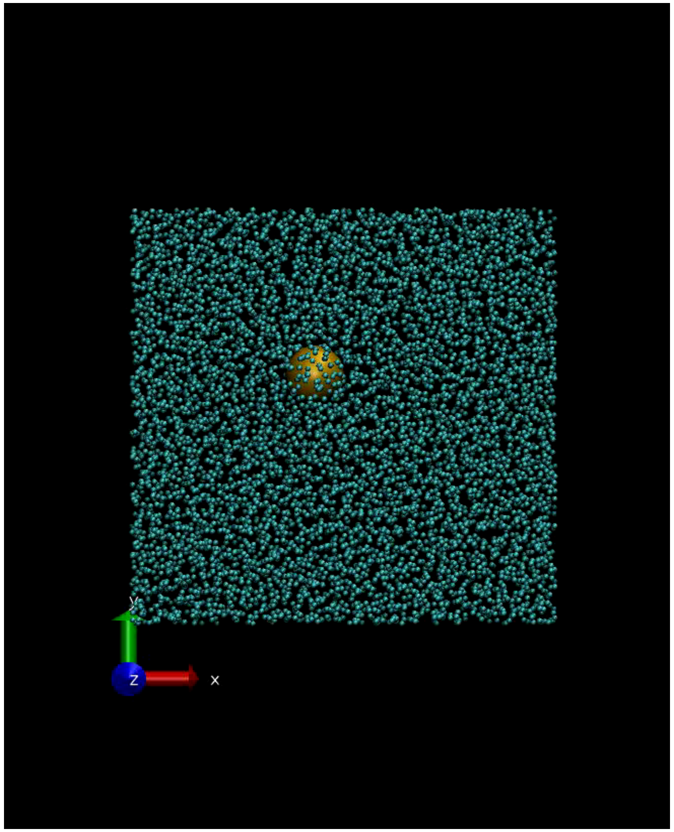
ICTS-NESP2015, Bengaluru, India

Molecular Dynamics Study on the Nonequilibrium Motion driven by an External Torque



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   2) Equilibrium vs nonequilibrium
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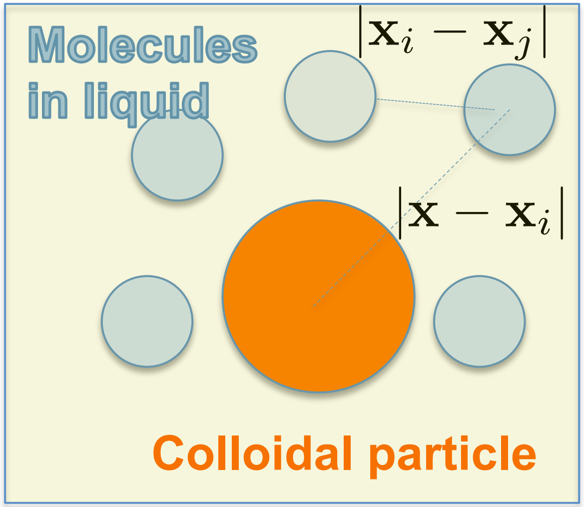
I. Molecular dynamics for nonequilibrium



Lenard-Jones Potential

$$V(r;\sigma,\epsilon) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$m\dot{\mathbf{v}}_i = -\sum_{j(\neq i)} \boldsymbol{\nabla}_i V(|\mathbf{x}_i - \mathbf{x}_j|;\epsilon,\sigma) - \boldsymbol{\nabla}_i V(|\mathbf{x} - \mathbf{x}_i|;\epsilon',\sigma')$$

$$-\gamma\mathbf{v}_i + \sqrt{D}\boldsymbol{\xi}_i(t)$$

Langevin thermostat $D = \gamma k_B T$

maintains the reservoir (liquid) in equilibrium at T

Colloidal particle

$$M\dot{\mathbf{v}} = -\nabla V + \mathbf{f}_{\rm nc} + \mathbf{f}_{\rm res}$$

$$= -k\mathbf{x} - \mathsf{A}\mathbf{x} - \sum_i \boldsymbol{\nabla} V(|\mathbf{x} - \mathbf{x}_i|;\sigma',\epsilon') \qquad \mathsf{A} = \begin{pmatrix} 0 & \alpha & 0 \\ \beta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$\alpha \neq \beta \rightarrow \nabla \times \mathbf{f}_{\rm nc} \neq 0$

torque

1st law of thermodynamics

$$\dot{E} = \dot{W} - \dot{Q} \qquad \left(E = \frac{M\mathbf{v}^2}{2} + \frac{k\mathbf{x}^2}{2}\right)$$

Work production rate

$$\dot{W} = \mathbf{v}\cdot\mathbf{f}_{nc} = -\mathbf{v}\cdot\mathsf{A}\cdot\mathbf{x}$$

Heat production rate into the reservoir

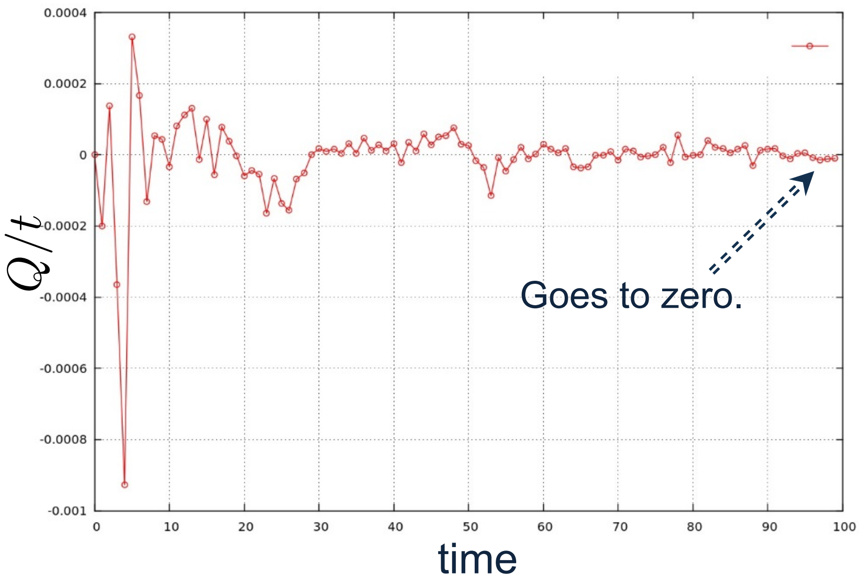
$$\dot{Q} = -\mathbf{v}\cdot\mathbf{f}_{\rm res}$$

Equilibrium vs Nonequilibrium

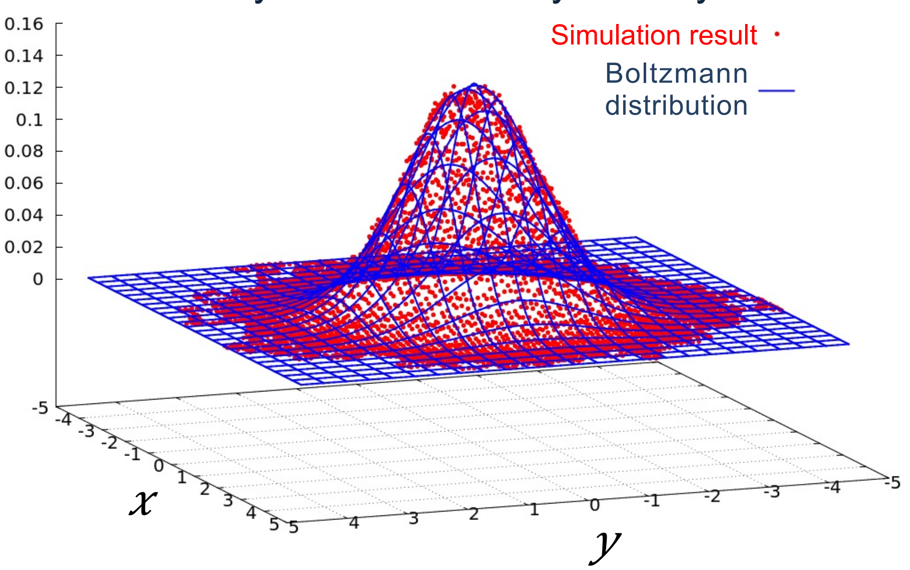
◆ Equilibrium $\alpha = \beta = 0,\ \mathbf{f}_{\mathrm{nc}} = 0,\ \dot{W} = 0$

$$\text{As } t \to \infty,\quad \langle \dot{E} \rangle = -\langle \dot{Q} \rangle \to 0$$

$$P(x,y) \propto e^{-(x^2+y^2)/(2k_B T)} \quad \text{(Boltzmann)}$$



The steady-state Probability Density function



◆ Nonequilibrium $\alpha \neq \beta, \quad \dot{W} \neq 0$

$$\text{As } t \to \infty \text{ (nonequilibrium steady state, NESS)}$$

$$\langle \dot{E} \rangle = \langle \dot{W} \rangle - \langle \dot{Q} \rangle \to 0, \quad \langle \dot{W} \rangle = \langle \dot{Q} \rangle > 0$$

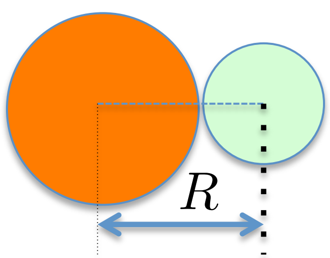
- ✓ Non-Boltzmann NESS
- ✓ Incessant production of work, heat, total entropy (EP)
- ✓ Jarzynski equality
- ✓ Fluctuation theorems → irreversibility, inequality (2^{nd} law)
- ✓ Hatano-Sasa relation for excess entropy (transient,non-adiabatic)
- ✓ Housekeeping EP (time-persistent, adiabatic)
- ✓ Breakage of detailed balance
- ✓ Nonzero NESS current in phase space
- ✓ Large deviation nature for long time for work, heat, EP
- ✓ Initial-memory everlasting in heat distribution
- ✓ etc

- ❑ Theory/simulation: Langevin equation, master equation, etc
- ❑ Experiment: small-system in optical trap, electric circuit, etc
- ❑ MD simulation: not many studies

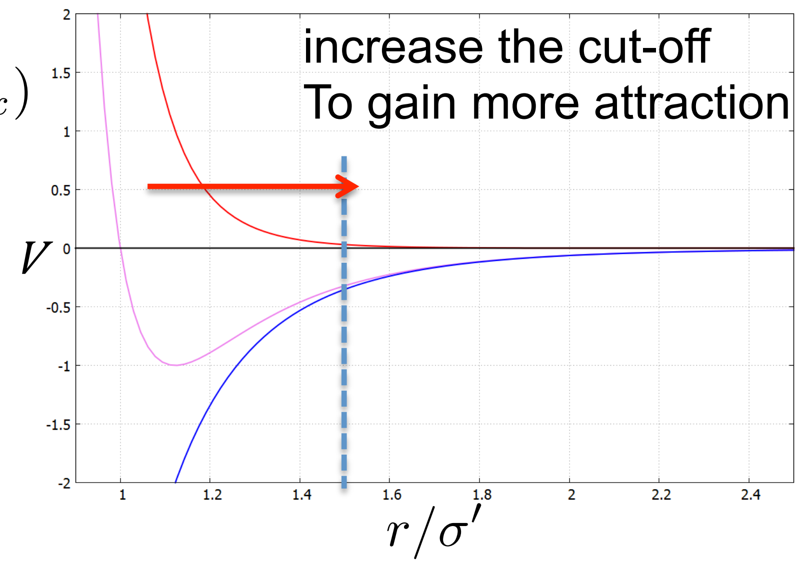
II. Preparation for overdamped limit

- To mimic many experiments in overdamped limit
- To compare with theoretical results from the overdamped Langevin equation

Overdamped limit $\dfrac{\gamma_c}{M} \gg \dfrac{k}{\gamma_c} \quad (\tau_p \ll \tau_x)$



The larger R, the larger γ_c.



Stokes' relation $\gamma_c = 4\pi\eta R$

Need to increase $\sigma' \propto R$

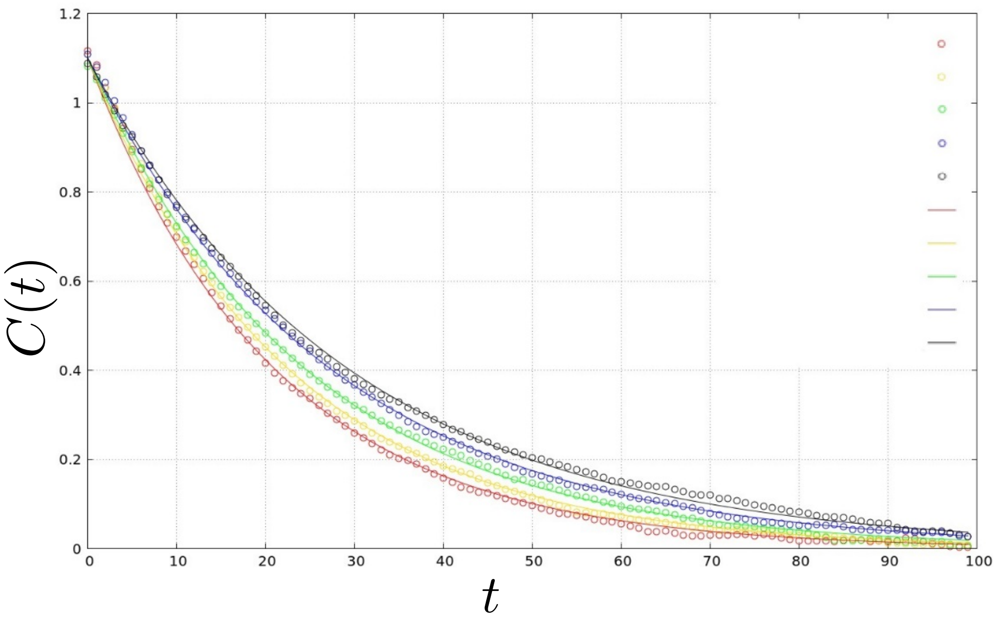
$r_{\text{cut-off}} = 2.2\sigma' \quad \text{(water)}$

Auto-correlation function for the position in time, from the Langevin equation

$$C(t) = \langle x(t)x(0)\rangle = \langle x(0)^2\rangle e^{-kt/\gamma_c}, \quad \text{for } \mathbf{f}_{\text{nc}} = 0$$

$$= \frac{k_B T}{k} e^{-kt/\gamma_c}, \quad \text{for initial equilibration}$$

$$\sigma' = 1.000(red), 1.125(yellow), 1.150(green), 1.275(blue), 1.500(black)$$

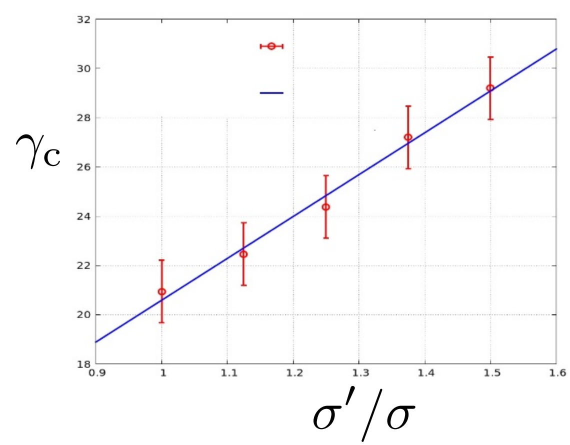


$$T = 1.1, \ M = 10 \ \ (k_B = k = m = 1)$$

$$\text{Fitting to} \ \ C(t) = ae^{-t/b}$$

$$a \simeq 1.1 \qquad b = \gamma_c$$

σ'/σ	γ_c	γ_c/M	k/γ_c
1.000	20.9463	2.09463	0.04774
1.125	22.4648	2.24648	0.04451
1.250	24.3773	2.43773	0.04102
1.375	27.2066	2.72066	0.03676
1.500	29.1974	2.91974	0.03425



Stokes' law confirmed

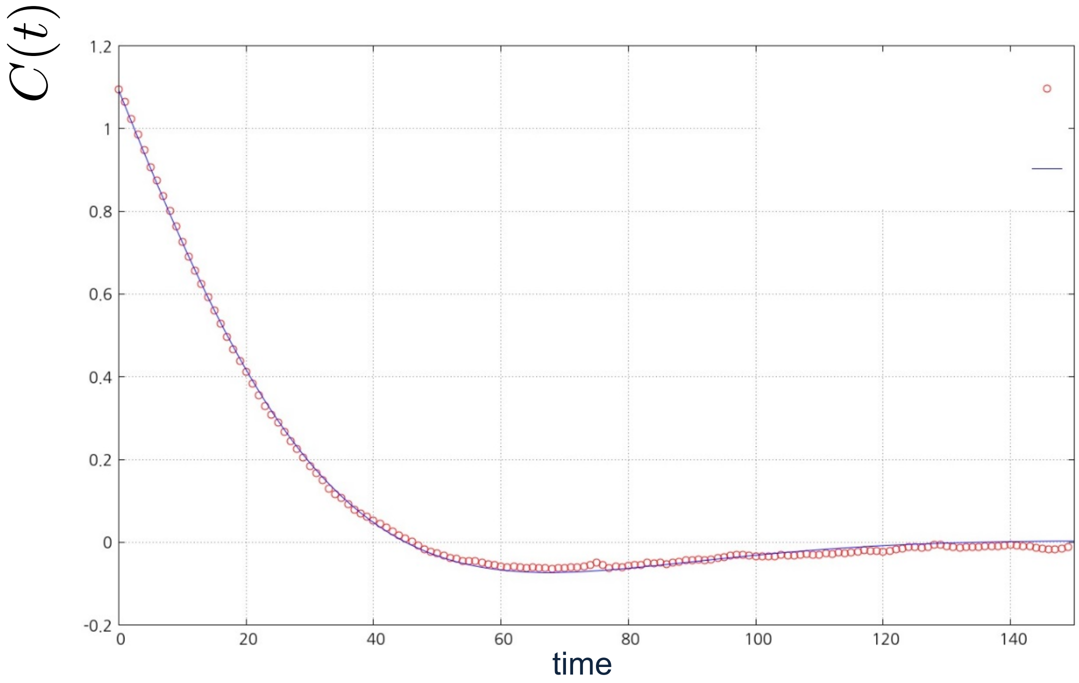
$$\gamma_c = 4\pi\eta R \propto \sigma'$$

III. Nonequilibrium measurements

$$M = 10,\ \sigma' = 1.5\ (\gamma_{\rm c} \simeq 28.19)$$
$$\text{setting}\ (m = k = \gamma = \sigma = \epsilon = 1,\ T = 1.1,\ r_{\rm cut-off} = 2.2)$$

Auto-correlation function for nonzero $\mathbf{f}_{\rm nc}$

From the Langevin equation $$C(t) = C(0) e^{-kt/\gamma_c} \cos\left[\frac{\sqrt{-\alpha\beta}t}{\gamma_{\rm c}}\right]$$



$$\alpha = -\beta = 1,\ k = 1,\ T = 1.1$$

$$C(0) \simeq 1.092,\ \gamma_c \simeq 28.67$$

Good agreement

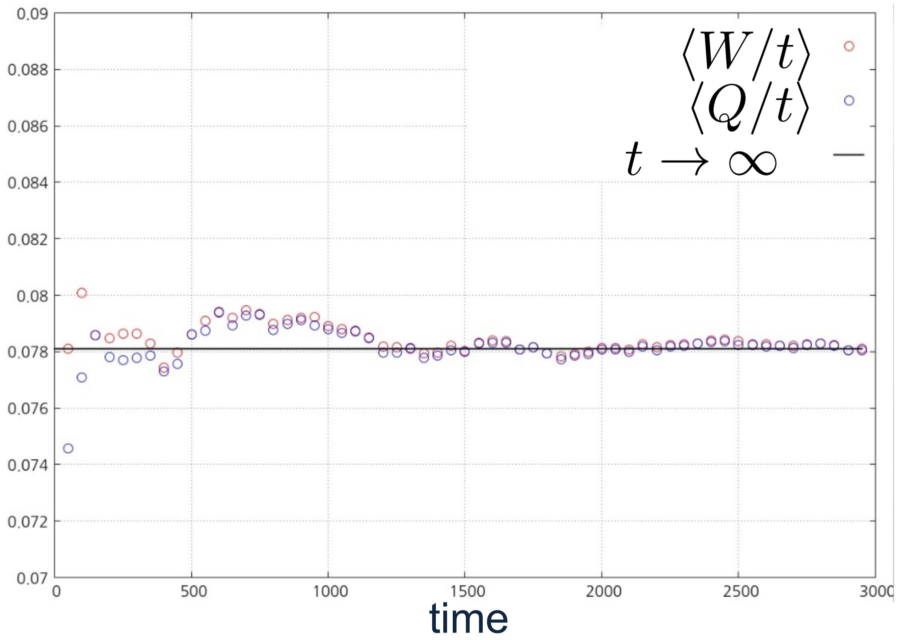
Work and heat production rates

Overdamped Langevin equation
C.Kwon, J.D. Noh, H. Park, PRE, 2011

$$\langle W/t \rangle = \langle Q/t \rangle = \frac{(\alpha - \beta)^2}{2k\gamma_c} k_B T$$

$$= \frac{2.2}{\gamma_c}$$

for $k = k_B = \alpha = -\beta = 1, \; T = 1.1$

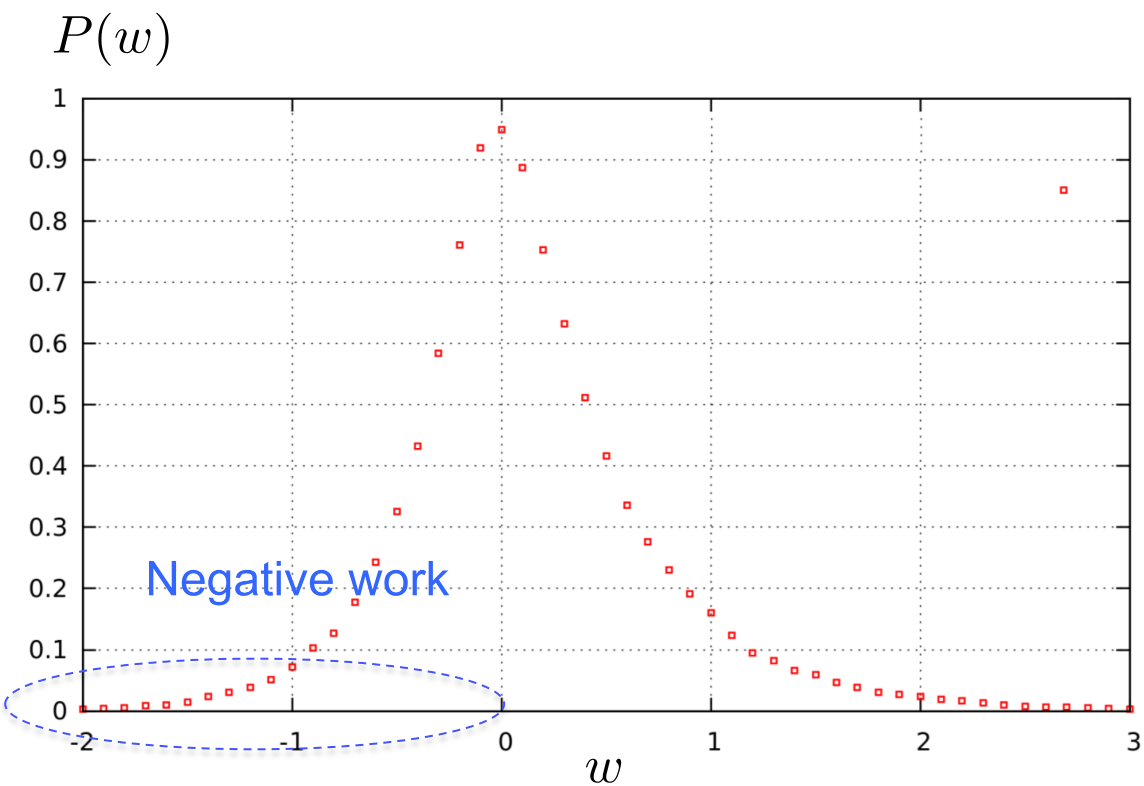


Reproducing successfully

$$\gamma_c \simeq 28.17$$

Distribution for work fluctuations

$$P(w),\ w = W/t = -\frac{1}{t}\int_0^t dt' \mathbf{v}\cdot \mathsf{A}\cdot \mathbf{x}$$



$$k = 1,\ \alpha = -\beta = 1,\ T = 1.1$$

at $t = 1$

$$\langle w \rangle = 0.1586$$

For large t, $P(w) \sim e^{-tf(w)}$

large deviation function $f(w)$

The average rate is positive, but the negative value is possible.
The violation of 2nd law is observable by chance, whlle $\langle W \rangle > 0$.

IV. Fluctuation theorems

Evans, Cohen, Morris (1993); Jarzynski (1997); Crooks (1998),; Kurchan (1998); Lebowitz and Spohn (1999); Speck and Seifert (2005); Esposito and Van den Broeck (2010); etc

$$\text{FT}\begin{cases}\text{time-accumulated } \mathcal{R} \text{ for } 0 < t < \tau \\ \text{initial PDF } \rho_0 \text{ \& arbitrary } \rho_\tau \text{ at } \tau\end{cases}$$

$$\mathcal{R} = -\beta^{-1}\ln\frac{\rho_\tau}{\rho_0} + Q$$

Infinitely many R's

(i) $\rho_0,\ \rho_\tau$: real PDFs, $R = T\Delta S_{tot}$ $\quad \Delta S_{\mathrm{tot}} = \Delta(-k_B \ln \rho) + Q/T$

(ii) $\rho_0,\ \rho_\tau$: EQ Boltzmann, $R = W - \Delta F$ (irreversible work)

(iii) $\rho_0,\ \rho_\tau$: uniform, $\infty - T$ dist, $R = Q$

Integral FT: $\langle e^{-\beta\mathcal{R}}\rangle = 1$ for all cases

Detailed FT: $\dfrac{P(\mathcal{R})}{P(-\mathcal{R})} = e^{\beta\mathcal{R}}$ for (ii), (iii)

$\langle R\rangle \geq 0$, 2nd law

$$\begin{cases}\text{Jarzynsky's equality: } \langle e^{-\beta(W-\Delta F)}\rangle = 1 \\ \text{Crooks' FT: } \dfrac{P(W)}{P(-W)} = e^{\beta(W-\Delta F)}\end{cases}$$

The initial PDF is important for FT!

EQ

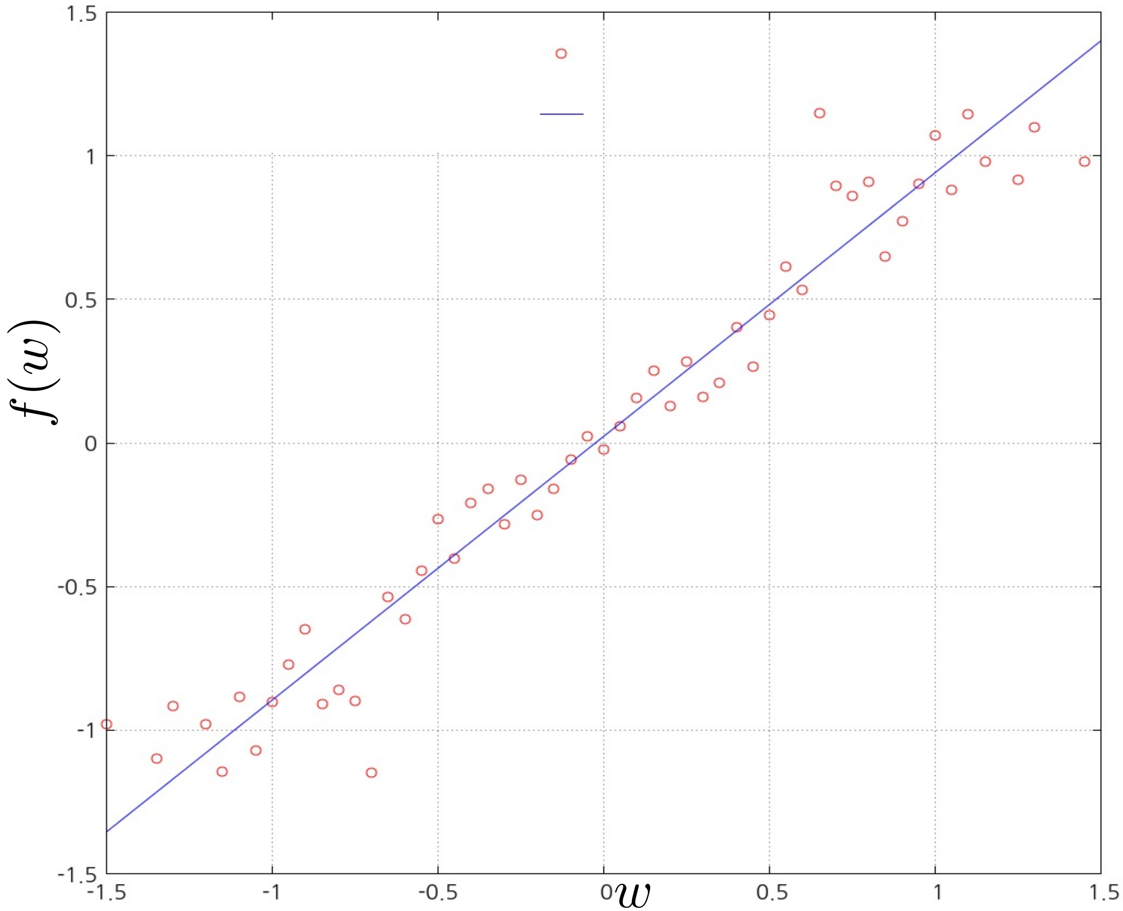
NESS

$\alpha = \beta = 0$ $t = 0$ $\alpha, \beta \neq 0$ $t = \tau$

waiting for a sufficient time longer than relaxation time $\sim \gamma_c / k$

$\Delta F = 0$

Expect the FT for work



$$f(w) = \frac{1}{\tau} \ln \frac{P(w)}{P(-w)}$$

$$= w$$

Confirmed successfully

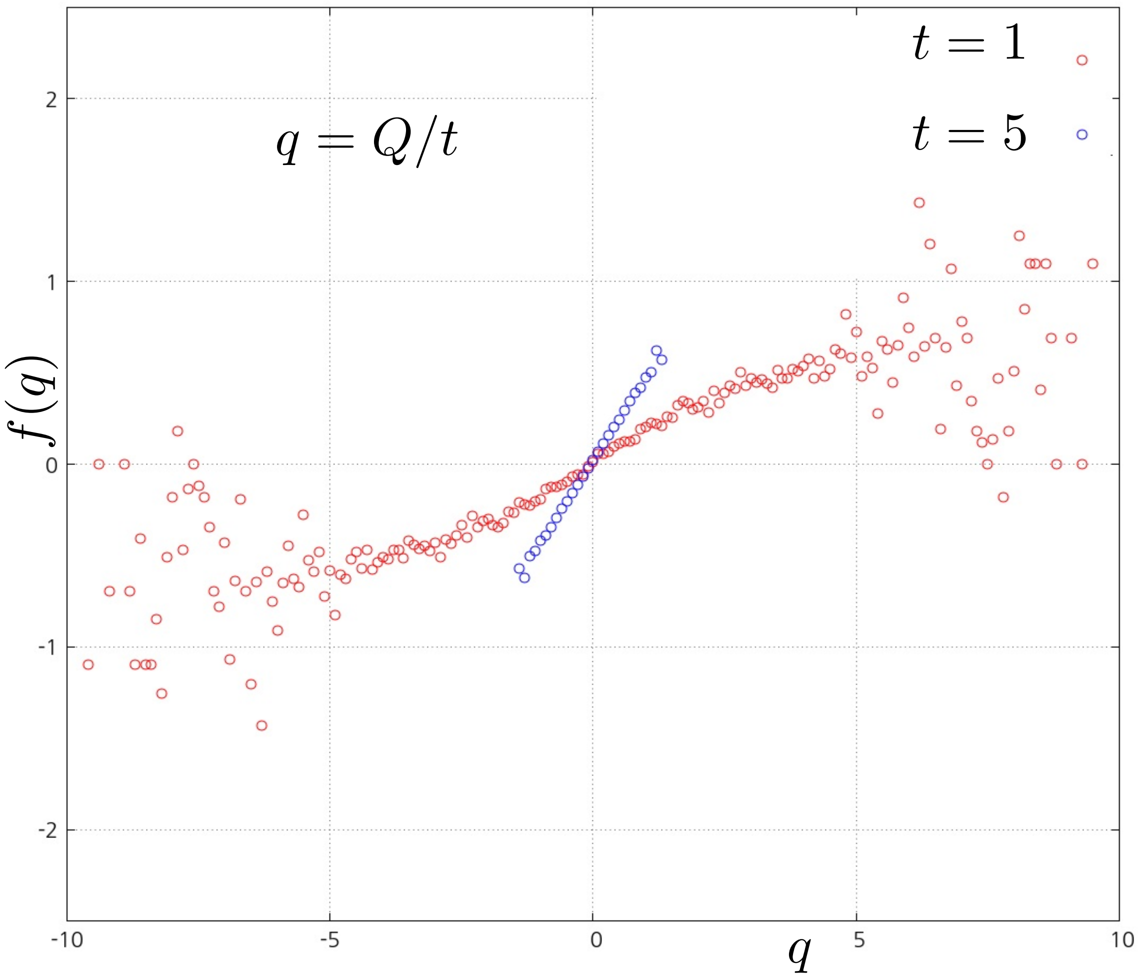
For large t, $Q \simeq W \propto t$. Does FT hold approximately?

$$Q = W - \Delta E$$

$|\Delta E| \to large$

for large initial or final energy

for unbound energy



FT holds near the center as time increases, while It deviates severely in the tail.

Initial-memory everlasting In heat distribution.

(moving potential)

Zon and Cohen, PRE, PRL (2003); Lee,Kwon, Park, PRE, JSTM (2013); Kim, Kwon, Park, PRE (2014)

V. Summary

- We used the MD simulation to study the nonequilibrium motion of a colloidal particle in a liquid driven out of equilibrium by an external torque.
- We designed the MD simulation to mimic an experiment in the overdamped limit.
- We compare the results with those obtained from the Langevin equation and found the two approaches to be in good agreement.
- We confirmed the (Crooks) FT for work and observed the FT for heat to hold only near the center of the range of heat.

Collaborators

Fluctuation Theorem, NEQ Entropy production, FDR violation, Feedback control, information thermodynamic, etc

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FDR violation

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Large deviation
Heat fluctuation
Multi reservoirs

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Information engine

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Experiment
FT for colloidal Particle In optical tweezers

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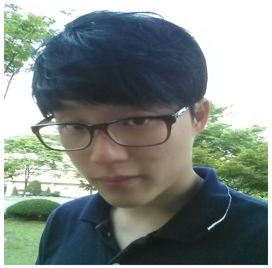

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Multiplicative noise

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