International Symposium on Quantum Thermodynamics
Stuttgart, 13.9. to 17.9.2010

Energy and information flow at nano-scale under wet conditions

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Subject

Heat transfer within a heat-bath

Main message

“Heat is scale-dependent.”

Introduction

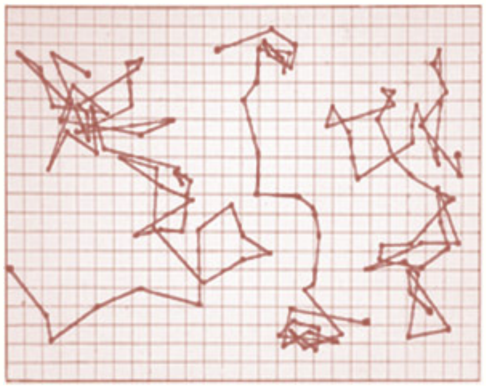
A few key papers of theory of fluctuations …

1905 – *Einstein's relation* (Fluctuation and dissipation)
1906 – Smoluchowski (diffusion process)
1908 – Langevin's equation (equation of *stochastic* motion)
1915 – Fokker (diffusion process)
1917 – Planck (diffusion process)
…
1940 – Kramers' equation (Brownian motion and chemical reaction)
1951 – Itô; "*On stochastic differential equations*" (mathematization!)
1960 – Zwanzig's *projection method* (from Liouville eq. to *diffusion*)
1963 – Feyman's ratchet wheel and pawl (mesoscopic heat engine)
1965 – *Mori's formula* (from Hamiltonian to linear Langevin eq.)
1973 – *Kawasaki's identity* (non-linear extension of *Mori's formula*)
…
1990's – Jarzynski's equality, Fluctuation Theorems, *StEng*

Introduction

A few key papers of mesoscopic experiments …

Brownian motion – Robert *Brown* (1827)
Les Atomes – Perrin (1913)
X-ray structure of protein – Perutz *et al.* (1960)
GRP, Shimomura (1960's)
Optical tweezer – Ashkin (1970)
STM, AFM – Bennig *et al.* (1980's)
Single filament dynamics – Yanagida, *et al.* (1984)
X-ray structure of *myosin* – Rayment (1993)
Single protein probe (1990')



Perrin 1913

Introduction

A few key papers of mesoscopic experiments …

Brownian motion – Robert *Brown* (1827)
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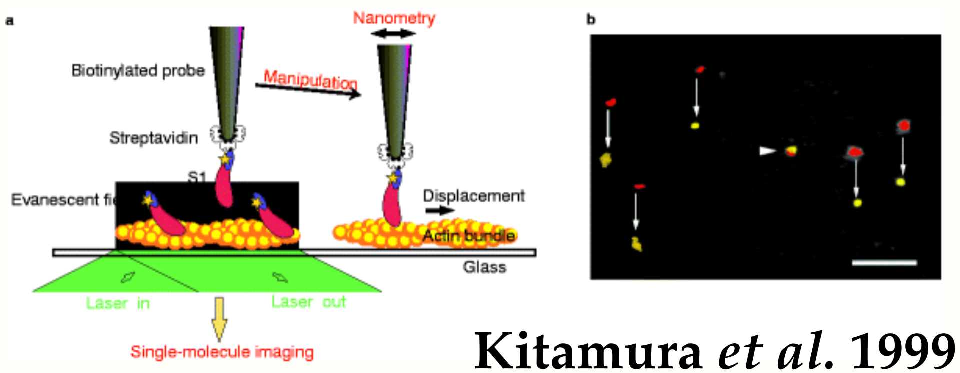
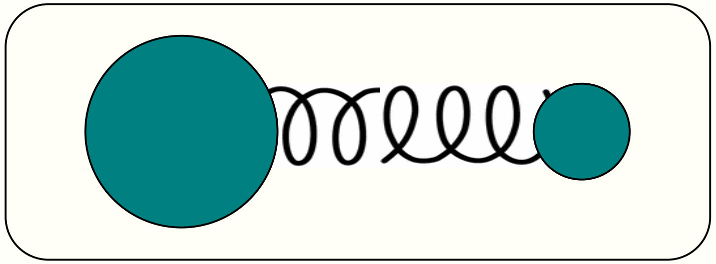


Kitamura *et al.* 1999

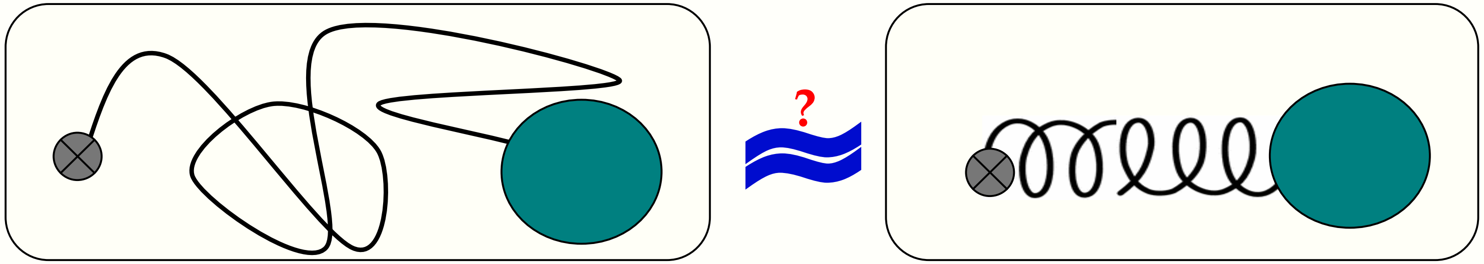
Simple example : two beads tied with a coil spring



energy transferred between remote points ?

asymmetry of heat exchange ?

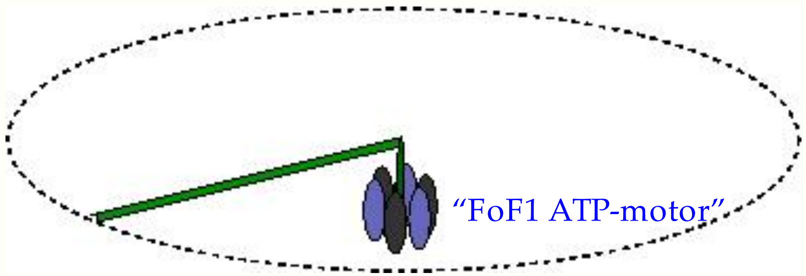
More example : a bead leashed by a polymer chain



condition for “slow”, bead motion?

only entropic ? energetics ?

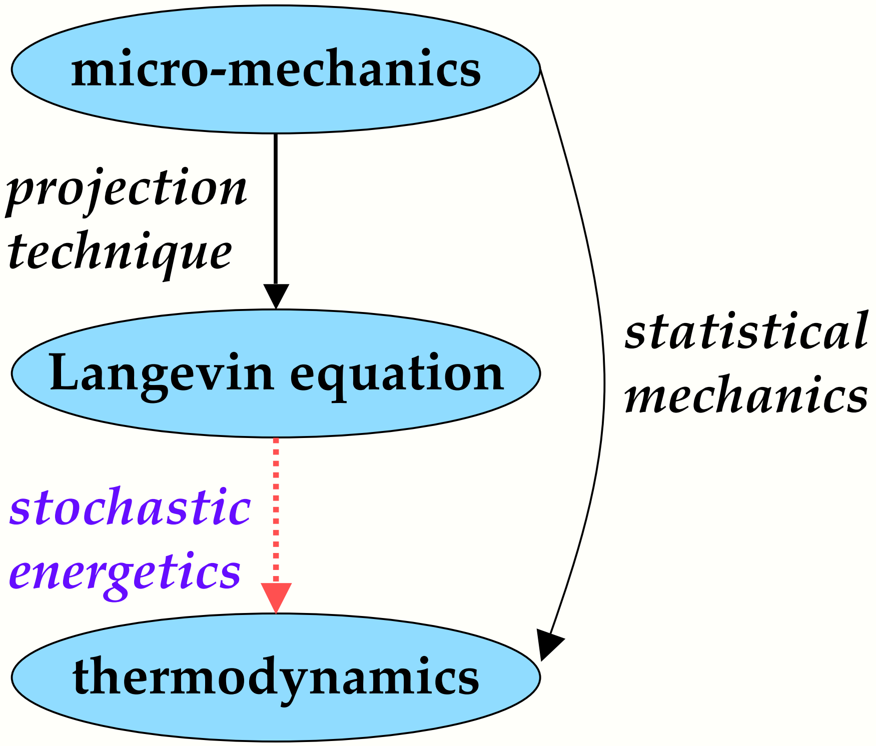
Further example : F1ATPase with actin filament



the filament generates a ***work*** or a ***heat*** ?

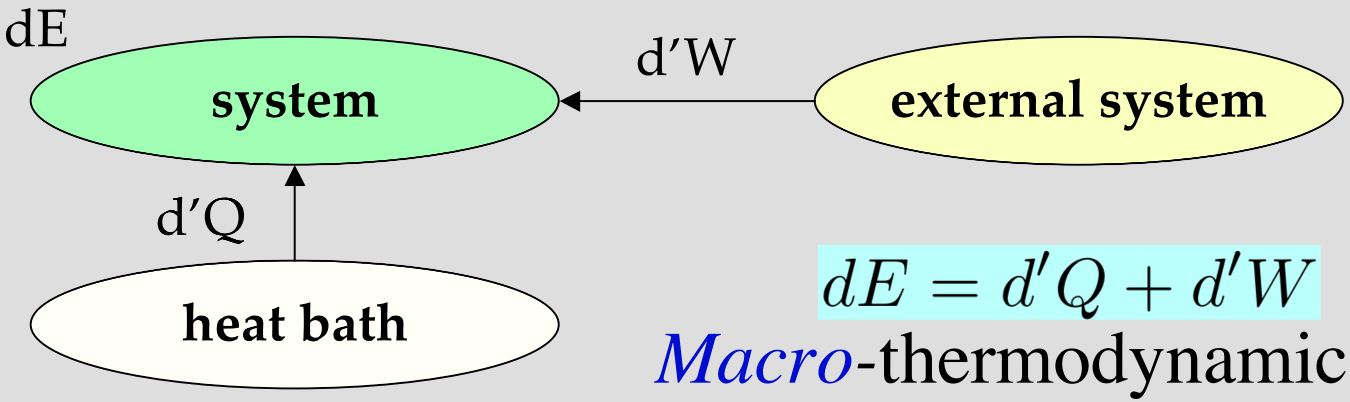
Basics of "**stochastic energetics**"

1. link between the stochastic dynamic description and thermodynamics



cf. Known : steady-state of Langevin eq ←→ canocnical ensemble

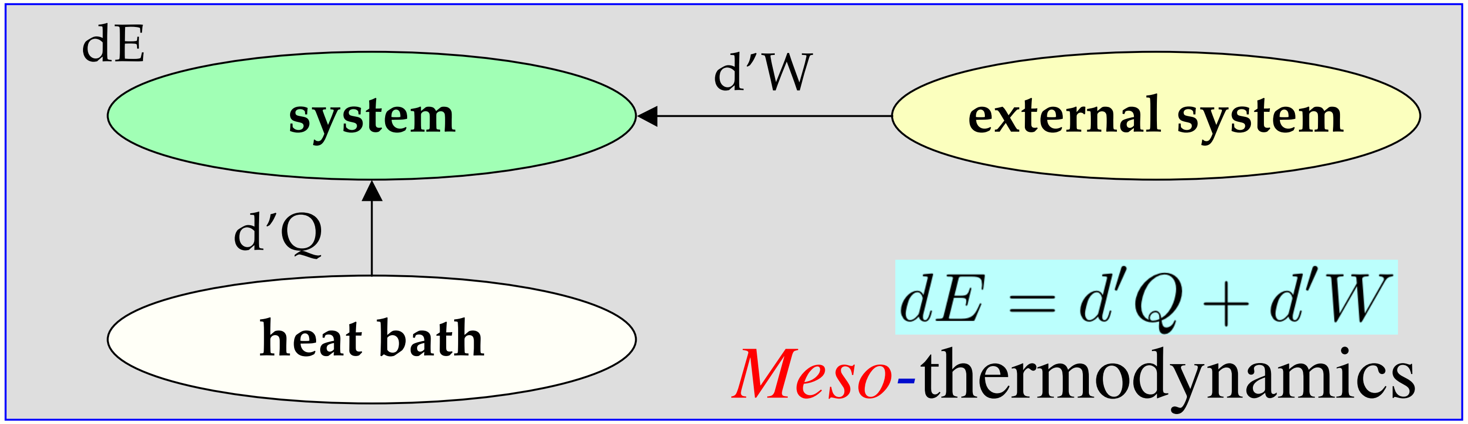
"thermodynamic structure" in different scales



$$dE = d'Q + d'W$$

Macro-thermodynamics

“thermodynamic structure” in different scales



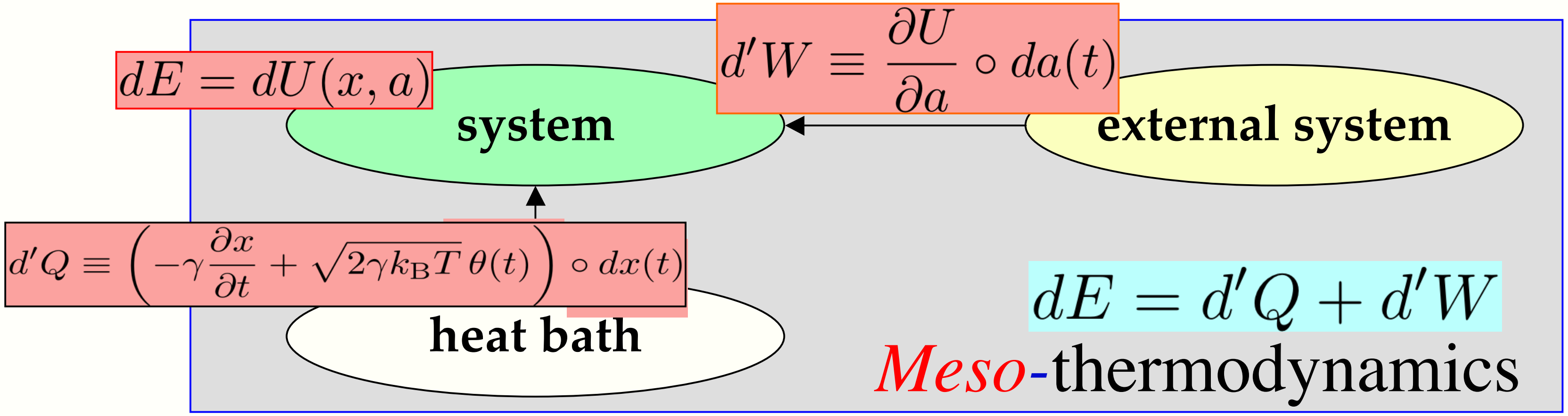
Langevin equation

$$0 = -\frac{\partial U(x,a)}{\partial x} - \gamma \frac{dx}{dt} + \sqrt{2\gamma k_{\mathrm{B}} T}\,\theta(t), \quad \langle \theta(t) \rangle = 0, \quad \langle \theta(t)\theta(t') \rangle = \delta(t-t')$$

$\theta(t)$: white Gaussian process
($\int_0^t \theta(s)ds = B_t$: Wiener process)

a : control parameter (by an external system)

“thermodynamic structure” in different scales



$$A(t) \circ dx(t) \equiv \frac{A(t+dt) + A(t)}{2} [x(t+dt) - x(t)]$$

STRATONOVICH type product

Langevin equation

$$0 = -\frac{\partial U(x,a)}{\partial x} - \gamma \frac{dx}{dt} + \sqrt{2\gamma k_{\rm B} T}\, \theta(t), \quad \langle \theta(t) \rangle = 0, \quad \langle \theta(t)\theta(t') \rangle = \delta(t - t')$$

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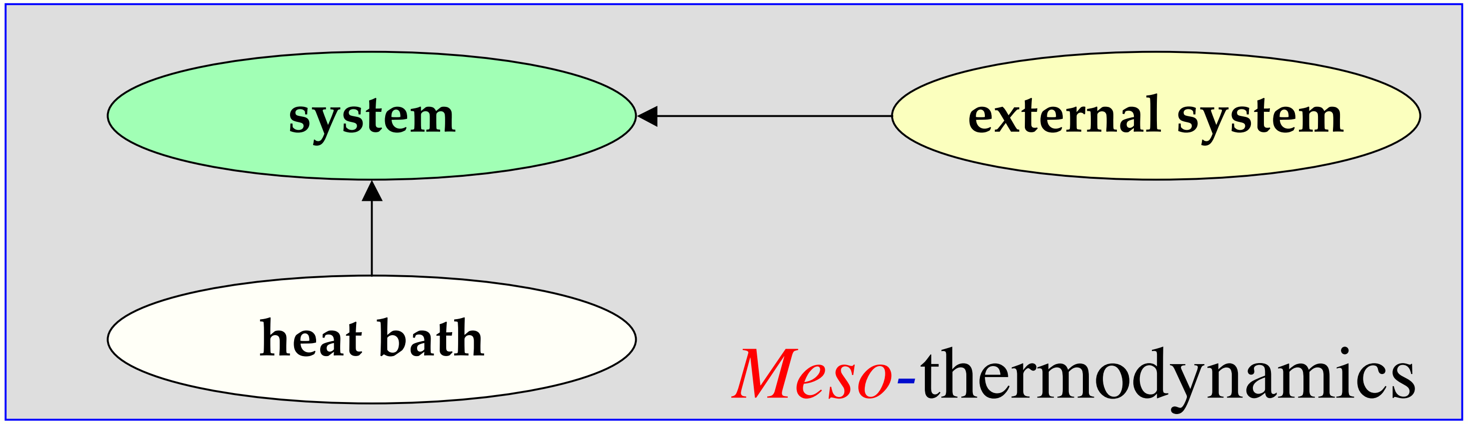


$$d'Q \equiv \left(-\gamma \frac{\partial x}{\partial t} + \sqrt{2\gamma k_{\mathrm{B}} T}\,\theta(t) \right) \circ dx(t)$$

$$d'W \equiv \frac{\partial U}{\partial a} \circ da(t)$$

$$dE = dU(x, a)$$

$$dE = d'Q + d'W$$

1st law for individual realization of stochastic process
2nd law for ensemble of realizations
good model when L-eq. is a valid description.

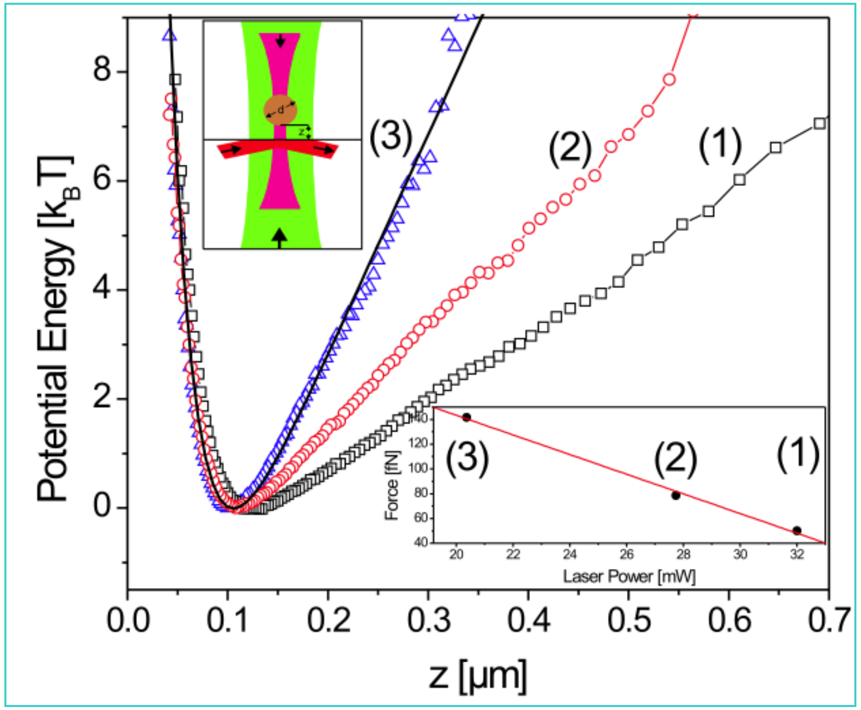
(cf. steady-state thermodyn., Q’m entangling,…)

Experimental demonstrations of ***energy balance***

PRL **96,** 070603 (2006) PHYSICAL REVIEW LETTERS week ending 24 FEBRUARY 2006

Thermodynamics of a Colloidal Particle in a Time-Dependent Nonharmonic Potential

V. Blickle,[1] T. Speck,[2] L. Helden,[1] U. Seifert,[2] and C. Bechinger[1]



***z*(*t*)** : Single-Particle Tracking (SPT)

a **:** laser force ↑

***U*(*z*,*a*)** : equilibrium distribution data

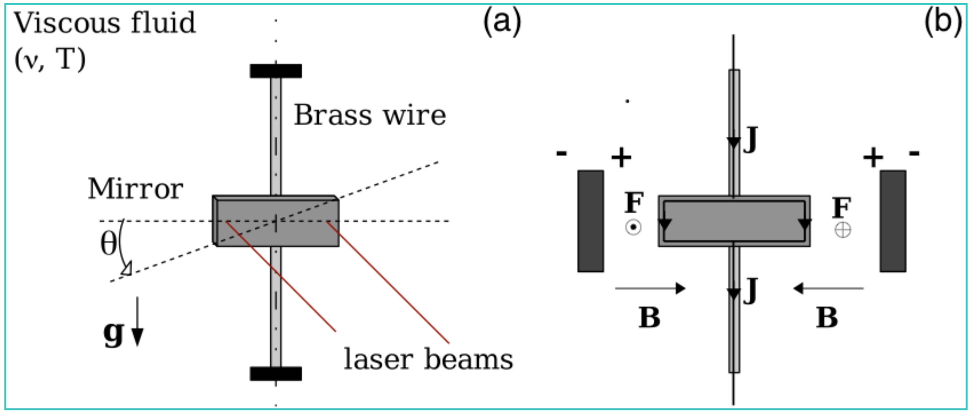
Experimental demonstrations of ***energy balance***

Journal of Statistical Mechanics: Theory and Experiment
An IOP and SISSA journal

stacks.iop.org/JSTAT/2007/P09018

Fluctuation theorems for harmonic oscillators

S Joubaud, N B Garnier and S Ciliberto



θ(t): tilt angle

$$I_{\mathrm{eff}} \frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} + \nu \frac{\mathrm{d}\theta}{\mathrm{d}t} + C\theta = M + \sqrt{2k_{\mathrm{B}}T\nu}\,\eta,$$

$$\begin{aligned} Q_\tau &= \Delta U_\tau - W_\tau \\ &= -\frac{1}{k_{\mathrm{B}}T}\int_{t_i}^{t_i+\tau} \nu \left[\frac{\mathrm{d}\theta}{\mathrm{d}t}(t')\right]^2 \mathrm{d}t' + \frac{\sqrt{2k_{\mathrm{B}}T\nu}}{k_{\mathrm{B}}T}\int_{t_i}^{t_i+\tau} \eta(t') \frac{\mathrm{d}\theta}{\mathrm{d}t}(t')\,\mathrm{d}t'. \end{aligned}$$

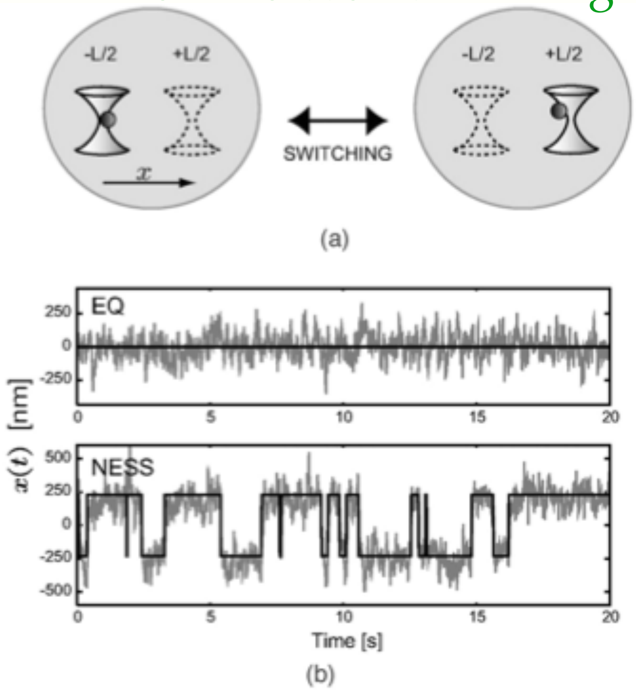
Experimental demonstrations of ***energy balance***

PHYSICAL REVIEW E **75**, 011122 (2007)

Experimental test of a new equality: Measuring heat dissipation in an optically driven colloidal system

Shoichi Toyabe,[1,*] Hong-Ren Jiang,[1] Takenobu Nakamura,[2] Yoshihiro Murayama,[1] and Masaki Sano[1,†]

Random Poisson switching



Harada-Sasa* identity : (*PRL '05)

$$\langle J\rangle_0=\gamma\int_{-\infty}^{\infty}[\tilde{C}(\omega)-2k_BT\tilde{R}'(\omega)]\frac{d\omega}{2\pi},$$

deviation from equilibrium F-D relation

f^p :probe force

$$\gamma\dot{x}(t)=F(x(t),t)+\varepsilon f^p(t)+\hat{\xi}(t),$$

heat : $\langle J\rangle=\langle F(x(t),t)\circ v(t)\rangle,$

correlation : $C(t)\equiv\langle\dot{x}(t)\dot{x}(0)\rangle_0.$

response :

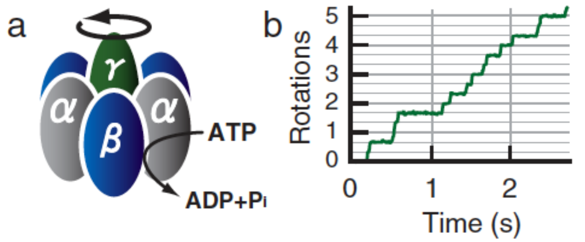
$$\langle\dot{x}(t)\rangle_\varepsilon-v_s=\varepsilon\int_{-\infty}^{t}R(t-s)f^p(s)ds+o(\varepsilon^2),$$

Experimental demonstrations of ***energy balance***

PRL **104**, 198103 (2010) PHYSICAL REVIEW LETTERS week ending 14 MAY 2010

Nonequilibrium Energetics of a Single F_1-ATPase Molecule

Shoichi Toyabe,[1] Tetsuaki Okamoto,[1] Takahiro Watanabe-Nakayama,[2] Hiroshi Taketani,[1] Seishi Kudo,[3] and Eiro Muneyuki[1,*]

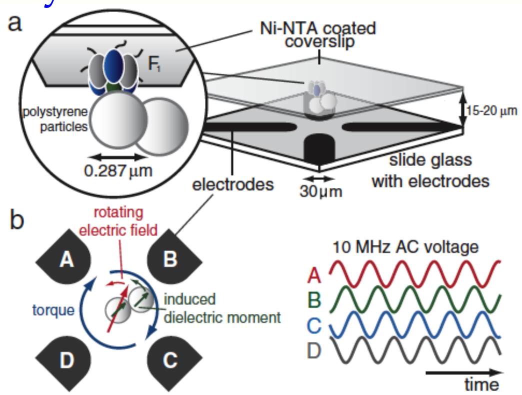


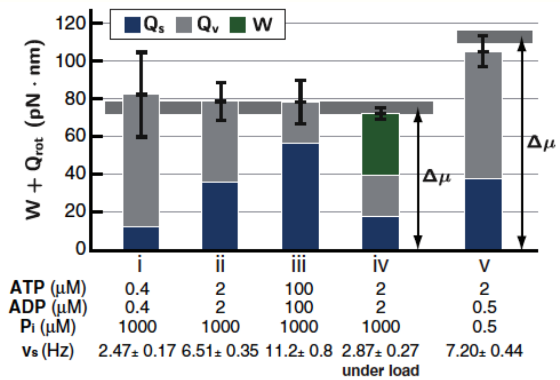
heat : $J \equiv \langle [\Gamma v(t) - \xi(t)] \circ v(t) \rangle = \left\langle \frac{d'Q}{dt} \right\rangle$

Harada-Sasa *equality* :

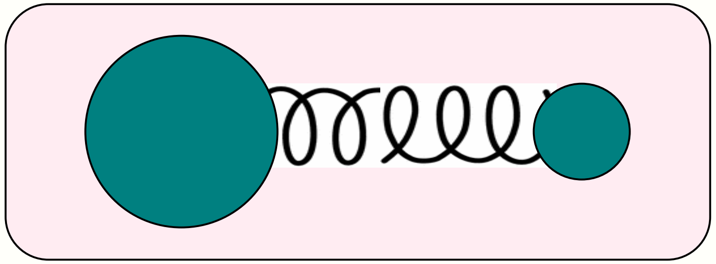
$$J = \Gamma v_s^2 + \Gamma \int_{-\infty}^{\infty} df[\tilde{C}(f) - 2T\tilde{R}'(f)],$$

Torque by electric field :





Simple example : **two beads tied with a coil spring** (VdW, for example)



system, energy balance, statistics

$$
\begin{aligned}
0 &= -\gamma_1 \dot{x}_1 + \xi_1 - k(x_1 - x_2) \\
0 &= -\gamma_2 \dot{x}_2 + \xi_2 + k(x_1 - x_2)
\end{aligned}
$$

*assumed: $\langle \xi_1(t)\xi_2(t') \rangle = 0$

motion : the smaller particle undergoes restrained Brownian motion around a slow Brownian motion of bigger particle

heat
$$
d'Q_1(t) = (-\gamma_1 \dot{x}_1 + \xi_1(t)) \circ dx_1
$$
$$
d'Q_2(t) = (-\gamma_2 \dot{x}_2 + \xi_2(t)) \circ dx_2
$$

autocorrelation:

$$
\left\langle \frac{d'Q_1(t)}{dt} \frac{d'Q_1(t')}{dt'} \right\rangle = 2(k_{\mathrm{B}}T)^2 \left(\frac{k}{\gamma_1}\delta(t-t') - (\frac{k}{\gamma_1})^2 e^{-2\kappa|t-t'|} \right)
$$

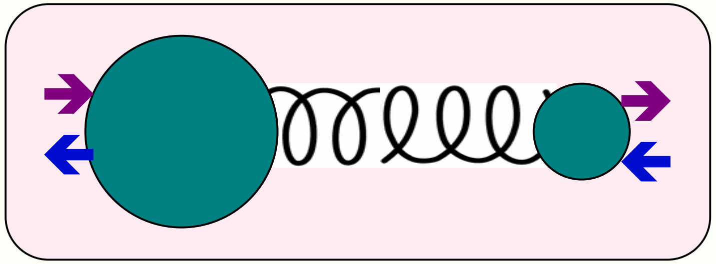
, similar for "2"

$$
\kappa = \frac{k}{\gamma_1} + \frac{k}{\gamma_2}
$$

➔ $$
\left| \frac{d'Q_1(t)}{dt} \right| \ll \left| \frac{d'Q_2(t)}{dt} \right| \qquad \text{for} \quad \gamma_1 \gg \gamma_2
$$

main exchange of energy between system-bath occurs through the smaller bead

+ limit of large bead: no energy exchange (but with momentum exchange)



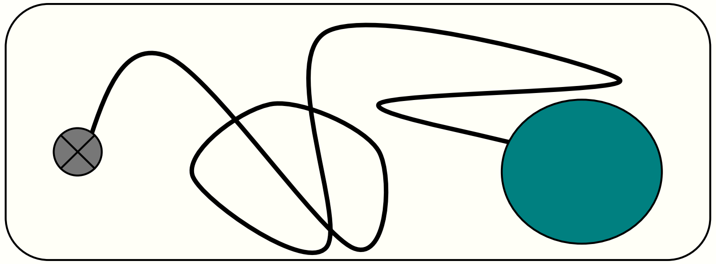
heat
cross-correlation: $$\left\langle \frac{d'Q_1(t)}{dt} \times \frac{d'Q_2(t')}{dt'} \right\rangle = -\frac{2k^2(k_\mathrm{B}T)^2}{\gamma_1\gamma_2} e^{-2\kappa|t-t'|}$$

anti-correlation

➔ heat is transferred within a bath through mechanical coupling

(heat diffusion) $$\left\langle \left(\int_t^{t+\Delta t} d'Q_1 \right)^2 \right\rangle \simeq \frac{2k}{\gamma_1+\gamma_2}(k_\mathrm{B}T)^2 \Delta t$$

Brownian particle leashed by a polymer chain



Model :

1D model — Gaussian chain : springs+ "monomer" (position R_n ; $0 \le n \le N-1$)

$$k = \frac{3k_{\mathrm{B}}T}{b^2}$$: effective spring constant

b : Kuhn (persistence) length – sub nm.

Rouse model — no hydrodynamic interactions (cf. Zimm model)

(+ continuum approximation)

$$\zeta \frac{\partial R_n}{\partial t} = -k \frac{\partial R_n}{\partial n^2} + f_n \qquad \langle f_n \rangle = 0 \qquad \langle f_n(t) f_m(t') \rangle = 2\zeta k_{\mathrm{B}} T \delta(t-t') \delta(n-m)$$

ζ : drag coefficient for monomer

$$R_0 = 0$$

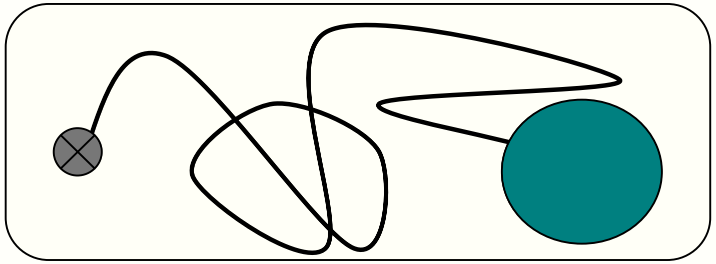
$$\Gamma \frac{dR_B}{dt} = -k \left. \frac{\partial R_n}{\partial n} \right|_{n=N} + \Xi(t)$$

$$\langle \Xi \rangle = 0 \qquad \langle \Xi(t) \Xi(t') \rangle = 2\Gamma k_{\mathrm{B}} T \delta(t-t')$$

Γ : drag coefficient for **Brownian particle**

— coupled Langevin equations

Brownian particle leashed by a polymer chain



Equilibrium thermodynamic properties

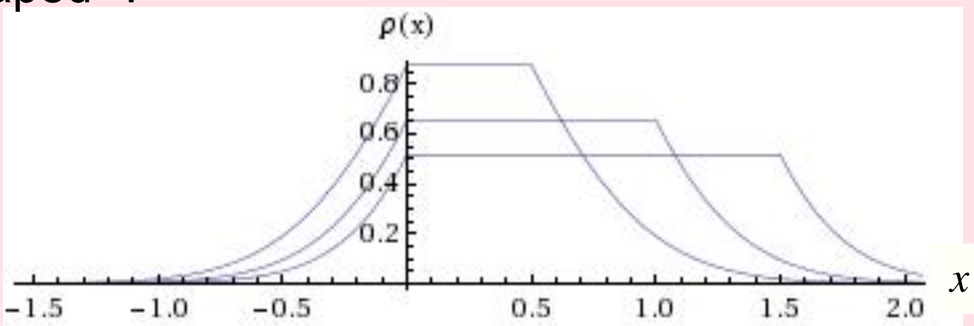
$\simeq$ ideal gas (energy *independent of* $k_B T$)

➔ [work done] = [released *calorimetric* heat]

Equilibrium statistical properties

Density of monomers : $\rho(x) = N \int_0^1 \frac{e^{-\frac{(x-uL)^2}{2Nb^2 u(1-u)}}}{\sqrt{2\pi N b^2 u(1-u)}} du$

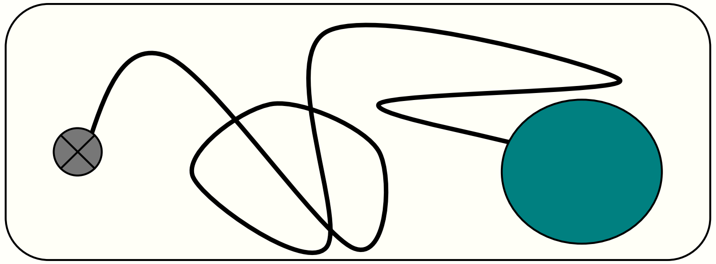
➔ cigar-shaped* : $\rho(x) = \text{const.} \quad (0 \le x \le L)$



x : in units of $R_g = N^{1/2} b$

*Brownian bridge: J.Pitman, in *Seminaire de Probabilités XXXIII*, LNM, vol.1709 (Springer, Berlin / Heidelberg, 1999) pp.388-394

Brownian particle leashed by a polymer chain



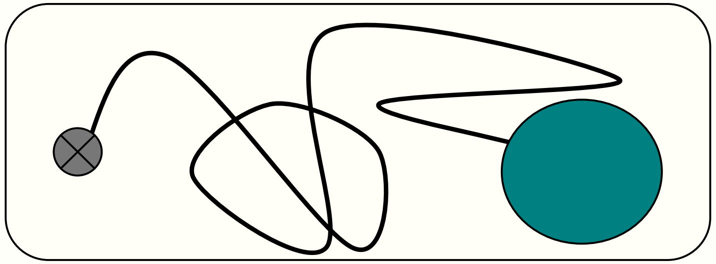
Energetics of *monomer resolution* (polymer chain + Brownian particle)

$$d'Q = \int \left[(-\zeta \frac{\partial R_n}{\partial t} + f_n(t)) \circ dR_n \right] dn + \left(-\Gamma \frac{dR_B}{dt} + \Xi(t) \right) \circ dR_B(t)$$

$$U = \frac{k}{2} \int \left(\frac{\partial R_n}{\partial n} \right)^2 dn \qquad k = \frac{k_\mathrm{B} T}{b^2}$$

$$dU = d'Q + 0$$

Brownian particle leashed by a polymer chain



Solution for $R_B(t)$ in time-Laplace transform, $\hat{R}_B(\eta)$

ellimination of monomer motions (cf. Zwanzig, 73)

$$\hat{R}_B(\eta) = \sqrt{\frac{2}{N}} \sum_{p=0}^{N-1} (-1)^p \underbrace{\frac{1}{\eta + k_p} \left(\frac{\alpha}{1+N\alpha} \frac{1}{1 - \frac{\alpha}{1+N\alpha} \sum_{q=0}^{N-1} \frac{k_q}{\eta + k_q}} \sum_{r=0}^{N-1} \frac{k_r}{\eta + k_r}\right.}_{\textit{memory effects}} \left.\hat{\mu_r}(\eta) + \hat{\mu_p}(\eta) \right)$$

$$\hat{\mu_p}(\eta) = \frac{1}{\zeta} \sum_{q=0}^{N-1} (\delta_{p,q} - \frac{\alpha}{1+N\alpha})(-1)^q \hat{\nu}_q(\eta)$$

$$k_p = \frac{k}{\zeta} \frac{\pi}{N} \left(p + \frac{1}{2} \right)$$

relaxation rate of *p*-th mode

$$\tilde{\nu}_p(t) = \sum_{n=1}^{N} \phi_p(n) f_n(t) + \sqrt{\frac{2}{N}} (-1)^p \Xi(t)$$

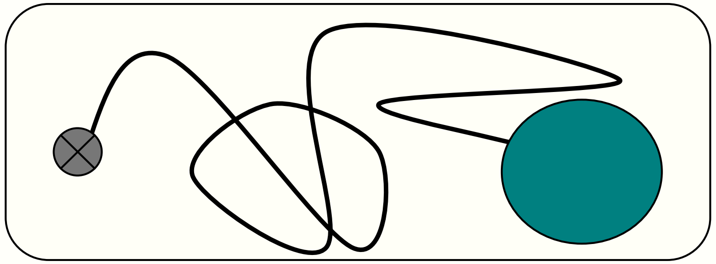
composite random force; 1 / …/1, $\alpha^{1/2}$

$$\phi_p(n) = \sqrt{\frac{2}{N}} \sin\left(\frac{\pi}{N} (p + \frac{1}{2}) n \right)$$

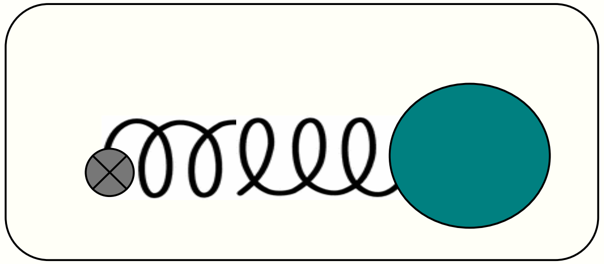
$$\alpha = \frac{2\Gamma}{N\zeta}$$

relative importance of *B*-particle

Brownian particle leashed by a polymer chain



Conditions for $\approx$



i) Process : $\alpha = \dfrac{2\Gamma}{N\zeta}$

(B-particle's diffusion time) >>(polymer's largest relaxation time)

$$\tau_B \sim \frac{R_g^2}{2D_B} \sim \frac{Nb^2\Gamma}{2k_\mathrm{B}T} \qquad \tau_\mathrm{Rouse} \sim \frac{N^2\zeta}{\pi^2 k} \sim \frac{N^2 b^2 \zeta}{\pi^2 k_\mathrm{B} T}$$

$$\frac{\tau_B}{\tau_\mathrm{Rouse}} \sim \frac{\pi^2}{4}\alpha \gg 1 \;\Rightarrow\; N \ll \frac{\pi^2}{2}\left(\frac{\Gamma}{\zeta}\right) \sim \frac{\pi^2}{2}\left(\frac{R_B}{b}\right)$$

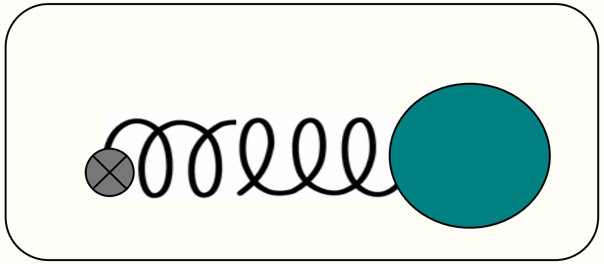
$$\sim 10^3\text{-}10^4 \quad \text{for } R_B = 1\mu\mathrm{m}$$

i) Time resolution : >>(polymer's largest relaxation time)

$$\Rightarrow\; \eta \ll k_{p=0}$$

Brownian particle leashed by a polymer chain

Effective dynamics for



$$\boxed{\Gamma \frac{dR_B}{dt} \simeq -k_{\rm eff} R_B + \Xi(t),} \qquad k_{\rm eff} = \frac{k}{N}$$

Effective energetics :

$$d' Q_B = k_{\rm eff} R_B \circ dR_B$$

$$E_B = \frac{k_{\rm eff}}{2} {R_B}^2$$

cf. microscopic model : $E^{(\rm m)} \equiv 0$

Different heats for different scales

resolution	atomic	“monomer”	Brownian particle
energetics	$E^{(\mathrm{m})} \equiv 0$	$k = \frac{k_\mathrm{B}T}{b^2}$ $U = \frac{k}{2}\int\left(\frac{\partial R_n}{\partial n}\right)^2 dn$ $dE = d'Q + 0$	$k_\mathrm{eff} = \frac{k}{N}$ $U_B = \frac{k_\mathrm{eff}}{2}{R_B}^2$ $d'Q_B = k_\mathrm{eff} R_B \circ dR_B$

Mesoscopic potentials include *entropic free-energy* of fast fluctuations

Different heats for different scales

General: **Link between mesoscopic heat Q_{eff} and *calorimetric* heat $Q^{(\mathrm{m})}$** *

*K. Sekimoto, Phys. Rev. E, 76, 060103(R) (2007)

resolution

energetics

	molecular scale	mesoscopic scale
	$E^{(\mathrm{m})}$	U_{eff}
	$Q^{(\mathrm{m})}$	Q_{eff}
	$dE^{(\mathrm{m})} = d'Q^{(\mathrm{m})} + d'W$	$dU_{\mathrm{eff}} = d'Q_{\mathrm{eff}} + d'W$

separation of timescale   e.g. change of R_B : adiabatic displacement for "short" polymer

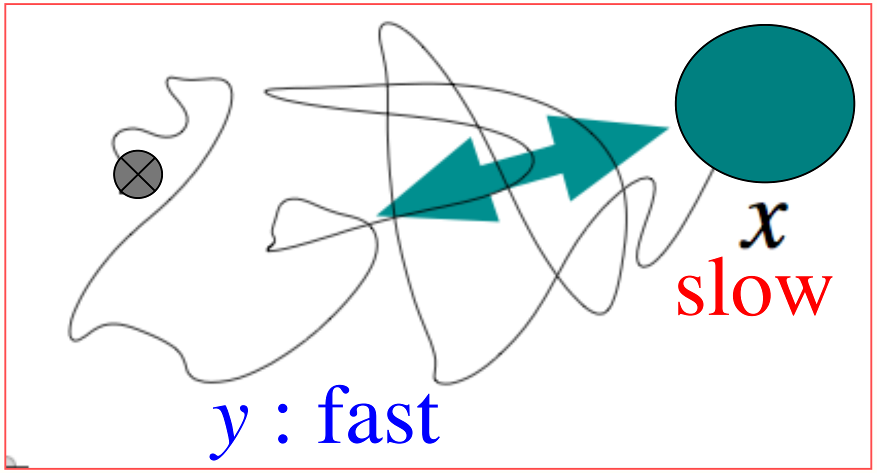
→ *quasi-equilibrium* correction term

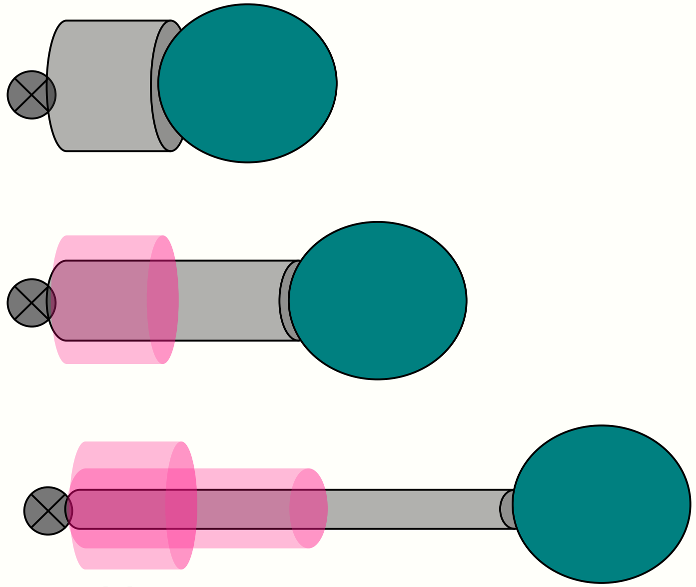
$$\mathrm{d}U_{\mathrm{eff}} \mapsto \mathrm{d}E^{(\mathrm{m})} \equiv \mathrm{d}U_{\mathrm{eff}} - T\,\mathrm{d}\left(\frac{\partial U_{\mathrm{eff}}}{\partial T}\right)$$

$$\mathrm{d}'Q_{\mathrm{eff}} \mapsto \mathrm{d}'Q^{(\mathrm{m})} \equiv \mathrm{d}'Q_{\mathrm{eff}} - T\,\mathrm{d}\left(\frac{\partial U_{\mathrm{eff}}}{\partial T}\right)$$

$$\mathrm{d} = \mathrm{d}x\,\frac{\partial}{\partial x} + \mathrm{d}a\,\frac{\partial}{\partial a}$$

➔ local spontaneous energy transfer (heat⇔work) in the heat bath





adiabatic work *on* R_B : compensated by released heat

local T-gradient : very weak $\quad D_{\rm th} \sim 10^{-3}{\rm cm}^2/{\rm s} \qquad D_{\rm B} = \frac{k_{\rm B}T}{6\pi\eta r_B} \sim (2/3\pi)10^{-8}{\rm cm}^2/{\rm s}$

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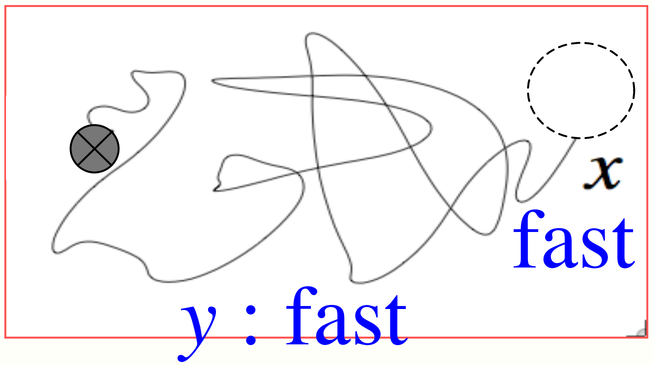
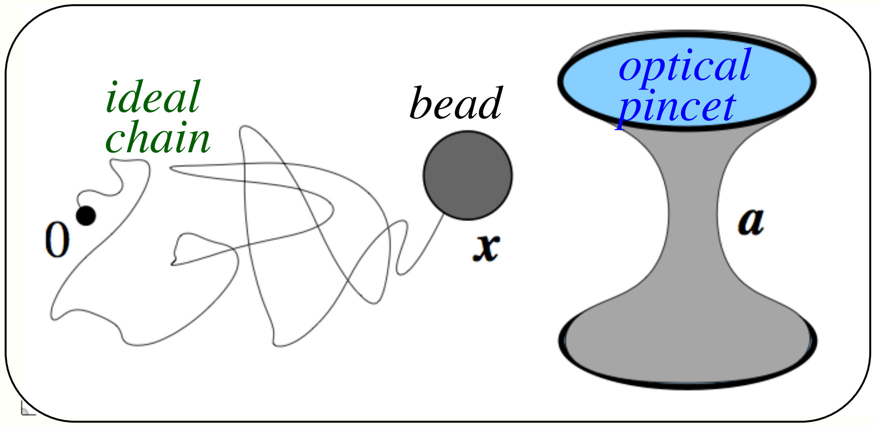
cf.



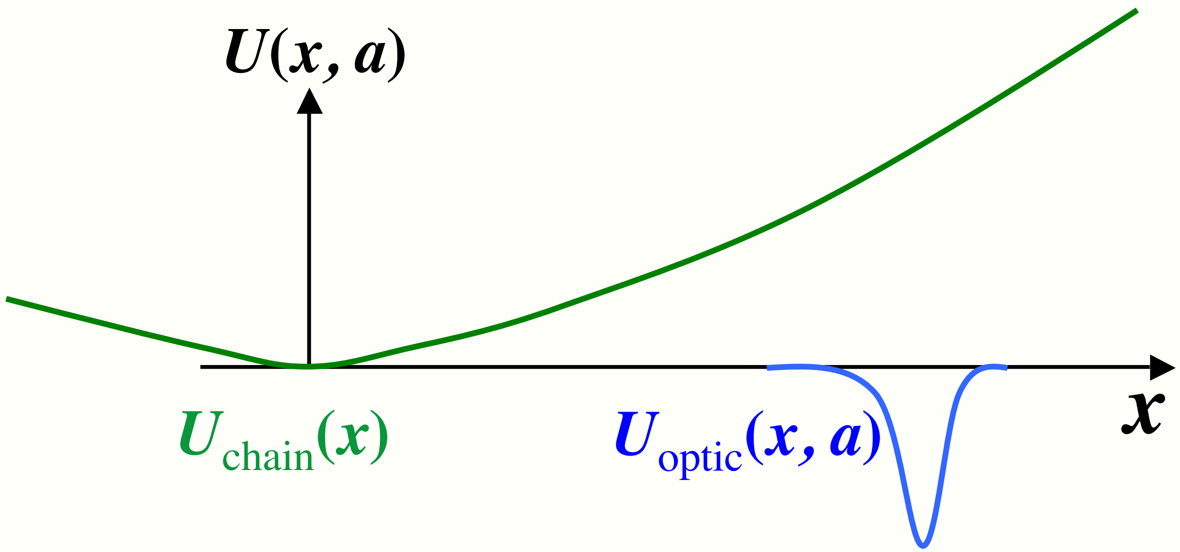
No calorimetric heat

Example

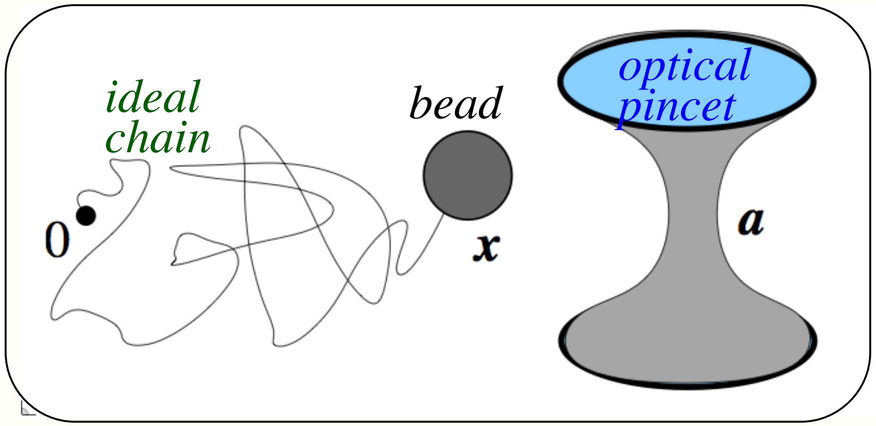


$$U(x,a) = U_{\text{chain}}(x) + U_{\text{optic}}(x,a)$$

$$0 = -\frac{\partial U(x,a)}{\partial x} - \gamma \frac{dx}{dt} + \sqrt{2\gamma k_{\mathrm{B}} T}\theta(t)$$



Example



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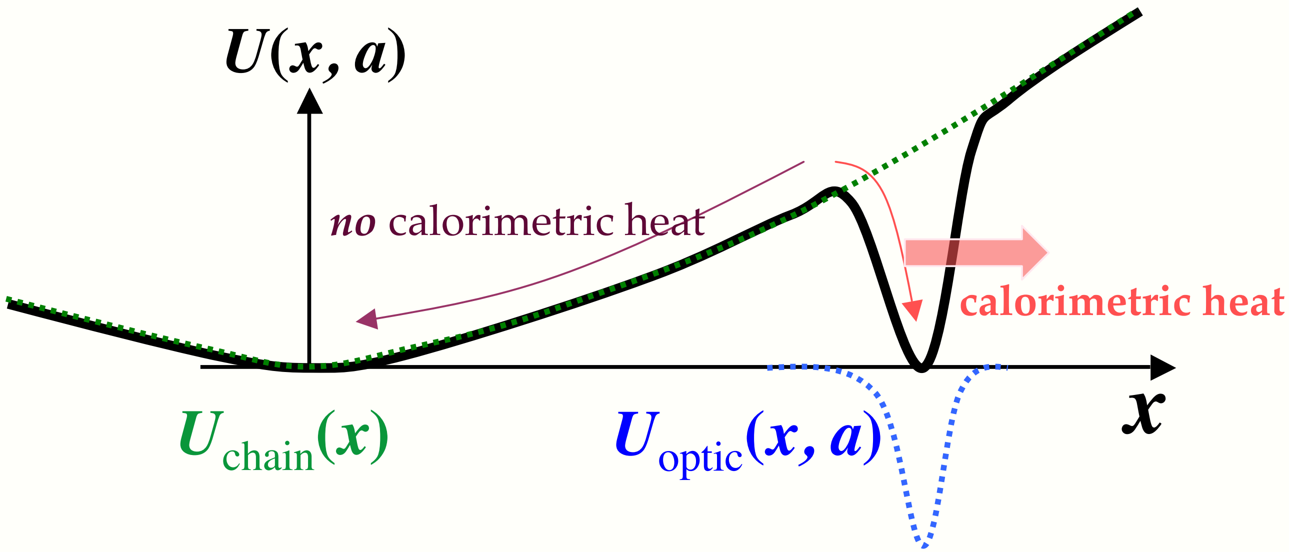
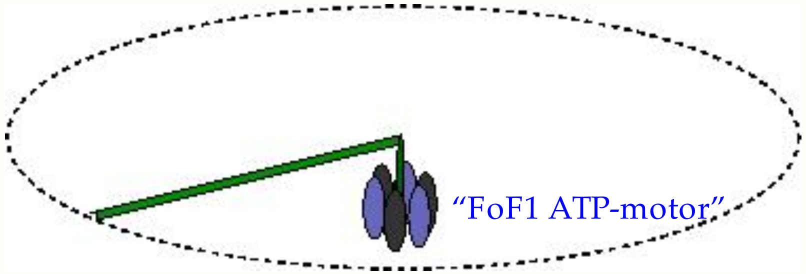
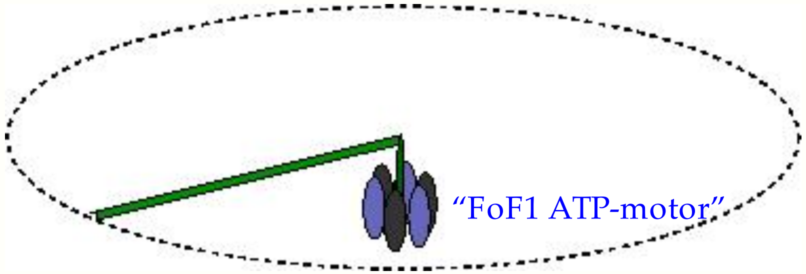


F1ATPase with actin filament



the filament generates a ***work*** or a ***heat*** ?

F1ATPase with actin filament



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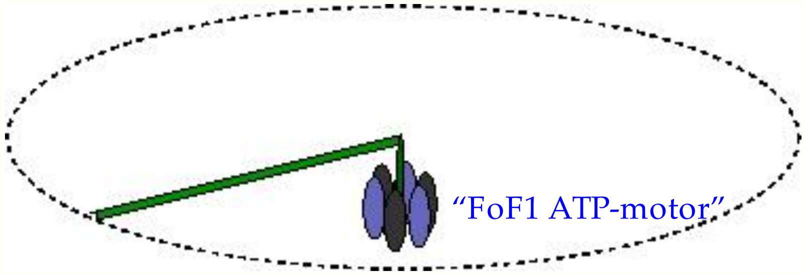
Answer with *scale-dependent heat* :

resolution	$\ell \gg$ (filament length) :	**heat**
	$\ell \leq$ (filament length) :	**work (*retreavable energy*)**

F1ATPase with actin filament



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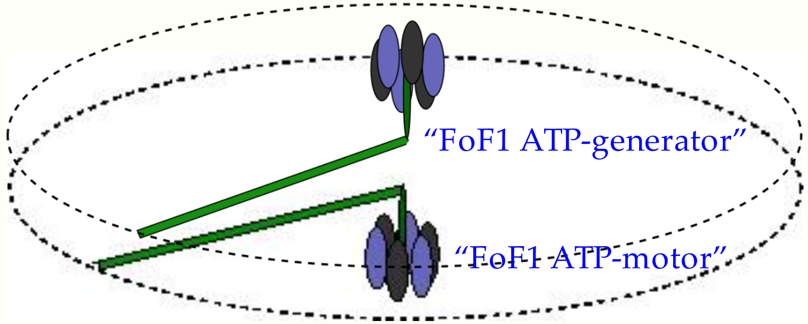
coupling though “heat”



Subject

Heat transfer within a heat-bath

Main message

“Heat is scale-dependent.”


Thank you for your attention

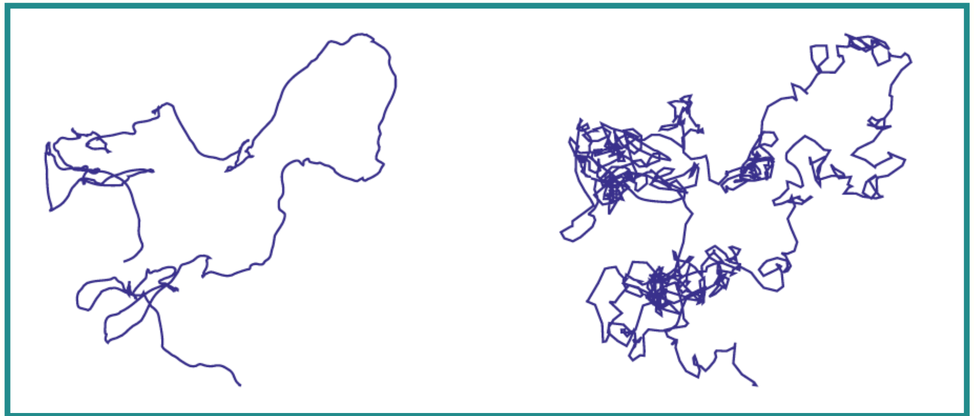
Different heats for different Langevin desriptions

under-damped : $\dfrac{dp}{dt} = -\dfrac{\partial U(x,a)}{\partial x} - \gamma \dfrac{dx}{dt} + \sqrt{2\gamma k_{\rm B} T}\,\theta(t), \qquad \dfrac{dp}{dt} = \dfrac{p}{m}$

time coarse graining

$$\gamma[x(t+\Delta t) - x(t)] = \sqrt{2\gamma k_{\rm B} T(x(t))}[B_{t+\Delta t} - B_t] - \frac{\partial U(x(t), a(t))}{\partial x}\Delta t + k_{\rm B} T'(x(t))\{[B_{t+\Delta t} - B_t]^2 - \Delta t\} + o(\Delta t),$$

over-dumped : $0 = -\dfrac{\partial U(x,a)}{\partial x} - \gamma \dfrac{dx}{dt} + \sqrt{2\gamma k_{\rm B} T}\,\theta(t)$



under-damped over-damped

2^{nd} law of stochastic energetics

$$a(t_0) = a_i \downarrow a(t_1) = a_f$$

Irreversible work : $W_{irr} \equiv W - \Delta F$

$$= \int_{a_i}^{a_f} \left\{ \frac{\partial U(x(t),a(t))}{\partial a} - \left\langle \frac{\partial U(x,a(t))}{\partial a} \right\rangle_{\mathrm{can};T} \right\} da(t).$$

$F: \; e^{-F/k_B T} = \int e^{-U(x,a)/k_B T} dx$

Quasi-static limit : $W_{irr} \to 0, \quad (prob.1)$

i.e. $W \to \Delta F$ *without ensemble averages*

Jarzynski equality (Jarzynski, PRL97, Crooks, JSP98)

$$1 = \left\langle e^{-\beta W_{irr}} \right\rangle_{\mathrm{eq.at}\ t=0} \quad \Rightarrow \quad \langle W_{irr} \rangle_{\mathrm{eq.at}\ t=0} \geq 0$$

Complementarity: $\langle W_{irr} \rangle \, \Delta t \geq S(a_i, a_f) \qquad (\Delta t \to \infty)$

(correction : initial condition sensitive)

abstract

- what loss of energy and of information are associated to irreversible process?
- how can "heat" do "work" when different spatiotemporal scales come into play ?
- why a motor which is passive by itself looks active and intelligent ?