Diffusion and response of Brownian particles in confined structures (restricted RWs)

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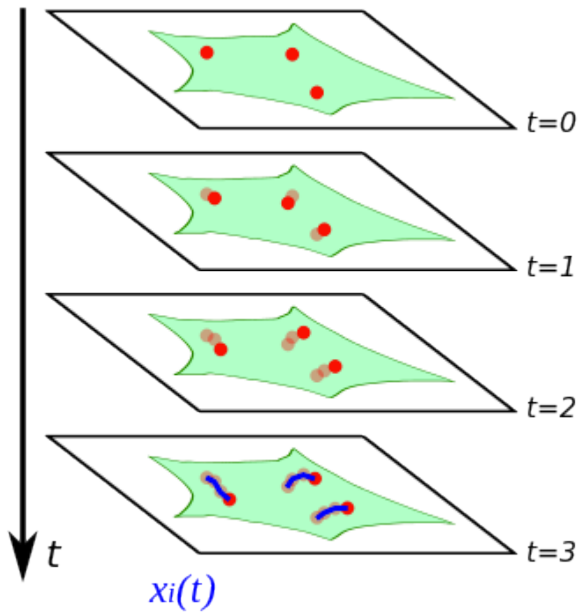
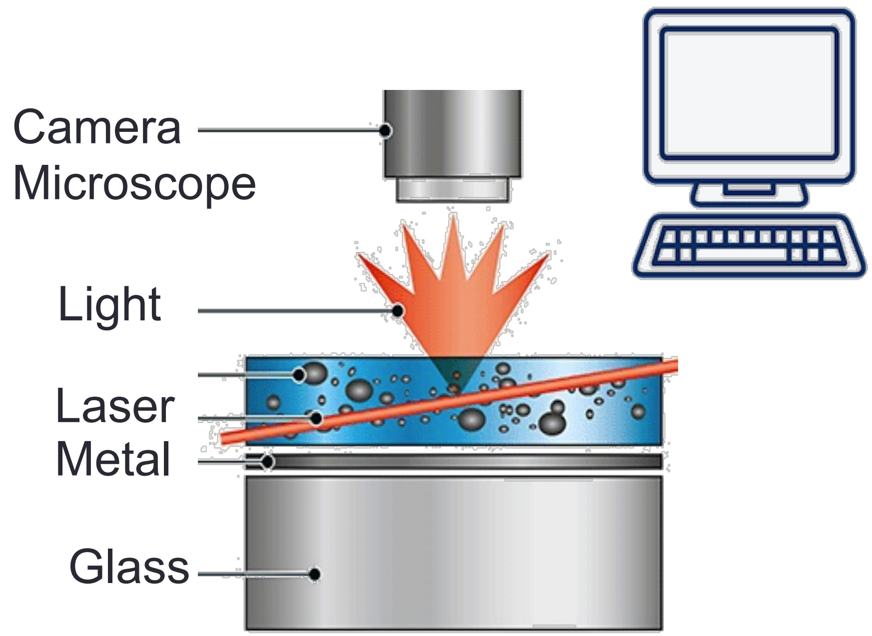
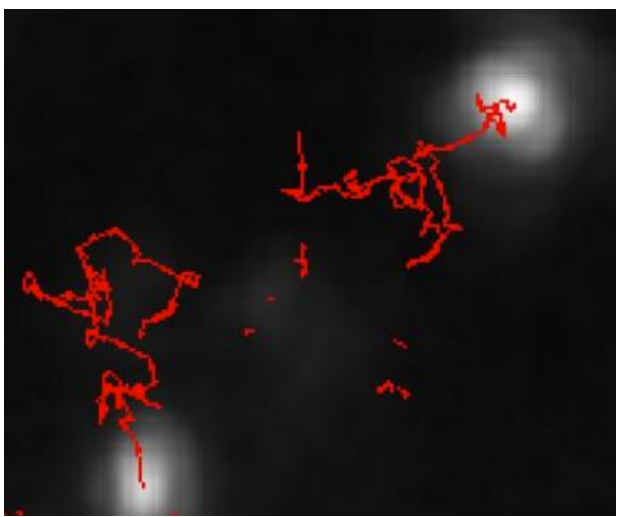
Outline of this talk

- Single Particle tracking technique
- Nano-Micro Confinement
  (size and dimensional reduction)
- Confined Random Walks
- Central Limit Theorem: Violations
- Standard versus Anomalous
- Example of Diffusion on:
  Branched structures,
  Fractal Trees, Channels

Single molecule tracking







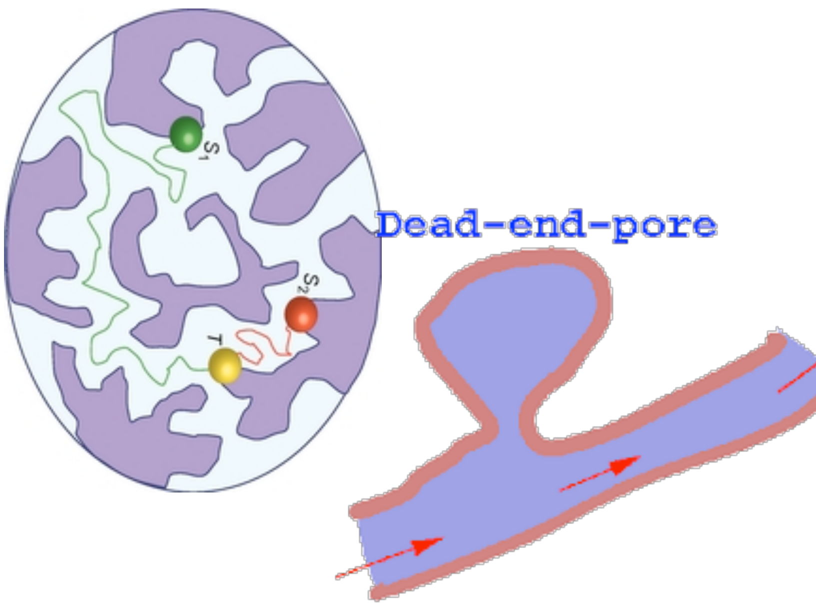
Ultra-Microscope + Laser illumination
CCD camera + Software
Particle Position

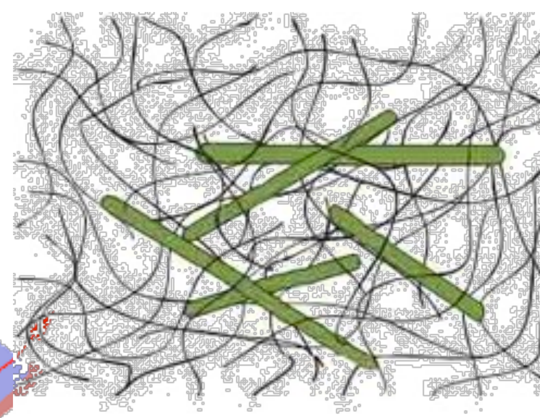
method to study
Nano-Micro Confinement

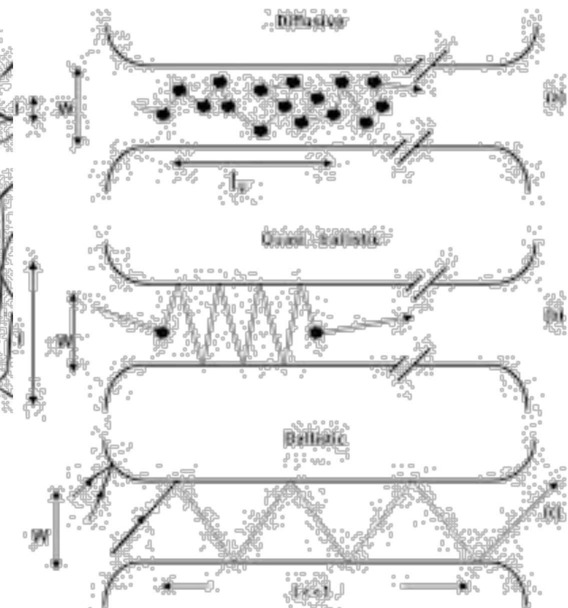
Nano-Micro confinement

PHENOMENOLOGY of GEOMETRY CONTROLLED TRANSPORT

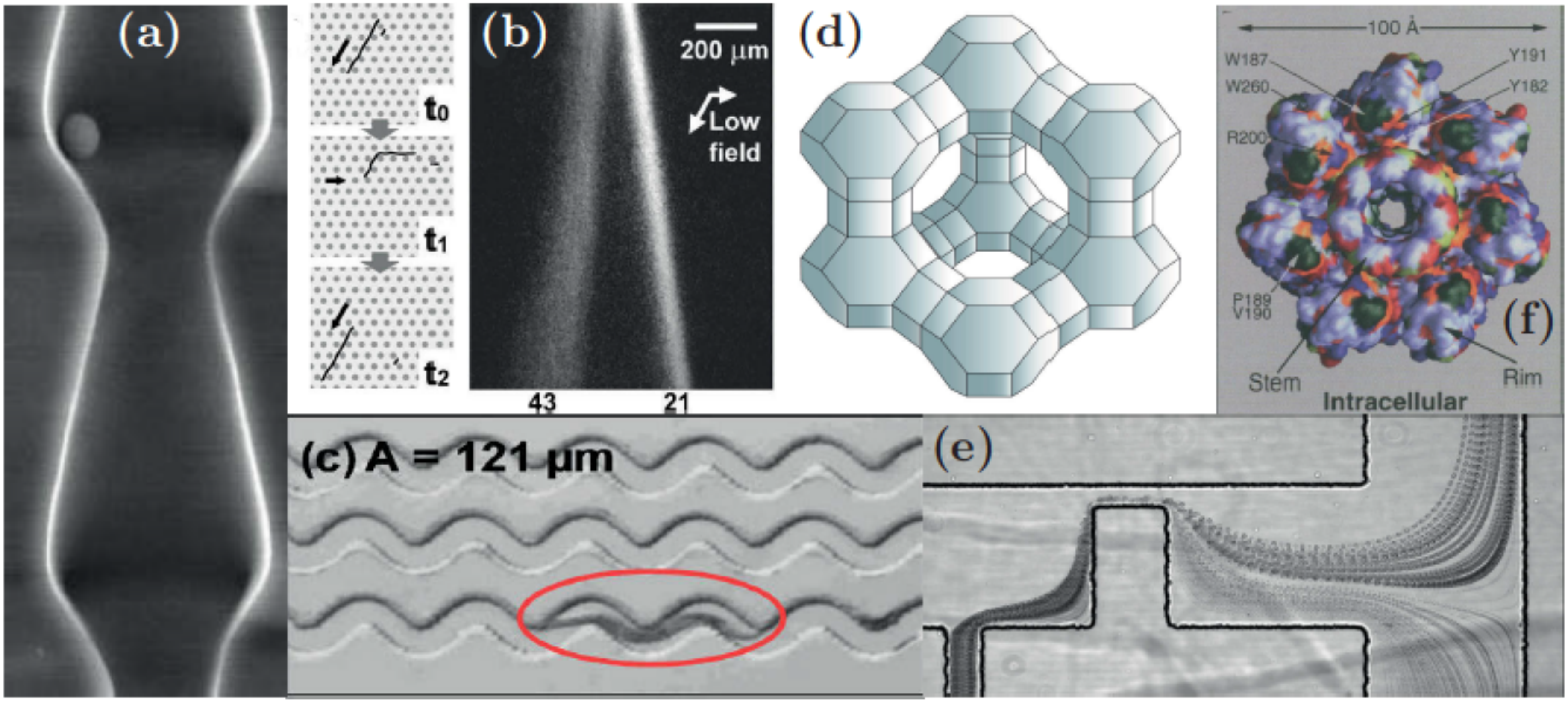
- Biology: transport in tissues, targeting,
  microtubules of cytoskeleton, cell motility
- Chemistry: controlled reaction, filtering
- Physics: porous media, low-dim transport, microfluidic
- Nanotechnology: nanodevices, chemical delivery
- Mathematics: discrimination normal--anomalous







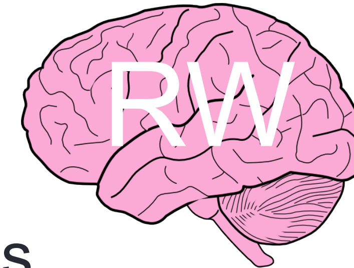
Collage from high impact journals



solid-state pore zeolites (aluminum-silicate) bio-nanopore

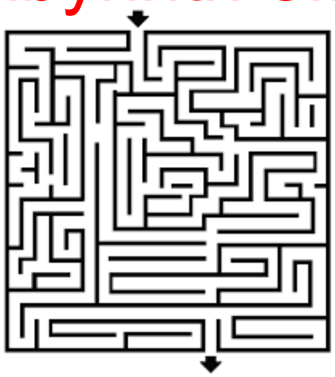
c-elegans in micro-channel

Confined Random Walks



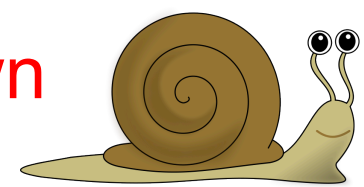
Geometric constraint: narrow path, compartments, branching, self-similarity (fractals), discontinuity (boundaries)

"labyrinth effect"



Two-state transport:
Active (ON) or Stalled (OFF)

Transport
- hindered or slowed down
  less: mobility, diffusivity
- anomalous sub-diffusion



Violation of Central Limit Theorem

Sum of displacements $$\left\langle \left|\mathbf{R}_N\right|^2 \right\rangle = \sum_{i=1}^{N} \left\langle \left|\delta\mathbf{R}_i\right|^2 \right\rangle + 2\sum_{i>j}^{N} \left\langle \delta\mathbf{R}_i \cdot \delta\mathbf{R}_j \right\rangle$$

does not satisfy C.L.T

Main reasons:

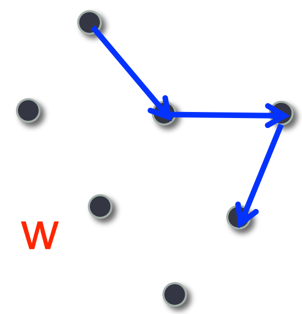
Not negligible correlation between displacements

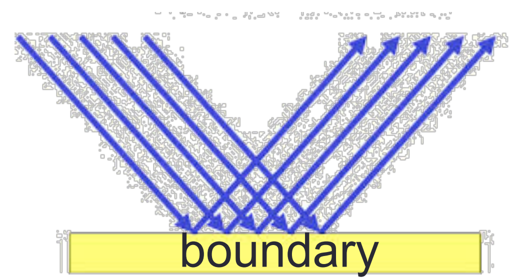
breaking of symmetry or isotropy

(spatial correlations)

Non-asymptotic regimes

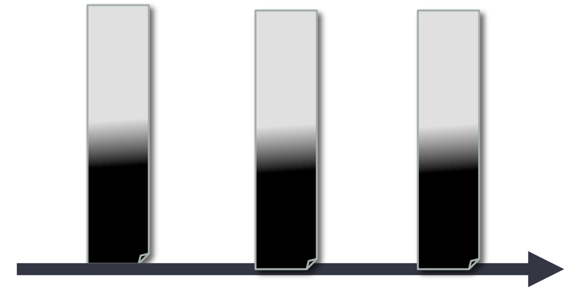
Mean-free path ~ confining section w



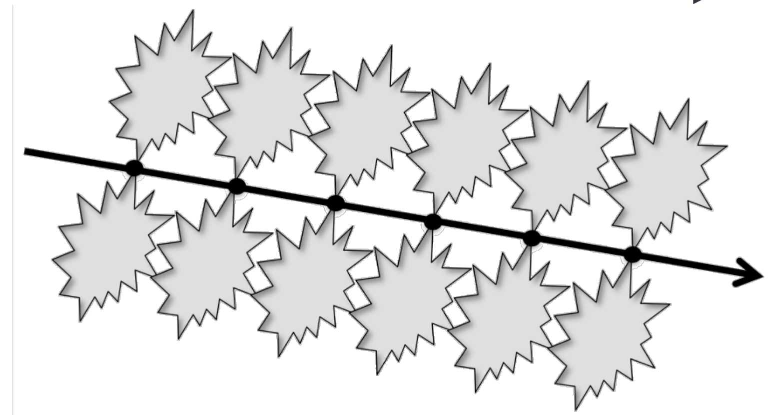


Violation of CLT ➔ NON STANDARD BEHAVIOUR

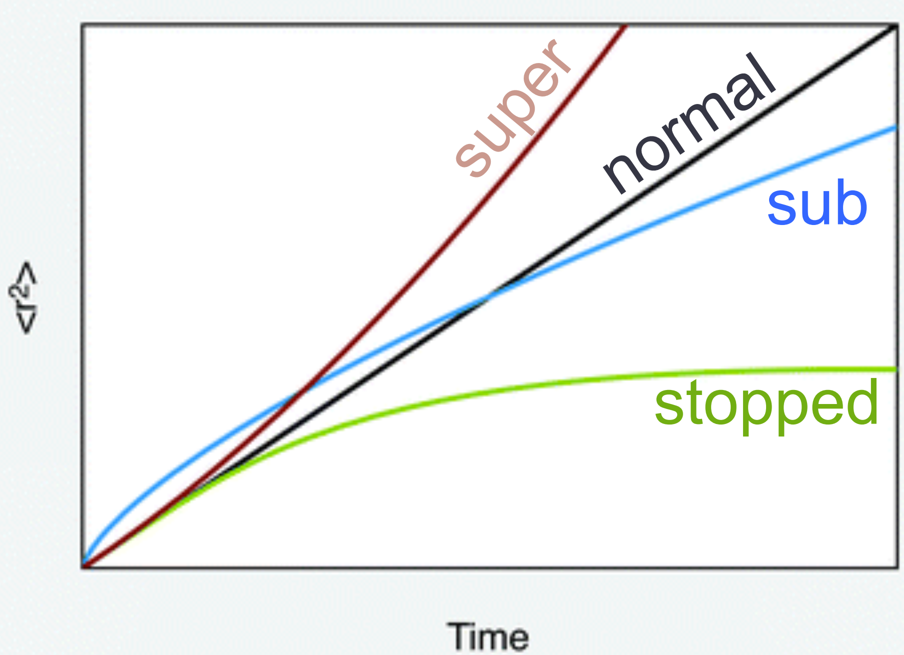
Strong anisotropy



$$\mathrm{M.S.D.} = \left\langle \left|\mathbf{r}(t) - \mathbf{r}(0)\right|^2 \right\rangle$$



$$MSD_{//}(t) + MSD_{\perp}(t)$$



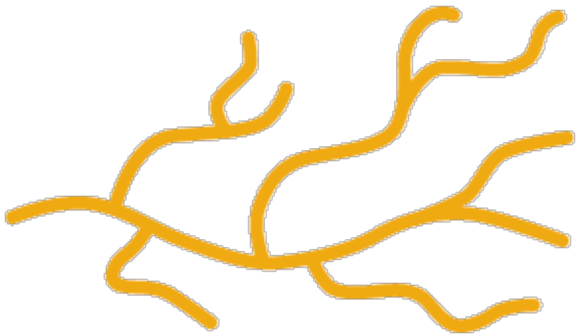
Competition: Backbone Sidebranches

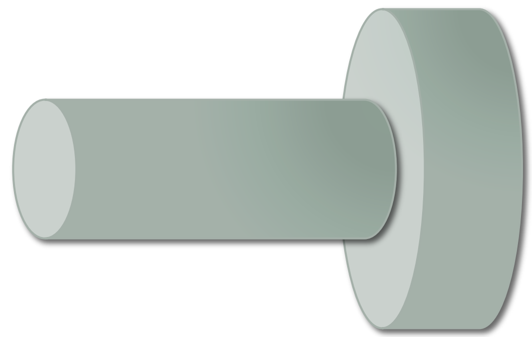
Turnover from: Anomalous => Standard

Theoretical description

We focus on

BRANCHED STRUCTURES and CHANNELS





Theory: main difficulty is taking into account
- Complexity of the support of motion
- Boundary conditions

Continuous time RW

Natural framework for trapping (waiting time)

$$\mathbf{r}(t) = \mathbf{r}_0 + \sum_{n=0}^{N(t)} \delta\mathbf{r}_n$$

simple RW $N(t) = t/\tau$

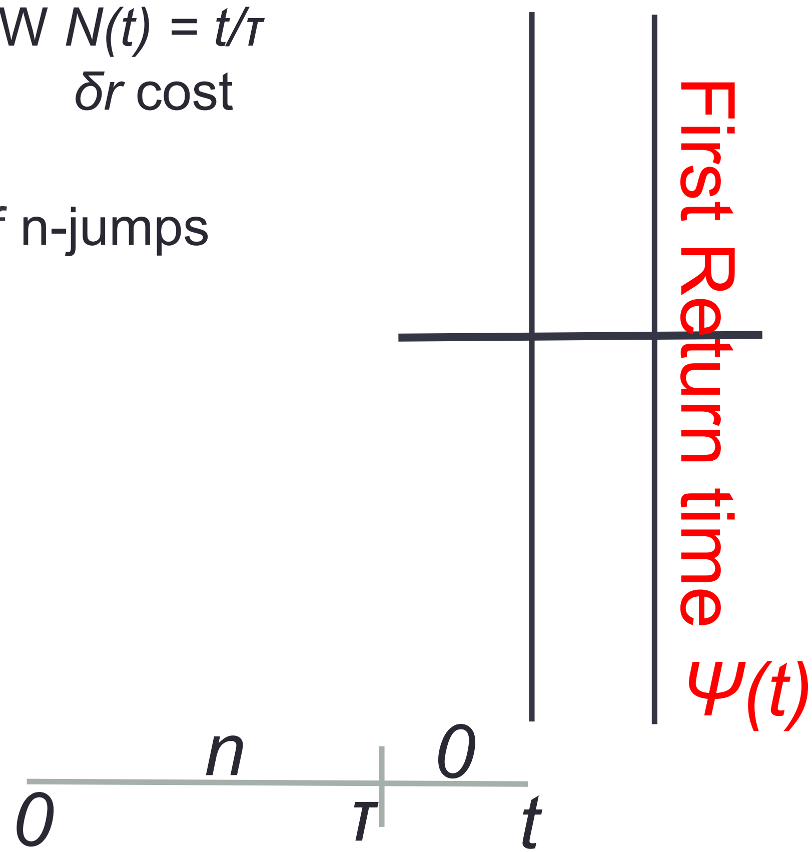
δr cost

Pr. of n-jumps

$$p(\boldsymbol{r}, t) = \sum_{n=0}^{\infty} P_n(t)\, p_n(\boldsymbol{r})$$

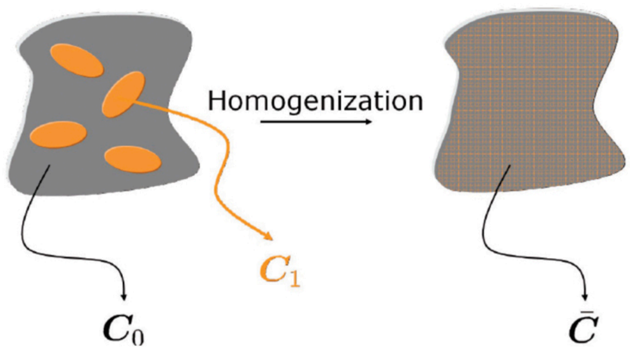
Pr. at r after n-jumps

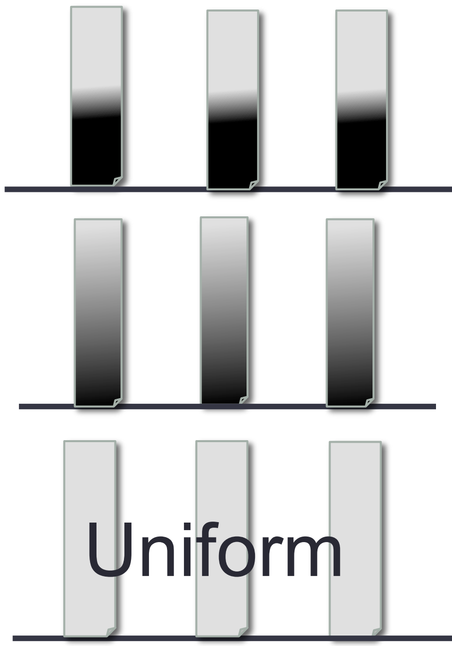
$$P_n(t) = \int_0^t \phi(t-\tau)\psi_n(\tau)\mathrm{d}\tau$$



Simpler method: Invoking HOMOGENIZATION !

Invoking Homogenization





Applied to system with strong anisotropy
= transversal diffusion “saturated”

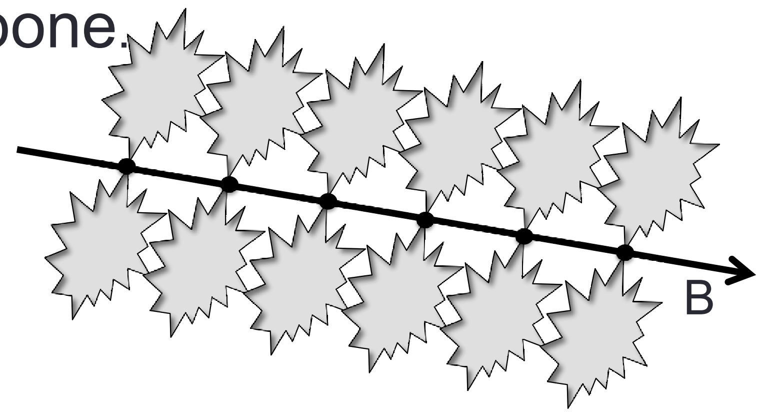
$$MSD_{//}(t) + MSD_{\perp}(t)$$

1) Asymptotic — Standard $D_0 \longrightarrow D_{eff}$

2) Pre-asymptotic — Not Standard, System dependent

Branched structures: comb-like

Diffusion along the backbone (B) depends on shape & size of Side-Branches. Anomalous regimes arise from their geometrical importance over the backbone.



$$\langle \Delta x^2(t) \rangle = \sum_{ij} \langle \delta_i \delta_j \rangle = \sum_{i}^{t} \langle \delta_i^2 \rangle + 2 \sum_{i}^{t} \sum_{j=i+1}^{t} \cancel{\langle \delta_i \delta_j \rangle}$$

$<\delta^2> = 1/2$

$$\delta_j = \begin{cases} 1 & \mathbf{r}_j \in B \\ 0 & \mathbf{r}_j \notin B \end{cases}$$

MSD

$$\langle \Delta x^2(t) \rangle = \frac{t}{2} P_B(t) \qquad D \sim \lim_{t \to \infty} P_B(t)$$

$<\delta>_\varepsilon = \varepsilon$ DRIFT

$$\langle \Delta x(t) \rangle_e = \varepsilon t \, P_B(t)$$

$$R(t) = \frac{\langle \Delta x^2(t) \rangle_0}{\langle \Delta x(t) \rangle_\varepsilon} = \frac{1}{2\varepsilon}$$

exact simplification

FDR

Effective diffusion coefficient

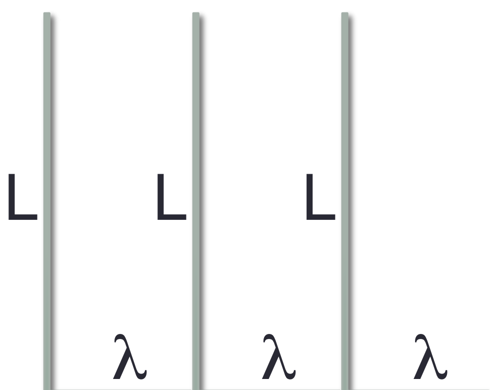
After homogenization
Standard diffusion on the Backbone occurs with a renormalized coefficient $D < D_{free} = D_0$

$$D(L) = D_0 P_B(\infty)$$

P_B asymptotic probability to occupy Backbone sites

Homogenization: all the M_{sb} sites on the SB are equally probable
$p_s = 1/M_{sb}$

$$D(L) = D_0 \frac{M_B(L)}{M_{sb}(L) + M_B(L)}$$

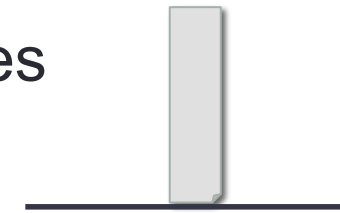


$$D(L) = D_0 \frac{\lambda}{L + \lambda} \qquad D(L) = D_0 \frac{\lambda}{L^d + \lambda} \sim L^{-d}$$

Homogenization time $t_*(L)$

$t_*(L)$ shortest timescale after which longitudinal diffusion becomes standard.

$t_*(L)$ ~ time taken by RW to visit most of $M_{sb}(L)$ sites in a single Side-Branch of size L.



$$t_*(L) = g[M_{sb}(L)]$$

Crossover An. - Std.

$$\left\langle x^2(t) \right\rangle_0 \sim \begin{cases} t^{2\nu} & t < t_*(L) \\ D(L)\ t & t > t_*(L) \end{cases}$$

Matching argument at $t_*(L)$

$$t_*(L)^{2\nu} = D(L)\ t_*(L)$$

Anomalous scaling

$$t_*(L) \sim L^u \qquad D(L) \sim L^{-d}$$

Distinct sites on SB visited by RW: S(t)

Bouchaud, Georges Phys. Rep. (1990)

$$S_{sb}(t) \sim \begin{cases} \sqrt{t} & d=1 \\ t/\ln(t) & d=2 \\ t & d>2 \end{cases}$$

$$S_{sd}[t_*(L)] \sim M_{sb}(L) \sim L^d$$

$$t_*(L) \sim \begin{cases} L^2 & d=1 \\ L^2 \ln(L) & d=2 \\ L^d & d>2 \end{cases}$$

$$\left\langle \Delta x^2(t) \right\rangle_{An} \sim \begin{cases} t^{1/2} & t<t_* & d=1 \\ \ln(t) & t<t_* & d=2 \\ c & t<t_* & d=2 \end{cases}$$

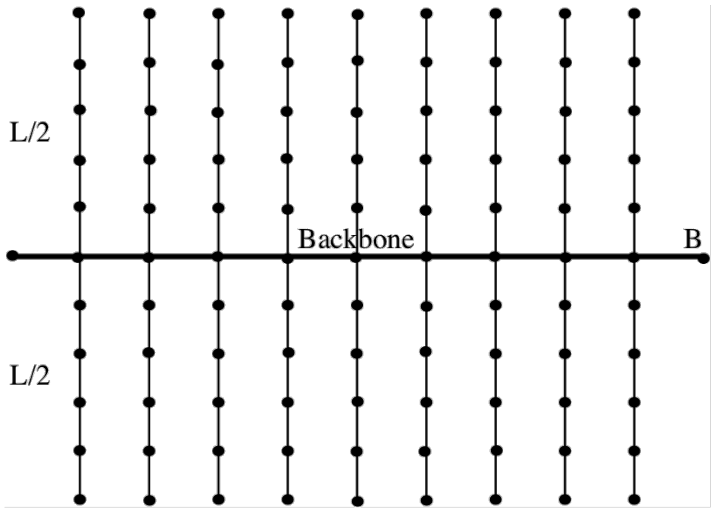
fractals

$$S(t) \sim t^{d_s/2} \qquad d_s = 2d/d_w$$

$$t_*(L) \sim L^{2d/d_s} \qquad 2\nu = 1 - d_s/2$$

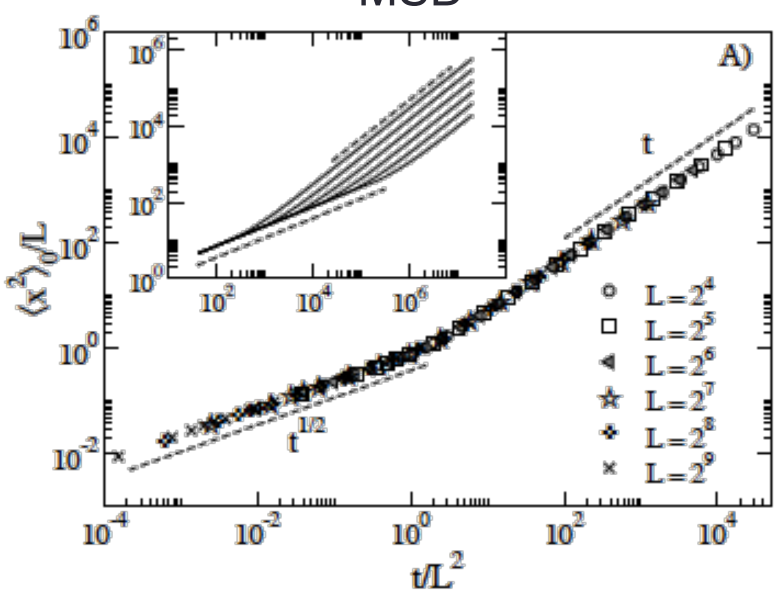
$$\left\langle \Delta x^2(t) \right\rangle \sim t^{1-d_s/2}$$

Side-branch d = 1

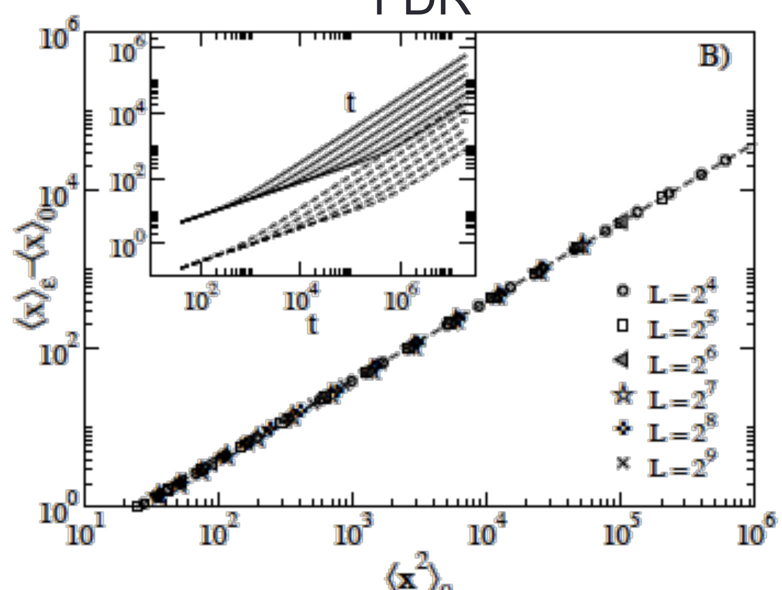


Simple comb lattice

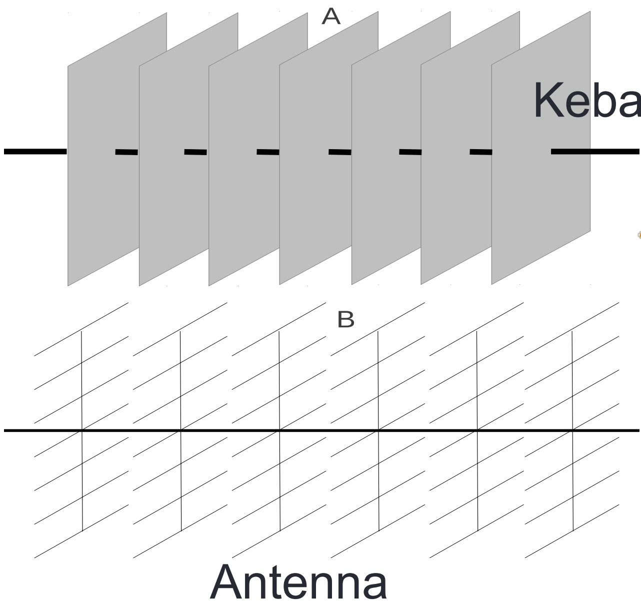
MSD



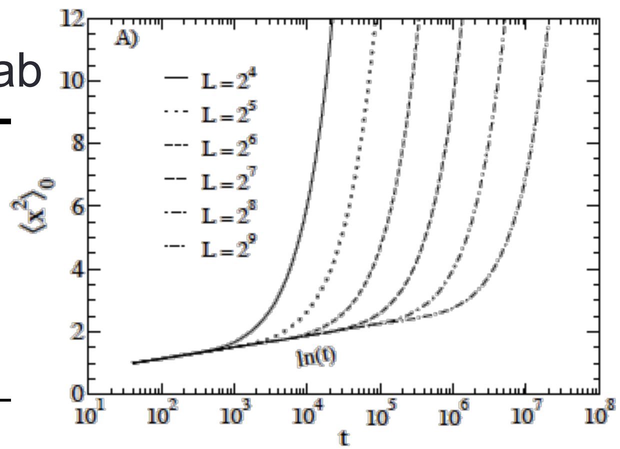
FDR



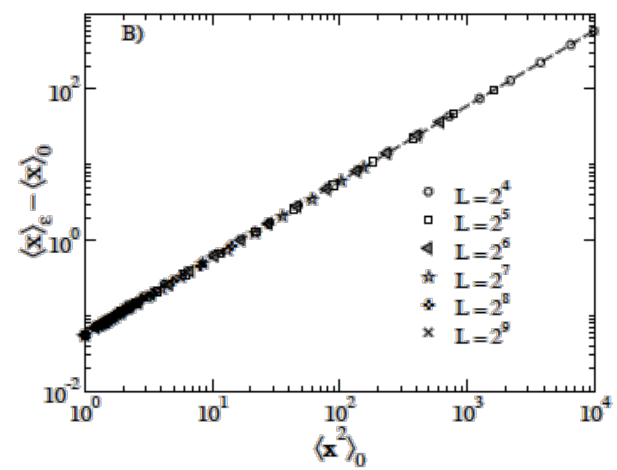
Side-Branch d = 2



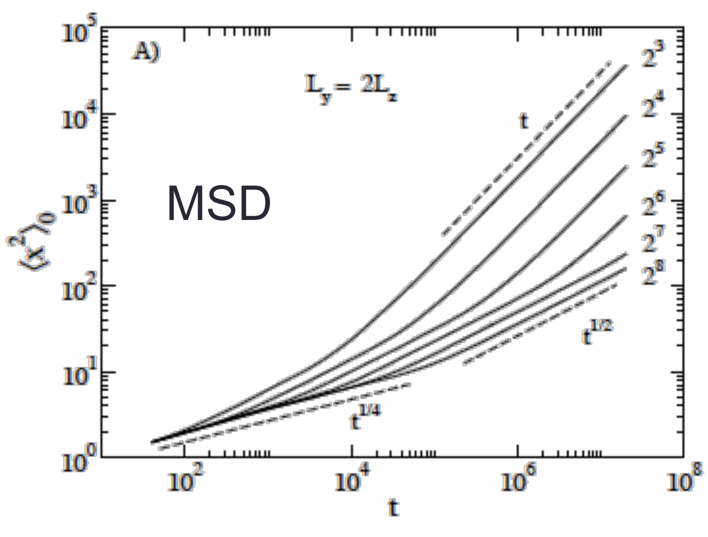
MSD

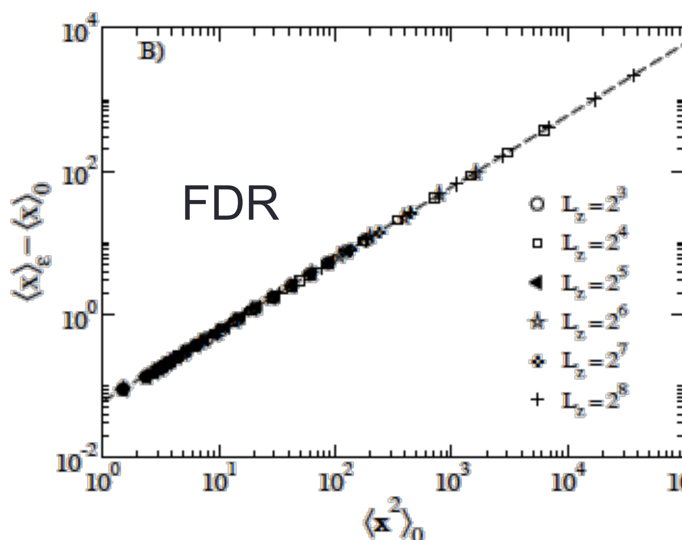


FDR

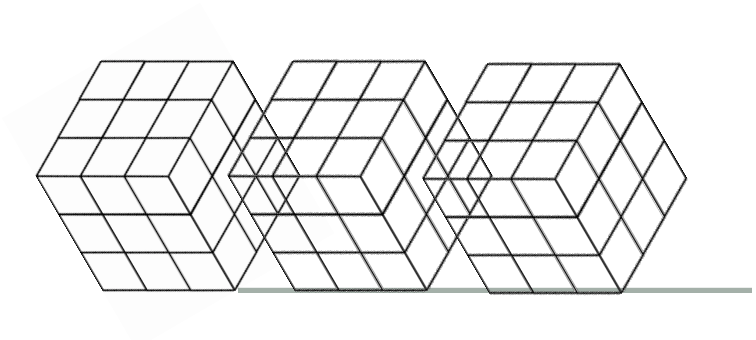


$d_s = 3/2$



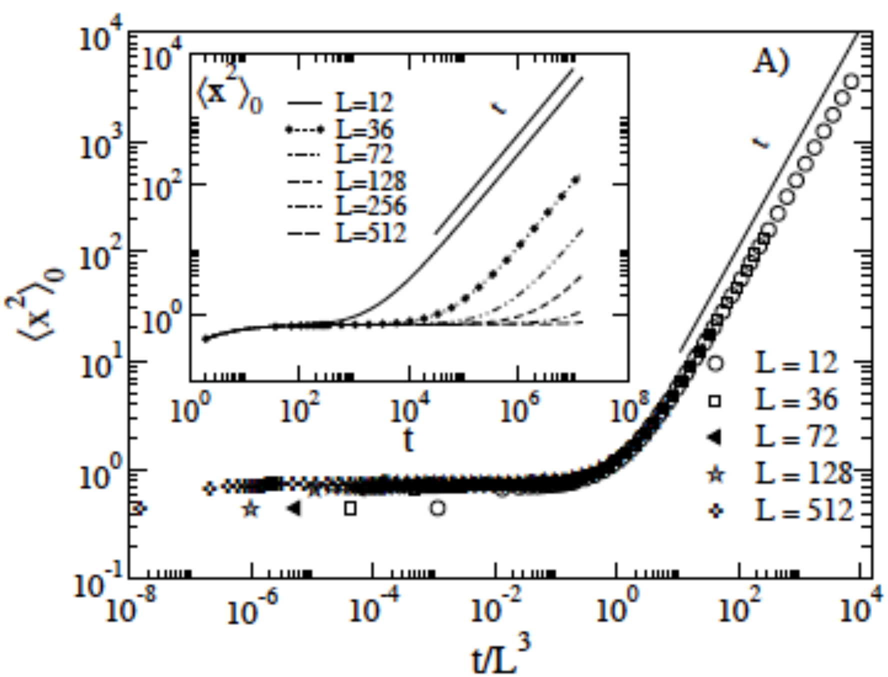


Side-branch d = 3

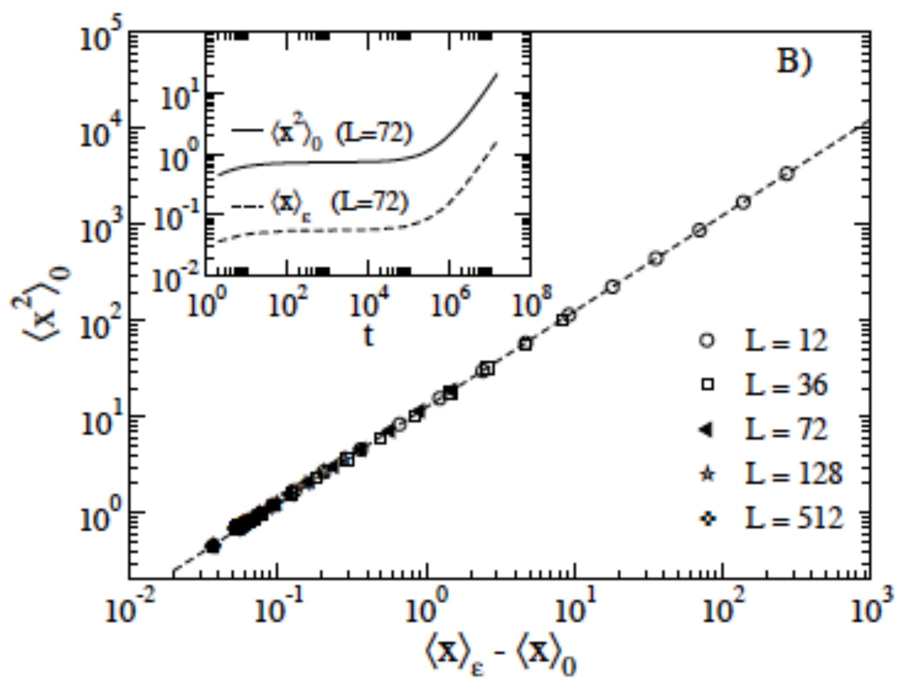


SB = CUBES along the Backbone

MSD



FDR



More complex scenario

Discrimination standard - diffusion requires spectrum of all moments $\left\langle x^q(t) \right\rangle$

a) Simple scaling (collapse)

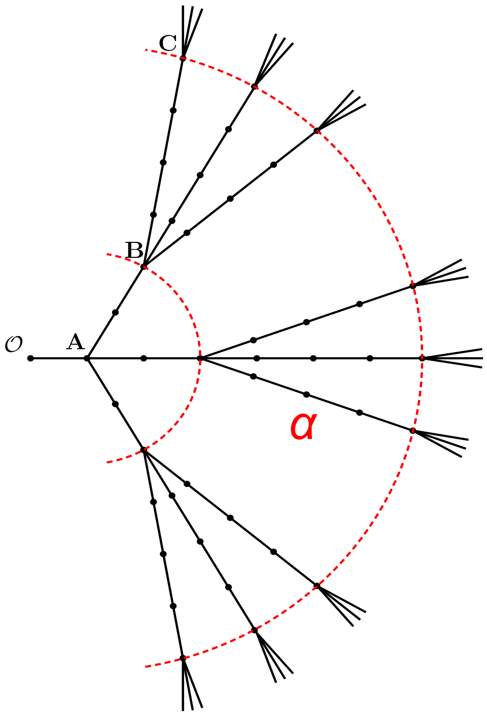
$$P(x,t) = \frac{1}{\lambda(t)} F\left(\frac{x}{\lambda(t)}\right)$$

$$\left\langle x^q(t) \right\rangle \sim \lambda(t)^q = t^{\nu q}$$

b) Strong anomalous diffusion (Multi-scaling)

$$\left\langle x^q(t) \right\rangle \sim t^{q\iota(q)}$$

RW on Fractal branched structures



Example of a complex graph NT_k

RW exhibits standard MSD

$$d_f = d_s = 1 + \frac{\ln(k)}{\ln(2)}$$

$$\langle x^2(t) \rangle \sim t^{d_s/d_f} = t$$

What about the $Q_t(\alpha,x)$??

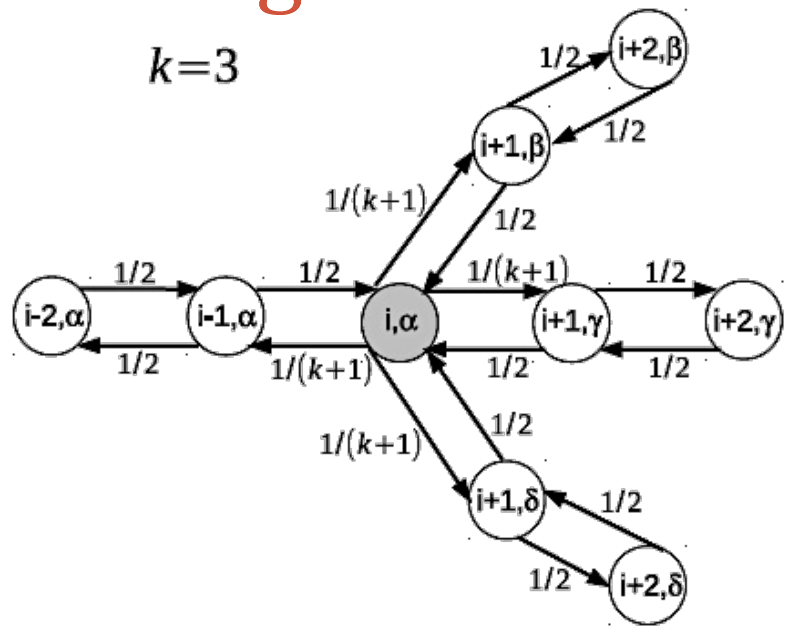
Write a Master Equation for $Q_t(\alpha,x)$ probability RW occupies the Site x in the Branch α $\quad$ x = distance from O

Distance from the origin

A walker on a branching point

$x_{t+1} = x_t + 1$ in k possibilities

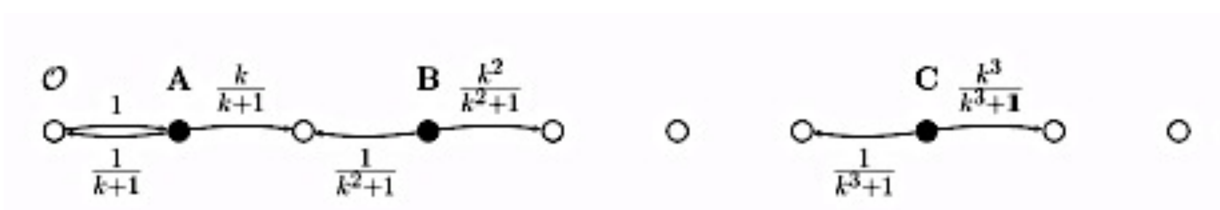
$x_{t+1} = x_t - 1$ in 1 possibility



$$w(x+1|x) = \begin{cases} \dfrac{k}{k+1}, & \text{if } x = 2^n - 1 \\ 1/2, & \text{elsewhere} \end{cases}$$

$$w(x-1|x) = \begin{cases} \dfrac{1}{k+1}, & \text{if } x = 2^n - 1 \\ 1/2, & \text{elsewhere} \end{cases}$$

The RW on NT_k is reduced to 1D RW with DEFECTS spaced of 2^n (branch. points)

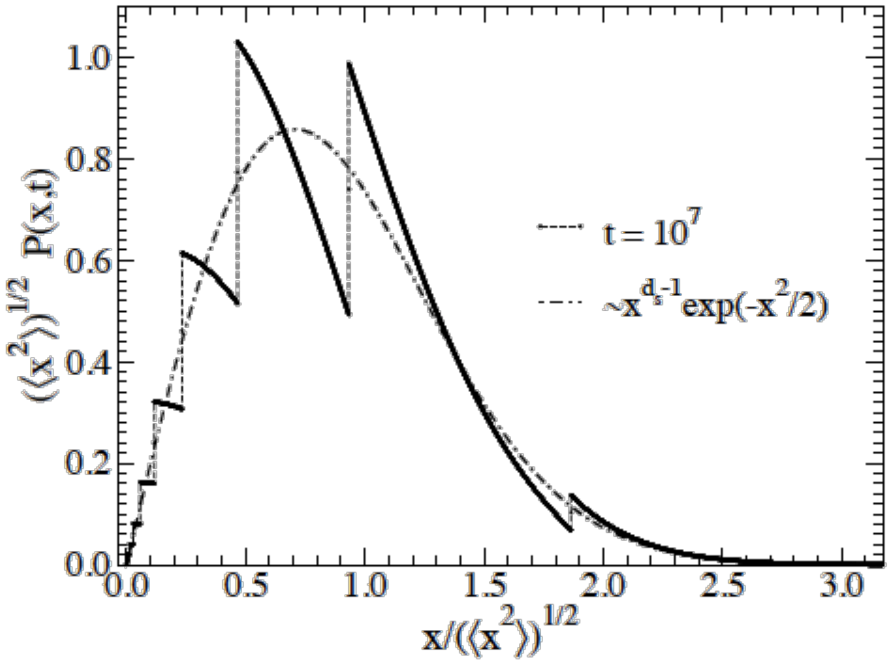


Distribution

$$P_{t+1}(x-1) = \frac{1}{2}P_t(x-2) + \frac{1}{k+1}P_t(x)$$

$$P_{t+1}(x) = \frac{1}{2}P_t(x-1) + \frac{1}{2}P_t(x+1)$$

$$P_{t+1}(x+1) = \frac{k}{k+1}P_t(x) + \frac{1}{2}P_t(x+2)$$



Approximation

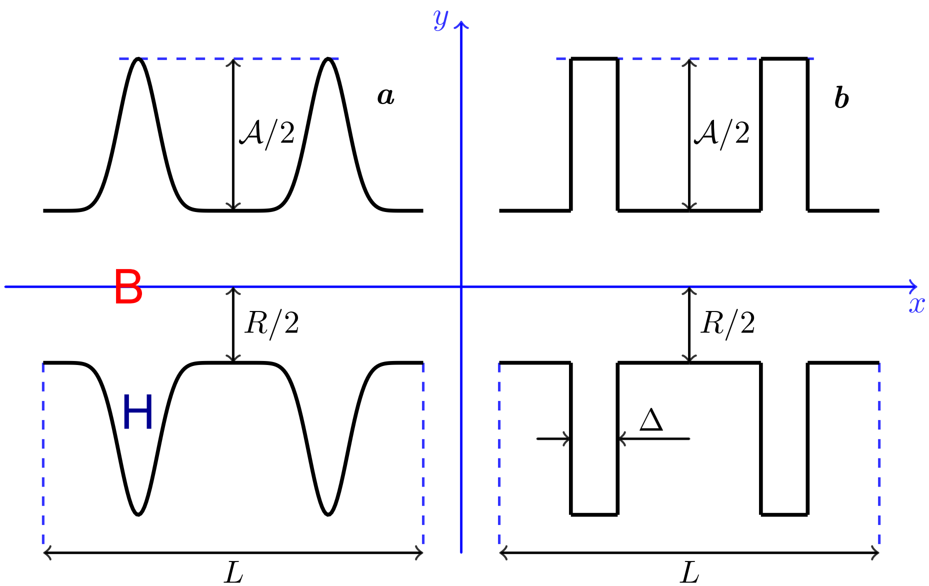
$$\mathscr{F}_t(x) = \frac{2}{\Gamma(d_s/2)(2t)^{d_s/2}} x^{d_s-1}\,\mathrm{e}^{-x^2/2t}$$

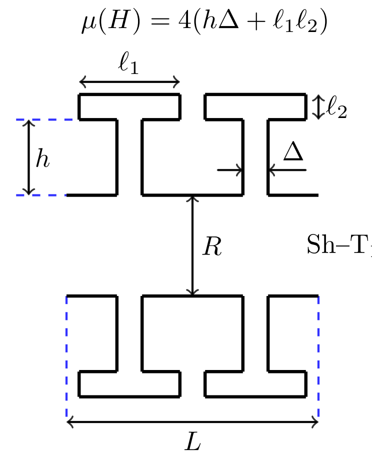
"Radial" Gaussian distribution

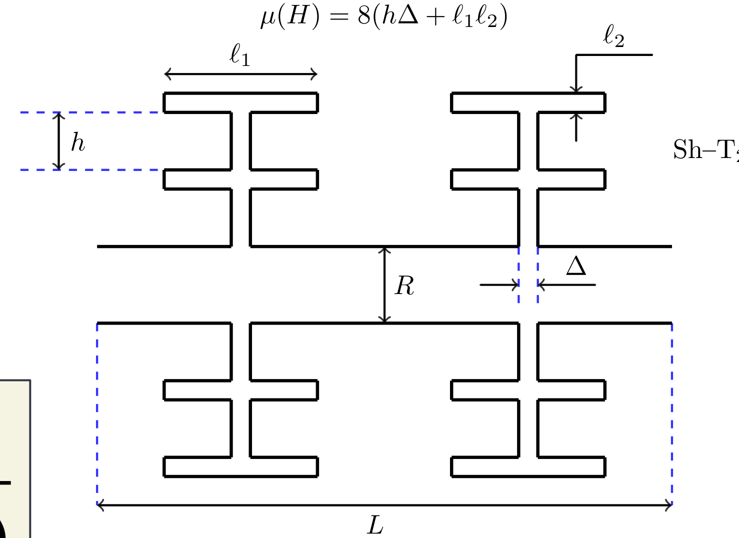
$$\langle x^q(t)\rangle = \int_0^\infty dx x^q \mathscr{F}_t(x) \sim t^{q/2}$$

Gaussian Scaling of moments

Simpler approach: homogenization



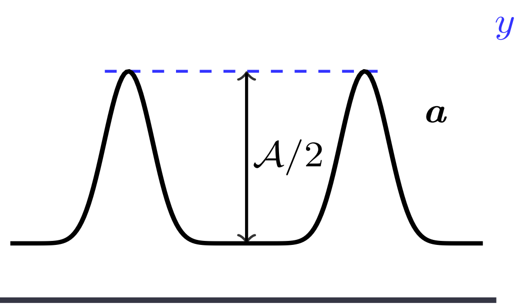




Test of homogenization formula

$$D = D_0 P_B(\infty) = D_0 \frac{\mu(B)}{\mu(H) + \mu(B)}$$

Periodically corrugated channels

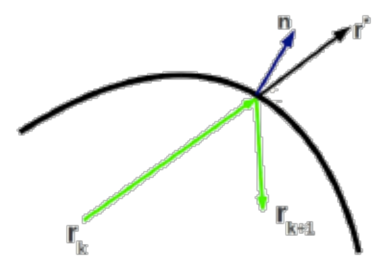


$$\frac{\partial P}{\partial t} = D_0 \left(\frac{\partial^2 P}{\partial^2 x} + \frac{\partial^2 P}{\partial^2 y} \right)$$

Fick-Jacobs Theory

$$Q(x,t) = \int_0^{w(x)} dy P(x,y,t)$$

No flux boundaries



Substitute in original Equation

+ factorization $\quad P(x,y,t) = Q(x,t)\, R(y,t|x)$

+ homogenization $\quad R(y,t|x) \sim 1/w(x)$

+ no-flux boundary conditions

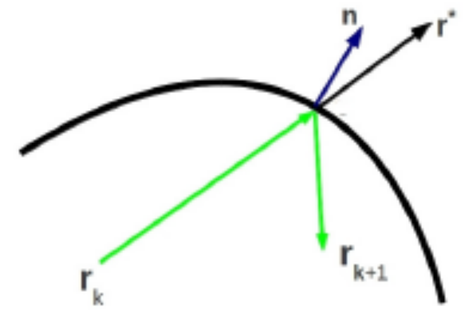
$$\frac{\partial Q}{\partial t} = D_0 \frac{\partial}{\partial x} \left(w(x) \frac{\partial}{\partial x} \frac{Q}{w(x)} \right)$$

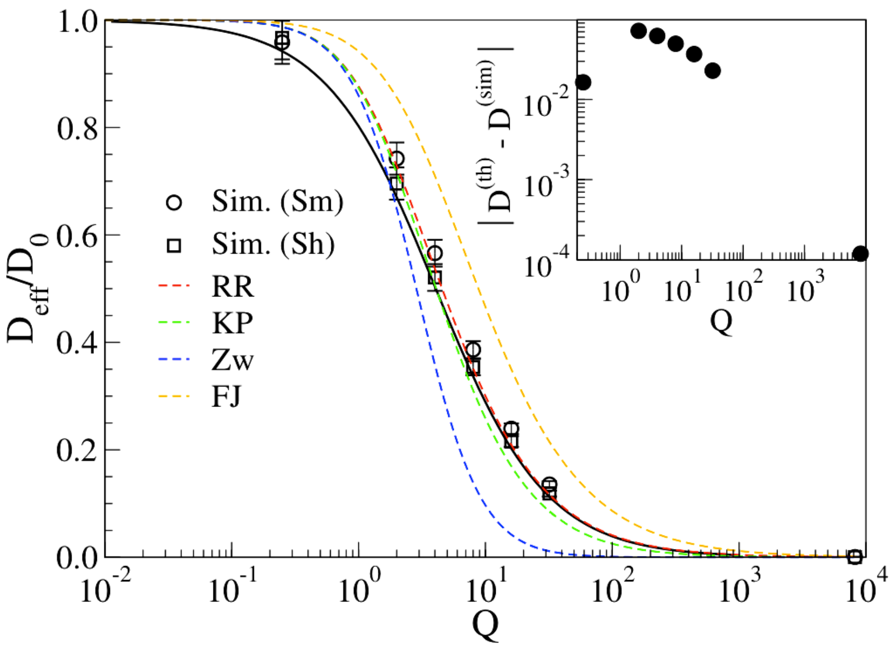
1-d

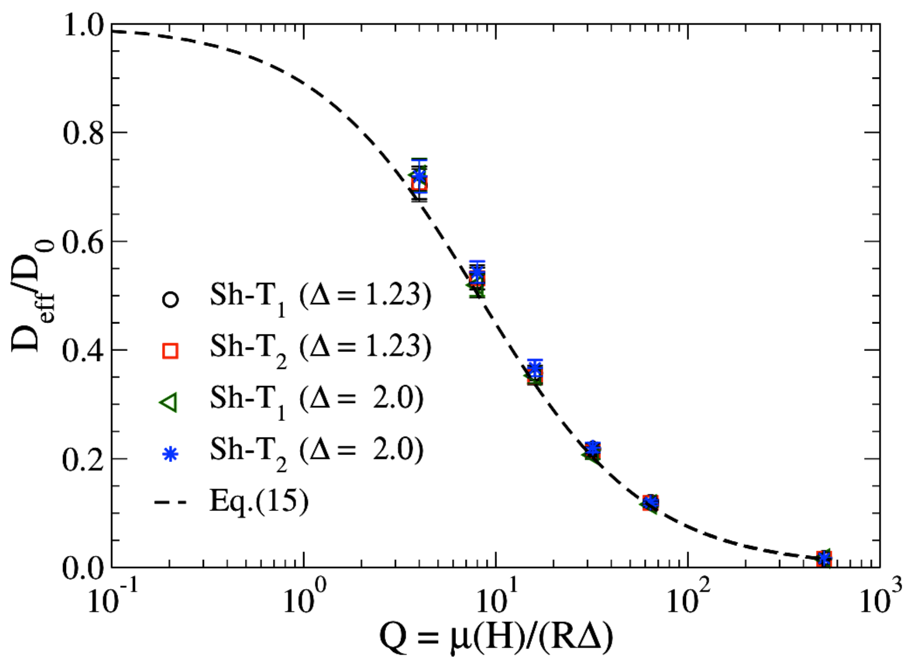
Asymptotic diffusion in PCC

$$\frac{d\mathbf{r}}{dt} = -\frac{\nabla V(\mathbf{r})}{\eta} + \sqrt{2D_0}\xi_t$$

No flux boundaries







Pre-asymptotic behavior

2 State Model H,B

$$\left\langle \Delta x^2(t) \right\rangle = 2D_0 \int_0^t du\, P_B(u)$$

$$\frac{dP_B(t)}{dt} = -k_B(t) P_B(t) + k_H(t)\,[1 - P_B(t)]$$

$$k_B(t) \sim a/\sqrt{t} \quad k_H(t) \sim b/\sqrt{t}$$

Solution

$$P_B(t) = P_s(0) + e^{-\sqrt{t/t_0}} + \frac{D}{D_0}\left(1 - e^{-\sqrt{t/t_0}}\right)$$

$$\left\langle \Delta x^2(t) \right\rangle = 2Dt + C\left[1 - e^{-\sqrt{t/t_0}}(\sqrt{t/t_0} + 1)\right]$$

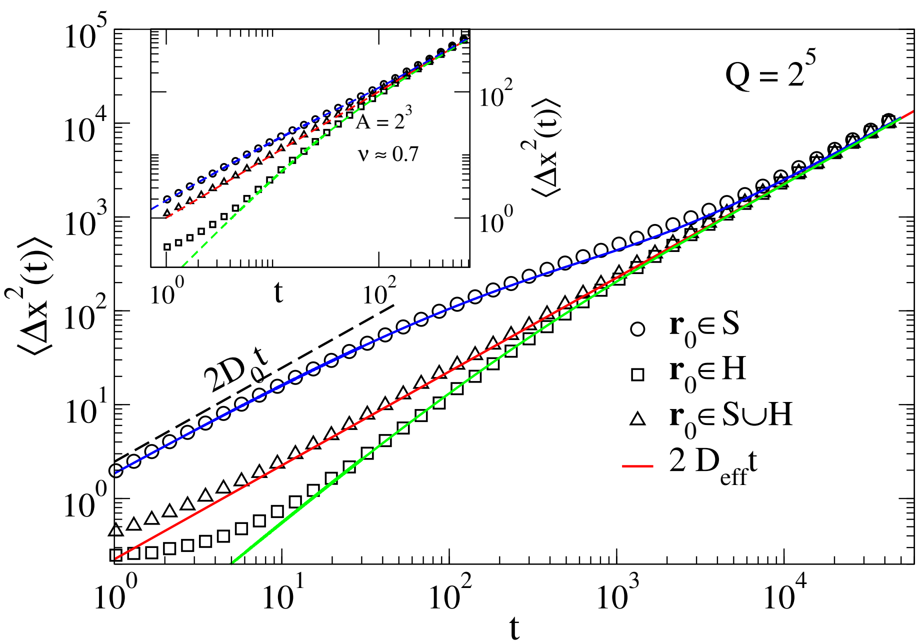
$$C = 4D_0 t_0 \left[P_B(0) - D/D_0\right]$$

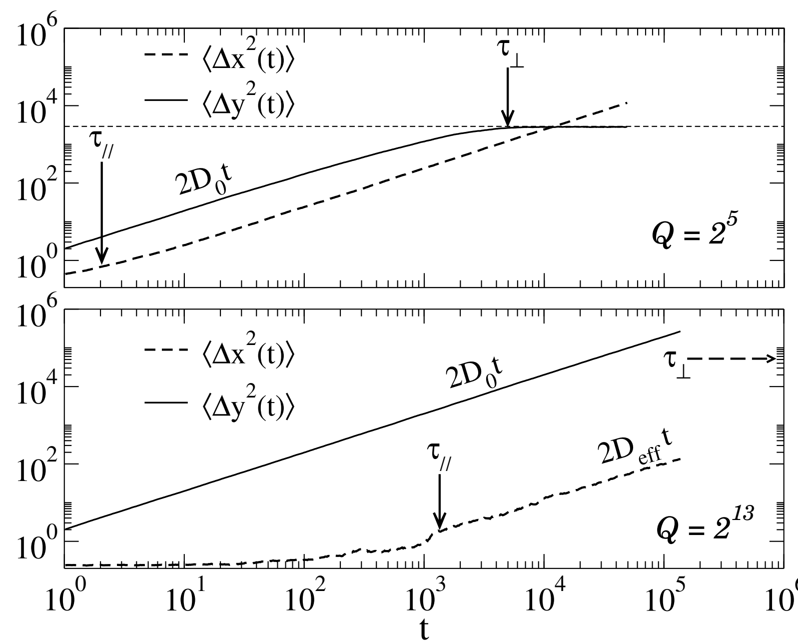
- Backbone $P_B(0)=1$
- Humps $P_B(0)=0$
- Uniform $P_B(0)=D/D_0$

Dependence on I.C.: constant C

Pre-asymptotic behavior

- Backbone $P_B(0) = 1$ $C > 0$
- Humps $P_B(0) = 0$ $C < 0$
- Uniform $P_B(0) = D/D_0$ $C = 0$





Conclusions

- CONFINED RW on branched structures and corrugated channels
- HOMOGENIZATION meaning and implications
- CROSSOVER from Anomalous to Standard
- MATCHING ARGUMENT → Anomalous Scaling
- GENERALIZATION of FDR (standard and anomalous)
- CHECK formula for Deff and FDR in channels