# A Monte Carlo approach for diffusion in inhomogeneous media and the “Ito – Stratonovich dilemma”

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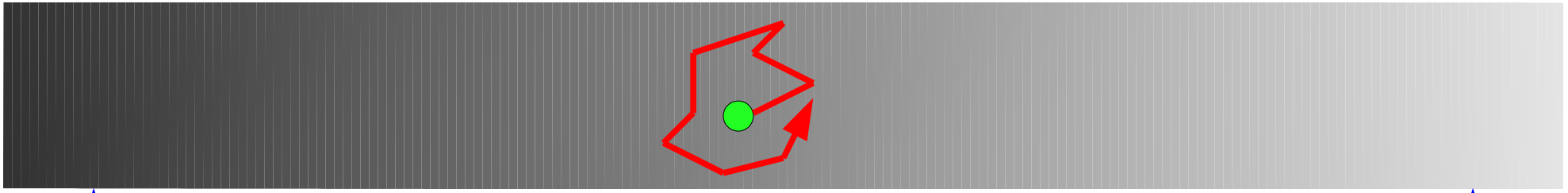
## Diffusion in a medium with the diffusion constant (diffusivity) varying in space



low diffusivity

high diffusivity

E.g., a colloidal particle in a fluid with a viscosity gradient

Overdamped limit is often appropriate. Overdamped Langevin equation:

$$\frac{dx}{dt}=\sqrt{2\,D(x)}\,R(t)$$

Noise $R(t)$: $\langle R(t)\rangle=0,\ \langle R(t)\,R(t')\rangle=\delta(t-t')$

$$\int_t^{t+\Delta t} R(t')\,dt'=\frac{r}{\Delta t},\ \langle r\rangle=0,\ \langle r^2\rangle=1$$

$$x(t+\Delta t)=x(t)+\int_t^{t+\Delta t}\sqrt{2\,D(x(t'))}\,R(t')\,dt'\approx x(t)+\begin{cases} r\sqrt{2\,D(x(t))\,\Delta t}, & \text{or} \\ r\sqrt{2\,D(x(t+\Delta t))\,\Delta t}, & \text{or, generally,} \\ r\sqrt{2\,D((1-\alpha)\,x(t)+\alpha\,x(t+\Delta t))\,\Delta t} & \end{cases}$$

Different definitions of the integral ("**calculi**"). Determined by parameter **α**.

$$x(t+\Delta t)=x(t)+r\sqrt{2\,D\big((1-\alpha)\,x(t)+\alpha\,x(t+\Delta t)\big)\,\Delta t}$$

| | | | |
|---|---|---|---|
| $\alpha=0$ | – | $D(x(t))$ | Ito calculus |
| $\alpha=1$ | – | $D(x(t+\Delta t))$ | “Isothermal” calculus |
| $\alpha=1/2$ | – | $D\left(\frac{x(t)+x(t+\Delta t)}{2}\right)$ | Stratonovich calculus |

Differences are significant: e.g., in the stationary state on an interval with reflecting boundaries the particle concentration

$$\rho(x)\propto D^{\alpha-1}$$

Uniform distribution for isothermal ($\alpha = 1$); more particles in regions with lower diffusivity otherwise ($\alpha < 1$).

What calculus is appropriate depends on the details of the system

If the overdamped Langevin equation is viewed as the limit of the 2nd order equation with the inertial term:

$$\frac{dx}{dt} = -\frac{m}{\zeta}\frac{d^2x}{dt^2} + \sqrt{\frac{2k_BT}{\zeta}}R(t)$$

$\zeta$ – friction coefficient

$T$ – temperature

$$\frac{k_BT}{\zeta} = D$$

$$m/\zeta \to 0$$

1) if $\zeta = \text{const}$, $T = T(x)$ – Ito

2) if $\zeta = \zeta(x)$, $T = \text{const}$ – isothermal (hence the name)

3) if $\zeta = \zeta(x)$, $T = \text{const}$, but noise correlation time, while approaching zero, is $>> m/\zeta$ – Stratonovich

Potential energy landscapes [I. M. Sokolov, Chem. Phys. 375 (2010) 359]:

isothermal Ito Stratonovich

Suppose we know what calculus a given system corresponds to.

## Simulation approaches

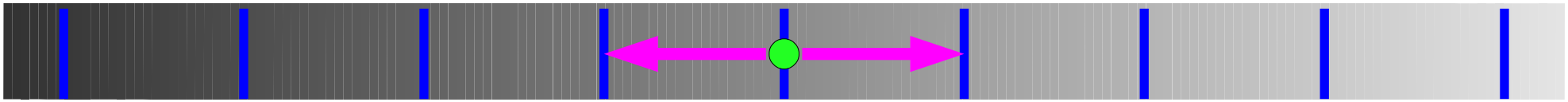
Standard molecular dynamics approaches correspond to different calculi:

Brownian Dynamics (BD): $x(t+\Delta t)=x(t)+r\sqrt{2\,D(x(t))\,\Delta t}$ – Ito

Langevin Dynamics (LD): solving numerically (e.g., using Verlet algorithm)

$$m\frac{d^2x}{dt^2}=-\zeta(x)\frac{dx}{dt}+\sqrt{2k_BT\,\zeta(x)}\,R(t)$$ – isothermal

## A Lattice Monte Carlo method

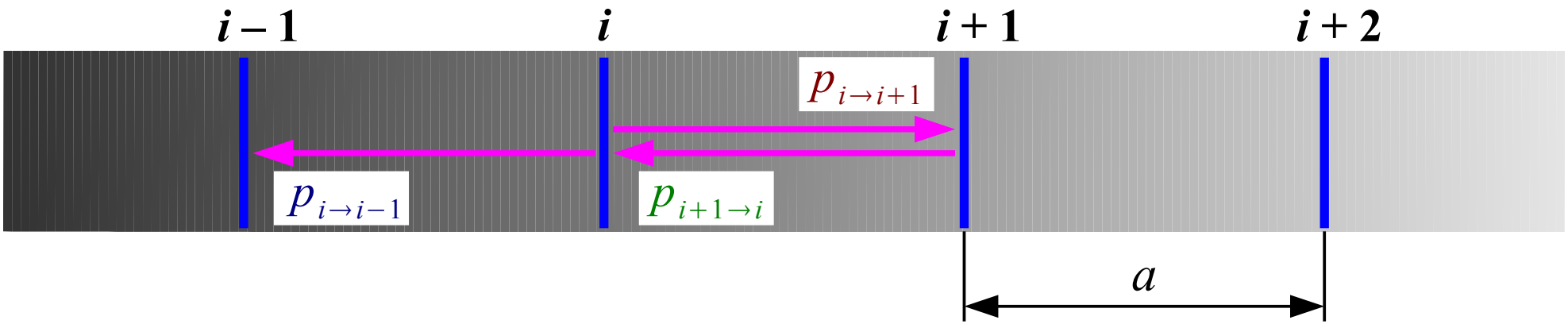


1) A common approach for all calculi;

2) Unlike, e.g., Metropolis MC, get the dynamics right (not just equilibrium);

3) A constant time step.

Some advantages compared to MD (even in accuracy).




Assume for now that *D* varies smoothly and the change between neighboring sites is small ⇒ bias is weak, probabilities of moves out of a site are ≈ same.

1) Detailed balance. The number of particles in a site in equilibrium $n_i \propto D_i^{\alpha-1}$.

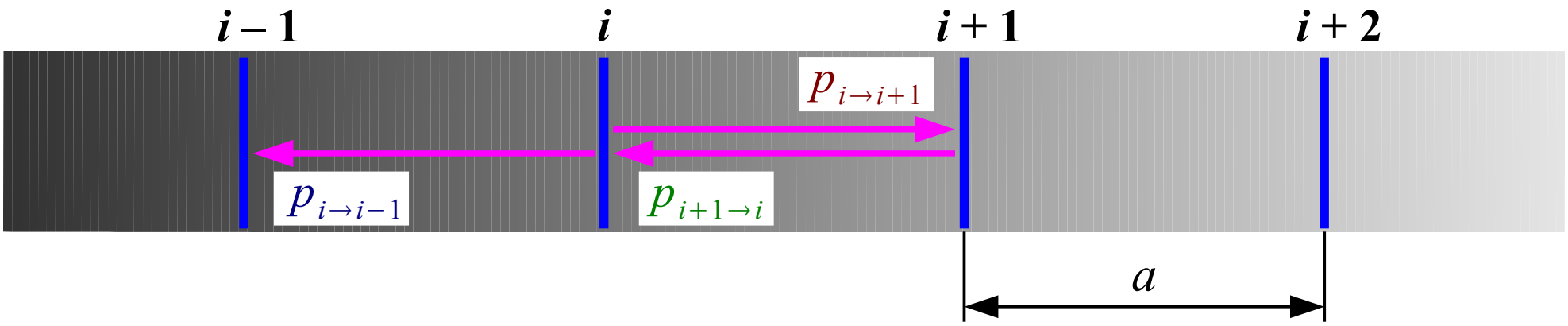
$$\frac{p_{i\to i+1}}{p_{i+1\to i}} = \frac{D_{i+1}^{\alpha-1}}{D_i^{\alpha-1}} = \exp\left[-(\epsilon_{i+1}-\epsilon_i)/k_B T\right], \quad \text{where} \quad \epsilon_i = (1-\alpha) k_B T \ln D_i$$

2) Dynamics. For a particle in site $i$, in one step

$$\langle \Delta x^2 \rangle = a^2 (p_{i\to i-1} + p_{i\to i+1}) \approx 2 D_i \Delta t \quad \Rightarrow \quad p \approx D \Delta t / a^2$$

Based on this, choose

$$p_{i\to i+1} + p_{i+1\to i} = (D_i + D_{i+1}) \Delta t / a^2$$

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if there is an external force

Based on this, choose

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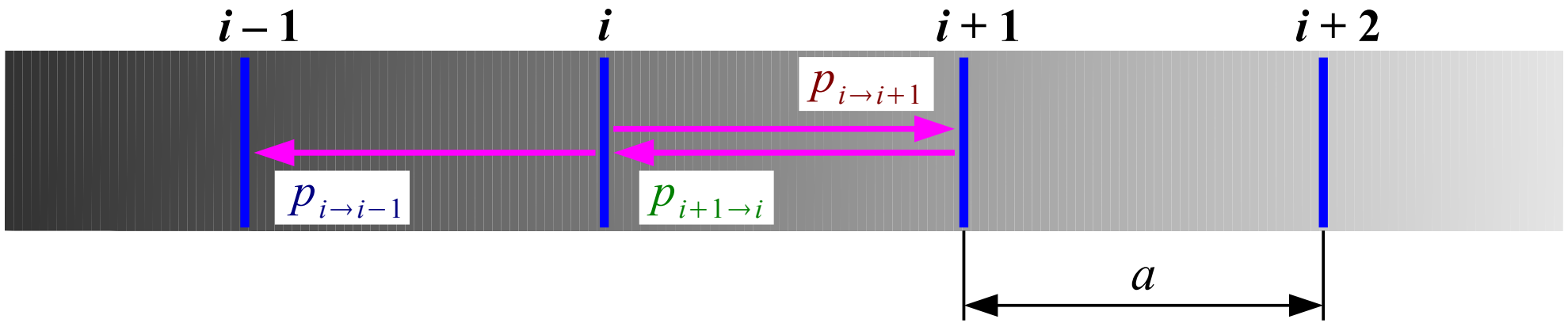
Straightforward to generalize to higher dimensions




$$\frac{p_{i\to i+1}}{p_{i+1\to i}}=\frac{D_{i+1}^{\alpha-1}}{D_i^{\alpha-1}}=\exp\left[-(\epsilon_{i+1}-\epsilon_i)/k_BT\right],\ \text{where}\ \epsilon_i=(1-\alpha)\ln D_i+E_i\ ;\ \ p_{i\to i+1}+p_{i+1\to i}=(D_i+D_{i+1})\Delta t/a^2$$

$$p_{i\to i+1}=\frac{(D_i+D_{i+1})\Delta t}{a^2}\times\frac{\exp\left[-(\epsilon_{i+1}-\epsilon_i)/k_BT\right]}{1+\exp\left[-(\epsilon_{i+1}-\epsilon_i)/k_BT\right]}$$

$$p_{i+1\to i}=\frac{(D_i+D_{i+1})\Delta t}{a^2}\times\frac{1}{1+\exp\left[-(\epsilon_{i+1}-\epsilon_i)/k_BT\right]}$$

Generally, $p_{i\to i+1}+p_{i\to i-1}\neq 1$. Probability to stay put $p_{i\to i}=1-p_{i\to i+1}-p_{i\to i-1}$.

$p_{i\to i}\approx 1-2D\Delta t/a^2$. Higher in regions of lower diffusivity.

$\Delta t<\approx a^2/2D_{\max}$ so $p_{i\to i}\geq 0$ .

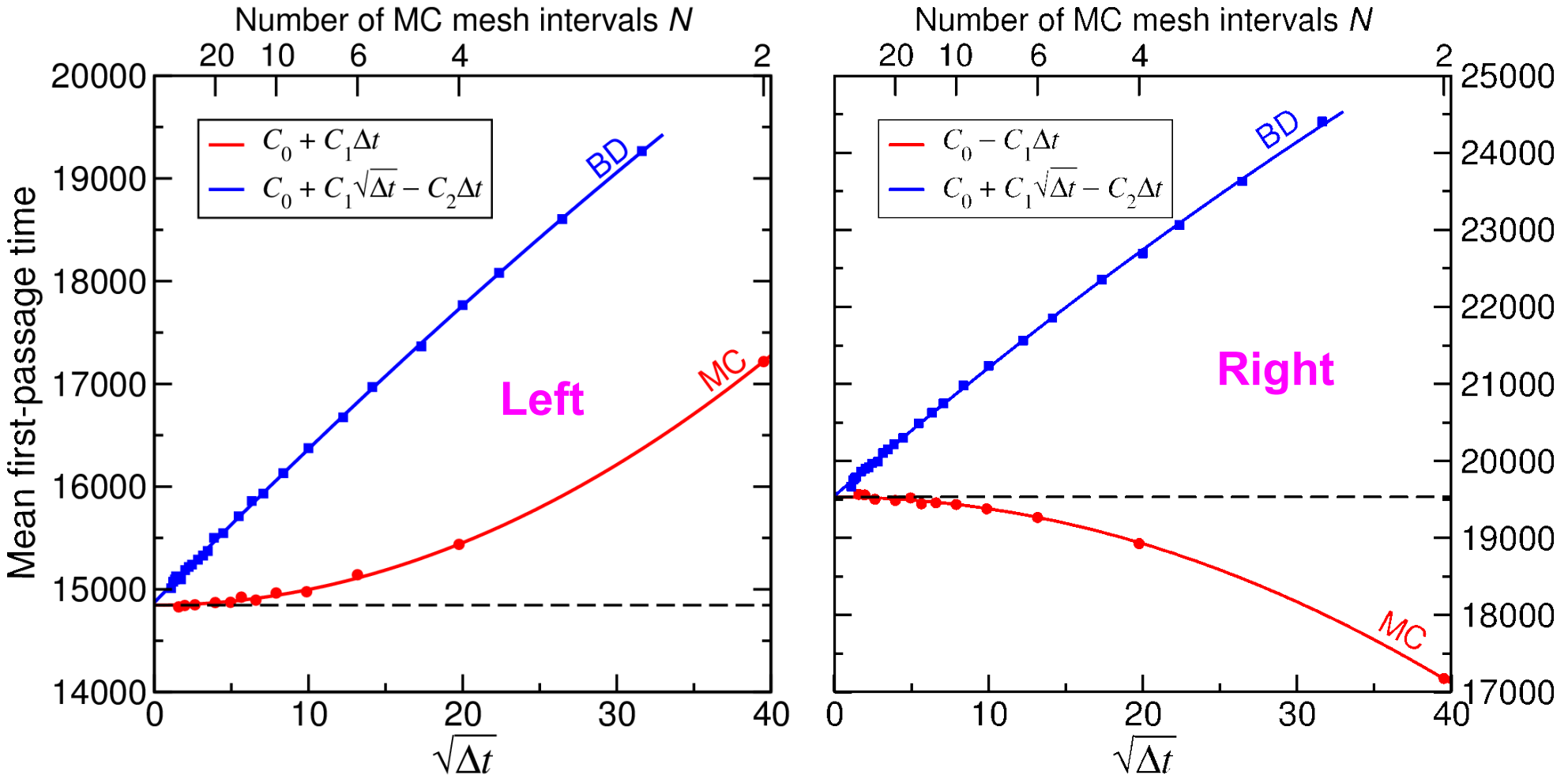
Note for $p_{i\to i}(D)=\text{const}$ $\Delta t\propto a^2\propto 1/N^2$, where $N$ is the number of intervals between lattice sites.

Example: an interval with absorbing boundaries, $\alpha = 0$. Start in the middle.

$x = 0$ $x = L$

Friction $\zeta = \zeta_L + (\zeta_R - \zeta_L)(x/L)$. Diffusivity $D = 1/\zeta$ $(k_B T \equiv 1)$. $\zeta_L = 10$, $\zeta_R = 100$, $L = 50$

Brownian Dynamics vs. Monte Carlo. **Conditional MFPTs** (left and right boundaries).




MC converges faster than BD as a function of the time step (linear vs. $\sqrt{\Delta t}$).

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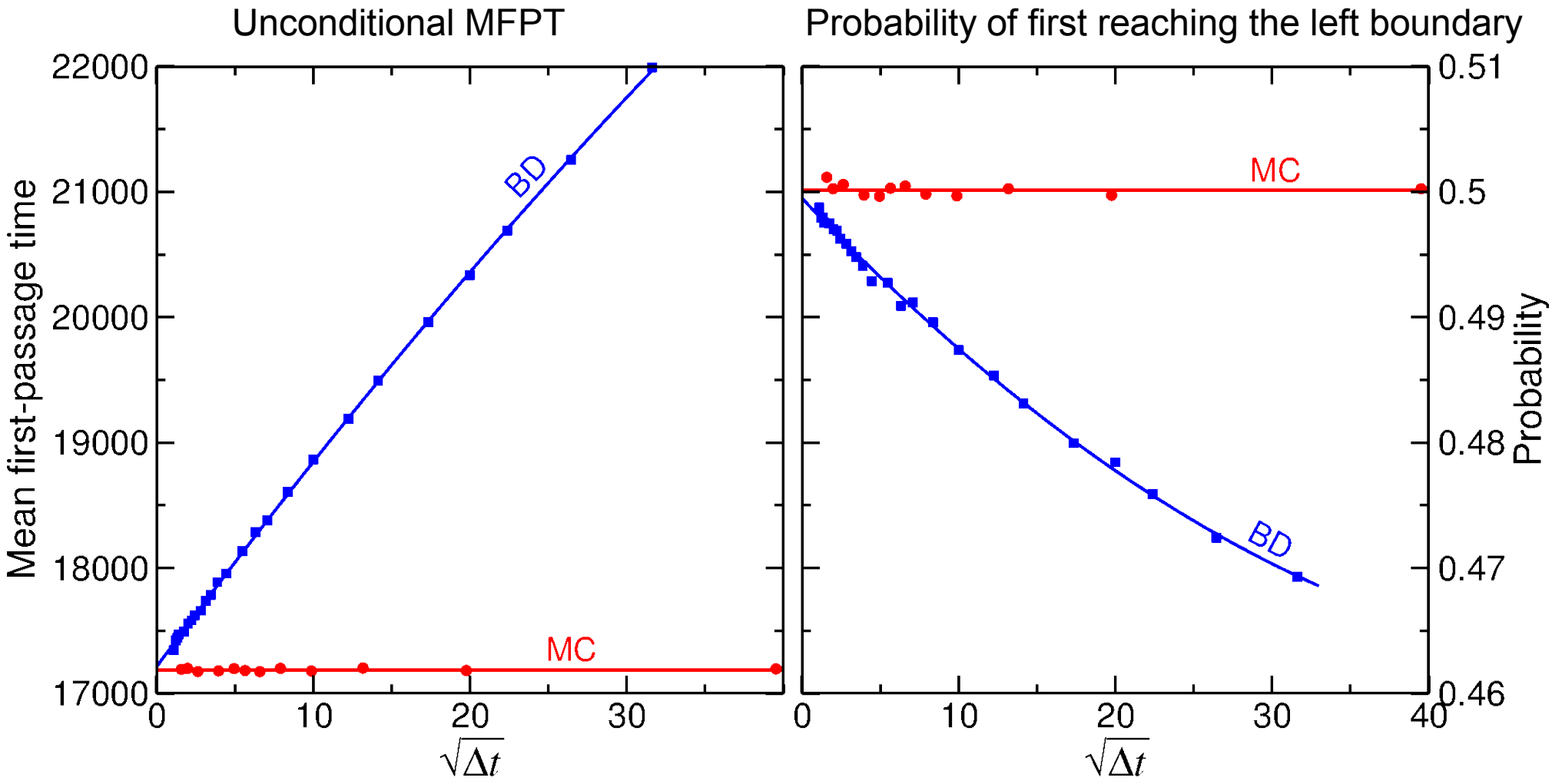
Brownian Dynamics vs. Monte Carlo



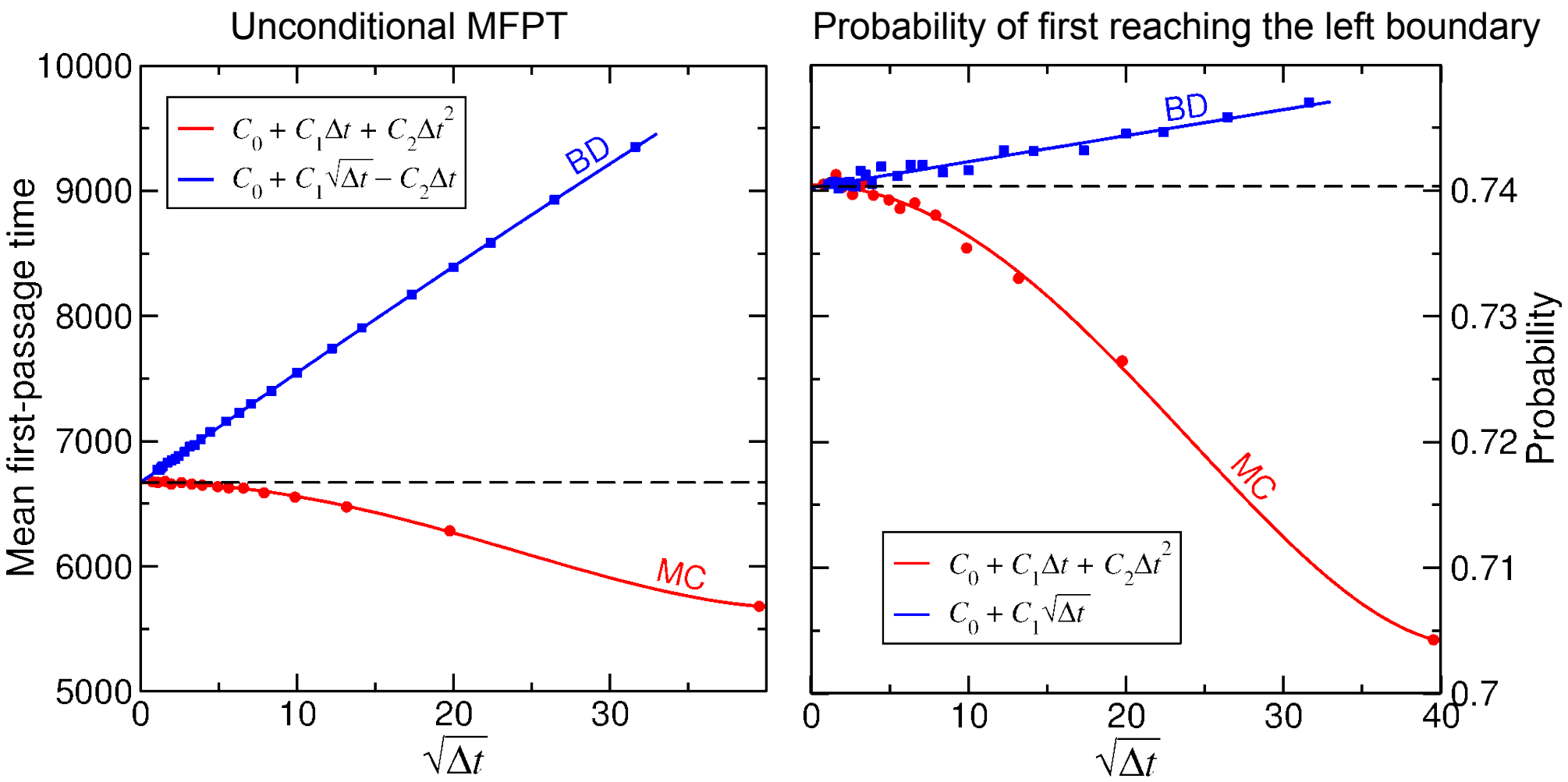

"Accidental" – only for Ito and linear friction dependence.

LMC reproduces the general property of Ito calculus – reaching either boundary is equiprobable. Does not depend on $D(x)$.

For other calculi and diffusivity dependences, MFPT and probabilities are not exact, but still converge linearly as a function of $\Delta t$.

Isothermal ($\alpha = 1$). Linear $D = D_L + (D_R - D_L)(x/L)$. $D_L = 0.1$, $D_R = 0.01$, $L = 50$

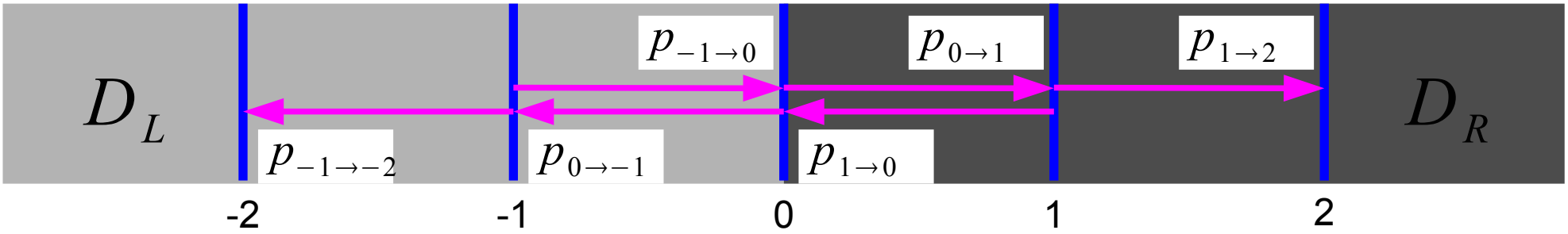
Compare to BD with an additional force.




Possible to modify the algorithm to always get correct probabilities, but more complicated and probably not generalizable to higher dimensions.

So far, have assumed that the diffusivity change is gradual.

A sharp interface. Assume that it coincides with a lattice site.




Not clear what value to take for $D_0$. Also, using our algorithm literally,

$p_{-1\to 0}+p_{0\to -1}=2D_L^*\Delta t/a^2$, where $D_L^*=\dfrac{D_{-1}+D_0}{2}$, but would some other mean be better?

By considering the first-passage problem from site 0 to its neighbors:

$$D_0=\left(\frac{D_L^{\alpha-1}+D_R^{\alpha-1}}{2}\right)^{\frac{1}{\alpha-1}}$$

Harmonic mean for $\alpha=0$,

$\to$ geometric mean for $\alpha\to 1$.

$$D_L^*=\frac{D_L^{\alpha}\left(D_L^{1-\alpha}+D_0^{1-\alpha}\right)}{2}$$

Arithmetic mean for $\alpha=0$,

simply $D$–1 for $\alpha\to 1$.

An interval with absorbing boundaries, interface in the middle. Particles starting at the interface.

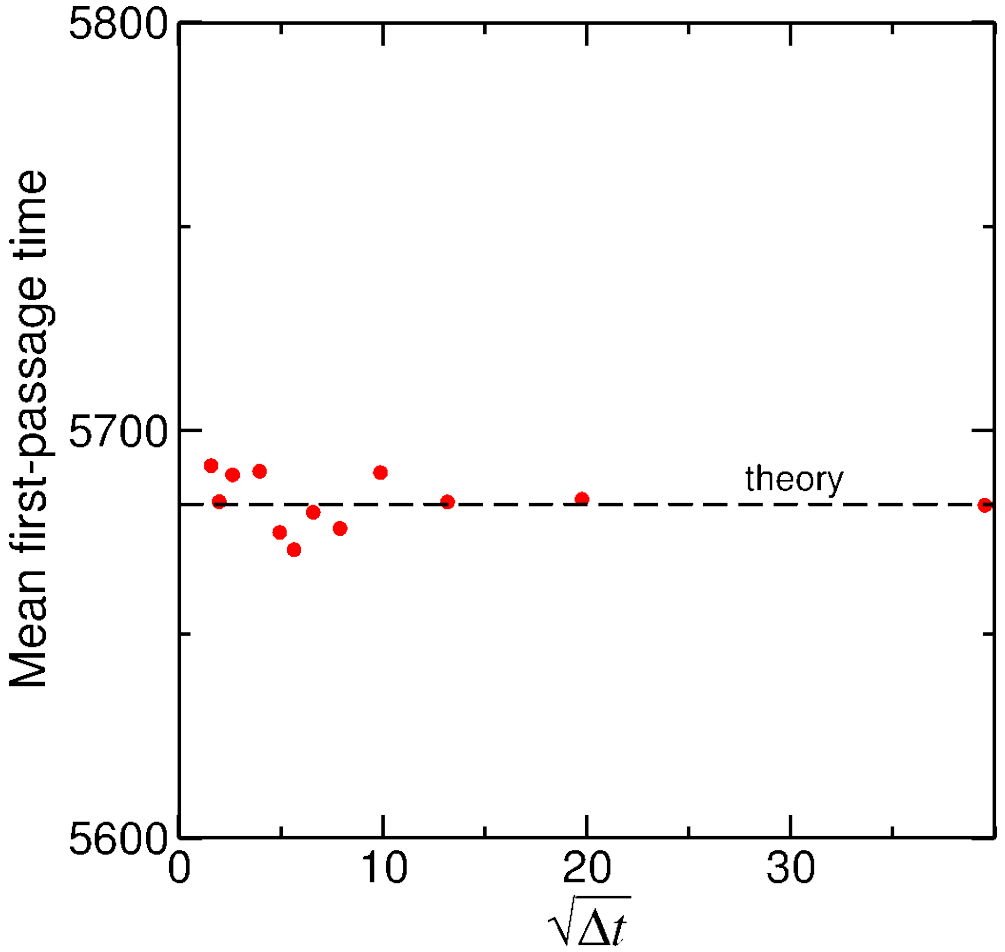
Isothermal ($\alpha = 1$)

$D_L = 0.1, \quad D_R = 0.01, \quad L = 50$

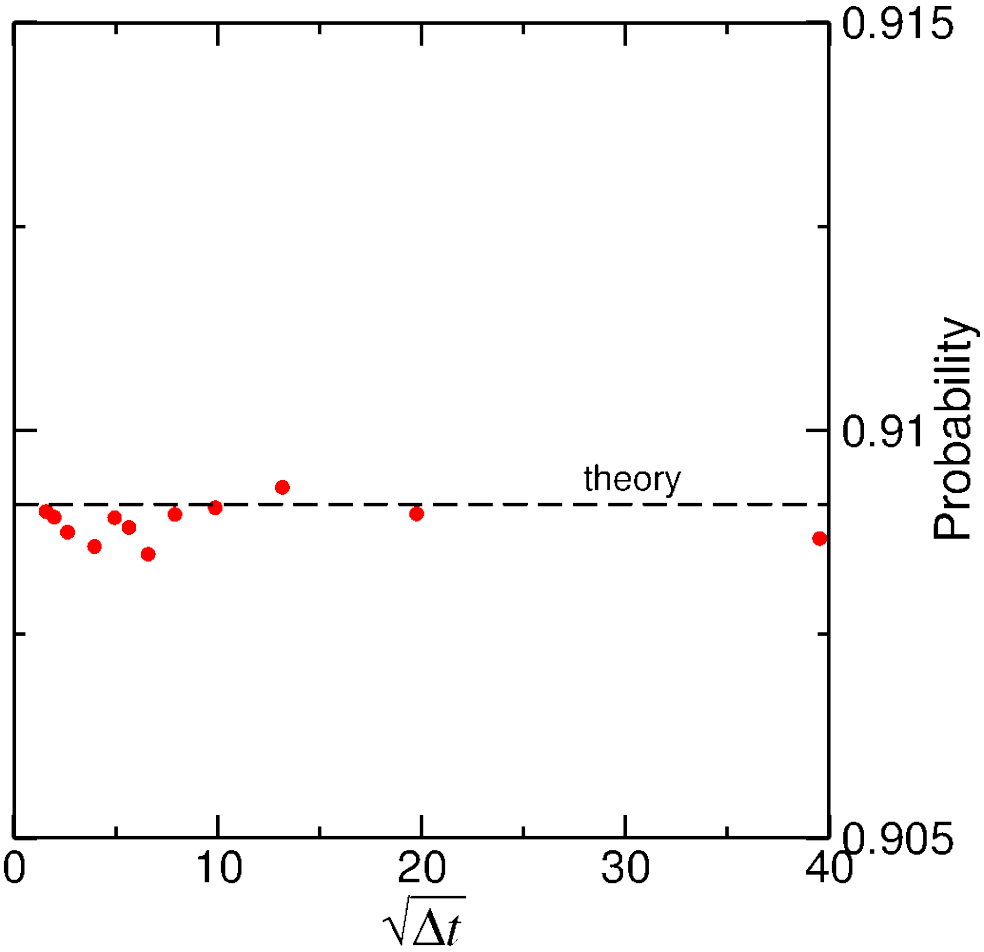
$$\mathrm{MFPT} = \frac{L^2}{8} \frac{D_L^{1-\alpha} + D_R^{1-\alpha}}{D_L^{1-\alpha} D_R^{1-\alpha} \left( D_L^{\alpha} + D_R^{\alpha} \right)} = \frac{L^2/4}{D_L + D_R} \approx 5682$$

$$P_L = \frac{D_L^{\alpha}}{D_L^{\alpha} + D_R^{\alpha}} = \frac{D_L}{D_L + D_R} = 10/11$$

Unconditional MFPT



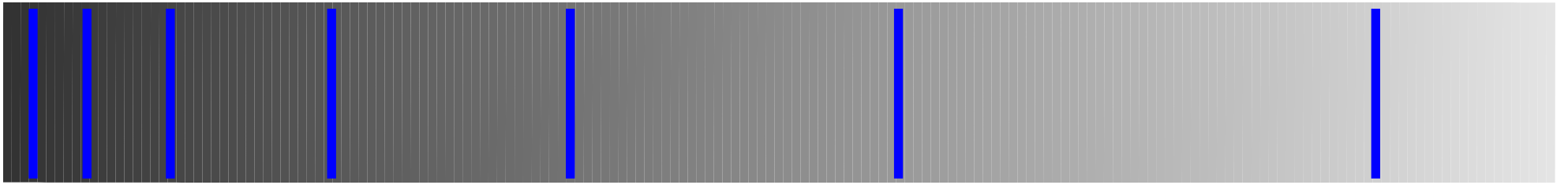

Probability of first reaching the left boundary




Also exact for other calculi.

# Additional remarks

1. Given that $D \approx pa^2/\Delta t$ , can keep $p$ constant and vary $a$ instead.



2. The problem of particle diffusion with a single viscosity interface is surprisingly rich and interesting. See arXiv:1208.5081.

3. In the future, apply this approach to a more complex situation, e.g., a lattice model of a polymer.

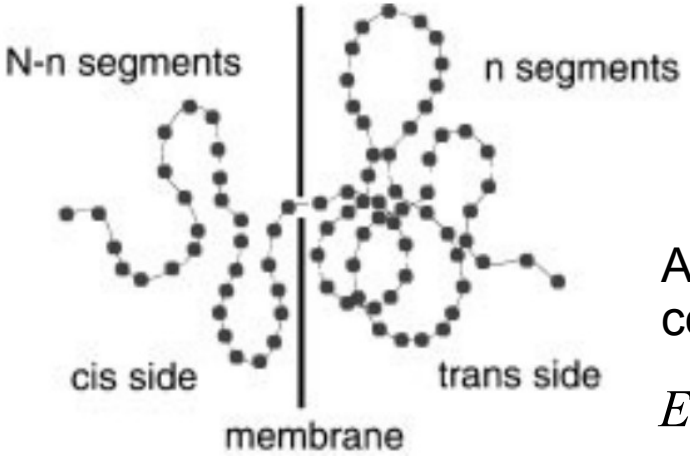
# Why is BD worse?

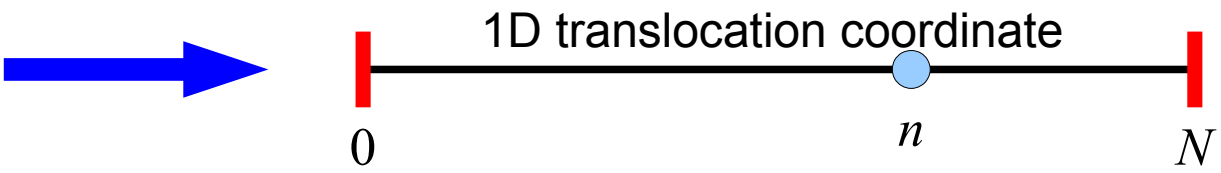
A step originating in the high-*D* region near the interface goes relatively far into the low-*D* region. But the converse is not true.

In MC, the step length is always the same.

# Example: a 1D polymer translocation model

W. Sung and P.J. Park, PRL 77 (1996) 783; M.G. Gauthier and G.W. Slater, JCP 128 (2008) 065103




Assuming both parts stay in equilibrium, the entropic contribution to the free energy is

$$E(n)/k_BT = (1-\gamma)[\ln(n)+\ln(N-n)]; \quad \gamma = 0.69 \quad \text{for SAW}$$

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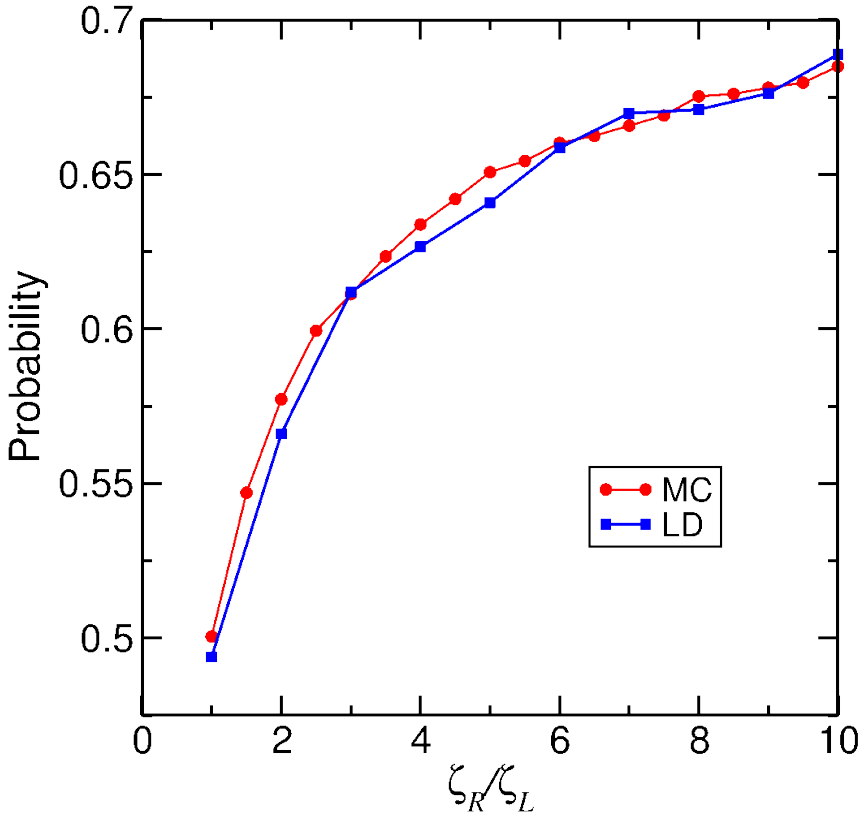



If the viscosities on the two sides are different, in the 1D model this corresponds to linear friction dependence

$$\zeta = \zeta_L + (\zeta_R - \zeta_L)(n/N)$$

On physical grounds, $\alpha = 1$ (isothermal calculus)

$N = 50$ (also # mesh intervals in MC).

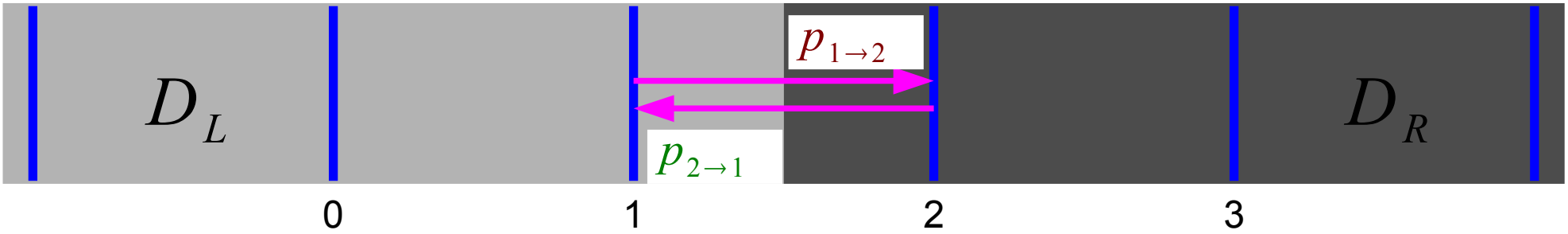
In LD, $m/\zeta_{\min}$ = 1.0; $\Delta t = 0.02$.

For $\alpha = 1$, there would be no bias, even in the presence of the entropic force.

So far, have assumed that the diffusivity change is gradual.

A sharp interface

E.g., useful when simulating a full 3D lattice model of translocation.




$$p_{1\to 2}+p_{2\to 1}=2\frac{D_L+D_R}{2}\Delta t/a^2$$

Arbitratily chose the arithmetic mean. An important issue when $D_L$ and $D_R$ are very different.

More generally, $p_{1\to 2}+p_{2\to 1}=2D^*\Delta t/a^2$. Choose $D^*$ so that the probability of reaching site 2 before site 0 starting at site 1 is correct (and likewise for reaching 3 before 1 starting at 2).

$$D^*=\frac{D_L^{\alpha}D_R^{\alpha}\left(D_L^{1-\alpha}+D_R^{1-\alpha}\right)}{D_L^{\alpha}+D_R^{\alpha}}$$

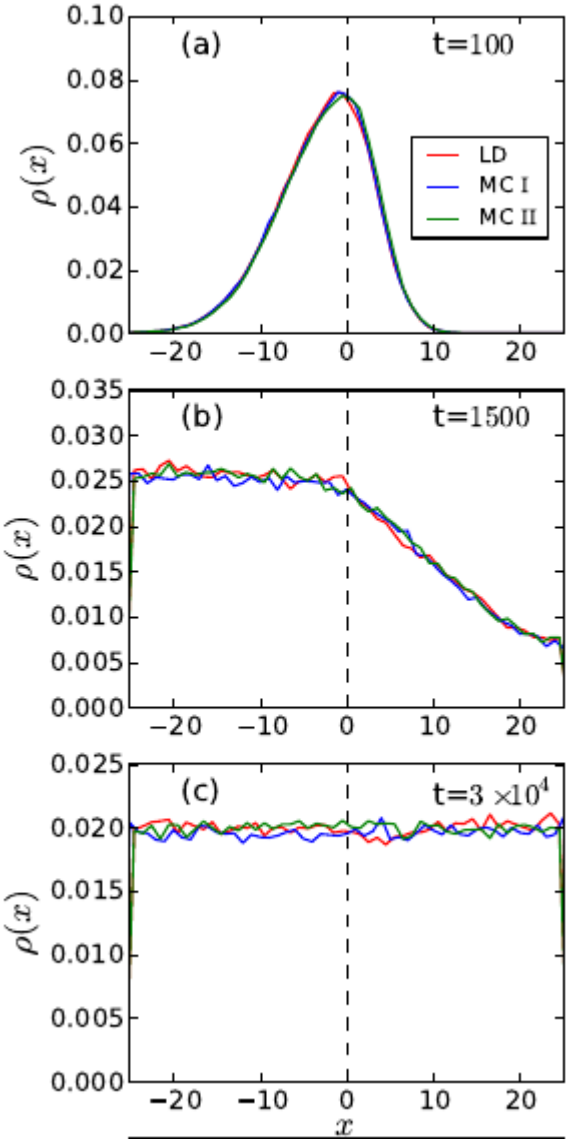
Arithmetic mean for Ito ($\alpha = 0$)

Geometric mean for Stratonovich ($\alpha = 1/2$)

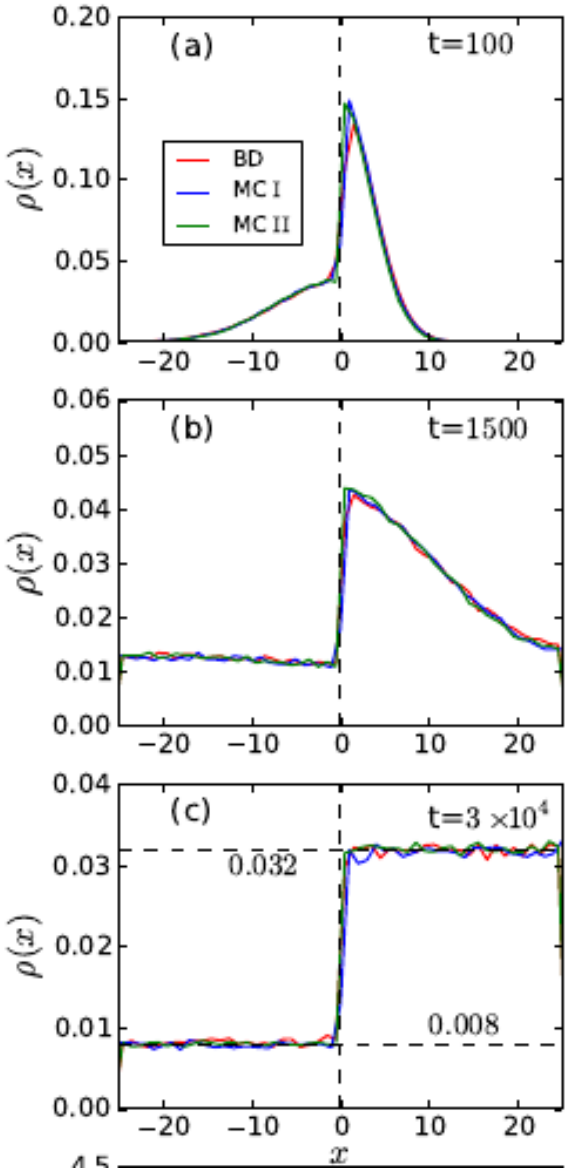
Harmonic mean for isothermal ($\alpha = 1$)

An interval with reflecting boundaries, interface in the middle. Particles starting at the interface.

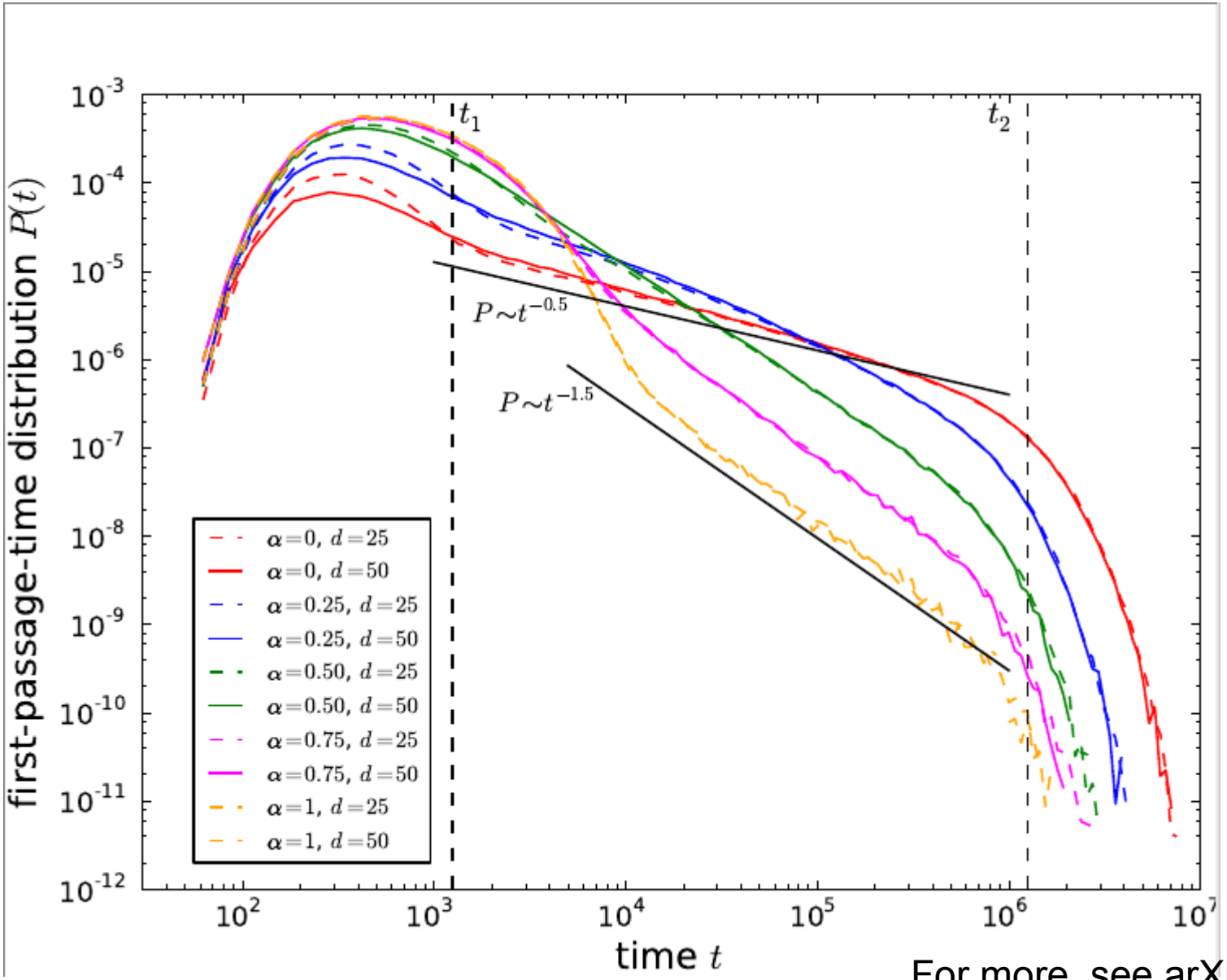
isothermal




Ito



A simple system, but some interesting results, especially in the high-diffusivity-ratio limit. Example: the conditional first-passage-time distribution for particles reaching the wall on the high-diffusivity side




$D_L = 0.5$

$D_R = 0.0005$

An intermediate power-law region with the exponent depending on the calculus:

$-1/2$ for $\alpha = 0$,

$-3/2$ for $\alpha \geq 1/2$,

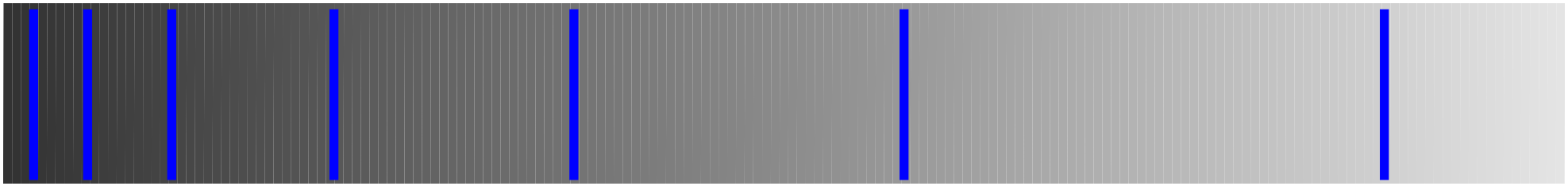
a combination of these with a crossover between them for $0 < \alpha < 1/2$.

For more, see arXiv:1208.5081

# Another MC approach

Probability of a move $p \approx D\,\Delta t / a^2$ had to be varied to keep $\Delta t$ and $a$ constant.

Alternatively, can vary $a$ and keep $p$ constant. Then $a \propto \sqrt{D}$.



If in equilibrium the average number of particles per site is constant, then the concentration $\propto 1/\sqrt{D}$, as in Stratonovich calculus. The effective energy is then $\epsilon_i = (1/2 - \alpha) \ln D_i$.

Unfortunately, hard to generalize to higher dimensions.

Need to make sure that $m/\zeta$ is small, but the time step is even smaller.

The higher $\Delta t$, the more efficient the simulation,but it may make sense to keep $\Delta t$ lower than max so $p_{i \to i}$ is not too close to 0 to avoid simulation artifacts.