Plan du cours

1. *Rappel des notions de la mécanique statistique d'équilibre - liens avec la réponse linéaire*
   - états de Gibbs
   - Théorème de Fluctuation-Dissipation, relations de Kramers-Kronig
   - applications à la calibration de micro-systèmes (oscillateur harmonique, circuit électronique, pièges optiques, microscope à force atomique)

2. *Modélisation de la dynamique hors d'équilibre*
   - systèmes déterministes : forces conservatives et non conservatives, systèmes thermostatés
   - systèmes aléatoires : processus de Markov, dynamique de Langevin
   - Thermodynamique stochastique

3. *Relations de Fluctuation transitoires*
   - renversement temporaire
   - égalités de Jarzynski et relations de Crooks
   - lien avec la 2ème Loi de la Thermodynamique
   - relations de Evans-Searles et de Hatano-Sasa
   - application à l'oscillateur harmonique, mesure sur molécule unique et piège optique hors d'équilibre

4. *Relations de Fluctuations stationnaires*
   - états stationnaires hors d'équilibres (NESS)
   - grandes déviations
   - Théorème de Gallavotti-Cohen
   - relations stationnaires pour la dynamique de Langevin
   - exemples d'applications expérimentales dans des systèmes linéaires et non linéaires
   - utilisation des relations de fluctuation pour mesurer la puissance d'un moteur moléculaire

5. *La réponse linéaire hors d'équilibre - théorie et expérience*
   - généralisations autour des NESS
   - le cas de la dynamique de relaxation

Measuring out of equilibrium fluctuations

Out of equilibrium fluctuations :

1. Chaotic dynamics

2. Stochastic systems
   a. System in contact with an out of equilibrium bath
   b. System in contact with several heat baths at different temperatures
   c. System driven by an external force

What can be measured in these systems?

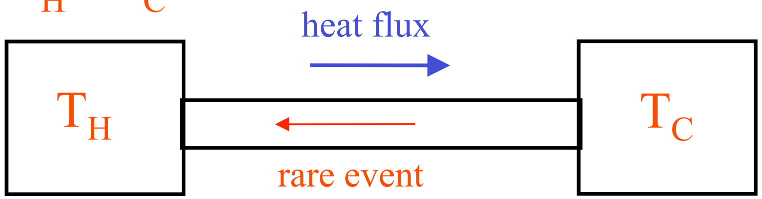
- Fluctuation Dissipation Theorem
- Fluctuation Theorem for work, heat and entropy
- Jarzinsky equality
- Time reversal symmetry and entropy production

Fluctuations in out of equilibrium systems

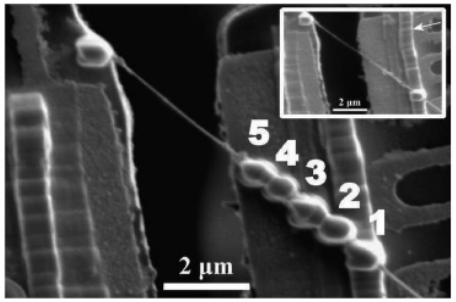
Steady current through a system in contact between two reservoirs

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

$T_H > T_C$

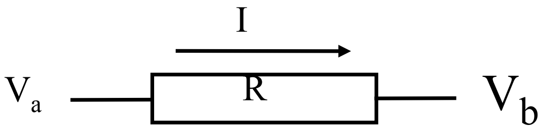


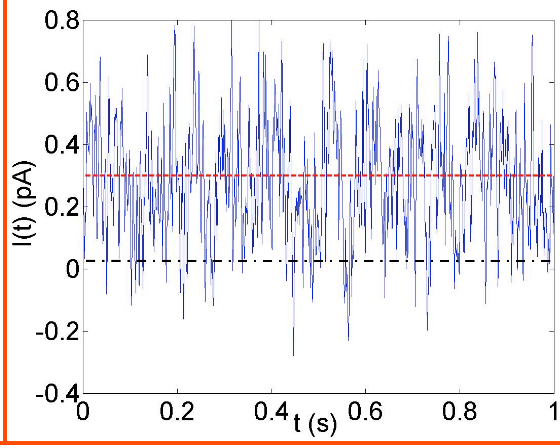
Thermal conductivity in nanotubes



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)

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

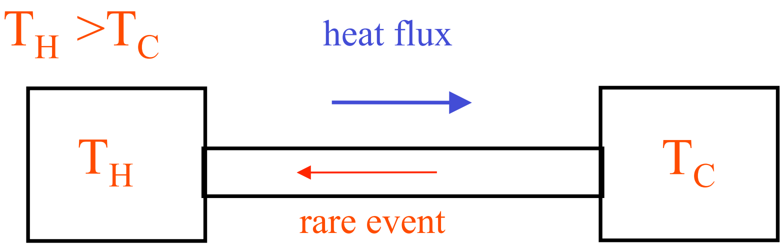
Injected power

$10^{-19} W$

Fluctuations in out of equilibrium systems

Steady current through a system in contact between two reservoirs

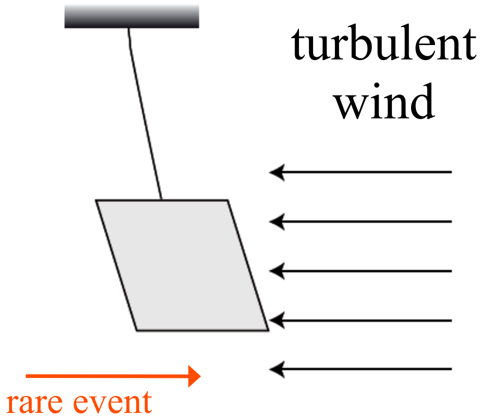
What is the probabilty that the heat flows from the cold to the hot reservoir ?



injected power $10^{-19} W$

Fluctuation Theorem ?

Fluctuations in dynamical systems



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

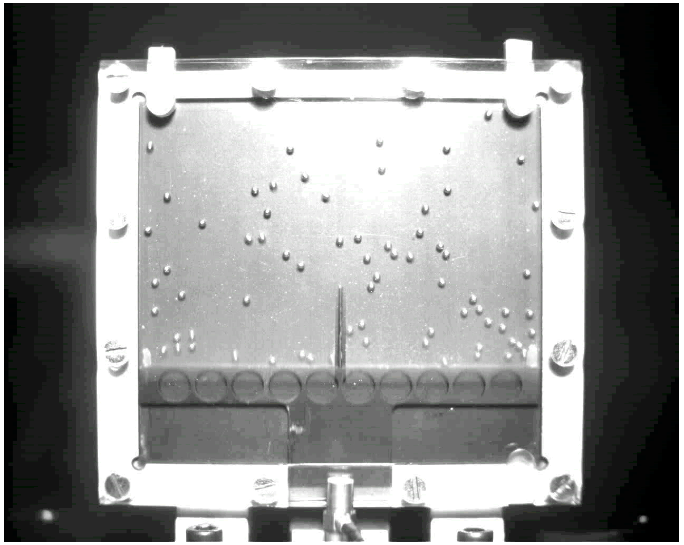
injected power $0.1 W$

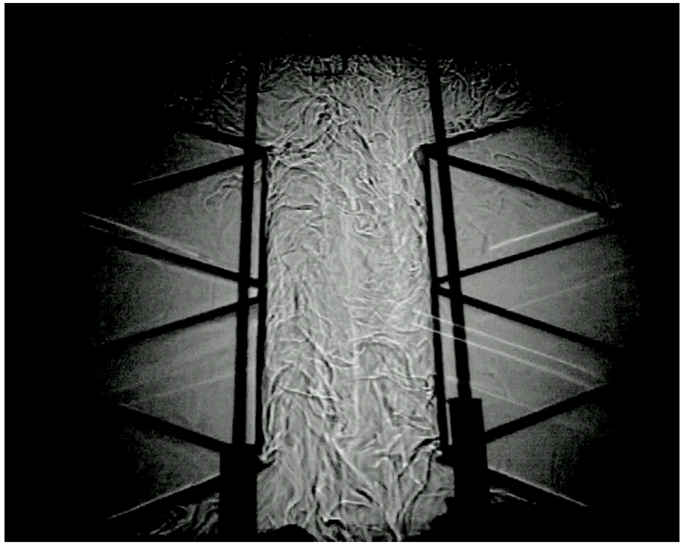
Examples of Dynamical Systems

Vibrated granular media

Thermal convetion in a fluid

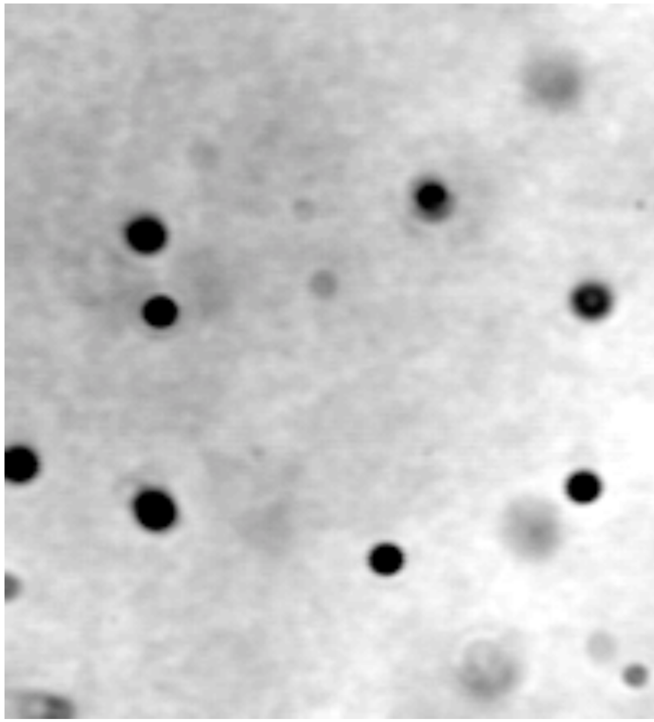
Cooled from above

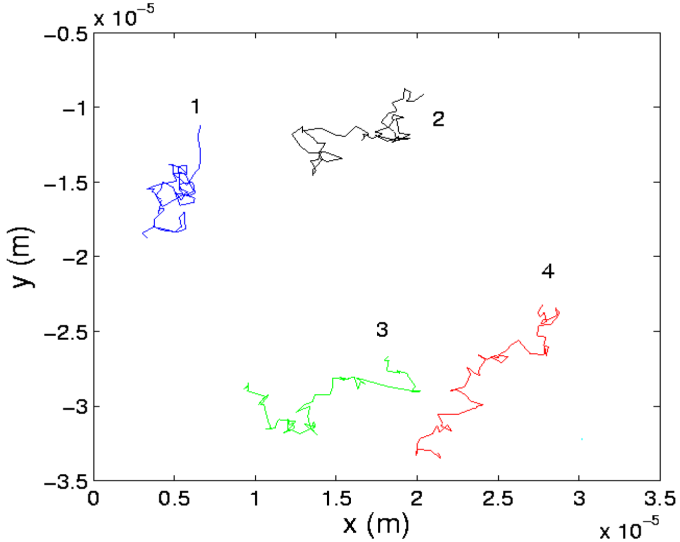


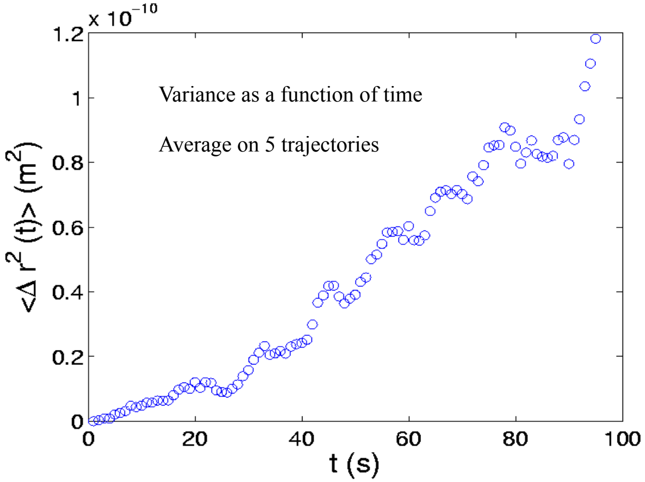


Heated from below

Brownian motion EQUILIBRIUM

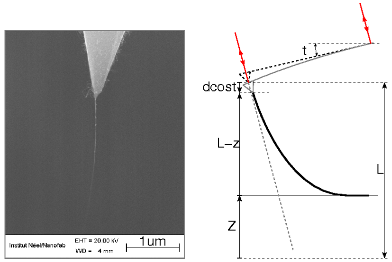




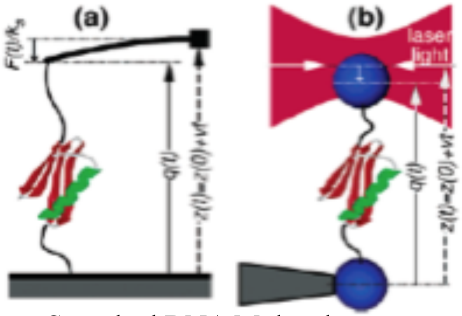


10 times faster than reality

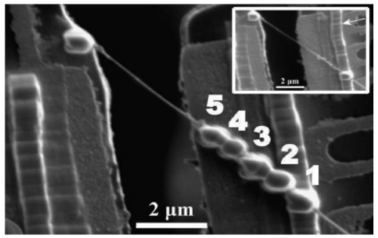
Examples of stochastic systems



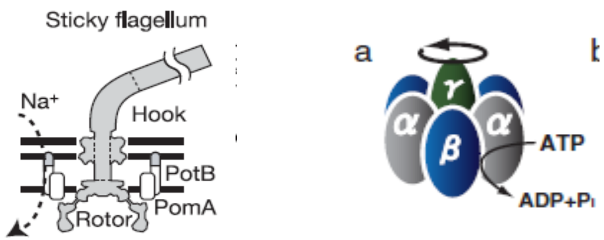
Mechanical properties of nanotubes



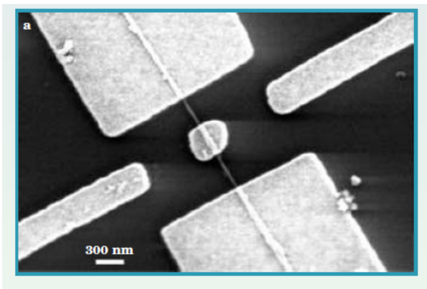
Stretched DNA Molecules



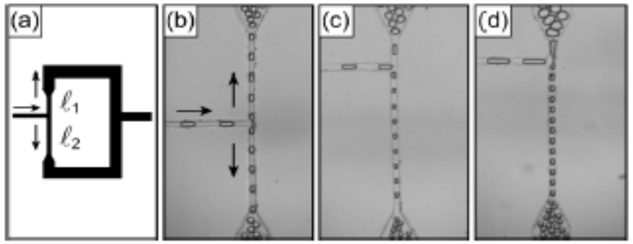
Thermal conduction in nanotubes



Molecular motors

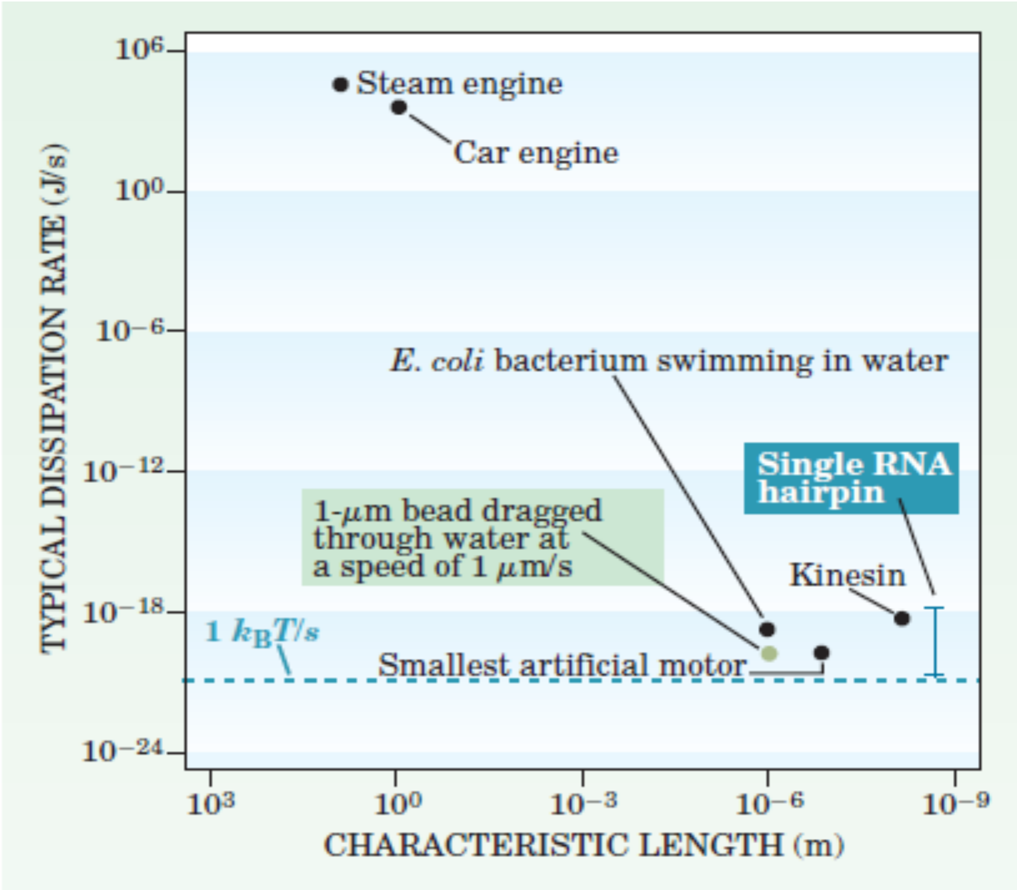


Micro Electro Mechanical Devices

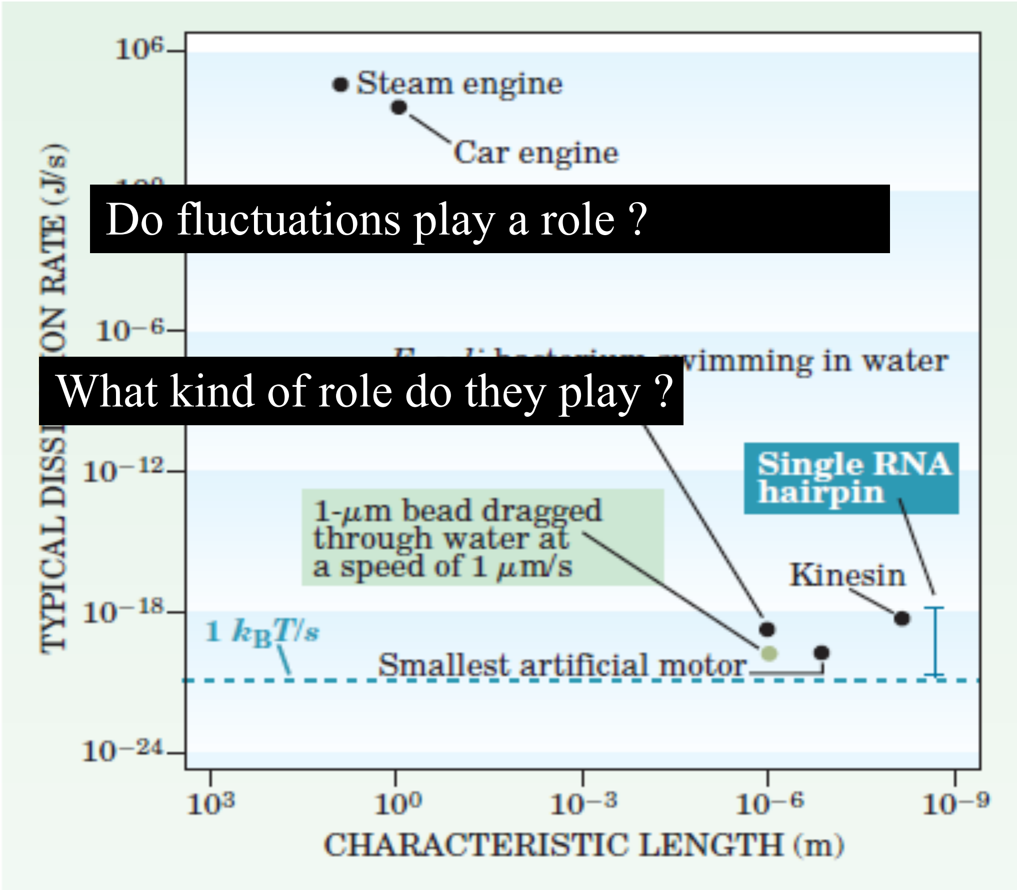


Micro hydrodynamics

Dissipation



Dissipation



Do fluctuations play a role ?

What kind of role do they play ?

The Optical Tweezers

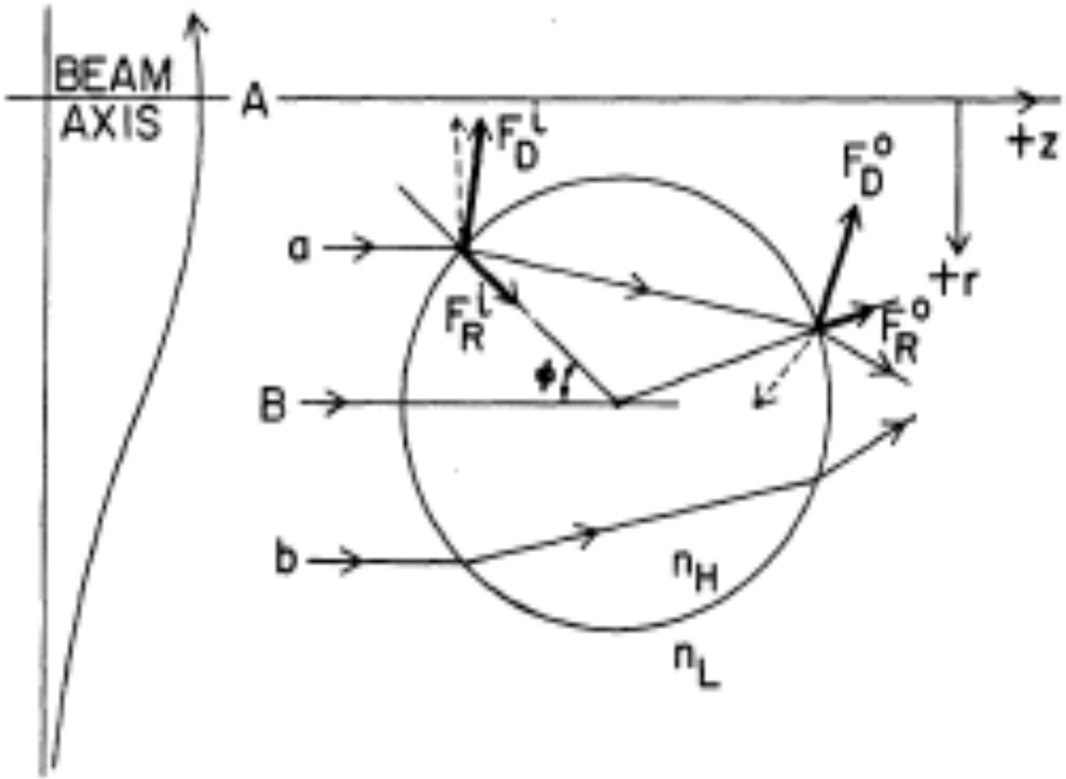
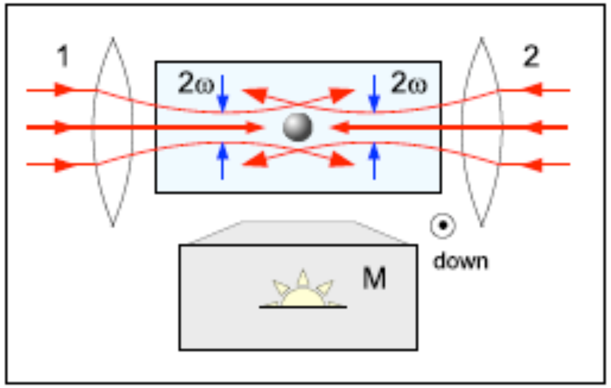
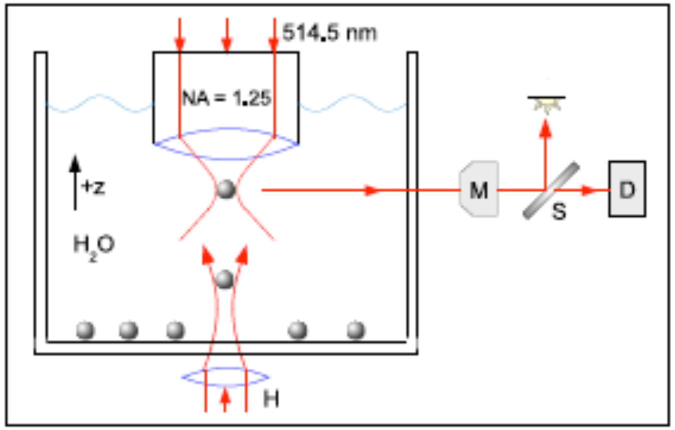


FIG. 2. A dielectric sphere situated off the axis A of a TEM_{00}-mode beam and a pair of symmetric rays a and b. The forces due to a are shown for $n_H > n_L$. The sphere moves toward $+z$ and $-r$.

First trapping experiments



(a)



(b)

The Optical Tweezers

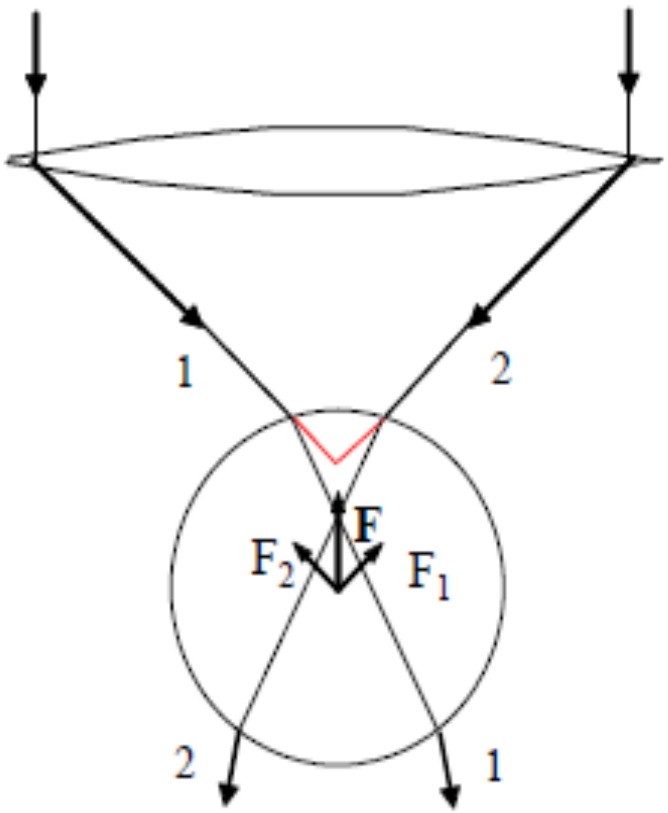


Figure 1. Schematic diagram showing the force on a dielectric sphere due to refraction of two rays of light, 1 and 2. The resultant force on the bead due to refraction is towards the focus.

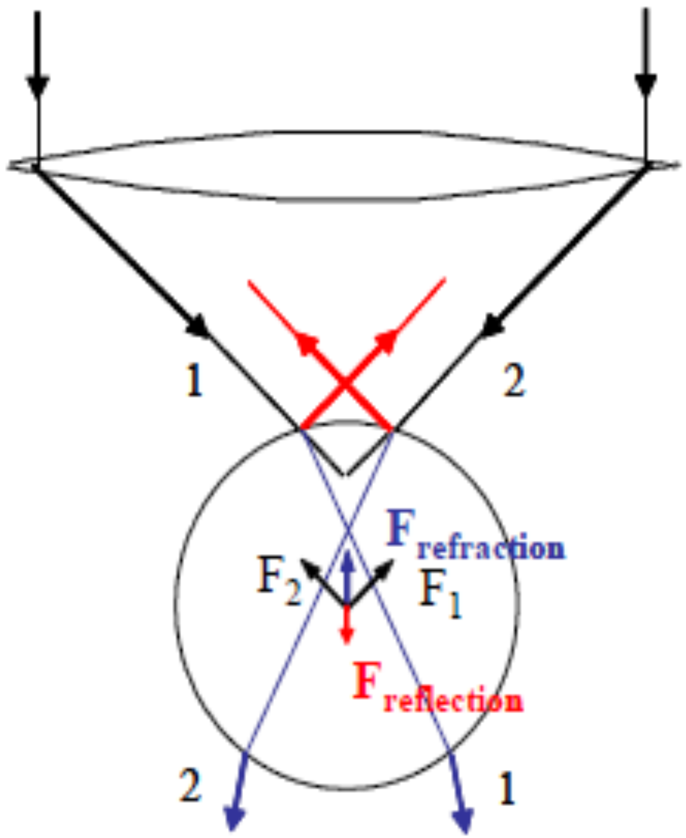


Figure 2. Schematic diagram showing the force on a dielectric sphere due to both reflection and refraction of two rays of light.

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:

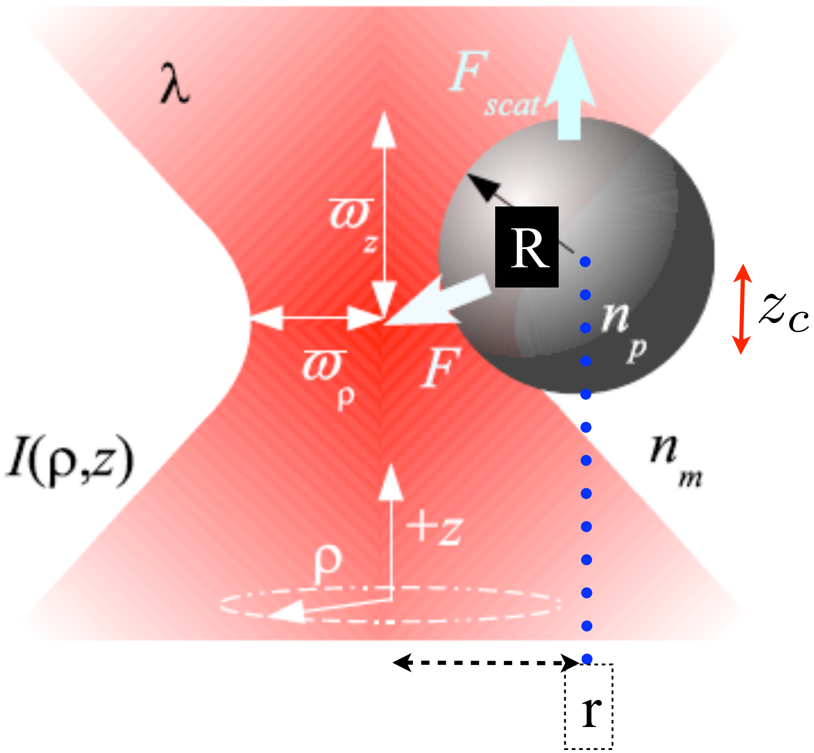
$$U = -\int_V P_i E_{oi} \; dv$$

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:

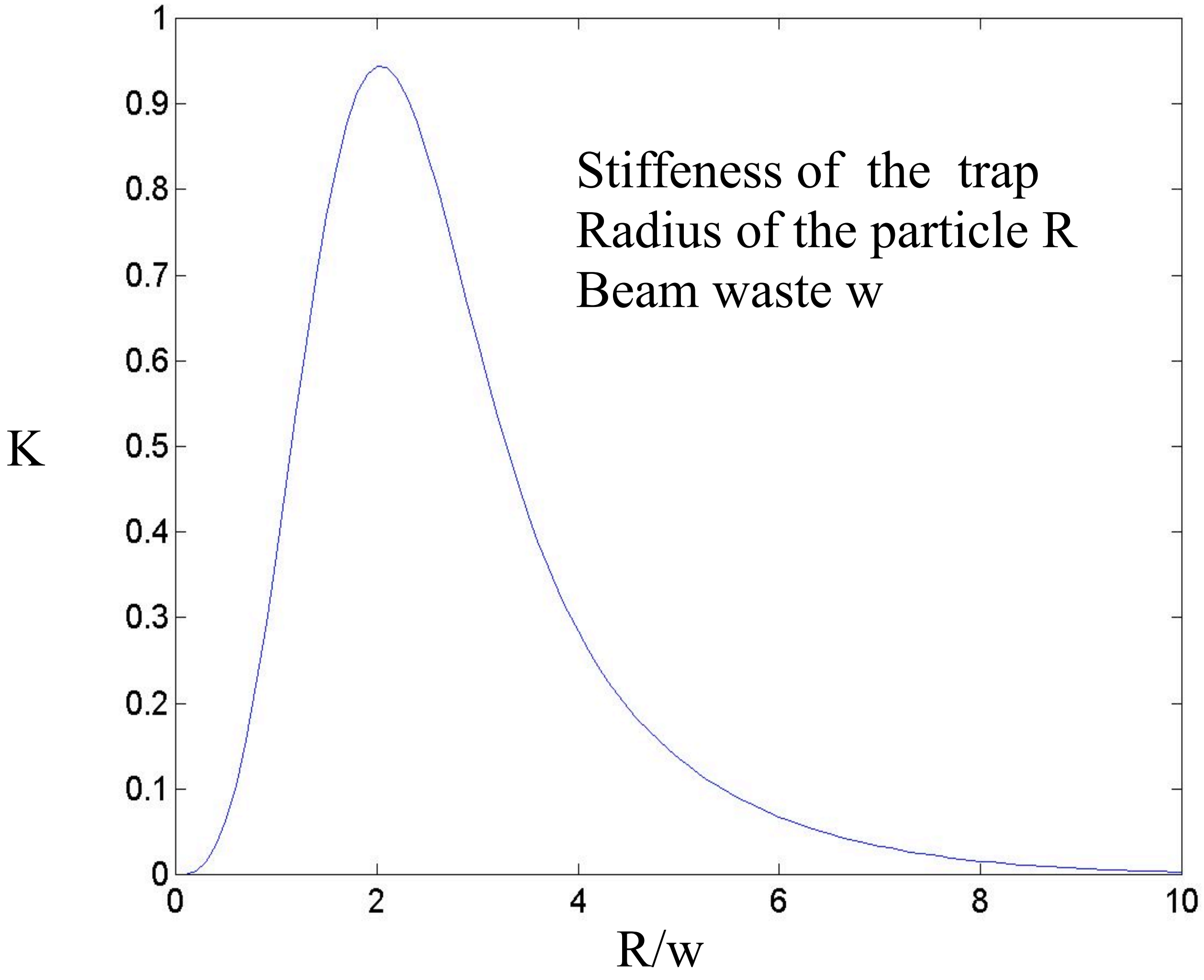
$$F(X) = \frac{2\pi\ \alpha\ I_o \bar{\omega}^2}{X^2} \exp\left(-\frac{R^2 + X^2}{2\bar{\omega}^2}\right) \left[\sinh\left(\frac{RX}{\bar{\omega}^2}\right) - \frac{RX}{\bar{\omega}^2} \cosh\left(\frac{RX}{\bar{\omega}^2}\right)\right]$$

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

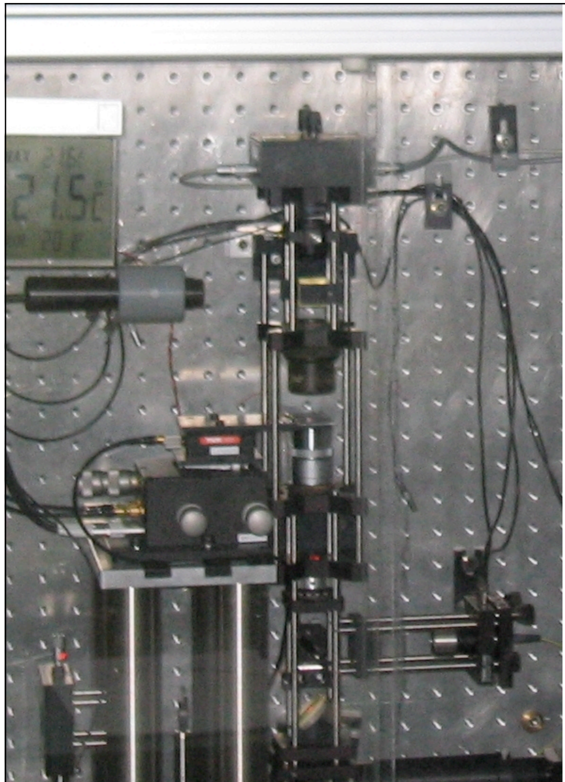
For small X $$F(X) \simeq -\frac{2\pi\alpha I_o \bar{R}^3}{3\bar{\omega}^2} \exp\left(-\frac{R^2}{2\bar{\omega}^2}\right)\ X$$

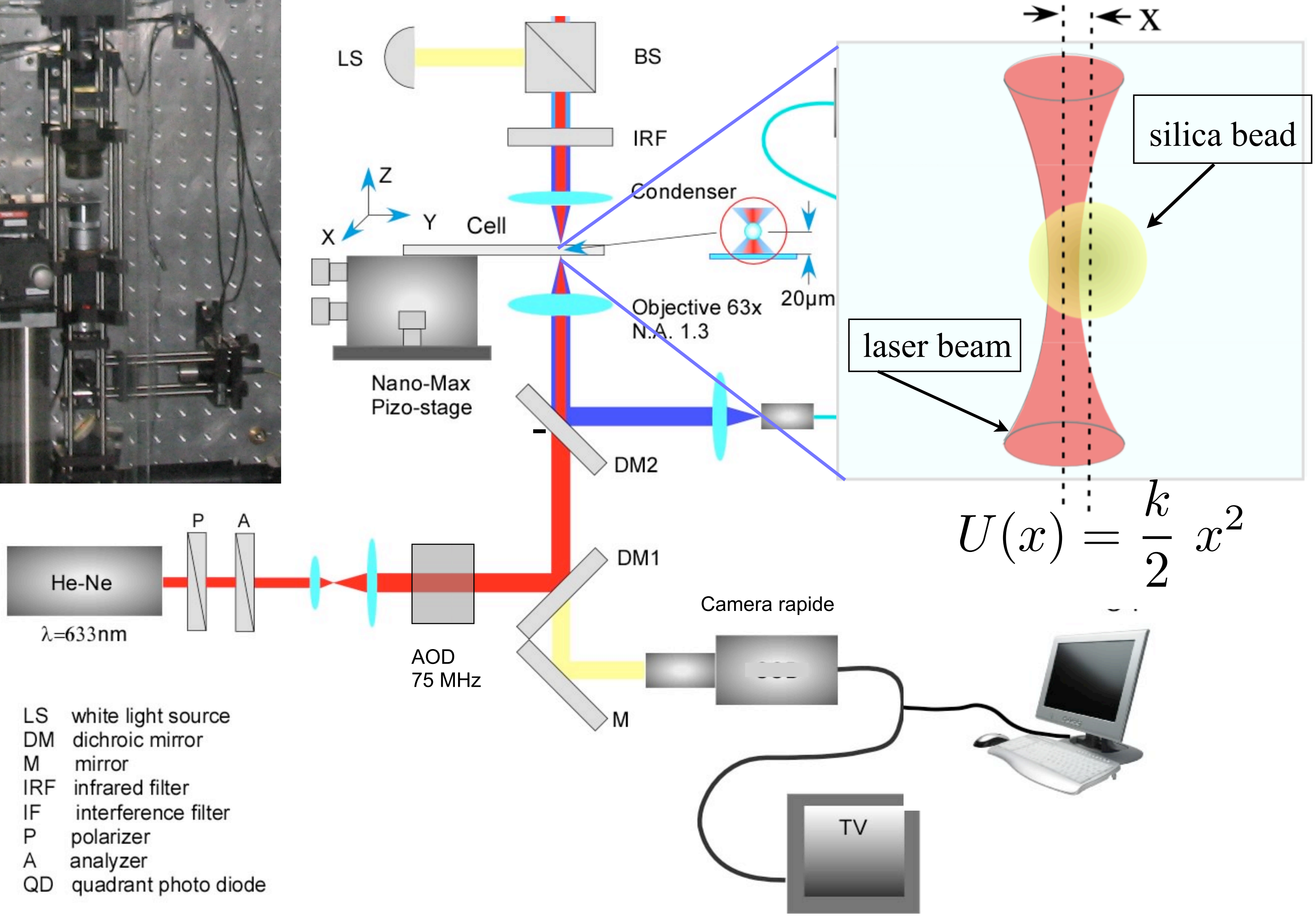
The Optical Tweezers

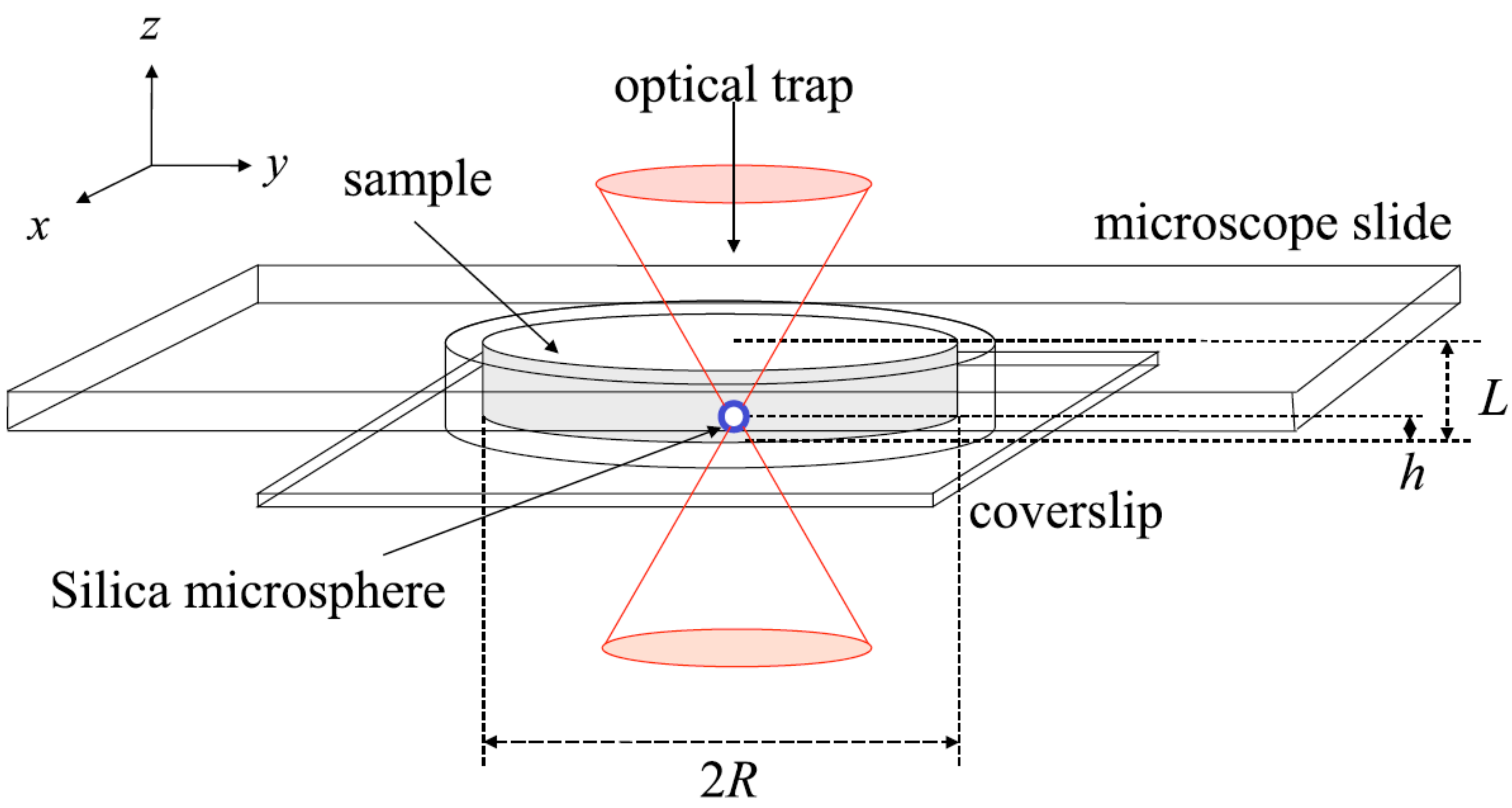
Then, the optical gradient force is simply given by the change of U in response to a change of the particles coordinates.



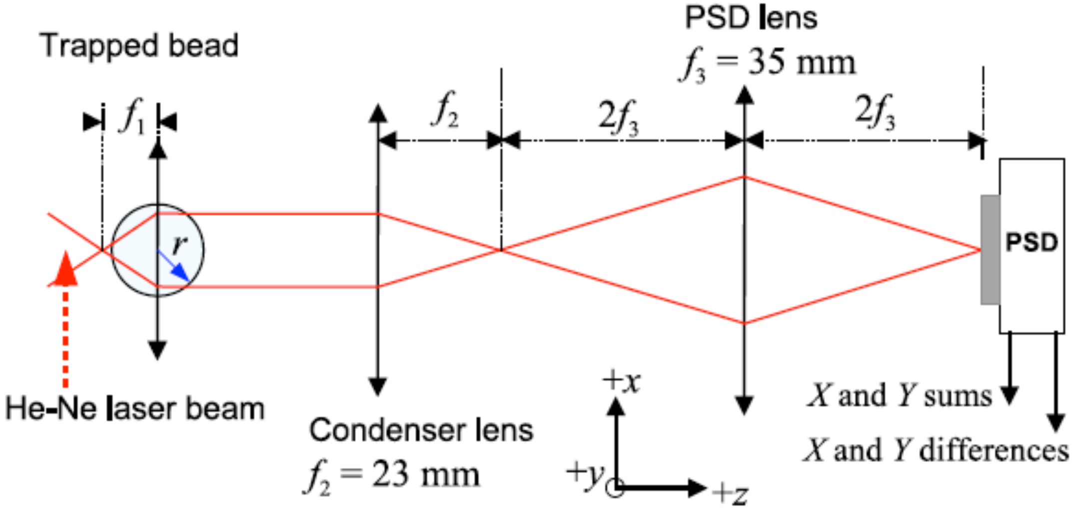
Experimental set-up Optical trap



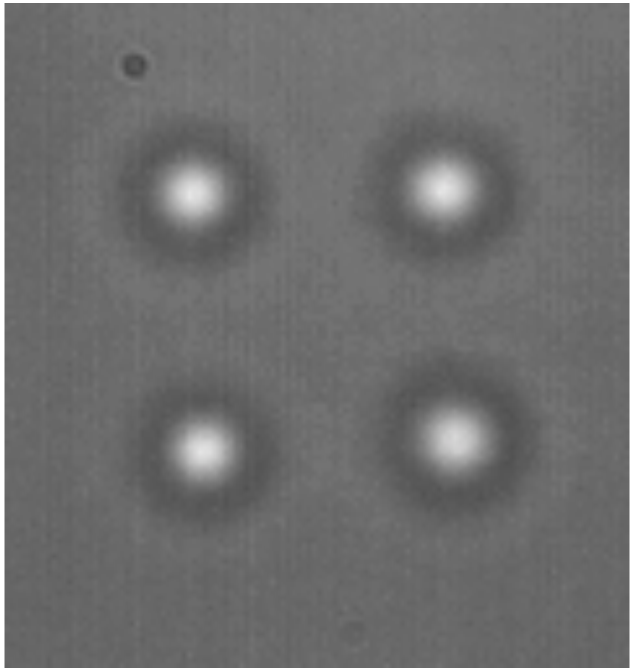


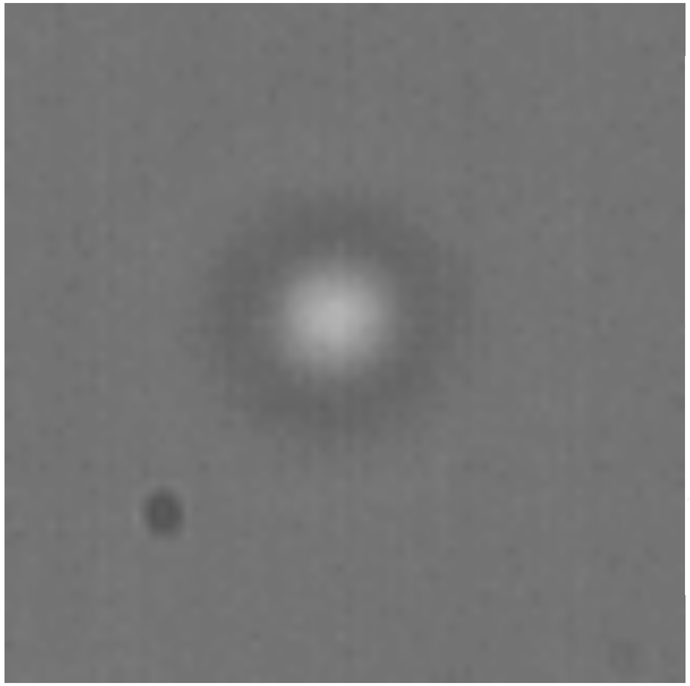

z
y
x
optical trap
sample
microscope slide
L
h
coverslip
Silica microsphere
2R

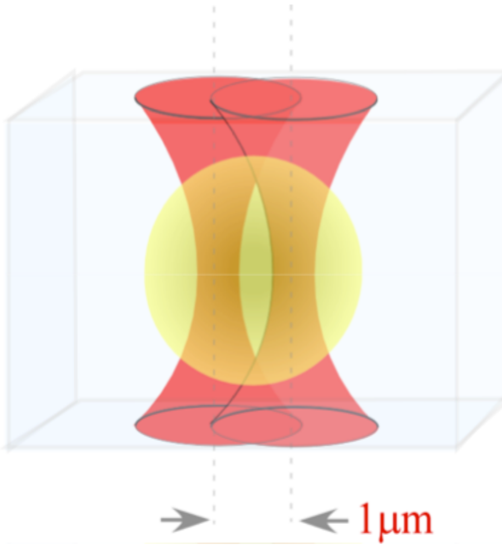
Detecting the bead position



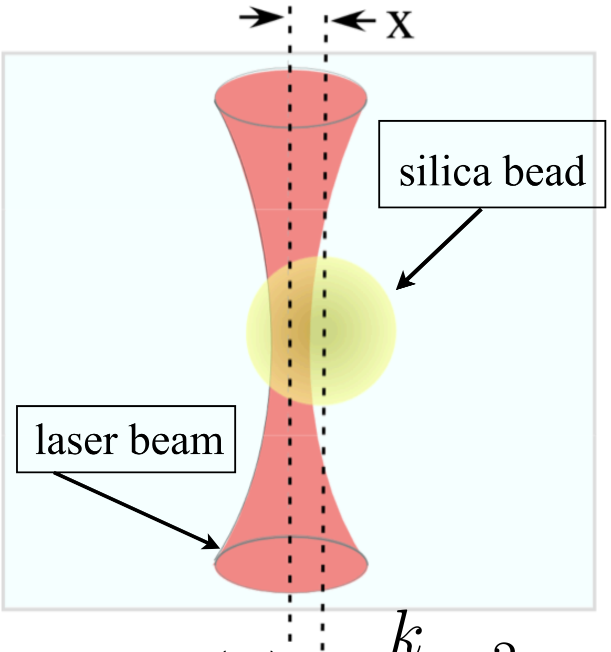
Examples of traps



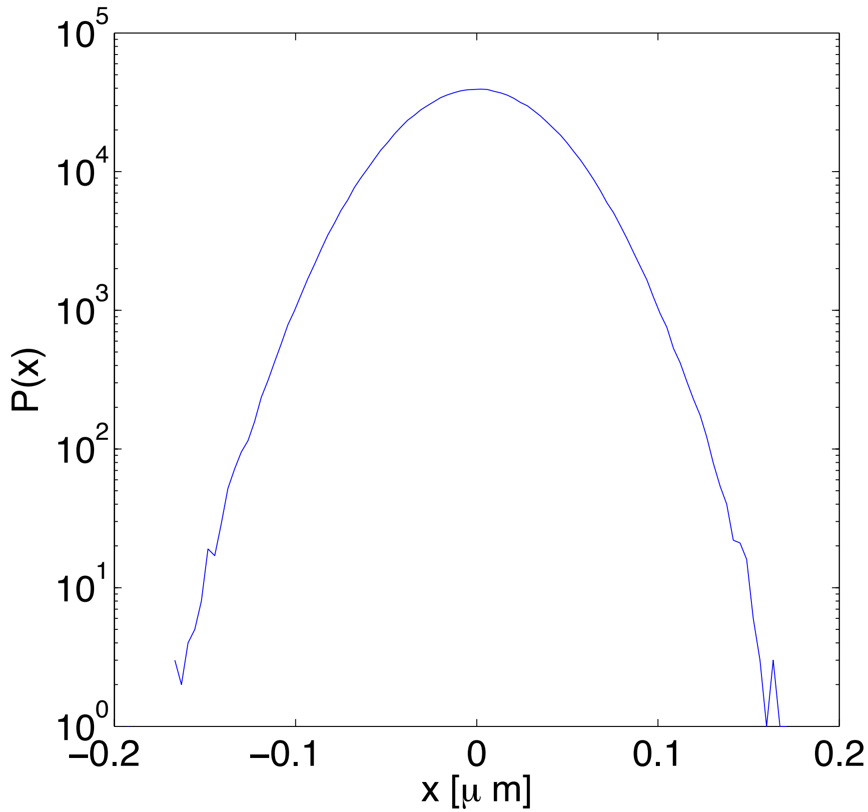




Calibration of an optical trap



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



Calibration of an optical trap

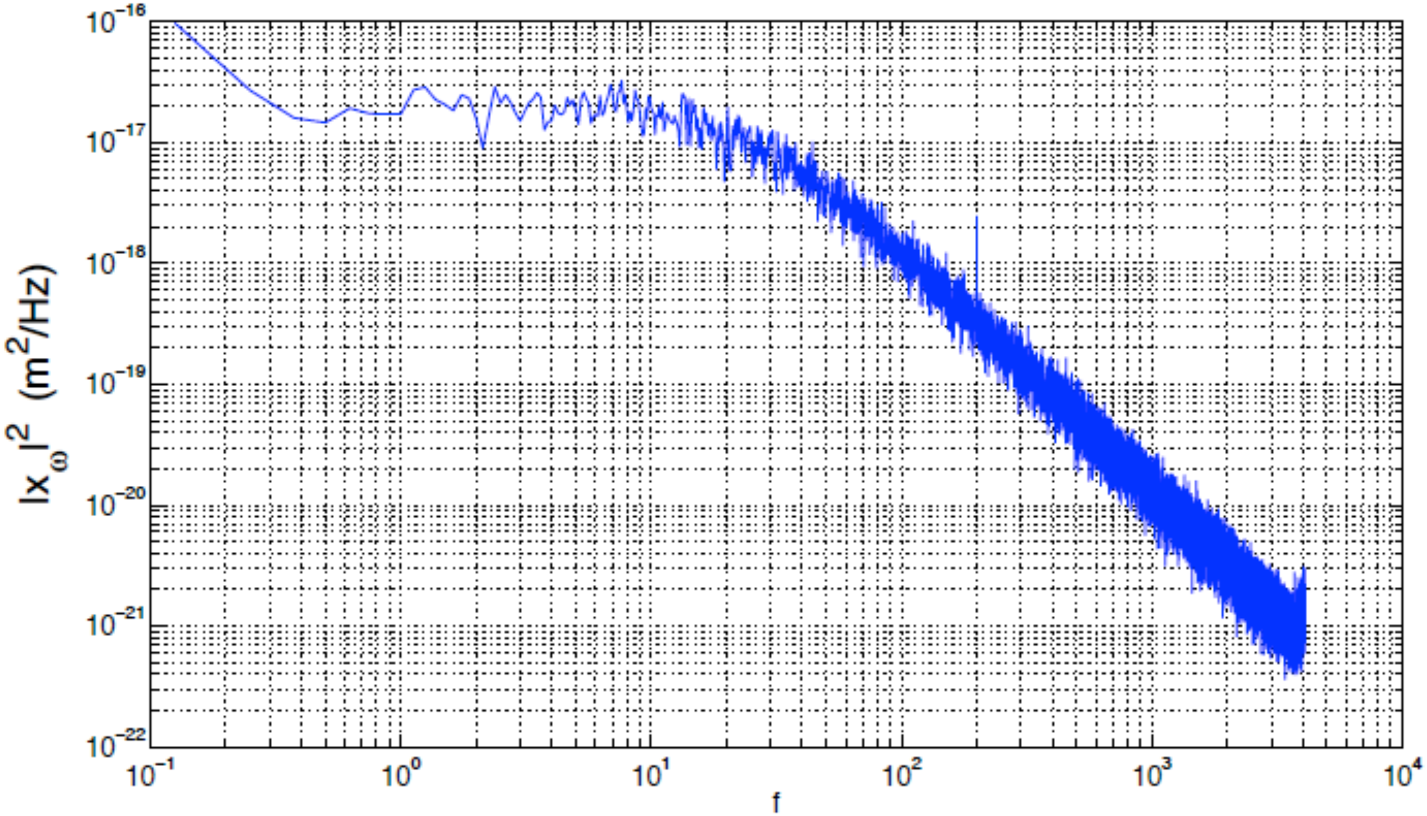
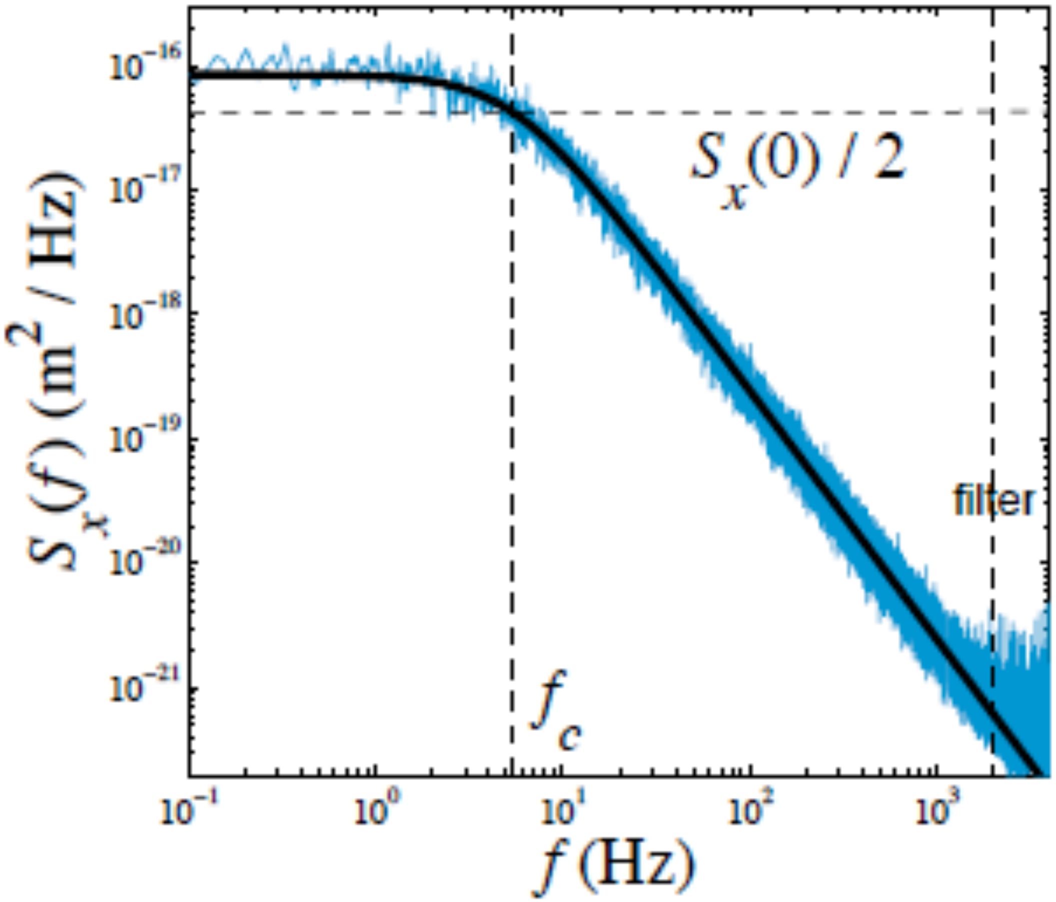


FIGURE 1 – Spectre de puissance de la position d'une particule piégée par un piège optique dans un fluide visqueux.



10^{-16}
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
$S_x(f)$ (m^2 / Hz)
$S_x(0)$ / 2
filter
f_c
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
f (Hz)

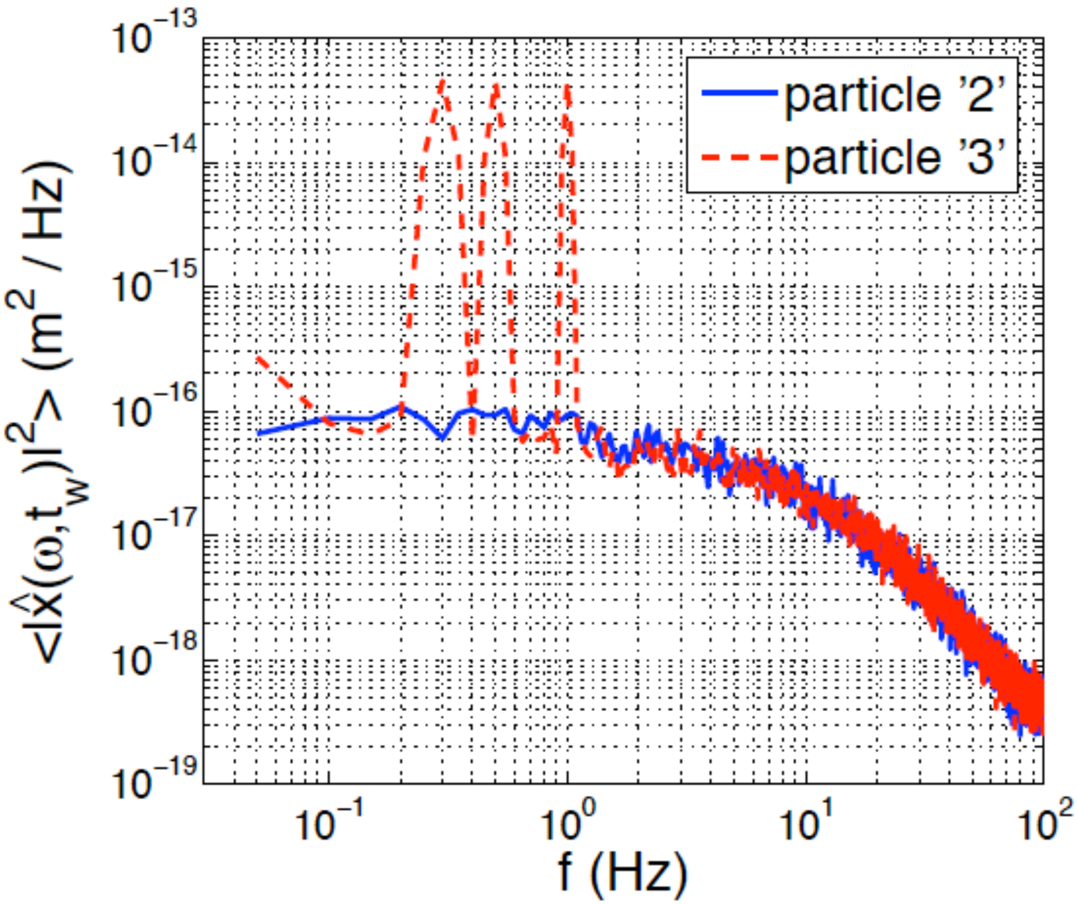
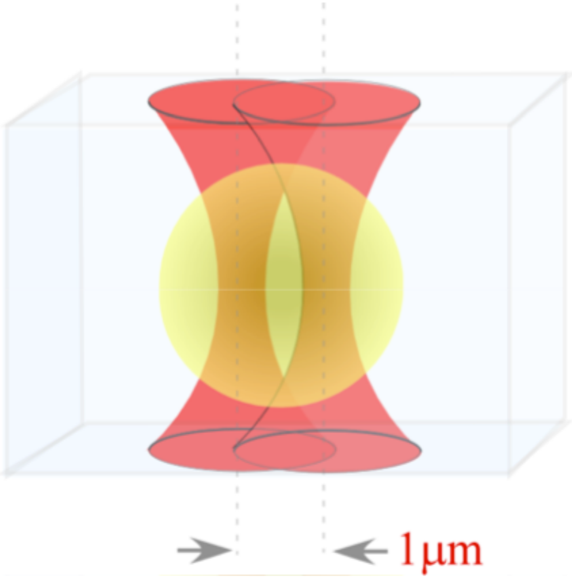
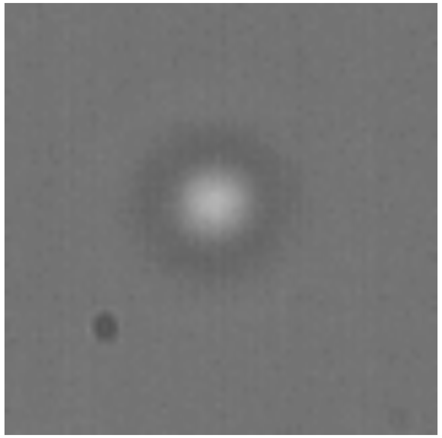
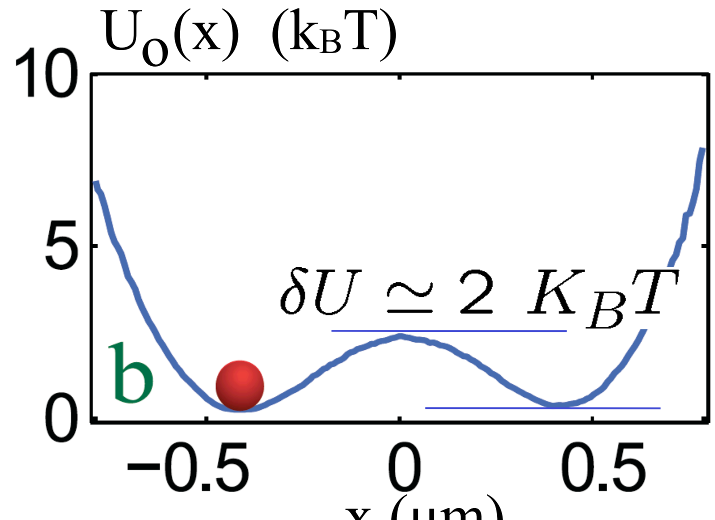


FIGURE 2 – Spectres de puissance de la position d'une particule piégée à l'équilibre et soumise à une force externe.

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

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

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

Fluctuation Dissipation Theorem

Observable : $O(t)$ 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

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

FDT from time to frequency

From Wiener-Khinchin theorem

$$< x(\tau)x(0) >= C(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} S(\omega)\exp(-i\omega\tau)\ d\omega \tag{1}$$

thus

$$\partial_\tau C(\tau) = -\frac{1}{2\pi}\int_{-\infty}^{\infty} i\omega\ S(\omega)\exp(-i\omega\tau)\ d\omega \tag{2}$$

and

$$\int_{-\infty}^{\infty} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau = -i\omega\ S(\omega) \tag{3}$$

As a consequence we may write

$$S(\omega) = -\frac{1}{i\omega}\int_{-\infty}^{\infty} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau \tag{4}$$

$$= \frac{i}{\omega}\left[\int_{-\infty}^{0} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau + \int_{0}^{\infty} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau\right] \tag{5}$$

FDT from time to frequency

Let us consider $\int_{-\infty}^{0} \partial_\tau C(\tau)\exp(-i\omega\tau)\ d\tau$ and change $\tau \to -\tau'$

$$\begin{aligned}
\int_{-\infty}^{0} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau &= \int_{\infty}^{0} \partial_{\tau'} C(-\tau')\exp(-i\omega\tau')\ d\tau' && (6)\\
&= -\int_{0}^{\infty} \partial_{\tau'} C(-\tau')\exp(-i\omega\tau')\ d\tau' && (7)\\
&= -\int_{0}^{\infty} \partial_{\tau'} C(\tau')\exp(-i\omega\tau')\ d\tau' && (8)\\
&= -\left[\int_{0}^{\infty} \partial_{\tau'} C(\tau')\exp(i\omega\tau')\ d\tau'\right]^* && (9)
\end{aligned}$$

where we used $C(-\tau') = C(\tau')$ and $[\cdot]^*$ stands for complex conjugate
Thus replacing this result in eq.5

$$\begin{aligned}
S(\omega) &= \frac{i}{\omega}\left[-\left(\int_{0}^{\infty} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau\right)^* + \int_{0}^{\infty} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau\right] && (10)\\
&= \frac{-2}{\omega}\ Imag\left[\int_{0}^{\infty} \partial_\tau C(\tau)\exp(i\omega\tau)\ d\tau\right] && (11)
\end{aligned}$$

FDT from time to frequency

Now we know that FDT imposes that for $\tau > 0$

$$\partial_\tau C(\tau) = -K_B \, T R(\tau)$$

thus

$$S(\omega) = \frac{2K_B T}{\omega} \; Imag\left[\int_0^\infty R(\tau)\exp(i\omega\tau)\; d\tau\right] \qquad (12)$$

$$= \frac{2K_B T}{\omega} \; Imag\left[R(\omega)\right] \qquad (13)$$

Furthermore as $S(\omega) = S(-\omega)$ then

$$< x^2 > = \frac{1}{2\pi}\int_{-\infty}^{\infty} S(\omega) d\omega \qquad (14)$$

$$= \frac{1}{2\pi}\int_0^\infty 2S(\omega) d\omega \qquad (15)$$

$$= \int_0^\infty S_x(f) df \qquad (16)$$

where we have defined $S_x(f) = 2S(\omega)$ and $2\pi f = \omega$. Finally we get

$$S_x(f) = \frac{4K_B T}{\omega} \; Imag\left[R(\omega)\right] \qquad (17)$$

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