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Invited Article

Adsorption–desorption phenomenon and the kinetic equation at interfaces in liquid crystalline systems

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The adsorption–desorption phenomenon in a sample having the shape of a slab is investigated by using a particular form for the kinetic equation at the limiting surfaces. A closed solution for the time evolution of the ion density in a nematic liquid crystal sample submitted to an external field is obtained in the limit in which the effective field coincides with the external field. In this framework it is shown that the intrinsic time connected with the presence of the electric field is proportional to the drift time. The constant of proportionality is of the order of the ratio between the thermal agitation energy and the electrostatic energy. In a similar manner, the time evolution of the bulk and surface densities, in the case of neutral particles, is also determined in a closed form by means of a simple expression. A microscopic model giving rise to a kinetic equation, similar to the one used in the analysis, is presented. We propose a statistical interpretation of the adsorption–desorption phenomenon in the framework of Maxwell–Boltzmann statistics, in which the relationship between the phenomenological parameters, entering into the kinetic equation at the boundary surfaces, with the microscopic model is derived. The analysis is suitable for the description of the adsorption phenomena of neutral particles (dyes) as well as charged particles (ions) in nematic liquid crystals.

1. Introduction

In recent years several investigations on nematic liquid crystals doped with dyes have been published [1–5]. The main interest of this kind of research is connected with the possibility to modify the nematic orientation with light [6–15]. According to the experimental studies, the dye initially dissolved in the nematic liquid crystal is selectively adsorbed by the limiting surfaces, and oriented by the nematic field. When incident light strives the surface covered by the dye, for the adsorption phenomenon, a structural transformation is induced, which is responsible for the change of the easy axis characterizing the substrate–nematic interface. Preliminary studies on the adsorption phenomenon of neutral particles have been reported [16, 17]. The importance of the adsorption phenomenon on the surface properties of nematic liquid crystals was first recognized by Pieranski and Jerome [18, 19] and by Teixeira and Sluckin [20, 21].

The influence of ions on the optical properties of a nematic liquid crystal sample has been the subject of intensive research. In the pioneering papers the analysis was mainly focused on the re-normalization of the anchoring energy and flexoelectric coefficients due to the presence of the ions, and limited to considering the static situation [22–33]. Investigations of the influence of ions on the dynamical properties of nematic samples have been presented by several groups, mainly for practical applications [34–47]. In the relevant theoretical analysis, the characteristic times are the diffusion time and the drift time [48]. An open fundamental problem is the analysis of the drift–diffusion problem of the impurities in a sample of liquid. In this framework, it is important to have information on the relaxation of the density of impurities when an external field is present, by taking into account the diffusion phenomenon [49].

The purpose of the present paper is twofold. First, we consider the ionic distribution in a sample in the shape of a slab, submitted to an external field. The sample is assumed to be filled with an isotropic liquid containing impurities that can be dissociated by means of a chemical reaction. We limit our investigation to the case in which the bulk density of ions is so small that the back electric field of ionic origin is negligible with

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respect to the applied field. In this framework, we show that the intrinsic time connected with the presence of the electric field is proportional to the drift time, but strongly depends on the temperature. Our results can be directly applied to nematic liquid crystal samples uniformly oriented, in a planar or homeotropic manner, when the electric field is smaller than the critical field to induce the Fréedericksz transition. In fact, in this case the nematic sample behaves as an isotropic medium in terms of the dielectric constant and the diffusion coefficient. However, as will be shown, our analysis gives the correct order of magnitude of the relaxation time, even in the case in which the nematic sample is distorted, i.e. the nematic orientation is not uniform across the sample. For this reason, this problem is also important for liquid crystals displays.

Secondly, we analyse the adsorption phenomenon, obtaining a closed solution for the time evolution of the adsorbed neutral particles (e.g. dyes) in terms of a series. We consider a simple type of kinetics at the limiting surface to describe the adsorption–desorption phenomenon. Different regimes, according to the adsorption energies of the dyes, are found. Furthermore, by means of a simple microscopic model, based on the van der Waals interaction of the dye molecule with the substrate, we show that it is possible to justify the kinetic equation describing the adsorption phenomenon. Finally, we investigate how to connect the phenomenological parameters entering into the kinetic equation with the parameters of the model. We show that this equation is in agreement with Maxwell–Boltzmann statistical mechanics. A simple model to deduce separately the phenomenological coefficients entering into the kinetic equation is presented.

Our review paper gives a recently proposed unified point of view on the dynamical aspects of the adsorption–desorption phenomenon [50–53], and is organized as follows. In § 2 the drift–diffusion problem is analysed. We discuss the rôle of the intrinsic characteristic times and establish a closed solution for the time evolution of the density of ions in the presence of an external field. We also show the results obtained numerically relevant to the time evolution of the distribution of ions across the sample. The applicability of the results of our model to nematic liquid crystal samples is discussed. In § 3 the adsorption phenomenon from the surfaces is explicitly considered. The time evolution of the bulk and surface densities is numerically investigated, showing that the behaviour is governed by the largest among the two characteristic times entering in the problem, when the diffusion time is maintained constant. In § 4 we propose a statistical interpretation for the kinetic equation in relation to the adsorption phenomenon. Finally, § 5 is dedicated to some concluding remarks.

2. Drift-diffusion problem

We consider a sample in the shape of a slab of thickness d. The Cartesian reference frame used in the analysis has the z-axis perpendicular to the bounding surfaces, located at $z=\pm d/2$ (see figure 1).

The problem is considered as one-dimensional, i.e. all physical quantities depend only on the z-coordinates. Let $\rho(z, t)$ be the density of impurities in the dielectric liquid. In practical cases, $\rho(z, t)$ can represent the density of a dye dissolved in the liquid crystal sample [6–15], or the density of ions resulting from molecular dissociation (intrinsic) or from the dissociation of impurities present in the liquid. Consider that on ρ acts an external force $\mathbf{F}=-\nabla U(z)$, where $U(z)$ is the potential of $\mathbf{F}$. In this case $\mathbf{F}$ is responsible for a net current which, in the limit of small $|\mathbf{F}|$, is given by $\mathbf{j}_{\mathrm{F}}=\mu\rho\mathbf{F}$, where μ is the mobility and $\mathbf{j}_{\mathrm{F}}$ is the drift-current due to $\mathbf{F}$. The total current is then

$$\mathbf{j}=\mathbf{j}_{\mathrm{D}}+\mathbf{j}_{\mathrm{F}}=-D\nabla\rho+\mu\rho\,\mathbf{F} \tag{1}$$

where $\mathbf{j}_{\mathrm{D}}$ is the diffusion current and D is the diffusion coefficient. The continuity equation for this problem is

$$\frac{\partial\rho}{\partial t}=\nabla\cdot(D\nabla\rho+\mu\rho\nabla U) \tag{2}$$

which, in the one-dimensional case, is reduced to

$$\frac{\partial\rho}{\partial t}=\frac{\partial}{\partial z}\left(D\frac{\partial\rho}{\partial z}+\mu\rho\frac{\mathrm{d}U}{\mathrm{d}z}\right) \tag{3}$$

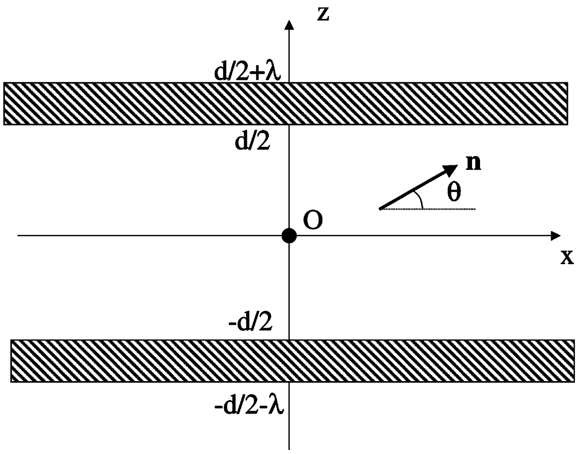

Figure 1. Nematic sample considered in the analysis. The surface anchoring energy is assumed strong. λ represents a typical length scale in which the interaction energy is supposed to be localized, see § 4.2.

where $\mu/D=1/k_BT$, in which k_B is the Boltzmann constant and T the absolute temperature, is the Einstein–Smoluchowski relation [48].

An ideal case relevant to a solution of particles in an external field is now considered. If the particles are neutral, for example, dye molecules in a liquid crystal, the homogeneous external field can be identified with that due to gravity. If the particles are electrically charged, the external field is due to an external power supply. However, since in the analysis the external field is assumed constant, the density of ions is considered to be so small that the actual electric field across the sample coincides with the external field. We consider the simple case in which $dU/dz=h$ is a constant. It is assumed that there is no adsorption from the limiting surfaces. In this case, equation (3) has to be solved by imposing the conditions

$$\int_{-d/2}^{d/2} \rho(z,\,t)\mathrm{d}z=\rho_0 d \tag{4}$$

where $\rho_0=\rho(z,\,t=0)$ is the initial homogeneous density across the sample, and

$$j(\pm d/2,\,t)=0, \quad \forall t. \tag{5}$$

Equation (4) is the conservation of the number of particles per unit area in the cell. By putting $\rho(z,\,t)=\rho_{\mathrm{eq}}(z)+\delta\rho(z,\,t)$, where $\rho(z,\,0)=\rho_0$, $\rho_{\mathrm{eq}}(z)=\lim_{t\to\infty}\rho(z,\,t)$, and hence $\lim_{t\to\infty}\delta\rho(z,\,t)=0$, one obtains

$$\rho_{\mathrm{eq}}(z)=\rho_{\mathrm{eq}}(0)\exp(-2\Omega z) \tag{6}$$

where $\Omega=\mu h/(2D)$. The integration constant ρ_{eq} is obtained by substituting equation (4). One obtains

$$\rho_{\mathrm{eq}}(0)=\rho_0\frac{\Omega d}{\sinh(\Omega d)}. \tag{7}$$

From equation (7) it follows that for $\Omega=0$, i.e. $h=0$, $\rho_{\mathrm{eq}}(0)=\rho_0$, and, hence, $\rho_{\mathrm{eq}}(z)=\rho_0$. In this case, $\delta\rho(z,\,t)=0$, for all $-d/2\leqslant z\leqslant d/2$ and $0\leqslant t<\infty$. In other words, in the absence of adsorption phenomena at the limiting surfaces, without the external field, the diffusion phenomenon is clearly absent.

2.1. *Intrinsic characteristic times*

The function $\delta\rho(z,\,t)$ is the solution of the linear partial differential equation

$$\frac{\partial(\delta\rho)}{\partial t}=D\frac{\partial^2(\delta\rho)}{\partial z^2}+\mu h\frac{\partial(\delta\rho)}{\partial z}. \tag{8}$$

A solution to equation (8) has the form

$$\delta\rho(z,\,t)=\exp\left(-\beta^2 t\right)\phi_\beta(z) \tag{9}$$

where $\beta\neq 0$. By substituting equation (9) into (8) one concludes that $\phi_\beta(z)$ is the solution of the ordinary differential equation with constant coefficients:

$$\frac{d^2\phi_\beta(z)}{\mathrm{d}z^2}+2\Omega\frac{\mathrm{d}\phi_\beta(z)}{\mathrm{d}z}+\frac{\beta^2}{D}\phi_\beta(z)=0. \tag{10}$$

The characteristic exponents relevant to $\phi_\beta(z)$ are then $m_\beta=-\Omega\pm i\omega_\beta$, where

$$\omega_\beta=\left(\frac{\beta^2}{D}-\Omega^2\right)^{\frac{1}{2}}. \tag{11}$$

It follows that

$$\phi_\beta(z)=\exp(-\Omega z)\left[a_\beta\cos\left(\omega_\beta z\right)+b_\beta\sin\left(\omega_\beta z\right)\right]. \tag{12}$$

Consequently, if use is made of equation (9), one has for $\delta\rho(z,\,t)$ the expression

$$\delta\rho(z,\,t)=\exp\left(-\beta^2 t-\Omega z\right)\left[a_\beta\cos\left(\omega_\beta z\right)+b_\beta\sin\left(\omega_\beta z\right)\right] \tag{13}$$

whose functional dependence on t and z is typical of a drift in the presence of diffusion. The total current density, equation (1), is in the present case given by

$$j=-D\frac{\partial\rho}{\partial z}-\mu h\rho. \tag{14}$$

By taking into account that $\rho(z,\,t)=\rho_{\mathrm{eq}}(z)+\delta\rho(z,\,t)$, where $\rho_{\mathrm{eq}}(z)$ is given by equation (6), one obtains

$$j=-D\frac{\partial(\delta\rho)}{\partial z}-\mu h(\delta\rho) \tag{15}$$

which for equation (13), can be rewritten as

$$\begin{aligned} j=\exp&\left(-\beta^2 t-\Omega z\right)\times\\ &\left\{\omega_\beta\left[-a_\beta\sin\left(\omega_\beta z\right)+b_\beta\cos\left(\omega_\beta z\right)\right]\right.\\ &\left.+\Omega\left[a_\beta\cos\left(\omega_\beta z\right)+b_\beta\sin\left(\omega_\beta z\right)\right]\right\}. \end{aligned} \tag{16}$$

The boundary conditions $j(\pm d/2,\,t)=0$ give the homogeneous system

$$\begin{aligned} &a_\beta\left(\Omega\cos X_\beta-\omega_\beta\sin X_\beta\right)\\ &\qquad+b_\beta\left(\Omega\sin X_\beta+\omega_\beta\cos X_\beta\right)=0\\ &a_\beta\left(\Omega\cos X_\beta+\omega_\beta\sin X_\beta\right)\\ &\qquad-b_\beta\left(\Omega\sin X_\beta-\omega_\beta\cos X_\beta\right)=0 \end{aligned} \tag{17}$$

where $X_\beta=\omega_\beta d/2$. A non-trivial solution for a_β and b_β is possible when the determinant of the coefficients of the system (17) vanishes. This condition gives $\left[\Omega^2+\omega_\beta^2\right]\sin\left(2X_\beta\right)=0$, from which it follows that $X_n=\omega_n d/2=n\pi/2$, where $n=1,\,2,\,\ldots$. Hence $\omega_n=n\pi/d$ and $\beta_n^2=D\left[\Omega^2+n^2\pi^2/d^2\right]$. The characteristic times

$\tau_n = 1/\beta_n^2$ are then given by

$$\tau_n = \frac{1}{\beta_n^2} = \frac{1}{1/\tau_\mathrm{h} + n^2/\tau_\mathrm{D}} \tag{18}$$

where $\tau_\mathrm{h}=1/(\Omega^2 D)$ is an intrinsic time connected with the presence of the external field, and $\tau_\mathrm{D}=d^2/(\pi^2 D)$ is the diffusion time in the present case. The longest characteristic time, for $n=1$, is then

$$\tau_1 = \frac{1}{1/\tau_\mathrm{h} + 1/\tau_\mathrm{D}} = \frac{\tau_\mathrm{D}\tau_\mathrm{h}}{\tau_\mathrm{h} + \tau_\mathrm{D}}. \tag{19}$$

For $\tau_\mathrm{D} \ll \tau_\mathrm{h}$, i.e. $\pi/d \gg \Omega$, from equation (19), it follows that

$$\tau_1 \sim \tau_\mathrm{D}. \tag{20}$$

In the opposite case where $\pi/d \ll \Omega$ one finds

$$\tau_1 \sim \tau_\mathrm{h}. \tag{21}$$

If the diffusing particles are ions contained in an isotropic liquid, and the drift is due to an external electric field, equation (21), by taking into account that $h=qE$, where q is the electric charge of the ion, and $\mu/D=1/k_\mathrm{B}T$, reads

$$\tau_1 \sim \tau_\mathrm{E} = 4\left(\frac{d^2}{\mu q V_0}\right)\frac{k_\mathrm{B}T}{qV_0} \tag{22}$$

where V_0 is the applied voltage. Equation (22) holds in the hypothesis that the concentration of ions is so low that the effective electric field in the sample practically coincides with the external field. This characteristic time is usually determined in elementary textbooks as $\tau_\mathrm{d}=d/v_\mathrm{d}=d/(\mu q E)=d^2/(\mu q V_0)$. From the expression of τ_d we derive that it depends on the temperature by means of the ion mobility μ. Consequently, the relative variation of τ_d occurring for a variation of the temperature T of δT is

$$\frac{\delta\tau_\mathrm{d}}{\tau_\mathrm{d}} = \frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}T}\delta T. \tag{23}$$

The relationship for τ_1 shows that $\tau_1 = a\tau_\mathrm{d}$, where $a=4k_\mathrm{B}T/(qV_0)$ represents the importance of the thermal agitation energy with respect to the potential energy responsible for the drift. It follows that when T changes by δT, the relative variation of the relaxation time is

$$\frac{\delta\tau_1}{\tau_1} = \left(\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}T} + \frac{1}{T}\right)\delta T. \tag{24}$$

To evaluate $\mathrm{d}\mu/\mathrm{d}T$ we assume, for the temperature dependence of the diffusion coefficient of the ions in the nematic material, that predicted by the Stokes–Einstein law [54], $D=k_\mathrm{B}T/(6\pi\eta R_0)$, where $\eta(T)$ is the viscosity of the ion in the nematic liquid, and R_0 an average dimension of the ion. By taking into account the Einstein–Smoluchowski relationship we get for the ion mobility the expression $\mu(T)=1/[6\pi\eta(T)R_0]$, from which we obtain

$$\frac{1}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}T} = -\frac{1}{\eta}\frac{\mathrm{d}\eta}{\mathrm{d}T}. \tag{25}$$

If we identify $\eta(T)$ with the viscosity of the nematic liquid crystal, $(1/\eta)$ $(\mathrm{d}\eta/\mathrm{d}T)\sim 10^{-2}$ [55]. In this case $\delta\tau_1/\tau_1$ differs from $\delta\tau_\mathrm{d}/\tau_\mathrm{d}$ for the term $\delta T/T$, which is not negligible with respect to $(1/\eta)$ $(\mathrm{d}\eta/\mathrm{d}T)$.

Note that τ_1, given by equation (22), represents the time necessary for the system to reach equilibrium, where the drift current is balanced by the diffusion current. By contrast, τ_d represents the time required by an ion to travel across the entire sample. Usually $\tau_1 < \tau_\mathrm{d}$ because not all the ions have to be moved to reach equilibrium.

2.2. *Time evolution of the ion density*

Since equation (8) is linear, the general solution for the problem can be written in the form

$$\delta\rho(z,t) = \sum_n \exp\left(-\beta_n^2 t\right)\phi_n(z) \tag{26}$$

where

$$\phi_n(z) = \exp(-\Omega z)[a_n\cos(\omega_n z) + b_n\sin(\omega_n z)]. \tag{27}$$

Note that the parameters

$$p_n = \frac{a_n}{b_n} = \frac{\omega_n\cos X_n + \Omega\sin X_n}{\omega_n\sin X_n - \Omega\cos X_n} \tag{28}$$

are known quantities when the eigenvalues have been determined. Consequently, it is possible to rewrite equation (26) in the form

$$\delta\rho(z,t) = \exp(-\Omega z)\sum_n b_n\exp\left(-\beta^2 t\right)\psi_n(z) \tag{29}$$

where

$$\psi_n(z) = \sin(\omega_n z) + p_n\cos(\omega_n z). \tag{30}$$

From equation (30) it follows that

$$\int_{-d/2}^{d/2}\psi_n(z)\psi_m(z)\mathrm{d}z = 0 \tag{31}$$

for $n \neq m$, and

$$\int_{-d/2}^{d/2}\exp(-\Omega z)\psi_n(z)\mathrm{d}z = 0. \tag{32}$$

Note that

$$\begin{aligned}&\int_{-d/2}^{d/2}\delta\rho(z,\,t)\mathrm{d}z=\sum_n b_n\exp\left(-\beta^2 t\right)\\&\int_{-d/2}^{d/2}\exp(-z)\psi_n(z)\mathrm{d}z=0\end{aligned}\tag{33}$$

for equation (32). Consequently, equation (4) is verified for all t, as required.

It is now possible to determine the coefficients b_n appearing in equation (29). From the expression $\rho(z, t)=\rho_{\mathrm{eq}}(z)+\delta\rho(z, t)$ one has, in the limit $t=0$,

$$\delta\rho(z,\,0)=\rho_0-\rho_{\mathrm{eq}}(z).\tag{34}$$

By taking into account equation (29), one can rewrite (34) in the form

$$\sum_n b_n\psi_n(z)=f(z)\tag{35}$$

where, for equation (7),

$$\begin{aligned}f(z)&=\exp(z)\delta\rho(z,\,0)\\&=\rho_0\left[\exp(z)-\frac{d}{\sinh(d)}\exp(-z)\right]\end{aligned}\tag{36}$$

From equation (35), for (31), one obtains

$$b_m=\frac{1}{N_m}\int_{-d/2}^{d/2}f(z)\psi_m(z)\mathrm{d}z\tag{37}$$

where $N_m=<\psi_m|\psi_m>$ is the square of the modulus of the eigenfunction ψ_m.

In figure 2 we show the time evolution of $\rho(z, t)=\rho_{\mathrm{eq}}+\delta\rho(z, t)$ for three typical values of the external field h, such that $\tau_1\sim\tau_{\mathrm{D}}$, $\tau_1\sim\tau_{\mathrm{D}}\tau_{\mathrm{h}}/(\tau_{\mathrm{D}}+\tau_{\mathrm{h}})$, and $\tau_1\sim\tau_{\mathrm{h}}$. As is evident from figure 2 (*c*) in the limit of large external field, which in practical units means $V_0\gg\pi(k_{\mathrm{B}}T/q)\approx0.075\,\mathrm{V}$, the equilibrium distribution is reached after a time $t_{\mathrm{eq}}\approx0.4\tau_{\mathrm{D}}$.

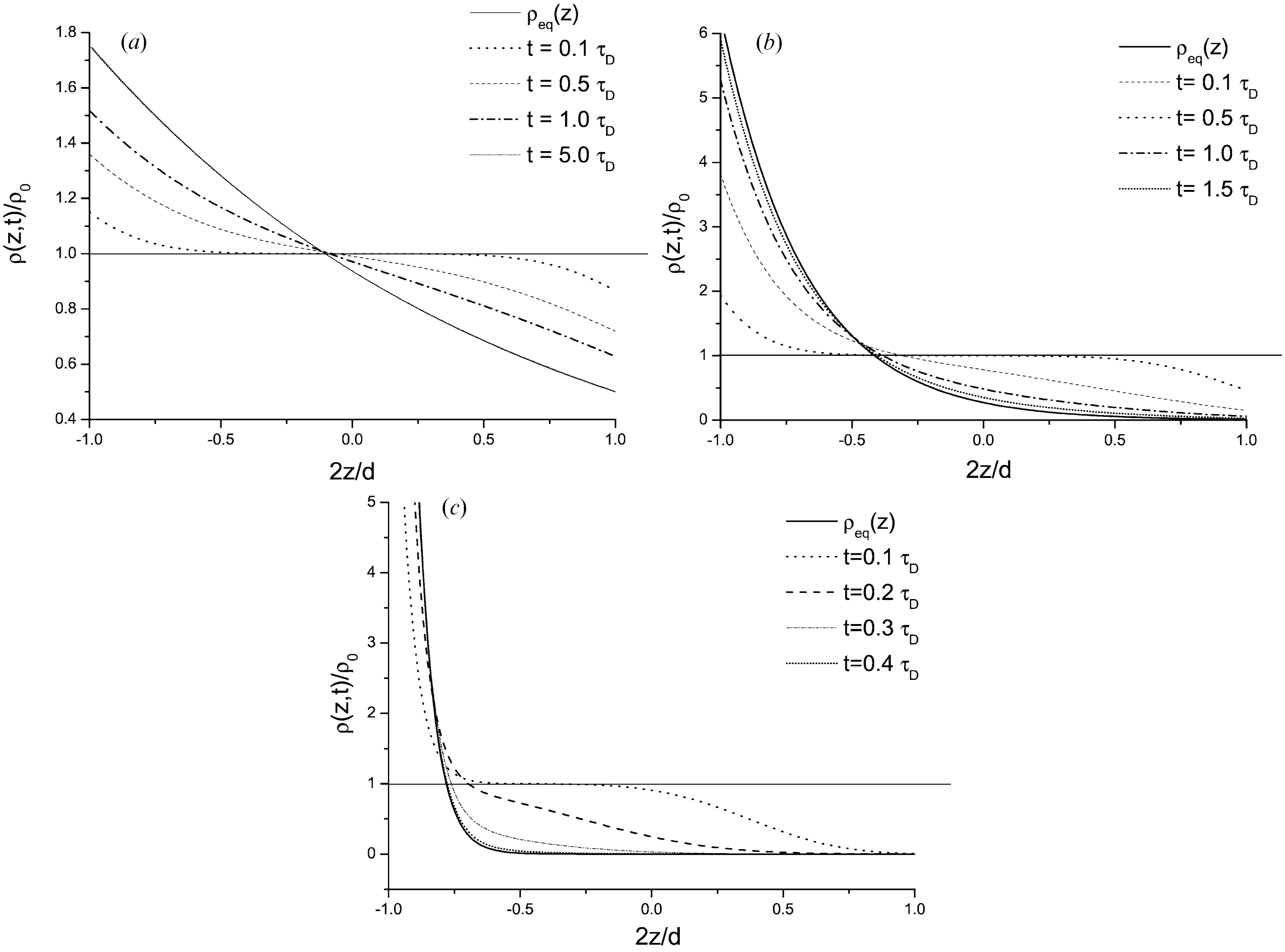

Figure 2. Time evolution of $\rho(z, t)$ for three typical values of the external voltage $V_0=\alpha\pi(k_{\mathrm{B}}T/q)$ for (*a*) $\alpha=1/5$, (*b*) $\alpha=1$ and (*c*) $\alpha=5$.

2.3. *Drift-diffusion phenomenon in nematic liquid crystals*

The analysis reported is, strictly speaking, valid only for isotropic liquids. The application of our results to nematic liquid crystals requires some additional hypothesis. As is known, nematic liquid crystals are anisotropic liquids, whose optical axis coincides with the average molecular orientation, called the nematic director and denoted by **n**. The physical parameters of nematic materials are described by symmetric second order tensors [56]. In particular, the dielectric constant, diffusion coefficient, and the ion mobility of the nematic medium have different values along and perpendicular to the director. Their representing tensors are of the kind

$$\begin{aligned} \varepsilon_{ij} &= \varepsilon_\perp \delta_{ij} + \varepsilon_\mathrm{a} n_i n_j \\ D_{ij} &= D_\perp \delta_{ij} + D_\mathrm{a} n_i n_j \\ \mu_{ij} &= \mu_\perp \delta_{ij} + \mu_\mathrm{a} n_i n_j \end{aligned} \tag{38}$$

where $\varepsilon_\mathrm{a}=\varepsilon_\parallel-\varepsilon_\perp$, and $\parallel$ and $\perp$ refer to **n**. Similar considerations hold for the tensors of diffusion and ion mobility. This circumstance implies that the effective dielectric constant, diffusion coefficient and ion mobility depend on the nematic orientation, described by **n**.

Since we are considering a nematic sample submitted to an external field, other limitations on the values of the field have to be imposed. Nematic materials present an electric polarization connected with the nematic distortion that has not been considered in our analysis [57]. Furthermore, if the electric field is strong enough it can induce a distortion. It follows that our results are valid also for nematic liquid crystals only if they are uniformly oriented. This implies that the external field has to be smaller than the critical field for the Fréedericksz transition. In this case our results can be directly applied to analyse the typical relaxation time in a drift-diffusion phenomenon. However, since the values of the parameters along and normal to the director are of the same order of magnitude [37], the analysis presented above gives the correct order of magnitude of the relaxation time for the ions in a nematic liquid crystal even in the case in which it is distorted.

It follows that we can apply our result to typical experimental situations concerning nematic liquid crystals. By assuming $d\sim 8\,\mu\mathrm{m}$, $D\sim 10^{-11}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ [44], we have $\tau_\mathrm{D}=d^2/(\pi^2 D)\sim 0.65\,\mathrm{s}$, and hence $\tau_\mathrm{eq}\approx 0.26\,\mathrm{s}$. This means that the ions follow the external field variations, if the external field is changing with a characteristic time larger than 0.3 s. However, in the case in which the ions are macroparticles arising from the deterioration of the aligning layers [44], the scale times can be completely different. In this case for $D\sim 10^{-12}\,\mathrm{m}^2\,\mathrm{s}^{-1}$, which corresponds to a radius of the ion of the order of 20 nm [44], we have $\tau_\mathrm{D}\sim 6.5\,\mathrm{s}$ and hence $\tau_\mathrm{eq}\sim 2.6\,\mathrm{s}$. In this situation, if the external field is changing with a period of the order of 1 s, the macroparticles arising from the surfaces do not participate in the phenomenon. Of course, ions dissolved in the liquid crystal, for which $D\sim 10^{-11}\,\mathrm{m}^2\,\mathrm{s}^{-1}$, by contrast, do participate. This conclusion can be of some importance in the experimental determination of physical parameters of nematic liquid crystals when external electric fields are applied [34–36].

3. Adsorption from surfaces

If the adsorption phenomenon from the surfaces is taken into account, and no external fields are present, the bulk density of particles $\rho(z, t)$ is the solution of the diffusion equation:

$$\frac{\partial \rho}{\partial t} - D\frac{\partial^2 \rho}{\partial z^2} = 0 \tag{39}$$

where D is the diffusion coefficient. The current density is, in this case, $j=-D\partial\rho/\partial z$. If we consider identical surfaces, we have furthermore $\rho(z, t)=\rho(-z, t)$. The surface density of adsorbed particles will be denoted by $\sigma=\sigma(t)$. The requirements to be fulfilled are expressed by

$$2\sigma(t) + \int_{-d/2}^{d/2} \rho(z, t)\mathrm{d}z = \rho_0 d \tag{40}$$

and [58]

$$j(\pm d/2, t) = -D\frac{\partial \rho}{\partial z} = \frac{\mathrm{d}\sigma}{\mathrm{d}t} \tag{41}$$

where $\rho_0=\rho(z, t=0)$ is the initial homogeneous density across the sample. To investigate the physical consequences of the phenomenon of adsorption, a kinetic equation at the limiting surfaces has to be imposed. A widely used balance equation at the boundary is [40]

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = \kappa\rho(-d/2, t) - \frac{1}{\tau}\sigma(t) \tag{42}$$

where κ and τ are parameters describing the adsorption phenomenon. Equation (42) simply states that the time variation of the surface density of adsorbed particles depends on the bulk density of particles just in front of the adsorbing surface, and on the surface density of particles already adsorbed. The statistical meaning of equation (42) will be discussed in detail in §4. In equation (42), τ has the dimension of time, and κ that of length/time. Consequently, if the adsorption phenomenon is present, there are two new intrinsic times, τ and $\tau_\kappa=d/2\kappa$.

3.1. *Time evolution of $\delta\rho(z, t)$*

To solve the problem one assumes that $\rho(z, t)=\rho_{\mathrm{eq}}(z)+\delta\rho(z, t)$, where $\rho_{\mathrm{eq}}(z)=\lim_{t\to\infty}\delta\rho(z, t)$ is the distribution of the particles in the steady state. Hence, $\lim_{t\to\infty}\delta\rho(z, t)=0$. We assume also that $\sigma(t)=\sigma_{\mathrm{eq}}+\delta\sigma(t)$, where $\lim_{t\to\infty}\delta\sigma(t)=0$. Simple considerations show that ρ_{eq} is z-independent.

In the limit $t\to\infty$, from equation (42) one obtains $\sigma_{\mathrm{eq}}=\kappa\tau\rho_{\mathrm{eq}}$. Equation (40), in the limit $t\to\infty$, becomes $2\sigma_{\mathrm{eq}}+\rho_{\mathrm{eq}}d=\rho_0 d$. Consequently, ρ_{eq} and σ_{eq} are found to be

$$\rho_{\mathrm{eq}}=\frac{\rho_0}{1+2\kappa\tau/d}\ \text{and}\ \sigma_{\mathrm{eq}}=\frac{\kappa\tau/d}{1+2\kappa\tau/d}\rho_0 d. \tag{43}$$

The time evolution of $\delta\rho(z, t)$ and $\delta\sigma(z, t)$ can now be determined. By substituting $\rho(z, t)=\rho_{\mathrm{eq}}+\delta\rho(z, t)$ into equation (39) one obtains

$$\frac{\partial(\delta\rho)}{\partial t}=D\frac{\partial^2(\delta\rho)}{\partial z^2} \tag{44}$$

whose solution can be written in the form

$$\delta\rho(z, t)=\sum_\beta C_\beta\cos(\omega_\beta z)\exp(-\beta^2 t) \tag{45}$$

where $\omega_\beta=\beta/\sqrt{D}$, with $\beta\neq 0$. Moreover, by substituting the expressions for $\rho(z, t)$ and $\sigma(t)$ into equation (42), one has

$$\frac{\mathrm{d}(\delta\sigma)}{\mathrm{d}t}=\kappa\delta\rho-\frac{1}{\tau}\delta\sigma. \tag{46}$$

From equations (33) and (46), one obtains

$$\delta\sigma=M\exp(-t/\tau)+\sum_\beta\delta\sigma_\beta\exp(-\beta^2 t) \tag{47}$$

where

$$\delta\sigma_\beta=\kappa\frac{C_\beta}{\tau^{-1}-\beta^2}\cos(\omega_\beta d/2) \tag{48}$$

and M has to be determined by means of the condition concerning the conservation of the number of particles. By substituting $\rho(z, t)$ and $\sigma(t)$ into equation (40) one gets

$$2\delta\sigma(t)+\int_{-d/2}^{d/2}\delta\rho(z, t)\mathrm{d}z=0 \tag{49}$$

which, from equations (45) and (47), can be written as

$$M\exp(-t/\tau)+\sum_\beta\left[\delta\sigma_\beta+\frac{C_\beta}{\omega_\beta}\sin(\omega_\beta d/2)\right]\exp(-\beta^2 t)=0 \tag{50}$$

from which, by taking into account equation (48), one obtains $M=0$ and $\tan(\omega_\beta d/2)=[\kappa/(\beta^2-\tau^{-1})]\omega_\beta$, which determines the eigenvalues of the problem and can be rewritten as

$$\tan X=\left(\frac{\tau_{\mathrm{D}}}{4\tau_\kappa}\right)\frac{X}{X^2-\tau_{\mathrm{D}}/4\tau} \tag{51}$$

where $X=\omega_\beta d/2$. In summary, three time scales govern the entire phenomenon, namely, $\tau_{\mathrm{D}}=d^2/D$, $\tau_\kappa=d/2\kappa$, and τ. The eigenvalues of the problem depend on the two ratios $\tau_{\mathrm{D}}/\tau_\kappa$ and τ_{D}/τ. In figure 3 the graphical solutions of equation (51) are illustrated.

In a practical problem it is important to know the first eigenvalue $\beta\neq 0$ responsible for the lowest relaxation time in the phenomenon under consideration. The function on the right hand side of equation (51) has a vertical asymptote at $X_\beta=(\tau_{\mathrm{D}}/4\tau)^{\frac{1}{2}}$. If $\tau_{\mathrm{D}}\ll\tau$, equation (51) can be approximated by $X_\beta\tan X_\beta=\tau_{\mathrm{D}}/(4\tau_\kappa)$, showing that X_β depends on $\tau_{\mathrm{D}}/\tau_\kappa$. For $\tau_{\mathrm{D}}\ll\tau_\kappa$, $X_\beta\sim(\tau_{\mathrm{D}}/4\tau_\kappa)^{\frac{1}{2}}$. In this case ($\tau_{\mathrm{D}}\ll\tau$, $\tau_{\mathrm{D}}\ll\tau_\kappa$, and $\tau_k\ll\tau$), one gets $\beta^2=1/\tau$. This means that when the diffusion process is a rapid phenomenon, the time dependence of the particle distribution is τ. In the opposite limit of $\tau_{\mathrm{D}}\gg\tau$, equation (51) gives $\tan X_\beta=-(\tau/\tau_\kappa)X_\beta$, whose solution is $\pi/2<X_\beta<\pi$, and the relevant relaxation time τ_{R} is in the range $\tau_{\mathrm{D}}/(4\pi^2)\leqslant\tau_{\mathrm{R}}\leqslant\tau_{\mathrm{D}}/\pi^2$. Finally, from equation (51) it follows that, for large X_β, i.e. $X_\beta\gg(\tau_{\mathrm{D}}/4\tau)^{\frac{1}{2}}$ the eigenvalues are $X_n\approx n\pi$.

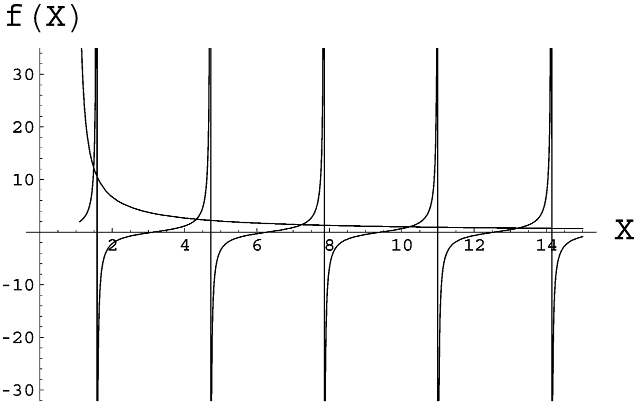

Figure 3. Illustration of the solution of equation (51) for $\tau_{\mathrm{D}}/4\tau=1$ and $(\tau_{\mathrm{D}}/4\tau_\kappa)=10$. $f(X)$ denotes the right and the left hand side of equation (51) depicted on the same axes.

3.2. *Time evolution of the bulk and surface densities*

If the eigenvalues are known, one can calculate the coefficients C_β appearing in equation (45), by means of which one determines the time evolution of $\delta\rho(z, t)$ and $\delta\sigma(t)$. From $\rho(z, t)=\rho_{\mathrm{eq}}+\delta\rho(z, t)$, written in the limit of $t\to 0$, one has $\delta\rho(z, 0)=2(\tau/\tau_\kappa)/(1+\tau/\tau_\kappa)\ \rho_0=2\sigma_{\mathrm{eq}}/d$, which, by using equation (45), becomes

$$\sum_\beta C_\beta \cos(\omega_\beta z)=\frac{2\sigma_{\mathrm{eq}}}{d}. \tag{52}$$

The main problem is that the eigenvectors $u_\beta=\cos(\omega_\beta z)$ are not orthogonal. In this case one can orthogonalize the set of eigenvectors by a procedure similar to the Schmidt approach [59]. By indicating the eigenvalues with $\beta_1(\neq 0)$, β_2, β_3, …, β_n, … one writes $u_i=\cos(\omega_{\beta_i} z)$, where u_i are linearly independent. It is possible to set, using Einstein's convention on the repeated indices, $v_i=\lambda_{ij}u_{\mathrm{j}}$, where $\lambda_{ij}=0$ for $i<j$, and $\lambda_{ii}=1$. Thus, the matrix Λ, of elements λ_{ij} is such that $\det\Lambda=1$. The coefficients λ_{ij} for $i>j$ are determined by putting

$$\langle v_i|v_j\rangle=\int_{-d/2}^{d/2} v_i(z)v_j(z)\,\mathrm{d}z=0 \tag{53}$$

for $i\neq j$. The relation among v_i and u_i can be written in the matrix form as $\mathbf{v}=\Lambda\boldsymbol{u}$, from which $u_i=(\Lambda^{-1})_{ij}v_j$. Consequently, if equation (52) is written as $C_\beta u_\beta(z)=2\sigma_{\mathrm{eq}}/d$ one gets $C_\beta(\Lambda^{-1})_{\beta j}\ v_j=2\sigma_{\mathrm{eq}}/d$, from where

$$C_\beta\left(\Lambda^{-1}\right)_{\beta j}\langle v_j|v_k\rangle=\frac{2\sigma_{\mathrm{eq}}}{d}\langle v_k\rangle \tag{54}$$

with

$$\langle v_k\rangle=\int_{-d/2}^{d/2} v_k(z)\,\mathrm{d}z. \tag{55}$$

Since $v_i(z)$ form a set of orthogonal functions, $<v_j|v_k>=N_k\delta_{jk}$, where $N_k=<v_k|v_k>$. Consequently, from equation (54), one deduces that $(\Lambda^{-1})_{\beta k}C_\beta=(2\sigma_{\mathrm{eq}}/d)<v_k>/N_k$. In the matrix form one has for the preceding equation:

$$\mathbf{C}=\frac{2\sigma_{\mathrm{eq}}}{d}\Lambda^{\mathrm{T}}\mathbf{R} \tag{56}$$

where $\mathbf{R}$ is the vector of elements $R_k=<v_k>/N_k$ and $\Lambda^{\mathrm{T}}_{ij}=\Lambda_{ji}$. The coefficients one is looking for are then given by

$$C_\beta=\frac{2\sigma_{\mathrm{eq}}}{d}\Lambda_{\alpha\beta}R_\alpha \tag{57}$$

which represents the solution of the problem. There is another way to obtain explicit equations connecting v_q with u_q, which gives directly the elements of the matrix Λ, and, consequently, the coefficients C_β. It can be written in the form [60]:

$$v_q=\sum_{n=1}^{q}\frac{M_{nq}}{M_{qq}}u_n \tag{58}$$

where M_{nq} is the minor of the element

$$d_{nq}=\int_{-d/2}^{d/2} u_n(z)u_q(z)\,\mathrm{d}z$$

in the determinant D_q defined as

$$D_1=d_{11}$$

$$D_2=\begin{vmatrix} d_{11} & d_{12}\\ d_{21} & d_{22}\end{vmatrix}$$

$$D_3=\begin{vmatrix} d_{11} & d_{12} & d_{13}\\ d_{21} & d_{22} & d_{23}\\ d_{31} & d_{32} & d_{33}\end{vmatrix};\quad \text{etc.}$$

This alternative way is more suitable for numerically implementation.

To study the time evolution of the densities, it is useful to rewrite the final equations governing them. The coefficient of the cosine in equation (48) can be put in the form

$$\kappa\frac{C_\beta}{\tau^{-1}-\beta^2}=\frac{d}{2}\left(\frac{\tau_{\mathrm{D}}}{4\tau_\kappa}\right)\frac{C_\beta}{\left(\frac{\tau_{\mathrm{D}}}{4\tau}-X_\beta^2\right)}$$

which, by using (51), can be cast in the final form:

$$\kappa\frac{C_\beta}{\tau^{-1}-\beta^2}=-\frac{d}{2}\frac{\tan X_\beta}{X_\beta}C_\beta.$$

This permits the rewriting of (48) as

$$\delta\sigma_\beta=-\frac{d}{2}\frac{\sin X_\beta}{X_\beta}C_\beta$$

giving for $\sigma(t)$ the re-scaled form:

$$\frac{2\sigma(t^*)}{d}=\rho_0\frac{r_1/r_2}{1+r_1/r_2}-\sum_\beta\frac{\sin X_\beta}{X_\beta}C_\beta\exp\left(-X_\beta^2 t^*\right) \tag{59}$$

where $r_1=\tau_{\mathrm{D}}/4\tau_\kappa$, $r_2=\tau_{\mathrm{D}}/4\tau$, and $t^*=4t/\tau_{\mathrm{D}}$. In the same manner, by considering that $\rho_{\mathrm{eq}}=\rho_0-2\sigma_{\mathrm{eq}}/d$, and using equation (45), one obtains:

$$\rho(Z, t^*)=\rho_0\frac{1}{1+r_1/r_2}+\sum_\beta C_\beta\cos(X_\beta Z)\exp\left(-X_\beta^2 t^*\right) \tag{60}$$

where $-1\leqslant Z=2z/d\leqslant 1$.

In Figure 4 the behaviour of $\rho(Z, t^*)/\rho_0$ versus Z, as predicted by equation (60), is shown for a significant set of parameters giving the ratios of the characteristic times entering in the problem. The curves show that as r_2 increases in comparison with r_1, i.e. as the importance of κ decreases when compared with τ, there is an increasing accumulation of particles near the surfaces, placed at $Z = \pm 1$. This indicates that the time characterizing the adsorption phenomenon, represented by τ_κ, becomes increasingly large, leading to an accumulation of particles (not adsorbed) near the limiting surfaces.

In figure 5 the behaviour of $2\sigma(t)/\rho_0 d$, as predicted by equation (59), is shown as a function of the rescaled time $t^* = 4t/\tau_D$ for three representative set of ratios r_1 and r_2. The solid curve shows the case for $r_1 = 10$ and $r_2 = 1$, i.e. for $\tau_D = 4\tau = 40\tau_\kappa$. The curve indicates that the characteristic time governing the behaviour of $\sigma(t)$ is such that $t^* = 4t/\tau_D \approx 1$. For this case, numerical calculations give the first non-zero eigenvalue as $X_1 = 1.5$, $\tau_D \approx 4$, and $\tau \approx 1$ and $\tau_\kappa \approx 0.10$. Therefore, the time behavior of $\sigma(t)$ is governed by τ which is the greater of τ and τ_κ. The dotted curve depicts $r_1 = r_2 = 1.0$, i.e., for $\tau_D = 4\tau = 4\tau_\kappa$. The first non-zero eigenvalue is $X_1 = 1.21$, $\tau_D \approx 4$, and $\tau_\kappa \sim \tau \approx 1$. In this case, both characteristic times are important for the behaviour of $\sigma(t)$. The dashed curve refers to $r_1 = 1$ and $r_2 = 5$, i.e. for $\tau_D = 20\tau = 4\tau_\kappa$. Numerical calculations give $X_1 = 2.01$, $\tau_D \approx 3.05$, and $\tau_\kappa \approx 0.9$, $\tau \approx 0.2$. In this case, the time behaviour of $\sigma(t)$ is governed by τ_κ.

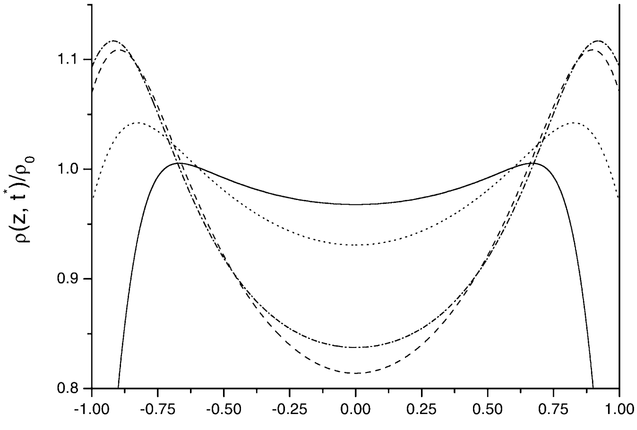

Figure 4. Behaviour of $\rho(Z, t^*)/\rho_0$ versus Z, as predicted by equation (60) for $t^* = 4t/\tau_D = 0.01$. The curves are depicted for a representative set of the parameters r_1 and r_2. Solid line corresponds to $r_1 = 10.0$ and $r_2 = 1.0$, dotted line to $r_1 = 1.0$ and $r_2 = 1.0$, dashed line to $r_1 = 1.0$ and $r_2 = 5.0$, and dashed-dotted line to $r_1 = 1.0$ and $r_2 = 10.0$.

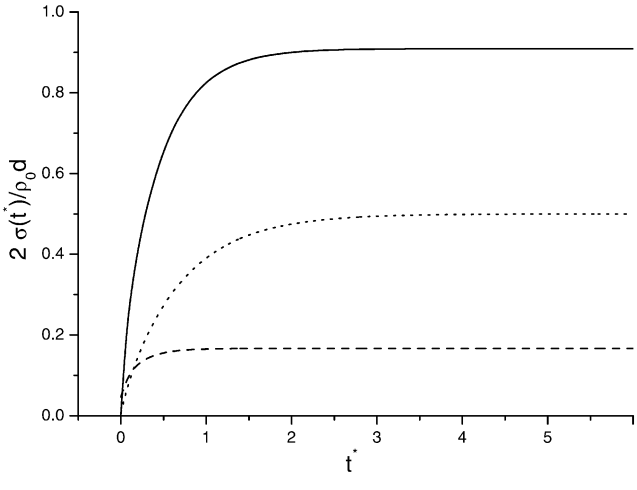

Figure 5. Behaviour of $2\sigma(t^*)/\rho_0 d$ versus $t^* = 4t/\tau_D$. Solid line depicts $r_1 = 10.0$ and $r_2 = 1.0$, dotted line $r_1 = 1.0$ and $r_2 = 1.0$, and dashed line $r_1 = 1.0$ and $r_2 = 5.0$.

The entire analysis, carried out with the help of numerical calculations, shows that, as expected on analytical grounds, the time behaviour of the surface density of particles is governed by the larger among the two characteristic times τ_κ and τ when τ_D is kept unchanged.

4. Statistical interpretation of the kinetic equation and the adsorption phenomenon

The adsorption phenomenon requires that a molecule loses sufficient energy during its collision with the surface that it can be trapped in the physisorption well. When the atom or molecule strikes the surface, it excites vibrational modes in the surface and, if the energy exchange is greater than the initial collision energy, it will be trapped in the well. We can calculate the adsorption rate for a bulk molecule just in front of the surface by means of the kinetic theory. The number of molecules incident on the surface, per unit area, per unit time, is the normal component of the current density defined as the product of the particle bulk density, just in front the surfaces, multiplied by the velocity of the particles. The adsorption rate is given by the product of the incoming flux with the suitably defined sticking coefficient. This kind of analysis holds when the molecules from the liquid are adsorbed on the surface when they hit an empty site, and during the adsorption phenomenon the molecule does not change its structure. Within this framework the adsorption phenomenon can be treated as a first order chemical reaction and from the preceding discussion, the rate of adsorption is proportional to the density just in front of the surface. This is the so called Langmuir approximation [61]. The desorption phenomenon is the reverse of the adsorption phenomenon and requires that an adsorbed molecule gains sufficient energy from the surface to break its bonding with the surface. If in the desorption phenomenon the adsorbate remains intact on the surface, and desorbs reversibly, then the desorption rate is just proportional to the surface coverage, i.e. to the surface density of already adsorbed particles. In this case the desorption is first order. Of course, more complicated situations, in which the structure of the molecule changes during adsorption, can also occur. For instance, if two incident molecules X are adsorbed as a molecule XX, the adsorption rate is proportional to the square of the density. In the same manner, the desorption rate strongly depends on the order of the chemical reaction describing the phenomenon [61, 62]. In the present investigation our analysis is limited to the case in which the adsorption–desorption phenomenon can be described by first order chemical kinetics, because we are mainly interested in the description of the adsorption–desorption of dyes from the surfaces. Furthermore, we have assumed that the system is far from reaching saturation in the covering ratio. Obviously, the analysis can be extended to consider more complicated cases. With our simplifying hypotheses, the kinetic equation at the surfaces, equation (42), is written in the form of a balance of the adsorption effect proportional to the density of the particles just in front of the surface, and the desorption effect proportional to the already adsorbed density of particles. We now show that this equation is in agreement with Maxwell–Boltzmann statistical mechanics; we also propose a simple model to deduce separately the phenomenological coefficients entering into the kinetic equation.

4.1. *1D lattice gas model*

We still suppose that the system has the shape of a slab of thickness d, limited by two surfaces that are perpendicular to the z-axis. Discretization can be achieved by assuming that the slab is formed by N identical planes intersecting the z-axis at equally spaced points, labelled by $m=1, 2, \ldots, N$. The 'bulk planes' are $N-2$ of them, and the 'surface planes' are the remaining two. In each one of these planes there are N_S sites that can be occupied by a particle. Actually, this assumption is necessary only for the 'surface planes' at which, in fact, the particles may attach themselves when the adsorption phenomenon is present, but for simplicity we assume the same for all the planes. Consequently, since the planes are identical, the system can be treated as a 1D lattice gas formed by N equally spaced planes that can be occupied by N_S of the n particles forming the entire system. Let us assume now that a particle in the 'surface plane' interacts with the surface and the adsorption energy, in $k_B T$ units, is $-A$. In this situation, the partition function of the thermodynamical system under consideration is obtained by taking into account that the energy of a particle in a given plane is such that $E_1=E_N=-A$, and $E_m=E_B=0$, for $m=2, \ldots, N-1$. Consequently, the single particle canonical partition function assumes the same form as the one representing a system of N degenerate states whose degeneracy is $g_m=N_S$, namely [63]

$$Z=\sum_{m=1}^{N} g_m \exp(-E_m)=N_S[2\exp(A)+N-2]. \qquad (61)$$

It follows that the thermodynamical probability for a particle to be on a bulk plane ($m=2, 3, \ldots, N-1$) and on a surface plane are, respectively,

$$p_B=\frac{N-2}{2\exp(A)+N-2} \quad \text{and} \quad p_S=\frac{2\exp(A)}{2\exp(A)+N-2}. \qquad (62)$$

Thus, the average numbers of bulk and surface particles are, respectively,

$$n_B=n p_B \quad \text{and} \quad n_S=n p_S. \qquad (63)$$

As expected, $n_B+n_S=n$. In terms of bulk and surface densities we can consider that $\rho_0 dS=n$, $\rho^*_{eq} d\,S=n_B$, and $2\sigma^*_{eq} S=n_S$, where S is the area of each plane. This relation implies that $\rho^*_{eq} d+2\sigma^*_{eq}=\rho_0 d$. Consequently, by using equation (63) one finds

$$\rho^*_{eq}=\frac{1}{1+(2\Delta/d)\exp(A)}\rho_0 \qquad \sigma^*_{eq}=\frac{(\Delta/d)\exp(A)}{1+(2\Delta/d)\exp(A)}\rho_0 d, \qquad (64)$$

where we have introduced the quantity $\Delta=\mathrm{d}/(N-2)$, whose meaning will be discussed later.

According to equation (64), in the limit $A\to 0$ we obtain

$$\rho^*_{eq}(0)=\frac{1}{1+2(\Delta/d)}\rho_0 \qquad \sigma^*_{eq}(0)=\frac{\Delta/d}{1+2(\Delta/d)}\rho_0 d \qquad (65)$$

indicating that even if $A=0$ at the surfaces the particle surface density is not zero. However, in the adsorption–desorption phenomenon one is interested in the variation of the surface density on the limiting surfaces due to the presence of the surfaces. For this reason in our analysis we will consider the effective bulk and surface densities of particles, in the adsorption problem under investigation, defined by $\rho_{eq}=\rho^*_{eq}+(2/d)\sigma^*_{eq}(0)$ and by $\sigma_{eq}=\sigma^*_{eq}-\sigma^*_{eq}(0)$. By definition ρ_{eq} and σ_{eq} are such that

$\rho_{\rm eq}(0)=\rho_0$ and $\sigma_{\rm eq}(0)=0$. By taking into account equation (64) and (65) we obtain for $\rho_{\rm eq}$ and $\sigma_{\rm eq}$ the expressions

$$\begin{aligned}\rho_{\rm eq}&=\left[\frac{1}{1+2(\Delta/d)\exp(A)}+2\frac{\Delta/d}{1+2(\Delta/d)}\right]\rho_0\\ \sigma_{\rm eq}&=\left[\frac{(/d)\exp(A)}{1+2(/d)\exp(A)}-\frac{\Delta/d}{1+2(\Delta/d)}\right]\rho_0 d.\end{aligned}\tag{66}$$

The quantity $\sigma_{\rm eq}$ given by equation (66) can be rewritten as

$$\sigma_{\rm eq}=\frac{\Delta}{d}\frac{\exp(A)-1}{[1+2(\Delta/d)][1+2(\Delta/d)\exp(A)]}\rho_0 d.\tag{67}$$

In the limit of large A, ($A\gg1$), from equation (67) we get

$$\sigma_{\rm eq}(A\gg1)=\frac{1}{2}\rho_0 d\tag{68}$$

whereas for small A, ($A\ll1$), the surface density is found to be

$$\sigma_{\rm eq}(A\ll1)=A\rho_0\Delta\tag{69}$$

since $\Delta\ll d$, as will be shown later. The relative increasing of the surface density of particles due to the adsorption phenomenon, according to the definition of $\sigma_{\rm eq}$ is given by the ratio

$$r=\frac{\sigma_{\rm eq}}{\sigma^*_{\rm eq}(0)}=\frac{\exp(A)-1}{1+2(\Delta/d)\exp(A)}.\tag{70}$$

The surface density in the limit of large adsorption energy given by equation (68) is an expected result, because in this limit all the particles (assumed dimensionless) present in the bulk are adsorbed. In this case from equation (70) we obtain $r\sim d/(2\Delta)\gg1$. In the opposite limit of small A, $r\sim A$. This result indicates that in the case of small adsorption energy, A represents the relative increase of the surface density of particles. By assuming $\rho_0\sim10^{20}$ particles per m^3, $\Delta\sim10^{-9}$ m [40], and taking $A\sim0.1$, one gets $\sigma_{\rm eq}\sim10^{10}$ particles per m^2, which represents 10% of the surface density of particles in the absence of adsorption. This quantity can be easily detected.

If we now compare equation (43), obtained by using the kinetic equation, with (66) we deduce that

$$\frac{\kappa\tau}{\Delta}=\frac{\exp(A)-1}{1+4(\Delta/d)+4(\Delta/d)^2\exp(A)}\tag{71}$$

which, by taking into account that $\Delta\ll d$, can be rewritten in the approximated form

$$\frac{\kappa\tau}{\Delta}=\exp(A)-1.\tag{72}$$

As expected, for $A\rightarrow0$, $\kappa\tau/\Delta\rightarrow0$.

4.2. *Microscopic model*

An alternative manner for the deduction of equation (72) is based on a particular model of a physical system. To this end, let us consider a sample in the shape of a slab containing particles. We can assume that the interaction of the particles with the limiting surfaces is short range and limited to two surface layers of thickness λ, where the interaction energy is localized. In this framework, the evolution of the bulk density is obtained by solving the diffusion equation in the three regions: $\mathcal{R}_1:-d/2\le z\le -z^*$, $\mathcal{R}_B:-z^*\le z\le z^*$, and $\mathcal{R}_2:z^*\le z\le d/2$, where $z^*=d/2-\lambda$ and λ is in the mesoscopic scale. For the sake of simplicity we assume that the surface potential, in $k_{\rm B}T$ units, is

$$U(z)=\begin{cases}U_1=U(\mathcal{R}_1)=\dfrac{U_0}{\lambda}(z+z^*)\\ U_{\rm B}=U(\mathcal{R}_{\rm B})=0\\ U_2=U(\mathcal{R}_2)=-\dfrac{U_0}{\lambda}(z-z^*).\end{cases}\tag{73}$$

The form proposed above for the potential illustrates, in a simple manner, the main feature to be explored in our analysis; that is, the fact that the interaction responsible for the adsorption phenomenon has a defined penetration range, here represented by λ. Since we approximate $U(z)$ by means of a linear function, our analysis is, actually, valid only for small U_0. In particular, the relation that we will obtain for $\kappa\tau$ will be meaningful only in the limit of $U_0\rightarrow0$. This point of the analysis can be improved by considering more realistic forms for the surface potential, such as those having the power-law decaying or other non-linear spatial dependence. Typical examples are (i) the van der Waals potential, $U(z)=A_{\rm H}/z^3$, where $A_{\rm H}$ is the Hammaker constant, for the first case, and (ii) $U(z)=U_0\cosh(z/\lambda)/\cosh[d/(2\lambda)]$, for the second case, i.e presenting a strong subsurface variation, and written for a system in which the surfaces are placed at $z=\pm d/2$. There are other choices for the potential [64] but they do not change the main conclusions of our analysis, as we have demonstrated in another context [65]. However, at the end of this section we will indicate a generalization of the analysis developed for the case in which $U(z)$ is given by equation (73).

Let us indicate the density by $\rho_i=\rho(\mathcal{R}_i)$ and the current density in the region $\mathcal{R}_i$ by

$$j_i=j(\mathcal{R}_i)=-D\frac{\partial\rho_i}{\partial z}-\varepsilon_i\mu h\rho_i\tag{74}$$

where $\varepsilon_1=1$, $\varepsilon_{\rm B}=0$ and $\varepsilon_2=-1$. In equation (74) μ is the mobility and $h=U_0/\lambda$. The continuity equations

$$\frac{\partial\rho_i}{\partial t}=-\frac{\partial j_i}{\partial z} \tag{75}$$

for $i=1$, B, 2, have to be solved by imposing the matching conditions

$$\rho_1(-z^*,t)=\rho_{\rm B}(-z^*,t) \quad \text{and} \quad \rho_{\rm B}(z^*,t)=\rho_2(z^*,t) \tag{76}$$

for the densities, and

$$\begin{aligned} &j_1(-d/2,t)=0, \quad j_1(-z^*,t)=j_{\rm B}(-z^*,t)\\ &j_{\rm B}(z^*,t)=j_2(z^*,t), \quad j_2(d/2,t)=0 \end{aligned} \tag{77}$$

for the current densities. The conditions $j_1(-d/2, t)=0$ and $j_2(d/2, t)=0$ simply state that the particles cannot leave the sample. By putting, as usual, $\rho_i(z, t)=\rho_{\rm eqi}(z)+\delta\rho_i(z, t)$ where $\rho_{\rm eqi}(z)$ are the densities in the steady state, a simple calculation gives

$$\rho_{{\rm eq}\,i}=p\exp(-U_i). \tag{78}$$

In deriving equation (78) we have used the Einstein–Smoluchowski relation. The constant p has to be determined by imposing that

$$\int_{-d/2}^{d/2}\rho(z,t){\rm d}z=\rho_0 d. \tag{79}$$

We get

$$\rho_{\rm eq}=\rho_{\rm eq\,B}=p=\left[\frac{1}{1+2R}\right]\rho_0 \tag{80}$$

where

$$R=\frac{\lambda}{d}\left[\frac{\exp(U_0)-1}{U_0}-1\right]. \tag{81}$$

The equivalent surface density, in the steady state, is defined by

$$\sigma_{\rm eq}=\int_{z^*}^{d/2}\left[\rho_{\rm eq2}(z)-\rho_{\rm eqB}\right]{\rm d}z=\left(\langle\rho_{\rm eq2}\rangle_\lambda-\rho_{\rm eqB}\right)\lambda \tag{82}$$

where

$$\langle f(z)\rangle_\lambda=\frac{1}{\lambda}\int_{d/2-\lambda}^{d/2}f(z){\rm d}z. \tag{83}$$

It follows that for equations (73), (78) and (80), $\sigma_{\rm eq}$ defined by (82) is

$$\sigma_{\rm eq}=\frac{R}{(1+2R)}\rho_0 d. \tag{84}$$

By comparing equations (80) and (84) with (43), we get

$$\frac{\kappa\tau}{\lambda}=\frac{\exp(U_0)-1}{U_0}-1\approx\frac{U_0}{2} \tag{85}$$

since $U_0\ll 1$ in our analysis. The result (85) coincides with (72) if Δ is of the order of λ, which is reasonable, and A is identified with the average value of the potential energy in the surface layer of thickness λ. In fact, in the present calculation λ represents the penetration of the surface forces, whereas when we analysed the statistical problem we considered the surface layers localized at the surface. Hence, the particles in the bulk were those at a distance Δ from the surface. This fact can be easily understood. Since $N\gg 2$ we can write $\Delta\approx d/N$, which represents the spacing between the planes in this 1D lattice gas model. It is not arbitrary but, on the contrary, it is connected with the penetration length of the forces giving rise to the adsorption. More precisely, Δ is a parameter connected with the separation between bulk and surface particles. It can be estimated by considering the first two planes N_1 and N_2, which represent, respectively, the surface itself ($m=1$) and the first plane of the bulk ($m=2$). The spacing between these planes has to be of the order of λ. Therefore, $\Delta\approx\lambda$ and $N=d/\Delta$ is a quantity fixed by the thickness of the sample and by the penetration of the surface forces.

We can now generalize the analysis presented above to the case of generic surface potential $U(z)$, which is, however, assumed localized in a surface layer of mesoscopic thickness. In this case equation (78) becomes

$$\rho_{\rm eq}(z)=\mathcal{P}\exp[-U(z)]. \tag{86}$$

The quantity $\mathcal{P}$ is again determined by means of equation (79). A simple calculation gives

$$\mathcal{P}=\frac{\rho_0}{\langle\exp[-U(z)]\rangle_d} \tag{87}$$

where

$$\langle f(z)\rangle_d=\frac{1}{d}\int_{-d/2}^{d/2}f(z){\rm d}z. \tag{88}$$

Consequently

$$\rho_{\rm eq}(z)=\rho_0\frac{\exp[-U(z)]}{\langle\exp[-U(z)]\rangle_d}. \tag{89}$$

In particular, since $U(0)=0$, we have from (89)

$$\rho_{\rm eq}(0)=\mathcal{P}. \tag{90}$$

The surface density of particles, that in this context is given by

$$\sigma_{\mathrm{eq}}=\frac{1}{2}\int_{-d/2}^{d/2}\left[\rho_{\mathrm{eq}}(z)-\rho_{\mathrm{eq}}(0)\right]\mathrm{d}z \tag{91}$$

is

$$\sigma_{\mathrm{eq}}=\frac{1}{2}\rho_0 d\frac{\langle\exp[-U(z)]\rangle_d-1}{\langle\exp[-U(z)]\rangle_d}. \tag{92}$$

By comparing equation (92) with (43) we get

$$\frac{\kappa\tau}{d}=\frac{\langle\exp[-U(z)]\rangle_d-1}{2}. \tag{93}$$

Now we can take into account the hypothesis that $U(z)$ is localized in a surface layer of mesoscopic thickness λ. In this case we have

$$\langle\exp[-U(z)]\rangle_d=2\frac{\lambda}{d}(\langle\exp[-U(z)]\rangle_\lambda-1)+1. \tag{94}$$

By substituting equation (94) into (93) we obtain, finally,

$$\frac{\kappa\tau}{\lambda}=\langle\exp[-U(z)]\rangle_\lambda-1 \tag{95}$$

which generalizes (85) to the case of arbitrary $U(z)$.

4.3. *Comparison between the phenomenological and the microscopic model*

In the two analyses presented above, only information on the product $\kappa\tau$ has been obtained because only the steady state was considered. To proceed further, and connect κ and τ with the parameters of the model, i.e. the adsorption energy and the range of the surface forces, it is possible to follow two different approaches. One is to consider the statistical mechanics of systems out of the equilibrium, and to solve the relevant equation for the detailed balance. The other is to solve the diffusion equation by taking into account the time evolution of the system. We will adopt the latter.

From equation (75) for $i=2$ one can write, for a surface layer of thickness λ, that

$$\int_{z^*}^{d/2}\frac{\partial\rho_2}{\partial t}\mathrm{d}z=-\int_{z^*}^{d/2}\frac{\partial j_2}{\partial z}\mathrm{d}z \tag{96}$$

which is equivalent to

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{z^*}^{d/2}\rho_2(z,t)\mathrm{d}z=-[j_2(d/2,t)-j_2(z^*,t)]. \tag{97}$$

The surface density in the surface layer is introduced as

$$\sigma(t)=\int_{z^*}^{d/2}[\rho_2(z,t)-\rho_{\mathrm{B}}(z,t)]\mathrm{d}z\approx\int_{z^*}^{d/2}\rho_2(z,t)\mathrm{d}z \tag{98}$$

because λ is of mesoscopic length. We observe that, if the surface density is considered as a useful quantity, in the surface layer $\rho_2(z,t)$ is expected to be very large with respect to ρ_{B} in order that equation (98) gives a finite quantity. In this framework $\rho_{\mathrm{B}}\ll\rho_2$. From the fourth of equations (77) one knows that $j(d/2,t)=0$. Therefore, equation (97), by using (98), is reduced to [58]

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t}=j_2(z^*,t). \tag{99}$$

At first sight equations (99) and (41) seem incompatible. The consistence between the two equations can be understood taking into account that in the present context the surface density is defined by means of the bulk density of particles in the surface layer. Consequently its increase is due to particles coming form the bulk, whose current density is $j_{\mathrm{B}}(z^*,t)$.

On the other hand, substitution of one of the equations (74), relevant to $i=2$, into (99) yields

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t}=\mu h\,\rho_2(z^*,t)-D\left[\frac{\partial\rho_2(z,t)}{\partial z}\right]_{z=z^*}. \tag{100}$$

To proceed further, one can assume that $\rho_2(z,t)$, in the surface layer, can be approximated by

$$\rho_2(z,t)=\rho_2(z^*,t)+\left(\frac{\partial\rho_2}{\partial z}\right)_{z=z^*}(z-z^*). \tag{101}$$

By taking into account that $\rho_2(z,t)\gg\rho_2(z^*,t)=\rho_{\mathrm{B}}(z^*,t)$, by substituting equation (101) into (98) one easily obtains

$$\sigma(t)=\frac{1}{2}\left(\frac{\partial\rho_2}{\partial z}\right)_{z=z^*}\lambda^2 \tag{102}$$

from which

$$\left(\frac{\partial\rho_2}{\partial z}\right)_{z=z^*}=\frac{2}{\lambda^2}\sigma(t). \tag{103}$$

Substitution of equation (103) into (100) yields

$$\frac{\mathrm{d}\sigma(t)}{\mathrm{d}t}=\mu h\,\rho_2(z^*,t)-\frac{2D}{\lambda^2}\sigma(t). \tag{104}$$

Moreover, if use is now made of the continuity condition (76), namely $\rho_{\mathrm{B}}(z^*,t)=\rho_2(z^*,t)$, it is possible to rewrite (104) in the final form

$$\frac{d\sigma(t)}{dt} = \mu h \rho_B(z^*, t) - \frac{2D}{\lambda^2}\sigma(t) \tag{105}$$

which coincides with the kinetic equation written phenomenologically at the adsorbing surface. It follows that

$$\kappa = \mu h \quad \text{and} \quad \frac{1}{\tau} = 2\frac{D}{\lambda^2}. \tag{106}$$

In this manner

$$\frac{\kappa\tau}{\lambda} = \frac{U_0}{2} \tag{107}$$

which has to be compared with (85). With this type of analysis it is possible to relate, separately, κ and τ with the microscopic parameters of the model U_0 and λ. In particular, τ is of the order of the diffusion time of the particles in the surface layer [66].

5. Concluding Remarks

We have analysed the diffusion phenomenon in a sample in the shape of a slab, in the presence of the adsorption phenomenon. The kinetic equation on the limiting surfaces describing the adsorption process is assumed to have two terms. One proportional to the bulk density of particles just in front to the adsorbing surfaces, the other proportional to the surface density of particles already adsorbed. The first term gives a positive contribution, whereas the second gives a negative contribution to the time variation of the surface density of adsorbed particles. We evaluate the time variation of the bulk and surface density of particles, and the characteristic times entering the problem. We have determined, in the limit of small ionic density, the intrinsic time related to the presence of the external field on the ion redistribution. It has been found proportional to the drift-time, and dependent on the temperature by means of the ratio k_BT/qV_0, representing the importance of the thermal agitation energy with respect to the electrostatic potential energy. We have also solved, in this framework, the full continuity equation, obtained the eigenvalues of the problem, and found the time evolution of the particle density across the sample. The possible application of our analysis to the drift-diffusion of ions in a nematic sample in the shape of a slab is discussed. In this case, we have shown that, although the mathematical description of the phenomenon under consideration is more complicated, our model gives the correct order of magnitude of the relaxation time. Finally, we have also presented a statistical description of the adsorption phenomenon in the framework of Maxwell–Boltzmann statistics. By means of a simple model system the adsorption parameters governing the kinetic adsorption at the surfaces have been related to the adsorption energy, and to the thickness of the effective surface layer in which it can be considered delocalized.

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