Adsorption–desorption phenomena and diffusion of neutral particles in the hyperbolic regime

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Abstract
The adsorption phenomenon of neutral particles from the limiting surfaces of the sample in the Langmuir approximation is investigated. The diffusion equation regulating the redistribution of particles in the bulk is assumed to be of hyperbolic type, in order to take into account the finite velocity of propagation of the density variations. We show that in this framework the condition on the conservation of the number of particles gives rise to a non-local boundary condition. We solve the partial differential equation relevant to the diffusion of particles by means of the separation of variables, and present how it is possible to obtain approximated eigenvalues contributing to the solution. The same problem is faced numerically by a finite difference algorithm. The time dependence of the surface density of adsorbed particles is deduced by means of the kinetic equation at the interface. The predicted non-monotonic behavior of the surface density versus the time is in agreement with experimental observations reported in the literature, and is related to the finite velocity of propagation of the density variations.

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(Some figures may appear in colour only in the online journal)
1. Introduction

The standard analysis of the adsorption phenomenon is made by means of the diffusion equation, in the framework of the Langmuir approximation [1]. In this scenario, to dynamically describe the adsorption–desorption process in confined systems, the diffusion equation has to be solved in order to obtain the bulk density of particles, and a kinetic balance equation has to be imposed at the interface to determine the time dependence of the particles’ surface density [1, 2]. For some systems, the temporal behavior of the surface density of adsorbed particles may be non-monotonic, presenting some kind of oscillatory behavior, and tending to a saturation value only for large enough time [3]. This may happen because, in the complex adsorption phenomenon occurring at a solid surface, the collision of a molecule can be represented by at least three different processes. The simplest one is an elastic scattering that occurs when there is no loss of translational energy during the collision of the molecule at the interface. Frequently, however, if the molecule is in a weakly bound state, then the thermal motion of the surface atoms can cause the molecule to undergo desorption. Finally, when the molecule collides with the surface, it may lose energy and is converted into a state where it remains on the surface for a reasonable time, i.e., it sticks [4]. Thus, for a more general process it is reasonable to assume that the actual position of the molecule on the surface has some kind of ‘memory’ of its incoming state, eventually modifying the adsorption–desorption rates. One way of incorporating memory effects in the adsorption phenomena is to propose a modified kinetic equation in which the suitable choice for a temporal kernel in the desorption rate can account for the relative importance of physisorption or chemisorption, according to the time scale governing the adsorption phenomena [3, 6]. This approach focuses on the surface behavior. Another way to face the problem is to consider that the density becomes a non-Markovian process and the diffusion equation is given by a persistent-random-walk process [8]. To account for this new effect, the current density of diffusing particles is assumed to satisfy the non-Fickian Maxwell–Cattaneo relationship. Indeed, in 1948 Cattaneo proposed a new constitutive equation that contains a new term and changes the Fourier equation into a hyperbolic one, whose solution propagates at finite velocity [9, 10]. In this modified scenario, the behavior of the bulk density of particles is governed by Cattaneo’s equation, while the usual kinetic equation governs the adsorption–desorption rates at the interface (Langmuir’s approximation). This implies that the diffusional process will not be described in the parabolic regime, as is usually done in the classical Fourier approach for heat propagation, but will be considered in the hyperbolic regime [11]. In this framework, due to the finite velocity propagation of the solution in a confined sample, one expects that a non-monotonic behavior for the density of particles at the surface may be found for suitable values of the parameters entering the model. Recently, a comparative analysis of the predictions of the diffusive models in the hyperbolic and parabolic regimes was carried out theoretically [12]. By employing two types of initial Gaussian-type distributions of the diffusing particles, namely, one centered around the symmetry surface in the middle of the sample and another localized close to the limiting surfaces, it was shown that the evolution toward the equilibrium distribution is not monotonic.

An alternative approach that considers the diffusion processes in a more general framework may be represented by the use of fractional operators, i.e. derivatives with non-integer orders [13]. In this case, the fractional exponent of the time derivative is assumed to lie between 1 and 2, representing the two limit situations of a parabolic equation and a hyperbolic equation. In describing anomalous transport in the framework of the fractional dynamics [14], even the generalized Cattaneo equation may be used to approach anomalous transport processes [15]. In general, anomalous behavior is usually related to the non-Markovian [7] characteristics of the
systems such as memory effects, fractality and interactions. This rich class of phenomena may be conveniently faced by the methods recently proposed to investigate anomalous diffusion, employing the techniques of fractional calculus and its applications in physics [16–23]. Thus, the physical scenarios represented by Cattaneo-like approaches and fractional calculus may be connected to explore non-usual diffusive behavior. In this optic, the present analysis may be revealed to be useful to also generalize the results recently found investigating the diffusion process in non-local solid mechanics [24, 25].

The organization of the paper and the main achievements are as follows. In section 2, a statement of the mathematical problem is given in terms of the usual diffusion equation and the kinetic equation at the interface is introduced. The condition stating the conservation of the number of particles is also imposed and a set of fundamental equations governing the parabolic regime is established. In section 3, the problem is reformulated in terms of a hyperbolic diffusion equation to account for the finite velocity of propagation of the density variations. There it is shown that the condition on the conservation of the number of particles leads to a non-local boundary condition. In section 4, we formally solve the partial differential equation relevant to the diffusion of particles by means of the separation of variables, and show how it is possible to obtain approximated values for the eigenvalues for the considered problem. In section 5, analytical results for the bulk and surface densities are obtained by means of an orthogonalization process that is also discussed in some detail. Since the same problem is numerically solved (section 6), we dedicate section 7 to present some relevant results obtained by the two strategies employed in the paper. The paper ends with some concluding remarks on the predictions of the hyperbolic model and its relevance in experimental contexts.

2. Position of the problem

In the following, we will consider the simple case of a confined sample in the shape of a slab of thickness \(d\), limited by two identical, adsorbing surfaces. In this case the problem is one-dimensional. We use a Cartesian reference frame having the \(z\)-axis perpendicular to the limiting surfaces, placed at \(z = \pm d/2\). We assume that at \(t = 0\) the distribution of particles across the sample is constant, characterized by a bulk density \(n_0\), and the adsorbing surfaces are not working. For \(t > 0\), the surfaces start to adsorb the particles, and the bulk density of particles changes with \(t\), until a new equilibrium distribution is reached, \(n_{eq}\). We assume that the adsorption phenomenon is related to a localized (short range) energy due to the surfaces. In this situation, the bulk density of equilibrium is homogeneous across the sample, and the adsorption phenomenon is related to the surface density of adsorbed particles, \(\sigma\). Hence, in the case we are considering \(n(z, t)\) passes from \(n_0\) to \(n_{eq}\) and \(\sigma\) from 0 to \(\sigma_{eq}\). In this case the fundamental equation of the problem is

\[
\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2},
\]

(1)

for the bulk, that has to be solved with the kinetic equation at the surfaces

\[
\frac{d\sigma}{dt} = k_d n_i(t) - \frac{1}{\tau_a} \sigma(t),
\]

(2)

where \(n_i(t) = n(\pm d/2, t)\) is the density of particles just in front of the limiting surfaces, and \(k_d\) and \(\tau_a\) are two phenomenological parameters related to the adsorption phenomenon in the Langmuir approximation. Since the particles cannot leave the sample we also have the condition

\[
\int_{-d/2}^{d/2} n(z, t) \, dz + 2\sigma(t) = n_0 d,
\]

(3)
in our symmetric problem, where \(\sigma(t)\) is the surface density of an adsorbed particle on the surfaces at \(z = \pm d/2\). In the simple case where the bulk differential equation is the diffusion equation, (1), equation (3) is equivalent to
\[
-D \left( \frac{\partial n}{\partial z} \right) = \frac{d\sigma}{dt},
\]
at \(z = \pm d/2\). Note that with our hypotheses \(n(z, t) = n(-z, t)\) and the two boundary conditions (4) reduce to only one equation, which is of local type. This means that \((\partial n/\partial z)(\pm d/2, t)\) depends only on surface density \(\sigma_{\pm}(t)\).

The solution of this problem predicts a monotonic increasing of \(\sigma\) from 0 to \(\sigma_{eq}\) [1]. On the contrary, experimental observations indicate a non-monotonic increasing of \(\sigma = \sigma(t)\) [3, 26].

3. Hyperbolic generalization

A theoretical attempt to interpret the experimental data has been done by modifying the kinetic equation at the limiting surfaces [5–7]. As stated above, according to this point of view, the non-monotonic behavior of the surface density of adsorbed particles versus the time has a surface origin, and it is taken into account by a modification of the standard Langmuir adsorption isotherm. Our aim is to show that non-monotonic behavior of \(\sigma = \sigma(t)\) could also have a bulk origin, related to the finite velocity of the bulk variation density.

As is well known, equation (1) is based on the assumption that the transmission of bulk density takes place with infinite velocity [27]. For this reason we modify equation (1) in an equation of hyperbolic type as follows [9]
\[
\tau_r \frac{\partial^2 N}{\partial t^2} + \frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial z^2},
\]
where \(\tau_r\) is a characteristic time related to the medium in which the particles are dispersed, and \(c_{\text{b}} = \sqrt{D/\tau_r}\) is the velocity of the bulk variations of density. The fundamental equations of our problem are equation (5), that has to be solved with equation (2) describing the adsorption phenomenon, and equation (3), stating the conservation of the number of particles. Note that the present case, from equation (3), does not follow a boundary condition of type (4) because the density of the current is no longer given by \(j = -D(\partial n/\partial z)\). In other words, when the fundamental equation of the problem is equation (5), equation (3) cannot be reduced to a local boundary condition.

We write equations (2)–(5) in dimensionless form. To this end we introduce the quantities \(N = nd, L = k_0\tau_a/d, A = \tau_a/\tau_D, B = \tau_r/\tau_D\), the reduced coordinates \(z^* = z/d\) and \(t^* = t/\tau_D\), where \(\tau_D = d^2/D\) is the standard diffusion time. Note that \(\ell = k_0\tau_a\) is an intrinsic length related to the adsorption. In terms of the reduced coordinates the equations of the problem are
\[
\frac{B}{\tau^*} \frac{\partial^2 N}{\partial t^*^2} + \frac{\partial N}{\partial t^*} = \frac{\partial^2 N}{\partial z^*^2},
\]
for \(-1/2 \leq z^* \leq 1/2\), with the kinetic equation
\[
A \frac{d\sigma}{d t^*} = LN_{\sigma}(t^*) - \sigma(t^*),
\]
where \(N_{\sigma}(t^*) = N(\pm 1/2, t^*)\), and the equation stating the conservation of particles
\[
\int_{-1/2}^{1/2} N(z^*, t^*) \, dz^* + 2\sigma(t^*) = N_0,
\]
where \( N_0 = n_0 d \). For \( t^* = 0 \) the surface density of the particle is such that \( \sigma(0) = 0 \). Consequently the initial time derivative of \( \sigma \), as it follows from equation (7), is

\[
\left( \frac{d\sigma}{dt^*} \right)_0 = \frac{L}{A} N_i(0),
\]

independent of \( B \).

In the final state of equilibrium, for \( t^* \to \infty, N \to N_{eq} \) and \( \sigma \to \sigma_{eq} \). These quantities, according to equations (7) and (8), are given by

\[
N_{eq} = N_0 \left( \frac{1}{1 + 2L} \right) \quad \text{and} \quad \sigma_{eq} = N_0 \frac{L}{1 + 2L}.
\]

The equations of the problem, equations (6)–(8), have to be solved by taking into account the initial distribution of particles, i.e. the distribution of \( N(z^*, t^*) \) and its \( t^* \)-derivative at \( t^* = 0 \). A simple inspection allows us to show that these two quantities are not independent. In fact, from equation (8) it follows that

\[
\sigma(t^*) = \frac{1}{2} \left[ N_0 - \int_{-1/2}^{1/2} N(z^*, t^*) \, dz^* \right],
\]

whose \( t^* \)-derivative is, for \( t^* \geq 0 \),

\[
\left( \frac{d\sigma}{dt^*} \right) = -\frac{1}{2} \int_{-1/2}^{1/2} \frac{\partial N}{\partial t^*} \, dz^*.
\]

In the limit \( t^* \to 0 \), equation (12) yields

\[
\left( \frac{d\sigma}{dt^*} \right)_0 = -\frac{1}{2} \int_{-1/2}^{1/2} \left( \frac{\partial N}{\partial t^*} \right)_0 \, dz^*.
\]

By comparing equation (13) with equation (9), one obtains

\[
\int_{-1/2}^{1/2} \left( \frac{\partial N}{\partial t^*} \right)_0 \, dz^* = -2 \frac{L}{A} N_i(0).
\]

As stated above, for a regular solution of our problem \( N \) and its \( t^* \)-derivative have to satisfy a condition of compatibility. In our analysis, the particles can be found in the volume or on the surface, but for \( t^* = 0 \) all the particles are only in the bulk. For this reason, we assume that for \( t^* = 0 \) the initial distribution of particles \( N(z^*, 0) \) is such that \( N_i(0) = N(\pm 1/2, 0) = 0 \), and \( N(z^*, 0) = N_0 \) for \( z^* \neq \pm 1/2 \). With this assumption, from equation (14) we get for the initial conditions of the problem relevant to the regular solution

\[
\left( \frac{\partial N}{\partial t^*} \right)_0 = 0, \quad \text{and} \quad N(z^*, 0) = N_0 [\theta(z^* + 1/2) - \theta(z^* - 1/2)],
\]

where \( \theta(x) \) is the Heaviside step function such that \( \theta(x) = 0 \) for \( x < 0 \), and \( \theta(x) = 1 \) for \( x > 0 \). In this framework, from equation (9) it follows that

\[
\left( \frac{d\sigma}{dt^*} \right)_{t^*=0} = 0,
\]

indicating that for \( t^* = 0 \) the time derivative of the surface density of adsorbed particles is continuous.

4. Eigenvalues and eigenvectors

We look for a solution of equation (6), with the conditions (7) and (8), of the form

\[
N(z^*, t^*) = N_{eq} + \eta(z^*, t^*) \quad \text{and} \quad \sigma(t^*) = \sigma_{eq} + s(t^*),
\]

indicating that for \( t^* = 0 \) the time derivative of the surface density of adsorbed particles is continuous.
where
\[
\lim_{t^* \to \infty} \eta(z^*, t^*) = 0 \quad \text{and} \quad \lim_{t^* \to \infty} s(t^*) = 0.
\] (18)

In terms of \(\eta(z^*, t^*)\) and \(s(t^*)\), equations (6)–(8) read
\[
B \frac{\partial^2 \eta}{\partial t^* \partial z^*} + \frac{\partial \eta}{\partial t^*} = \frac{\partial^2 \eta}{\partial z^* \partial z^*}, \quad (19)
\]
\[
A \frac{ds}{dt^*} = L \eta - s, \quad (20)
\]
\[
\int_{-1/2}^{1/2} \eta(z^*, t^*) \, dz^* + 2s(t^*) = 0. \quad (21)
\]

In equation (19), \(B\) is a small parameter, since we expect the velocity of the transmission of the information to be finite, but large. However, the limit operation of \(B \to 0\) cannot be directly performed because in this limiting operation the differential equation passes from the hyperbolic to the parabolic type. The point \(B = 0\) is thus a singular point [28]. Equations (6)–(8) can be solved by separating the variables. By putting
\[
\eta(z^*, t^*) = U(z^*) V(t^*), \quad (22)
\]
equation (19) can be rewritten as
\[
\frac{1}{V} \left( B \frac{d^2 V}{dt^*^2} + \frac{dV}{dt^*} \right) = \frac{1}{U} \frac{d^2 U}{dz^*^2} = -\alpha^2, \quad (23)
\]
where the separation constant \(\alpha^2\) has its real part positive, in such a manner that equation (18) are verified. From equation (23) we get
\[
B \frac{d^2 V}{dt^*^2} + \frac{dV}{dt^*} + \alpha^2 V = 0 \quad (24)
\]
\[
\frac{d^2 U}{dz^*^2} + \alpha^2 U = 0. \quad (25)
\]
Since equation (24) has constant coefficients, its solutions are of the kind \(V = P \exp(\mu t^*)\), where the characteristic exponents are given by
\[
\mu_{1,2}(\alpha) = -\frac{1}{2B} \left( 1 \pm \sqrt{1 - 4\alpha^2 B} \right). \quad (26)
\]
Note that, for fixed \(\alpha\), in the limit \(B \to 0\), from equation (26) we get \(\mu_1 \to -1/B\), and \(\mu_2 \to -\alpha^2\). This means that in the considered limit \(\mu_1 \to -\infty\), whereas \(\mu_2\) tends to a finite quantity.

The function \(V(t^*)\) we are looking for is
\[
V_\alpha(t^*) = P_{1\alpha} \exp(\mu_1 t^*) + P_{2\alpha} \exp(\mu_2 t^*), \quad (27)
\]
where \(P_{1\alpha}\) and \(P_{2\alpha}\) are the integration constants to be determined. By taking into account the symmetry of the problem, the solution of equation (25) is
\[
U_\alpha(z^*) = Q_\alpha \cos(\alpha z^*), \quad (28)
\]
where \(Q_\alpha\) is a new constant to be determined. The solution of equation (19) can be expressed in the form
\[
\eta_\alpha(z^*, t^*) = \eta_{1\alpha}(z^*, t^*) + \eta_{2\alpha}(z^*, t^*), \quad (29)
\]
where
\[
\eta_{1\alpha}(z^*, t^*) = S_{1\alpha} \cos(\alpha z^*) \exp(\mu_1 t^*), \quad (30)
\]
with $S_1(\alpha) = P_{1,\alpha} Q_{\alpha}$, and similar relations being valid for $\eta_{2\alpha}(z^*, t^*)$ and $S_{2\alpha}$. The functions $\eta_{1\alpha}$ and $\eta_{2\alpha}$ are two linearly independent solutions.

Let us now consider equation (20). After integration we get

$$s(t^*) = e^{-t^*/\Lambda} \left[ \frac{L}{A} \int_0^{t^*} e^{t^*/\Lambda} \eta(1/2, t) \, dt + M \right].$$

(31)

This relation, written for the mode $\eta_{1\alpha}(z^*, t^*)$, after taking equation (30) into account, becomes

$$s_{1\alpha} = \frac{L}{1 + \mu_1 A} S_{1\alpha} \cos(\alpha/2) \left[ e^{t^*/\Lambda} + \frac{M_{1\alpha} - L}{1 + \mu_1 A} S_{1\alpha} \cos(\alpha/2) \right] e^{-t^*/\Lambda}.$$

(32)

A similar relation holds for $s_{2\alpha}$. By imposing now condition (21) for the mode $\eta_{1\alpha}(z^*, t^*)$ and $\eta_{2\alpha}(z^*, t^*)$ we get the eigenvalues equations

$$f_1(\alpha') = \frac{1}{\alpha'} \tan(\alpha'/2) + \frac{L}{1 + \mu_1 A} = 0$$

(33)

$$f_2(\alpha'') = \frac{1}{\alpha''} \tan(\alpha''/2) + \frac{L}{1 + \mu_2 A} = 0,$$

(34)

for the eigenvalues $\alpha'$ and $\alpha''$, and

$$M_{1\alpha} = \frac{L}{1 + \mu_1 A} S_{1\alpha} \cos(\alpha'/2)$$

(35)

$$M_{2\alpha} = \frac{L}{1 + \mu_2 A} S_{2\alpha} \cos(\alpha''/2),$$

(36)

for the integration constants appearing in equation (31) for the two modes. A simple analysis allows us to verify that the eigenfunctions $\varphi_{\alpha} = \cos(\alpha z^*)$ are not orthogonal in $-1/2 \leq z^* \leq 1/2$. In fact, for two different $\alpha$, solutions of equation (33) we call $\alpha_a$ and $\alpha_b$, we have

$$(\varphi_a, \varphi_b) = \int_{-1/2}^{1/2} \cos(\alpha_a z^*) \cos(\alpha_b z^*) \, dz^* = -2 \frac{L}{\alpha_a^2 - \alpha_b^2} \frac{\alpha_a^2}{1 + \mu_1 \alpha_a A} - \frac{\alpha_b^2}{1 + \mu_1 \alpha_b A} \cos(\frac{\alpha_a}{2}) \cos(\frac{\alpha_b}{2}) = 0.$$}

(37)

Hence, to use the eigenfunctions we have to orthogonalize the set of $\varphi_{\alpha} = \cos(\alpha z^*)$.

By taking into account equation (26), it follows that the critical exponents $\mu_{1,2}$ are real only for $\alpha < 1/(2\sqrt{B})$. Since the physical meaning of $\alpha^2$ is the relaxation time, it follows that the dimensionless relaxation time related to the phenomenon under investigation has a critical behavior around $4B$, or, in absolute units, around $4\tau_c$. Note that, for $\alpha > 1/(2\sqrt{B})$, equations (33) and (34) have no solutions. This means that the number of eigenvalues is finite for $B = 0$. Consequently the number of eigenfunctions is finite too, and the relevant set of eigenfunctions is not complete. It follows that is impossible to satisfy the initial boundary conditions of the problem if one tries to solve it by means of the separation of variables.

In figure 1 we show, for a given set of $A$, $B$, and $L$, the eigenvalues determined by means of equations (33) and (34). As is clear, the eigenvalues $\alpha'$ and $\alpha''$ are close to $\alpha_m = 2n\pi$, where $m$ is an integer. As underlined above, for $\alpha > 1/(2\sqrt{B})$ the characteristic exponents are complex and conjugated, and given by

$$\mu_{1,2} = -\frac{1}{2B} \left( 1 \pm i \sqrt{4\alpha^2 B - 1} \right).$$

(38)

In this framework the real and imaginary parts of the eigenvalue equation $\mathcal{E}$ are

$$\text{Re}[\mathcal{E}] = \frac{1}{\alpha} \tan\left(\frac{\alpha}{2}\right) + \frac{2B(2B - A)}{(2B - A)^2 + A^2(4\alpha^2 B - 1)},$$

(39)
Figure 1. The behavior of $f_1(\alpha)$, given by equation (33) (black), and of $f_2(\alpha)$, given by equation (34) (red), versus $\alpha$ showing the zeros corresponding to the eigenvalues $\alpha'$ and $\alpha''$, for $A = 0.5, B = 10^{-3}$ and $L = 0.1$.

\[
\text{Im}[\mathcal{E}] = \pm \frac{2BA\sqrt{4\alpha^2B - 1}}{(2B - a)^2 + A^2(4\alpha^2B - 1)}, \tag{40}
\]

where $+$ and $-$ refer to $\alpha'$ and $\alpha''$, respectively. A simple inspection shows that $\text{Re}[\mathcal{E}] = 0$ has infinite solutions, whereas $\text{Im}[\mathcal{E}] = 0$ has no solutions. In figure 2 we show $\text{Re}[\mathcal{E}]$ and $\text{Im}[\mathcal{E}]$ versus $\alpha$. As is clear from the figure, for a given $\alpha$, different from the solution of $\text{Re}[\mathcal{E}] = 0$, $\text{Re}[\mathcal{E}] \gg \text{Im}[\mathcal{E}]$. In addition, we underline that, for $\alpha < 1/(2\sqrt{B})$, the eigenvalues of equation (34) are very close to those of $\text{Re}[\mathcal{E}] = 0$. The same conclusion holds true for the eigenvalues of equation (33), except for the first one. For this reason, in the following we neglect the small imaginary part of the eigenvalue equation, and assume that the solutions of $\text{Re}[\mathcal{E}] = 0$ represent an approximation for the eigenvalues of the problem, which we indicate simply by $\alpha$.

5. Initial conditions

The solution of the problem under study, due to the linear character of equation (19) and of the conditions (20) and (21), is

\[
\eta(z^*, t^*) = \sum_{\{\alpha\}} \left[ S_{1,\alpha} \exp[\mu_1(\alpha)t^*] + S_{2,\alpha} \exp[\mu_2(\alpha)t^*] \right] \cos(\alpha z^*), \tag{41}
\]

where the $\alpha$ are the solutions of $\text{Re}[\mathcal{E}] = 0$, $\mu_{1,2}(\alpha)$ given by equations (26), and $S_{1,\alpha_1} = 0$ for the reason discussed above. The coefficients $S_{1,\alpha}$ and $S_{2,\alpha}$ have to be determined by means of the initial conditions on $N(z^*, t^*)$ and $\partial N/\partial t^*$ for $t^* = 0$.

The initial conditions on $\eta(z^*, t^*)$ are such that

\[
\eta(z^*, 0) = N(z^*, 0) - N_{\text{eq}} \quad \text{and} \quad \left( \frac{\partial \eta}{\partial t^*} \right)_{t^*=0} = 0, \tag{42}
\]
Figure 2. (a) The behavior of the real part of equations (33) (black thick lines), (34) (red dashed lines) and \( \text{Re}[\xi] \) (blue dotted lines), as given by equation (39), versus \( \alpha \) for \( A = 0.5, B = 10^{-3} \) and \( L = 0.1 \). (b) The same for the imaginary part of equations (33) (black thick lines) and the negative of the imaginary part of equations (34) (red dashed lines).

where \( N(z^*, 0) \) is defined in equation (15). By means of equation (41), equation (42) can be rewritten as

\[
\sum_{\alpha} (S_{1,\alpha} + S_{2,\alpha}) \cos(\alpha z^*) = N(z^*, 0) - N_{eq} \tag{43}
\]

\[
\sum_{\alpha} [\mu_1(\alpha) S_{1,\alpha} + \mu_2(\alpha) S_{2,\alpha}] \cos(\alpha z^*) = 0. \tag{44}
\]

From equation (44) it follows that

\[
S_{2,\alpha} = -\frac{\mu_1(\alpha)}{\mu_2(\alpha)} S_{1,\alpha}, \tag{45}
\]

and equation (43) becomes

\[
\sum_{\alpha} S_{1,\alpha} \left[ 1 - \frac{\mu_1(\alpha)}{\mu_2(\alpha)} \right] \cos(\alpha z^*) = \sum_{\alpha} C_\alpha \varphi_\alpha(z^*) = N(z^*, 0) - N_{eq}. \tag{46}
\]
Equation (46) has to be inverted to determine $S_{1\alpha}$ and then $S_{2\alpha}$, by means of which we can evaluate $\eta(z^*, t^*)$ and finally $s(t^*)$. As stated above, this is a difficult task since the eigenfunctions $\psi_\alpha(z^*)$ are not orthogonal. To orthogonalize them, we assume that it is possible to expand $\psi_\alpha(z^*)$ in terms of an orthogonal set $\psi_\alpha(z^*)$ such that

$$\psi_\alpha(z^*) = \sum_{\alpha} U_{\alpha l} \psi_l(z^*). \quad (47)$$

In this manner, equation (46) can be rewritten as

$$R_j = \sum_{\alpha} U_{\alpha j} C_\alpha, \quad (48)$$

where

$$R_j = \int_{1/2}^{1/2} [N(z^*, 0) - N_{eq}] \psi_j(z^*) \, dz^*$$

$$= \int_{1/2}^{1/2} \psi_j(z^*) \psi_j(z^*) \, dz^*.$$

In matrix notation, equation (48) becomes $R = UC$, from which it follows that $C = V^T R$, where $V = U^{-1}$. To obtain the elements of $V$, we can implement a method which is more suitable to be handled numerically [29, 30], namely

$$\psi_q(z^*) = \sum_{\alpha=1}^q M_{\alpha q} \psi_\alpha(z^*) = \sum_{\alpha=1}^q V_{\alpha q} \psi_\alpha(z^*), \quad (49)$$

where $M_{\alpha q}$ is the minor of the element

$$d_{\alpha q} = \int_{1/2}^{1/2} \psi_\alpha(z^*) \psi_q(z^*) \, dz^*$$

in the determinant $D_q$ defined as

$$D_1 = d_{11}$$

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

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

This procedure allows us to obtain the coefficients $C_\alpha$ and then, using (45), $S_{1\alpha}$ and $S_{2\alpha}$ giving the solutions $\eta(z^*, t^*)$ and $s(t^*)$ in closed analytical form. In particular, the surface density of particles may be rewritten as

$$\sigma(t^*) = \sigma_{eq} - \sum_{\alpha} \frac{1}{\alpha} \left[ S_{1\alpha} e^{\mu_1(\alpha)t^*} + S_{2\alpha} e^{\mu_2(\alpha)t^*} \right] \sin(\alpha/2), \quad (50)$$

and is shown in figure 3 for two illustrative cases. These results are impressive. In the framework of Langmuir’s approximation for the adsorption phenomenon the expected temporal behavior of $\sigma(t)$ is monotonous, with the density reaching a saturation value for large enough time in the parabolic approximation for the diffusion equation. The presence of the second derivative in equation (5) (accounted for by $B \neq 0$) is clearly responsible for the oscillating behavior of $\sigma$ shown in figure 3. As mentioned before, this results is in good qualitative agreement with the experimental data reported in [3]. The non-monotonic behavior found here is strongly dependent on the values of the parameters $A$ and $L$, but the choice of the value of $B$ is crucial in determining this behavior, as will be discussed in detail in section 7. The slope of $\sigma(t^*)$ at the origin is practically independent of the value of $L$. Likewise, the positions of the maxima of $\sigma(t^*)$ are also essentially independent of $L$. Notice, however, that the value of $\sigma(t^*)$ at the maximum is clearly sensible to the value of $L$, as will be discussed below.
6. Numerical procedure

The finite-difference-based procedure exploited to solve the problem described by equations (6)–(8) is now outlined. Thanks to the symmetry, only half the geometry can be considered. Let us thus partition the spatial domain $0 \leq z^* \leq 0.5$ into $n_{z^*}$ segments of length $h = 0.5/n_{z^*}$, and the time domain $[0, T]$ under consideration into $n_t$ segments of length $k = T/n_t$. By assuming that $N(z^*, t^*) = N_{i,j}$ and that $\lambda = k/h$, the numerical algorithm for the inner points of the spatial domain $(i = 2, \ldots, n_{z^*})$ reads:

- $j = 0$:
  $$N_{i,0} = N_0$$

- $j = 1$ ($g_i = (\frac{\partial N}{\partial z^*})_{i,0}$):
  $$N_{i,1} = \frac{\lambda^2}{2B} (N_{i+1,0} + N_{i-1,0}) + \frac{B - \lambda^2}{B} N_{i,0} + \frac{(2B - k)k}{2B} g_i$$

- $j = 2, \ldots, n_{t^*} + 1$
  $$N_{i,j} = \frac{2\lambda^2}{2B + k} (N_{i+1,j-1} + N_{i-1,j-1}) + \frac{4(B - \lambda^2)}{2B + k} N_{i,j-1} - \frac{2B - k}{2B + k} N_{i,j-2}.$$

As concerns the boundary conditions ($i = 1$ and $i = n_{z^*} + 1$), the following relationship is imposed to satisfy the symmetry condition:

$$N_{1,j} = N_{2,j}.$$

On the other hand, as regards $N_{n_{z^*}+1,j}$, its values are obtained at each time $j$ by inserting equation (8) into (7) and approximating the integrals by means of the simple trapezoidal rule:

$$\int_a^b f(x) \, dx \approx \frac{b - a}{2} \sum_{k=1}^{n_{t^*}} (f(x_{k+1}) + f(x_k)),$$
In the procedure described above it is important to underline that the numbers of spatial and time intervals, \( n_z \) and \( n_t \), respectively, should be increased until convergence occurs. Moreover, \( \lambda \) must be kept sufficiently small in order to prevent numerical instabilities. The problem is more complicated than that related to classical differential equations, e.g. the wave equation, according to which the condition \( \lambda < 1 \) must be satisfied. This is due to the nonlocal condition 8 coupled with 7: at each time, the density \( N(0.5, t^*) \) depends on the solution throughout the sample. Indeed, for what concerns the results presented in section 7, it is found that the value of \( \lambda \) is affected by the parameters considered in the analysis, and especially by \( B \): the lower is \( B \), the lower must be \( \lambda \). For \( B = 10^{-3} \), \( \lambda \) is assumed to be equal to \( 2.5 \times 10^{-2} \).

### 7. Results

The numerical procedure discussed in section 6 is now implemented for a more detailed investigation of the behavior of \( \sigma(t^*) \) and \( N(z^*, t^*) \) as a function of the characteristic times \( \tau_r, \tau_D, \tau_a \) and lengths \( d \) and \( \kappa_a \tau_a \). By comparing the results with those presented in figure 3, the approximated method to obtain the eigenvalues of the problem by solving \( \text{Re}[\mathcal{E}] = 0 \) presented in section 4 is validated. Notice again that initial conditions (16) are satisfied as shown in the inset of figure 3.

In figure 4, the surface density of particles is shown as a function of \( t^* \) for different ratios between the characteristic desorption time \( \tau_a \) and the diffusion time \( \tau_D \). For \( \tau_a < \tau_D \) (\( A < 1.0 \)), the desorption process is significant for initial times and a kind of ‘competing effect’ with adsorption and diffusion may be found at the surface. This competition for short times is probably the main mechanism underlying the non-monotonic trend of \( \sigma \). In figure 5, the varying quantity is the ratio between a characteristic ‘adsorption length’ (represented by \( \ell = \kappa_a \tau_a \)) and the thickness of the sample. For \( \ell \ll d \) (\( L \ll 1 \)), the adsorption–desorption process occurs over a very short distance, i.e., it is strongly localized near the surface and is not conspicuous. The number of particles on the surface is very small. As \( L \) increases, the ‘adsorption length’ also increases and an increasingly high number of particles takes part into the adsorption–desorption phenomena. For \( L \gg 1 \), the adsorption–desorption phenomena is
expected to involve all the particles in the sample. This explains the high value of the surface density and also the different values of $\sigma$ at the maxima found in figure 3 when $L \gg 1$. In all the cases in which the desorption process is present, the non-monotonic behavior is assured by the small value of $B$. Indeed, in figure 6, the values of $B$ are chosen to illustrate the role of the second derivative in equation (5). For very small values of $B$ ($B = 10^{-3}$ and $B = 10^{-2}$) the adsorption phenomenon presents the expected monotonic behavior of Langmuir’s approximation. As $B$ increases, the oscillating behavior arises in the system and is very clear for the initial times when $B = 0.1$ but is also present if one waits for longer, i.e., when $B = 1.0$ the maxima in the density are found for $t \gg \tau_D$. In this latter case, the characteristic time $\tau_r = \tau_D$, which implies that the velocity $c$ of the density wave becomes small. However, since the whole sample takes
part in the adsorption–desorption phenomenon (because $\ell = d$) the surface density increases before starting to oscillate for large $t$.

Another feature of the behavior of the surface density can be quantitatively understood from the previous figures. The velocity of the density wave, in the units we are using here, is given by $c = 1/\sqrt{B} \approx 3.16$, if $B = 0.1$. Now, if we consider the curve $\sigma(t^*)$ versus $t^*$, the first maximum may be found for $t^* = T \approx 0.32$, i.e., $1/c$. This is an expected result: when the concentration starts to vary in view of the adsorption phenomenon on the surface ($z^* = -1/2$, for instance), the more distant particles are located close to the second surface ($z^* = 1/2$), and they have to cover the distance 1 with velocity $c$. For this reason, the next maximum will be found after a time interval $T$. Finally, one notices that the slope of $\sigma(t^*)$ at the origin is of the order of $N_0 c$. For $t^* = 0$ the bulk density of particles just in front of the surface is $N_0$, and hence $j(0) = N_0 c$. Since this current density is responsible for the increase of the surface density of the particles, in a first approximation, by neglecting the diffusion phenomenon, $j = \frac{d\sigma}{dt^*}$.

The behavior of the bulk density of particles is shown in figure 7 in different positions inside the sample. The initial condition is such that $N(z^*, 0) = N_0$ for $|z^*| \neq 1/2$. The same considerations done on the behavior of $\sigma$ can be useful here for interpreting the behavior of the bulk density. For instance, if we consider the position $z^* = 0$, the distance from the surface is 1/2. Thus, the bulk density changes after an interval of $T^* = 0.5/c \approx 0.16$, as can be easily checked on figure 7. In the same manner, bearing in mind the positions $z^* = 0.25$ and $z^* = 0.75$, one notices that the maximum in the density may be found after a time interval $1/c$, because the density waves have to go toward the surface and come back. If we consider, for simplicity, the position $z^* = 0$, we notice that the density changes after a time interval $T^*$, when the particles start to move towards the surface. After a time $T^*$, the particles reach the surface.

Figure 7. $N(z^*, t^*)$ versus $t^*$ for $N_0 = 3, A = 0.01, B = 0.1$ and $L = 1.0$ at different positions inside the sample.
at which point a part of them is reflected (the other part may be adsorbed). This reflected part arrives again at the position $z^* = 0$, after a time $T^*$, where they interfere with the particles coming from the opposite surface. Consequently, at the time $T^*$ the density starts to change and after a time $2T^*$ it is recomposed, and so on. For very large time intervals, however, the surface density tends to a saturation while the bulk density tends to an almost constant value. The oscillations of the bulk density versus $t^*$, evident in figure 7, are related to numerical problems in facing the discontinuous initial conditions (15). For smoother distributions $N(z^*, 0)$, this oscillating behavior is no longer present: in figure 8 we show the evolution of the bulk density related to a parabolic initial distribution, vanishing at the limiting surfaces, i.e. proportional to $(\frac{1}{4} - Z^{*2})$.

8. Conclusions

The diffusion of particles in a finite-length sample is described here by a diffusion equation of hyperbolic type (Cattaneo’s equation). The solution of this equation is subjected to boundary conditions involving a kinetic balance equation at the surfaces. The problem was analytically solved by means of the separation of variables, invoking a detailed process for the orthogonalization of the eigenfunctions of the problem. In addition, a detailed numerical analysis allowed the exploration of the role of the model parameters on the temporal behavior of the bulk and surface density of particles. In contrast to the temporal behavior usually found in solving the diffusion equation of parabolic type (usually Fick’s law), the solutions show a remarkable oscillatory behavior, both in the bulk and in the surface, for the initial times. This kind of formalism may be helpful for exploring memory effects on the adsorption–desorption phenomenon at the limiting surfaces as well as on the bulk diffusion of neutral particles.

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