TALK

ENTROPIC PULLING AND DIFFUSION DIODE EFFECTS IN SYSTEMS WITH COORDINATE-DEPENDENT DAMPING

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IISER PUNE

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Hydrodynamics of low-dimensional interacting systems : Advances, challenges, and future directions
June 2-13, YITP, Kyoto university, Japan

Outline

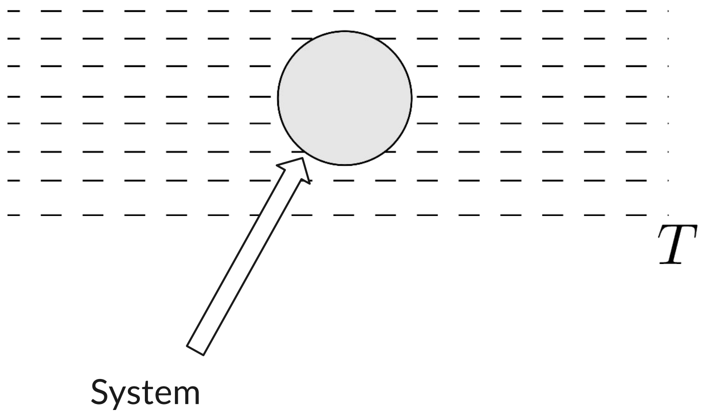
1. Langevin dynamics
    a. Recap and related works
    b. Basics of Itô process

2. Recent work
    a. Diffusion diode
    b. Entropic pulling of a chain

Langevin equation:

Constant damping coefficient

$$m\dot{v}_t = -\Gamma v_t + \sigma\eta(t), \quad \sigma = \sqrt{2\Gamma k_B T}$$



$\eta(t)$: Gaussian white noise

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

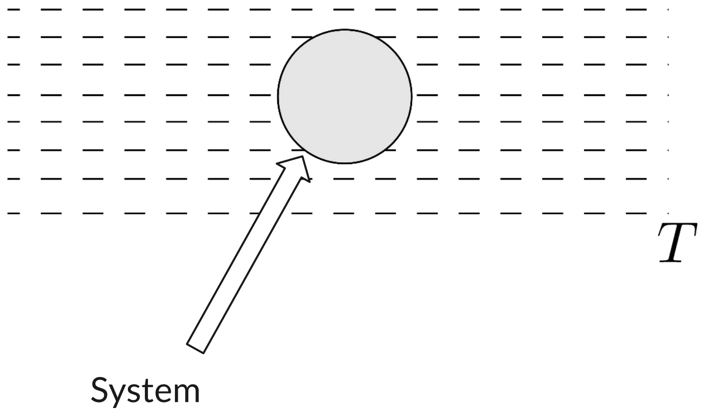
$$\langle \eta(t)\eta(t') \rangle = \delta(t - t')$$

Langevin equation:

Constant damping coefficient

$$m dv_t = -\Gamma v dt + \sigma dW_t, \quad \sigma = \sqrt{2\Gamma k_B T}$$

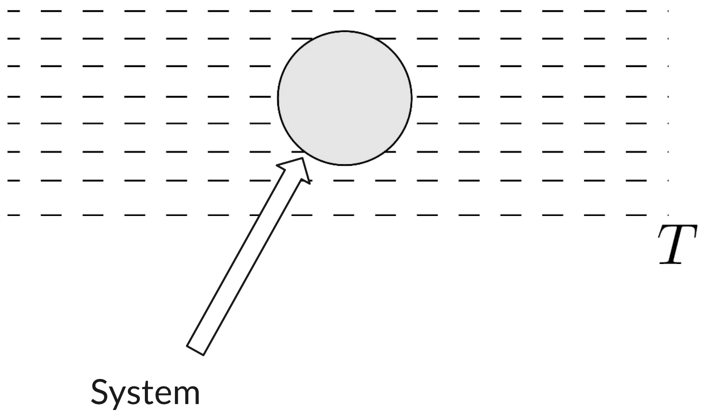
$$dW_t = \eta(t) dt$$



$\color{red}{W_t}$: Wiener process

Recap of Langevin dynamics

Langevin equation:



$$m dv_t = -\Gamma v dt + \sigma dW_t, \quad \sigma = \sqrt{2\Gamma k_B T}$$

K_t : Kinetic energy

$$K_t = \frac{1}{2} m v_t^2$$

Itô process

Using Itô lemma

$$dK_t = [-2\frac{\Gamma}{m}K_t + \frac{\sigma^2}{2m}]dt + \sigma\sqrt{\frac{2K_t}{m}}dW_t$$

Initial condition : $K_0 = \frac{1}{2}mv_0^2$

Itô process

Using Itô lemma

$$dK_t = [-2\frac{\Gamma}{m}K_t + \frac{\sigma^2}{2m}]dt + \sigma\sqrt{\frac{2K_t}{m}}dW_t \quad , \quad K_0 = 0$$

Using Itô lemma

Itô process

$$dK_t = [-2\frac{\Gamma}{m}K_t + \frac{\sigma^2}{2m}]dt + \sigma\sqrt{\frac{2K_t}{m}}dW_t \quad , \quad K_0 = 0$$

$$dK_t = \frac{\sigma^2}{2m}dt$$

Particle is pushed towards positive kinetic energy : Effect of thermal fluctuations

Using "normal" calculus

Stratonovich calculus

$$dK_t = -2\frac{\Gamma}{m}K_t dt + \sigma\sqrt{\frac{2K_t}{m}} \circ dW_t \qquad , \qquad K_0 = 0$$

$$\Downarrow$$

$$dK_t = 0$$

Absorbing state: the particle continuous to stay at rest.

Reference : Itô versus Hänggi–Klimontovich : Carlos Escudero and Helder Rojas

Using "normal" calculus

Stratonovich calculus

$$dK_t = -2\frac{\Gamma}{m}K_t dt + \sigma\sqrt{\frac{2K_t}{m}} \circ dW_t \quad , \quad K_0 = 0$$

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Absorbing state: the particle continuous to stay at rest. No effect of thermal fluctuation.

Using "normal" calculus

Stratonovich calculus

$$dK_t = -2\frac{\Gamma}{m}K_t dt + \sigma\sqrt{\frac{2K_t}{m}} \circ dW_t \qquad , \qquad K_0 = 0$$

$$\Downarrow$$

$$dK_t = 0$$

Absorbing state: the particle continuous to stay at rest. No effect of thermal fluctuation.

Unphysical !!

Chain rule corresponding to Anti- Itô Interpretation

Anti-Itô calculus

$$dK_t = -2\frac{\Gamma}{m}K_t dt - \frac{\sigma^2}{2m}dt + \sigma\sqrt{\frac{2K_t}{m}} \bullet dW_t \;, \qquad K_0 = 0$$

$$\Downarrow$$

$$dK_t = -\frac{\sigma^2}{2m}dt$$

Push the particle to negative kinetic energy

Anti-Ito calculus

$$dK_t = -2\frac{\Gamma}{m}K_t dt - \frac{\sigma^2}{2m}dt + \sigma\sqrt{\frac{2K_t}{m}} \bullet dW_t \;, \qquad K_0 = 0$$

$$\Downarrow$$

$$dK_t = -\frac{\sigma^2}{2m}dt$$

Push the particle to negative kinetic energy

Unphysical !!

Summary

Interpretation	**SDE**	**Behavior if** $K_0 = 0$	**Physical Plausibility**	**Solution Type**
Itô	$dK_t = [-2\frac{\Gamma}{m}K_t + \frac{\sigma^2}{2m}]dt + \sigma\sqrt{\frac{2K_t}{m}}dW_t$	Positive kinetic energy	Realistic: thermal fluctuations induce motion	Unique strong global solution
Stratonovich	$dK_t = -2\frac{\Gamma}{m}K_t dt + \sigma\sqrt{\frac{2K_t}{m}} \circ dW_t$	Absorbing state	Unphysical: particle stuck at rest	Infinitely many spurious solutions
Anti-Itô	$dK_t = -2\frac{\Gamma}{m}K_t dt - \frac{\sigma^2}{2m}dt + \sigma\sqrt{\frac{2K_t}{m}} \bullet dW_t$	Negative kinetic energy	Unphysical: negative/complex energy possible	No meaningful solution

The authors further discuss :

- Kinetic energy for Relativistic Brownian particle under three interpretations.
- Kinetic energy for two particle system in a heat bath under three interpretations

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- Kinetic energy for Relativistic Brownian particle under three interpretations.
- Kinetic energy for two particle system in a heat bath under three interpretations

- The authors show that Anti-Itô and Stratonovich description does not give physical solution.

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PAPER

Fluctuation-dissipation relation, Maxwell-Boltzmann statistics, equipartition theorem, and stochastic calculus

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Keywords: Forward stochastic differential equations, backward stochastic differential equations, Malliavin calculus, uniqueness of solution, multiplicity of solutions, Itô vs Stratonovich dilemma

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Topical Review

Brownian motion near a wall: the dilemma of Itô or Stratonovich

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Recap of Langevin dynamics

Langevin equation:

In presence of potential $U(x)$

$$m\dot{v}_t = -\Gamma v_t - \frac{\partial U(x)}{\partial x} + \sigma\eta(t), \quad \sigma = \sqrt{2\Gamma k_B T}$$

$$\Big\Downarrow \quad \text{Overdamped limit} \quad m\dot{v}_t \approx 0$$

$$\frac{dx}{dt} = -\frac{1}{\Gamma}\frac{\partial U(x)}{\partial x} + \sqrt{\frac{2k_BT}{\Gamma}}\eta(t)$$

- Experiments have shown that the diffusivity of a BP decreases (or damping increases) as it comes near to a wall/interface.

- Diffusivity (and damping) can becomes coordinate/ state dependent.

Overdamped Langevin equation:

$$\frac{dx}{dt} = -\frac{1}{\Gamma(x)}\frac{\partial U}{\partial x} + \sqrt{2D(x)}\eta(t)$$

Local Stokes-Einstein relation

$$D(x) = \frac{k_B T}{\Gamma(x)}$$

Overdamped Langevin equation:

ITÔ PROCESS

$$\frac{dx}{dt} = -\frac{1}{\Gamma(x)}\frac{\partial U}{\partial x} + \sqrt{2D(x)}\eta(t)$$

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Overdamped Langevin equation:

$$\frac{dx}{dt} = -\frac{1}{\Gamma(x)}\frac{\partial U}{\partial x} + \sqrt{2D(x)}\eta(t)$$

$$\Big\Downarrow \quad \text{Fokker Planck}$$

$$\frac{\partial}{\partial t}\rho(x,t) = -\frac{\partial}{\partial x}[-\frac{1}{\Gamma(x)}\frac{\partial U(x)}{\partial x}\rho(x,t) - \frac{\partial}{\partial x}(D(x)\rho(x,t))]$$

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Overdamped Langevin equation:

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$$\frac{\partial}{\partial t}\rho(x,t) = -\frac{\partial}{\partial x}[\underbrace{-\frac{1}{\Gamma(x)}\frac{\partial U(x)}{\partial x}\rho(x,t)}_{\text{Drift current}} - \overbrace{\frac{\partial}{\partial x}(D(x)\rho(x,t))}^{\text{Diffusion current}}]$$

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$$\xrightarrow[J(x,t)=0]{\text{Equilibrium}}$$

$$\rho(x) = C\frac{D_0}{D(x)}\exp(-\frac{U(x)}{k_B T})$$

Itô distribution

Itô distribution: $\rho(x) = C\frac{D_0}{D(x)}\exp(-\frac{U(x)}{k_BT})$

D_0 : Bulk Diffusivity

$D(x)$: State-dependent Diffusivity

Itô distribution: $\rho(x) = C\frac{D_0}{D(x)}\exp(-\frac{U(x)}{k_B T})$

Dimensionless density of states: $\Omega(x) = \frac{D_0}{D(x)}$

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Dimensionless density of states: $\Omega(x) = \frac{D_0}{D(x)}$

Excess entropy

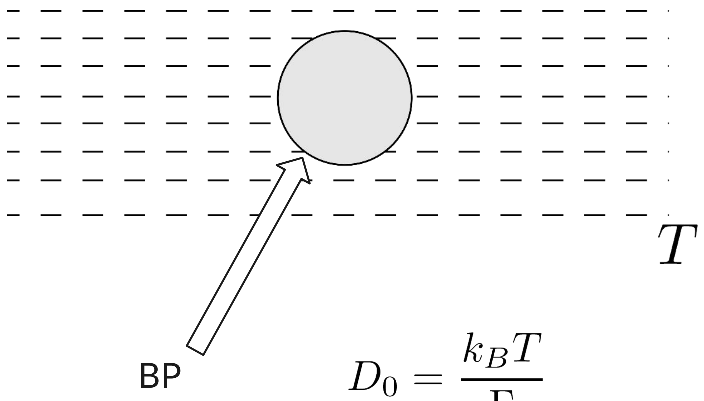
$$S(D(x)) = k_B \log\Omega(x) = k_B \log\frac{D_0}{D(x)}$$

Physical meaning ??

Langevin equation:

Constant damping coefficient

$$m\dot{v}_t = -\Gamma v_t + \sigma\eta(t), \quad \sigma = \sqrt{2\Gamma k_B T}$$



$$D_0 = \frac{k_B T}{\Gamma}$$

Langevin equation:

Constant damping coefficient

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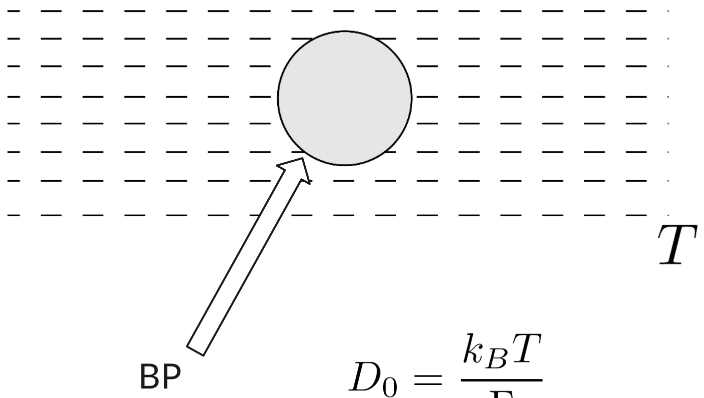

$$D_0 = \frac{k_B T}{\Gamma}$$

The velocity spread of BP after it has equilibrated : $\Delta v = \sqrt{\frac{k_B T}{m}}$

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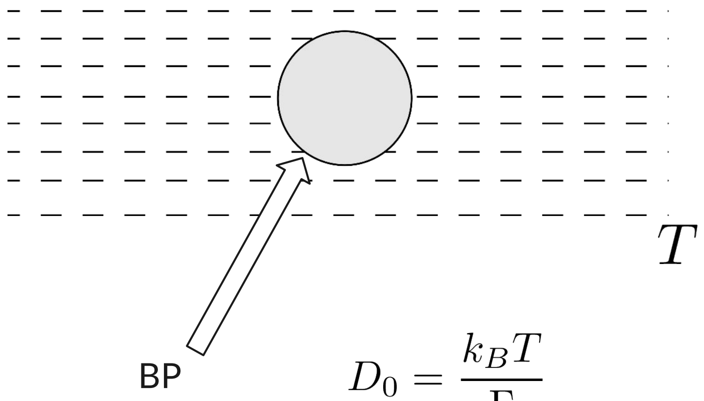

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The minimum average time BP takes to equilibrate : $\tau = \frac{m}{\Gamma}$

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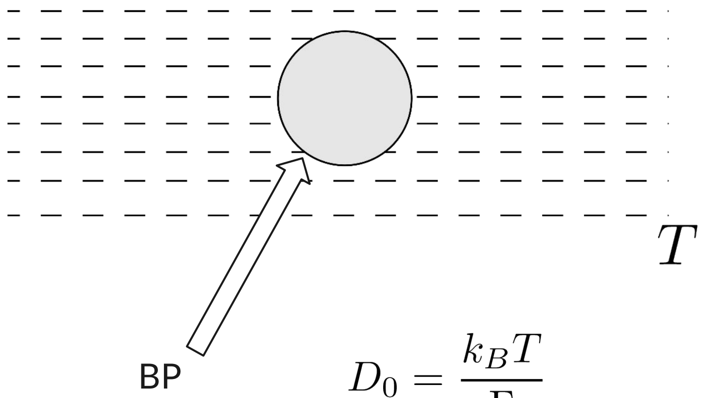

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The velocity spread of BP after it has equilibrated : $\Delta v = \sqrt{\frac{k_B T}{m}}$

The minimum average time BP takes to equilibrate : $\tau = \frac{m}{\Gamma}$

Corresponding uncertainty in position : $\Delta x = \Delta v \times \tau = \frac{\sqrt{m k_B T}}{\Gamma}$

$$\Delta x \times \Delta v = \frac{k_B T}{\Gamma} = D_0$$

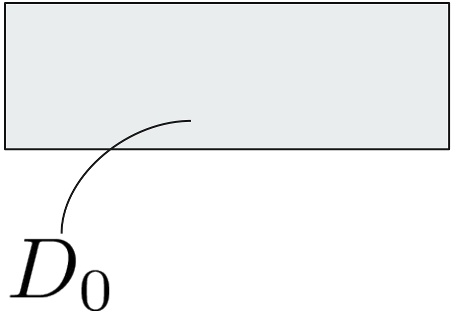
Minimum Phase space cell volume or cell size available to BP in Bulk: D_0

$$\Delta x \times \Delta v = \frac{k_B T}{\Gamma} = D_0$$

Minimum Phase space cell volume or cell size available to BP in Bulk: D_0

Classical analog to Planck's constant which sets lower bound to phase space volume

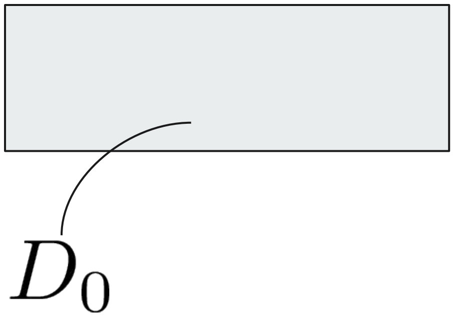
Minimum Phase space cell volume or cell size available to BP in Bulk: D_0



Minimum Phase space cell volume or cell size available to BP in Bulk: D_0

For a BP near interface, minimum phase space volume or cell size becomes : $D(x)$

$$D_0 \geq D(x)$$



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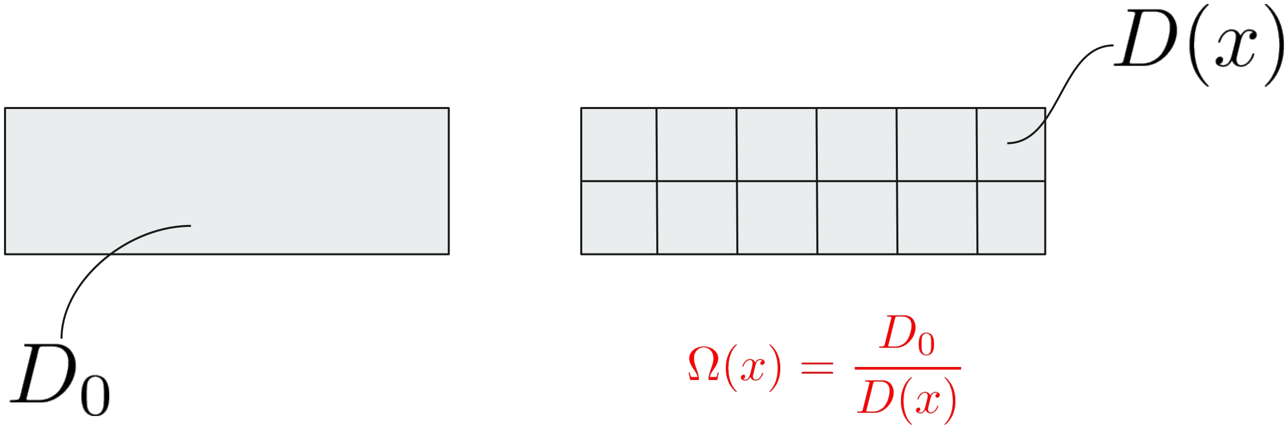
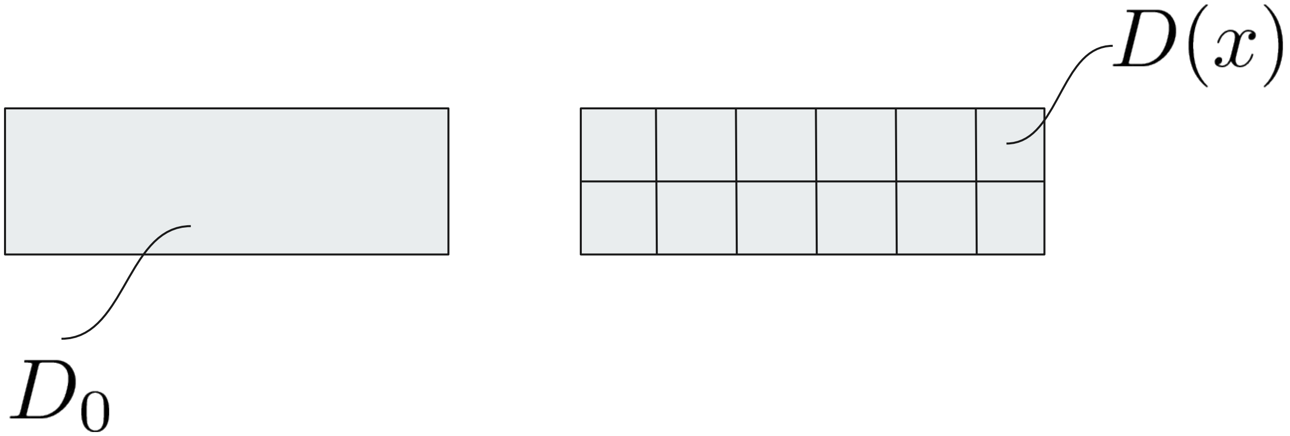


$$\Omega(x) = \frac{D_0}{D(x)}$$

Phase space perspective of the entropy term



$$D_0 \geq D(x)$$

$$\Omega(x) = \frac{D_0}{D(x)}$$

Micro-canonical Degeneracy

$$S(D(x)) = k_B \log \Omega(x)$$

Itô distribution:

$$\begin{aligned}\rho(x) &= C\frac{D_0}{D(x)}\exp\left(-\frac{U(x)}{k_BT}\right)\\ &= C\exp\left(-\frac{1}{k_BT}\left[U(x)-TS(D(x))\right]\right)\\ &= C\exp\left(-\frac{\mathcal{F}(x)}{k_BT}\right)\end{aligned}$$

$$\boxed{\mathcal{F}(x) = U(x) - TS(D(x))}$$

$$F_{ent}(x) = -\frac{d\mathcal{F}(x)}{dx} = T\frac{dS(D(x))}{dx} = -k_B T\frac{d}{dx} log D(x)$$

➔ Motion in direction of decreasing diffusivity.

Recent work

Physics Letters A 553 (2025) 130709

Contents lists available at ScienceDirect

Physics Letters A

journal homepage: www.elsevier.com/locate/pla

Letter

Entropic pulling and diffusion diode in an Itô process

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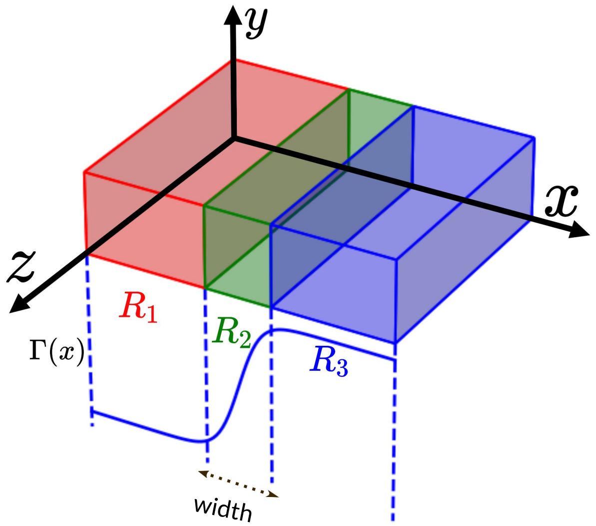
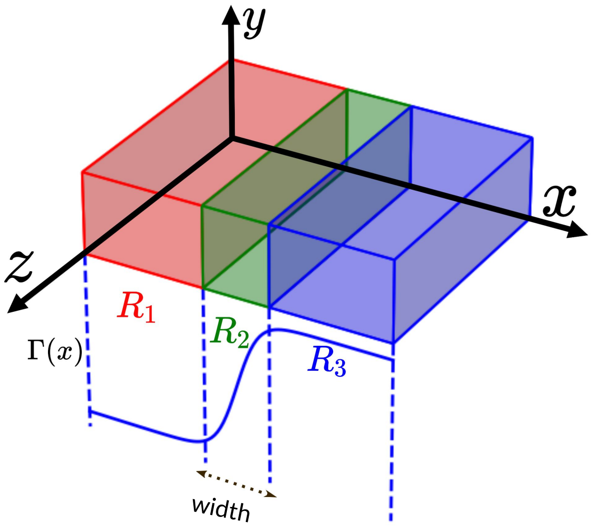
- Consider N Brownian particles confined inside a box in contact with a heat bath at temperature T.
- Box is divided into three cuboidal regions: R_1, R_2 and R_3.
- Regions R_1 and R_3 are geometrically identical

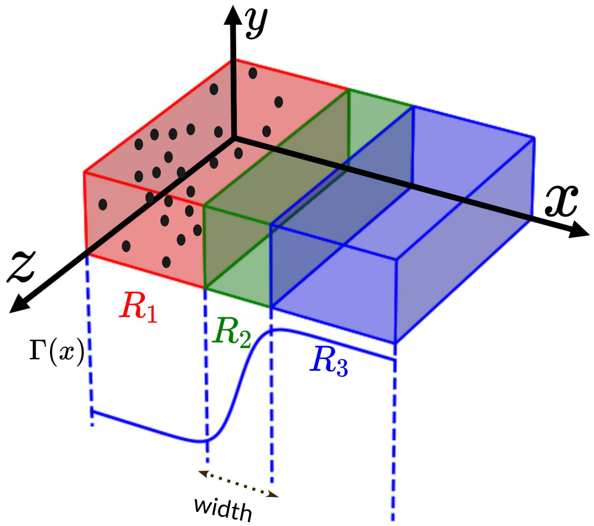


- Isotropic Coordinate dependent damping exists .
- Excluded volume interaction between particles
- Confining potential at boundaries .



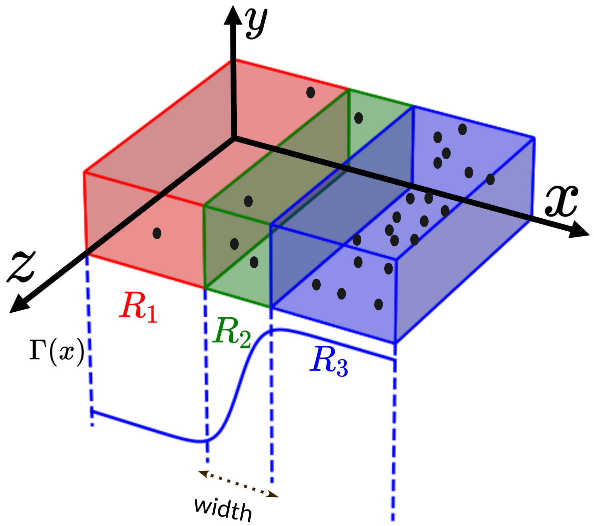
Case I

- Brownian particles are placed randomly in R_1 at start of simulation and allowed to evolve



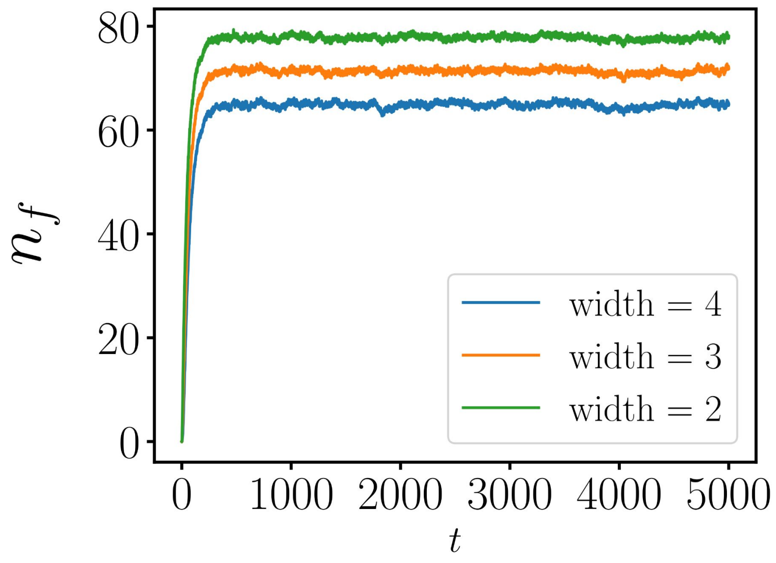
Case I

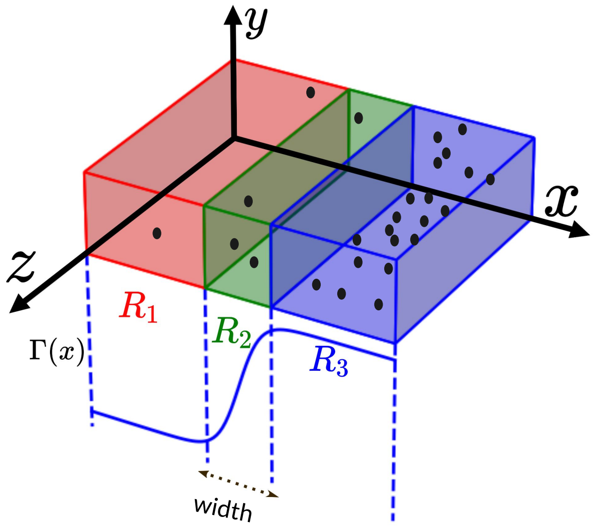
- Most of the particles reach R_3



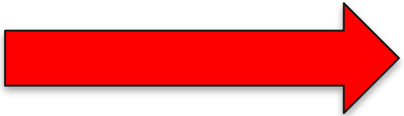
Case I

- Most of the particles reach R_3

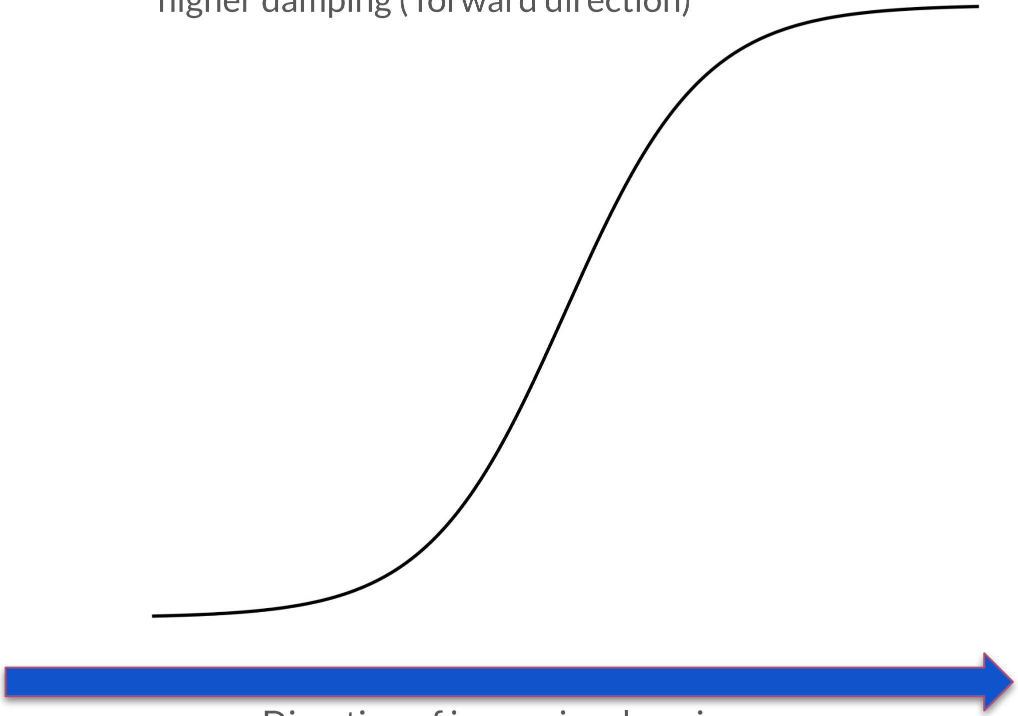




Mean occupation number of particles in R_3
for various widths of R_2



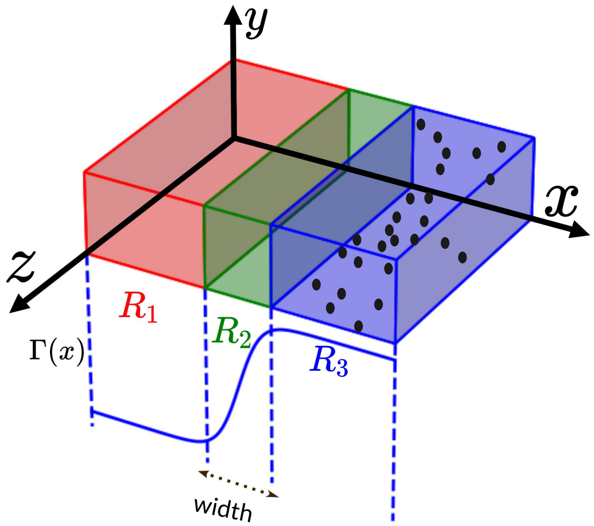
- Case I: Cooperation of particles motion in direction of higher damping (forward direction)



Direction of increasing damping

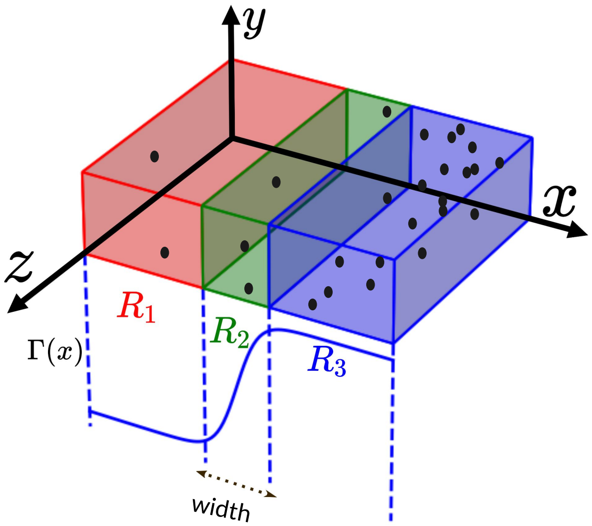
Case II

- Brownian particles are placed randomly in R_3 at start of simulation and allowed to evolve.

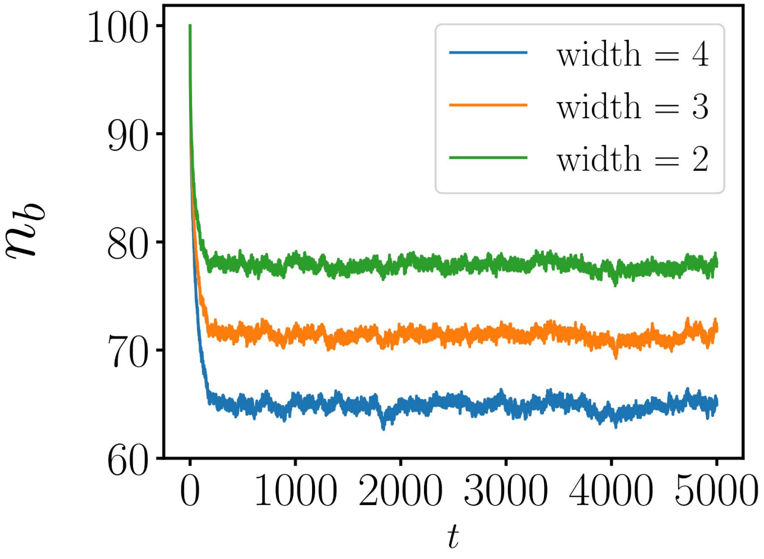


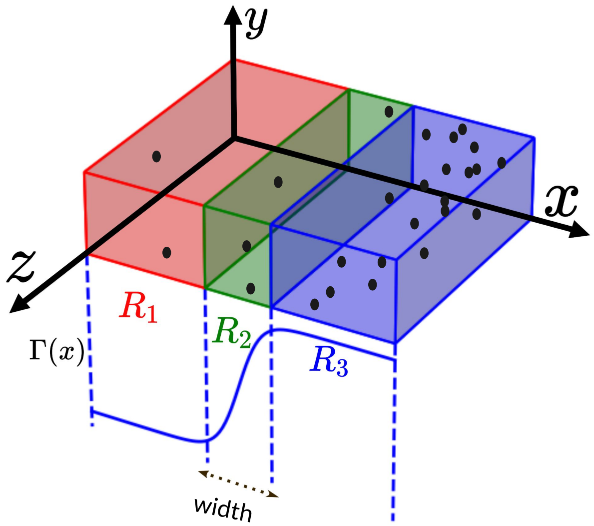
Case II

- Most of the particles are unable to cross via R_2.



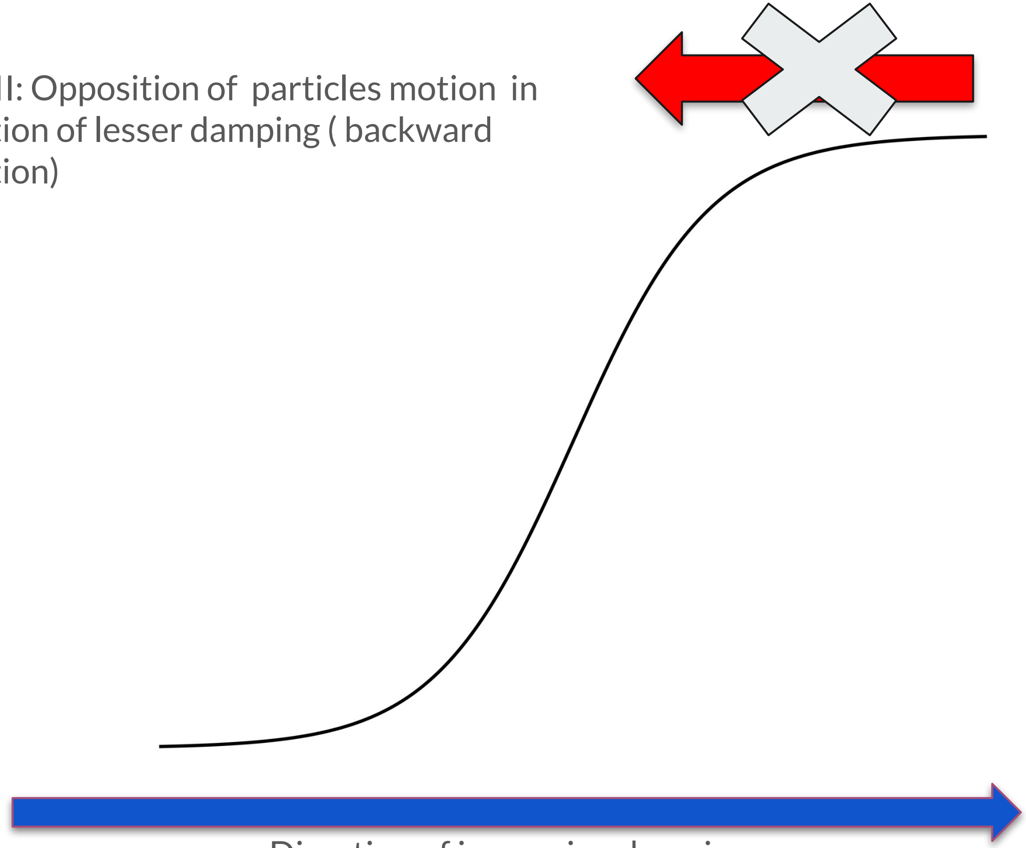
Case II





Mean occupation number of particles in R_3
for various widths of R_2

- Case II: Opposition of particles motion in direction of lesser damping (backward direction)

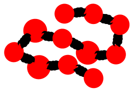


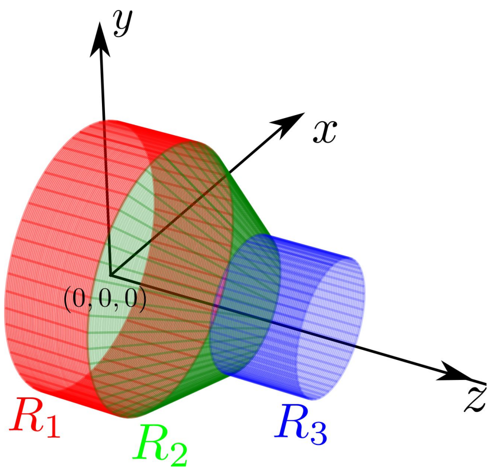
Direction of increasing damping

Conclusion

- Cooperation in particles motion towards regions of higher damping in presence of damping gradient.
- Opposition in particles motion towards regions of higher damping in presence of damping gradient.
- Entropic pulling in such systems can generate diffusion diode effect.

- Consider a Brownian chain confined inside a funnel like geometry in contact with a heat bath at temperature T.
- R_1 & R_3 : hollow right circular cylinder of radius $\mathcal{R}$ & r respectively.
- R_2 : frustum of cone with radii $\mathcal{R}$ & r , where $\mathcal{R} > r$.
- h : height of each region.





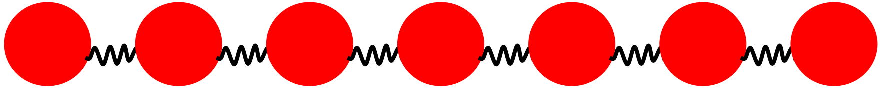
Case I

$$\Gamma_i = \frac{A}{\mathcal{S}_i}$$

$\mathcal{S}_i$: Cross- section radius

- Coordinate dependent damping experienced by a monomer in a region is inversely proportional to radius of circular cross-section in which it is present .

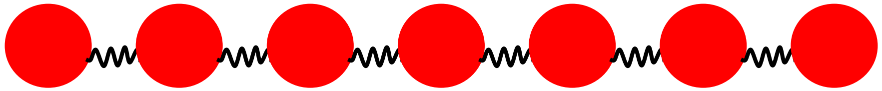
- Initial state of polymer : Linear unfolded configuration with chain lying on z axis in region R_1.



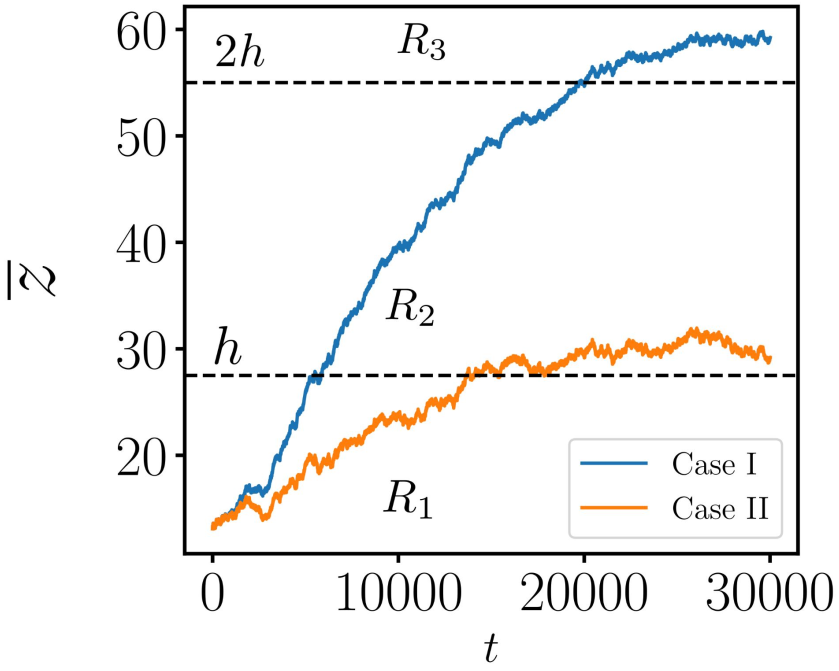
- Gaussian distributed random variable with zero mean, unit strength, no cross correlation.

Case II $\Gamma_i = constant$

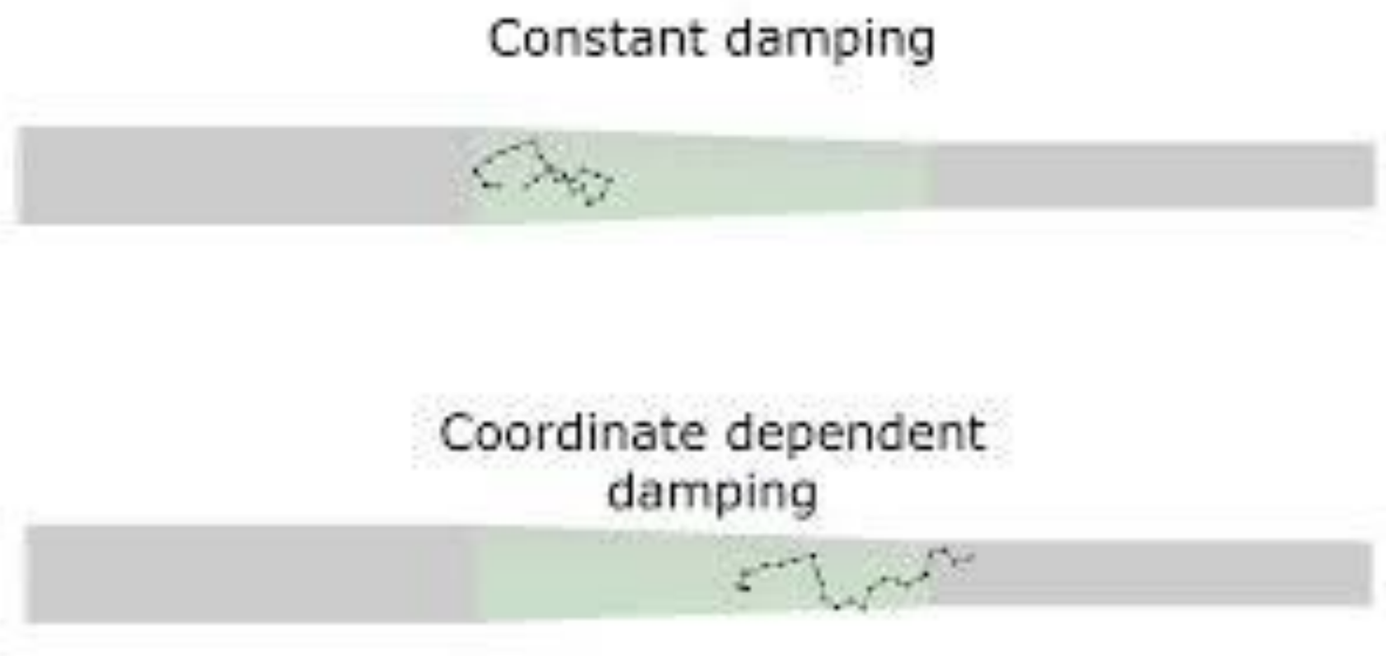
- Constant damping
- Initial state of polymer : Linear unfolded configuration with chain lying on z axis in region R_1.



- Random numbers used are same as in case I.



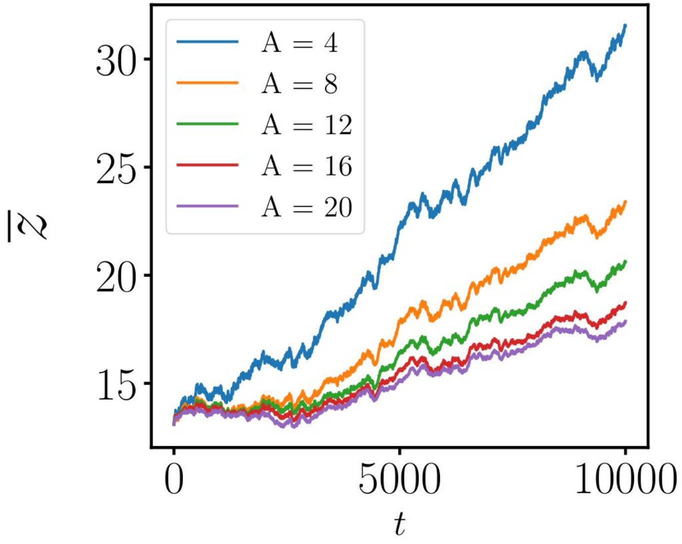
Average motion of centre of mass in z direction


Constant damping
Coordinate dependent damping

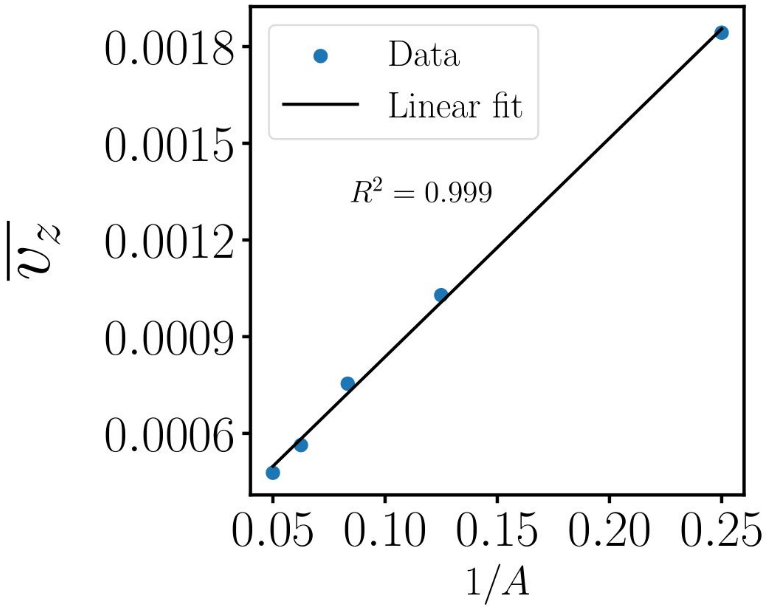
- Now, we remove regions R_1 & R_3.
- Only have region R_2. Compare transport for various damping strengths.

$$\Gamma_i = \frac{A}{\mathcal{S}_i}$$

A : Damping gradient strength



Variation of average position of centre of mass in z direction for various damping gradient.



1/A : Diffusivity gradient strength

Variation of average velocity of centre of mass in z direction for various diffusivity gradient.

Conclusion

- The Itô process facilitates the transport of mesoscopic object from a wider region to narrower one.

- This also means that the mesoscopic entity can remain trapped after reaching region of high damping.

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Single-molecule evidence of Entropic Pulling by Hsp70 chaperones

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Hsp70 chaperones are central components of the cellular network that ensures the structural quality of proteins. Despite crucial roles in processes such as protein disaggregation and protein translocation into organelles, their physical mechanism of action has remained hotly debated. To the best of our knowledge, no experimental data has directly proven any of the models proposed to date (Power Stroke, Brownian Ratchet, or Entropic Pulling) due to a lack of suitable methods. Here, we use nanopores, a powerful single-molecule tool, to investigate the mechanism of Hsp70s. We demonstrate that Hsp70s extract trapped polypeptide substrates from the nanopore by generating strong forces (equivalent to 46 pN over distances of 1 nm), that rely on the size of Hsp70. The findings provide unambiguous evidence of the Entropic Pulling mechanism, thus solving a long-standing debate, and proposing a potentially universal principle governing diverse cellular processes. Additionally, these results highlight the utility of biological nanopores for protein studies.

Authors : Rukes et al. (2024)

Thank you!!

Questions??