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Adsorption phenomenon of neutral particles and a kinetic equation at the interface

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The adsorption phenomenon of neutral particles in a sample having the shape of a slab is theoretically investigated by using a particular form for the kinetic equation at the limiting surfaces. The time evolution of the bulk and surface densities is determined in a closed form by means of a simple expression. A discussion on the characteristic times entering in the problem is reported. Finally, a microscopic model giving rise to a kinetic equation similar to the one used in the analysis is proposed, and the phenomenological parameters determined. The analysis is suitable for the description of the adsorption phenomena of dyes in nematic liquid crystals.

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I. INTRODUCTION

In recent years several investigations on nematic liquid crystals doped with dyes have been published [1–5]. The main interest in this kind of research work 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 are selectively adsorbed by the limiting surfaces, and oriented by the nematic field. When the light incides on the surface covered by the dyes, 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 were proposed in Refs. [16,17].

In the present paper we analyze, theoretically, the adsorption phenomenon, obtaining a closed solution for the time evolution of the adsorbed dyes in terms of a series. We consider a simple kind of kinetic at the limiting surface able to reproduce the main characteristics of the problem. 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. We show also how to connect the phenomenological parameters entering in the kinetic equation with the parameters of the model. Our paper is organized as follows. In Sec. II the mathematical problem for the diffusion in the presence of adsorption-desorption is formulated. The relevant equation for the eigenvalues is discussed in Sec. III, whereas in Sec. IV the time evolution of the bulk and surface density of the particles is derived in a closed form. In Sec. V a microscopic model for the kinetic equation describing the adsorption-desorption phenomenon is proposed. Section VI is devoted to the conclusion.

II. THE MATHEMATICAL 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 $z=\pm d/2$. The problem is supposed one dimensional, where all physical quantities depend only on the z coordinates. If the adsorption phenomenon from the surfaces is taken into account, the bulk density of particles $\rho(z,t)$ is solution of the diffusion equation

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

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

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

and $j(-d/2,t)=d\sigma/dt$ [18], 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 [19]

$$\frac{d\sigma}{dt} = \kappa\, \rho(-d/2,t) - \frac{1}{\tau}\sigma(t), \tag{3}$$

where κ and τ are parameters describing the adsorption phenomenon. Equation (3) 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. In Eq. (3), τ has the dimension of time, whereas κ of a length/time. Consequently, if the adsorption phenomenon is present, there are two new intrinsic times, τ and $\tau_\kappa=d/2\,\kappa$.

To solve the problem one assumes that $\rho(z,t)=\rho_{eq}(z)+\delta\rho(z,t)$, where $\rho_{eq}(z)=\lim_{t\to\infty}\rho(z,t)$ is the distribution of the particles in the steady state. Hence, $\lim_{t\to\infty}\delta\rho(z,t)=0$. We assume also that $\sigma(t)=\sigma_{eq}+\delta\,\sigma(t)$, 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 Eq. (3) one obtains $\sigma_{eq}=\kappa\,\tau\,\rho_{eq}$. Equation (2), in the limit $t\to\infty$, becomes $2\sigma_{eq}+\rho_{eq}\,d=\rho_0 d$. Consequently, ρ_{eq} and σ_{eq} are found to be

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$$\rho_{\rm eq} = \frac{\rho_0}{1+2\ \kappa\ \tau/d} \quad \text{and} \quad \sigma_{\rm eq} = \frac{\kappa\tau/d}{1+2\kappa\tau/d}\rho_0 d. \tag{4}$$

The time evolution of $\delta\rho(z,t)$ and $\delta\sigma(z,t)$ can be now determined. By substituting $\rho(z,t)=\rho_{\rm eq}+\delta\rho(z,t)$ into Eq. (1) one obtains

$$\frac{\partial(\delta\rho)}{\partial t} = D\frac{\partial^2(\delta\rho)}{\partial z^2}, \tag{5}$$

whose solution can be written in the form

$$\delta\rho(z,t) = \sum_\beta C_\beta \cos(\omega_\beta\ z)\ e^{-\beta^2\ t}, \tag{6}$$

where $\omega_\beta=\beta/\sqrt{D}$, with $\beta\neq 0$. Moreover, by substituting the expressions for $\rho(z,t)$ and $\sigma(t)$ into Eq. (3), one has

$$\frac{d(\delta\sigma)}{dt} = \kappa\delta\rho - \frac{1}{\tau}\delta\sigma. \tag{7}$$

By Eq. (6) and Eq. (7), one obtains

$$\delta\sigma = Me^{-t/\tau} + \sum_\beta \delta\sigma_\beta\ e^{-\beta^2 t}, \tag{8}$$

where

$$\delta\sigma_\beta = \kappa\frac{C_\beta}{\tau^{-1}-\beta^2}\cos(\omega_\beta d/2), \tag{9}$$

and M must be determined by means of the condition concerning the conservation of the number of particles.

III. THE EIGENVALUES OF THE MATHEMATICAL PROBLEM

By substituting $\rho(z,t)$ and $\sigma(t)$ into Eq. (2) one gets

$$2\ \delta\sigma(t) + \int_{-d/2}^{d/2} \delta\rho(z,t)dz = 0, \tag{10}$$

that, for Eqs. (6) and (8), can be written as

$$M\ e^{-t/\tau} + \sum_\beta \left[\delta\sigma_\beta + \frac{C_\beta}{\omega_\beta}\sin(\omega_\beta d/2)\right] e^{-\beta^2 t} = 0, \tag{11}$$

from which, by taking into account Eq. (9), 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

$$\tan X_\beta = \left(\frac{\tau_D}{4\tau_\kappa}\right)\frac{X_\beta}{X_\beta^2-\tau_D/4\tau}, \tag{12}$$

where $X_\beta=\omega_\beta d/2$. In summary, three time scales govern the entire phenomenon, namely, $\tau_D=d^2/D$, $\tau_\kappa=d/2\kappa$, and τ. The eigenvalues of the problem depend on the two ratios τ_D/τ_κ and τ_D/τ.

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 Eq. (12) has a vertical asymptote at $X_\beta=\sqrt{\tau_D/4\tau}$. If $\tau_D\ll\tau$, Eq. (12) can be approximated by $X_\beta \tan X_\beta=\tau_D/(4\tau_\kappa)$, showing that X_β depends on τ_D/τ_κ. For $\tau_D\ll\tau_\kappa$, $X_\beta\sim\sqrt{\tau_D/4\tau_\kappa}$. In this case ($\tau_D\ll\tau$, $\tau_D\ll\tau_\kappa$), 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 $\tau_D\gg\tau$, Eq. (12) 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 $\tau_D/(4\pi^2)\leqslant\tau_R\leqslant\tau_D/\pi^2$. Finally, from Eq. (12) it follows that, for large X_β, i.e., $X_\beta\gg\sqrt{\tau_D/4\tau}$ the eigenvalues are $X_n\approx n\ \pi$.

IV. TIME EVOLUTION OF THE BULK AND SURFACE DENSITIES

If the eigenvalues are known, one can calculate the coefficients C_β appearing in Eq. (6) and determine $\delta\rho(z,t)$ and $\delta\sigma(t)$. From $\rho(z,t)=\rho_{\rm eq}+\delta\rho(z,t)$, written in the limit of $t\to 0$, one has $\delta\rho(z,0)=2[\tau/(\tau_\kappa+\tau)]\rho_0=2\ \sigma_{\rm eq}/d$, that, by using Eq. (6), becomes

$$\sum_\beta C_\beta\cos(\omega_\beta\ z) = \frac{2\ \sigma_{\rm eq}}{d}. \tag{13}$$

The main problem is that the eigenvectors $u_\beta=\cos(\omega_\beta\ z)$ are not orthogonal. In this case one can orthogonalyze the set of eigenvectors by a procedure similar to the Schmidt approach [20]. By indicating the eigenvalues with $\beta_1(\neq 0)$, β_2, $\beta_3,\ldots$, $\beta_n,\ldots$ one writes $u_i=\cos(\omega_{\beta_i}z)$, where u_i are linearly independent. It is possible to set $v_i=\lambda_{ij}u_j$, where $\lambda_{ij}=0$ for $i<j$, and $\lambda_{ii}=1$. Thus, the matrix $\mathbf{\Lambda}$, of elements λ_{ij} is such that $\det\Lambda=1$. The coefficients λ_{ij} for $i>j$ are determined by setting

$$\langle v_i|v_j\rangle = \int_{-d/2}^{d/2} v_i(z)v_j(z)dz = 0, \tag{14}$$

for $i\neq j$. The relation among v_i and u_i can be written in the matrix form as $\mathbf{v}=\Lambda\mathbf{u}$, from which $u_i=(\Lambda^{-1})_{ij}\ v_j$. Consequently, if Eq. (13) is written as $C_\beta u_\beta(z)=2\ \sigma_{\rm eq}/d$ one gets $C_\beta(\Lambda^{-1})_{\beta j}\ v_j=2\ \sigma_{\rm eq}/d$, from where

$$C_\beta(\Lambda^{-1})_{\beta j}\langle v_j|v_k\rangle = \frac{2\ \sigma_{\rm eq}}{d}\langle v_k\rangle, \tag{15}$$

with

$$\langle v_k\rangle = \int_{-d/2}^{d/2} v_k(z)dz. \tag{16}$$

Since $v_i(z)$ form a set of orthogonal functions, $\langle v_j|v_k\rangle=N_k\delta_{jk}$, where $N_k=\langle v_k|v_k\rangle$. Consequently, from Eq. (15), one deduces that $(\Lambda^{-1})_{\beta k}C_\beta=(2\ \sigma_{\rm eq}/d)\langle v_k\rangle/N_k$. In the matrix form one has for the preceding equation,

$$\mathbf{C} = \frac{2\sigma_{\rm eq}}{d}\Lambda^{\rm T}\ \mathbf{R}, \tag{17}$$

where $\mathbf{R}$ is the vector of elements $R_k=\langle v_k\rangle/N_k$ and $\Lambda^{\rm T}_{\beta,\alpha}=\Lambda_{\alpha,\beta}$. The coefficients one is looking for are then given by

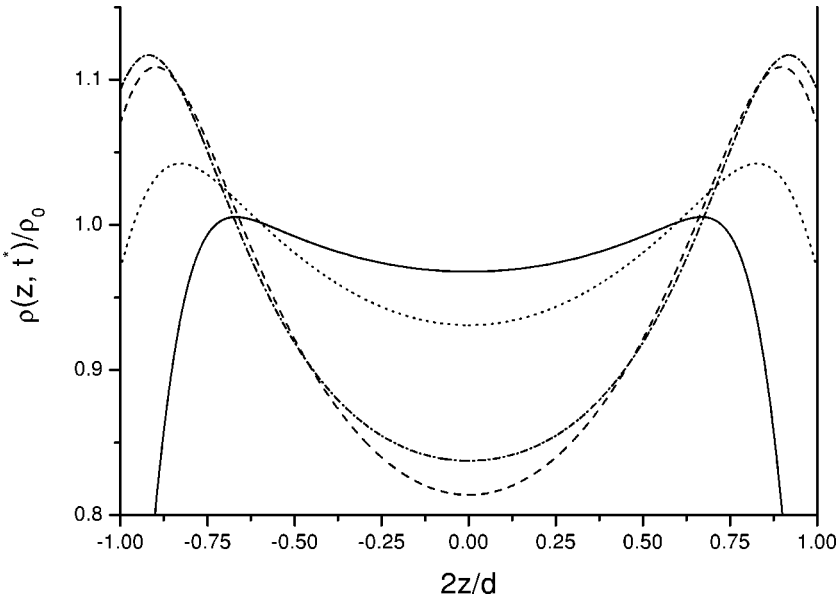

FIG. 1. Behavior of $\rho(Z,t^*)/\rho_0$ vs Z, as predicted by Eq. (21) for $t^*=4t/\tau_D=0.01$. The curves are depicted for a representative set of the parameters r_1 and r_2. Solid line corresponds to $r_1=10.0$ and $r_2=1.0$, dotted line to $r_1=1.0$ and $r_2=1.0$, dashed line to $r_1=1.0$ and $r_2=5.0$, and dashed dotted line to $r_1=1.0$ and $r_2=10.0$.

$$C_\beta = \frac{2\ \sigma_{\rm eq}}{d}\Lambda_{\alpha\beta}R_\alpha, \tag{18}$$

which represents the solution of the problem. There is another way to obtain explicit formulas connecting v_q with u_q, which gives directly the elements of the matrix Λ, and, consequently, the coefficients C_β. According to this alternative procedure the orthogonal vectors $v_k(z)$ are defined in terms of the vectors $u_n(z)$ by [21]

$$v_q = \sum_{n=1}^{q} \frac{M_{nq}}{M_{qq}} u_n, \tag{19}$$

where M_{nq} is the minor of the element

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

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 to be numerically implemented.

To study the time evolution of the densities, it is useful to rewrite the final equations governing them. The coefficient of the cosine in (9) can be set in the form

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

which, by using (12), 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 to rewrite (9) as

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

giving for $\sigma(t)$ the rescaled form,

$$\frac{2\ \sigma(t^*)}{d} = \rho_0\frac{r_1/r_2}{1+r_1/r_2} - \sum_\beta \frac{\sin X_\beta}{X_\beta}C_\beta\ e^{-X_\beta^2\ t^*}, \tag{20}$$

where $r_1=\tau_D/4\tau_\kappa$, $r_2=\tau_D/4\tau$, and $t^*=4t/\tau_D$. In the same manner, by considering that $\rho_{\rm eq}=\rho_0-2\sigma_{\rm eq}/d$, and using (6), one obtains

$$\rho(Z,t^*) = \rho_0\frac{1}{1+r_1/r_2} + \sum_\beta C_\beta\cos(X_\beta Z)\ e^{-X_\beta^2\ t^*}, \tag{21}$$

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

In Fig. 1 the behavior of $\rho(Z,t^*)/\rho_0$ vs Z, as predicted by Eq. (21), 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 Fig. 2 the behavior of $2\sigma(t)/\rho_0 d$, as predicted by Eq. (21), is shown as a function of the rescaled time $t^*=4t/\tau_D$ for three representative set of ratios r_1 and r_2. Solid curve was

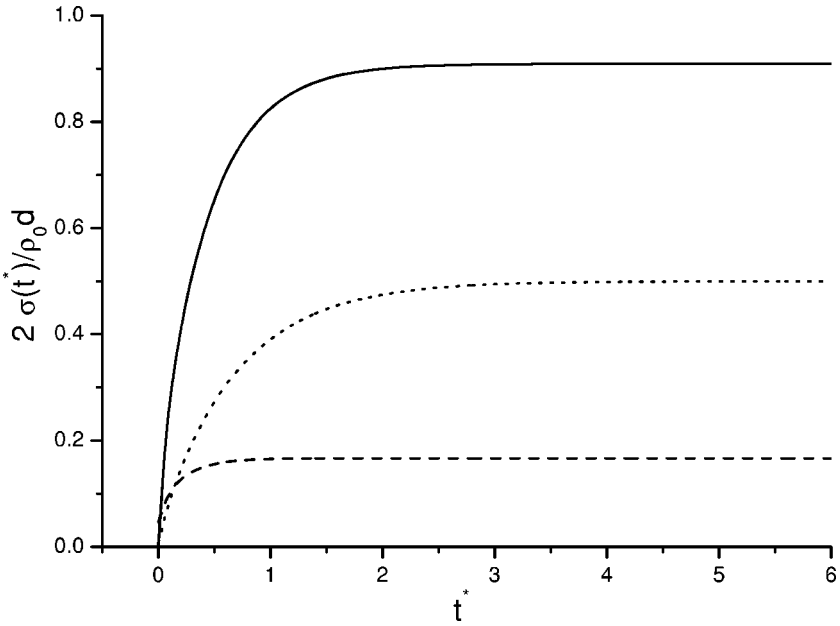

FIG. 2. Behavior of $2\sigma(t^*)/\rho_0 d$ vs $t^*=4t/\tau_D$. Solid line was depicted for $r_1=10.0$ and $r_2=1.0$, dotted line for $r_1=1.0$ and $r_2=1.0$, and dashed line for $r_1=1.0$ and $r_2=5.0$.

depicted 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 behavior of $\sigma(t)$ is such that $t^*=4t/\tau_D\approx 1$. For this case, numerical calculations give the first nonzero 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 greatest one among τ and τ_κ. Dotted curve was depicted for $r_1=r_2=1.0$, i.e., for $\tau_D=4\tau=4\tau_\kappa$. The first nonzero 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 behavior of $\sigma(t)$. Dashed curve refers to $r_1=1$ and $r_2=5$, i.e., for $\tau_D=20\tau=4\tau_\kappa$. Numerical calculations give $X_1=2.01$, $\tau_D\approx 3.5$, and $\tau_\kappa\approx 0.9$ *e* $\tau\approx 0.2$. In this case, the time behavior of $\sigma(t)$ is governed by τ_κ.

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

V. MICROSCOPIC MODEL FOR THE KINETIC EQUATION RELEVANT TO THE ADSORPTION-DESORPTION PHENOMENON

In a real problem one has a specie of particles interacting with the limiting surfaces via van der Waals forces, whose potential energy $U(z)$ is strongly localized close to the bounding surfaces [22]. In this situation, when the surfaces are absent, the density of particles is homogeneous across the sample. However, when the surfaces are switched-on, i.e., the interaction between the particles and the substrate is present, a current of drift takes place close to the boundary until the diffusion current balances the drift current. Our aim is now to show that the drift-diffusion problem in a system characterized by a potential localized on mesoscopic lengths close to the boundary can be used to interpret the kinetic equation at the adsorbing surface.

It is supposed that $U(z)$ can be approximated by

$$U(z)=\begin{cases} U_1(z)=h(z+z^*), & -d/2\leqslant z\leqslant z_1,\\ U_B(z)=0, & z_1\leqslant z\leqslant z_2,\\ U_2(z)=-h(z-z^*), & z_2\leqslant z\leqslant d/2,\end{cases} \tag{22}$$

where $h=dU/dz=U_0/\lambda$, $z_1=-z^*$, and $z_2=z^*$, with $z^*=d/2-\lambda$.

The problem under consideration concerns two surface layers where $dU(z)/dz=\text{const}$, and a bulk region where $U(z)=0$, and the current reduces to the diffusion current. The continuity equations in the three regions are

$$\frac{\partial\rho_\alpha}{\partial t}=-\frac{\partial j_\alpha}{\partial z}, \tag{23}$$

in the respective z regions, where $\alpha=1$, B, 2 and

$$j_\alpha=-\left(D\frac{\partial\rho_\alpha}{\partial z}+\varepsilon_\alpha\mu h\rho_\alpha\right) \tag{24}$$

with $\varepsilon_1=1$, $\varepsilon_B=0$, and $\varepsilon_2=-1$. Equation (23) must be solved with the boundary conditions

$$\rho_1(z_1,t)=\rho_B(z_1,t)\quad\text{and}\quad\rho_B(z_2,t)=\rho_2(z_2,t), \tag{25}$$

for what concerns the densities, and

$$j_1(-d/2,t)=0,\quad j_1(z_1,t)=j_B(z_1,t),$$

$$j_B(z_2,t)=j_2(z_2,t),\quad j_2(d/2,t)=0 \tag{26}$$

for what concerns the currents. By setting again $\rho_\alpha(z,t)=\rho_{\text{eq}\ \alpha}(z)+\delta\rho_\alpha(z,t)$, one obtains, by taking into account (25),

$$\rho_{\text{eq}\ \alpha}(z)=p\ \exp[-\mu\ U_\alpha(z)/D]. \tag{27}$$

The constant p is deduced by imposing

$$\int_{-d/2}^{d/2} \rho_{\rm eq}(z)dz = \rho_0\, d. \tag{28}$$

By using Eq. (27) and the Einstein-Smoluchowsky relation $\mu/D=1/k_BT$, we have

$$p = \rho_0\left\{1 + \frac{2\lambda}{d}\left[\frac{e^{U_0/k_BT}-1}{U_0/k_BT} - 1\right]\right\}^{-1}. \tag{29}$$

The functions $\delta\rho_\alpha(z,t)$ are solutions of the differential equations

$$\frac{\partial(\delta\rho_\alpha)}{\partial t} = D\frac{\partial^2(\delta\rho_\alpha)}{\partial z^2} - \varepsilon_\alpha \mu h \frac{\partial(\delta\rho_\alpha)}{\partial z}, \tag{30}$$

which are the continuity equations for the three layers.

For simplicity, in the analysis reported above, it is assumed that there is no adsorption on the limiting surfaces. However, since at the end, in the steady state, the density of the particles close to $z=\pm d/2$ will be larger than the one in the bulk, the considered system is, actually, a model for the adsorption. By comparing the results of the present analysis with the analysis of the adsorption from the surfaces, it is possible to connect the phenomenological parameters κ and τ appearing in Eq. (3) with the microscopic parameters U_0 and λ. According to Eq. (27), in the steady state the bulk density of particles is $\rho_{\rm eq}=\rho_{{\rm eq}\ B}=\rho_0/(1+2R)$, where, for Eq. (29),

$$R = \frac{\lambda}{d}\left[\frac{e^{U_0/k_BT}-1}{U_0/k_BT} - 1\right]. \tag{31}$$

Close to the bounding walls, for Eq. (27), the profiles of the particles density are $\rho_{{\rm eq}\ \alpha}=p\ \exp[-U_\alpha(z)/k_BT]$. Since $\lambda \ll d$ it is possible to introduce a surface density of particles by means of the relation

$$\sigma_{{\rm eq}\ 2} = \int_{z_2}^{d/2} [\rho_{{\rm eq}\ 2}(z) - \rho_{{\rm eq}\ {\rm B}}(z)]dz, \tag{32}$$

and a similar relation for $\sigma_{{\rm eq}\ 1}$. Simple calculations give $\sigma_{{\rm eq}\ 1}=\sigma_{{\rm eq}\ 2}=\sigma_{\rm eq}$, where $\sigma_{\rm eq}=[R/(1+2R)]\rho_0 d$.

By comparing $\rho_{\rm eq}$ and $\sigma_{\rm eq}$ obtained above with the ones given by (4) one obtains

$$\kappa\tau = \lambda\left[\frac{e^{U_0/k_BT}-1}{U_0/k_BT} - 1\right]. \tag{33}$$

In order to show that the system under consideration implies a kinetic equation at the surface of the kind (3), we define an effective surface density $\sigma(t)$ by means of the relation

$$\sigma_2 = \int_{z_2}^{d/2} [\rho_2(z,t) - \rho_{\rm B}(z,t)]\, dz \approx \int_{z_2}^{d/2} \rho_2(z,t)dz, \tag{34}$$

because λ is a mesoscopic length. We assume that in the surface layer the bulk density is well approximated by

$$\rho_2(z,t) = \rho_2(z_2,t) + \left(\frac{\partial\rho_2}{\partial z}\right)_{z_2}(z-z_2). \tag{35}$$

By substituting (35) into (34) we get

$$\left(\frac{\partial\rho_2}{\partial z}\right)_{z_2} \sim 2\frac{\sigma_2}{\lambda^2}. \tag{36}$$

Furthermore, from (34) by derivation with respect to t we have

$$\frac{d\sigma_2}{dt} \sim \int_{z_2}^{d/2} \frac{\partial\rho_2}{\partial t}dz, \tag{37}$$

that by using Eq. (23), the boundary conditions, Eqs. (25), (26), and (36) can be rewritten as

$$\frac{d\sigma_2(t)}{dt} = \mu\, h\rho_B(z_2,t) - \frac{2\,D}{\lambda^2}\sigma_2(t), \tag{38}$$

which coincides with the kinetic equation written on phenomenological ground at the adsorbing surface, i.e., Eq. (3). Hence, by comparing Eq. (38) with Eq. (3) we deduce that $\kappa=\mu\, h$ and $1/\tau=2D/\lambda^2$. Therefore $\kappa\,\tau/\lambda=U_0/(2\,k_BT)$, which coincides with the power expansion of Eq. (33) in the limit of $U_0 \ll k_BT$. With this type of analysis it is possible to connect, 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 [23].

To compare the predictions of our model with the experimental results is a difficult task for the following reason. The adsorption phenomenon is expected to play an important role on the surface properties of nematic liquid crystals doped with dyes, as discussed in the Introduction. However, no experiments on the time dependence of the surface concentration of dyes have been published until now. The experimental analysis quoted in the Introduction usually refer to the steady state, when σ has reached $\sigma_{\rm eq}$. We hope that our theoretical investigation can stimulate research work in this direction.

On the contrary, the time dependence of the adsorption phenomenon has been considered to analyze the influence of the ions on the optical transmission of a nematic cell submitted to an external electric field. According to Zhang and D'Have' $\kappa \sim 10^{-6}$ m/s and $\tau \sim 10^{-3}$ s [24]. By assuming $D \sim 10^{-12}$ m^2/s, as reported by Sawada *et al.* [25], for large ions, we obtain $U_0/(k_BT) \sim 0.1$ and $\lambda \sim 10$ nm. These values are quite reasonable when the adsorbed particles are ions in a nematic liquid crystal having an average dielectric constant of the order of 20 ϵ_0, where ϵ_0 is the dielectric constant of the vacuum. We are aware that this system is rather different from the one considered in our analysis, because in this case, in the bulk also a drift current is present. However, since for this system the proposed model predicts reasonable values for the adsorption energy and for the range of the surface forces, our assumptions are probably correct.

VI. CONCLUSION

We have theoretically analyzed the diffusion phenomenon in a sample in the shape of a slab, in the presence of the adsorption-desorption phenomenon. The kinetic equation on the limiting surfaces describing the adsorption process is assumed to have two terms. One proportional to the bulk den-

sity of particles just in front to the adsorbing surfaces and another one proportional to the surface density of particles already adsorbed. The first term gives a positive contribution, whereas the second term gives a negative contribution to the time variation of the surface density of adsorbed particles. We evaluated the time variation of the bulk and surface density of particles, and the characteristic times entering in the problem. Finally, by means of a simple microscopic model we have justified the kinetic equation used in our analysis and evaluated the phenomenological parameters entering in the kinetic equation at the interfaces. Our model predicts for the case in which the adsorbed particles are ions dissolved in a nematic liquid crystal reasonable values for the adsorption energy and range of the surface forces.

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