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Some considerations about the modelling of single file diffusion

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1. Introduction

Single file diffusion (SFD) is a one dimensional process, in which no mutual passage of the diffusing particles is allowed. In a recent paper [1] an interpretation of the SFD of water in the narrow straight channels of two different zeolites, as simulated by Molecular Dynamics calculations, was attempted within the fractional diffusion theory, which stems from the Continuous Time Random Walk (CTRW) scheme [2]. It was shown that, although some features of SFD, such as the dependence of the Mean Square Displacement (MSD) of a tagged particle on the *square root* of time was reasonably well reproduced, the functional form of the propagator expected from fractional diffusion equations did not correspond to that derived from the simulations, but agreed (only for long times) with the asymptotic behaviour resulting from statistical considerations [3].

In the present contribution the theoretical models proposed to describe SFD are considered and compared with the simulation data in more detail. Some suggestions are put forward, which could be useful in order to develop a satisfactory theory for SFD.

2. Experiments, numerical simulations and theoretical models

In the modelling of diffusive processes, the propagator (i.e., the probability $W(r,t)$ of finding a particle in the position *r* at the time *t*) contains all the relevant information about the process itself. A satisfactory theory of diffusion should yield a mathematical method (possibly an equation or an equation system) for evaluating the propagator of a system given its characteristics and the applied boundary conditions. For normal diffusion the propagator is represented by a Gaussian function with second momentum proportional to time. For SFD, from statistical theories the following form of time asymptotic propagator for an infinite system of fixed density ρ results: [3]

$$W(r,t) = \frac{\sqrt{\rho}}{2(\pi D_0 t)^{1/4}} exp\left\{-\rho r^2 \left[\pi/(16 D_0 t)\right]^{1/2}\right\}, \quad (1)$$

where D_0 is the diffusion coefficient the particle would have if it were the only particle in the infinite one-dimensional system. In order to fit experimental MSDs of silica colloid spheres suspended in water and confined in straight and narrow grooves, Lin *et al.* [4] proposed a general Gaussian form of the propagator and an ansatz was to describe the MSD over the entire time range (*F* is the single file mobility factor):

$$W(r,t) = \left(2\pi\langle r^2(t)\rangle\right)^{-1/2} exp\left\{-r^2(t)/2\langle r^2(t)\rangle\right\}; \qquad \frac{1}{\langle r^2(t)\rangle} = \frac{1}{2D_0 t} + \frac{1}{2Ft^{1/2}}, \quad (2)$$

Although Eq. (2) fitted reasonably the experimental MSDs reported in Ref. [4], it was not able to fit satisfactorily the propagators derived from our simulations. The fractional diffusion theory, as well as the CTRW models, does not take into account correlation of noise that, instead, appears to be the responsible for the achievement of the subdiffusivity in SF systems [6]. Such slow decaying power-law correlations can be introduced in the dynamics of a SF system through the Generalized Langevin Equation [5]

$$\ddot{x} + \int_0^t dt' \, \beta(t - t') \dot{x}(t') = \xi(t), \tag{3}$$

setting the memory kernel $\beta(t) = \gamma_d / \left[\Gamma(1/2) t^{1/2}\right]$, being $\gamma_d = 1/\tau_d^{3/2}$, where τ_d is the average time needed for a pair of particle to collide against its neighbours [8]. Thus the motion of a particle can be ruled by two different Langevin equations each one pertaining to different diffusional stages it exhibites during its motion:

$$\ddot{x} + \gamma \dot{x} = \xi(t) \text{ for } t \ll \tau_d \quad \text{and } \ddot{x} + \gamma_d \frac{\partial^{1/2}}{\partial t^{1/2}} \dot{x} = \xi_d(t) \text{ for } t \gg \tau_d, \tag{4}$$

where γ is a damping constant. The second of (4) is often called Fractional Langevin Equation [9]. Both noises in (4) satisfy the Generalized Fluctuation-Dissipation Theorem: $\langle \xi(t+\tau)\xi(t) \rangle = kT\beta(\tau)$ and the velocity autocorrelation function $C_v(t)$ turns out to reproduce exactly the numerical and analytical results given in [6]. From the dynamical representation of the motion given by (4) it is easy to pass to a probabilistic picture in terms of the diffusion equation for the propagator:

$$\frac{\partial}{\partial t} W(r,t) = D \frac{\partial^2}{\partial r^2} W(r,t) \text{ for } t \ll \tau_d \text{ and } \frac{\partial}{\partial t} W(r,t) = \frac{F t^{-1/2}}{2} \frac{\partial^2}{\partial r^2} W(r,t) \text{ for } t \gg \tau_d. \tag{5}$$

It is easy to recognize in the second of (5) the diffusion equation for Fractional Brownian Motion (FBM) [7], whose solution is a Gaussian as Eq. (1) with variance $2F\sqrt{t}$.

3. Conclusion

In conclusion we showed how the single file diffusion can be understood by means of the GLE and the related diffusion equation for FBM. However, the connection between the two diffusive regimes has to be still demonstrated, as a change in the time dependence of $C_v(t)$ corresponds to a change of timescales and noise amplitudes appearing in (4).

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