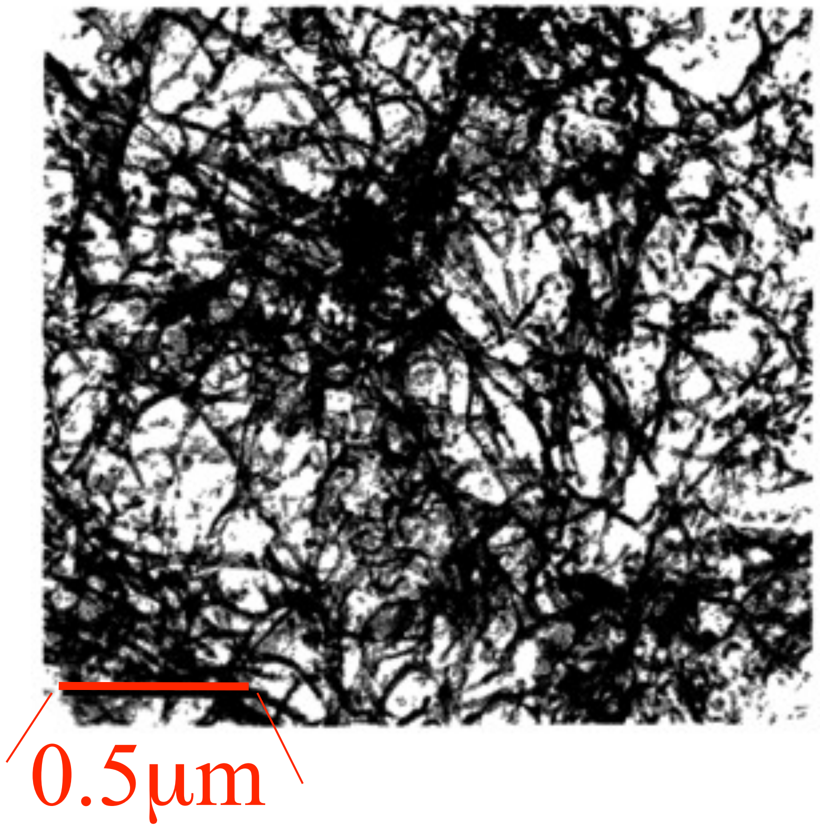
Gelatin liquid-solid transition



Gelatin :

liquid for Tm>32°C

solid for Tg< 28°C

In our experiment we use

10%wt concentration in water

For T<Tg gelatin presents : aging and memory effects

at 10%wt concentration after a cooling at 26°C it takes ~2h to solidify

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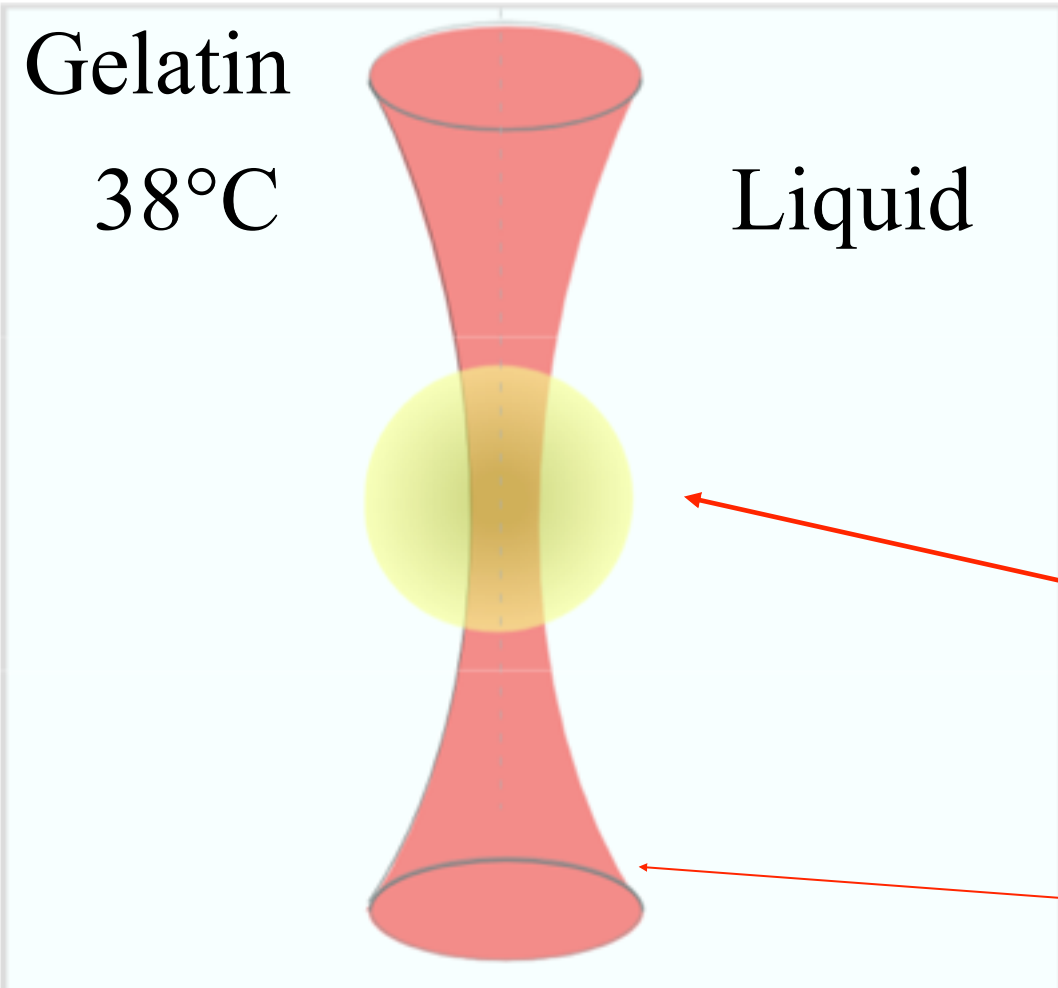

Trapped glass particle R=1µm

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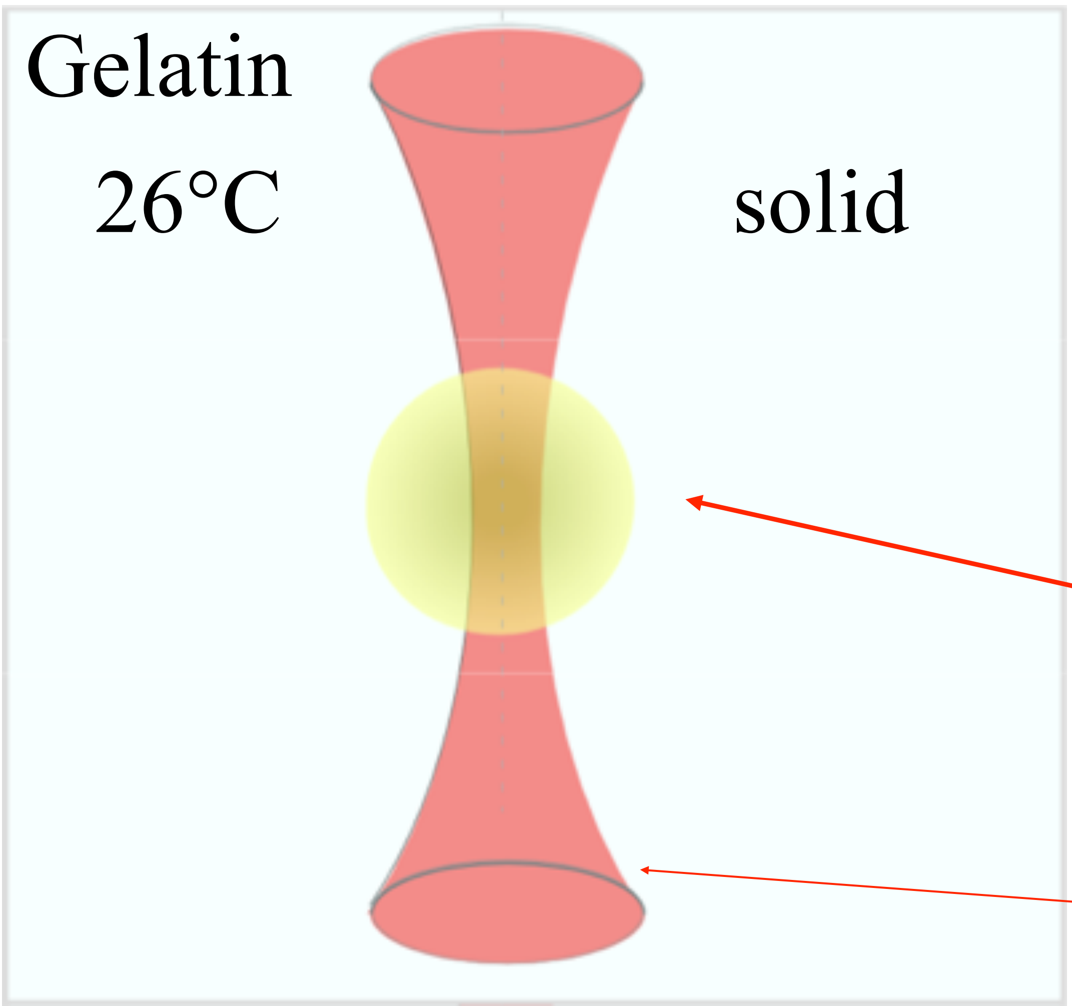

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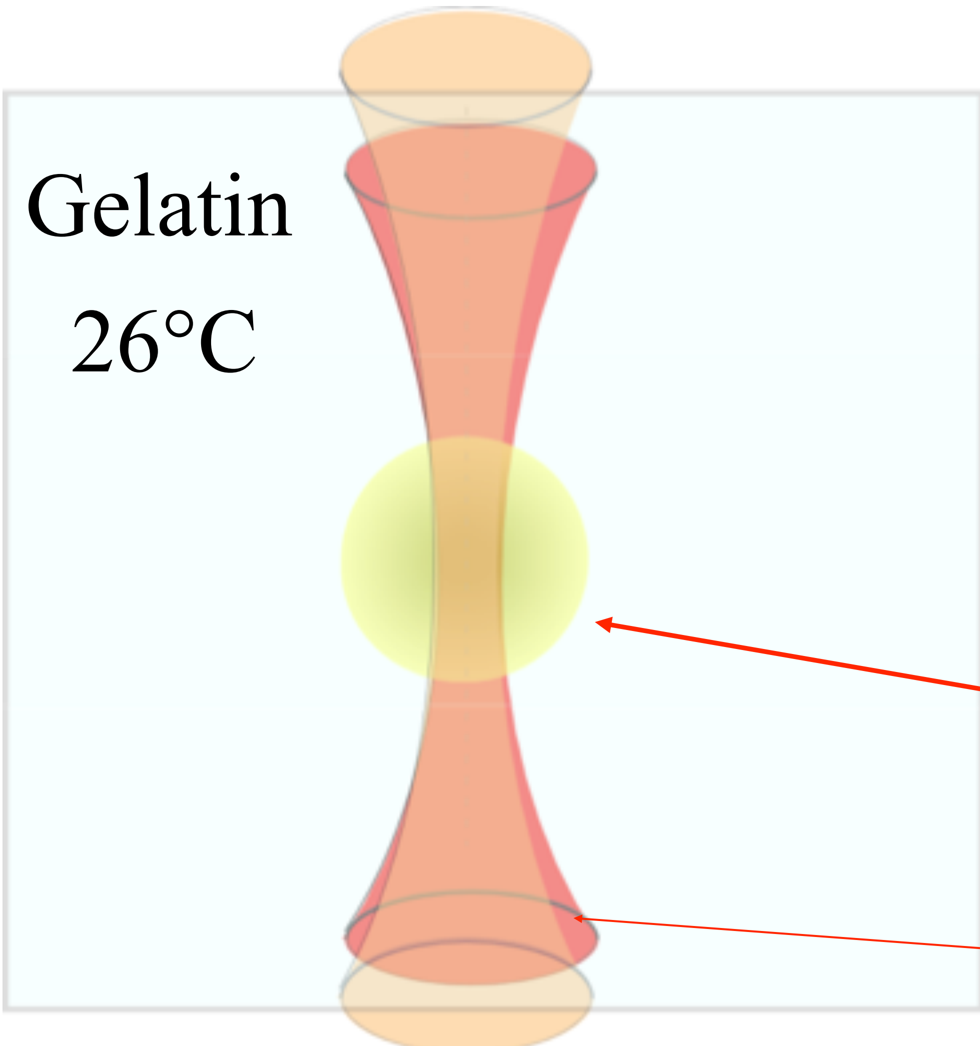

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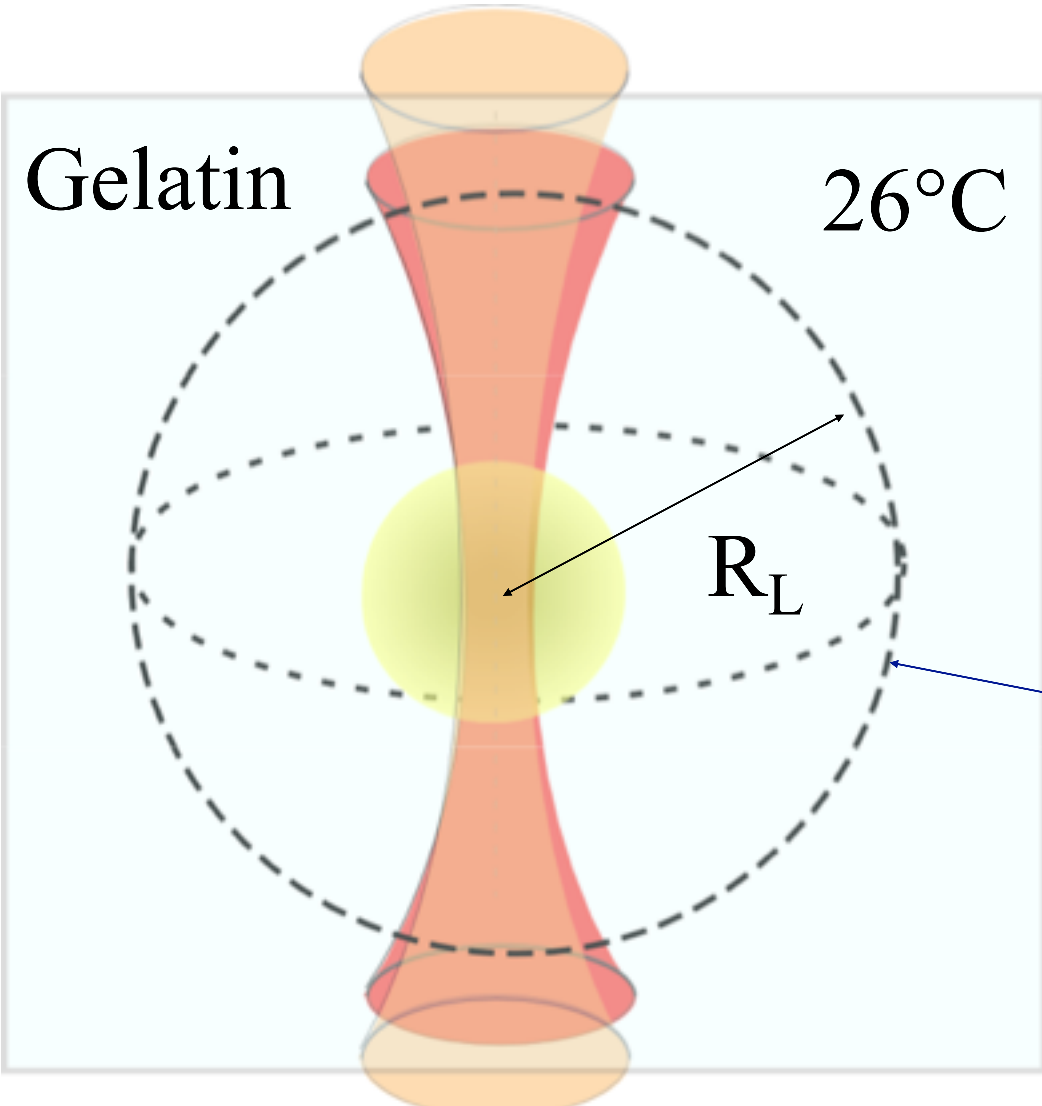
Trapping laser

Infrared Laser switched on for a few minutes

Gelatin liquid-solid transition (heating)

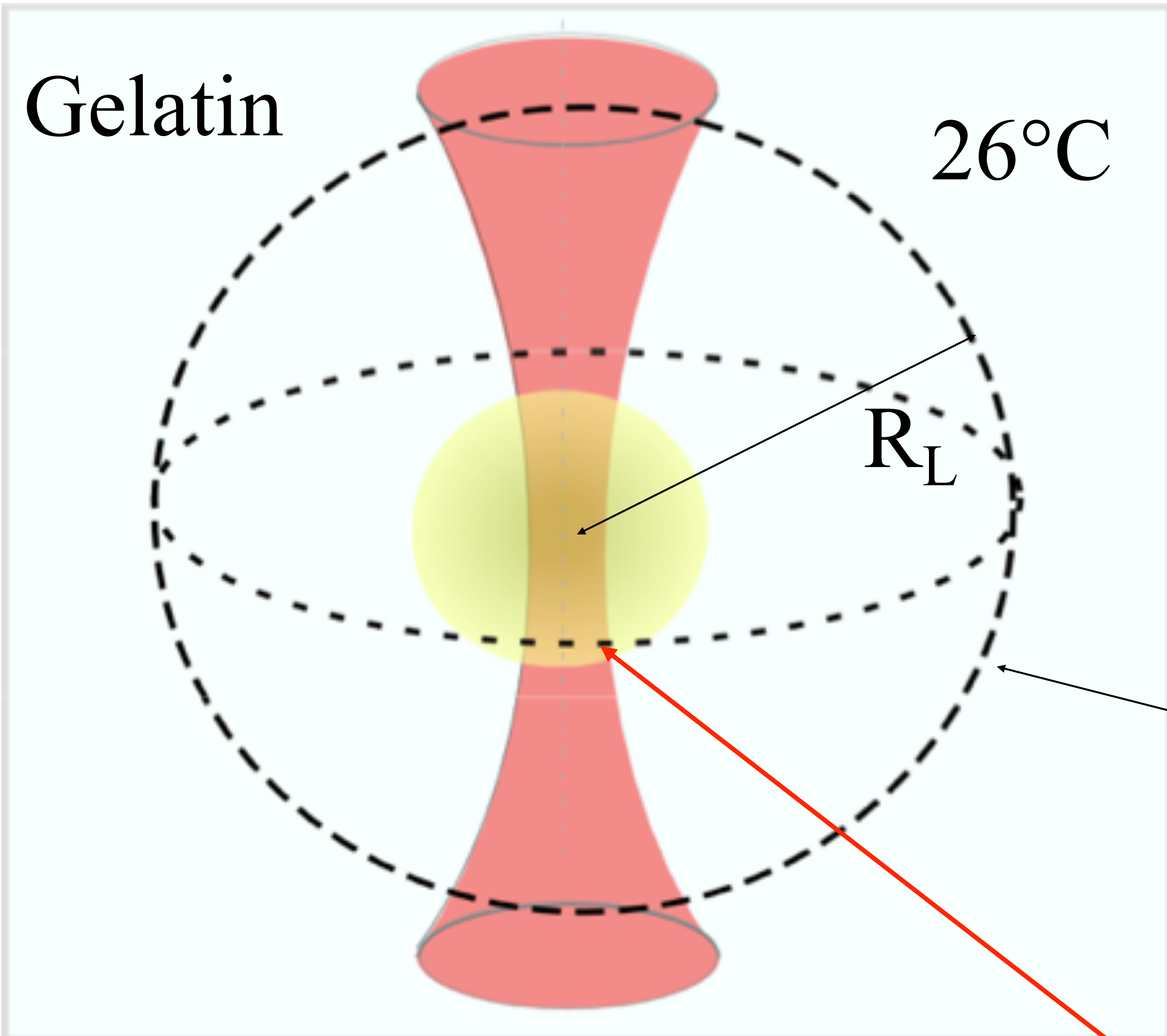


The temperature around the focus grows till 38°C and the gel melts

A drop of liquid of radius R_L=5 μm is formed

Infrared Laser switched on for a few minutes

Gelatin liquid-solid transition (quench)



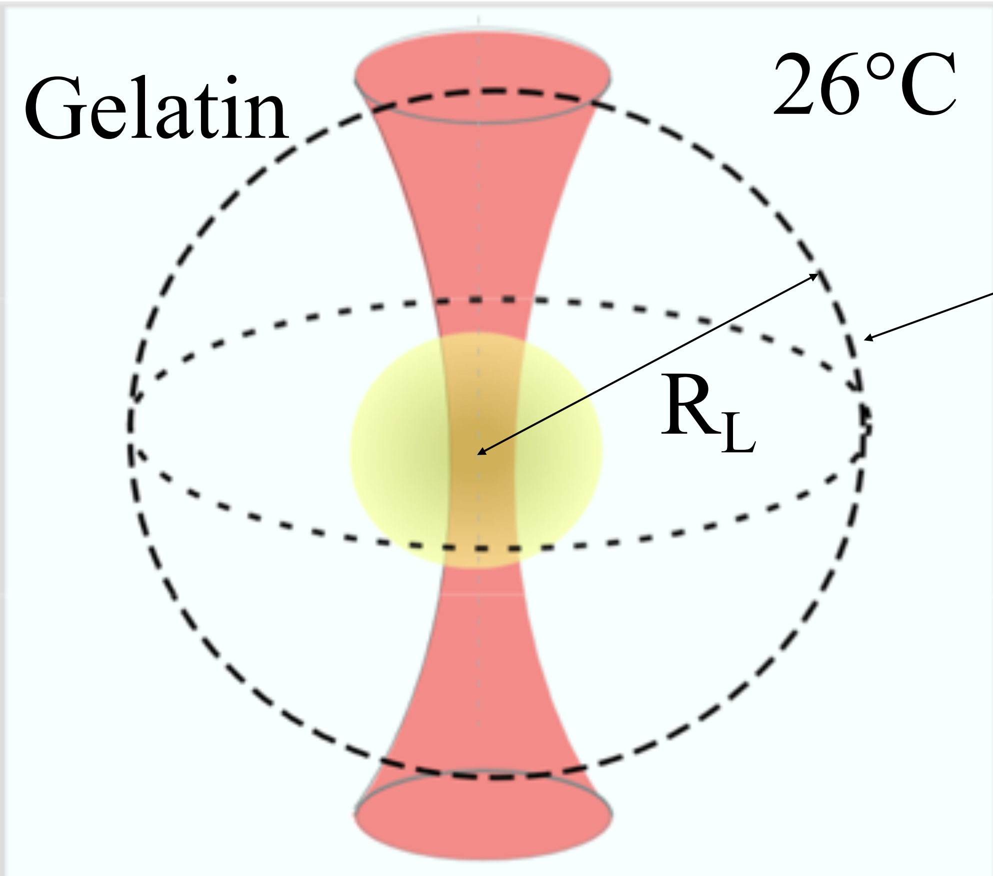
The infrared laser is switched off
and
the liquid drop cools very fast

At t=1ms after the switch off
we obtain:

A drop of an unstable liquid at 26°C inside a stable solid

Trapped glass particle R=1µm

Gelatin liquid-solid transition (quench)



Drop of an unstable liquid at 26°C inside a stable solid

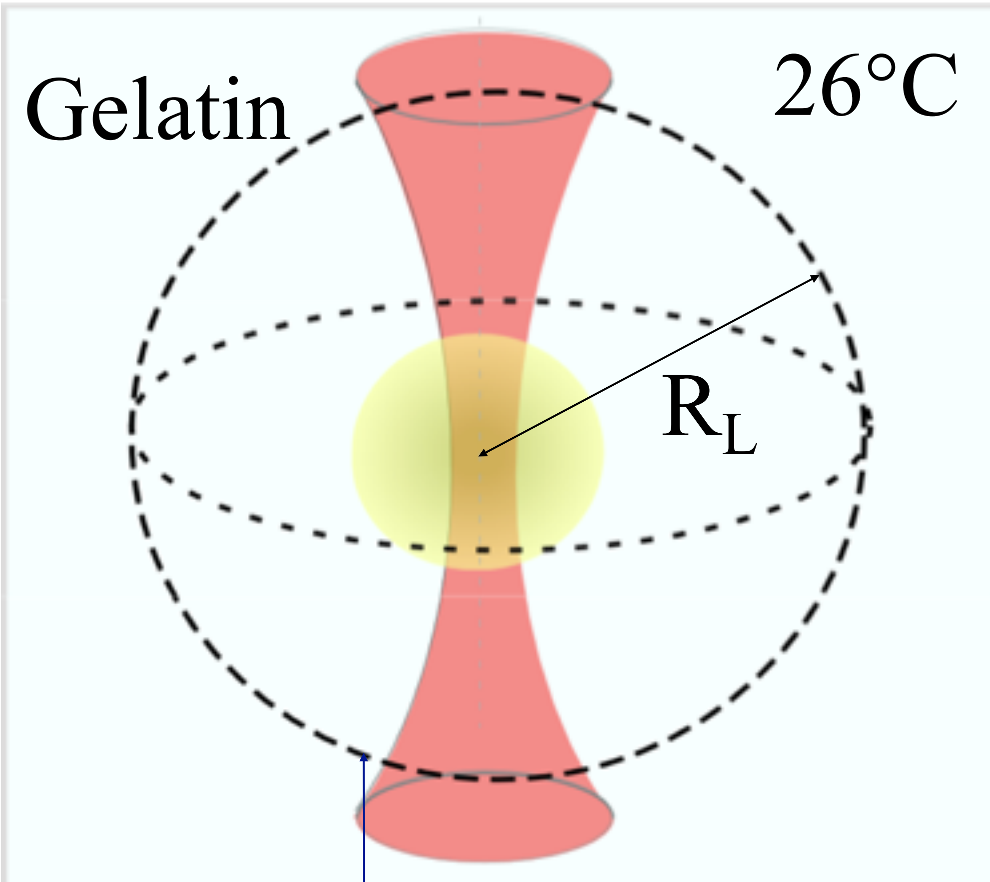
What happens ?

How long does it take to solidify ?

Does the transition start from the frontier ?

What is the nature of the bead fluctuations inside the drop ?

Dynamics of the bead



Drop of the
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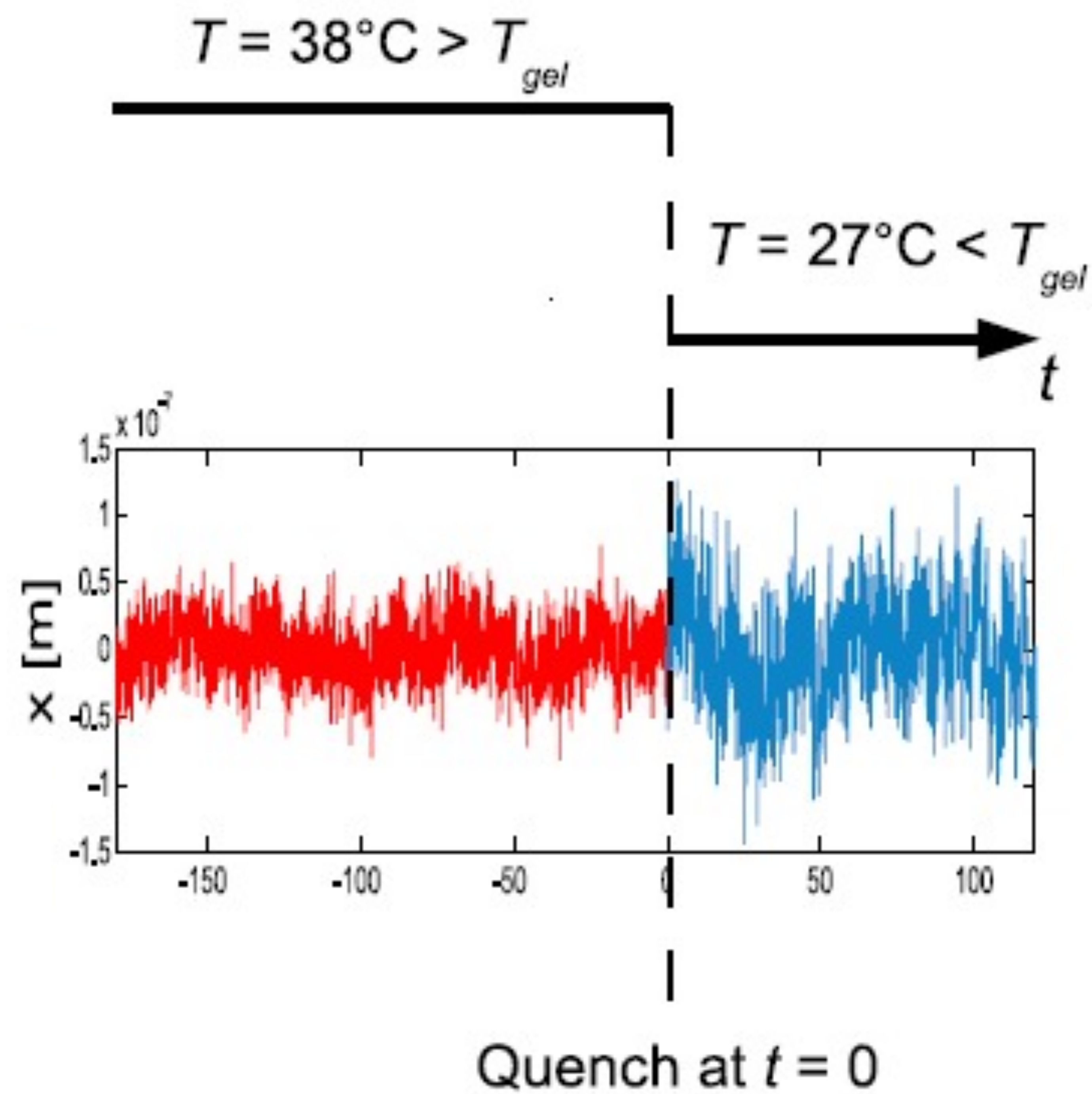
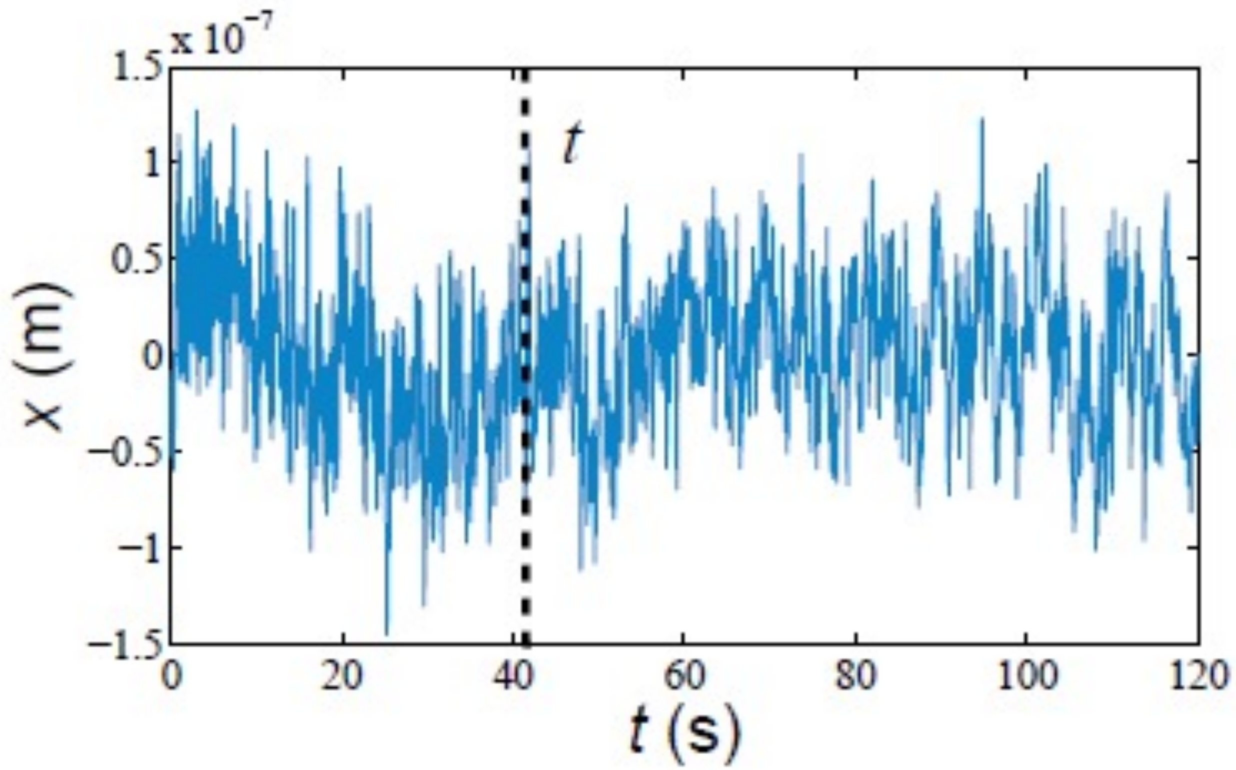


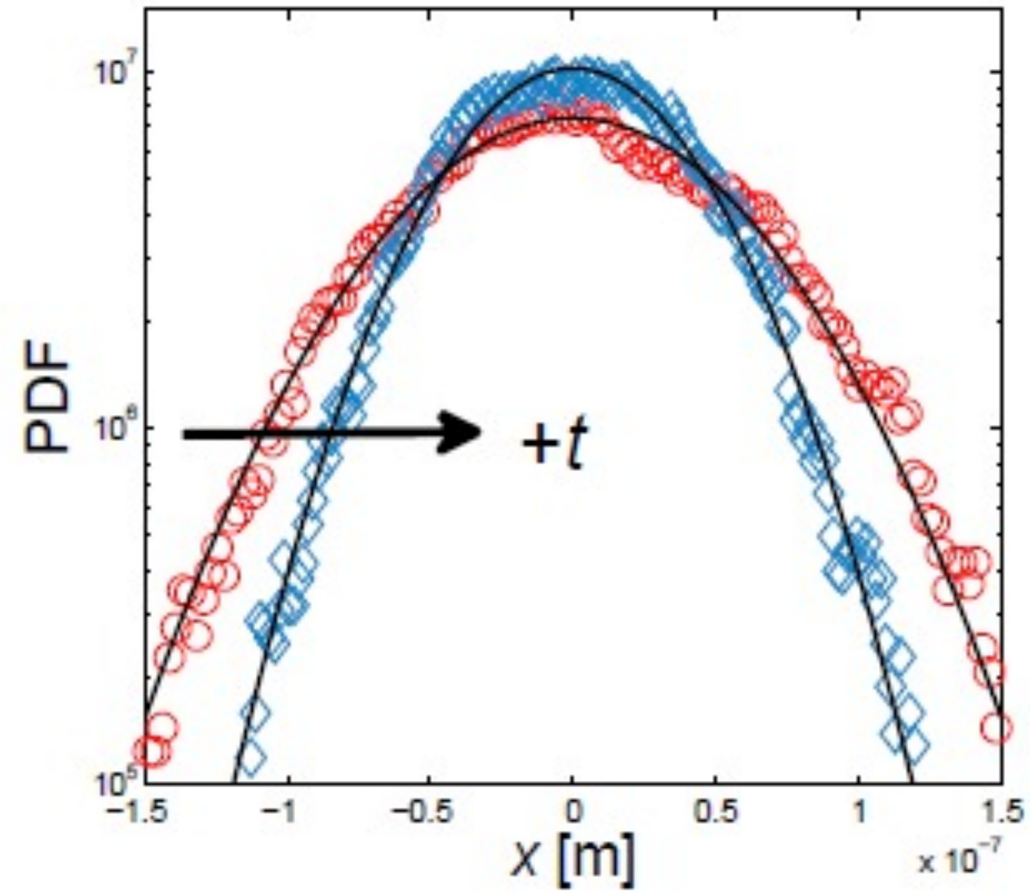
Dynamics of the bead

Particle motion during the gelation process

Probing nonequilibrium particle dynamics through the variance σ_x^2 of its position x [Gomez-Solano et al., arXiv:1102.4750]:

- Nonstationarity: $\sigma_x(t)$ computed at each t over an ensemble of independent quenches.
- Fluctuations of x are Gaussian for all $t \geq 0$.



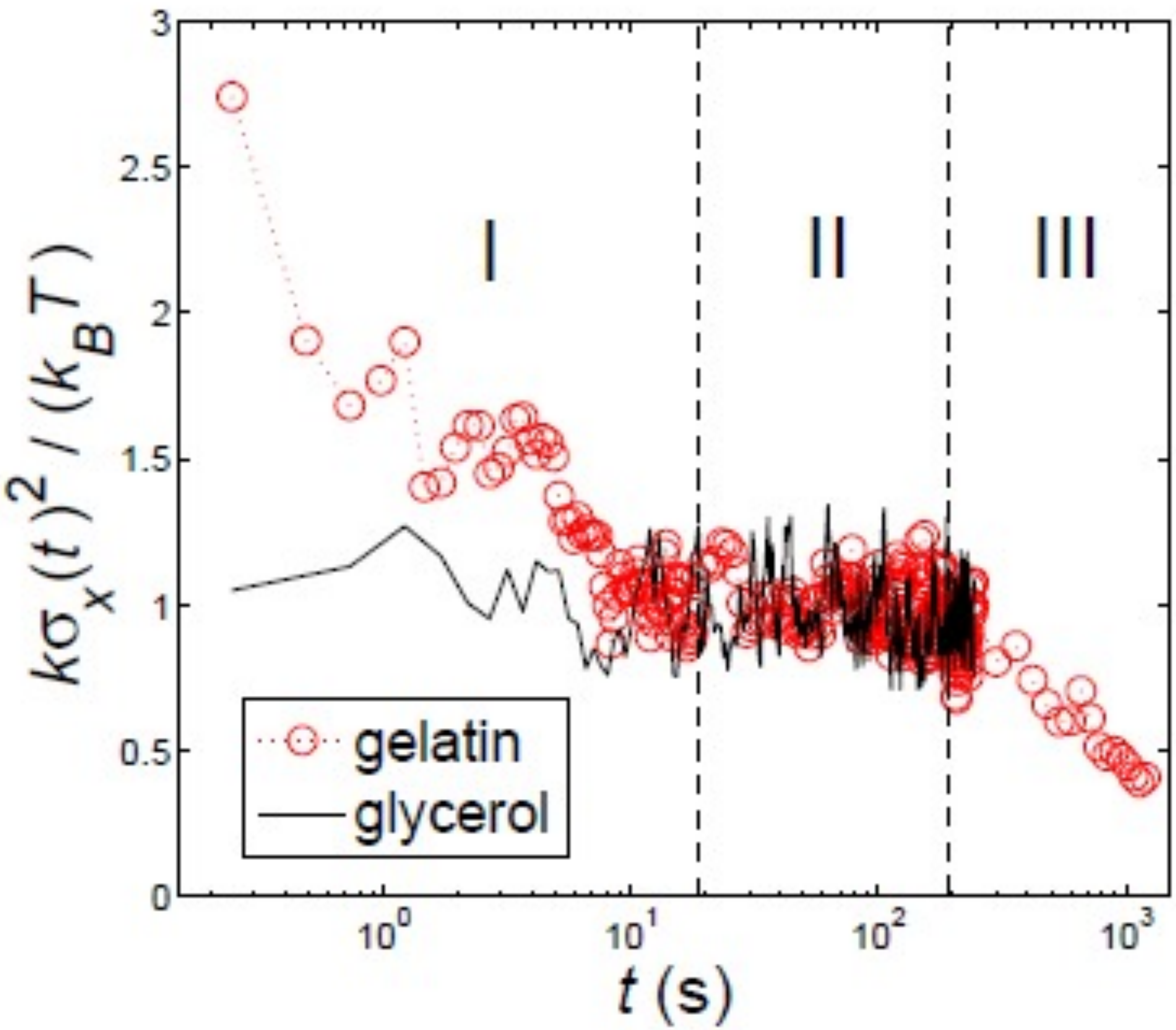


Time evolution of the variance

The measured $\sigma^2(t)$ is compared to the equilibrium value σ_{eq}^2 of the trap

From equipartition

$$\sigma_{eq}^2 = \frac{k_B\ T}{k}$$



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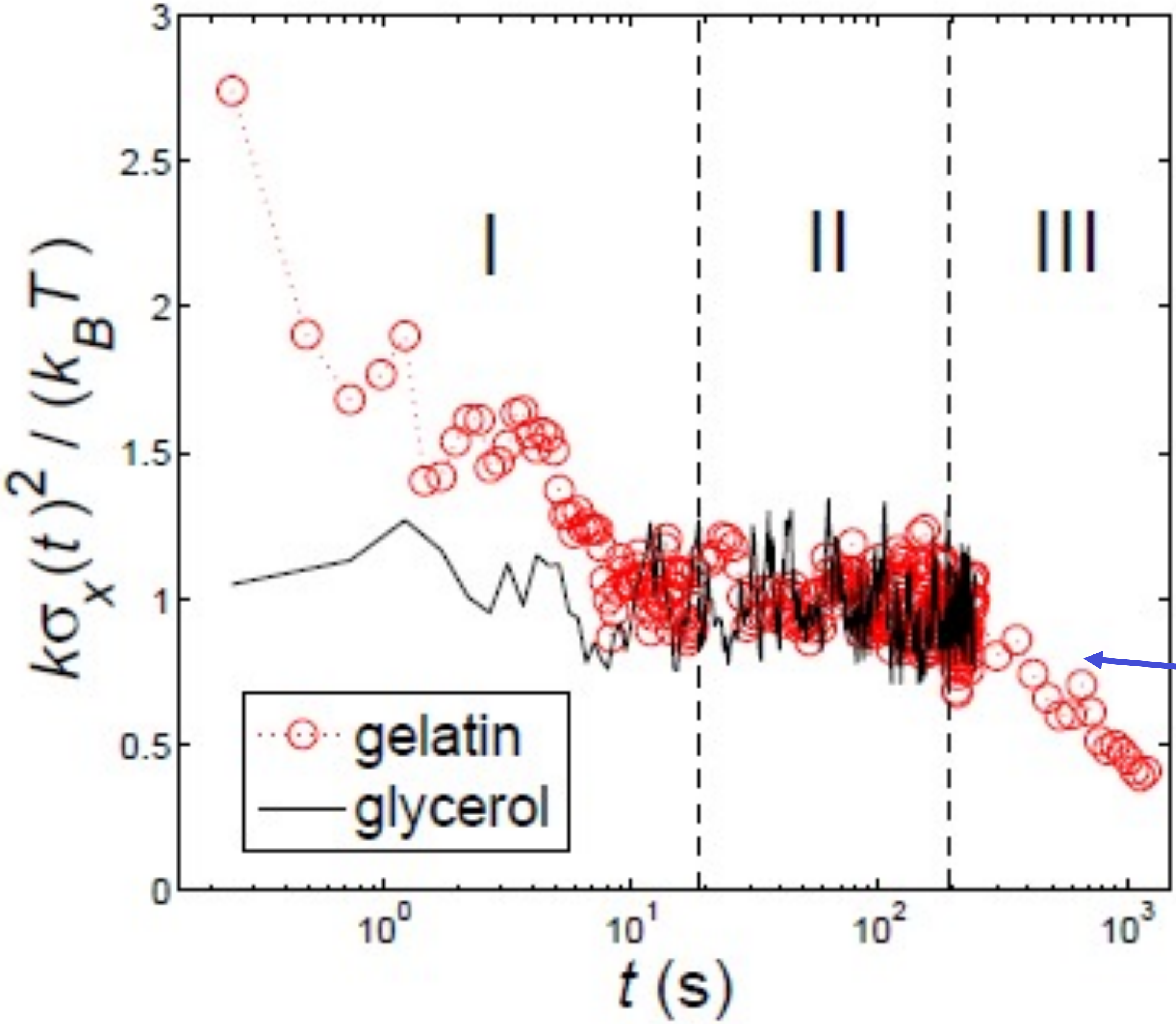


$$\sigma^2(t) = \frac{k_B\ T}{(k + \tilde{k}_{gel})}$$

Active microrheology

Motion of a Brownian particle trapped by a laser Beam

Viscoelastic Langevin dynamics

$$\int_{-\infty}^{t} \Gamma(t-t', t_w)\dot{x}(t')dt' + k\ (x - x_o) = \xi(t),$$

The applied oscillating force $f_o(t) = \ k\ x_o(t)$

The linear response $\hat{\chi}(\omega, t_w) = \dfrac{\hat{x}(\omega, t_w)}{\hat{f}_0(\omega)}$

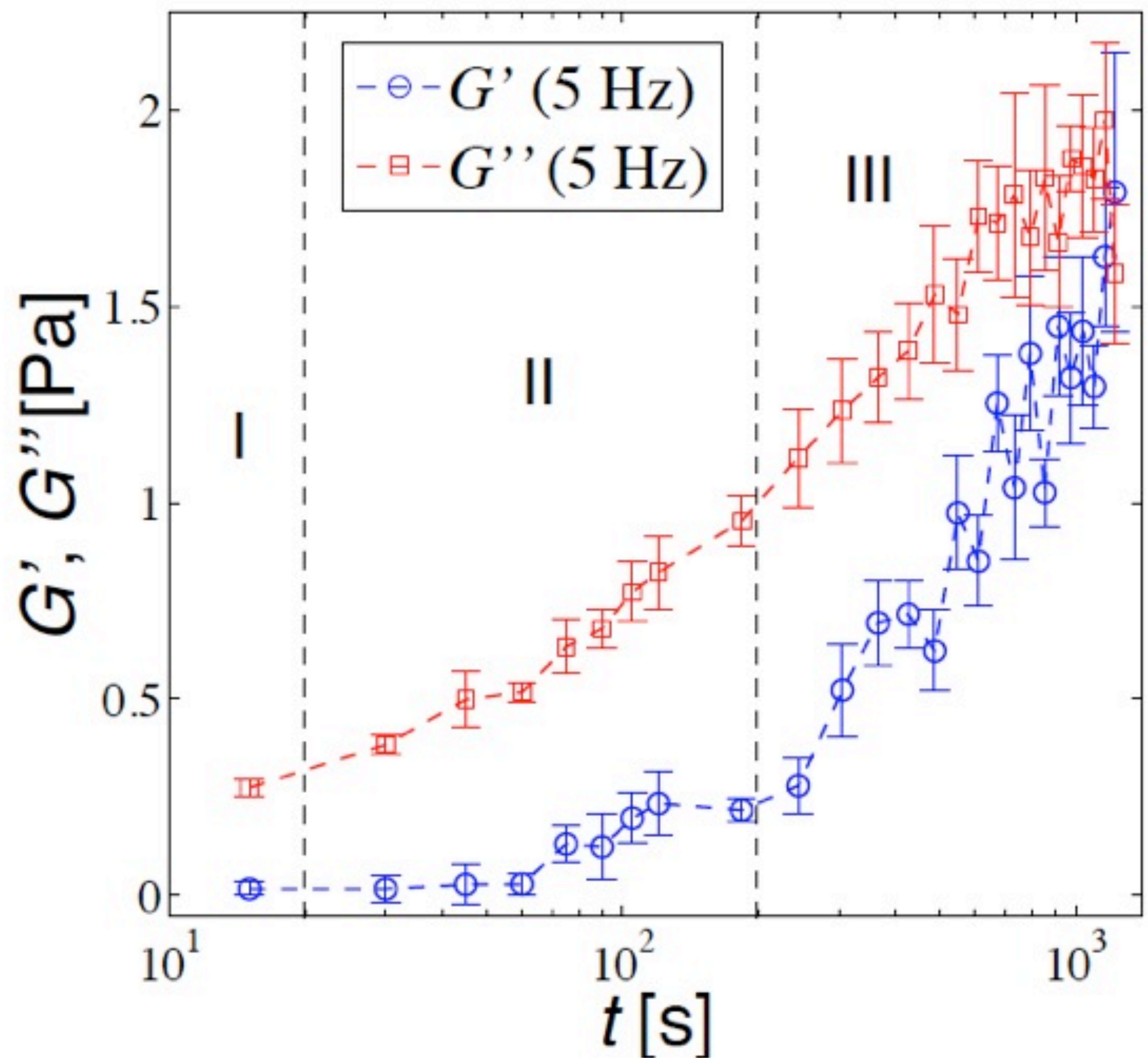
$$G'(\omega, t_w)\ 6\ \pi\ r = Re\left[\frac{1}{\chi(\omega, t_w)}\right] - k$$ Elastic modulus

$$G''(\omega, t_w)\ 6\ \pi\ r = Im\left[\frac{1}{\chi(\omega, t_w)}\right] / \omega$$ Viscosity

Gelatine liquid-solid transition

Time evolution of the viscous and elastic modulus

I. Pure viscous
II. Negligible elasticity
III. Logarithmic growth of G' etG''



Heat Fluctuations

$$\Delta U_\tau(t_w) - W_\tau = Q_\tau(t_w),$$

For $F = 0$: $W_\tau = 0$ and

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$$\Delta U_\tau(t_w) = \frac{1}{2}k(x(t_w+\tau)^2 - x(t_w)^2) + \int_{t_w}^{t_w+\tau} \dot{x}(t)(K_t * x)(t,t_w)dt,$$

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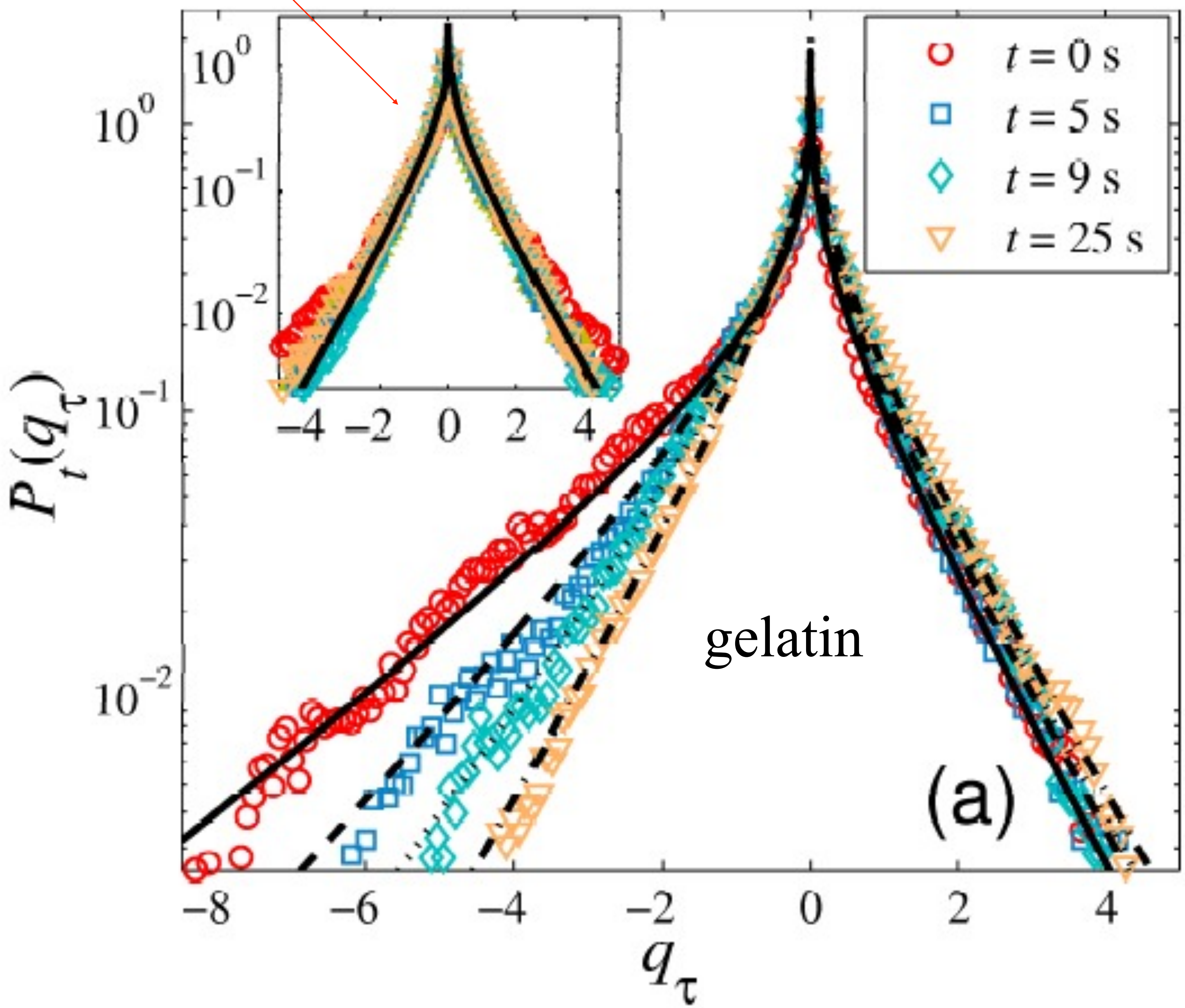
For $t_w < 200$s, Q_τ can be computed from ΔU_τ.

Energy PDF

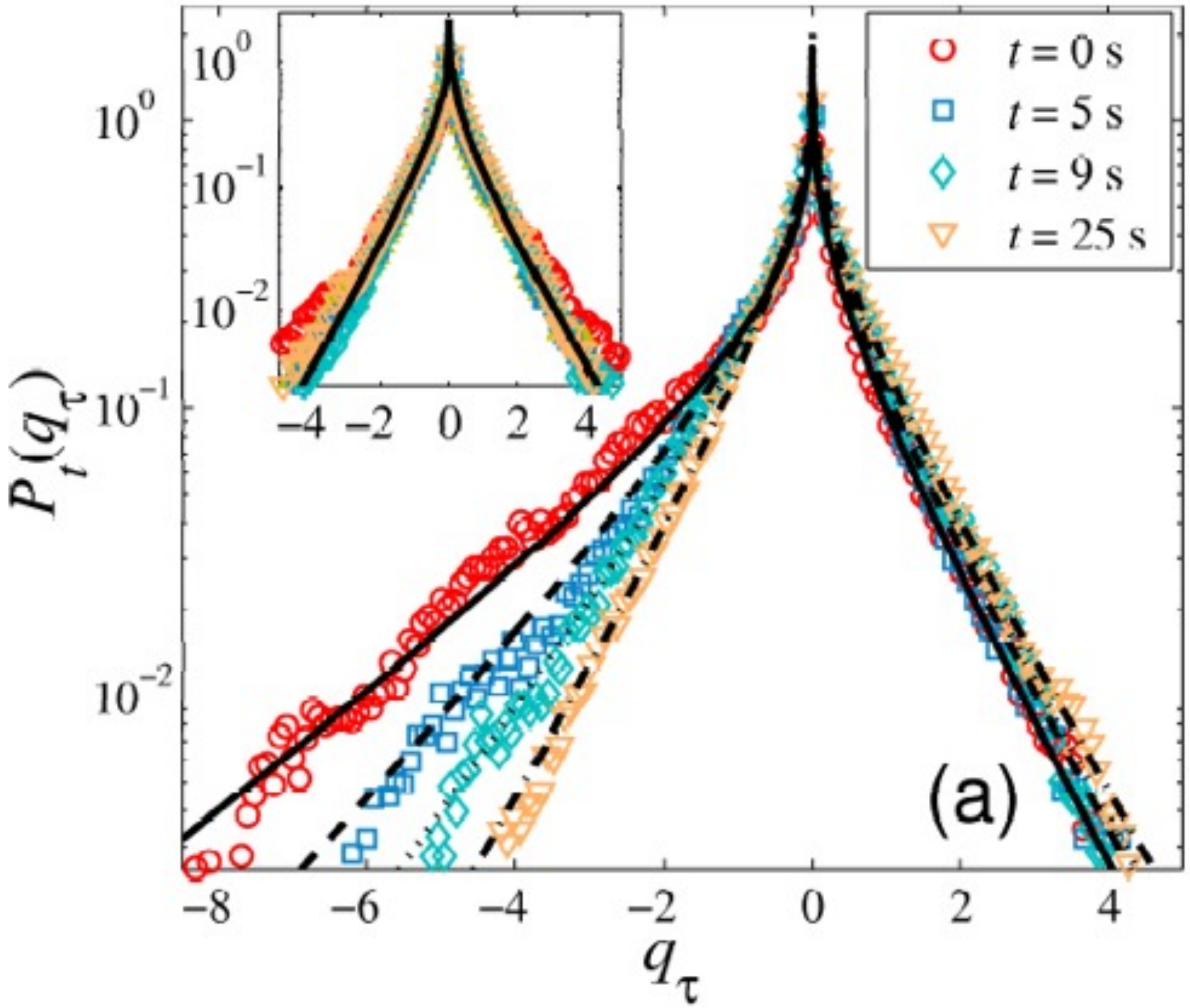
glicerol

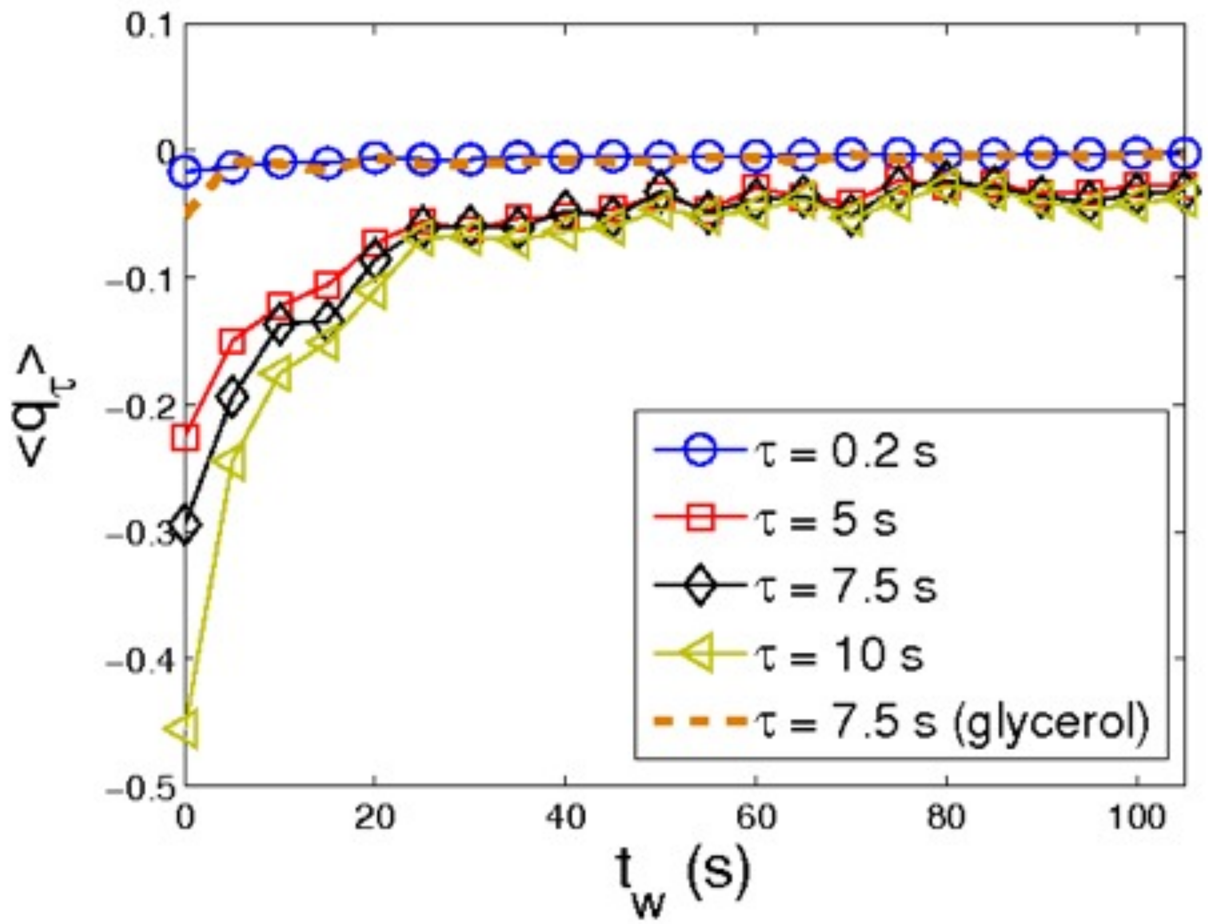
$$q_\tau = \frac{Q_\tau}{k_B\ T}$$



Energy PDF and mean heat

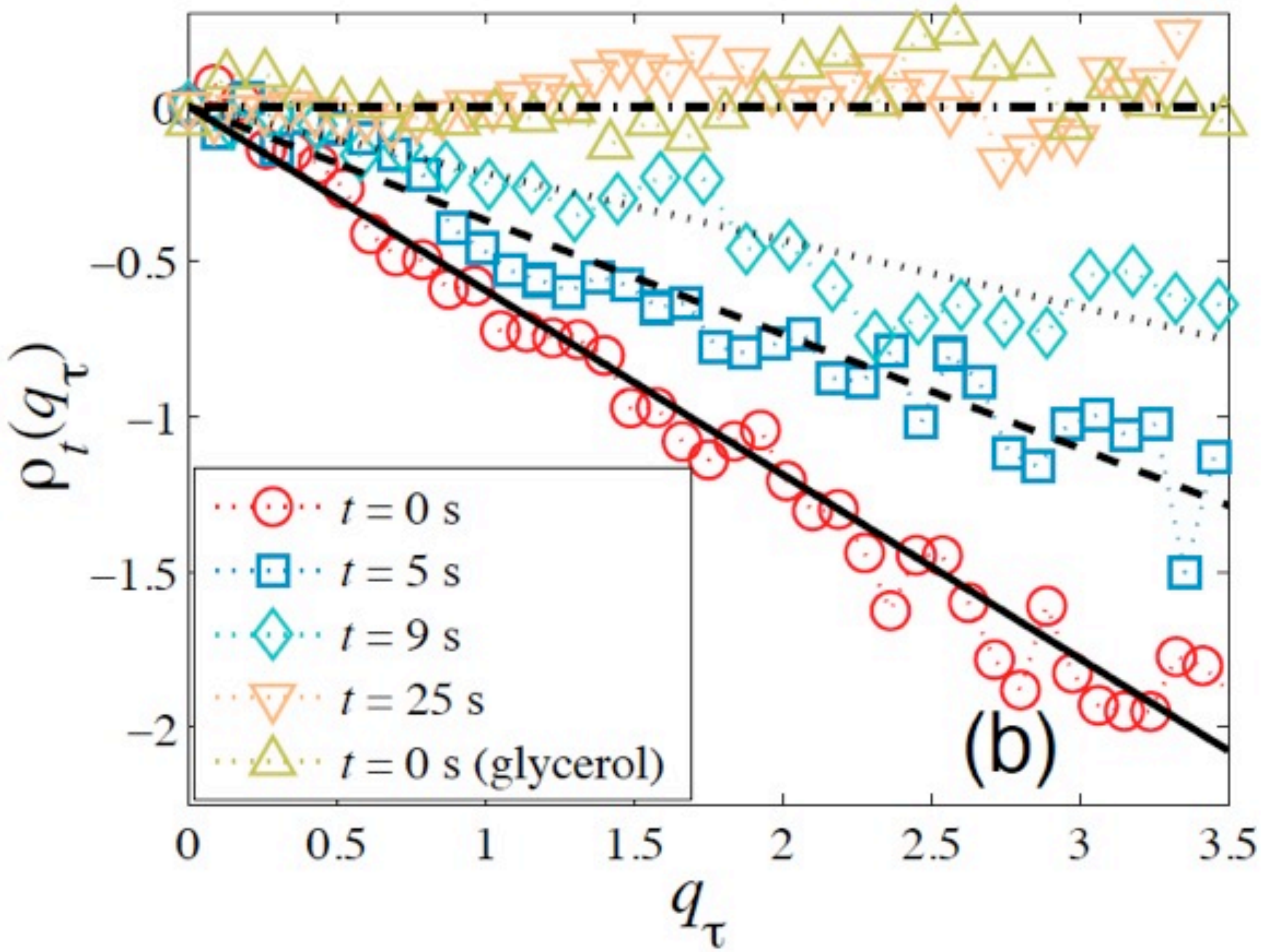
$$q_\tau = \frac{Q_\tau}{k_B\ T}$$





Mean heat

Fluctuation theorem



FT fixes the symmetries of the PDF $\rho(q_\tau) = \log \frac{P(q_\tau)}{P(-q_\tau)}$

$$\rho(\tau) = \Delta\beta_{t,\tau}\ q_\tau \text{ for } \tau \to \infty$$

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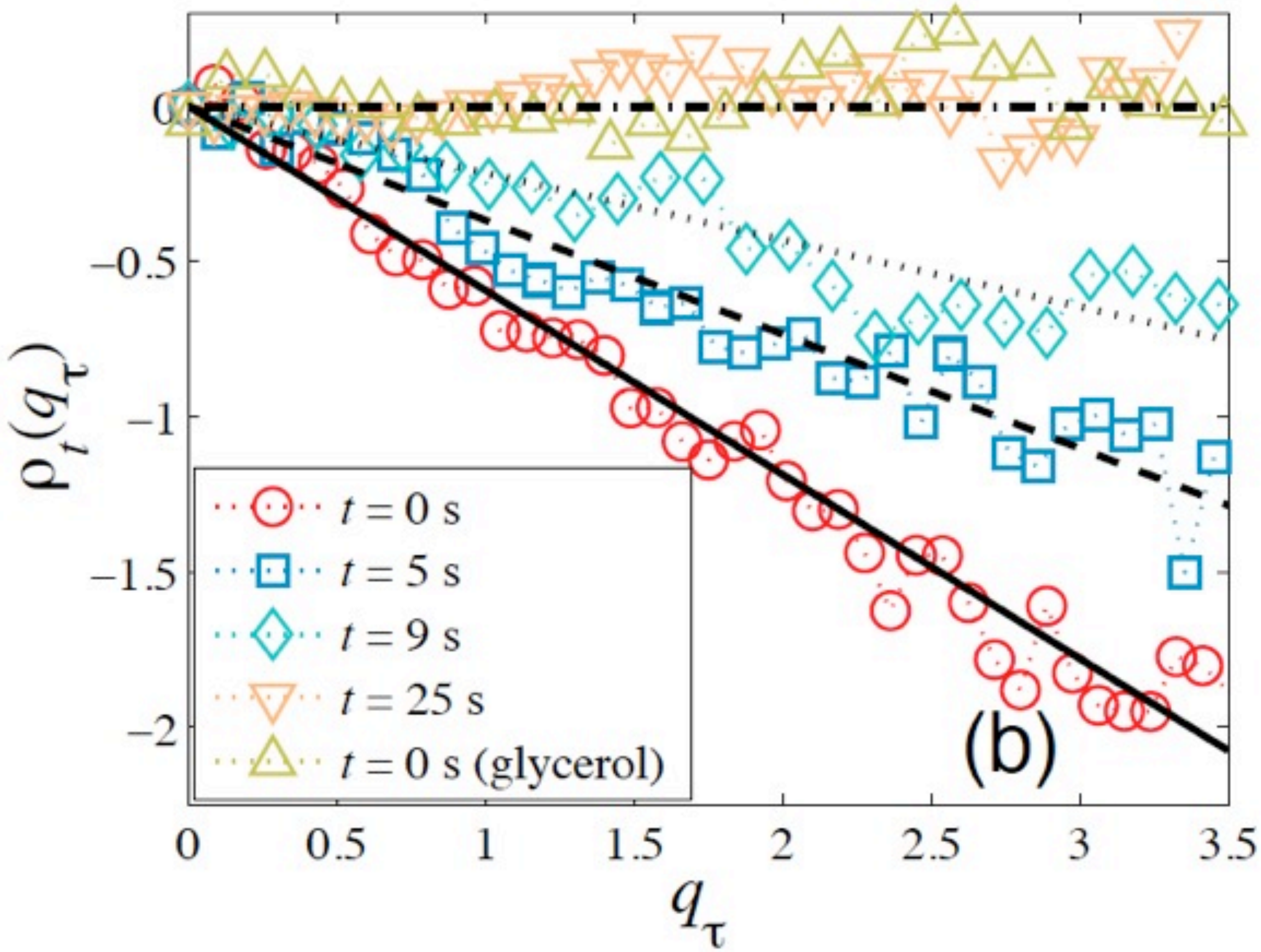

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What is the value ?

Data analysis

Using the experimental observation that P(x) are Gaussian
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One gets from a simple model in the limit of large τ :

$$P_t(q_\tau) = \frac{A_{t,\tau}}{\pi} K_0\left(B_{t,\tau}|q_\tau|\right) \exp\left(-\frac{\Delta_{t,\tau} A_{t,\tau}}{2} q_\tau\right),$$

where K_0 is the zeroth-order modified Bessel function of the second kind,

$$\Delta_{t,\tau} = \frac{\sigma_x(t)}{\sigma_x(t+\tau)} - \frac{\sigma_x(t+\tau)}{\sigma_x(t)}, \quad A_{t,\tau} = \frac{k_B T}{k\sigma_x(t)\sigma_x(t+\tau)} \text{ and } \quad B_{t,\tau} = A_{t,\tau}\sqrt{1+\Delta^2_{t,\tau}/4}$$

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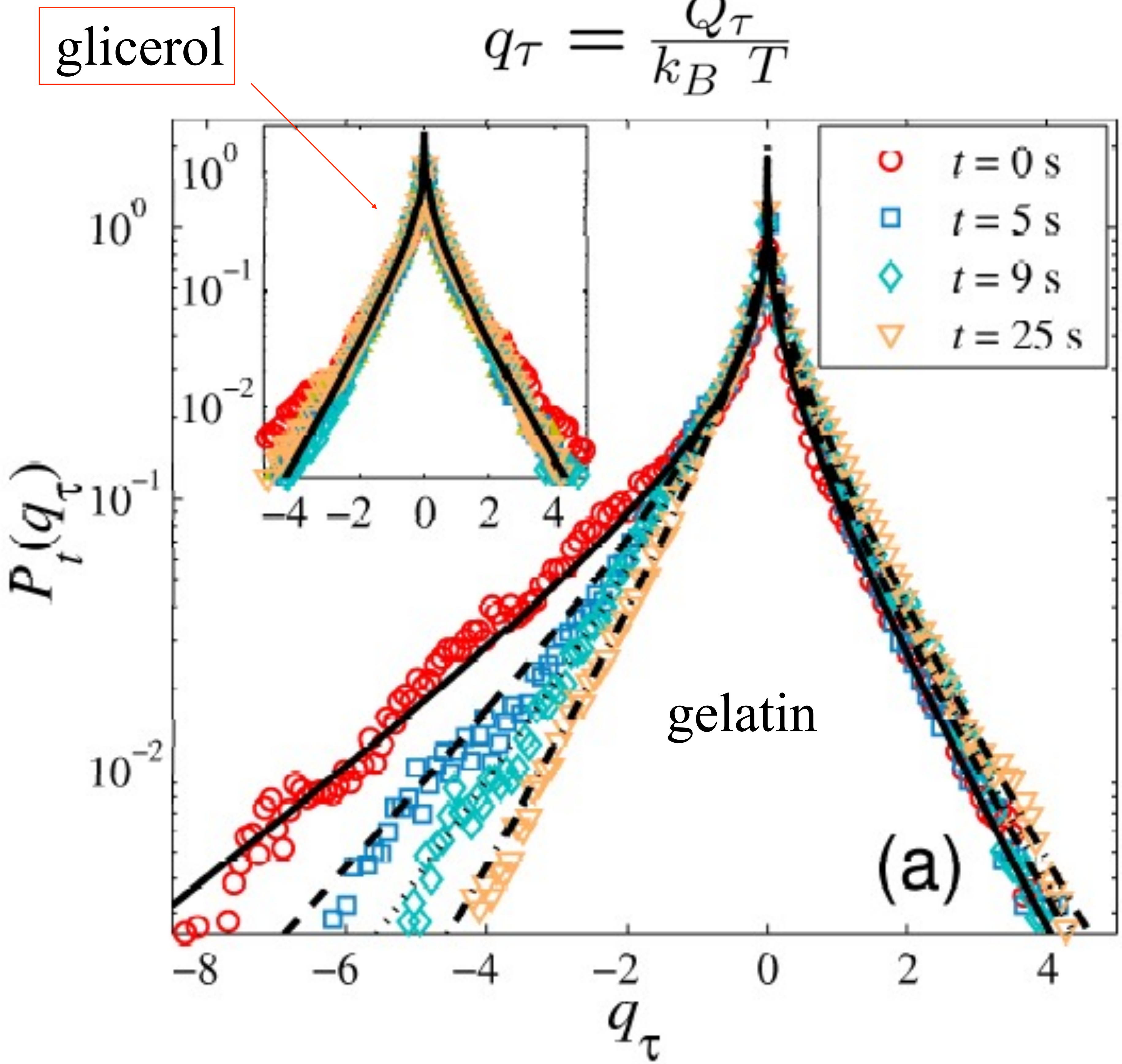
from which

$$\Delta\beta_{t,\tau} = \frac{k_B T}{k}\left[\frac{1}{\sigma_x(t+\tau)^2} - \frac{1}{\sigma_x(t)^2}\right].$$

Hence, the linearity of $\rho_t(q_\tau)$ is analytically satisfied

Energy PDF

$$q_\tau = \frac{Q_\tau}{k_B\ T}$$



Comparisons with other results

Using an equipartition-like relation : $k_B T_{eff}(t) = k\sigma_x(t)^2$

$$\Delta\beta_{t,\tau} = \left[1/T_{eff}(t+\tau) - 1/T_{eff}(t)\right] T,$$

Similar relations have been theoretically derived :

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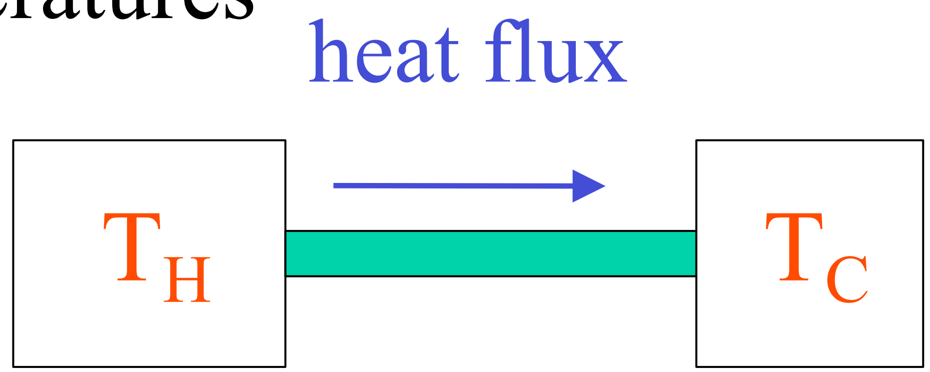
Similar relations have been theoretically derived :

A) In the stationary case for the heat flux between two reservoirs at different temperatures

$$\ln \frac{P(Q_\tau)}{P(-Q_\tau)} = \left(\frac{1}{T_C} - \frac{1}{T_H}\right) \frac{Q_\tau}{k_B}$$



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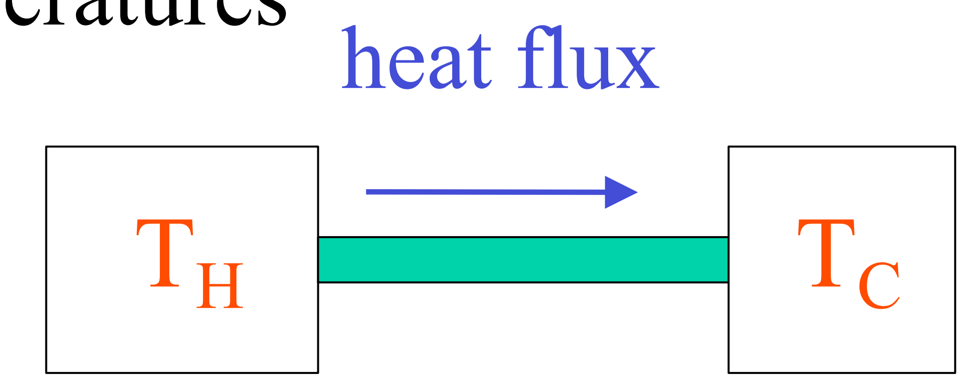

B) In the non-stationary case during the aging of spin glasses

A. Crisanti and F. Ritort, Europhys. Lett. 66, 253 (2004).

What this is useful for ?

From Fluctuation Theorem

$$\Delta S_\tau = -k_B \Delta\beta_{t,\tau} q_{t,\tau}$$

is the entropy production rate of the relaxation process

Comparing this result with numerical data of aging spin-glasses

Aging can be interpreted as an heat transfer (cooling) of the slow modes towards the heat bath

A. Crisanti and F. Ritort, Europhys. Lett. **66**, 253 (2004).

Conclusions

The liquid-solid transition is studied inside a drop of liquid after a very fast quench.

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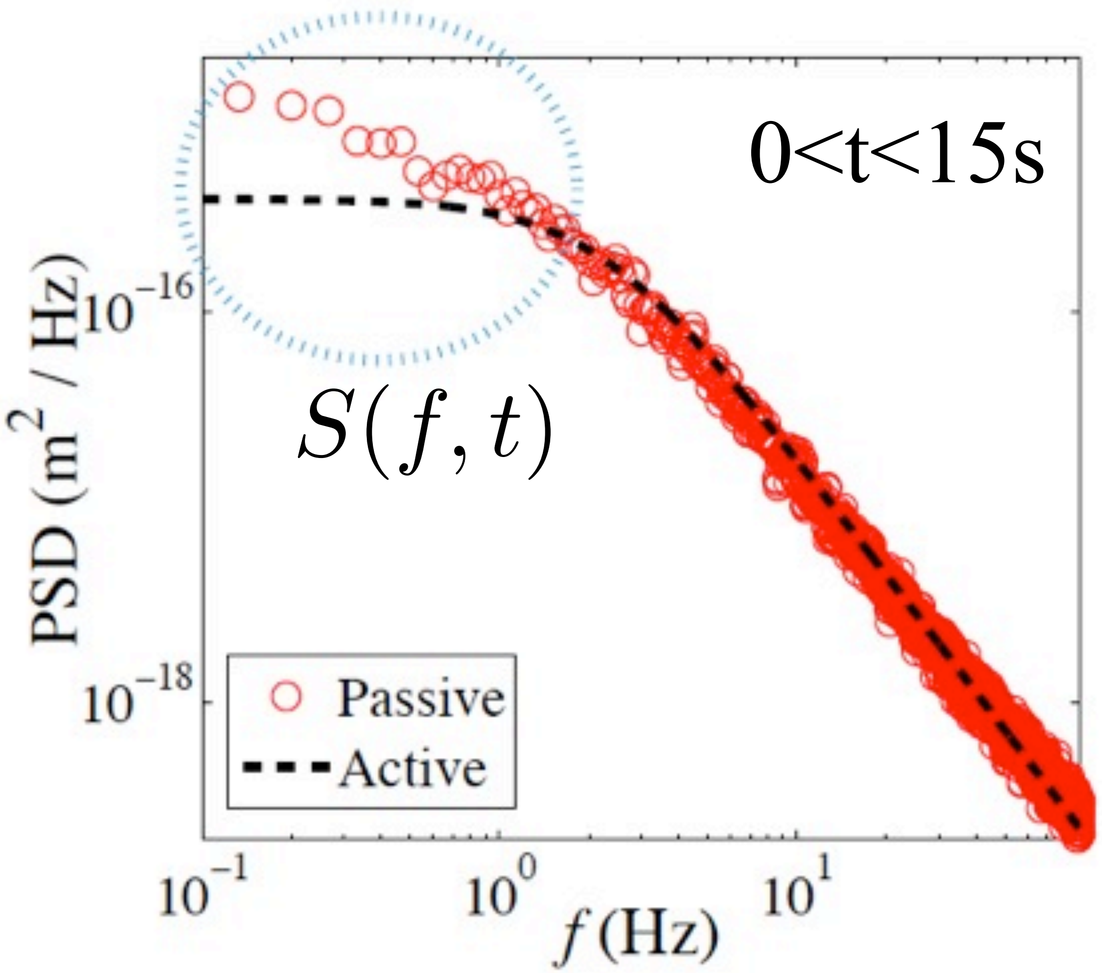
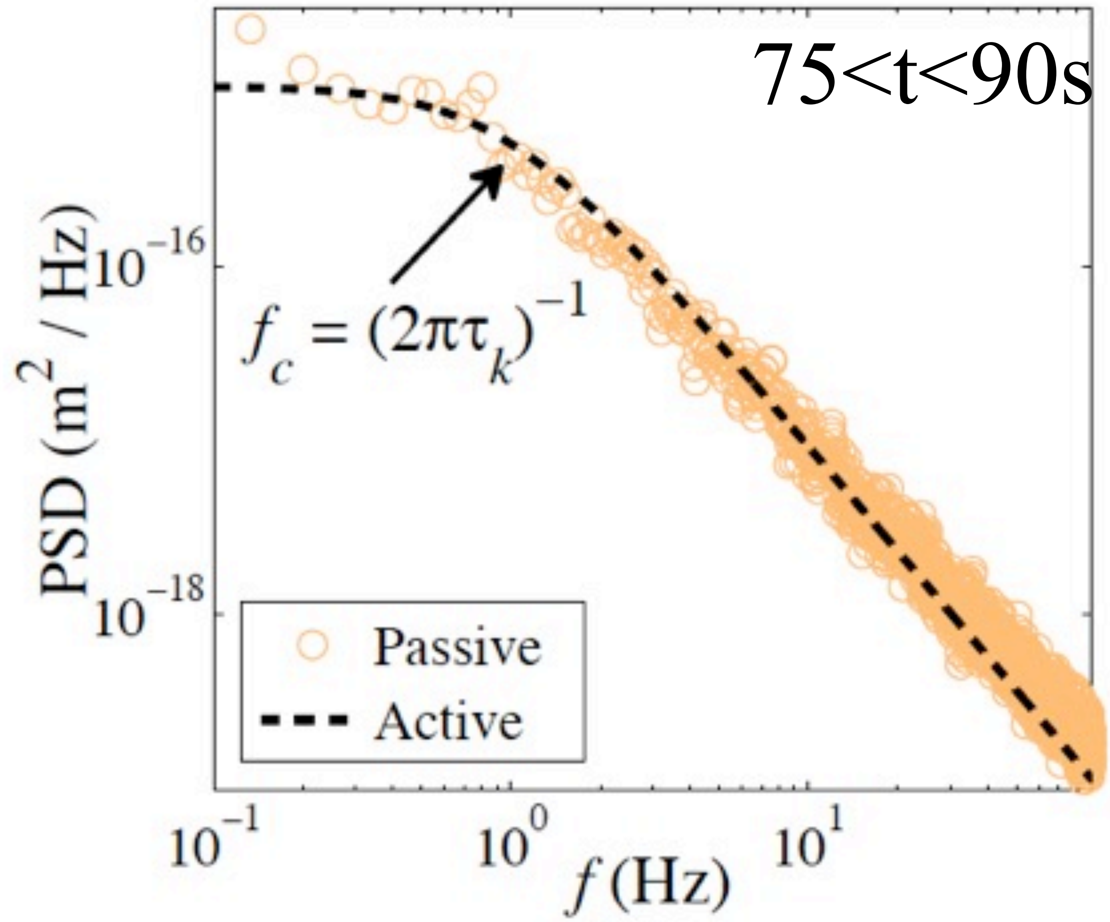
c) The Fluctuation Dissipation Theorem is violated

Fluctuations and Linear response





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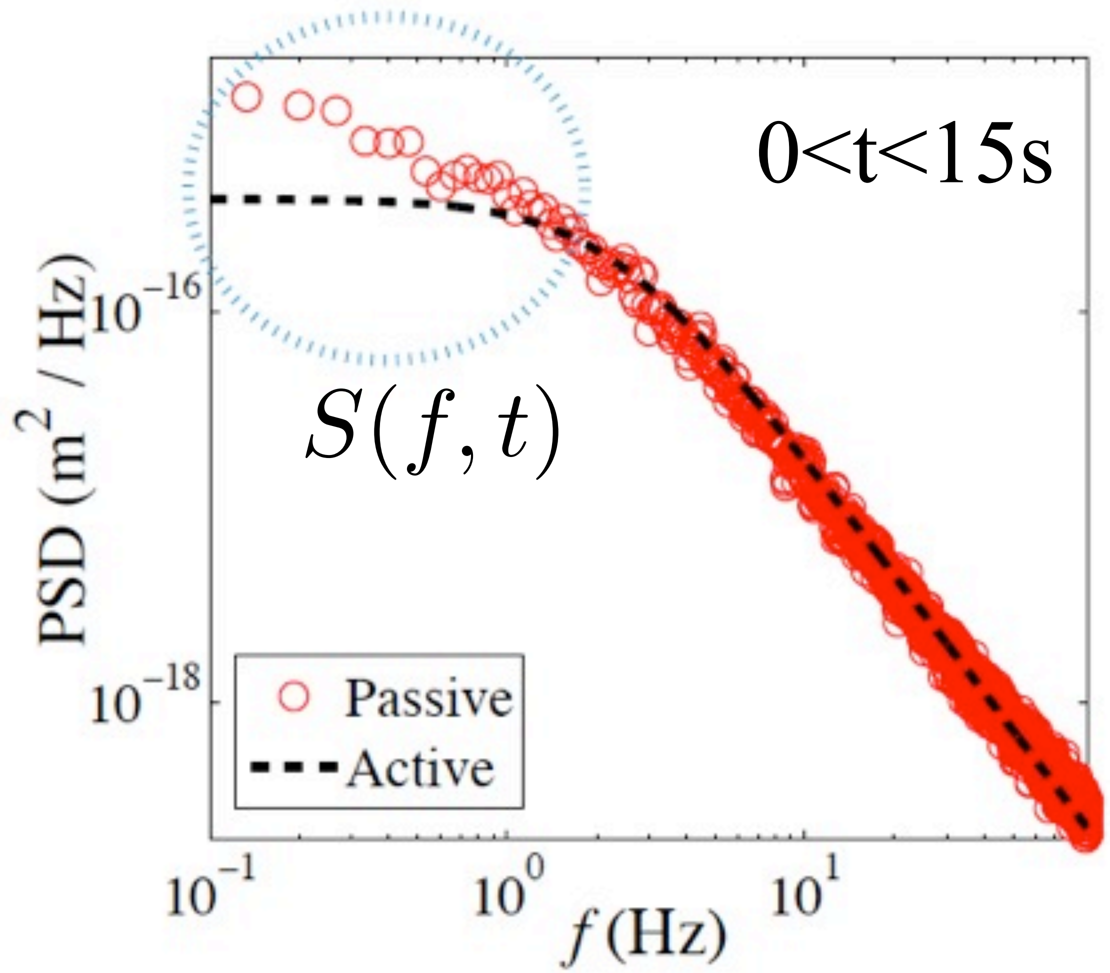
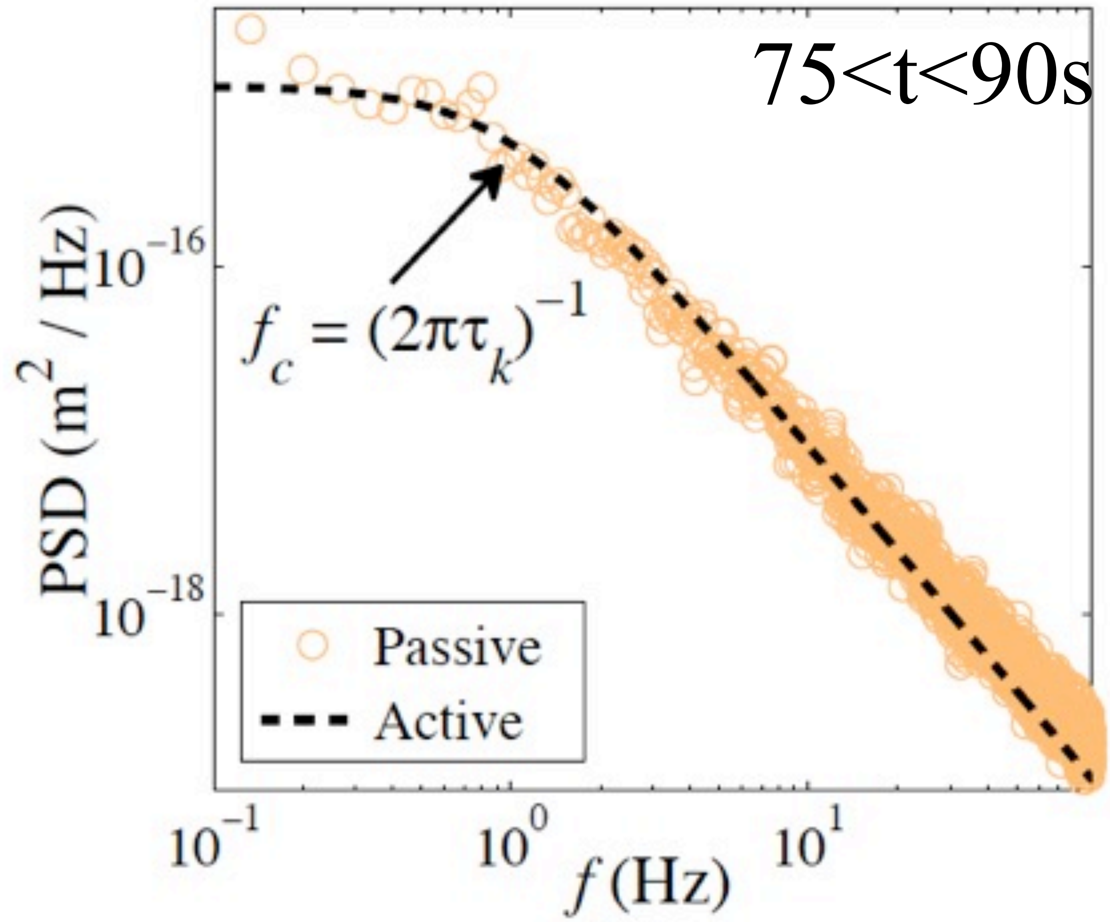


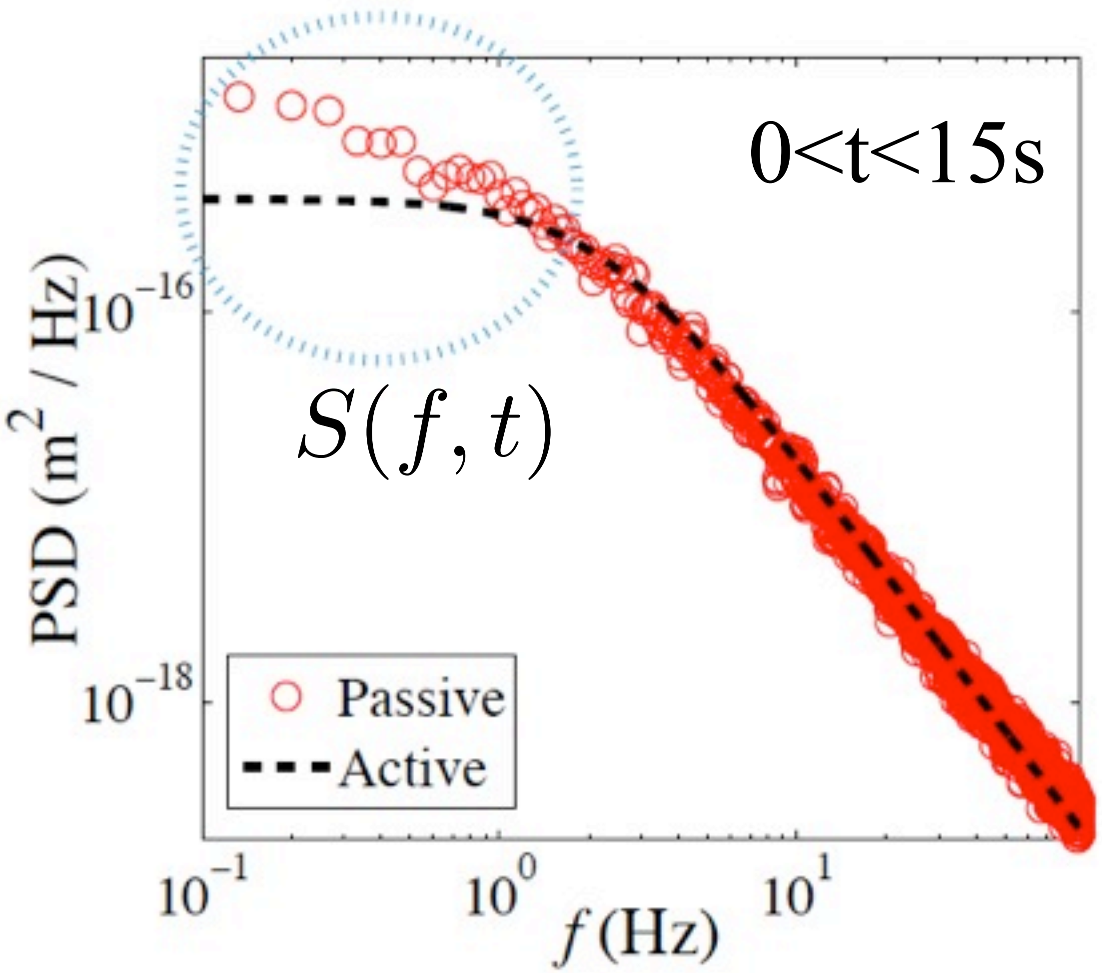


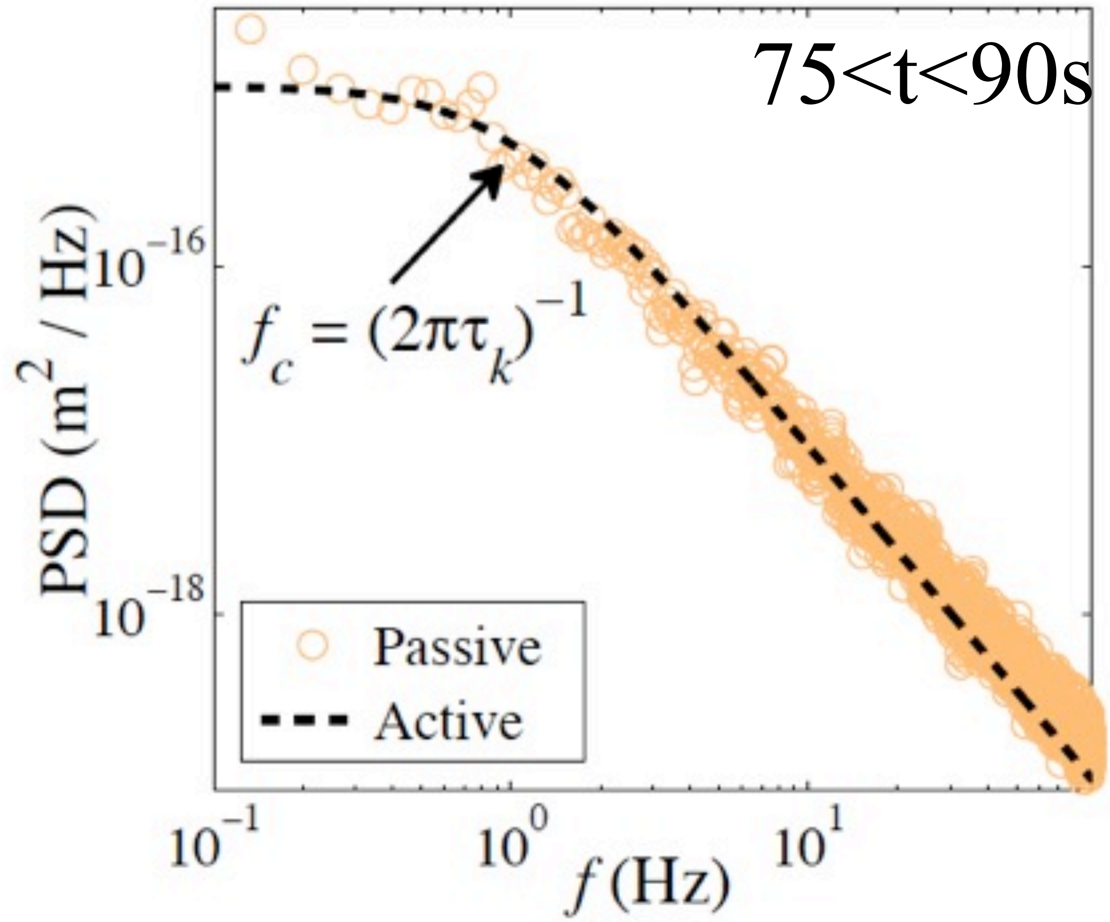
$$S(f,t) = \frac{2k_B\,T}{\pi f} Im[R(f,t)]$$

FDT

in equilibrium

Fluctuations and Linear response

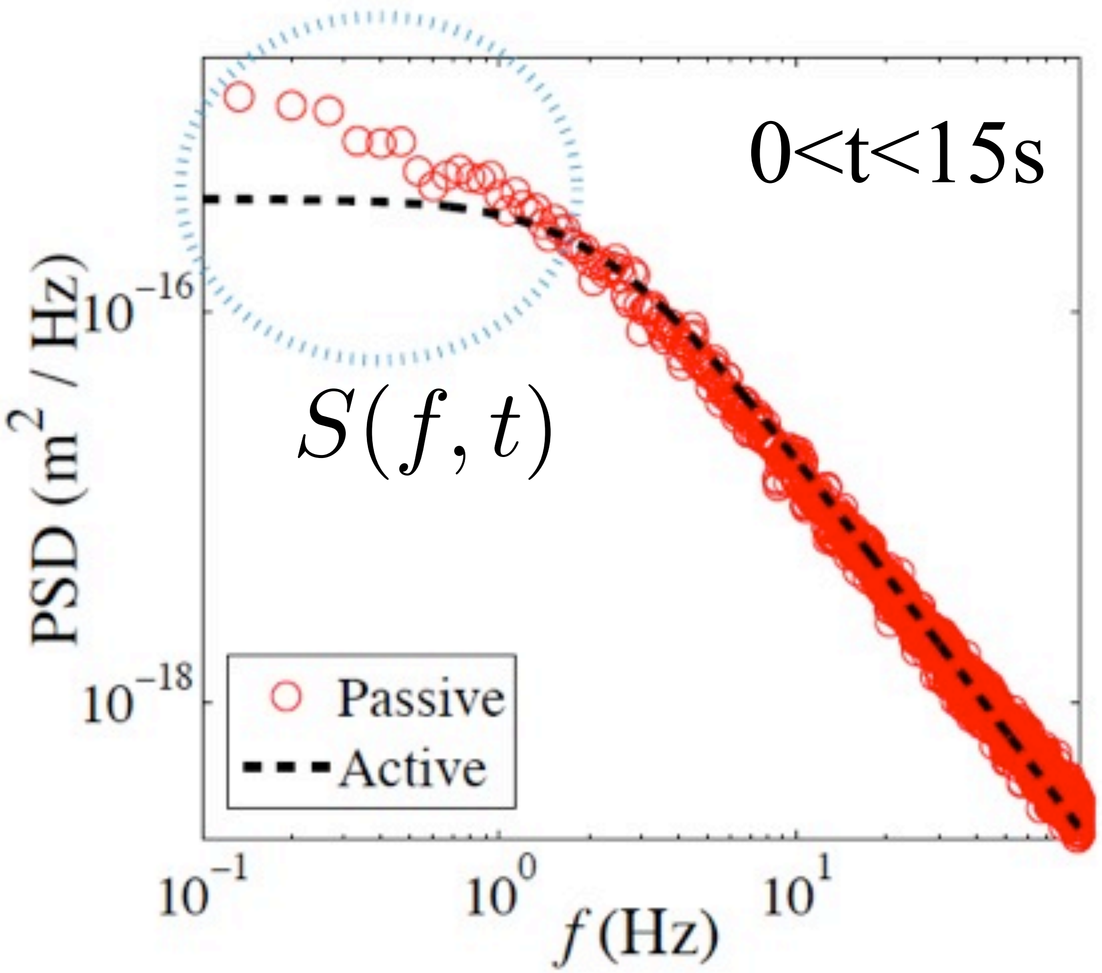


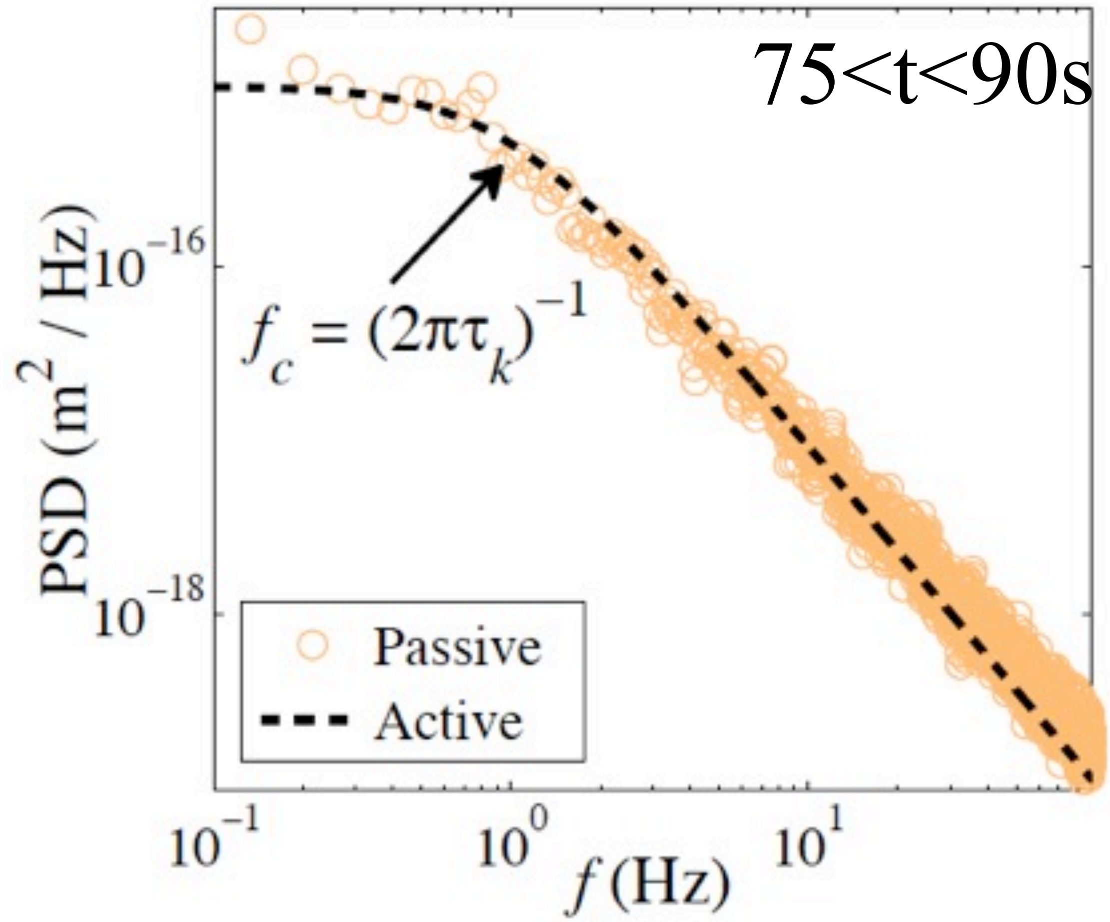


$$S(f,t) \neq \frac{2k_B\,T}{\pi f} Im[R(f,t)] \quad \text{out of equilibrium}$$

FDT is violated in our experiment

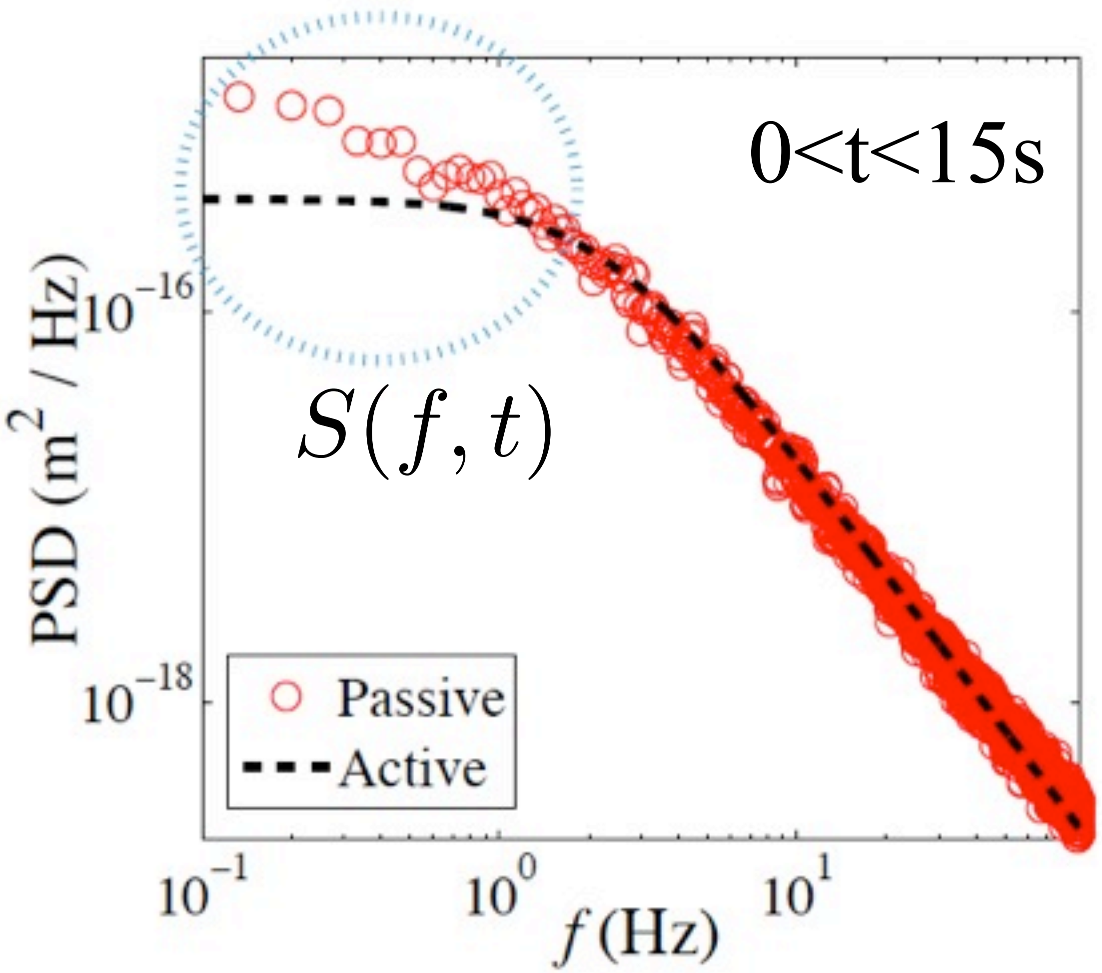
Fluctuations and Linear response

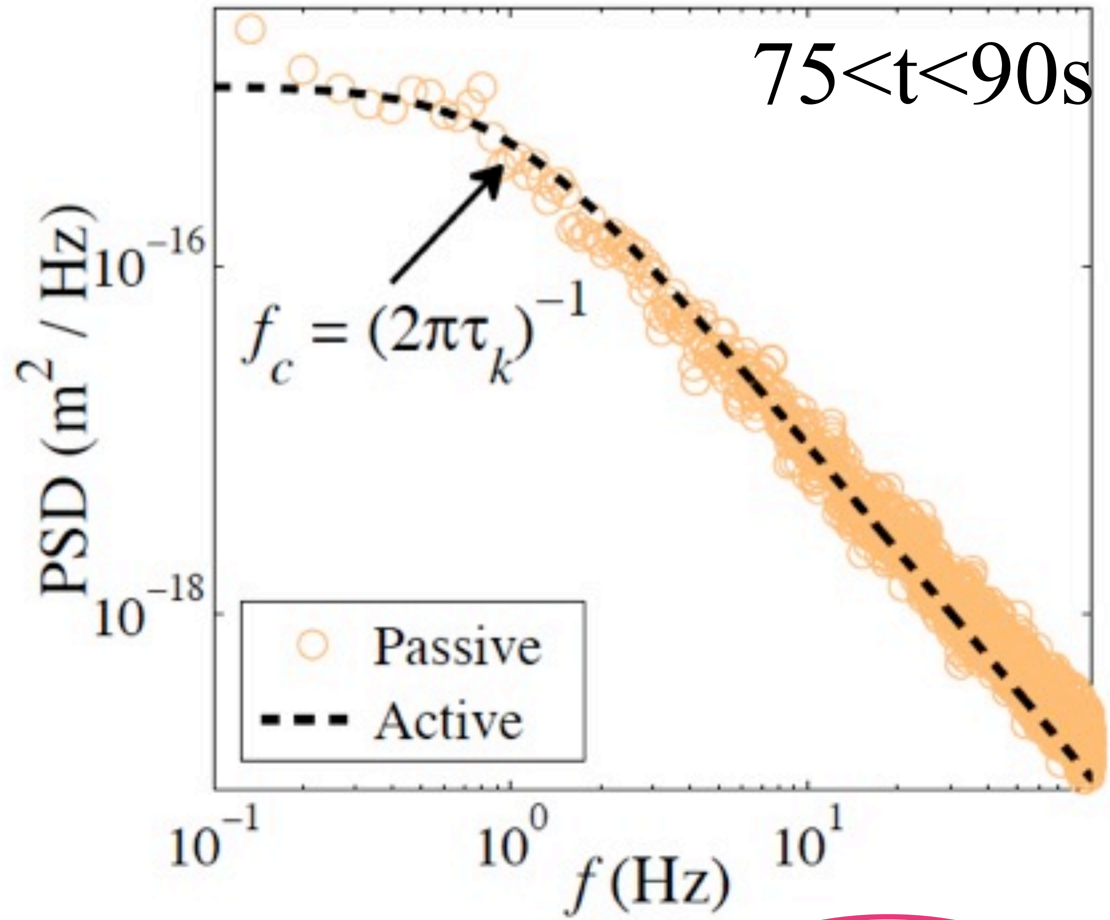




$$\int_0^{\infty} \left[S(f,t) - \frac{2k_B\,T}{\pi f} Im\{R(f,t)\} \right] df = \frac{2\,\overline{Q}_{t,\Delta t}}{k}$$

Fluctuations and Linear response





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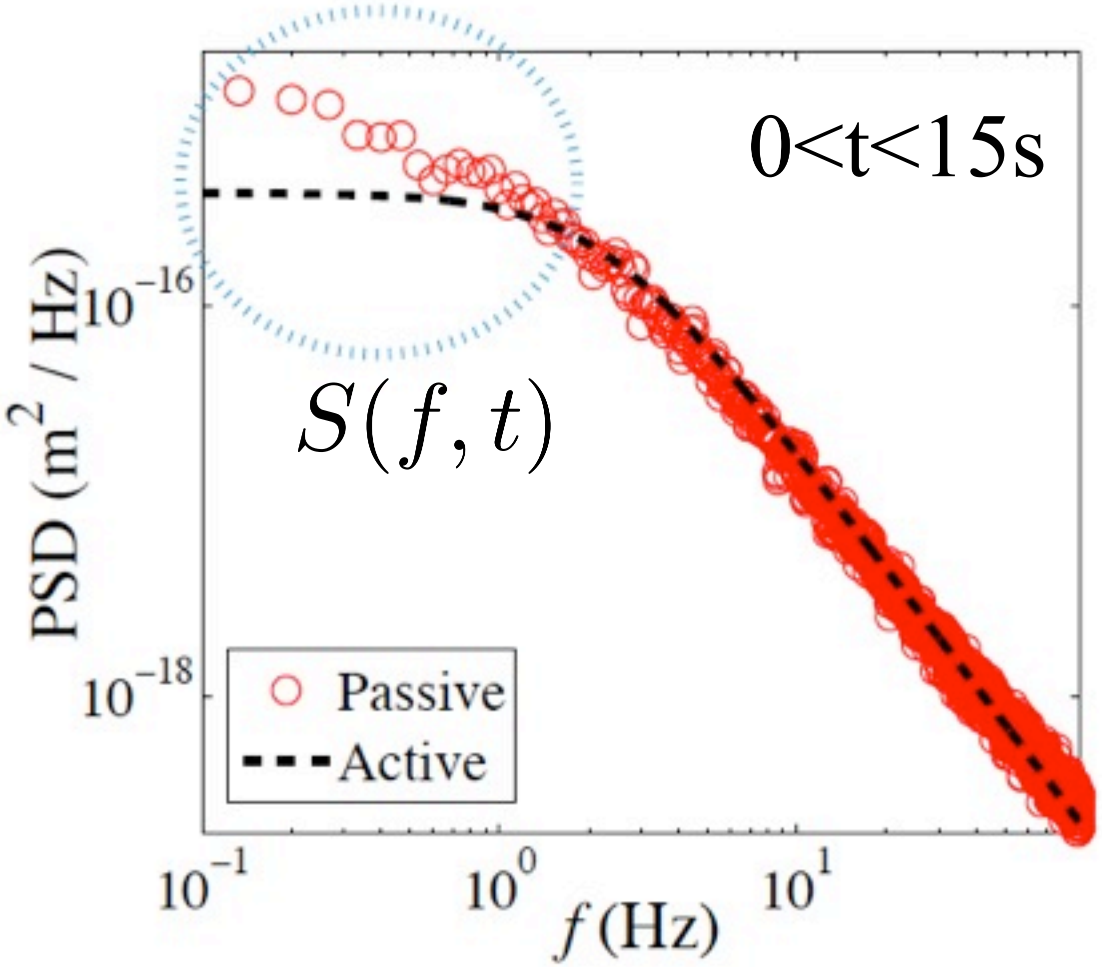
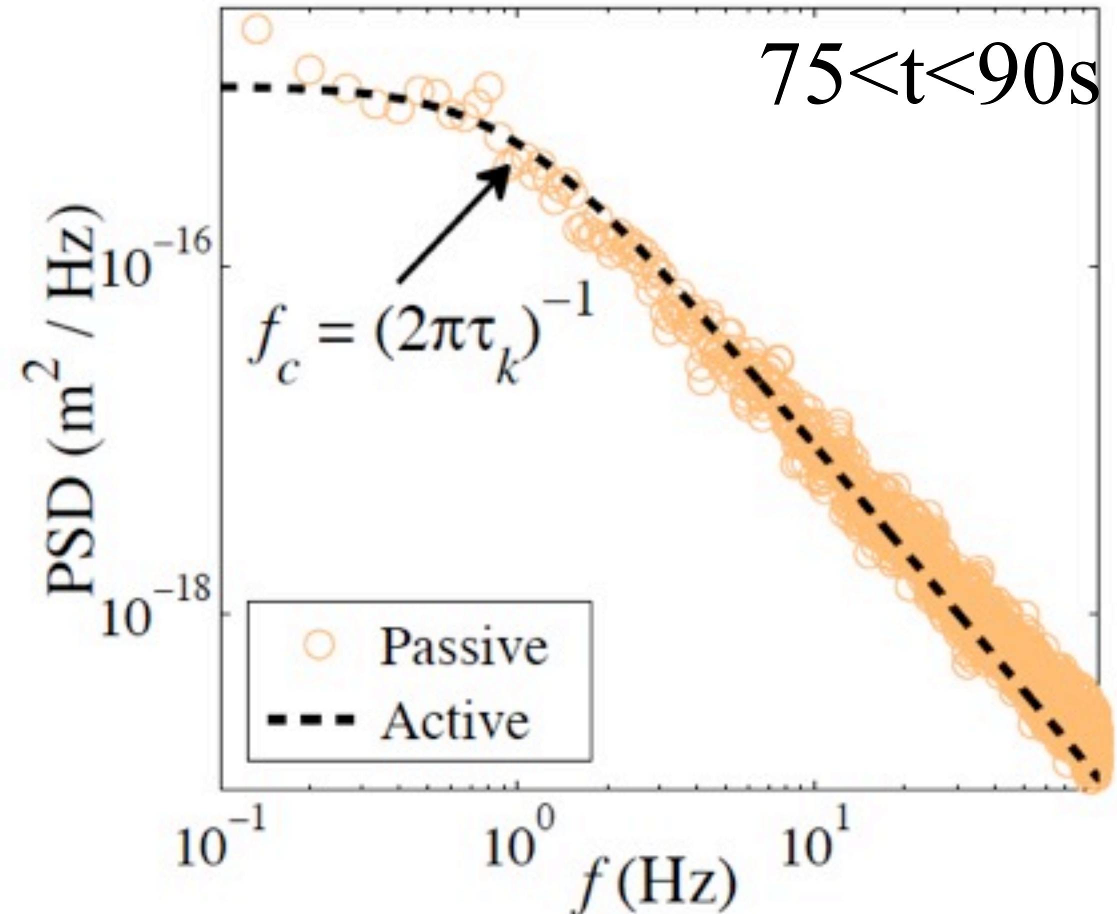
heat dissipated in the time interval [t,t+Δt]

Fluctuations and Linear response





$$\int_0^\infty \left[S(f,t) - \frac{2k_B\, T}{\pi f} Im\{R(f,t)\} \right] df = \frac{2\, \overline{Q}_{t,\Delta t}}{k}$$

As in the generalized FDT for NESS the extra additive term is related to the heat flux.
(Chetrite, Gawedzki, Seifert Speck, Maes, Lipiello, Corberi)

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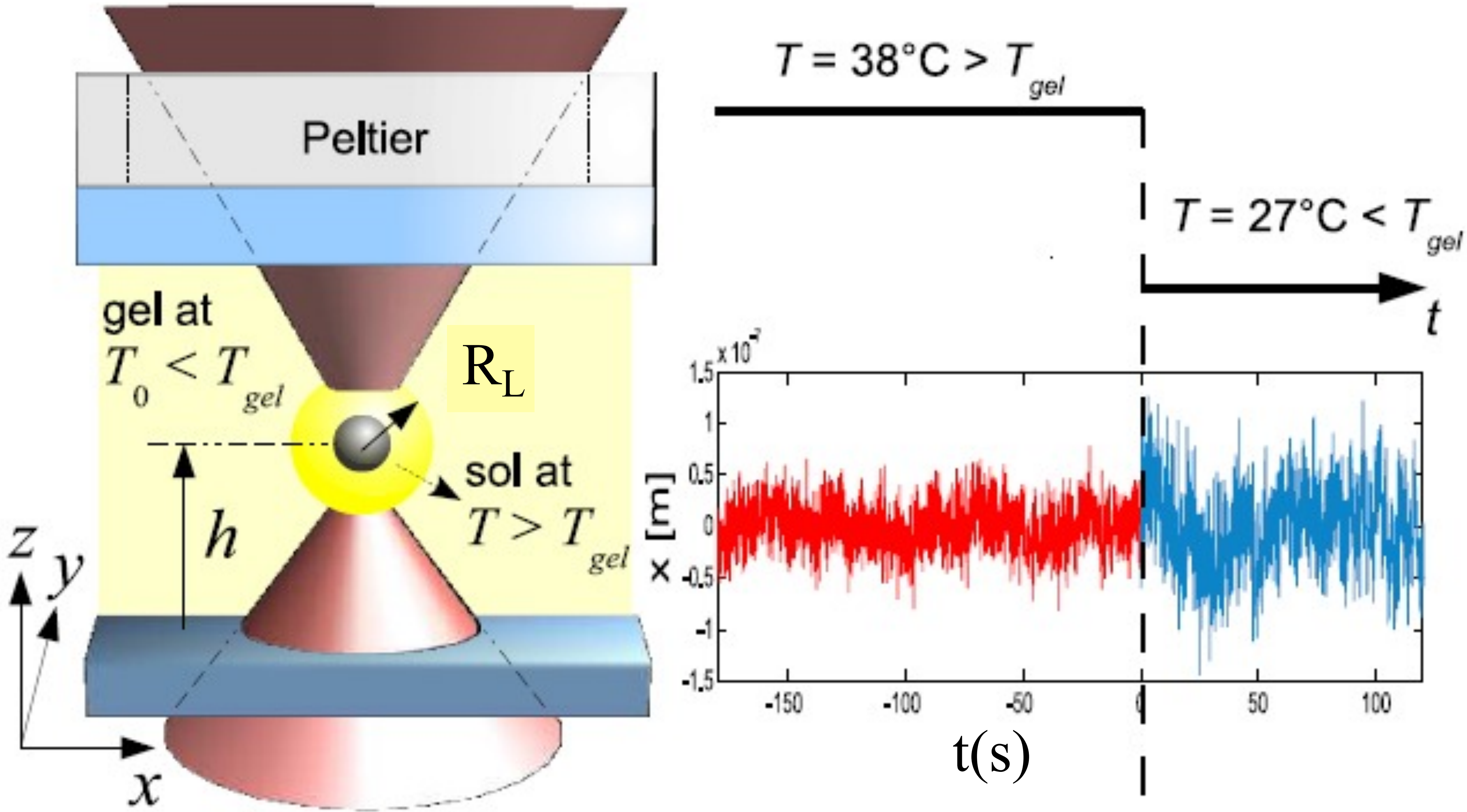
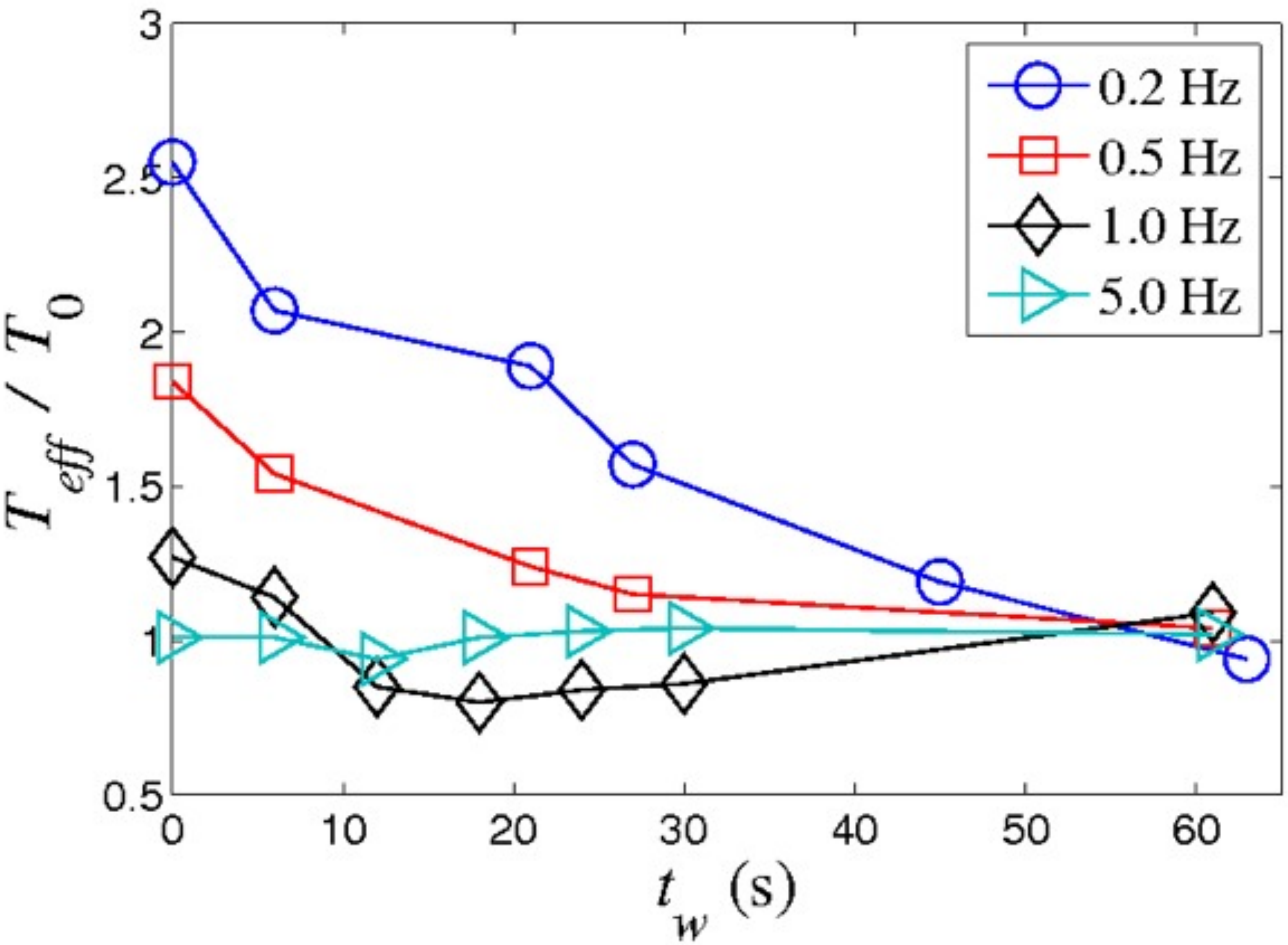
b) The Fluctuation Theorem is satisfied in a non-stationary regime

c) The Fluctuation Dissipation Theorem is violated.
The amount of the violation is related to the heat flux as for the Generalized FDT for NESS.

- Fast quench of the droplet to $T = 27^\circ$ C $< T_{gel}$ by decreasing the laser power: heat diffusion into the gel bulk in $\sim$1 ms.



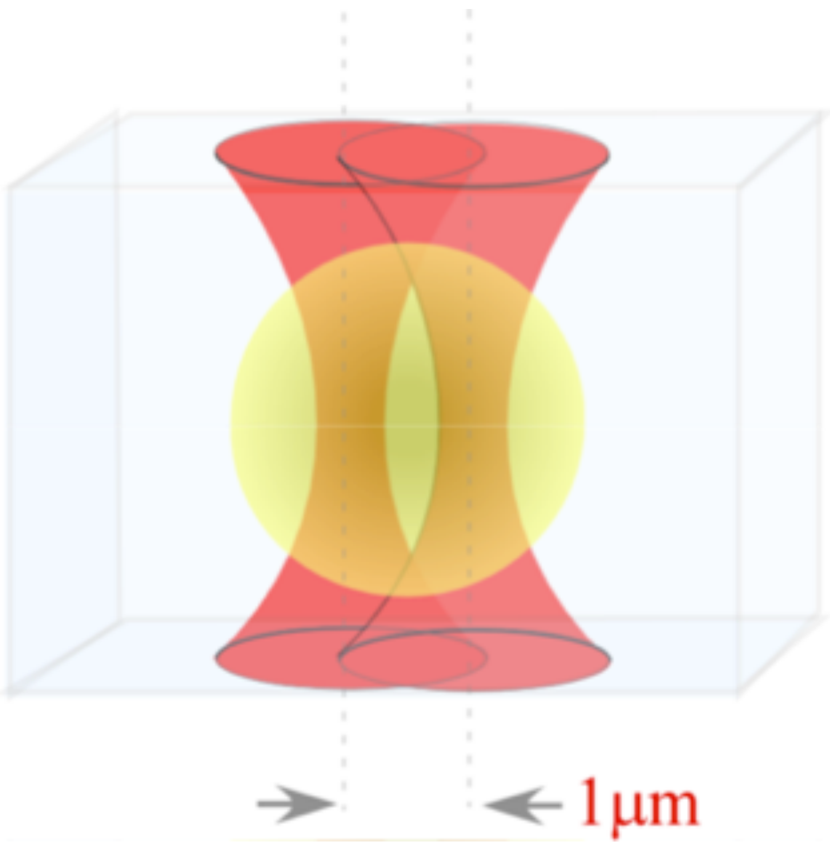


Experiment in gelatine
at 10%wt
sol-gel transition at 28°C

The stochastic resonance and Fluctuation Theorem

P.Jop. A. Petrosian, S. Ciliberto, Eur. Phys. Lett. **81,** 50005 (2008)

Brownian particle trapped by two laser beams



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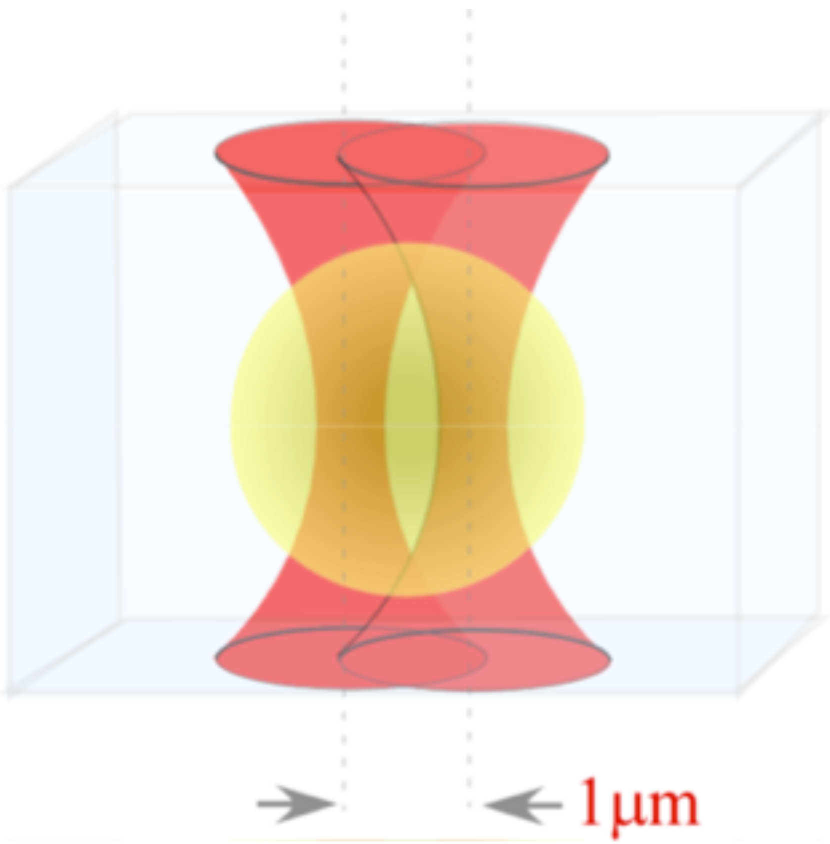
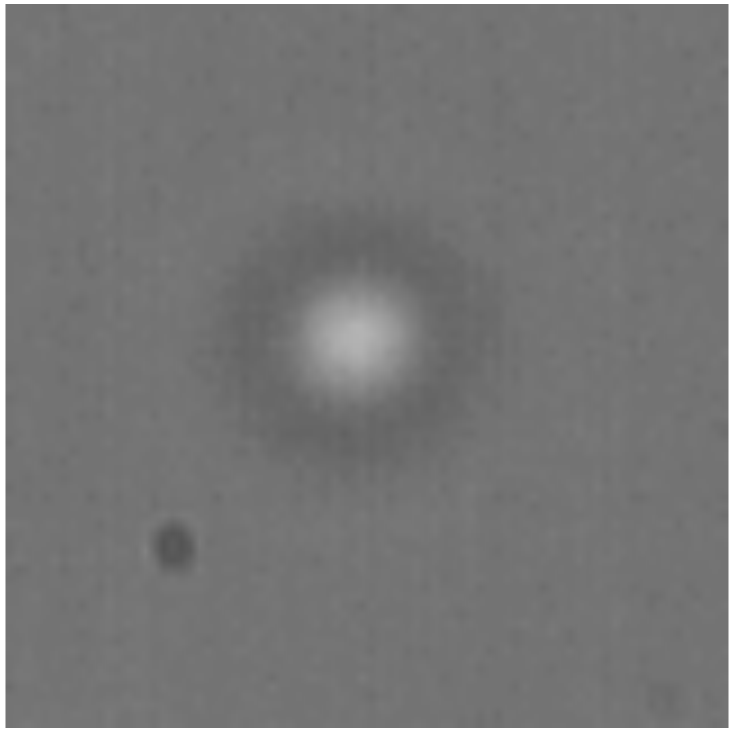
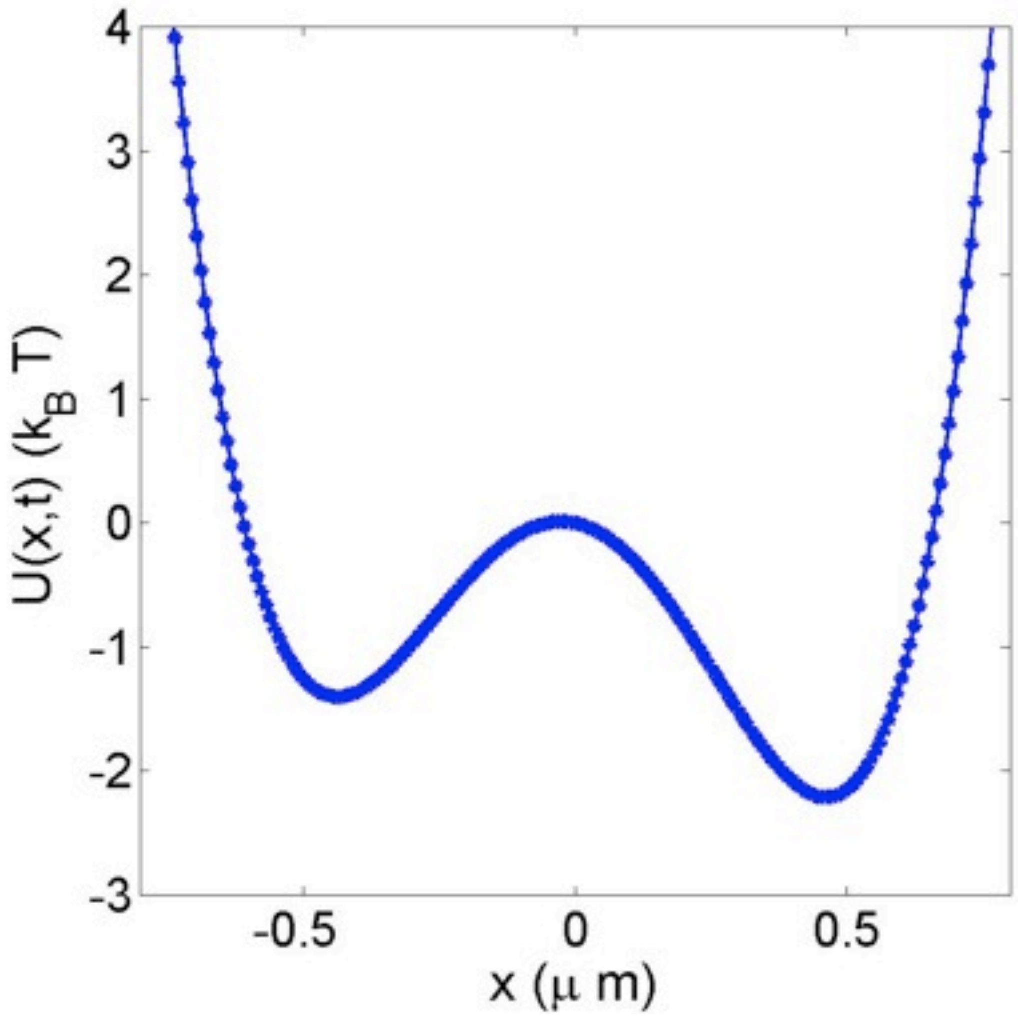




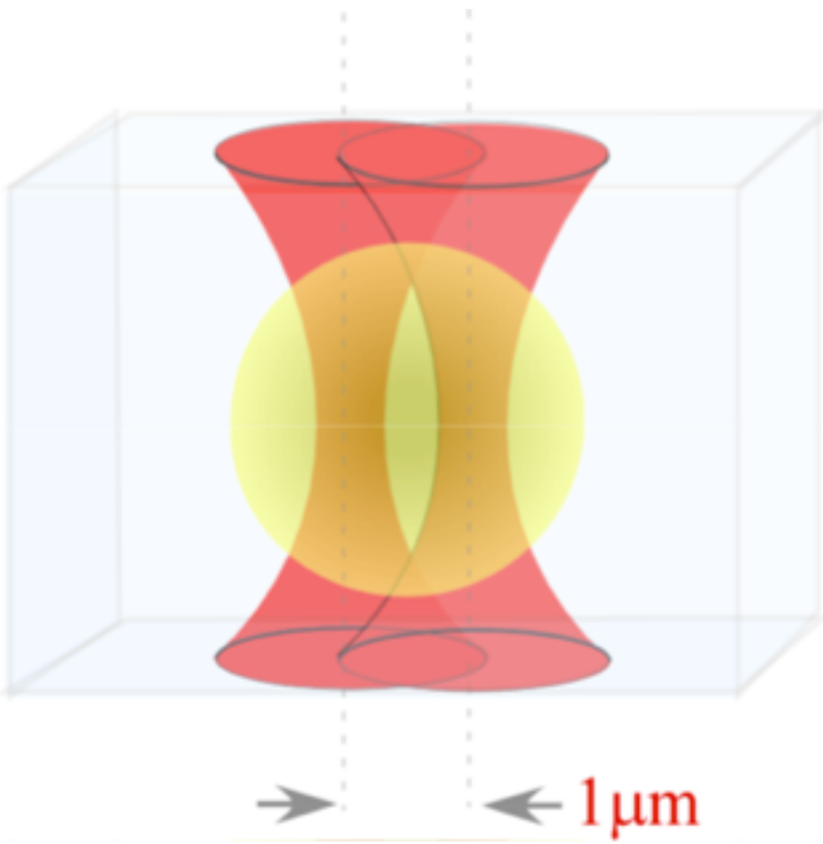


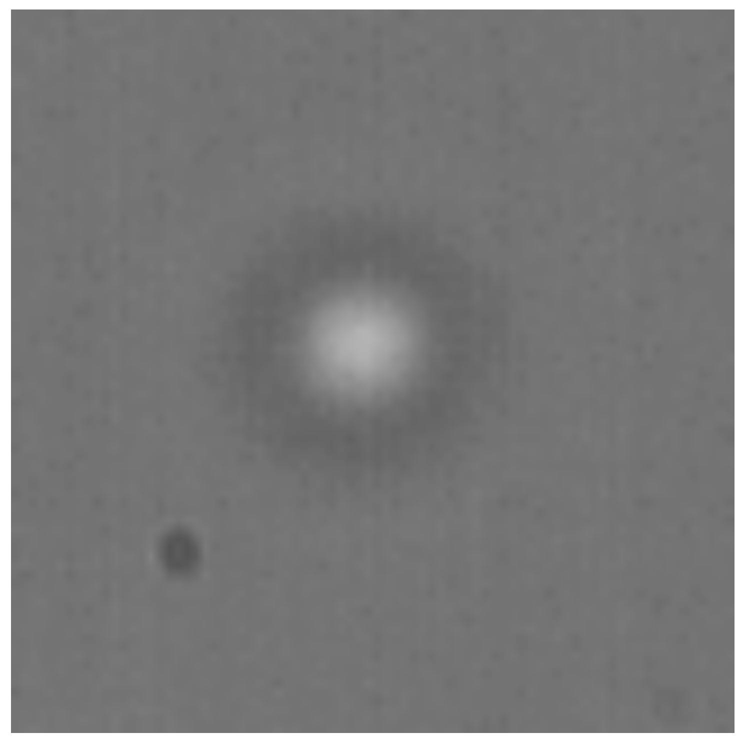
$$U_0(x) = ax^4 - bx^2 - dx$$

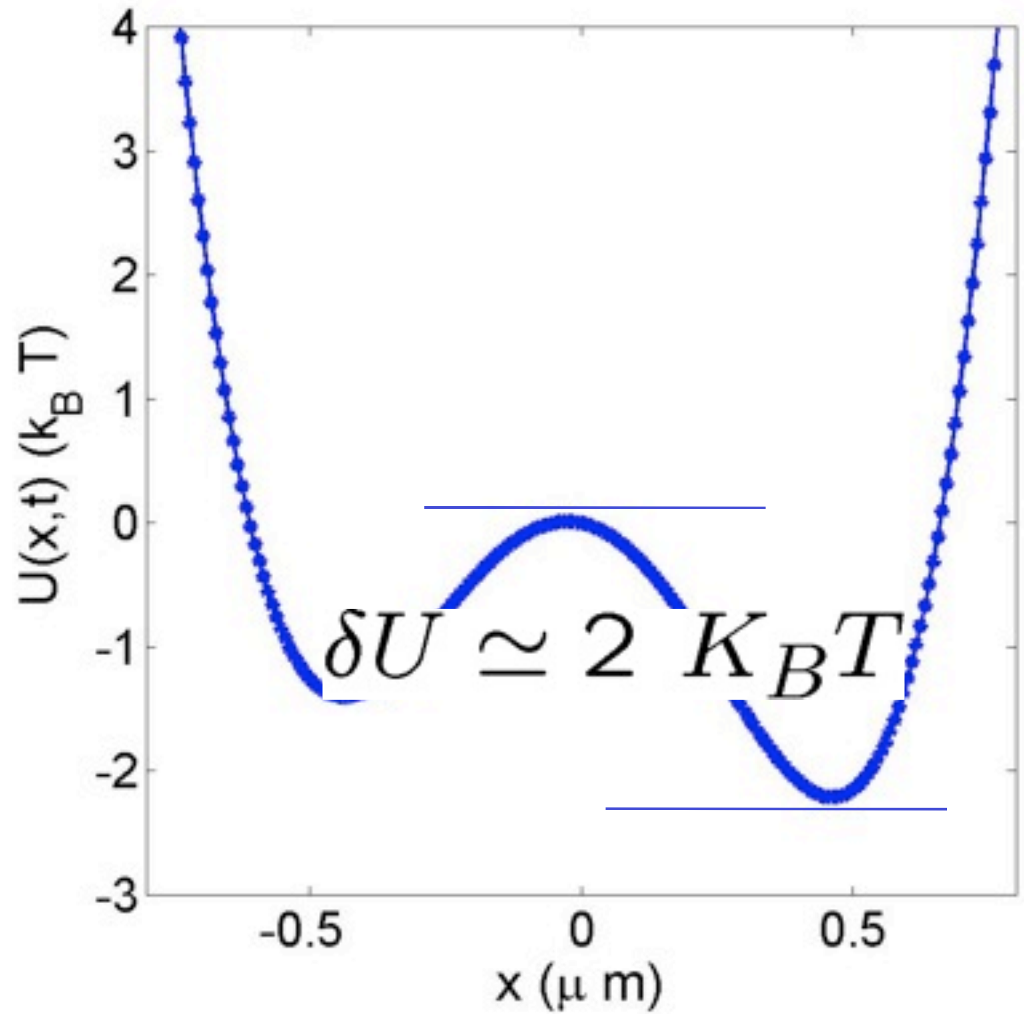
The stochastic resonance and Fluctuation Theorem

P.Jop. A. Petrosian, S. Ciliberto, Eur. Phys. Lett. **81,** 50005 (2008)

Brownian particle trapped by two laser beams







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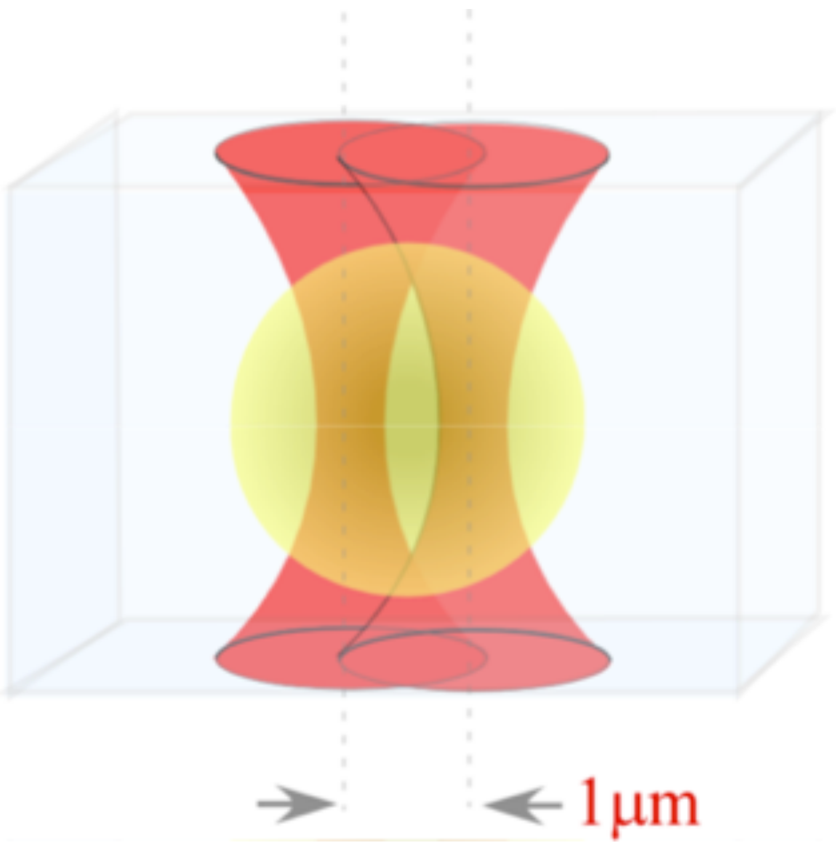

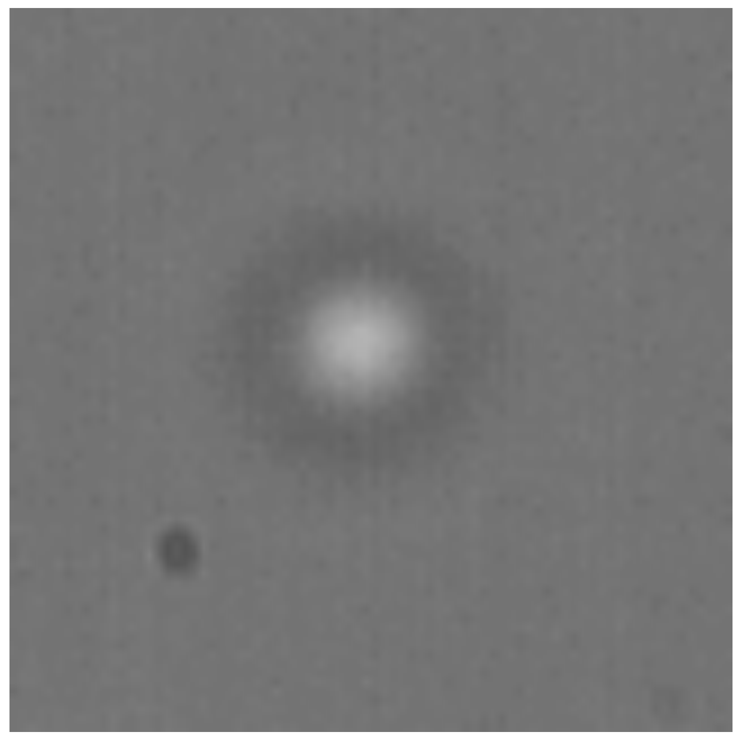

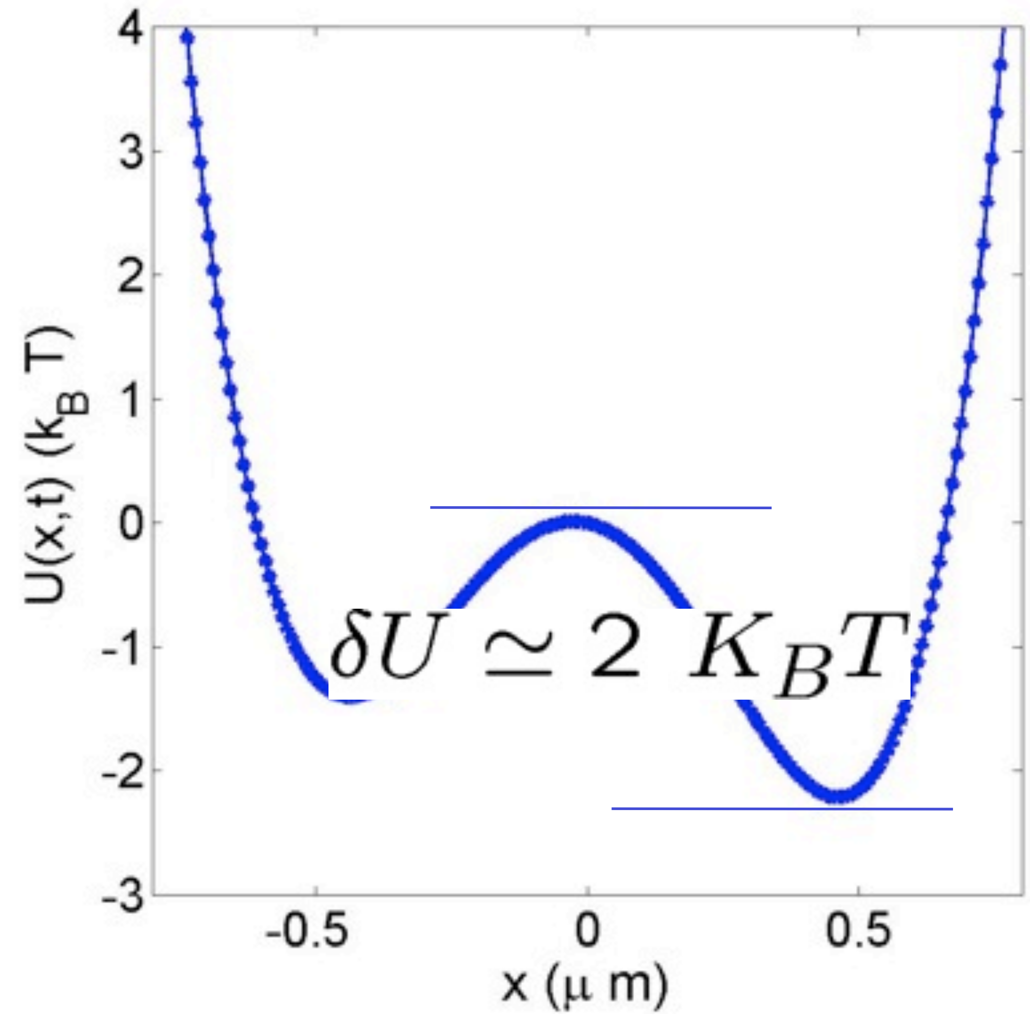

The Kramer rate is

$$r_k = \tau_o^{-1} \exp(-\frac{\delta U}{k_B T})$$

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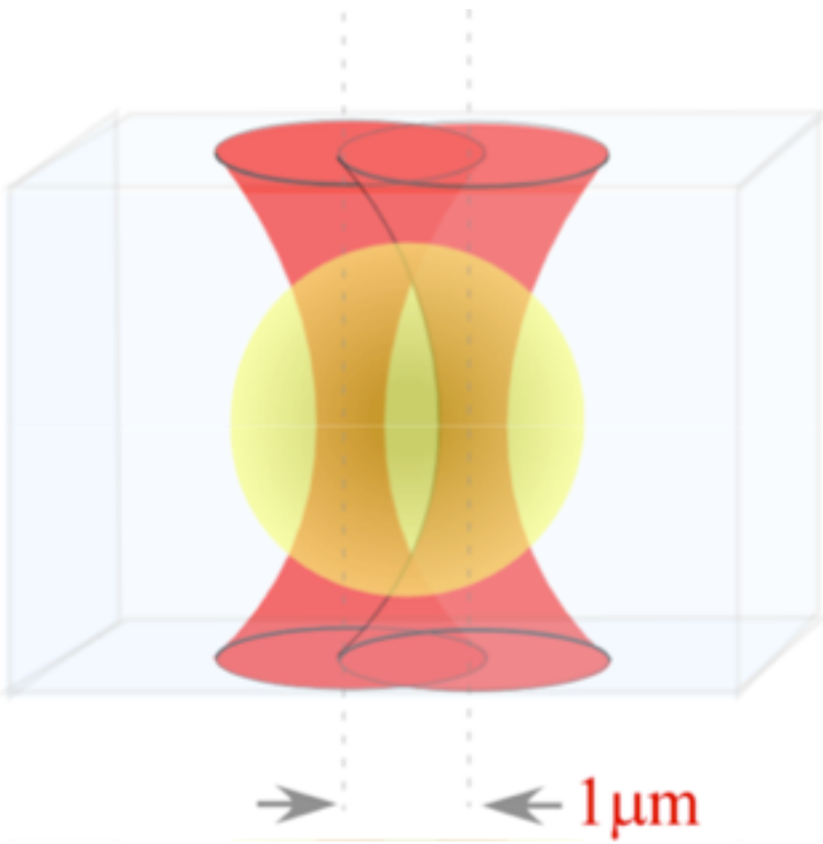

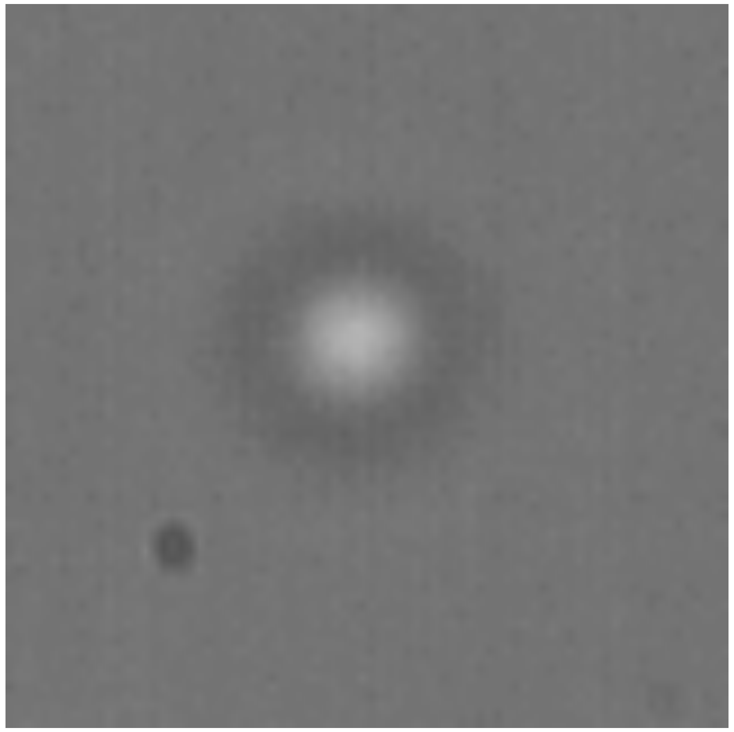

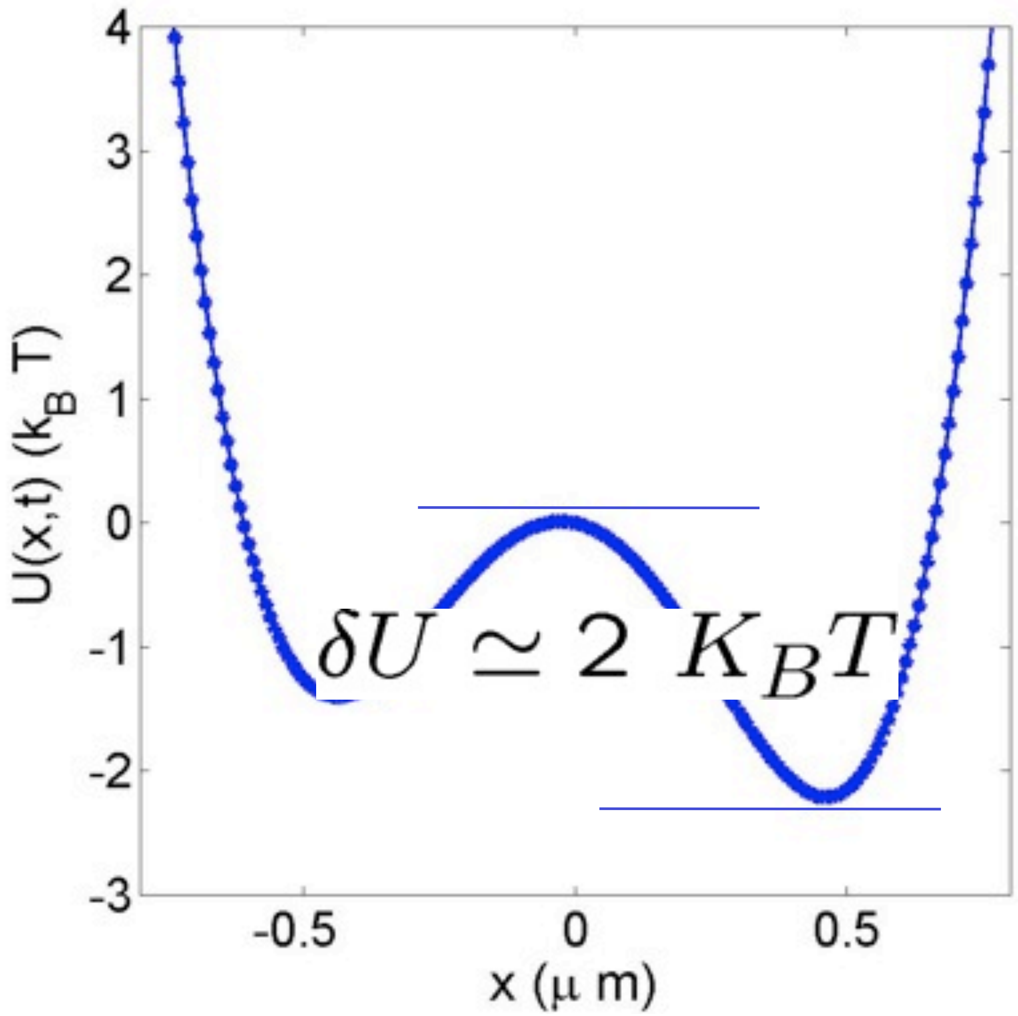

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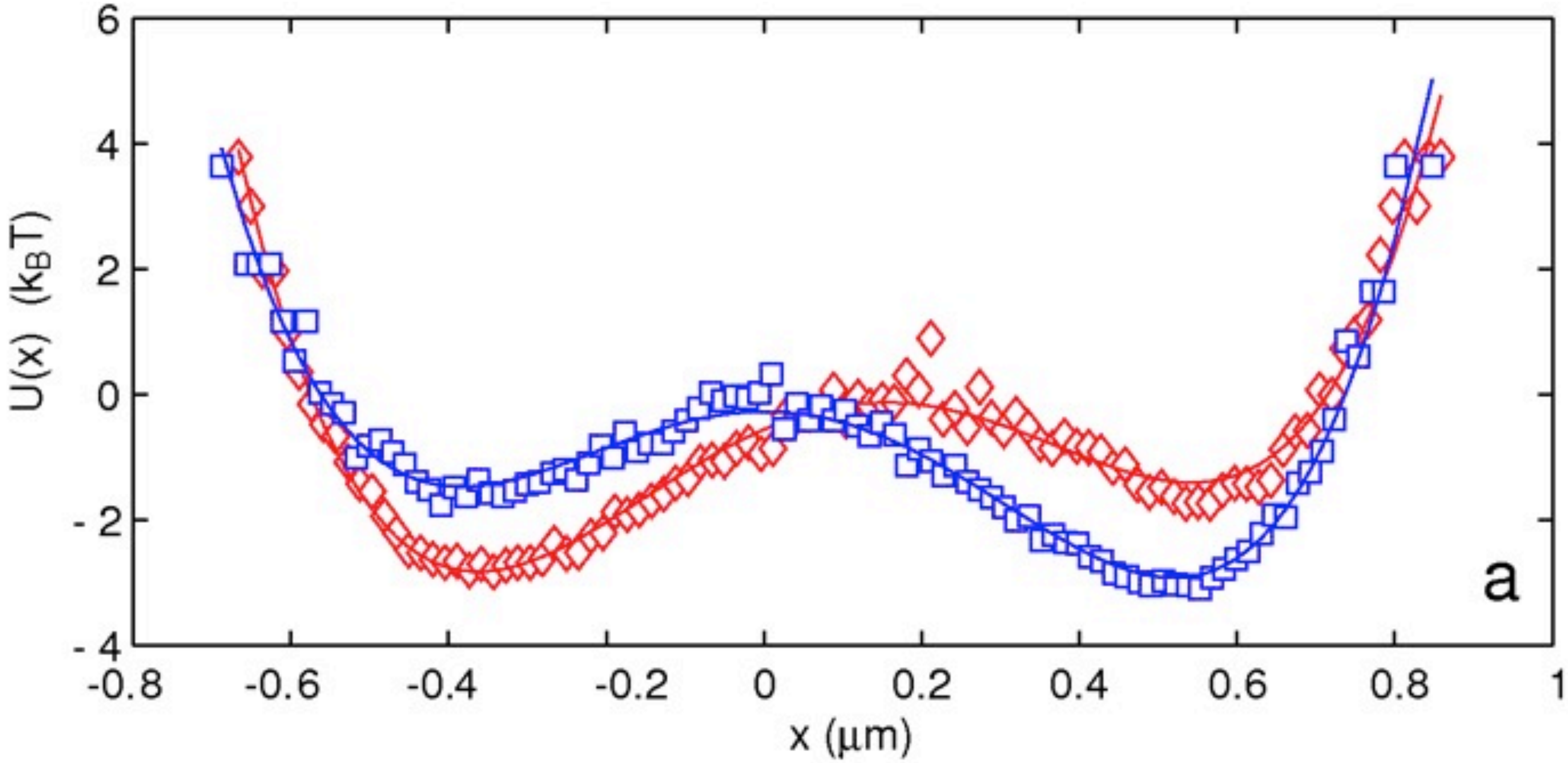
The non linear potential



Kramer rate

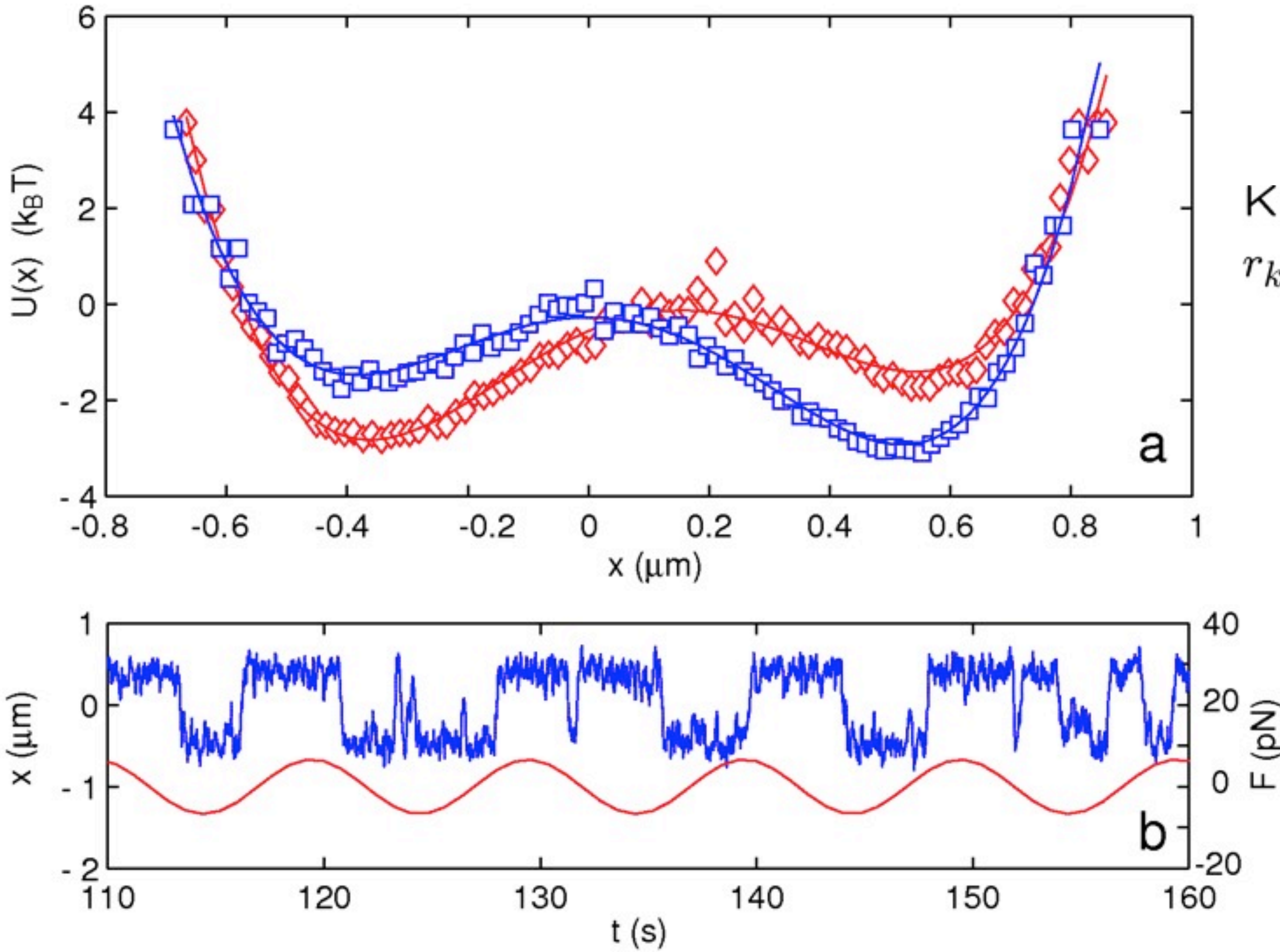
$$r_k = \tau_o^{-1} \exp(-\frac{\delta U}{k_B T})$$

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

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

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

The non linear potential



Kramer 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

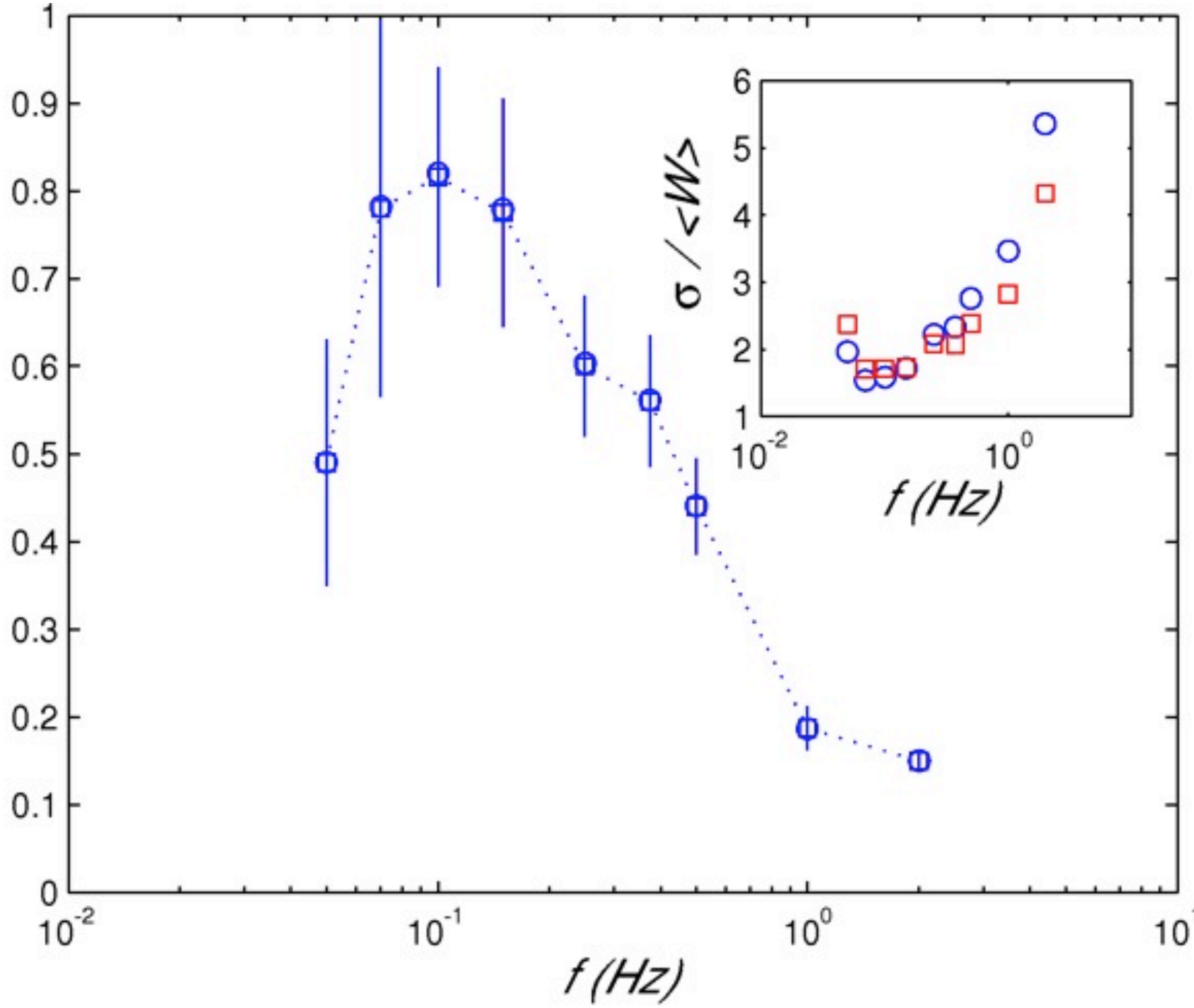
Stochastic Resonance

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

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

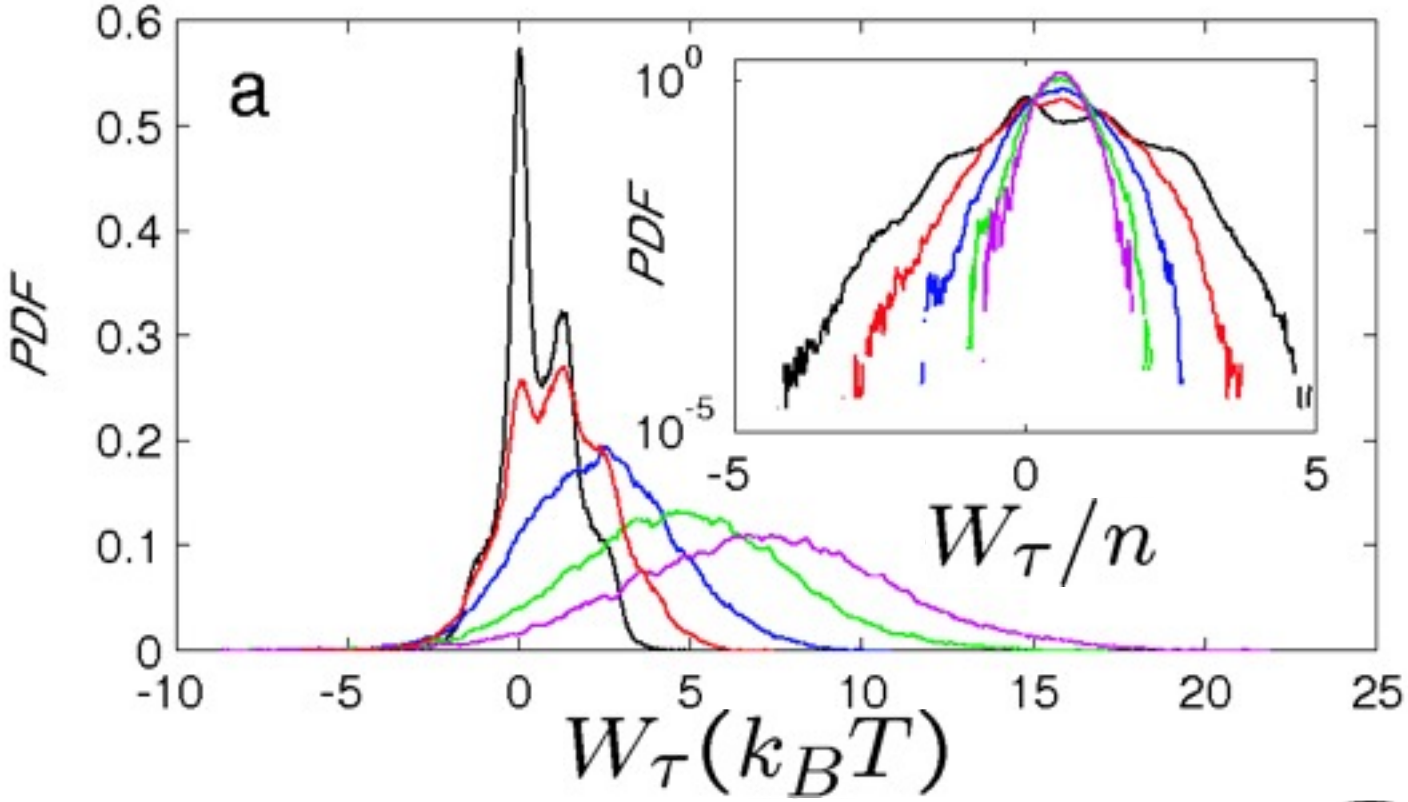
$< W_\tau >$

$n = 1$



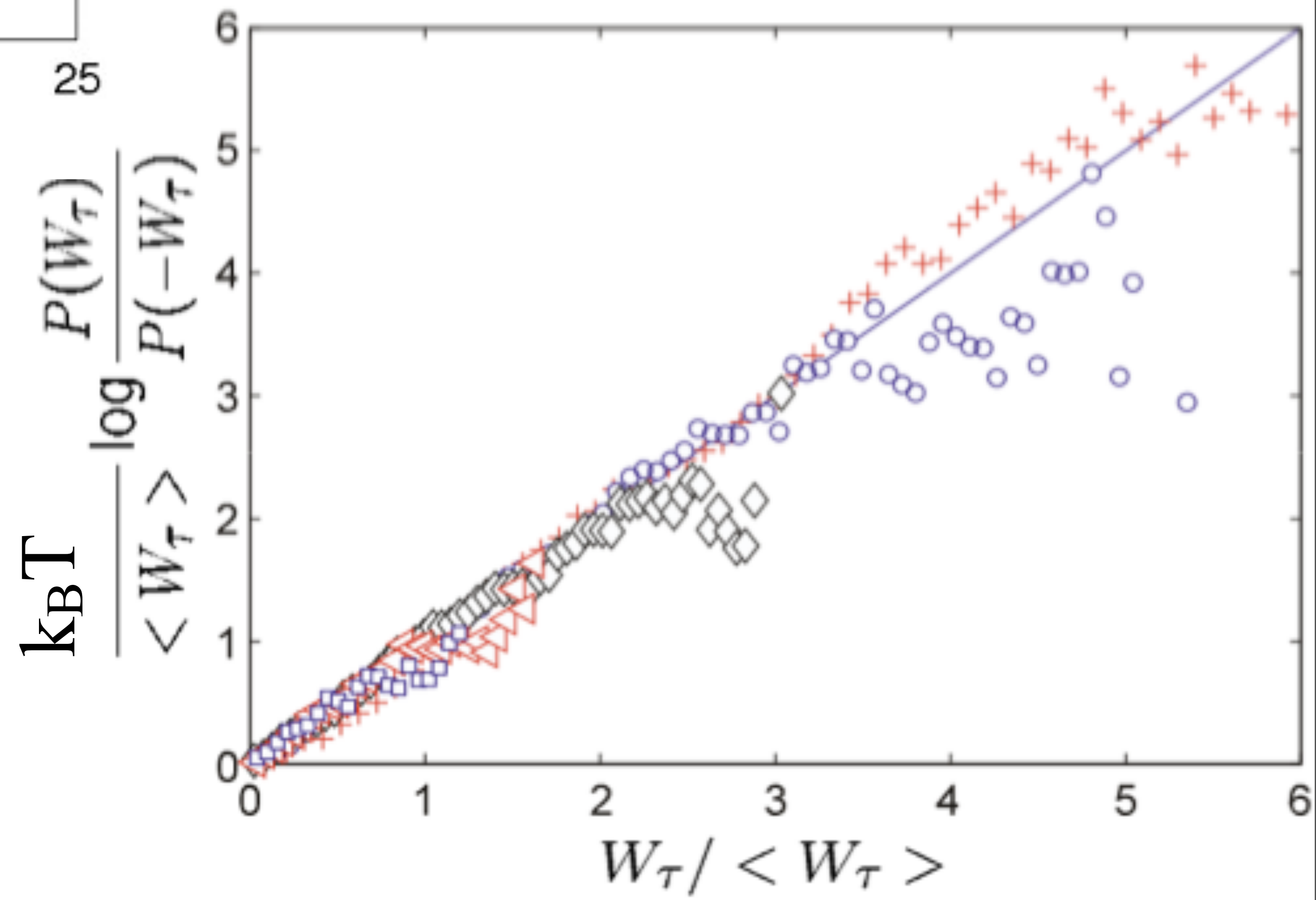
Fluctuation Theorem for W

f=0.25Hz and τ= n / f



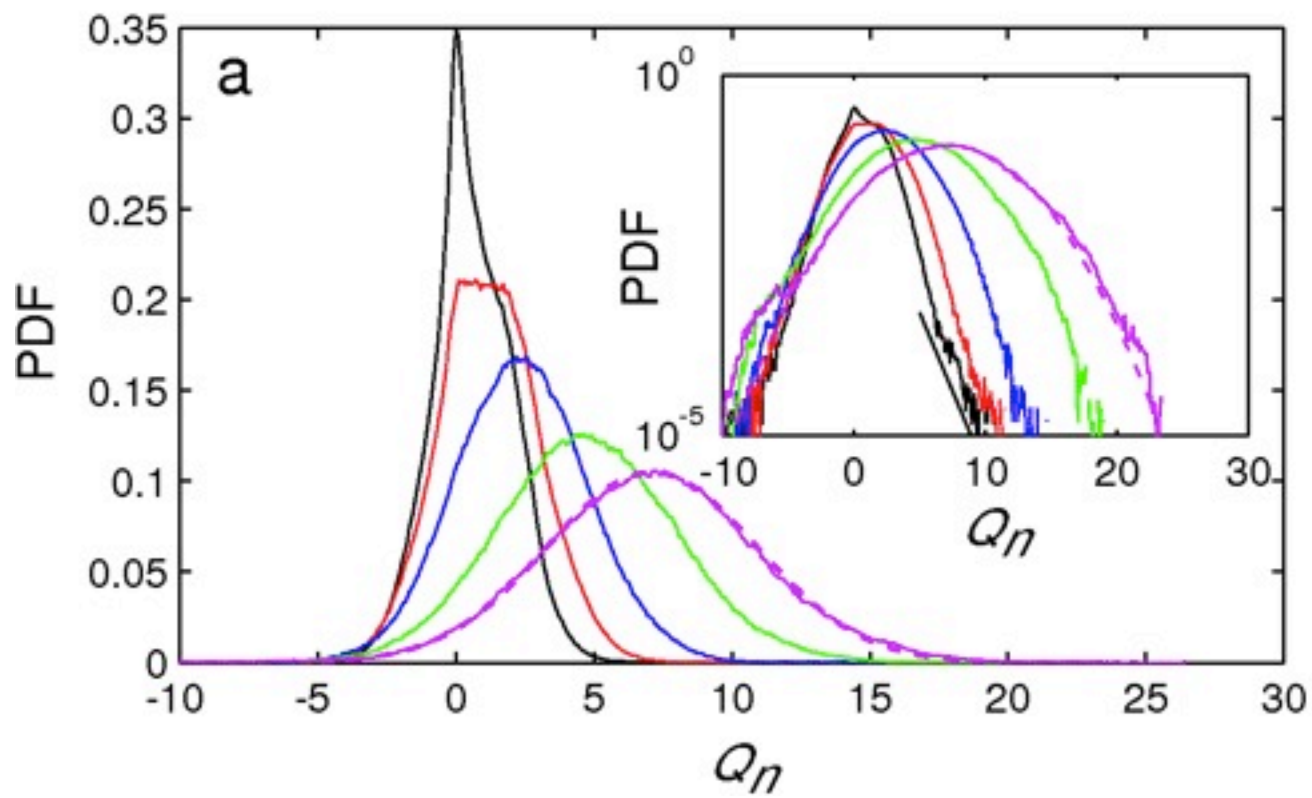
$n = 1, 4, 8$ and 12

$n = 1$ (+), 2 (○), 4 (◇), 8 (△), 12 (□)



Fluctuation Theorem for Q

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



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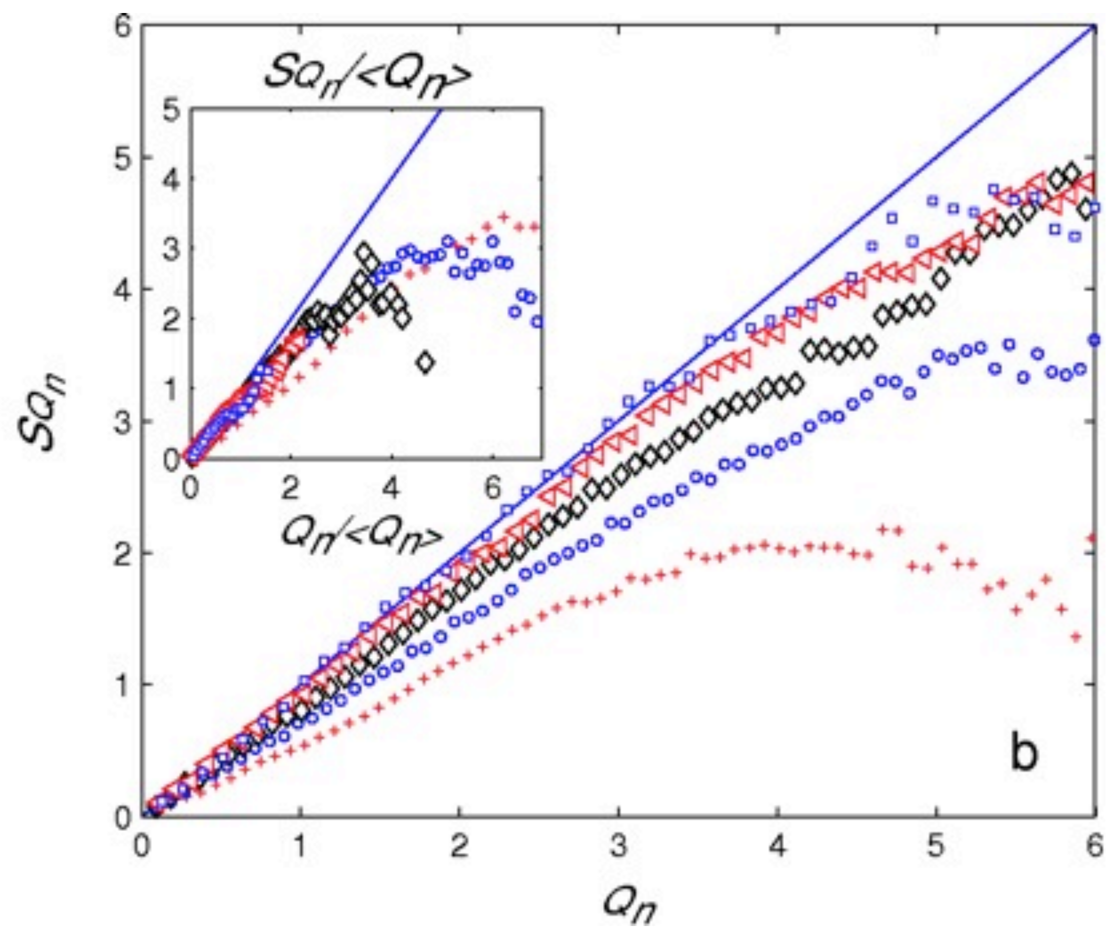


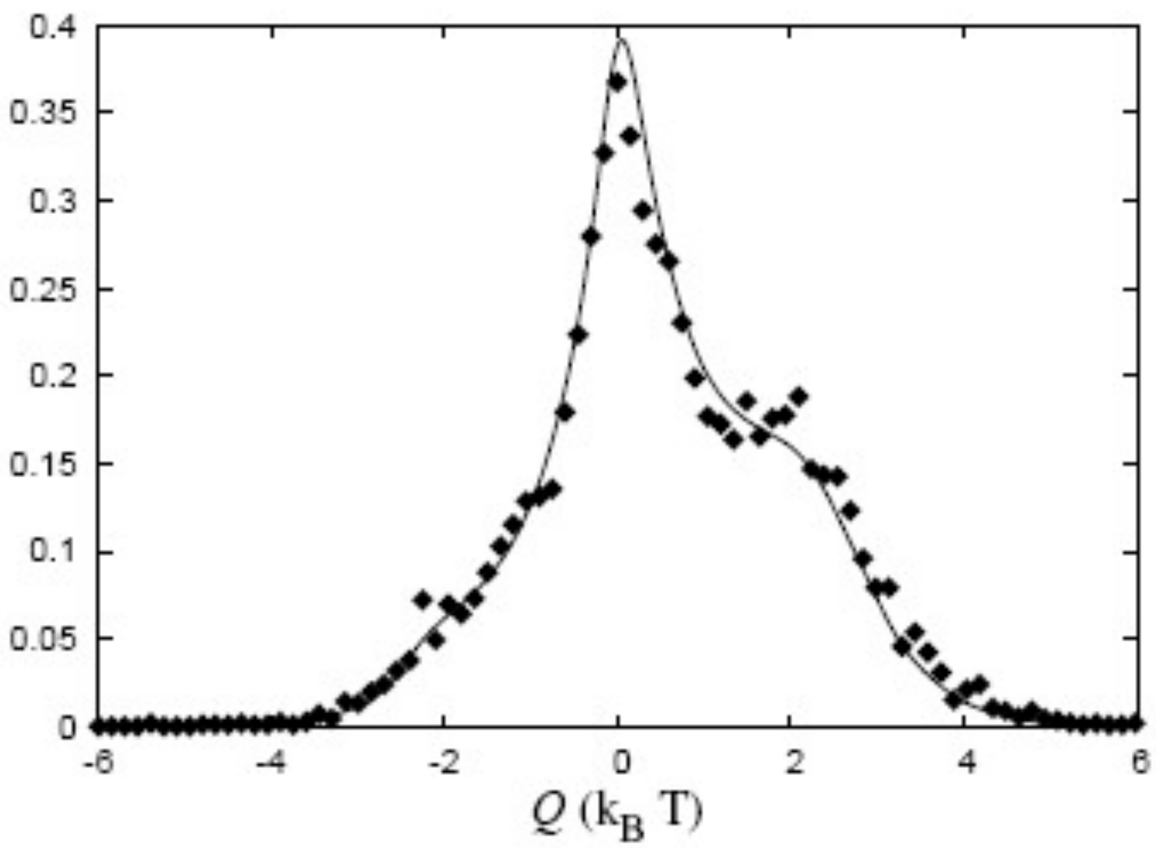
$n = 1$ (+), 2 ($\circ$), 4 ($\diamond$), 8 ($\triangle$), 12 ($\square$)

Theoretical comparison

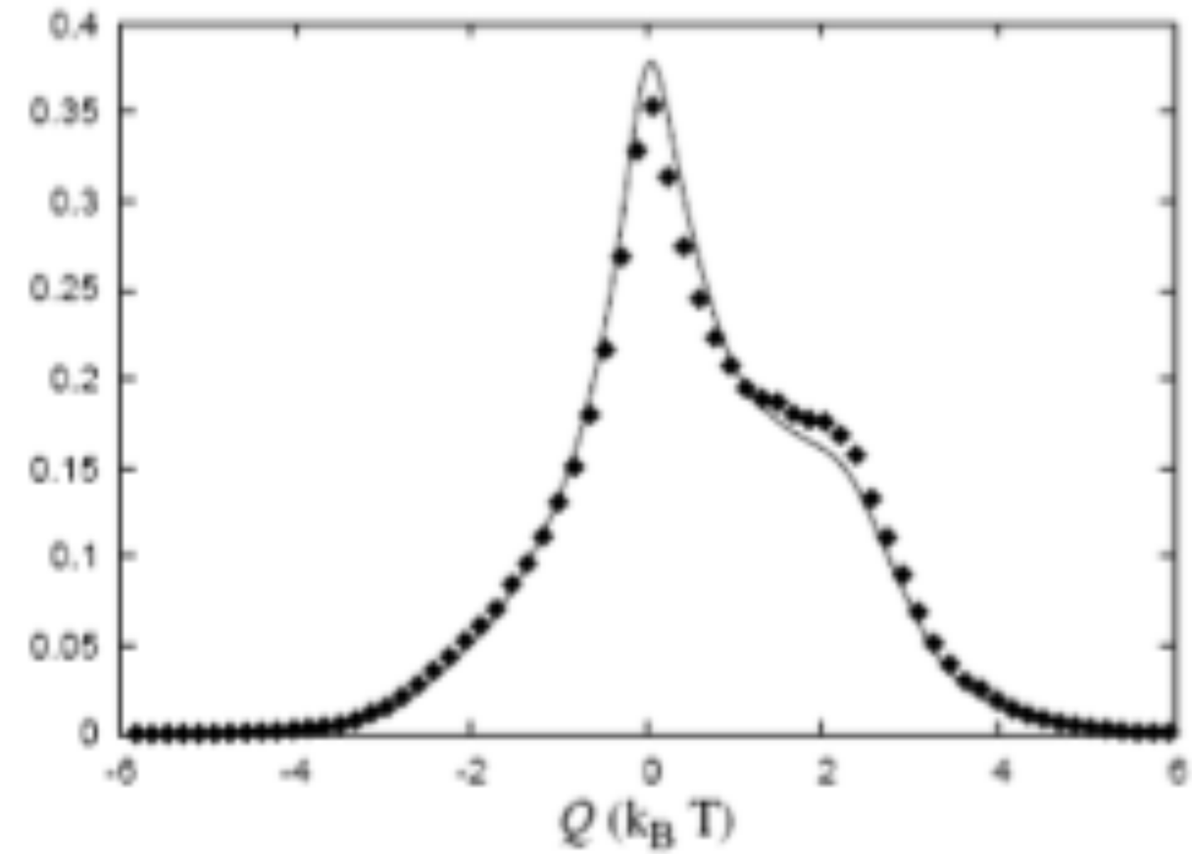
A. Imparato, P. Jop, A. Petrosyan and S. Ciliberto, J. Stat. Mech. (2008) P10017

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

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**.

- We have applied also **SSFT** to the strongly non-linear case of the **stochastic resonance**