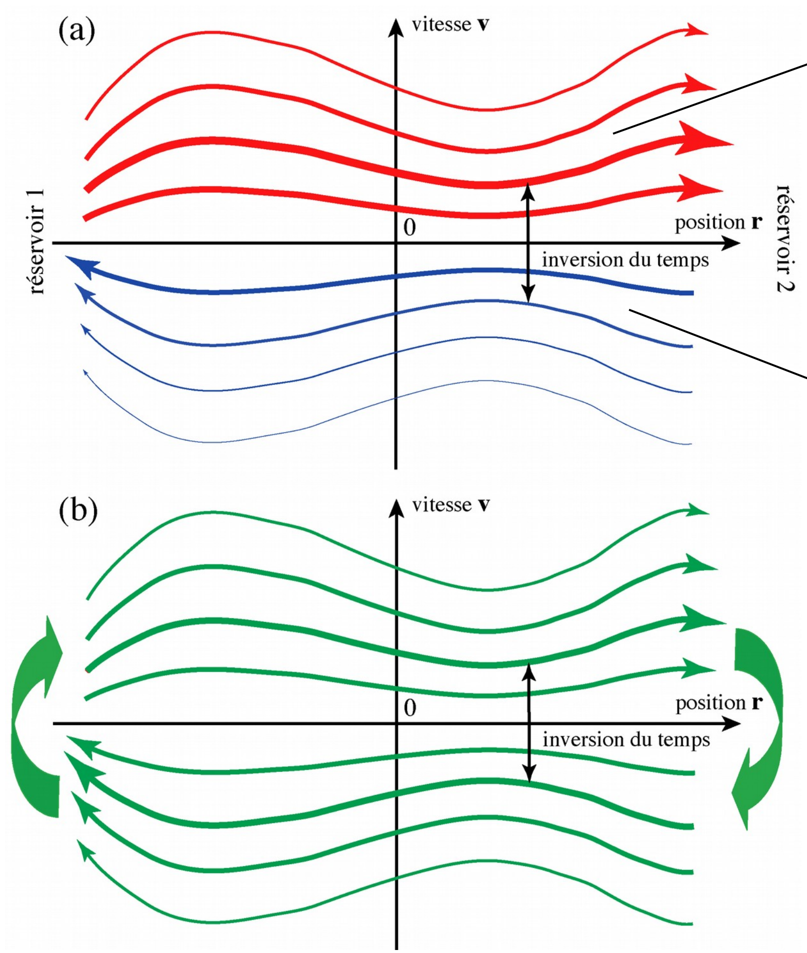
Brisure explicite de symétrie: *par les conditions aux bords dans les systèmes ouverts.*

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

Asymetrie temporelle dans la description statistique

non-équilibre

production d'entropie
dissipation d'énergie



trajectoires
les plus probables

Asymétrique sous inversion du temps

trajectoires
remontant le temps,
moins probables

équilibre

entropie constante

symétrique sous inversion du temps

Remarque: La microréversibilité est toujours satisfaite.

Nanosystems dehors equilibrium: theoremes de fluctuations

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  - Jarzynski relation
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Dynamique microscopique Hamiltonienne

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

Fonction hamiltonienne: $H = \sum_{i=1}^{N} \frac{p_i^2}{2\, m_i} + U(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N)$

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: $t \rightarrow -t \qquad \hat{\Theta}(\boldsymbol{q}, \boldsymbol{p}) = (\boldsymbol{q}, -\boldsymbol{p})$

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

Theoreme de Liouville & équation de Liouville

Equations d'Hamilton:

$$\dot{\boldsymbol{q}}_i = +\frac{\partial H}{\partial \boldsymbol{p}_i} \qquad \dot{\Gamma} = J \cdot \nabla H$$

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

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:

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

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

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

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

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:

$$d\Gamma(t) = d\Gamma(0)$$

$$d\boldsymbol{q}(t)\, d\boldsymbol{p}(t) = d\boldsymbol{q}(0)\, d\boldsymbol{p}(0)$$

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

Driven Hamiltonian Systems

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

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

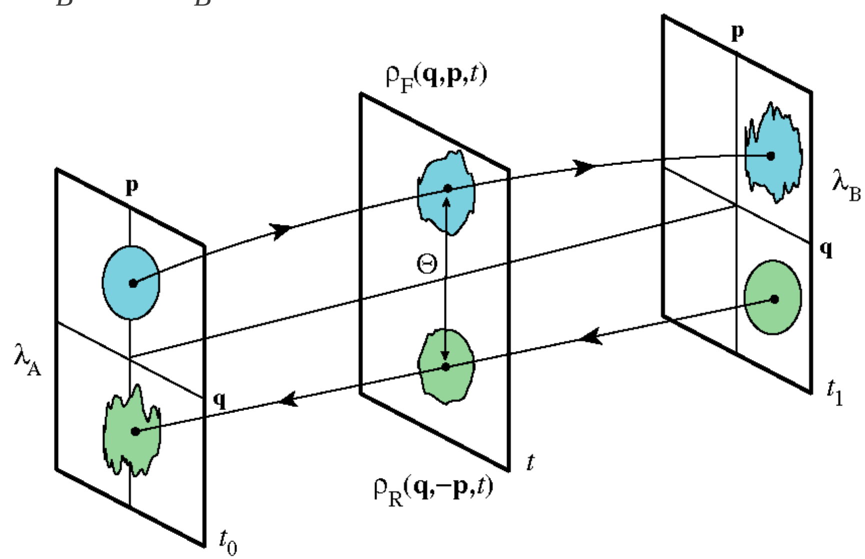
initial state in the canonical ensemble: $\rho(\Gamma)=\frac{1}{Z_A}e^{-\beta H(\Gamma,\lambda_A)}\equiv\frac{1}{Z_A}e^{-\beta H_A(\Gamma)}$

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: $\rho(\Gamma)=\frac{1}{Z_B}e^{-\beta H(\Gamma,\lambda_B)}\equiv\frac{1}{Z_B}e^{-\beta H_B(\Gamma)}$

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



Fluctuation theorem for the nonequilibrium work

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

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

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

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

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

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

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

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

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

using microreversibility & Liouville's theorem:

Crooks fluctuation theorem (1999):

$\Delta F=F_B-F_A$

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

Nonequilibrium work fluctuation theorem : proof

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

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

$$p_F(W)\equiv\langle\delta\left(W-\left(H_B(\Gamma(T;\Gamma_0))-H_A(\Gamma_0)\right)\right)\rangle_{0,A}$$
$$=\frac{1}{Z_A}\int d\Gamma_0\, e^{-\beta H_A(\Gamma_0)}\,\delta\left(W-\left(H_B(\Gamma(T;\Gamma_0))-H_A(\Gamma_0)\right)\right)$$
$$=\frac{1}{Z_A}\int d\Gamma_0\, e^{-\beta(H_B(\Gamma(T;\Gamma_0))-W)}\,\delta\left(W-\left(H_B(\Gamma(T;\Gamma_0))-H_A(\Gamma_0)\right)\right)$$
$$=\frac{Z_B}{Z_A}\frac{1}{Z_B}\int d\Gamma\, e^{-\beta(H_B(\Gamma)-W)}\,\delta\left(-W-\left(H_A(\Gamma_0(\Gamma;-T))-H_B(\Gamma)\right)\right)$$

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):

$$\boxed{\langle e^{-\beta W}\rangle = e^{-\beta \Delta F}} \qquad \beta = (k_B T)^{-1}$$

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: $\langle W \rangle \geq \Delta F$ $\qquad \langle e^x \rangle \geq e^{\langle x \rangle}$

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

The isothermal-isobaric case

Jarzynski nonequilibrium work theorem (1997):

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

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

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):

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

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

$0 < t < t_1$

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

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

average work: by Liouville's theorem & microreversibility

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

R. Kawai, J.M.R. Parrondo, & C. Van den Broeck, Phys. Rev. Lett. **98** (2007) 080602

Kullback-Leibler distance

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

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

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

Corollaries

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

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

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

Jarzynski nonequilibrium work theorem (1997):

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

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

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

(proof: exercise)

A generalization for Markovian dynamics

Hatano T and Sasa S, 2001 Phys. Rev. Lett. 86 3463

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

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Notez que

$$\left\langle \frac{P_{SS}(\Gamma_N;\alpha_N)}{P_{SS}(\Gamma_N;\alpha_{N-1})}\frac{P_{SS}(\Gamma_{N-1};\alpha_{N-1})}{P_{SS}(\Gamma_{N-1};\alpha_{N-2})}\dots\frac{P_{SS}(\Gamma_1;\alpha_1)}{P_{SS}(\Gamma_1;\alpha_0)}\right\rangle$$
$$=\int d\Gamma_0\dots d\Gamma_N\frac{P_{SS}(\Gamma_N;\alpha_N)}{P_{SS}(\Gamma_N;\alpha_{N-1})}\dots P(\Gamma_2,t_2|\Gamma_1,t_1;\alpha_1)\frac{P_{SS}(\Gamma_1;\alpha_1)}{P_{SS}(\Gamma_1;\alpha_0)}P(\Gamma_1,t_1|\Gamma_0,t_0;\alpha_0)P_{SS}(\Gamma_0,t_0;\alpha_0$$
$$=\int d\Gamma_N P_{SS}(\Gamma_N;\alpha_N)=1$$

Définissez

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

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

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

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

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

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

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

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

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

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

Quantum work relation and response theory

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

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

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

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

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

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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

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

$\hat{\Theta} i = -i \hat{\Theta}$

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

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

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

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

Quantum work relation and response theory

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

Theorem:

Étant donné

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

Fonction arbitraire $\lambda(t)$

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

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

Preuve:

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

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

Quantum work relation and response theory

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

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

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,

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

et

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

Quantum work relation and response theory

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

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

Consequnce 1: $\lambda(t)=0 \Rightarrow \langle e^{-\beta H_F(T)} e^{\beta H(0)} \rangle_{F,B} = e^{-\beta\Delta F}$ Generalized Jarzynski relation.

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

Consequnce 2: Response

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

$$\Rightarrow \langle A_F(s) e^{-\beta H_F(T)} e^{\beta H(0)} \rangle_{F,B} = e^{-\beta\Delta F} \langle \epsilon_A A_R(T-s) \rangle_{R,-B}, \quad 0 \le s \le T$$

$$\Rightarrow \langle A_F(T) e^{-\beta H_F(T)} e^{\beta H(0)} \rangle_{F,B} = e^{-\beta\Delta F} \langle \epsilon_A A_R(0) \rangle_{R,-B}$$

Choisissez $H(t;B) = H(B) + bX(t), \quad X(t\le 0) = X(t \ge T) = 0 \Rightarrow H(0;B) = H(T;B) = H(B)$

$$\epsilon_A \langle A_R(0) \rangle_{R,-B} = \epsilon_A \langle A(0) \rangle_{0,-B} = \langle A(0) \rangle_0$$

$$\Delta F = 0$$

$$\langle A_F(T) e^{-\beta H_F(T)} e^{\beta H(0)} \rangle_{F,B} = \langle A(0) \rangle_{0,-B}$$

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 2: Response $$\left\langle A_F(T)\, e^{-\beta H_F(T)}\, e^{\beta H(0)} \right\rangle_{F,B} = \langle A(0) \rangle_{0,-B}$$

$$H(t;B) = H(B) + bX(t), \quad X(t<0) = X(t>T) = 0$$

Puis, $$\frac{d}{dt} H_F(t;B) = U_F^t(t;B)\, \frac{\partial H(t;B)}{\partial t}\, U_F(t;B)$$
$$= U_F^t(t;B)\, b\, U_F(t;B)\, \dot{X}(t)$$
$$\equiv b_F(t;B)\, \dot{X}(t)$$

$$\frac{d}{dt} H_F(t;B) = b_F(t;B)\, \dot{X}(t)$$
$$\Rightarrow H_F(t;B) = H(0;B) + \int_0^t dt \;\; b_F(t;B)\, \dot{X}(t)$$
$$\Rightarrow H_F(t;B) = H(0;B) - \int_0^t dt \;\; \dot{b}_F(t;B)\, X(t)$$

Quantum work relation and response theory

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

Consequence 2: Response

$$\langle A_F(T)\, e^{-\beta H_F(T)}\, e^{\beta H(0)}\rangle_{F,B} = \langle A(0)\rangle_{0,-B}$$

$$H_F(t;B) = H(0;B) - \int_0^t dt \;\; \dot{b}_F(t;B)\, X(t)$$

En utilisant l'identitie $e^{\beta(P+Q)}e^{-\beta P} = 1 + \int_0^\beta du \;\; e^{u(P+Q)}\, Q e^{-uP}$

$$\begin{aligned} e^{-\beta H_F(T)} e^{\beta H(0)} &= 1 + \int_0^\beta du \;\; e^{-u H_F(T)}\left(\int_0^T dt \;\; \dot{b}_F(t;B)\, X(t)\right) e^{u H(0)} \\ &= 1 + \int_0^\beta du \;\; e^{-u H(0)}\left(\int_0^t dt \;\; \dot{b}_0(t;B)\, X(t)\right) e^{u H(0)} + O(X^2) \\ &= 1 + \int_0^T dt\, X(t) \int_0^\beta du \;\; \dot{b}_0(t + i\hbar u; B) + O(X^2) \end{aligned}$$

$$\begin{aligned} \langle A_F(T)\, e^{-\beta H_F(T)} e^{\beta H(0)}\rangle_{F,B} &= \langle A_F(T)\rangle_{0,B} + \int_0^T dt\, X(t) \int_0^\beta du \;\; \langle A(T)\, \dot{b}_0(t + i\hbar u; B)\rangle_{0;B} + O(X^2) \\ &= \langle A_F(T)\rangle_{0,B} + \int_0^T dt\, X(T-t) \int_0^\beta du \;\; \langle A(t)\, \dot{b}_0(-i\hbar u; B)\rangle_{0;B} + O(X^2) \end{aligned}$$

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 2: Response

$$\left\langle A_F(T)\, e^{-\beta H_F(T)}\, e^{\beta H(0)} \right\rangle_{F,B} = \left\langle A(0) \right\rangle_{0,B}$$

$$\left\langle A_F(T)\, e^{-\beta H_F(T)}\, e^{\beta H(0)} \right\rangle_{F,B} = \left\langle A_F(T) \right\rangle_{0,B} + \int_0^T dt\, X(T-t) \int_0^\beta du \;\; \left\langle A(t)\, \dot{b}_0(-i\hbar u; B) \right\rangle_{0;B} + O(X^2)$$

$$\boxed{\left\langle A_F(T) \right\rangle_{0,B} = \left\langle A(0) \right\rangle_{0,B} - \int_0^T dt\, X(T-t) \int_0^\beta du \;\; \left\langle A(t)\, \dot{b}_0(-i\hbar u; B) \right\rangle_{0;B} + O(X^2)}$$

"Linear-Response + Green-Kubo relation"

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

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

electric potential: $$\Phi(\boldsymbol{q})=V_0\frac{2\mathrm{z}^2-x^2-y^2}{r_0^2+2\mathrm{z}_0^2}$$

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

Hamiltonian in the Larmor rotating framework with rescaled variables:

$$H_0=\sum_{i=1}^{N}\left[\frac{1}{2}P_i^2+\left(\frac{1}{8}-\frac{g^2}{4}\right)\left(X_i^2+Y_i^2\right)+\frac{g^2}{2}Z_i^2\right]+\sum_{1\le i<j\le N}\frac{1}{R_{ij}}$$

elongated trap: $|g|<\frac{1}{\sqrt{6}}$

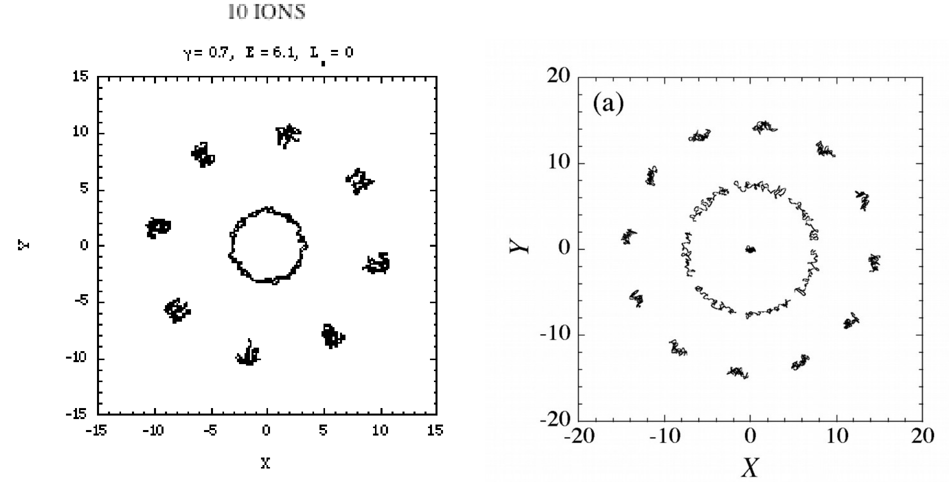
trap parameter: $$g\equiv\frac{\omega_z}{\omega_c}$$

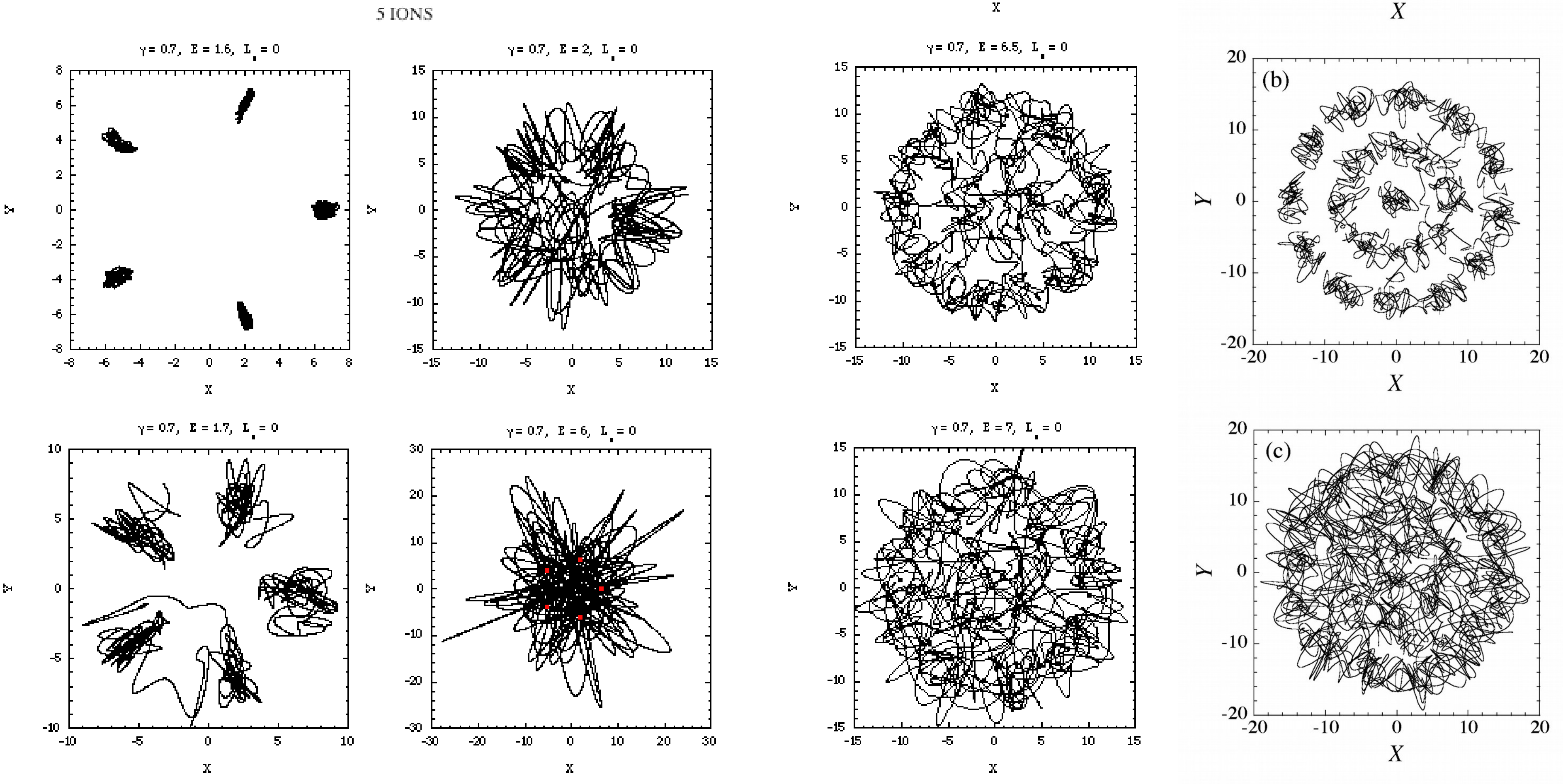
spherical trap: $|g|=\frac{1}{\sqrt{6}}$

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

MICROPLASMAS
ION TRAJECTORIES

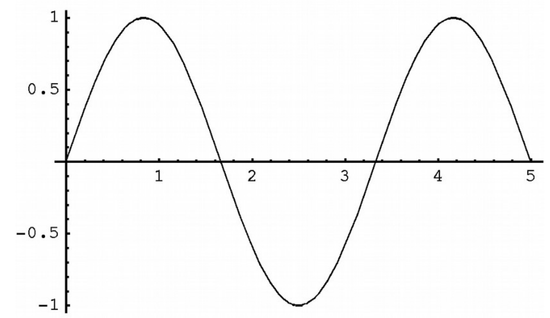
quasi 2D trap





Nonequilibrium work in microplasmas

external forcing



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

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

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

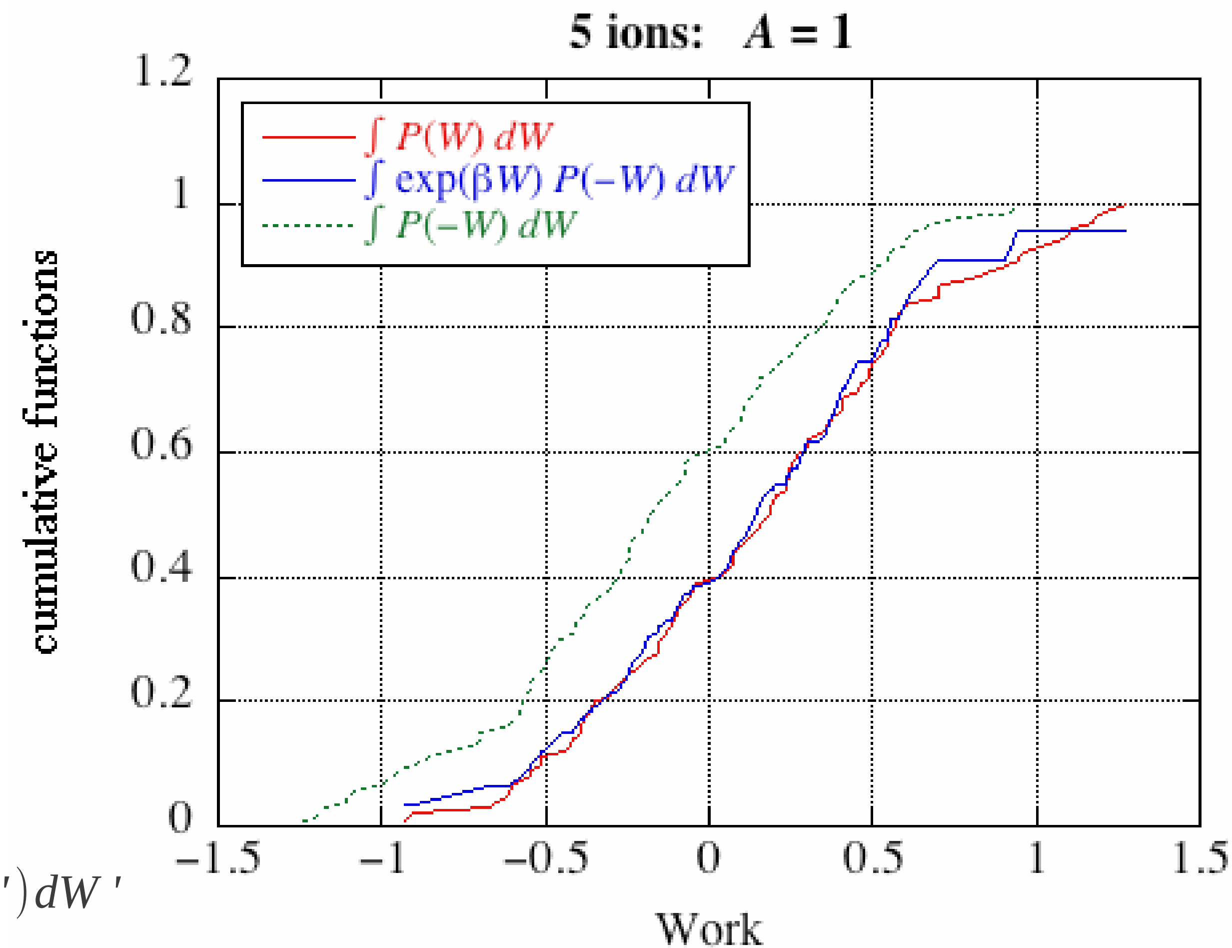
$$\Delta F = 0$$

Nonequilibrium work fluctuation theorem:

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

after integration:

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



RNA unfolding & refolding

C. Bustamante, Quart. Rev. Biophys. (2006)].

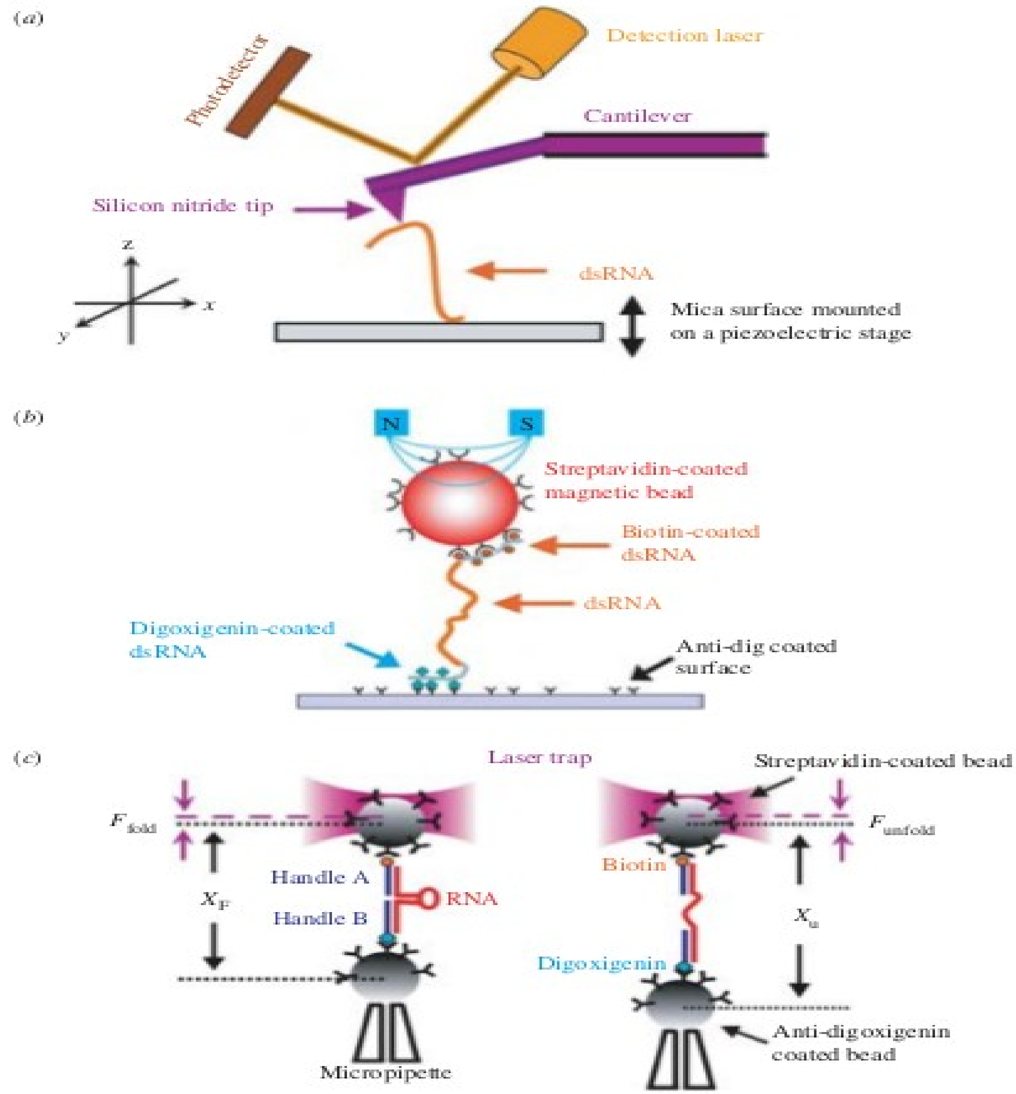
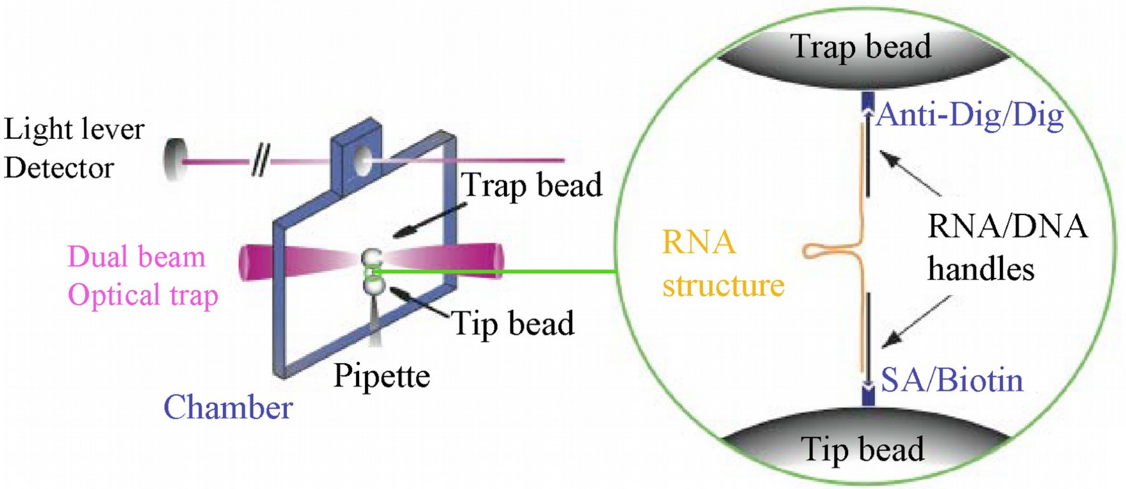
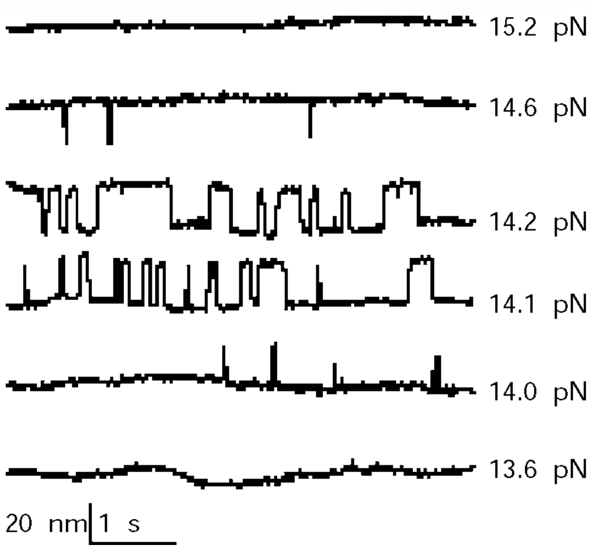


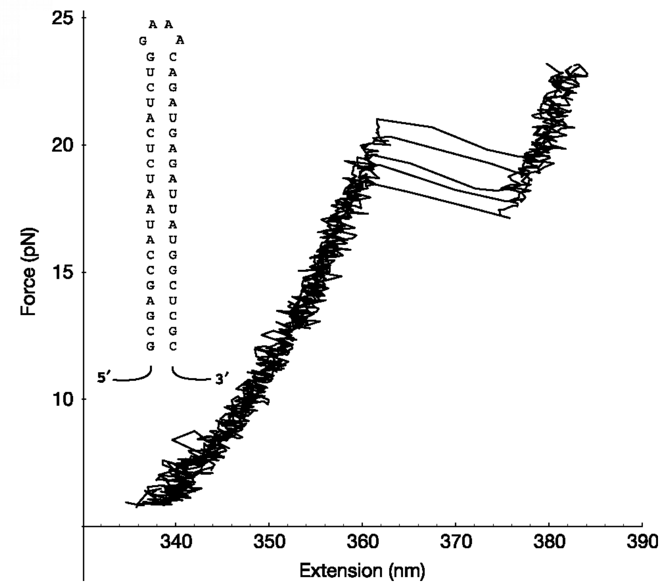
Fig. 1. Experiment set-ups for mechanical studies of RNA. (*a*) Atomic force microscopy (Rief *et al.* 1997). The 'pulling' AFM consists of a cantilever, a laser detection system and a moveable surface. The silicon nitride tip of the cantilever picks up RNA molecules by 'tapping' on the surface. The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







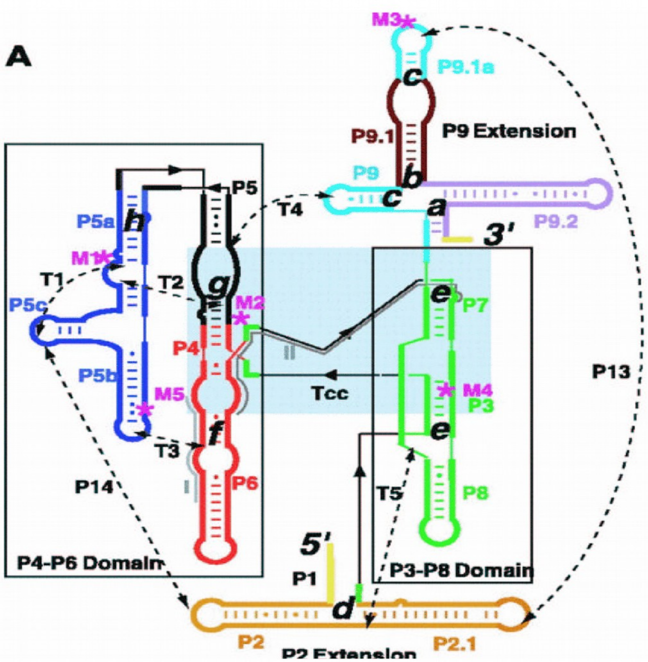
Distance between the beads versus time for different tensions
[C. Bustamante, Quart. Rev. Biophys. (2006)].

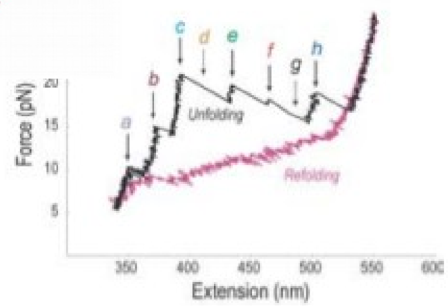
Five unfolding force-extension curves
for the RNA hairpin (loading rate of 7.5 pN s^{-1}).

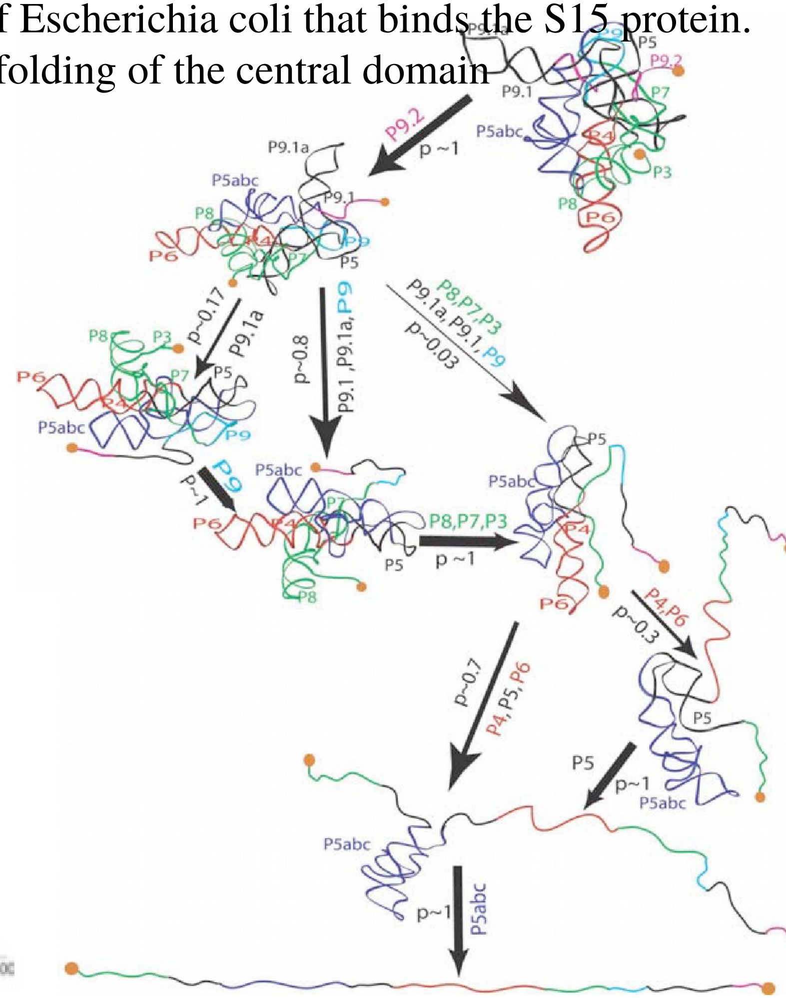
rRNA

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.

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

D. Collin, F.Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr. & C. Bustamante,
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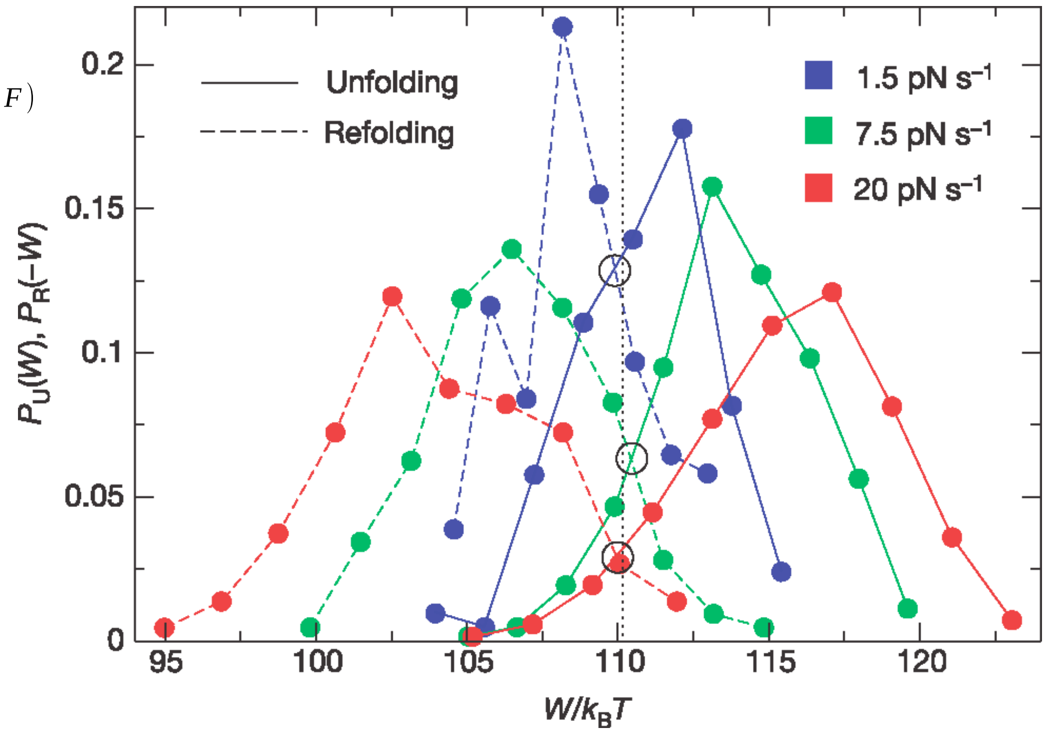
$$\frac{p_F(W)}{p_R(-W)} = e^{\beta(W-\Delta F)}$$



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 ΔG = 110.3 k_BT.

RNA FOLDING FREE ENERGIES: WILD-TYPE & MUTANT

D. Collin, F.Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr. & C. Bustamante,
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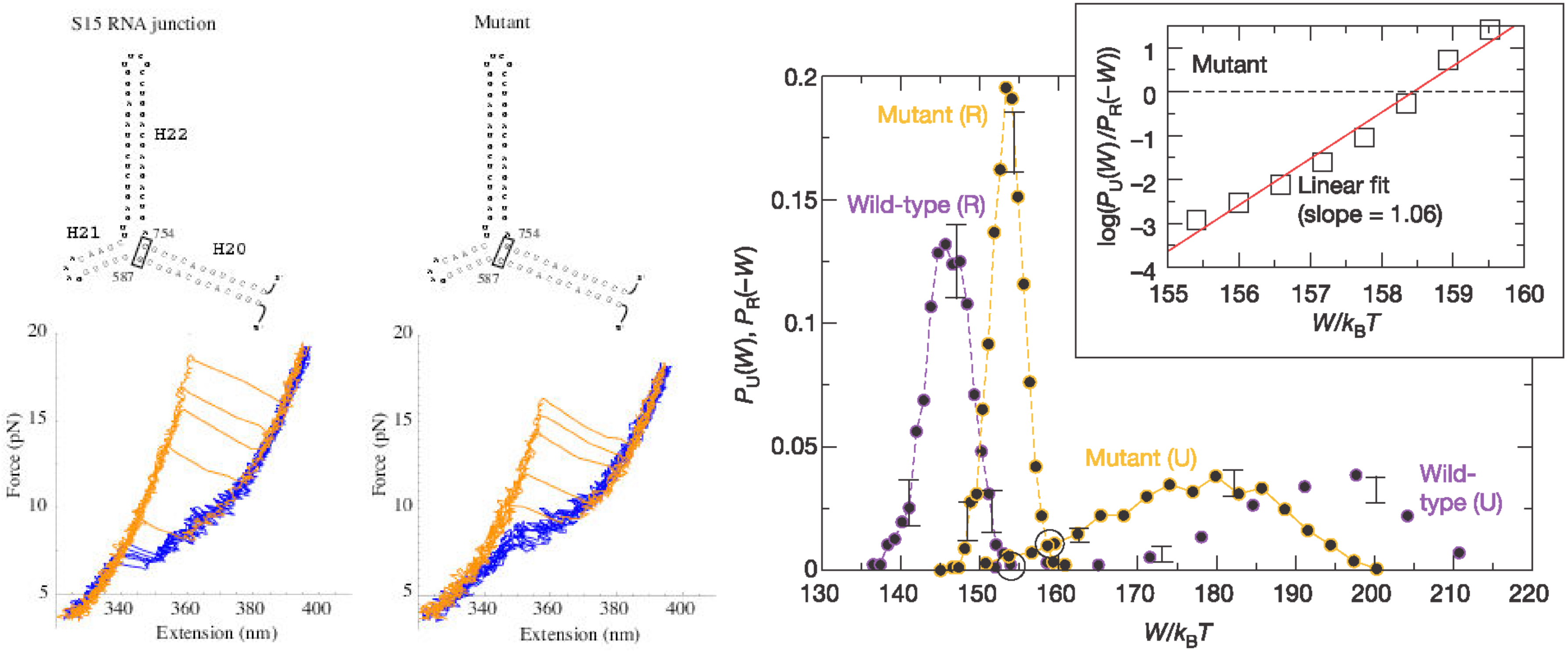

Free-energy recovery and test of the Crooks fluctuation theorem for non-Gaussian work distributions. Experiments carried out on the wild-type and mutant S15 three-helix junction without Mg2+. Unfolding (continuous lines) and refolding (dashed lines) work distributions. Statistics: 900 pulls and two molecules (wild type, purple); 1200 pulls and five molecules (mutant type, orange). Inset, test of the CFT for the mutant.

ΔG = 154.1±0.4 k_BT for unfolding the wild type and ΔG = 157.9±0.2 k_BT for unfolding the mutant type.

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

Connection to the steady-state fluctuation theorem

transient driven process:

Crooks fluctuation theorem (1999):

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

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

Jarzynski's nonequilibrium work relation (1997):

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

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: $X = F = E - T S$
closed system, isothermal-isobaric ensemble, Gibbs free enthalpy: $X = G = F + P V$
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 $P_{\rm st}(w)$
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:

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

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

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

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

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

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

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

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

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

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

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

Entropy & fluctuation theorem

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

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

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

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

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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