Non-Equilibrium Fluctuations in Expansion/Compression Processes of a Single-Particle Gas

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Nonequilibrium Thermodynamics in Quantum and Classical Physics

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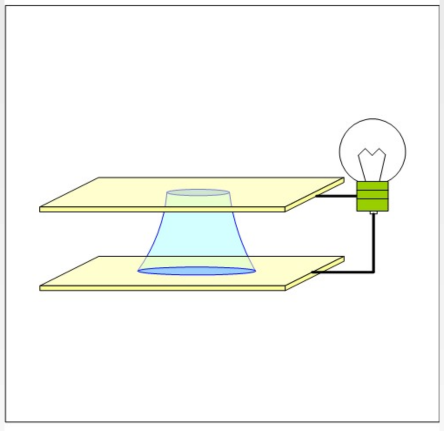
What happens at soft matter interfaces?

How to explain non-equilibrium phenomena?

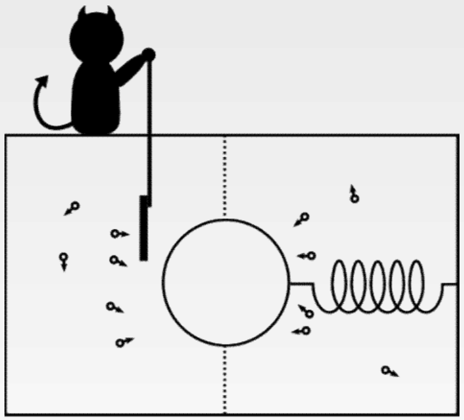
- Electrical Properties at Solid-Liquid Interfaces
- Non-Equilibrium Fluctuations in Very Small Systems
- Colloid and Nano Particles at Interfaces
- Hydrodynamics in Small Systems
- Wetting and Electro-wetting

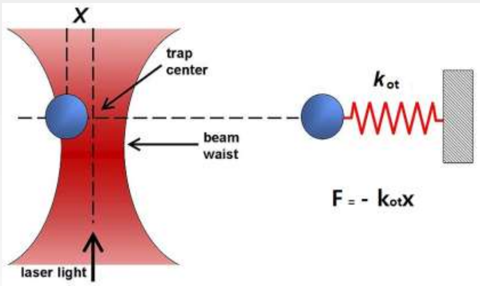
Electrical Properties at Solid-Liquid Interfaces



- **Electric power generation by modulating the metal-water interface.**
- **Interfacial charge density between solid and liquid.**
- **The influence of pH solution on solid-liquid interfaces.**

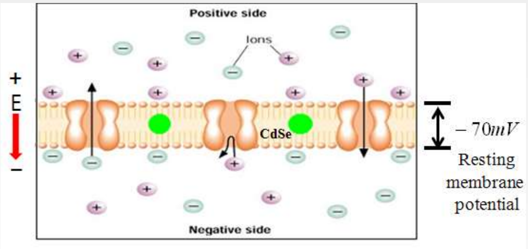
Non-Equilibrium Fluctuations in Very Small Systems

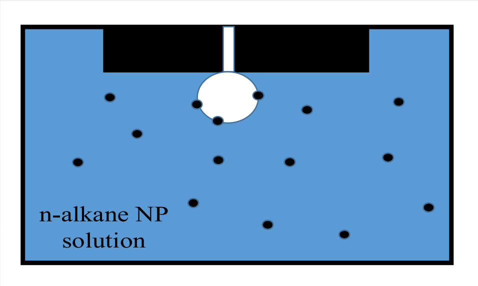


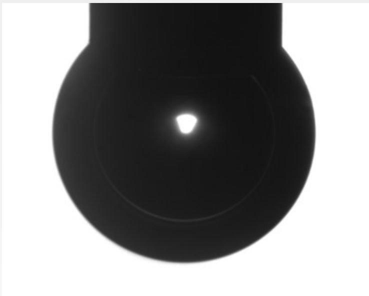


- **Realization of a Brownian motor through feedback control.**
- **Optical tweezers studying micro-size systems**
- **The influence of pH solution on solid-liquid interfaces.**

Colloid and Nano Particles at Interfaces







- **Electrical phenomena across bio-membrane**
- **Hydrodynamics of colloid particles near interfaces**
- **Nano particle adsorption at the liquid-vapor**

Soft Matter Physics Research Group

Contributors:

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Fluctuation theorem

- **Most interesting processes in the nature occur far from equilibrium.**
- **The second law of thermodynamics predicts that the entropy of an isolated system should tend to increase until it reaches equilibrium.** $\langle \Delta s \rangle > 0$.
- **In statistical mechanics, the second law is only a statistical one. There should always be some nonzero probability that the entropy of an isolated system might spontaneously *decrease*** $(\Delta s < 0)$**; the fluctuation theorem precisely quantifies this probability.**
- **Fluctuation theorem deals with the relative probability that the entropy of a system far from equilibrium will increase or decrease over a given amount of time.**

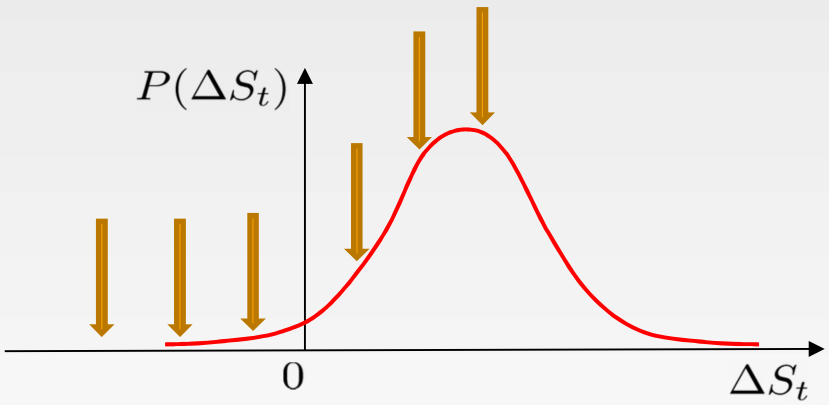
Discovery of Fluctuation Theorems (FT)

Evans, Cohen, Morris (1993)
Evans & Searls (1994), Gallavotti & Cohen (1995)

Gallavotti-Cohen Symmetry

$$\frac{P(\Delta S_t)}{P(-\Delta S_t)} = e^{\Delta S_t}$$

Detailed FT



$$\int_{-\infty}^{\infty} P(\Delta S_t) d\Delta S_t = \int_{-\infty}^{\infty} e^{\Delta S_t} P(-\Delta S_t) d\Delta S_t = \int_{-\infty}^{\infty} e^{-\Delta S_t} P(\Delta S_t) d\Delta S_t = \boxed{\langle e^{-\Delta S_t} \rangle = 1}$$

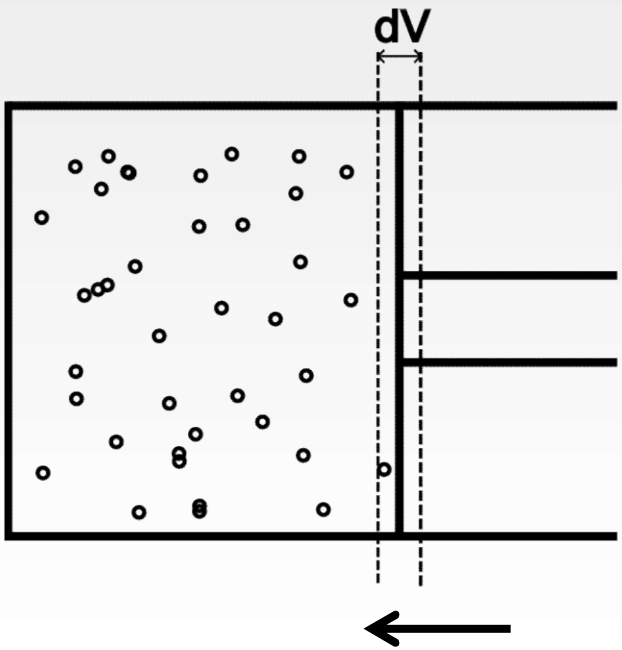
Integral FT

Using Jensen's inequality $\langle e^x \rangle \geq e^{\langle x \rangle} \longrightarrow e^0 = \langle e^{-\Delta S_t} \rangle \geq e^{\langle -\Delta S_t \rangle} \longrightarrow \langle \Delta S_t \rangle \geq 0$

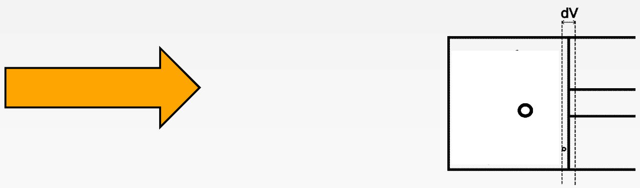
Thermodynamic 2nd law is a corollary of G-C symmetry!!

Fluctuations depending on the size of the system

Macroscopic system



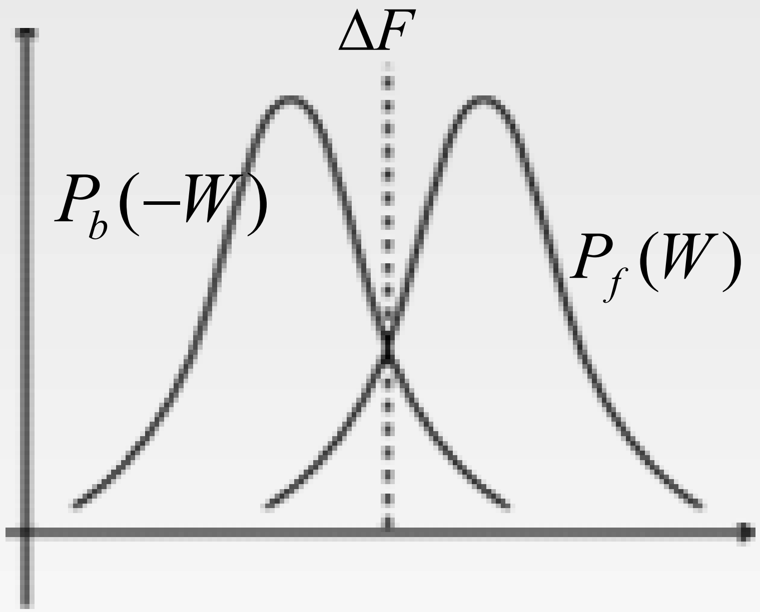
Microscopic system



Fluctuations in thermodynamic variables are **negligible**.

Fluctuations in thermodynamic variables are **very visible**.

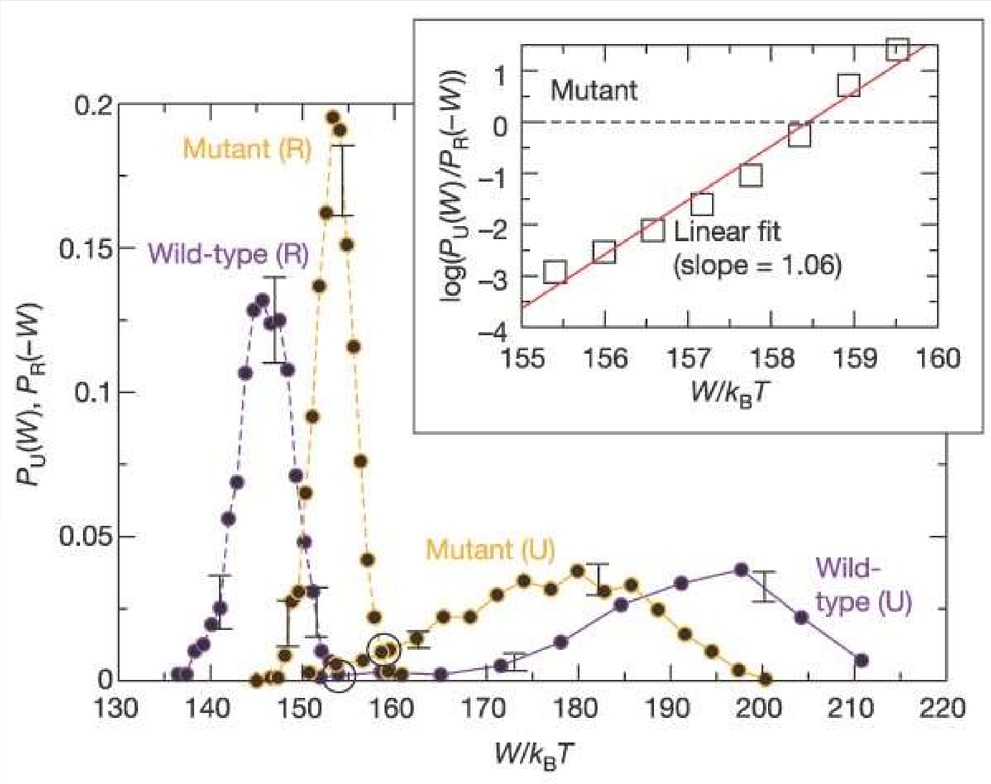
Crooks Fluctuation Theorem (CFT, G. E. Crooks 1998)



$$\frac{P_f(W)}{P_b(-W)} = \exp[\beta(W - \Delta F)]$$

- **CFT has drawn a lot of attention because of its usefulness in experiment. This theorem makes it possible to experimentally measure the free energy difference of the system during a non-equilibrium process.**

Why fluctuation theorem is important?



Collin, Bustmante *et. al.* Nature(2005)

Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies

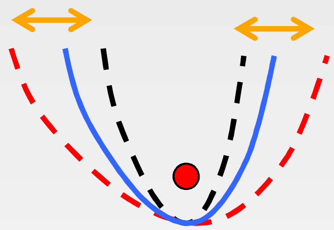
$$\frac{P_f(W)}{P_b(-W)} = \exp[\beta(W - \Delta F)]$$

Idea

- **Consider a particle trapped in a 1D harmonic potential**

$$V(x) = kx^2 / 2$$

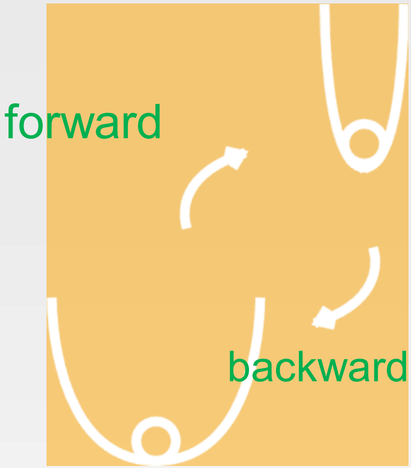
where k **is a trap strength of the potential.**



- **When the trap strength is either increasing or decreasing isothermally in time, the particle is driven from equilibrium.**
- **Since the size of the system is finite, one can test the fluctuation theorems in this system.**
- **We measure the work distribution and determine the free energy difference of the process by using Crooks fluctuation theorem.**

DY Lee, C. Kwon & H. K. Pak PRL, 114, 060603 (2015)

Free Energy Difference of the System



- **Harmonic oscillator (in 1D)**
  - Hamiltonian is given by

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

  - Partition function is

$$Z = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp - \beta H(x,p)dxdp / h = 1/\beta\hbar\omega, \qquad \omega = \sqrt{k/m}$$

  - Free energy difference between two equilibrium states (k_i, k_f) at the same temperature is

$$\beta\Delta F = (-\ln Z_f) - (-\ln Z_i) = 1/2 \ln \frac{k_f}{k_i}$$

  - Forward quasi-static process : $k_f > k_i \quad \rightarrow \quad \Delta F > 0 \quad (\Delta S < 0)$

    Backward quasi-static process: $k_f < k_i \quad \rightarrow \quad \Delta F < 0 \quad (\Delta S > 0)$
  - During these processes: $U \equiv \langle E \rangle = k_B T$

1D Brownian Motion of Single Particle in Heat Bath

$$\begin{cases} \dot{x} = \dfrac{p}{m} \\ \dot{p} = -\nabla V\big(x, \lambda(t)\big) - \gamma \dfrac{p}{m} + z(t), \end{cases} \qquad \langle z(t) z(t') \rangle = 2D\delta(t - t')$$

$$\dot{p} \cdot \frac{p}{m} = -\nabla V \cdot \frac{p}{m} + \left[-\gamma \frac{p}{m} + z(t)\right] \cdot \frac{p}{m}, \qquad dV\big(x, \lambda(t)\big) = \nabla V \cdot dr + \frac{\partial V}{\partial t} dt$$

$$\frac{d}{dt}\left(\frac{p^2}{2m}\right) = -\frac{d}{dt} V(x) + \frac{\partial V}{\partial \lambda} \dot{\lambda} + \left[-\gamma \frac{p}{m} + z(t)\right] \frac{p}{m}$$

$$\frac{d}{dt}\left(\frac{p^2}{2m} + V\right) = \underline{\frac{\partial V}{\partial \lambda} \dot{\lambda}} + \underline{\left[-\gamma \frac{p}{m} + z(t)\right] \frac{p}{m}}$$

$$\frac{dE}{dt} = \dot{W} - \dot{Q}$$

Thermodynamic 1st Law

1D Brownian Motion of Single Particle in Heat Bath

$$\frac{d}{dt}\left(\frac{p^2}{2m}+V\right) = \underline{\frac{\partial V}{\partial \lambda}\dot{\lambda}} + \underline{\left[-\gamma\frac{p}{m}+z(t)\right]\frac{p}{m}}$$

$$\frac{dE}{dt} = \dot{W} - \dot{Q}$$

Thermodynamic 1st Law

$$\dot{W} = \frac{\partial V}{\partial \lambda}\dot{\lambda} = \frac{\partial}{\partial k}\left(\frac{1}{2}kx^2\right)\dot{k} = \frac{1}{2}x^2\dot{k} \longrightarrow W = \int_0^\tau \dot{W}dt = \frac{1}{2}\int_{k_i}^{k_f} x^2 dk$$

In equilibrium, $\lambda = const \quad \rightarrow \quad \dot{W}=0$, $\quad \frac{dE}{dt} = -\dot{Q}$

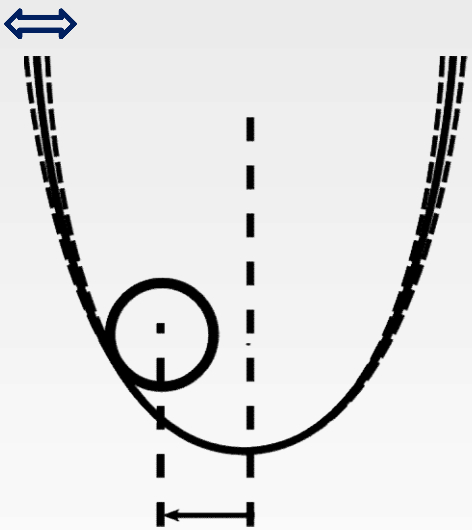
In non-equilibrium steady state,

$$\dot{\rho}_{ss}(x,p) = 0,\ \langle E\rangle = const,\ \ \frac{d}{dt}\langle E\rangle = 0$$

$\langle\dot{W}\rangle = \langle\dot{Q}\rangle > 0$ Work done by external source converts to heat in

$\Delta S_{env} = \frac{\Delta Q}{T} > 0$ the heat bath.

Single Particle Gas under a Harmonic Potential
→ Quasi-static process (Equilibrium process)



- **Thermodynamic work:**

$$W = -\int dt\dot{\lambda}\frac{\partial H}{\partial \lambda} = \frac{1}{2}\int dk\, x^2$$

Here, $\lambda = k$ **(external parameter)**

- **dk/dt→0 :**
  (Quasi-static process)

$$\left\langle x^2 \right\rangle^{eq} = \left\langle x^2 \right\rangle_f = \left\langle x^2 \right\rangle_b = k_B T/k$$

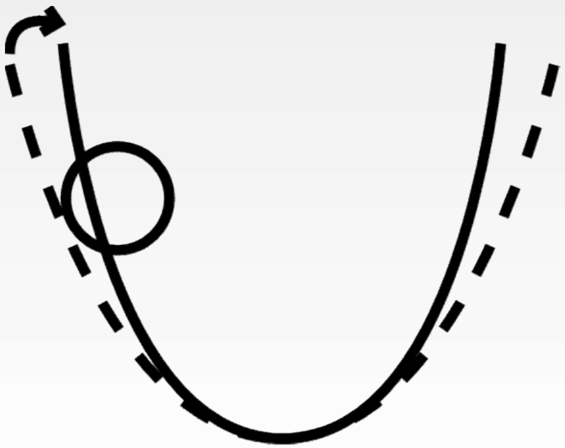
$$< dW_f >=< d(-W_b) >= \frac{1}{2}\left\langle x^2 \right\rangle^{eq}|dk| = \frac{1}{2}\frac{k_B T}{k}|dk|$$

$$W =< W >_f =< -W_b >= \frac{1}{2\beta}\ln\frac{k_f}{k_i} = \Delta F$$

$$P_f(W) = P_b(-W) = \delta(W - \Delta F)$$

Single Particle Gas under a Harmonic Potential → Non-equilibrium process(dk/dt=finite)

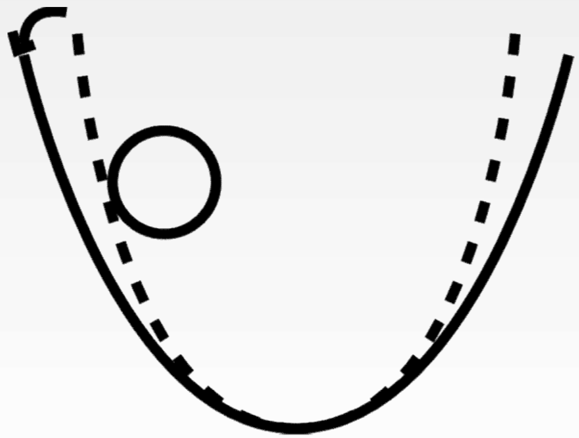
- **Forward process (dk/dt>0)**



$$\langle x^2 \rangle_f \geq \langle x^2 \rangle^{eq}$$

$$\rightarrow \langle d(W_f^{neq}) \rangle \geq \langle d(W_f^{eq}) \rangle$$

- **Backward process (dk/dt<0)**



$$\langle x^2 \rangle_b \leq \langle x^2 \rangle^{eq}$$

$$\rightarrow \langle d(-W_b^{neq}) \rangle \leq \langle d(-W_b^{eq}) \rangle$$

$$\Rightarrow \quad \langle -W \rangle_b \leq \langle W \rangle^{eq} = \Delta F \leq \langle W \rangle_f$$

Single Particle under a Harmonic Potential
→ Extreme limit of non-equilibrium process (dk/dt=infinite)

- **The system remembers its previous state.**
- **Consider a sudden change limit**

  (dk/dt → ∞)

  - The particle is still at initial position.
  - Position distribution is given by the initial equilibrium Boltzmann distribution
    - Using Equi-partition theorem

$$W = 1/2\int_{k_i}^{k_f} dk\, x^2 \;\; and \;\; \langle x^2 \rangle = k_B T / k_i$$

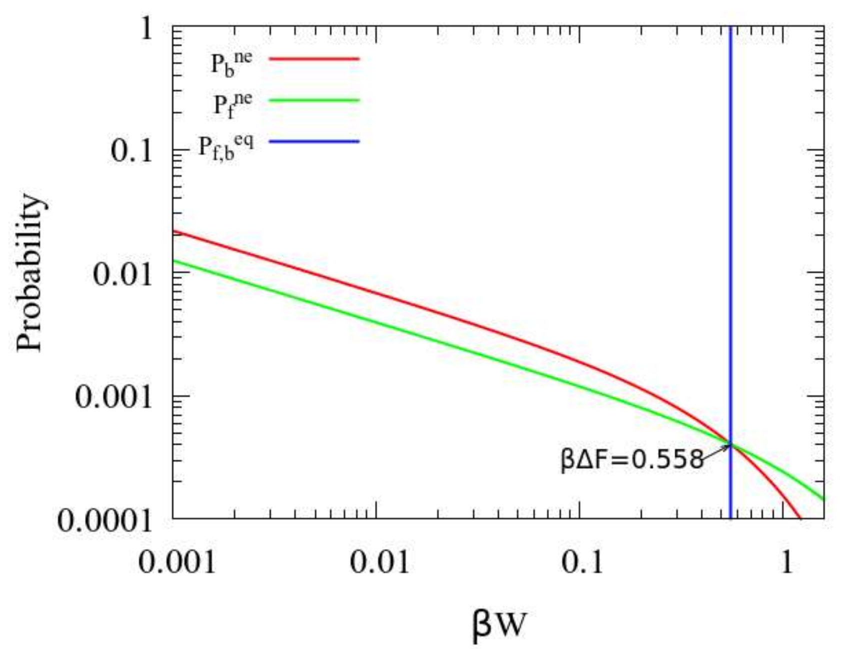
$$\rightarrow \langle W \rangle^{neq} = \frac{k_B T}{2}\frac{k_f - k_i}{k_i}$$

$$\Rightarrow \langle -W \rangle_b < \langle W \rangle^{eq} < \langle W \rangle_f$$

Using recent theoretical result,

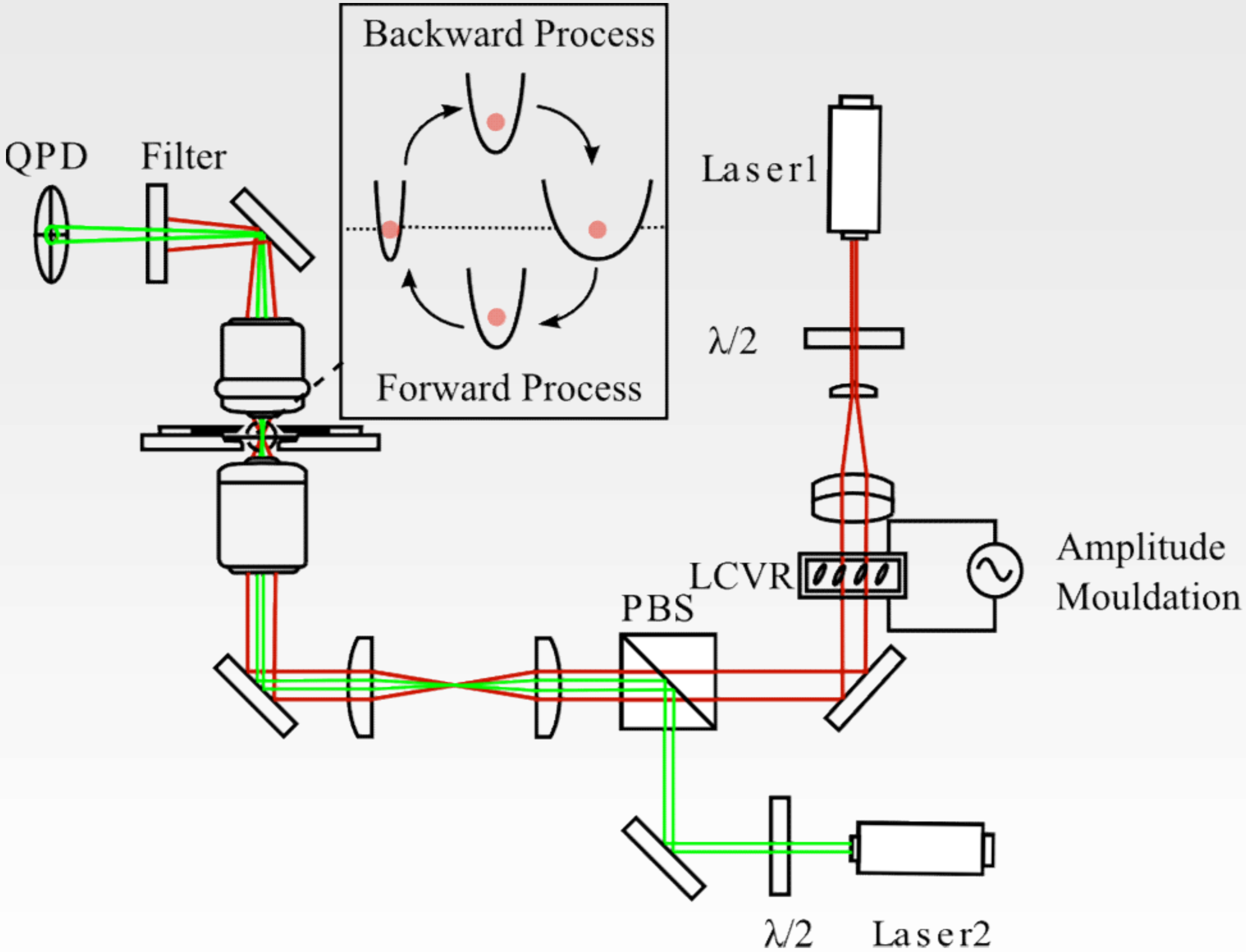
$$P_{f,b}(W) = \theta(\mp W)\sqrt{\frac{|a|}{\pi}}(\mp\beta W)^{-1/2} e^{-|a|\beta W}$$

$$a = k_i / (k_f - k_i)$$



Kwon, Noh, Park, PRE 88 (2013)

Experimental Setup – Optical Tweezers with time dept. trap strength

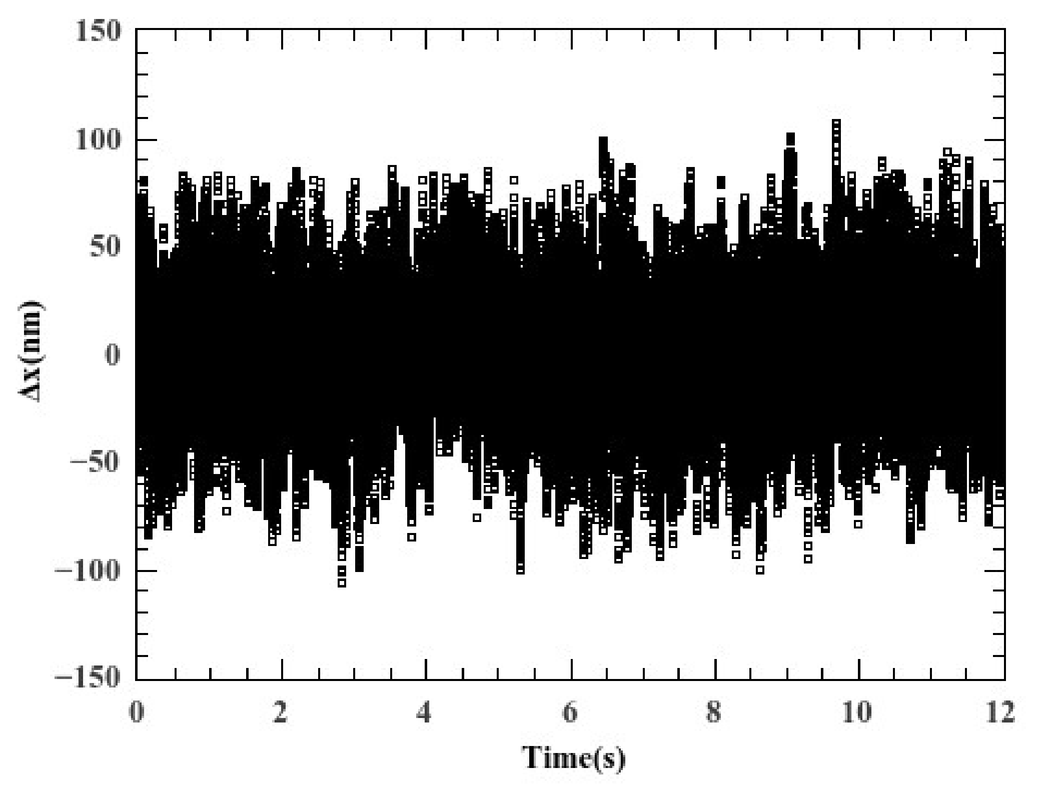


**$2\mu m$ PMMA particle in do-decane liquid

Temp. of the system is maintained at 27°± 0.1°.

Particle position is measured with 1nm resolution.

Measurements of Optical Trap Strength



$$k_{ot} = 2.87\, pN / \mu m$$

Measurements of Optical Trap Strength

- **The optical trap strength is calibrated with three different methods**
  - **Equi-partition theorem**

$$\frac{1}{2}k\langle x^2\rangle = \frac{1}{2}k_B T$$

  - **Boltzmann distribution method**

$$\rho(x)dx = Ce^{-\beta U(x)}dx,\ V(x) = \frac{1}{2}kx^2$$

  - **Oscillating optical tweezers method**

$$m\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + kx = A\cos(\omega t)$$

$$x = D(\omega)\cos(\omega - \delta),\ \delta = \tan^{-1}\left(\frac{\gamma\omega}{k}\right)$$

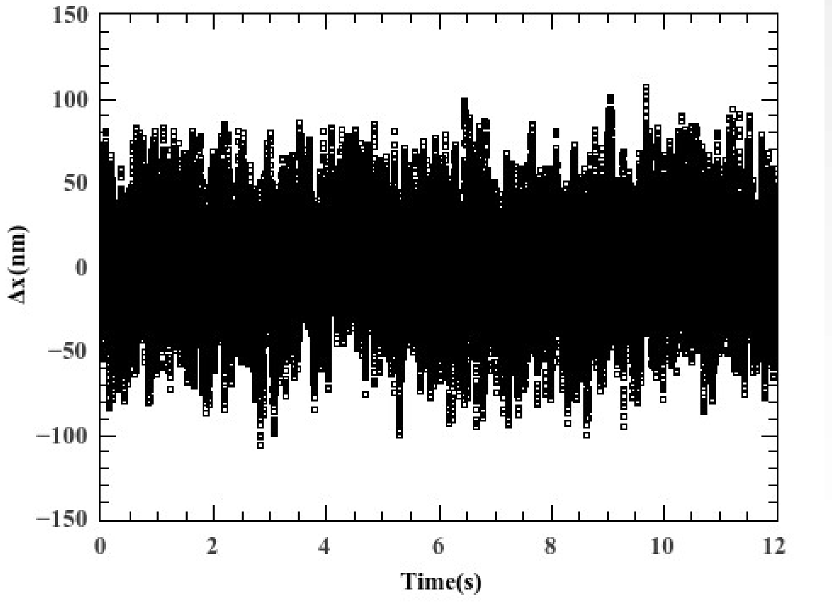
Passive Method of Measuring Optical Trap Strength

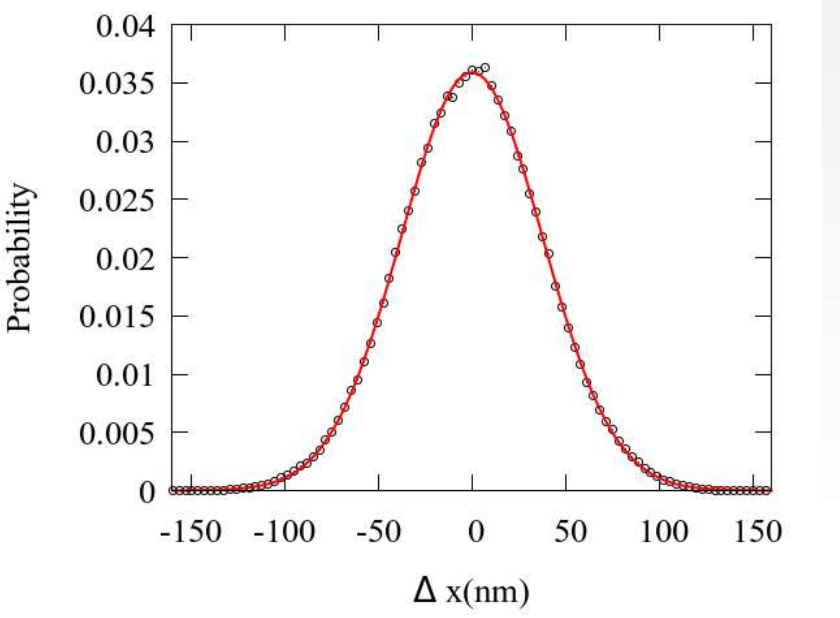
- **Equi-partition theorem**

$$\frac{1}{2}k\langle x^2\rangle = \frac{1}{2}k_BT$$

- **Boltzmann distribution**

$$p(x)dx = Ce^{-\beta V(x)}dx,\ V(x) = \frac{1}{2}kx^2$$



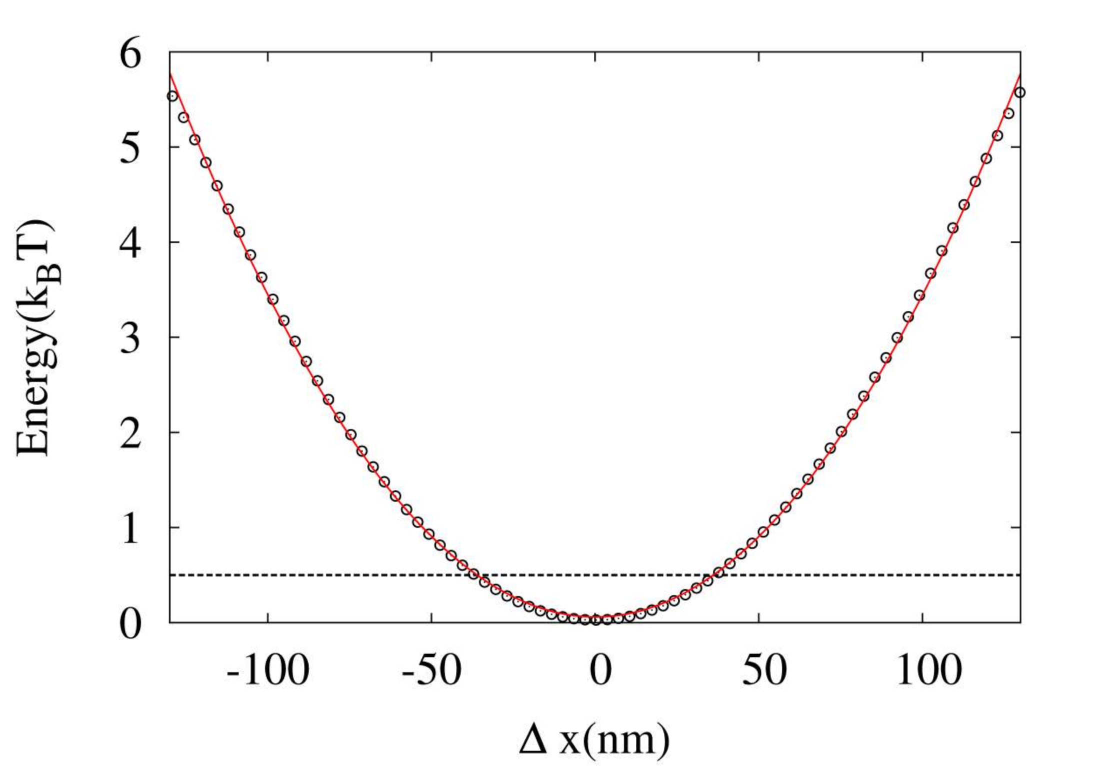


$$k_{ot} = 2.87\, pN/\mu m$$

Profile of 1D Harmonic Potential

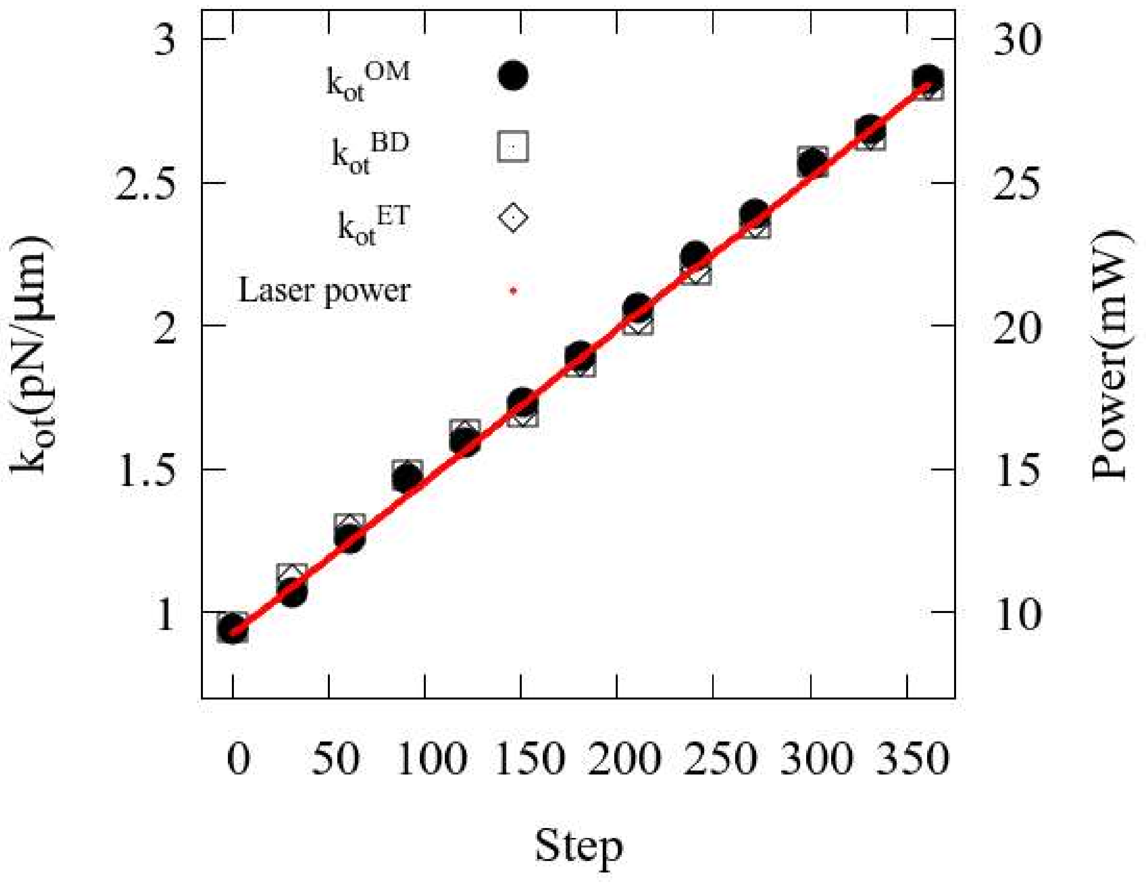
$$p(x)\,dx = Ce^{-\frac{V(x)}{k_B T}}\,dx \quad in\ 1Dim$$

$$V(x) = -k_B T \ln p(x) + k_B T \ln C$$



$$k_{ot} = 2.87\,pN/\mu m$$

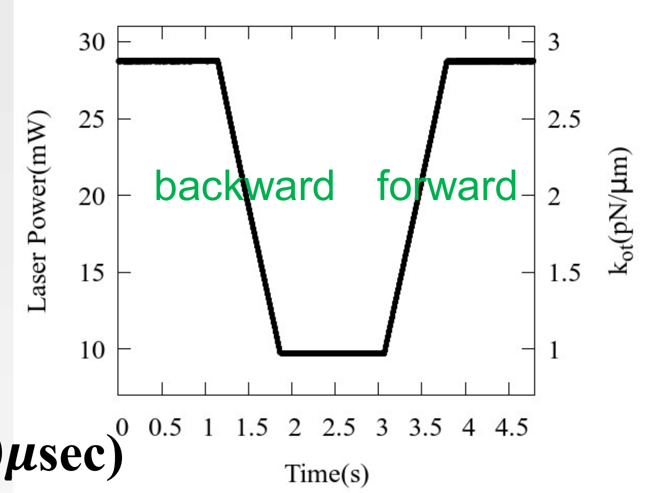
Measurements of Optical Trap Strength with Controlled Laser Power



Experimental Method

- **Using a PMMA particle of 2μm diameter in do-decane solvent**
- **Linearly changing the trap strength in time**
  - From 2.87 to 0.94pN/μm (backward process)
  - From 0.94 to 2.87pN/μm (forward process)
  - Theoretical free energy difference :

$$\beta\Delta F = 1/2\ln(k_f / k_i) = 0.558$$

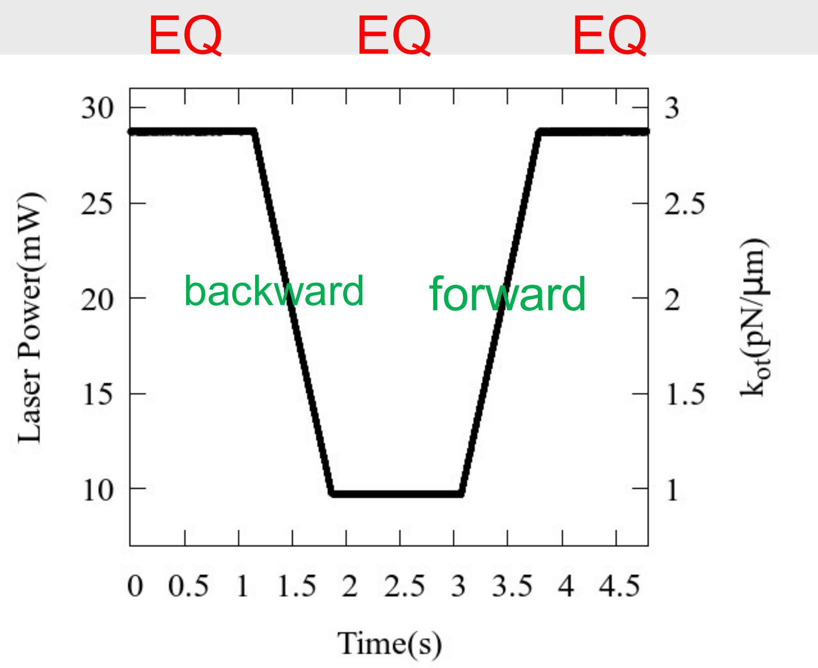


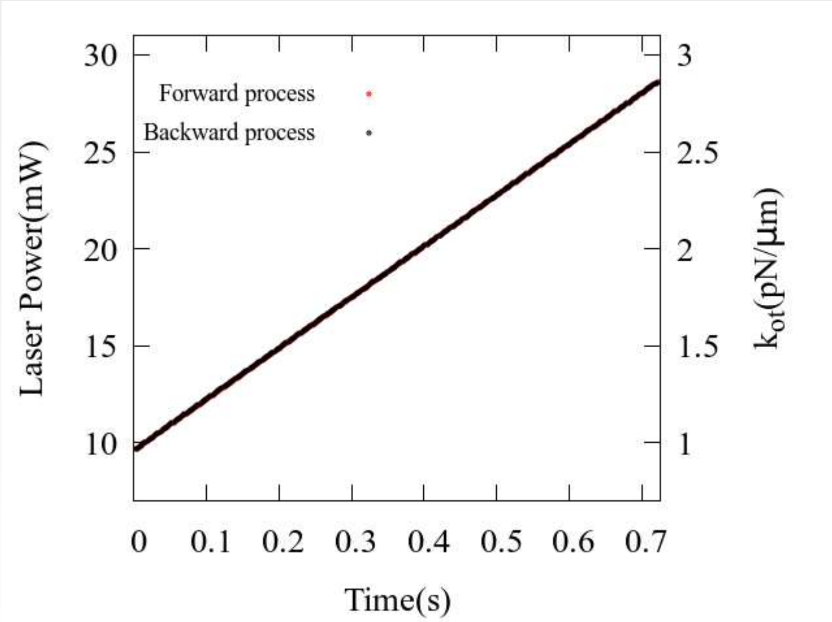
- **Data sampling :10kS/s (sampling in every 100μsec)**
- **Repetition is over 40000 times**
- **Total number of steps : 360**
- **Rate of changing trap strength(pN/μm·s) : 0.268, 0.536, 2.68, 5.36**

  by changing the time difference between the neighboring steps

  from 1msec to 20msec

Laser Power and Trap Strength in Time





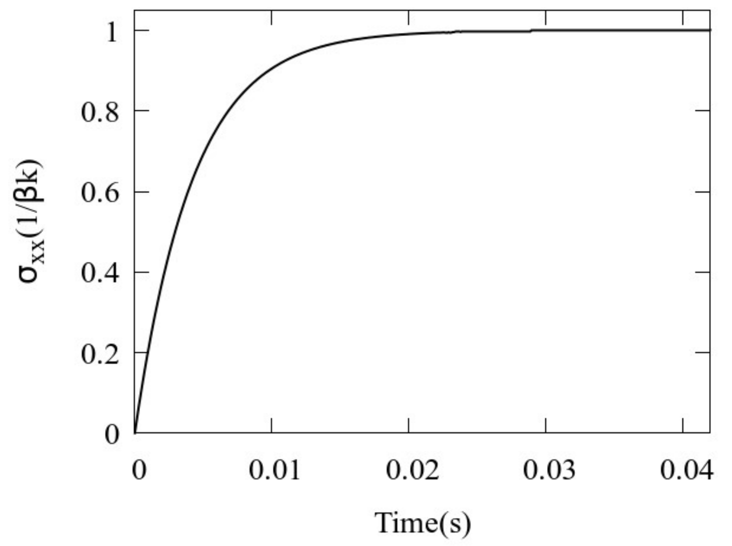
$$\dot{k} = \pm 0.536\, pN / \mu m \cdot s$$

Characteristic equilibration time in this system

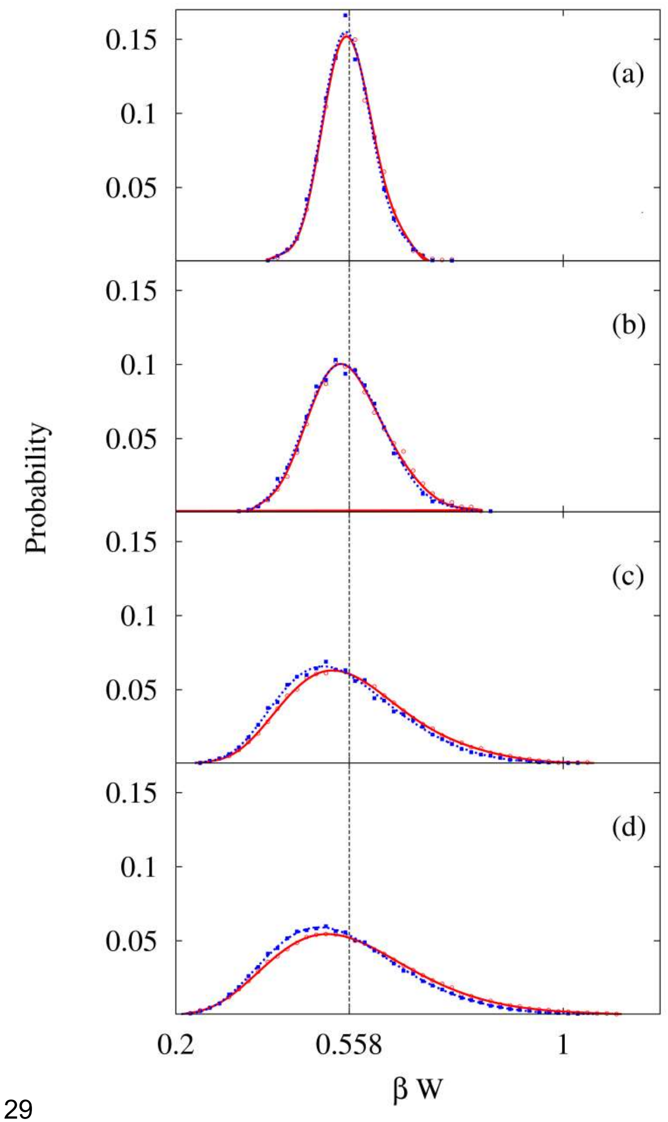
- **In non-equilibrium process, the external parameters have to be changed before the system relaxes to the equilibrium state.**
- **Mean squared displacement:** $\sigma_{xx} = \left\langle \left[x(t) - < x(0) > \right]^2 \right\rangle$
  - After the particle loses its initial information then σ_{xx} obeys the equi-partition theorem.
  - In our system, **the characteristic equilibration time(τ)** is about **20ms**.

$$\rightarrow t >> \tau, \quad \sigma_{xx} = k_B T / k$$

(equi-partition theorem)



Work Probabilities for Four Different Protocols



: forward

: backward

$\dot{k} = 0.268 \text{pN/μm·s}$

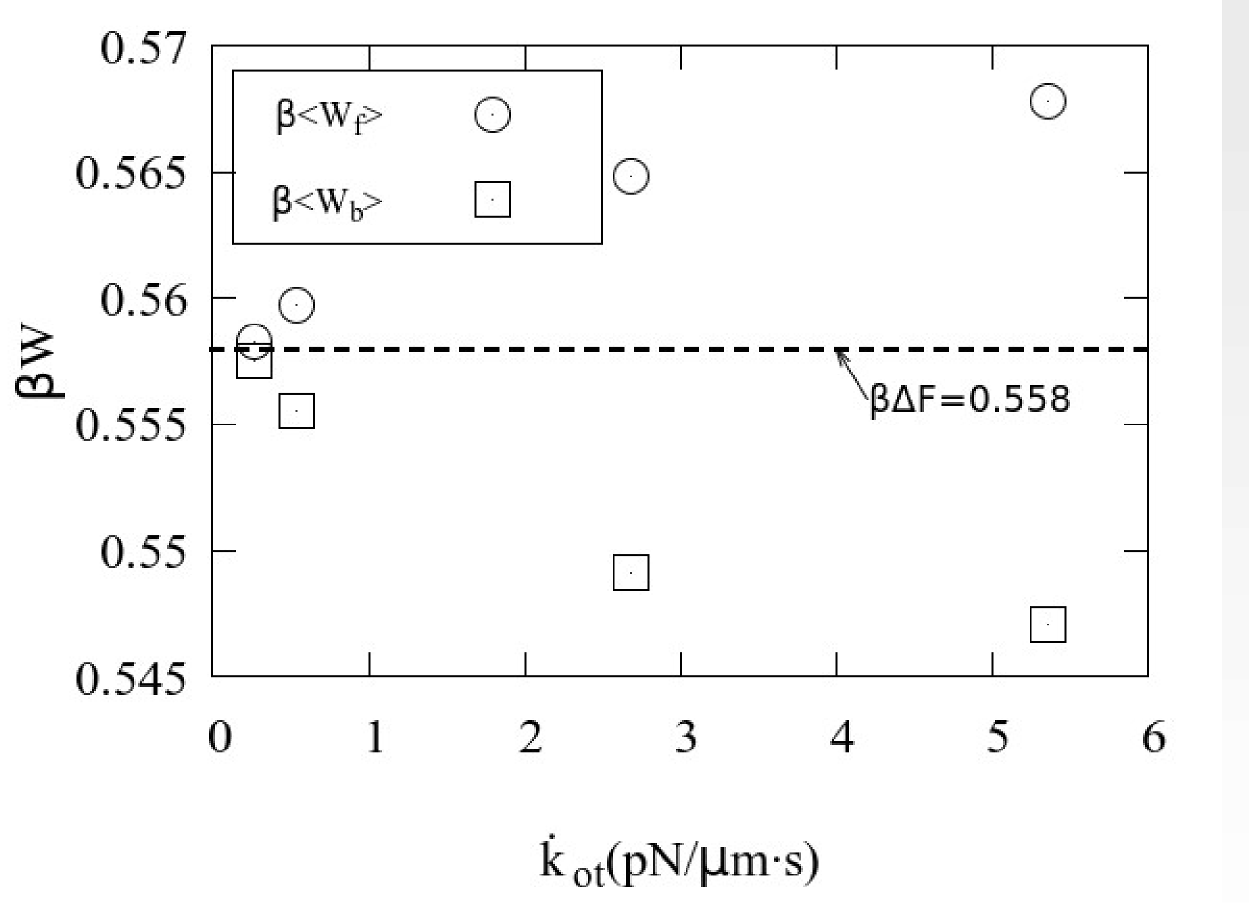
$\dot{k} = 0.536 \text{pN/μm·s}$

$\dot{k} = 2.68 \text{pN/μm·s}$

$\dot{k} = 5.36 \text{pN/μm·s}$

$$\frac{P_f(W)}{P_b(-W)} = \exp[\beta(W - \Delta F)]$$

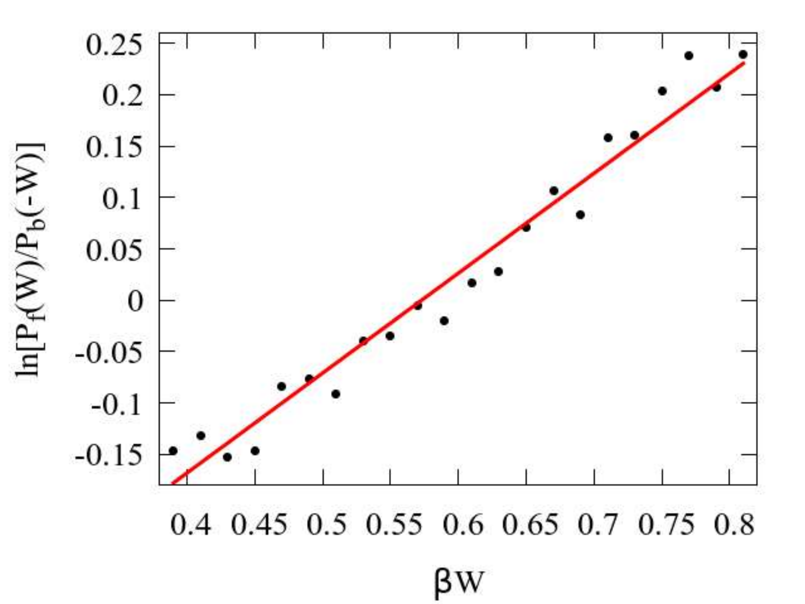
Mean Work Value and Expected Free Energy Difference



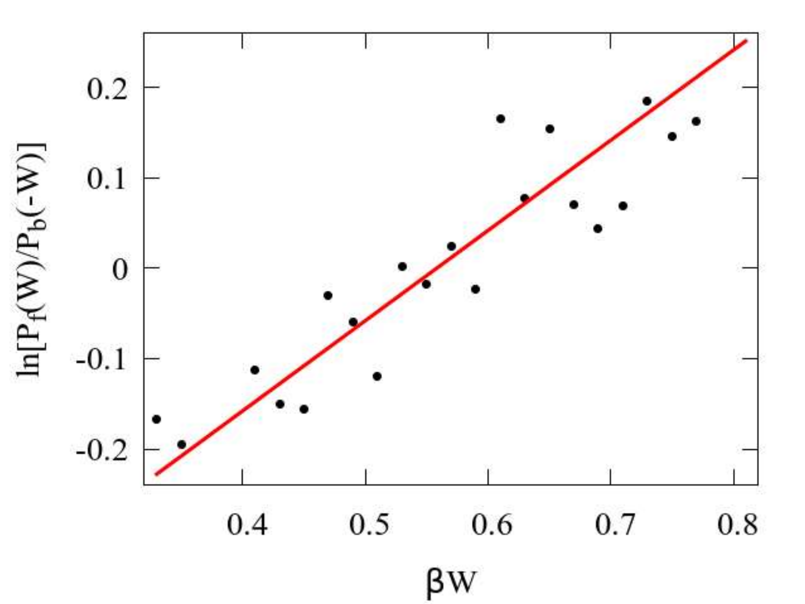
$$\langle -W \rangle_b \leq \langle W \rangle^{eq} = \Delta F \leq \langle W \rangle_f$$

Verification of Crooks Fluctuation Theorem

- **Fastest protocol, $\dot{k} = 5.36\text{pN}/\mu\text{m}\cdot\text{s}$**



- **Fast protocol, $\dot{k} = 2.68\text{pN}/\mu\text{m}\cdot\text{s}$**



$$\frac{P_f(W)}{P_b(-W)} = \exp[\beta(W - \Delta F)]$$

Conclusion

- **We experimentally demonstrated the CFT in an exactly solvable real system.**

$$\frac{P_f(W)}{P_b(-W)} = \exp[\beta(W - \Delta F)]$$

- **We also showed that mean works obey in non-equilibrium processes.** $\langle -W \rangle_b \le \langle W \rangle^{eq} \le \langle W \rangle_f$

- **Useful to make a micrometer-sized stochastic heat engine.**

DY Lee, C. Kwon & H. K. Pak PRL, 114, 060603 (2015)