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Molecular Intermittent Dynamics in Interfacial Confinement

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1. Introduction

Porous materials, concentrated colloidal suspensions are example of confining systems developing large specific surface, presenting a rich variety of shapes and exhibiting complex and irregular morphologies on a large length scale. Such a confinement strongly influences the molecular dynamics of embedded fluids and the diffusive motion of particles entrapped inside these materials. As shown in fig 1, the particle trajectory can be described as an alternate succession of surface adsorption steps and confining bulk relocations. The full transport process appears as an intermittent dynamics. This question related to a first passage problem is discussed in this presentation

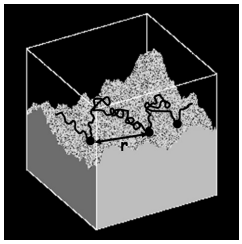

Figure 1. An Intermittent Brownian Dynamics (I.B.D) near a rough interface.

2. Intermittent dynamics in confinement: a spectral analysis

The confined Brownian diffusion of a particle inside an interfacial medium is an intermittence of adsorption steps near the interface and Brownian excursion in the bulk. The time evolution can be described using a indicator function I(t) equals to one in the adsorption state and zero in the bulk. This random signal is associated to two probability distribution functions (p.d.f), $\Psi_R(t)$ and $\Psi_A(t)$. $\Psi_R(t)$ provides the time distribution spend in the bulk before a readsorption on the surface and $\Psi_A(t)$ characterized the way that an adsorbed molecules is released in the bulk. A way to characterize the statistical nature of the intermittent dynamics is to compute the average time auto-correlation R(t) of the random signal I(t). As shown elsewhere [1], it is more convenient to compute its spectral density J(ω). Assuming a statistical independence between successive adsorption and relocation, we can write that [1]:

$$J(\omega) = \frac{\sigma}{\omega^2} \mathrm{Re}\, al\left(\frac{(1-\tilde{\Psi}_R(\omega))(1-\tilde{\Psi}_A(\omega))}{1-\tilde{\Psi}_R(\omega).\tilde{\Psi}_A(\omega)}\right) \qquad \text{Eq(1)}$$

where σ is normalization constant and $\tilde{\Psi}_R(\omega)$ and $\tilde{\Psi}_B(\omega)$ are the time Fourier transforms of $\Psi_R(t)$ and $\Psi_B(t)$ respectively. Analytical expressions of J(ω).can be computed for various interfacial geometries [1,2,3,5] showing its strong ability to capture the fluid-surface interaction and the bulk geometrical confinement.

3. The case of water Dynamics in hydrophilic or hydrophobic Pores

In order to gain insights into the intermittent dynamics of confined fluid, we have performed an atomic–scale simulation results for water fluid confined in siliceous slit nanopores [4]. The dynamics of the confined fluid is determined using Molecular Dynamics simulations (MD) at constant temperature. $\Psi_R(t)$, $\Psi_A(t)$ and $R(t)$ were computed independently. Our analysis shows clearly that adsorption layer is restricted to two water layers. The self diffusion can be described as an intermittent dynamics between this two layers proximal region and the distal confined bulk. A similar approach is developed to describe the confining dynamics of water inside a hydrophobic pore (a carbon nanotube) and an interesting comparison between hydrophilic and hydrophobic pores can be outlined.

4. Probing adsorption and relocation statistics in confinement: NMRD Experiments

The Nuclear Magnetic Relaxation Dispersion technique (NMRD) is an effective experimental method to follow an intermittent dynamics near an interface. Under some general conditions of relaxation [1]; the related spin-lattice relaxation rate $R_1(\omega)$ is directly proportional to $J(\omega)$. Various experimental studies of the intermittent dynamics, using NMRD were recently performed (plaster pastes [5], flat colloidal clay particles [1], long and stiff nanometric strands [3]) with a special emphasis on the fluid-surface interaction in term of "nano-wettability" [5].

3. Conclusion

The former analysis of the intermittent dynamics provides a simple description of the local exploration of an interfacial medium by a particle and/or a molecule. This coarse grained description allows to quantify the influence of the "local" confining geometry and also to estimate the degree of interaction during the adsorption step. As recently discussed [6], another important aspect of the intermittent dynamics is related to its efficiency to optimize the research of a surface target which puts forward a general mechanism of enhancement and regulation of chemical reactivity.

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