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Nonlinear waves in electromigration dispersion in a capillary

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HIGHLIGHTS

- Exact solutions are constructed for electromigration dispersion waves.
- Reduction to a Darboux equation is achieved under a traveling-wave ansatz.
- Integral curves connecting equilibria are completely characterized.
- Bistability results in the coexistence of kink solutions.

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ABSTRACT

We construct exact solutions to an unusual nonlinear advection–diffusion equation arising in the study of Taylor–Aris (also known as shear) dispersion due to electroosmotic flow during electromigration in a capillary. An exact reduction to a Darboux equation is found under a traveling-wave ansatz. The equilibria of this ordinary differential equation are analyzed, showing that their stability is determined solely by the (dimensionless) wave speed without regard to any (dimensionless) physical parameters. Integral curves, connecting the appropriate equilibria of the Darboux equation that governs traveling waves, are constructed, which in turn are shown to be asymmetric kink solutions (*i.e.*, non-Taylor shocks). Furthermore, it is shown that the governing Darboux equation exhibits bistability, which leads to two coexisting non-negative kink solutions for (dimensionless) wave speeds greater than unity. Finally, we give some remarks on other types of traveling-wave solutions and a discussion of some approximations of the governing partial differential equation of electromigration dispersion.

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1. Introduction

From the early work on Taylor cones and jetting [1] and the Taylor–Melcher leaky dielectric model [2] to modern microfluidics applications [3,4], such as electrophoretic separation of mixtures [5], electrokinetic and electrohydrodynamic phenomena remain an active topic of research [6] in physicochemical hydrodynamics [7, Chapters 6–7] (see also [8, Chapters 8–10]). A related topic is the phenomenon of Taylor–Aris dispersion [9,10], which is one example of a macrotransport process [11] describing the spread of the cross-sectionally averaged concentration of a tracer in a laminar flow far downstream from the point of injection. For example, in a pressure-driven laminar flow (mean speed \bar{u}) of a Newtonian fluid in a planar slot of height h_0 , a dispersivity $\mathcal{D} = D + h_0^2 \bar{u}^2 / (210D)$ is found for the case of a tracer of diffusivity D [11, Chapter 2]. The cross-sectionally averaged concentration is, then, advected downstream with constant speed \bar{u} and spreads with an effective diffusivity equal to the dispersivity \mathcal{D} .

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The classical dispersion equation is a linear advection–diffusion equation, which is solvable by classical techniques (integral transforms, self-similarity methods, separation of variables, etc. [12]). However, different physical contexts present new aspects to dispersion. For example, streamwise variations of the mean flow in a radial geometry [13] leads to nonstandard self-similarity exponents (specifically $t^{1/4}$ instead of $t^{1/2}$), while a shear-rate dependent diffusivity turns out to yield the classical Taylor–Aris dispersion equation albeit with different numerical pre-factors [14]. The effect of geometry has also been addressed [15–17] due to its implications for microfluidic devices [3], in which case a surprising result arises: the dispersivity scales with the width and not the height of the channel.

While the latter examples all involve dispersion equations that are *linear*, recent work on Taylor–Aris dispersion of concentrated suspensions has yielded *nonlinear* governing equations. For example, if the diffusivity is made concentration-dependent [18] due to the effects of shear-induced migration of finite-sized particles in a laminar flow [19,20], the dispersion equation becomes an advection–diffusion equation with nonlinear diffusivity. In this case, self-similar solutions can still be found analytically [18, Eq. (16)]. If a suspension–balance approach is used to fully account for the suspended particles' effect on the laminar flow field, then the dispersion equation has both nonlinear advective and nonlinear diffusive terms [21, Eq. (4.1)]. In the latter case, however, the form of the nonlinearity is quite involved, precluding any analytical results. Returning to the electroosmotic flow context [22–24], dispersion is considered a hinderance for lab-on-a-chip technologies if the goal is separation and fractionation [5,25], while the enhanced mixing due to dispersion is sought out for other applications [3, Section 3]. Either way, it is clear that accurate model equations and their solutions (analytical, if possible) are needed to gain practical understanding and determine conditions for minimizing/maximizing dispersion [26]. More recently, Ghosal and Chen [27–30] have undertaken the study of electromigration and dispersion of analytes with and without a background electroosmotic flow.

In particular, in [30], a *nonlinear* electromigration dispersion equation that models Taylor–Aris (shear) dispersion in a capillary in the presence of electroosmotic flow was derived. This equation [30, Eq. (3.23)], which features both nonlinear advective and nonlinear diffusive terms is unlike [21, Eq. (4.1)], in that the nonlinearities are elementary functions of the dependent variable. Such equations are generally of interest in mechanics and applied mathematics because of what Crighton [31] has termed, in the context of hydrodynamics, the *Taylor–Lighthill balance*: the tendency of (linear or nonlinear) dissipation such as diffusion to counteract wavefront steepening due to advective nonlinearities in the governing equations [31,32]. The Taylor–Lighthill balance results in smooth waveforms, often termed *kinks* (to be precisely defined below), in the traveling wave context [33]. (In higher-order evolution equations, such as the celebrated Korteweg–de Vries model, this balance produces *solitons* [34, Section 2.1].) Ghosal and Chen [27–30] presented numerical evidence, and analytical results in some special cases, showing that the Taylor–Lighthill balance yields permanent traveling electromigration waveforms. However, a detailed mathematical analysis of [30, Eq. (3.23)] is lacking. Additionally, in [30], the authors also suggested the use of a modified version of the original nonlinearities (specifically, a Taylor-series expansion keeping only a few terms) of the electromigration dispersion equation. It is known, however, that such modifications of the nonlinearities are not always valid and can lead to significant differences between the original and approximate equations in the context of nonlinear acoustics [35,36]. Therefore, there is an impetus to obtain *exact* results regarding the *full* nonlinear electromigration dispersion equation.

To this end, in the present work, we show that exact traveling wave solutions can be constructed for the electromigration dispersion equation, and the latter can be well approximated by Taylor shock (*i.e.*, “tanh”) [37,31] profiles. Aside from the fundamental, mathematical interest in obtaining an exhaustive classifications of various solutions to field theories [38], it is important to understand traveling electromigration wave phenomena [39] (also known as *isotachophoretic boundaries* [40] in other contexts) because, for example, such traveling waves can be used as the basis for electrophoretic separation methods [40]. In this context, being able to generate and propagate a concentration kink through an ionic solution leads to the partitioning of the solution into zones of nearly uniform compositions [40], effectively separating analytes of different conductivities. Alternatively, a traveling-wave can be imposed by applying an external electric field, which also yields an effective separation technique for microfluidic devices [41].

2. Problem formulation

Ghosal and Chen [18, Eq. (3.23)] derived the following macrotransport equation for the cross-sectionally averaged sample concentration $\bar{\phi}(x, t)$ (relative to the background):

$$\frac{\partial \bar{\phi}}{\partial t} + \frac{\partial}{\partial x} \left[\left(u_{eo} + \frac{v_0}{1 - \alpha \bar{\phi}} \right) \bar{\phi} \right] = \frac{\partial}{\partial x} \left\{ \left[D + \frac{ku_{eo}^2 w_0^2}{D} \left(\frac{\alpha \bar{\phi}}{1 - \alpha \bar{\phi}} \right)^2 \right] \frac{\partial \bar{\phi}}{\partial x} \right\} \quad (0 < \bar{\phi} < 1/\alpha), \quad (1)$$

where t is time, x is the streamwise coordinate, the positive constant u_{eo} is the mean electroosmotic flow speed, the positive constant v_0 is the migration velocity of any isolated ion, α is a constant parameter used in [27] to characterize the nonlinearity, D is the constant diffusivity of each ion species (all equal in this case), w_0 is the planar capillary's constant half-width and $k = 2/105$.

To simplify the analysis, we rescale $\bar{\phi}$ and switch to the moving frame of the mean flow:

$$x^* = x - u_{eo}t, \quad t^* = t, \quad \bar{\phi}^*(x^*, t^*) = \alpha \bar{\phi}(x, t), \quad (2)$$

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