Confined Brownian motion as applied to grain-growth processes

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1 Purpose of the visit

The aim of my short visit to Barcelona was to start a cooperation with prof. J. Miguel Rubí from University of Barcelona on a subject of confined Brownian motion considered in entropic context, potentially useful to describe grain-growth processes. Firstly, I was going to research more in area of transport in confined media through channels of various-diameter passages, corresponding to one-dimensional Fick-Jacobs diffusion. Next, I wanted to formulate a problem with prof. Rubí on elaboration of the above mentioned scenario in order to apply it to (soft-matter) grain growth. And finally, I planed to build a computer simulation which could help solve the stated problem.

2 Description of the work carried out during the visit

Looking on polycrystal grain growth as a process depending on motions of unreacted particles (of nano- or mesoscale) randomly moving between matured grains, and as a process depending on geometry of the grains, we expect that Fick-Jacobs transport equation, with confinements, can be helpful in understanding the properties of many (soft-matter) polycrystal materials in terms of dynamics, viscoelasticity, thermal or electrical conductivity, etc. In such a system the presence of entropy barriers is a common feature.

The motions of unreacted particles can be stated as entropy driven diffusion process characterized by a presence of entropic barriers which can be described, in probabilistic way, by mesoscopic non-equilibrium thermodynamics (MNET)[1, 3]. This approach provides a derivation of a generalized Fick-Jacobs formula for the constrained dynamics of the mesoscopic degree of freedom. In [3] Rubí and Reguera have shown that entropically originating confinement can be involved into MNET in natural way in a definition of chemical potential. A basic confinements in the problem of particles' motion between growing grains are grain boundaries, thus, a local curvatures emerging during the grain growth. Grain boundaries create sometimes narrow (funnel-like) and sometimes wide channels, cf. Fig. 1.

During the short visit, a very interesting problem to take on was to apply the Fick-Jacobs transport to activation processes, which in many cases takes place in confined media (e.g. self-assembly, association of biomolecules, binding, transport in ion channels, chemical reactions and other barrier crossing dynamics). Finding the activation regime could be very interesting issue. We supposed that the activation should depend on a size of the channel, a characteristic angle of the "funnel", an energy supplied to the randomly walking particles, etc.

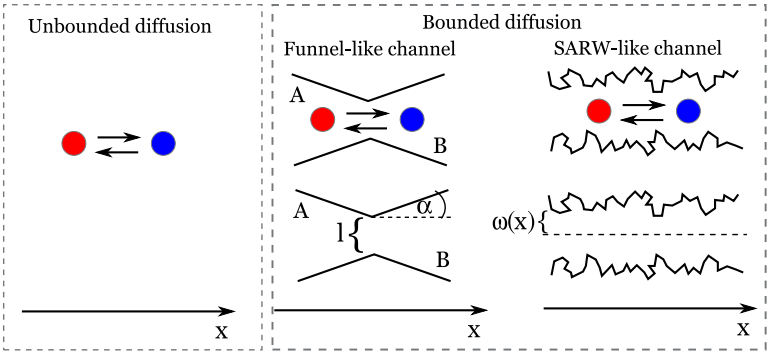

Figure 1: RW particles without and with boundaries.

Additionally, in the case of polycrystal grain boundary, their geometry is non-regular and can be described as self-avoiding polygon (SAP; fractal structure) [4, 5] thus a channel created by polycrystal grains has also fractal (self-avoiding random walk, SARW) nature [2]. Thus, a second interesting problem was to check if Fick-Jacobs approach is able to describe transport through fractal-like channel.

2.1 Activation driven by the entropy

In the case of transport through funnel-like channel, flow activation rates are affected by confinement. We consider the transport as one-dimensional flow along coordinate x. Entropy production, following from MNET theory [3], is given by

$$\sigma = -\frac{1}{T} J \frac{\partial \mu}{\partial x}, \tag{1}$$

where T is a temperature, $J \equiv J(x,t)$ a flux and $\mu \equiv \mu(x,t) = kT \ln \rho + \phi$ is non-equilibrium chemical potential with ϕ being a potential barrier (minimal work needed to move system from one stage to another), $\rho \equiv \rho(x,t)$ - concentration of particles and k - a Boltzmann constant. This equation can also be written, using flux-force relation and assuming coarsening, as

$$J = -\frac{kL}{\rho} e^{-\phi/kT} \frac{\partial}{\partial x} e^{\mu/kT}, \tag{2}$$

where L is Onsager coefficient. The equation (2), after differentiation and integration from state 1 (μ_1, ρ_1, ϕ_1) to state 2 (μ_2, ρ_2, ϕ_2), can be expressed as

$$J \propto \left(\rho_2 e^{\frac{\phi_2}{kT}} - \rho_1 e^{\frac{\phi_1}{kT}} \right). \tag{3}$$

When we consider the work, ϕ, disjointly from one related to energetic contribution ϕ_{energ} and second related to entropic work ϕ_{entrop}, then chemical potential

$$\mu = kT \ln \rho + \phi_{energ} + \phi_{entrop}. \tag{4}$$

Denoting $a = e^{\phi_{entrop}/kT}$ as activity coefficient, the above equation can be rewritten as

$$\mu = kT \ln a\rho + \phi_{energ}. \tag{5}$$

Figure 2: Two containers with big channels between them. 400 particles move randomly inside them drawing lines from light (early stage of moves) to dark (later stage of moves) color.

Then, a flux equation is

$$J \propto \left(a_2 \rho_2 e^{\frac{\phi_{energ,2}}{kT}} - a_1 \rho_1 e^{\frac{\phi_{energ,1}}{kT}} \right). \tag{6}$$

Noticing that $\phi_{entrop} = T \triangle S$, where $\triangle S = k \ln \frac{A}{A_0}$ is entropic potential [1] (A_0 is a cross-sectional area of a channel's neck, $A \equiv A(x)$ is an cross-sectional area of a channel in a function of x) we can write $a = e^{\triangle S/k} = \frac{A}{A_0}$.

During the short visit, we prepared a plan of Monte Carlo two-dimensional simulation of one-dimensional transport phenomenon through a channel between two (or more) containers containing RW particles, to compare the flux obtained as simulation result with the analytic J function (cf., Eq. (3)).

Alongside the analytical work done in the course of the visit first implementation of the program have been created using Java 8 technology (see, Fig. 2). The simulation allows, in this early stage of our study, to:

- build containers with reflecting walls where RW particles can move,
- include channel walls which allow a particle to move through them changing this way the containers,
- apply periodic boundary conditions which simulate infinity of a space,
- put into containers N number of RW particles with energies E (each container can have their own temperature T and size),
- create outputs of calculated mean-squared displacement (MSD), concentration, flux (as a difference if concentrations),
- visualize the diffusion of RW particles.

Based on a knowledge of flux in the process we can now approximate the function to a power-law and compare simulation results with its analytic counterparts. Additionally, based on a knowledge of MSD of RW particles, we are able to describe some viscoelastic properties of the system.

2.2 Random walk between polycrystals' grains

Assuming that the polycrystal grain boundaries have a shape of self-avoiding polygon (SAP) [5], we would like to apply Fick-Jacobs equation to describe a transport between two SAP grains. The case of transport through periodic (sinusoidal) tube has been studied [6] and with well defined differentiable radius of the tube (or a half-width of the channel in two-dimensional case), $\omega(x)$, it is possible to get information about the dynamics of the system. Diffusion coefficient, chemical potential, flux of matter are the physical quantities which can be computed based on the first derivative of the $\omega(x)$, cf. Eqs (3)-(7b) in [6]. This approach is in principle valid for $|\frac{d\omega(x)}{dx}| \ll 1$.

The first question, which we were trying to answer during the short visit, was: if we can write, e.g. while based on the sinusoidal example, an analog of a differential (thus, difference) equation for $\omega(x)$ in the case of self-avoiding random walk (SARW) curve (a fragment of SAP boundary). We started from searching analytic approximation of SARW curve using a Fourier-type noise equation which can be composition of sinusoidal functions, for example

$$f(x) = \sum_{i=1}^{n} \frac{1}{i^2} \sin(i\omega_0 x). \tag{7}$$

We assumed that only determinant of obtaining SARW-like curve is fractal dimension which in case of SARW is $d_f = d + 2/3$ (with the qualitatively different RW limit at $d = 4$, d is a dimension of Euclidean space). Our considerations were situated in two-dimensional space, thus, $d = 2$.

As a continuation, if the Fourier-type functions will not be satisfying, we will search a different type functions for example the ones flowing out from natural structures such as sea surface (cf. Fig. 1 in [7]).

For the purpose of computing the fractal dimension for a curve generated by equation of type Eq. (7), and further of each type of equations which we were to check to be best fitted to SARW fractal, we created a project of computer application. A first implementation of the program was made during the short visit using Java 8, and had the task of drawing the function and computing fractal dimension using the box counting method.

All the simulation environments, created during the visit, were programmed with extensibility and further reuse in mind as we are looking for longtime scientific cooperation.

3 Description of the main results obtained

To analyze more carefully the two problems stated above, a few representative examples of simulation results have been selected for presentation in a form (see, Figs 3-6). Those results require more in depth analysis in further studies to answer the stated questions.

3.1 Main results on activation driven by the entropy

During the short visit, we have conducted running first bath of simulation through the created application and gathered first results for different simulation parameters from which we choose six representative examples. The performed simulations' environment contains two containers of the same sizes and two channels between them (with periodic boundary conditions).

For this two containers (denoted by A and B) we assumed the following parameters:

	l	N_A	N_B	s_A	s_B	α	S
a	50	200	200	10	10	55	74156
b	50	0	400	10	10	55	74156
c	50	200	200	10	20	55	74156
d	6	200	200	10	10	55	59988
e	6	0	400	10	10	55	59988
f	6	200	200	10	20	55	59988

where l is size of channel, N_X - number of RW particles in container X, s_X - length of single allowable RW particle's jump which is related with energy of particle inside container X its temperature of the container, α - angle adjacent to channel passage, and S is the containers' area. The sizes of l, s_X, S are given in the simulation space unit of length. The fluxes for six situations mentioned above are presented on the Figure 3. They are computed as a difference

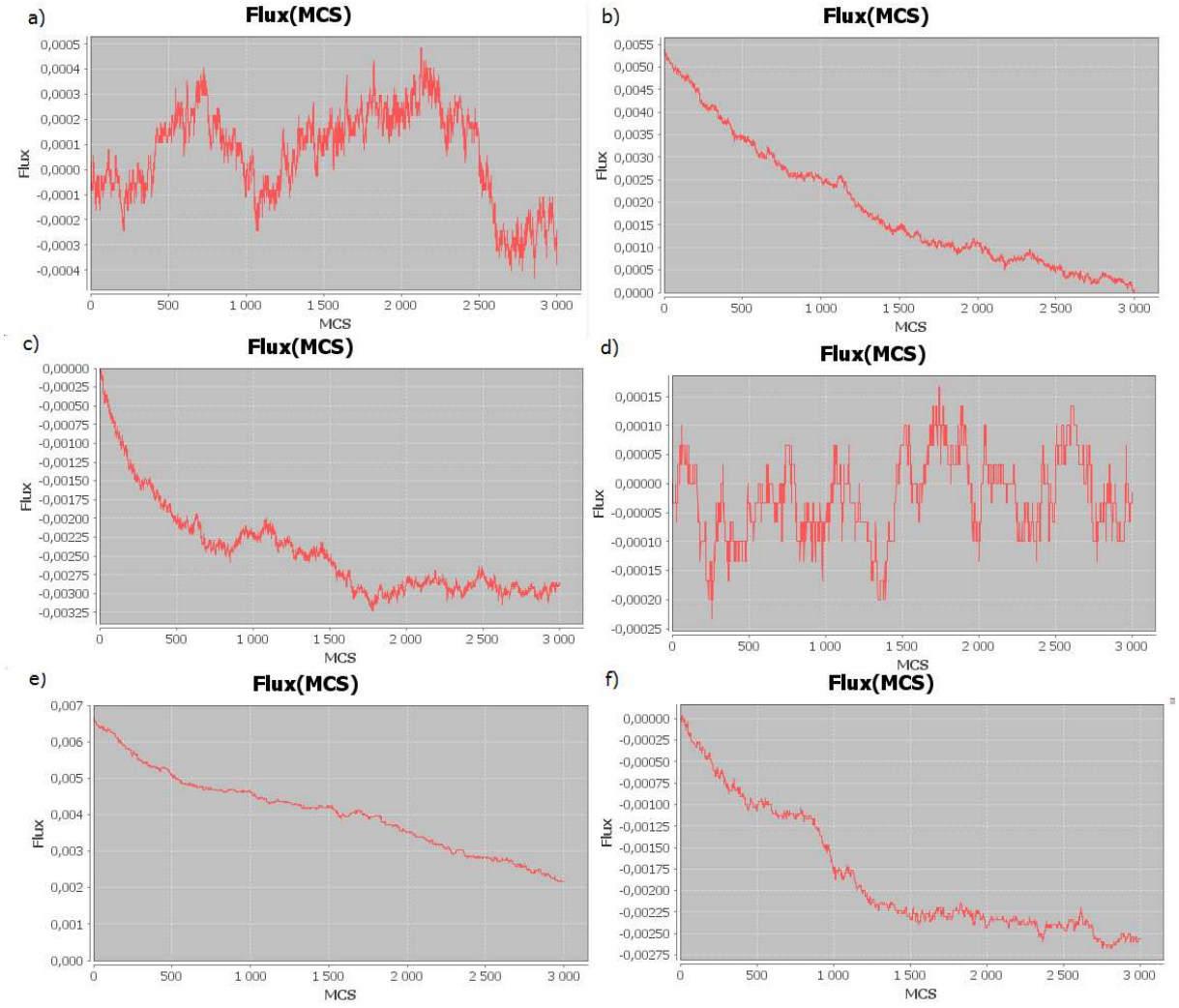

Figure 3: Flux as a function of time (measured in Monte Carlo Steps, MCS) for six different simulation environments. Cases a,b and c are obtained from simulation of wide channel ($l = 50$); cases d, e, f are obtained from simulation of tight channel ($l = 6$) (cf. Tab. 3.1).]

in concentrations between containers, $J(t) \propto \rho_B(t) - \rho_A(t)$, where concentration ρ_X are telling

us how many RW particles are traveling inside container X. The particles did not interfere with each other - excluded volume effect is not added on this stage of study. First three results (a-c) are obtained from simulation for wide channel ($l = 50$) and rest of the results (d-f) are generated for more close-packed structures creating tight channel ($l = 6$). Cases a and d show an equilibrium state. No significant flux is obtained (its value randomly fluctuates about zero) due to a lack of force (no concentration or temperature differences between containers). When we change the concentration in containers we obtain greater concentration in B than in A (cases b and e), the system strives for equilibrium by equalizing the concentration - flux starts from positive value and approaches zero. It can be fitted to exponential function as shown in a Fig. 4. A comparison of the fitting functions y with flux obtained analytically (cf. Eq.

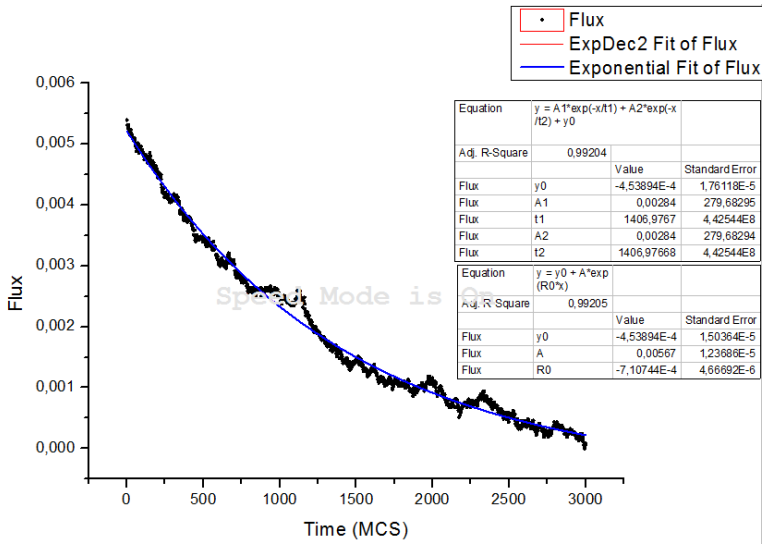

Figure 4: Flux, from the case b, as a function of time, fitted to two different exponential functions. Origin 8 software was used for function fitting.

(3)) will be a main topic of further study. The most interesting cases, however, are those with different energy of RW particles in each container. The systems (cases c and f) starting from equilibrium show an interesting behaviors lowering exponentially to negative values. In these examples a temperature gradient has been added, thus, an analytical counterpart of flux should have different form (with Soret effect) as has been proposed in [8].

MSD for two completely different situations (cases a and f) are presented in the Fig. 5. Due to a periodic boundaries added in a form of two channels, the figures are very close to diffusive ones where the MSD is proportional to time. When the size of channel is small ($l = 6$) (close-packed system) the bend on the MSD curve is clearly seen. The bend grows when the channel's size is lowered. On the next stage of the study the activation regime will be searched. Also a viscoelastic properties of the system can be studied based on the knowledge of MSD by finding a complex shear modulus of probe particles pushed through the matter.

3.2 Main results on random walk between polycrystals' grains

A first attempt of drawing an approximation function of fractal-like grain boundary have been made during the short visit (see, Fig. 6). A computation of its fractal dimension has been

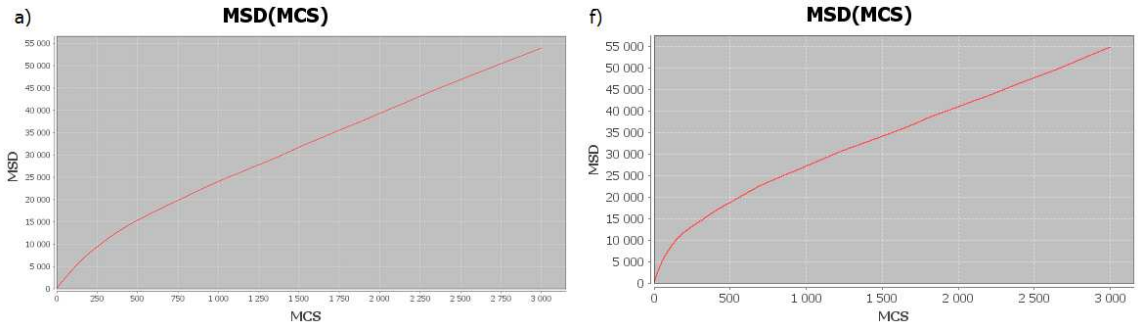

Figure 5: MSD as a function of time for six different simulation environments.

also obtained using the box-counting method. The results have been compared to Fractalyse 2.4 application. Fractal dimension D_f is still too low to treat the function as approximation

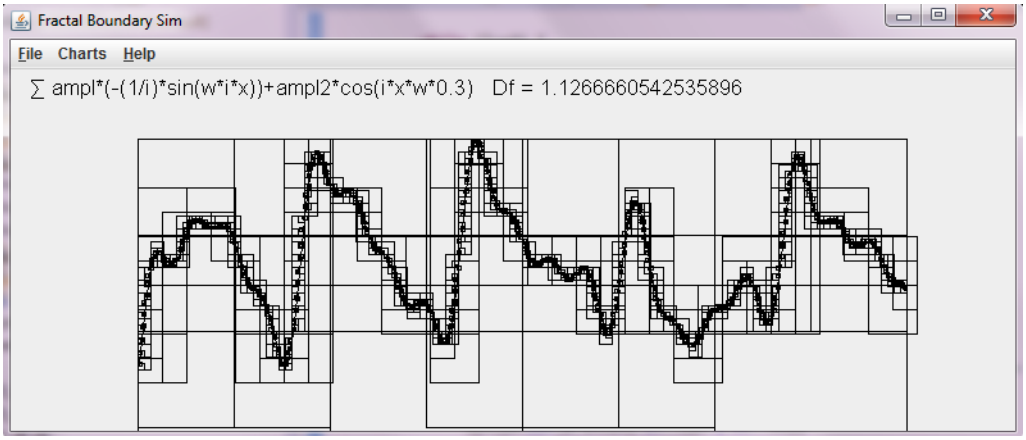

Figure 6: An example of single boundary generated by equation $f(x) = \sum_{i=1}^{n}(-X_1\frac{1}{i}\sin(i\omega_0 x)+ X_2\cos(0.3i\omega_0 x))$, where $x \in < 0, 600 >$, $n = 4$, $X_1 = 50$, $X_2 = 20$, $\omega_0 = 0.05$. The black boxes, seen on the curve, are used to count fractal dimension D_f.

of SARW boundary. The finding of proper approximation function will be a topic of further study.

4 Future collaboration with host institution

Beyond completing the research mentioned above, as a future work, we aim to study the activation problem applied to grain-growth processes where x will be threated as a grain size or volume in analogy with [9], thus, in the phase space (x-space) of grain sizes. Adding external forces to the simulations to check how it will change the results will also be a very promising issue, as has preliminary been announced by our recent [10].

5 Projected publications / articles resulting or to result from the grant

On the basis of the studies done during the visit in Barcelona, we plan to publish at least two papers in international journals:

1. J.M. Rubí, N. Kruszewska, A. Gadomski, "Activation driven by the entropy",
2. N. Kruszewska, J.M. Rubí, A. Gadomski, "Random walk between polycrystals' grains".

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