# Normal and anomalously slow diffusion under external fields

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1827, Brown observed the irregular unceasing motion of the pollen in water (1765, Ingenhousz)

1905, Einstein's explanation of diffusion, Pearson's random walk:

1) the existence of a mean free path
2) the existence of a mean time taken to perform a step or between collisions

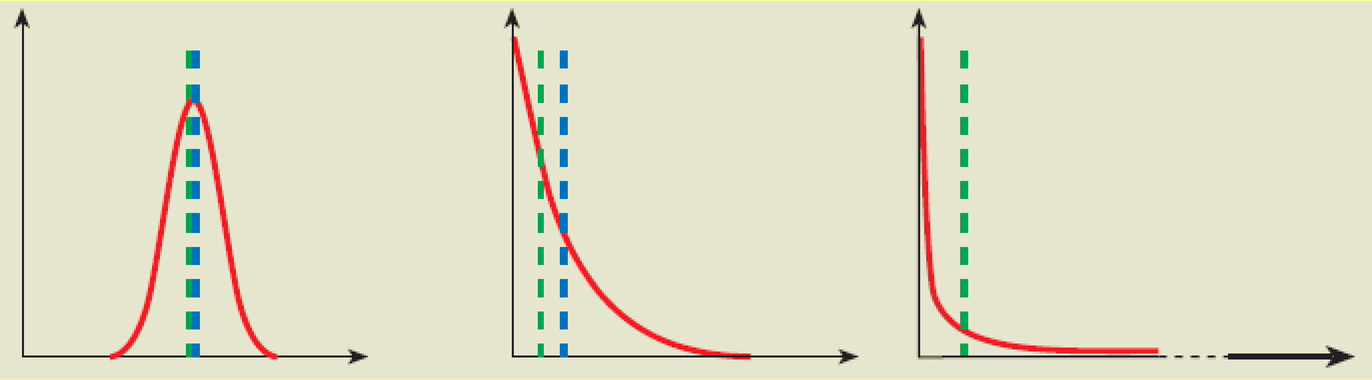
1906, Smoluchowski
1908, Langevin

the theoretical works of Einstein, Smoluchowski and Langevin on Brownian motion guided the experimentalists toward meaningful measurements.

what happens if the assumptions made by Einstein and Pearson do not hold ?!

experiments in the early 1970s:
movement of the charge carriers in amorphous semiconductors could not be described by the classic diffusion equation.

1975, Scher, Montroll:
charges moving in amorphous media tend to get trapped by local imperfections and then released due to thermal fluctuations. The trapping times are more likely to be described by a Pareto distribution with an infinite mean value than by a Gaussian distribution.

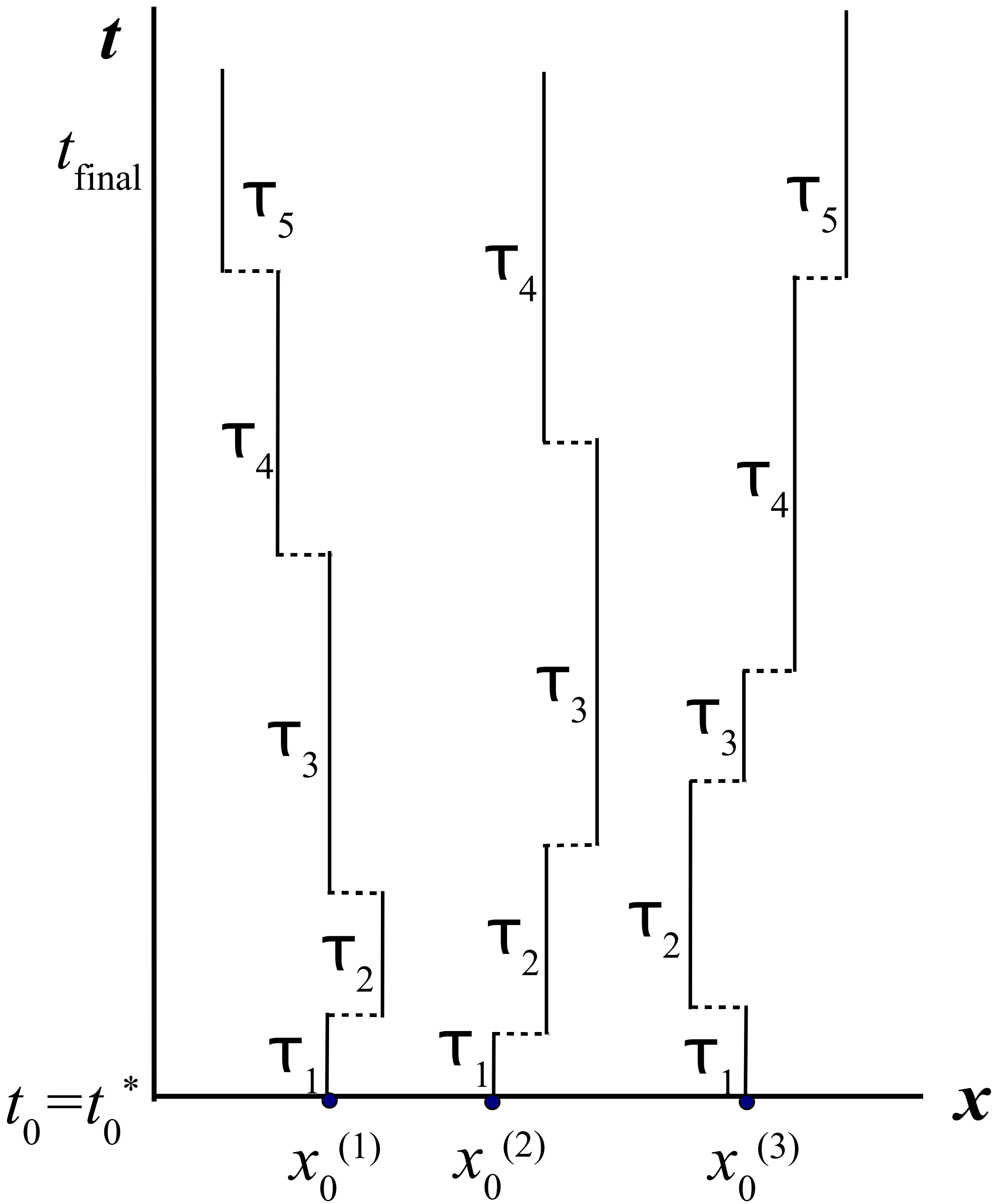


green – median
blue – mean

Gaussian exponential Pareto

This idea was not accepted easily by other researchers because it implied that a distribution that did not have a mean value might have a **physical meaning**.

# 1965, Montroll and Weiss,
## continuous time random walk model:




1D lattice $\{ x_i = i\,\Delta x \}$

initial positions $x^{(n)}(t_0) = x_0^{(n)}$

after a random waiting time τ drawn from a residence time distribution (RTD) $\psi_i(\tau)$, the particle jumps with probability $q_i^{\pm}$ $(q_i^{+} + q_i^{-} = 1)$ from site $\boldsymbol{i}$ to site $\boldsymbol{i}$ **±1:**

$$x^{(n)} \to x^{(n)} \pm \Delta x\,,$$
$$t^{(n)} \to t^{(n)} + \tau\,;$$

fractional hopping rates are:

$$g_i^{\pm} = \frac{\kappa_\alpha}{\Delta x^2} \exp\left[ -\frac{\beta\left(U_{i\pm 1} - U_i\right)}{2} \right];$$

$$q_i^{\pm} = \frac{g_i^{\pm}}{g_i^{+} + g_i^{-}}$$

exponential RTD → normal diffusion

Pareto or Mittag-Leffler RTD

↓

subdiffusion

$$\langle \delta r^2(t) \rangle \propto t$$
$$\langle r(t) \rangle \propto t$$

normal diffusion

$$\xrightarrow{\alpha \neq 1}$$

$$\langle \delta r^2(t) \rangle \propto t^{\alpha}$$
$$\langle r(t) \rangle \propto t^{\alpha}$$

$0 < \alpha < 1$ – subdiffusion

$\alpha > 1$ – superdiffusion

diffusion coefficient: $[\kappa] = \mathrm{cm}^2\,\mathrm{s}^{-1} \rightarrow [\kappa_\alpha] = \mathrm{cm}^2\,\mathrm{s}^{-\alpha}$

current: $[v] = \mathrm{cm}\,\mathrm{s}^{-1} \rightarrow [v_\alpha] = \mathrm{cm}\,\mathrm{s}^{-\alpha}$

Anomalous diffusion has been known since Richardson's treatise on turbulent diffusion in 1926.
Within transport theory it has been studied since the late 1960s.

anomalous diffusion is relevant in many problems in physics and chemistry, in particular in electrochemistry, in geophysics and environmental physics, in biology and microbiology, medicine, in complex systems, and finance

superdiffusion:

- Richardson turbulent diffusion
- special domains of rotating flows
- collective slip diffusion on solid surfaces
- layered velocity fields
- bulk-surface exchange controlled dynamics in porous glasses
- the transport in micelle systems
- heterogeneous rocks
- quantum optics
- single molecule spectroscopy
- the transport in turbulent plasma
- bacterial motion

subdiffusion:

- charge carrier transport in amorphous semiconductors
- glasses
- nuclear magnetic resonance
- diffusion in percolative and porous systems
- transport on fractal geometries
- dynamics of a bead in a polymeric network
- protein conformational dynamics
- molecular motors
- DNA unzipping

diffusion equation describing normal Brownian motion:

$$\frac{\partial}{\partial t} P(x,t) = \kappa \frac{\partial^2}{\partial x^2} P(x,t)$$

**fractional** diffusion equation describing subdiffusion:

$$\frac{\partial}{\partial t} P(x,t) = {}_0\hat{D}_t^{1-\alpha} \kappa_\alpha \frac{\partial^2}{\partial x^2} P(x,t),$$

$${}_0\hat{D}_t^{1-\alpha} \chi(t) = \frac{1}{\Gamma(\alpha)} \frac{\partial}{\partial t} \int_0^t dt' \frac{\chi(t')}{(t-t')^{1-\alpha}}$$

Riemann-Liouville fractional derivative; $0 < \alpha < 1$

or

$$D_*^\alpha P(x,t) = \kappa_\alpha \frac{\partial^2}{\partial x^2} P(x,t),$$

$$D_*^\alpha P(x,t) = \frac{1}{\Gamma(1-\alpha)} \int_0^t dt' \frac{1}{(t-t')^\alpha} \frac{\partial}{\partial t'} P(x,t')$$

Caputo fractional derivative

master equation corresponding to the random walk:

$$\frac{\partial P_i(t)}{\partial t} = g^{+}_{i-1} P_{i-1}(t) + g^{-}_{i+1} P_{i+1}(t) - (g^{+}_{i} + g^{-}_{i}) P_i(t)$$

**fractional master equation** corresponding to the CTRW:

$$\frac{\partial P_i(t)}{\partial t} = {}_0\hat{D}_t^{1-\alpha} \{ g^{+}_{i-1} P_{i-1}(t) + g^{-}_{i+1} P_{i+1}(t) - (g^{+}_{i} + g^{-}_{i}) P_i(t) \}$$

or

$$D^{\alpha}_{*} P_i(t) = g^{+}_{i-1} P_{i-1}(t) + g^{-}_{i+1} P_{i+1}(t) - (g^{+}_{i} + g^{-}_{i}) P_i(t)$$

## fractional calculus:

One way to formally introduce **fractional derivatives** proceeds from the repeated differentiation of an integral power:

$$\frac{\mathrm{d}^n}{\mathrm{d}\,x^n}x^m=\frac{m!}{(m-n)!}x^{m-n}$$

For an arbitrary power $\mu$, repeated differentiation gives

$$\frac{\mathrm{d}^n}{\mathrm{d}\,x^n}x^\mu=\frac{\Gamma(\mu+1)}{\Gamma(\mu-n+1)}x^{\mu-n},$$

with gamma functions replacing the factorials.
The gamma functions allow for a generalization to an arbitrary order of differentiation $\alpha$,

$$\frac{\mathrm{d}^\alpha}{\mathrm{d}\,x^\alpha}x^\mu=\frac{\Gamma(\mu+1)}{\Gamma(\mu-\alpha+1)}x^{\mu-\alpha}$$

The latter equation corresponds to the **Riemann-Liouville derivative**.
It is sufficient for handling functions that can be expanded in Taylor series.

September 30th 1695 L'Hopital wrote to Leibniz asking him about a particular notation he had used in his publication for the *n*th-derivative of the linear function $f(x) = x$:

$$\frac{\mathrm{d}^n f(x)}{\mathrm{d}x^n}$$

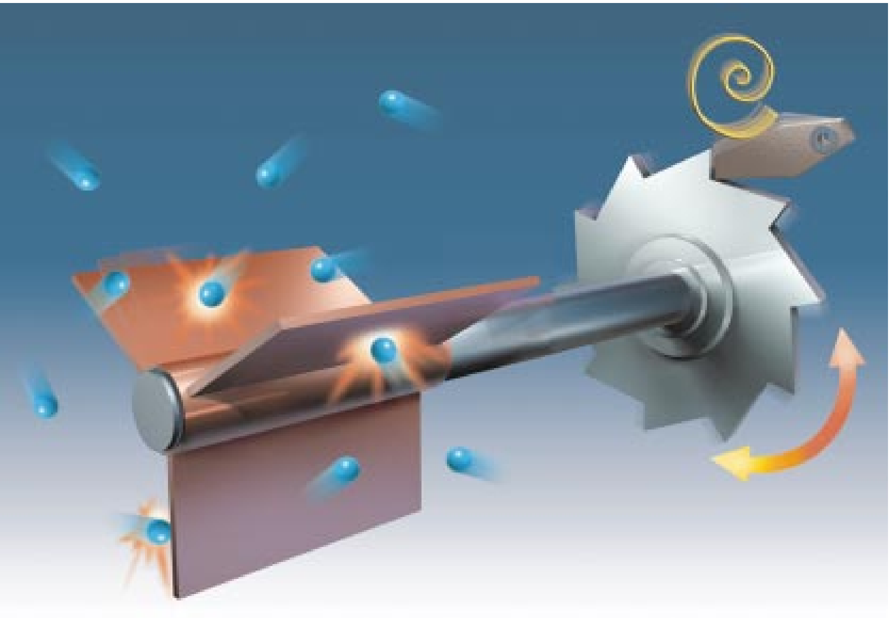
– What would the result be if $n = ½$ ?

Leibniz's response: "An apparent paradox, from which one day useful consequences will be drawn."

The derivatives of integer order and their inverse operations – integrations – provide the language for formulating and analyzing many laws of physics.
However, about 300 years had to pass before what is now known as fractional calculus was slowly accepted as a practical instrument in physics.

"Leibniz's response has proven at least half right. Within the 20th century especially numerous applications and physical manifestations of fractional calculus have been found. However, these applications and the mathematical background surrounding fractional calculus are far from paradoxical. While the physical meaning is difficult (arguably impossible) to gasp, the definitions themselves are no more rigorous than those of their integer order counterparts." [Adam Loverro]

# diffusion on periodic substrates:



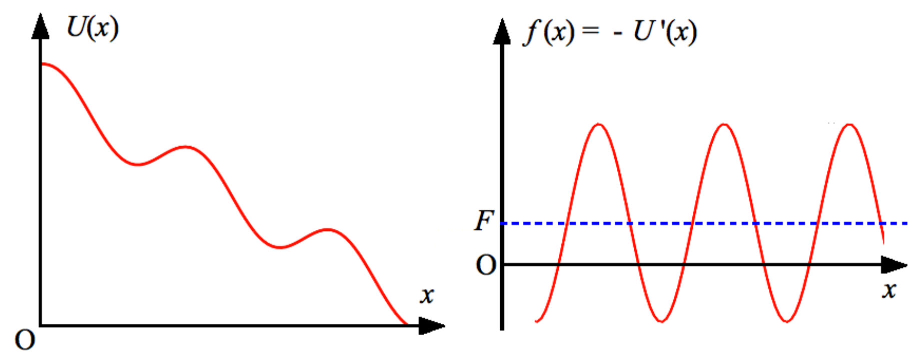
**Smoluchowski-Feynman ratchet:**
is it possible to convert Brownian motion into useful work?

$$\eta \frac{dx(t)}{dt} = -\frac{dU(x)}{dx} + \xi(t)$$

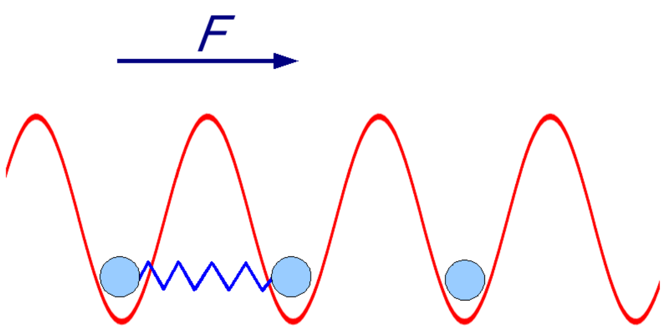
$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2\eta k_B T \delta(t-t')$$

$$U(x) = U_0(x) - Fx$$

$$U_0(x) = U_0(x+L), \quad F = \text{const}$$



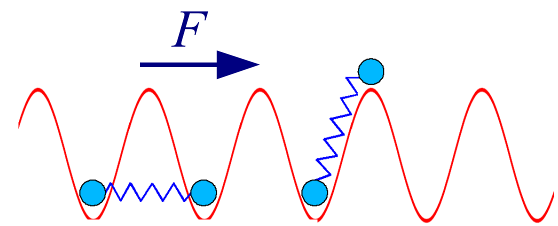
- normal Brownian motion of monomers and dimers under the influence of a spatially periodic forces
- anomalously slow diffusion on periodic substrates




applications in physics, chemistry, nanotechnology, molecular biology:

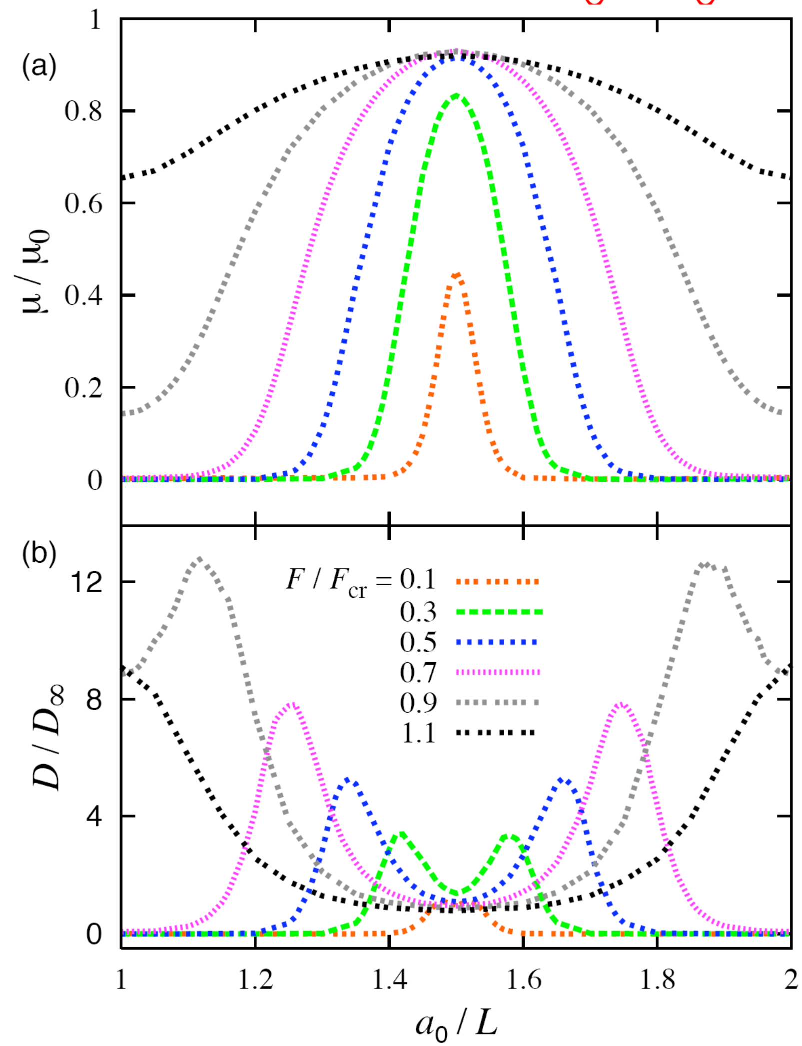
- Josephson junctions diffusion of
- rotating dipoles in external fields
- particle separation by electrophoresis
- charge density waves
- mode locking in laser gyroscopes
- plasma accelerators
- neural activity
- intracellular transport
- DNA unzipping
- diffusion of atoms and molecules (e.g. dimers) on crystal surfaces
- motion of dissociated dislocations

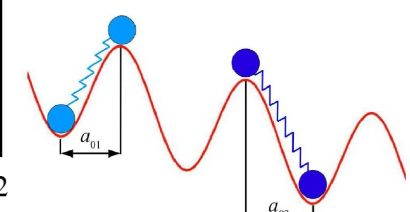
motion of dimers (harmonically interacting Brownian particles):




directed motion (current) is larger for the dimers with the length of half period of the potential period

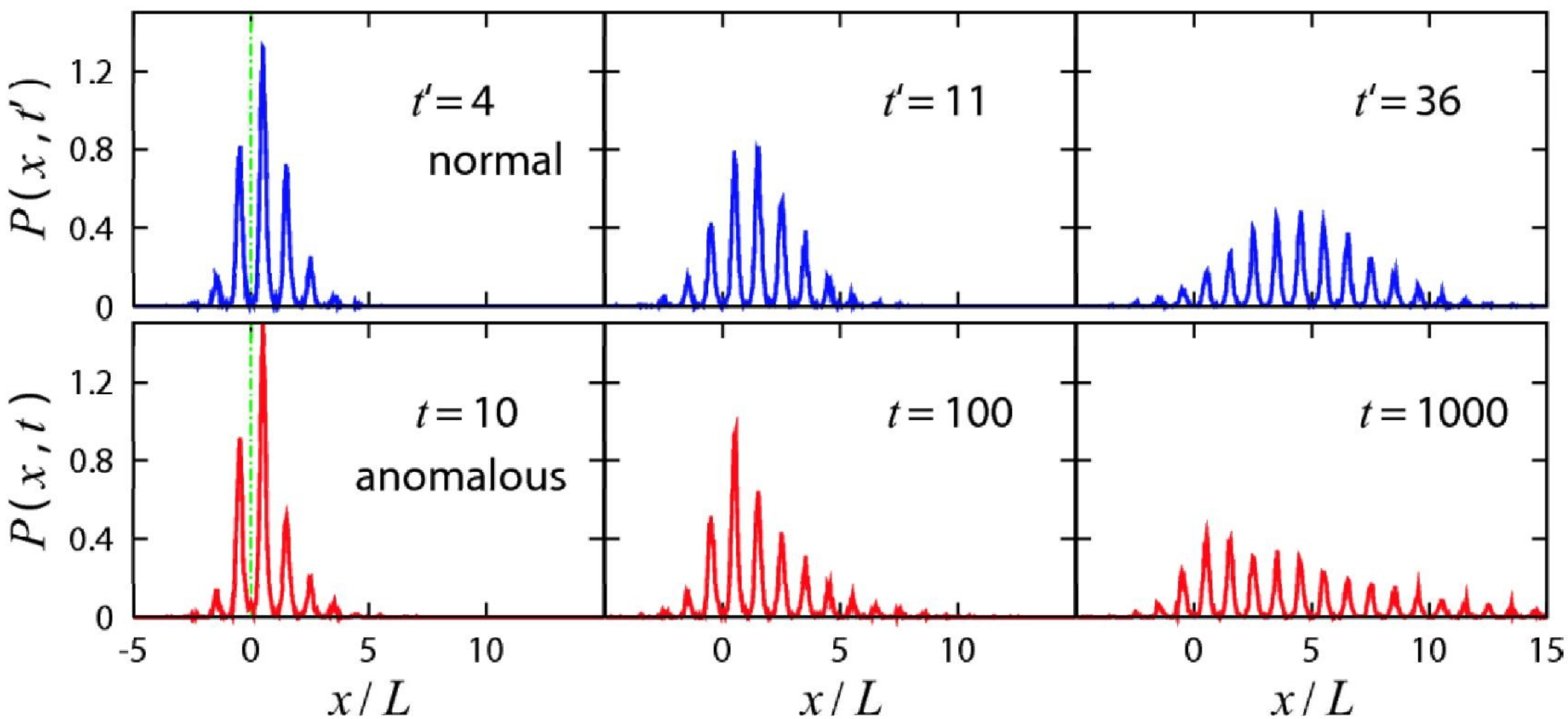
diffusion coefficient is larger for the dimer configurations such that one of the particles is in the minimum of the washboard potential and the other one on the top of the potential barrier



motion of a monomer in a periodic substrate under the influence of an external bias: normal versus anomalously slow motion

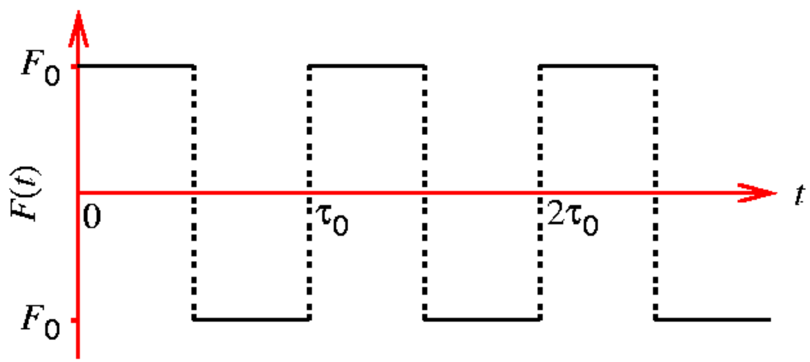
normal Brownian motion: the probability density is spreading and its maximum is moving in the direction of the external bias

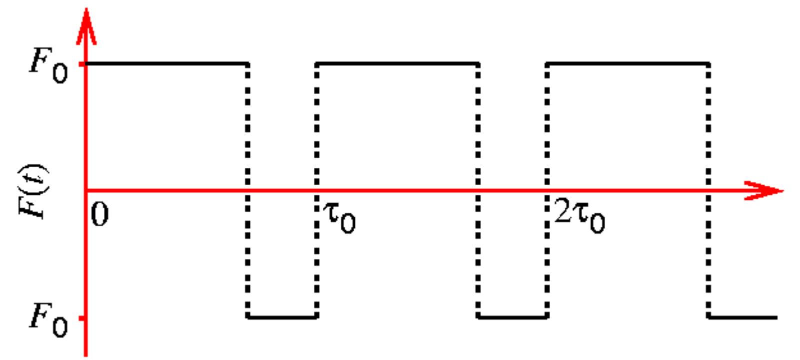


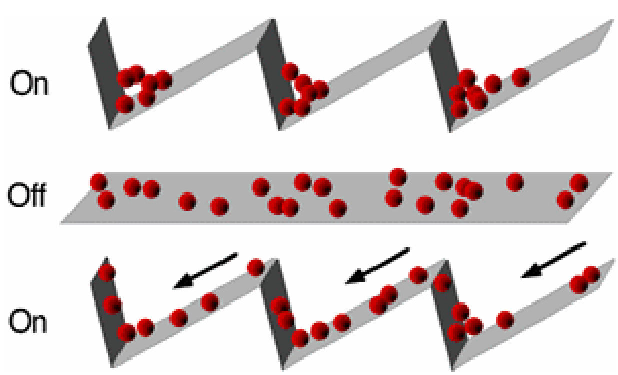

subdiffusion: the probability density is spreading in the direction of the external bias but the maximum remains close to the initial position, i.e. the system has memory

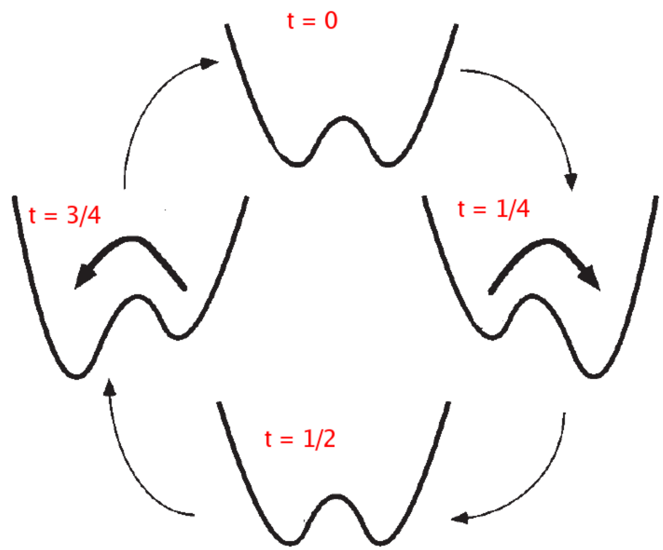
# subdiffusion in time dependent fields:

$$f(t) = \pm F_0, \quad F_0 = \text{const}, \quad \tau_0 = \text{ time period}$$

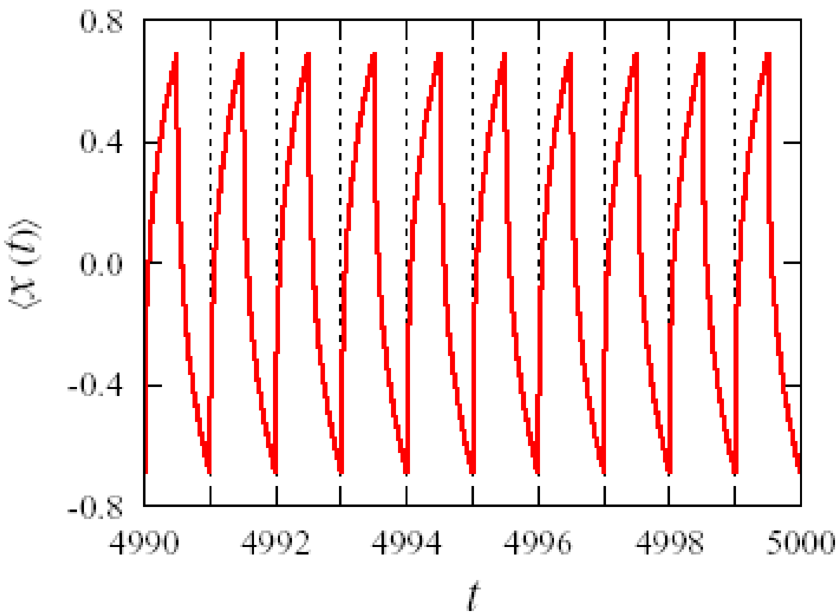


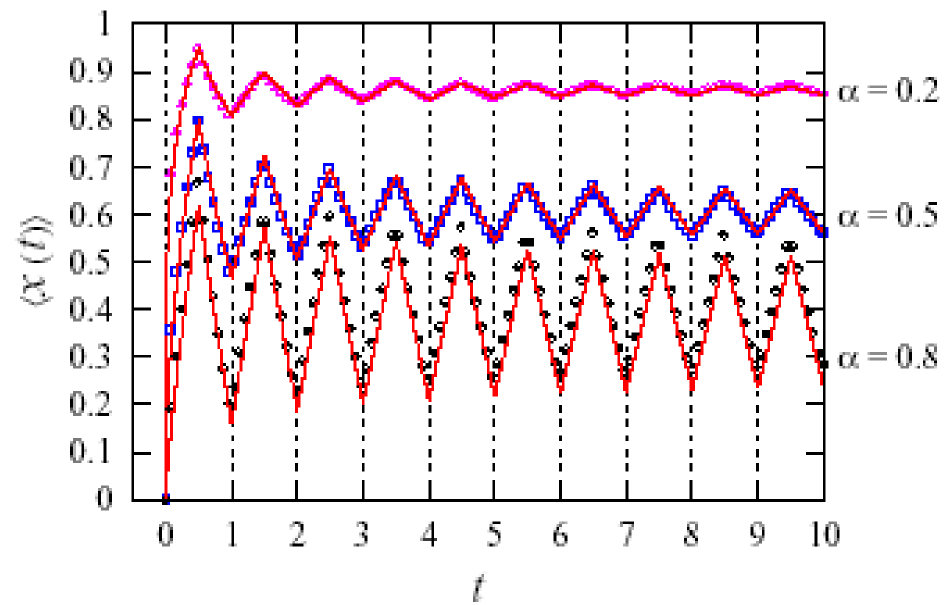



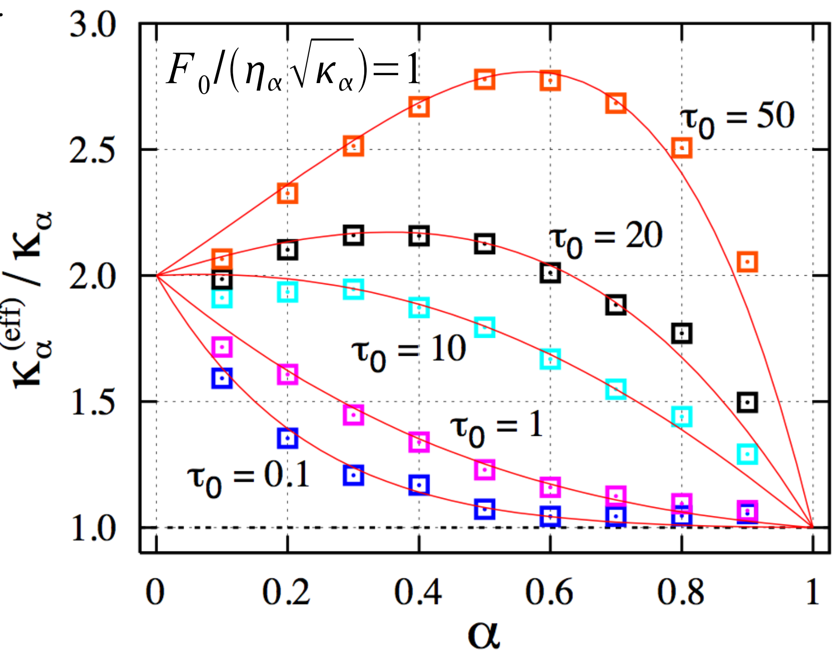
$\langle F(t) \rangle_{\tau_0} = 0$ – average force is zero




normal:

- mean particle position fluctuates around the initial condition;
- diffusion coefficient is equal to the free diffusion coefficient




anomalous:

- in the long time limit the particles will not respond to the external force!
- diffusion coefficient is larger than the free diffusion coefficient!

## more information in:

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## the study was carried out in collaboration with:

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