

## Memory effect in the adsorption phenomena of neutral particles

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The adsorption-desorption phenomenon of neutral particles dissolved in an isotropic fluid is investigated by using a nonsingular kernel in the kinetic equation at the limiting surfaces. To account for the relevance of a memory effect, three types of kernels in the kinetic equation are considered. Similar kernels have been used to investigate nonexponential relaxation including several contexts such as dielectric relaxation, diffusion-controlled relaxation in liquids, liquid crystals, and amorphous polymers. A suitable choice for a temporal kernel can account for the relative importance of physisorption or chemisorption, according to the time scale governing the adsorption phenomena, and can be the key mechanism to understand the specific roles of both processes. By using a general procedure, the time evolution of the density of particles is determined in closed analytical form. The analysis is relevant in the description of the adsorption phenomena in general.

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Adsorption phenomena in nematic liquid crystal (NLC) cells have been investigated mainly in connection with their effect on the anchoring energy [1]. Adsorption of dyes is of particular importance in this context because it can be responsible for a change of the easy axis characterizing the substrate-nematic interface [2,3], thus permitting the possibility to modify the NLC orientation with light [4–9]. Recently, the dynamical aspects of the adsorption and desorption of dyes have been investigated theoretically as well as experimentally in order to clarify the role of the adsorbed dyes in the surface properties of an NLC cell [10,11]. In a previous work, we considered the time evolution of the surface density of adsorbed particles from a solid surface of an adsorbate dissolved in an isotropic liquid. For this problem we got a closed analytical solution, obtained in the framework of a simple kind of kinetic equation at the interface [10]. In the present paper we analyze, theoretically, the dynamics of the adsorption-desorption phenomenon of neutral particles in a sample of isotropic fluid by incorporating a kind of memory effect in the kinetic equation at the substrate-fluid interface. An effect of this kind is expected because, in the adsorption phenomenon by a solid surface, the collision of a molecule can be represented by three different processes. An elastic scattering occurs when there is no loss of translational energy during the collision; however, if the molecule is still in a weakly bound state, even if it is on the surface, the thermal motion of the surface atoms can cause the molecule to desorb. Finally, when the molecule collides with a surface, it loses energy and is converted into a state where it remains on the surface for a reasonable time; one says that the molecule sticks [12]. These phenomena indicate that the actual position of the molecule on the surface has a memory of its incoming state, eventually modifying the adsorption-desorption rates. In order to describe this memory effect, we consider a modified kinetic equation in which the suitable choice for a kernel in the desorption rate can account for the importance of the physisorption or of the chemisorption, according to the time scale governing the adsorption phenomena. Exact analytical solutions are obtained for the time evolution of the bulk and surface densities of particles in the sample, showing that the memory effect in

the kinetic equation is the way by which physical and chemical adsorption are taken into account in the sample.

We consider a sample of isotropic fluid in the shape of a slab of thickness  $d$ , containing neutral particles that can be adsorbed at the surfaces. The Cartesian reference frame has the  $z$  axis perpendicular to the limiting surfaces, located at  $z = \pm d/2$ , and the problem can be considered as one dimensional. The behavior of the bulk density of particles  $\rho(z, t)$ , in a medium whose diffusion coefficient is  $D$ , is governed by the diffusion equation

$$\frac{\partial \rho}{\partial t} - D \frac{\partial^2 \rho}{\partial z^2} = 0, \quad (1)$$

to be solved by considering that, for identical surfaces,  $\rho(z, t) = \rho(-z, t)$ . A Laplace transform can be used to put Eq. (1) in the form

$$D \frac{d^2}{dz^2} \rho(z, s) = s \rho(z, s) - \rho(z, 0), \quad (2)$$

where  $\rho(z, s) = \mathcal{L}\{\rho(z, t)\}$  [ $\mathcal{L}\{\dots\} = \int_0^\infty (\dots) e^{-st} dt$ ] and  $\rho(z, 0) = \rho_0$  is the initial homogeneous density across the sample. The solution for the above equation, by taking the previous boundary condition into account, is given by

$$\rho(z, s) = \frac{\rho_0}{s} + \mathcal{B}(s) \cosh(\sqrt{s/D} z). \quad (3)$$

If we denote by  $\sigma(t)$  the surface density of adsorbed particles, conservation of the number of particles in the system requires that  $2\sigma(t) + \int_{-d/2}^{d/2} \rho(z, t) dz = \rho_0 d$ . For the balance equation at the boundary we propose

$$\frac{d\sigma}{dt} = \kappa \rho(-d/2, t) - \int_0^t \mathcal{K}(t-\bar{t}) \sigma(\bar{t}) d\bar{t}, \quad (4)$$

where  $\kappa$  is a parameter connected with the adsorption phenomenon. It can be related to a characteristic time  $\tau_\kappa$  for the adsorption phenomenon in a sample of thickness  $d$  by means of the relation  $\tau_\kappa = d/2\kappa$ .

Equation (4) is an extension of the usual balance equation [13] that incorporates a more complex desorption rate by means of the kernel  $\mathcal{K}(t)$ . A similar equation has been used to

investigate nonexponential (or non-Debye) relaxation [14] including several contexts such as dielectric relaxation, diffusion-controlled relaxation in liquids, liquid crystals, and amorphous polymers. In particular, nonexponential relaxation implies memory [14] and consequently a nontrivial [14,15] choice to the kernel present in Eq. (4). In the context of this work, Eq. (4) can be interpreted as stating that the time variation of the surface density of particles depends on the bulk density of particles in front of the adsorbing surface and on the surface density of particles already adsorbed, but taking into account a memory for this process, which depends on the choice of the kernel by  $\mathcal{K}(t)$ . It has to take into account the loss of energy of the particle during the collision with the surface in the previous adsorption processes. Memory effects in NLC samples have been considered in the last two decades in connection with bulk and surface properties [16–26]. Here, we propose to investigate their relevance in the adsorption of particles at the interface by explicitly considering a balance equation embodying this

possibility. To proceed, we take the Laplace transform of Eq. (4), to obtain

$$s\mathcal{G}(s) - \sigma(0) = \kappa\rho(-d/2, s) - \mathcal{K}(s)\mathcal{G}(s), \quad (5)$$

where  $\mathcal{G}(s) = \mathcal{L}\{\sigma(t)\}$  and  $\sigma(t=0)$  is the initial surface density of adsorbed particles. To obtain  $\mathcal{G}(s)$  from Eq. (5) we can use Eq. (3) which enables us to obtain

$$\mathcal{G}(s) = \frac{\kappa\rho_0}{s[s + \mathcal{K}(s)]} + \frac{\kappa \cosh[\sqrt{s/D}d/2]}{s + \mathcal{K}(s)}\mathcal{B}(s), \quad (6)$$

since  $\sigma(t=0)=0$ . Using Eqs. (6) and (3) in the conservation of the number of particles, we can obtain  $\mathcal{B}(s)$  as follows:

$$\mathcal{B}(s) = - \frac{\kappa\rho_0}{\kappa s \cosh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right] + \sqrt{\frac{D}{s}}s[\mathcal{K}(s) + s]\sinh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right]}. \quad (7)$$

By using the above result, the Laplace transform of the surface density of adsorbed particles is given by

$$\mathcal{G}(s) = \frac{\kappa\rho_0}{s[s + \mathcal{K}(s)]} - \frac{\kappa^2\rho_0 \cosh[\sqrt{s/D}d/2]}{s[s + \mathcal{K}(s)]\{\kappa \cosh[\sqrt{s/D}d/2] + \sqrt{D/s}[s + \mathcal{K}(s)]\sinh[\sqrt{s/D}d/2]\}}. \quad (8)$$

Now, let us address our discussion concerning Eq. (8) by choosing three kernels. Let us consider first the case

$$\mathcal{K}(t) = \frac{1}{\tau^2} \delta(t/\tau). \quad (9)$$

This case corresponds to the usual limit of Eq. (4)—namely,  $d\sigma/dt = \kappa\rho(-d/2, t) - \sigma(t)/\tau$ , where  $\tau$  is a parameter connected with the desorption rate. It represents the characteristic time connected with the desorption rate in a way similar to  $\tau_\kappa$  being related to the adsorption rate. From a microscopic perspective, the product of the phenomenological parameters  $\kappa\tau$  is of the order of the range of the physical interactions responsible for the adsorption phenomenon [1].

This case is relevant to a pure chemisorption process. In this case, we are assuming that the molecule on the surface has lost the memory of the preceding state. For this reason, the kernel is a localized function of the time. In the theory of dielectric relaxation a kernel of this kind takes into account the rapid answer of the dielectric material to an external excitation and it is connected to  $\epsilon_\infty$  [27].

The inverse of Eq. (9) is  $\mathcal{K}(s) = 1/\tau$ . In this manner,  $\mathcal{G}(s)$ , given by Eq. (8), becomes

$$\mathcal{G}(s) = \frac{\kappa\rho_0}{s(s + 1/\tau)} - \frac{\kappa^2\tau^2\rho_0}{s(1 + s\tau)\{\kappa\tau + \sqrt{D/s}(1 + s\tau)\tanh[\sqrt{s/D}d/2]\}}, \quad (10)$$

and  $\sigma(t)$  is found by inverting Eq. (10). The first term is

easily inverted by writing it in terms of partial fractions, whereas the second one is simply the convolution of two functions. The inversion can be performed by using a Bromwich's integral in the complex plane. The poles arising in the integration process are periodic and given by the eigenvalue equation

$$\tan[X_\beta] = \left(\frac{\tau_D}{4\tau_\kappa}\right) \frac{X_\beta}{X_\beta^2 - \tau_D/4\tau}, \quad (11)$$

where  $\tau_D = d^2/D$  and  $d\beta_n/2\sqrt{D} = X_\beta$ , with  $\beta_n$  being the roots of Eq. (11). This equation coincides with the one obtained in Ref. [10]. In this manner, the results obtained in [10] by means of a series expansion of the solution of Eq. (1) can be obtained here by an analysis based on the Laplace transform method. In particular, the temporal behavior of  $\sigma(t)$  is monotonically increasing with  $t$ , as reported in [10].

Let us consider, as a second example, the kernel

$$\mathcal{K}(t) = \frac{1}{\tau\tau_a} e^{-t/\tau_a}, \quad (12)$$

where  $\tau_a$  is a characteristic time. The kernel (12) is similar to the one introduced in the theory of dielectrics to describe relaxation phenomena in these media when subjected to external fields which are time dependent. In that case, the relaxation time is connected to friction describing the interaction of a given electrical dipole with the surrounding medium. This intrinsic time of the problem is of the order of the time needed by the dipole to follow the time variation of the external electric field. It is then connected to a kind of

“memory” of the dielectric medium. We assume that, in this process, the molecule on the surface has a memory of the preceding state, represented by a kernel which has a nonzero

width in time; i.e., the memory effect is relevant for short periods of time. The Laplace transform of kernel (12) is  $\mathcal{K}(s)=1/[(s+1/\tau_a)\tau\tau_a]$ . For this case, Eq. (8) becomes

$$\mathcal{G}(s) = \frac{\kappa\rho_0}{s\left[s + \frac{1/\tau_a}{(s+1/\tau_a)\tau}\right]} - \frac{\kappa^2\rho_0 \cosh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right]}{s\left[s + \frac{1/\tau_a}{(s+1/\tau_a)\tau}\right] \left\{ \kappa \cosh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right] + \sqrt{\frac{D}{s}}\left(s + \frac{1/\tau_a}{(s+1/\tau_a)\tau}\right) \sinh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right] \right\}}. \quad (13)$$

Again, an inversion process, similar to the one applied to Eq. (10), has to be carried out, requiring an integration in the complex plane, by means of the residues technique. The process has two steps as before. The inversion of the second part of Eq. (13) shows the existence of an infinite number of poles given by the equation

$$\tan[X_\beta] = \frac{X_\beta\left(4X_\beta^2\frac{\tau_a}{\tau_D} - 1\right)\frac{\tau}{\tau_\kappa}}{1 - 4X_\beta^2\frac{\tau}{\tau_D}\left(1 - 4X_\beta^2\frac{\tau_a}{\tau_D}\right)}, \quad (14)$$

which reduces to Eq. (11) in the limit  $\tau_a \rightarrow 0$ , as expected. For the inversion of Eq. (13) one has to take into account that it can be faced again as the convolution of two terms. This task can be accomplished by a procedure that although delicate, presents no particular difficulty. In this manner, the expression for  $\sigma(t)$  can be obtained in closed analytical form which, despite being very simple, is rather long to be presented. In Fig. 1(a) the time dependence of the surface density of adsorbed particles is presented. The memory effect, connected with the kernel (12), is responsible for a non-monotonic behavior of  $\sigma = \sigma(t)$ . This can be interpreted in the

following manner. When the adsorption phenomenon starts, a large number of particles coming from the bulk are adsorbed. They are trapped in energy wells at the surface. However, their energy is still rather large and, for this reason, they are desorbed soon losing a part of the energy in this adsorption step. When they are trapped again, a further amount of energy is lost, and again they are desorbed. The phenomenon continues until the energy lost from the particle is such that the steady state is reached after a characteristic time  $\tau_a$ .

As the last example, let us consider a mixed kernel—i.e., a combination of the last two ones. This case is relevant to a system in which both physisorption and chemisorption processes are conspicuous and have two different characteristic times  $\tau_1$  and  $\tau_2$ . We have

$$\mathcal{K}(t) = \frac{1}{2\tau_1\tau_a}e^{-t/\tau_a} + \frac{1}{2\tau_2\tau}\delta(t/\tau), \quad (15)$$

whose Laplace transform is

$$\mathcal{K}(s) = \frac{1/\tau_a}{2(s+1/\tau_a)\tau_1} + \frac{1}{2\tau_2}. \quad (16)$$

For this case, by considering  $\tau_2 = \tau$ , Eq. (8) gives

$$\mathcal{G}(s) = \frac{\kappa\rho_0}{s\left[s + \frac{1/\tau_a}{2(s+1/\tau_a)\tau_1} + \frac{1}{2\tau}\right]} - \frac{\kappa^2\rho_0 \cosh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right]}{s\left[s + \frac{1/\tau_a}{2(s+1/\tau_a)\tau_1} + \frac{1}{2\tau}\right] \left\{ \kappa \cosh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right] + \sqrt{\frac{D}{s}}\left(s + \frac{1/\tau_a}{2(s+1/\tau_a)\tau_1} + \frac{1}{2\tau}\right) \sinh\left[\sqrt{\frac{s}{D}}\frac{d}{2}\right] \right\}}. \quad (17)$$

The surface density of particles can be obtained again by the inversion process described in the previous cases. The temporal behavior of  $\sigma(t)$  is exhibited in Fig. 1(b).

The analysis presented above is valid for a sample in the shape of a slab of thickness  $d$ , where the number of adsorbate particles is fixed, as the dye molecules in a nematic liquid crystals cell considered in [3]. However, experimental measurements of the adsorption are, usually, performed by considering an adsorbing surface in contact with a reservoir. This is equivalent to considering a sample of infinite thick-

ness. In short, to compare our model with the experimental results, in the equations reported above, the limit  $d \rightarrow \infty$  has to be performed. In this case, the bulk density of adsorbed particles is fixed by the experimental conditions. This means that, in Eq. (4),  $\rho$  has to be considered constant. It follows that  $\sigma(t)$  is determined by Eq. (4) only. We have solved this equation with the kernels considered above. The trends of  $\sigma(t)$  are similar to the ones reported in Figs. 1(a) and 1(b). However, in these cases the typical times of the problem depend only on the adsorption process—i.e., on  $\tau$  and  $\tau_a$ . In

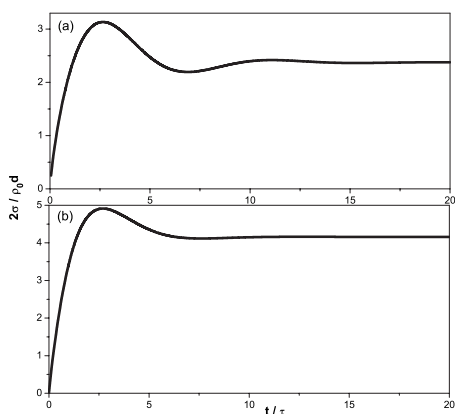


FIG. 1. (a) Behavior of  $2\sigma(t)/\rho_0d$  vs  $t$  for  $\tau_D=4\tau$ ,  $\tau_K=\tau/10$ , and  $\tau_a=1.5\tau$  for the kernel (12). (b) The same for  $\tau_D=4\tau$ ,  $\tau_1=0.8\tau$ ,  $\tau_K=\tau/10$ , and  $\tau_a=1.5\tau$ , for the kernel (15).

Fig. 2, we report the theoretical  $\sigma(t)$  dependence when the kernel is given by Eq. (15), and in the inset we show the superposition of experimental data relative to chemisorption and physisorption processes from Refs. [28,29]. The theoretical behavior is qualitatively very similar to the behavior of some acid monolayers whose adsorption is governed by physical forces, but in which the role of the head group is conspicuous [28]. A behavior like the one depicted in Fig. 1(b) is in agreement with the quantitative behavior found by Fourier transform IR spectroscopy for siloxane polymers chemisorbing to alumina [28,29]. In this system, measurements of the variation of physically adsorbed and chemically adsorbed segments show that the physisorption process is strong in the first minutes, presenting a pronounced maximum and tending to a small value; the chemisorption process, on the contrary, follows a curve very similar to the one shown in Ref. [10]—i.e., tends to a saturation value. When these effects are combined, because they occur during the same process, the resulting curve has a shape very similar to the one shown in Fig. 1(b).

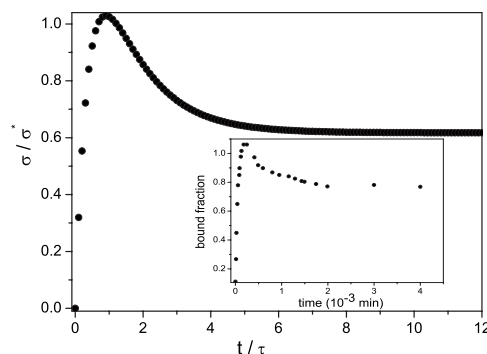


FIG. 2. Behavior of  $\sigma(t)/\sigma^*$  vs  $t/\tau$  for  $\tau_1=\tau_2=\tau_a=\tau/3$ .  $\sigma^*$  is the maximum value of the surface density of adsorbed particles. The inset refers to the superposition of experimental data relative to chemisorption and physisorption processes from Refs. [28,29].

An adsorbing gas is usually assumed to be chemisorbed when the adsorption energy is higher than the energy required for physisorption (typically less than 10 kcal/mol). On the other hand, a given molecule can usually physisorb and chemisorb on the same surface, or in other terms, a molecule first physisorbs and then is converted into a chemisorbed state. The most common equilibrium situation is, thus, the existence of a mixture of physisorbed and chemisorbed molecules on the surface. For this reason, a more realistic description of the kinetics at the interface should be developed by taking into account both processes. The description we are proposing here to account for these processes is to consider a temporal kernel in the adsorption-desorption rates. This approach is equivalent to considering that the adsorption process is well described if one considers the memory of the preceding state for the molecules being adsorbed at the surface.

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