Solitary Waves of Molecular Distributions in Liquids Generated by Electrophoresis and Optical Fields

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The physical problem of molecular distribution dynamics in liquids which contain applied electric fields and electromagnetic radiation is modeled. In particular, the effect of electrophoretic mobility changes of dissolved molecules due to radiation excitation is included in the present model. The resulting set of coupled nonlinear partial differential equations governing the spatial motion of these molecular distributions over time exhibit solitary wave solutions for some values of the equation parameters. Higher resolutions of two components in capillary electrophoresis are predicted.

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Trapping atoms in a vacuum using optical fields is a beautiful topic in both theoretical and experimental physics [1]. However, trapping atoms and molecules inside a liquid using optical fields is a hard task. In part, these difficulties are due to the large momentum transferred by thermal collisions between the solution constituents at ordinary temperatures. Therefore higher mean forces, which are competitive to diffusion and other dispersing mechanisms, are required to observe compression or trapping effects of molecular distributions in liquid solutions.

Electrophoresis is an interesting effect that has recently attracted attention. Gel electrophoresis [2–4] and particularly capillary electrophoresis [5,6] are promising techniques with applications in DNA sequencing, protein mapping, and general analytical biochemistry [7].

A wide class of molecules exhibit a translational movement when dissolved in aqueous solutions subjected to electrical fields. This electrophoretic velocity is proportional to the applied electric field. This proportionality constant is called electrophoretic mobility and is related to some physical properties of the liquid medium and the moving molecules. Consequently, in stationary liquids without mass convection, and subjected to applied electric fields, the molecular distribution packets move due to this electrophoresis and spread according to the diffusion equation.

In this Letter we model and report the results of the dynamics in one spatial dimension of these molecular distributions when dissolved in liquids which contain electric fields and electromagnetic radiation propagating through these media. Some molecules, e.g., some phototautomers [8,9], exhibit a different electrophoretic mobility when at an excited state. Thus the presence of radiation is responsible for the nonlinear dynamics in this model. As we shall see, this causes distribution compression, resulting in moving or stationary solitary waves of molecular distributions. In principle, this effect should be experimentally observed in a great variety of situations, such as electrophoresis in viscous fluids, gel electrophoresis with radiation transparent gels, or capillary electrophoresis. The possibility of covalently binding these molecules (e.g., phototautomers) to other molecules gives this effect special interest, as it can be extended to a wide class of chemicals and biochemicals.

If only one kind of molecules is dissolved in a liquid with applied electric and optical fields, then, in terms of electrophoretic mobility, this molecular distribution $C(\mathbf{r},t)$ can be seen as the sum of two distributions: (a) the distribution $C_2(\mathbf{r},t)$ which represents the excited molecules with electrophoretic mobility μ_2 and decaying rate Γ and (b) $C_1(\mathbf{r},t)$ which represents the molecules with electrophoretic mobility μ_1. The functions C_1 and C_2 have units of concentration (number of molecules per unit volume) and satisfy Fick's first law with the two following additional velocity terms:

$$\mathbf{J}_1 = -D_1\nabla C_1 + \mu_1\mathbf{E}C_1 + \mathbf{v}C_1\,, \tag{1a}$$

$$\mathbf{J}_2 = -D_2\nabla C_2 + \mu_2\mathbf{E}C_2 + \mathbf{v}C_2\,, \tag{1b}$$

where $\mathbf{J}_i$ is the molecular current (net flow of molecules C_i per unit area per unit time) and D_i their diffusion coefficient (taken as a constant). $\mathbf{E}$ denotes the electric field and $\mathbf{v}$ the velocity of the liquid medium as a whole with respect to the frame of reference. It is considered that molecular diffusion alone is responsible for band broadening. If radiation is present then absorbing and decaying terms must be added to the continuity equations

$$\frac{\partial C_1}{\partial t} = -\nabla\cdot\mathbf{J}_1 + \Gamma C_2 - kIC_1\,, \tag{2a}$$

$$\frac{\partial C_2}{\partial t} = -\nabla\cdot\mathbf{J}_2 - \Gamma C_2 + kIC_1\,. \tag{2b}$$

Here, $I = I(\mathbf{r},t)$ is the monochromatic radiation intensity (number of photons crossing unit area per unit time) and k the absorption coefficient of molecules C_1. For simplicity, the absorption coefficient of molecules C_2 is

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assumed to be zero in this model. Molecules C_2 decay to molecules C_1 at a rate Γ. Stimulated decaying processes are considered negligible. If the electric field $\mathbf{E}$ is position and time independent, then, introducing Eqs. (1) in (2), in one spatial dimension results in the following:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} - v_{1x} \frac{\partial C_1}{\partial x} + \Gamma C_2 - kIC_1 , \quad (3a)$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} - v_{2x} \frac{\partial C_2}{\partial x} - \Gamma C_2 + kIC_1 , \quad (3b)$$

$$\frac{\partial I}{\partial x} = akIC_1 . \quad (3c)$$

Equation (3c) expresses Beer's law and is added to obtain the $I(x,t)$ variation, $v_{1x} = \mu_1 E_x + v_x$ and $v_{2x} = \mu_2 E_x + v_x$. It is supposed that the liquid is transparent to the monochromatic radiation and that there is radiation propagating in one direction only. The constant a expresses this direction of propagation. If radiation is propagating from positive to negative values of the x coordinate then $a = +1$ and, conversely, if radiation is propagating from negative to positive values of the x coordinate then $a = -1$. The incident radiation intensity is denoted as $I_0 = I(a\infty, t)$. In this work we consider D_1, D_2, I_0, Γ, and $k \geq 0$.

A physical system which closely meets the model summarized in Eqs. (3) is optical fibers with a liquid core. When radiation is propagating through that optical fiber, in some operation conditions, Eq. (3c) gives a reasonable description of $I(x,t)$. Furthermore, if a capillary electrophoresis [5] experiment is carried out in this system by subjecting the fiber (capillary) ends to an electrostatic potential difference, then the molecular distribution dynamics along the capillary should in good approximation be described by Eqs. (3). In this system the function $C(x,t)$ [$C(x,t) = C_1(x,t) + C_2(x,t)$] represents the band or zone. The velocity term v_x, liquid velocity with respect to the capillary wall, is called electro-osmotic velocity [10]. If there are no pressure gradients and if E_x is constant along the capillary, then this liquid velocity is constant [11] over practically the entire cross section area of the liquid core inside the capillary as predicted using the Debye-Hückel approximation [10]. Reynolds' numbers for aqueous solutions filling capillaries with $r = 25 \times 10^{-4}$ cm internal radius and subjected to velocities of 10^{-1} cm/s are of order 10^{-2}. Under these conditions the main band broadening mechanism in this system is diffusion, since there are no Poisseuille [10] flow terms and turbulences are minimal.

To analyze the solutions of this set of three coupled nonlinear partial differential equations, we take first $k = v_{1x} = v_{2x} = 0$ and $\Gamma > 0$. Then, $C_1(x,t)$ and $C_2(x,t)$ spread according to the diffusion equation, the distribution C_1 increases at a rate of ΓC_2, and C_2 decreases at a rate of $-\Gamma C_2$. However, if $k > 0$ and $I_0 > 0$, then the fraction of excited molecules reaches an equilibrium value. And, if there is a difference between v_{1x} and v_{2x}, then these two distributions will move at different velocities, and this will cause either dispersion or the compression of the total distribution $C(x,t)$. To show this time evolution we integrated Eqs. (3) using an iterative second order Runge-Kutta method. In all following integrations the numerical values used for the parameters in Eqs. (3) are $D_1 = D_2 = 10^{-4}$ cm^2 s^{-1}, $k = 5 \times 10^8$ cm^2 mol^{-1}, $I_0 = 16 \times 10^{-8}$ mol cm^{-2} s^{-1}, and $\Gamma = 250$ s^{-1}. A number of $N = 5 \times 10^{-13}$ mol of molecules are dissolved in the transparent liquid, and they have a spatial distribution along x coordinate at time $t = 0$ given by Gaussians of standard deviations $\sigma(0)$ and variances $\sigma^2(0)$. The liquid core of the capillary has a radius $r = 25 \times 10^{-4}$ cm.

Figures 1 and 2 show some results of this integration. Figure 1 shows the variance of the total distribution $C(x,t)$ vs time for various values of the compression parameter $\alpha = a(v_{1x} - v_{2x})$. In this figure the same initial conditions are used for all integrations, $C(x,0)$ being Gaussians with variances 4×10^{-3} cm^2. In order to avoid divergences at time $t = 0$, the optical field is turned on smoothly between $t = 0$ and $t = 1$ s according to $I(a\infty, t) = I_0(1 - \cos \pi t)/2$. This is only a numerical requirement. But for $t > 1$ s then $I(a\infty, t) = I_0$; I_0 is a constant. If $\alpha = 0$, then the distribution spreads according to the diffusion equation. If $\alpha < 0$, then the total distribution is dispersed faster than by diffusion alone. But, if $\alpha > 0$, a compression of the distribution is observed.

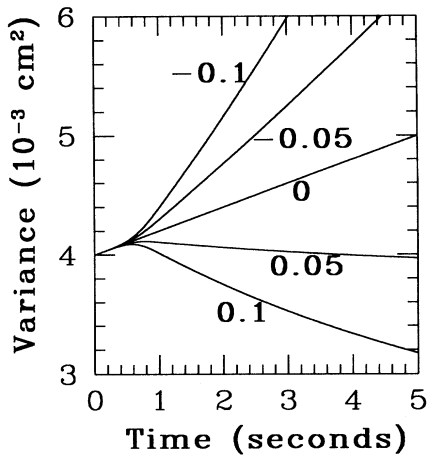

FIG. 1. Variance of the total distribution $C(x,t)$ vs time for many values of the parameter α, $\alpha = a(v_{1x} - v_{2x})$. The same initial conditions are used for all integrations. For $\alpha = 0$, which means no electrophoretic velocity differences, the molecular distribution variance grows in time according to the diffusion equation. For $\alpha < 0$ the total distribution is dispersed faster than by diffusion alone. For $\alpha > 0$ a compression of the molecular distribution occurs.

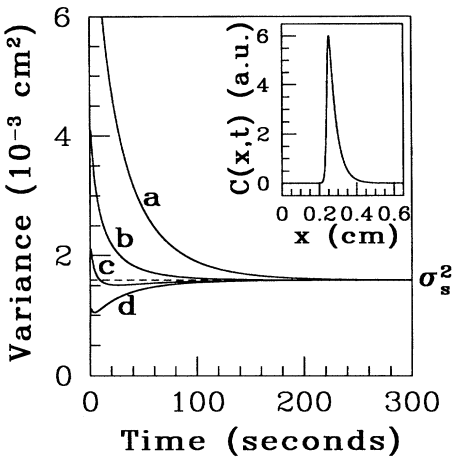

FIG. 2. Variance of the total distribution $C(x,t)$ vs time for various initial conditions. Here $\alpha = 0.1$ cm s^{-1} for all integrations and $C(x,0)$ being Gaussians with variances: *a*, $\sigma^2 = 0.01$; *b*, $\sigma^2 = 0.004$; *c*, $\sigma^2 = 0.002$; and *d*, $\sigma^2 = 0.001$ cm^2. The remaining conditions are the same as in Fig. 1. Notice that molecular distribution variance converges to the same value σ_s^2, which is the solitary wave variance. The solitary wave shape is plotted in the small box at the top, which shows molecular distribution along the spatial coordinate.

Figure 2 shows variance of the total distribution $C(x,t)$ vs time using $\alpha = 0.1$ cm s^{-1} for all runs. The remaining conditions are the same as in Fig. 1, except for the initial variances of $C(x,0)$. For all initial conditions the distribution $C(x,t)$ reaches the same stationary variance σ_s^2. The steady state solutions are solitary waves (monomodal distributions) which propagate with constant velocity v_s, constant area $(N/\pi r^2)$, and without change of form. The shape of these solitary waves is shown in the small box at the top in Fig. 2.

From Eqs. (3), it can be shown that this solitary wave velocity v_s along the capillary is given by

$$v_s = \frac{v_{1x} + v_{2x}(\gamma/\beta)(1 - e^{-\beta})}{1 + (\gamma/\beta)(1 - e^{-\beta})}, \qquad (4)$$

where $\gamma = kI_0/\Gamma$, $\beta = \lambda + W(\gamma e^{-\lambda})$, $\lambda = (kN/\pi r^2) - \gamma$, and $W(x)$ is Lambert's function of principal branch, $W(0,x)$. In capillary electrophoresis, the electro-osmotic velocity v_x may be adjusted in such a way that solitary wave velocity is zero. From Eq. (4), this velocity is given by

$$v_x = -\frac{\mu_1 E_x + \mu_2 E_x(\gamma/\beta)(1 - e^{-\beta})}{1 + (\gamma/\beta)(1 - e^{-\beta})}. \qquad (5)$$

With this electro-osmotic velocity, the molecular distribution is trapped in a small region of space. Different kinds of trapping in the domain of DNA gel electrophoresis are reported [12]. Fundamentally, this difference resides on the solitary wave nature of the present trap.

As Eqs. (3) show, if k is small, then the amount of total molecules N required to obtain small values of σ_s^2 must be large enough to guarantee at least a little damping of $I(x,t)$ while traveling through the distribution. But if k is large, then the amount of molecules N may be smaller. From Eqs. (3b) and (3c) we conclude that if Γ is small then I_0 must be small too to avoid saturation. But if Γ is large, then I_0 may be larger. For fixed values of D_i, r, α, k, and N there exists an optimum value [13] for I_0/Γ, which gives minimum stationary variances. If molecules C_2 absorb significantly, then the term ak_2IC_2 must be added to Eq. (3c), and this will enhance the compression effect.

In the discussions above E_x and I_0 are constants. But E_x and I_0 may be varied in time, and the direction of light propagation a may be changed synchronically with E_x. This allows a large number of layouts, which may increase the compression effect of the distribution in 1D, 2D, and 3D experiments.

The results above were obtained for liquids which contain dissolved in it only one component C_1 (and their excited molecules C_2). When two components are present, for example, C_1 (and C_2) and C_1' (and C_2'), then Eqs. (3), (4), and (5) do not remain valid. Equations (3) are split into five. If only molecules C_1 and C_1' absorb, then Eq. (3c) will have the additional term $ak'IC_1'$. Now if $\alpha > 0$ and $\alpha' = a(v_{1x}' - v_{2x}') > 0$, then two solitary waves with stationary variances σ_s^2 and $\sigma_s'^2$ may occur, depending on the parameters $r, N, N', I_0, k, k', \Gamma$, and Γ'. Consequently, if σ_s^2 and $\sigma_s'^2$ exist and have a finite value, then any two components of a mixture with $v_s \neq v_s'$ may be separated. A detailed analysis of the influence of all parameters on σ_s^2, $\sigma_s'^2$, v_s, and v_s' would determine which two components may be separated in how long of time [13]. Integration of this last set of five coupled nonlinear partial differential equations allows us to study the interesting phenomena of collision [13]. When two solitary waves of this dynamical system collide they do not break up and disperse. The two solitary waves emerge from the collision region with the same area but with different velocities and stationary variances. In some aspects these solitary waves behave like solitons. This integration allows us to calculate a second and very useful quantity called resolution. The resolution (R) of two bands is defined [14] as the distance between their centers of mass divided by $4\bar{\sigma}$, where $\bar{\sigma}$ is the average of the two standard deviations.

Figure 3 shows the resolution of a two-component mixture vs electrophoresis time for three distinct conditions. All curves of this figure are obtained using the following conditions: $C_2(x,0) = C_2'(x,0) = 0$, $C_1(x,0) = C_1'(x,0)$ [being Gaussians with initial variances $\sigma^2(0) = \sigma'^2(0) = 0.005$ cm^2], $N = N' = 2.5 \times 10^{-13}$ mol, $D_1 = D_2 = D_1' = D_2' = 10^{-4}$ cm^2 s^{-1}, $\Gamma = \Gamma' = 250$ s^{-1}, $I_0 = 20 \times 10^{-8}$ mol cm^{-2} s^{-1}, and $v_{1x}' - v_{1x} = 10^{-2}$ cm s^{-1}. Curve *a* shows the result for a

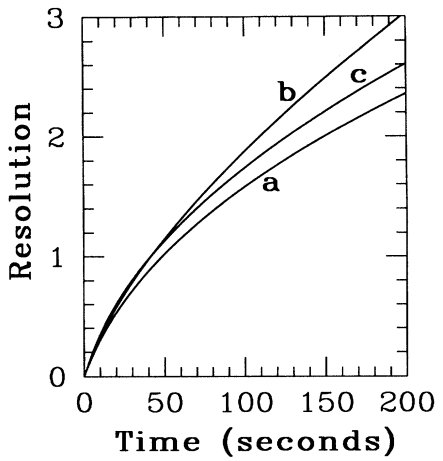

FIG. 3. Resolution of a two-component mixture vs electrophoresis time. Curve a shows the result for $\alpha = \alpha' = 0$, which means a normal capillary electrophoresis run; in curve b, $\alpha = \alpha' = 5 \times 10^{-2}\ \mathrm{cm\,s^{-1}}$; and in curve c, $\alpha = 0$ and $\alpha' = 5 \times 10^{-2}\ \mathrm{cm\,s^{-1}}$. The initial variances are $\sigma^2(0) = \sigma'^2(0) = 0.005\ \mathrm{cm^2}$. Higher resolutions are observed under conditions b and c.

normal capillary electrophoresis run, $\alpha = \alpha' = 0$. In this $R \propto t^{1/2}$ as $t \to \infty$. Notice that higher resolutions are obtained at least in two situations: b, $\alpha = \alpha' = 5 \times 10^{-2}\ \mathrm{cm\,s^{-1}}$ and $k = k' = 5 \times 10^{7}\ \mathrm{cm^2\,mol^{-1}}$; and in c, $\alpha = 0$, $\alpha' = 5 \times 10^{-2}\ \mathrm{cm\,s^{-1}}$, and $k = k' = 2 \times 10^{8}\ \mathrm{cm^2\ mol^{-1}}$.

In conclusion, in the present model molecular distribution dynamics exhibits solitary wave solutions from which propagating velocity is deduced, as given by Eq. (4). Adjusting electro-osmotic velocity according to Eq. (5) causes molecular distribution to be trapped with a static distribution. A generalization to multicomponent capillary electrophoresis is a simple step, as shown. In particular, an increase of resolution of a two-component mixture electrophoresis is observed in this model. This scheme may have interesting implications in analytical biochemistry and molecular physics studies. Although, some experimental difficulties are expected: First, the requirement of medium transparency is not met in all practical situations. Second, the need for covalently binding labels (e.g., phototautomers) to molecules such as DNA and proteins probably restricts its practical applicability. We suggest the use of Bäcklund transformations or the inverse scattering method to obtain exact solutions for $C_1(x,t)$, $C_2(x,t)$, and $I(x,t)$ in Eqs. (3). To our knowledge, this is the first example of solitary waves of molecular distributions in liquids generated by electrophoresis and optical fields.

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