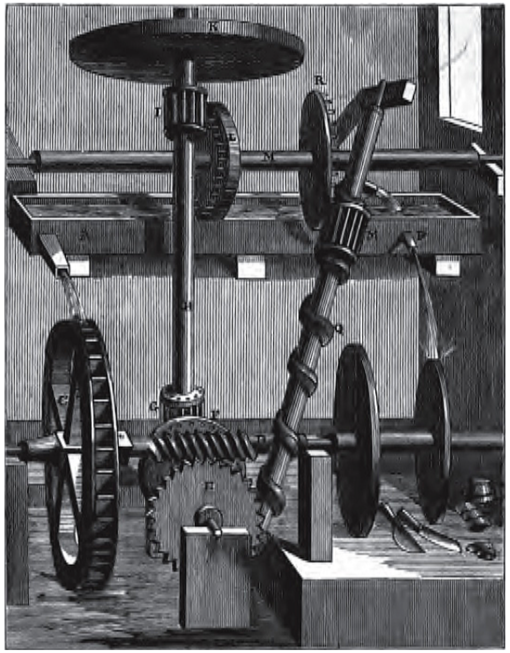
How thermodynamics becomes stochastic — a short exploration of recent advances in statistical physics

Ralf Eichhorn

NORDITA

The 2nd law of thermodynamics

$$\boxed{\Delta S \geq 0}$$

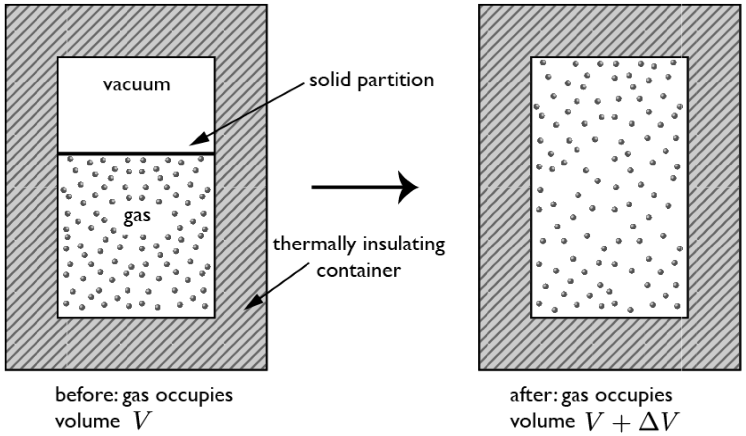


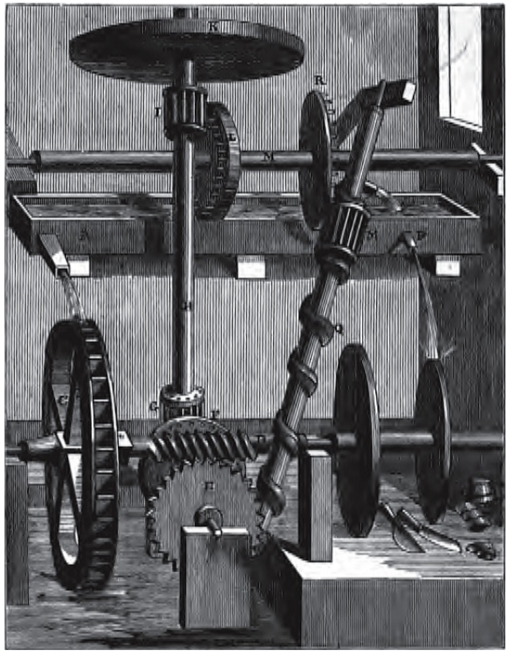
- forbids perpetual motion machines
- limits the efficiency of heat engines
- thermodynamic arrow of time
- ...

The 2nd law of thermodynamics

$$\Delta S \geq 0$$

An irreversible process: the (adiabatic) ***free expansion*** of an ideal gas





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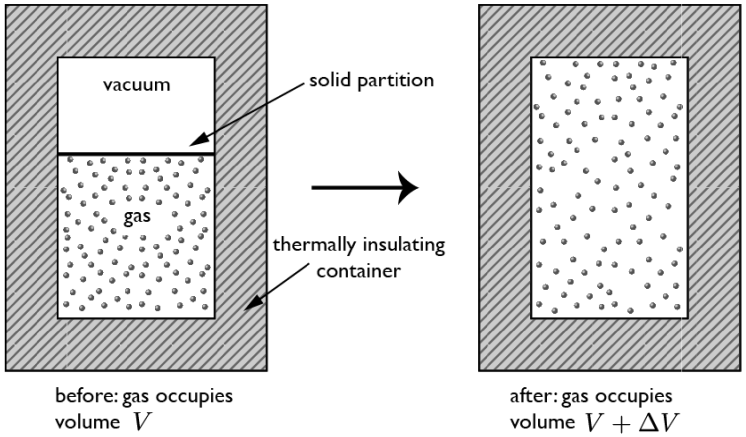

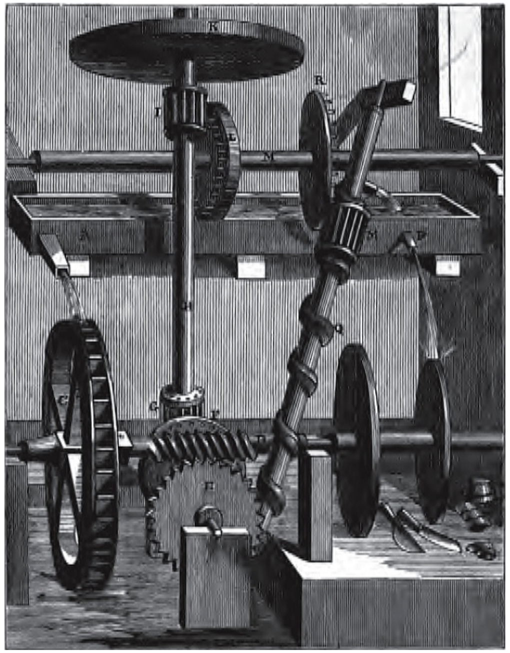

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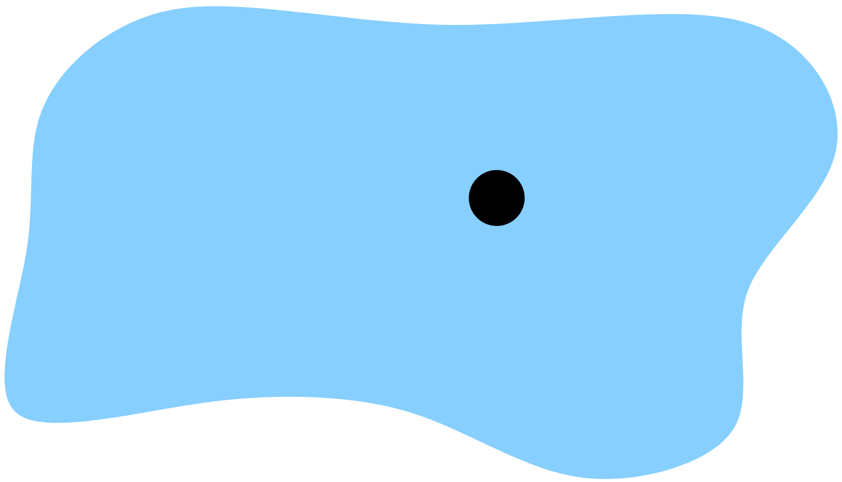
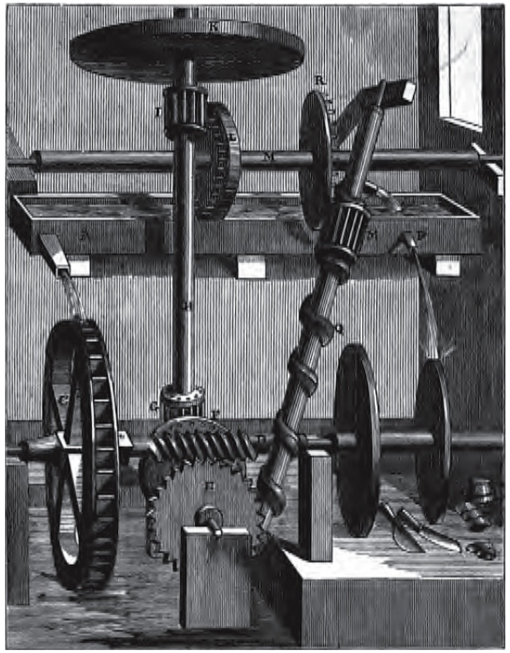


thermal fluctuations!



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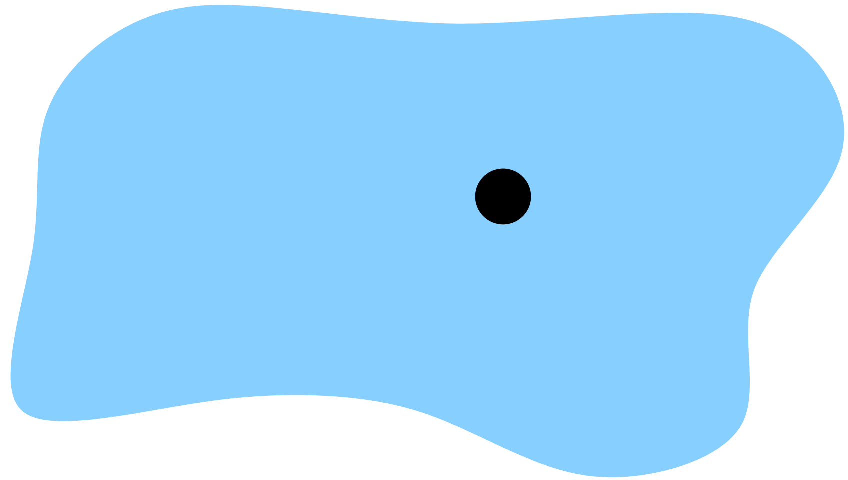
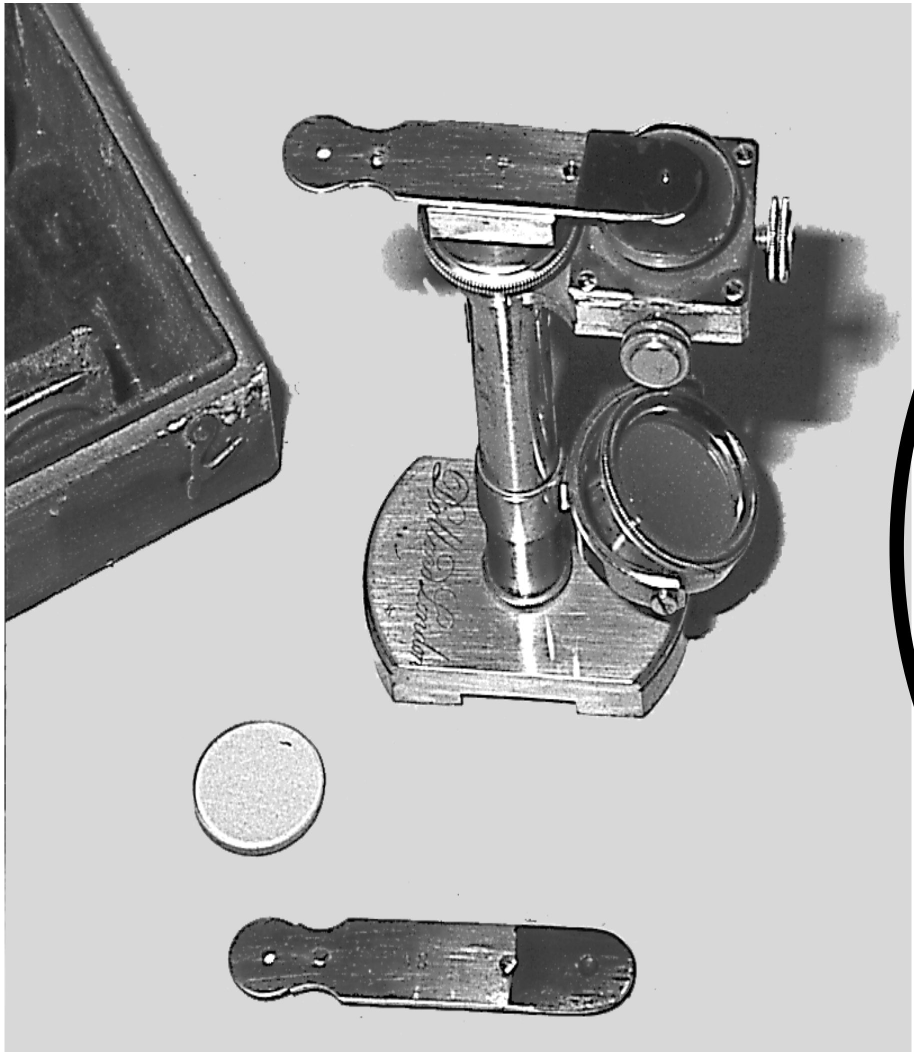


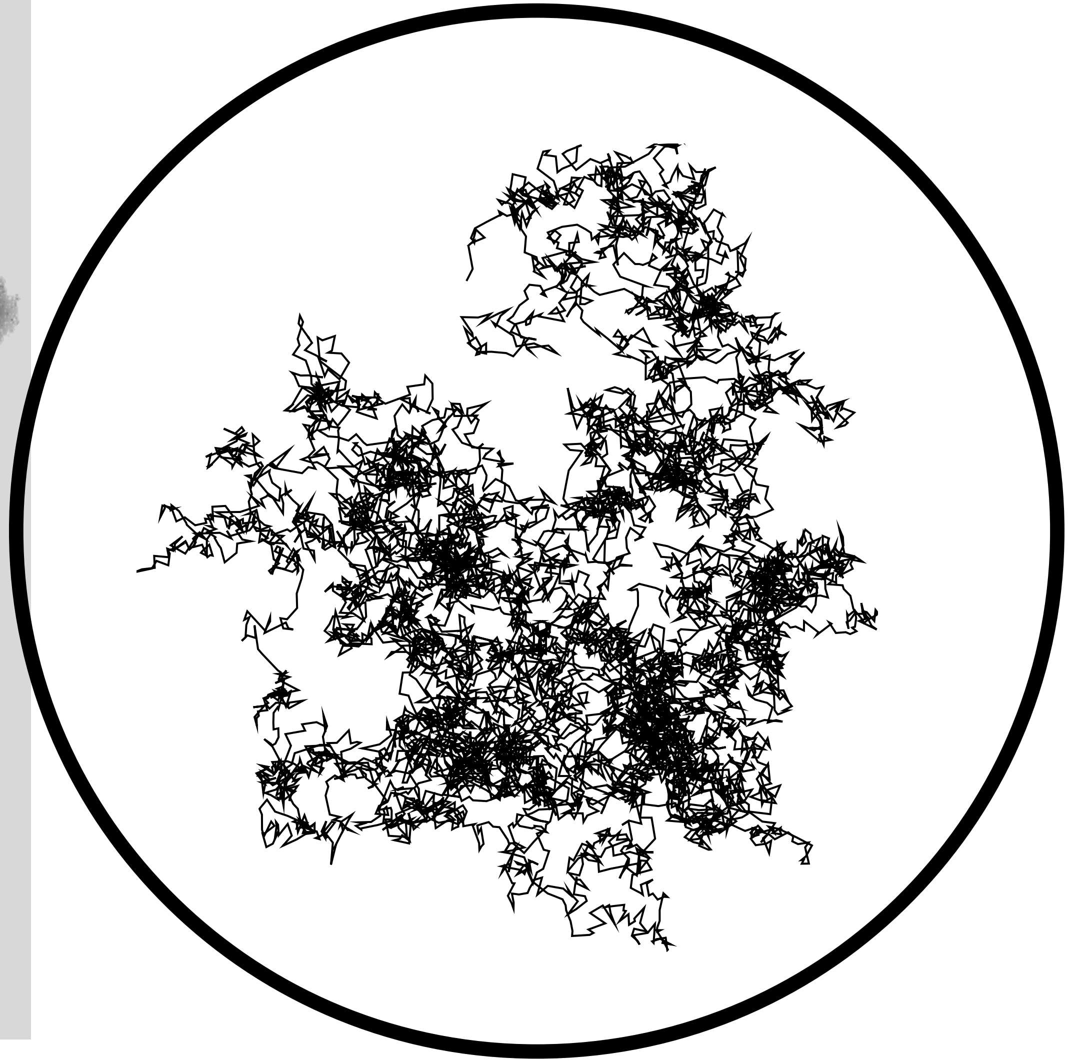
thermal fluctuations!

(far) away from thermal equilibrium???

Brownian motion

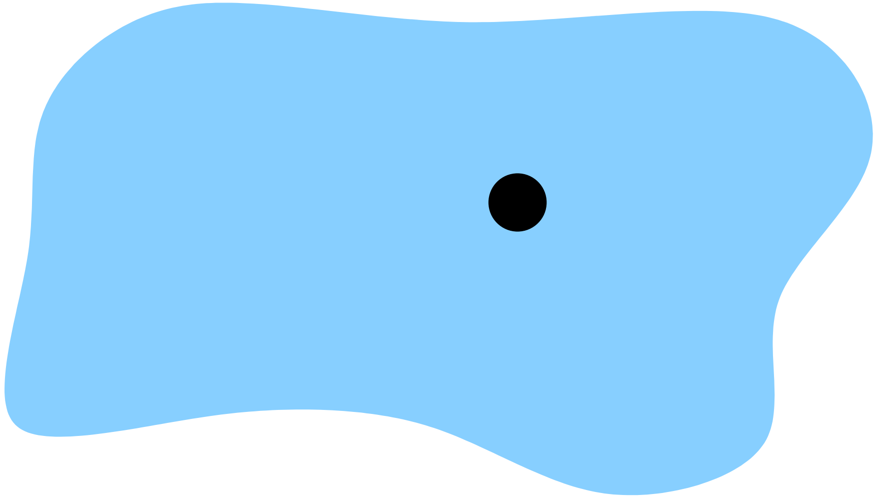
Robert Brown (1827): pollen in water

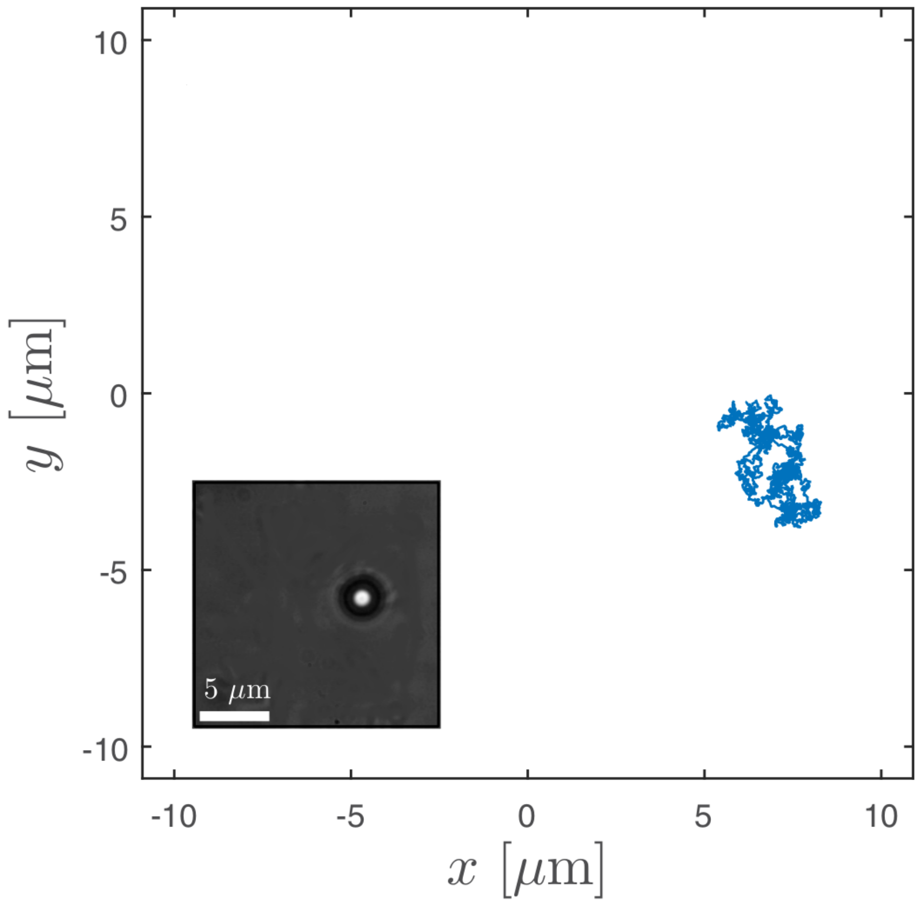




[A. P. Philipse, *Notes on Brownian Motion* (Utrecht University)]

Roadmap





[Argun et al, PRE **94**, 062150 (2016)]

model class: Langevin-equation

Stochastic dynamics . . .

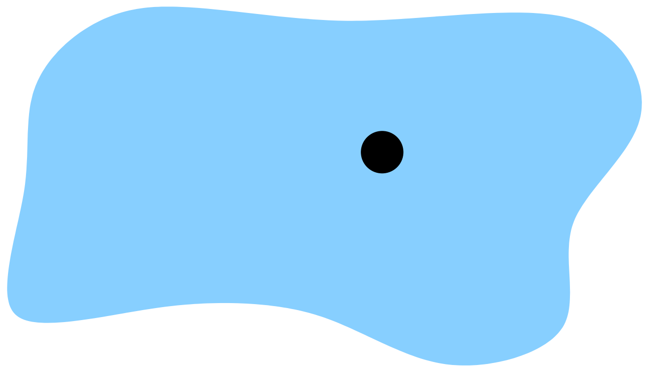
Stochastic energetics . . .

Stochastic thermodynamics . . .

. . . central results & perspective

Langevin-equation

$$\boxed{ma = F}$$



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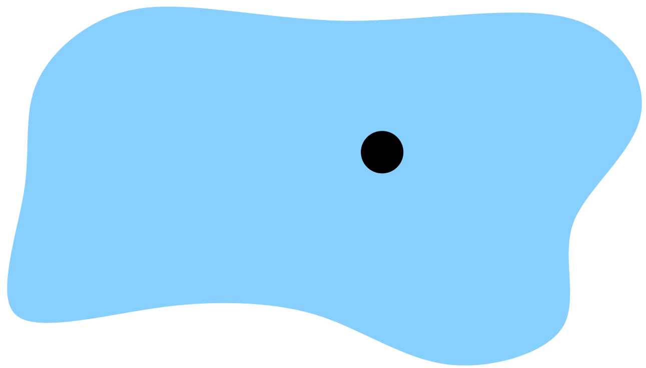

friction force: $F_{\text{friction}} = -\gamma v$

"Brownian motion force" $F_{\text{noise}} = \gamma\sqrt{2D}\,\xi(t)$

(random walk) $\langle \xi(t) \rangle = 0,\ \langle \xi(t)\,\xi(s) \rangle = \delta(t-s)$

$$\boxed{D = \frac{k_{\mathrm{B}}T}{\gamma}}$$

Einstein-relation

Langevin-equation

$$\boxed{m\ddot{x}(t) = -\gamma\dot{x}(t) + \sqrt{2k_{\mathrm{B}}T\gamma}\,\xi(t) + f(x(t),t)}$$

friction force: $F_{\text{friction}} = -\gamma v$

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(random walk) $\langle\xi(t)\rangle = 0,\ \langle\xi(t)\,\xi(s)\rangle = \delta(t-s)$

$$\boxed{D = \frac{k_{\mathrm{B}}T}{\gamma}}$$ Einstein-relation

Langevin-equation

Life at low Reynolds number

E. M. Purcell
Lyman Laboratory, Harvard University, Cambridge, Massachusetts 02138
(Received 12 June 1976)

Editor's note: This is a reprint (slightly edited) of a paper of the same title that appeared in the book *Physics and Our World: A Symposium in Honor of Victor F. Weisskopf*, published by the American Institute of Physics (1976). The personal tone of the original talk has been preserved in the paper, which was itself a slightly edited transcript of a tape. The figures reproduce transparencies used in the talk. The demonstration involved a tall rectangular transparent vessel of corn syrup, projected by an overhead projector turned on its side. Some essential hand waving could not be reproduced.

American Journal of Physics, Vol. 45, No. 1, January 1977

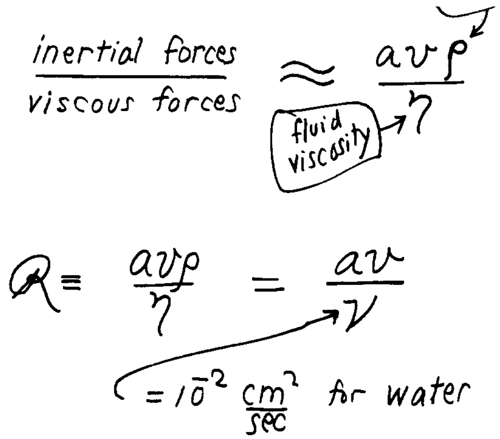


Figure 1.

ment, it's about 10^{-4} or 10^{-5}. For these animals inertia is totally irrelevant. *We* know that $F = ma$, but they could scarcely care less. I'll show you a picture of the real animals in a bit but we are going to be talking about objects which are the order of a micron in size (Fig. 4). That's a micron scale, not a suture, in the animal in Fig. 4. In water where the kinematic viscosity is 10^{-2} cm/sec these things move around with a typical speed of 30 μm/sec. If I have to push that animal to move it, and suddenly I stop pushing, how

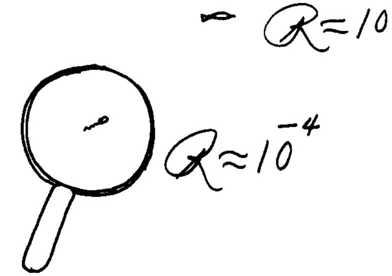


Figure 3.

far will it coast before it slows down? The answer is, about 0.1 Å. And it takes it about 0.6 μsec to slow down. I think this makes it clear what low Reynolds number means. Inertia plays no role whatsoever. If you are at very low Reynolds number, what you are doing at the moment is entirely determined by the forces that are exerted on you *at that moment*, and by nothing in the past.[2]

It helps to imagine under what conditions a man would be swimming at, say, the same Reynolds number as his own sperm. Well, you put him in a swimming pool that is full of molasses, and then you forbid him to move any part of his body faster than 1 cm/min. Now imagine yourself in that condition: you're under the swimming pool in molasses, and now you can only move like the hands of a clock. If under those ground rules you are able to move a few meters in a

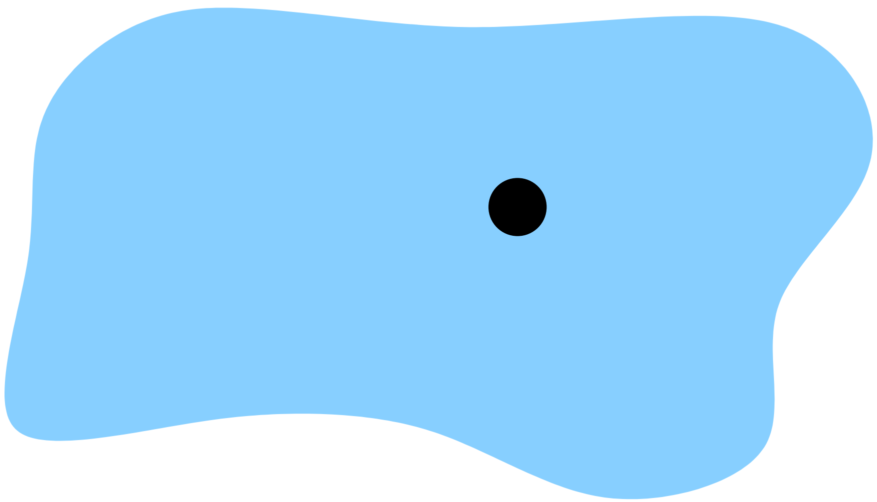
time and length scale of frictional relaxations:

$$m/\gamma = \mathcal{O}(1\,\mu\mathrm{s})$$
$$d = \mathcal{O}(0.1\,\text{Å})$$

$$m\ddot{x}(t) = -\gamma\dot{x}(t) + f(x(t),t) + \sqrt{2k_\mathrm{B}T\gamma}\,\xi(t)$$

$$\longrightarrow \quad \gamma\dot{x}(t) = f(x(t),t) + \sqrt{2k_\mathrm{B}T\gamma}\,\xi(t)$$

Roadmap



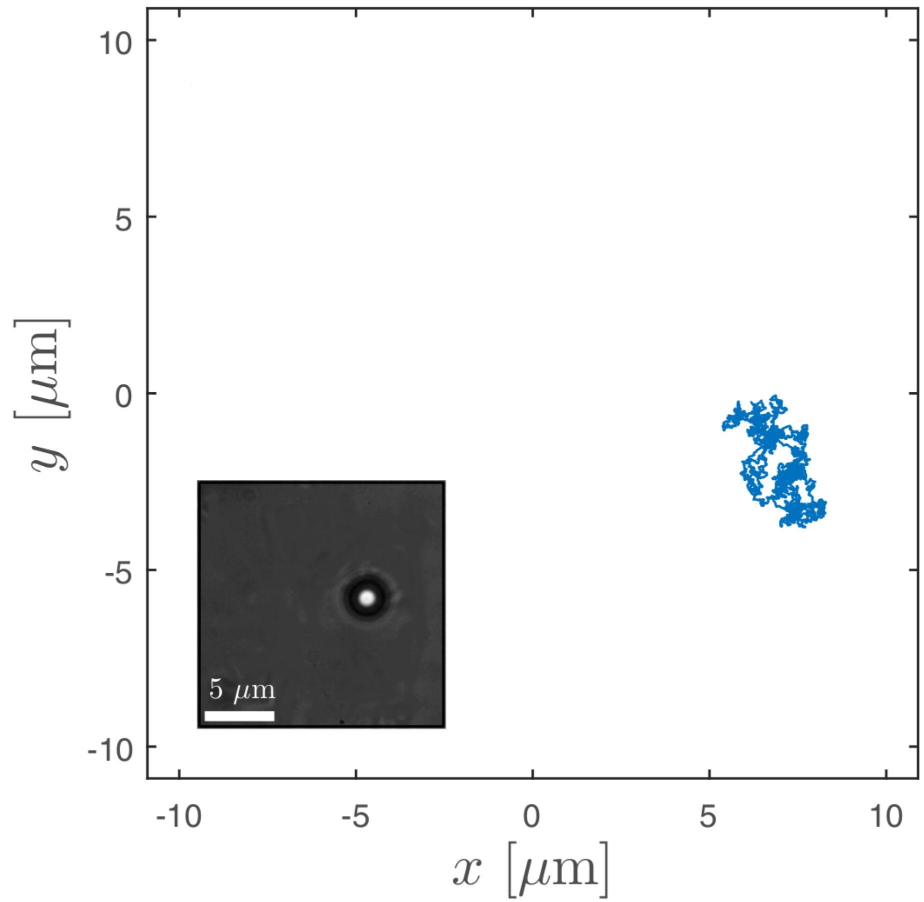
model class: Langevin-equation

Stochastic dynamics . . .

Stochastic energetics . . .

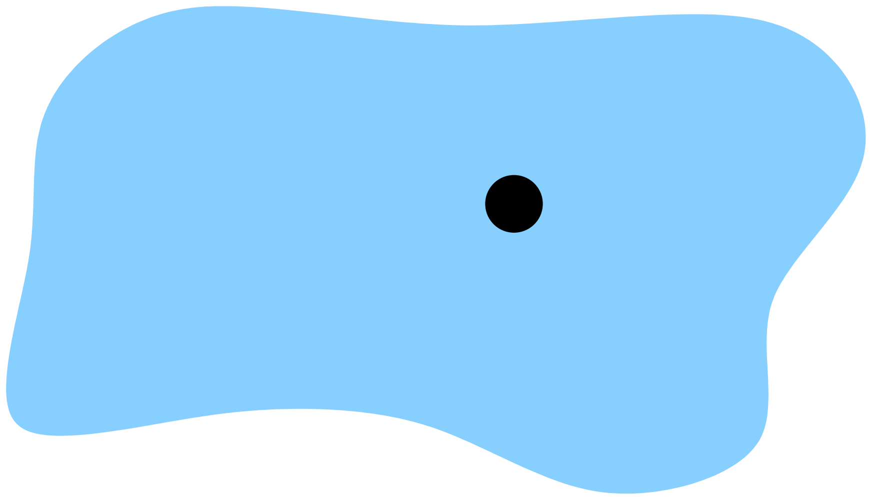
Stochastic thermodynamics . . .

. . . central results & perspective

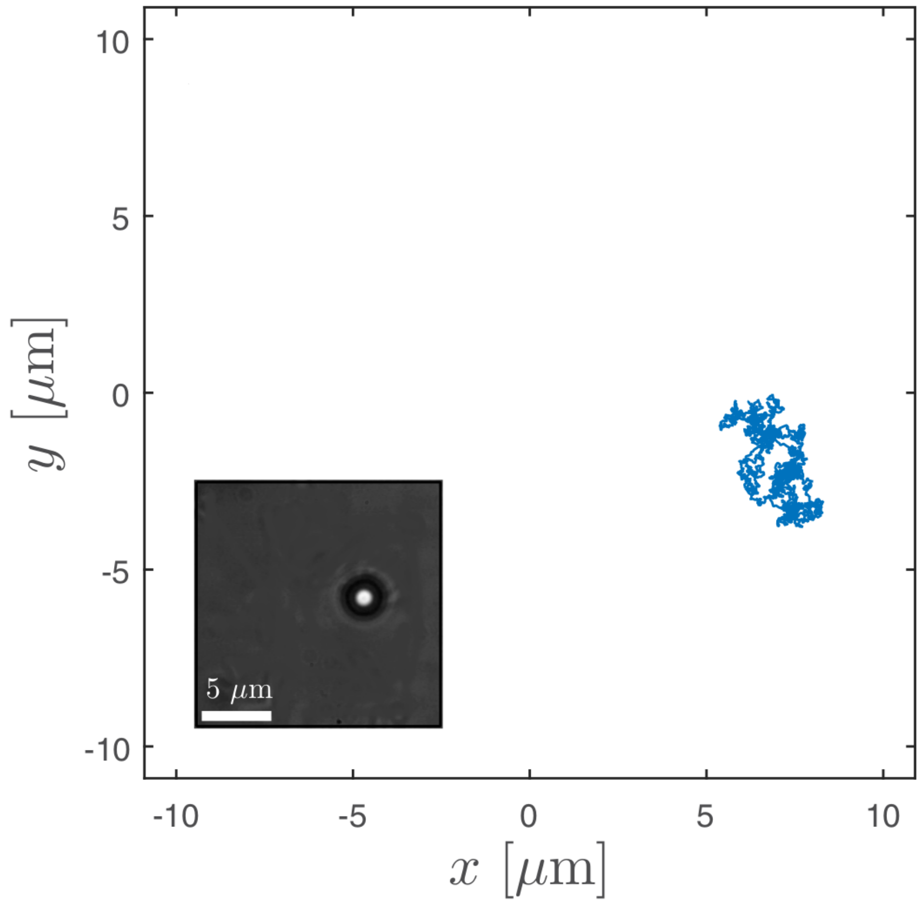


[Argun et al, PRE **94**, 062150 (2016)]

Stochastic energetics



$$\gamma\dot{\boldsymbol{x}}(t) = -\boldsymbol{\nabla}U(\boldsymbol{x}(t),t) + \sqrt{2k_{\mathrm{B}}T\gamma}\,\boldsymbol{\xi}(t)$$



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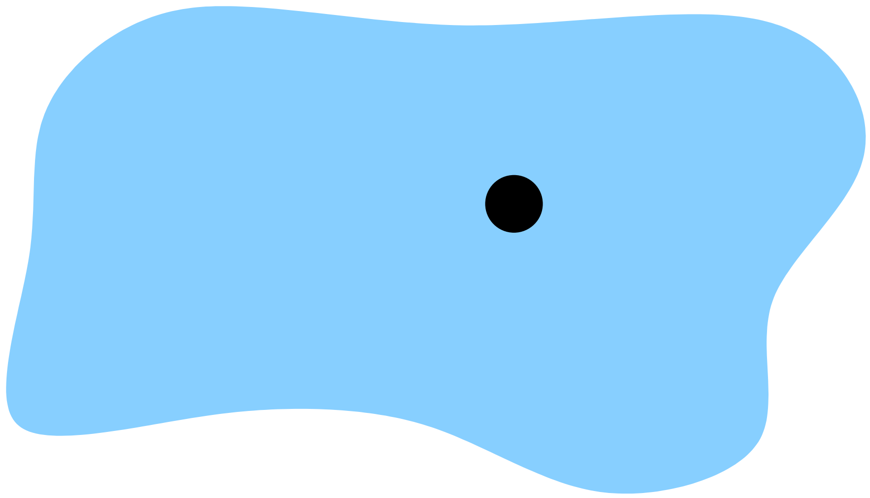
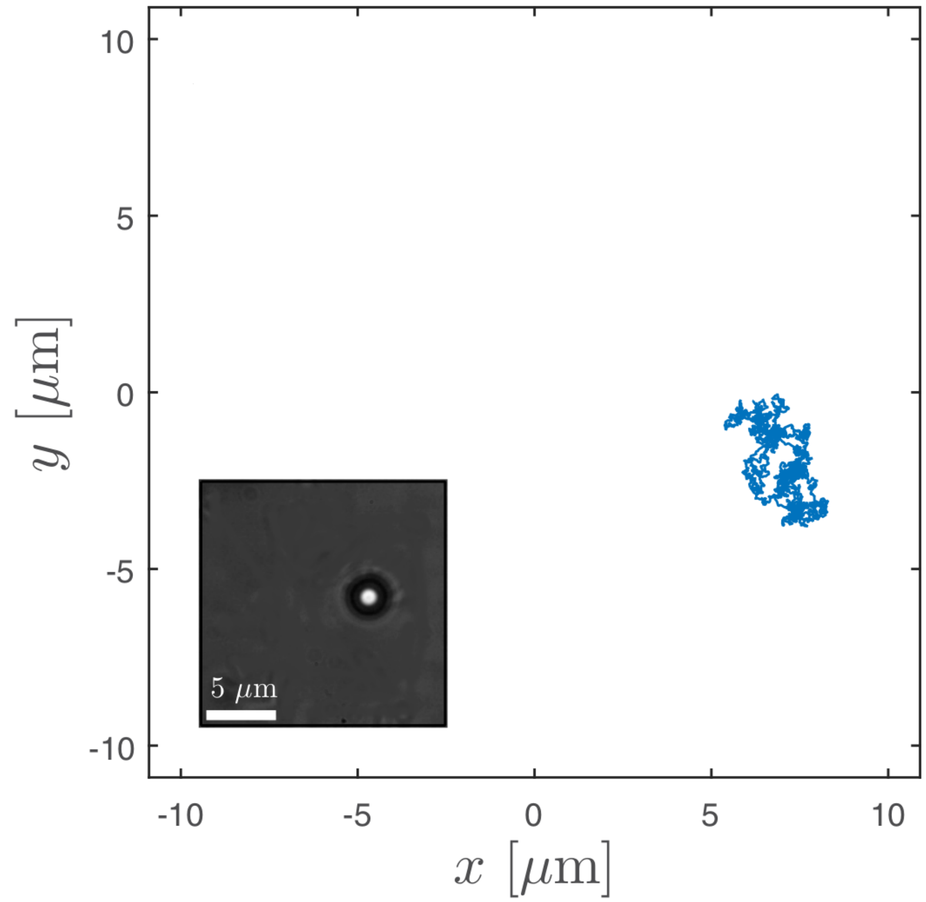




[Argun et al, PRE **94**, 062150 (2016)]

$$\gamma \dot{\boldsymbol{x}}(t) = -\boldsymbol{\nabla} U(\boldsymbol{x}(t), t) + \sqrt{2k_{\mathrm{B}}T\gamma}\, \boldsymbol{\xi}(t)$$

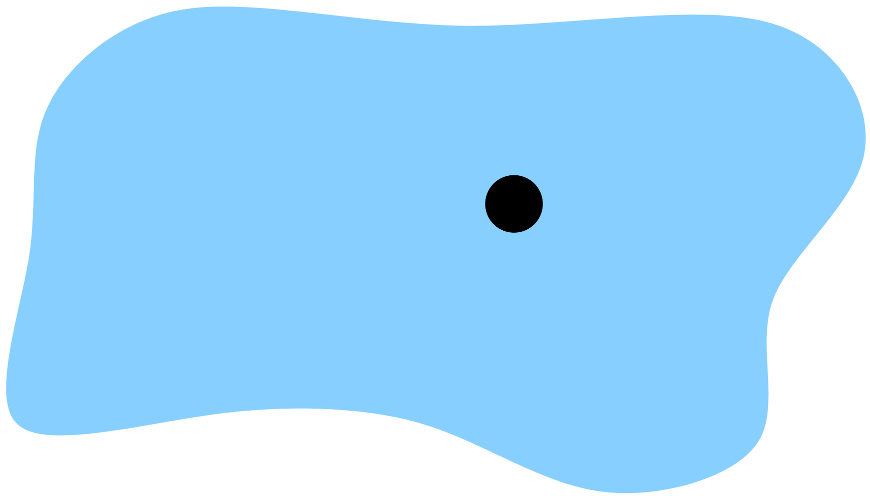
$$\mathrm{d}U = U(\boldsymbol{x}(t+\mathrm{d}t), t+\mathrm{d}t) - U(\boldsymbol{x}(t), t)$$

$$= \underbrace{\boldsymbol{\nabla} U(\boldsymbol{x}(t), t) \circ \mathrm{d}\boldsymbol{x}}_{=\delta Q} + \underbrace{\frac{\partial U(\boldsymbol{x}(t), t)}{\partial t} \mathrm{d}t}_{=\delta W}$$

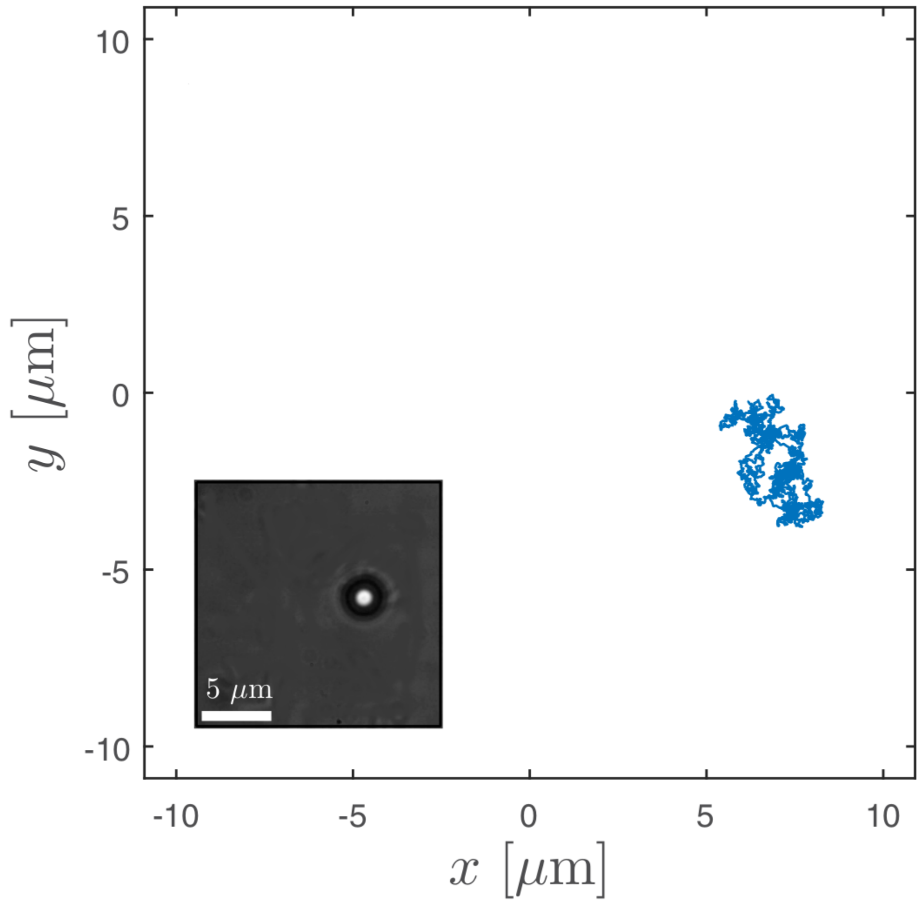
$$\delta Q = \left(-\gamma \dot{\boldsymbol{x}}(t) + \sqrt{2k_{\mathrm{B}}T\gamma}\, \boldsymbol{\xi}(t)\right) \circ \mathrm{d}\boldsymbol{x} = \boldsymbol{\nabla} U(\boldsymbol{x}(t), t) \circ \mathrm{d}\boldsymbol{x} = -\boldsymbol{f}(\boldsymbol{x}(t), t) \circ \mathrm{d}\boldsymbol{x}$$

$$\Rightarrow \quad \boxed{\mathrm{d}U = \delta W + \delta Q} \qquad \text{(first law)}$$

Stochastic thermodynamics



$$\gamma\dot{\boldsymbol{x}}(t) = \boldsymbol{f}(\boldsymbol{x}(t), t) + \sqrt{2k_{\mathrm{B}}T\gamma}\,\boldsymbol{\xi}(t)$$



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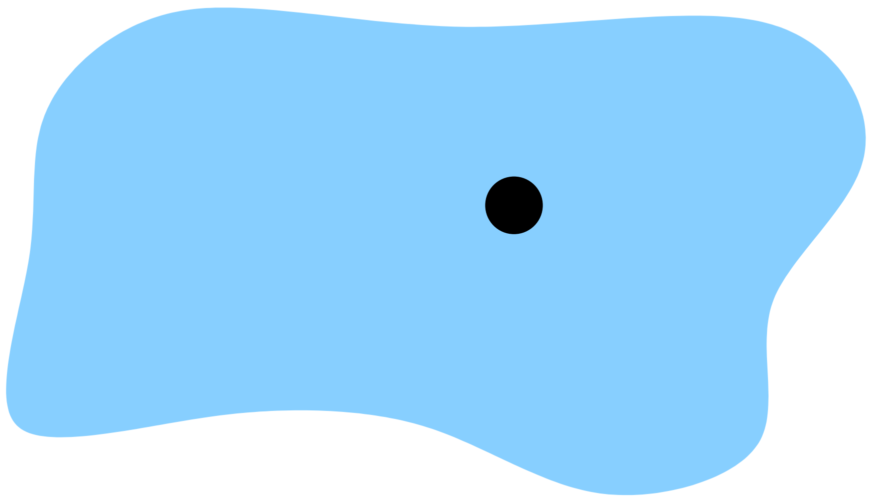
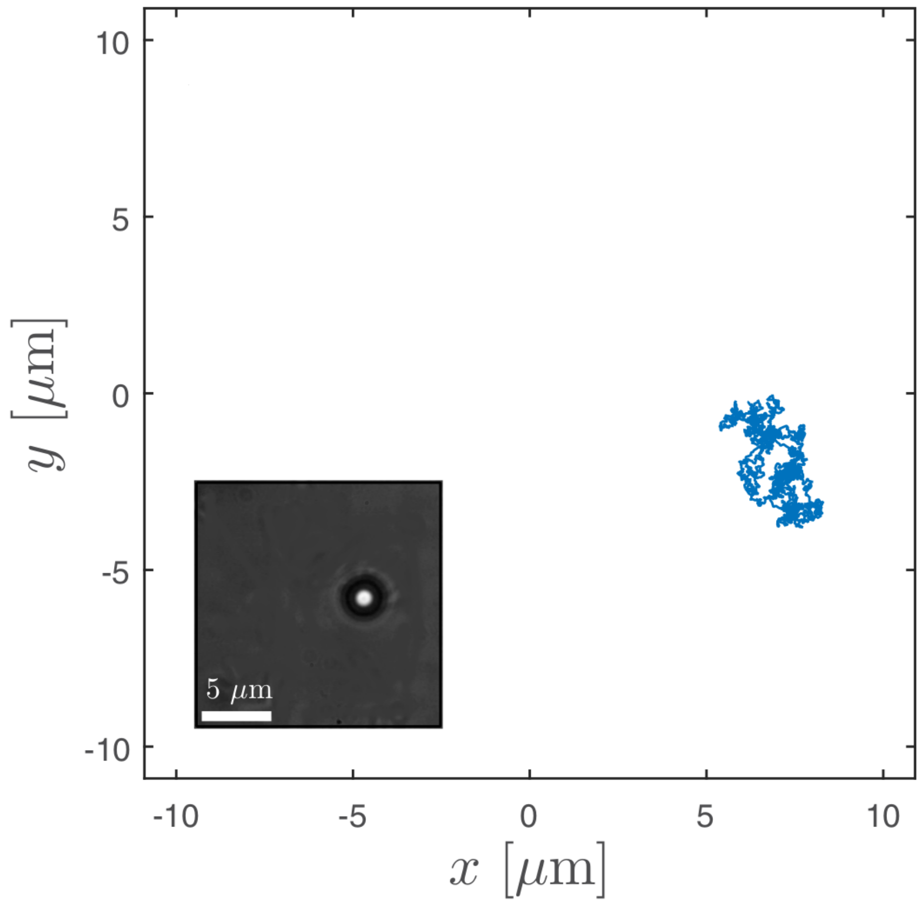




[Argun et al, PRE **94**, 062150 (2016)]

$$\gamma \dot{\boldsymbol{x}}(t) = \boldsymbol{f}(\boldsymbol{x}(t), t) + \sqrt{2 k_{\mathrm{B}} T \gamma}\, \boldsymbol{\xi}(t)$$

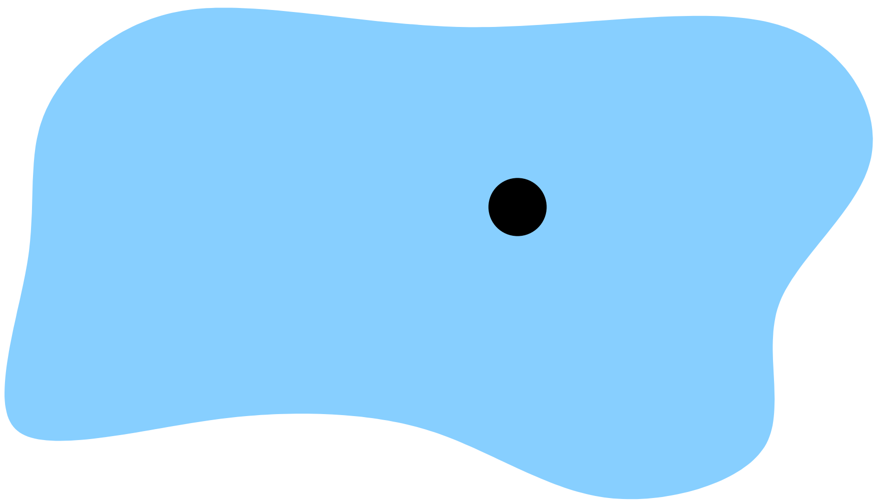
$$\boxed{\frac{\tilde{\mathfrak{p}}[\tilde{\overline{\boldsymbol{x}}}]}{\mathfrak{p}[\overline{\boldsymbol{x}}]} = e^{-\Delta S[\overline{\boldsymbol{x}}]/k_{\mathrm{B}}}}$$

$$\Delta S[\overline{\boldsymbol{x}}] = -\frac{\Delta Q[\overline{\boldsymbol{x}}]}{T} + \Delta S_{\mathrm{sys}}(\boldsymbol{x}_0, \boldsymbol{x}_\tau)$$

$$\Delta Q[\overline{\boldsymbol{x}}] = -\int_0^\tau \boldsymbol{f}(\boldsymbol{x}(t), t) \circ \mathrm{d}\boldsymbol{x}(t)$$

$\hookrightarrow$ **trajectory-wise thermodynamics**

Roadmap



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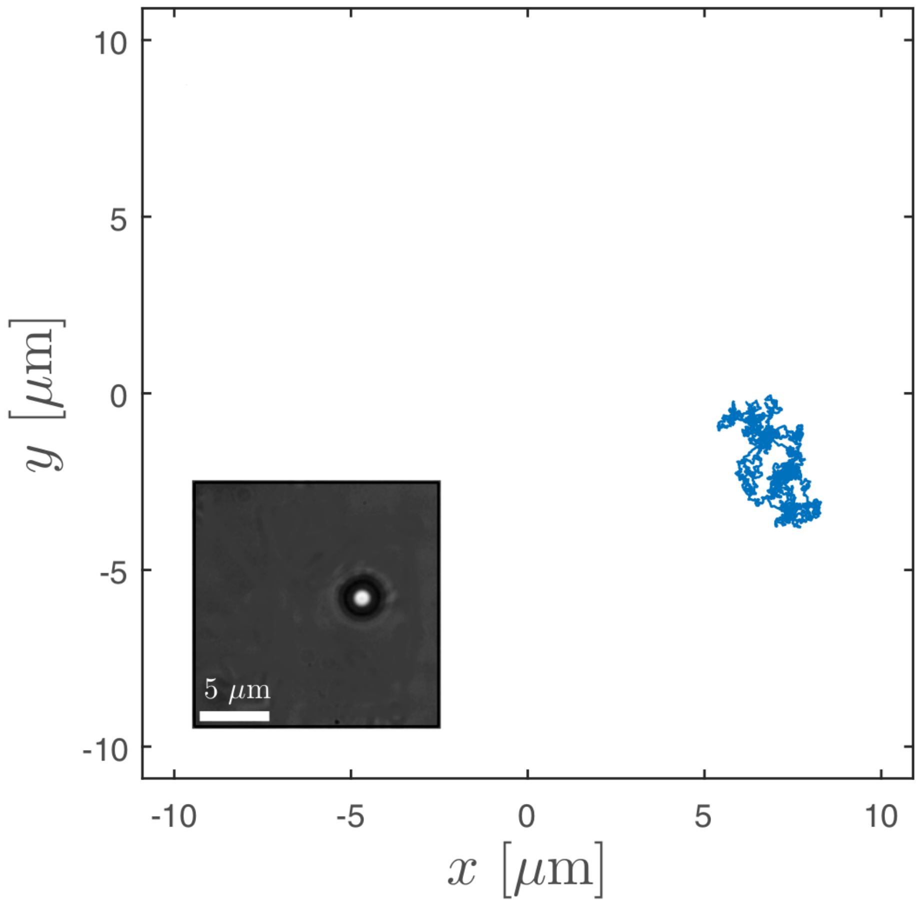
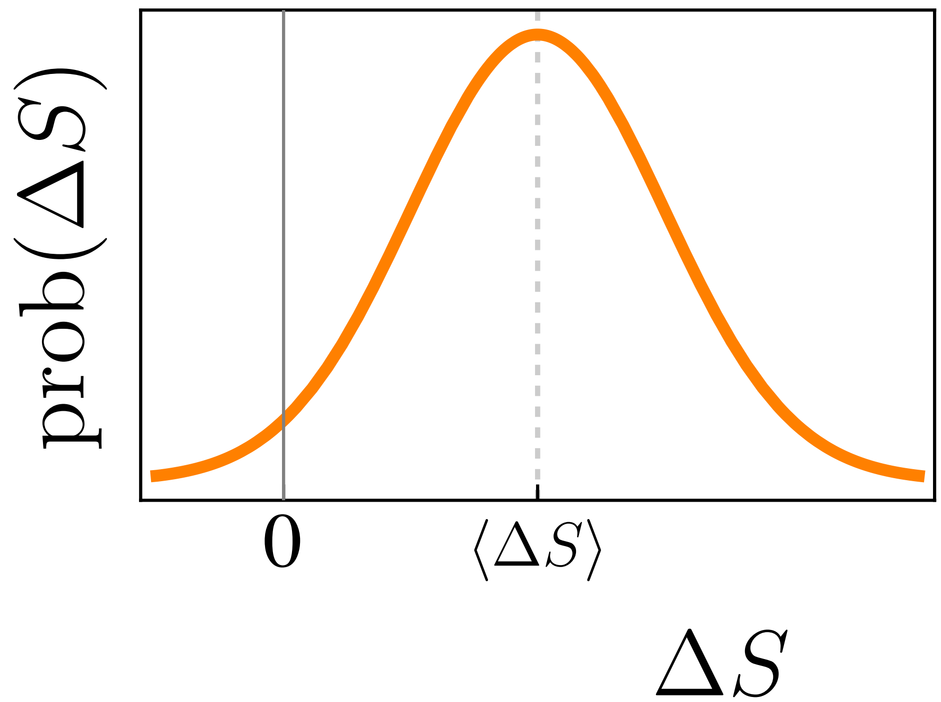


[Argun et al, PRE **94**, 062150 (2016)]

The fluctuation theorem

$$\gamma \dot{\boldsymbol{x}}(t) = \boldsymbol{f}(\boldsymbol{x}(t), t) + \sqrt{2 k_B T \gamma}\, \boldsymbol{\xi}(t)$$



$$\frac{\tilde{\mathfrak{p}}[\tilde{\overline{\boldsymbol{x}}}]}{\mathfrak{p}[\overline{\boldsymbol{x}}]} = e^{-\Delta S[\overline{\boldsymbol{x}}]/k_B}$$

$$\frac{p(-\Delta S)}{p(\Delta S)} = e^{-\Delta S/k_B}$$

$$\left\langle e^{-\Delta S[\overline{\boldsymbol{x}}]/k_B} \right\rangle = 1 \quad \Rightarrow \quad \langle \Delta S \rangle \geq 0$$

"refinement of the second law"

Jarzynski relation

$$\gamma \dot{\boldsymbol{x}}(t) = -\boldsymbol{\nabla} U(\boldsymbol{x}(t), t) + \sqrt{2 k_{\mathrm{B}} T \gamma}\, \boldsymbol{\xi}(t)$$

first law: $\Delta U(\boldsymbol{x}_0, \boldsymbol{x}_\tau) = \Delta W[\overline{\boldsymbol{x}}] + \Delta Q[\overline{\boldsymbol{x}}]$

entropy: $\Delta S[\overline{\boldsymbol{x}}] = -\dfrac{\Delta Q[\overline{\boldsymbol{x}}]}{T} + \Delta S_{\mathrm{sys}}(\boldsymbol{x}_0, \boldsymbol{x}_\tau)$

$$\Rightarrow \Delta F = \Delta U - T \Delta S_{\mathrm{sys}} = \Delta W - T \Delta S$$

$$\Rightarrow \boxed{\left\langle e^{-\Delta W / k_{\mathrm{B}} T} \right\rangle = e^{-\Delta F / k_{\mathrm{B}} T} \quad \Rightarrow \quad \Delta F \leq \langle \Delta W \rangle}$$

from the fluctuation theorem $\left\langle e^{-\Delta S / k_{\mathrm{B}}} \right\rangle = 1$

Crooks relation

Vol 437|8 September 2005|doi:10.1038/nature04061 nature

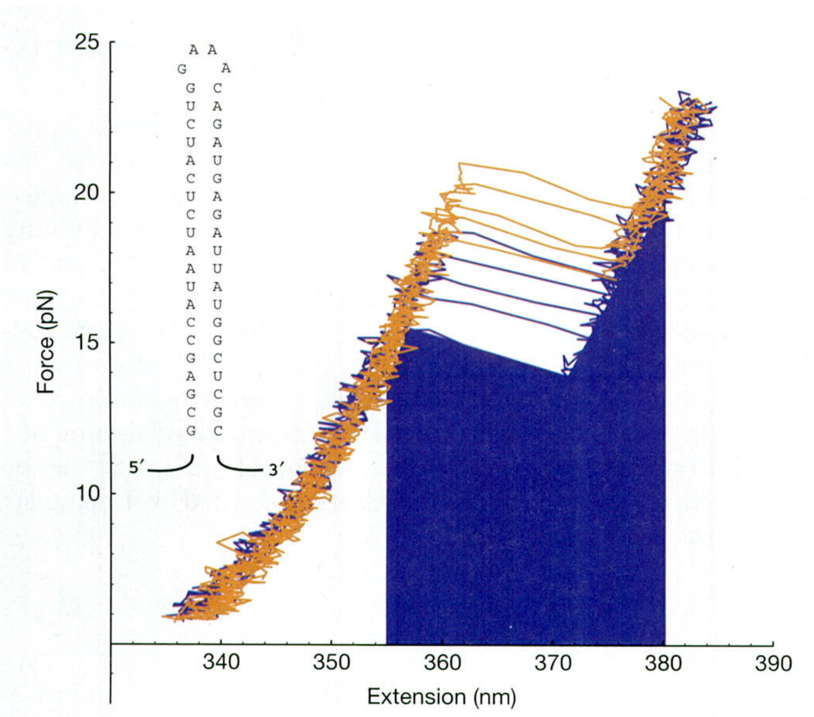
LETTERS

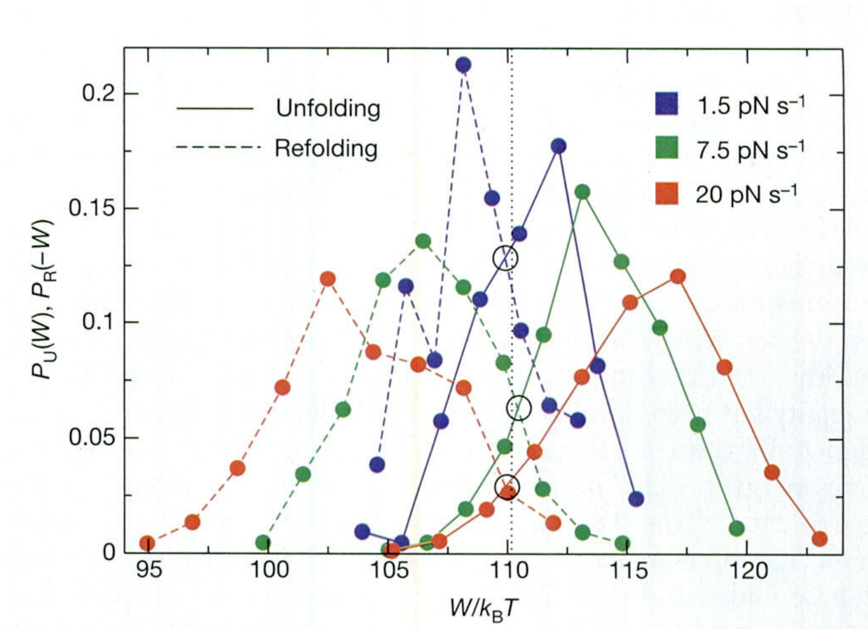
Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies

D. Collin[1]*, F. Ritort[2]*, C. Jarzynski[3], S. B. Smith[4], I. Tinoco Jr[5] & C. Bustamante[4,6]

$$\frac{p(W)}{\tilde{p}(-W)} = e^{(W-\Delta F)/k_{\mathrm{B}}T}$$

$$p(W) = \tilde{p}(-W) \Leftrightarrow W = \Delta F$$





Stochastic heat engine

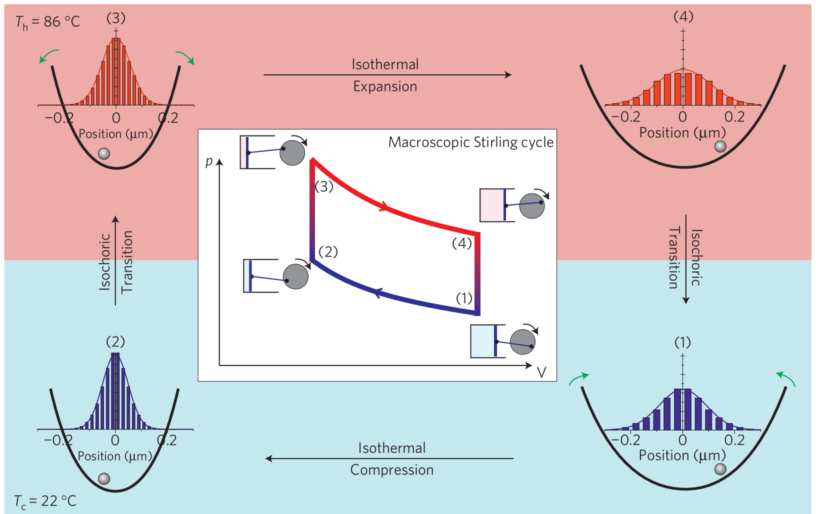
with Brownian particle(s) as working medium

nature physics | LETTERS

PUBLISHED ONLINE: 11 DECEMBER 2011 | DOI: 10.1038/NPHYS2163

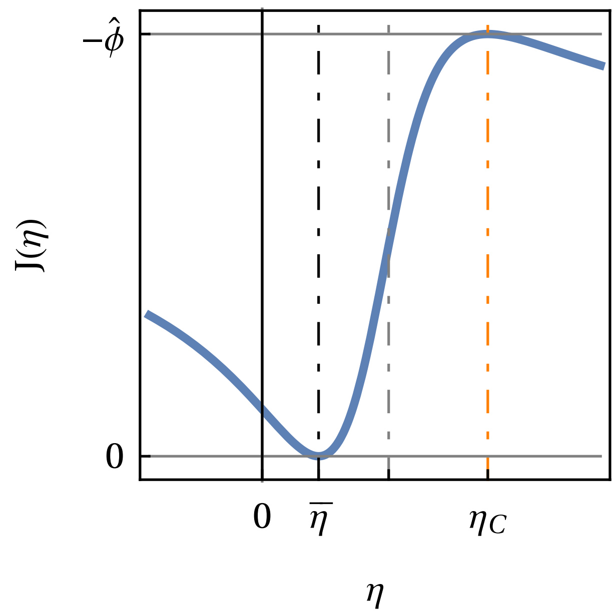
Realization of a micrometre-sized stochastic heat engine

Valentin Blickle[1,2]* and Clemens Bechinger[1,2]



$$\eta = -\frac{\Delta W}{\Delta Q_{\mathrm{h}}}$$

$$p(\eta) \sim e^{-\tau J(\eta)} \quad (\tau \to \infty)$$



Are there universal laws (far) away from equilibrium?

fluctuation theorem	$\left\langle e^{-\Delta S/k_{\mathsf{B}}} \right\rangle = 1$
Jarzynski relation	$\left\langle e^{-\Delta W/k_{\mathsf{B}}T} \right\rangle = e^{-\Delta F/k_{\mathsf{B}}T}$
efficiency fluctuations	$p(\eta) \sim e^{-\tau J(\eta)}$
thermodynamic uncertainty relation	$\dfrac{\mathrm{Var}(J_\tau)}{\langle J_\tau \rangle^2} \geq \dfrac{2k_{\mathsf{B}}}{\Delta S}$
generic properties of ΔS	$p_{\mathrm{inf}}(-s) = \dfrac{e^{-s/k_{\mathsf{B}}}}{k_{\mathsf{B}}}$

A (subjective) selection of references...

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Key results

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And more...

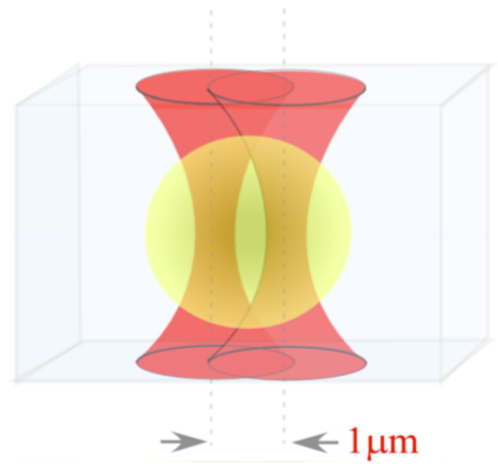
- biological systems
  (evolution, adaption, self-replication, reaction networks...)
- active matter
- quantum mechanics
- the role of information
- ...

LETTER

doi:10.1038/nature10872

Experimental verification of Landauer's principle linking information and thermodynamics

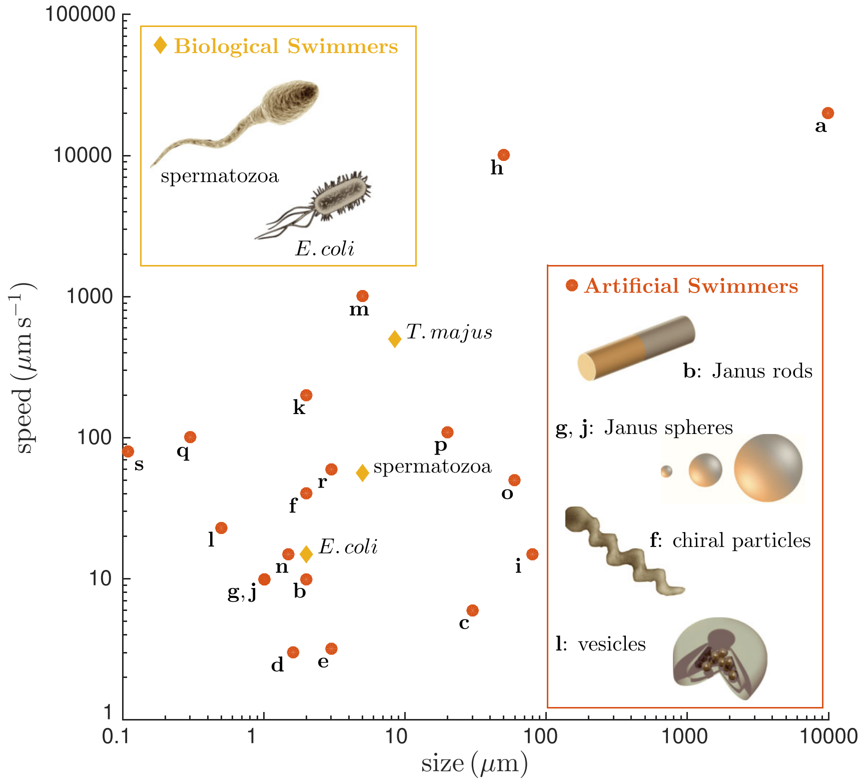
Antoine Bérut[1], Artak Arakelyan[1], Artyom Petrosyan[1], Sergio Ciliberto[1], Raoul Dillenschneider[2] & Eric Lutz[3]†



Active matter systems

collection of motile macro- or microorganisms

(human crowd, herds of land animals, flocks of birds, schools of fish, ant colonies, bacteria, etc)



[Bechinger et al, Rev Mod Phys **88**, 045006 (2016)]

self-propelled Brownian particles (biological or man-made)

passive Brownian particle in a "bath" of active Brownian particles

Active matter systems

Active matter are driven systems in which (unlimited) energy is supplied directly, isotropically and independently at the level of the individual constituents–active particles–which, in dissipating it, generally achieve some kind of systematic movement.

[Ramaswamy, J Stat Mech 054002 (2017)]

	active matter	**condensed matter** [passive (soft) matter]
driving	force-free	external forces or field
direction of motion	particle orientation	direction of external field
energy input	homogeneously at particle scale	at boundaries
non-equilibrium (breaking of detailed balance or time-reversal symmetry)	for individual components	by external driving

Active matter systems

Collective behavior in biological systems is a complex topic, to say the least. It runs wildly across scales in both space and time, involving taxonomically vastly different organisms, from bacteria and cell clusters, to insect swarms and up to vertebrate groups. It entails concepts as diverse as coordination, emergence, interaction, information, cooperation, decision-making, and synchronization. Amid this jumble, however, we cannot help noting many similarities between collective behavior in biological systems and collective behavior in statistical physics, even though none of these organisms remotely looks like an Ising spin. Such similarities, though somewhat qualitative, are startling, and regard mostly the emergence of global dynamical patterns qualitatively different from individual behavior, and the development of system-level order from local interactions. It is therefore tempting to describe collective behavior in biology within the conceptual framework of statistical physics, in the hope to extend to this new fascinating field at least part of the great predictive power of theoretical physics.

[Andrea Cavagna]

Grand aim of the active-matter paradigm:
[Ramaswamy, J Stat Mech 054002 (2017); Bechinger et al, Rev Mod Phys **88**, 045006 (2016)]

- to bring living systems into the inclusive ambit of condensed matter physics
- to understand the dynamics of active particles in real-life environments
- to discover the emergent statistical and thermodynamic laws governing matter made of intrinsically driven particles

Stochastic thermodynamics...

... of active Brownian particles??
(Brownian motion with "self-propulsion")

$$\left\langle e^{-\Delta S+\Delta \mathcal{I}} \right\rangle = 1$$

[Lennart Dabelow, Stefano Bo, RE, PRX **9**, 021009 (2019)]

Machine learning techniques...

Machine learning the thermodynamic arrow of time

Alireza Seif,[1,2] Mohammad Hafezi,[1,2,3] and Christopher Jarzynski[1,4]

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The mechanism by which thermodynamics sets the direction of time's arrow has long fascinated scientists. Here, we show that a machine learning algorithm can learn to discern the direction of time's arrow when provided with a system's microscopic trajectory as input. The performance of our algorithm matches fundamental bounds predicted by nonequilibrium statistical mechanics. Examination of the algorithm's decision-making process reveals that it discovers the underlying thermodynamic mechanism and the relevant physical observables. Our results indicate that machine learning techniques can be used to study systems out of equilibrium, and ultimately to uncover physical principles.

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