# Concentration profiles and reaction fronts in $A+B\rightarrow C$ type processes: Effect of background ions

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The diffusion and reaction of initially separated ions $A^-$ and $B^+$ in the presence of counterions $\hat{A}^+$ and $\hat{B}^-$ are studied. The dynamics is described in terms of reaction-diffusion equations obeying local electroneutrality, and the time evolution of ion concentrations is determined. We find that, in the absence of reactions, unequal mobility of ions generates nontrivial features in the macroscopically observable concentration profiles. Switching on the reaction $A^-+B^+\rightarrow C$ leads to the formation of a localized, diffusive reaction front, and one finds that the properties of the front (e.g., the effective diffusion constant) are affected by the background ions. The consequences of this effect on the formation of Liesegang patterns are discussed.

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## I. INTRODUCTION

The reaction-diffusion process $A+B\rightarrow C$ has long been studied. This conceptually simple process displays a rich variety of phenomena (nonclassical reaction kinetics [1,2], clustering and segregation [3,4], front formation [5,6]) and, depending on the interpretation of $A$ and $B$ (particles, quasiparticles, topological defects, chemical reagents, etc.), it provides a model for a number of phenomena in physics, chemistry, and biology.

In many cases of interest, $A$ and $B$ are ions ($A^-$ and $B^+$) and these ions are initially separated from each other. An example we shall discuss below is the formation of Liesegang bands [7,8], where an electrolyte $A^-\hat{A}^+$ diffuses into a gel column containing another electrolyte $\hat{B}^-B^+$. The concentration of $A$'s is taken to be much larger than that of the $B$'s; thus the reaction front $A^-+B^+\rightarrow C$ moves along the column. An appropriate choice of reagents then leads to quasiperiodic precipitation ($C\rightarrow D$) in the wake of the front (Fig. 1).

In general, the background ions ($\hat{A}^+$ and $\hat{B}^-$) are expected to play a role in the process described above. Nevertheless, the usual approach is to neglect them and consider only a contact interaction between the neutral reagents $A$ and $B$. This approximation is based on the argument that the background ions provide only screening and, furthermore, the screening length is much smaller than the scale of concentration variations relevant in the formation of a macroscopic pattern. Although the argument sounds compelling, one should note that the background ions may generate macroscopic effects even if the screening length is negligible. Indeed, if the mobility of one of the background ions ($\hat{A}^+$ in the Liesegang case) is much smaller than the other mobilities, then the motion and properties of the reaction front are altered. Since the properties of the reaction front are crucial in determining the pattern [9–11], one expects that the presence of background ions will give rise to macroscopic changes in the observed patterns.

Our aim with this work is to verify the above expectation and to investigate how the diffusion and front formation are affected by unequal mobilities of background ions. More precisely, we shall study the time evolution of ion concentrations in the process

$$A^-+\hat{A}^++B^++\hat{B}^-\rightarrow C+\hat{A}^++\hat{B}^-, \tag{1}$$

where the reaction product $C=A^-B^+$ is assumed to vanish from the system. The process starts at $t=0$ from an initial condition where the electrolytes $A^-\hat{A}^+$ and $B^+\hat{B}^-$ are separated and their concentrations $(a^+,\hat{a}^-,b^-,\hat{b}^+)$ are constant in the left $(x<0)$ and right $(x>0)$ half spaces, respectively,

$$\begin{aligned} a^-(x,t=0)&=\hat{a}^+(x,t=0)=a_0\theta(-x),\\ b^+(x,t=0)&=\hat{b}^-(x,t=0)=b_0\theta(x), \end{aligned} \tag{2}$$

where $\theta(x)$ is the step function. Such an initial state with $a_0\gg b_0$ is actually used in Liesegang experiments, and this choice is also motivated by the fact that investigations of front formation from such an initial state have proved to be instrumental in understanding the $A+B\rightarrow C$ process [5].

The study of motion of ions is not an easy task and we must simplify the problem to make it tractable. We believe, however, that our approximations listed below are appropriate at least for the description of the Liesegang experiments.

(1) It is assumed that the phenomena can be described by reaction-diffusion equations. This appears to be a correct assumption for reactions taking place in a gel where convection is absent.

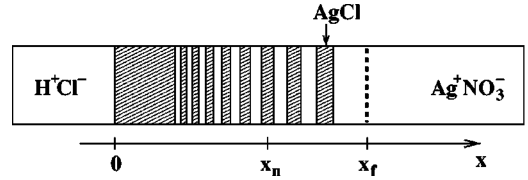


FIG. 1. Schematic picture of Liesegang phenomena. The correspondence with the notation in the text is given by $A^-=Cl^-$, $\hat{A}^+=H^+$ (outer electrolyte); $B^+=Ag^+$, $\hat{B}^-=NO_3{}^-$ (inner electrolyte); and $D=AgCl$ (precipitate). The initial interface between electrolytes is at $x=0$. The precipitation bands (shaded regions) emerge in the wake of the moving reaction-diffusion front (dashed line at $x_f$).

 

(2) The screening length is assumed to be negligible and screening is taken into account by enforcing local electroneutrality. At characteristic ion concentrations ($10^{-3}M$–$1M$) present in Liesegang experiments, the screening length is indeed small ($\sim 10^{-9}$ m) compared both to the characteristic diffusion length ($\sim 10^{-2}$ m) and to the width of the reaction zone ($\sim 10^{-6}$ m). Further discussion can be found in Sec. II.

(3) The concentration profiles are assumed to depend only on one spatial coordinate ($x$ in Fig. 1). Although a one-dimensional geometry can be set up in experiments on Liesegang phenomena (the length of the gel column can be made much larger than its width), one should note that the finite extent of the sample in the transverse direction poses nontrivial problems with edge effects. It appears, however, that these effects can be neglected since the final pattern is usually one dimensional to good accuracy.

(4) The mobilities of the reagents and of the background ions are, in general, different. For simplicity, we shall consider the case with one of the background ions having a significantly distinct diffusion coefficient:

$$D_a = D_b = D_{\hat{b}} \equiv D \neq D_{\hat{a}} \equiv \hat{D}. \tag{3}$$

This is just a technical assumption to keep the number of parameters small, and this also appears to be the most interesting case for Liesegang phenomena where $a_0 \gg b_0$.

Once the above approximations are made one arrives at a problem that can be studied numerically and, in some limits, analytically. The process is now simple enough so that the numerical analysis is not hindered by computer time and memory problems, or by difficulties arising from discretization.

In order to arrive at the results, we shall proceed as follows. First we discuss how to take into account the electroneutrality constraint in the reaction-diffusion equations (Sec. II). Then the case without reaction is studied and we show that interesting concentration profiles emerge even in the pure diffusion process (Sec. III). The effects of reactions are considered in Sec. IV, where the properties of the reaction front are calculated. Finally, the implications for understanding the Liesegang phenomena are discussed in Sec. V.

## II. EQUATIONS IN THE ELECTRONEUTRALITY APPROXIMATION

In a medium such as a gel, the ions move by diffusion and, in the presence of an electric field $\vec{E} = -\vec{\nabla}\varphi$, the flux of ions $\vec{j}_i$ is given by the Nernst-Planck relation [12]

$$\vec{j}_i = \vec{j}_{i,\mathrm{diff}} + \vec{j}_{i,\mathrm{drift}} = -D\left(\vec{\nabla} n_i + \frac{z_i}{\varphi_0} n_i \vec{\nabla}\varphi\right). \tag{4}$$

Here $n_i$ is the concentration of the $i$th ions of integer charge $z_i$, $D_i$ is their diffusion coefficient, and $\varphi_0 = RT/F$ is a constant combining the temperature $T$, the gas constant $R$, and the Faraday number $F$. The potential $\varphi$ is determined from the Poisson equation

$$\Delta\varphi = -\frac{F}{\varepsilon_r \varepsilon_0} \sum_i z_i n_i, \tag{5}$$

where $\varepsilon_0$ is the permittivity of free space while $\varepsilon_r$ is the dielectric constant of the system.

An important quantity in ionic diffusion is the Debye length $r_D$ which gives the characteristic length scale associated with charge imbalances,

$$r_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 RT}{F^2 n_0}}, \tag{6}$$

where $n_0$ is the characteristic scale of ionic concentrations. In a Liesegang experiment, one usually has $n_0 \approx 10^{-3}M$–$1M$ and the process takes place in an aqueous medium ($\varepsilon_r \approx 80$). Thus $r_D \approx 10^{-10}$–$10^{-8}$ m, and one can see that $r_D$ is much smaller than the scale of the macroscopic pattern (e.g., the width of the bands, $\approx 10^{-3}$–$10^{-2}$ m). As a consequence, one can use the electroneutrality approximation which consists of replacing Eq. (5) by the constraint

$$\sum_i z_i n_i = 0. \tag{7}$$

Denoting now the rate of reaction of the $i$th ion with the others by $R_i(\{n\})$ and assuming that the reaction does not violate electroneutrality ($\Sigma_i z_i R_i = 0$), Eq. (4) together with the constraint (7) yields the following equations for the time evolution of the concentration fields:

$$\partial_t n_i = D_i[\Delta n_i - z_i \vec{\nabla}\cdot(n_i \vec{\mathcal{E}})] - R_i(\{n\}) \tag{8}$$

where the appropriately scaled electric field is given by

$$\vec{\mathcal{E}} = \frac{\Sigma_i z_i D_i \vec{\nabla} n_i}{\Sigma_i z_i^2 D_i n_i}. \tag{9}$$

At first sight, the origin of this electric field is not obvious since $\vec{\mathcal{E}}$ emerges in an electroneutral system. One should remember, however, that constraints generate forces, and it is the electroneutrality constraint that generates the above field. In reality, the ionic diffusion does produce unbalanced charges, which, in turn, do generate an electric field $\vec{\mathcal{E}}_r$. The charge densities, however, are much smaller than the typical ion concentrations, $\Sigma_i z_i n_i \ll n_j$, and $\vec{\mathcal{E}}_r$ is actually a field that allows diffusion in nearly electroneutral conditions. The electroneutrality approximation [12] replaces the nearly electroneutral conditions with exact electroneutrality by replacing $\vec{\mathcal{E}}_r$ with a field $\vec{\mathcal{E}}$ [Eq. (9)] such that the diffusive dynamics is constrained to keep the charge imbalances at zero.

It should be noted that there is an extra term in $\vec{\mathcal{E}}$ if a steady global current flows through the system. Such a current is not present in the Liesegang problem and, trying to keep the discussion as simple as possible, we shall assume that the global current is zero.

For the process of actual interest Eq. (1), reaction takes place only between the ions $A^-$ and $B^+$ and their rate of reaction is given by $ka^-b^+$ where $k$ is the rate constant. Thus the above equations in a one-dimensional geometry take the form

$$\partial_t a^- = D[\partial_x^2 a^- + \partial_x(a^-\mathcal{E})] - ka^-b^+ \tag{10}$$

$$\partial_t b^+ = D[\partial_x^2 b^+ - \partial_x(b^+\mathcal{E})] - ka^-b^+, \tag{11}$$

$$\partial_t \hat{a}^+ = \hat{D}[\partial_x^2 \hat{a}^+ - \partial_x(\hat{a}^+\mathcal{E})], \tag{12}$$

$$\partial_t \hat{b}^- = D[\partial_x^2 \hat{b}^- + \partial_x(\hat{b}^-\mathcal{E})], \tag{13}$$

with

$$\mathcal{E} = \frac{D\partial_x(-a^- + b^+ - \hat{b}^-) + \hat{D}\partial_x\hat{a}^+}{D(a^- + b^+ + \hat{b}^-) + \hat{D}\hat{a}^+}. \tag{14}$$

Equations (10)–(14) together with the initial conditions (2) provide the mathematical formulation of our problem.

Before turning to the solution of the above equations, let us mention that the diffusion-reaction problem of ions in one-dimensional geometry can be tackled numerically without assuming the electroneutrality condition. The only difficulty is that the discretization of space must be on a finer scale than the Debye length and so, in the range of physical parameters where $r_D$ is exceedingly small, the calculation becomes impractical. One expects (and we verified it for some cases) that the solution of the full problem will approach the solution of the corresponding ''electroneutral'' problem as $r_D$ is decreased.

## III. CONCENTRATION PROFILES WITH NO REACTIONS

Let us begin the analysis of Eqs. (10)–(14) by considering the case of no reactions ($k=0$) and let us further restrict our study to the case of $a_0 \gg b_0$ corresponding to the Liesegang initial conditions. The limit of $b_0=0$ is especially simple and treated in textbooks. In this case, the two ions $A^-$ and $\hat{A}^+$ must move together; thus an electric field is generated that slows down the more mobile ions and accelerates the slower ions. The result is an effective diffusion with a diffusion coefficient $D_{\text{eff}} = 2D\hat{D}/(D+\hat{D})$ [13].

The presence of a small amount of $B$'s ($a_0 \gg b_0$) does not significantly change the motion of $A$'s. The ions $A^-$ and $\hat{A}^+$ can separate now but only by a small amount, which is compensated by the motion of $B$'s. In Fig. 2, we can see the results for the case of $b_0/a_0 = 0.01$ and $\hat{D}/D = 0.1$ (slow background ions $\hat{A}^+$). The electric field is mainly generated by the motion of the majority $A$ ions and, in turn, this field is the determining factor in the motion of the minority $B$ ions. Since this field, shown in Fig. 2(b), moves the $\hat{A}^+$ ($A^-$) ions in the $+x$ ($-x$) direction, a similar effect is felt by the $B$ ions. Indeed, as one can see in Fig. 2(c), the $B^+$'s are repelled from the region the $A$ ions moved into, while the ions $\hat{B}^-$ are pulled through this region. As a result, a region emerges where the ionic and diffusive drifts of the $B$'s are in opposite directions.

It should be noted that the profiles shown in Fig. 2 keep their shape in time. The pictures at $t'$ are obtained from those at $t=1$ h by rescaling the $x$ axis by a factor $\sqrt{t'/t}$. This numerical observation is the consequence of the fact that the Debye length is zero and the initial conditions (2) do not contain any length scales. As a consequence, all the length scales are diffusive lengths proportional to $\sqrt{t}$. The above argument can be seen to work explicitly in the limit $\hat{D}=0$

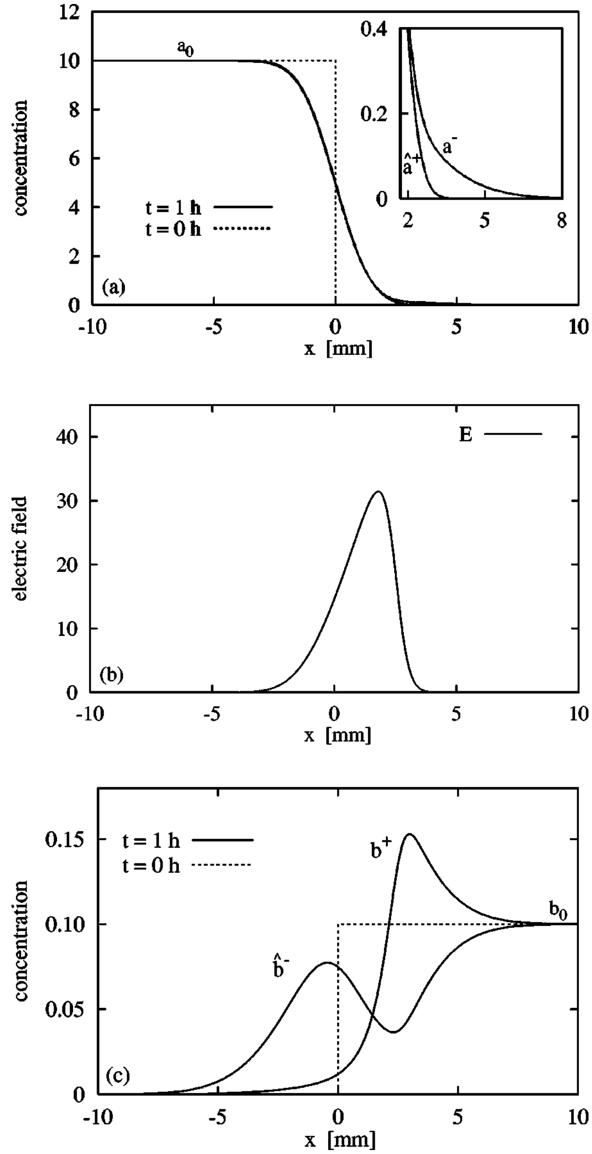


FIG. 2. Concentration profiles of the $A$ and $B$ ions [(a) and (c), respectively] and the electric field (b) generated by them. The concentration is measured in $0.1M$ while the unit of the electric field is V/m. The results are for the case of $b_0 = 0.01a_0$ with the diffusion coefficients given by $D = 10^{-9}$ m$^2$/s and $\hat{D} = 0.1D$. Inset in (a) shows that region where relative separation of the $A$ ions is significant.

where an analytic calculation [14] gives the concentration profiles, which can be expressed through error functions of argument $x/\sqrt{t}$.

The complexity of the concentration profiles shown in Figs. 2(a) and 2(c) suggests that if reactions are switched on between the ions $A^-$ and $B^+$ then the emerging reaction front may be rather different from that in the case of neutral reagents. This is what we shall study in Sec. IV.

## IV. REACTION FRONT

The full reaction-diffusion process is described by Eqs. (10)–(14) and the solution of these equations with initial condition (2) provides the description of the reaction front. Indeed, once the concentration profiles are known, the location and the time evolution of the production of $A^-+B^+\to C$ particles are given by

$$R(x,t)=ka^-(x,t)b^+(x,t). \tag{15}$$

The properties of $R(x,t)$ are well known for the case of neutral reagents ($\mathcal{E}=0$) [5]. In that case, the reaction takes place in a narrow, moving region whose width is much smaller than the diffusive scales. The motion of the reaction zone is ''diffusive'' characterized by a diffusion constant $D_f$

$$x_f=\sqrt{2D_ft}. \tag{16}$$

Another important feature of the front is that it leaves behind a density of $C$'s [10],

$$c_0=\int_0^\infty R(x,t)dt, \tag{17}$$

which is independent of $x$.

The parameters $D_f$ and $c_0$ can easily be determined for the neutral case by exploiting the smallness of the width of the reaction zone. The reaction zone is replaced by a point where the diffusion equations are supplemented by boundary conditions and as a result the parameters $D_f$ and $c_0$ are given as functions of $a_0$, $b_0$, $D_a$, and $D_b$ [5,15].

The presence of a localized, diffusive front is an essential ingredient in the theories of Liesegang phenomena [9–11], and the parameters of the front (especially $D_f$ and $c_0$) are known to influence the properties of the patterns. Thus the next step is now to find out how the above picture is modified as a result of the ionic character of the reagents.

Equations (10)–(14) with initial condition (2) can be studied by straightforward numerical methods and one finds that the localized-diffusive-front picture does hold, and, furthermore, the scaling properties (16) and (17) also remain valid when the ionic interactions are switched on. The actual values of the parameters $D_f$ and $c_0$, however, are affected by the presence of background ions.

In order to understand how these results arise, let us begin with the numerical observation that the reaction front remains narrow even if the ionic interactions are switched on. Indeed, for characteristic values of $a_0\approx 100b_0\approx 1M$, $D_a\approx D_b\approx 10^{-10}$ m$^2$/s, and $k\approx 10^{10}$ $M^{-1}$ s$^{-1}$ [16], we find that the width is in the mesoscopic range ($\sim 10^{-6}$ m) at all times available in a Liesegang experiment. Thus, on diffusive length scales, the reaction zone can be treated as a point (as in the neutral case) and one arrives at equations with no reaction terms:

$$\partial_t n_i=D_i[\partial_x^2 n_i - z_i\partial_x(n_i\mathcal{E})]. \tag{18}$$

The reactions are taken into account by the following boundary conditions at the front:

$$\begin{aligned} &a^-(x_f)=b^+(x_f)=0,\\ &|j_{a^-}(x_f)|=|j_{b^+}(x_f)|. \end{aligned} \tag{19}$$

The meaning of the above conditions is that the concentrations of the reagents are zero at the front and the fluxes of ions $A^-$ and $B^+$ to the reaction zone are equal.

Let us now suppose that $x_f(t)$ and $n_i(x,t)$ are the solutions of the above equations (18) and (19) with the initial condition (2). Then one can easily verify that the front position $\lambda x_f(t/\lambda^2)$ and the concentrations $n_i(x/\lambda,t/\lambda^2)$ also solve the same problem for an arbitrary $\lambda>0$ (note that the initial conditions do not contain any length scale). Thus the functions $n_i(x,t)$ and $x_f(t)$ must satisfy the conditions $n_i(x,t)=n_i(x/\lambda,t/\lambda^2)$ and $x_f(t)=\lambda x_f(t/\lambda^2)$. As a consequence, we find that the concentration profiles obey the scaling form

$$n_i(x,t)=\Phi_i\left(\frac{x}{\sqrt{t}}\right), \tag{20}$$

and the front moves diffusively even if the ionic interactions are taken into account,

$$x_f\sim\sqrt{t}. \tag{21}$$

The above relationship (21) defines the diffusion constant $D_f$ through $x_f=\sqrt{2D_ft}$.

The scaling of the concentrations Eq. (20) together with Eq. (14) imply scaling for the electric field,

$$\mathcal{E}(x,t)=\frac{1}{\sqrt{t}}\Psi\left(\frac{x}{\sqrt{t}}\right). \tag{22}$$

These scaling results allow us to investigate the production of $C$ particles. The number of $C$'s arising in the reaction zone in a unit time is given by the flux of one of the reagents (e.g., $j_{a^-}$) entering the front. According to Eqs. (20)–(22), $j_{a^-}$ at $x_f$ is proportional to $1/\sqrt{t}$ and the velocity of the front decays in time in the same way, $x_f\sim 1/\sqrt{t}$. It follows then that the density of the $C$'s emerging in the wake of the front is a constant,

$$c=\frac{j_{a^-}}{\dot{x}_f}=\text{const}=c_0. \tag{23}$$

The results (20)–(23) given by the above analytical argument have been confirmed by computer simulations. An example of such a numerical calculation can be seen in Fig. 3.

Having established the same scaling properties of the front [Eqs. (21),(23)] as in the case of neutral reagents, we turn now to the actual values of the parameters $D_f$ and $c_0$. Since the motion of the reagents is modified by the electric field (22), one expects that $D_f$ and $c_0$ will depend not only on the properties of the reagents but also on the properties of the background ions.

We studied the effect of the background ions by changing the diffusion coefficient $\hat{D}$ [Eq. (3)] and keeping all the other parameters $(a_0,b_0,D)$ fixed. The numerical results for $D_f$ and $c_0$ as functions of $\hat{D}$ are shown in Fig. 4. As one can see, $c_0$ does not change significantly in the physically relevant range of $0.1<\hat{D}<10$ [Fig. 4(b)]. The reason for this insensitivity of $c_0$ is that the density of the reaction product for $a_0\gg b_0$ and $D_a\approx D_b$ is mainly determined by the concentration $b_0$ [10].

The parameter $D_f$ is much more sensitive to the mobility of the counterions, as shown in Fig. 4(a). Although the mo-

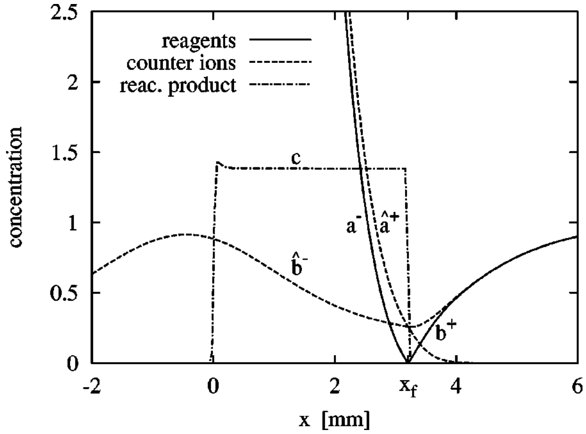


FIG. 3. Concentration profiles of the $A$ and $B$ ions when the reaction is switched on. The initial state is given by Eq. (2). The results are shown at time 1 h for the case of $b_0=0.01a_0=0.01M$ with the diffusion coefficients given by $D=10^{-9}$ m$^2$/s and $\hat{D}=0.1D$. The concentration is measured in units of $0.01M$.

tion of the front is determined by the interplay of all four types of ions and the process is rather complex, the result in Fig. 4(a) can be easily understood. For $a_0 \gg b_0$, the main effect comes from the counterions $\hat{A}^+$ slowing down or speeding up the motion of the $A^-$'s. If the diffusion coefficient $\hat{D}$ is smaller than $D$, the $A^-$ ions are pulled back by the $\hat{A}^+$'s (otherwise the slow $\hat{A}^+$ ions would form positive charge density in the left region); thus fewer $A^-$ particles enter the front, which yields a smaller value of $D_f$. A similar argument leads to the opposite effect for the case of $\hat{D}>D$. The case $\hat{D}=D$ is special in the sense that the electric field (14) vanishes and the result corresponds to the case of neutral reagents.

In the next section we turn to the theory of Liesegang phenomena in order to demonstrate the relevance of the above results in the description of a relatively simple pattern-forming process.

## V. IMPLICATIONS FOR LIESEGANG THEORIES

The Liesegang patterns described in Sec. I have been much investigated for about a century [7,8,17]. The gross features of *normal* patterns in reproducible experiments are rather simple, namely, the distance between consecutive bands $x_{n+1}-x_n$ increases with band order $n$ and the positions of the bands obey a *spacing law* [18,19]:

$$\frac{x_{n+1}}{x_n} \equiv 1+p_n \xrightarrow{n \gg 1} 1+p, \tag{24}$$

where $1+p$ is called the spacing coefficient and $p>0$.

Currently, the Liesegang phenomenon is mainly studied as a nontrivial example of pattern formation in the wake of a moving front [9,20] and the theories of normal patterns revolve around the calculation of $p$. The main feature of these theories is that the precipitate appears as the system goes through some nucleation [9,20–24], spinodal [11], or coagulation [25] thresholds. Most of these theories are rather complicated, however, and have been developed only recently to the level [10,11] that $p$ can be investigated in detail, and, in

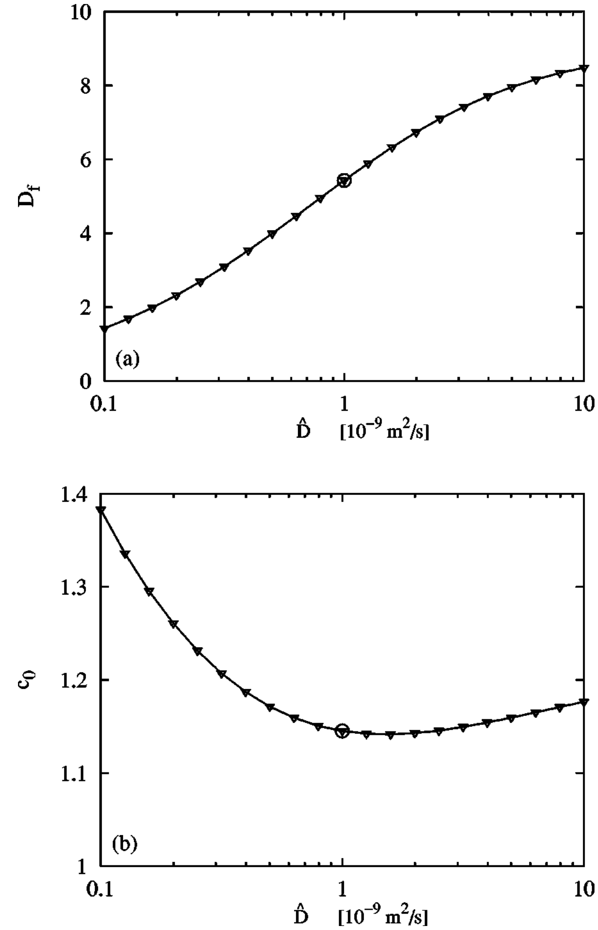


FIG. 4. The diffusion coefficient of the reaction front ($D_f$) and the concentration of the reaction product ($c_0$). $\hat{D}$ is the diffusion coefficient of the $\hat{A}^+$ ions while $D$ for the other ions is $10^{-9}$ m$^2$/s. The units of $D_f$ and $c_0$ are $10^{-9}$ m$^2$/s and $0.01M$, respectively. The initial concentrations are given by $b_0=0.01a_0=0.01M$. The points indicated by the circles correspond to the case when the background ions have no effect on the dynamics.

particular, its dependence on the initial concentrations $a_0$ and $b_0$ can be determined, and connection can be made to the experimentally established Matalon-Packter law [26,27].

None of the above theories addresses the question of how the Liesegang patterns are affected by the presence of background ions although the existence of such an effect is expected. Indeed, let us take, for example, the expression for $p$ obtained in a simple version of the *nucleation and growth* theory [see Eq. (25) in [10]],

$$p \approx \frac{D_c c^*}{D_f(c_0-c^*)}, \tag{25}$$

where $D_c$ is the diffusion coefficient of the $C$ particles while $c^*$ is the threshold concentration of $C$'s. The meaning of $D_f$ (the diffusion coefficient of the front) and $c_0$ (the concentration of $C$'s left behind the front) is the same as defined in this paper. As one can see from Eq. (25), the spacing coefficient depends on both $D_f$ and $c_0$. Thus, on the basis of our results (see Fig. 4), we expect $p$ to be affected by the background ions.

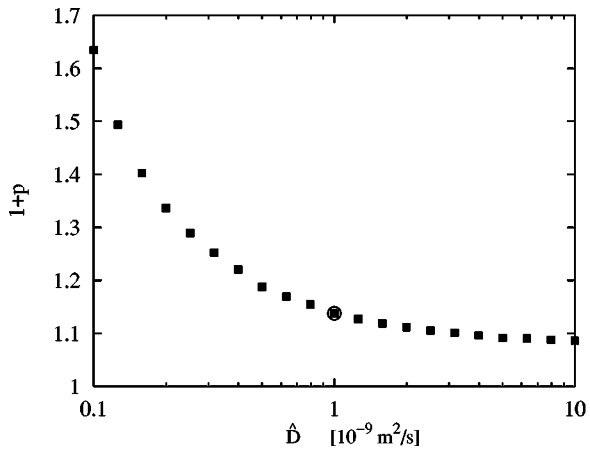


FIG. 5. Spacing coefficient as a function of the diffusion coefficient ($\hat{D}$) of the background ions ($\hat{A}^+$) for a case with $b_0/a_0 = 0.01$. The circle corresponds to equal diffusion coefficients where the description in terms of neutral reagents is valid.

In order to put our expectation on a firmer basis, we calculated $p$ numerically by employing a recent theory [11] where the addition of the background ions is straightforward. The main ingredients in this theory are (i) a moving reaction front that leaves behind the particles $C$, and (ii) a Cahn-Hilliard type phase-separation dynamics for the $C$ particles. This theory yields the spacing law, and the results for $p$ are in agreement with the Matalon-Packter law. Thus it appears to be a good candidate for the description of the Liesegang process. Since the reaction front enters the description only as a source in the Cahn-Hilliard equation [see Eq. (3) in [11]], one can study the effect of background ions by modifying the source according to the description in Sec. IV. The results of our numerical work for a particular case with $b_0/a_0 = 0.01$ (the parameters in the Cahn-Hilliard equation were set to unity) are displayed in Fig. 5.

As can be seen from Fig. 5, $p$ does depend on $\hat{D}$ and, actually, $p$ can change by a factor of 5 compared to the neutral case ($\hat{D} \approx D$) provided $\hat{D}$ decreases by a factor of 10. One can also observe that the ionic effect is larger when the counterion $A^+$ is slower than $A^-$. These observations and the overall picture are in agreement with the result (25) obtained in the nucleation and growth theory. Indeed, $c_0$ is weakly dependent on $\hat{D}$; thus the main effect comes from $D_f$. As Fig. 4 shows, $D_f$ is a smooth, monotonically increasing function of $\hat{D}$ and this translates through Eq. (25) into a monotonically decreasing $p(\hat{D})$.

We have thus shown that the background ions cannot be neglected in the description of the Liesegang phenomena unless the diffusivities of the ions are roughly equal. Although this conclusion appears to complicate the description significantly, the reassuring aspect of the result is that all the complications can be absorbed into the parameters ($D_f$ and $c_0$) of the front. As a consequence, previous ideas about the pattern formation remain intact apart from the need to take account of the renormalization of the parameters $D_f$ and $c_0$.

## VI. FINAL REMARKS

A general conclusion we can draw from the present work is that the dynamics of reaction fronts is strongly altered if the diffusivities of the reacting ions differ significantly from those of the background ions. This conclusion is based on the nontrivial density profiles found in a study of the the simplest reaction scheme $A+B \rightarrow C$ assuming negligible screening length (electroneutrality approximation). We believe, however, that some aspects of our results (the reaction front can still be characterized by an effective diffusion constant and it still leaves behind a constant density of reaction product) are robust since they appear to follow from more general considerations, and thus they should be applicable to more complicated cases.

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