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thermodynamics of colloidal particles

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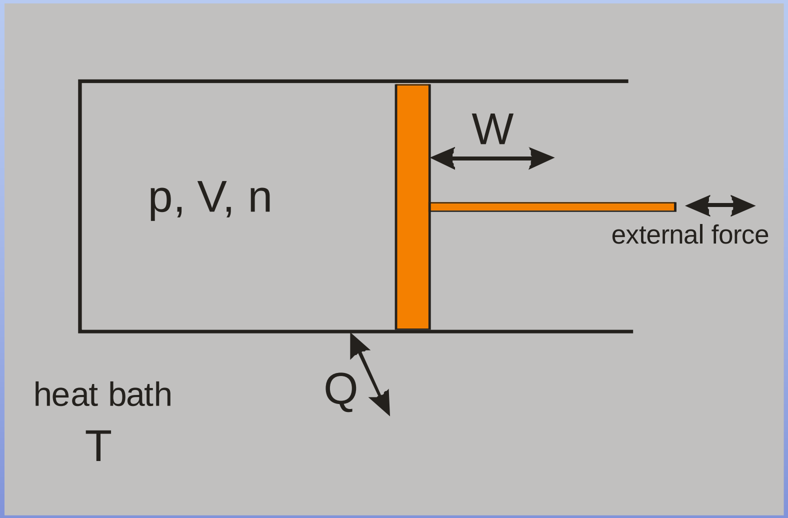
- mesoscopic thermodynamics
- TIRM experiment
- energy conservation
- work distribution / fluctuation theorems

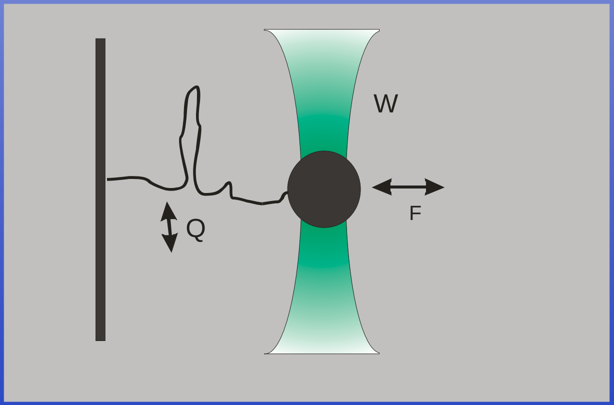
thermodynamics

macroscopic:

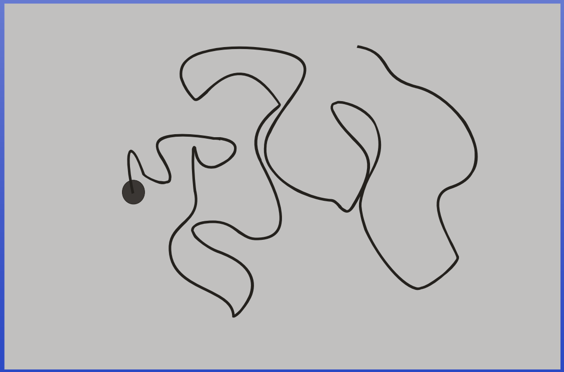


ideal gas

mesoscopic:

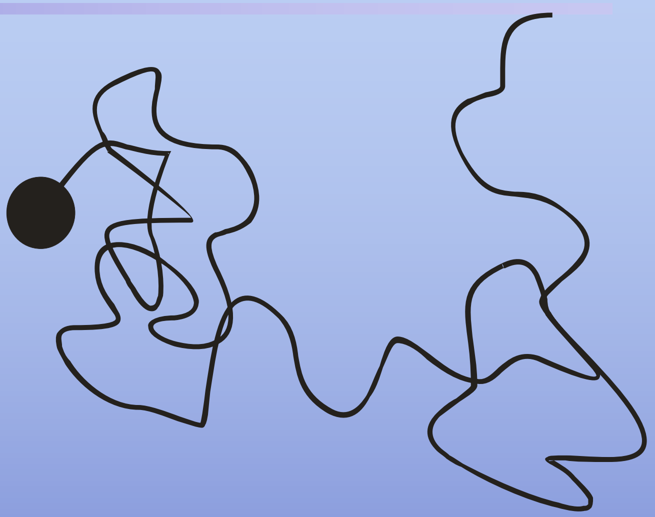


- suspended colloidal particle
- protein pulling
- Brownian motion
- fluctuations



brownian motion

Brownian particle: random walk



Langevin equation

$$m\cancel{\frac{d^2z}{dt^2}} + \gamma\frac{dz}{dt} = -\frac{\partial V}{\partial z} + \xi(t)$$

overdamped system

friction coefficient

external potential

stochastic force:

$$\langle \xi(t) \rangle = 0$$

$$\langle \xi(t) \bullet \xi(t') \rangle = 2\gamma T \delta(t - t')$$

(Sekimoto 1998)

energy balance: equilibrium

time-independent potential: $\frac{dV}{dt} = 0$ V only z dependent

Langevin equation $\gamma \frac{dz}{dt} = -\frac{\partial V}{\partial z} + \xi(t)$

$$0 = -[-\gamma \frac{dz}{dt} + \xi(t)]dz + \frac{\partial V}{\partial z} dz$$

$$dQ \equiv -[-\gamma \frac{dz}{dt} + \xi(t)]dz$$ heat

$$dV \equiv \frac{\partial V}{\partial z} dz$$ potential difference

$$0 = dQ + dU$$ energy balance

energy balance: time dep. potentials

$V[z,\lambda(t)]$ $\quad \lambda(t)$ control parameter

e.g.: $\lambda(t) = \sin(\omega t)$

no total differential

add: $\dfrac{\partial V(z,\lambda(t))}{\partial \lambda} d\lambda$

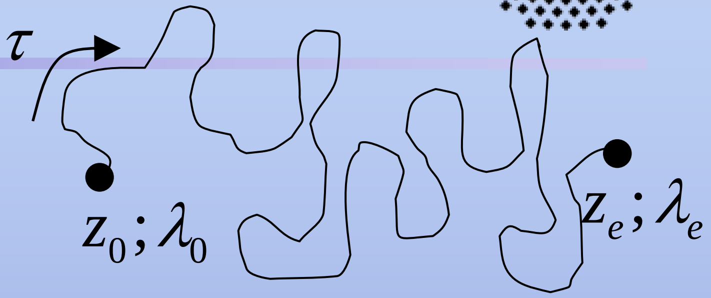
$$0 = -[-\gamma \frac{dz}{dt} + \xi(t)]dz + \frac{\partial V(z,\lambda(t))}{\partial z} dz$$

$$\underbrace{\frac{\partial V(z,\lambda(t))}{\partial \lambda} d\lambda}_{dW} = \underbrace{-[-\gamma \frac{dz}{dt} + \xi(t)]dz}_{dQ} + \underbrace{\frac{\partial V(z,\lambda(t))}{\partial z} dz + \frac{\partial V(z,\lambda(t))}{\partial \lambda} d\lambda}_{dV}$$

work $\qquad$ heat $\qquad$ potential difference

microscopic energy balance

trajectory picture



parametric trajectory

$$dQ = -[-\gamma \frac{dz}{dt} + \xi(t)]dz = -\frac{\partial V}{\partial z} dz$$

Langevin equation

$$\gamma \frac{dz}{dt} = -\frac{\partial V}{\partial z} + \xi$$

integration along trajectory

$$Q = \int_{z_0,\lambda_0}^{z_e,\lambda_e} -\frac{\partial V}{\partial z} dz = \int_{t_0}^{t_e} -\frac{\partial V}{\partial z} \dot{z}\, d\tau$$

$$W = \int_{t_0}^{t_e} \frac{\partial V}{\partial \lambda} \dot{\lambda}\, d\tau$$

$$\Delta V = V(t_e) - V(t_0)$$

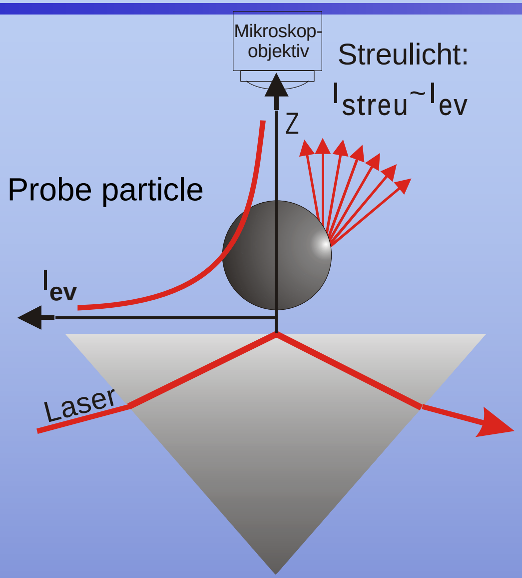
trajectory

determination of Q,W, and V

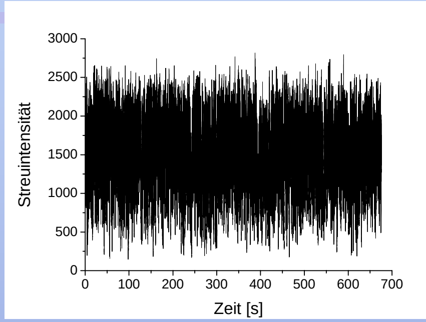
experiment

- exact measurement of the trajectory
- externally controllable force to drive particle into non equilibrium

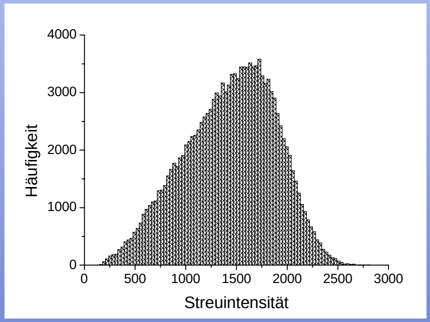
TIRM Technique



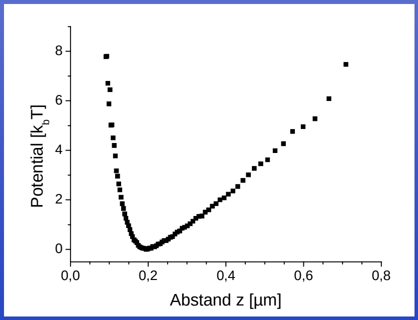
Scattering signal



Histogram



Inversion of the
Boltzman
distribution

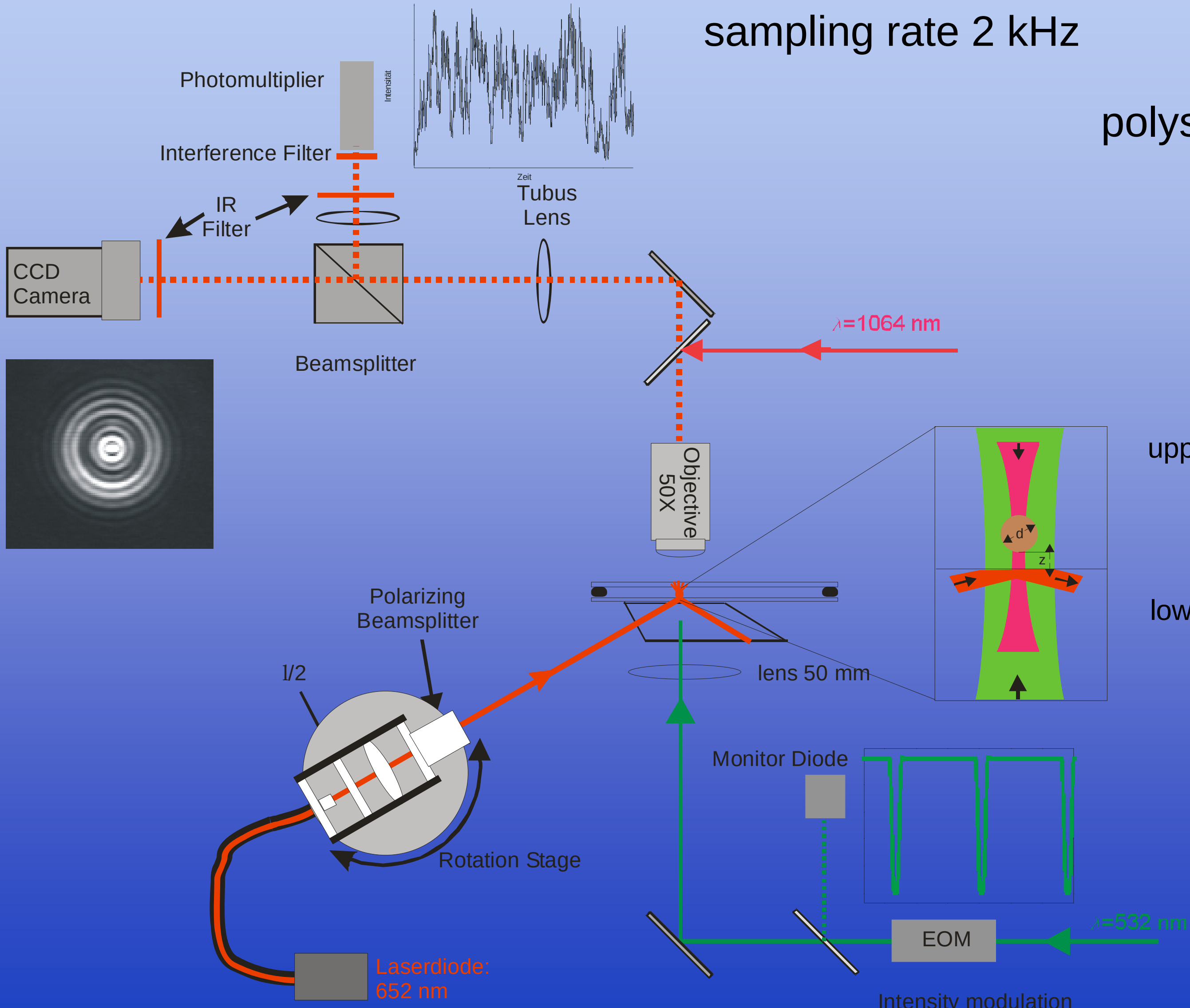


Potential

- Creation of an evanescent wave
- Exponentially decaying scattering itensity

- Determination of the particle wall distance z

experiment



sampling rate 2 kHz

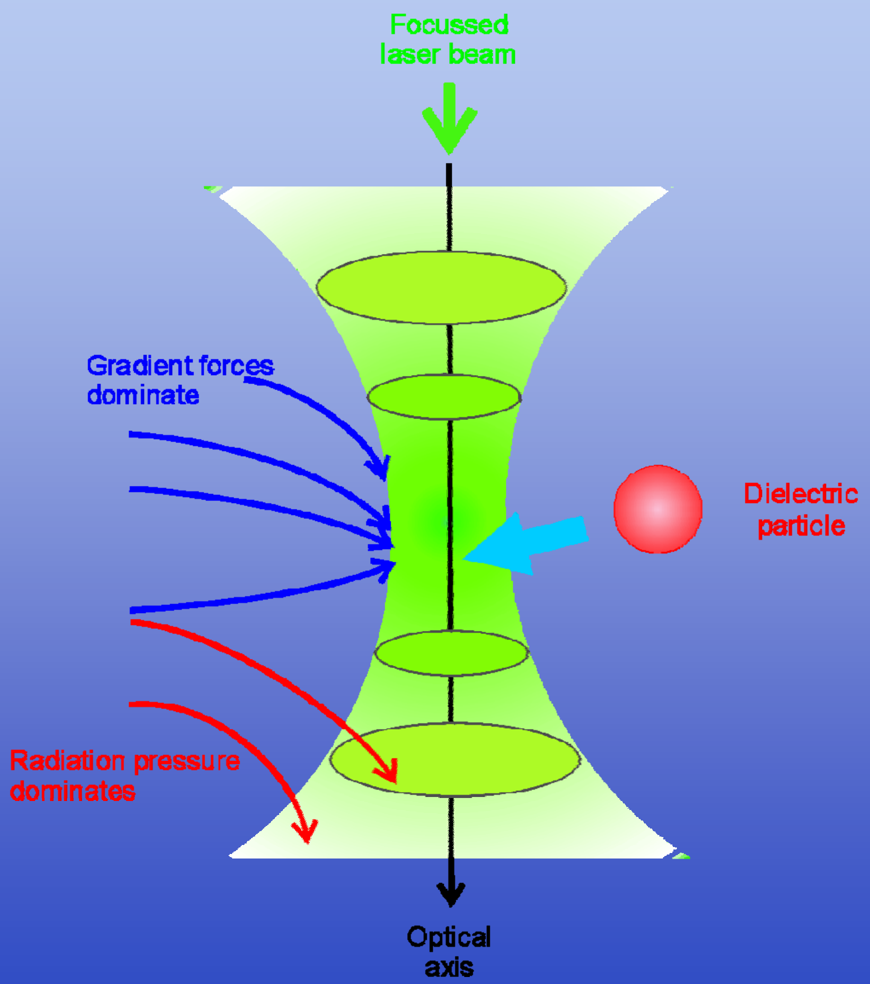
polystyrene particles

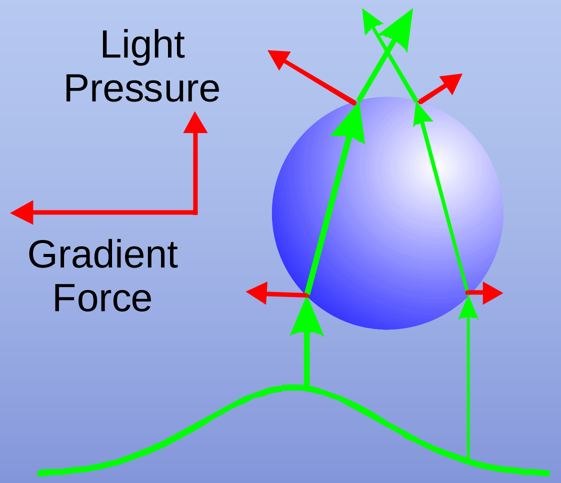
d=4 µm

upper tweezers 10mW

lower tweezers 300mW

optical tweezers





Dipole interaction energy for a particle in an electric field:

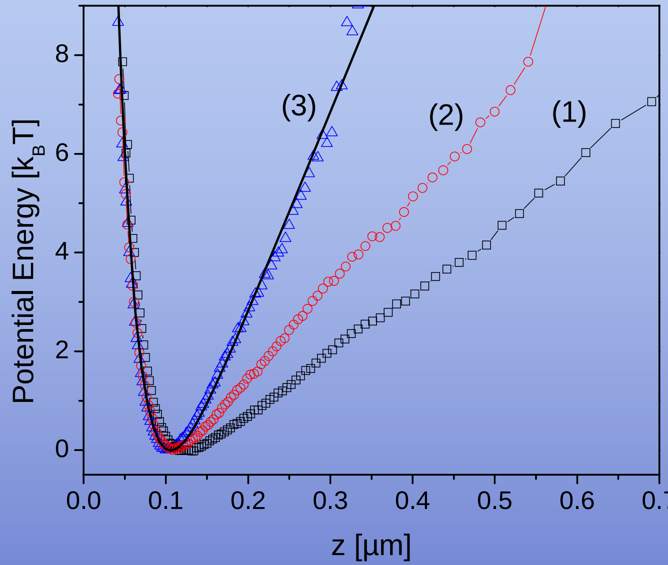
$$W \propto -\alpha \int E^2 \, dV$$

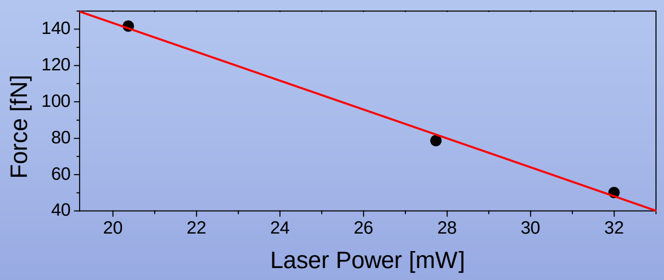
$$\alpha = \varepsilon_{particle} / \varepsilon_{outside} - 1$$

$\Rightarrow$ Particle moves towards higher fields.

lower tweezers calibration

- increasing tweezers intensity





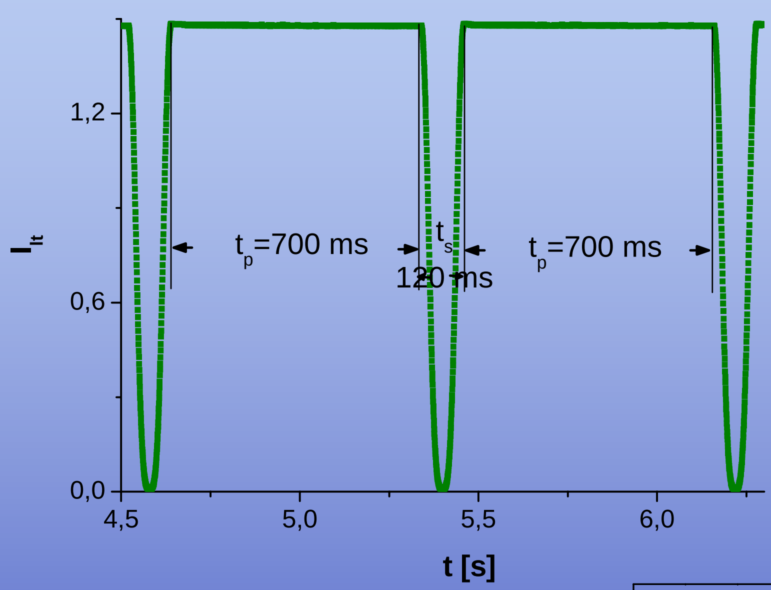
- linear dependance of light pressure
- tweezers calibration

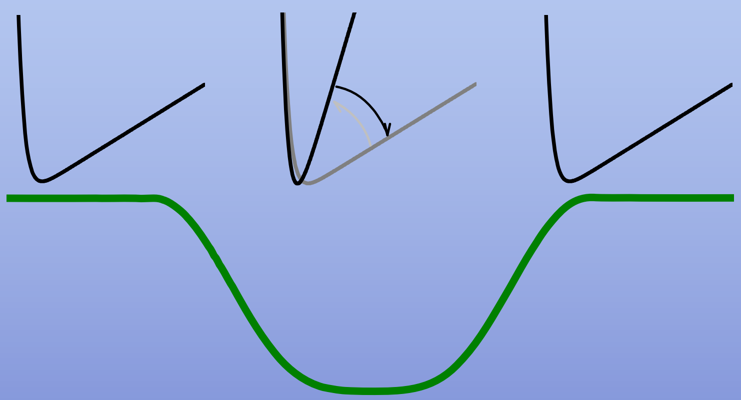
$$V_l = c \bullet I_l \bullet z$$

interaction potential

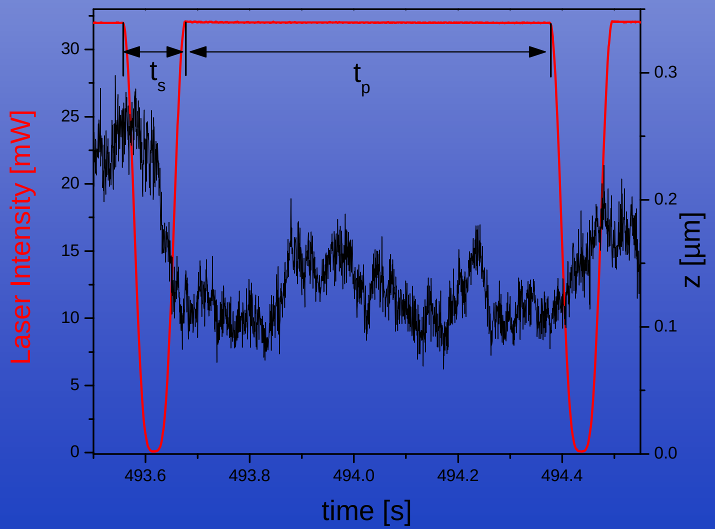
$$V[z(\tau),\lambda(\tau)] = A \cdot e^{-\kappa z} + B_0 \cdot z + I_{lt}[\lambda(\tau)] \cdot c \cdot z$$

pulse protocol





• strong coupling to the bath

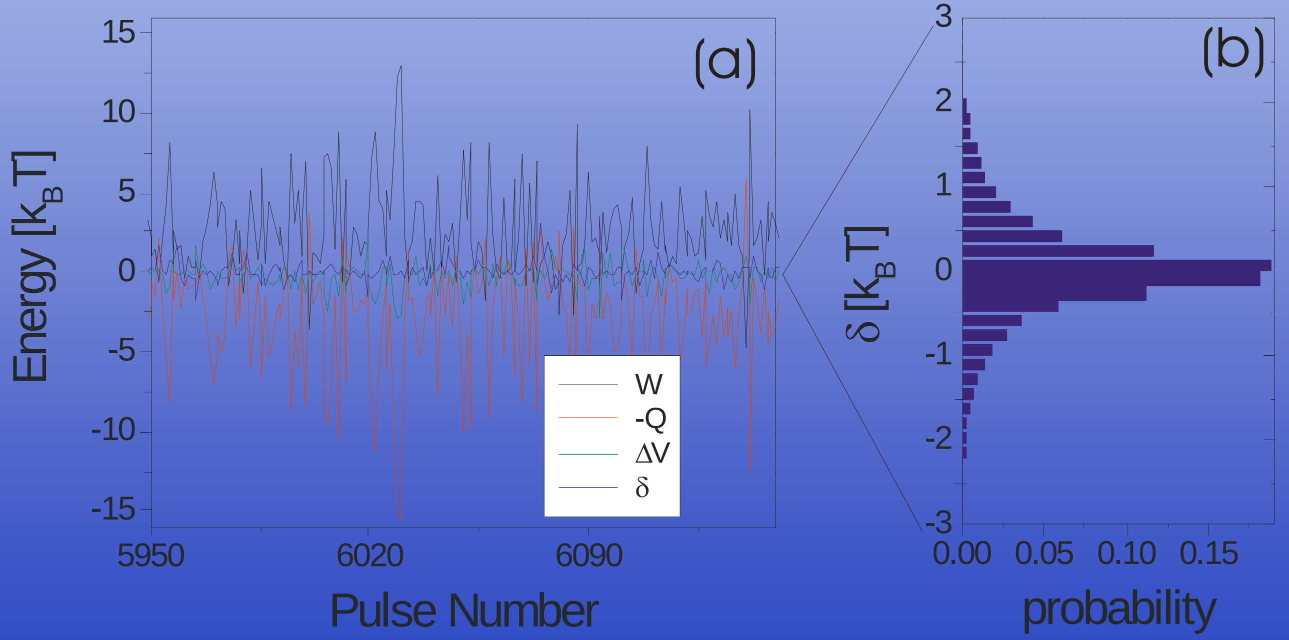


energy conservation

$$W = -\int_{t_0}^{t_e} \frac{\partial V}{\partial \lambda} \dot{\lambda}(t) d\tau = -\frac{c}{\nu} \sum_{\tau} \dot{I}_{lt} \cdot z(\tau)$$

$$Q = -\int_{t_0}^{t_e} \frac{\partial V}{\partial z} \dot{z} \, d\tau = -\frac{1}{\nu} \sum_{\tau} \frac{\partial V}{\partial z} \dot{z}(\tau)$$

energy balance: $\delta = W - Q + \Delta V = 0$



energy resolution about 0.25 kT

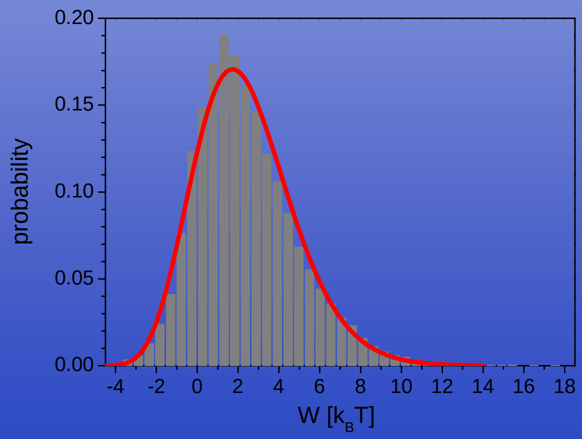
work distribution

particle wall potential is not harmonic

harmonic potentials → symmetric gaussian work distribution

• demonstrated with colloidal particles in 3d traps

non harmonic potentials → theory predicts:
asymmetric non gaussian distribution

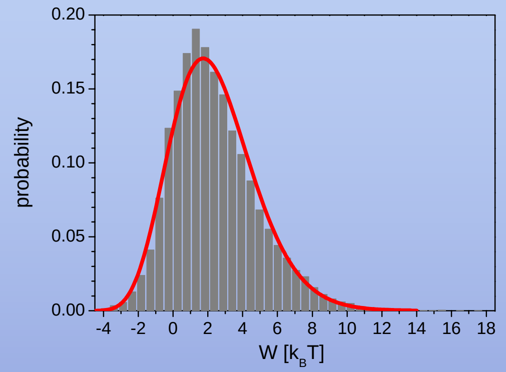


theory:
•no fit parameters

<W>=2.4 kT

fluctuation theorems

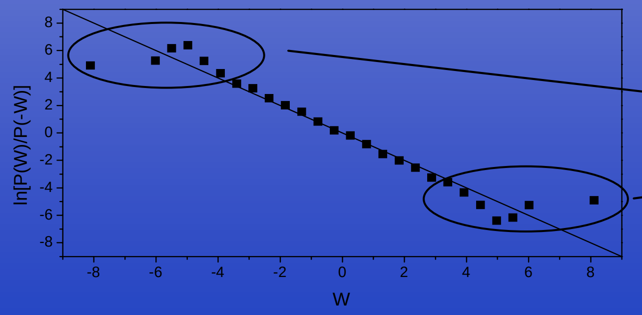
symmetric protocol: $\Delta F = 0$



Jarzynski relation:

exp. $$< e^{-\beta W} > = 1.03$$

detailed fluctuation theorem: $$\frac{P(-W)}{P(W)} = e^{-\beta W}$$



statistics!