Brownian Transport at the Nano-scales

- Brownian transport in confined geometries subjected to external fields of force

- Brownian transport in inhomogeneous media, ie, with position dependent diffusion

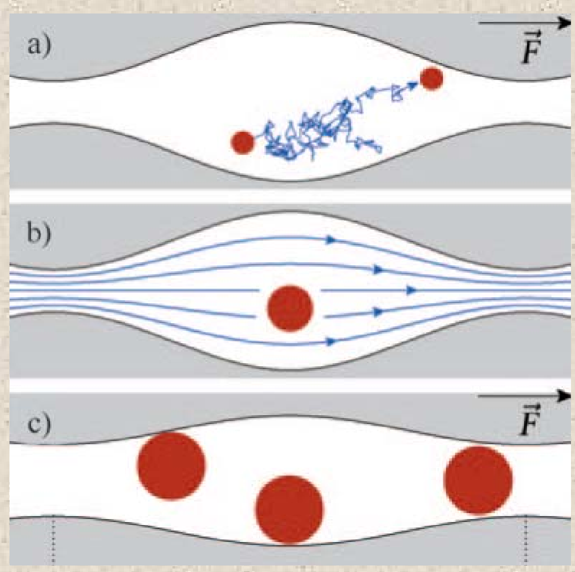
P. Hänggi & FM, Rev Mod Phys, 81 (2009) 387

P.S. Burada et al., ChemPhysChem 10 (2009) 45

Erice, July 2012

Part 1: Brownian Transport in Narrow Channels

- bio-systems, porous media
- artificial submicron devices
- noise rectification mechanisms



Burada et al, ChemPhysChem 10 (2009) 45

Entropic channels

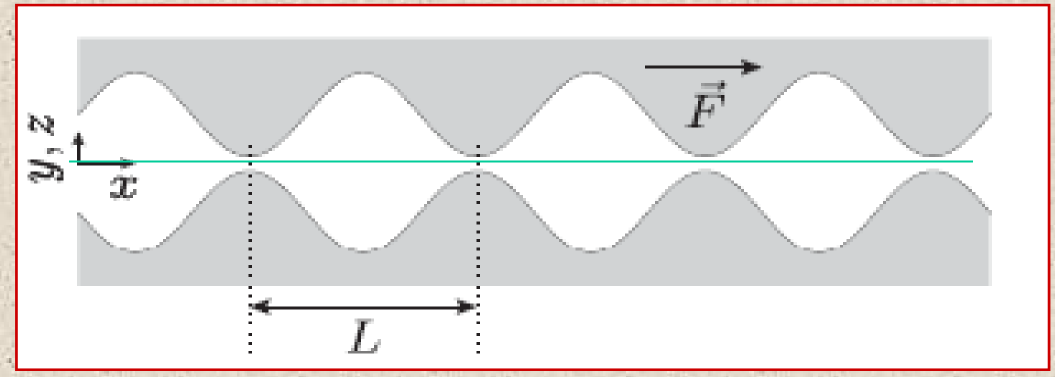
$$\dot{\vec{r}} = F\,\vec{e}_x + \sqrt{D_0}\,\vec{\xi}(t)$$

$\xi(t)$: Gaussian, $\langle \xi_i(t) \rangle = 0$

$\langle \xi_i(t)\xi_j(0) \rangle = 2\delta_{ij}\delta(t)$

$w(x)$: channel radius/profile

$w(x) = (1/2)[\Delta + (y_L - \Delta)\sin(\pi x/L)]$



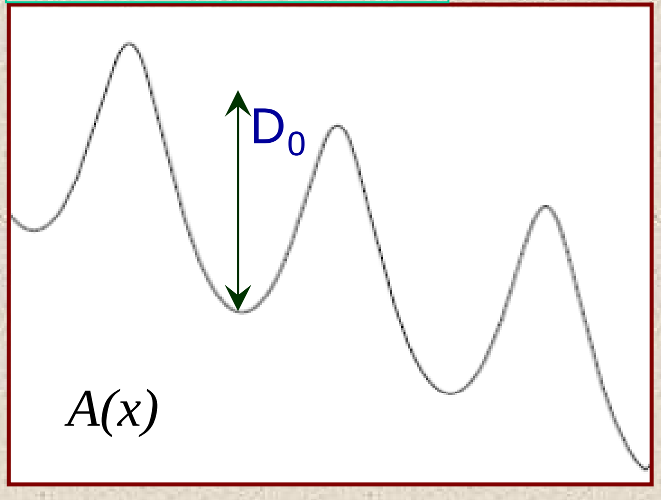
overdamped, or Smoluchowski approximation: infinite damping (or zero mass) as in most biological physics systems

no analytical methods to describe transport in a generic profile w(x); approximate techniques are needed

$$\partial_t P(x,y;t) = \left[-F\partial_x + D_0(\partial_x^{\,2} + \partial_y^{\,2})\right]P(x,y;t)$$

- dimension reduction techniques: from 3D, 2D to 1D effective transport equations

$$P(x;t) = \int_{-w(x)}^{w(x)} P(x,y;t)\,dy$$



narrow pores, $w_{min} << w_{max}$

$$\partial_t P(x;t) = \partial_x D(x)\left[\partial_x + A'(x)/D_0\right]P(x;t)$$

$A(x) = -Fx - D_0 \ln\sigma(x)$ entropic term

$\sigma(x) = 2w(x)$ in 2D

$= \pi w(x)^2$ in 3D

channel cross section

Zwanzig-Fick-Jacobs (ZFJ) scheme

Zwanzig, JCP, 1992

- technical difficulty: an uncontrolled expansion

$D(x) = D_0/[1+w'(x)^2]^\alpha$, α =1/2 (in 3D)

=1/3 (in 2D)

Reguera & Rubi, PRE64, 2001

ZFJ →1D Langevin equation (LE)

$$\dot{x} = -A'(x) + \sqrt{D_0}\,\xi(t)$$

mobility

$$\mu(F) = \langle \dot{x} \rangle / F$$

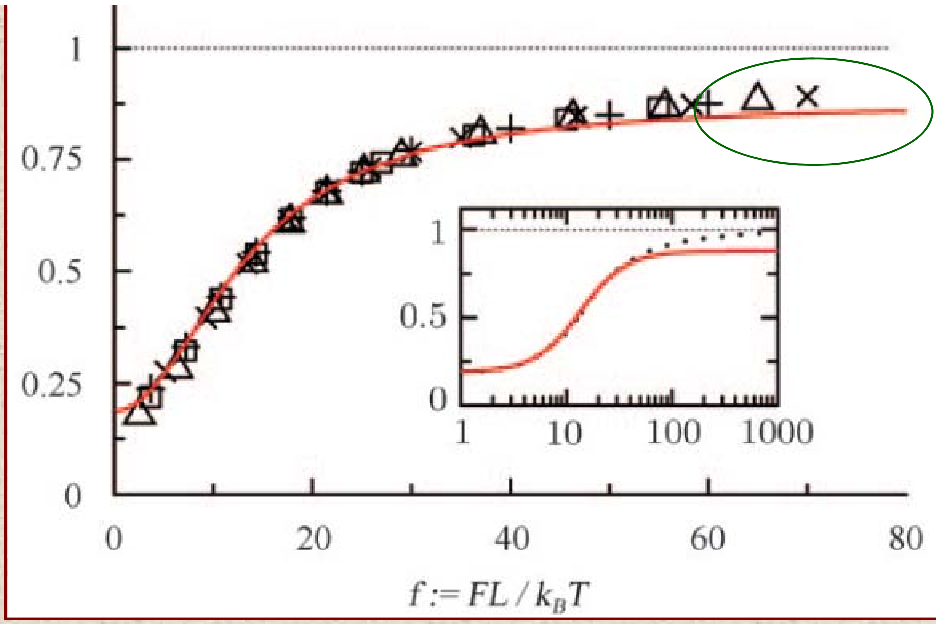
$$\langle \dot{x} \rangle = \lim_{t\to\infty} [\langle x(t) \rangle - x(0)] / t$$

$\mu(F) \to 1$, for $F \to \infty$ theory fails

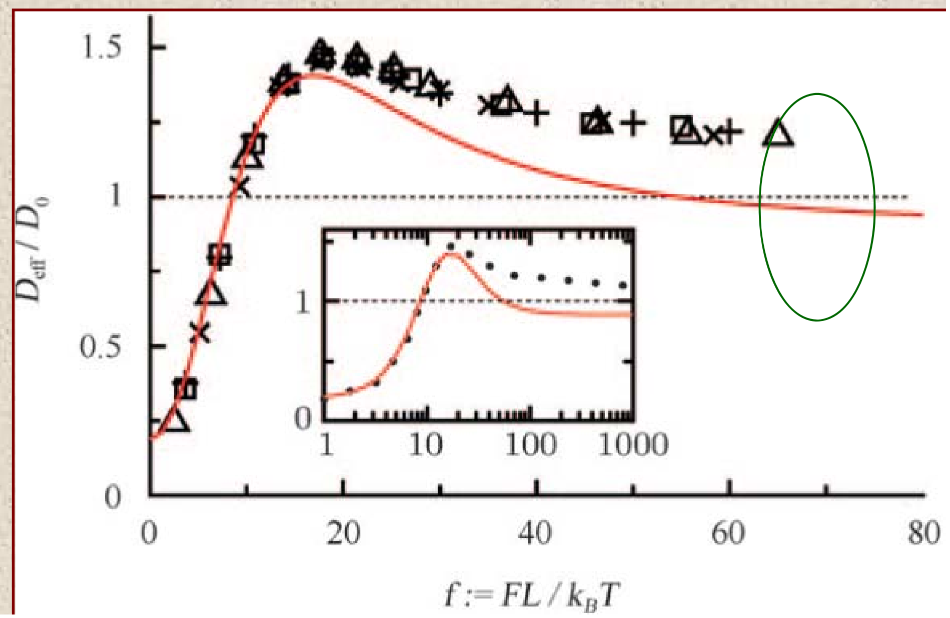
diffusivity

$$D = \lim_{t\to\infty} [\langle x^2(t) \rangle - \langle x(t) \rangle^2] / 2t$$

D(F) goes through a depinning peak, and $D(F) \to D_0$ for $F \to \infty$



Costantini, FM, EPL 48, 1999



validity

1. narrow pores

2. fast transverse re-equilibration

$\tau_y << \max\{\tau_x, \tau_F\}$

$\tau_y = w^2_{max}/2D_0$ transverse diffusion

$\tau_x = L^2/2D_0$ longitudinal diffusion

$\tau_F = L/F$ drift

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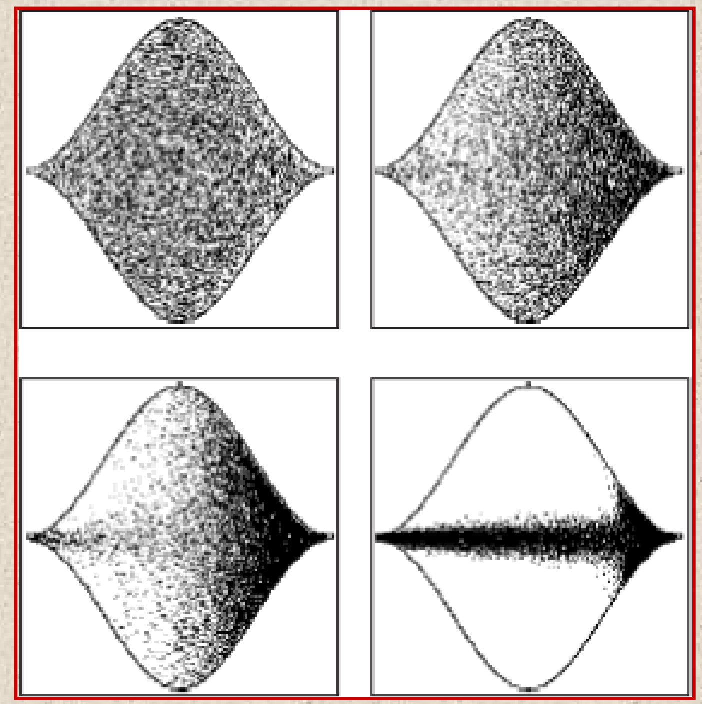
3. For smooth channel

$w'(x) << \min\{1, D_0/FL\}$

more stringent for large drives



$P(\delta x) \approx F/D_0 \; \exp(-F\delta x/D_0)$

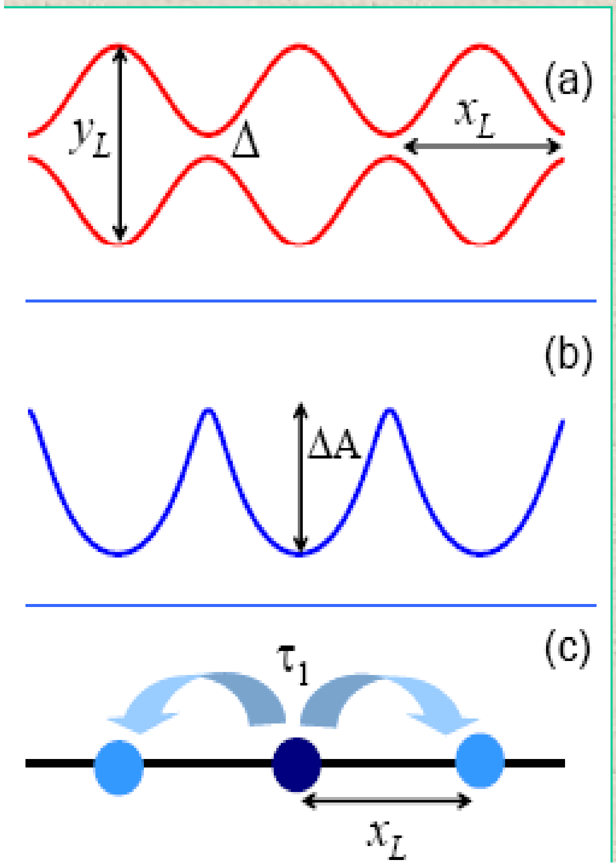
despite much effort,
validity of ZFJ scheme
remains very limited

Laachi et al, EPL 80, 2007

Random walker model

alternative approach based on discretizing x(t) with steps of $L=x_L$

the particle is trapped in a compartment for a time τ_1; τ_1 is the MFET through either opening



Assume F=0: the diffusion constant is then

$$D(F=0)=\frac{x_L^2}{2\tau_1}$$

zero drive

(A) reduced 1D dynamics

$$\tau_1=\frac{1}{D_0}\int_0^{x_L/2}\frac{dy}{P_{st}(y)}\int_{-x_L/2}^{y}P_{st}(x)dx \qquad P_{st}(x)=\frac{A(x)}{\int_0^{x_L}A(z)dz}$$

$$\tau_1=\frac{x_L^2}{4D_0}\sqrt{\frac{y_L}{\Delta}}\left[1+\frac{\Delta}{y_L}\right]$$

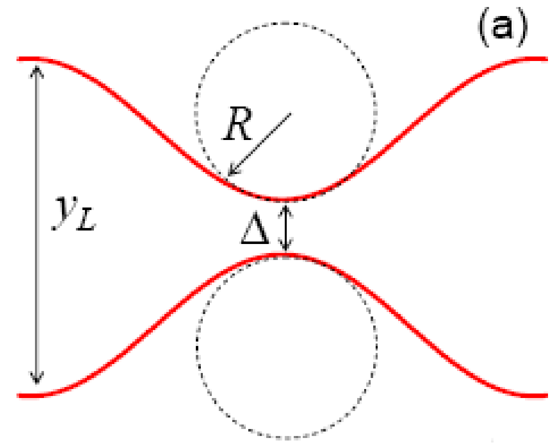
(B) 2D direct calculation (Holcman et al, 2011)

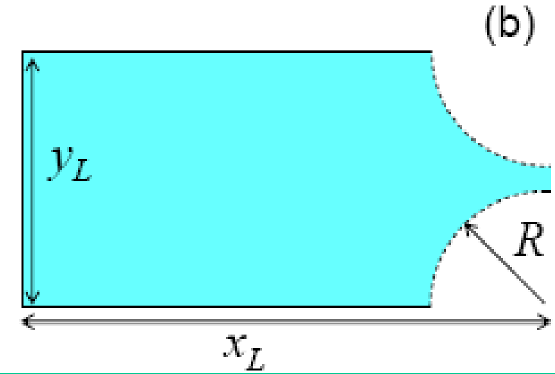
$$\tau_1 = \frac{\pi\Omega}{2D_0}\sqrt{\frac{R}{\Delta}}\left[1+O\left(\frac{\Delta}{R}\right)\right]$$

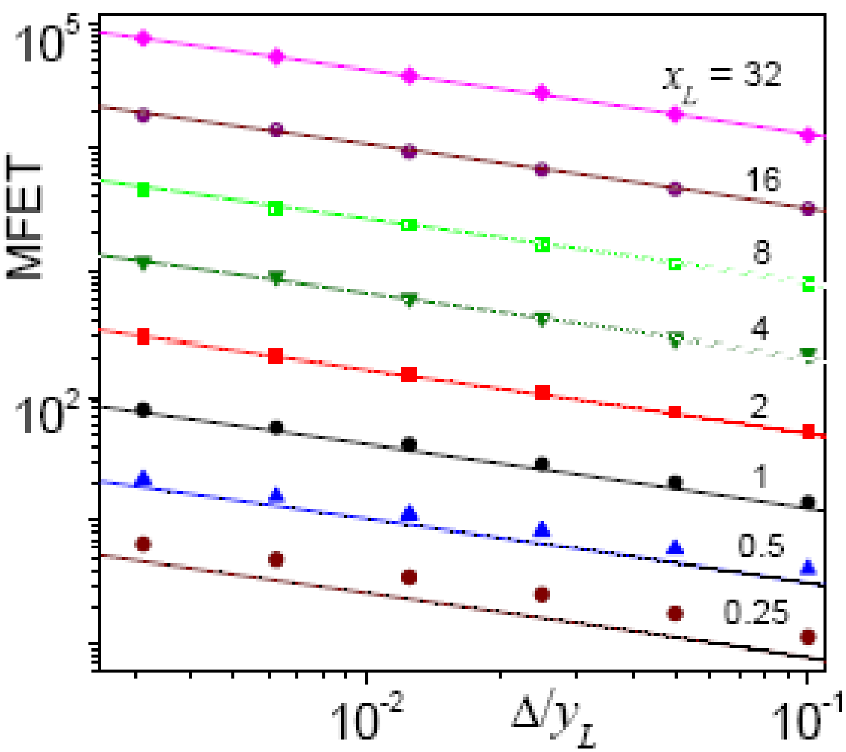
zero drive

for a rounded pore with radius R and volume Ω

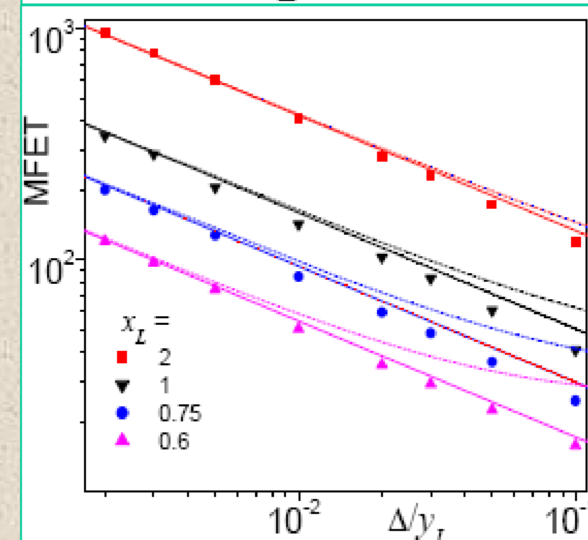
$$R = \frac{x_L^2}{\pi^2(y_L-\Delta)} \simeq \frac{x_L^2}{\pi^2 y_L}, \qquad \Omega = 2\int_0^{x_L} w(x)\,dx \simeq \frac{x_L y_L}{2}$$







independent check



Geometric effects

Brownian transport can be studied under more general conditions:

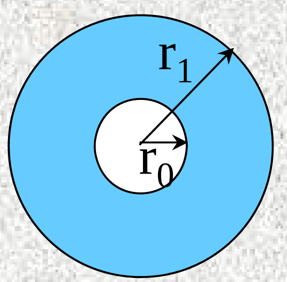
narrow pores, only

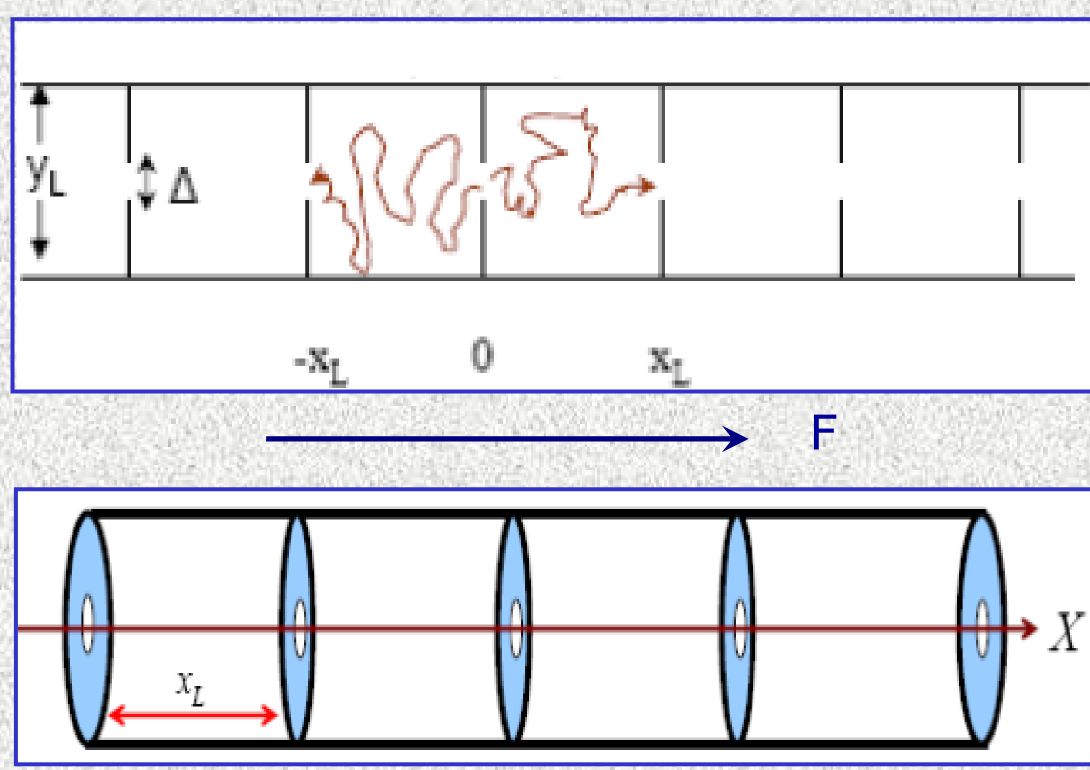
$$\dot{\vec{r}} = F\,\vec{e}_x + \sqrt{D_0}\,\vec{\xi}(t)$$

ZFJ scheme fails even

at F=0 as w'(x) diverges

at partitions

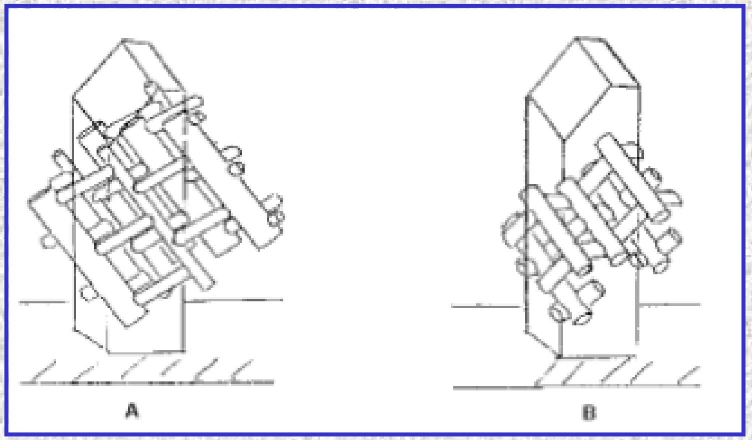




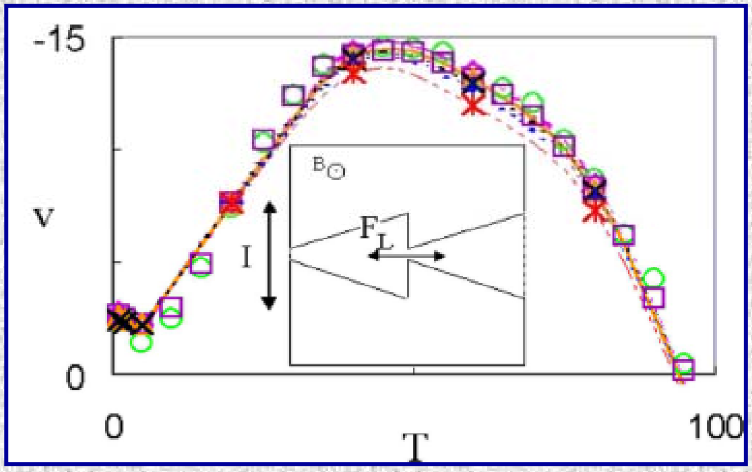
interest not conceptual only

applications

channel networks in natural and artificial porous media (zeolites, membranes, etc)



particle ratcheting in 2D and 3D channels is more effective for sharp boundaries (eg. magnetic vortices in type-II superconductors)



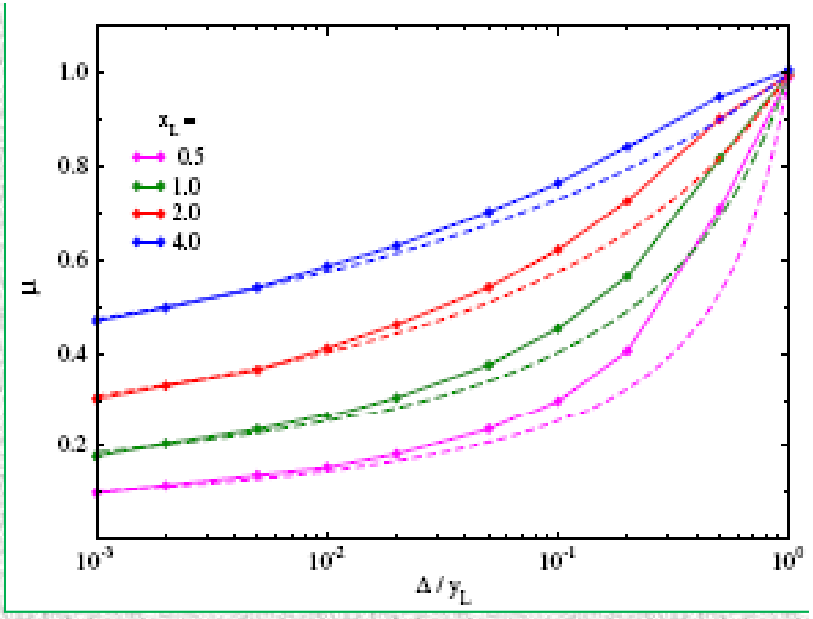
Wambaugh et al, PRL 83, 1999

Example: 2D narrow septate channels

$$x_L >> y_L; \Delta << y_L$$

Mobility

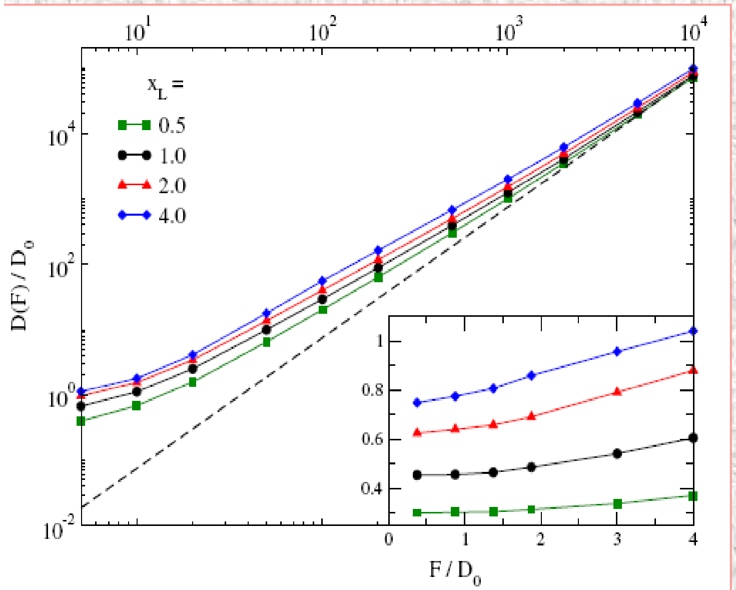
$$\mu(0) = \frac{D(0)}{D_0} = \left[1 - \frac{2}{\pi}\frac{y_L}{x_L}\ln\left(\frac{\Delta}{y_L}\right)\right]^{-1} \quad F=0$$



Diffusivity

$$\frac{D(F)}{D_0} = \frac{\Delta}{12}\left(1 - \frac{\Delta}{y_L}\right)^3\left(\frac{F}{D_0}\right)^2 \quad \text{large F}$$

$$\mu(F \to \infty) = \frac{\Delta}{y_L}$$



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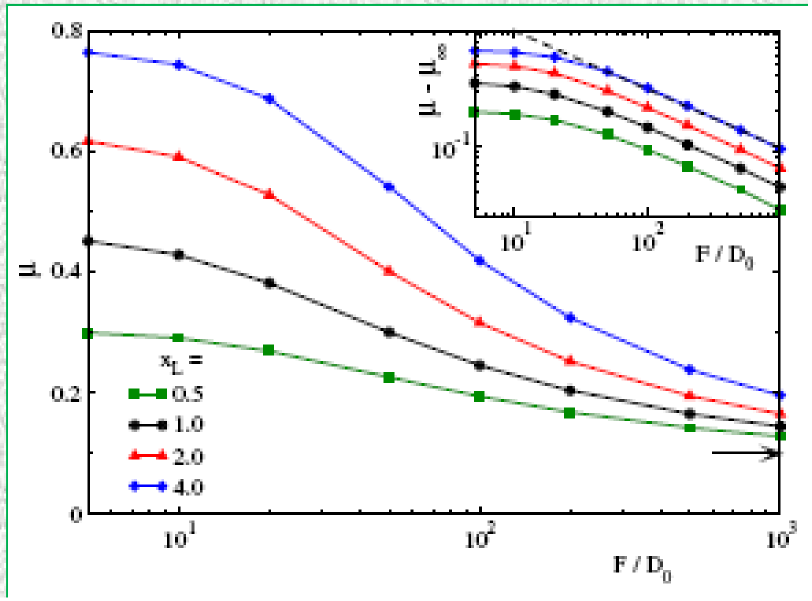
Taylor's like

F dependence



Inertia effects

- large damping is the rule eg in biological systems → bulk diffusion is overdamped …

$$m\ddot{\vec{r}} = -\gamma\dot{\vec{r}} + F\,\vec{e}_x + \sqrt{\gamma kT}\,\vec{\xi}(t)$$

ξ(t): Gaussian, $\langle \xi_i(t) \rangle = 0$

$\langle \xi_i(t)\xi_j(0) \rangle = 2\delta_{ij}\delta(t)$

$\gamma = 1$

- …under certain conditions (Smoluchowski approximation), ie

$$\Delta l_{obs} >> l_T \equiv \sqrt{kT}/\gamma$$

thermal length

$$\Delta t_{obs} >> 1/\gamma$$

irrelevant relaxation details

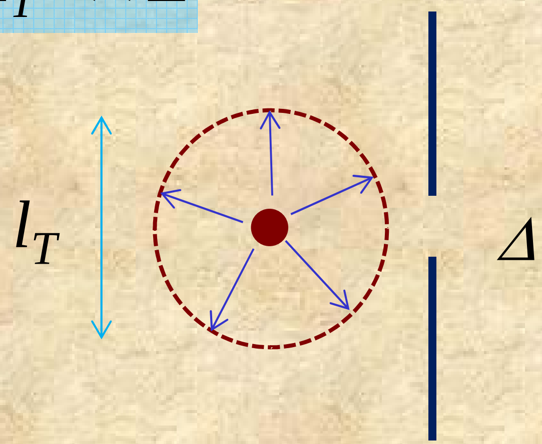
$$Fl_T << kT \quad \text{or} \quad F/\gamma << \sqrt{kT}$$

external work negligible

drift << thermal

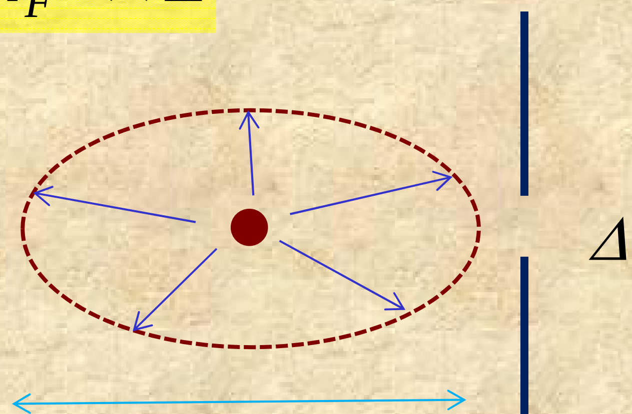
- conditions to be specialized for constrained geometries

$l_T \ll \Delta$



$$\gamma \gg \gamma_T \equiv \sqrt{kT} / \Delta$$

$l_F \ll \Delta$



$$l_F \equiv F / \gamma^2$$

$$\gamma \gg \gamma_F \equiv \sqrt{F / \Delta}$$

… which surely fail in the limit $\Delta \to 0$

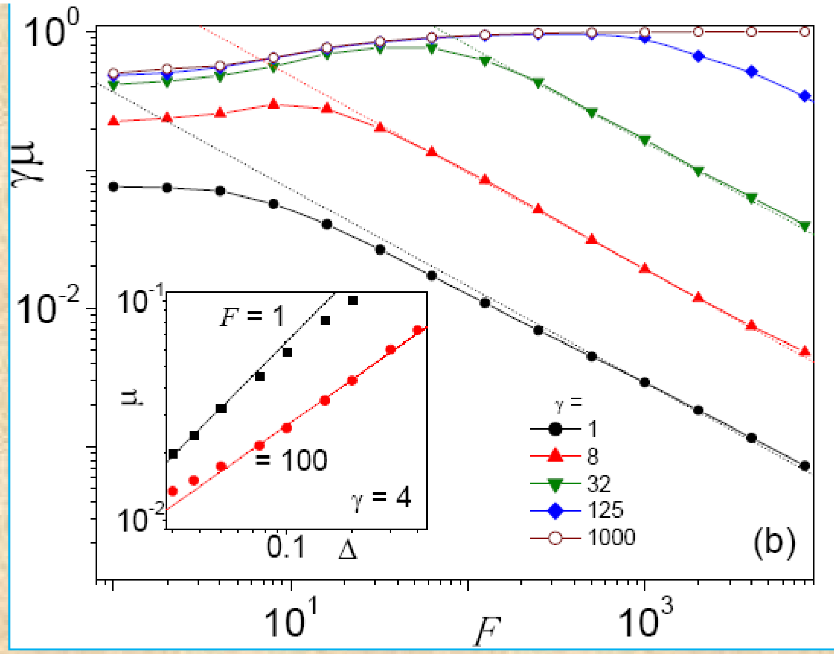
- inertia suppresses transport

  $\mu(F)$ decays with F

  D(F) increases with F

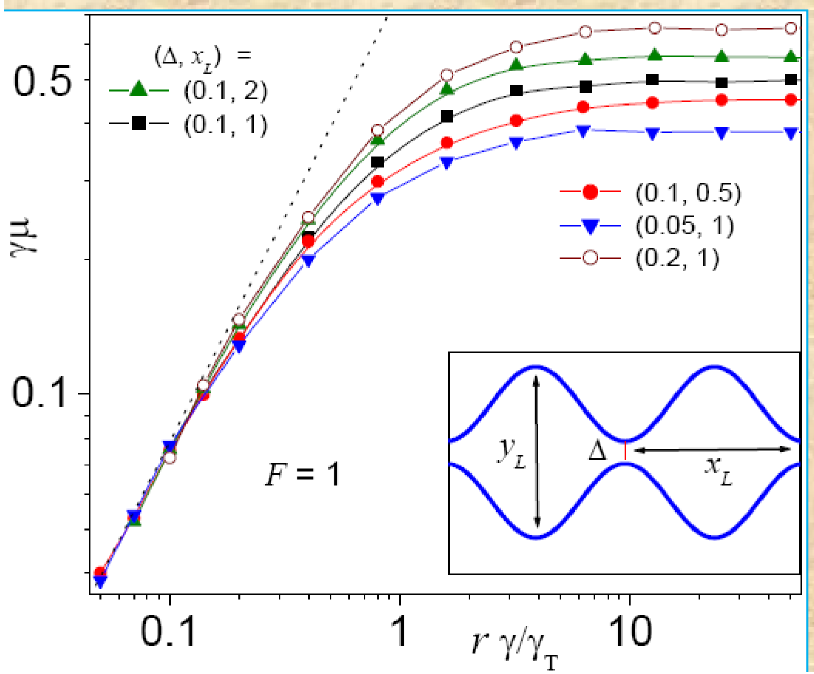
- measurable effect,

  eg in colloidal suspensions



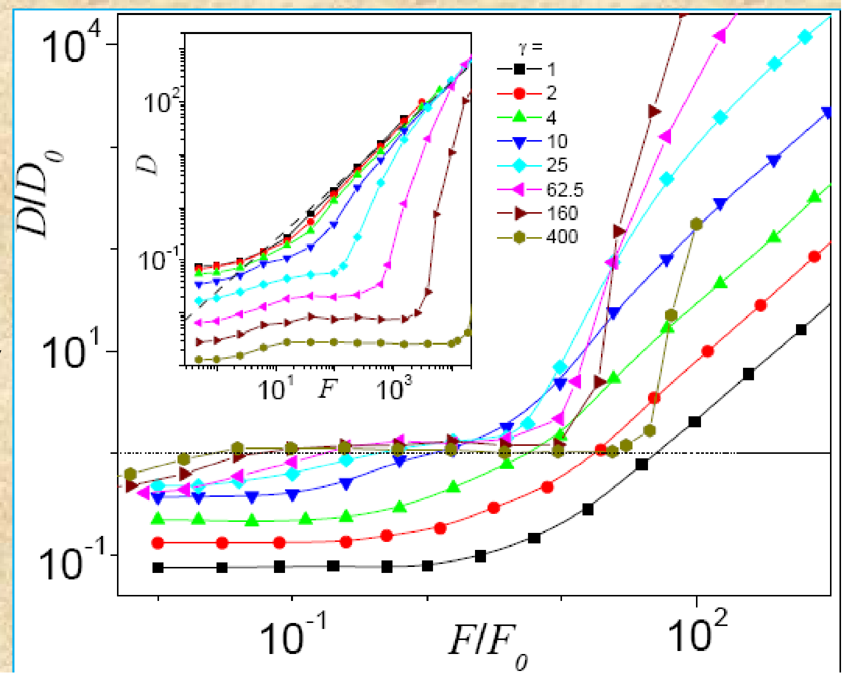
low F

large F



Ghosh et al,

EPL 2012



Part 2: Brownian Transport and State-Dependent Diffusion

- how can we extract useful work from the environment (without violating the II law of thermodynamics)? $\rightarrow$ ratchet mechanisms

  P. Hänggi & FM, Rev Mod Phys, 81 (2009) 387

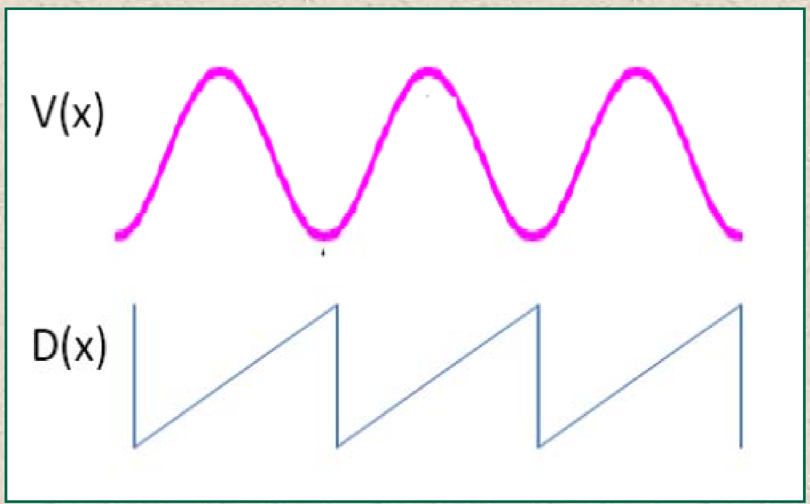
- noise rectification mechanisms in the absence of external drives (passive devices)
- inhomogeneous environments

} NanoPower

Büttiker's model

consider an overdamped particle on a 1D periodic substrate V(x+L)=V(x)

let the diffusivity D of the substrate also be periodically modulated with period L



with Langevin equation

$$\dot{x} = -V'(x) + \sqrt{D(x)} \circ \xi(t)$$

$\xi(t)$: Gaussian, $\langle \xi_i(t) \rangle = 0$

$\langle \xi_i(t) \xi_j(0) \rangle = 2\delta_{ij}\delta(t)$

and FPE (Ito scheme)

$$\frac{\partial}{\partial t} P(x,t) = \frac{\partial}{\partial x}\left[V'(x) + \frac{\partial}{\partial x}\sqrt{D(x)}\frac{\partial}{\partial x}\sqrt{D(x)}\right] P(x,t)$$

on solving the FPE for periodic b.c. $P_{st}(x+L)=P_{st}(x)$

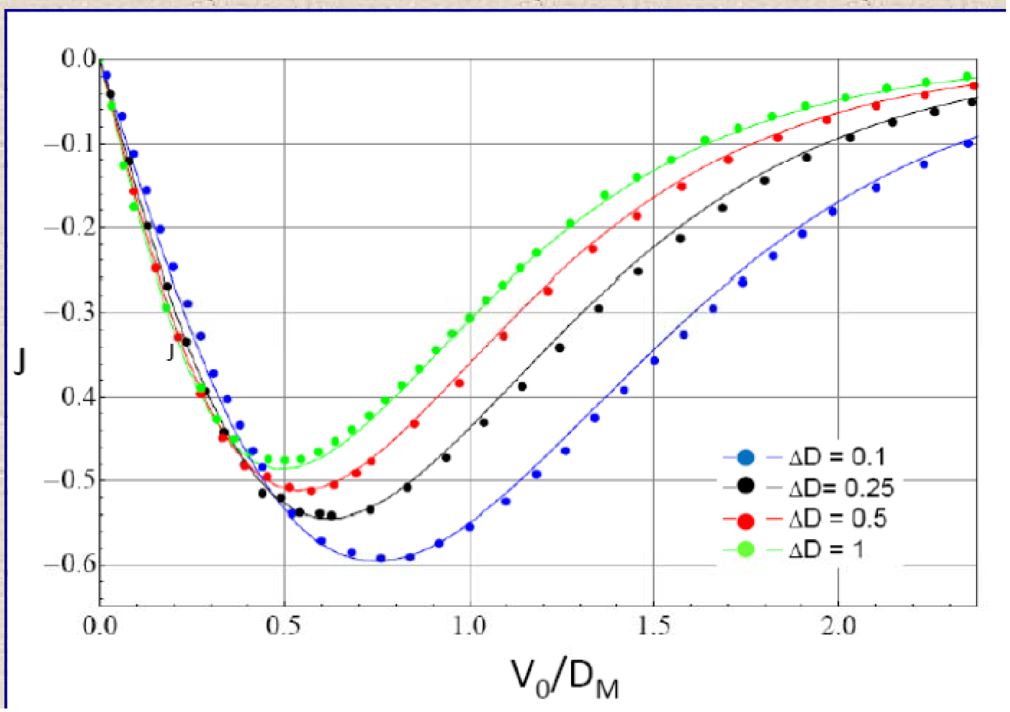
$$J = \frac{1 - e^{\Delta F}}{\int_0^L \frac{e^{-F(x)}}{D(x)} dx \int_x^{x+L} e^{F(y)} dy}.$$

with $$F(x) = \int_0^x \frac{V'(y)}{D(y)} dy$$

rectification condition, $j \neq 0$

$$\Delta F = \int_0^L \frac{V'(x)}{D(x)} dx \neq 0$$

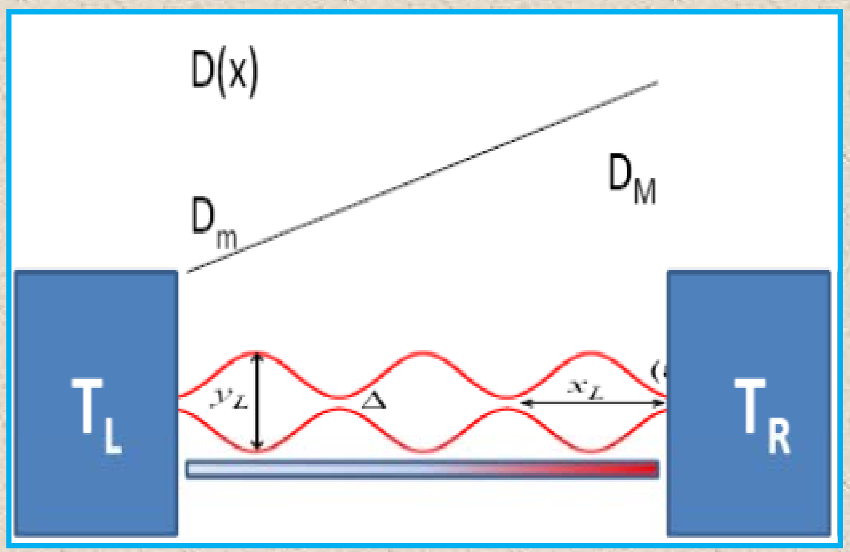
one can play with V(x), D(x) profiles and relative phase.



Extension to narrow channels

consider an overdamped particle
narrow channel $w(x+L)=w(x)$

let the diffusivity D of the substrate also be periodically modulated with period nL, $T_L=T_R$



FJZ approach assuming Ito scheme

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x}\left[V'(x) + \frac{\partial}{\partial x}\sqrt{D(x)}\frac{\partial}{\partial x}\sqrt{D(x)}\right]P(x,t)$$

$$V'(x) \to D(x)A'(x) = -D(x)w'(x)/w(x)$$

hence

$$\Delta F = \int_0^{x_L}\frac{A'(x)}{D(x)}dx = -\int_0^{x_L}\frac{w'(x)}{w(x)}dx = -\ln w(x)\,|_0^{x_L} = 0.$$

no rectification!

Meaning of $\sqrt{D(x)} \circ \xi(t)$

- during a time interval Δt, $t \to t+\Delta t$, the particle moves from $x=x(t)$ to $x(t+\Delta t)=x \pm \Delta x$ with $\Delta x^2 = 2D\Delta t$;
- what if $D=D(x)$? what is the appropriate choice for D in $\Delta x^2 = 2D\Delta t$?
- $D \to D(x+\alpha\Delta x)$ the choice $0 \leq \alpha \leq 1$ depending on the underlying dynamics

➢ Ito ($\alpha = 0$) vs Stratonovitch ($\alpha = 1/2$) dilemma, see standard textbooks; answer follows from a more detailed microscopic modeling of the process

$$\dot{x} = v$$
$$\dot{v} = -\gamma v + \sqrt{D(x)}\,\xi(t)$$
$$\gamma \to \infty$$

$\alpha = 0$

Ito

$$\dot{x} = \sqrt{D(x)}\,\eta$$
$$\dot{\eta} = -\frac{\eta}{\tau} + \frac{\xi(t)}{\tau}$$
$$\tau \to 0$$

$\alpha = 1/2$

Stratonovitch

α dependent drift: on expanding in leading (stochastic) order of Δt

$$D(x+\alpha\Delta x) = D(x) + \alpha \frac{dD}{dx}\Delta x;$$

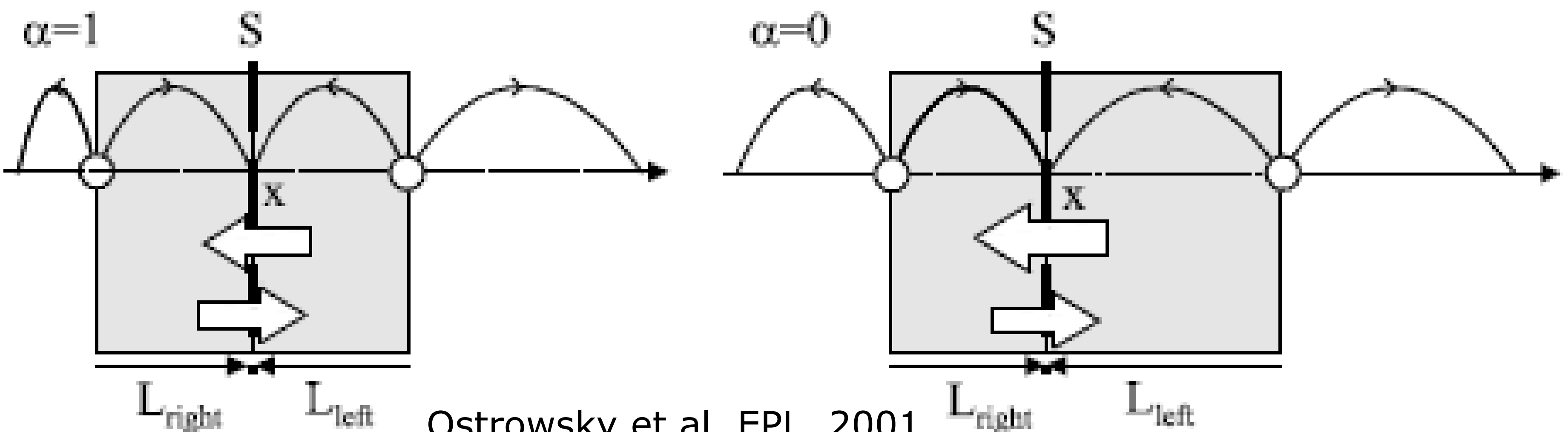
$$x(t+\Delta t) = x(t) + \alpha \frac{dD}{dx}\Delta t \pm \sqrt{2D[x(t)]\Delta t}$$

$$\langle \dot{x} \rangle = \alpha \frac{dD}{dx}$$

α dependent current density: assume $P_{st}(x) = P_0$

$$J(x) = \frac{P_0}{2}\frac{S(L_R - L_L)}{S\Delta t} = -P_0(1-\alpha)\frac{dD(x)}{dx}$$

$$L_{R/L} = \pm(\alpha - 1)\frac{dD}{dx}\Delta t + \sqrt{2D[x(t)]\Delta t}$$



Ostrowsky et al, EPL, 2001

for a generic $P_{st}(x)$ and $0 \leq \alpha \leq 1$

$$J(x) = -(1-\alpha)\frac{dD(x)}{dx}P_{st}(x) - D(x)\frac{dP_{st}(x)}{dx}$$

$$\bar{J} = \int_0^L J(x)dx \neq \frac{\langle \dot{x} \rangle}{L}$$

seemingly counterintuitive

two simple cases for $dD(x)/dx = \Delta D/L$ constant

case $\alpha = 0$: (Ito)

$$\langle \dot{x} \rangle = 0$$

$$\bar{J} = 0$$

$$P_{st}(x) \propto D(x)^{-1}$$

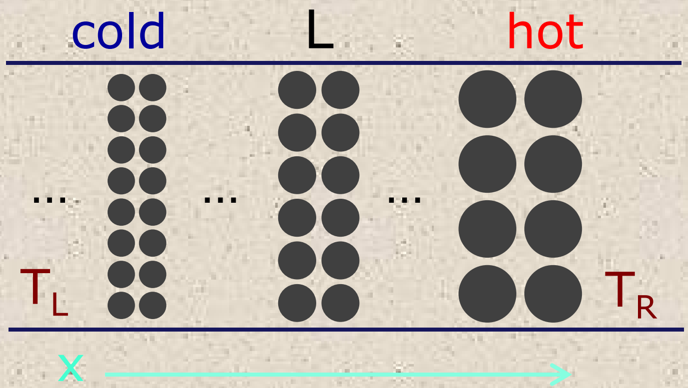
case $\alpha = 1$: (anti-Ito)

$$\langle \dot{x} \rangle = \Delta D/L$$

$$\bar{J} = 0$$

$$P_{st}(x) = 1/L$$

Artificial materials



consider a graded 2D lattice strip of length L>>R; easily mapped to an entropic channel

• R and Δ increase linearly with x,

R(x) $\to \kappa$R, Δ(x) $\to \kappa\Delta$, with $\kappa^2(x)=1+\delta(x/L)$

• Δ/R and the free space fraction

$$\phi = \pi R^2 / x_L^2 = 1-(\pi/4)(1-\Delta/x_L)^2$$ constant

• hence an effective x-dependent T (i.e. D): T(x)=T $\kappa^2(x)$

• and a constant $P_{st}(x) \propto \phi$

$\to$ FJZ channel: 1D LE with linear D(x), anti-Ito scheme $\alpha=1$

a new class of Brownian rectifiers:

zero current (isothermal), net (measurable) drift

generalization for any choice of α: choosing $\kappa(x)$ and $\Delta/R(x)$ we can tune the x-dendence of $\phi = \phi(\Delta/R)$ and D – recall that $D=x_L^2/4\tau_1$ with τ_1 known function of the local lattice parameters

eg: $D(x)P_{st}(x) = \text{const} \rightarrow \alpha=0$ (Ito scheme)

Büttiker rectifier:

zero current and zero drift

Conclusions

Part 1

- 2D and 3D narrow channels show geometric and inertial properties unaccounted for by Zwanzig-Fick-Jacobs scheme
- more should be done to incorporate hydrodynamics

Part 2

- graded (ordered viz. disordered) structures are modeled by x-dependent diffusivity
- different transport transport