Experiments in stochastic thermodynamics

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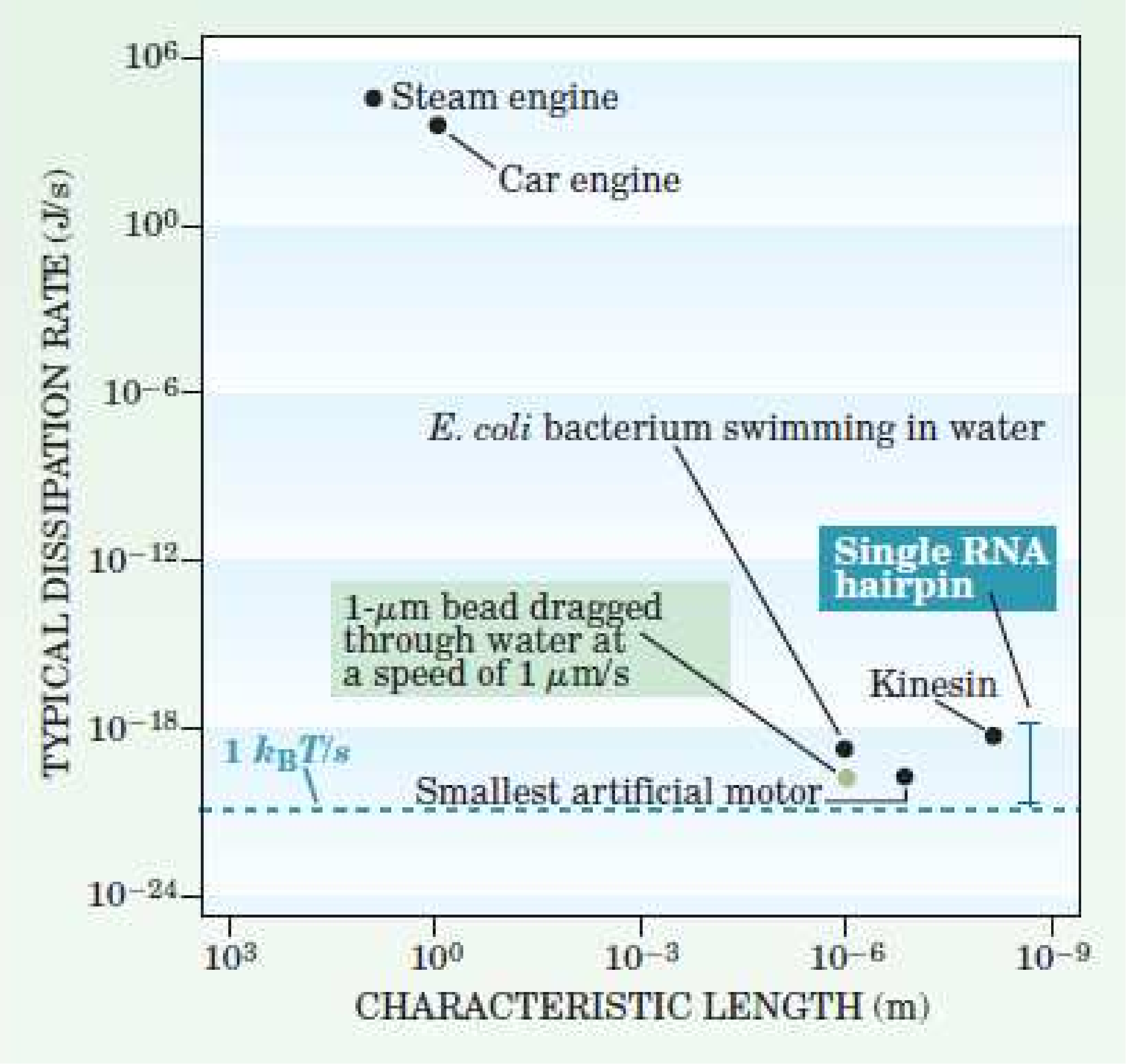
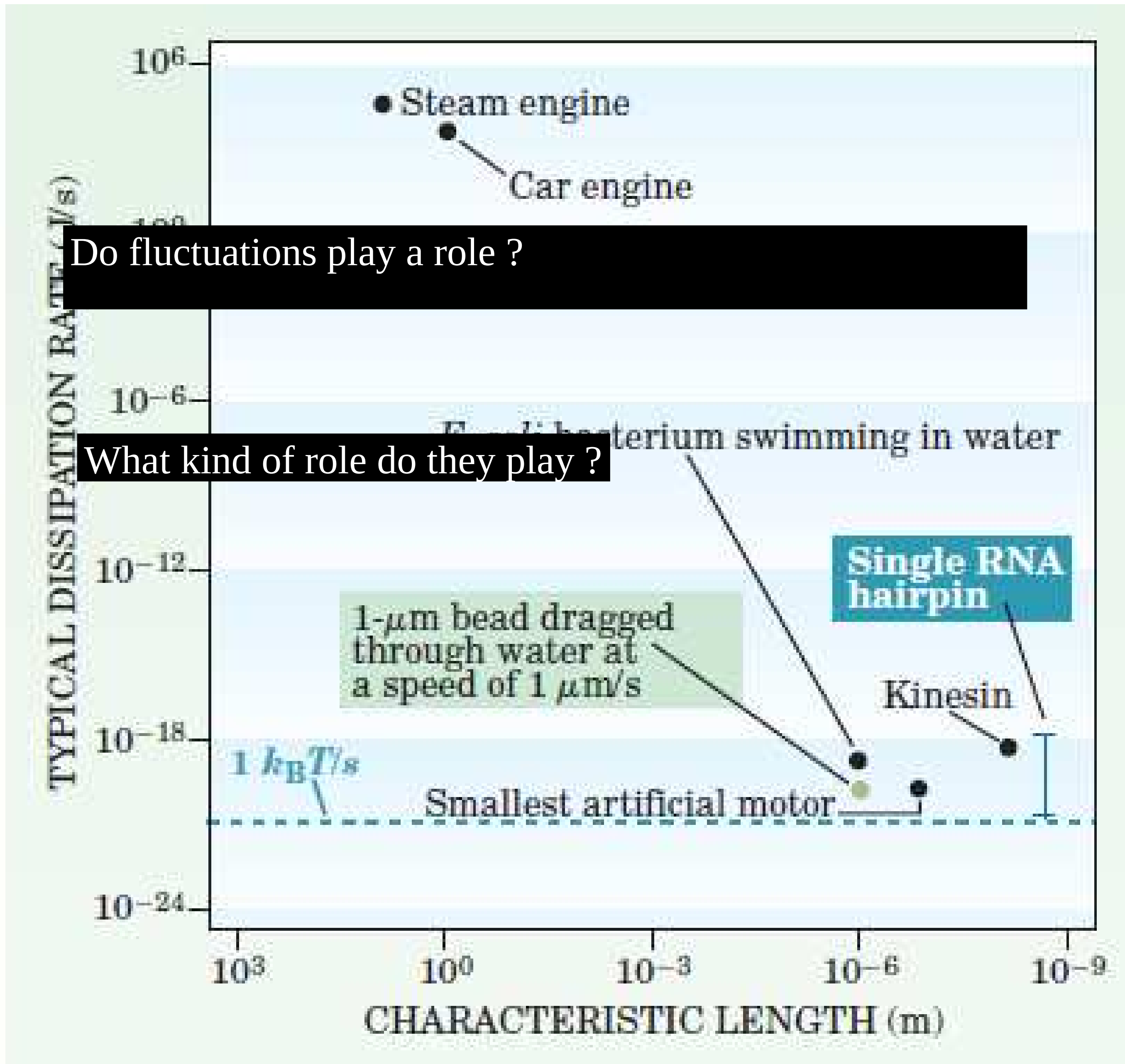
Dissipation



Dissipation

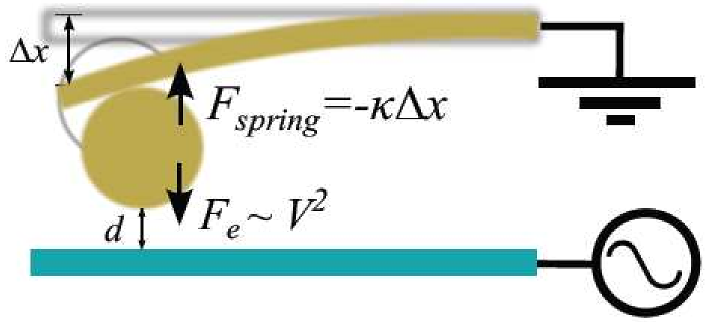


Do fluctuations play a role ?

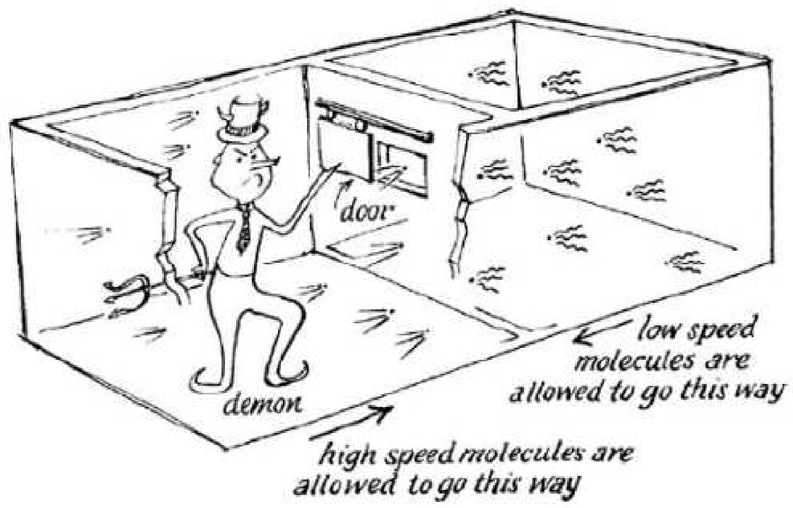
What kind of role do they play ?

Experiments in stochastic thermodynamics

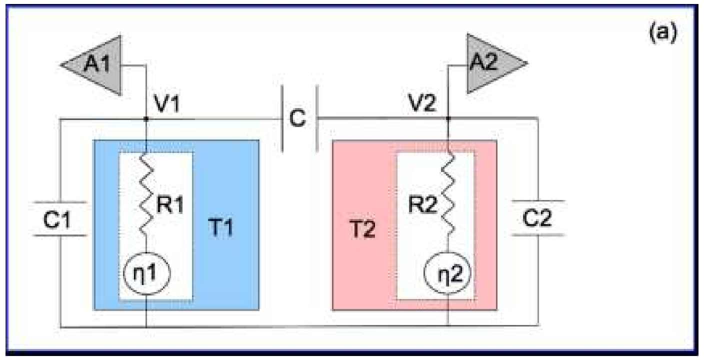
Brownian particles driven in a NESS



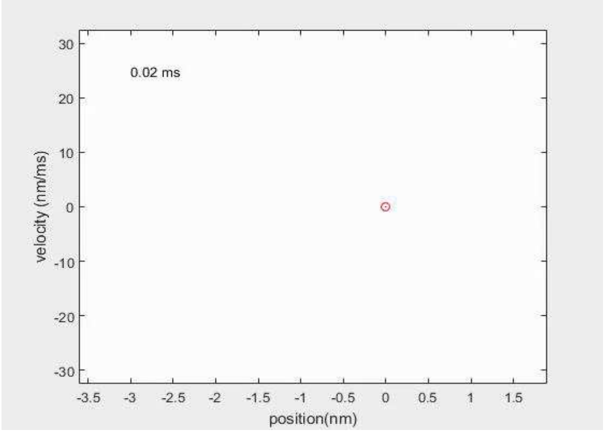
Micro actuator



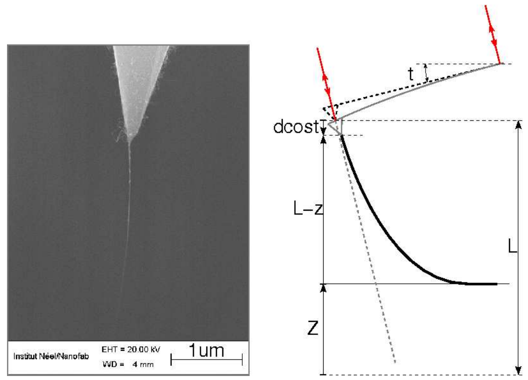
The Maxwell demon



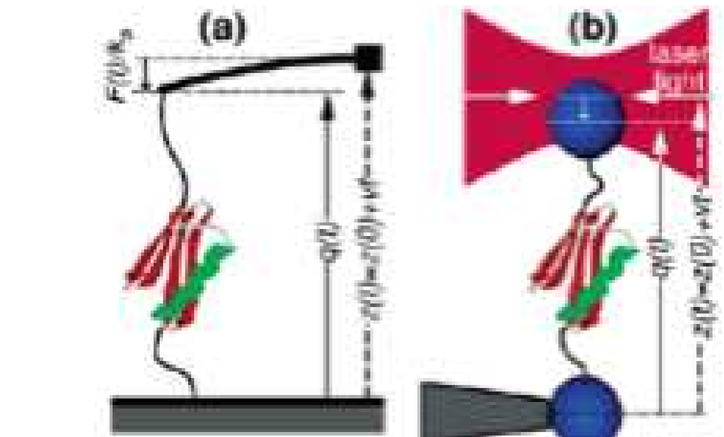
Fluctuation driven heat transfer



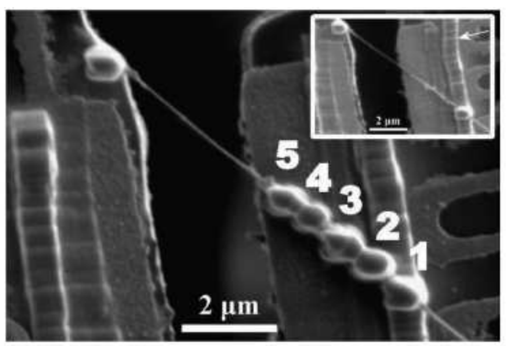
Examples of stochastic systems



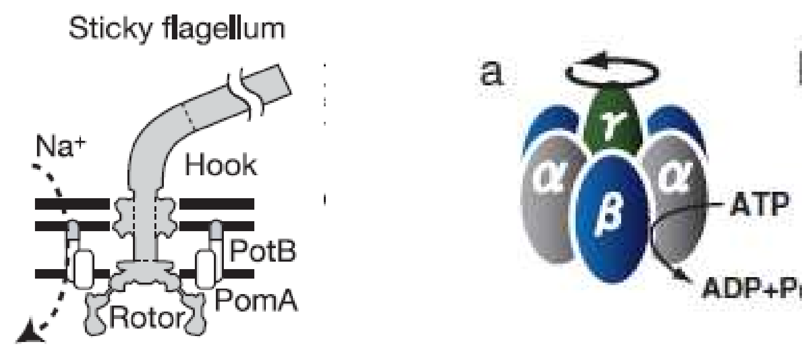
Mechanical properties of nanotubes



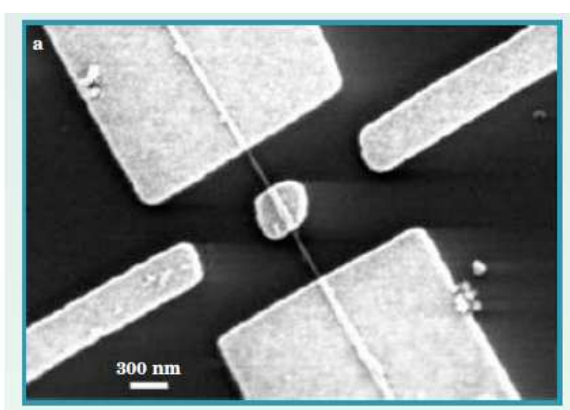
Stretched DNA Molecules



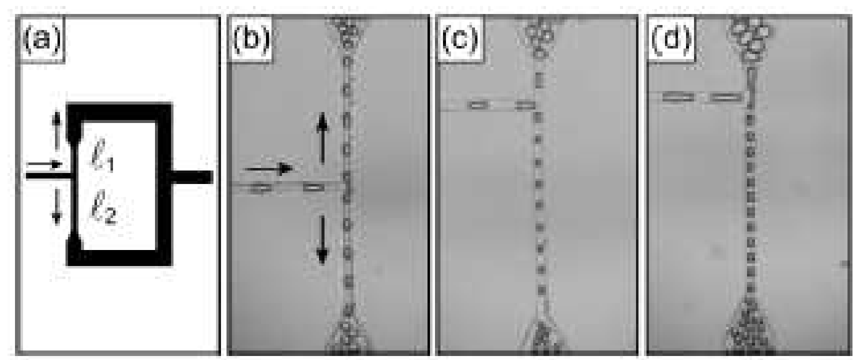
Thermal conduction in nanotubes



Molecular motors



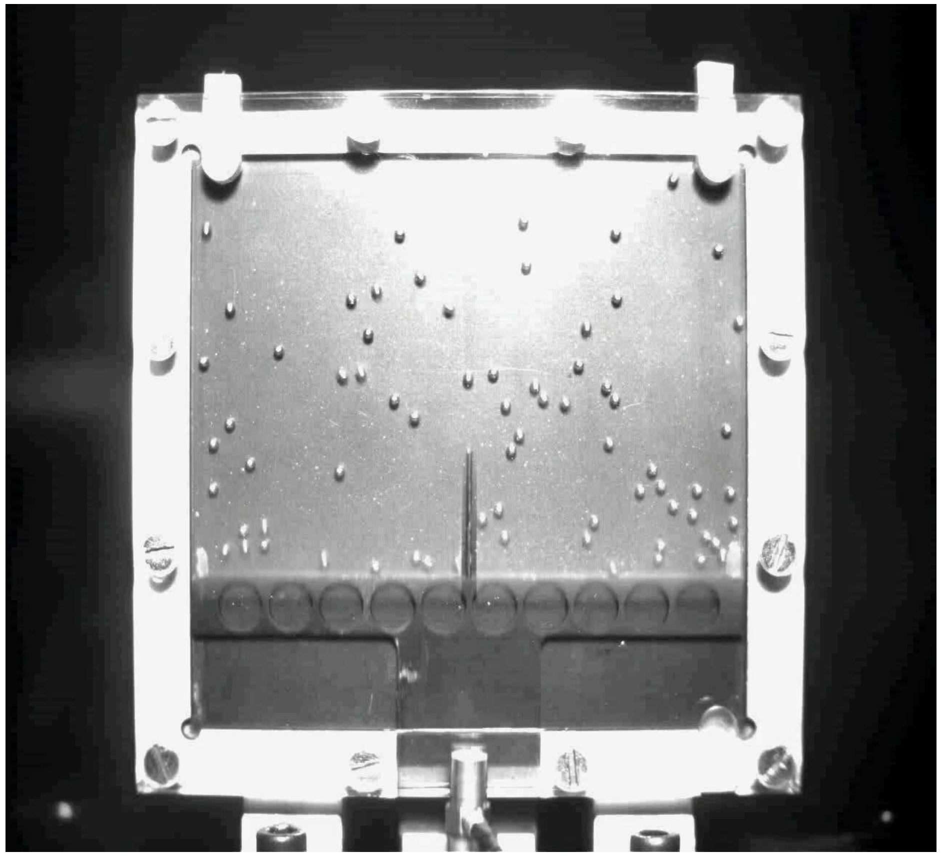
Micro Electro Mechanical Devices



Micro hydrodynamics

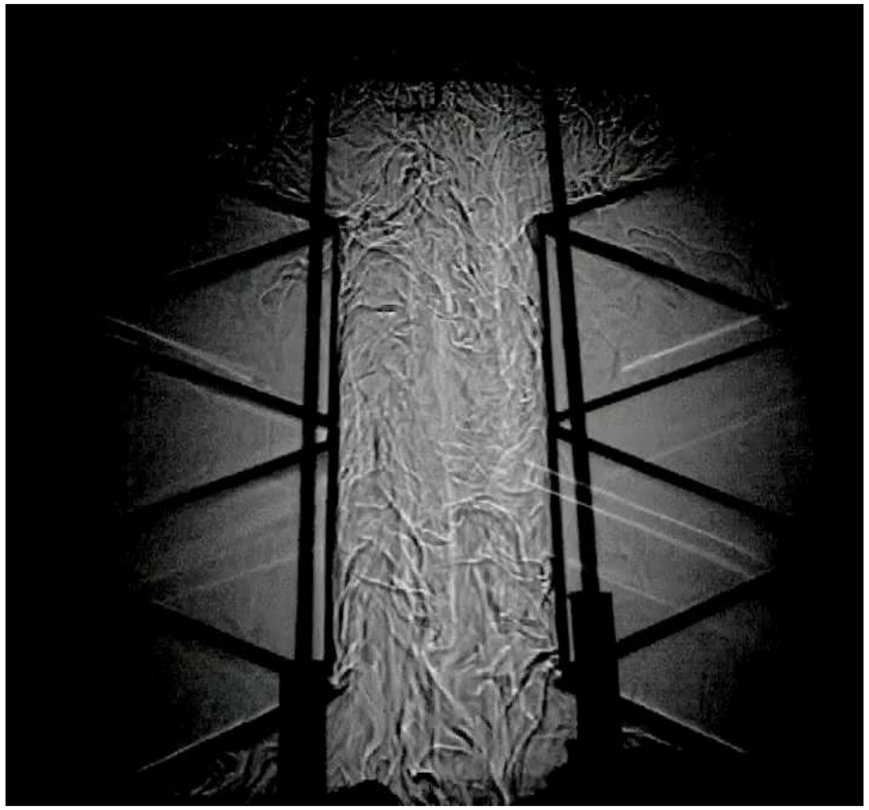
Examples of Dynamical Systems

Vibrated granular media



Thermal convection in a fluid

Cooled from above



Heated from below

Fluctuations in Macroscopic systems

Outline

1) Basic notions of thermodynamics and of equilibrium statistical physics

2) Calibrate instruments using equilibrium statistical physics

- Optical Tweezers
- Active and passive Microrheology
- Electric circuits analogies and differences
- Harmonic oscillator

3) Out of equilibrium and stochastic thermodynamics

What is stochastic thermodynamics useful for ?

- Fluctuation theorems (FT)
- Jarzynski and Crooks equality
- The stochastic entropy

Experimental approach

- FT in harmonic oscillators
- FT in stochastic resonance
- Fluctuation driven heat fluxes

- Application of FT, Jarzynski and Crooks equality

Outline

4) Stochastic thermodynamics and the dynamical systems. Experiments on turbulent flow, granular media and mechanical waves

5) The Maxwell demon and the connection between information and thermodynamics

6) Fluctuation Dissipation Theorems in non equilibrium steady state (NESS)

7) Engineered Swift Equilibration. How to reach equilibrium arbitrary fast.

Main Laws of Thermodynamics I

Clausius

The **First Law of Thermodynamics** is a version of the **Law of Conservation of Energy**

Clausisus statement of **the First Law**

In a thermodynamic process, the increment in the internal energy of a system is equal to the difference between the heat exchanged by the system with the heat bath and the increment of work done on it.

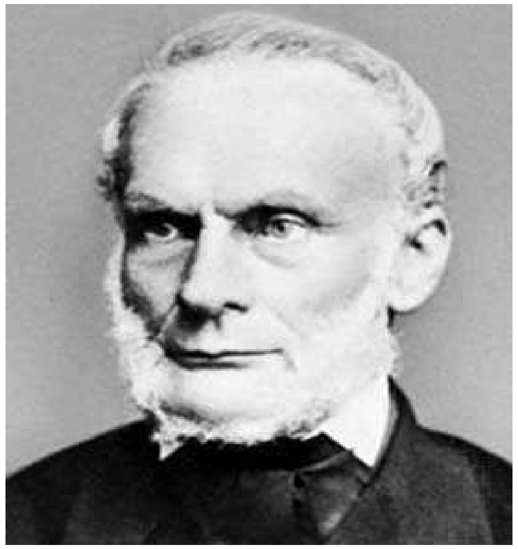
$$\Delta U_{A,B} = W_{A,B} - Q$$

Main Laws of Thermodynamics II

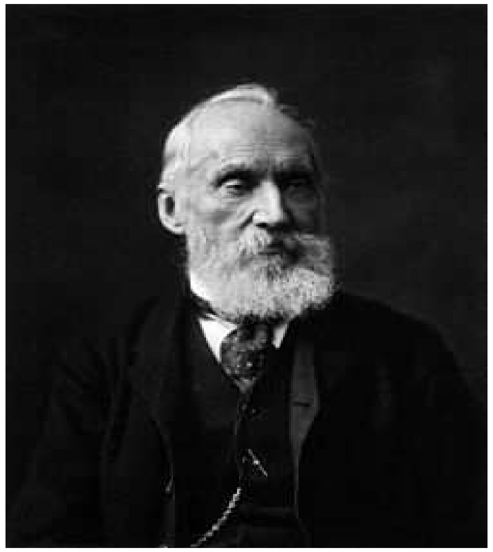
The Second Law is a statement about irreversibility.
It is usually stated in physical terms of impossible processes.

Sadi Carnot was the first to give a formulation of this principle

Sadi Carnot



Rudolf Clausius



Lord Kelvin

Clausius Statement of the Second Law: *Heat can never pass from a colder to a warmer body without some other change*

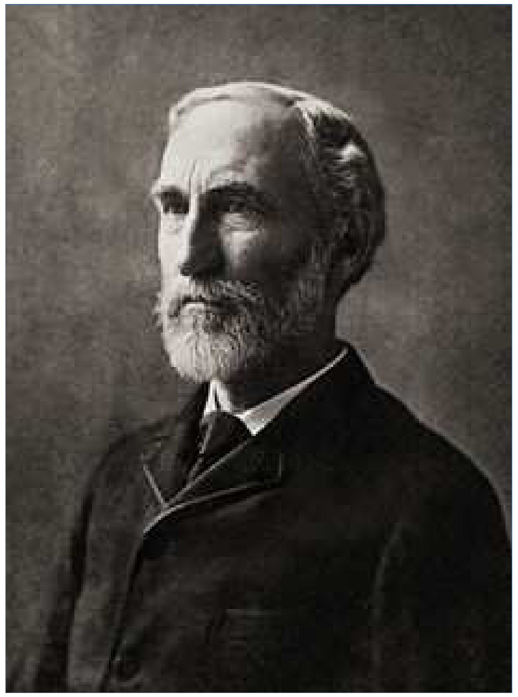
Lord Kelvin Statement of *the Second Law: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.*

Main Laws of Thermodynamics III

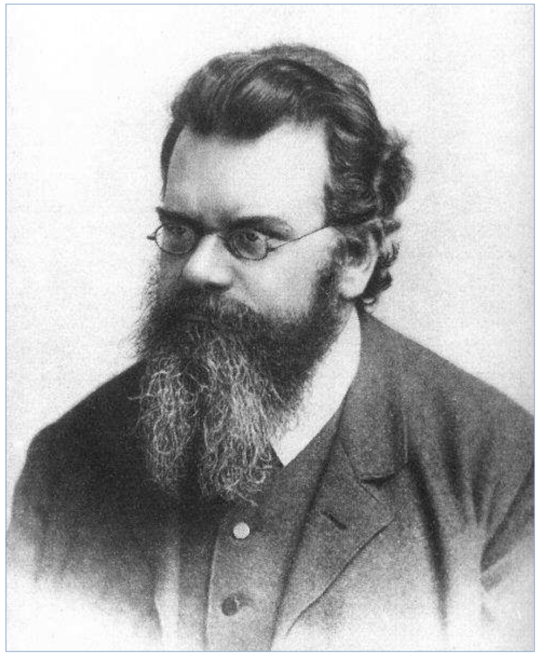
The **Second Law of Thermodynamics** is related to the concept of **Entropy**

$$\Delta S = \frac{Q}{T}$$

$$\Delta S_{tot} \geq 0$$



Gibbs

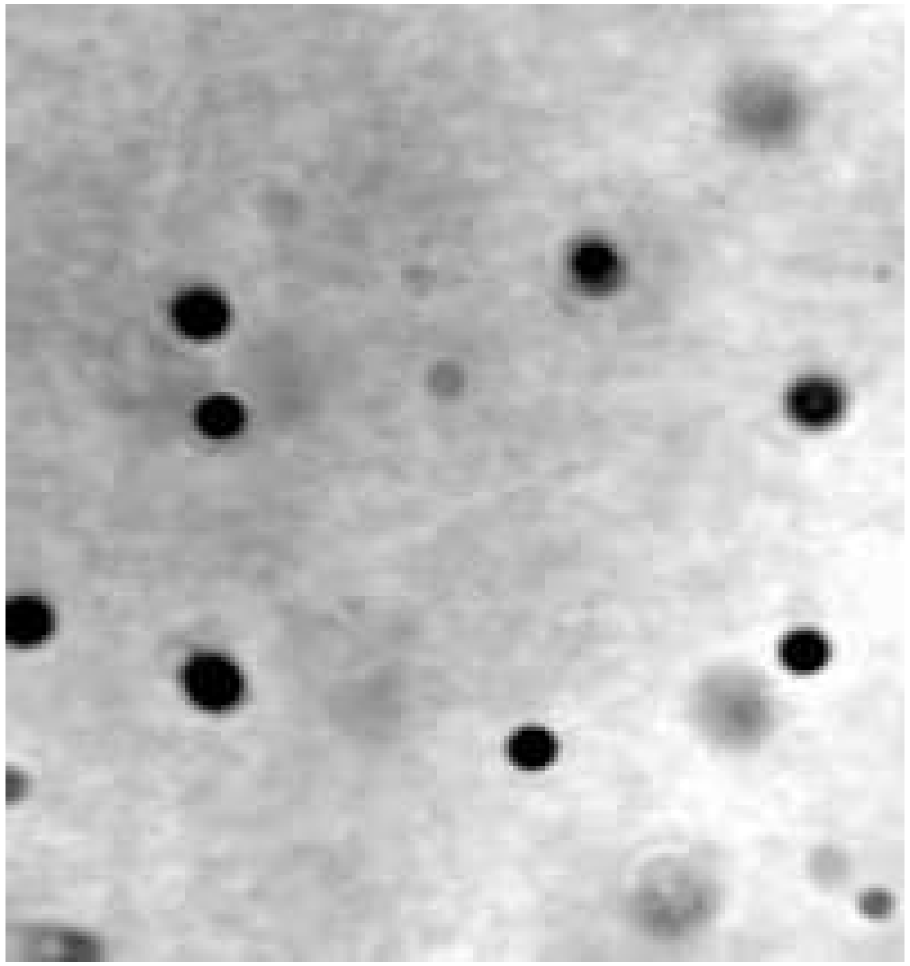


Boltzmann

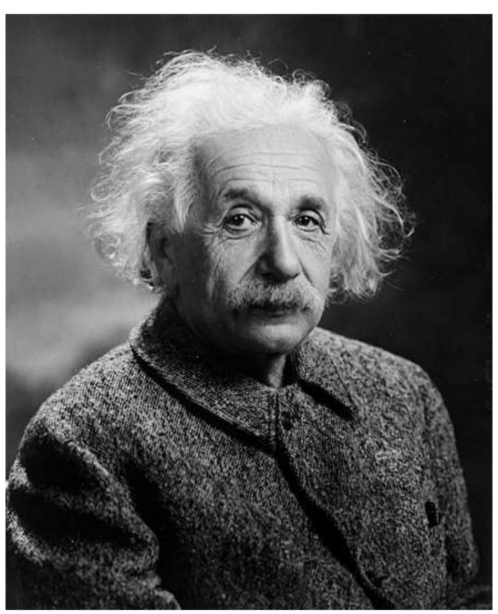
In **statistical mechanics**,**Entropy** is related to the probability of the microstates, correponding to a particular macrostate:

$$S = -k_B \Sigma_i p_i \log p_i$$

Brownian motion EQUILIBRIUM

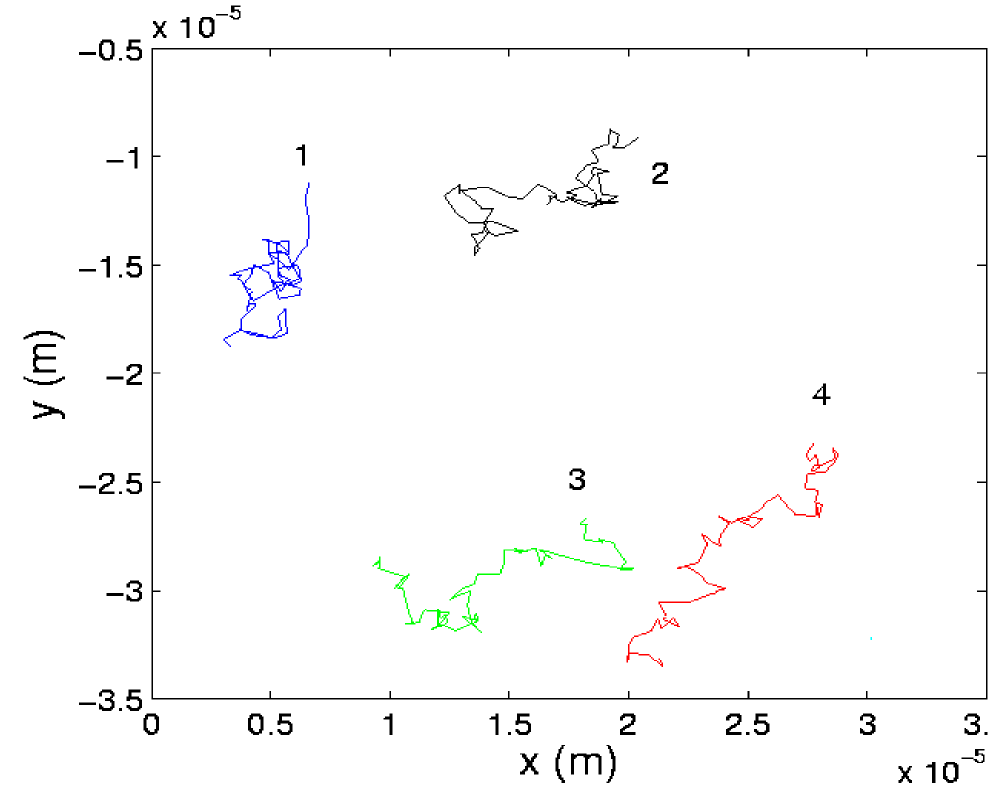


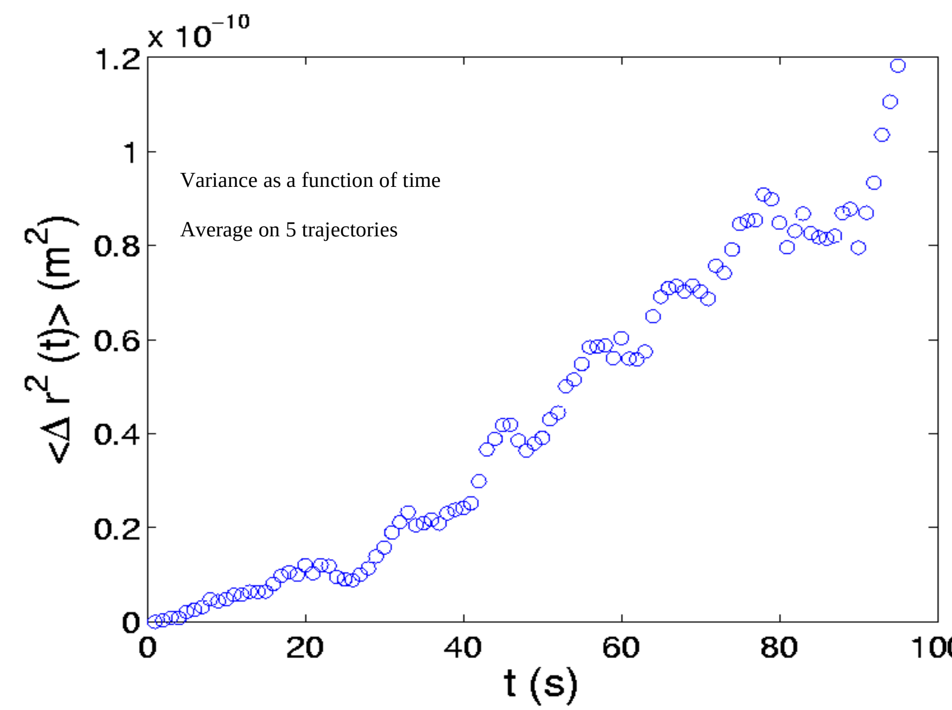
10 times faster than reality



A.Einstein

J. Perrin





$$< x^2 > = 2\ D\ t \qquad D = \frac{k_B\ T}{\Gamma}$$

$$\Gamma = 6\ \pi\ \eta\ R$$

The Nyquist problem

JULY, 1928 *PHYSICAL REVIEW* *VOLUME 32*

THERMAL AGITATION OF ELECTRIC CHARGE IN CONDUCTORS*

BY H. NYQUIST

ABSTRACT

The electromotive force due to thermal agitation in conductors is calculated by means of principles in thermodynamics and statistical mechanics. The results obtained agree with results obtained experimentally.

DR. J. B. JOHNSON[1] has reported the discovery and measurement of an electromotive force in conductors which is related in a simple manner to the temperature of the conductor and which is attributed by him to the thermal agitation of the carriers of electricity in the conductors. The work to be resported in the present paper was undertaken after Johnson's results were available to the writer and consists of a theoretical deduction of the electromotive force in question from thermodynamics and statistical mechanics.[2]

Consider two conductors each of resistance R and of the same uniform temperature T connected in the manner indicated in Fig. 1. The electromotive force due to thermal agitation in conductor I causes a current to be set up in the circuit whose value is obtained by dividing the electromotive force by $2R$. This current causes a heating or absorption of power in conductor II, the absorbed power being equal to the product of R and the square of the current. In other words power is transferred from conductor I to conductor II. In precisely the same manner it can be deduced that power is transferred from conductor II to conductor I. Now since the two conductors are at the same temperature it follows directly from the second law of thermodynamics that the power flowing in one direction is exactly equal to that flowing in the other direction. It will be noted that no assumption has been made as

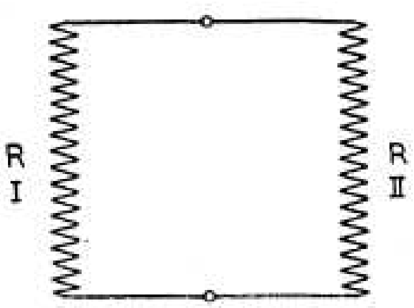
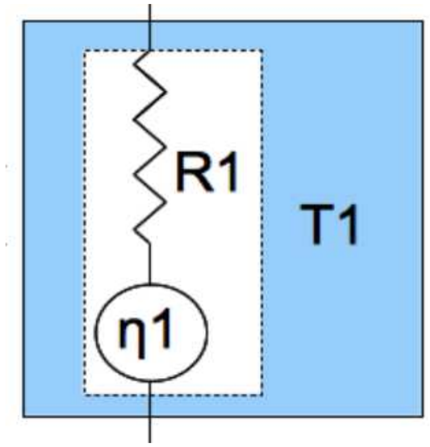


Fig. 1.

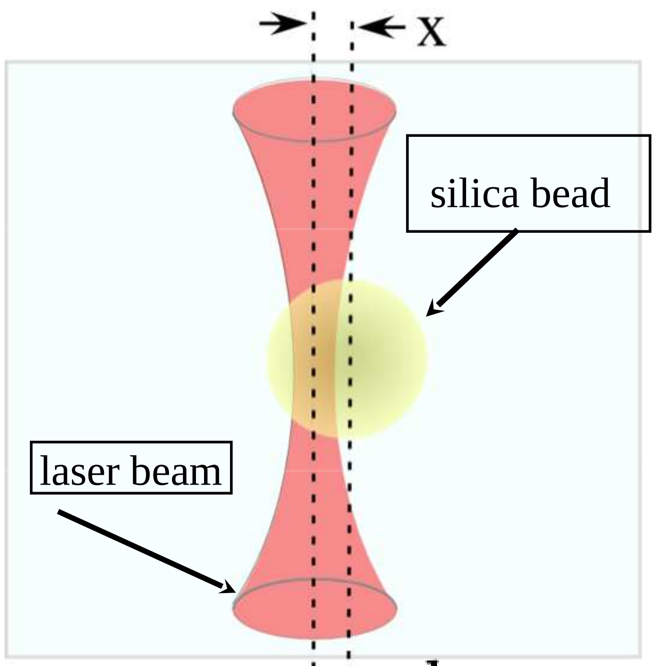
Power spectral density of the electric noise

$$|\tilde{\eta}|^2 = 4k_B R T$$



In 1928 well before Fluctuation Dissipation Theorem (FDT), this was the second example, after the Einstein relation for Brownian motion, relating the dissipation of a system to the amplitude of the thermal noise.

Confining fluctuations

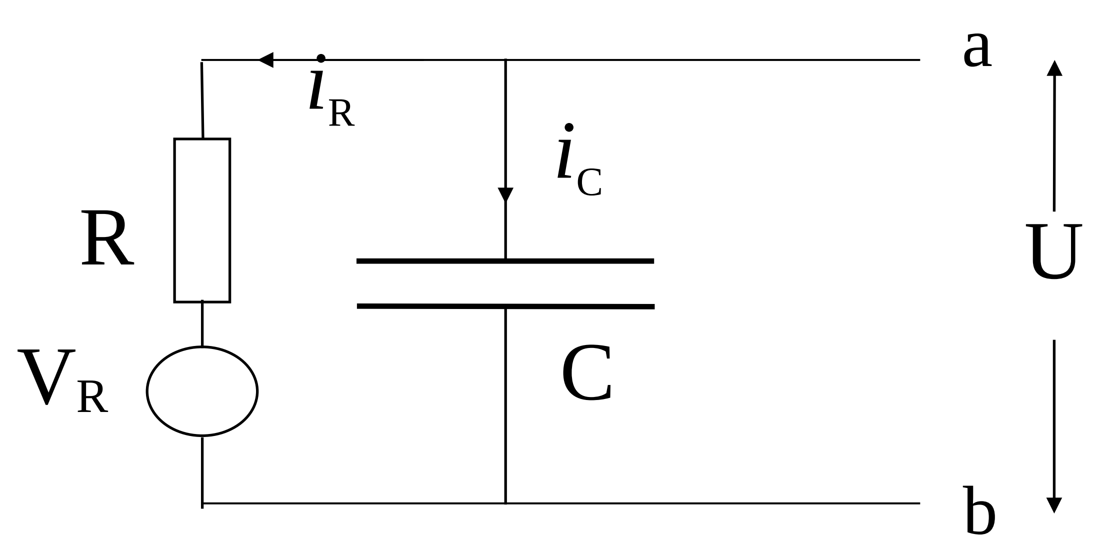


$$U(x) = \frac{k}{2}\, x^2$$

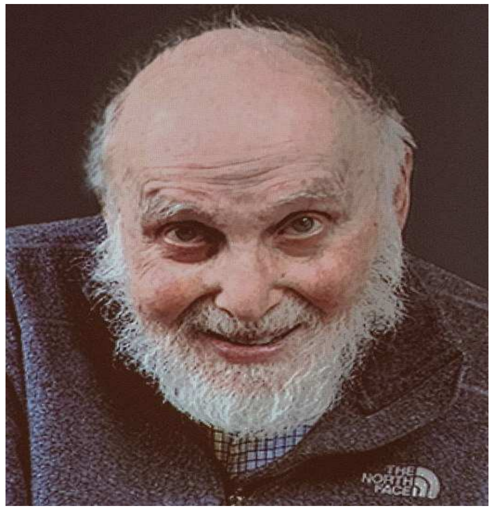
In an optical trap for a colloid

By a capacitance for the electronic noise

Equivalent circuit



The Optical Tweezers



A Ashkin
Physics Nobel Price in 2018 for the invention of optical tweezers

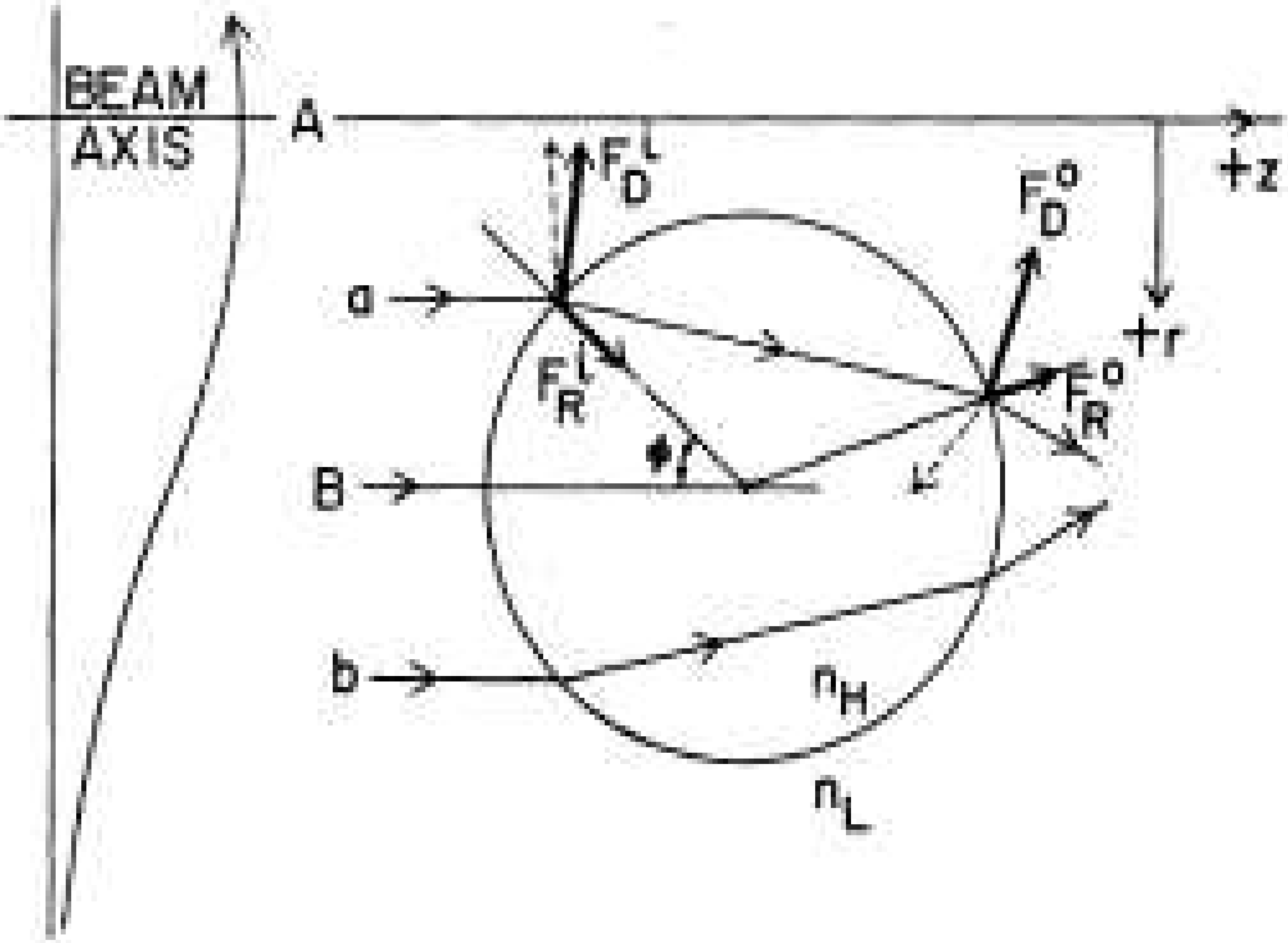
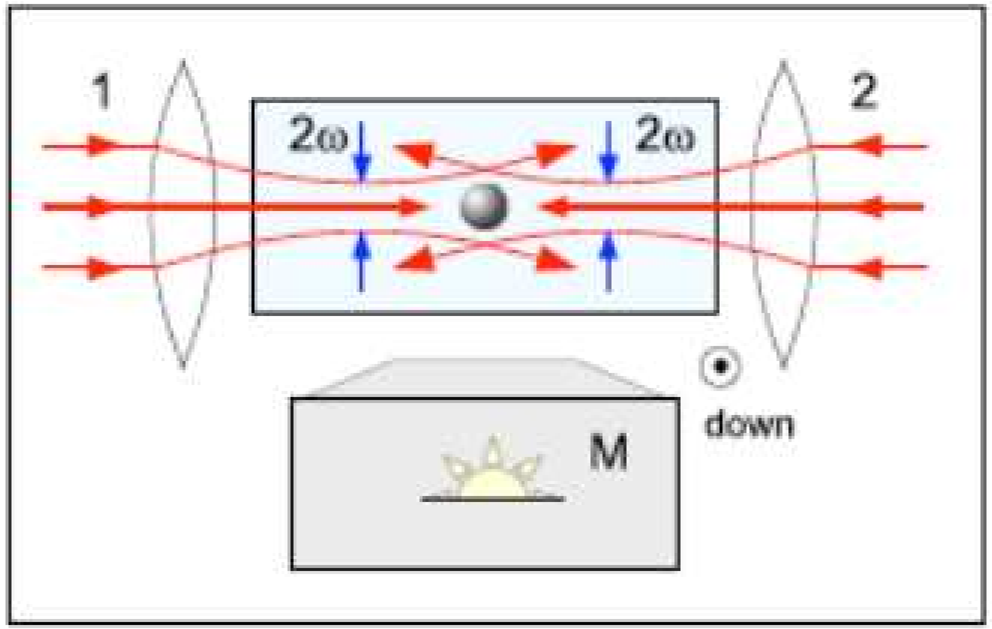
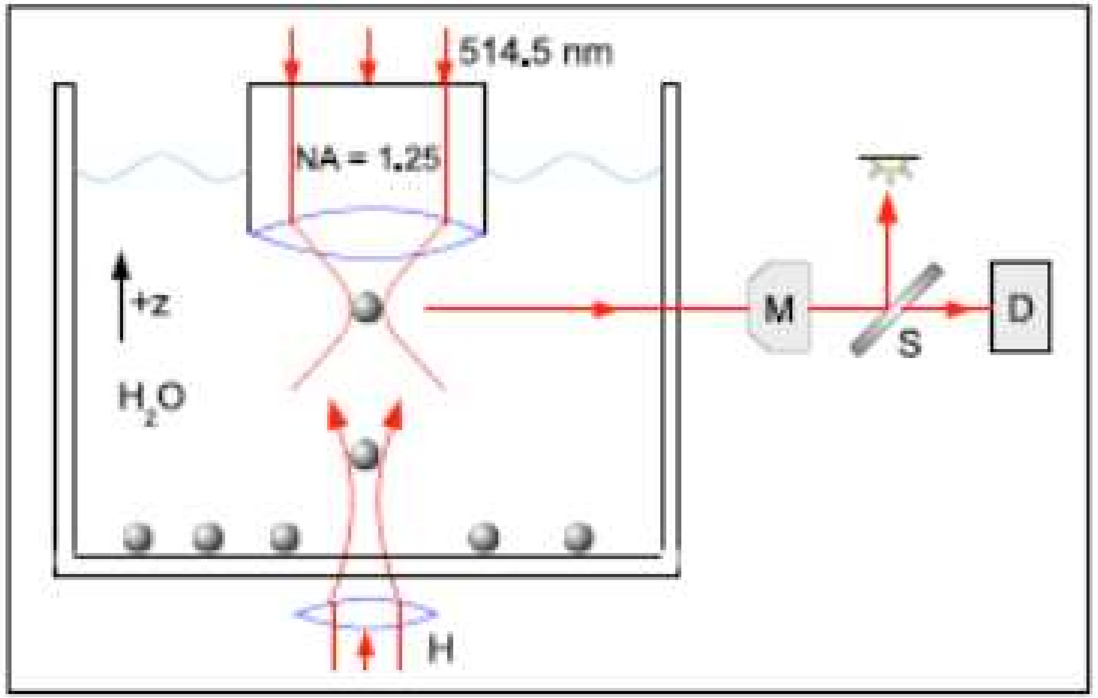


FIG. 2. A dielectric sphere situated off the axis A of a TEM_{00}-mode beam and a pair of symmetric rays a and b. The forces due to a are shown for $n_H > n_L$. The sphere moves toward $+z$ and $-r$.

First trapping experiments



(a)



(b)

The Optical Tweezers

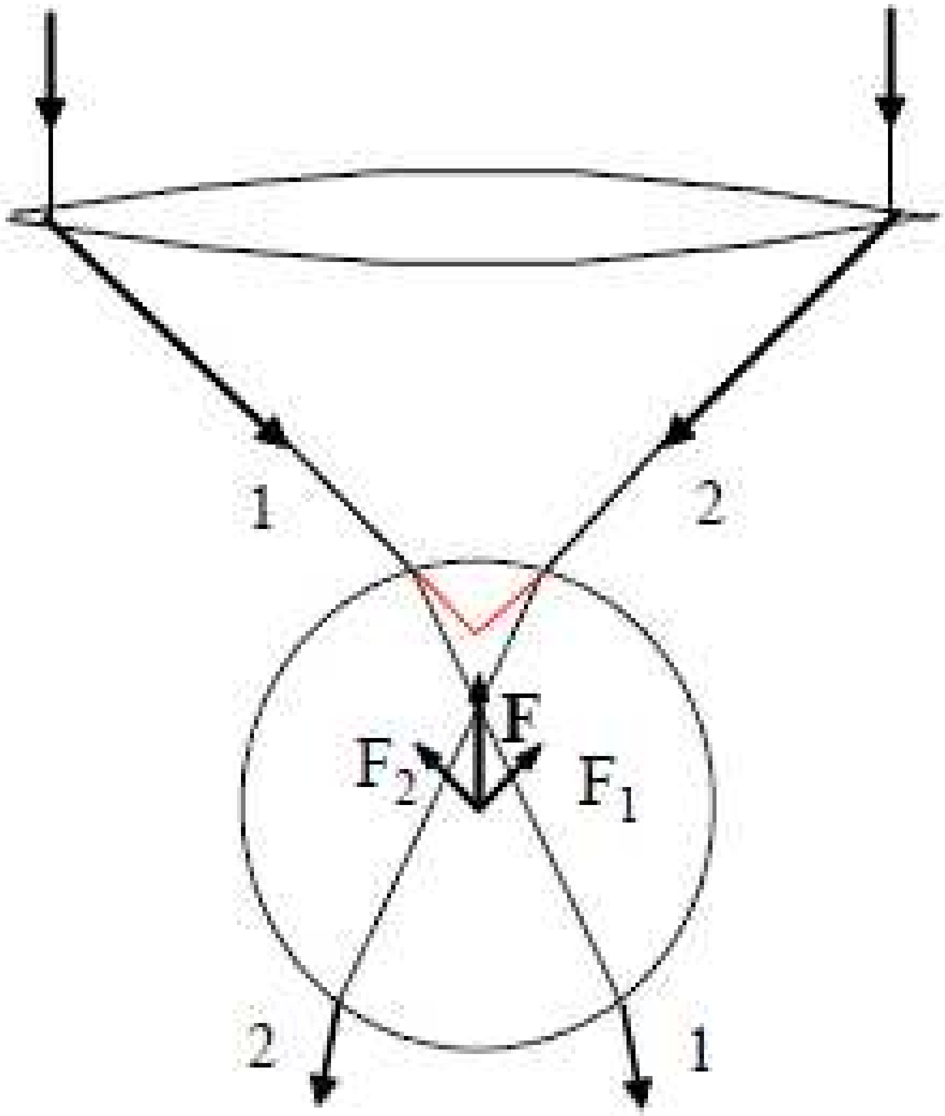


Figure 1. Schematic diagram showing the force on a dielectric sphere due to refraction of two rays of light, 1 and 2. The resultant force on the bead due to refraction is towards the focus.

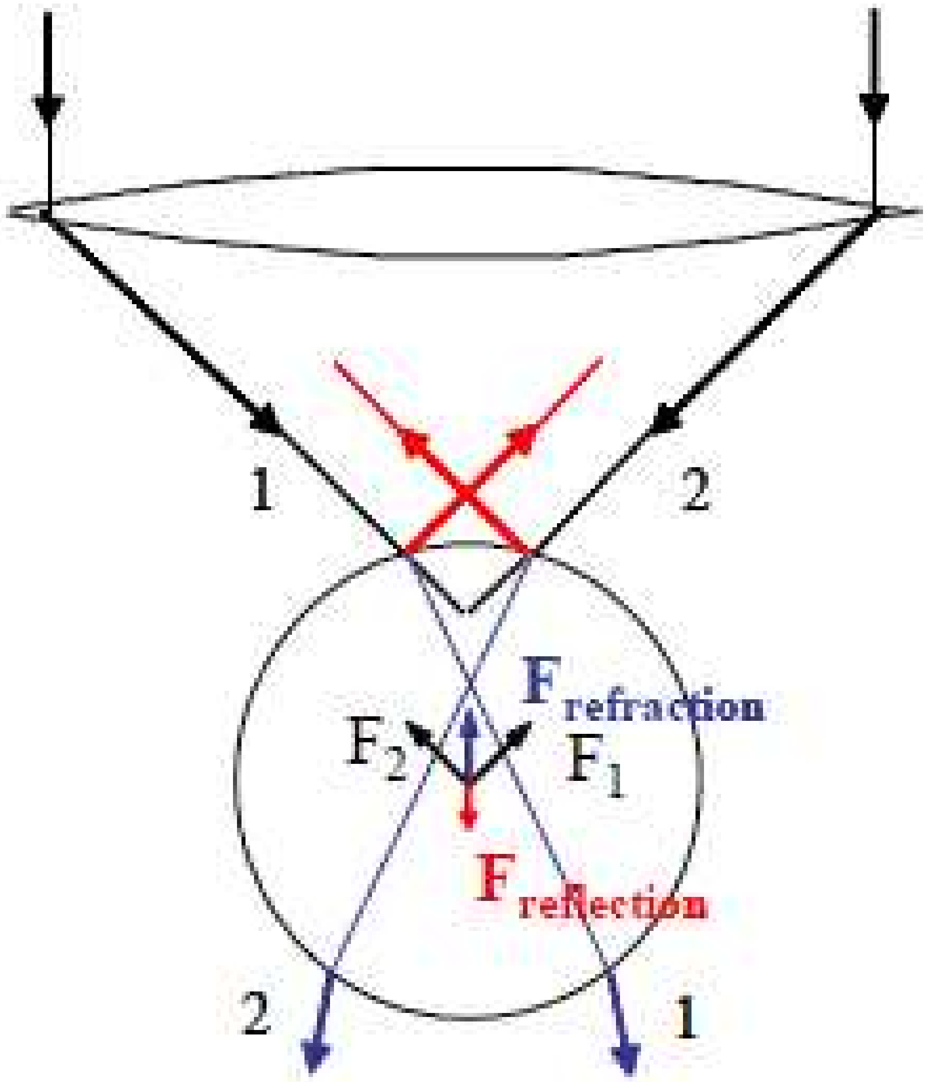


Figure 2. Schematic diagram showing the force on a dielectric sphere due to both reflection and refraction of two rays of light.

The Optical Tweezers

For dielectric particles in presence of a strongly focused beam the main contribution is coming from the electric field. Thus the total energy variation can be expressed as the dipole interaction:

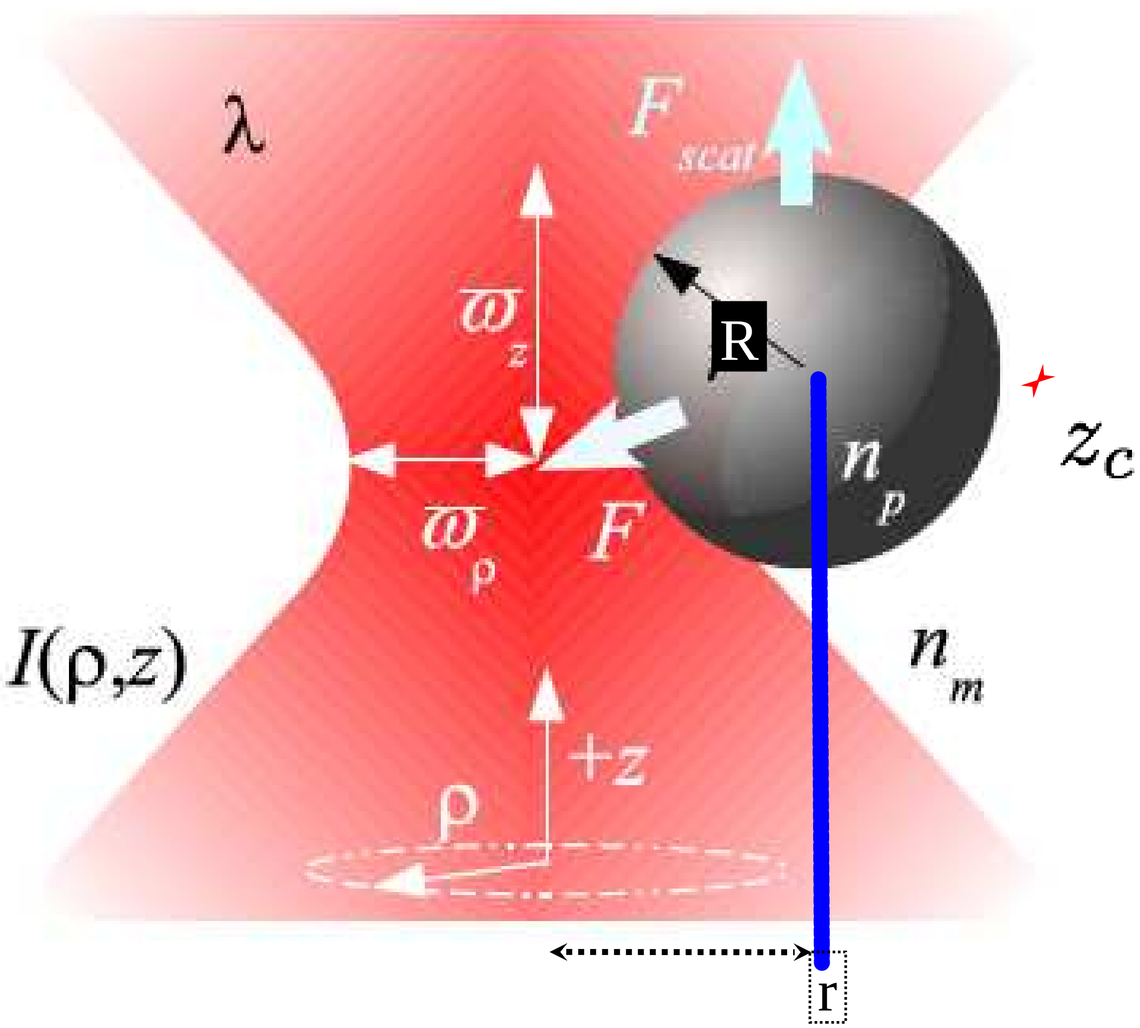
$$U = -\int_V P_i E_{oi}\ dv$$

where $P_i = \epsilon_0 \chi E_{oi}$, E_{oi} is the incident field and $\chi = \epsilon - 1$. This reduce the dipole interaction energy to

$$U = -\alpha \int_V I\ dv$$

where $I = \epsilon_f \epsilon_0 E_0^2$ is the intensity of the laser beam and $\alpha = \frac{\epsilon_p}{\epsilon_f} - 1 = \frac{n_p^2}{n_f^2} - 1$

ϵ_f and ϵ_p are the dielectric constant of the fluid and of the particle.



Assuming :

$$I(\rho, z) = I_0 \exp\left(-\frac{\rho^2}{2\varpi_\rho^2} - \frac{z^2}{2\varpi_z^2}\right)$$

In the approximation $\varpi_\rho = \varpi_z = \varpi$

the force is:

$$F(X) = \frac{2\pi\ \alpha\ I_o \bar{\omega}^2}{X^2} \exp(-\frac{R^2 + X^2}{2\bar{\omega}^2}) \left[\sinh(\frac{RX}{\bar{\omega}^2}) - \frac{RX}{\bar{\omega}^2} \cosh(\frac{RX}{\bar{\omega}^2})\right]$$

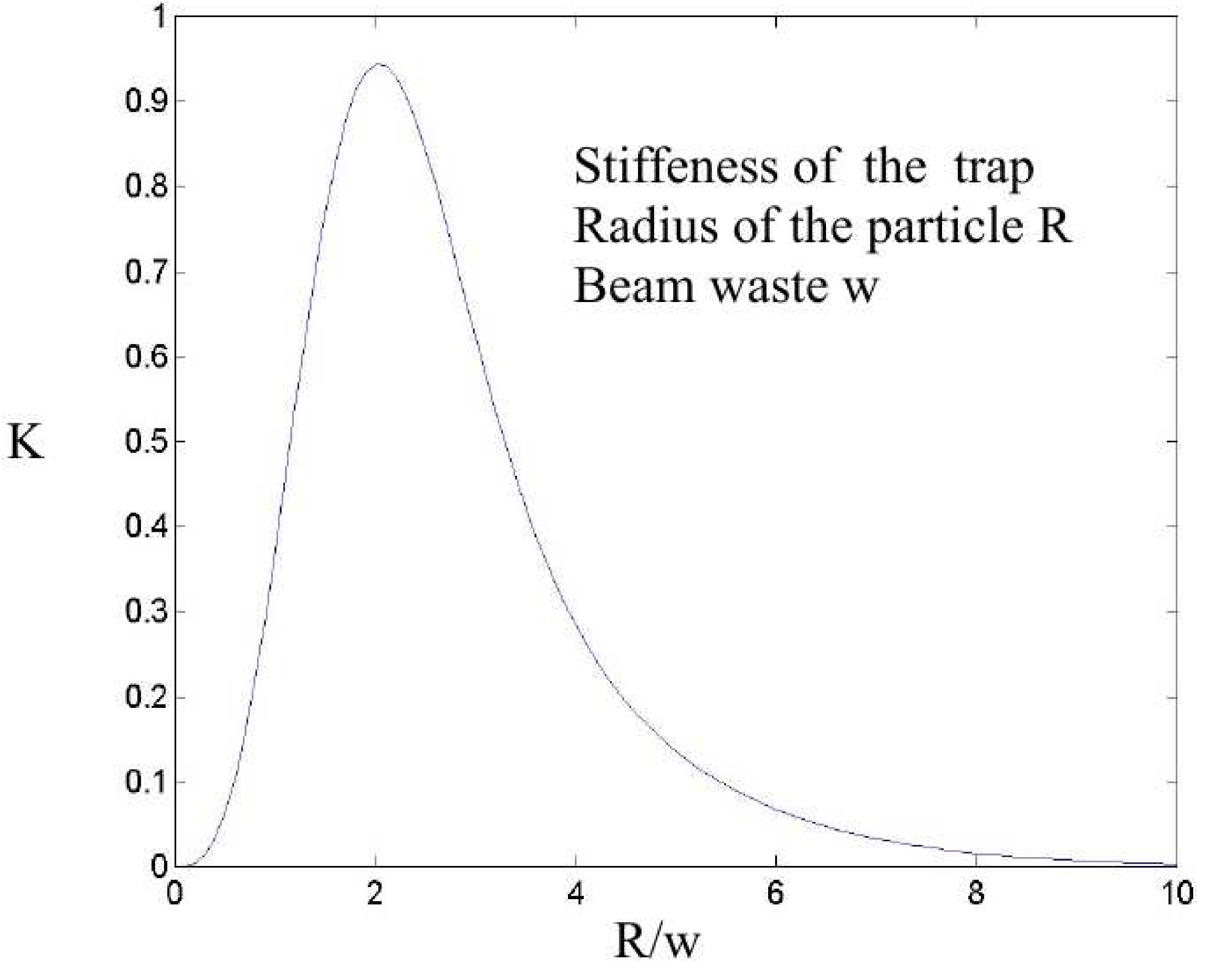
$$X = \sqrt{r^2 + z_c^2}$$

For small X

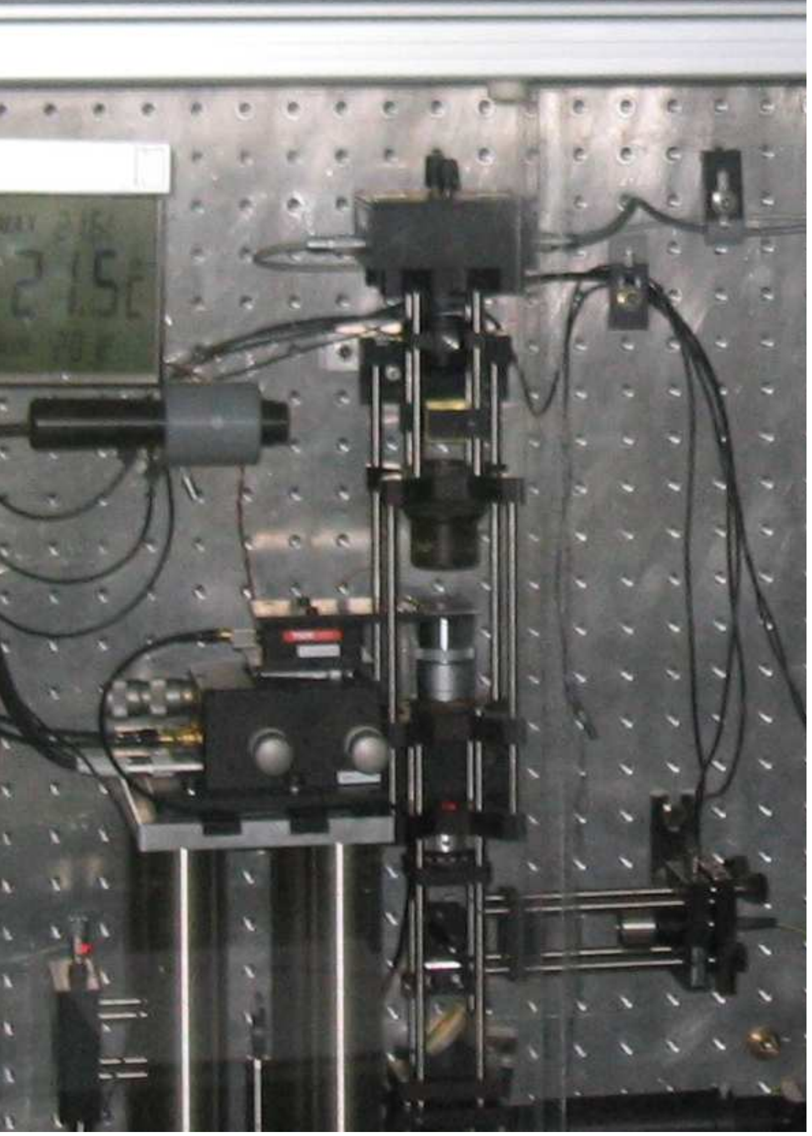
$$F(X) \simeq -\frac{2\pi\alpha I_o \bar{R}^3}{3\bar{\omega}^2} \exp(-\frac{R^2}{2\bar{\omega}^2})\ X$$

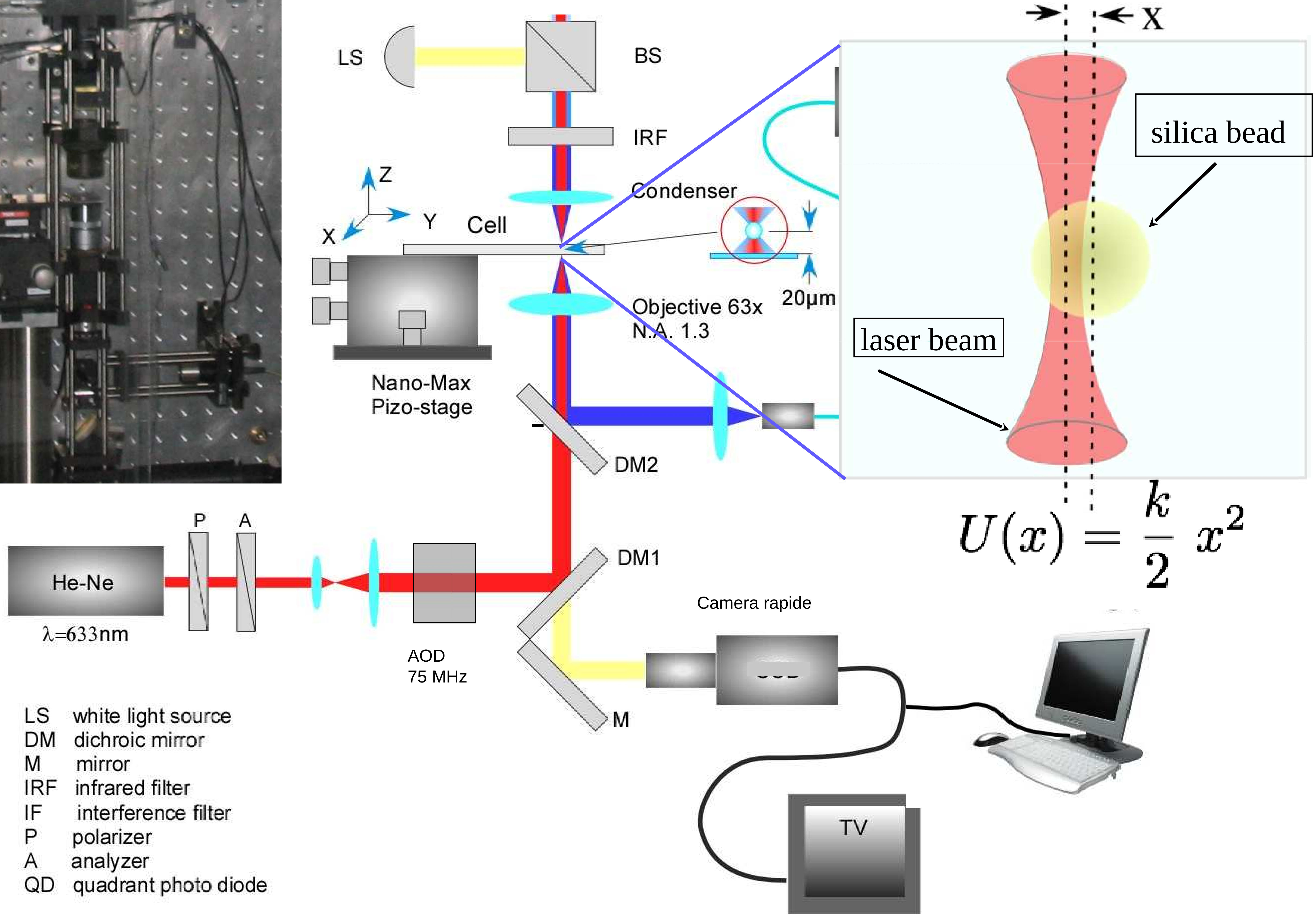
The Optical Tweezers

Then, the optical gradient force is simply given by the change of U in response to a change of the particles coordinates.

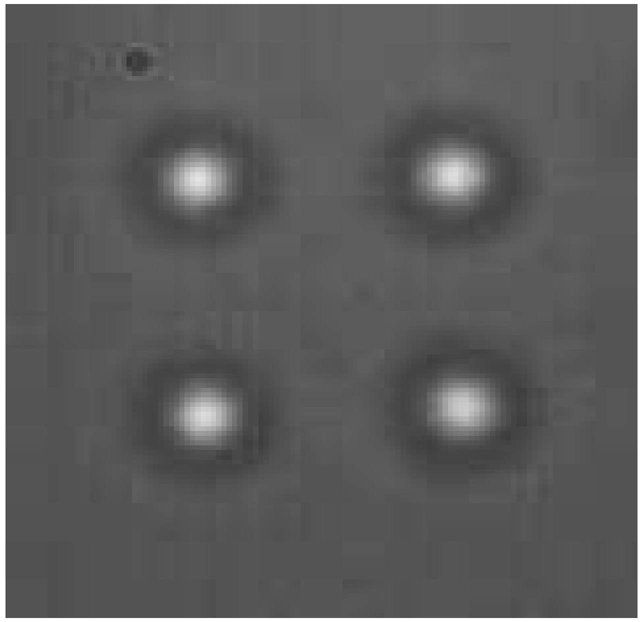


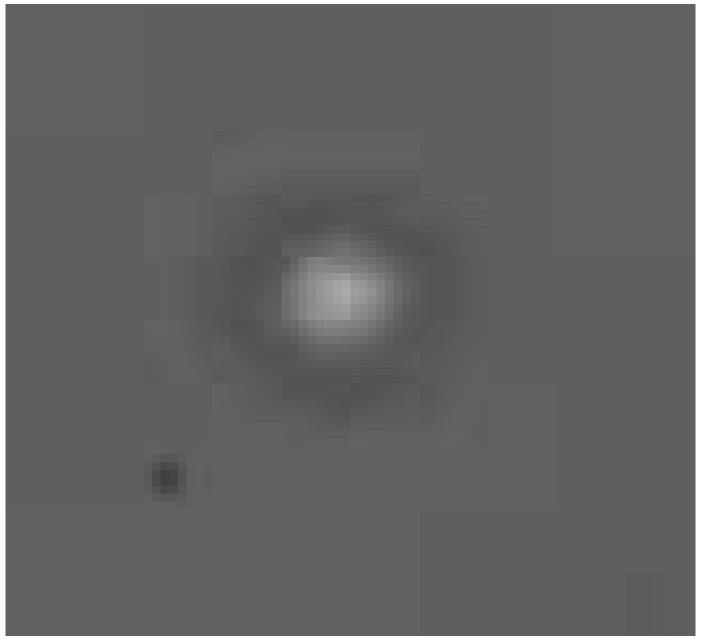
Experimental set-up Optical trap

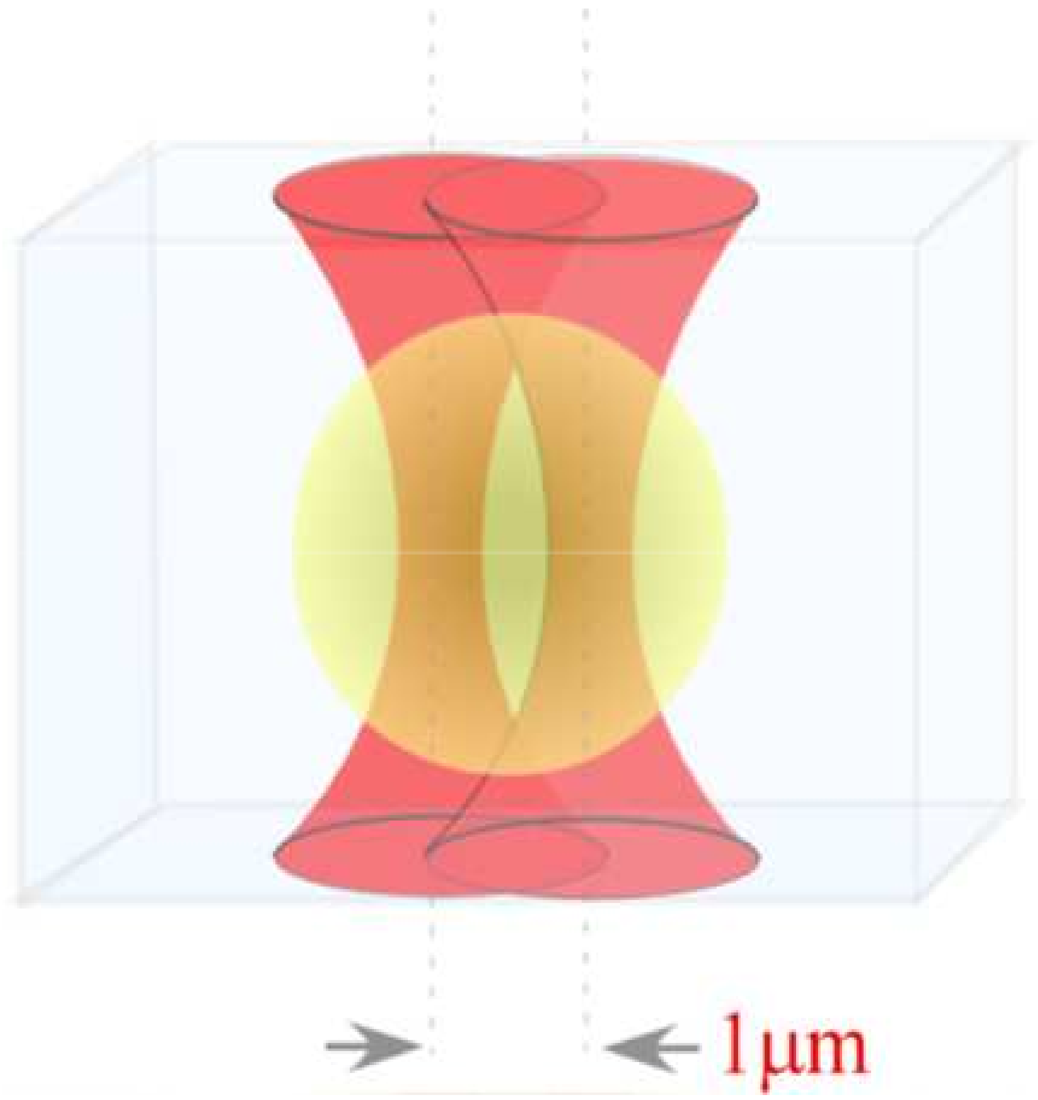




Examples of traps

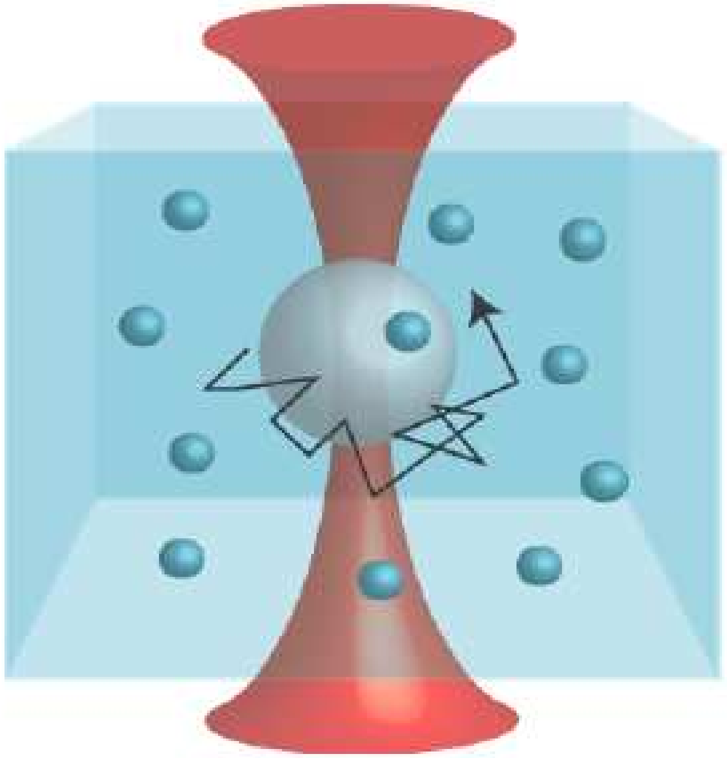






The dynamics of the trapped particle

The equation of motion of the particle in the trap is



$$\gamma \dot{x} = -k(t)x + \sqrt{D}\gamma\xi(t)$$

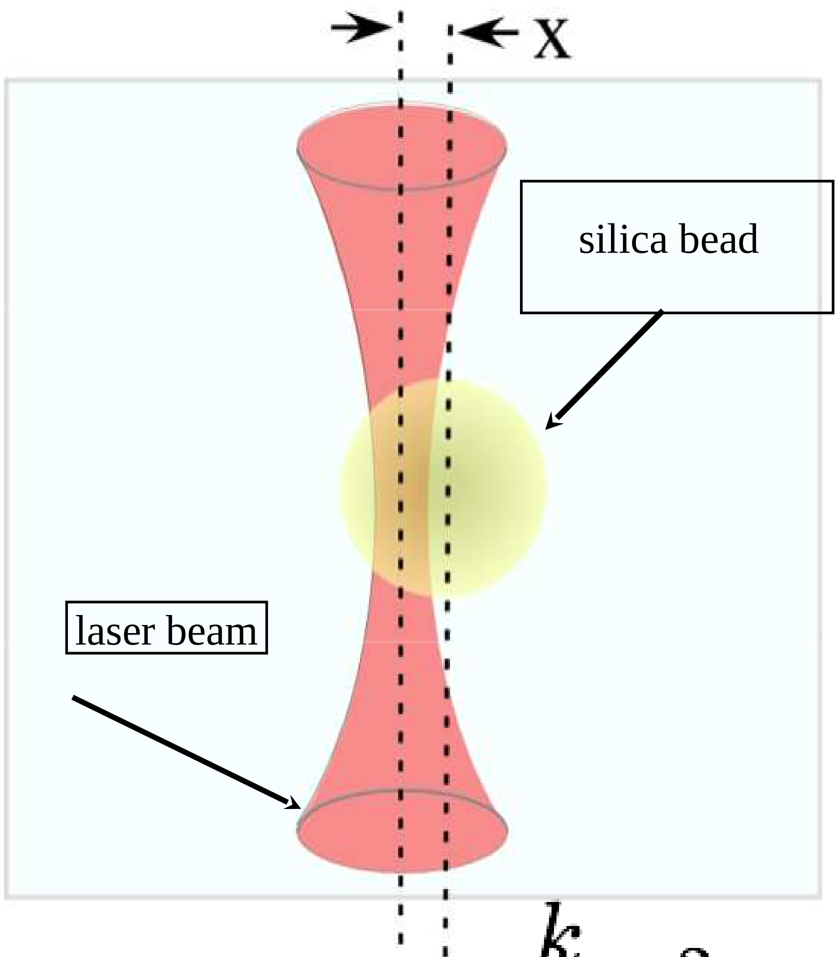
$$\tau_{relax} = k/\gamma \qquad D = k_B T/\gamma$$

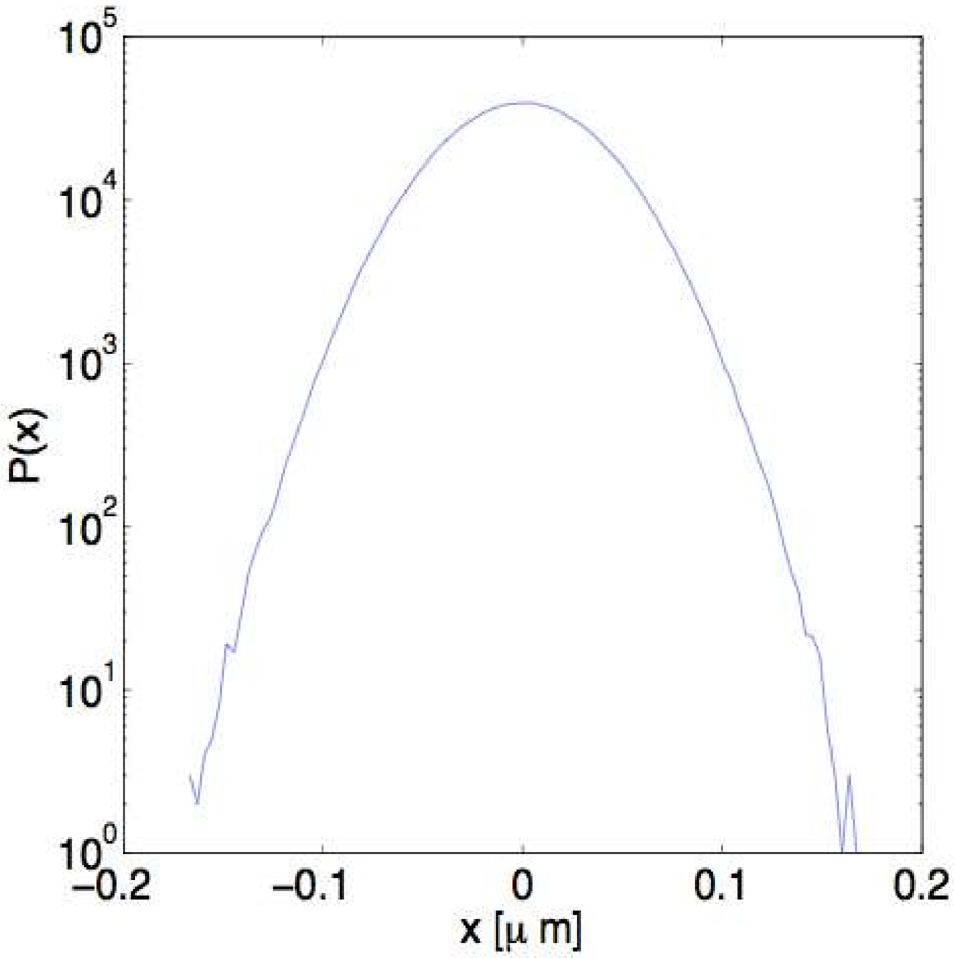
$$< \xi(t')\xi(t) >= 2\delta(t'-t)$$

$$\rho(x) = \frac{1}{\sqrt{\pi\sigma_x^2}} \exp[-\frac{k\ x^2}{2\ k_B T}] \quad \text{with} \quad \sigma_x^2 = \frac{k_B T}{k}$$

Typical values are $k_i = 0.5pN/\mu m$ and $\tau_{relax} \simeq 15ms$.

Calibration of an optical trap





$$\rho(x) \propto \exp[-\frac{U(x)}{k_B T}]$$

$$U(x) = \frac{k}{2}\ x^2$$

$$\rho(x) = \frac{1}{\sqrt{\pi\sigma_x^2}} \exp[-\frac{k\ x^2}{2\ k_B T}] \quad \text{with} \quad \sigma_x^2 = \frac{k_B T}{k}$$

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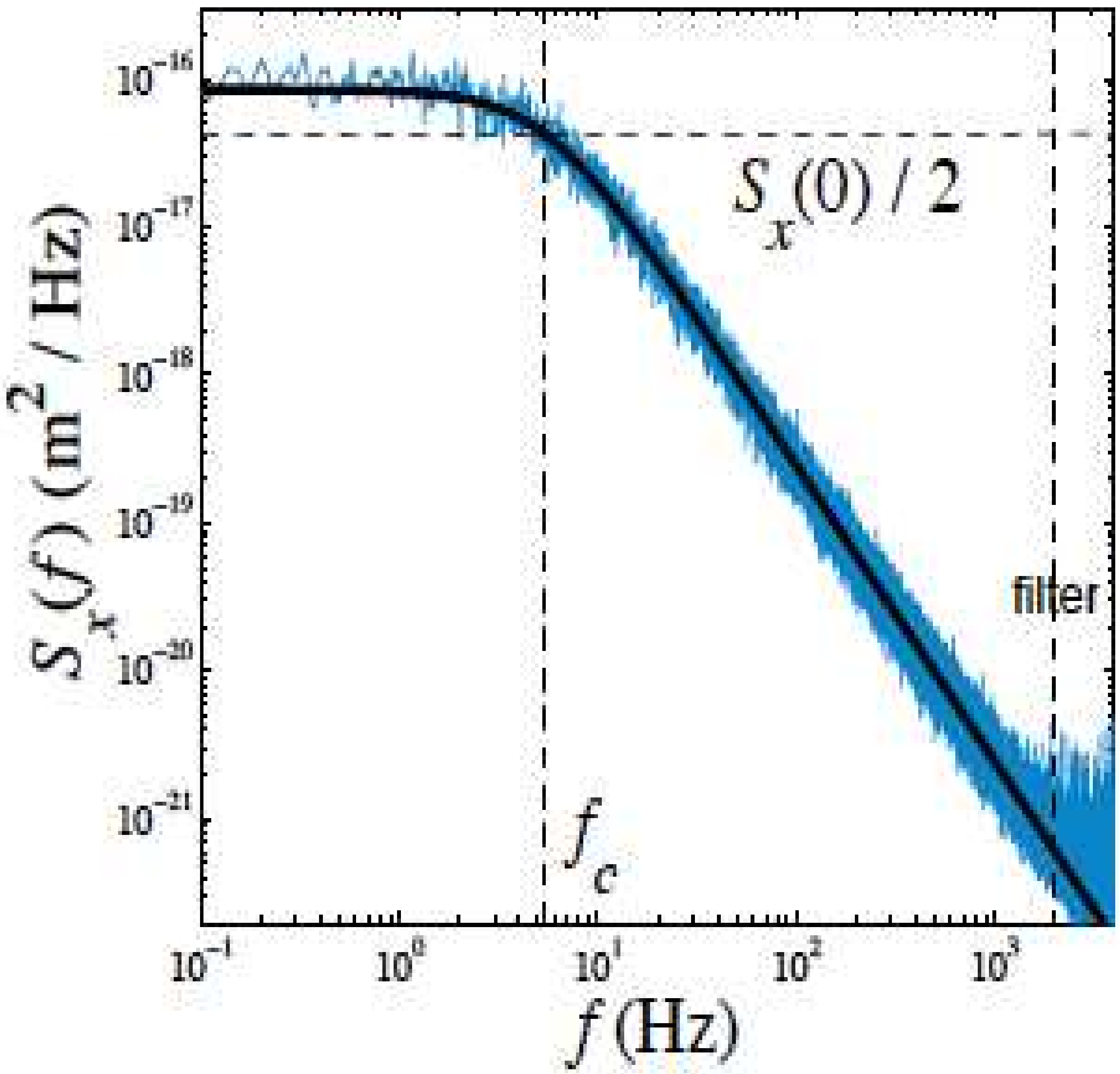
Calibration of an optical trap

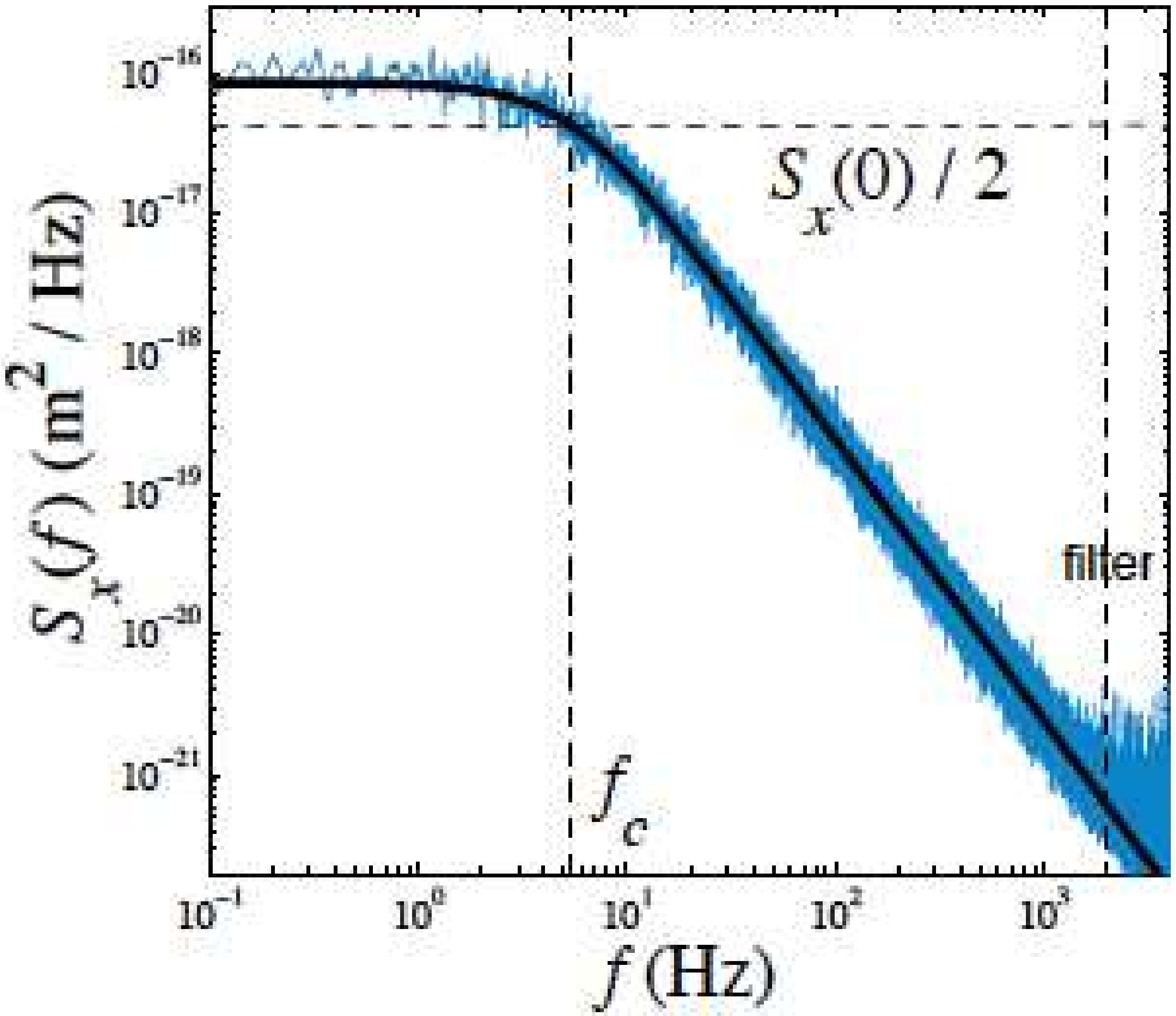


$$S_x(f) = \frac{4k_B T\gamma}{k^2 + \gamma^2\omega^2}$$

$$\gamma = 6\pi\ \eta\ R$$

$$2\pi\ f_c = \frac{\gamma}{k}$$

Passive Rheology using FDT



$$S_x(f) = \frac{4k_BT\ \gamma}{k^2 + \omega^2}$$

$$\gamma = 6\pi\ \eta\ R$$

$$2\pi\ f_c = \frac{\gamma}{k}$$

$$S_x(f) = \frac{4k_BT}{\omega} Imag[\mathrm{Resp}(\omega)]$$

Real Part can be measured using Kramers-Kroening

Fluctuation Dissipation Theorem

$\text{Observable}: O(t)$ $\quad$ $\text{conjugated variable}: h$

$$\text{response function}: R(t,s) = \frac{\delta O(t)}{\delta h}$$

$$\text{correlation function}: C(t,s) =< O(t)O(s) >$$

$$\partial_s C(t,s) = -k_B T \; R(t,s)$$ FDT

$$C(t,t) - C(t,s) = k_B T \; \chi(t,s)$$ Integral form

$$\text{Integral response function}: \chi(t,s)$$

For the spectrum

$$S_x(f) = \frac{4k_B T}{\omega} Imag[\text{Resp}(\omega)]$$

Kramer Kroening

$$S_j(\omega) = \frac{4\ k_B T}{\omega} \chi''_j(\omega)$$

$$\tilde{\chi}'_j(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\xi \tilde{\chi}''_j(\xi)}{\xi^2 - \omega^2} d\xi = \frac{1}{2\pi k_B T} P \int_0^\infty \frac{\xi^2 S_j(\xi)}{\xi^2 - \omega^2} d\xi$$

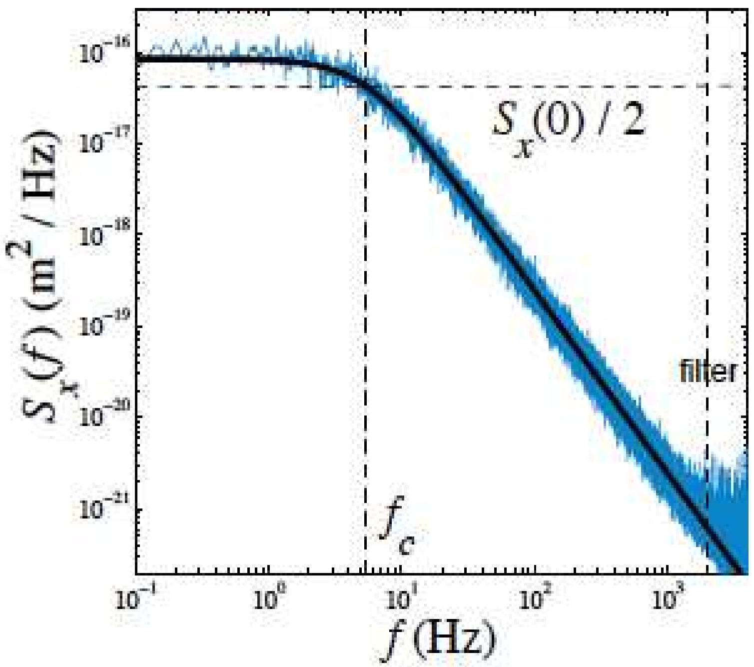
i.e. $\tilde{\chi}''_j(\xi, t_w) = \omega S_j(\omega, t_w)/(4 k_B T)$.

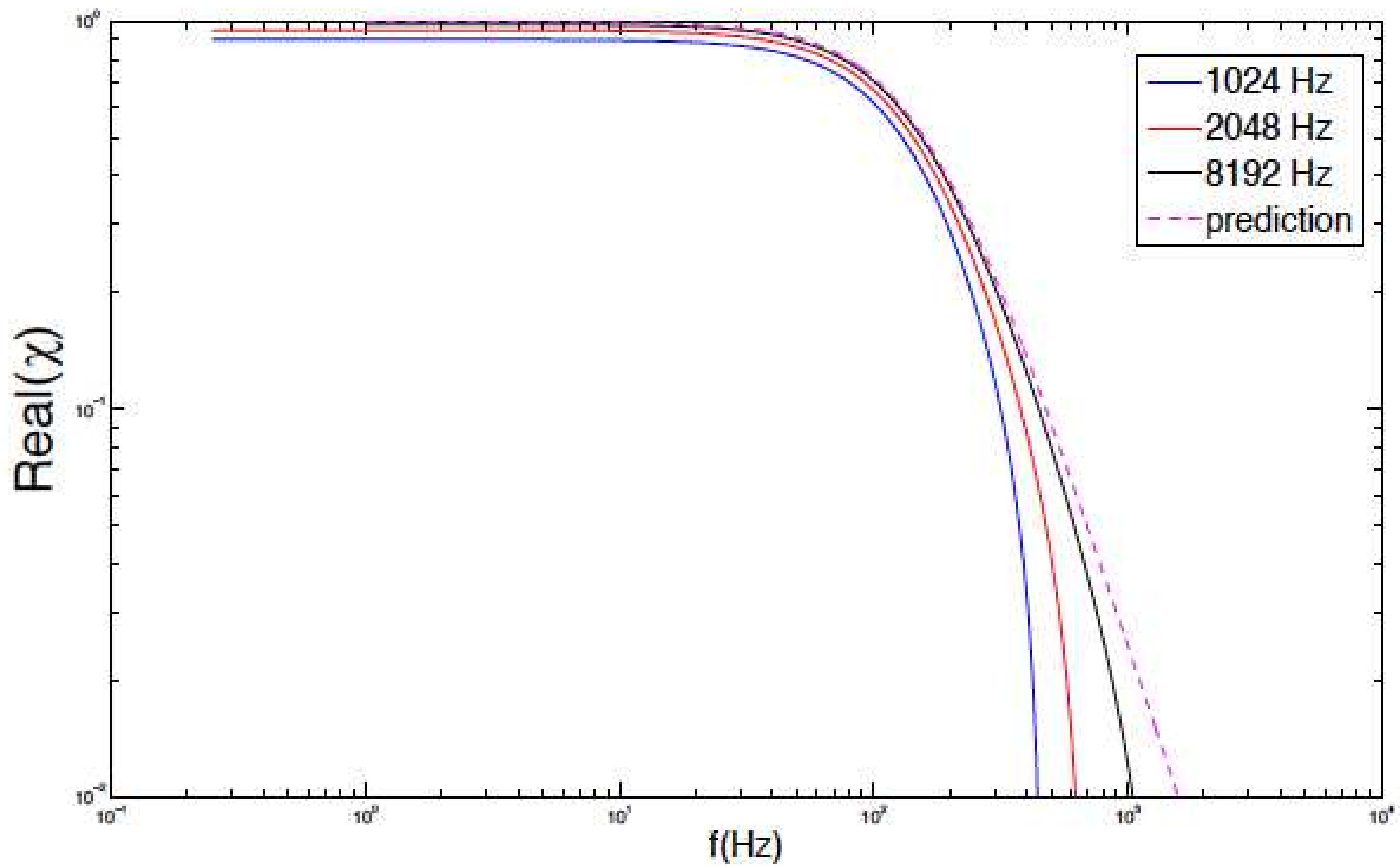
To compute $\tilde{\chi}'_j$ we use a Fourier transform algorithm that is:

$$\tilde{\chi}'_j(\omega) = \frac{1}{2\pi k_B T} \int_0^{1/\omega_{min}} \cos(\omega\ t)\ dt\ \int_0^{\omega_{max}} \xi^2 S_j(\xi)\ \sin(\xi\ t) d\xi,$$

where ω_{min}, ω_{max} are the minimum and maximum of the spectrum.

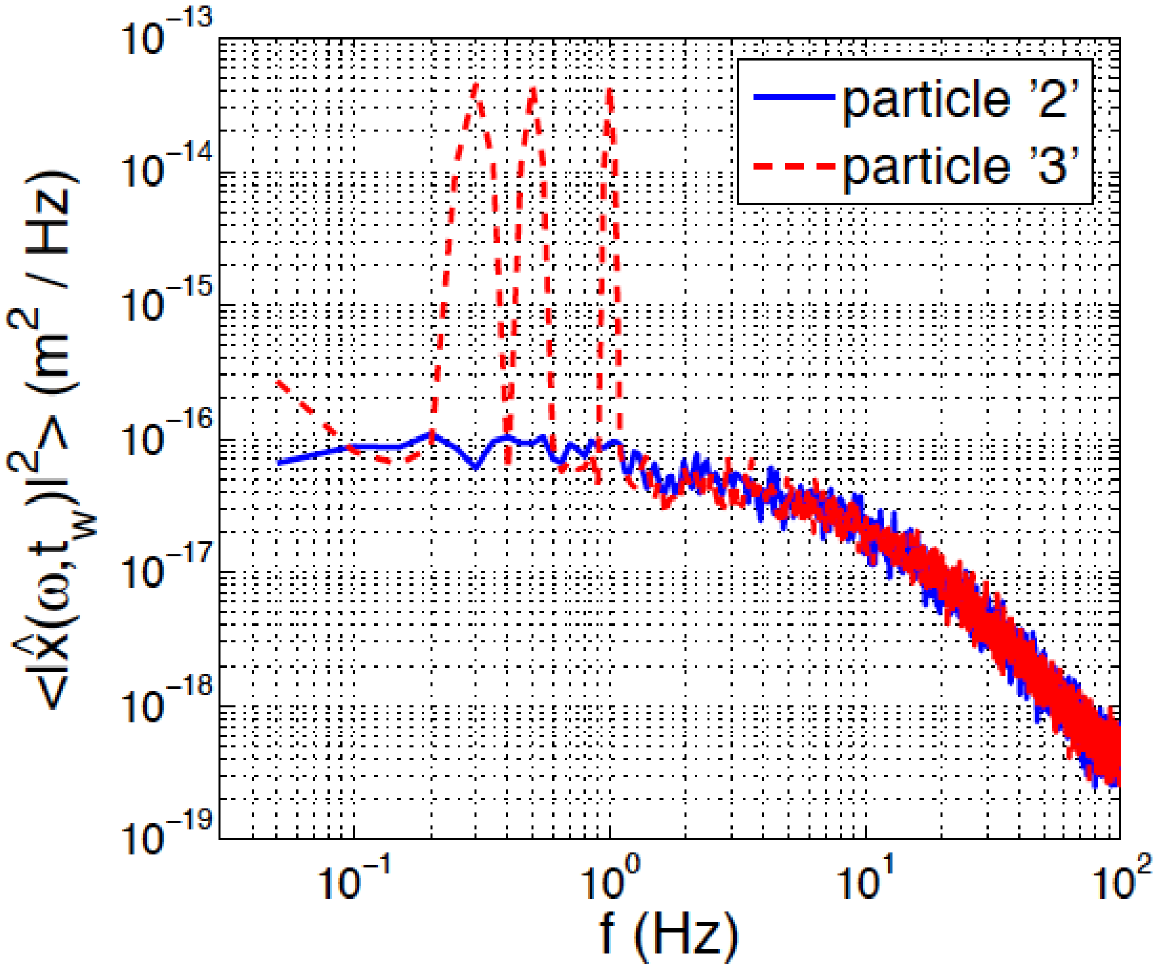
Test of the method of Kramers-Kroening
Using the spectra of the trapped Brownian particle





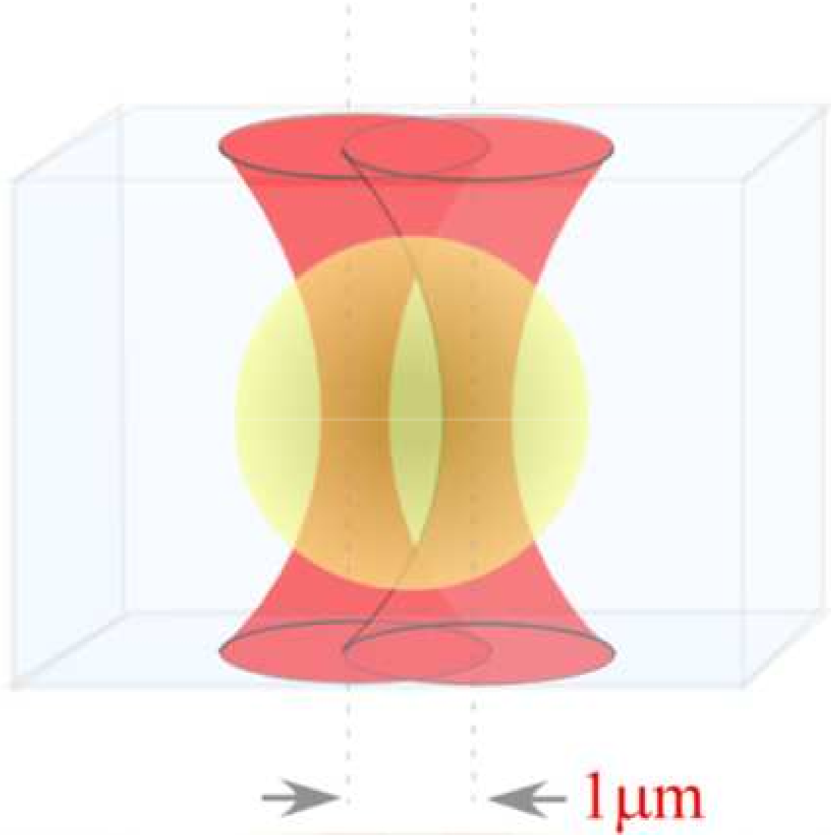
Active Rheology

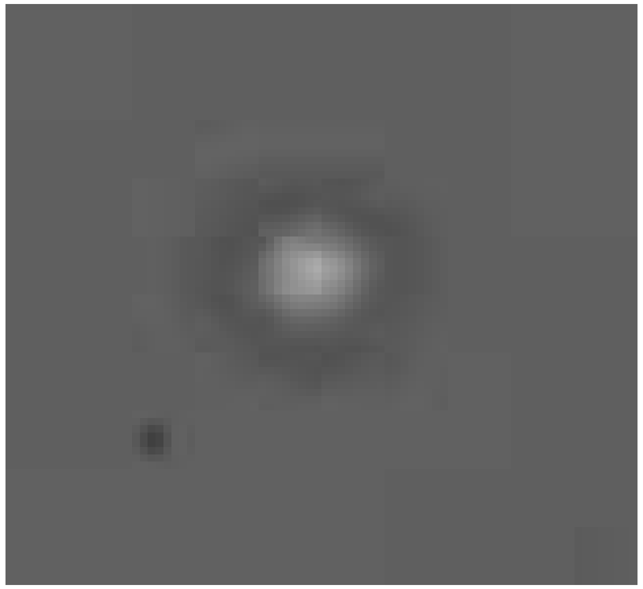
$$\gamma \dot{x} = -k[x - x_o(t)] + \xi \qquad \mathrm{Resp}(\omega) = < \frac{\tilde{x}(\omega)}{k\tilde{x}_o(\omega)} >$$

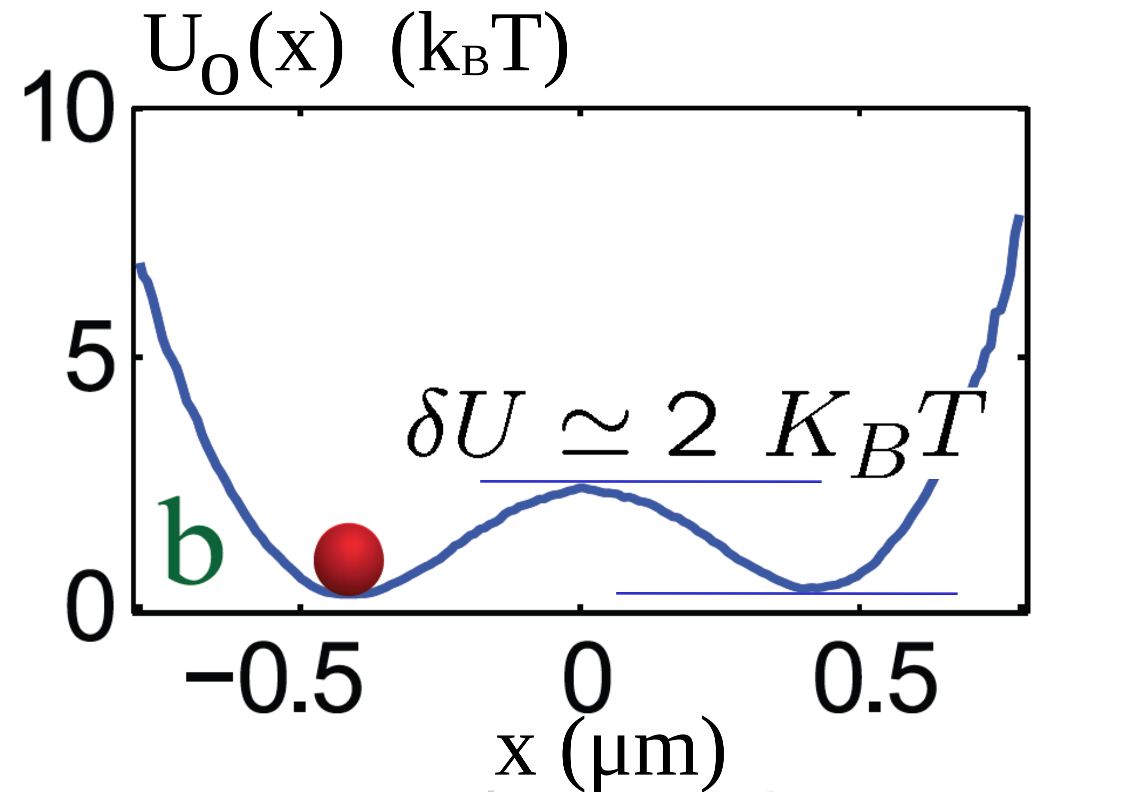


Direct measure of the response function

Brownian particle trapped by two laser beams







$$U_o(x) = a\,x^4 - b\,x^2 + d\,x$$

The Kramers time

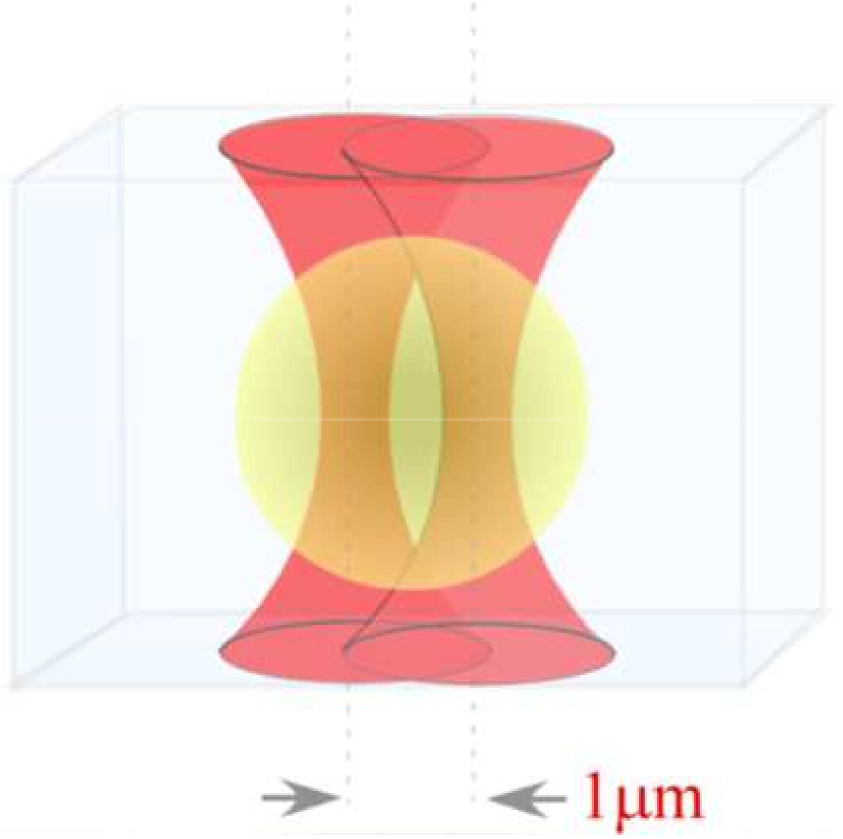
$$\tau_K = \tau_o \ \exp[\frac{\delta U}{k_B T}]$$

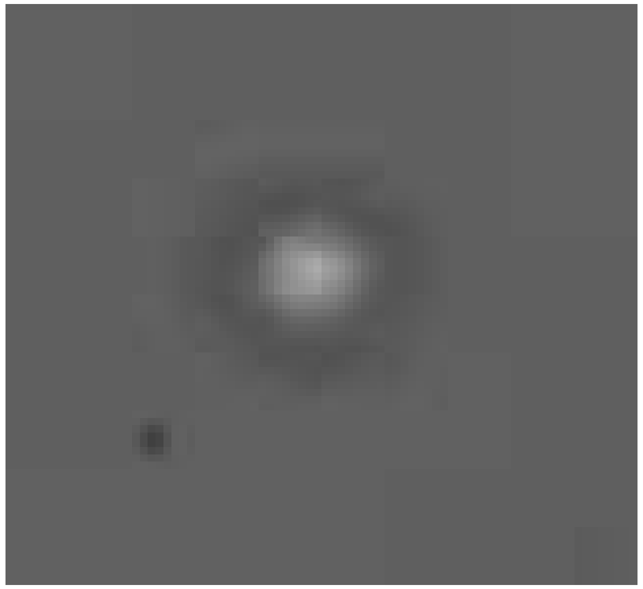
with $\tau_o = 1\ s$

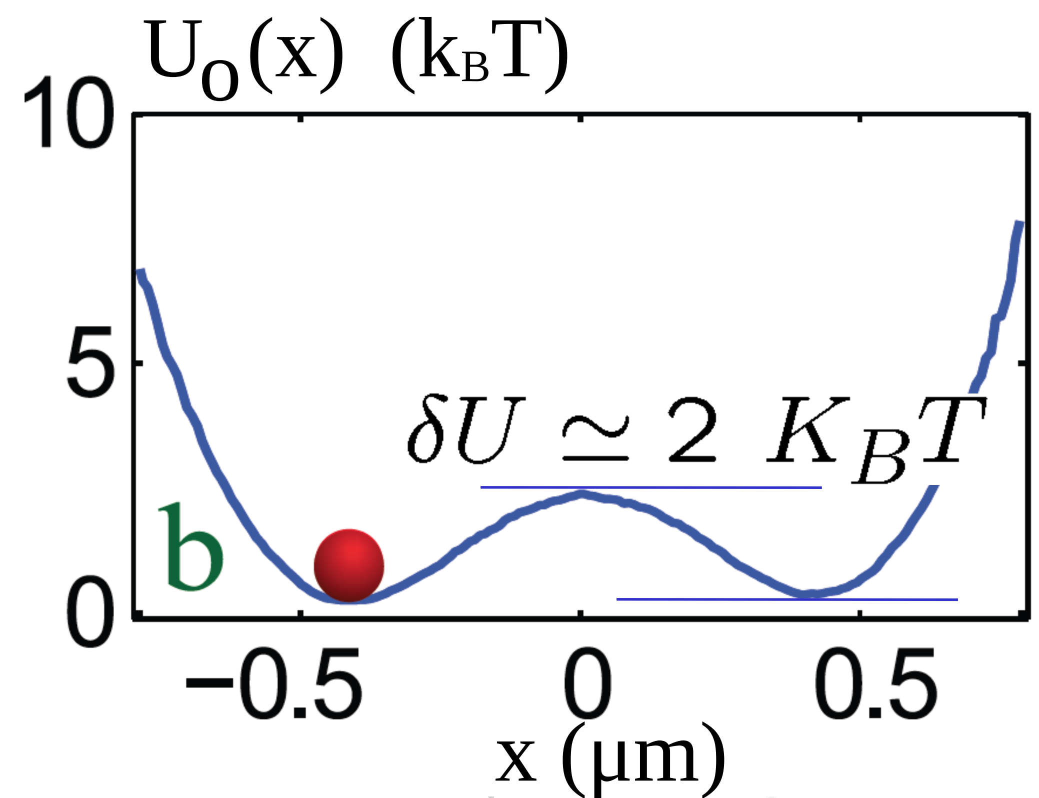
Potential measured using the probability density function of $x(t)$

$$P(x) \propto \exp\left(\frac{-U(x)}{k_B T}\right)$$

Brownian particle trapped by two laser beams







The Kramers time

$$\tau_K = \tau_o \ \exp[\frac{\delta U}{k_B T}]$$

with $\tau_o = 1\ s$

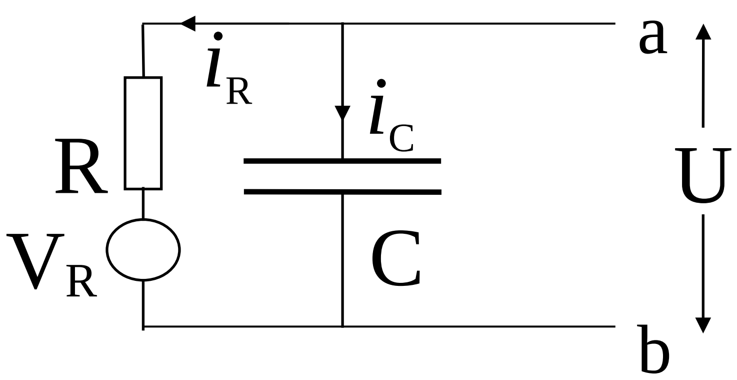
$$U_o(x) = a\ x^4 - b\ x^2\ +\ d\ x$$

Potential measured using detailed balance

$$\frac{\omega_{i \to j}}{\omega_{j \to i}} = e^{-\frac{\Delta U_{j,i}}{k_B T}}$$

with $\Delta U_{j,i} = U(x_j) - U(x_i)$

Electric circuit



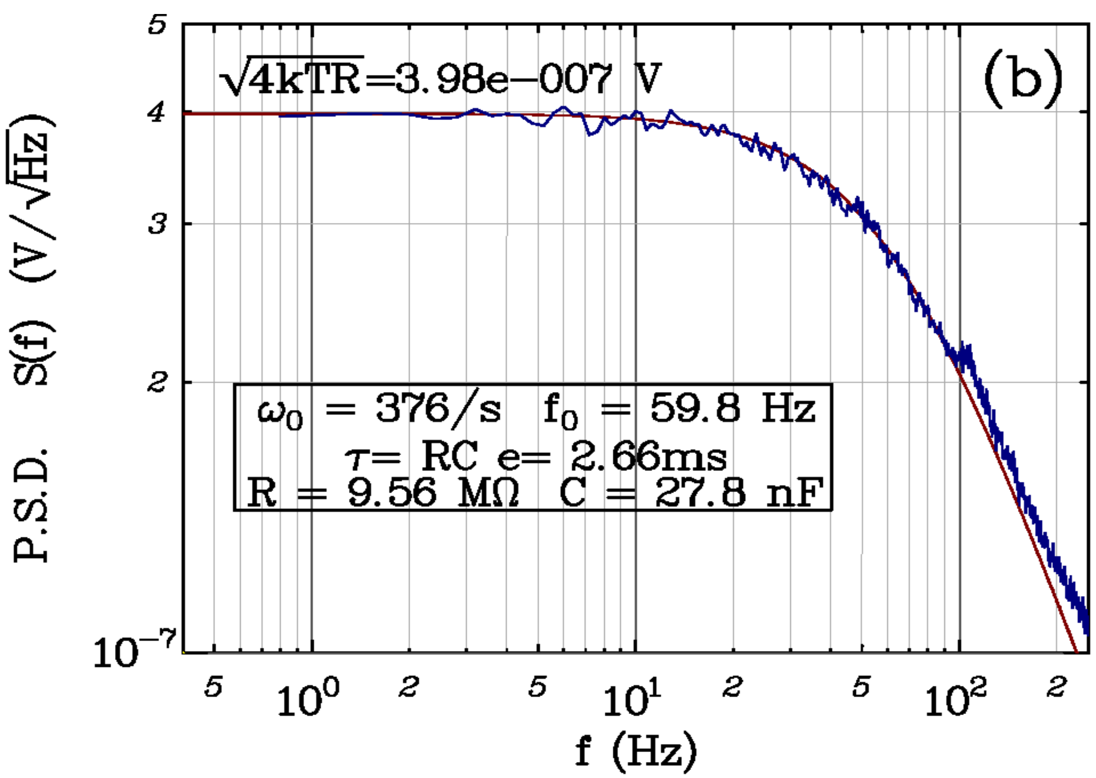
$$R = 9.52\ M\Omega$$

$$C = 200\ pF$$

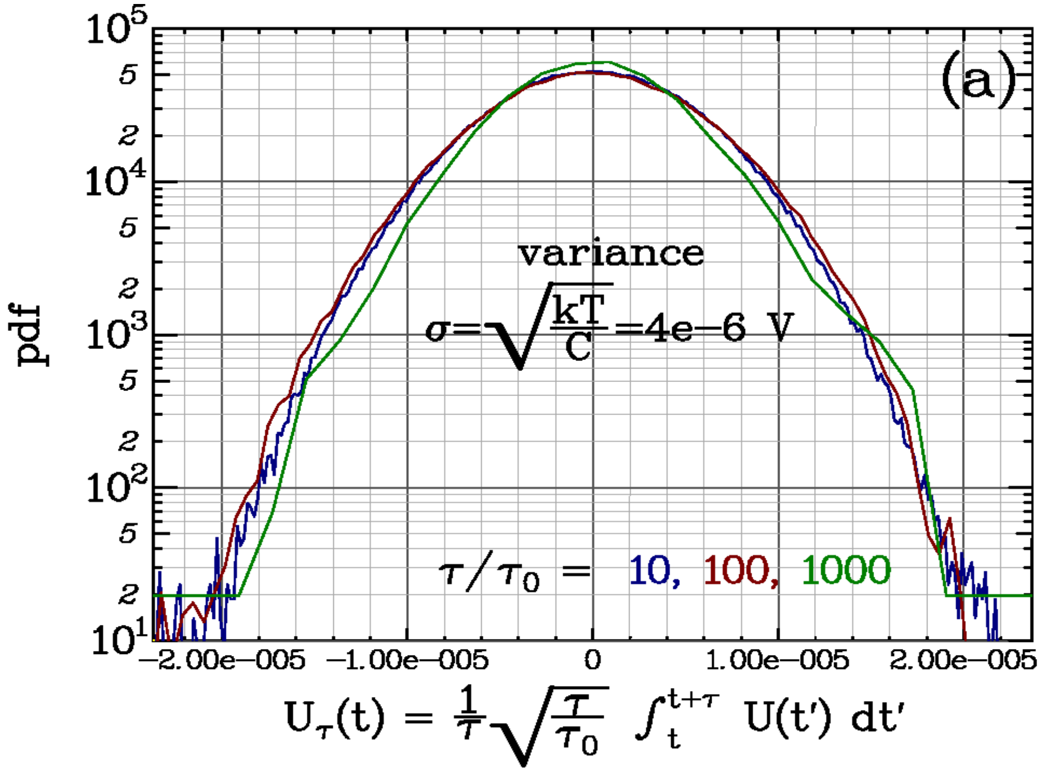
$$\tau_o = R\ C = 3ms$$

$$S_U(f) \simeq 400 \frac{nV}{\sqrt{Hz}} \text{ for } f < 1/(2\pi\ \tau_o)$$

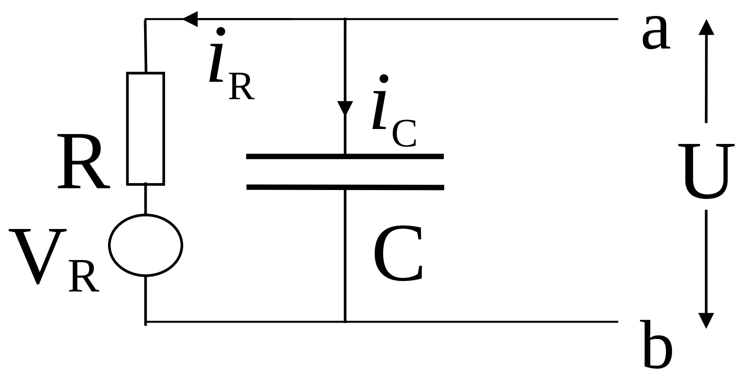
Noise spectrum



Pdf of U



Langevin equation for a resistance in equilibrium



$$U = i_R \; R \; + \; V_R(t)$$

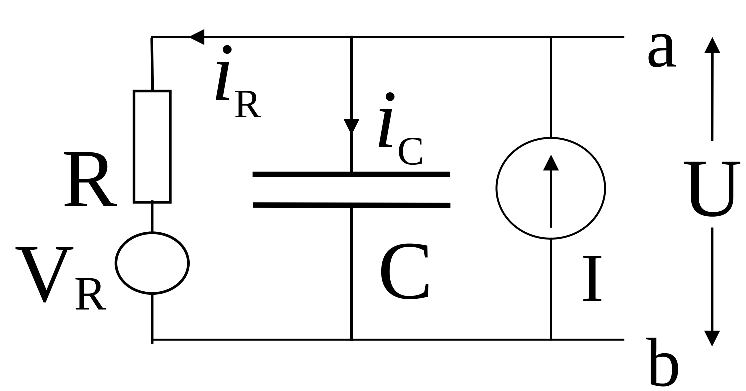
$$\frac{dq_R}{dt} = i_R, \qquad U = \frac{q_C}{C}, \qquad i_R + i_C = 0$$

$$R\,C\frac{dU}{dt} = -U + V_R(t)$$

$$R\frac{dq_R}{dt} = -V_R(t) - \frac{q_R}{C},$$

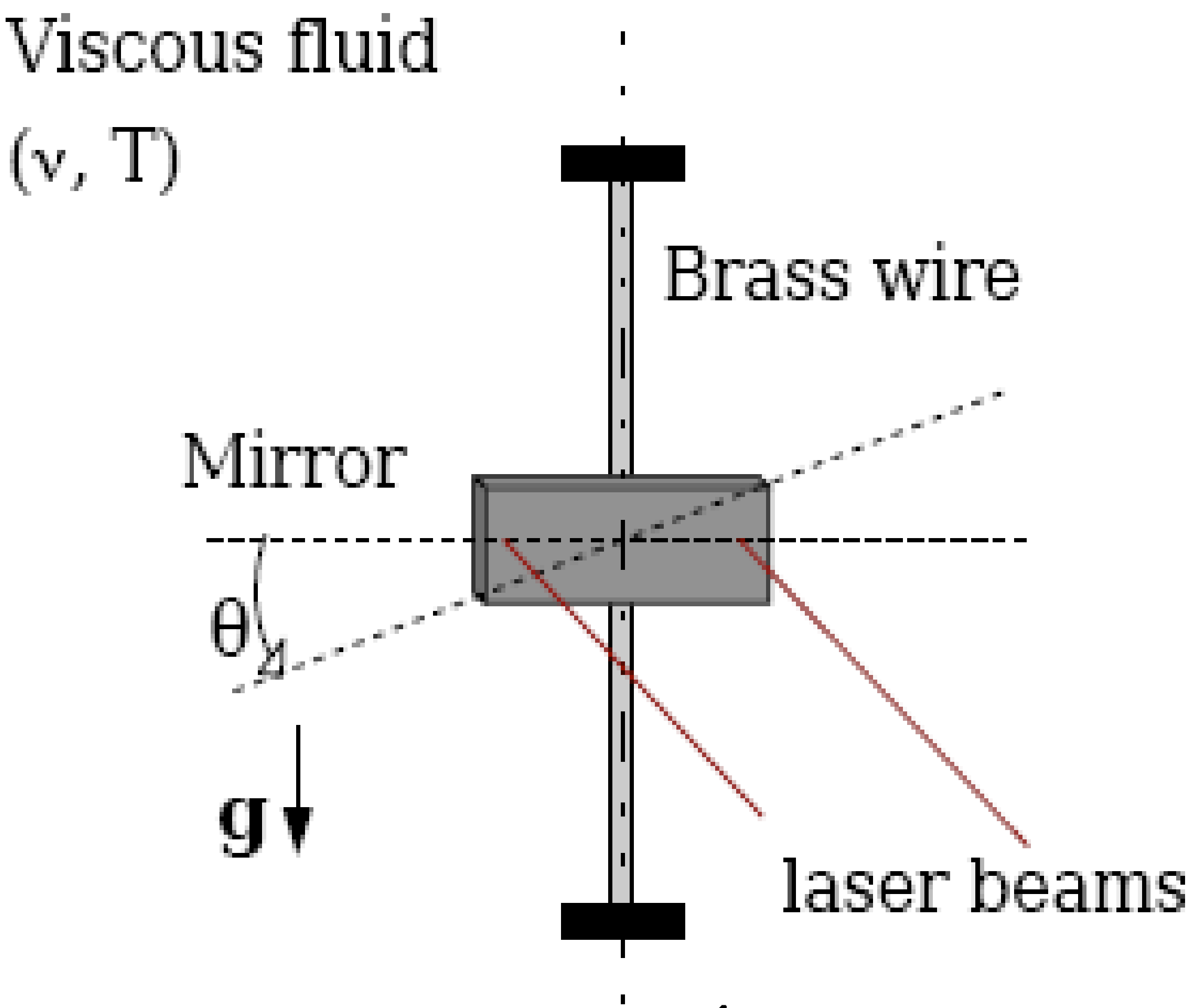
$$S_U(f) = \frac{4k_BT\;R}{(R^2C^2\omega^2+1)} = 4k_BT\,Real[Z(\omega)] = \frac{4k_BT}{\omega}Imag[\frac{\tilde{V}(\omega)}{\tilde{q}(\omega)}]$$

$$Z(\omega) = \frac{\tilde{V}(\omega)}{\tilde{I}(\omega)} = \frac{\tilde{V}(\omega)}{i\omega\tilde{q}(\omega)}$$



$$< U^2 >= k_BT/C$$

The torsion pendulum



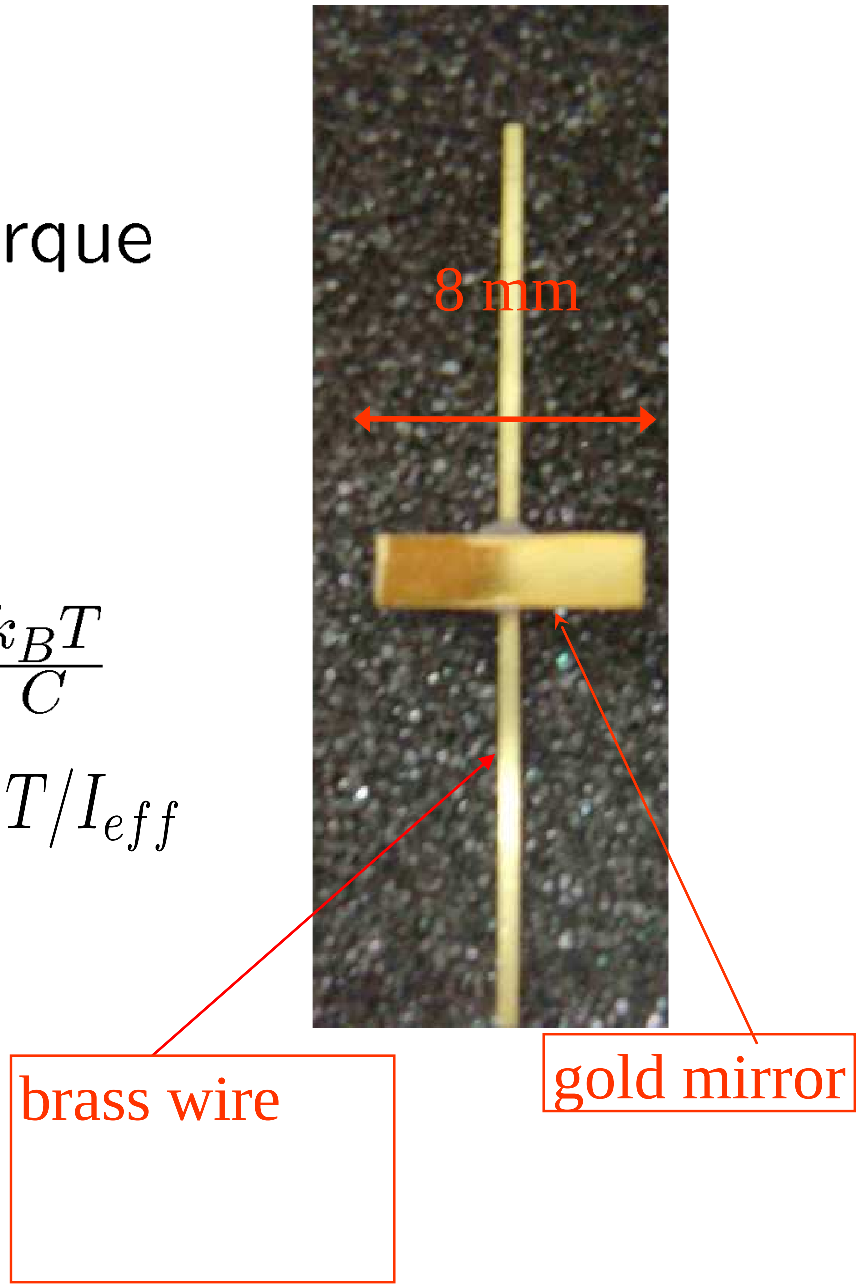
Elastic torque

$M_e = C\ \theta$

Variance

$< \theta^2 >= \frac{k_B T}{C}$

$< \dot{\theta}^2 >= K_B T / I_{eff}$



- stiffness $C = 4.7\ 10^{-4}$ Nm/rad
- typical displacement : $\sqrt{< \theta^2 >} = \sqrt{\frac{K_B\ T}{C}} \simeq$ 3nrad
- A differential interferometer is used to measure θ
- Measurement noise $\simeq$ 25 prad. Signal to noise ratio $\simeq$ 100.

Equation of motion

$$I_{\mathsf{eff}}\,\ddot\theta + \int_{-\infty}^{t} G(t-t')\,\dot\theta(t')\;dt' + C\theta = M + \eta,$$

In Fourier space

$$[-I_{\mathsf{eff}}\,\omega^2 + \widehat{C}]\,\widehat{\theta} = \widehat{M},$$

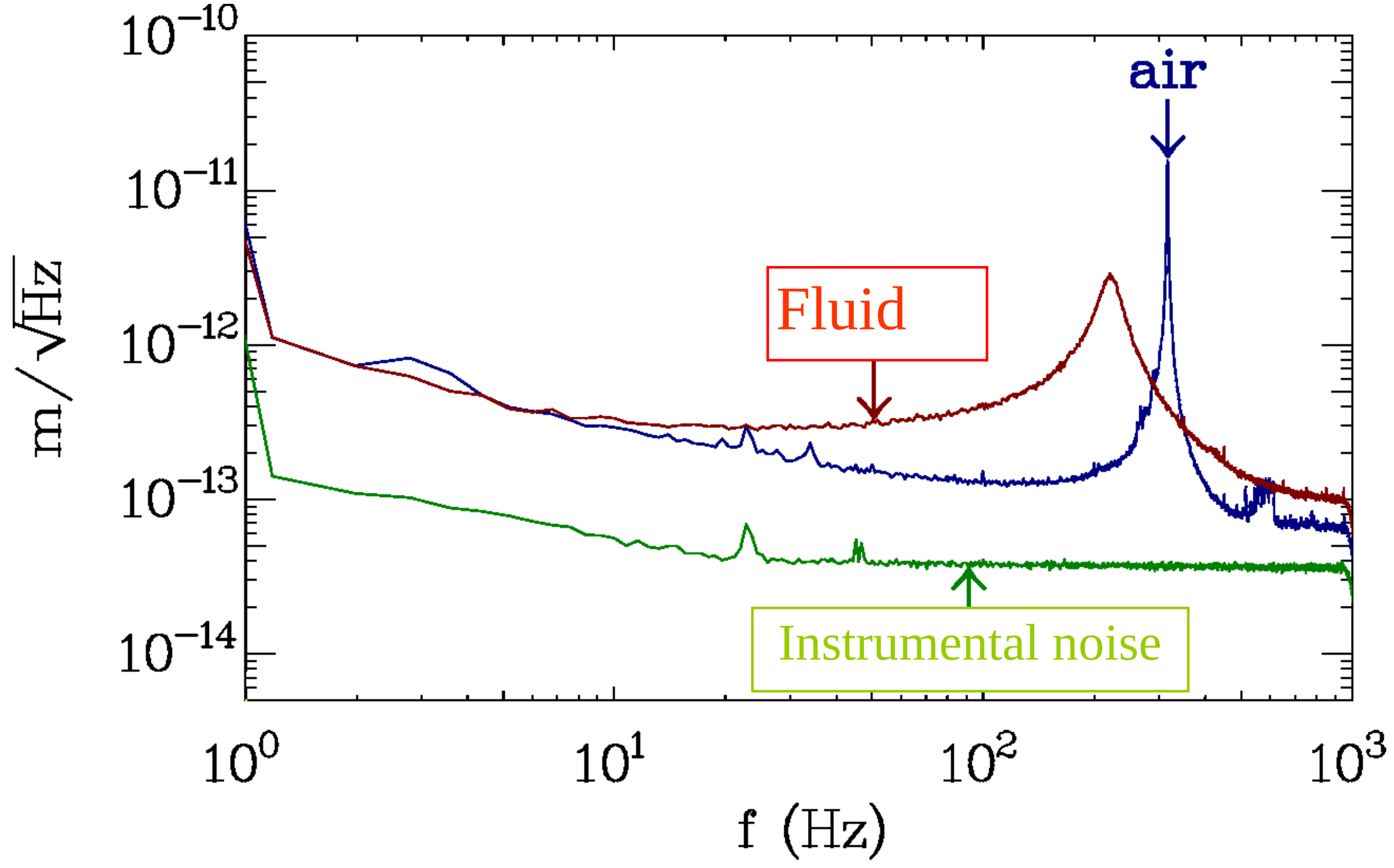
where $\widehat{C} = C + i[C_1'' + \omega\nu]$ is the complex frequency-dependent elastic stiffness

The response function is $\hat\chi = \dfrac{\widehat{\theta}}{\widehat{M}}$

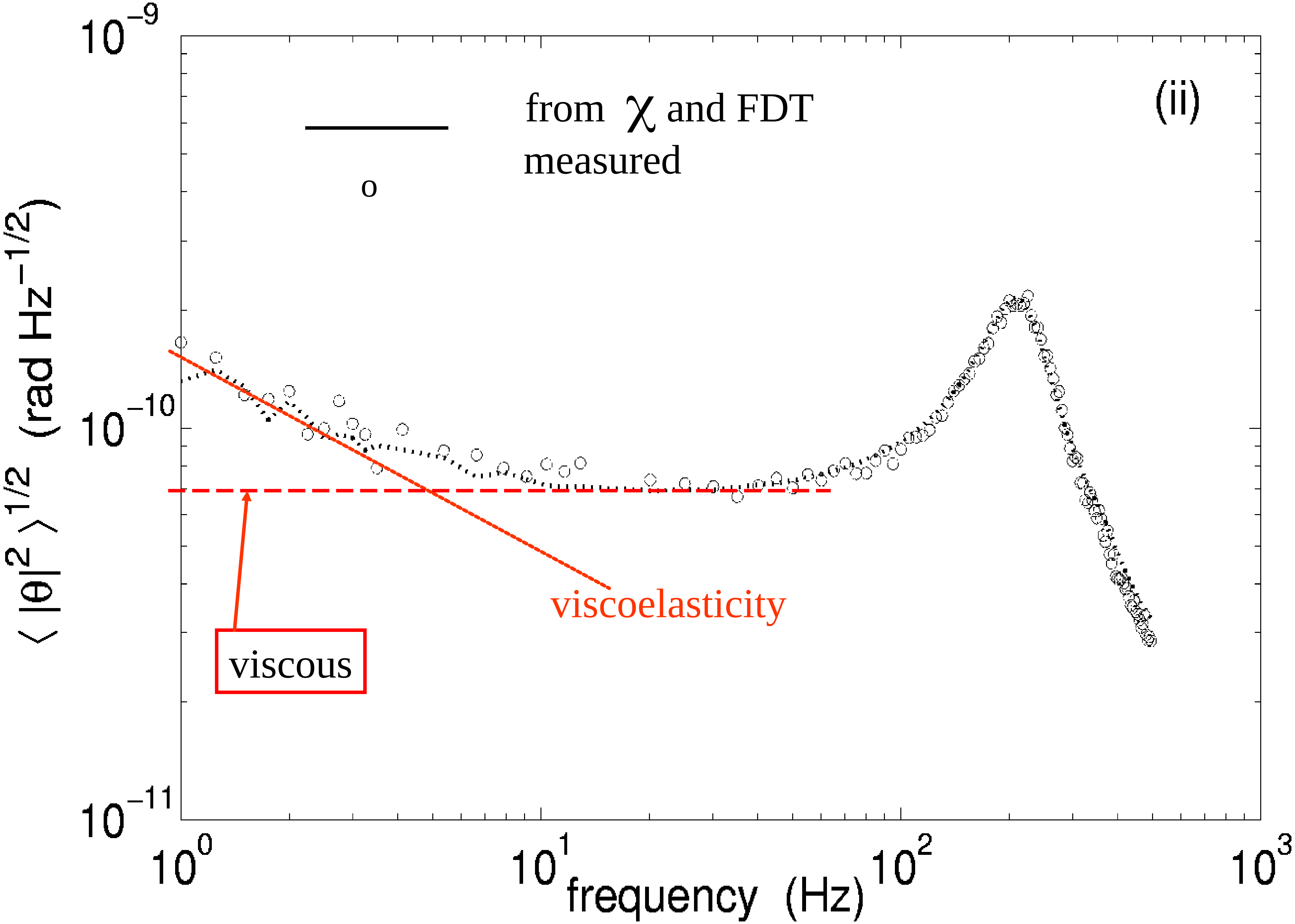
The thermal fluctuation power spectral density is given by FDT

$$\langle|\widehat{\theta}|^2\rangle = \frac{4k_BT}{\omega}\,\mathrm{Im}\,\hat\chi = \frac{4k_BT}{\omega}\frac{C_1'' + \omega\,\nu''}{[-I_{\mathsf{eff}}\,\omega^2 + C]^2 + [C_1'' + \omega\,\nu]^2}.$$

Thermal Noise of Torsion pendulum



Fluctuation Spectrum



$$f_o = \sqrt{C/I_{\text{eff}}}/(2\pi) = 217\text{Hz}$$

relaxation time $\tau_\alpha = 2I_{\text{eff}}/\nu = 9.5\text{ms}.$

Conclusions about the application of equilibrium statistical physics to experiment

Equipartition $k\ x^2 = k_B\ T$

Gibbs Statistics, $P(x) \propto \exp[-\frac{U(x)}{k_B T}]$

detailed balance, $\frac{\omega_{i\to j}}{\omega_{j\to i}} = e^{-\frac{\Delta U_{j,i}}{k_B T}}$ $\Delta U_{j,i} = U(x_j) - U(x_i)$

FDT, $S_x(f) = \frac{4k_B T}{\omega} Imag[\mathrm{Resp}(\omega)]$

allow us to fully calibrate optical traps, electric circuits and harmonic oscillators

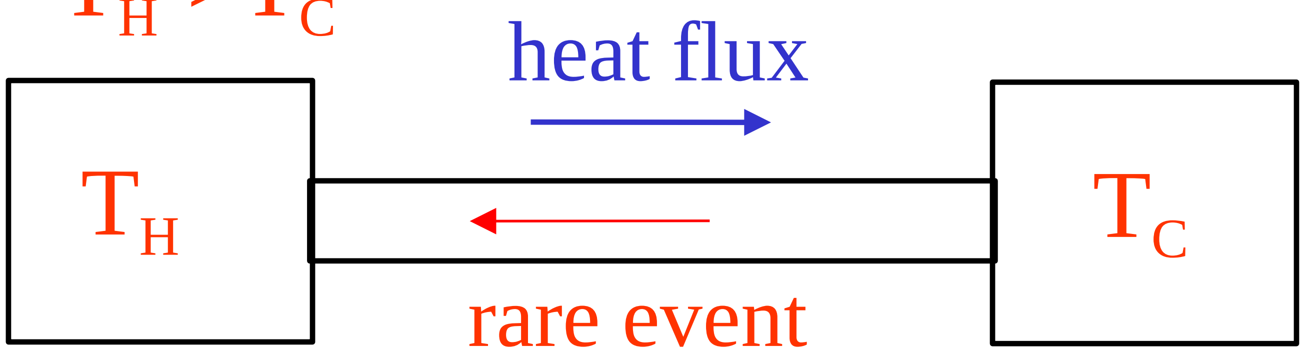
Using FDT and Kramers-Kroening relations one can extract the response of the system using only the thermal fluctuations.

Fluctuations in out of equilibrium systems

ENS DE LYON

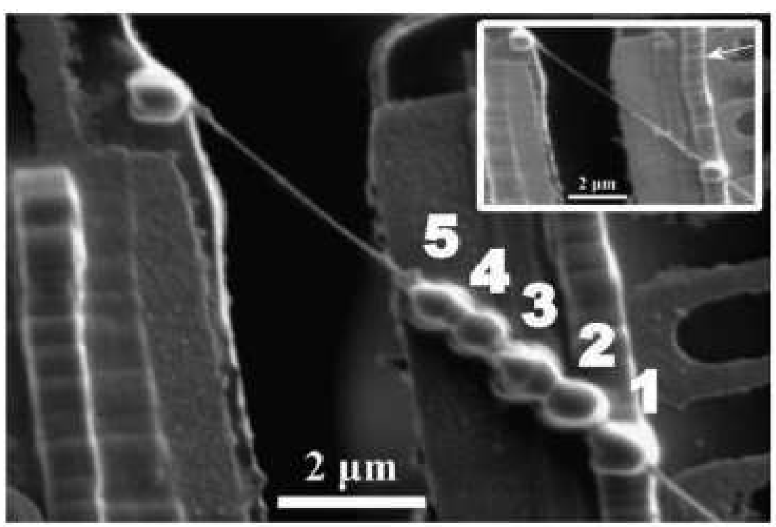
Steady current through a system in contact between two reservoirs

$T_H > T_C$



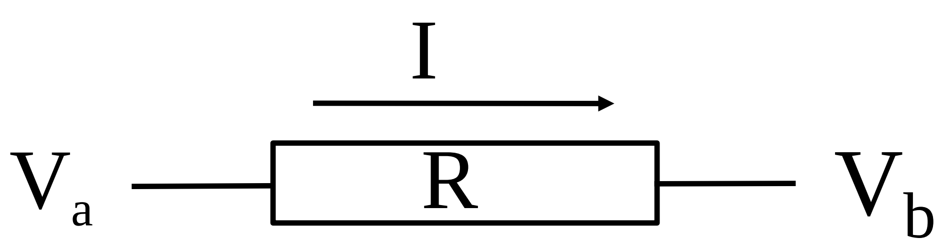
What is the probabilty that the heat flows from the cold to the hot reservoir ?

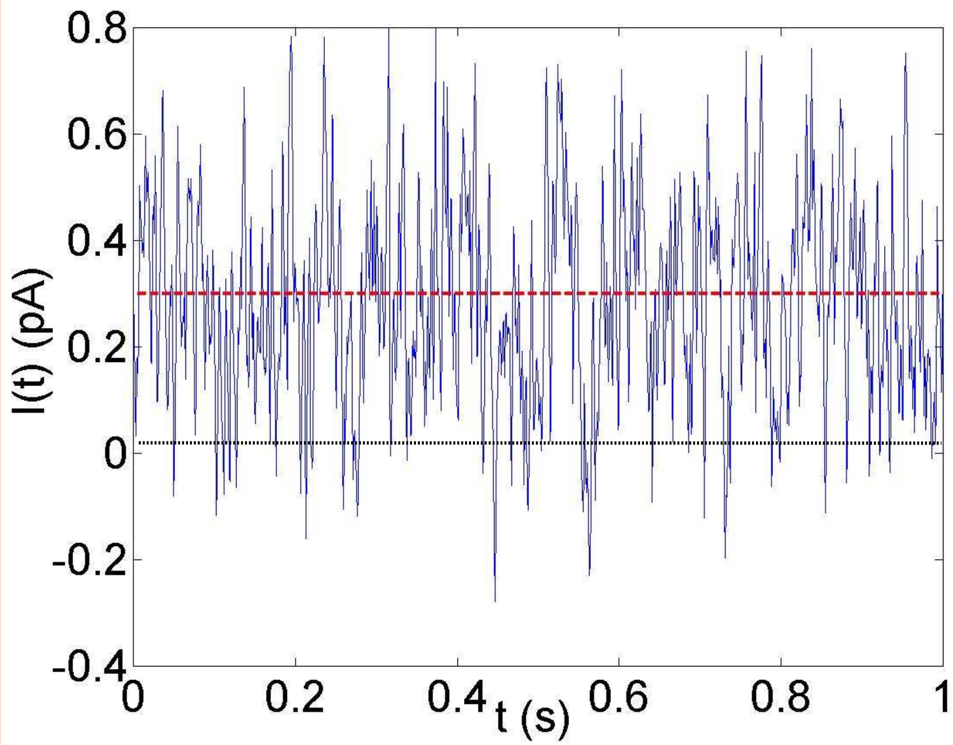
Thermal conductivity in nanotubes



C.W. Chang, et al.
PRL 101, 075903 (2008)

Electric current





R.Van Zon, et al
PRL 92, 130601 (2004).

N. Garnier, S. Ciliberto
PRE 71, 060101 (2005)

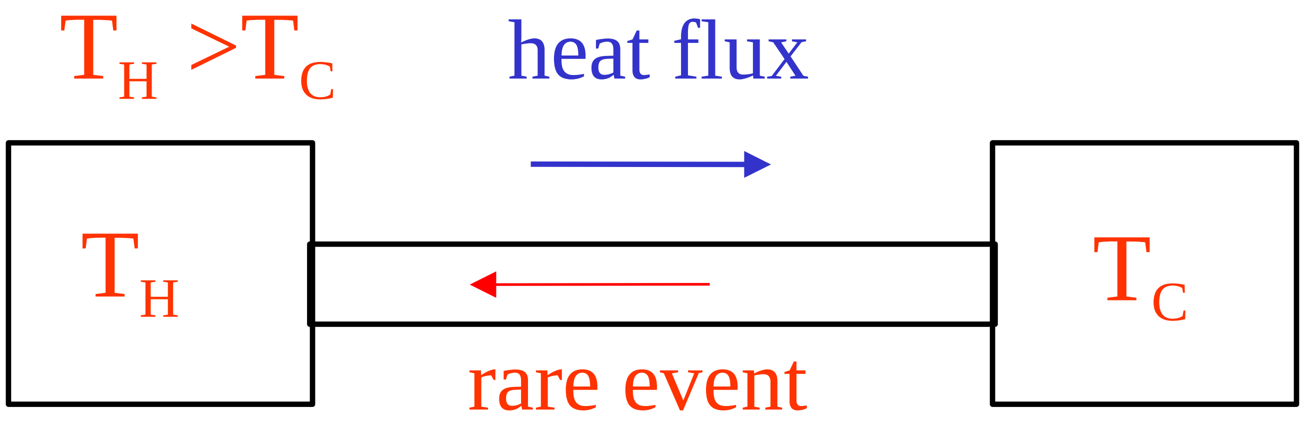
$$\bar{I} = \frac{(V_b - V_a)}{R}$$

Injected power

$10^{-19} W$

Fluctuations in out of equilibrium systems

Steady current through a system in contact between two reservoirs



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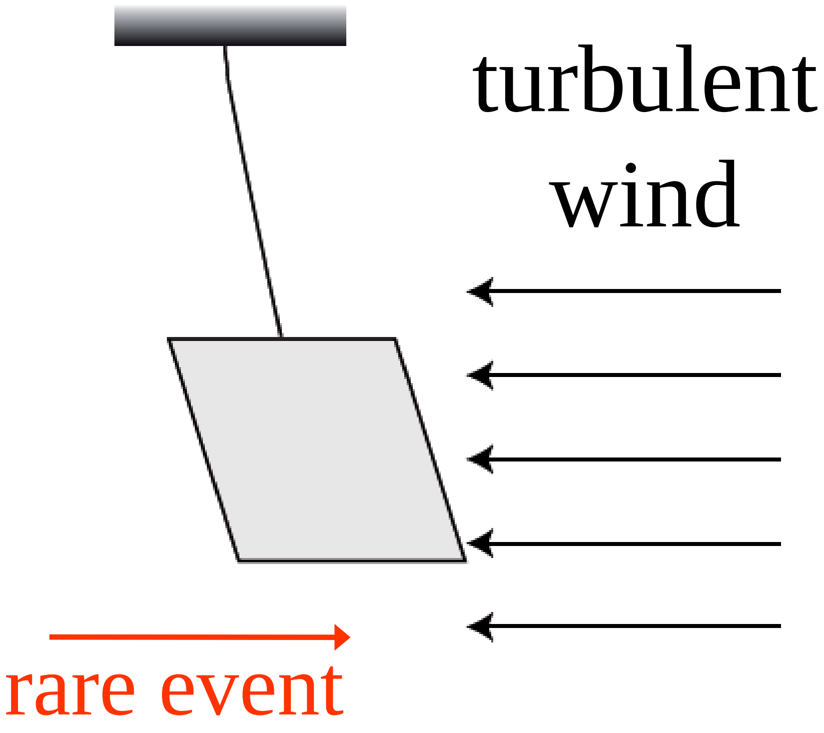
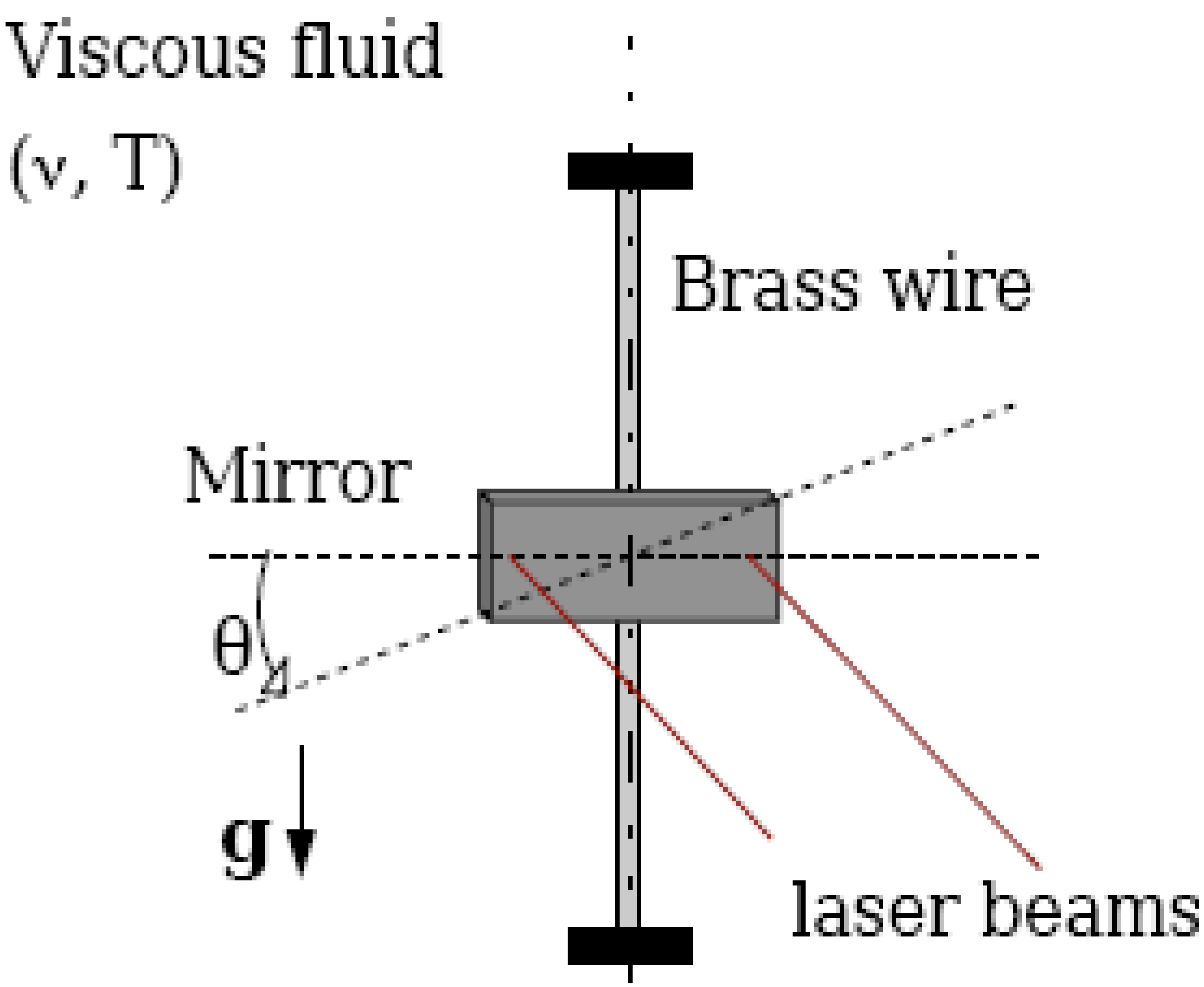


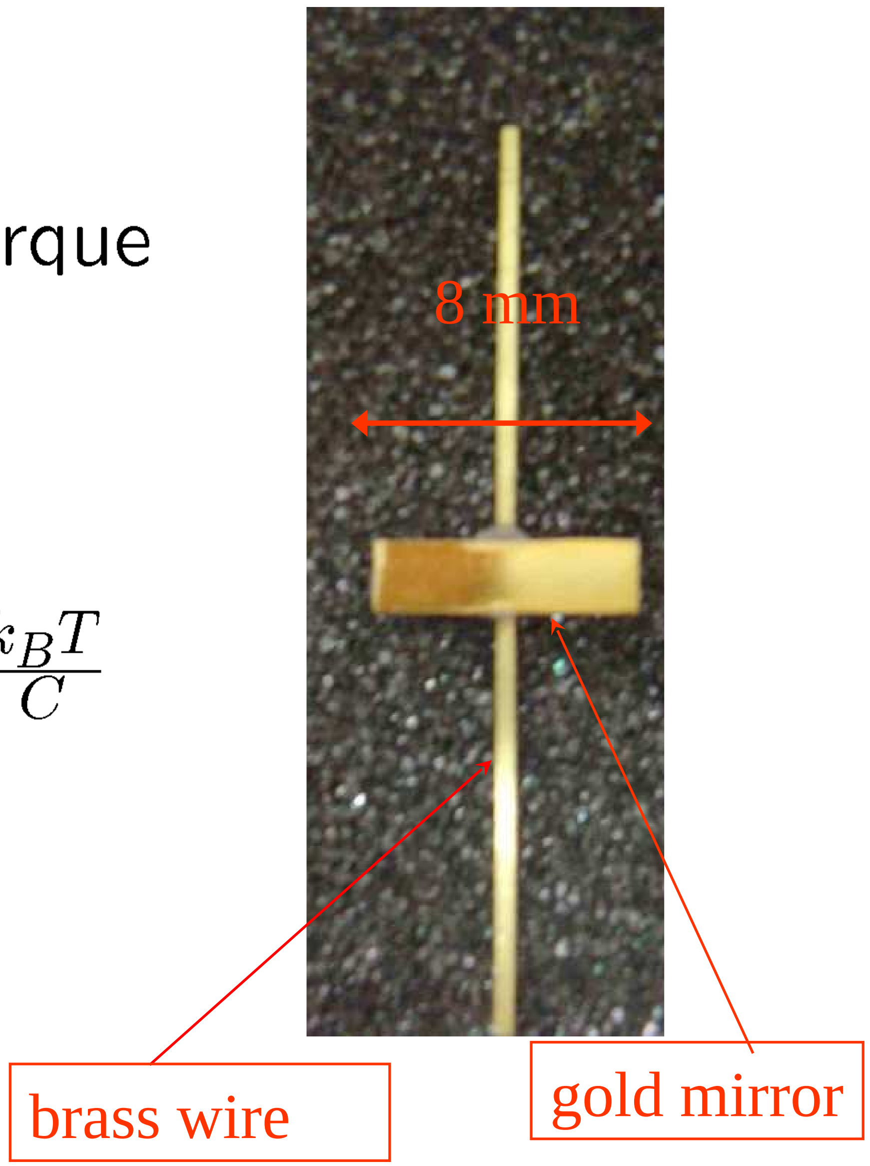
What is the probability that the object moves against the wind ?

The torsion pendulum



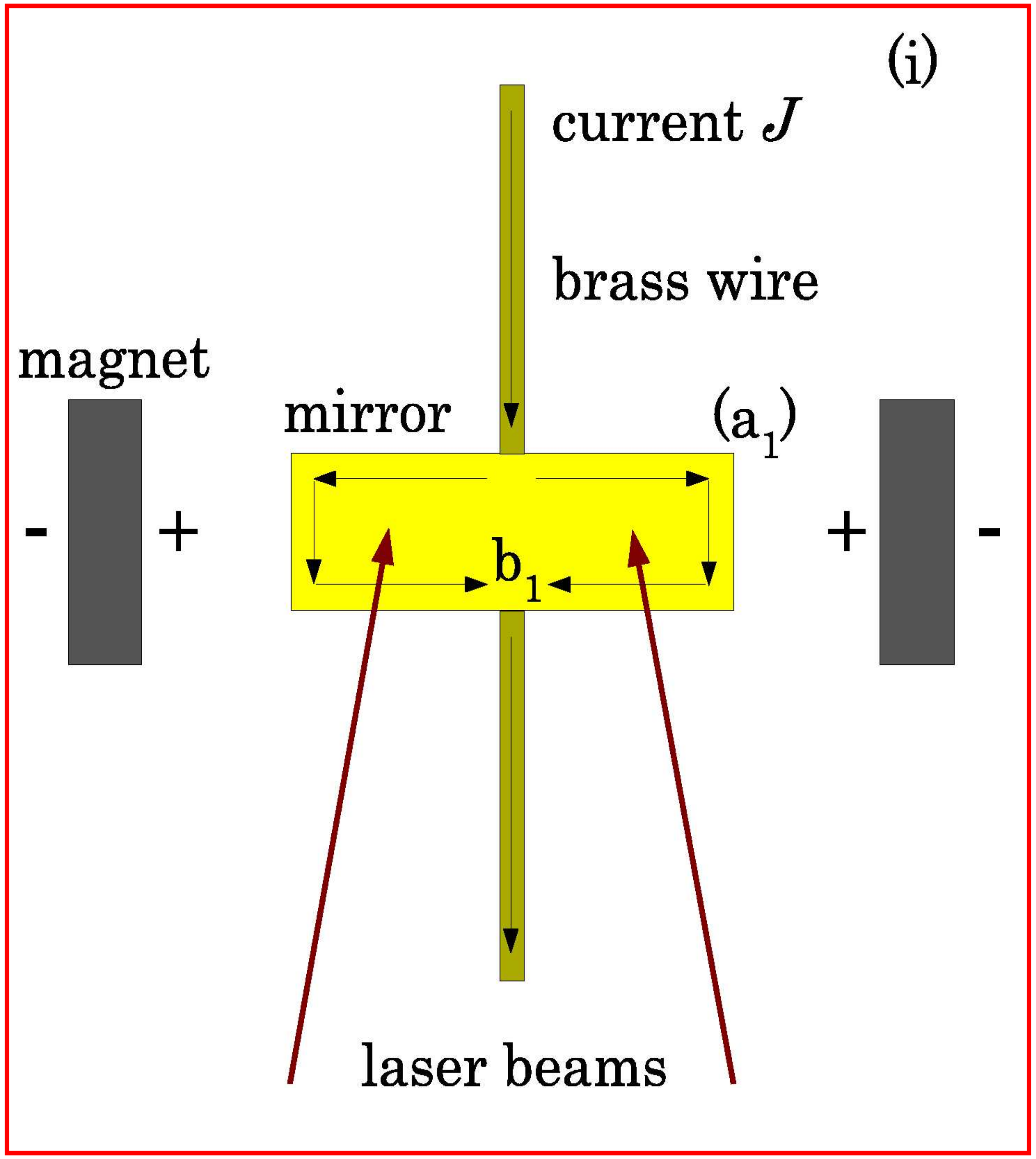
Elastic torque
$M_e = C\ \theta$

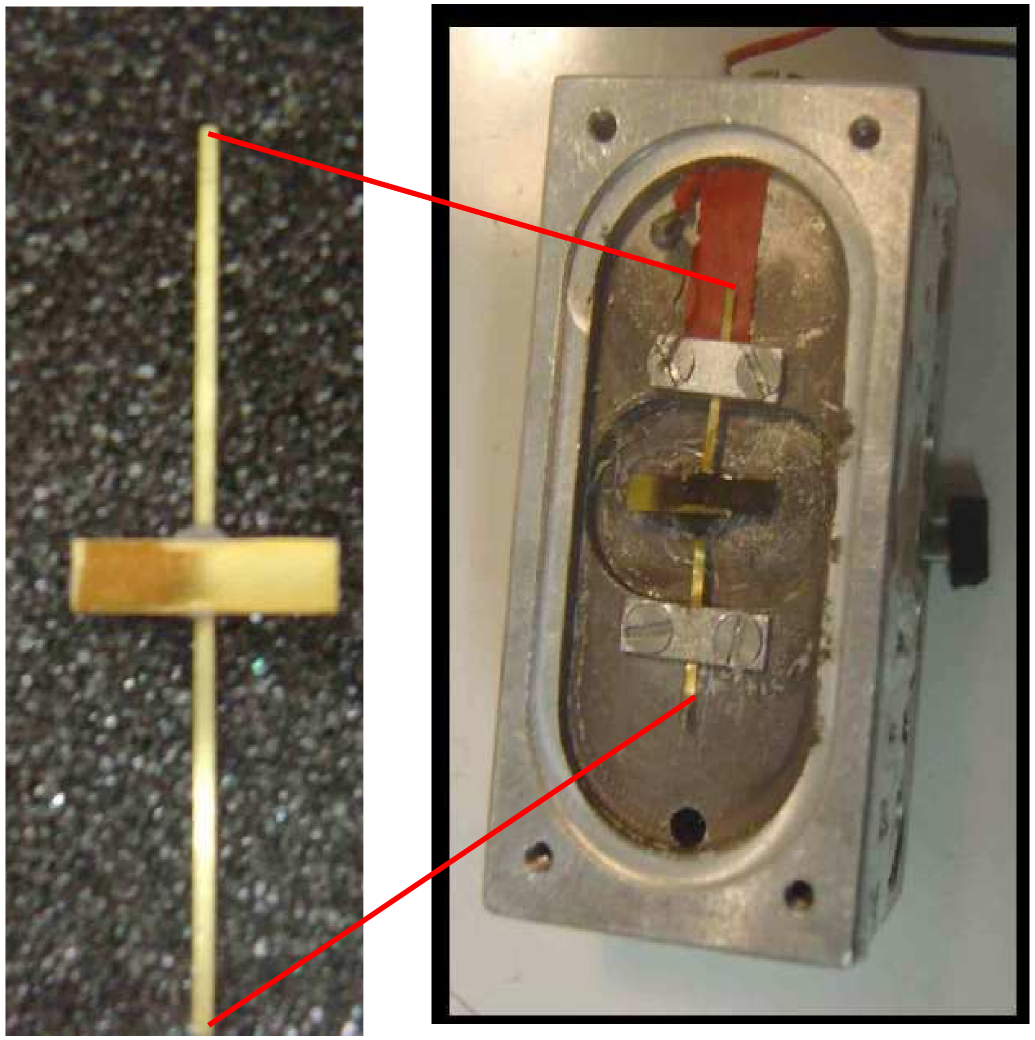
Variance
$< \theta^2 >= \frac{k_B T}{C}$



- stiffness $C = 4.7\ 10^{-4}$ Nm/rad
- typical displacement : $\sqrt{< \theta^2 >} = \sqrt{\frac{K_B\ T}{C}} \simeq$ 3nrad
- A differential interferometer is used to measure θ
- Measurement noise $\simeq$ 25 prad. Signal to noise ratio $\simeq$ 100.

External Forcing





The applied torque $M \propto J$

Typical applied torque < 50pN m

$$I_{\text{eff}} \frac{d^2\theta}{dt^2} + \nu \frac{d\theta}{dt} + C\theta = M + \eta$$

Equation of motion

$$I_{\text{eff}}\,\ddot{\theta} + \int_{-\infty}^{t} G(t-t')\,\dot{\theta}(t')\;dt' + C\theta = M + \eta,$$

In Fourier space

$$[-I_{\text{eff}}\,\omega^2 + \widehat{C}]\,\widehat{\theta} = \widehat{M},$$

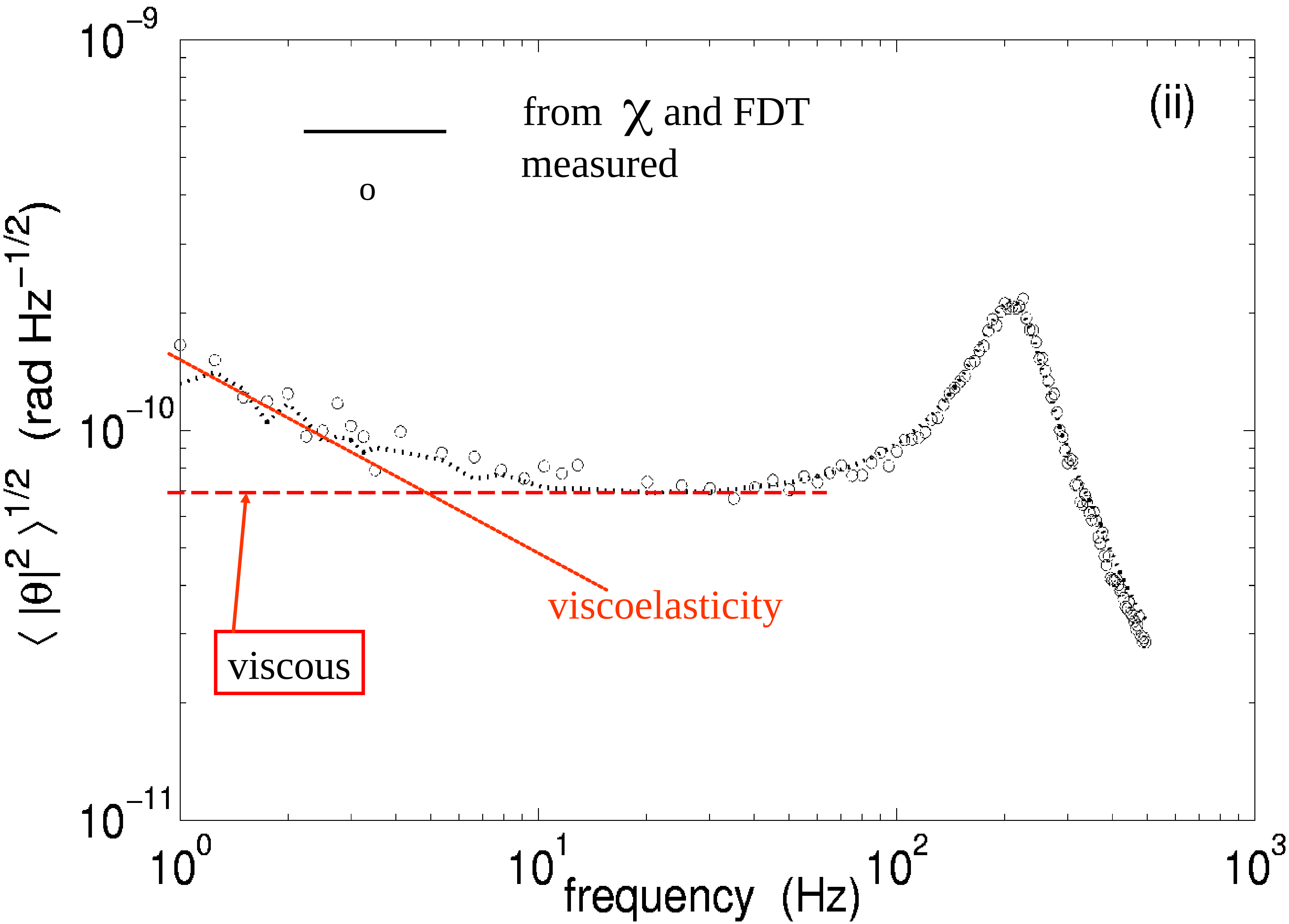
where $\widehat{C} = C + i[C_1'' + \omega\nu]$ is the complex frequency-dependent elastic stiffness

The response function is $\hat{\chi} = \dfrac{\widehat{\theta}}{\widehat{M}}$

The thermal fluctuation power spectral density is given by FDT

$$\langle|\widehat{\theta}|^2\rangle = \frac{4k_BT}{\omega}\,\text{Im}\,\hat{\chi} = \frac{4k_BT}{\omega}\frac{C_1'' + \omega\,\nu''}{[-I_{\text{eff}}\,\omega^2 + C]^2 + [C_1'' + \omega\,\nu]^2}.$$

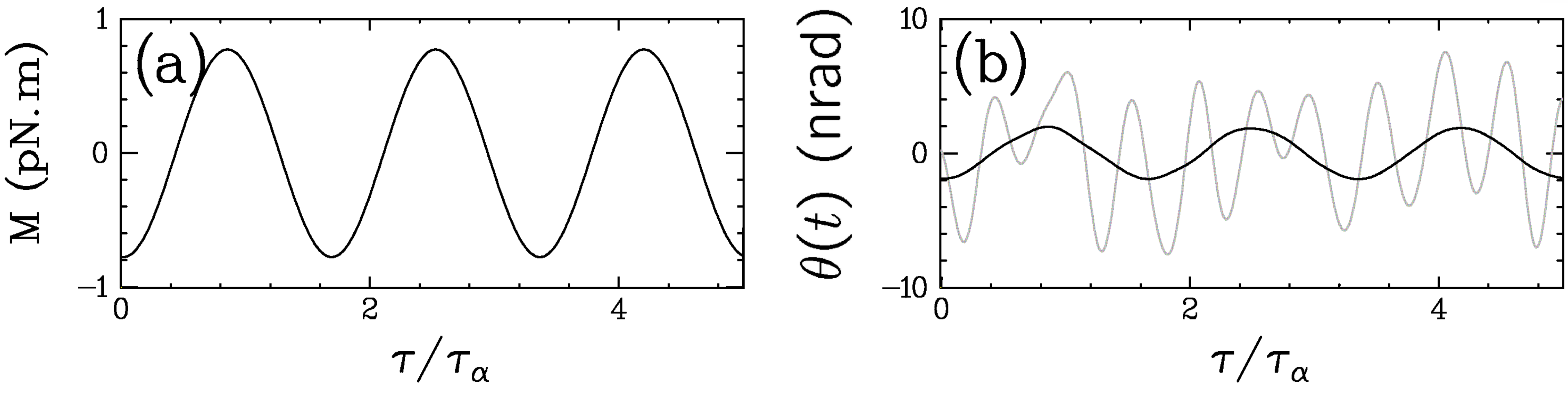
Fluctuation Spectrum



$f_o = \sqrt{C/I_{\text{eff}}}/(2\pi) = 217\text{Hz}$

relaxation time $\tau_\alpha = 2I_{\text{eff}}/\nu = 9.5\text{ms}$.

Work during periodic forcing



$$M(t) = M_o \sin \omega_d t$$

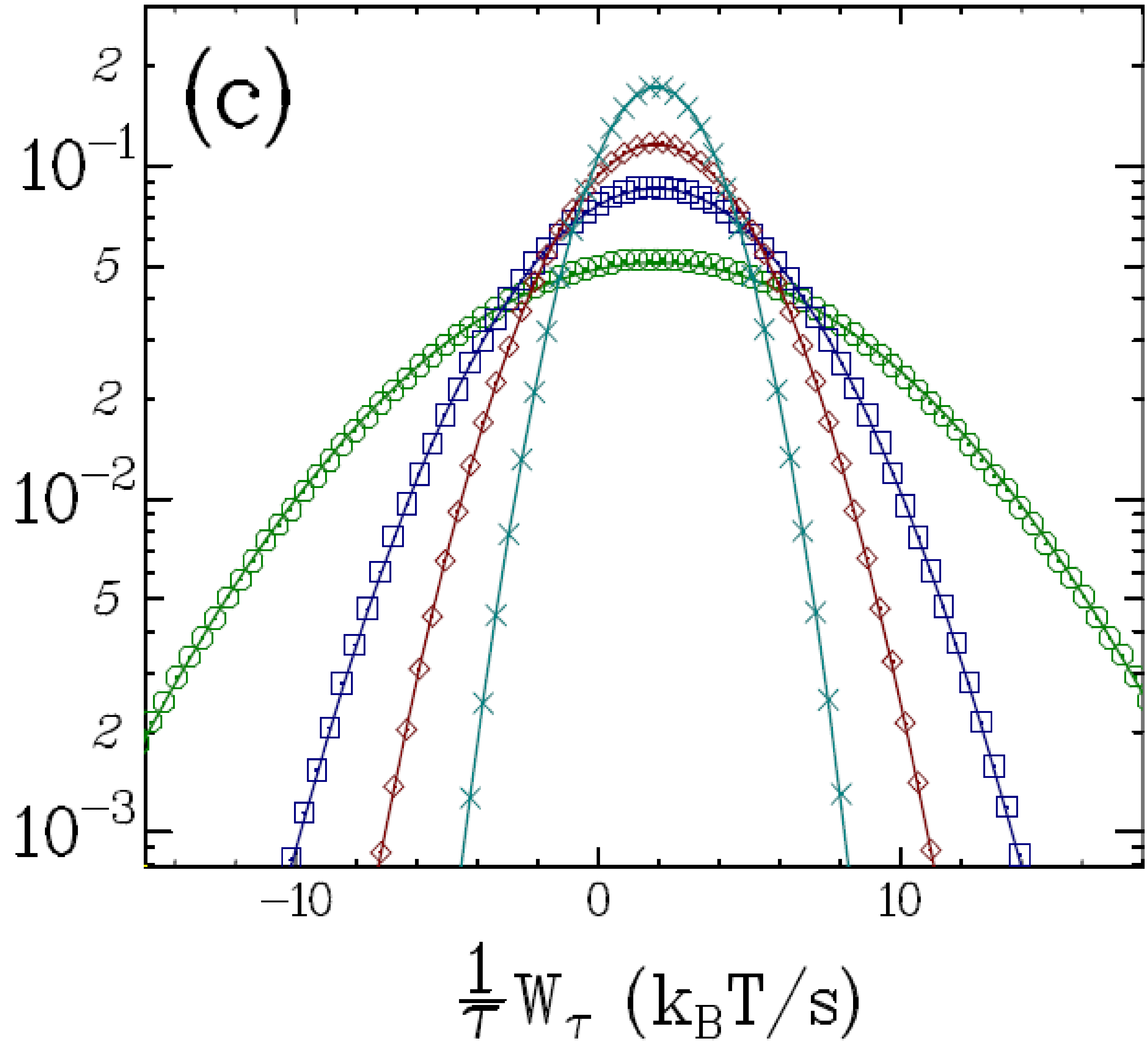
$$W_n = W_{\tau=\tau_n} = \int_{t_i}^{t_i+\tau_n} M(t) \frac{d\theta}{dt} dt \,,$$

with $\tau_n = n 2\pi/\omega_d$

W_τ is a fluctuating quantity

PDF of the work

$n = 7$ (○), $n = 15$ (□), $n = 25$ (◇) and $n = 50$ (×).



Energy Balance (I)

Sekimoto K, Progress of Theoretical Phys. supplement (130), 17 (1998).

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

- We multiply this equation by $\dot{\theta}$ and we get : $\frac{dU(t)}{dt} = P_{inj}(t) - P_{dis}(t)$

- The injected power : $P_{inj}(t) = M(t)\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}$

- The dissipated power : $P_{diss}(t) = \nu \left[\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}\right]^2 - \sqrt{2k_B T \nu}\ \ \eta(t)\ \frac{\mathrm{d}\theta(t)}{\mathrm{d}t}.$

- The internal energy : $U(t) = \left\{\frac{1}{2} I_{\text{eff}} \left[\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}\right]^2 + C\ \theta(t)^2\right\}.$

Energy Balance (II)

Sekimoto K, Progress of Theoretical Phys. supplement (130), 17 (1998).

$$\frac{dU(t)}{dt} = P_{inj}(t) - P_{dis}(t)$$

- We integrate over a time τ starting at a time t_i. We get:

$$\Delta U_\tau = U(t_i+\tau) - U(t_i) = W_\tau - Q_\tau$$

- W_τ is the work done on the system over a time τ :

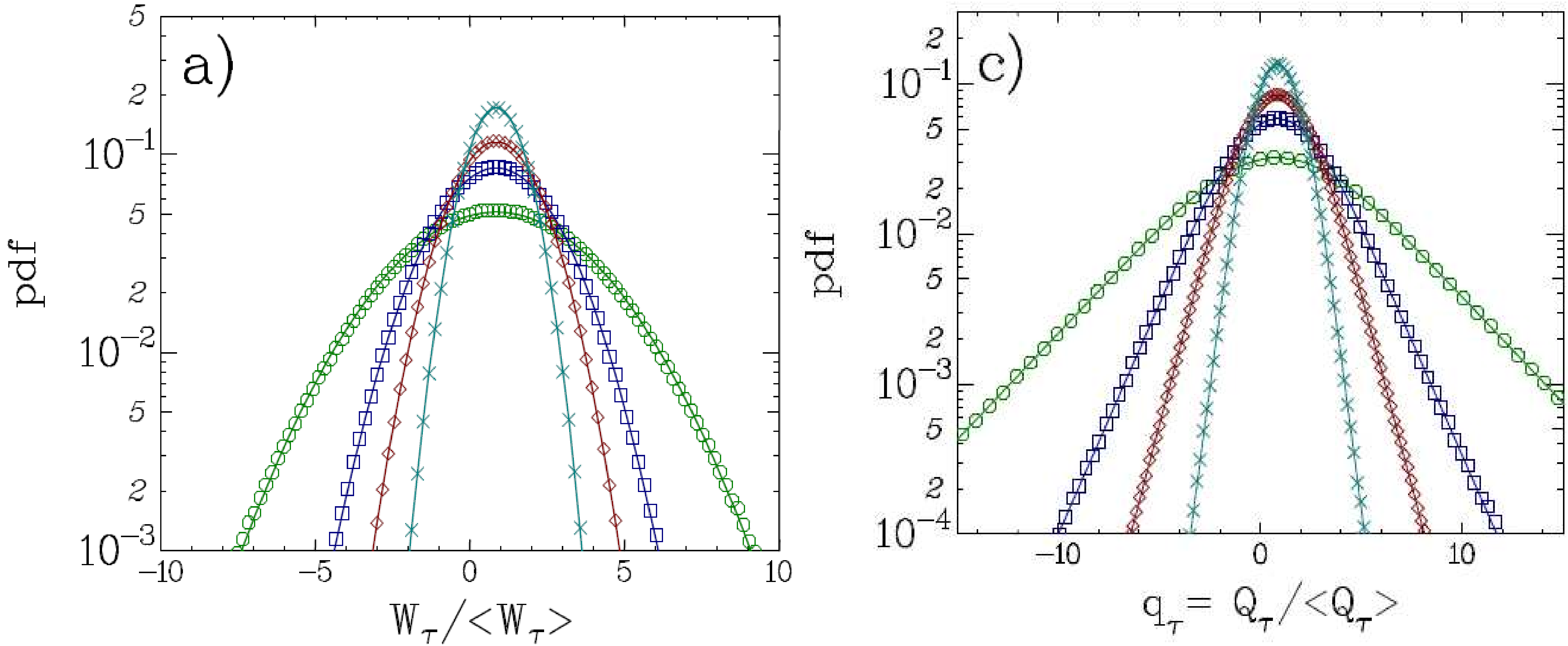
$$W_\tau = \int_{t_i}^{t_i+\tau} M(t') \frac{\mathrm{d}\theta}{\mathrm{d}t}(t') \mathrm{d}t'$$

- $Q_\tau = W_\tau - \Delta U_\tau$ is the heat dissipated by the system.

We study the fluctuations of W_τ, Q_τ and
the Fluctuation Theorem for these two quantities

PDF of the work and of the heat

$n = 7$ ($\circ$), $n = 15$ ($\square$), $n = 25$ ($\diamond$) and $n = 50$ ($\times$).



$$< W_\tau > = < Q_\tau > \simeq 0.04\ n\ (k_B T)$$

Stationary State Fluctuation Theorem (SSFT)

(stochastic systems)

$$\log \frac{P(X_\tau)}{P(-X_\tau)} = \frac{X_\tau}{k_B T}\,\Sigma(\tau)$$

where $\Sigma(\tau) \to 1$ for $\tau \to \infty$

X_τ stands either for Q_τ or for W_τ

The Fluctuation Theorem fixes the symmetry of P(X) around zero

Transient Fluctuation Theorem (TFT)

At $\tau = 0$ the system is in equilibrium

$$\Sigma(\tau) = 1 \qquad \forall \tau$$

Short comment on FT for Gaussian P(Xτ)

FT imposes that:

$$\log \frac{P(X_\tau)}{P(-X_\tau)} = \frac{X_\tau}{k_B T} \Sigma(\tau)$$

if $$P(X_\tau) = A \ \exp[-\frac{(X_\tau - < X_\tau >)^2}{2\delta_\tau^2}]$$

then from FT $$\delta_\tau^2 = 2 \ k_B \ T \ < X_\tau >$$

and $$\frac{\delta_\tau}{< X_\tau >} = \sqrt{\frac{2 \ k_B \ T}{< X_\tau >}}$$

The Fluctuation Theorem (FT)

- 1993 First numercial evidence of fluctuations relations
  D. Evans, E.D.G. Cohen and G. P. Morris.

- 1994 Proof of the transient fluctuation theorem (TFT)
  D. Evans and D.J.Searles

- 1995 Proof of the Stationary State Fluctuation Theorem (SSFT) for dynamical systems.
  G.Gallavotti and E.D.G. Cohen.

- 1997 Later proofs of FT for systems with stochastic dynamics were given by
  J. Kurchan, J. Lebowitz and E. Spohn, J. Farago.

- 2003 R. van Zon and E.G.D. Cohen extended the results
  to the heat fluctuations in stochastic systems

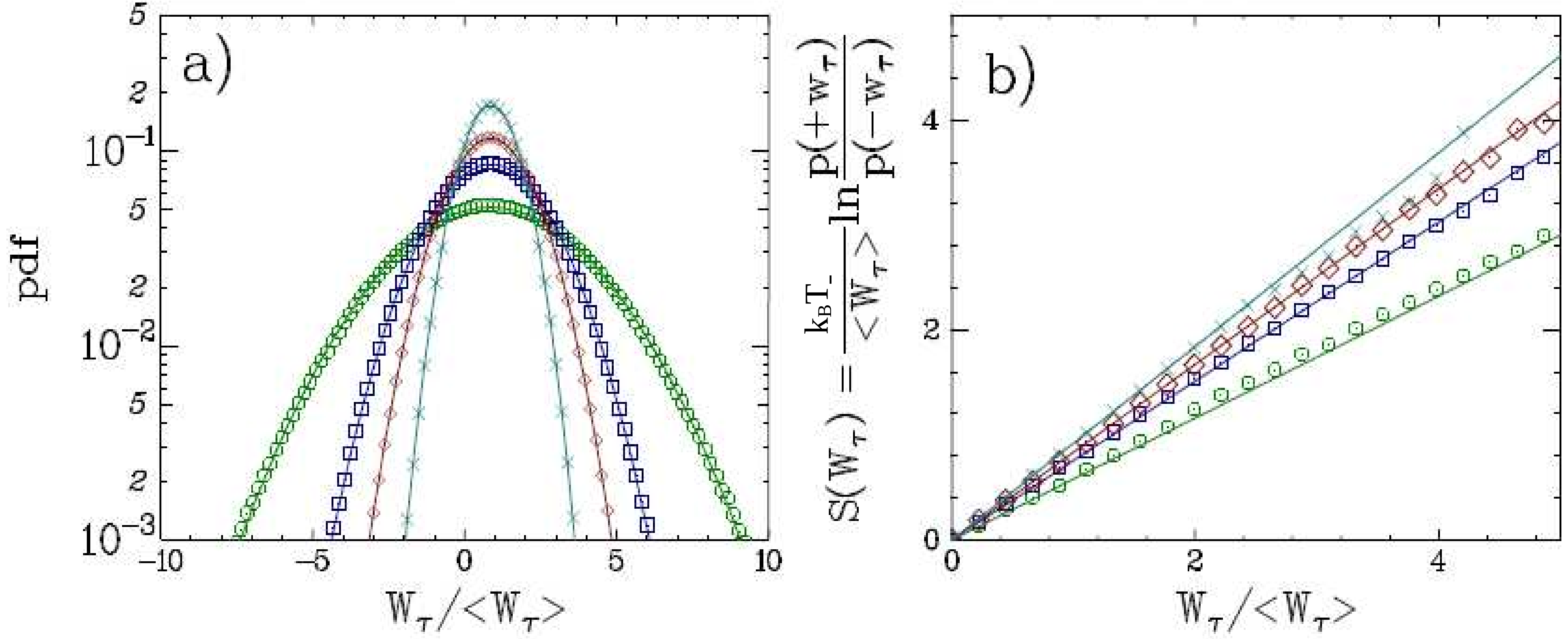
- New kinds of relations for suitably defined entropies have been proposed for stochastic system.
  K. Sekimoto, S. Sasa, U. Seifert, P. Gaspard, C. Maess, K. Gadwedzky,
  M. Esposito, C. Van den Broeck

SSFT periodic forcing: W

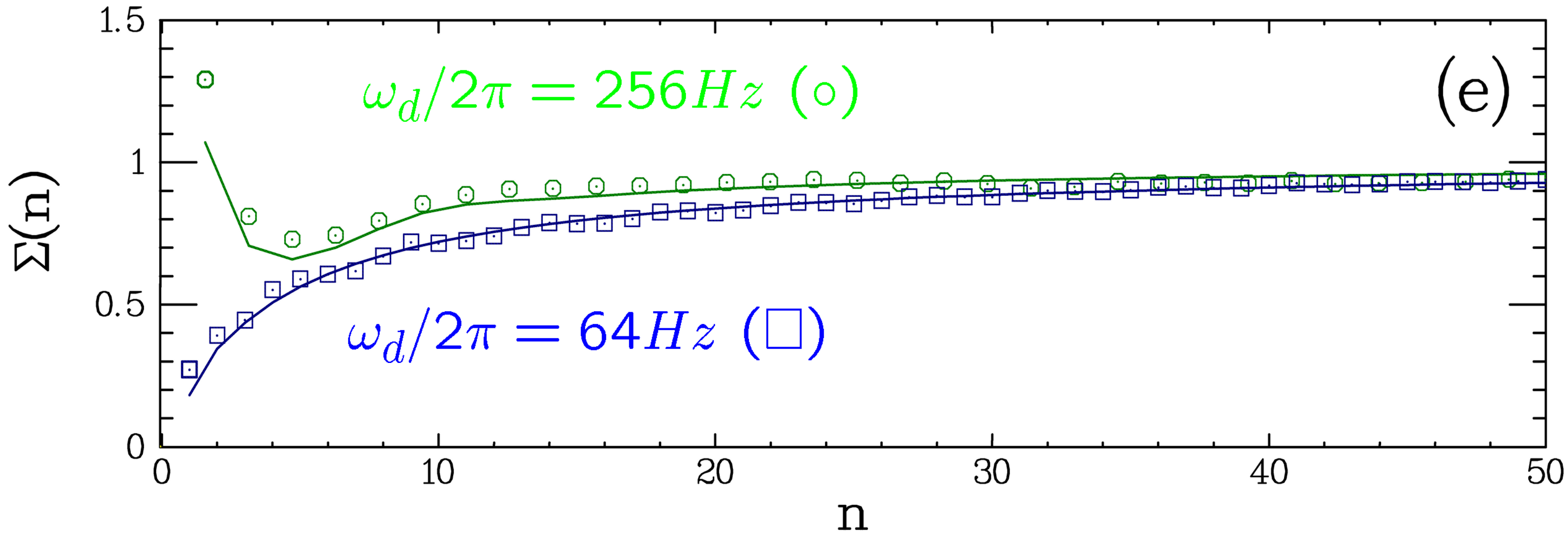
$$\frac{k_B\ T}{< W_\tau >} \log \frac{P(W_\tau)}{P(-W_\tau)} = \frac{W_\tau}{< W_\tau >} \Sigma(\tau)$$

$$\omega_d/2\pi = 64\text{Hz} < \omega_o/2\pi$$

$n = 7$ ($\circ$), $n = 15$ ($\square$), $n = 25$ ($\diamond$) and $n = 50$ ($\times$).



SSFT periodic forcing: Σ for W



$$\frac{k_B\ T}{< W_\tau >} \log \frac{P(W_\tau)}{P(-W_\tau)} = \frac{W_\tau}{< W_\tau >} \Sigma(\tau)$$

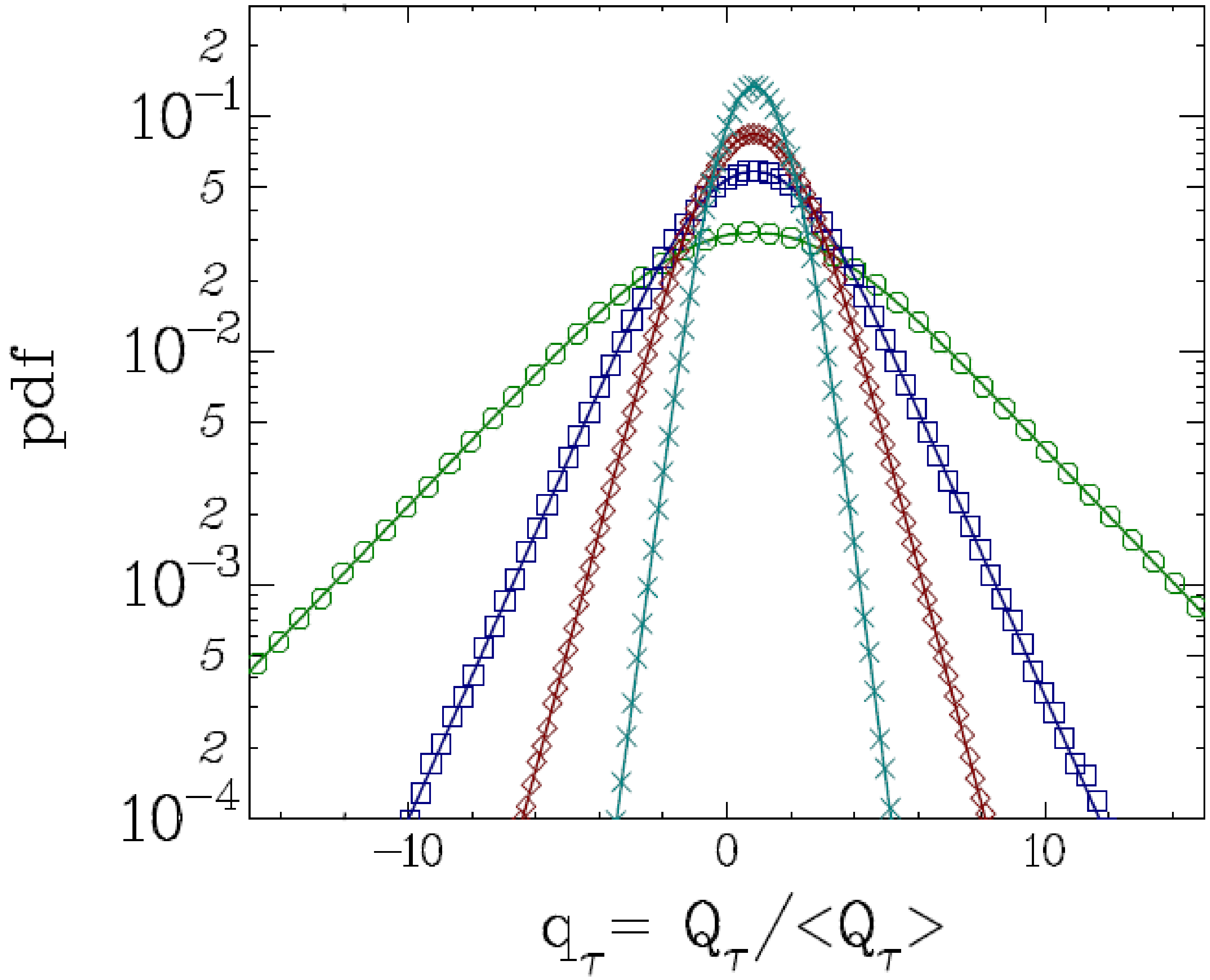
Analytically computed from the Langevin equation using two experimental observations

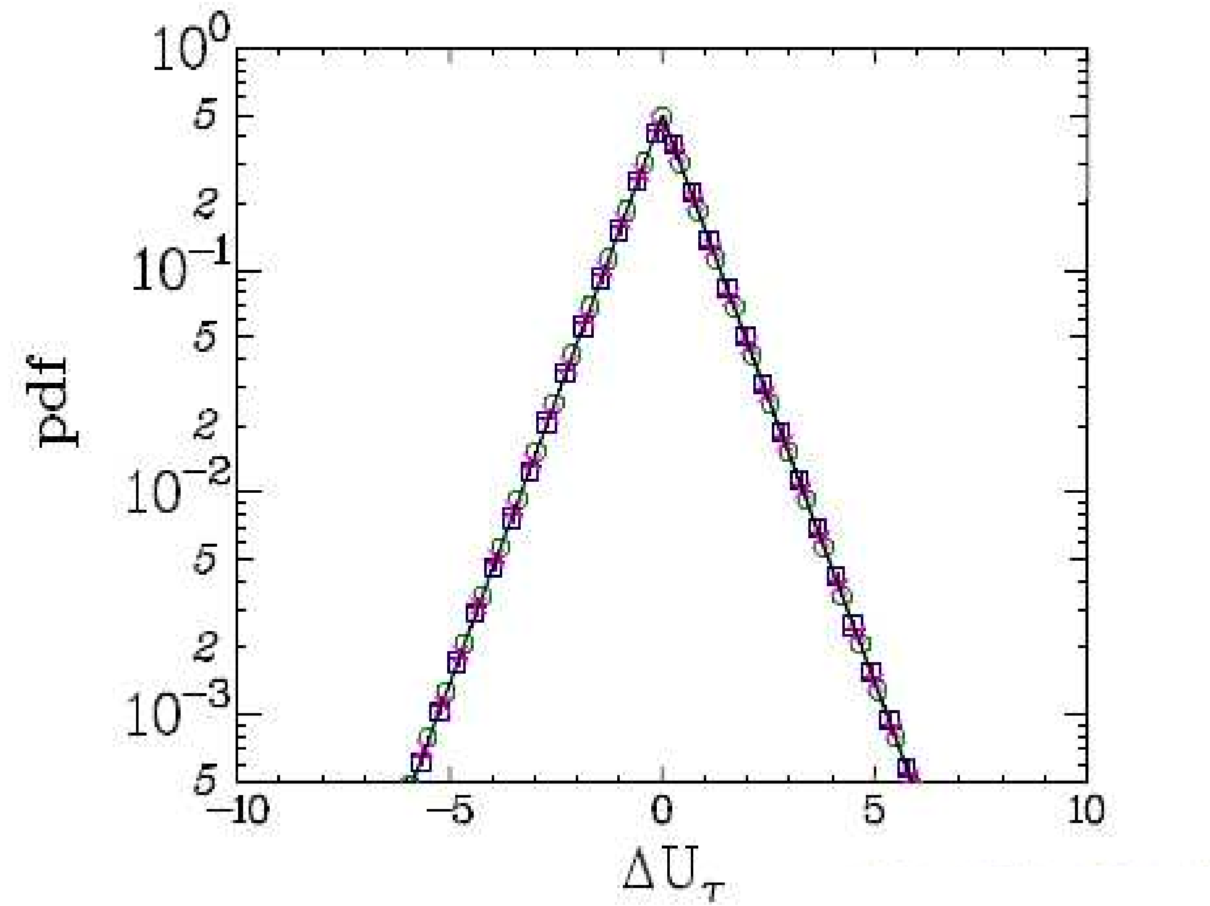
- The statistical properties of the bath are not modified by the driving
- The fluctuations of the work are Gaussian

S. Joubaud, N. B. Garnier, S. Ciliberto, J. Stat. Mech., P09018 (2007)

SSFT periodic forcing: Q

$n = 7$ ($\circ$), $n = 15$ ($\square$), $n = 25$ ($\diamond$) and $n = 50$ ($\times$).



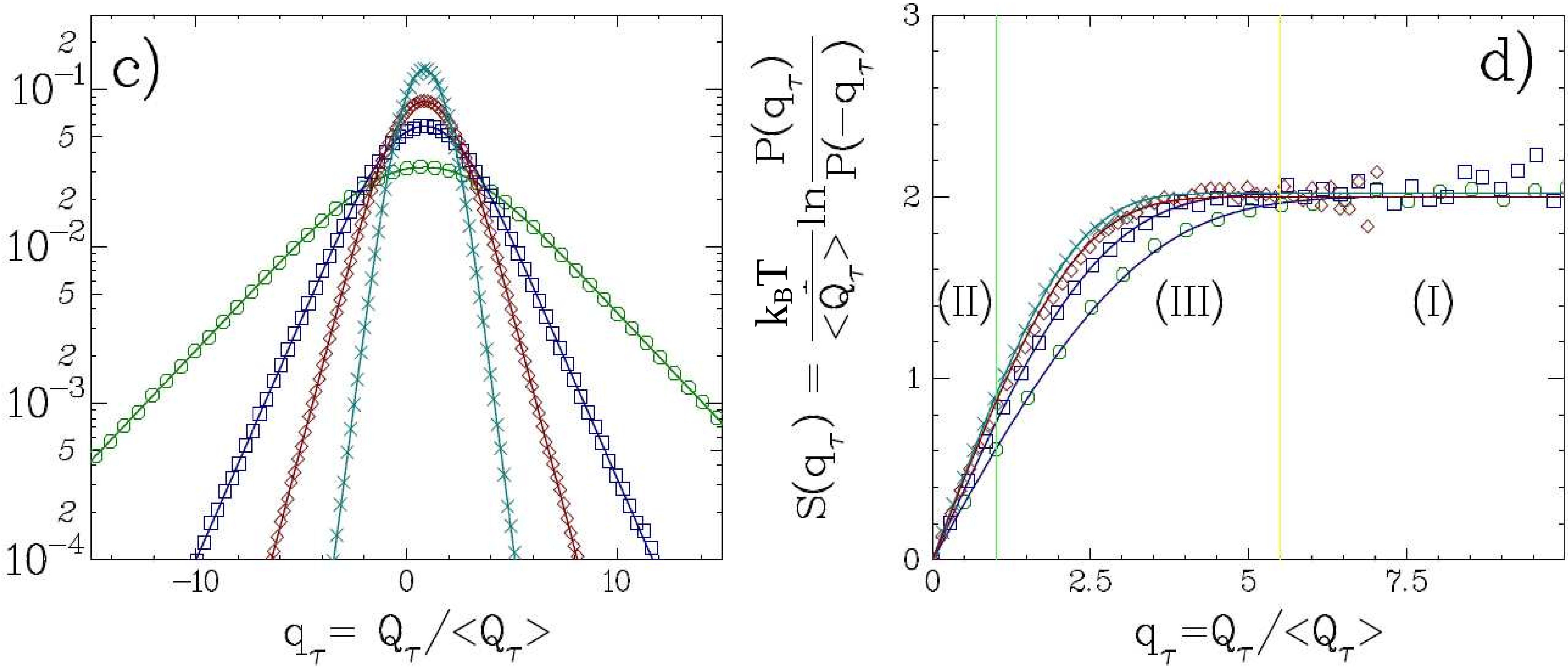


$$P(q) = \frac{\exp\left(\frac{\sigma^2}{2}\right)}{4}\left(\exp(q-\bar{q})\left[erfc\left(\frac{q-\bar{q}+\sigma_W^2}{\sqrt{2\sigma_W^2}}\right)\right] + \exp(-(q-\bar{q}))\left[erfc\left(\frac{-q+\bar{q}+\sigma_W^2}{\sqrt{2\sigma_W^2}}\right)\right]\right)$$

S. Joubaud, N. B. Garnier, S. Ciliberto, J. Stat. Mech., P09018 (2007)

SSFT periodic forcing: Σ for Q

$n = 7$ (○), $n = 15$ (□), $n = 25$ (◇) and $n = 50$ (×).



3 regions :

(I) Large fluctuations are exponential: $S(q_\tau) = 2$ for $q_\tau > 3$

(II) for $q_\tau < 2$, $S(q_\tau) = \Sigma(n)\ q_\tau$ with $\Sigma(n) \to 1$ for $n \to \infty$

(III) Smooth connection .

Stationary State Fluctuation Theorem (SSFT)

(stochastic systems)

$$\log \frac{P(X_\tau)}{P(-X_\tau)} = \frac{X_\tau}{k_B T} \Sigma(\tau)$$

where $\Sigma(\tau) \rightarrow 1$ for $\tau \rightarrow \infty$

X_τ stands either for Q_τ or for W_τ

The Fluctuation Theorem fixes the symmetry of P(X) around zero

Transient Fluctuation Theorem (TFT)

At $\tau = 0$ the system is in equilibrium

$$\Sigma(\tau) = 1 \qquad \forall \tau$$

Trajectory dependent entropy

- U. Seifert, Phys. Rev. Lett., 95, 040602, (2005), for Langevin dynamics
- A. Puglisi, L. Rondoni, A. Vulpiani, J. Stat. Mech.: Theory and Experiment, P08010,(2006) for Markov process

Heat dissipated by the system towards the heat bath:

$$Q_\tau = W_\tau - \Delta U_\tau \,.$$

we define the entropy variation in the system during a time τ as :

$$\Delta s_{\mathrm{m},\tau} = \frac{1}{T} Q_\tau$$

For thermostated systems, entropy change in medium behaves like the dissipated heat. The non-equilibrium Gibbs entropy is :

$$S(t) = -k_B \int \; d\vec{x} \; p(\vec{x}(t), t, \lambda_t) \ln p(\vec{x}(t), t, \lambda_t) = \langle s(t) \rangle$$

Trajectory dependent entropy

$s(t) \equiv -k_B \ln p(\vec{x}(t), t, \lambda_t)$ " trajectory dependent entropy "

The total entropy $s_{\text{tot}}(t) = s_{\text{m}}(t) + s(t)$

The variation $\Delta s_{\text{tot},\tau}$ of $s_{\text{tot}}(t)$:

$$\Delta s_{\text{tot},\tau} \equiv s_{\text{tot}}(t+\tau) - s_{\text{tot}}(t) = \Delta s_{\text{m},\tau} + \Delta s_\tau$$

We are interested in studying the fluctuations of $\Delta s_{\text{tot},\tau}$.

Trajectory dependent entropy

For the torsion pendulum the "trajectory-dependent" entropy is :

$$\Delta s_{\tau_n} = -k_B \ln \left(\frac{p(\theta(t_i+\tau_n),\varphi).p(\dot{\theta}(t_i+\tau_n),\varphi)}{p(\theta(t_i),\varphi).p(\dot{\theta}(t_i),\varphi)} \right)$$

with starting phase $\varphi = t_i \omega_d$ and $\tau_n = n\ 2\pi/\omega_d$

Computing the total entropy

- Compute $p(\theta(t_i),\varphi)$ and $p(\dot{\theta}(t_i),\varphi)$ for each initial phase φ.
- Compute the "trajectory-dependent" entropy.
- As fluctuations of θ and $\dot{\theta}$ are independent of φ. Average Δs_{τ_n} over φ.

Computing the total entropy

- Compute $p(\theta(t_i), \varphi)$ and $p(\dot\theta(t_i), \varphi)$ for each initial phase φ.
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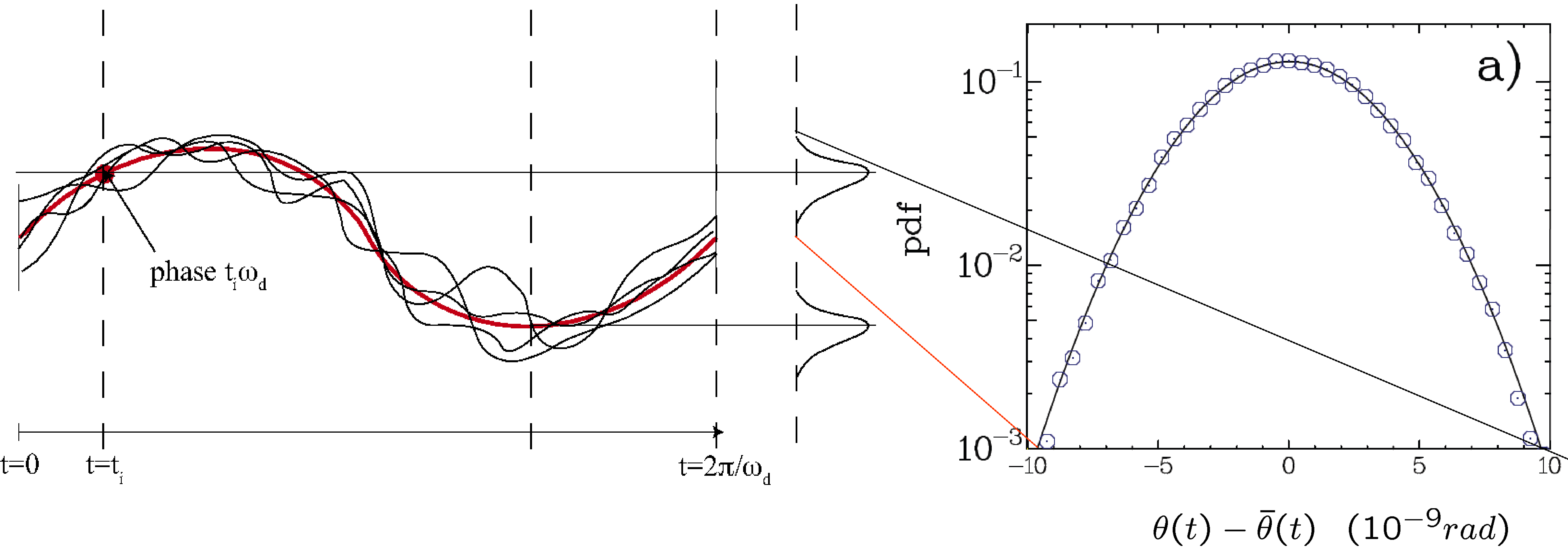
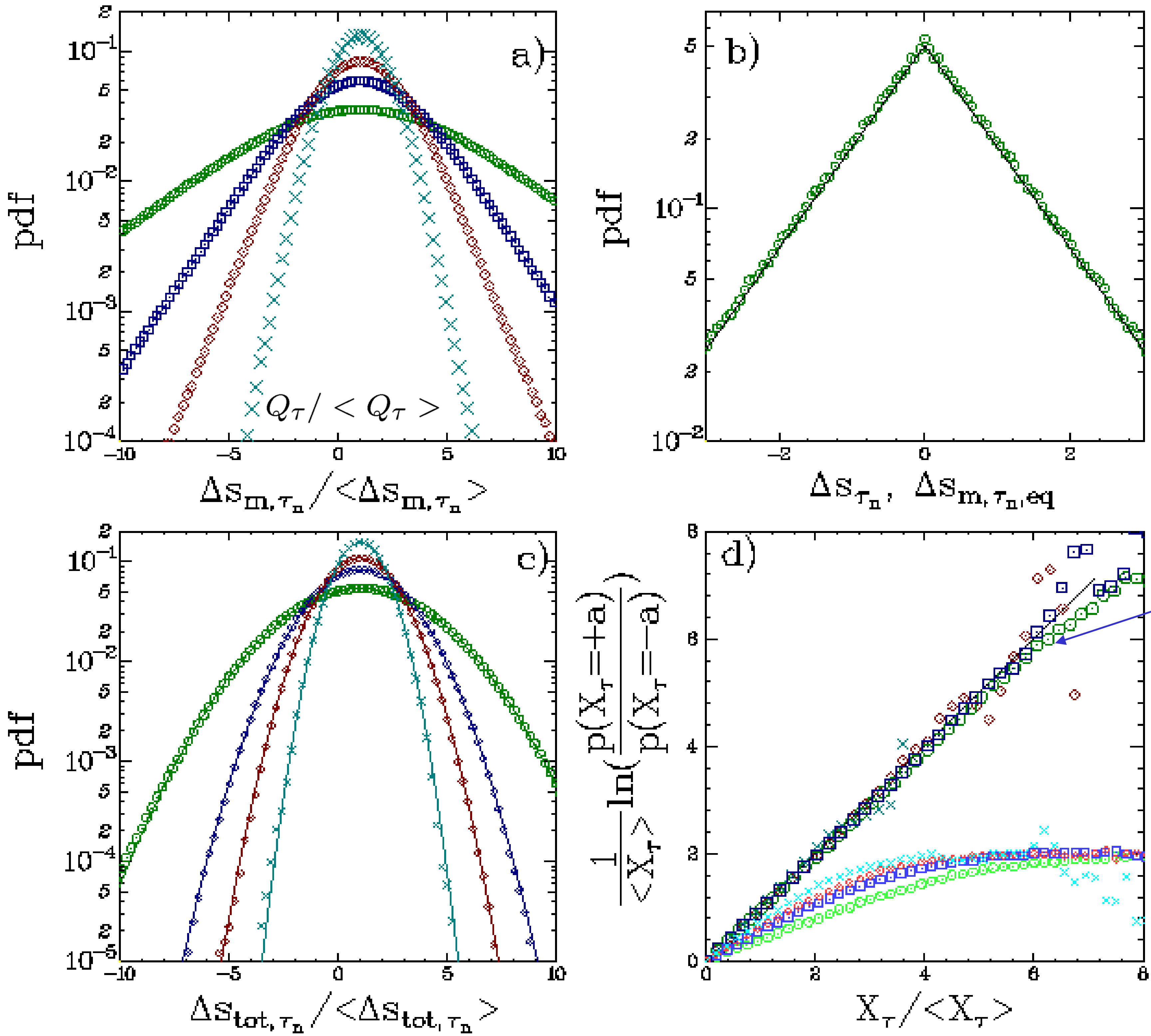


Fluctuations of the total entropy

n=7 (○), n=15 (□), n=25 (◊), n=20 (×)



— $\Delta s_{m,\tau_n,eq} = \frac{\Delta U_\tau}{T}$ at $M = 0$

○ Δs_{τ_n}

$X_\tau = \Delta S_{tot}$

$X_\tau = \Delta S_{m,\tau_n}$

FT for total entropy

$$\ln\left(\frac{P(\Delta s_{\text{tot},\tau_n})}{P(-\Delta s_{\text{tot},\tau_n})}\right) = \frac{\Delta s_{\text{tot},\tau_n}}{k_B} \quad \forall\ \tau_n$$

FT for total entropy

$$T.\Delta s_{\text{tot},\tau_n} = Q_\tau + T.\Delta s_{\tau_n} = W_{\tau_n} - \Delta U_{\tau_n} + T.\Delta s_{\tau_n}$$

The data show that : $T\ \Delta s_{\tau_n} = (\Delta U_{\tau_n})_{\text{equilibrium}}$

Out of equilibrium :

$$T.\Delta s_{\text{tot},\tau_n} = Q_\tau + T.\Delta s_{\tau_n} = W_{\tau_n} - (\Delta U_{\tau_n})_{\text{out\_equilibrium}} + (\Delta U_{\tau_n})_{\text{equilibrium}}$$

In equilibrium :

$W_{\tau_n} = 0,\qquad Q_\tau = -(\Delta U_{\tau_n})\qquad$ and $\qquad T.\Delta s_{\text{tot},\tau_n} = 0$

Conclusions on FT (partial)

- We have studied the energy fluctuations of a harmonic oscillator driven out of equilibrium by an external force.

- We have measured the **finite time corrections** for SSFT and compared to the theoretical predictions. TFT is instead verifed for all times.

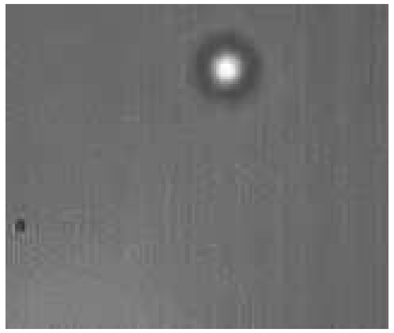
- The ‘’ **trajectory dependent entropy** ‘’ has been measured and we checked that SSFT is verified for all times for the ‘’**total entropy’’**.

- We have shown that in this specific example the **‘’total entropy’’** takes into account only the entropy produced by the external driving, without the **entropy fluctuations at equilibrium**.

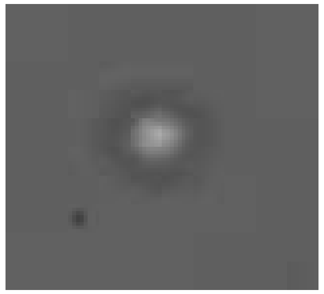
What does it happen in the non linear case ?

A Brownian particle trapped in a laser beam

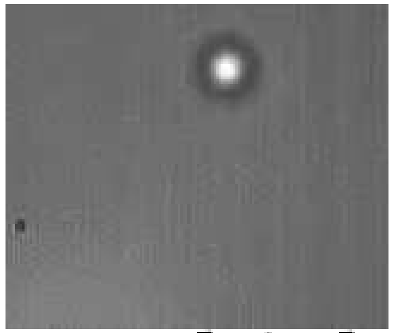
Basic Concepts on Stochastic Thermodynamics



$$\nu \dot{x} = -\frac{\partial U_o(x,t)}{\partial x} + f(t) + \eta$$



Basic Concepts on Stochastic Thermodynamics



$$\nu \dot{x} = -\frac{\partial U_o(x,t)}{\partial x} + f(t) + \eta$$

multiplying by $\dot{x}$ and integrating for a time τ we get :

$$\Delta U_\tau = W_\tau - Q_\tau$$

Stochastic thermodynamics

$$\Delta U_\tau = -\int_0^\tau \frac{\partial U_o}{\partial x}\ \dot{x}\ dt$$

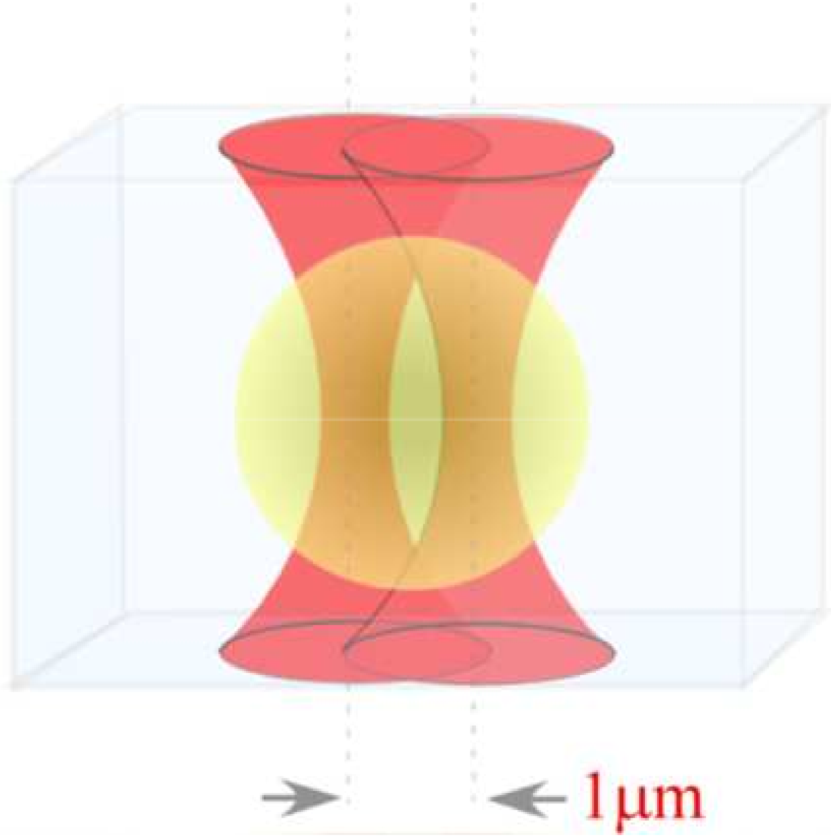
$$W_\tau = \int_0^\tau f\ \dot{x}\ dt$$

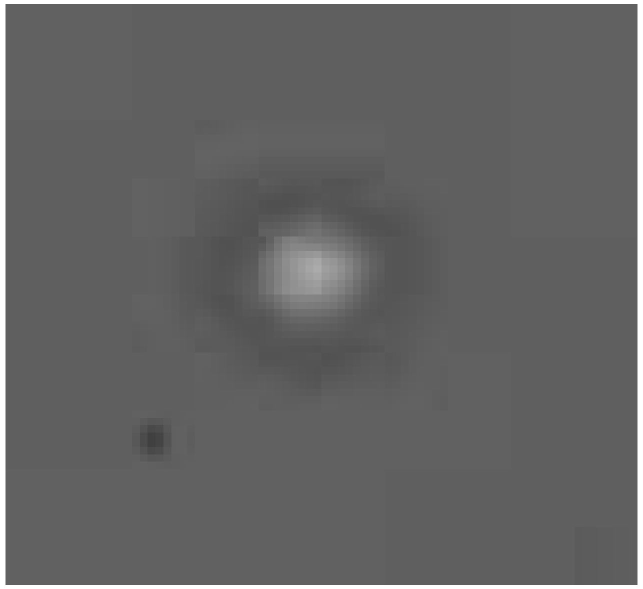
$$Q_\tau = \int_0^\tau \nu \dot{x}^2\ dt - \int_0^\tau \eta \dot{x}\ dt$$

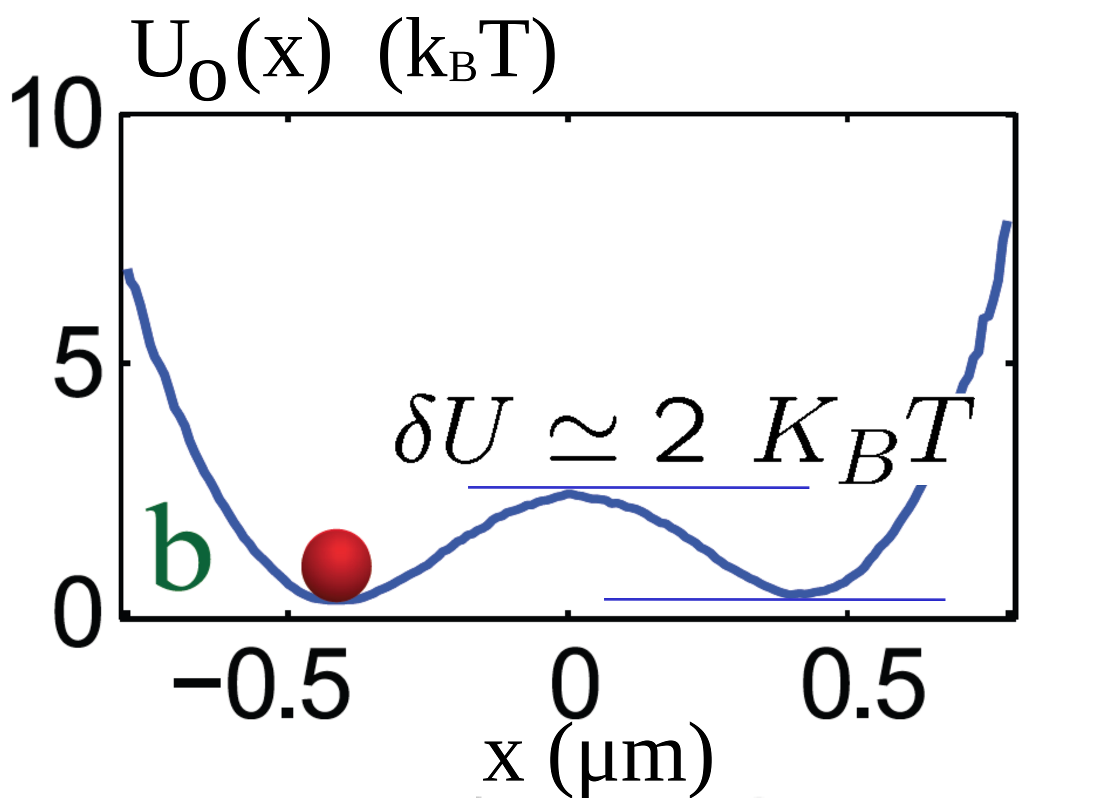
Sekimoto K, Progress of Theoretical Phys. supplement (130), 17 (1998).

FT and the stochastic resonance

Brownian particle trapped by two laser beams







The Kramers time

$$U_o(x) = a\,x^4 - b\,x^2 + d\,x$$

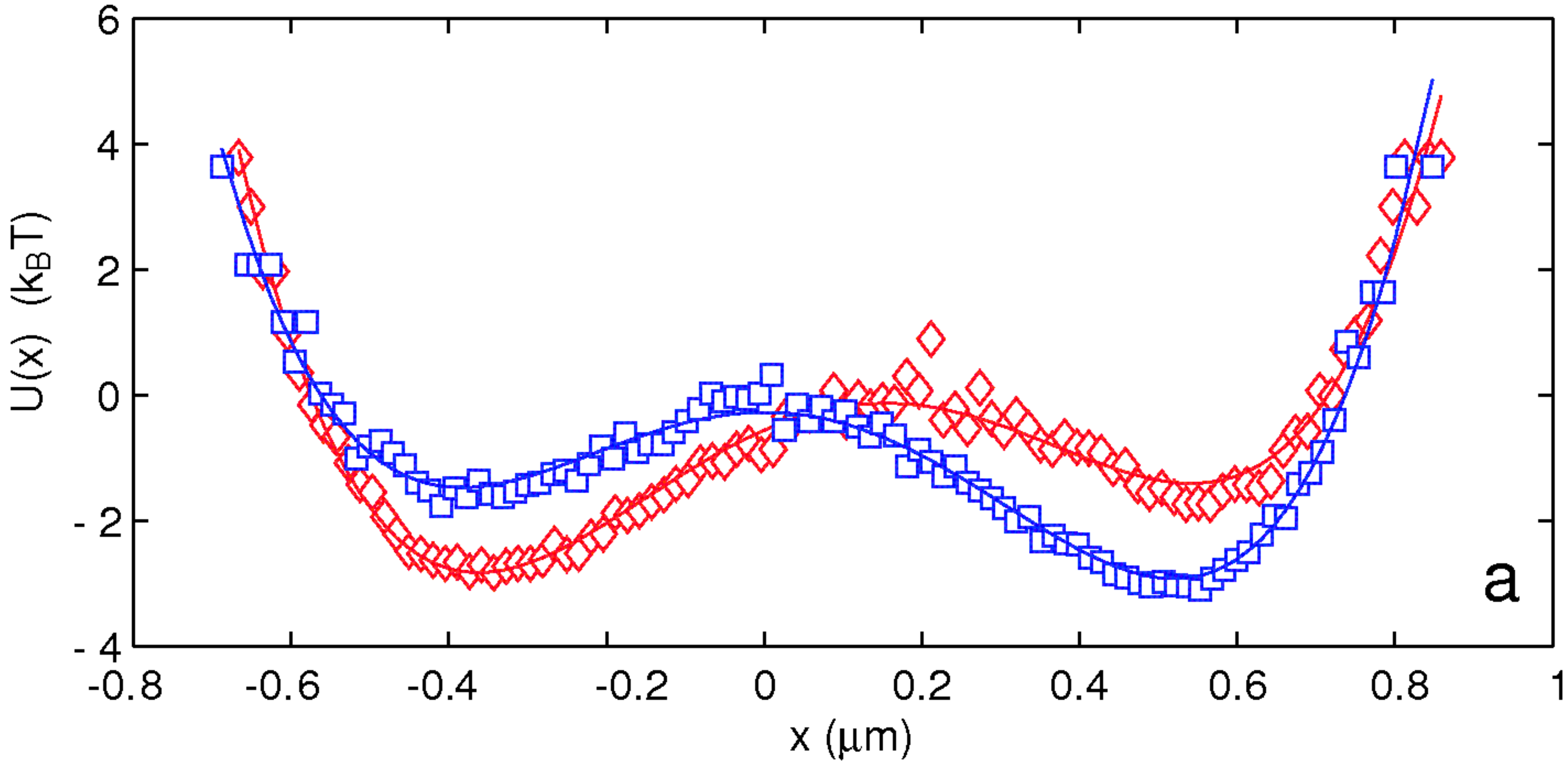
$$\tau_K = \tau_o\ \exp[\frac{\delta U}{k_B T}]$$

with $\tau_o = 1\ s$

Potential measured using the probability density function of $x(t)$

$$P(x) \propto \exp\left(\frac{-U(x)}{k_B T}\right)$$

FT and the stochastic resonance
The non linear potential



Kramers rate

$$r_k = \tau_o^{-1} \exp[-\frac{\Delta U}{k_B T}]$$

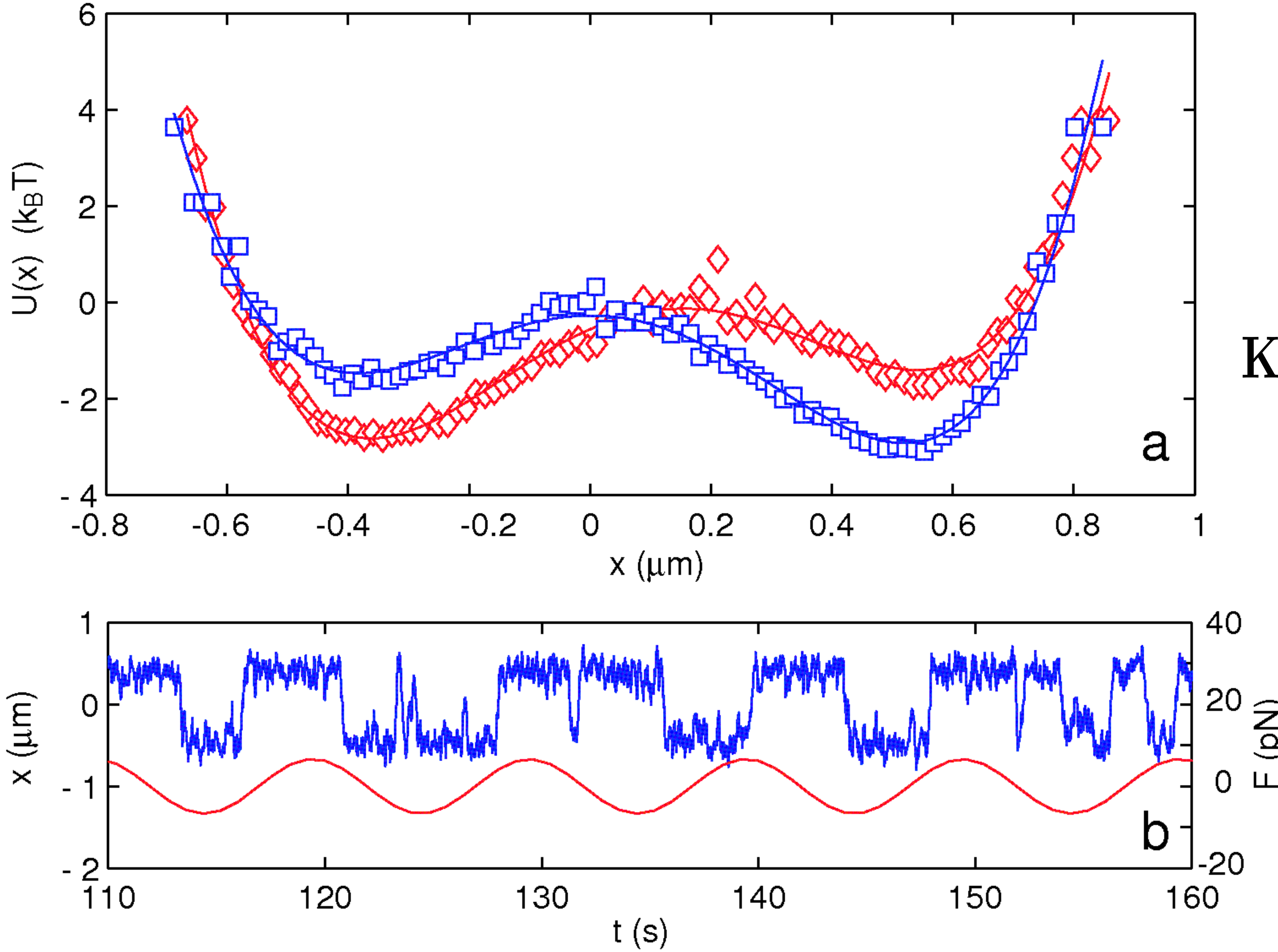
$$U_0(x) = ax^4 - bx^2 - dx$$

$$U(x,t) = U_0(x) + U_p(x,t) = U_0 + c\ x\ \sin(2\pi f t),$$

$$\nu\ \dot{x} = -\frac{\partial U_o(x)}{\partial x} - c\ \sin(2\pi f t) + \eta$$

FT and the stochastic resonance

The non linear potential



Kramers rate

$$r_k = \tau_o^{-1} \exp[-\frac{\Delta U}{k_B T}]$$

f=0.1Hz

At $f \simeq r_k$ the hops of the particle synchronise with the external forcing

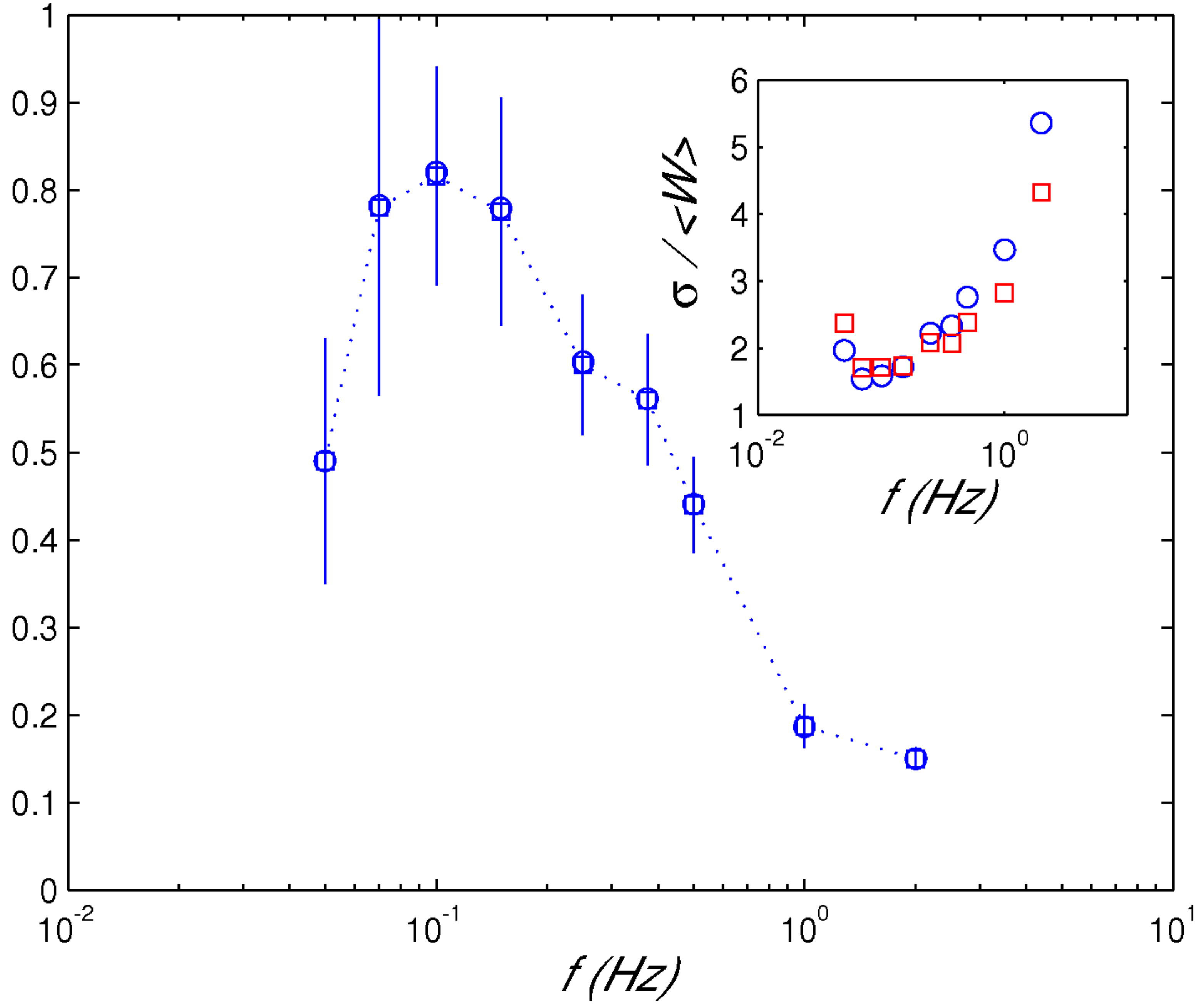
Stochastic Resonance

At $f \simeq r_k$ the hops of the particle synchronise with the external forcing

$$W_\tau = c \int_{t_i}^{t_i+\tau_n} \dot{x} \ \sin(2\pi f t) dt \quad \text{with } \tau_n = n/f$$

$< W_\tau >$

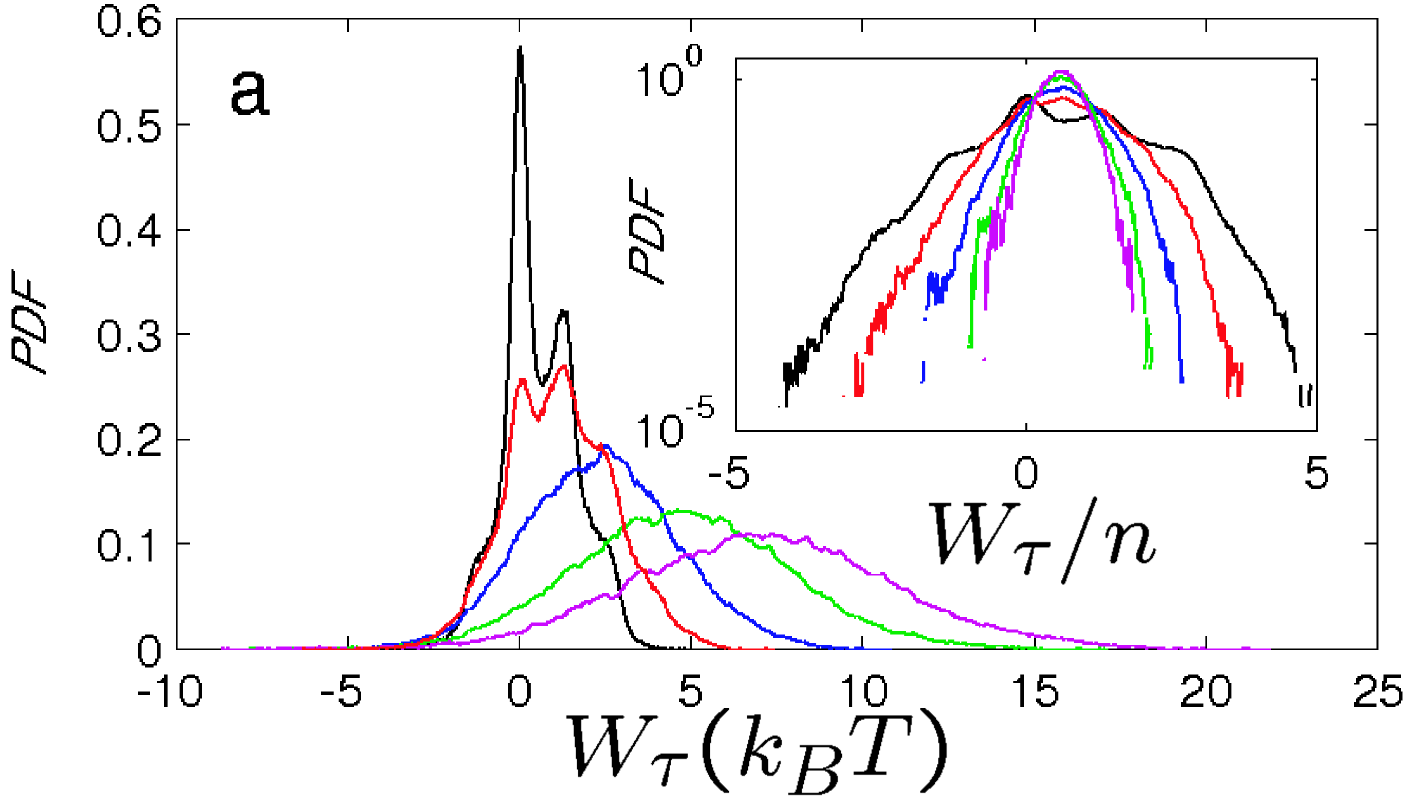
$n = 1$



FT and the stochastic resonance

Fluctuation Theorem for W

f=0.25Hz and τ= n / f



$$\log \frac{P(X_\tau)}{P(-X_\tau)} = \frac{X_\tau}{k_B T}\,\Sigma(\tau)$$

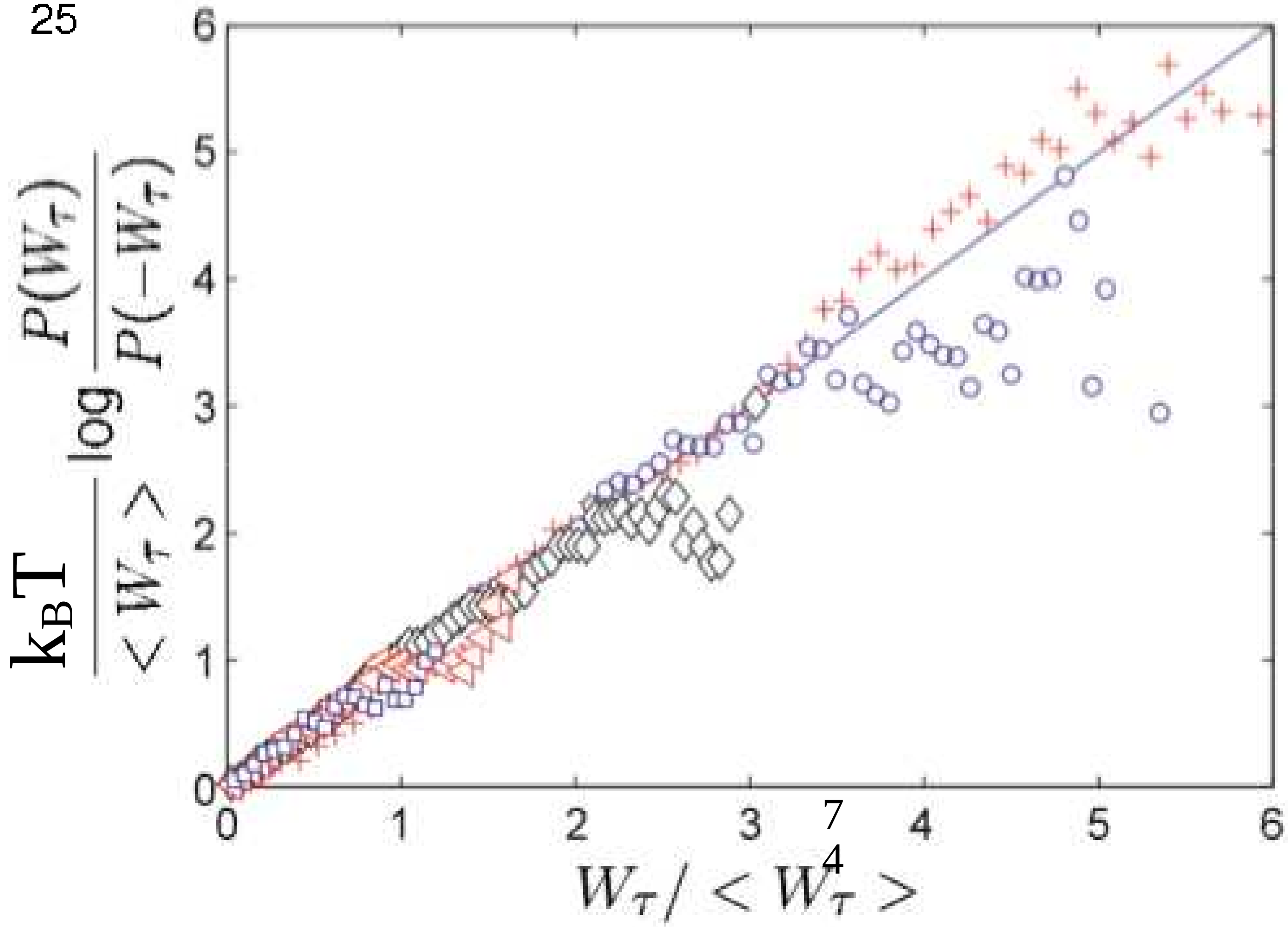
where $\Sigma(\tau) \to 1$ for $\tau \to \infty$

$n = 1$ (+), 2 ($\circ$), 4 ($\diamond$), 8 ($\triangle$), 12 ($\square$)

$n = 1$, 4, 8 and 12

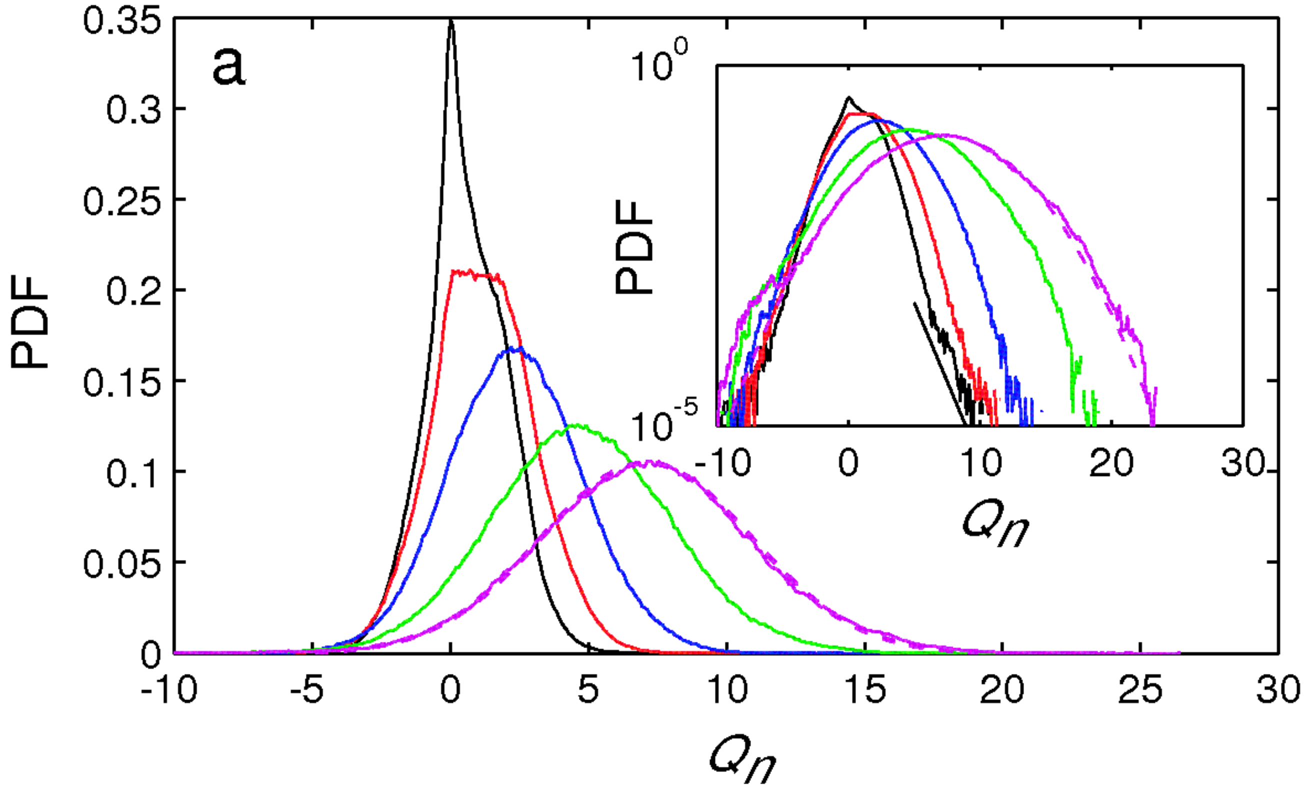
$$W_\tau = c \int_{t_i}^{t_i+\tau_n} \dot{x}\ \sin(2\pi f t)\,dt$$

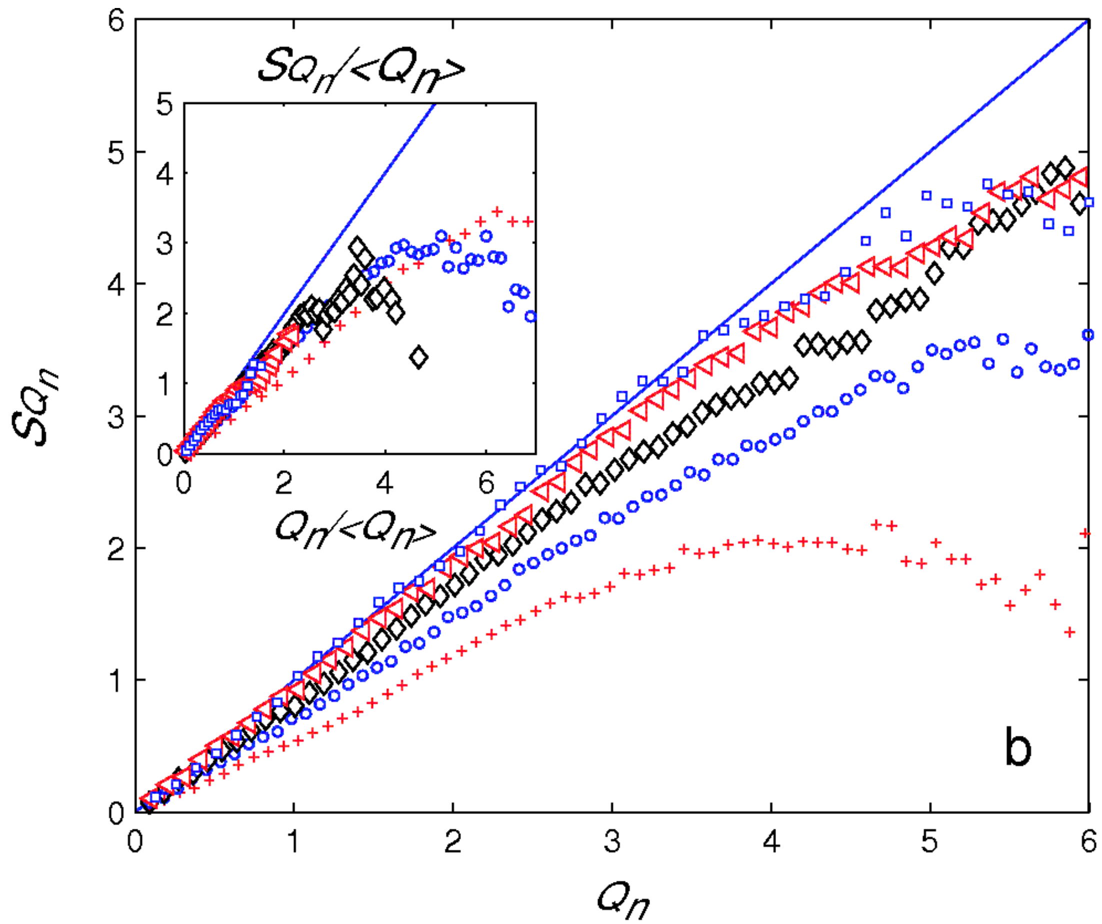
with $\tau_n = n/f$



Fluctuation Theorem for Q

$$Q_\tau = -\Delta U_{o,\tau} + W_\tau$$





$n = 1$, 4, 8 and 12

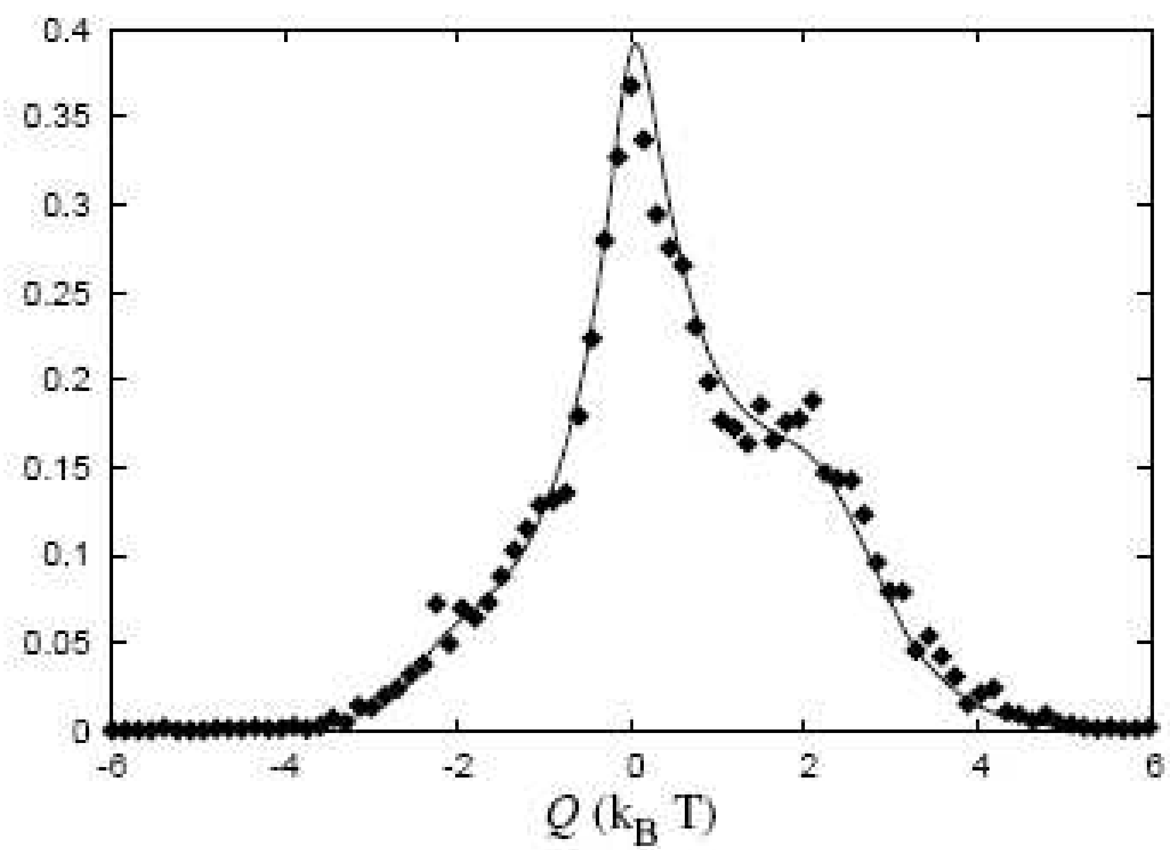
$n = 1$ $(+)$, 2 $(\circ)$, 4 $(\diamond)$, 8 $(\triangle)$, 12 $(\square)$

Theoretical comparison

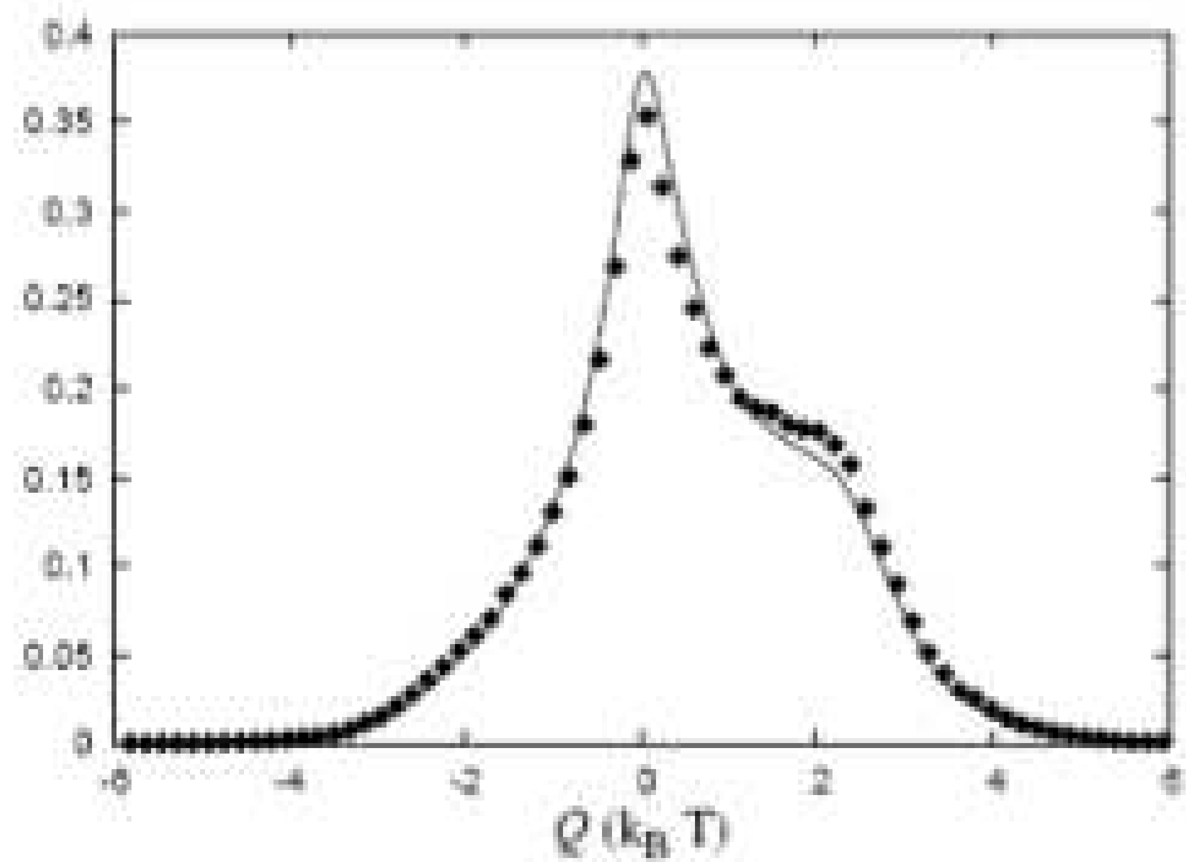
A. Imparato, P. Jop, A. Petrosyan and S. Ciliberto, J. Stat. Mech. (2008) P10017

PDF of the heat computed on a single period :

(initial phase=0)



(averaged over different initial phases)



♦ Experimental data

—— Theoretical prediction based on Fokker-Planck equation

The Nyquist problem

JULY, 1928 *PHYSICAL REVIEW* *VOLUME 32*

THERMAL AGITATION OF ELECTRIC CHARGE IN CONDUCTORS*

BY H. NYQUIST

ABSTRACT

The electromotive force due to thermal agitation in conductors is calculated by means of principles in thermodynamics and statistical mechanics. The results obtained agree with results obtained experimentally.

DR. J. B. JOHNSON[1] has reported the discovery and measurement of an electromotive force in conductors which is related in a simple manner to the temperature of the conductor and which is attributed by him to the thermal agitation of the carriers of electricity in the conductors. The work to be resported in the present paper was undertaken after Johnson's results were available to the writer and consists of a theoretical deduction of the electromotive force in question from thermodynamics and statistical mechanics.[2]

Consider two conductors each of resistance R and of the same uniform temperature T connected in the manner indicated in Fig. 1. The electromotive force due to thermal agitation in conductor I causes a current to be set up in the circuit whose value is obtained by dividing the electromotive force by $2R$. This current causes a heating or absorption of power in conductor II, the absorbed power being equal to the product of R and the square of the current. In other words power is transferred from conductor I to conductor II. In precisely the same manner it can be deduced that power is transferred from conductor II to conductor I. Now since the two conductors are at the same temperature it follows directly from the second law of thermodynamics that the power flowing in one direction is exactly equal to that flowing in the other direction. It will be noted that no assumption has been made as

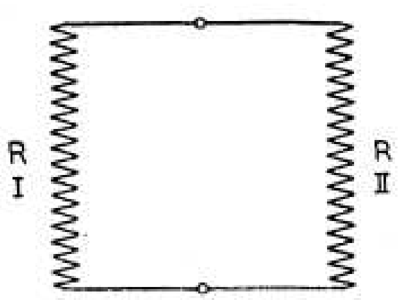
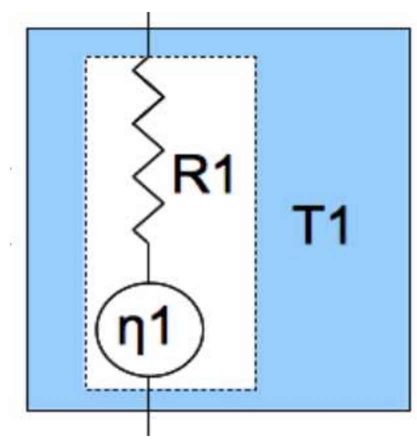


Fig. 1.

Power spectral density of the electric noise

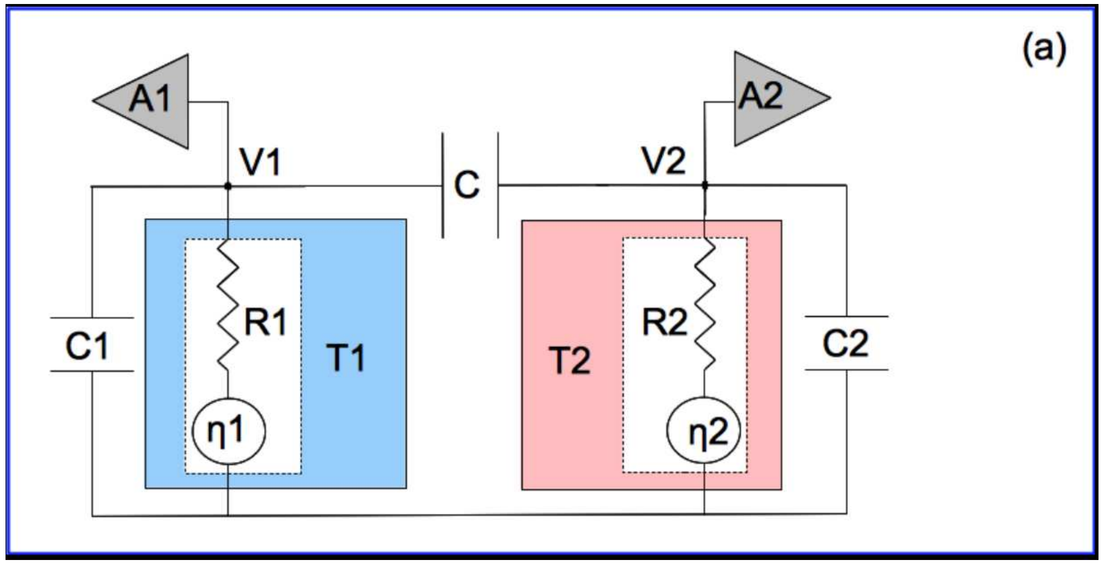
$$|\tilde{\eta}|^2 = 4 k_B R T$$

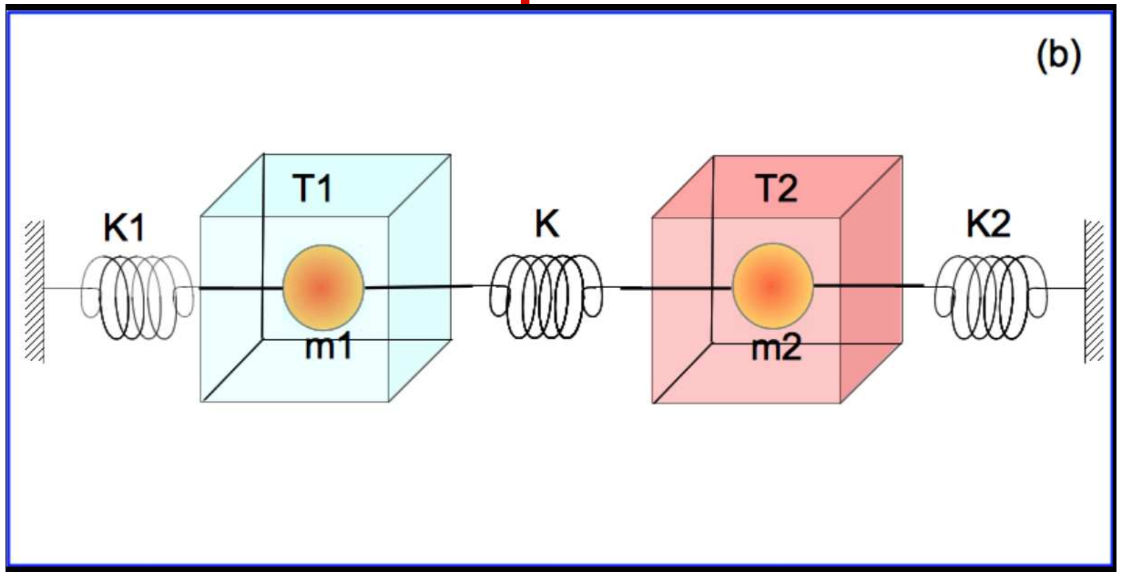


In 1928 well before Fluctuation Dissipation Theorem (FDT), this was the second example, after the Einstein relation for Brownian motion, relating the dissipation of a system to the amplitude of the thermal noise.

Two heat baths coupled by fluctuations

Electric Circuit and mechanical equivalent





$$R_1 \dot{q}_1 = -q_1 \frac{C_2}{X} + (q_2 - q_1)\frac{C}{X} + \eta_1$$
$$R_2 \dot{q}_2 = -q_2 \frac{C_1}{X} + (q_1 - q_2)\frac{C}{X} + \eta_2$$

$$\langle \eta_i(t)\eta_j(t')\rangle = 2\delta_{ij} k_B T_i R_j \delta(t - t')$$

$$X = C_2\, C_1 + C\,(C_1 + C_2)$$

q_m the displacement of the particle m

i_m its velocity

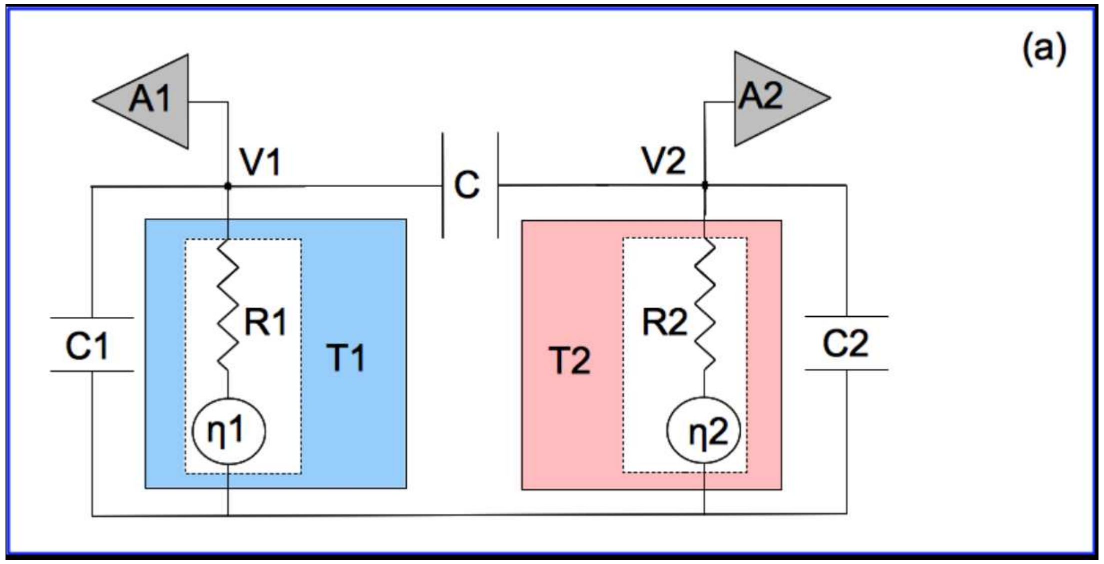
$K_m = 1/C_m$ the stiffness of the spring m

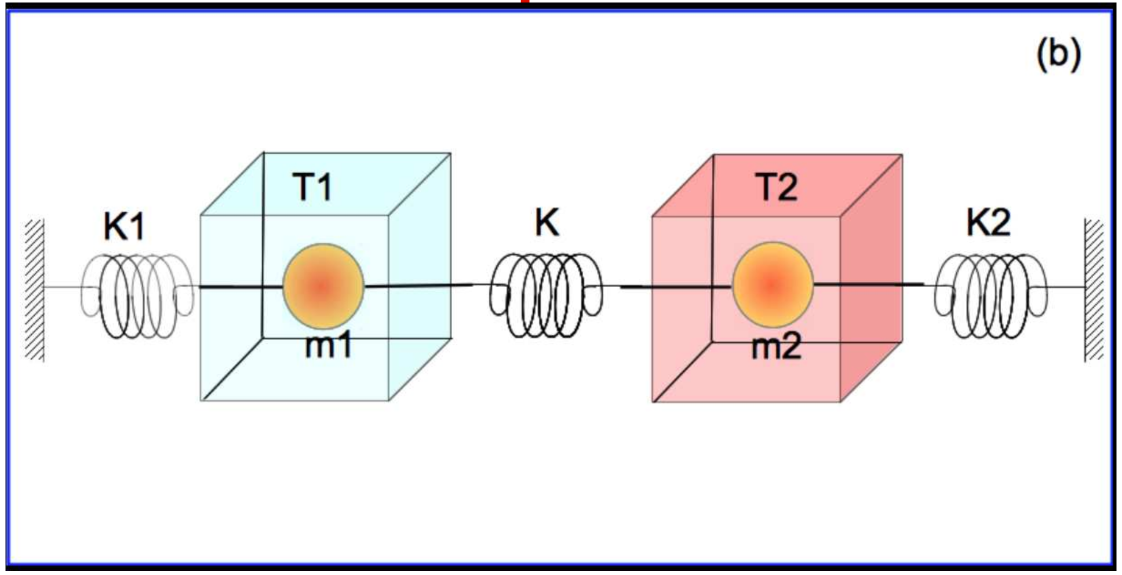
$K = 1/C$ the stiffness of the coupling spring

R_m the viscosity.

Two heat baths coupled by fluctuations

Electric Circuit and mechanical equivalent





$$(C_1 + C)\dot{V}_1 = C\dot{V}_2 + \frac{1}{R_1}(\eta_1 - V_1),$$

$$(C_2 + C)\dot{V}_2 = C\dot{V}_1 + \frac{1}{R_2}(\eta_2 - V_2).$$

$$\langle \eta_i(t)\eta_j(t')\rangle = 2\delta_{ij}k_B T_i R_j \delta(t - t')$$

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R_m the viscosity.

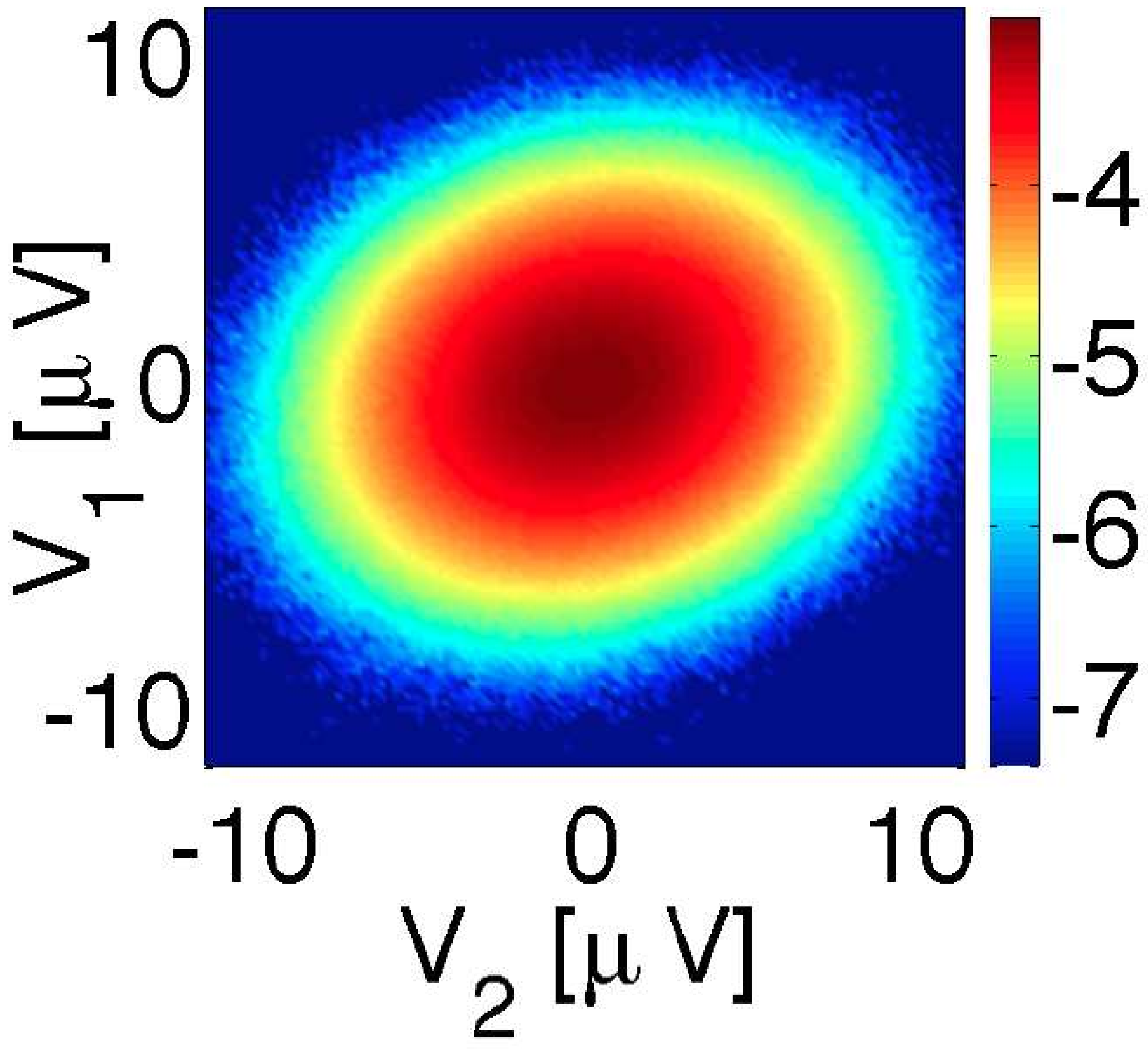
Two heat baths coupled by fluctuations

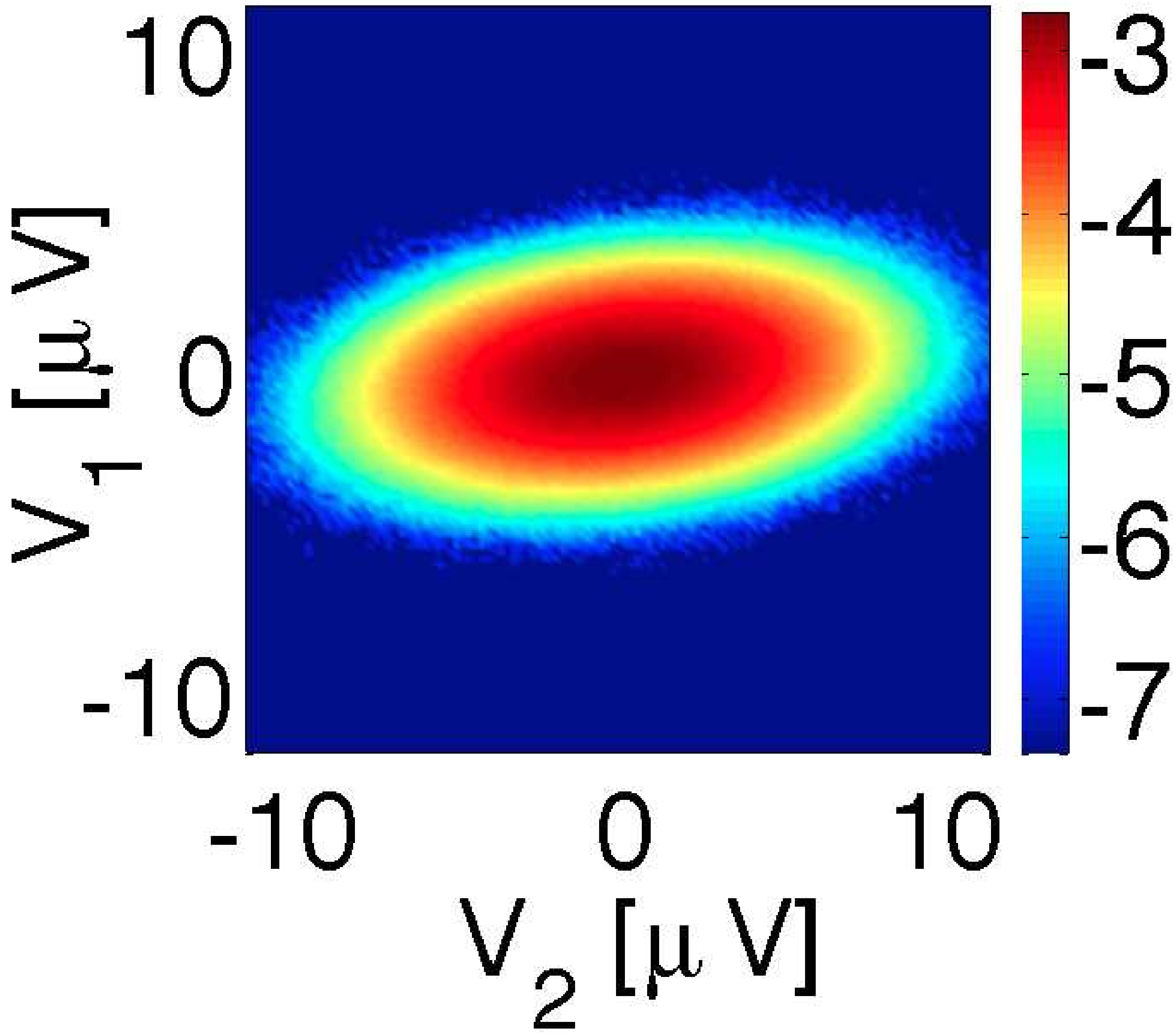
Joint probability of V_1 and V_2

$$\log_{10} P(V_1, V_2)$$
at $T_1 = T_2 = 296k$

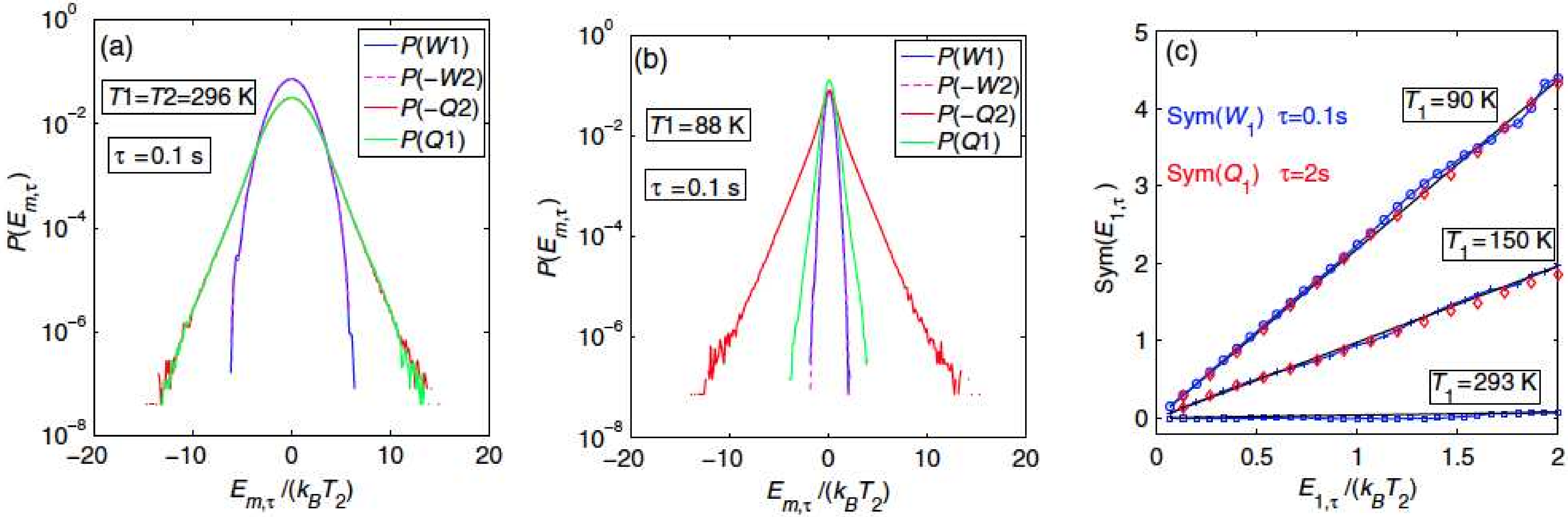
$$\log_{10} P(V_1, V_2)$$
at $T_1 = 88K$ and $T_2 = 296K$

Statistic of the work and heat





Two heat baths coupled by fluctuations



FT for W_τ et Q_τ
for $\tau \to \infty$

$$Sym(E_{m,\tau}) = \log \frac{P(E_{m,\tau})}{P(-E_{m,\tau})} = \Delta\beta \frac{E_{m,\tau}}{k_B T_2}$$

with $\Delta\beta = (T_2/T_1 - 1)$

Two heat baths coupled by fluctuations

Entropy produced

$$\Delta S_{r,\tau} = Q_{1,\tau}/T_1 + Q_{2,\tau}/T_2$$

related to the heat exchanged with the reservoirs

Statistical properties of the total entropy

Following Seifert, (PRL 95, 040602, 2005) who developed this concept for a single heat bath, we introduce a trajectory entropy for the evolving system

$$S_s(t) = -k_B \log P(V_1(t), V_2(t))$$

and the entropy production on the time τ

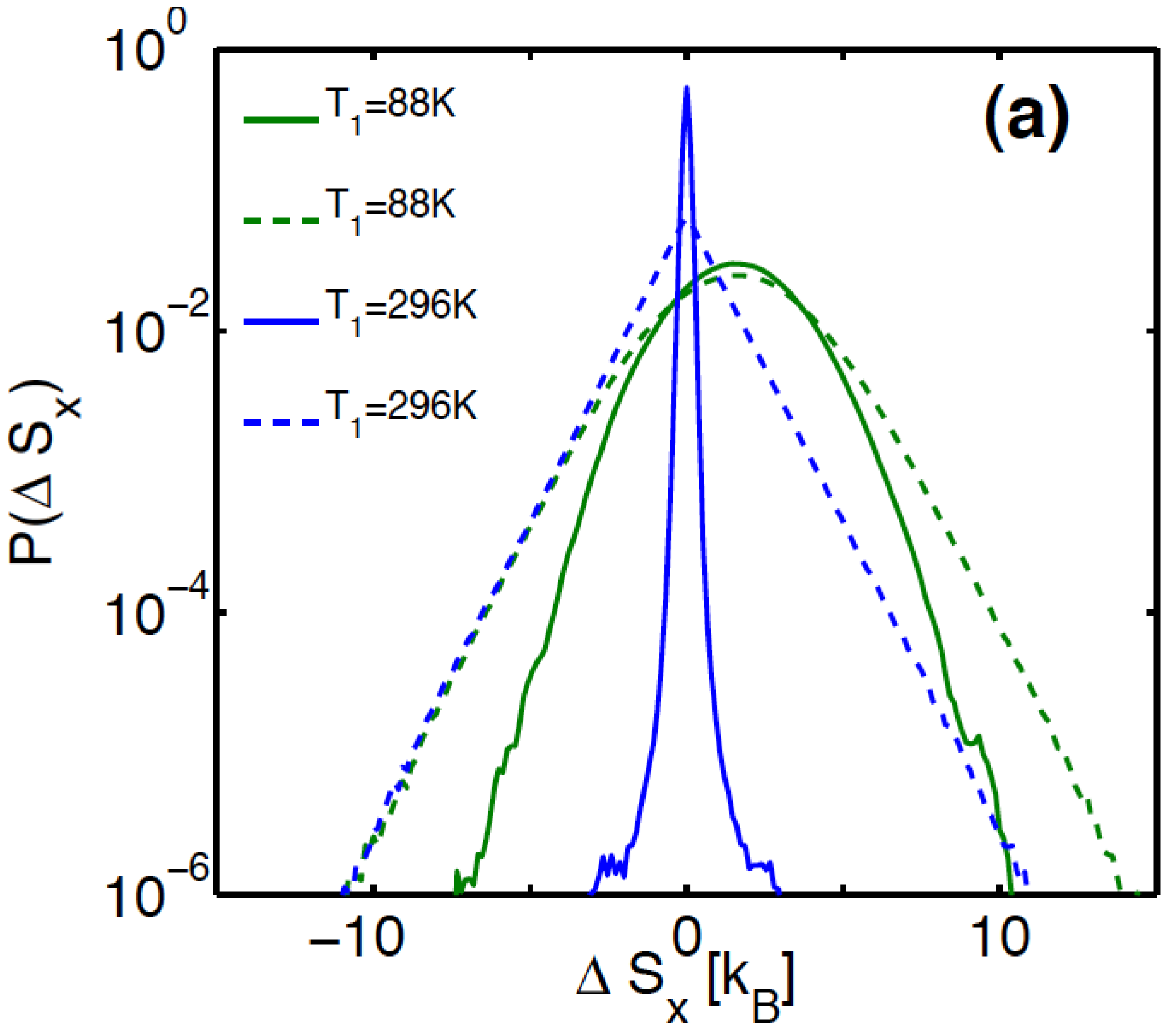
$$\Delta S_{s,\tau} = -k_B \log \left[\frac{P(V_1(t+\tau), V_2(t+\tau))}{P(V_1(t), V_2(t))} \right].$$

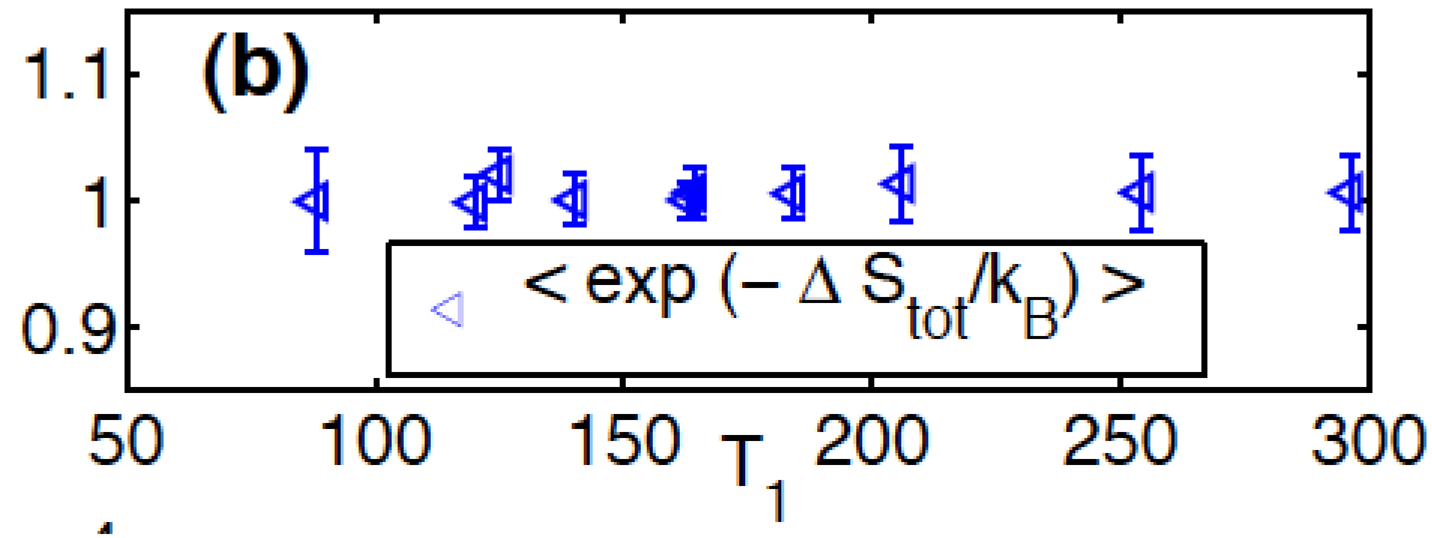
The total entropy is :

$$\Delta S_{tot,\tau} = \Delta S_{r,\tau} + \Delta S_{s,\tau}$$

Two heat baths coupled by fluctuations

$$\Delta S_{tot,\tau} = \Delta S_{r,\tau} + \Delta S_{s,\tau}$$





$\Delta S_{tot,\tau}$ (solid line)

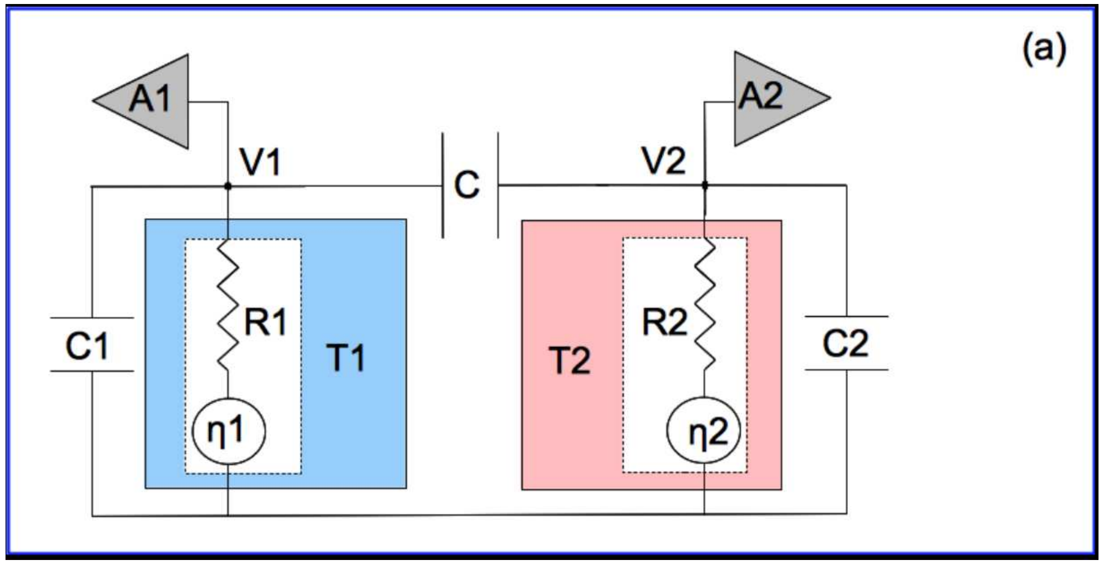
$\Delta S_{r,\tau}$ (dotted line)

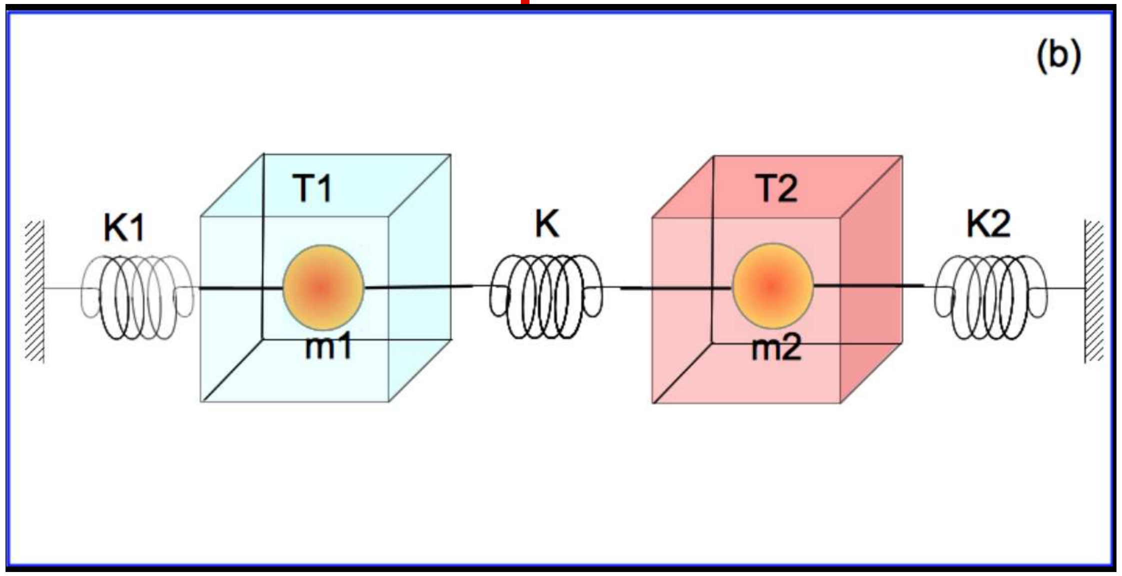
independently of ΔT and of τ,
the following equality always holds

$$\langle \exp(-\Delta S_{tot}/k_B) \rangle = 1$$

Two heat baths coupled by fluctuations

Electric Circuit and mechanical equivalent





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$$\langle \eta_i(t)\eta_j(t')\rangle = 2\delta_{ij} k_B T_i R_j \delta(t - t')$$

$$X = C_2\, C_1 + C\,(C_1 + C_2)$$

q_m the displacement of the particle m

i_m its velocity

$K_m = 1/C_m$ the stiffness of the spring m

$K = 1/C$ the stiffness of the coupling spring

R_m the viscosity.

Fluctuation Dissipation Theorem in out of equilibrium

Power Spectral Density of V1 and V2

$$Sp_1(\omega) = \frac{4k_B T_1 R_1[1+\omega^2(C^2R_1R_2+R_2^2(C_2+C)^2)]}{(1-\omega^2 X R_1R_2)^2+\omega^2Y^2} + \frac{4k_B(T_2-T_1)\,\omega^2\,C^2R_1^2R_2}{(1-\omega^2 X R_1R_2)^2+\omega^2Y^2}$$

$$Sp_2(\omega) = \frac{4k_B T_2 R_2[1+\omega^2(C^2R_1R_2+R_1^2(C_1+C)^2)]}{(1-\omega^2 X R_1R_2)^2+\omega^2Y^2} + \frac{4k_B(T_1-T_2)\,\omega^2\,C^2R_2^2R_1}{(1-\omega^2 X R_1R_2)^2+\omega^2Y^2}.$$

Equilibrium | Out of Equilibrium

The variance of V1 and V2

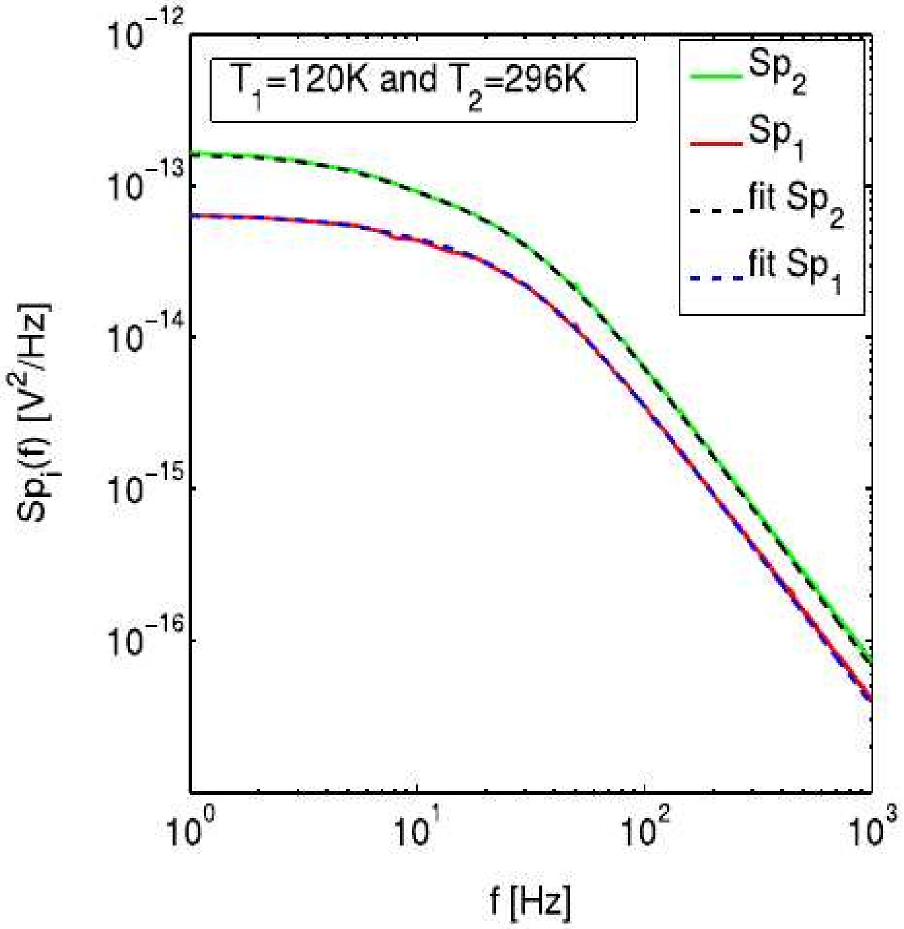
$$\sigma_1^2 = k_B\frac{T_1(C+C_2)Y+(T_2-T_1)C^2R_1}{XY}$$

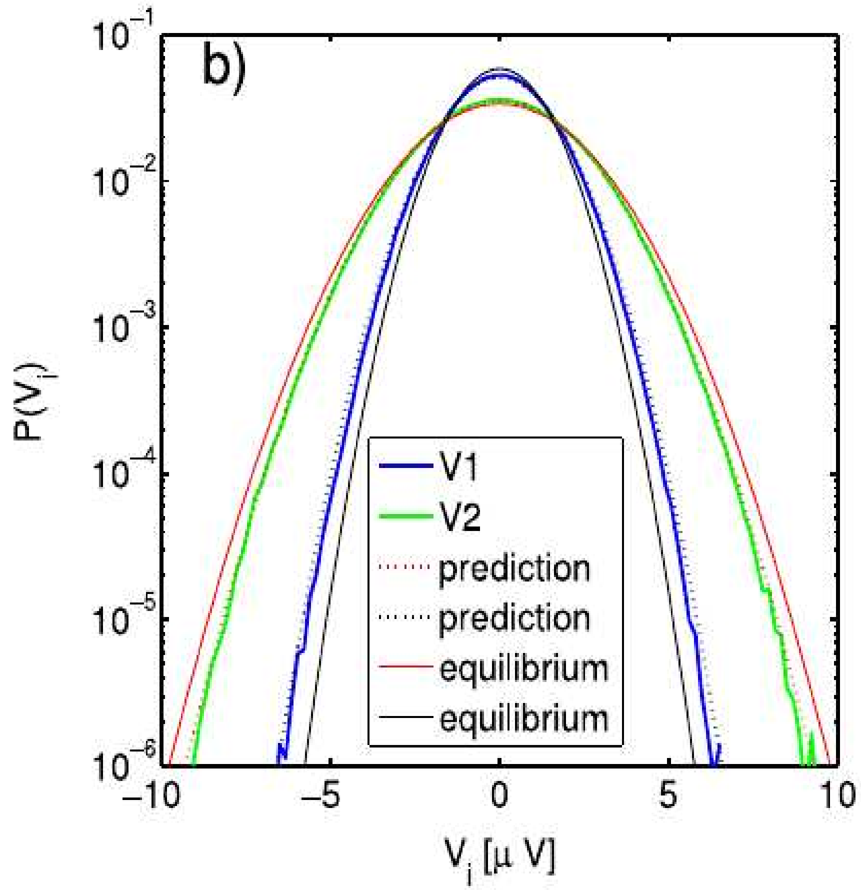
$$\sigma_2^2 = k_B\frac{T_2(C+C_1)Y-(T_2-T_1)C^2R_2}{XY}.$$

$$\sigma_m^2 = \sigma_{m,\mathrm{eq}}^2 + \langle\dot{Q}_m\rangle R_m$$

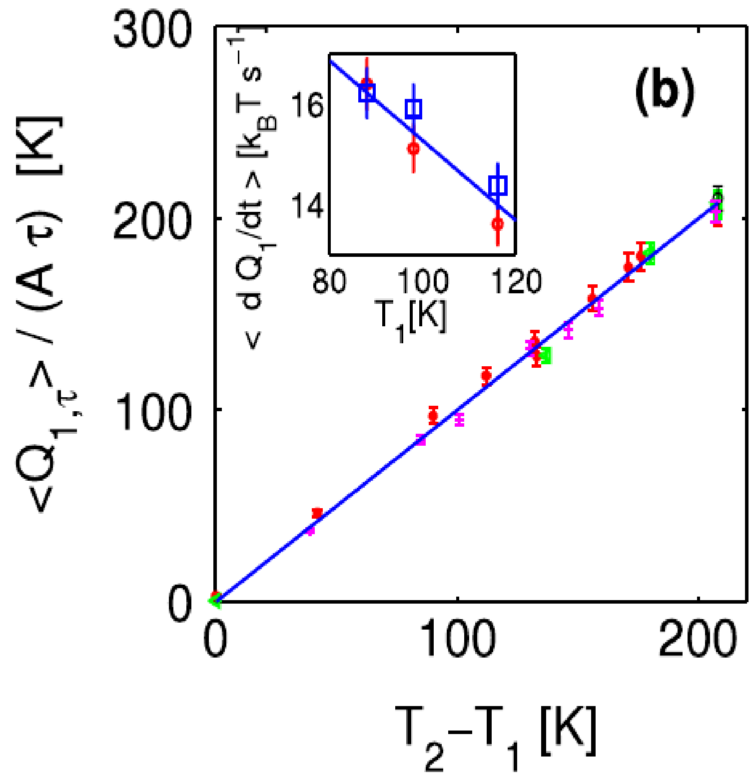
which is an extension to two temperatures of the Harada-Sasa relation

Fluctuation Dissipation Theorem
in out of equilibrium





$$Q_{m,\tau} = \int_{t_0}^{t_0+\tau} i_m(t) V_m(t)\,\mathrm{d}t = \int_{t_0}^{t_0+\tau} V_m \left[C\dot{V}_{m'} - (C_m + C)\dot{V}_m \right]\,\mathrm{d}t.$$



What Stochastic Thermodynamics is useful for ?

1) Jarzinsky and Crooks equalities are useful to compute the free energy difference bewteen two equilibrium states using any kind of transformation

2) Hatano-Sasa relation and the Fluctuation Dissipation Theorem for non equilibrium steady states(NESS). These are useful to compute the response function of NESS.

3) The measure of energy fluctautions allows us to estimate tiny amount of heat exchanged bewteen the system and its heat bath.

4) Calibration of an out of equilibrium system (the force, the offset, the mean injected power).

5) The role of hidden variables and the stochastic inference. *To what extent the fact that FT and FDT do not* hold can give information on hidden variables ?

6) Efficiency of nano and micro motors

7) Energy information connection and the role of Maxell's demon.

8) Engineered Swift equilibration (ESE)

Jarzynski equality

Consider a system whose energy is: $H(\Gamma, \lambda)$
Here $\lambda(t)$ is an externally controlled parameter.
We consider a transformation from an initial equilibrium state, $\lambda = A$ to another equlibrium state $\lambda = B$. Thus we have

$$H(\Gamma_r, B) - H(\Gamma_0, A) = W^J$$

where

$$W^J = \int_0^{\tau} dt \, \frac{d\lambda}{dt} \frac{\partial H}{\partial \lambda}$$

If ΔF is the free energy difference between the two equilibrium states A and B then the **Jarzynski Equality** (JE) states that:

$$< \exp(-\beta \, W^J) > = \exp(-\beta \Delta F)$$

If W^J has a Gaussian PDF then the JE takes a simple form:

$$\Delta F = < W^J > - \frac{\sigma_W^2}{2 \, K_B \, T}$$

Crooks identity

Crooks considered the forward (F) and reverse processes (R). During the F processes λ goes from A to B. During the R the inverse path is done.

Crooks derived the following identity:

$$\frac{P_F(W^J)}{P_R(-W^J)} = \exp\left(\frac{W^J - \Delta F}{K_B T}\right) = \exp\left(\frac{W_{dis}}{K_B T}\right)$$

simple manipulation of this ratio and integration gives:

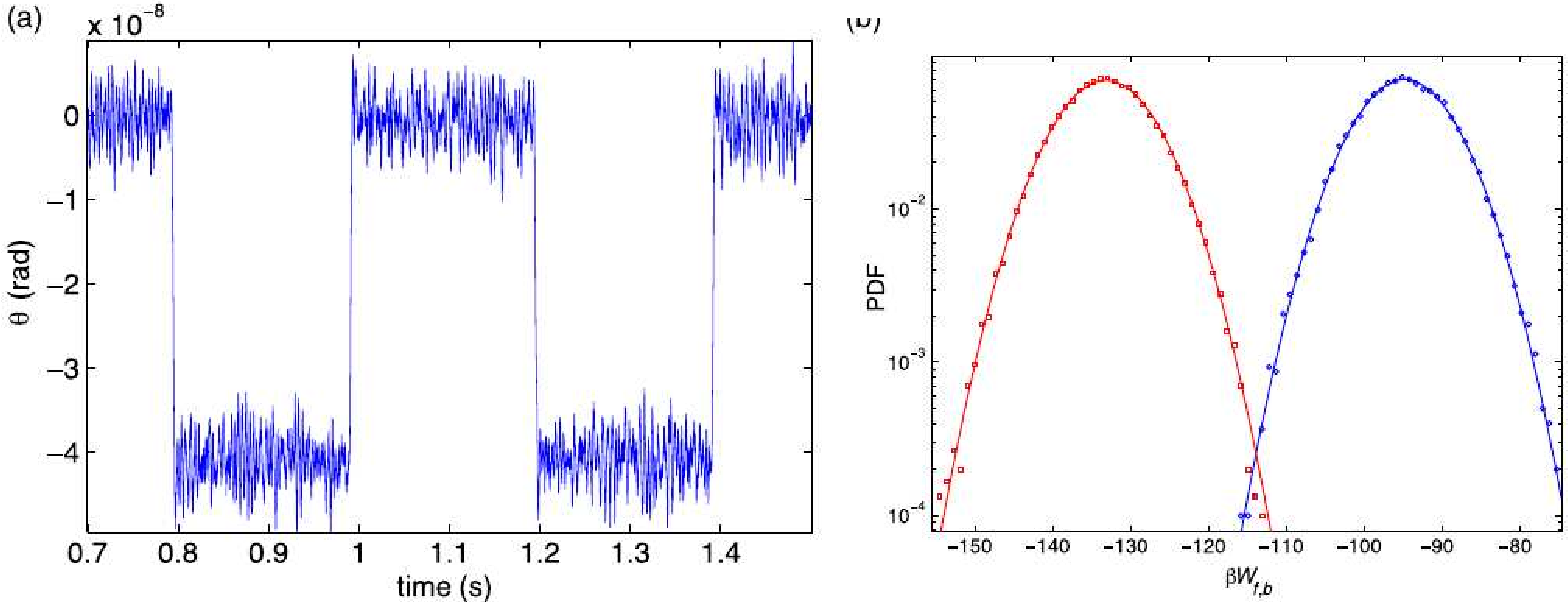
$$\int_{-\infty}^{\infty} P_F(W^J)\ \exp\left(-\frac{W^J}{K_B T}\right)\ dW^j = \exp\left(-\frac{\Delta F}{K_B T}\right)$$

which is the Jarzynski equality:

$$<\ \exp(-\beta\ W^J)\ > = \exp(-\beta \Delta F)$$

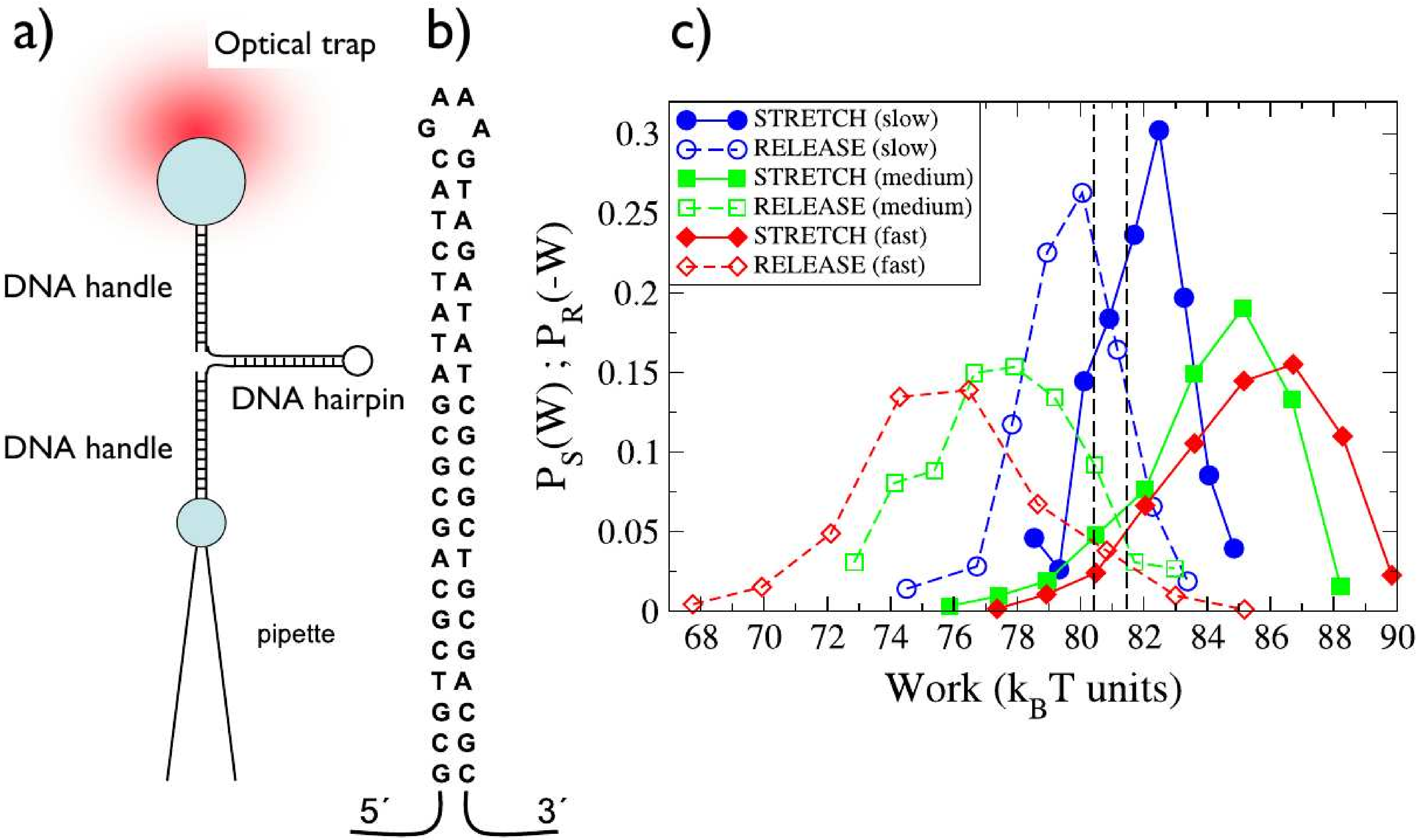
Free energy difference in the torsion pendulum

$$I_{\text{eff}} \frac{d^2\theta}{dt^2} + \nu \frac{d\theta}{dt} + C\theta = M + \eta$$



(a) Time evolution of θ when a periodic torque $M(t)$ drives the oscillator from A ($\theta = 0$) to B [$\theta = 41$nrad) and vice versa. In this specific case the stiffness is $C \simeq 5.5$Nm, the transition time is $t_s \simeq 0.1\tau_{relax}$, and $M = 22.4$pNm/ rad.
(b) Probability distribution functions of the work for the forward (blue curve) and backward (red curve) transformation. The crossing point of the two PDFs determines the value of $\Delta F_{A,B}$. The crossing point is at $W \simeq 112 k_B T$, which is within experimental errors of the expected theoretical $\Delta F_{A,B} \simeq 110 k_B T$.

Application of Crooks equation to the measure of the free energy of DNA hairpin



A. Mossa, M. Manosas, N. Forms, J.M. Huguet, and Felix Ritort. Dynamic force spectroscopy of dna hairpins: I. Force kinetics and free energy landscapes. J. Stat. Mech., page P02060, 2009.

Reversed dynamics

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

$P_+[z_t|z_0]$ Probability of observing the trajetory z_t

$P_-[z_t^R|z_0^R]$ probability to observe the reversed path having also reversed the driving

Q_t Heat dissipated along the path z_t

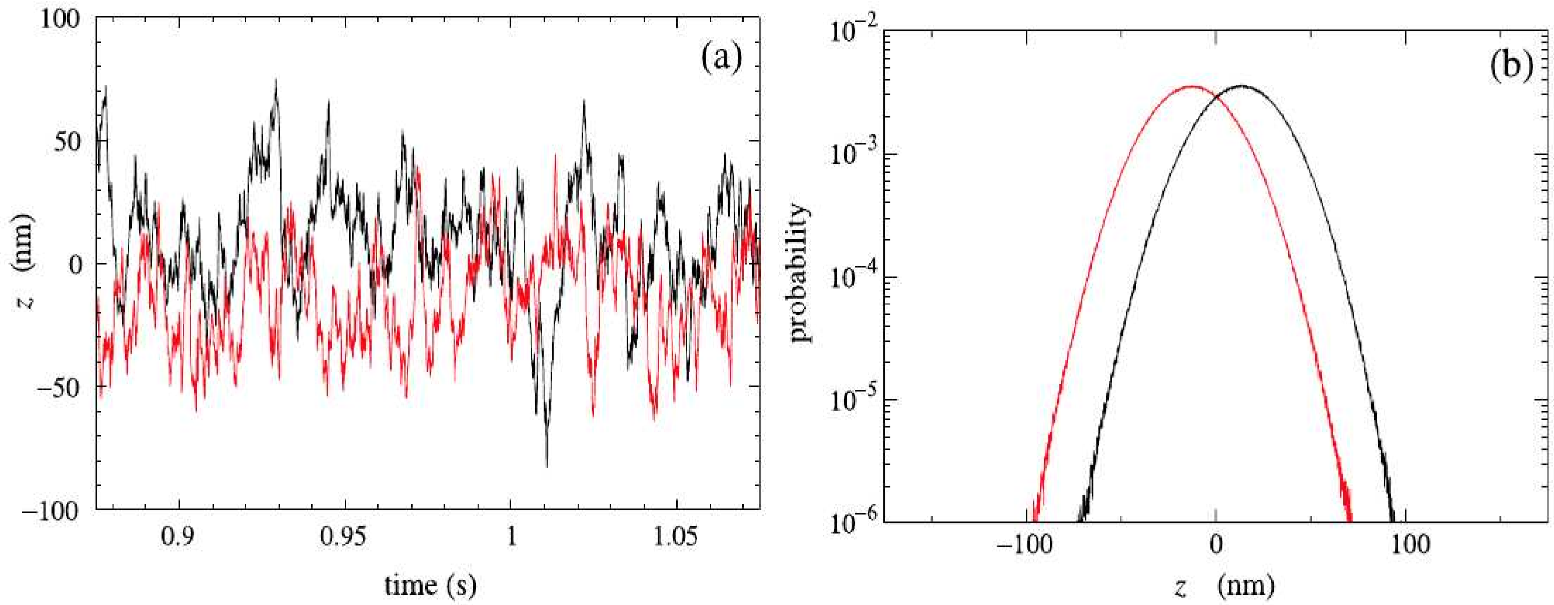
Onsager L and Machlup S, 1953 Phys. Rev. 91 1505

Crooks G E, 1999 Phys. Rev. E 60 2721

D Andrieux et al. 2008, JSTAT P01002

Time arrow in non-equilibrium fluctuations

Andrieux D, Gaspard P, et al. PRL, 98, 150601 (2007), JSTAT P01002 (2008).



Brownian particle in fluid moving at speed u

$$\alpha\ \dot{z} = -k\ z + \alpha\ u + \eta(t)$$

$$W_t = -\int_0^t u\, F(z_{t'})\, \mathrm{d}t'$$

$$Q_t = \int_0^t (\dot{z}_{t'} - u)\, F(z_{t'})\, \mathrm{d}t'.$$

The entropy production rate

$$\frac{\mathrm{d_i}S}{\mathrm{d}t} = \lim_{t\to\infty}\frac{1}{t}\frac{\langle Q_t\rangle}{T} = \lim_{t\to\infty}\frac{1}{t}\frac{\langle W_t\rangle}{T} = \frac{\alpha u^2}{T}$$

The entropy production rate in a NESS can also be computed using the thermodynamic time asymmetry of the non-equilibrium fluctuations.

No knowledge of the parameters of the system is required. We need only

1) to measure the position of the particle without calibration.
2) the possibility of driving with u and - u

ENS DE LYON

Time arrow in non-equilibrium fluctuations

Andrieux D, Gaspard P, et al. PRL, 98, 150601 (2007), JSTAT P01002 (2008).

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

1) Construct a reference vector $\boldsymbol{Z}_m = [Z(m\tau),\ldots,Z(m\tau+n\tau-\tau)]$

2) Measure de probability $P_+(\boldsymbol{Z}_m;\varepsilon,\tau,n) = \frac{1}{L'}\mathrm{Number}\{\boldsymbol{Z}_j : \mathrm{dist}_n(\boldsymbol{Z}_m,\boldsymbol{Z}_j)\leq\varepsilon\}$

3) Average $H(\varepsilon,\tau,n) = -\frac{1}{M}\sum_{m=1}^{M}\ln P_+(\boldsymbol{Z}_m;\varepsilon,\tau,n)$

4) $h(\varepsilon,\tau) = \lim_{n\to\infty}\lim_{L',M\to\infty}\frac{1}{\tau}\left[H(\varepsilon,\tau,n+1) - H(\varepsilon,\tau,n)\right].$

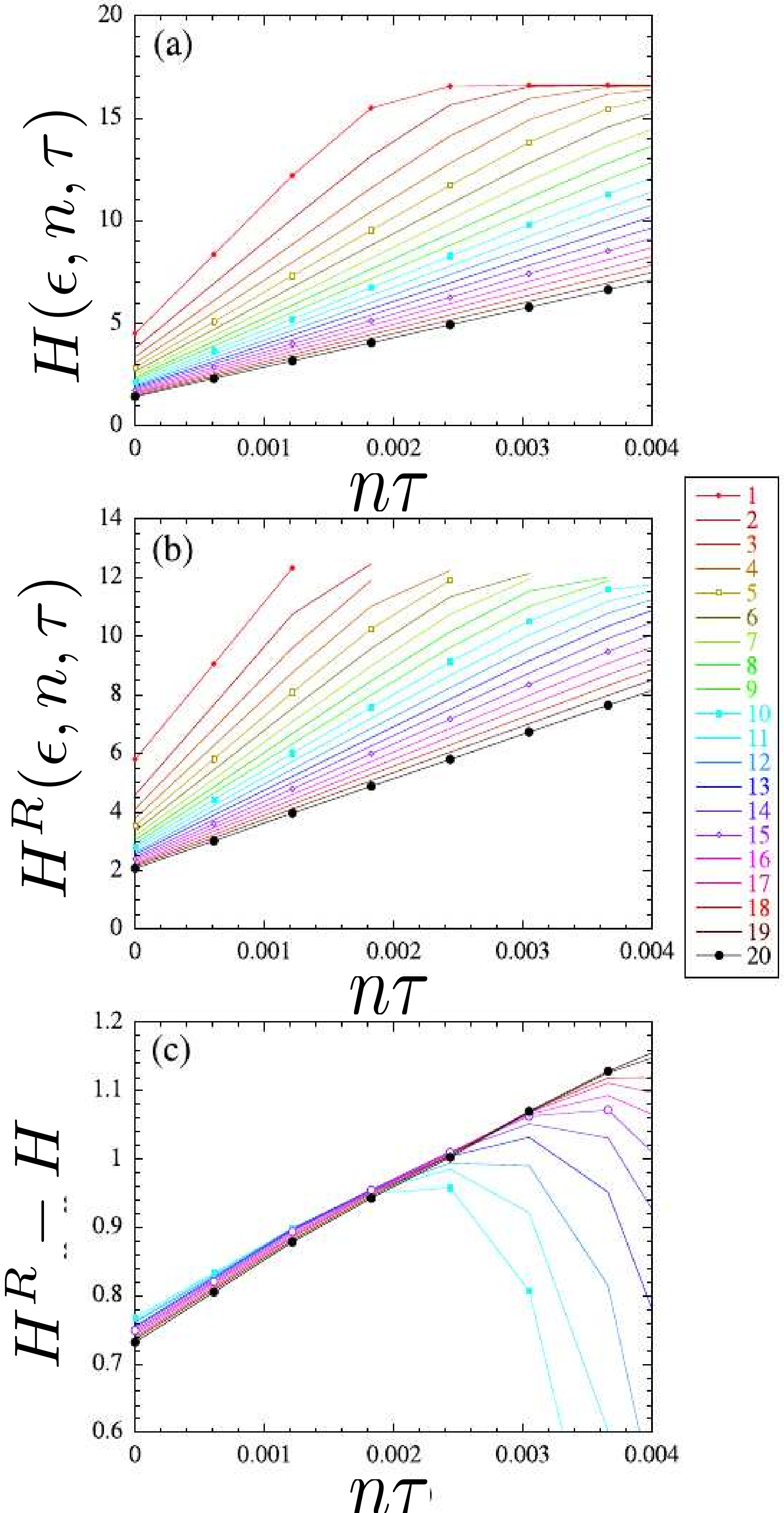
Algorithm similar to the Grassberger-Procaccia method for fractal dimension

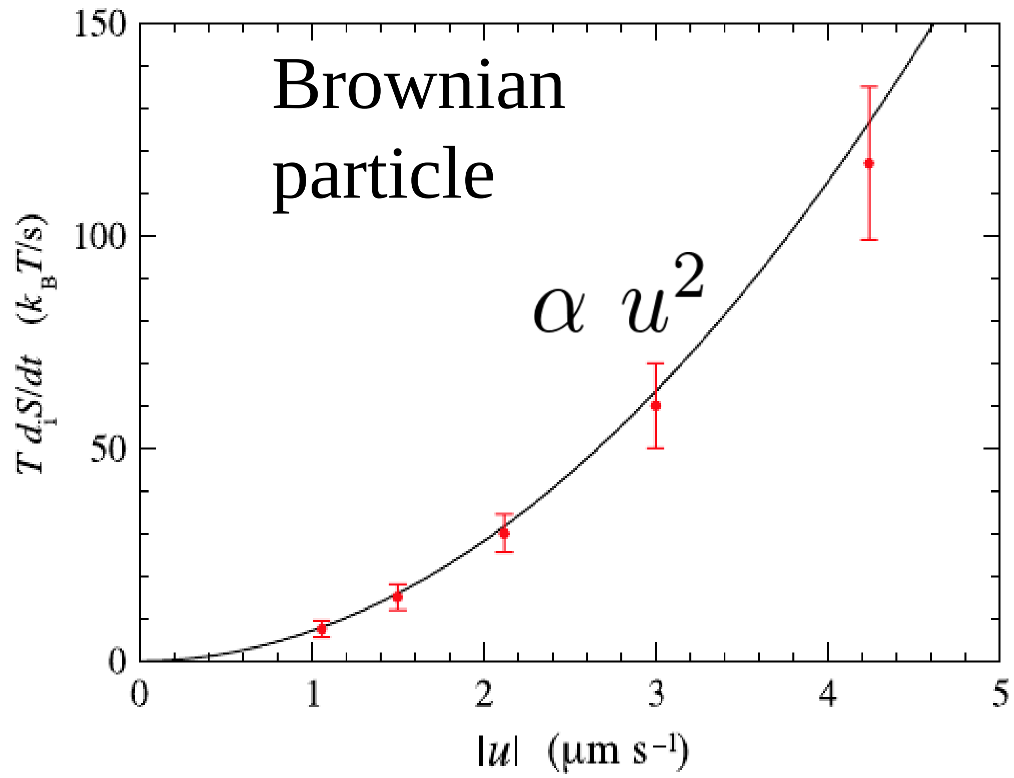
5) Repeat the previous steps for the system driven backward and with the inverted Zm

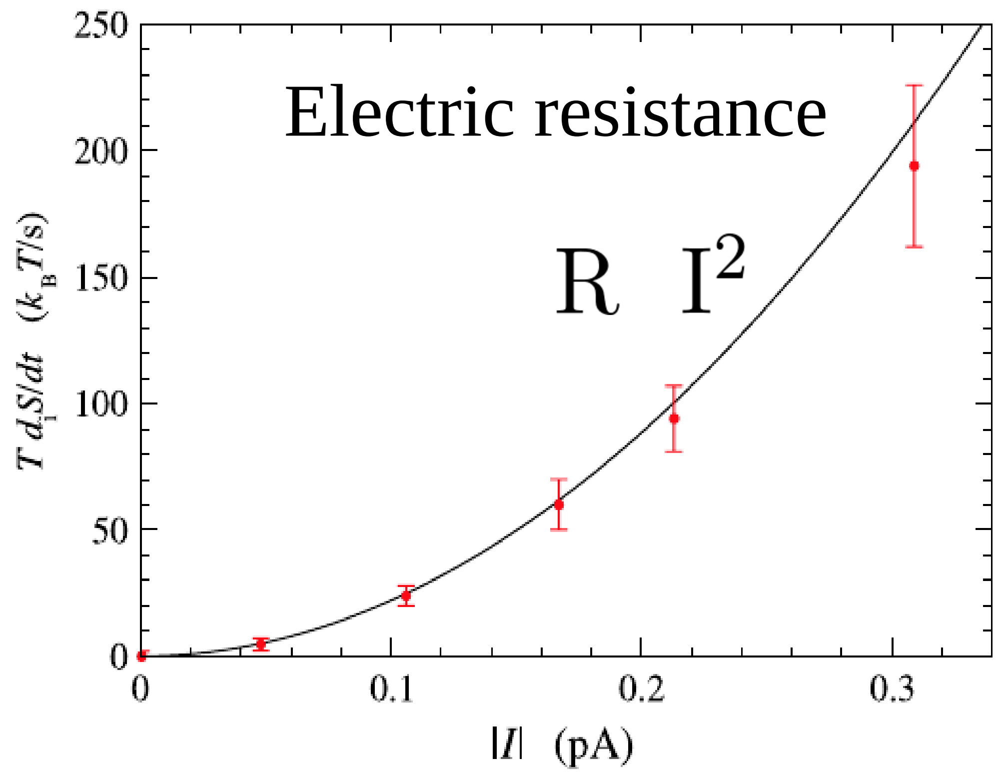
$$P_-(\boldsymbol{Z}_m^{\mathrm{R}};\varepsilon,\tau,n) = \frac{1}{L'}\mathrm{Number}\{\tilde{\boldsymbol{Z}}_j : \mathrm{dist}_n(\boldsymbol{Z}_m^{\mathrm{R}},\tilde{\boldsymbol{Z}}_j)\leq\varepsilon\}$$

Time arrow in non-equilibrium fluctuations

Andrieux D, Gaspard P, et al. PRL, 98, 150601 (2007), JSTAT P01002 (2008).







Conclusion

The entropy production rate is measured using the breaking of the time reversal symmetry out of equilibrium.

What Stochastic Thermodynamics is useful for ?

1) Jarzinsky and Crooks equalities are useful to compute the free energy difference bewteen two equilibrium states using any kind of transformation

2) Hatano-Sasa relation and the Fluctuation Dissipation Theorem for non equilibrium steady states(NESS). These are useful to compute the response function of NESS.

3) The measure of energy fluctautions allows us to estimate tiny amount of heat exchanged bewteen the system and its heat bath.

4) Calibration of an out of equilibrium system (the force, the offset, the mean injected power).

5) The role of hidden variables and the stochastic inference. *To what extent the fact that FT and FDT do not* hold can give information on hidden variables ?

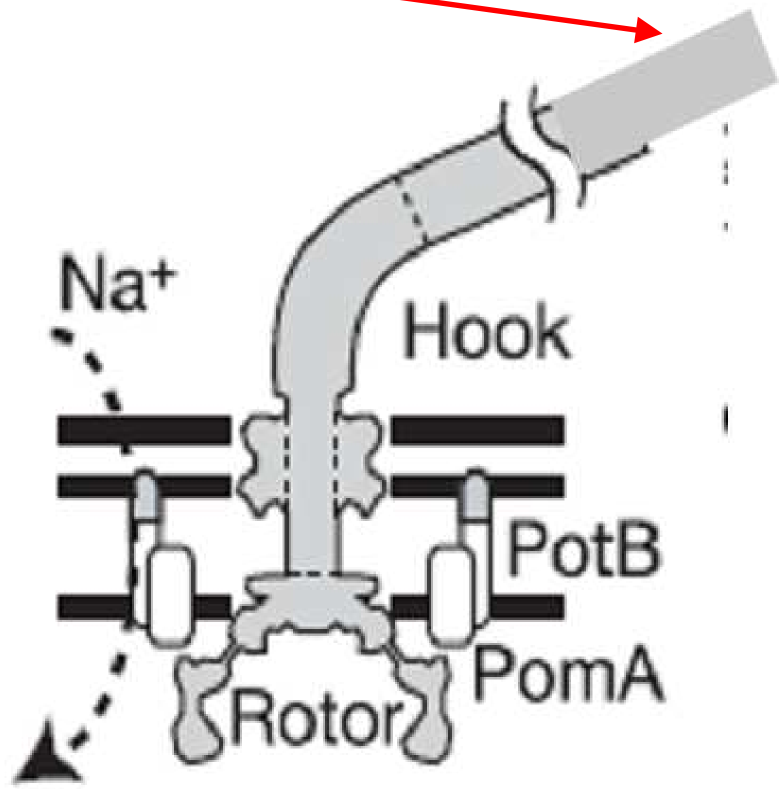
6) Efficiency of nano and micro motors

7) Energy information connection and the role of Maxell's demon.

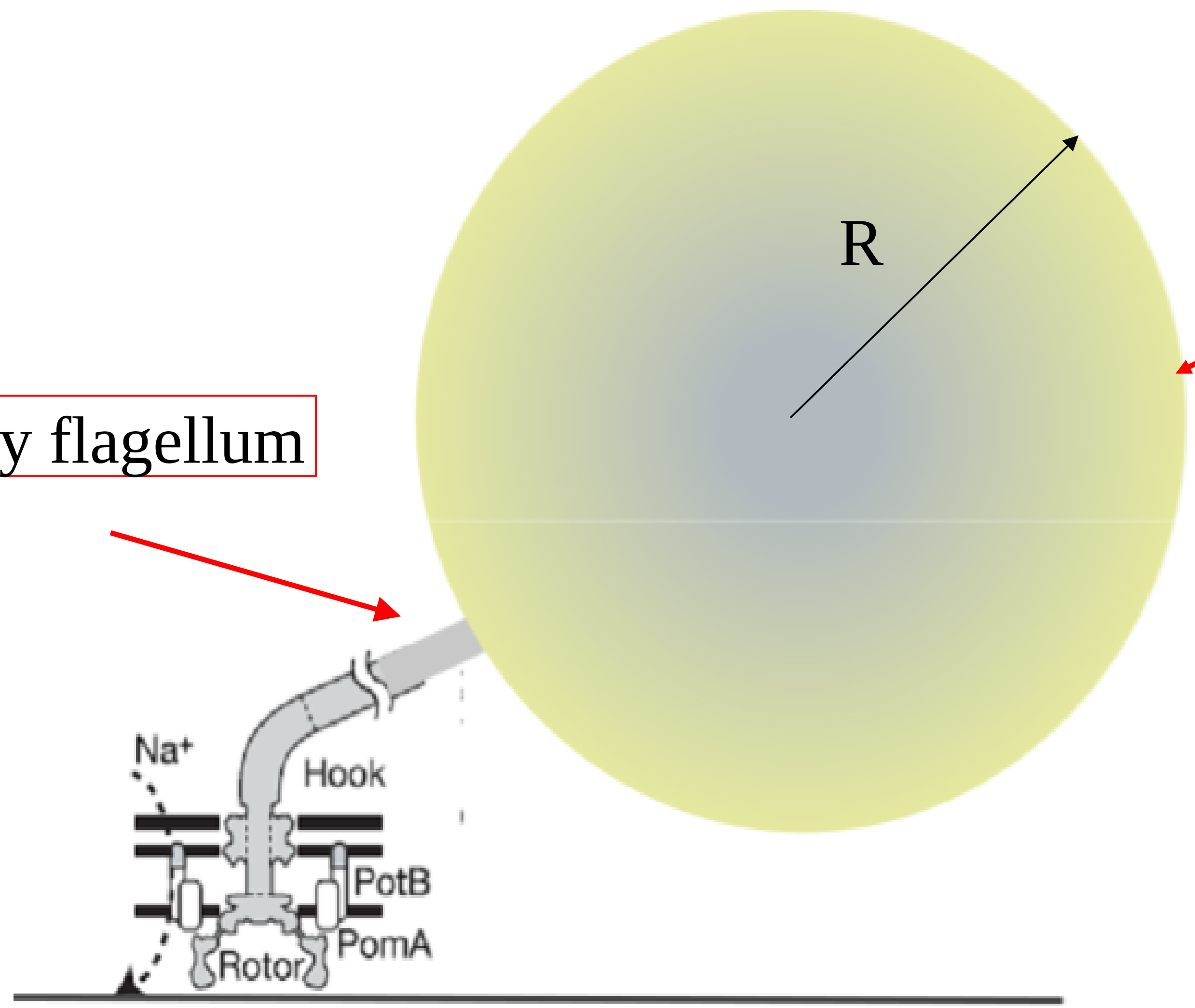
8) Engineered Swift equilibration (ESE)

Molecular motor and FT

Sticky flagellum



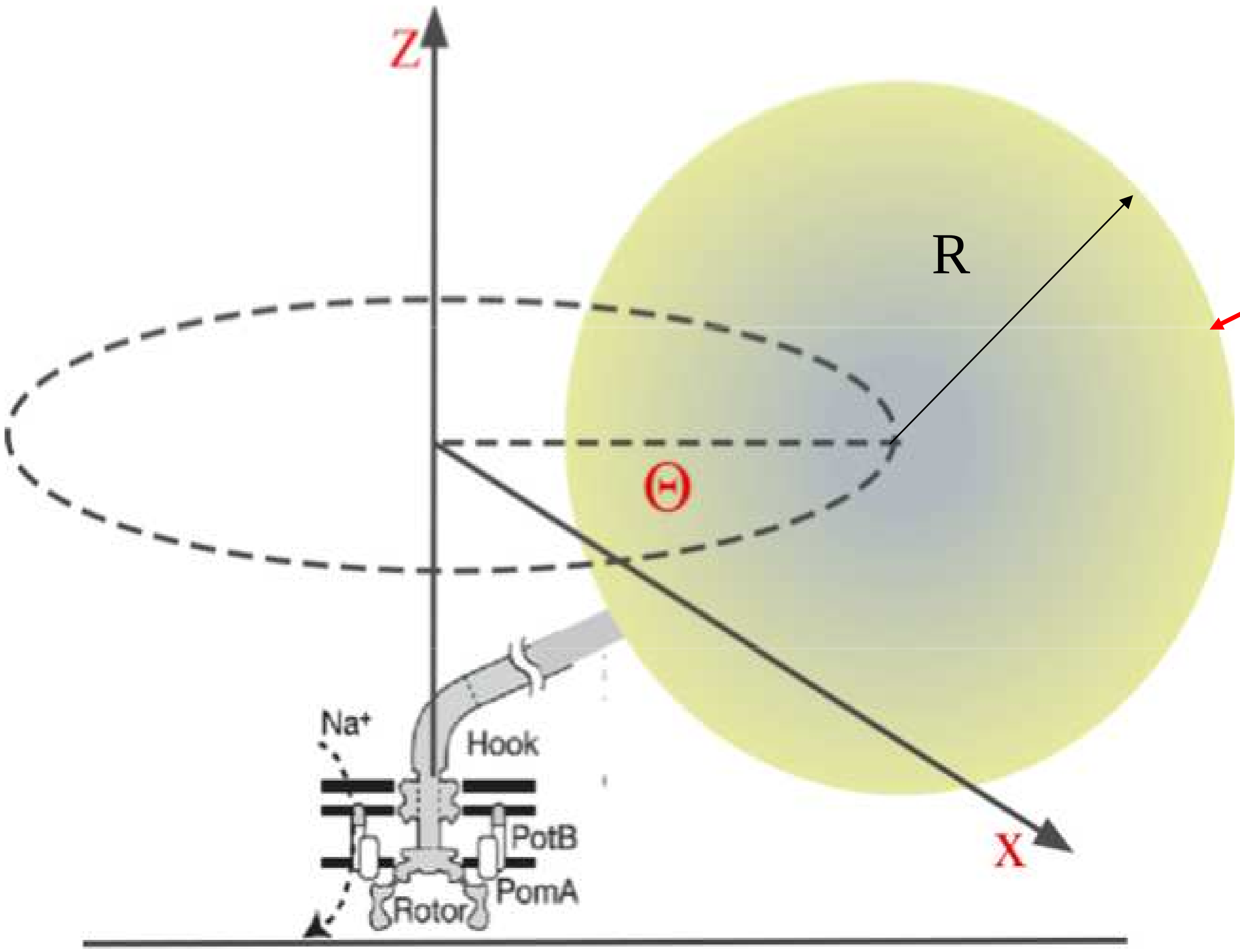
Molecular motor and FT



$$R \simeq 0.5\mu m$$

(drawing not in scale)

Molecular motor and FT



polystyrene bead

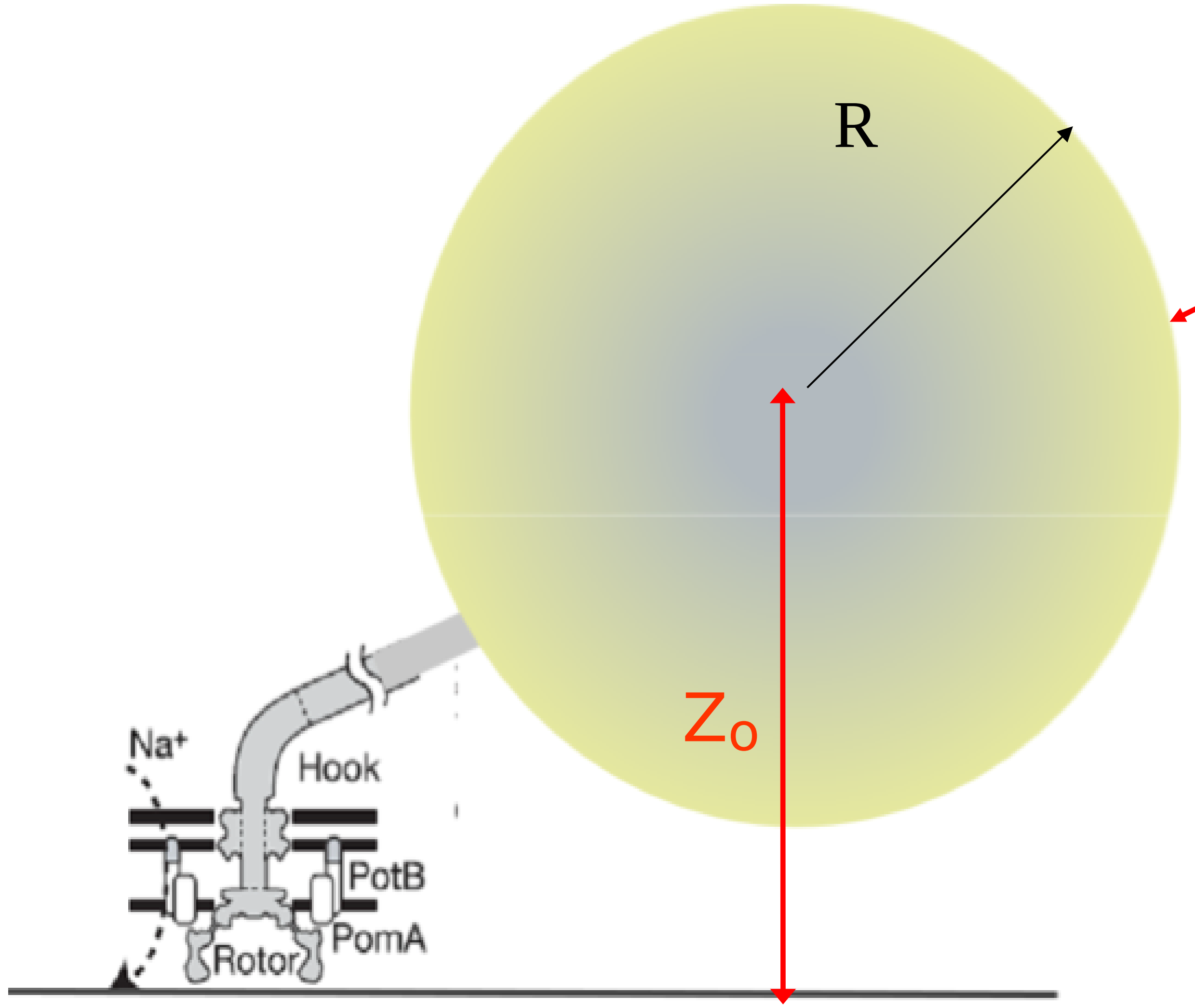
$$R \simeq 0.5\mu m$$

$$\gamma\dot{\theta} = N + \eta$$

Standard method to determine the torque N

$$N = \frac{<\dot{\theta}>}{\gamma}$$

Molecular motor and FT



$$R \simeq 0.5\mu m$$

$$\gamma \dot{\theta} = N + \eta$$

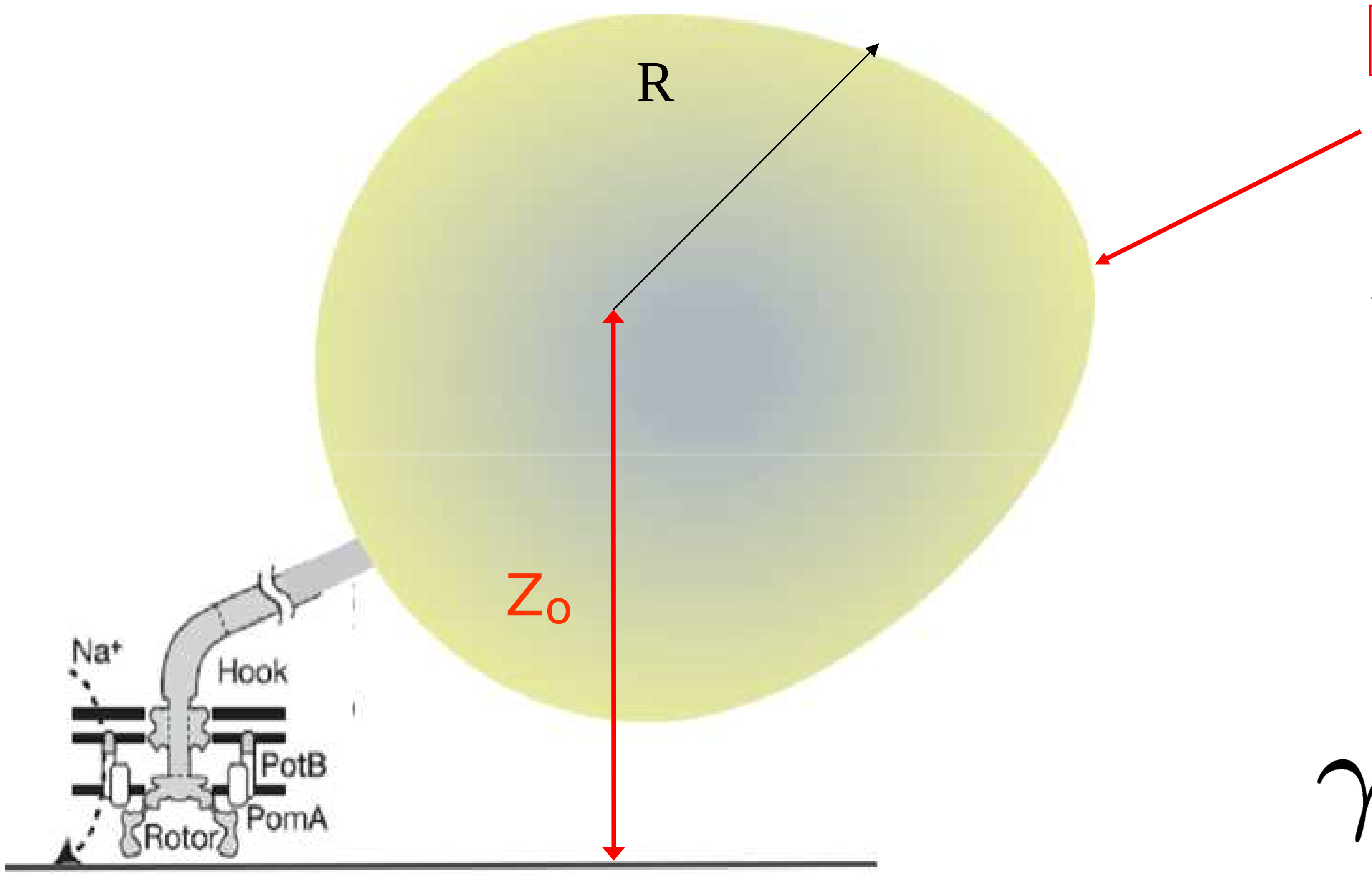
Standard method to determine the torque N

$$N = \frac{<\dot{\theta}>}{\gamma}$$

but

$$\gamma(R, Z_0)$$

Molecular motor and FT



$$R \simeq 0.5 \mu m$$

$$\gamma \dot{\theta} = N + \eta$$

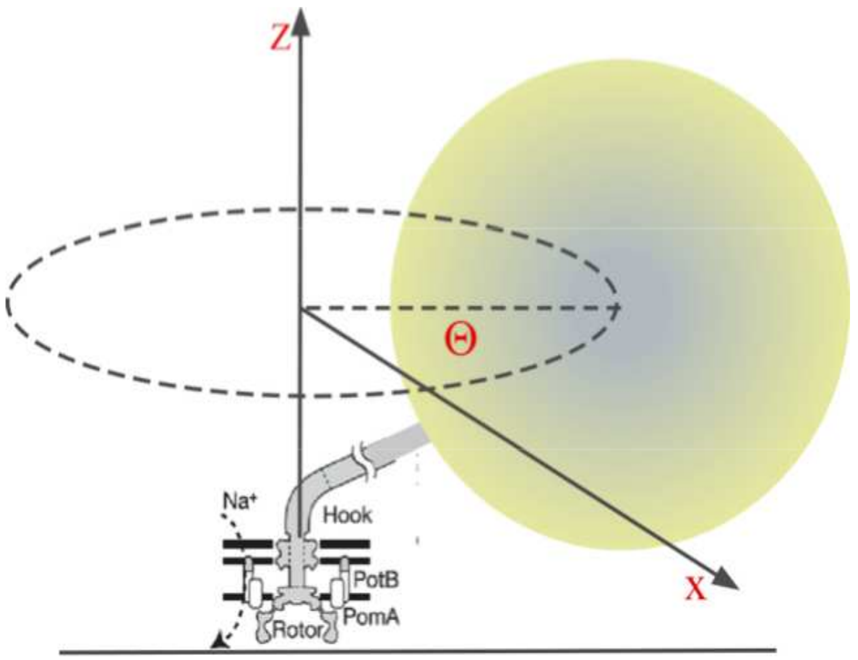
Standard method to determine the torque N

$$N = \frac{<\dot{\theta}>}{\gamma}$$

but $\gamma(R, Z_0)$

and of the shape

Molecular motor and FT



New method based on FT to determine the torque N

$$\gamma \dot{\theta} = N + \eta$$

$$W_\tau = N \int_t^{t+\tau} \dot{\theta} \; dt = N \; \Delta\theta_\tau \quad \text{where } \Delta\theta_\tau = (\theta(t+\tau) - \theta(t))$$

SSFT for W_τ

$$\log\left(\frac{P(\Delta\theta_\tau)}{P(-\Delta\theta_\tau)}\right) = \Sigma(\tau) \; N \; \frac{\Delta\theta_\tau}{k_B T}$$

γ is not needed

with $\Sigma(\tau) \to 1$ for $\tau \to \infty$

Molecular motor and FT

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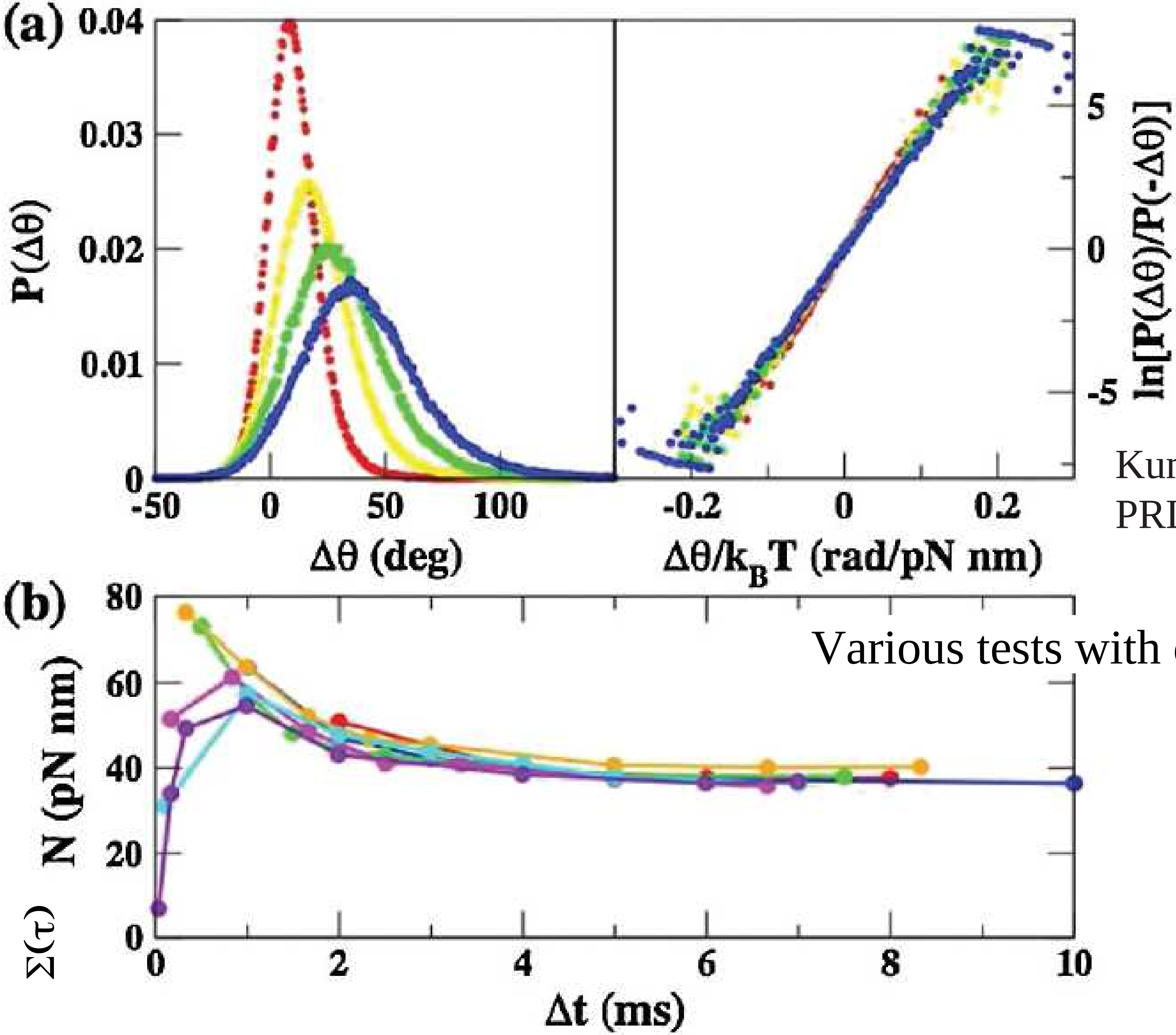
$$\log\left(\frac{P(\Delta\theta_\tau)}{P(-\Delta\theta_\tau)}\right) = \Sigma(\tau)\ N\ \frac{\Delta\theta_\tau}{k_B T}$$



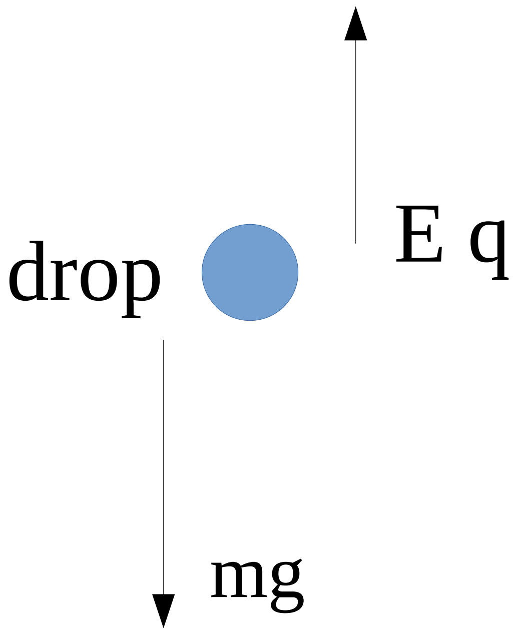
Kumiko Hayashi et al.,
PRL 104, 218103 (2010)

Various tests with different beads

(size and shape)

Using FT for calibration

The Millikan experiment



$$\gamma \dot{x} = -m\ g + E\ q + \eta$$

$$< \dot{x} >= -mg/\gamma$$

$$qE = mg$$

Standard method

Determination of m

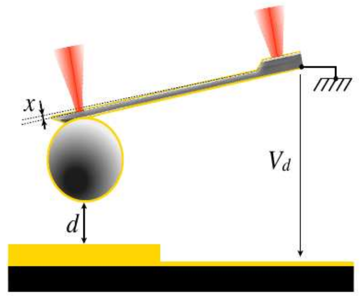
and then measure of q

Using FT for calibration

$$W = (-mg + Eq)\ x$$

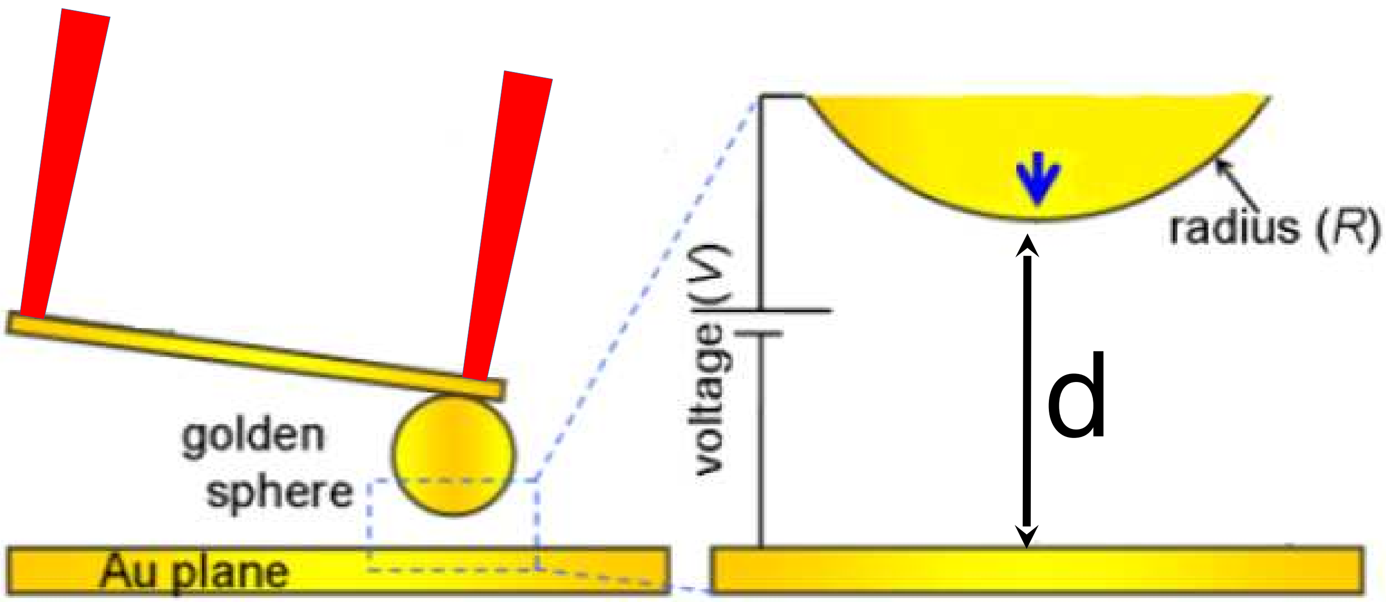
$$\log \frac{P(x)}{P(-x)} = \frac{W}{k_B T}$$

$$\log \frac{P(x)}{P(-x)} = \frac{-mg + Eq}{k_B T}\ x$$

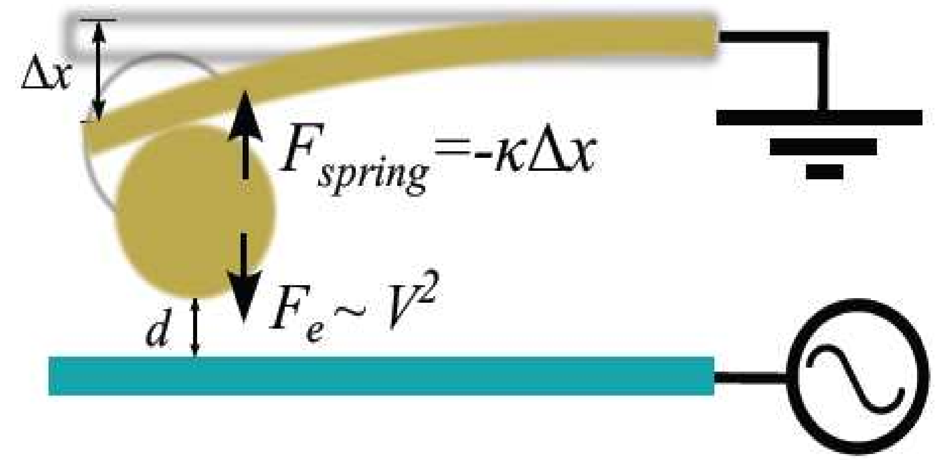


Transient Fluctuation Theorem
Force Measurement with an Atomic Force Microscope
without calibration

The AFM cantilever



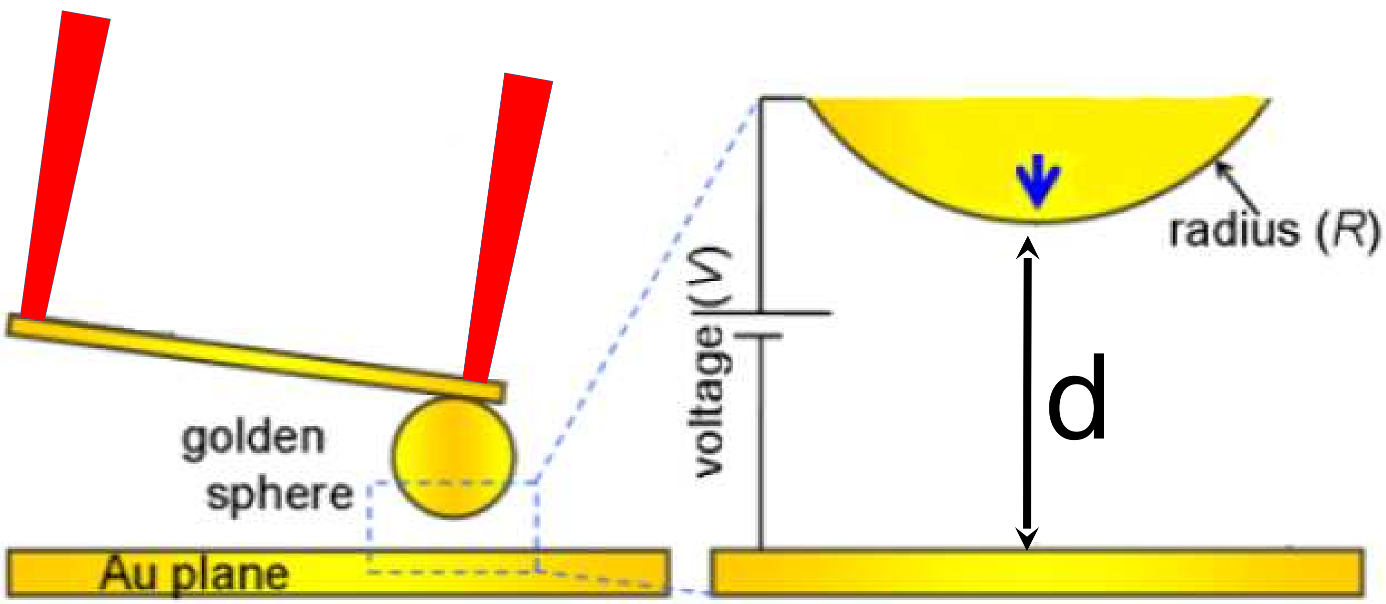
$$F_e = \frac{4\pi_0 R V^2}{d}$$



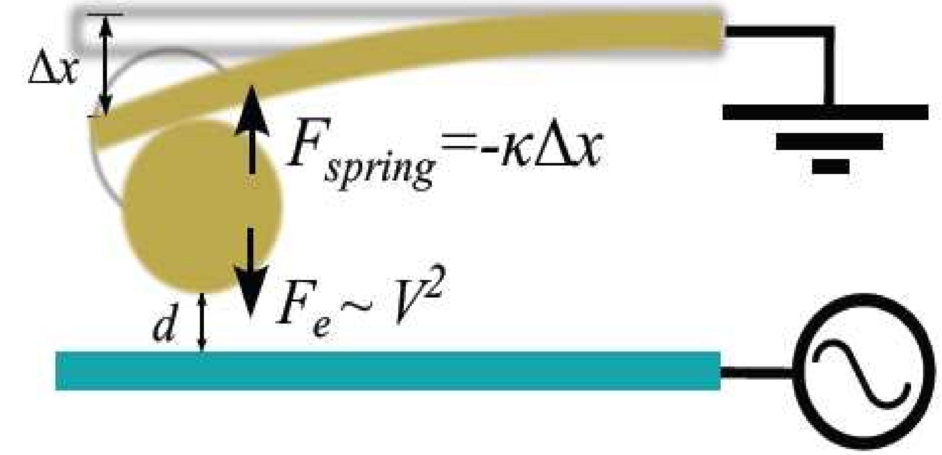
F=k $\times \Delta x$

Δx interferometric measure
k need to be calibrated

The AFM cantilever



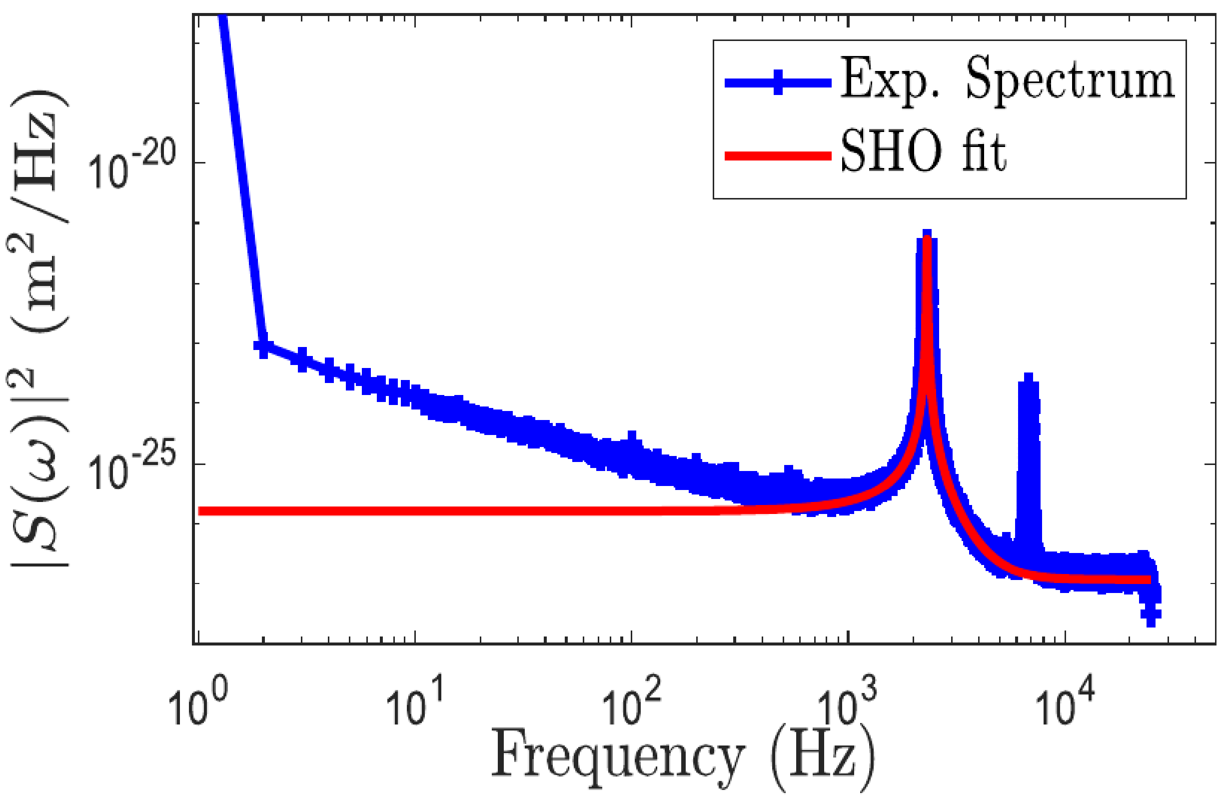
$$F_e = \frac{4\pi_0 R V^2}{d}$$



$F = k \times \Delta x$

Δx interferometric measure
k need to be calibrated

Standard Calibration



- Langevin equation for one vibration mode :

$$m \ddot{x} + \gamma \dot{x} + k x = \xi(t)$$

- Predict the fluctuations spectrum and adjust the parameters

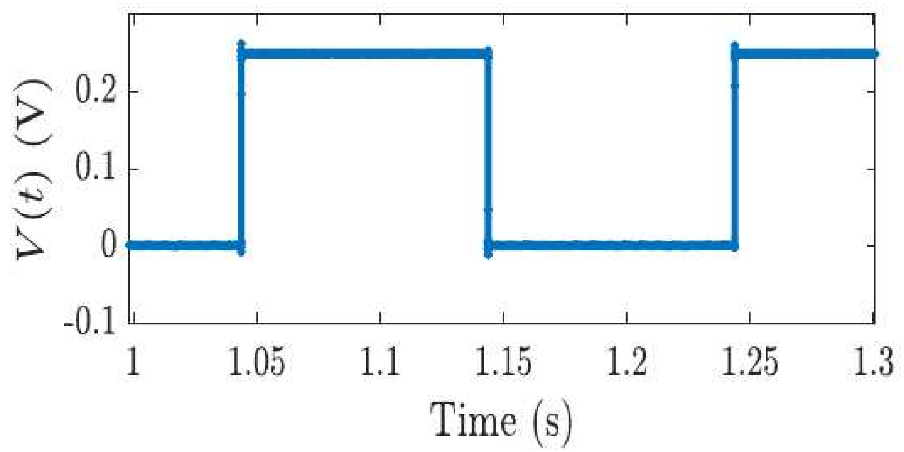
Using Transient Fluctuation Theorem

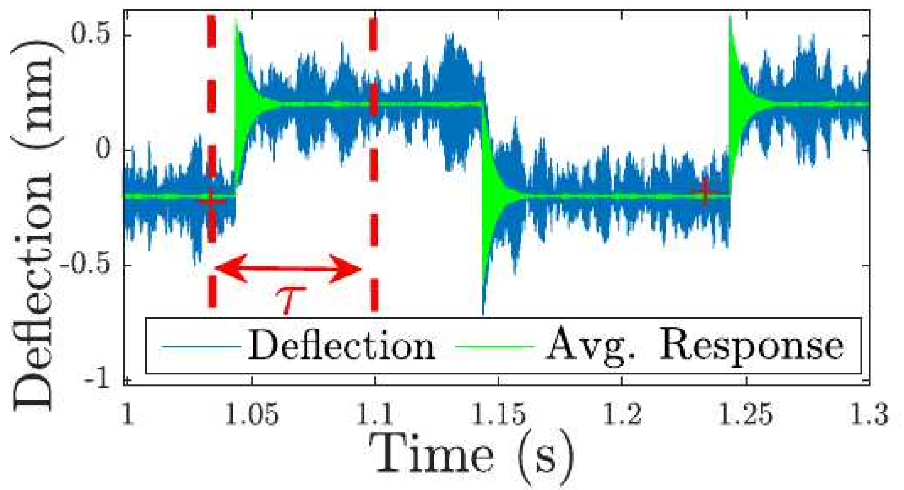
Transient fluctuation Theorem (TFT) for a system in equilibrium at t=0.

W_τ is the work performed by the external forces in a time τ

$$\ln\left(\frac{\mathcal{P}(W_\tau)}{\mathcal{P}(-W_\tau)}\right) = \frac{W_\tau}{k_B T}, \qquad \forall\tau.$$

Apply a periiodic voltage





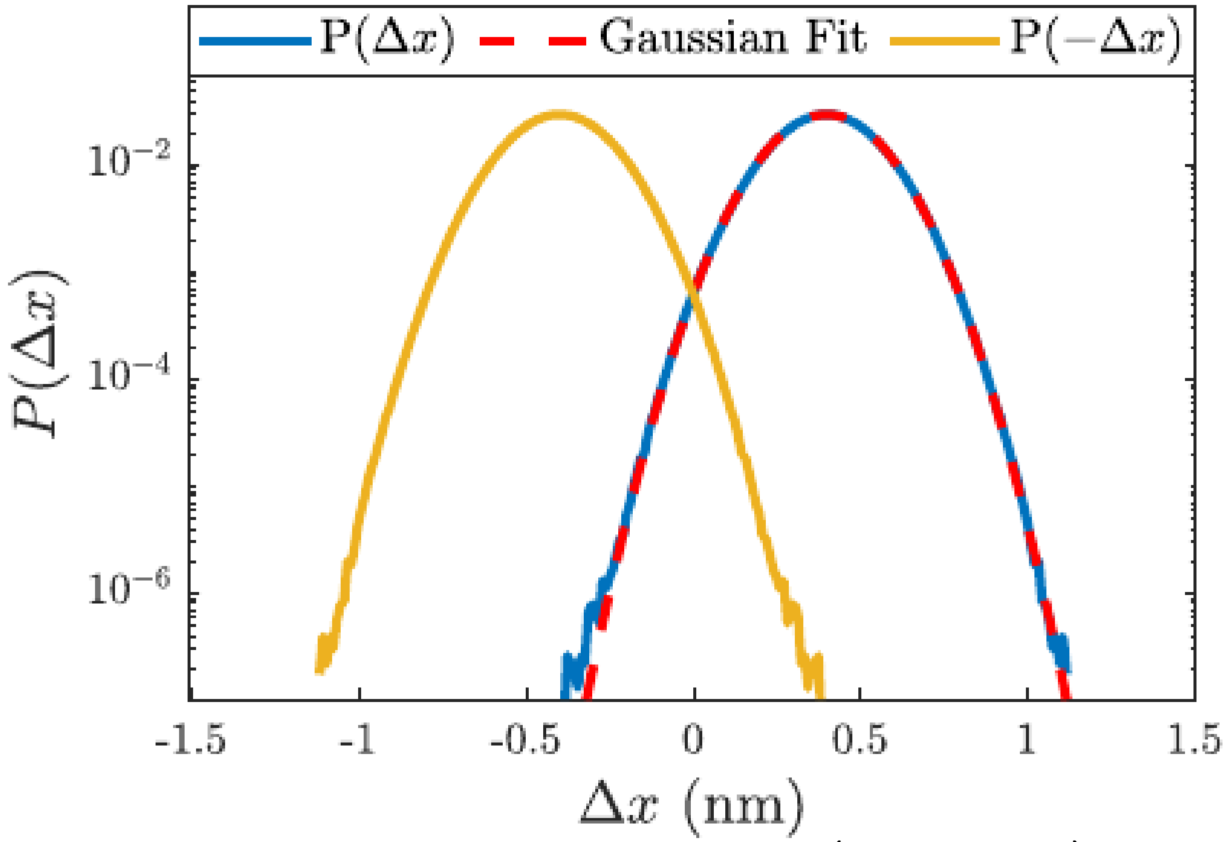
$$W_\tau = F\int_0^\tau \dot{x}\,\mathrm{d}t = F\,\Delta X_\tau$$

$$\Delta X_\tau = x_f(\tau) - x_i(0)$$

$$\Phi(W_\tau) = \log\left(\frac{P(W_\tau)}{P(-W_\tau)}\right) = \Phi(\Delta X_\tau)$$

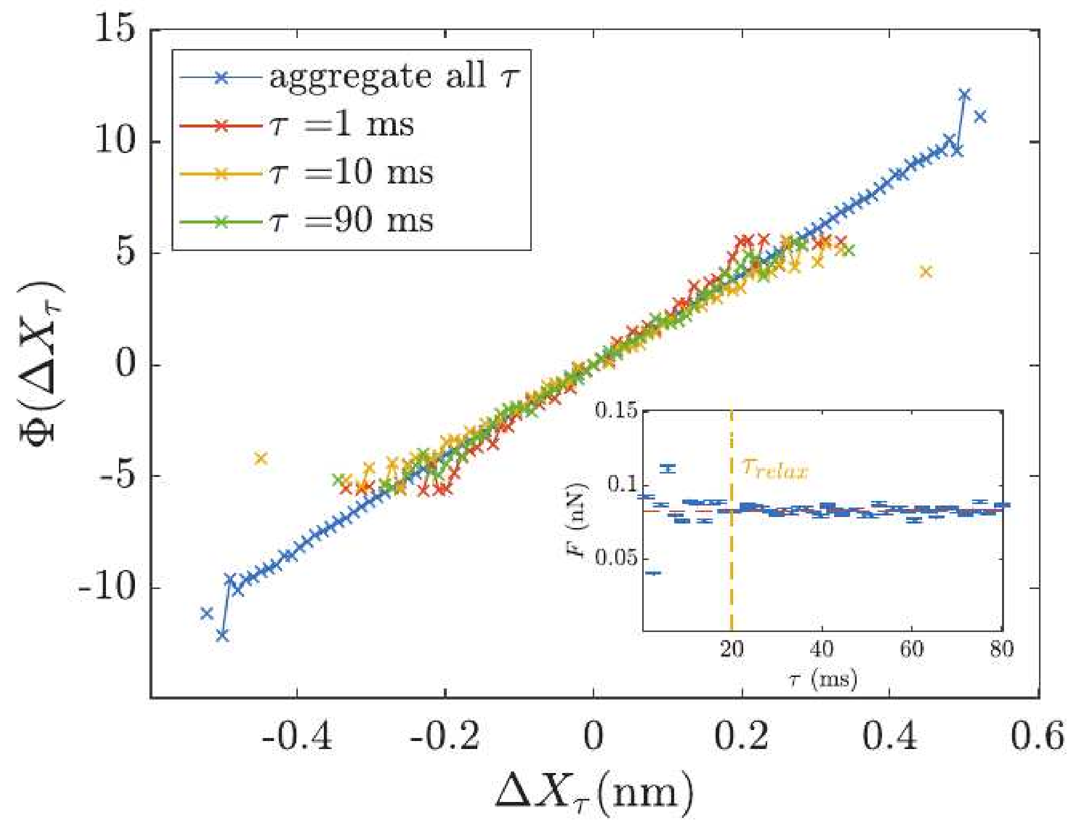
TFT : $\quad \Phi(\Delta X_\tau) = \dfrac{F\Delta X_\tau}{k_B T}$

Using Transient Fluctuation Theorem



$$\Phi(\Delta X_\tau) = \log\left(\frac{P(\Delta X_\tau)}{P(\Delta X_\tau)}\right)$$

TFT : $\Phi(\Delta X_\tau) = \frac{F\Delta X_\tau}{k_B T}$



Conclusions

1) We get the value of the sphere-plane interaction force without doing any hypothesis on the experimental apparatus.

2) Extension to non controlled forces ⇒ Step in distance instead of force

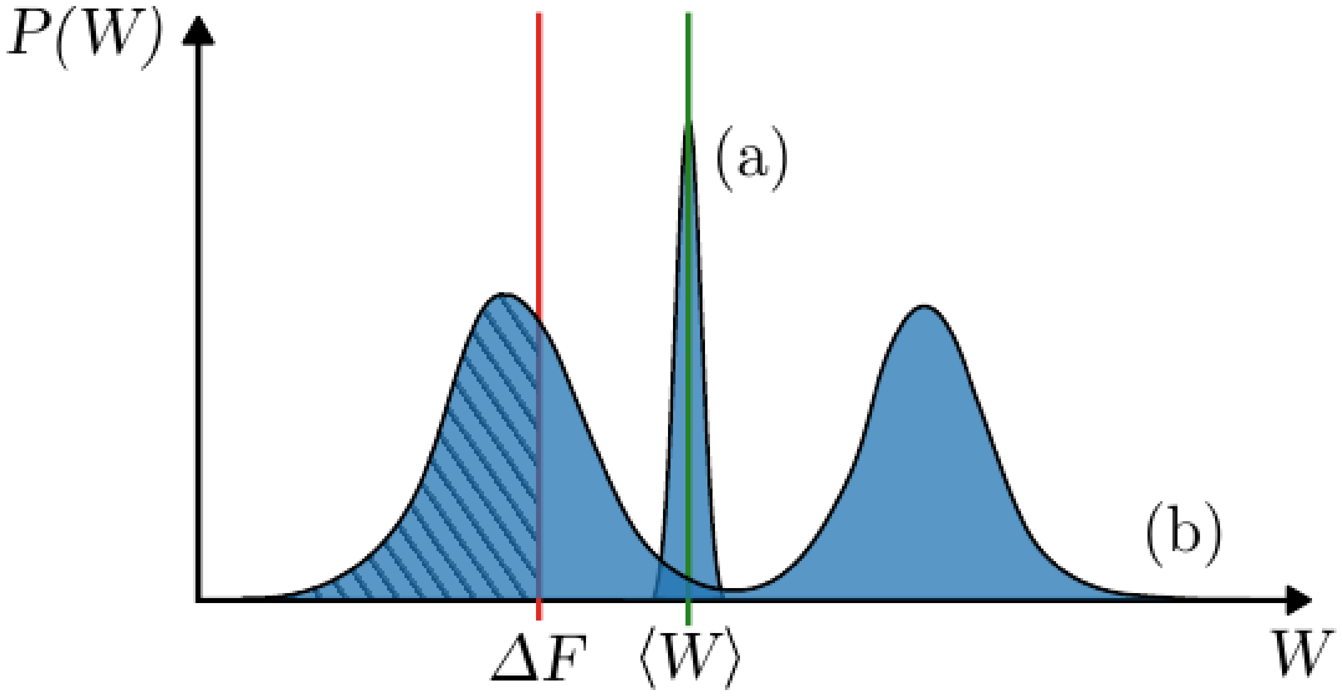
S. Albert, A. Archambault, A. Petrosyan, C. Crauste, L. Bellon, S. C., EPL , 131(1) :10008 (2020)

Probabilistic work extraction on a classical oscillator beyond the second law

Nicolas Barros , SC, and Ludovic Bellon

arXiv:2402.18556

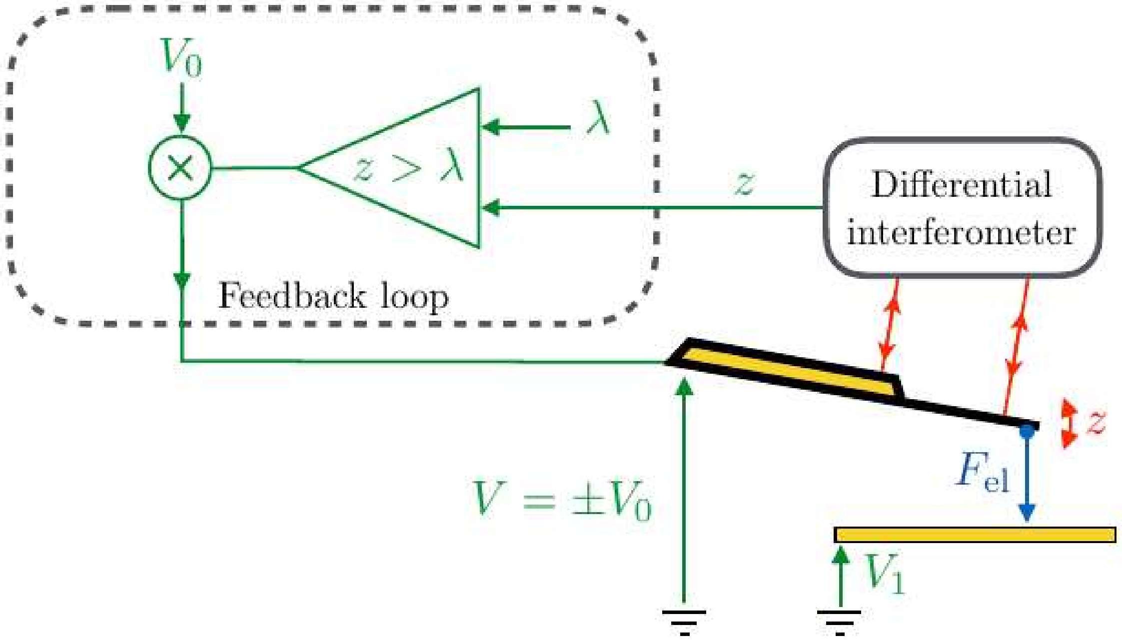
Drive a system from an equilibrium state A to another equilibrium state B



Probability distribution of the work

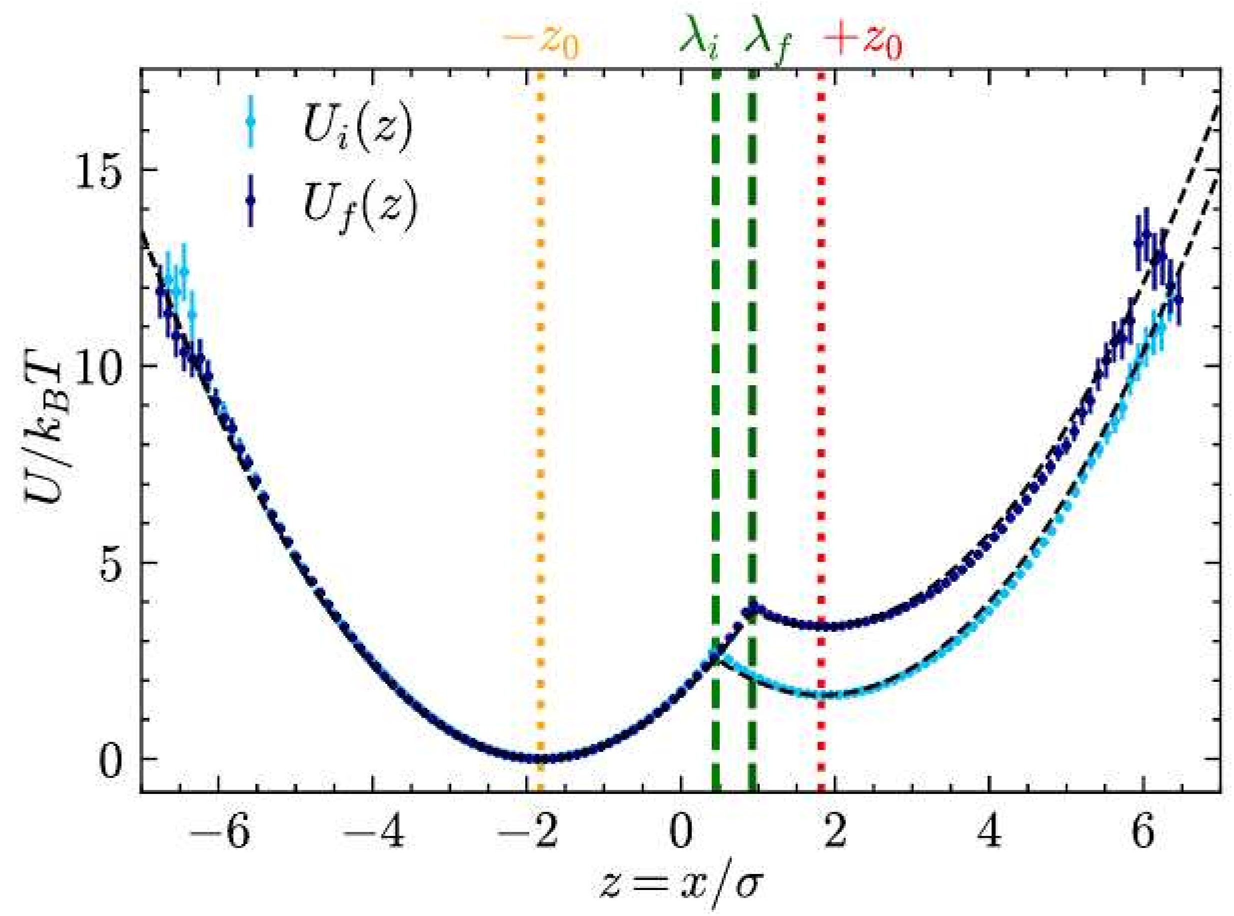
Can we design a protocol in which the second principle is violated more than 90% of the times ?

Probabilistic work extraction on a classical oscillator beyond the second law

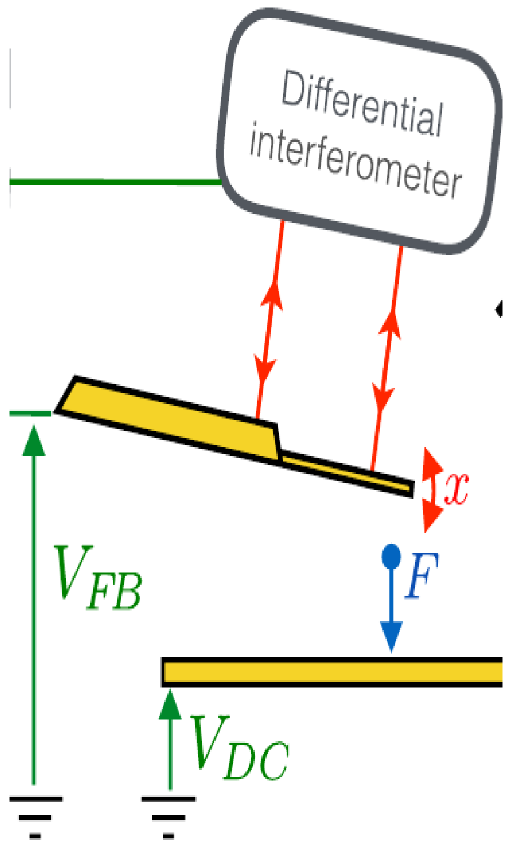


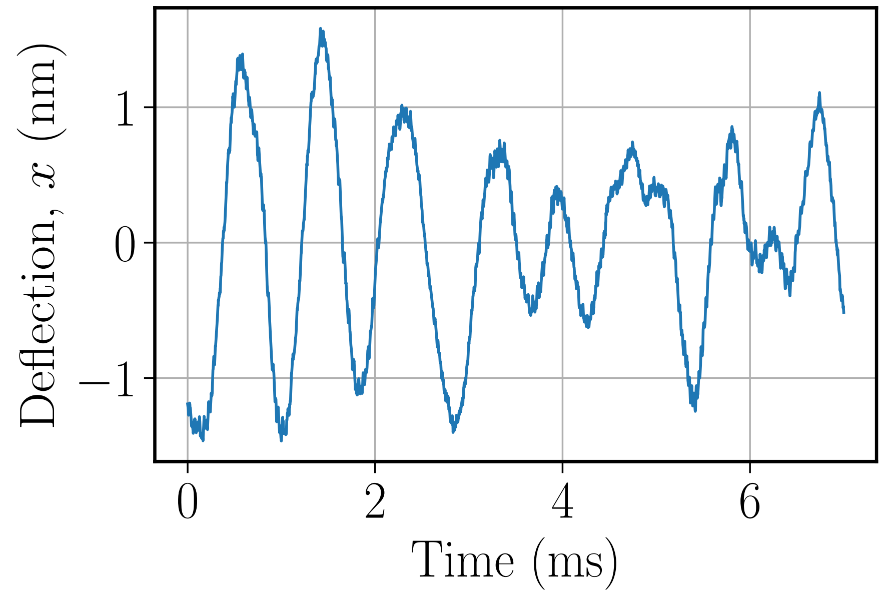
The experimental apparatus

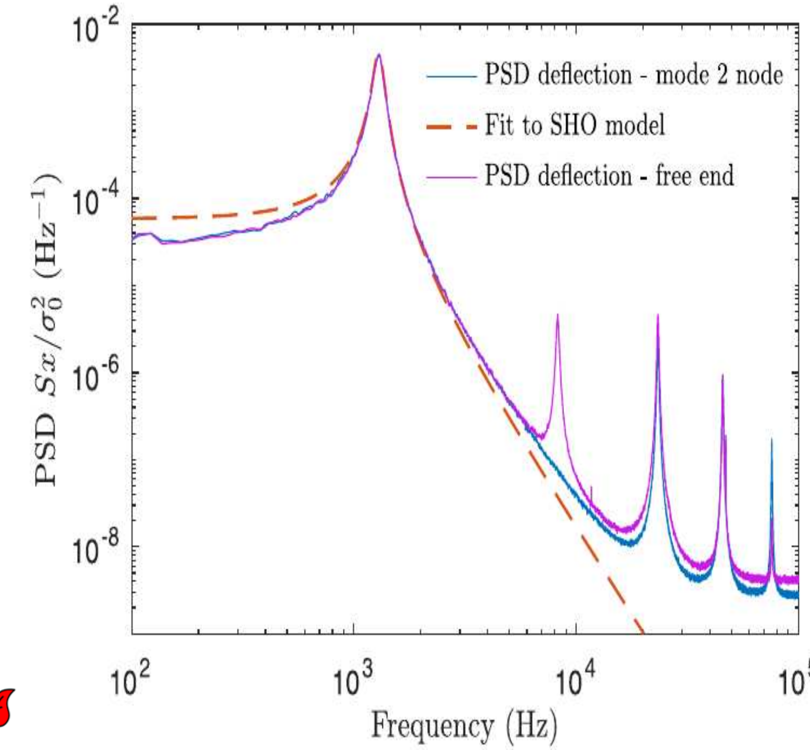
$$U(z, \lambda, z_0) = \frac{1}{2}\left(z - S(z-\lambda) z_0\right)^2 + \lambda z_0 \left(S(z-\lambda) + S(\lambda)\right)$$



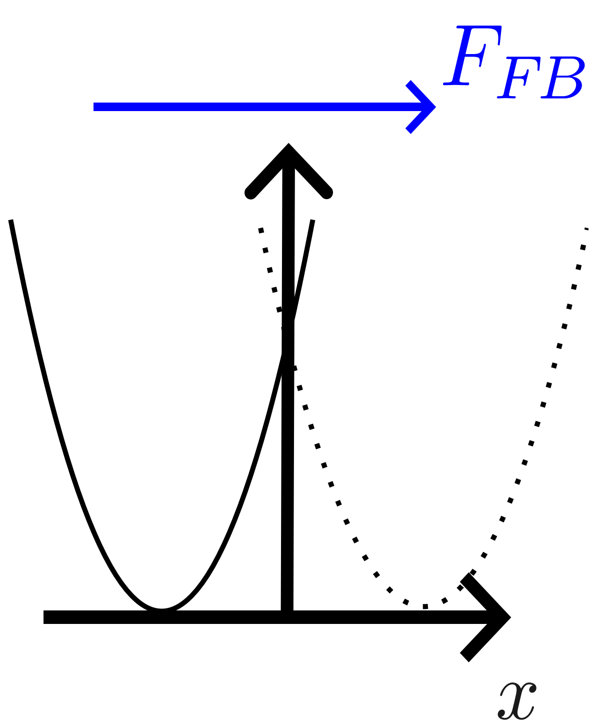
Microcantilever, a model for Brownian particle



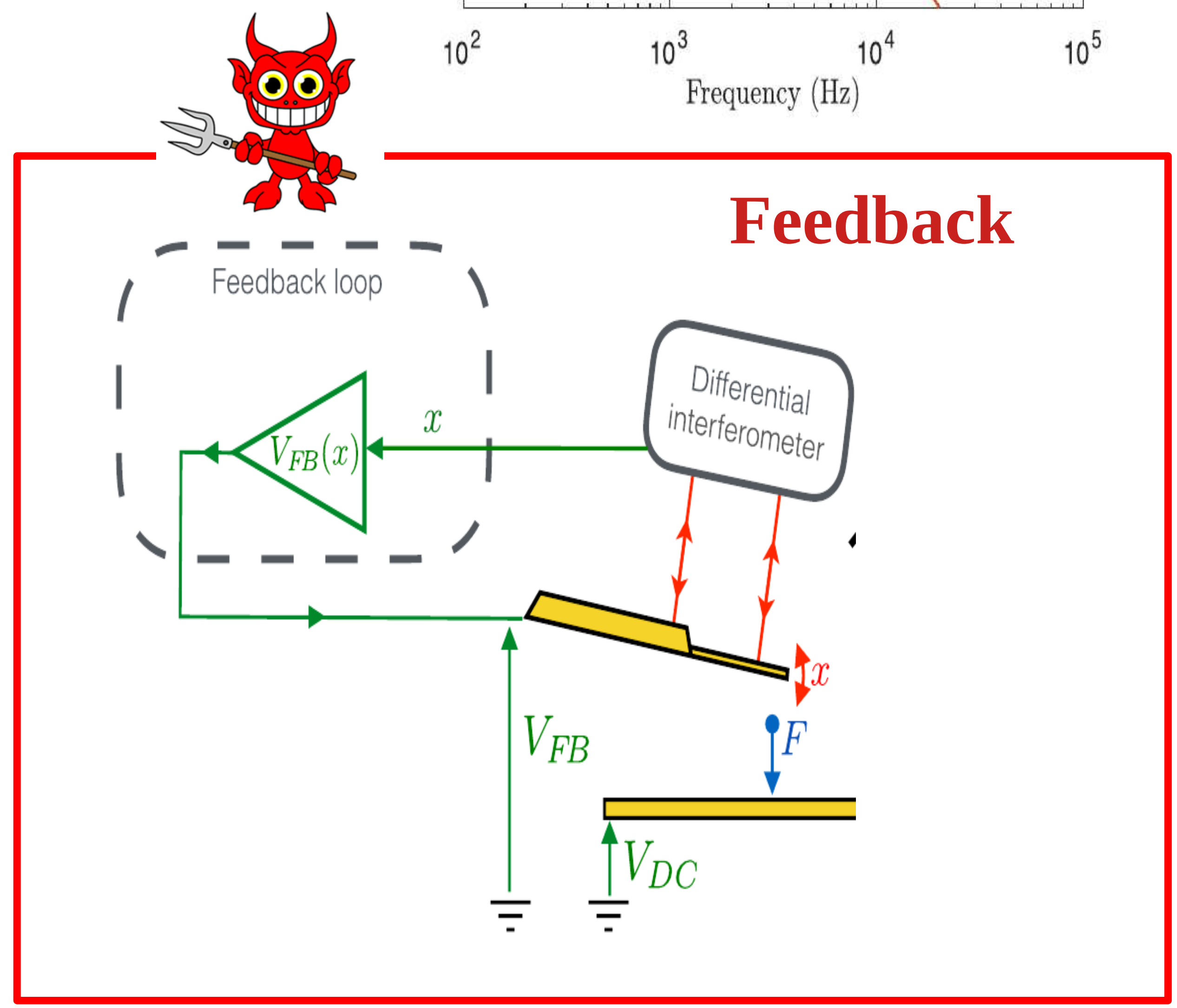


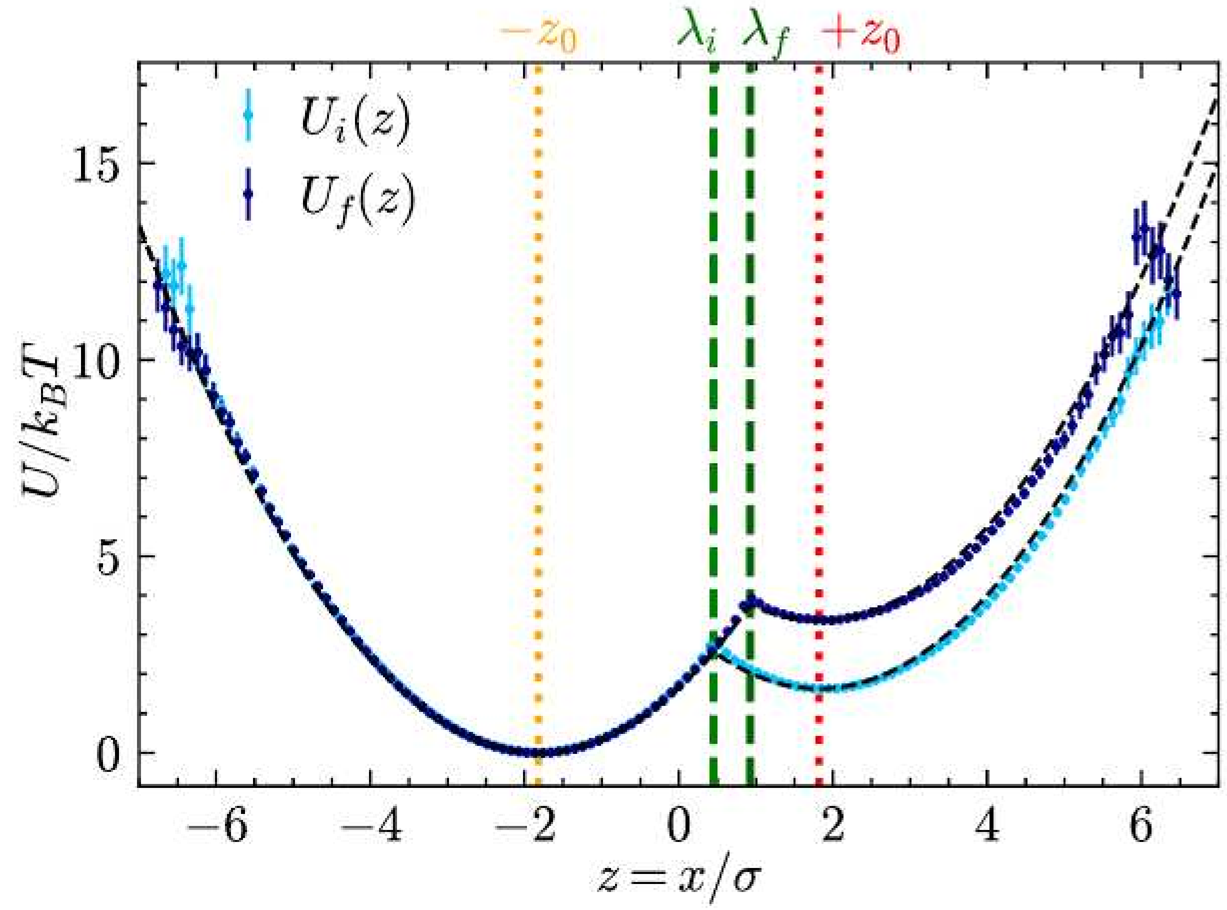


$$m\ddot{x} + \gamma\dot{x} + kx = \xi(t) + F_{FB}(t)$$



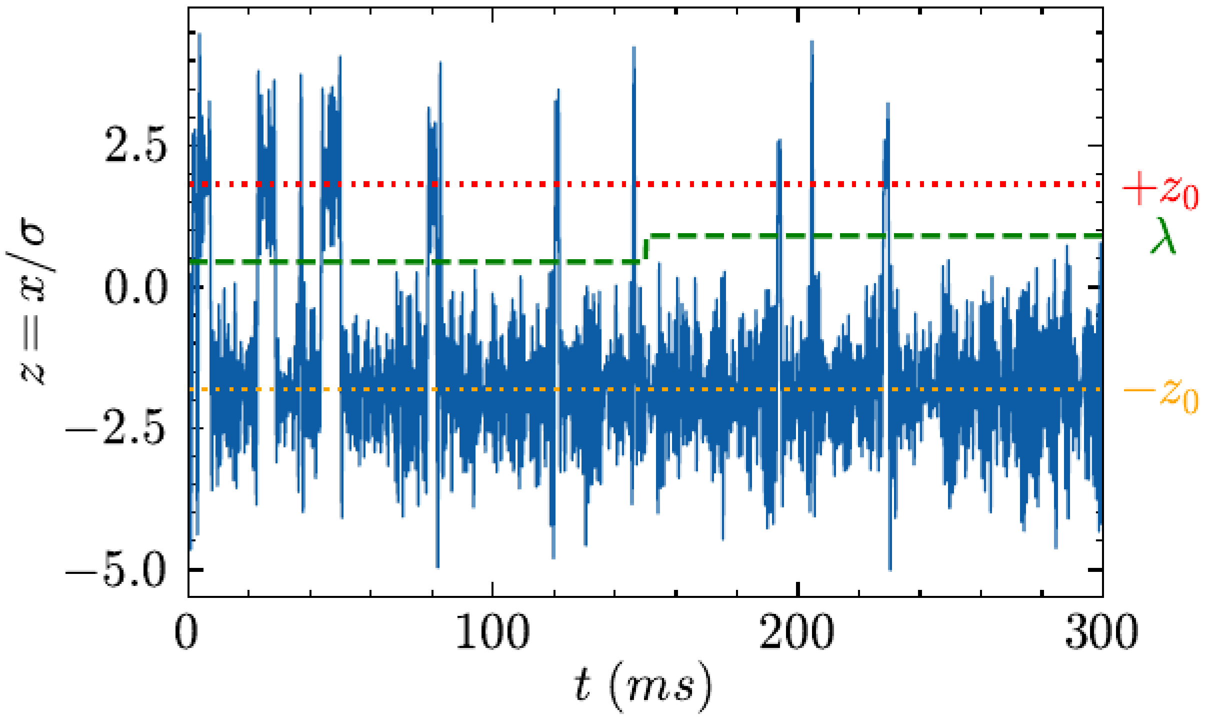
$$F_{FB} \propto V_{FB}$$

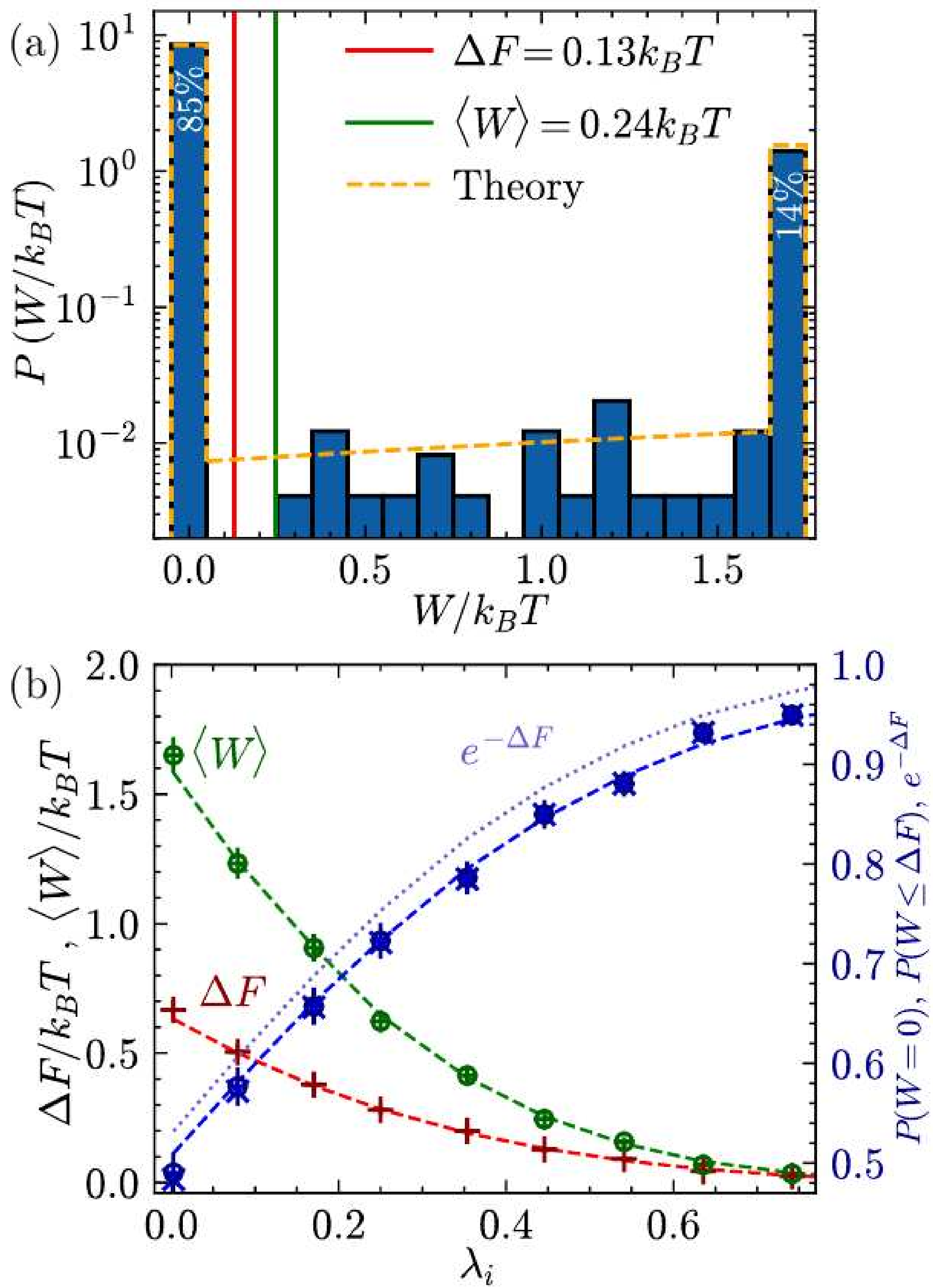




$$U(z, \lambda, z_0) = \frac{1}{2}\left(z - S(z-\lambda)z_0\right)^2 + \lambda z_0\left(S(z-\lambda) + S(\lambda)\right)$$

Time series





Proability distribution of the work

The second principle is violated by 90% of the trajectories but not in average

The system produces energy for 90% of the trajectories

In order to use this energy surplus one has to introduce a Maxwell demon which spends energy to elaborate information

What Stochastic Thermodynamics is useful for ?

1) Jarzinsky and Crooks equalities are useful to compute the free energy difference bewteen two equilibrium states using any kind of transformation

2) Hatano-Sasa relation and the Fluctuation Dissipation Theorem for non equilibrium steady states(NESS). These are useful to compute the response function of NESS.

3) The measure of energy fluctautions allows us to estimate tiny amount of heat exchanged bewteen the system and its heat bath.

4) Calibration of an out of equilibrium system (the force, the offset, the mean injected power).

5) The role of hidden variables and the stochastic inference. *To what extent the fact that FT and FDT do not* hold can give information on hidden variables ?

6) Efficiency of nano and micro motors

7) Energy information connection and the role of Maxell's demon.

8) Engineered Swift equilibration (ESE)

FT in dynamical systems

For stochastic systems FT can be safely used for applications

What about dynamical systems ?

$$\log \frac{P(X_\tau)}{P(-X_\tau)} = \frac{X_\tau}{k_B T_{eff}} \Sigma(\tau)$$

Dynamical systems

What is this prefactor ?

$$\log \frac{P(A_\tau)}{P(-A_\tau)} = \frac{\gamma \ \tau}{< A_\tau >} A_\tau \ \Sigma(\tau)$$

Dynamical systems

where γ is the phase space contraction rate

and A_τ is identified as the entropy production in the time τ

FT in dynamical systems

1) Turbulent flows

2) Granular media

3) Mechanical waves

FT in dynamical systems

Turbulent flows

Turbulence convection: Ciliberto S and Laroche C, 1998 J. Physique IV 8 215

Wind pressure : Ciliberto S et al. 2004 Physica A 340 240

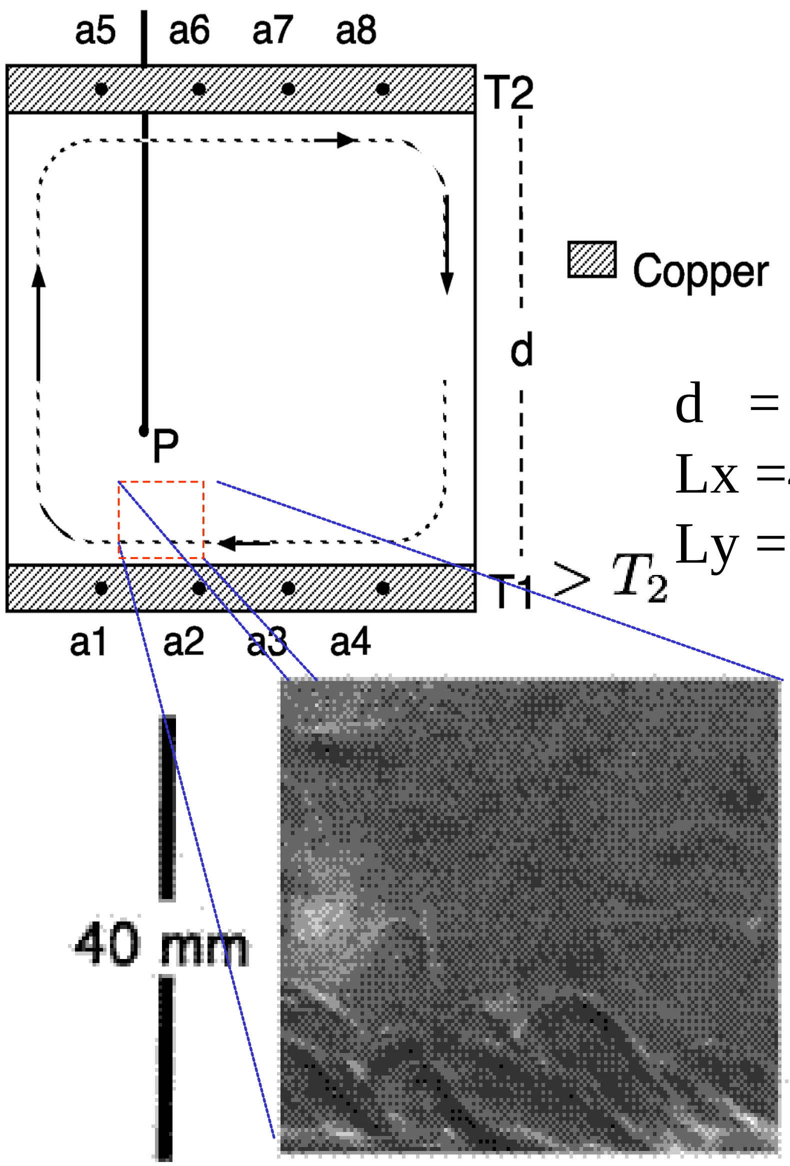
FT in dynamical systems

Turbulent flows

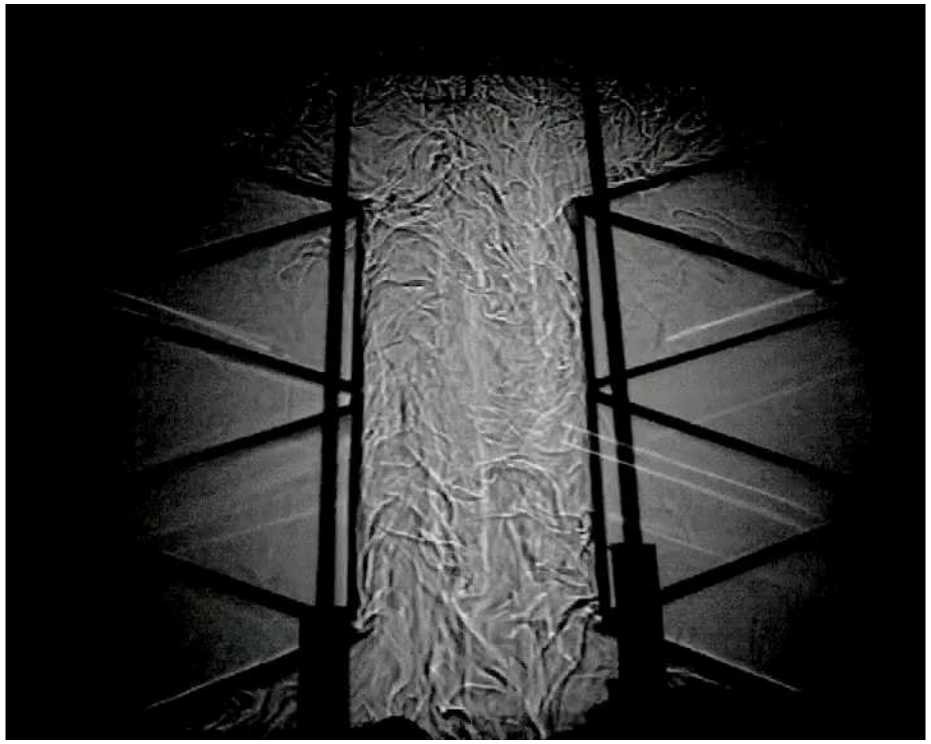
Turbulence convection: Ciliberto S and Laroche C, 1998 J. Physique IV 8 215

Inspired by :

Lepri S.,Livi R, Politi A.,Energy transport in anharmonic lattices close and far from equilihrium Physica D. 1998



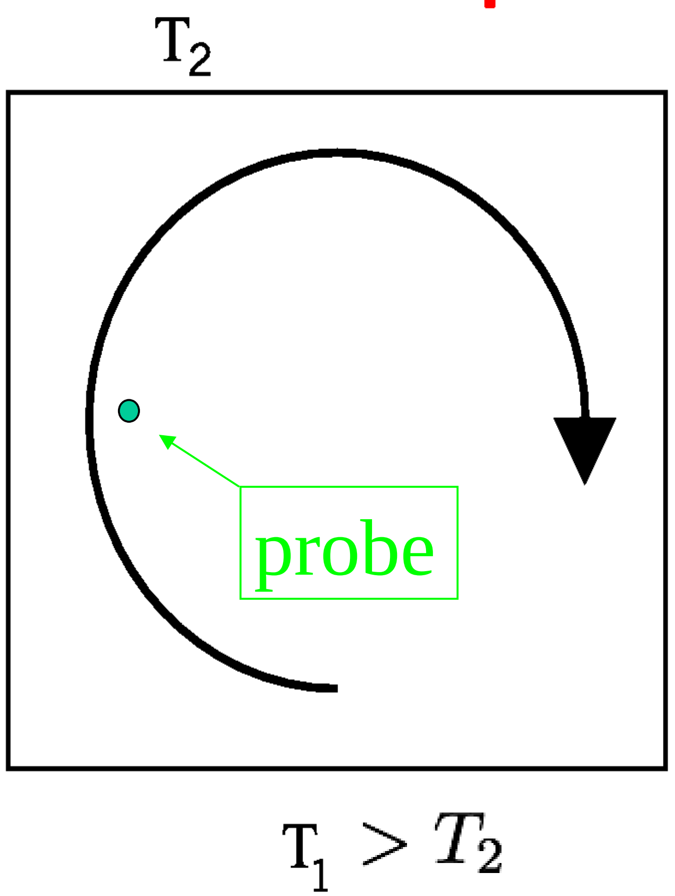
d = 20 cm
Lx =40 cm
Ly = 10 cm



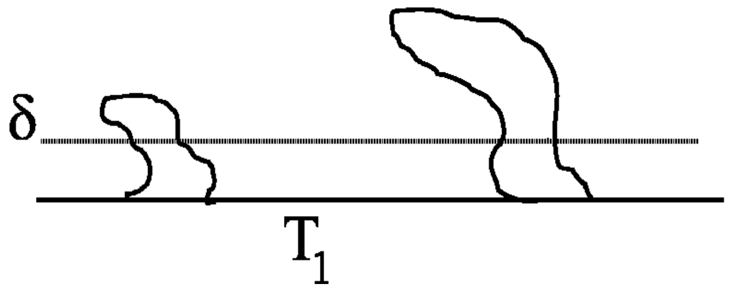
FT in dynamical systems

Heat transport in turbulent convection

Heat transport mechanisms



The large scale circulation flow does not transport heat



The largest part of heat is transported by the plumes

The probe measures the local heat flux Φ

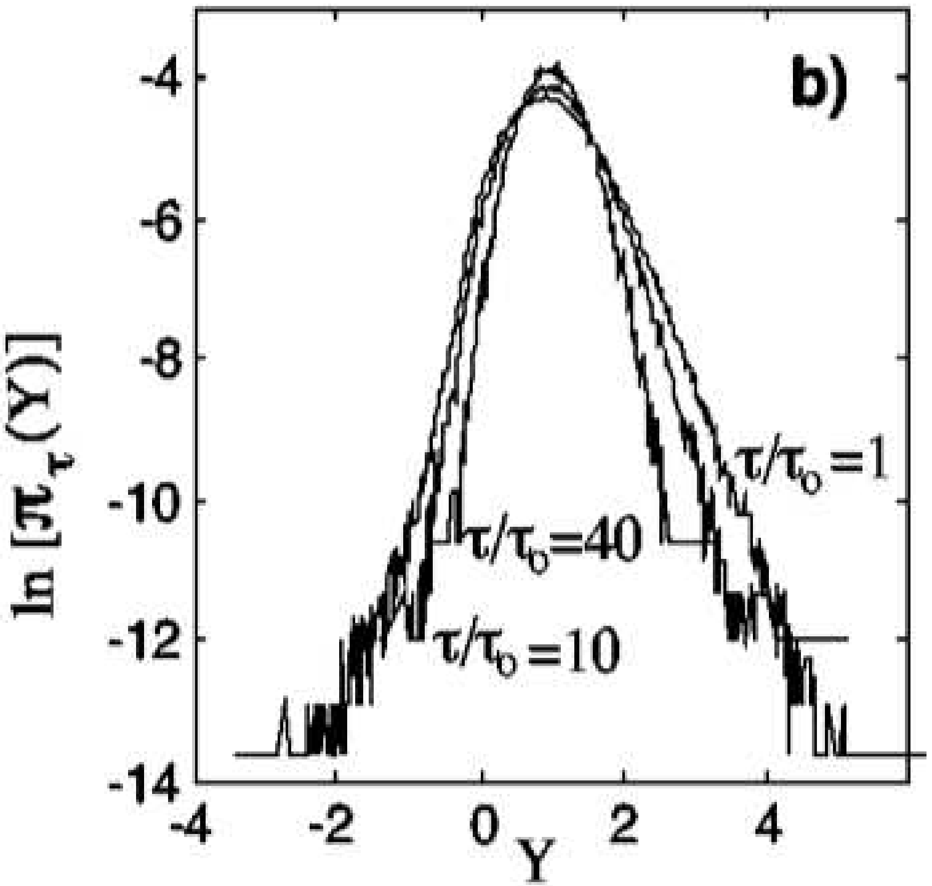
$$Y = \frac{\Phi_\tau}{\Phi_o}$$

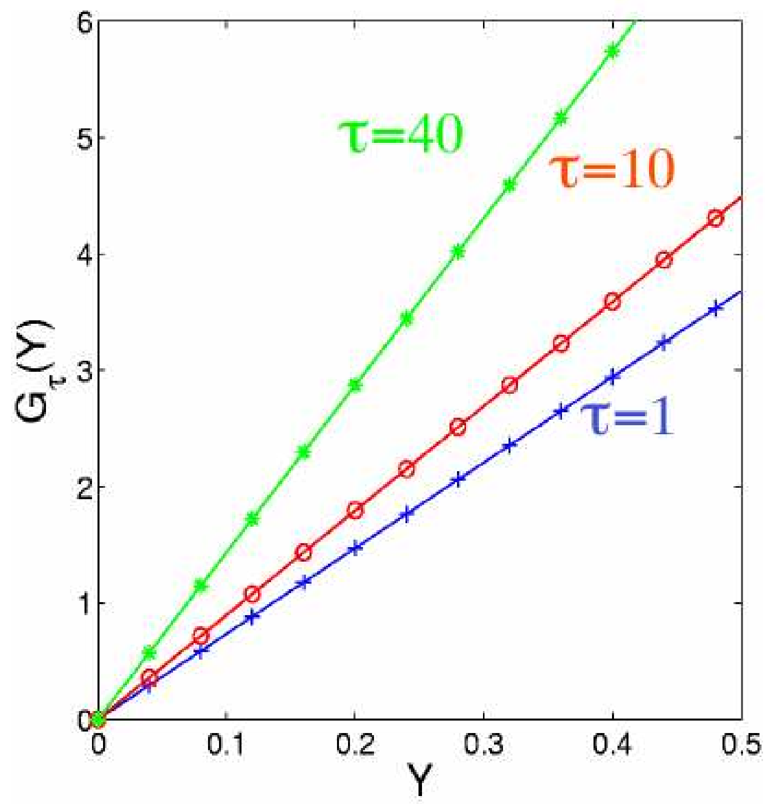
$$\Phi_\tau = \frac{1}{\tau}\int_t^{t+\tau} \Phi(t')dt'$$

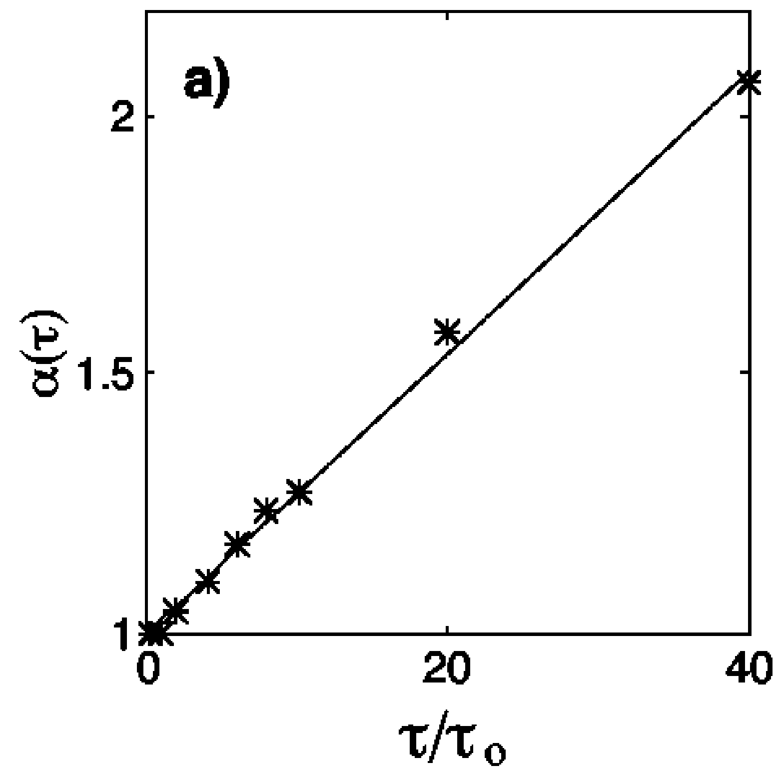
$$\phi_o = \lim_{\tau\to\infty} \Phi_\tau$$

FT in dynamical systems

PDF of the heat flux at Ra=10^{10}







We compute

$$G_\tau(Y) = ln\frac{\pi_\tau(Y)}{\pi_\tau(-Y)}$$

We find: $G_\tau(Y) \propto \alpha(\tau)\ Y$ with $\alpha(\tau) = \left(\gamma\frac{\tau}{\tau_o} + 1\right)$

Therefore the heat flux PDF verifies

$$\ln\frac{\pi_\tau(Y)}{\pi_\tau(-Y)} = \alpha(\tau)\ Y\ \beta$$

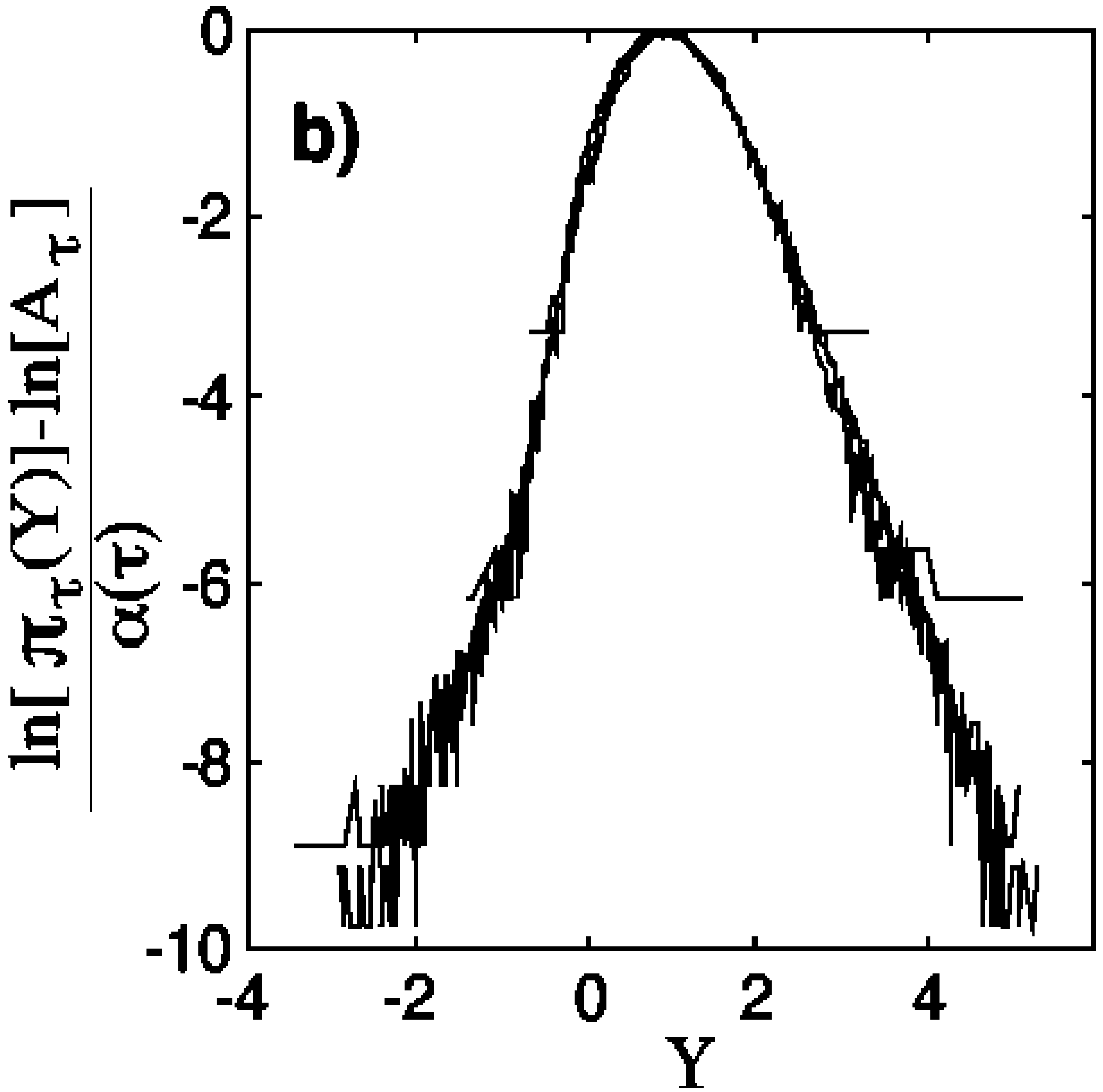
Heat transport in turbulent convection

We construct a large deviation function in the following way:

$$\pi_\tau(y) = A_\tau \exp(\zeta(y)\alpha(\tau))$$

then

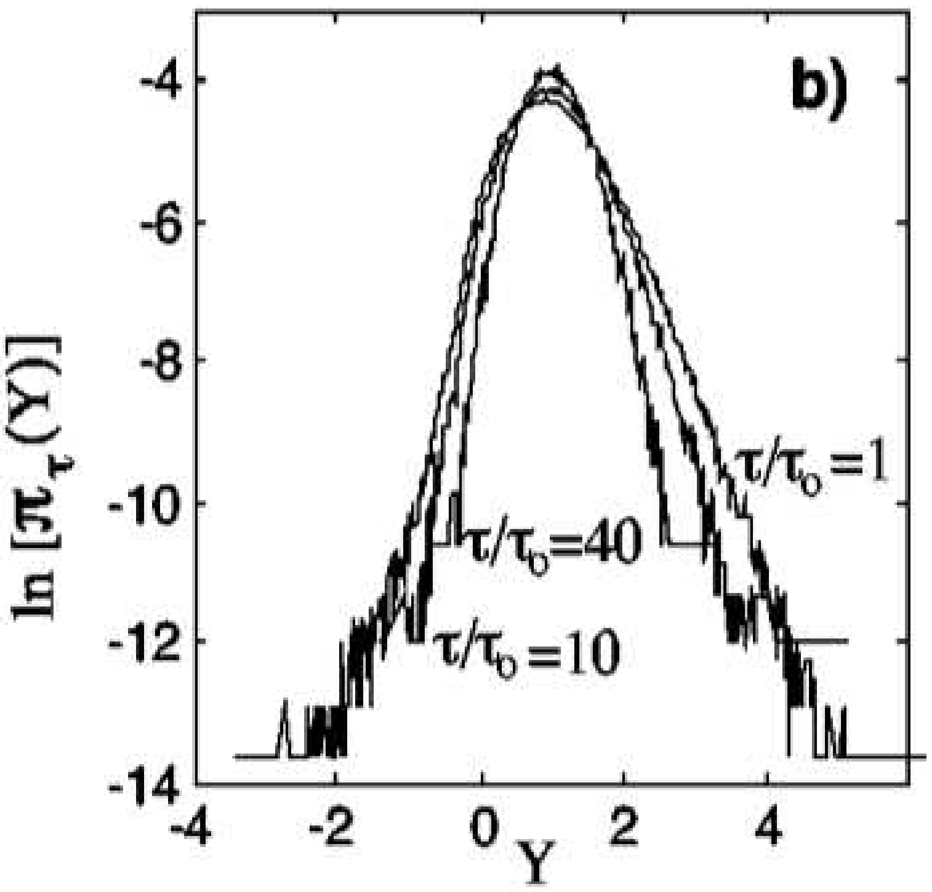
$$\zeta(y) = \frac{\ln(\pi_\tau(y)) - \ln(A_\tau)}{\alpha(\tau)}$$

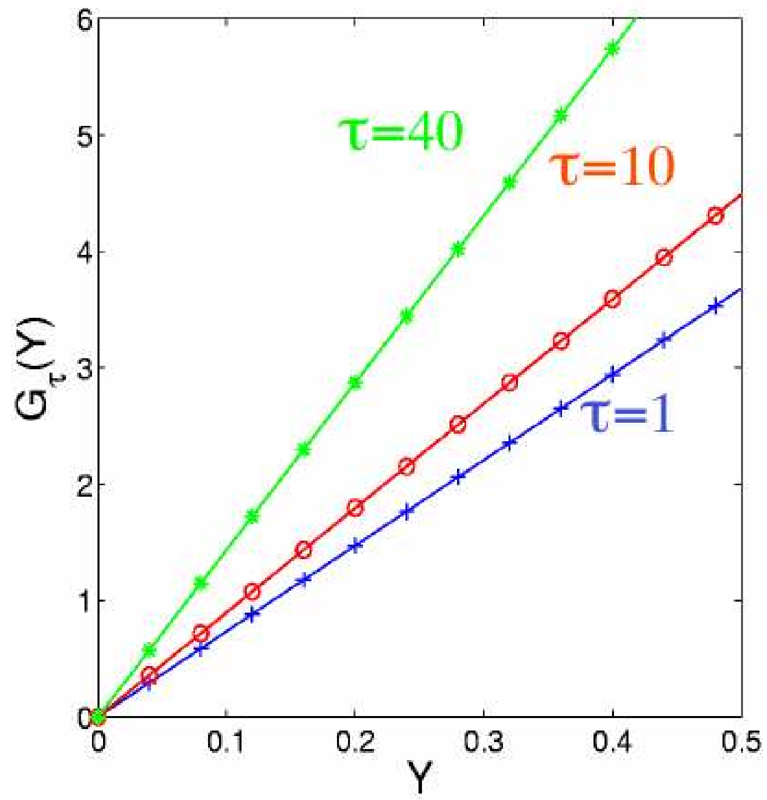


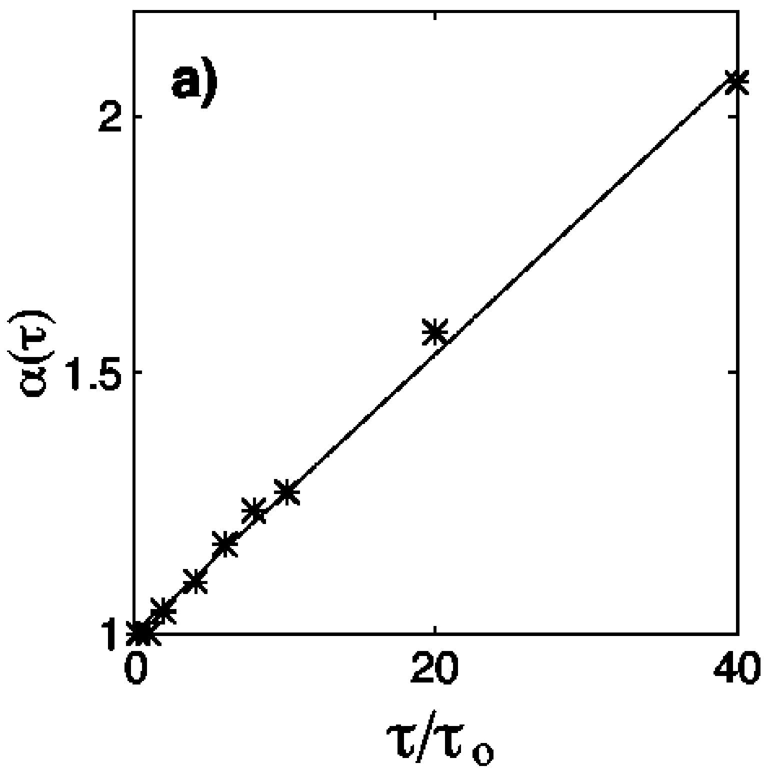
A good rescaling of the PDF is obatined for all values of τ

FT in dynamical systems

PDF of the heat flux at Ra=10^{10}







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$$\ln\frac{\pi_\tau(Y)}{\pi_\tau(-Y)} = \alpha(\tau)\ Y\ \beta$$

What is this ?

FT in dynamical systems

1) Turbulent flows

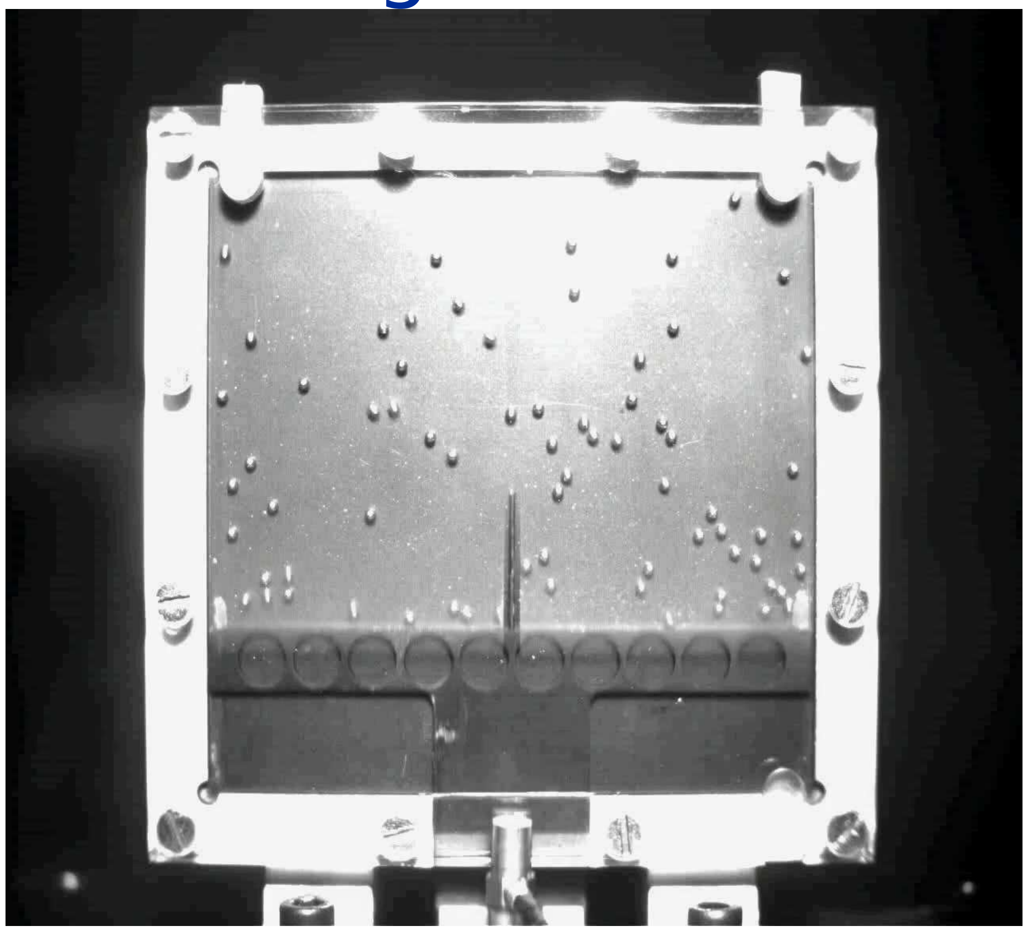
2) Granular media

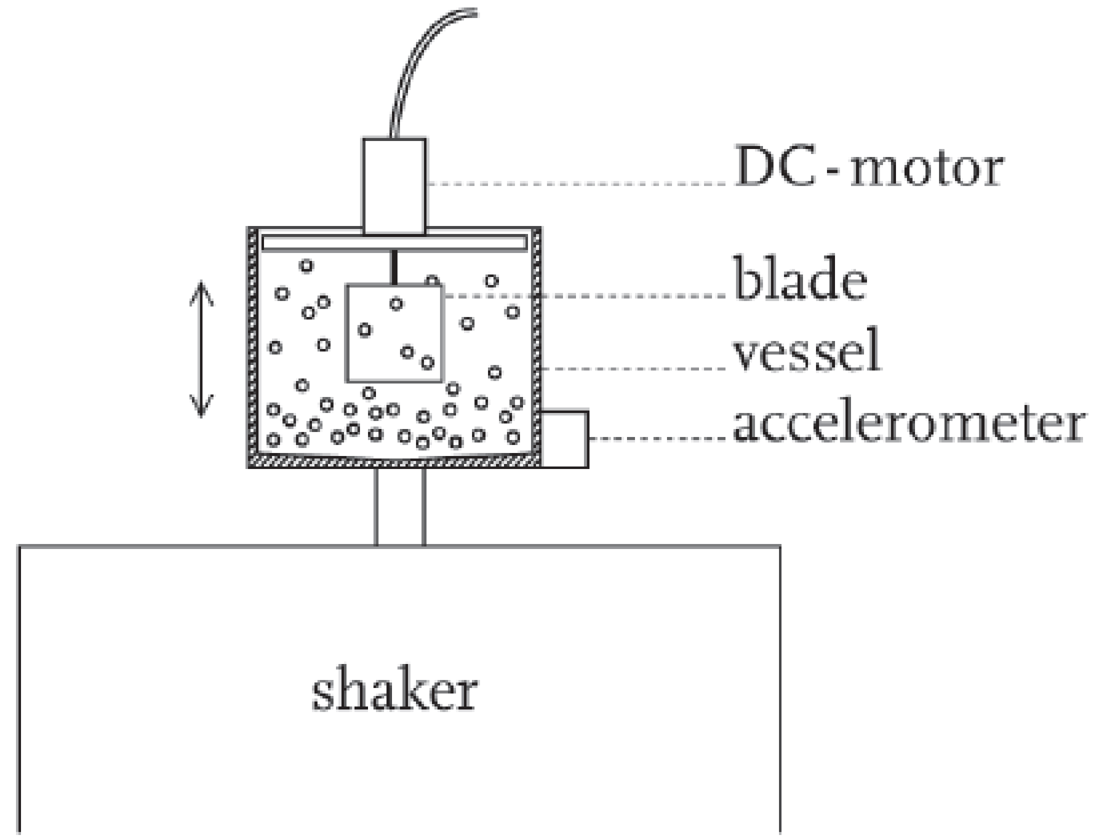
3) Mechanical waves

FT in dynamical systems

The granular media

Vibrated granular media





S. Joubaud, D. Lohse, D. van der Meer Phys. Rev. Lett. 108, 210604 (2012)

A.Naert, EPL 97, 20010 (2012)

FT in dynamical systems

The granular media

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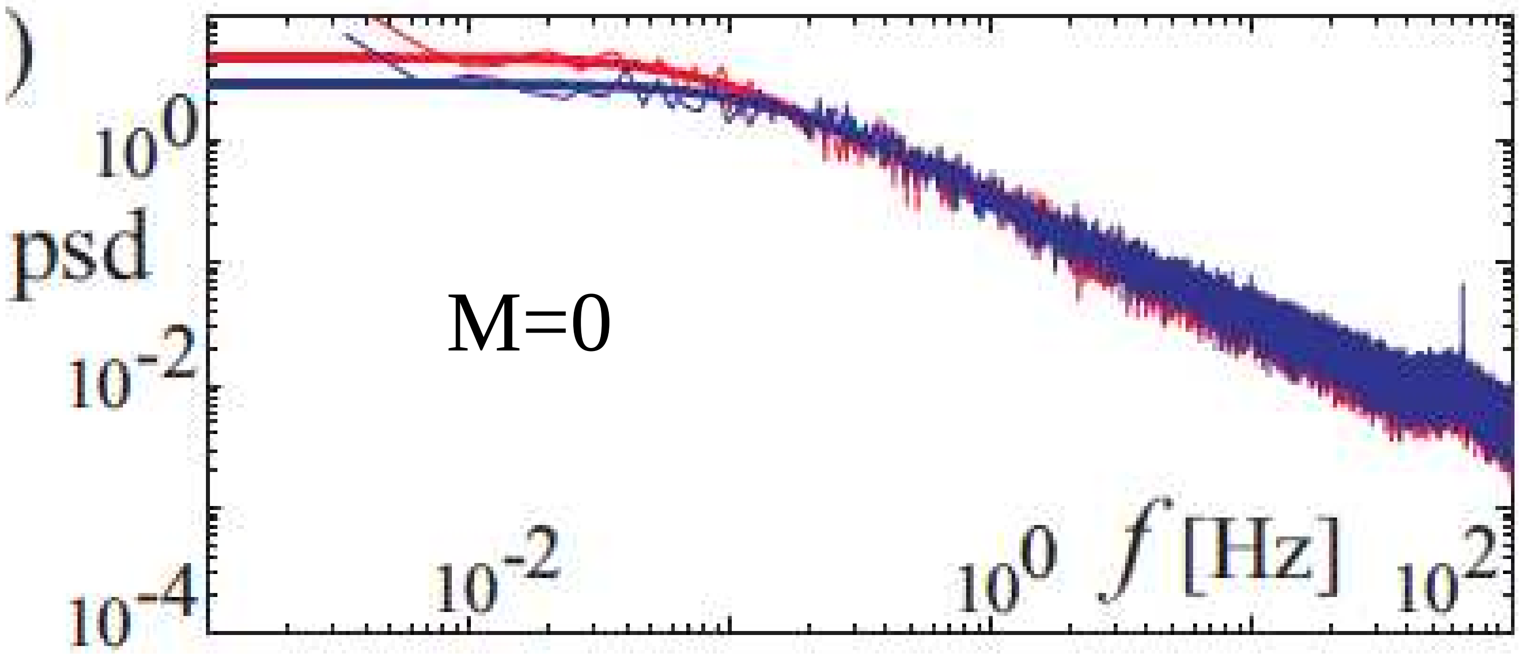
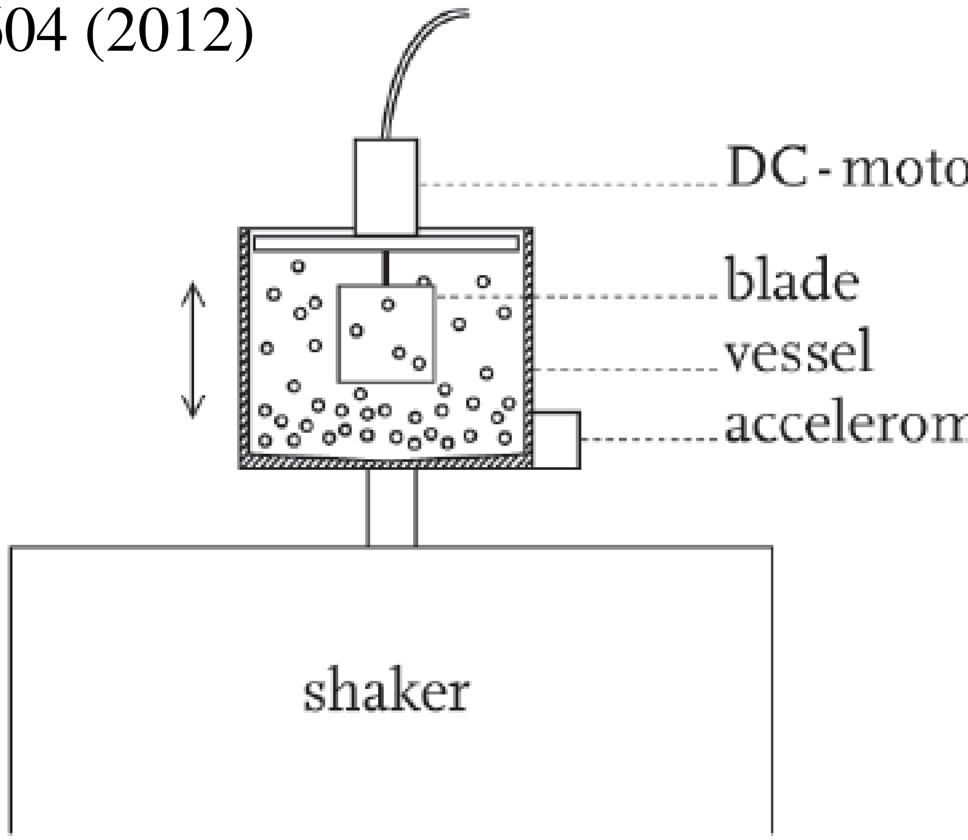
A.Naert, EPL 9)7, 20010 (2012)

angular velocity power spectra





$$I\frac{d\omega}{dt} = -\gamma\omega + M_{\partial e} + \eta$$

An effective temperature and viscosity can be estimated

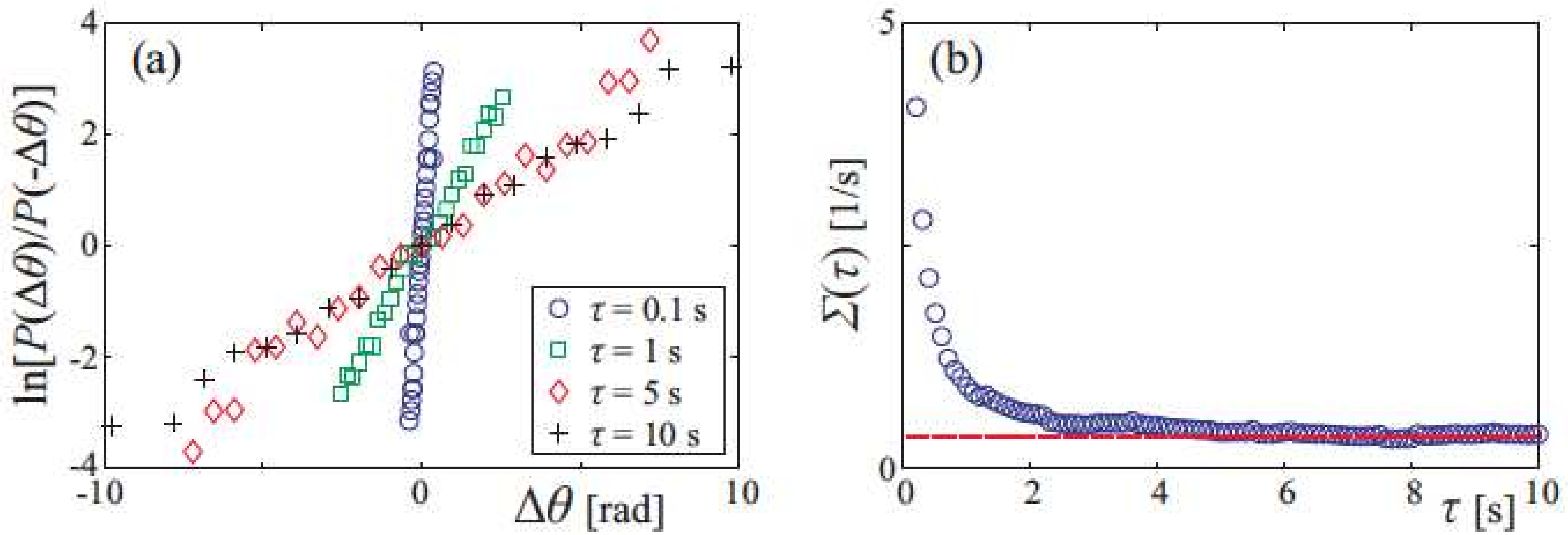
FT in dynamical systems

The granular media

$$M_{\partial_\epsilon} \neq 0$$

$$I\frac{\mathrm{d}\omega}{\mathrm{d}t} = -\gamma\omega + M_{\partial e} + \eta \qquad W_\tau = \int_t^{t+\tau} M_{\partial_\epsilon}\omega(t')dt' = M_{\partial_\epsilon}\Delta\theta$$

$$\ln\left(\frac{P(W_\tau)}{P(-W_\tau)}\right) = \ln\left(\frac{P(\Delta\theta)}{P(-\Delta\theta)}\right) = \frac{M_{\partial e}\Delta\theta}{T_{\mathrm{r}}} \qquad \Delta\theta \equiv \theta(t+\tau) - \theta(t)$$



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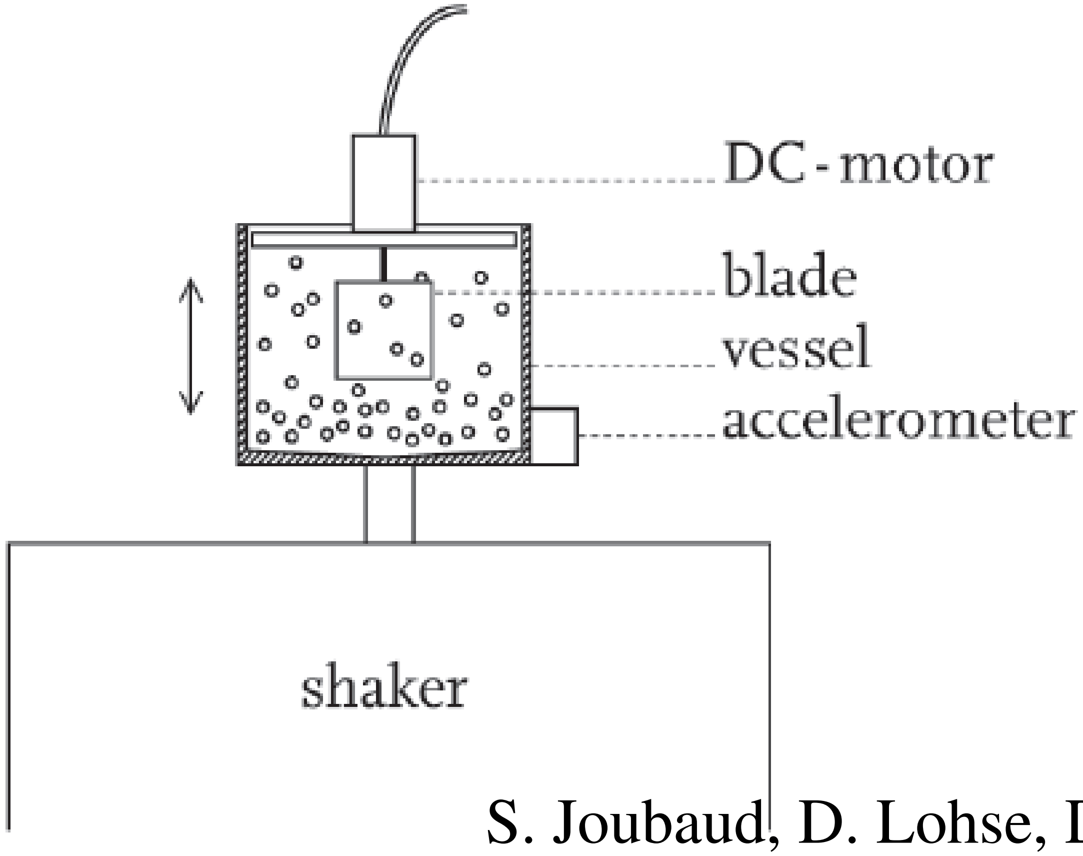
FT in dynamical systems

The granular media



Tracer inside a granular gas

S. Joubaud, D. Lohse, D. van der Meer Phys. Rev. Lett. 108, 210604 (2012)

A.Naert, EPL 97, 20010 (2012)

Warning: Energy flow inside the gas

Experiment: Feitosa K and Menon N, 2004 Phys. Rev. Lett. 92 164301

Theory: Puglisi A, Visco P, Barrat A, Trizac E and van Wijland F, 2005 Phys. Rev. Lett. 95 110202

FT in dynamical systems

1) Turbulent flows

2) Granular media

3) Mechanical waves

FT in dynamical systems

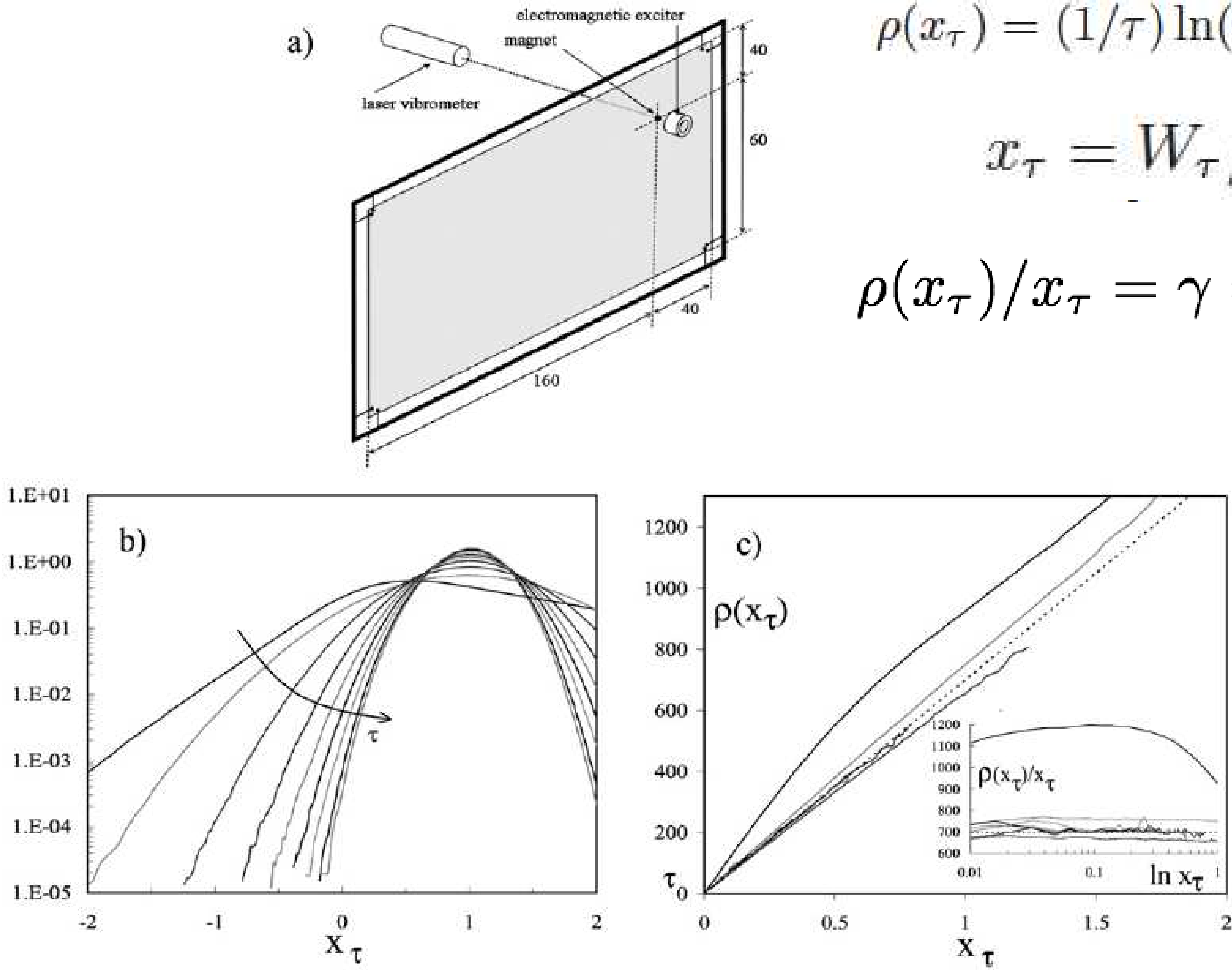
Mechanical Waves

Cadot O, Boudaoud A and Touz C, 2008 Eur. Phys. J. B 66 399

$$\rho(x_\tau) = (1/\tau)\ln(P(x_\tau)/P(-x_\tau))$$

$$x_\tau = W_\tau / \langle W_\tau \rangle$$

$$\rho(x_\tau)/x_\tau = \gamma =$$ phase space contraction rate



= mean relaxation time of the plate vibrational mode

Conclusions on the applications of stochastic thermodynamics

- For stochastic systems: it can be safely used for applications

This is true when the driving force is deterministic
Several problems may arise when the driving force is random

R. Solano et al, EPL, 89 (2010) 60003
E. Dieterich et al. Nat. Phys. 11, 971 (2015).

- For dynamical systems: the connection between experiments and theory is not yet very well established.

Difficulties in estimating the characteristic time and energy scales in the experiments