Controlled dispersion in periodic microchannels and regular obstacle parks

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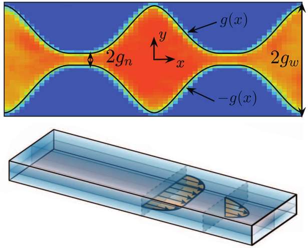
Dispersion in confined out-of-equilibrium systems

- How a cloud of Brownian particles disperses in an infinite medium over the time ? (no stationary distribution, $p(\mathbf{x}, t)$ unknown).

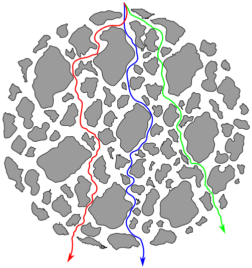
microchannels



Yang *et al.*, PNAS (2017).

Aminian *et al.*, Science (2016).

pollutant in porous media

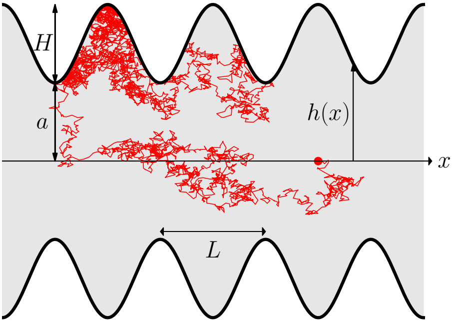


Leitmann and Franosch, Phys. Rev. Lett. (2017).

- Stationary state described by the long-time effective diffusivity (in 2d)

$$D_e = \lim_{t\to\infty} \frac{\overline{\mathbf{x}^2(t)}}{4t}.$$

Dispersion in 2d symmetric and periodic microchannels



- Periodicity of the channel : L.
- Minimal height : a.
- Variation height : H.
- Two dimensionless parameters :

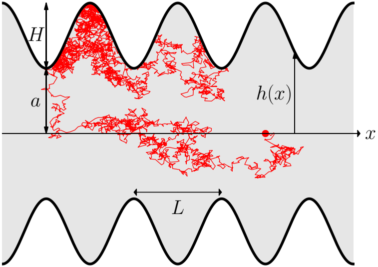
$$\varepsilon = a/L \text{ and } \xi = H/a.$$

- Height of the channel :

$$h(x) = \varepsilon\zeta(x).$$

- Constant microscopic diffusivity D_0.
- Stationary probability density is constant over a period : $P_s = 1/|\Omega|$.

Traditional approach : reduction to one-dimensional problem



- Marginal stationary probability density

$$p_s^*(x) \propto h(x) \propto \exp[-\beta\varphi(x)].$$

- Effective one-dimensional potential

$$-\beta\varphi(x) = \ln h(x) \Leftrightarrow s(x) = k_B \ln h(x).$$

- narrow regions = entropic barriers.
- wide regions = entropic traps.
- Slowing down of the dispersion : $D_e \leq D_0$.

Jacobs, Diffusion Processes (1935).

- Improvement : Introduction of an effective one-dimensional diffusivity

$$\frac{D(x)}{D_0} = 1 - \frac{1}{3}h'(x)^2 + \cdots$$

Zwanzig, J. Chem. Phys. (1991).

Reguera and Rubí, Phys. Rev. E (2001).

Kalinay and Percus, Phys. Rev. E (2006).

Determination of the effective diffusivity

- From the one-dimensional approach (Fick-Jacobs' approximation)

$$D_e = \frac{1}{\langle h\rangle\langle D^{-1}h^{-1}\rangle}.$$

Lifson and Jackson, J. Chem. Phys. (1961).

  - Spatial average

$$\langle h\rangle = \frac{1}{L}\int_0^L dx\ h(x).$$

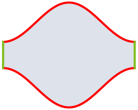
  - Approximation valid only for slowly varying channels ($h'(x) \ll 1$).

- Our approach : exact Kubo formulas

$$\frac{D_e}{D_0} = 1 - \frac{1}{\langle h\rangle}\int_0^L dx\ h'(x)\ f(x,h(x)) = \frac{C}{\langle h\rangle}$$

Guérin and Dean, Phys. Rev. E (2015).
Mangeat *et al.*, J. Stat. Mech. (2017).

  - Partial differential equations for the auxilliary function $f(x,y)$



$$\nabla^2 f(x,y) = 0 \qquad f(x,y) = \mathrm{Re}\, w(x+iy)$$

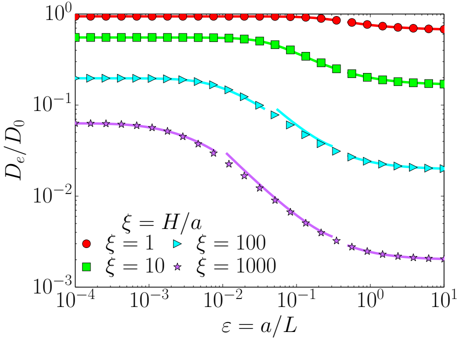
$$\mathbf{n}\cdot\nabla f(x,y=h(x)) = \mathbf{n}\cdot\mathbf{e_x} \qquad \mathrm{Im}\, w(x+ih(x)) = h(x) - C$$

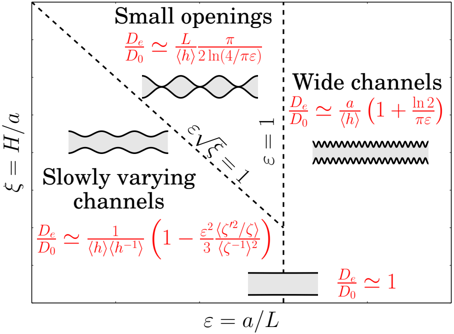
$$f(x+L,y) = f(x,y) \qquad w(z+L) = w(z)$$

  - Valid for all shapes of channels !

Classification of different regimes of dispersion

- Identification of three regimes of dispersion :
  - $\varepsilon \ll 1$ and $\varepsilon\sqrt{\xi} \ll 1$: Slowly varying channels (FJ approximation valid).
  - $\varepsilon \ll 1$ and $\varepsilon\sqrt{\xi} \gg 1$: Small opening channels (FPT approach valid).
  - $\varepsilon \gg 1$: Wide channels (new result).

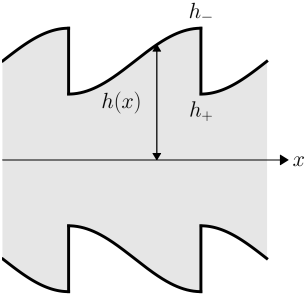




Mangeat *et al.*, EPL (2017).

- The dispersion is controlled by the geometry of the channel.

Dispersion in discontinuous channels



- Failure of perturbation theory $\left(h'(x) = \infty\right)$.
- Discontinuity at $x = 0[L]$.
- Ratio of discontinuity

$$\nu = \frac{h_+}{h_-} \leq 1$$

- Long-time effective diffusivity, with a correction $\mathcal{O}(\varepsilon)$ instead of $\mathcal{O}(\varepsilon^2)$!

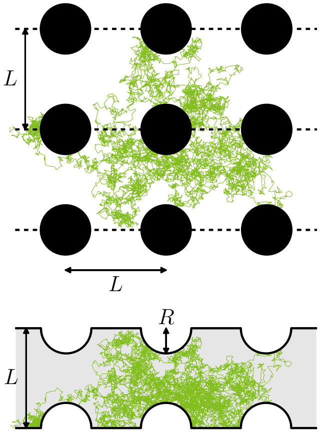
$$\frac{D_e}{D_0} \simeq \frac{1}{\langle h \rangle \langle h^{-1} \rangle} \left(1 - \varepsilon \frac{\gamma(\nu)}{\pi \langle \zeta^{-1} \rangle} \right)$$

$$\gamma(\nu) = \frac{1+\nu^2}{\nu} \ln \frac{1+\nu}{1-\nu} - 2 \ln \frac{4\nu}{1-\nu^2}$$

- The discontinuity plays the role of a local trap.

Mangeat *et al.*, J. Chem. Phys. (2018).

Dispersion in regular obstacle parks



- Periodicity of the square lattice : L
- Radius of the obstacles (disks) : R
- Only one dimensionless parameter :

$$\lambda = \frac{2R}{L} \in [0, 1].$$

- Volume fraction of obstacles : $\varphi = \pi R^2 / L^2$.

- Analogy with a channel of height

$$h(x) = \frac{L}{2} - \sqrt{R^2 - x^2}\,\Theta\left(R - |x|\right).$$

Dagdug *et al.*, J. Chem. Phys. (2012).

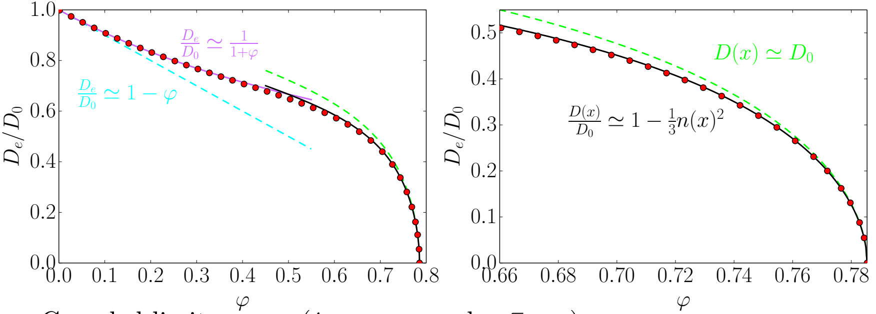
Effective diffusivity deduced from the microchannel's one

- Link with the parameters of the channel :

$$\varepsilon = \frac{1-\lambda}{2}, \quad \xi = \frac{\lambda}{1-\lambda} \quad \Rightarrow \quad \varepsilon\sqrt{\xi} = \frac{\sqrt{\lambda(1-\lambda)}}{2}.$$

- Dilute limit : $\lambda \to 0$ $\left(i.\ e.\ \varepsilon \simeq 1/2 \text{ and } \varepsilon\sqrt{\xi} \ll 1\right)$
  - Regime of dispersion : $D_e/D_0 \simeq 1 - \varphi \simeq (1+\varphi)^{-1}$.

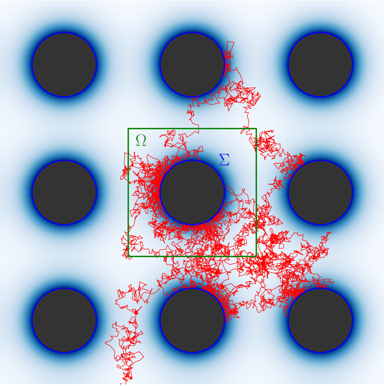
Maxwell, A Treatise on Electricity and Magnetism (1881).



- Crowded limit : $\lambda \to 1$ $\left(i.\ e.\ \varepsilon \ll 1 \text{ and } \varepsilon\sqrt{\xi} \ll 1\right)$
  - Regime of dispersion : slowly varying channel (FJ approximation relevant)
- The dispersion is well characterized by these two asymptotic regimes.

Mangeat *et al.*, in preparation.

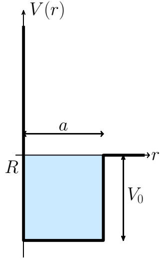
Physical problem in presence of *sticky spheres*

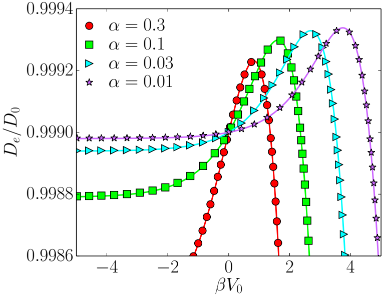


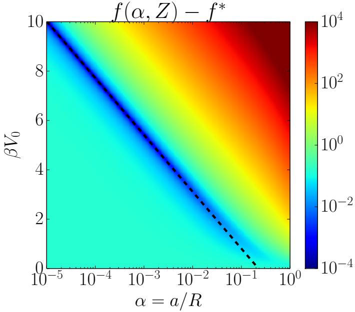
- Presence of obstacles :
  entropic trapping
- Presence of an attractive potential :
  energy trapping
- Observed effect : the dispersion is increased for a non vanishing attraction
  detrapping !

Putzel *et al.*, Phys. Rev. Lett. (2014).

Dispersion in the square-well potential







- Two dimensionless parameters : $\alpha = a/R$ and $Z = \exp(\beta V_0)$.
- Long-time effective diffusivity :

$$\frac{D_e}{D_0} \simeq 1 - \varphi f(\alpha, Z)$$

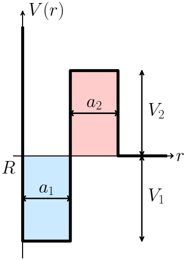
Cichocki et Felderhof, Langmuir (1992).

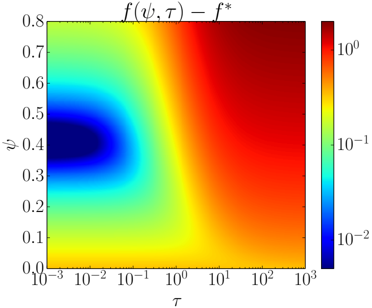
- Expression of the maximum of the effective diffusivity $(a \ll R)$:

$$\frac{D_e}{D_0} \simeq 1 - \varphi \frac{2\psi^2 - \psi + 1}{\psi + 1}, \qquad \psi = \alpha Z.$$

- Optimisation in 2d : $f^* \simeq 0.6569$ and $\psi^* \simeq 0.4142$.

Dispersion in the square-well potential with a barrier





- Four parameters : $\alpha_i = a_i/R$ and $Z_i = \exp(\beta V_i)$.
- Optimisation in 2d : $f^* \simeq 0.6569$, $\tau^* = 0$ and $\psi^* \simeq 0.4142$.
- Optimisation of the effective diffusivity for $a_1, a_2 \ll R$

$$\frac{D_e}{D_0} = 1 - \varphi \frac{2(\tau+1)\psi^2 - (1-\tau)\psi + 1}{(\tau+1)\psi + 1}, \qquad \psi = \alpha_1 Z_1 \text{ and } \tau = \alpha_2 Z_2$$

- Relations with the MFPT to leave (t_{esc}) and reach (t_Σ^*) the surface :

$$\psi \simeq \frac{t_{\mathrm{esc}}}{t_\Sigma^*} \qquad \text{and} \qquad \tau \simeq \frac{D_0}{R^2} t_\Sigma^*.$$

Mangeat *et al.*, in preparation.

- Exact Kubo formulas to characterize the dispersion for all shapes of channels.
- Identification of regimes of dispersion for continuous and discontinuous channels.
- Dispersion is controlled by the geometry of the channel.
- Analogy between the dispersion in regular obstacle parks and periodic microchannels.
- Dispersion is optimized for an attractive potential on the surface of obstacles.

- Study of the dispersion in presence of constant forces, or moving boundaries.
- Study of the dispersion in attractive obstacle parks in the crowded limit.

Aknowledgement : Prof. Dr. Heiko Rieger and SFB1027.

Thank you for your attention !

List of publications :

- *Geometry controlled dispersion in periodic corrugated channels*, EPL **118**, 40004 (2017).
- *Dispersion in two dimensional channels—the Fick–Jacobs approximation revisited*, J. Stat. Mech. (2017), 123205.
- *Dispersion in two-dimensional periodic channels with discontinuous profiles*, J. Chem. Phys. **149**, 124105 (2018).
- *Enhanced dispersion in attractive regular obstacle arrays*, in preparation.