# Mathematical analysis of electromigration dispersion fronts

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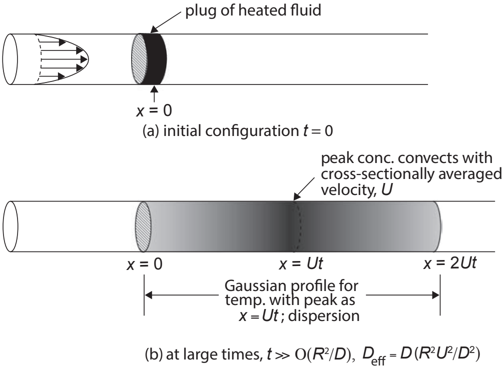
# Introduction: Taylor–Aris (shear) dispersion




"The transport process that leads to the spread of this cross-sectionally averaged temperature pulse turns out to resemble a pure axial conduction (or diffusion) process and is therefore called Taylor dispersion." (Leal, *Advanced Transport Phenomena*, 2007, §3-H-2)

- Key physics: shear enhances diffusion.
- Applications
  - measuring molecular diffusivity of solutes (Taylor, *Proc. R. Soc. A* 1954)
  - chromatography, separations (Golay, *Gas Chromatography* 1958)
  - but, limits throughput/ resolution in microfluidics (Bae *et al.*, *Lab Chip* 2009)
- What about migration of ions in electro-osmotic flows?

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# Theory of Taylor–Aris dispersion

- Diffusive passive tracer advected by a flow in 2D obeys

$$\frac{\partial c}{\partial t} + v_x(y)\frac{\partial c}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right).$$

- Let $c(x,z,t) = \bar{c}(x,t) + c'(x,y,t)$ and $v_x(y) = \overline{v_x} + v_x'(y)$.
- For $L/h \gg \overline{v_x}h/D_0$ and $|c'|/\bar{c} \ll 1$, can separate the evolution of the mean $\bar{c}$ from fluctuations $c'$ to obtain a macrotransport equation:

$$\frac{\partial \bar{c}}{\partial t} + \overline{v_x}\frac{\partial \bar{c}}{\partial x} \approx \frac{\partial}{\partial x}\left(\bar{D}\frac{\partial \bar{c}}{\partial x}\right) - \overline{v_x'\frac{\partial c'}{\partial x}},$$

$$\frac{\partial}{\partial y}\left(D\frac{\partial c'}{\partial y}\right) \approx v_x'\frac{\partial \bar{c}}{\partial x}.$$

- NB: 'dispersion' in the sense of 'dispersal' (not $\omega(k)$).

(G.I. Taylor, *Proc. R. Soc. A* 1953; Aris, *Proc. R. Soc. A* 1956; Brenner & Edwards, *Macrotransport Processes*, 1993, see also Griffiths & Stone, *EPL*, 2012; Christov & Stone, *Granular Matter*, 2014)

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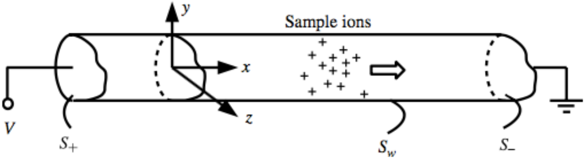
# Electromigration dispersion due to electro-osmotic flow




- Assuming infinitely thin Debye layers and simplest three-ion model (Ghosal & Chen, *J. Fluid Mech.* 2012; also APS DFD 2010 & 2011):

$$\Phi_t + \boldsymbol{\nabla}\cdot\big[(\boldsymbol{V}+\boldsymbol{E})\Phi\big] = Pe^{-1}\boldsymbol{\nabla}^2\Phi, \qquad \boldsymbol{n}\cdot\boldsymbol{\nabla}\Phi = 0 \;\; (\boldsymbol{x}\in S_w),$$
$$-\boldsymbol{\nabla}P + \boldsymbol{\nabla}^2\boldsymbol{V} = \boldsymbol{0}, \quad \boldsymbol{\nabla}\cdot\boldsymbol{V} = 0, \qquad V_1 = u_* E_1 \;\; (\boldsymbol{x}\in S_w),$$
$$\boldsymbol{\nabla}\cdot[(1-\Phi)\boldsymbol{E}] = 0, \quad \boldsymbol{\nabla}\times\boldsymbol{E} = \boldsymbol{0}, \qquad \boldsymbol{n}\cdot\boldsymbol{E} = 0 \;\; (\boldsymbol{x}\in S_w).$$

- The electromigration dispersion equation can derived by standard methods (e.g., Pagitas, Nadim & Brenner, *Physica A*, 1986), is

$$\frac{\partial\Phi}{\partial T} + \frac{\partial}{\partial X}\left(\frac{\Phi}{1-\Phi}\right) = \frac{1}{Pe}\frac{\partial}{\partial X}\left\{\left[1 + k u_*^2 Pe^2\left(\frac{\Phi}{1-\Phi}\right)^2\right]\frac{\partial\Phi}{\partial X}\right\},$$

where $0 < \Phi < 1$, $Pe = v_0 h/D (> 0)$ and $u_* = u_{\text{eo}}/v_0 (> 0)$.

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# Reduction to an ODE under the traveling wave ansatz

- For right-traveling waves $\Phi(X, T) = F(Z)$, $Z = (X - cT)Pe$, $c > 0$, letting $\kappa := ku_*^2 Pe^2 (> 0)$, we obtain after an integration:

$$F' = \underbrace{[1 - c(1 - F)](1 - F)F / \left[(1 - F)^2 + \kappa F^2\right]}_{=\mathfrak{G}(F)},$$

which is a form of Darboux's ODE (Murphy, *ODEs and their solutions*, 1960).

[Note that $(1 - F)^2 + \kappa F^2$ cannot be 0, and $0 < F < 1$!]

- Equilibria ($\mathfrak{G} = 0$) are $F_0 = 0$, $F_1 = 1 - 1/c$, $F_2 = 1$; their stability is determined by $\mathfrak{G}'(F_i)$.
- General solution exact solution can be found implicitly:

$$\left[(c-1)^2\kappa + 1\right] \ln[1 - c(1 - F)] - \left[(c-1)\kappa \ln(1 - F) + \ln F\right] c = (Z - Z_0)(c - 1)c.$$

- Goal: determine structure of allowed front-type ("kink") solutions based on this expression.

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# Step 1: Study stability diagram of equilibria

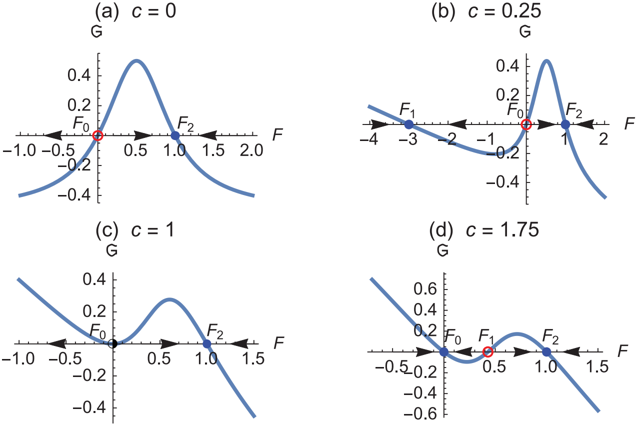


Figure: $\mathfrak{G}(F)$: RHS of the ODE; $\kappa = 1$ without loss of generality; equilibrium points are $F_{0,1,2}$ (open for unstable, filled for stable, half-filled for neutral).

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# Step 2: Construct kinks connecting stable equilibria

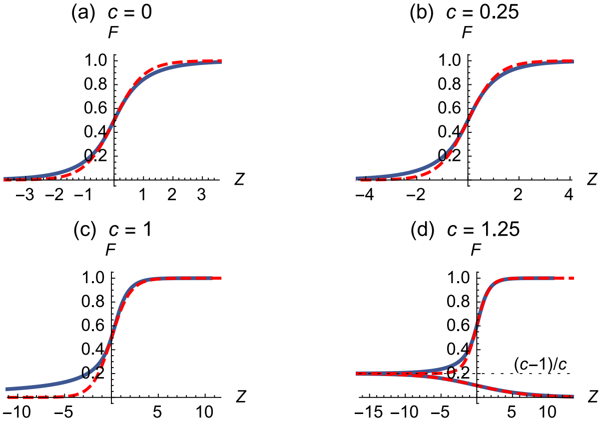


Figure: Solid: exact kink solutions illustrating all possible scenarios; Dashed: Taylor shock (G.I. Taylor, *Proc. R. Soc. Lond. A*, 1910) approximation:
$F(Z) \approx \frac{1}{2}\left[F(+\infty) + F(-\infty)\right] + \frac{1}{2}\left[F(+\infty) - F(-\infty)\right] \tanh(2Z/\ell)$, $\ell = \left|\frac{F(+\infty) - F(-\infty)}{F'(0)}\right|$.

# Summary

- Obtained and classified the exact front solutions to the equation of electromigration dispersion, via a reduction to Darboux's ODE.
  - *Permanent* waveforms *unlike* classical Taylor–Aris dispersion.
- Showed that for (dimensionless) front speeds $> 1$, bistability allows two co-existing front solutions (one increasing, one decreasing).
- Open problems:
  - Are the kink solutions "global attractors," emerging from any IC?
  - Can bistatiblity be exploited in applications to chromatography and separations? Traveling wave electrophoresis? (Edwards *et al.*, *Phys. Rev. Lett.*, 2009)
- Ref.: I.C. Christov, "Nonlinear waves in electromigration dispersion in a capillary," *Wave Motion* (2017) to appear; arXiv:1603.08277.

Thank you for your attention!

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