Anomalous diffusion and the adsorption-desorption process in anisotropic media

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Abstract – The diffusive process of dispersed particles in a semi-infinite cell of an anisotropic fluid limited by an adsorbing surface is theoretically investigated. The densities of bulk and surface particles are analytically determined, taking into account the conservation of the number of particles immersed in the sample. It is shown that an anomalous diffusion process can take place according to the time scale considered. For short time interval there is a sub-diffusion process, followed by a super-diffusive regime. For large time interval the diffusive process tends to a normal behavior. The analysis is suitable for the description of the adsorption phenomena of neutral as well as charged particles in anisotropic media.

We consider a general situation represented by a semi-infinite anisotropic medium in contact with a solid substrate at which an adsorption-desorption process takes place [1]. Initially, a defined number of particles is suspended or dispersed in the medium and an anisotropic diffusive process starts. The particles reaching the solid substrate can be adsorbed and desorbed in such a way that the kinetics of this process is governed by a typical balance equation characterizing a chemical reaction of first kind (Langmuir's approximation). The conservation of the number of particles is then invoked and the profiles of the surface as well as the bulk density of particles are analytically obtained by means of Laplace-Fourier techniques. The results for the momentum distribution show that the system exhibits anomalous diffusion [2] behavior, according to the values of the characteristic times entering the problem. More precisely, not only a single subdiffusive or superdiffusive motion can be found, but the system presents a multiple behavior that includes both modes of subdiffusion and superdiffusion and, for large times, the normal diffusive behavior. A system presenting a similar behavior can be found in the dynamics of vesicles driven by adhesion gradients of a Langmuir monolayer [3]. The same theoretical framework can be relevant to describe the diffusion process of suspended or dispersed particles in anisotropic media like liquid crystals [4] and effects of interfaces on diffusion [5]. In fact, dispersions of particles in an anisotropic host medium like nematic liquid crystals are responsible for a series of different physical scenarios deserving a more fundamental explanation [4]. Among the systems recently considered it is worth mentioning the suspension of magnetic grains [6], silica spheres [7], latex particles [8], oil droplets [9]. All the bulk effects in these systems have been object of attention in the last few years.

In this letter, we demonstrate that the presence of an anomalous diffusive behavior, which typically takes place on fractals [10], here is a consequence of a compromise between the diffusion of immersed particles in the host, together with the adsorption-desorption process at the interface when the conservation of the number of particles is invoked. In this sense, the results presented here are universal for this typical geometry and the theoretical framework presented can be widely applied to different physical contexts, as we show below.

To mathematically formulate the problem we consider a typical geometry for the sample such that the Cartesian reference frame has the z-axis perpendicular to the

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bounding surface, located at $z = 0$. If the system is a nematic liquid crystal, we can consider that in this geometry the sample is homeotropically oriented. In the general case of other host medium, it is enough to consider an anisotropic diffusion coefficient and the bulk density of particles $\rho(x, y, z; t)$ is governed by the anisotropic diffusion equation

$$\frac{\partial}{\partial t}\rho(x, y, z; t) = \mathcal{D}_{\perp}\left(\frac{\partial^2}{\partial x^2}\rho(x, y, z; t) + \frac{\partial^2}{\partial y^2}\rho(x, y, z; t)\right)$$
$$+ \mathcal{D}_{\parallel}\frac{\partial^2}{\partial z^2}\rho(x, y, z; t), \tag{1}$$

where $\mathcal{D}_{xx} = \mathcal{D}_{yy} = \mathcal{D}_{\perp}$ and $\mathcal{D}_{zz} = \mathcal{D}_{\parallel}$ are, respectively, the diffusion coefficients connected with the x, y and z directions. The bulk density of particles is subjected to the boundary conditions: $\rho(\pm\infty, y, z; t) = 0$, $\rho(x, \pm\infty, z; t) = 0$ and $\rho(x, y, \infty; t) = 0$. The boundary condition of $\rho(x, y, z; t)$ on the surface $z = 0$ is defined in terms of the surface density of particles, $\sigma(x, y; t)$, by the kinetic equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma(x, y; t) + \frac{1}{\tau}\sigma(x, y; t) = \kappa\rho(x, y, 0; t), \tag{2}$$

where κ and τ are parameters describing the adsorption phenomenon. For simplicity, we consider an arbitrary initial condition which is normalized, *i.e.*, $\rho(x, y, z; 0) = \widetilde{\rho}(x, y, z)$ with $\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\int_{0}^{\infty}\mathrm{d}z\rho(x, y, z; 0) = 1$. This quantity, $\widetilde{\rho}(x, y, z)$, can represent a definite amount of particles introduced in the host sample, at a given position. Other condition to be imposed to the system is a consequence of the first one, namely, the conservation of the number of particles

$$\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\sigma(x, y; t)$$
$$+ \int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\int_{0}^{\infty}\mathrm{d}z\rho(x, y, z; t) = 1, \tag{3}$$

and, for simplicity, we assume that $\sigma(x, y; 0) = 0$. Note that the first term of eq. (3) gives the quantity of particle adsorbed by the surface and the second term gives the quantity of particles present in the bulk. In particular, this quantity is known as survival probability $\mathcal{S}(t)$. To solve eq. (1) subjected to the conditions stated above, we use the Green's function approach and integral (Laplace and Fourier) transforms.

We start by applying the Laplace transform ($\mathcal{L}\{\ldots\} = \int_{0}^{\infty}\mathrm{d}t e^{-st}\ldots$ and $\mathcal{L}^{-1}\{\ldots\} = \frac{1}{2\pi i}\int_{-i\infty+c}^{i\infty+c}\mathrm{d}s e^{st}\ldots$) on the variable t and the Fourier transform ($\mathcal{F}\{\ldots\} = \frac{1}{2\pi}\int_{0}^{\infty}\mathrm{d}k_{\xi}e^{-ik_{\xi}\xi}\ldots$ and $\mathcal{F}^{-1}\{\ldots\} = \int_{0}^{\infty}\mathrm{d}\xi e^{ik_{\xi}\xi}\ldots$) on the variables x and y in eq. (1), which lead us to obtain the equation

$$\mathcal{D}_{\parallel}\frac{\mathrm{d}^2}{\mathrm{d}z^2}\rho(k_x, k_y, z; s)$$
$$- \left[s + \mathcal{D}_{\perp}\left(k_x^2 + k_y^2\right)\right]\rho(k_x, k_y, z; s) = -\widetilde{\rho}(k_x, k_y, z). \tag{4}$$

The solution to eq. (4) is formally given by

$$\rho(k_x, k_y, z; s) = -\int_{0}^{\infty}\mathrm{d}\overline{z}\,\widetilde{\rho}(k_x, k_y, \overline{z})\mathcal{G}(k_x, k_y, z, \overline{z}; s)$$
$$- \mathcal{D}_{\parallel}\rho(k_x, k_y, 0; s)\frac{\mathrm{d}}{\mathrm{d}\overline{z}}\mathcal{G}(k_x, k_y, z, \overline{z}; s)\bigg|_{\overline{z}=0}, \tag{5}$$

with the Green's function obtained from the equation

$$\mathcal{D}_{\parallel}\frac{\mathrm{d}^2}{\mathrm{d}z^2}\mathcal{G}(k_x, k_y, z, \overline{z}; s)$$
$$- \left[s + \mathcal{D}_{\perp}\left(k_x^2 + k_y^2\right)\right]\mathcal{G}(k_x, k_y, z, \overline{z}; s) = \delta(z - \overline{z}) \tag{6}$$

and subjected to the conditions $\mathcal{G}(k_x, k_y, 0, \overline{z}; s) = \mathcal{G}(k_x, k_y, \infty, \overline{z}; s) = 0$. By using the Fourier transform ($\mathcal{F}_s\{\ldots\} = \sqrt{\frac{2}{\pi}}\int_{0}^{\infty}\mathrm{d}k_z\sin(k_z z)\ldots$ and $\mathcal{F}_s^{-1}\{\ldots\} = \sqrt{\frac{2}{\pi}}\times\int_{0}^{\infty}\mathrm{d}z\sin(k_z z)\ldots$), it is possible to show that the solution to eq. (6) is given by

$$\mathcal{G}(k_x, k_y, z, \overline{z}; s) =$$
$$- \frac{2}{\pi}\int_{0}^{\infty}\mathrm{d}k_z\frac{\sin(k_z z)\sin(k_z \overline{z})}{s + \mathcal{D}_{\parallel}k_z^2 + \mathcal{D}_{\perp}\left(k_x^2 + k_y^2\right)}. \tag{7}$$

By performing the inverse Fourier and Laplace transforms, eq. (7) may be simplified to

$$\mathcal{G}(x, y, z, \overline{z}; t) =$$
$$- \frac{1}{\sqrt{4\pi\mathcal{D}_{\parallel}t}}\left(e^{-\frac{(z-\overline{z})^2}{4\mathcal{D}_{\parallel}t}} - e^{-\frac{(z+\overline{z})^2}{4\mathcal{D}_{\parallel}t}}\right)\frac{e^{-\frac{x^2+y^2}{4\mathcal{D}_{\perp}t}}}{4\pi\mathcal{D}_{\perp}t}, \tag{8}$$

and the solution is given by

$$\rho(x, y, z; t) =$$
$$- \int_{-\infty}^{\infty}\mathrm{d}\overline{x}\int_{-\infty}^{\infty}\mathrm{d}\overline{y}\int_{0}^{\infty}\mathrm{d}\overline{z}\,\widetilde{\rho}(\overline{x}, \overline{y}, \overline{z})\mathcal{G}(x - \overline{x}, y - \overline{y}, z, \overline{z}; t)$$
$$- \mathcal{D}_{\parallel}\int_{-\infty}^{\infty}\mathrm{d}\overline{x}\int_{-\infty}^{\infty}\mathrm{d}\overline{y}\int_{0}^{t}\mathrm{d}\overline{t}\rho(\overline{x}, \overline{y}, 0; \overline{t})$$
$$\times\frac{\mathrm{d}}{\mathrm{d}\overline{z}}\mathcal{G}(x - \overline{x}, y - \overline{y}, z, \overline{z}; t - \overline{t})\bigg|_{\overline{z}=0}. \tag{9}$$

To obtain the time dependent behavior of the quantity of adsorbed particles by the surface, *i.e.*, $\overline{\sigma}(t) = \int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\sigma(x, y; t)$, we consider eqs. (2), (3), and (9). After some calculation, using the Laplace transform, it is possible to show that

$$\overline{\sigma}(s) = \int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\int_{0}^{\infty}\mathrm{d}z\frac{\kappa\widetilde{\rho}(x, y, z)e^{-\sqrt{\frac{s}{\mathcal{D}_{\parallel}}}z}}{\kappa s + \sqrt{s\mathcal{D}_{\parallel}}\left(s + \frac{1}{\tau}\right)} \tag{10}$$

and, consequently, that

$$\overline{\sigma}(t) = \int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\int_{0}^{\infty}\mathrm{d}z\widetilde{\rho}(x, y, z)\int_{0}^{t}\mathrm{d}\overline{t}\frac{\Phi(\overline{t})e^{-\frac{z^2}{4\mathcal{D}_{\parallel}(t-\overline{t})}}}{\sqrt{\pi(t-\overline{t})}} \tag{11}$$
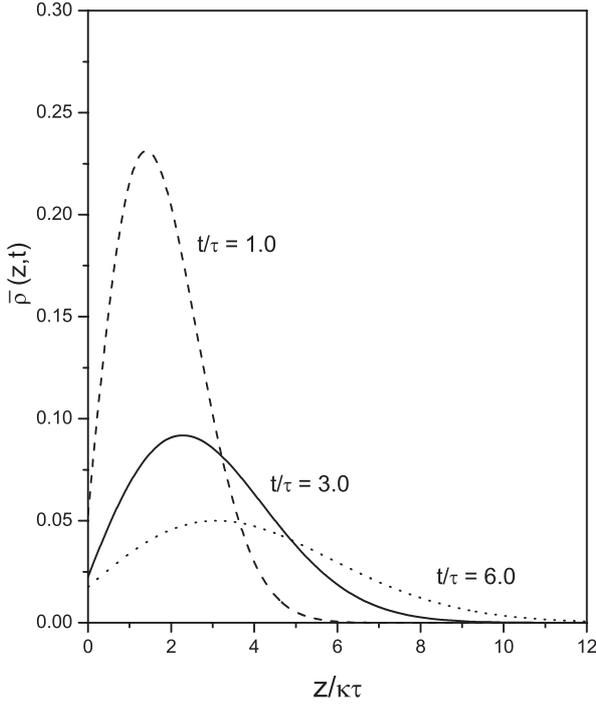
Fig. 1: Profile of the bulk density of particles $\overline{\rho}(z,t) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \rho(x,y,z;t)$ *vs.* z for three different values of the ratio t/τ by considering the initial condition $\widetilde{\rho}(x,y,z) = \delta(x)\delta(y)\delta(z-1)$. We consider for simplicity $\mathcal{D}_{\|} = 1$, $\kappa = 5$ and $\tau = 10$ ($\tau_{\mathrm{R}} \approx 7.9$).

with

$$\Phi(t) = \frac{\tau_{\mathrm{R}}}{\sqrt{\tau(\tau_{\mathrm{R}}^2 - 1)}} \left[\gamma_+ e^{\gamma_+^2 t/\tau} \operatorname{erfc}\left(\gamma_+ \sqrt{t/\tau}\right) \right.$$
$$\left. - \gamma_- e^{\gamma_-^2 t/\tau} \operatorname{erfc}\left(\gamma_- \sqrt{t/\tau}\right) \right], \tag{12}$$

where $\gamma_{\pm} = \tau_{\mathrm{R}} \pm \sqrt{\tau_{\mathrm{R}}^2 - 1}$ and erfc(x) is the complementary error function. Actually, $\overline{\sigma}(t)$ represents the number of particles on the surface, since we have performed an integration over x and y. In the preceding expressions, we have introduced the quantity

$$\tau_{\mathrm{R}} = \frac{\kappa}{2} \sqrt{\frac{\tau}{\mathcal{D}_{\|}}}, \tag{13}$$

that involves the characteristic parameters connected with the dynamics of the diffusion process and the kinetics of the adsorption phenomenon in the sample.

In fig. 1, the bulk density of particles integrated over x and y is shown as a function of $z/\kappa\tau$ for three different times, illustrating the spreading of the distribution in connection with the lowering of the bulk density near the surface limiting the samples.

In fig. 2, the relation of dispersion for the z-direction of the distribution function, *i.e.*, $(\Delta z)^2 = \langle (z - \langle z \rangle)^2 \rangle$, is shown as a function of the time (solid line with circles). It is remarkable that this simple system can exhibit anomalous diffusion behavior which becomes evident when we
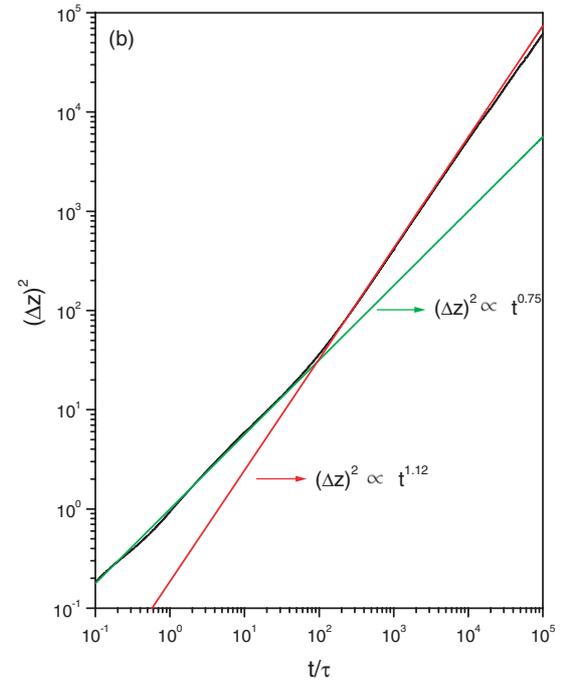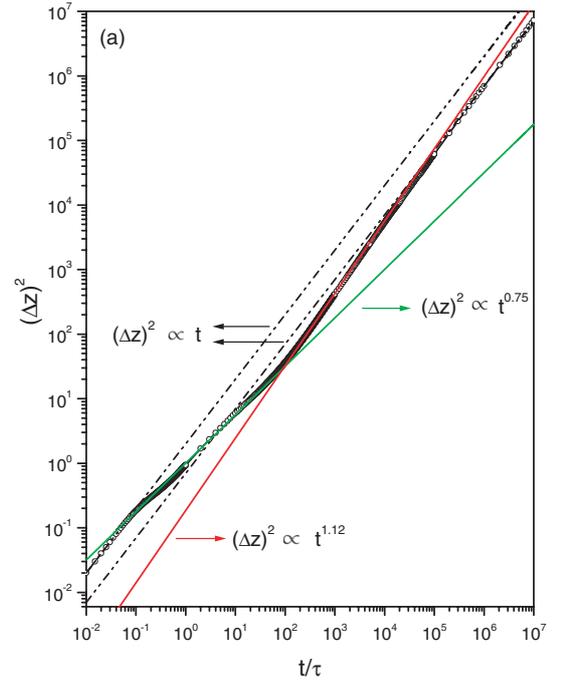

Fig. 2: Panel a) illustrates the behavior of $(\Delta z)^2$ *vs.* t/τ for the initial condition $\widetilde{\rho}(x,y,z) = \delta(x)\delta(y)\delta(z-1)$ ad shows the different diffusive regimes present by the system during the process. Panel b) focuses on the intermediate times were the anomalous regime is present. Note that the straight lines present in this figures are approximations used to evidence the different diffusion regimes in the time scale considered. We consider for simplicity $\mathcal{D}_{\|} = 1$, $\kappa = 5$ and $\tau = 10$ ($\tau_{\mathrm{R}} \approx 7.9$).

draw comparative straight lines characterizing the different diffusion regimes. In fact, after starting the diffusion process, which initially is usual for very small times, the
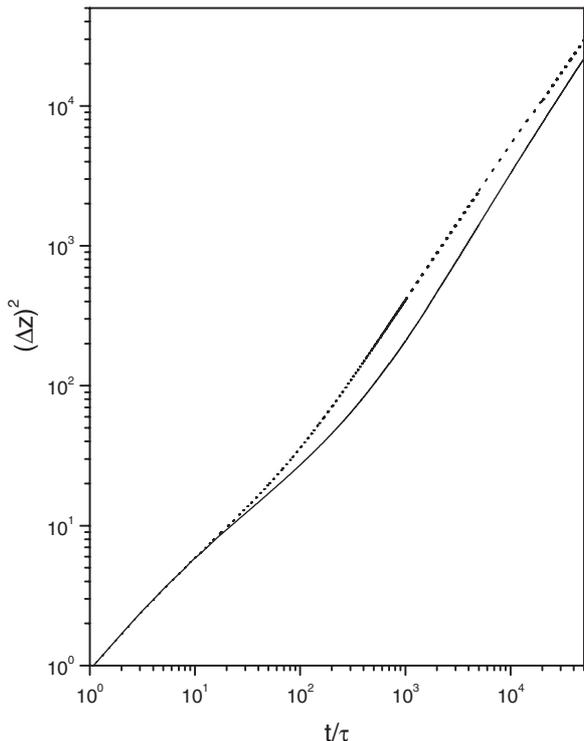
Fig. 3: The same as in fig. 2 in order to show the role of the parameter τ as crossover time in two illustrative situations: $\tau = 10$ ($\tau_{\mathrm{R}} \approx 7.9$) (dotted line) and $\tau = 50$ ($\tau_{\mathrm{R}} \approx 18$) (solid line).

Fig. 4: Adsorbed particles $\overline{\sigma}(t)$ given by eq. (11) (solid line) and survival probability $\mathcal{S}(t)$ (dotted line) *vs.* t for the initial condition $\widetilde{\rho}(x, y, z) = \delta(x)\delta(y)\delta(z - 1)$. We consider for simplicity $\mathcal{D}_{\parallel} = 1$, $\kappa = 5$ and $\tau = 10$ ($\tau_{\mathrm{R}} \approx 7.9$).

system exhibit a sub-diffusive regime for which $(\Delta z)^2 \propto t^{0.75}$ (dashed line). This initial regime indicates that the adsorption process on the surface plays the main role for initial times. After that, the process becomes super-diffusive with $(\Delta z)^2 \propto t^{1.12}$ (dotted line). The second regime reflects the effect of the desorption process of the particles by the surface $z = 0$ which dominates the solution for intermediate times. For long enough time, the system presents a normal diffusive behavior $(\Delta z)^2 \propto t$ (dashed-dotted line). The last behavior may be understood as a consequence of the absence of adsorption or desorption. This feature may be verified in fig. 3 which for long time shows that the particles initially adsorbed by the surface are essentially desorbed and remaining in the bulk. This anomalous behavior, in particular the presence of different regimes, is also related to the conservation of the number of particles (eq. (3)) imposed to the system. In fact, in our model the number of particles inserted in the system is fixed and the adsorption–desorption process, together with the necessity to conserve the total number of particles, leads to a different diffusive regimes according to the time scale considered. It is interesting to note that other models such as the ones based on fractional diffusion equations [11] have also been used to investigate anomalous diffusion and may exhibit different diffusive regimes [12]. However, the anomalous diffusion produced by these models are essentially due to the presence of fractional operator and not explicitly by the interaction
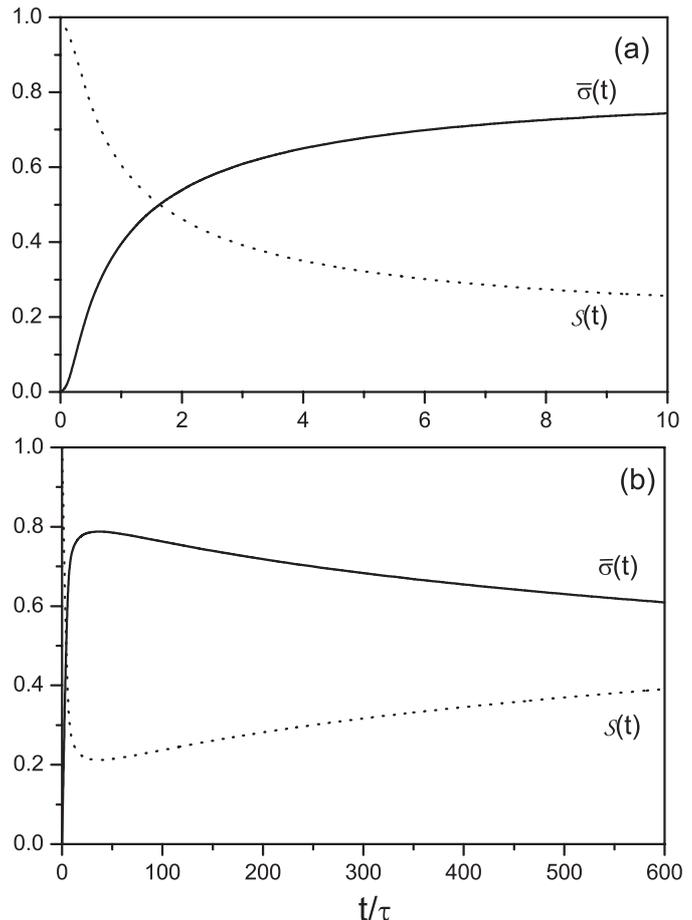
between the surface and the bulk (adsorption-desorption) as we have considered above for a fixed number of particles. In fig. 3, one observes a crossover time which is essentially governed by τ. This result is a manifestation of the importance of the desorption process, whose characteristic time is τ, in the anomalous behavior of the diffusion. The onset of this anomalous behavior is sensitive to the values of the model parameters. A simple criteria to be followed by them is that the characteristic times may be such that the diffusion process is followed by the adsorption and then by the desorption process. For what concerns the number of particles at the surface, here represented by $\overline{\sigma}(t)$, in fig. 4 one can find two typical behaviors according to the time scale considered. In fig. 4(a), this quantity is exhibited for $t < \tau$, where τ is a characteristic time connected with the desorption process. This means that after the diffusion takes place in the bulk, the surface adsorbs and the number of particles on it rapidly grows (solid line). In the same figure, the survival probability is shown as a function of the time. This quantity illustrates that particles present in the bulk are initially adsorbed by the surface $z = 0$ and after desorbed in the bulk. The behavior is in agreement
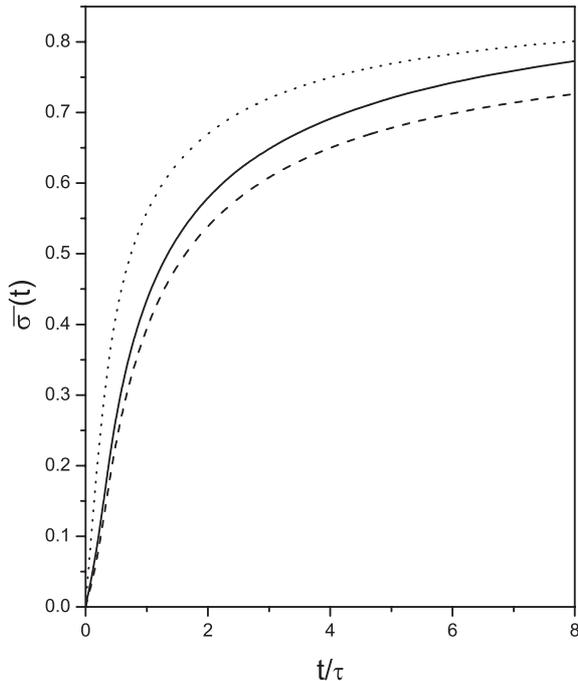
Fig. 5: Number of adsorbed particles $\overline{\sigma}(t)$ as given by eq. (11) vs. t/τ for different sets of parameters: $\mathcal{D}_{\parallel} = 3.0$, $\kappa = 7.0$, $\tau = 15.0$ ($\tau_R = 7.8$) (dotted line), $\mathcal{D}_{\parallel} = 1.0$, $\kappa = 5.0$, $\tau = 10.0$ ($\tau_R = 7.9$) (dashed line), and $\mathcal{D}_{\parallel} = 1.0$, $\kappa = 10.0$, $\tau = 10.0$ ($\tau_R = 15.8$) (solid line).

with the one shown in part (a), exhibiting a decreasing behavior. For $t \gg \tau$ the situation is different, as shown in fig. 4(b), where both quantities are shown for a large time interval. After a rapid increasing, $\overline{\sigma}(t)$ tends to decrease while $\mathcal{S}(t)$ shows the inverse behavior. The asymptotic limit for long time, i.e., for $t \gg \tau$ is $\overline{\sigma}(t) \sim \tau_R \sqrt{\tau/\pi t}$. Finally, in fig. 5 the short-time behavior of $\overline{\sigma}(t)$ illustrates its sensitivity to the values of the model parameters. Notice that from eq. (10) (or eq. (11)) only $\mathcal{D}_{\parallel}$ contributes to $\overline{\sigma}(t)$. This means that anomalous diffusion may also occur even in the case of isotropic diffusion constant.

This permits to conclude that after a short time interval, where the diffusion process together with the adsorption process works, the number of particles on the surface increase; after that, however, when a large number of particles have been adsorbed, the desorption process is operating and the bulk becomes again more populated. This behavior is a consequence of the boundary conditions imposed to the system and the absence of external forces. In fact, different boundary conditions (see, for example, the case worked out in [13,14]) or external forces applied in the system may lead us to a stationary solution for the density of particles, $\rho(x, y, z; t)$, and consequently a stationary rate of adsorption-desorption process on the surface $z = 0$.

In conclusion, we have demonstrated that anomalous diffusion can be found in those semi-infinite anisotropic systems for which the diffusive behavior is accompanied by

the adsorption-desorption process at a uniform interface, when the conservation of the number of particles is imposed to the entire system. Since this mechanism is general, the theoretical framework presented here can found applications in a wide variety of systems, and, in particular, in colloidal suspensions or any kind of dispersed particles that undergo diffusion through a host system. This happens because the flat interface, at which the adsorption-desorption phenomenon takes place, breaks the translational invariance and together with the adsorption-desorption process may represent the disappearing or appearing of a particle in a given system where particles can be confined in some phases. In some colloidal system, as the concentration in a dense colloidal suspension is increased, particles become confined in transient cages formed by their neighbors [15,16]. This prevents them from diffusing freely throughout the sample. Such an inhibition of the molecular motion is responsible for a subdiffusion process whose mechanisms are in many respects similar to the ones described in the theoretical framework we have discussed above. As a final remark, we would like to underline that a system composed by two adsorbing surfaces, i.e., in the slab shape, in one dimension does not exhibit anomalous behavior [13,17]. This reinforces the idea that to find anomalous diffusion behavior we have to consider a semi-infinite system limited by a surface in which the adsorption-desorption process is governed by a kinetic equation when the conservation of particle is imposed to the system. In fact, as stated above, for long enough time, $\overline{\sigma}(t) \propto 1/\sqrt{t}$. This means that, when the particles are inserted into the system, the diffusion process starts and, for short time intervals, the number of particles increases at the surface. However, in view of the desorption process and the semi-infinite character of the medium, for long enough time the overwhelming majority of the particles can be found again in the bulk. For this system, there is no stationary solution for the bulk density of particle as is found in the system in the slab shape.

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