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Intrinsic characteristic times in the drift-diffusion problem

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The redistribution of impurities in a sample in the shape of a slab filled with an isotropic liquid submitted to an external field is considered. The case in which the impurities are ions dissolved in the liquid, and the external field is an electric field is also investigated. 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. A closed solution for the time evolution of the density of particles is obtained. The importance of the effect on real situations is investigated. The possible application of these results to nematic samples submitted to an external electric field is discussed.

1. Introduction

The presence of impurities dissolved in a liquid can strongly modify the physical properties of the liquid itself. An open fundamental question 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 [1].

The aim of this work is to consider the distribution of impurities in a sample in the shape of a slab filled with an isotropic liquid submitted to an external field, by considering in particular the case in which the impurities are ions dissolved in the liquid. We will show that the intrinsic time connected with the presence of the electric field is proportional to the drift time, but it 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 what determines the dielectric, diffusion and ionic mobility physical properties. 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.

This problem is a rather important one in liquid crystal displays. The influence of ions on the optical properties of a nematic liquid crystal sample has been the subject of intensive research work. In earlier first papers the analysis was mainly on the importance of the ionic renormalization of the anchoring energy and flexoelectric coefficients by limiting the considerations to the static situation [2–13]. More recently, works devoted to the analysis of the optical response of a nematic sample submitted to a periodic square-wave signal have been published [14–16]. The studies of the influence of ions on the dynamical properties of nematic samples have been presented by several groups, mainly for practical applications [17–26]. In the relevant theoretical analysis, the characteristic times are the diffusion time and the drift time [27].

In this scenario our paper represents the first attempt to evaluate the relaxation time of the ionic redistribution in a nematic sample submitted to an external electric field, in an analytical way.

Our paper is organized as follows. In §2 the fundamental equations of the problem are given, and the simplifying hypotheses presented. The characteristic relaxation time for the redistribution of the impurities in the sample in the presence of the drift-diffusion phenomenon is evaluated in §3. The time evolution of the density of ions is analytically deduced in §4. In the

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same section we also show the results obtained numerically relevant to the time evolution of the distribution of ions across the sample. The applicability of the result of our model to nematic liquid crystal samples is discussed in § 5. The main results of our paper and conclusions are discussed in § 6. Finally, in the Appendix a discussion on the role of adsorption phenomenon on the drift-diffusion problem is reported.

2. Setting the problem

The sample is considered in the form of a slab of thickness d limited by two flat surfaces, placed at $z=\pm d/2$, which are not adsorbing (see the Appendix). The problem is assumed as being one-dimensional with all the quantities depending only on the z-coordinate, which is normal to the bounding plates. Let $\rho(z, t)$ be the density of impurities in the isotropic dielectric liquid. In practical cases, $\rho(z, t)$ can represent the density of neutral particles dissolved in the liquid, or the density of intrinsic ions connected with the molecular dissociation or with the impurities present in the liquid itself. 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 that, 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 $\mathbf{j}=\mathbf{j}_{\mathrm{D}}+\mathbf{j}_{\mathrm{F}}=-D\nabla\rho+\mu\rho\mathbf{F}$, where $\mathbf{j}_{\mathrm{D}}$ is the diffusion current. The continuity equation in this case reads

$$\frac{\partial\rho}{\partial t}=\nabla\cdot(D\nabla\rho+\mu\rho\nabla U) \tag{1}$$

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

$$\frac{\partial\rho}{\partial t}=\frac{\partial}{\partial z}\left(D\frac{\partial\rho}{\partial z}+\mu\rho\frac{\mathrm{d}U}{\mathrm{d}z}\right) \tag{2}$$

where $\mu/D=1/k_{\mathrm{B}}T$ is the Einstein–Smoluchowski relation [27]. In the following, we limit our investigation to the case in which only one kind of impurity is present in the liquid. However, our analysis can be easily generalized to the case in which there are several kinds of impurity present at the same time in the liquid under investigation. In this situation for each type of impurity we have to solve a problem similar to the one presented in the following, and the effective relaxation time will be determined by the group of impurities having the higher mobility.

We limit our investigation to the ideal case in which the external field can be assumed homogeneous: $\mathrm{d}U/\mathrm{d}z=h=$constant. If the particles are neutral the homogeneous external field can be identified with the one due to gravity. If the particles are electrically charged, the external field is due to an external power supply. However, since h is assumed constant, the density of ions has to be so small that the actual electric field across the sample coincides with the external one.

In this framework equation (2) has to be solved by imposing the conditions

$$\int_{-d/2}^{d/2}\rho(z, t)\,\mathrm{d}z=\rho_0\,d \tag{3}$$

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

$$j(\pm d/2, t)=0, \quad \forall t. \tag{4}$$

Equation (3) 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

$$\rho_{\mathrm{eq}}(z)=\rho_{\mathrm{eq}}(0)\exp(-2\Omega z) \tag{5}$$

where $\Omega=\mu h/(2D)$. The integration constant ρ_{eq} is obtained by imposing equation (3). One gets

$$\rho_{\mathrm{eq}}(0)=\rho_0\frac{\Omega d}{\sinh(\Omega d)}. \tag{6}$$

From equation (6) 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 $-d/2\leq z\leq d/2$ and $0\leq t<\infty$. In other words, in the absence of adsorption phenomena at the limiting surfaces, without the external field, the diffusion phenomenon is, obviously, absent.

3. Relaxation time

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

$$\frac{\partial(\delta\rho)}{\partial t}=D\frac{\partial^2(\delta\rho)}{\partial z^2}+\mu h\frac{\partial(\delta\rho)}{\partial z}. \tag{7}$$

A solution to equation (7) is sought in the form

$$\delta\rho(z, t)=\exp(-\beta^2 t)\phi_\beta(z) \tag{8}$$

where $\beta\neq 0$. By substituting equation (8) into (7) one concludes that $\phi_\beta(z)$ is a solution of the ordinary differential equation with constant coefficients

$$\frac{\mathrm{d}^2\phi_\beta(z)}{\mathrm{d}z^2}+2\Omega\frac{\mathrm{d}\phi_\beta(z)}{\mathrm{d}z}+\frac{\beta^2}{D}\phi_\beta(z)=0. \tag{9}$$

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

$$\omega_\beta=\left(\frac{\beta^2}{D}-\Omega^2\right)^{\frac{1}{2}}. \tag{10}$$

It follows that

$$\phi_\beta(z)=\exp(-\Omega z)\left[a_\beta\cos(\omega_\beta z)+b_\beta\sin(\omega_\beta z)\right] \tag{11}$$

and, making use of equation (8), one has for $\delta\rho(z, t)$ the expression

$$\delta\rho(z,\,t)=\exp\left(-\beta^2 t-\Omega\, z\right)\left[a_\beta\cos\left(\omega_\beta z\right)+b_\beta\sin\left(\omega_\beta z\right)\right] \tag{12}$$

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

$$j=-D\frac{\partial\rho}{\partial z}-\mu h\rho. \tag{13}$$

By taking into account that $\rho(z,\,t)=\rho_{\text{eq}}(z)+\delta\rho(z,\,t)$, where $\rho_{\text{eq}}(z)$ is given by equation (5), one obtains

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

that, for equation (12), can be rewritten as

$$\begin{aligned} j=&-D\exp\left(-\beta^2 t-\Omega\, z\right)\times\\ &\left\{\omega_\beta\left[-a_\beta\sin\left(\omega_\beta z\right)+b_\beta\cos\left(\omega_\beta z\right)\right]\right.\\ &\left.+\Omega\left[a_\beta\cos\left(\omega_\beta z\right)+b_\beta\sin\left(\omega_\beta z\right)\right]\right\}. \end{aligned} \tag{15}$$

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

$$\begin{aligned} &a_\beta\left(\Omega\cos X_\beta-\omega_\beta\sin X_\beta\right)\\ &\quad+b_\beta\left(\Omega\sin X_\beta+\omega_\beta\cos X_\beta\right)=0\\ &a_\beta\left(\Omega\cos X_\beta+\omega_\beta\sin X_\beta\right)\\ &\quad-b_\beta\left(\Omega\sin X_\beta-\omega_\beta\cos X_\beta\right)=0 \end{aligned} \tag{16}$$

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 (16) 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

$$\tau_n=\frac{1}{\beta_n^2}=\frac{1}{1/t_{\text{h}}+n^2/t_{\text{D}}} \tag{17}$$

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

$$\tau_1=\frac{1}{1/t_{\text{h}}+1/t_{\text{D}}}=\frac{t_{\text{D}}\,t_{\text{h}}}{t_{\text{h}}+t_{\text{D}}}. \tag{18}$$

For $t_{\text{D}}\ll t_{\text{h}}$, i.e. $\pi/d\gg\Omega$, from equation (18), it follows that $\tau_1\sim t_{\text{D}}$. In the opposite case where $\pi/d\ll\Omega$ one finds $\tau_1\sim t_{\text{h}}$.

If the diffusing particles are ions contained in an isotropic liquid, and the drift is due to an external electric field, by taking into account that $h=qE$, where q is the electric charge of the ion, and $\mu/D=1/k_{\text{B}}T$, the relation $\tau_1\sim t_{\text{h}}$ reads

$$\tau_1\sim t_{\text{E}}=4\left(\frac{d^2}{\mu\, q\, V_0}\right)\frac{k_B T}{q V_0} \tag{19}$$

where V_0 is the applied voltage. Equation (19) 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 text-books as $\tau_{\text{d}}=d/v_{\text{d}}=d/(\mu\ q\ E)=d^2/(\mu\ q\ V_0)$. From the expression of τ_{d} we derive, it depends on the temperature by means of the ions mobility μ. Consequently, the relative variation of τ_{d} occurring for a variation of the temperature T of δT is

$$\frac{\delta\tau_{\text{d}}}{\tau_{\text{d}}}=\frac{1}{\mu}\frac{\text{d}\mu}{\text{d}T}\delta T. \tag{20}$$

The relationship reported above for τ_1 shows that $\tau_1=a\tau_{\text{d}}$, where $a=4k_{\text{B}}T/(qV_0)$ 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

$$\frac{\delta\tau_1}{\tau_1}=\left[\frac{1}{\mu}\frac{\text{d}\mu}{\text{d}T}+\frac{1}{T}\right]\delta T. \tag{21}$$

To evaluate $\text{d}\mu/\text{d}T$ we assume for the temperature dependence of the diffusion coefficient of the ions in the nematic material the one predicted by the Stokes–Einstein law [28], $D=k_{\text{B}}T/(6\pi\eta R_0)$, 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 relation $\mu/D=1(k_{\text{B}}T)$, we get for the ion mobility the expression $\mu(T)=1/[6\pi\eta(T)R_0]$, from which we obtain

$$\frac{1}{\mu}\frac{\text{d}\mu}{\text{d}T}=-\frac{1}{\eta}\frac{\text{d}\eta}{\text{d}T}. \tag{22}$$

If we identify $\eta(T)$ with the viscosity of the nematic liquid crystal, $(1/\eta)(\text{d}\eta/\text{d}T)\sim 10^{-2}$ [29]. In this case $\delta\tau_1/\tau_1$ differs from $\delta\tau_{\text{d}}/\tau_{\text{d}}$ for the term $\delta T/T$, which is not negligible with respect to $(1/\eta)(\text{d}\eta/\text{d}T)$.

Note that τ_1, given by equation (19), 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 for an ion to travel across the entire sample. Usually $\tau_1<\tau_{\text{d}}$ because not all the ions have to move to reach the equilibrium.

4. Time evolution of the density of ions

Since equation (7) is linear, the general solution for the problem can be written in the form

$$\delta\rho(z,t)=\sum_n \exp\left(-\beta_n^2 t\right)\phi_n(z) \tag{23}$$

where

$$\phi_n(z)=\exp(-\Omega z)[a_n\cos(\omega_n z)+b_n\sin(\omega_n z)]. \tag{24}$$

The quantities

$$p_n=\frac{a_n}{b_n}=\frac{\omega_n\cos X_n+\Omega\sin X_n}{\omega_n\sin X_n-\Omega\cos X_n} \tag{25}$$

when the eigenvalues have been determined, are known quantities. Consequently, it is possible to rewrite equation (23) in the form

$$\delta\rho(z,t)=\exp(-\Omega z)\sum_n b_n\exp\left(-\beta^2 t\right)\psi_n(z) \tag{26}$$

where

$$\psi_n(z)=\sin(\omega_n z)+p_n\cos(\omega_n z). \tag{27}$$

From equation (27) it follows that

$$\langle\psi_n|\psi_m\rangle=\int_{-d/2}^{d/2}\psi_n(z)\psi_m(z)\,\mathrm{d}z=0 \tag{28}$$

for $n\neq m$, and

$$\langle\exp(-\Omega z)|\psi_m\rangle=\int_{-d/2}^{d/2}\exp(-\Omega z)\psi_n(z)\,\mathrm{d}z=0 \tag{29}$$

Notice that

$$\begin{aligned}&\int_{-d/2}^{d/2}\delta\rho(z,t)\mathrm{d}z=\\&\sum_n b_n\exp\left(-\beta^2 t\right)\int_{-d/2}^{d/2}\exp(-\Omega z)\psi_n(z)\,\mathrm{d}z=0\end{aligned} \tag{30}$$

for equation (29). Consequently, equation (3) is verified for all t, as required.

It is now possible to determine the coefficients b_n appearing in equation (26). From the expression $\rho(z,t)=\rho_{\mathrm{eq}}(z)+\delta\rho(z,t)$ one has, in the limit $t=0$,

$$\delta\rho(z,0)=\rho_0-\rho_{\mathrm{eq}}(z). \tag{31}$$

By taking into account equation (26), one can rewrite (31) in the form

$$\sum_n b_n\psi_n(z)=f(z) \tag{32}$$

where, for equation (6),

$$\begin{aligned}f(z)&=\exp(\Omega z)\delta\rho(z,0)\\&=\rho_0\left[\exp(\Omega z)-\frac{\Omega d}{\sinh(\Omega d)}\exp(-\Omega z)\right].\end{aligned} \tag{33}$$

From equation (32), for (28), one obtains

$$b_m=\frac{1}{N_m}\int_{-d/2}^{d/2}f(z)\psi_m(z)\,\mathrm{d}z \tag{34}$$

where $N_m=\langle\psi_m|\psi_m\rangle$ is the square of the modulus of the eigenfunction ψ_m.

In the figure 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 $\tau_1\sim t_{\mathrm{D}}$, $\tau_1\sim t_{\mathrm{D}}t_{\mathrm{h}}/(t_{\mathrm{D}}+t_{\mathrm{h}})$, and $t_1\sim t_{\mathrm{h}}$. As evident from the figure (*c*), in the limit of large external field, that in practical terms means $V_0\gg\pi(k_{\mathrm{B}}T/q)\approx 0.075\,\mathrm{V}$, the equilibrium distribution is reached after a time $t_{\mathrm{eq}}\approx 0.4t_{\mathrm{D}}$.

5. Drift-diffusion phenomenon in nematic liquid crystals

The analysis described is, strictly speaking, valid only for isotropic liquids. The application of our results to nematic liquid crystals requires some supplementary hypothesis. As is well known, nematic liquid crystal 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 tensors of second order [30]. In particular, the dielectric constant, diffusion coefficient, and the ion mobility of the nematic medium, have different values along and perpendicular to the director. The tensors representing these are of the form

$$\begin{aligned}\varepsilon_{ij}&=\varepsilon_\perp\delta_{ij}+\varepsilon_a n_i n_j,\\D_{ij}&=D_\perp\delta_{ij}+D_a n_i n_j,\\\mu_{ij}&=\mu_\perp\delta_{ij}+\mu_a n_i n_j,\end{aligned} \tag{35}$$

where $\varepsilon_a=\varepsilon_\parallel-\varepsilon_\perp$, 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 and ion mobility depend on the nematic orientation, described by **n**.

Since we are considering a nematic sample subjected to an external field, other limitations on the values of the field have to be imposed. The nematic materials present an electric polarization connected with the nematic distortion that we have not considered in our analysis. 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 [17], the

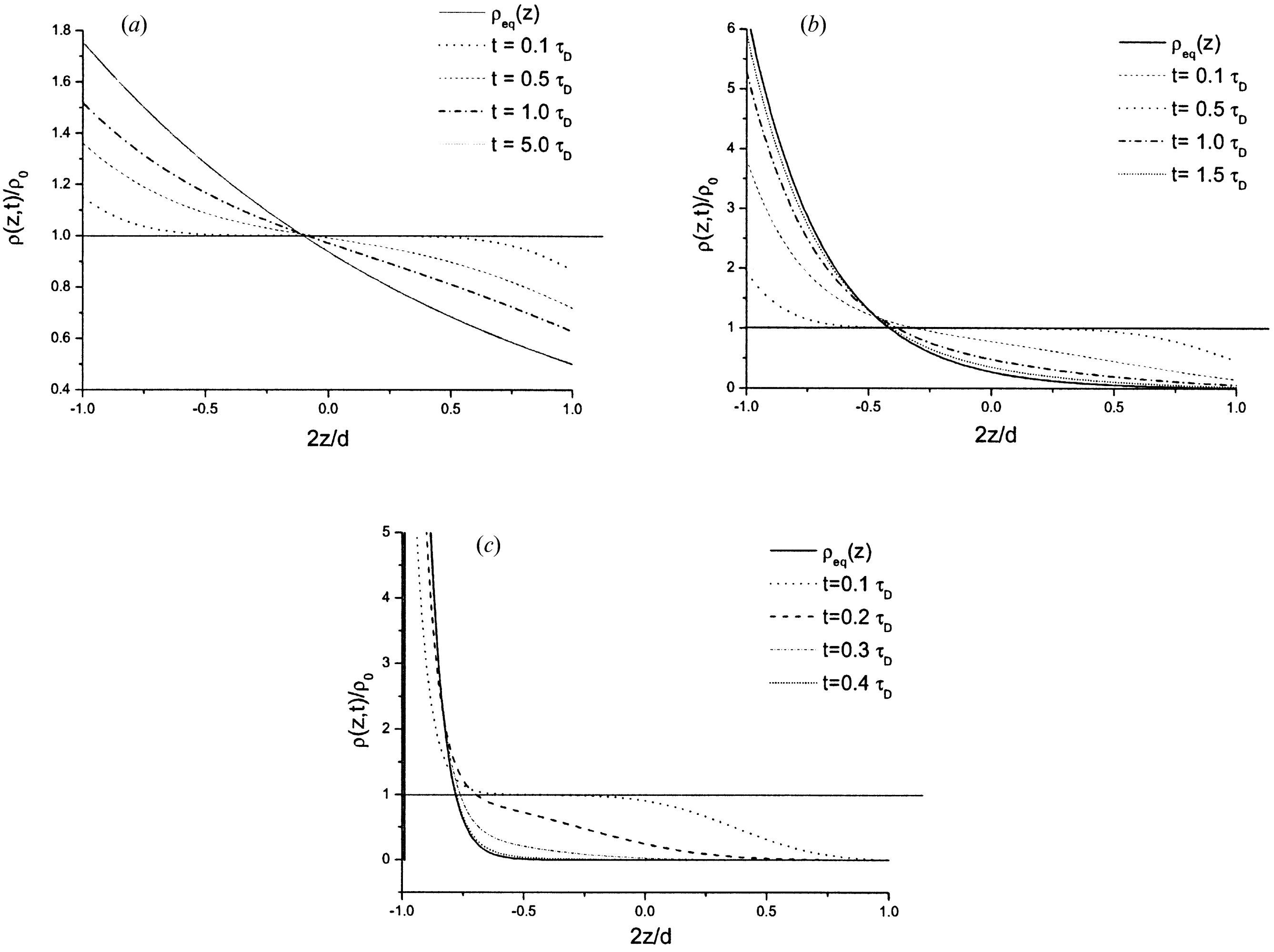

Figure. Time evolution of $\rho(z, t)$ for three typical values of the external voltage $V_0=\alpha\pi(k_BT/q)$ for (*a*) $\alpha=1/5$, (*b*) $\alpha=1$ and (*c*) $\alpha=5$.

analysis presented already gives the correct order of magnitude of the relaxation time for the ions in a nematic liquid crystals 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 $d\sim 8\,\mu m$, $D\sim 10^{-11}\,m^2\,s^{-1}$ [24] we have $t_D=d^2/(\pi^2 D)\sim 0.65\,s$, and hence $t_{eq}\approx 0.26\,s$. This means that the ions follow the external field variations, if the external field is changing with a characteristic time greater than 0.3 s. However, in the case in which the ions are macroparticles coming from the deterioration of the aligning layers [24], the time scale can be completely different. In this case for $D\sim 10-12\,m^2\,s^{-1}$, which corresponds to a radius of the ion of the order of 20 nm [24], we have $t_D\sim 6.5\,s$ and hence $t_{eq}\sim 2.6\,s$. In this situation, if the external field is changing with a period of the order of 1 s, the macroparticles coming from the surfaces do not contribute to the phenomenon. Of course, the ions dissolved in the liquid crystal, for which $D\sim 10-11\,m^2\,s^{-1}$, by contrast, do contribute. This conclusion may be of importance in the experimental determination of physical parameters of nematic liquid crystals when external electric fields are applied [14–16].

6. Conclusions

We have determined, in the limit of small ionic density, the intrinsic time connected with the presence of the external field on the ion redistribution. It has been found to be proportional to the drift-time and, depends 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, with 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.

Finally, the possible application of our analysis to the drift-diffusion of ions in nematic sample in the shape of a slab has been discussed. In this case we have shown that, although the mathematical description of the the phenomenon under consideration is more complicated, our model gives the correct order of magnitude of the relaxation time.

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Appendix

In our analysis we have solved the partial differential equation

$$\frac{\partial \rho}{\partial t}=D\frac{\partial^2 \rho}{\partial z^2}+\mu h\frac{\partial \rho}{\partial z} \tag{A1}$$

with the boundary condition

$$-D\frac{\partial \rho}{\partial z}-\mu h\rho=0 \tag{A2}$$

at $z=\pm d/2$, by taking into account the conservation of the number of particles expressed by the relation

$$\int_{-d/2}^{d/2}\rho(z,t)\,\mathrm{d}z=\rho_0 d. \tag{A3}$$

As stated in the text, equations (A1), (A2) and (A3) hold in the hypothesis that the adsorption from the surface can be neglected. The aim of this appendix is to discuss when this approximation works well.

In a real problem, when adsorption from the surface is present, the drift-diffusion equation has to be solved with the kinetic equation at the adsorbing surface. This equation describes the importance of the adsorption with respect to the desorption phenomenon. A form of this equation proposed by Maximus *et al.* [20] is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t}=\kappa\rho(-d/2,t)-\frac{1}{\tau}\sigma(t) \tag{A4}$$

where $\sigma(t)$ represents the surface density of adsorbed particles. The first contribution to the r.h.s of equation (A4), whose phenomenological coefficient is κ, is connected with the trapping of the particles from the bulk by the surface, whereas the second term is connected with the desorption of the particles already at the surface. The relevant phenomenological parameter is the desorption time τ. In this case equation (A1) has to be solved with the boundary condition

$$-D\frac{\partial \rho}{\partial z}-\mu h\rho=\frac{\mathrm{d}\sigma}{\mathrm{d}t} \tag{A5}$$

at $z=\pm d/2$. The new relationship taking into account the conservation of the number of particles is now

$$2\sigma(t)+\int_{-d/2}^{d/2}\rho(z,t)\,\mathrm{d}z=\rho_0 d. \tag{A6}$$

Let us introduce the reduced coordinates $z_{\mathrm{r}}=z/d$, $t_{\mathrm{r}}=t/\tau_{\mathrm{D}}$, and the characteristic times $\tau_{\mathrm{D}}=d^2/D$, $\tau_{\mathrm{F}}=d/(\mu h)$, $\tau_\kappa=d/(2\kappa)$, connected to the diffusion, to the drift under the external field, and to the adsorption, respectively. Finally we define the reduced densities $\rho_{\mathrm{r}}=\rho/\rho_0$, and $\sigma_{\mathrm{r}}=2\sigma/(\rho_0 d)$. In terms of the reduced quantities equations (A1), (A4) and (A6) read, respectively,

$$\frac{\partial \rho_{\mathrm{r}}}{\partial t_{\mathrm{r}}}=\frac{\partial^2 \rho_{\mathrm{r}}}{\partial z_{\mathrm{r}}^2}+\frac{\tau_{\mathrm{D}}}{\tau_{\mathrm{F}}}\frac{\partial \rho_{\mathrm{r}}}{\partial z_{\mathrm{r}}} \tag{A7}$$

$$\frac{\mathrm{d}\sigma_{\mathrm{r}}}{\mathrm{d}t_{\mathrm{r}}}=\frac{\tau_{\mathrm{D}}}{\tau_\kappa}\rho_{\mathrm{r}}(-1/2,t_{\mathrm{r}})-\frac{\tau_{\mathrm{D}}}{\tau}\sigma_{\mathrm{r}}(t_{\mathrm{r}}) \tag{A8}$$

and

$$\sigma_{\mathrm{r}}(t_{\mathrm{r}})+\int_{-1/2}^{1/2}\rho_{\mathrm{r}}(z_{\mathrm{r}},t_{\mathrm{r}})\,\mathrm{d}z_{\mathrm{r}}=1. \tag{A9}$$

From equation (A9) it follows that when $\tau_\kappa\gg\tau_{\mathrm{D}}$, and $\tau\gg\tau_{\mathrm{D}}$ the adsorbtion–desorption phenomenon from the limiting surfaces is negligible. Our analysis works in this case.

However, since we are mainly interested in the relaxation time of the ions dissolved in the liquid in the presence of an external electric field, our results are actually valid in general. The reason is the following. Usually, when an electric field is applied to a nematic liquid crystal the electrodes are covered with a thin layer of an insulating material, in order to avoid charge injection. This surface layer, in some cases, can also be used to orient the nematic liquid crystal. In this experimental situation, when the external field is switched on the ions present in the liquid crystal move close to the electrodes and screen the applied field. In any case, due to the presence of the insulating material, the current density $j(\pm d/2,t)=0$. Since, in our analysis the eigenvalues are connected with the boundary conditions $j(\pm d/2,t)=0$, the discussion presented in the paper relevant to the characteristic relaxation time remains unchanged.

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