

ENTROPY PRODUCTION OF REACTION-DIFFUSION SYSTEMS UNDER CONFINEMENT

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entropy
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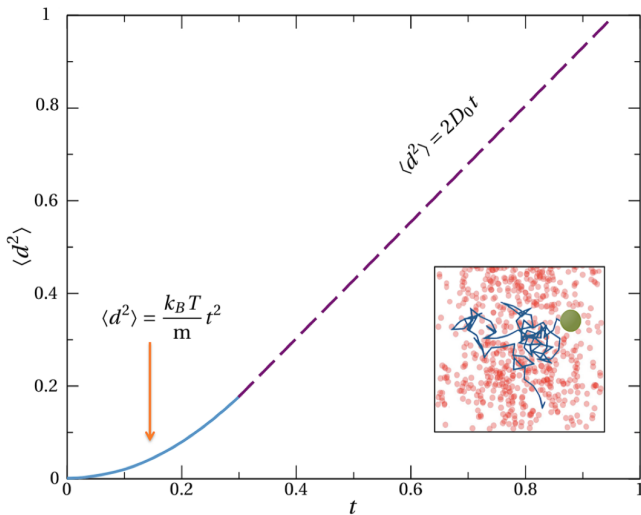

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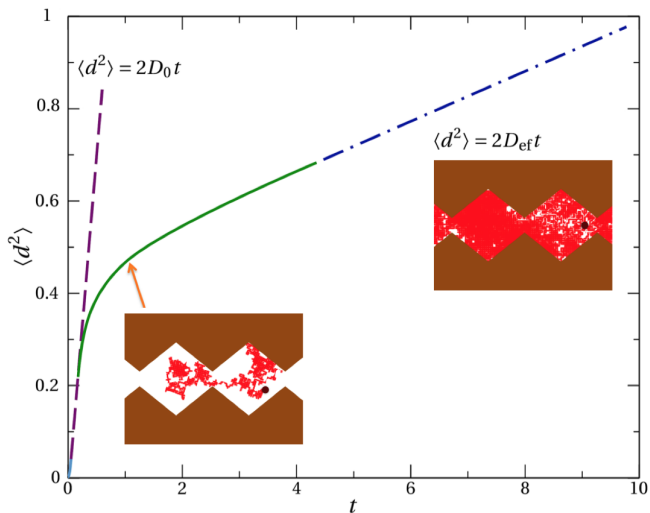
DIFFUSION ON NARROW CHANNELS

Mean square displacement



Channels

When diffusion occurs in bounded systems, the slope of the MSD, i.e. the diffusion coefficient is affected by boundaries



Effective 1D projection method

For narrow channels, there is a method that projects the 2D motion to an effective one-dimensional motion. From 2D diffusion equations:

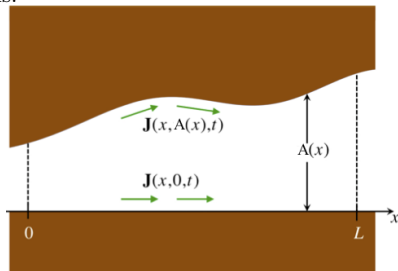
$$\frac{\partial}{\partial t} C(x, y, t) = D_x \frac{\partial^2}{\partial x^2} C(x, y, t) + D_y \frac{\partial^2}{\partial y^2} C(x, y, t),$$

we introduce the marginal distribution

$$c(x, t) = \int_{f_1(x)}^{f_2(x)} C(x, y, t) dy,$$

where $f_i(x)$ are the upper and lower boundaries of the channel, such that the width function is

$$w(x) = f_2(x) - f_1(x).$$



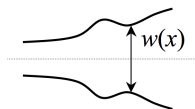
- After integration under reflecting boundary conditions, the so-called **Fick-Jacobs** equation is obtained:

$$\frac{\partial}{\partial t} c(x, t) = D_0 \frac{\partial}{\partial x} w(x) \frac{\partial}{\partial x} \frac{c(x, t)}{w(x)}.$$

The *entropic potential* $U(x) = -\ln w(x)$ which contains effects of the shape of the boundaries, is introduced.

- Zwanzig propose an adjustment due to variations of the diffusion coefficient:

$$\frac{\partial}{\partial t} c(x, t) = \frac{\partial}{\partial x} D(x) w(x) \frac{\partial}{\partial x} \frac{c(x, t)}{w(x)}, \quad (1)$$

$D(x)$ for 2D and 3D symmetric channels

Author

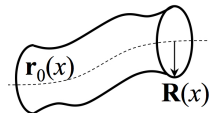
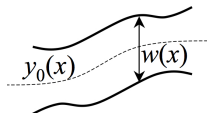
2D Channel

3D Tube

Jacobs (1967)	D_0	D_0
Zwanzig (1992)	$\frac{D_0}{1 + \frac{1}{12} w'(x)^2}$	$\frac{D_0}{1 + \frac{1}{2} R'(x)^2}$
Reguera y Rubí (2001)	$\frac{D_0}{\sqrt[3]{1 + \frac{1}{4} w'(x)^2}}$	$\frac{D_0}{\sqrt{1 + R'(x)^2}}$
Kalinay y Percus (2006)	$\frac{D_0}{w'(x)} \arctan \left[\frac{1}{2} w'(x) \right]$	$\frac{D_0}{\sqrt{1 + R'(x)^2}}$
García-Chung, Chacón-Acosta, Dagdug	JCP (2015)	JCP (2016)

Cuadro: $D(x)$ for symmetric. Width function in 2D is $w(x)$ and in 3D $\pi R(x)^2$.

$D(x)$ for 2D and 3D asymmetric channels



Author

2D Channel

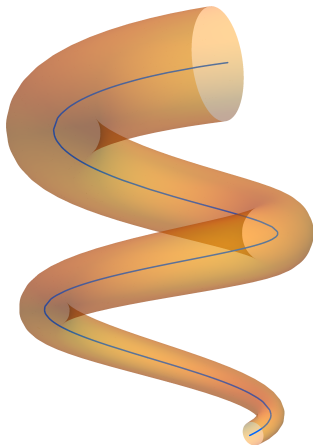
3D Tube

Bradley (2009)	$\frac{D_0}{1 + \frac{1}{12} w'(x)^2 + y_0'(x)^2}$	-
Berezhkovskii and Szabo (2001)	$\frac{D_0}{1 + \frac{1}{12} w'(x)^2 + y_0'(x)^2}$	$\frac{D_0}{1 + \frac{1}{2} R'(x)^2 + \mathbf{r}_0'(x)^2}$
Dagdug and Pineda (2012)	$\frac{D_0}{w'(x)} \left\{ \arctan \left[y_0'(x) + \frac{w'(x)}{2} \right] - \arctan \left[y_0'(x) - \frac{w'(x)}{2} \right] \right\}$	J. Cond. Matt. (2018)
Chávez, Chacón-Acosta, Dagdug	J. Cond. Matt. (2018)	JCP (2018)

Cuadro: $D(x)$ for asymmetric channels, the midline in 2D is $y_0(x)$ and in 3D is $\mathbf{r}_0(x)$. Width function in 2D is $w(x)$ and in 3D $\pi R(x)^2$.

$D(s)$ from the differential geometrical method

Different geometry methods show that when a tube has a constant cross-section, the diffusion coefficient takes the following form in the corresponding limit cases.



$$D_{\kappa}(s) \simeq 2D_0 \frac{1 - \sqrt{1 - (R\kappa)^2}}{(R\kappa)^2}, .$$

For $R\kappa \ll 1^a$.

$$D_{\tau}(s) \simeq D_0 \frac{\ln(1 + (R\tau)^2)}{(R\tau)^2},$$

For $R\tau \ll 1$.

For a variable cross-section $R \neq \text{const.}$, and when the channel has a twisted midline, one has^b

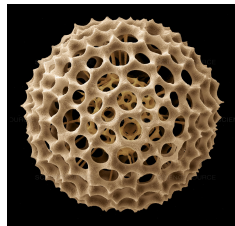
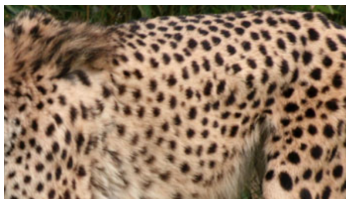
$$D(s) \approx D_0 \frac{\ln(1 + R'^2 + (R\tau)^2)}{R'^2 + (R\tau)^2},$$

^aOgawa PLA (2013).

^bChávez, Chacón-Acosta, Dagdug, JCP (2018).

PATTERN FORMATION ON NARROW CHANNELS

Turing mechanism for pattern formation



Turing mechanism for pattern formation

- The Reaction-Diffusion system:

$$\frac{\partial u}{\partial t} = \nabla^2 u + \gamma f(u, v), \quad \frac{\partial v}{\partial t} = d\nabla^2 v + \gamma g(u, v),$$

where u y v are the species' concentrations that diffuse and react according to the kinetics f and g . Here $d = D_u/D_v$ and γ is the relative strength of the reactions. The problem may have Neumann, Dirichlet, Robin, or periodic boundary conditions.

- The stationary state of the system is (u_0, v_0) , such that in the absence of diffusion $f = g = 0$.
- Under certain conditions of the values of the parameters, the system's state becomes unstable in the presence of diffusion.
- Turing conditions for pattern formation:

$$\begin{aligned} \text{tr}A &= f_u + g_v < 0, & \det A &= f_u g_v - f_v g_u > 0, \\ df_u + g_v &> 0, & (df_u + g_v)^2 - 4d(f_u g_v - f_v g_u) &> 0, \end{aligned}$$

where the derivatives are evaluated in the steady-state (u_0, v_0) .

- The system is linearized around (u_0, v_0) and the polynomial $\lambda(k)$ is the dispersion relation whose roots give the range of unstable wavenumbers

$$k_{\pm} = \sqrt{\frac{\gamma}{2d} \left((df_u + g_v) \pm \sqrt{(df_u + g_v)^2 - 4d \det A} \right)}, \quad (2)$$

Parameter formation on channels¹

- Let us consider two chemical species (u, v) confined in a channel whose longitudinal coordinate is larger than the transversal one. This system is then described by the Fick-Jacob-Zwanzig operator Eq. (1), which is rewritten as a Fokker-Planck operator:

$$\frac{\partial u(x, t)}{\partial t} = \underbrace{\frac{\partial}{\partial x} \left[\frac{\partial}{\partial x} (D(x)u(x, t)) - (B(x)u(x, t)) \right]}_{-J_u} + \gamma w(x) f\left(\frac{u}{w}, \frac{v}{w}\right), \quad (3)$$

$$\frac{\partial v(x, t)}{\partial t} = \underbrace{d \frac{\partial}{\partial x} \left[\frac{\partial}{\partial x} (D(x)v(x, t)) - (B(x)v(x, t)) \right]}_{-J_v} + \gamma w(x) g\left(\frac{u}{w}, \frac{v}{w}\right), \quad (4)$$

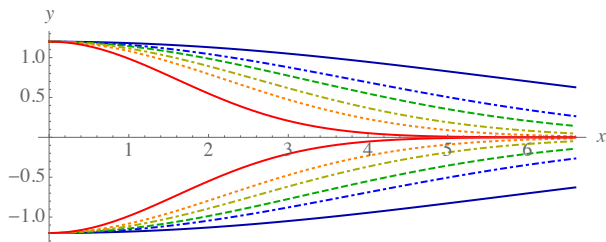
with the fluxes J_u, J_v and the advection coefficient

$$B(x) = \frac{\partial D(x)}{\partial x} + D(x) \frac{\partial \ln w(x)}{\partial x}.$$

- By doing an expansion of the concentrations around the steady-state and a rescaling of the coordinates as a function of $D(x)$, it is then possible to obtain a linearized set of equations for the perturbations that gives us a dispersion relation from where it is possible to analyze the stability of the system¹.
- We study the well-known Schnakenberg kinetics $f = \gamma(a - u + u^2v)$, $g = \gamma(b - u^2v)$.

¹Chacón-Acosta, Núñez-López, Pineda, JCP (2020).

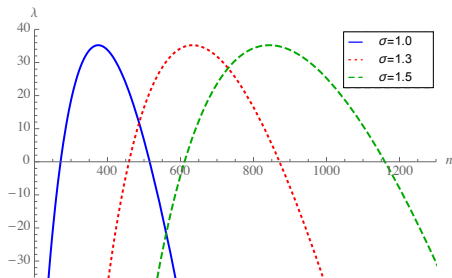
Funnel-like channel



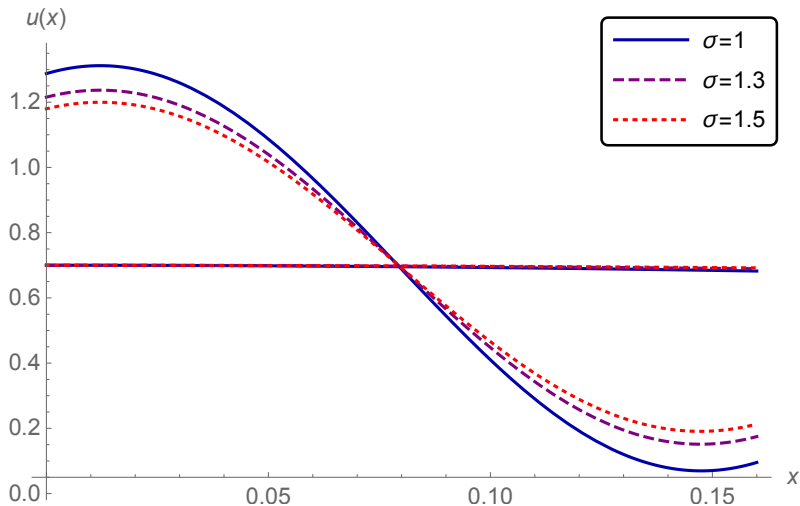
$$w(x) = A_0 \exp\left(-\frac{x^2}{2\sigma^2}\right),$$

Harmonic oscillator potential, with the shape parameter $1.5 \text{ (red)} \leq \sigma \leq 6 \text{ (blue)}$.

$$n_{\mp} = \frac{\gamma\sigma^2}{2d} \left[(df_u + g_v) \mp \sqrt{(df_u + g_v)^2 - 4d(f_u g_v - f_v g_u)} \right].$$



Funnel-like channel



Morphogen density u for Schnakenberg kinetics with $a = 0.2$, $b = 0.5$, $d = 2.95$, and $\gamma = 100$, for different values of σ .

ENTROPY PRODUCTION

Entropy production

- The entropy production rate of a reaction-diffusion system is given by the sum of two components: chemical reactions and by diffusion

$$\sigma = \sigma_R + \sigma_D \quad (5)$$

- Chemical contribution.** The entropy production rate per unit length due to chemical reactions is as follows²

$$\sigma_R = \sum_{i,j} S_{ij} \mathcal{J}_i \ln \left(\frac{c_j}{c_j^0} \right), \quad (6)$$

where S_{ij} are the stoichiometric coefficient for the reaction, \mathcal{J}_i is the i -th net chemical reaction current, and c_j, c_j^0 are the concentration and its equilibrium value respectively.

- The reversible part of the reactions is not considered to obtain S_{ij} , which avoids the thermodynamic study of pattern formation. However, we consider it as an approximation to study the geometric effects in these types of expressions.
- For the present reaction σ_R is

$$\sigma_R = \gamma \left(a + b - \frac{u}{w} \right) \left(\ln \left(\frac{u}{u_0} \right) + \ln \left(\frac{v}{v_0} \right) \right), \quad (7)$$

the total entropy production rate is the spatial integration of this term along the entire length of the channel.

²Mahara et al. JCP (2004).

Entropy production

- **Diffusion contribution.** The entropy production rate per unit length due to confined diffusion is³

$$\sigma_D = - \sum_i J_i \mathcal{F}_i, \quad (8)$$

where J_i are the fluxes (3)-(4), and \mathcal{F}_i the entropic driving force of each species.

- For the present process σ_D is

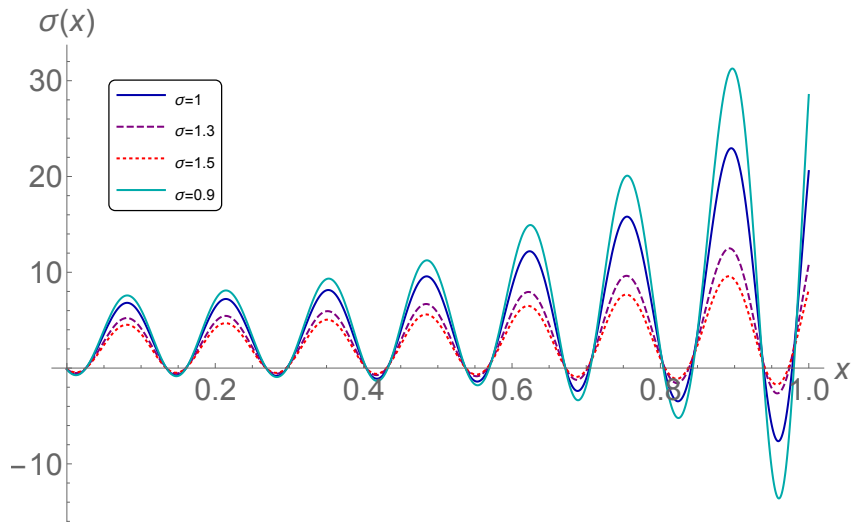
$$\begin{aligned} \sigma_D &= \left(\frac{\partial u}{\partial x} - u \frac{w'}{w} \right) \left(\frac{1}{u} \frac{\partial u}{\partial x} - u \frac{w'}{w} \right) + d \left(\frac{\partial v}{\partial x} - v \frac{w'}{w} \right) \left(\frac{1}{v} \frac{\partial v}{\partial x} - v \frac{w'}{w} \right), \\ \sigma_D &= u \left(\frac{\partial}{\partial x} \ln \left(\frac{u}{w} \right) \right)^2 + dv \left(\frac{\partial}{\partial x} \ln \left(\frac{v}{w} \right) \right)^2. \end{aligned} \quad (9)$$

- The entropy production of the entire system has proven to be a good scalar measure of the dynamics of global pattern formation². It is also related to the kind of diffusion in the system, either parabolic or hyperbolic diffusion

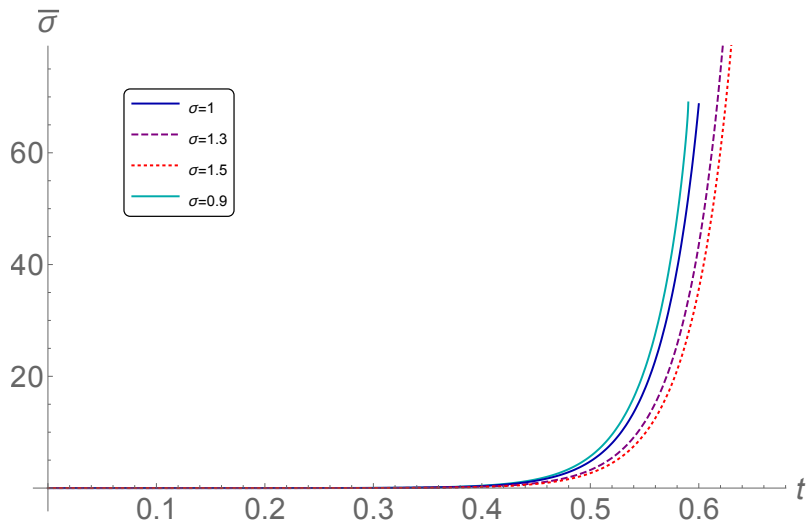
$$\bar{\sigma} = \int_0^L dx \sigma(x, t).$$

³Carusela, Rubi, J Cond. Matt. (2018).

Entropy production funnel-like channel



Entropy production funnel-like channel



SUMMARY

Summary

- Confinement influences the diffusivity of the system.
- Turing's mechanism gives us the range of unstable modes where the patterns can form for specific values of the parameters.
- When the system is under confinement, both the range of unstable modes and the pattern itself, change depending on the geometry of the channel.
- Also, the rate of entropy production grows faster as the width of the channel increases.

Gracias por su atención