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# Involutive formulation for electroneutral microfluids

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## Abstract

In this paper we study a microfluidic flow model where the movement of several charged species is coupled with electric field and the motion of ambient fluid. The main numerical difficulty in this model is the net charge neutrality assumption which makes the system essentially overdetermined. Hence we propose to use the involutive and the associated augmented form of the system in numerical computations. The numerical experiments show that our approach gives significantly better results than the standard approach. Our methodology is also applicable to other overdetermined systems.

*Key words:* electrophoresis, stacking, overdetermined PDE, involution  
*1991 MSC:* 35K55, 58J10, 65M60, 76W05

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## 1 Introduction

Over the past 15 years, integrated electrokinetic microsystems have been developed with a variety of functionalities including sample pretreatment, mixing, and separation. Electric fields are used either to generate bulk fluid motion (electroosmosis) or to separate charged species (electrophoresis). In this article we study a widely used mathematical model for electrophoresis [1,2,5,8,16,20].

Mathematically this leads to a complicated system of nonlinear PDEs. The system is naturally composed of 2 blocks. The first is the Stokes system which

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governs the motion of the ambient fluid where the charged species of interest are. The second block is a nonlinear convection diffusion system for charged species and elliptic equation for electric potential. The real challenge comes from the physically reasonable charge neutrality assumption: charge distributions for different species add up to zero. This constraint makes the system essentially overdetermined, and leads immediately to problems with standard numerical methods which are designed to deal only with square systems (as many equations as unknowns).

Our method, already used in [9,10], uses the involutive and its associated augmented form of the system in numerical computations. The augmented form can be constructed once the involutive system and its compatibility operator are known. Typically this leads us back to the class of square systems where again standard methods are applicable. All relevant constraints of the problem are now explicitly included in the augmented system, hence the numerical errors related to constraints can effectively be controlled. The computations thus become more stable because one does not need to worry about possible instabilities due to nonrespect of constraints. Also the results will be more reliable, and they are more likely to reproduce essential qualitative properties of the solution than the standard methods. An example of this is presented below. Note that our approach is not restricted to microfluidic systems, but on the contrary can be applied in a wide variety of situations.

The content of the article is as follows. In section 2 we briefly recall what is meant by involutive, completed and augmented systems. In section 3 we present the physical model and then in section 4 derive the corresponding completed systems, both in stationary and time dependent case. Then in section 5 the relevant augmented systems are introduced and in section 6 we present our numerical results. Our method gives clearly better results than the standard approach. Finally in section 7 we conclude with some perspectives for future work.

## 2 Involutive, completed and augmented systems

### 2.1 Involutive systems

The important concept of involutivity is unfortunately quite difficult to define precisely. However, for our purposes it is sufficient to explain the idea in concrete terms and indicate how to work with this notion constructively. For more details we refer to [3,6,7,9,10,15,18,19,21].

Let us consider the system  $\nabla \times y + y = 0$ . Taking the divergence we see that if

$y$  is a solution, then it must also satisfy  $\nabla \cdot y = 0$ . This new equation is called a *differential consequence* or *integrability condition* of the initial system. Hence we have two systems:

$$\mathcal{S} \quad : \quad \nabla \times y + y = 0 \qquad \mathcal{S}' \quad : \quad \begin{cases} \nabla \times y + y = 0 \\ \nabla \cdot y = 0 \end{cases} \quad (1)$$

We say that  $\mathcal{S}'$  is the involutive form of  $\mathcal{S}$  because no more new first order differential consequences can be found. So informally we may say that *a system is involutive, if it contains all its differential consequences (up to given order)*.

There are many tricky issues involved when one actually tries to compute the involutive form, but the important point is that these constructions can be in fact carried out. Hence the approach we are proposing here is potentially useful for solving quite general systems of PDE.

It turns out that for the purposes of numerical computation it is sometimes convenient to use not the “full” involutive form of the system, but to add just some of the integrability conditions to the original system. Hence we will use the term *completed system* to indicate that we may not use the full involutive system.

But since completed systems usually have more equations than unknowns while the numerical methods for PDEs are designed for square systems, it is not obvious how to generalize for example the finite element method to this more general case. We outline below one possible approach.

## 2.2 Augmented systems

Let us consider our problem in a general form

$$A_0 y = f \quad (2)$$

and let us suppose that  $A_0$  is already in completed form. Now since  $A_0$  is in general overdetermined, there are typically no solutions for arbitrary  $f$ ; hence there are some *compatibility conditions* for  $f$ . These conditions are given by a *compatibility operator*  $A_1$  such that  $A_1 A_0 = 0$  and (2) has a solution only if  $A_1 f = 0$ .

Let us now introduce some function spaces  $V_i$  such that  $A_i : V_i \rightarrow V_{i+1}$ . Let us suppose that  $A_0$  is injective,  $A_1$  is surjective, and that  $\text{image}(A_0) = \ker(A_1)$ ; in other words the following complex is exact:

$$0 \longrightarrow V_0 \xrightarrow{A_0} V_1 \xrightarrow{A_1} V_2 \longrightarrow 0$$

This suggests that we can decompose  $V_1$  as follows:

$$\text{image}(A_0) \oplus \text{image}(A_1^T) \simeq V_1$$

where  $A_1^T$  is the formal transpose of  $A_1$ . Of course to be able to write equality instead of  $\simeq$  we should specify carefully the relevant vector spaces. However, proceeding formally, this decomposition suggests that it is indeed possible to find some functional framework such that the combined operator  $(A_0, A_1^T)$  would be bijective or at least Fredholm.

So instead of trying to solve the original system (2) in some least square sense, we introduce an auxiliary variable  $\tilde{y}$  and solve

$$A_0 y + A_1^T \tilde{y} = f \tag{3}$$

We call this system the *augmented system*. This formulation is reasonable because the augmented system is square, hence standard software is readily available. Also all the relevant information about the original system is contained in the completed operator  $A_0$  which means that the results will be reliable. The drawback is that we have introduced an extra variable  $z$  which increases the computational cost. However, we can use  $\tilde{y}$  in error control as explained in [9].

### 3 Governing equations of ionic microfluids

#### 3.1 Physical background.

Electrokinetic systems have been developed to perform a variety of functions including chemical separations, pre-concentration, and mixing [2,20]. Examples of separation assays include on-chip capillary zone electrophoresis and isoelectric focusing. Preconcentration methods include field amplified sample stacking and isotachophoretic preconcentration. These applications involve the convective-diffusion-electromigration of multiple ionic and neutral species.

Below we will discuss a fairly general convective diffusion system of equations applicable to electrokinetic microfluidics. We assume uniform and constant electrical permittivity and low Reynolds number flows. We also assume species are dilute enough to apply the Nernst-Planck equations and the dilute approximation for Fick's law [16].

Our formulation is applicable in thin electrical double layers, and accounts for net charge accumulation in the bulk resulting from a coupling between electric fields and conductivity gradients. The principal computational difficulty in this

model is due to the net electroneutrality assumption. This assumption is valid on the length scales relevant to the phenomena under study [5,8,16].

### 3.2 Initial model.

Let us consider the case where we have  $m$  different charged species in some ambient fluid. Let  $\rho^e = F \sum_i z_i C^i = \sum_i z_i c^i$  be the net charge density where  $z_i \in \mathbb{Z}$  is the valence number of species  $i$ ,  $C^i$  is the molar concentration and  $F$  is the Faraday's constant. The charge induces an electric field which is supposed to come from the potential  $\phi$ . Hence we get our first equation

$$-\varepsilon \Delta \phi - \rho^e = 0$$

where  $\varepsilon$  is the permittivity of the ambient fluid. The motion of ambient fluid is governed by Navier-Stokes equations, but because in typical applications the Reynolds number is very low we can as well use the Stokes system. We will further suppose that the ambient fluid is incompressible. Hence the Stokes system in the presence of electric field can be written as

$$\begin{aligned} \rho u_t - \mu \Delta u + \nabla p - \rho^e \nabla \phi &= 0 \\ \nabla \cdot u &= 0 \end{aligned}$$

Here  $\rho$  is the density of the fluid and  $\mu$  is the dynamic viscosity. Now the movement of different species are governed by equations  $c_t^i + \nabla \cdot \mathbf{J}^i = 0$  where the current density  $\mathbf{J}^i$  is given by

$$\mathbf{J}^i = -\nu_i c^i \nabla \phi - d_i \nabla c^i + c^i u$$

where  $\nu_i$  is the mobility times the Faraday's constant and  $d_i$  the diffusivity of species  $i$ . We have now introduced all necessary variables and parameters. Taking into account that  $\nabla \cdot u = 0$  one has:

$$\nabla \cdot \mathbf{J}^i = -\nu_i \langle \nabla c^i, \nabla \phi \rangle - \nu_i c^i \Delta \phi - d_i \Delta c^i + \langle \nabla c^i, u \rangle$$

This gives the system

$$\begin{aligned} \rho u_t - \mu \Delta u + \nabla p - \rho^e \nabla \phi &= 0 \\ \nabla \cdot u &= 0 \\ c_t^i - d_i \Delta c^i - \nu_i c^i \Delta \phi - \nu_i \langle \nabla c^i, \nabla \phi \rangle + \langle \nabla c^i, u \rangle &= 0 \quad , \quad i = 1, \dots, m \\ -\varepsilon \Delta \phi - \rho^e &= 0 \\ \rho^e - \sum_i z_i c^i &= 0 \end{aligned}$$

In the following we will only consider the net neutrality assumption case where  $\rho^e = 0$ . Assuming this, and taking the divergence of the first equation and simplifying we obtain

$$\begin{aligned}
\rho u_t - \mu \Delta u + \nabla p &= 0 \\
- \Delta p &= 0 \\
\nabla \cdot u &= 0 \\
c_t^i - d_i \Delta c^i - \nu_i c^i \Delta \phi - \nu_i \langle \nabla c^i, \nabla \phi \rangle + \langle \nabla c^i, u \rangle &= 0 \quad , \quad i = 1, \dots, m \\
- \Delta \phi &= 0 \\
- \sum_i z_i c^i &= 0
\end{aligned} \tag{4}$$

Note that the system is naturally composed of 2 blocks: the Stokes system for variables  $(u, p)$  and a diffusion like system for variables  $(c, \phi)$ .

The main difficulty in solving (4) with standard methods is that the electroneutrality constraint (the last equation) is not respected. Of course one of the species could be deduced from the constraint:

$$c^m = -\frac{1}{z_m} \sum_{i=1}^{m-1} z_i c^i \tag{5}$$

However, this is a real limitation because in this case the physical characteristics of one species are not taken into account during integration. Hence it is definitely interesting to include the electroneutrality constraint explicitly in the numerical model.

To complete the model (4) we should now impose the relevant boundary conditions. However, now an essential difficulty appears concerning the potential  $\phi$ . On one hand from physical point of view it is clear that values of  $\phi$  on the boundary depend on other variables of the problem. However, in order to get physically reasonable boundary conditions one should model the quite complicated interactions of variables in a thin boundary layer. On the other hand in the intended application the precise behavior of the solution in the boundary layer is not very important and hence one would like to use some simple boundary conditions and model the interactions of potential with other variables in another way. Hence we drop the equation  $\Delta \phi = 0$  in (4) and proceed with

$$\begin{aligned}
\rho u_t - \mu \Delta u + \nabla p &= 0 \\
- \Delta p &= 0 \\
\nabla \cdot u &= 0 \\
c_t^i - d_i \Delta c^i - \nu_i c^i \Delta \phi - \nu_i \langle \nabla c^i, \nabla \phi \rangle + \langle \nabla c^i, u \rangle &= 0 \quad , \quad i = 1, \dots, m \\
- \sum_i z_i c^i &= 0
\end{aligned} \tag{6}$$

## 4 Completion of the initial model.

It is convenient to introduce the following quantities:

$$\begin{aligned}\beta &= \sum_i \frac{z_i \nu_i c^i}{d_i} & \eta &= \sum_i \frac{z_i c^i}{d_i} \\ \psi &= \sum_i z_i \nu_i c^i\end{aligned}\tag{7}$$

These are all different kind of weighted averages of concentration fields and they appear naturally in the analysis of the system (6).

### 4.1 Stationary case

Let us consider first the stationary case of (6):

$$\begin{aligned}-\mu \Delta u + \nabla p &= 0 \\ -\Delta p &= 0 \\ -\nabla \cdot u &= 0 \\ -d_i \Delta c^i - \nu_i \nabla \cdot (c^i \nabla \phi) + \langle \nabla c^i, u \rangle &= 0 \quad , \quad i = 1, \dots, m \\ -\sum_i z_i c^i &= 0\end{aligned}\tag{8}$$

There seems to be too few equations: there is apparently no “natural” 2nd order equation for  $\phi$ . However, we can get an independent equation for  $\phi$  using the “constraint”  $\sum_i z_i c^i = 0$ . Differentiating this we obviously have

$$\sum_i z_i \Delta c^i = 0$$

Multiplying the equations for  $c^i$  in (8) by  $z_i/d_i$  and adding them to the above equation we obtain

$$-\sum_i \frac{z_i \nu_i}{d_i} \nabla \cdot (c^i \nabla \phi) + \sum_i \frac{z_i}{d_i} \langle \nabla c^i, u \rangle = 0$$



Our current system can thus be written as

$$\begin{aligned}
& -\mu\Delta u + \nabla p = 0 \\
& -\Delta p = 0 \\
& -\nabla \cdot u = 0 \\
& -d_i\Delta c^i - \nu_i c^i \Delta \phi + \langle \nabla c^i, u - \nu_i \nabla \phi \rangle = 0 \quad , \quad i = 1, \dots, m \quad (9) \\
& -\nabla \cdot (\beta \nabla \phi) + \langle \nabla \eta, u \rangle = 0 \\
& -\sum_i z_i c^i = 0
\end{aligned}$$

Because the system is quasilinear, the principal symbol of its linearized version does not depend on the nonlinear terms of the original system. In fact the symbol is

$$\sigma L = |\xi|^2 \begin{pmatrix} L_1 & 0 \\ 0 & L_2 \end{pmatrix} \quad \text{where}$$

$$L_1 = \begin{pmatrix} \mu & 0 & 0 & 0 \\ 0 & \mu & 0 & 0 \\ 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad L_2 = \begin{pmatrix} d_1 & 0 & \dots & 0 & \nu_1 \bar{c}^1 \\ 0 & d_2 & \dots & 0 & \nu_2 \bar{c}^2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & d_m & \nu_m \bar{c}^m \\ 0 & 0 & \dots & 0 & \bar{\beta} \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Hence the linearised system is elliptic, if  $\bar{\beta} \neq 0$  because  $\sigma L$  is injective for all  $\xi \neq 0$  in this case. Here  $\bar{c}^i$  and  $\bar{\beta}$  indicate the reference solution around which the system is linearized.

#### 4.2 Time dependent case

Let us consider the system (6). To obtain an equation for  $\phi$  we now multiply the equations for  $c^i$  by  $z_i$ , then operate with  $\partial_t - a\Delta$  to the last equation and

add. This gives

$$\begin{aligned}
\rho u_t - \mu \Delta u + \nabla p &= 0 \\
-\Delta p &= 0 \\
-\nabla \cdot u &= 0 \\
c_t^i - d_i \Delta c^i - \nu_i \nabla \cdot (c^i \nabla \phi) + \langle \nabla c^i, u \rangle &= 0 \quad , \quad i = 1, \dots, m \quad (10) \\
-\nabla \cdot (\psi \nabla \phi) - \sum_i z_i (d_i - a) \Delta c^i &= 0 \\
-\sum_i z_i c^i &= 0
\end{aligned}$$

Now arguing as above in the stationary case we expect that the system is well-posed if  $\psi \neq 0$ , because the (linearised version of the) next to last equation is elliptic in this case.

Note that the system as a whole is not parabolic according to standard definitions [4]. Instead we could say that it is of *elliptic-parabolic type* in the following sense:

- putting  $p = \phi = 0$  the linearised system is parabolic for  $(u, c)$
- putting  $u = 0, c = 0$  the linearised system is elliptic for  $(p, \phi)$

Hence we could call  $(p, \phi)$  elliptic variables and  $(u, c)$  parabolic variables. It seems that there is no “general” theory for these kind of systems, although in addition to Stokes system there are apparently quite many models of this type, for example the chemotaxis model [12].

## 5 From completed to augmented systems.

### 5.1 Stationary case

Our next task is to construct the augmented system corresponding to (9), and in order to do that we need to find the compatibility operator. Let us denote  $y = (u^1, u^2, u^3, p, c^1, \dots, c^m, \phi)$  and write the system (9) as  $A_0 y = 0$ . Now the Stokes system is a subsystem of (9), hence one compatibility condition comes from that. The second one is simply given by our construction of the equation for  $\phi$ . So if we define

$$A_1 = \begin{pmatrix} \nabla \cdot 1 & -\mu \Delta & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & 0 & z_1/d_1 & \dots & z_m/d_m & -1 & -\Delta \end{pmatrix}$$

then it is easy to check that  $A_1 A_0 = 0$ . Now introducing  $\tilde{y} = (\tilde{y}^1, \tilde{y}^2)$  the augmented system  $A_0 y + A_1^T \tilde{y} = 0$  can be written as

$$\begin{aligned}
& -\mu\Delta u + \nabla p - \nabla \tilde{y}^1 = 0 \\
& -\Delta p + \tilde{y}^1 = 0 \\
& -\nabla \cdot u - \mu\Delta \tilde{y}^1 = 0 \\
& -d_i \Delta c^i - \nu_i \nabla \cdot (c^i \nabla \phi) + \langle \nabla c^i, u \rangle + \frac{z_i}{d_i} \tilde{y}^2 = 0 \quad , \quad i = 1, \dots, m \quad (11) \\
& -\nabla \cdot (\beta \nabla \phi) + \langle \nabla \eta, u \rangle - \tilde{y}^2 = 0 \\
& -\sum_i z_i c^i - \Delta \tilde{y}^2 = 0
\end{aligned}$$

Again linearized version of this is elliptic, if  $\beta \neq 0$ . Hence the system should be well-posed under the same hypothesis as the system (9). Note also that the system (11) is nicely decoupled in two blocks so that the auxiliary variables do not interact. Moreover the structure of the block for  $c^i$  and  $\phi$  is such that the principal part also has a block structure so that all variables can be solved cyclically.

## 5.2 Time dependent case

Denoting the system (10) by  $K_0 y = 0$  we get the following compatibility operator

$$K_1 = \begin{pmatrix} \nabla \cdot 1 & \rho \partial_t - \mu \Delta & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & 0 & z_1 & \dots & z_m & -1 & \partial_t - a \Delta \end{pmatrix}$$

Hence the augmented system  $K_0 y + K_1^T \tilde{y} = 0$  can be written as

$$\begin{aligned}
& \rho u_t - \mu \Delta u + \nabla p - \nabla \tilde{y}^1 = 0 \\
& -\Delta p + \tilde{y}^1 = 0 \\
& \rho \tilde{y}_t^1 - \nabla \cdot u - \mu \Delta \tilde{y}^1 = 0 \\
& c_t^i - d_i \Delta c^i - \nu_i \nabla \cdot (c^i \nabla \phi) + \langle \nabla c^i, u \rangle + z_i \tilde{y}^2 = 0 \quad , \quad i = 1, \dots, m \quad (12) \\
& -\nabla \cdot (\psi \nabla \phi) - \sum_i z_i (d_i - a) \Delta c^i - \tilde{y}^2 = 0 \\
& \tilde{y}_t^2 - a \Delta \tilde{y}^2 - \sum_i z_i c^i = 0
\end{aligned}$$

Note that this is also of elliptic–parabolic type and the auxiliary unknowns  $\tilde{y}$  are parabolic. Again we expect that the system is well-posed if  $\psi \neq 0$ . The parameter  $a$  can be freely chosen, but looking at the last equation we see that it should be positive. Note that dropping the time dependence in (12) gives an alternative formulation of the stationary problem which is a bit different from (11).

The auxiliary variables  $\tilde{y}^1$  and  $\tilde{y}^2$  satisfy  $K_1 K_1^T \tilde{y} = 0$  and writing this out gives

$$\begin{aligned}\rho^2 \tilde{y}_{tt}^1 - 2\rho\mu\Delta\tilde{y}_t^1 + \mu^2\Delta^2\tilde{y}^1 - \Delta\tilde{y}^1 + \tilde{y}^1 &= 0 \\ \tilde{y}_{tt}^2 - 2a\Delta\tilde{y}_t^2 + a^2\Delta^2\tilde{y}^2 + (1 + |z|^2)\tilde{y}^2 &= 0\end{aligned}$$

These are 2-parabolic equations [4] (the latter for  $a > 0$ ).

## 6 Implementation and examples

### 6.1 Physical setting

The derivation of completed and augmented systems presented above is valid in any dimension. Physically the problem is obviously strictly speaking 3 dimensional. In a typical application one could consider a horizontal channel of  $100\mu\text{m}$  wide,  $100\mu\text{m}$  deep and several centimeters long. However, the boundary layers along channel walls are only a few nanometers thick which implies that a 2 dimensional model is relevant and even a 1 dimensional model can be used [1]. Indeed when one is mainly interested in stacking (see below) already 1 dimensional model gives sufficiently accurate results. However, if one wants to simulate how the propagating front of some concentration is distorted for example in curved channels then one must use a 2 dimensional model.

We did some computations both with 2 and 1 dimensional models. The channel width was chosen as  $100\mu\text{m}$  and the length as 1mm. The computational cost of 2 dimensional case was about 100 times bigger than in 1 dimensional case. Such a dramatic difference is due to the fact that the resolution of the flow of the ambient fluid becomes trivial in 1 dimensional case. Hence we did only few test runs in 2 dimensional case and most of the computations were done with 1 dimensional model.

Because we have already analysed the augmented Stokes system in our previous papers [9,10] we will only discuss below how our formulation improves the quality of the solutions of concentrations of species  $c^i$ . This is also justified by the fact that in this model the main interest and the main computational difficulty is related to concentrations while the motion of the ambient fluid is relatively unimportant and in any case considerably easier to compute.

## 6.2 Stacking

The aim of stacking is to amplify the local concentrations of species to make them observable by existing devices. We consider the case of 3 ionic species. The third species is the sample species of interest whose molar concentration is low and one would like to increase it through stacking. Typically the sample species is three or four orders of magnitude smaller than other species and consequently one needs to stack the sample species by the factor of about 1000 to make it observable. Representative experimental conditions are described in [1,8,11].

To model a single interface of conductivities, we choose a simple error function profile for the initial concentration. We consider the following initial conditions for the species that reproduces well the experimental conditions:

$$\begin{aligned} c_{\text{init}}^1(x) &= \frac{1}{2} b_1 (\gamma + 1 - (\gamma - 1) \text{erf}(\alpha x)) \\ c_{\text{init}}^3(x) &= b_3 (1 + \text{erf}(\alpha x)) \\ z_2 c_{\text{init}}^2(x) &= -z_1 c_{\text{init}}^1(x) - z_3 c_{\text{init}}^3(x) \end{aligned} \quad (13)$$

where  $b_1 = 100$ ,  $b_3 = 0.1$ ,  $\alpha > 0$  and  $\gamma > 0$ . Note that  $\alpha$  controls the sharpness in the initial plug and  $\gamma$  indicates the initial concentration ratio between high and low conductivity regions in the sense that

$$\lim_{x \rightarrow -\infty} c_{\text{init}}^1(x)/b_1 = \gamma, \quad \lim_{x \rightarrow \infty} c_{\text{init}}^1(x)/b_1 = 1$$

In fact a more important property of  $\gamma$ , both experimentally and numerically, is that it also indicates the final stacking ratio of  $c^3$ . This can be seen as follows.

Let us consider the 1 dimensional model. Neglecting diffusion and the motion of the ambient fluid, the species conservation equation for different species becomes

$$c_t^i + \frac{\partial}{\partial x} (z_i \nu_i c^i \phi_x) = 0$$

A constant current density  $\mathbf{j}$  is applied in the axial direction defined by the difference of electric potential at the ends of the channel:

$$\mathbf{j} = \frac{V_{\text{left}} - V_{\text{right}}}{L} \sigma_{\text{total}}$$

where  $L$  is the length of the channel and

$$\sigma_{\text{total}} = \int_0^L \sigma(x, t) dx, \quad \sigma(x, t) = \sum_i z_i^2 \nu_i c^i$$

Let us further suppose that  $\sigma_{\text{total}}$  is independent of time. The electric field is

then locally defined as:

$$E = \phi_x = \frac{j}{\sigma}$$

Now in our setting of 3 species the concentration of sample species  $c^3$  increases as it migrates from a region of high conductivity to a region of lower drift velocity. Hence the stacked sample keeps increasing with time and the concentration progressively approaches a maximum steady value. Now in the steady state the net flux of the species  $c^3$  at the left and right edges balance:

$$(z_3\nu_3c^3E)|_{\text{left}} = (z_3\nu_3c^3E)|_{\text{right}}$$

Then considering the initial conditions (13) we have

$$\sigma_{\text{left}} = \sum_{i=1}^3 z_i^2 \nu_i c_{\text{left}}^i \approx z_1^2 \nu_1 c_{\text{left}}^1 + z_2^2 \nu_2 c_{\text{left}}^2 \approx (z_1^2 \nu_1 - z_1 z_2 \nu_2) b_1 \gamma$$

As  $j$  is constant this implies

$$\frac{c_{\text{left}}^3}{c_{\text{right}}^3} = \frac{E_{\text{right}}}{E_{\text{left}}} = \frac{\sigma_{\text{left}}}{\sigma_{\text{right}}} \approx \gamma$$

When diffusion and motion of the ambient fluid are present the above arguments can still be used to provide an upper bound for the stacking capacity. Indeed, both diffusion and the convective motion tend to distort the front where stacking happens and hence one expects a lower final stacking ratio in this case.

### 6.3 Boundary conditions

The boundary condition for the Stokes system is classical except along solid walls where, to avoid treating the nanometric double-layer region, one assumes the following slip boundary condition [5,16]:

$$u = -\zeta \nabla \phi$$

Here  $\zeta$  is a positive constant which depends on the material with which channels are built and also the fluid permittivity and dynamic viscosity. The flow is therefore parallel to the wall and to the electric field. For the electric potential we impose a Dirichlet boundary condition at the inlet and the outlet where a difference of potential is applied and homogeneous Neumann boundary condition is assumed along the wall. Together with the boundary condition for  $u$  along the wall, the former condition enforces the non-penetration boundary condition for the velocity.

The boundary condition for the concentration is Dirichlet at the inlet boundary, homogeneous Neumann along the walls and at the outlet. Initial and

boundary conditions for the auxiliary variables  $\tilde{y}$  are identically zero as these are compatible with the requirement that the solution of the initial and completed systems should match.

#### 6.4 Test cases

We have used the following parameters in our computations, given in SI units. Recall that mobility in our case is the usual mobility multiplied by Faraday's constant.

mobility	$\nu_1 = 5 \cdot 10^{-8}$	$\nu_2 = 3 \cdot 10^{-7}$	$\nu_3 = 3 \cdot 10^{-8}$
diffusivity	$d_1 = 2 \cdot 10^{-10}$	$d_2 = 3 \cdot 10^{-10}$	$d_3 = 2 \cdot 10^{-10}$
valence number	$z_1 = +1$	$z_2 = -1$	$z_3 = -2$

We chose the value  $\alpha = 4 \cdot 10^4$  in initial conditions (13) and  $a = (d_1 + d_2 + d_3)/3$  in (12). We tried also some other values for  $a$ , but the results were essentially the same as long as  $a$  was of the same order of magnitude as diffusivity. This requirement is quite natural, considering that  $a$  is the diffusivity for the auxiliary variable  $\tilde{y}^2$ .

As we showed above choosing the value of  $\gamma$  in (13) approximately determines the ultimate stacking ratio. Otherwise choosing different values gave qualitatively similar results. The main difference is that reaching a higher stacking ratio takes longer time and hence a longer channel is needed. For this reason we will show below results for just one value of  $\gamma$ . We chose a moderate value which allowed a relatively short channel and hence avoided excessive computational cost. In fact all computations were done with a standard laptop.

We will show that our formulation (12) gives better results than the standard approach which we may identify as the model (6). The effort to implement our method was relatively small because the augmented systems are so designed that the usual building blocks of numerical codes can quite easily be adapted to our context. Indeed our method was implemented by modifying the code which was used to obtain the results described in [1].

Let us make some general remarks of the code which apply as well to the initial code as to our improved code. The system has a block diagonal structure which makes it possible to solve different variables cyclically. We use an explicit time marching fixed point algorithm which produces fully implicit solution of the system [17]. The advection-diffusion equations of species are solved using a mixed finite volume Galerkin implementation providing suitable conservation properties [13]. Finally the equation for  $\phi$  is solved using a classical central difference scheme.

Let us then discuss the results obtained. Figure 1 shows instantaneous iso-contours of the electric field, velocity field, pressure, total charge density, as well as charge density of sample species for  $\gamma = 50$ . One can see that the propagating front for sample species where the stacking occurs is a little curved. Also it is clear that the errors in the total charge density are concentrated in this same region. To analyse the electroneutrality constraint and stacking in more detail we could now take slices of the solution in the middle of the channel, and see how they evolve in time. However, since the curving of the front does not play critical role here we may as well use 1 dimensional model to do this. In our test case doing 2 dimensional computations and then taking 1 dimensional slices produced essentially similar results as direct 1 dimensional simulations.

Figure 2 shows the time histories for  $c^3$ ,  $\tilde{y}^2$  and  $\rho^e$  when solving system (6) and (12) for  $\gamma = 50$ . To make stacking (and also the evolution of other quantities) easier to visualise we have plotted the solutions in different time instants so that the convective movement of the ambient fluid is eliminated. One can clearly see that our method preserves better the electroneutrality constraint. In addition, and perhaps even more importantly, our method respects the upper bound for stacking ratio given by  $\gamma$  while in the standard method there is quite significant overshoot.

We may interpret the results as follows. The solution is most sensitive to errors in the region where rapid changes occur, i.e. in the front where the sample species is stacked. Now the biggest errors are rather naturally in the same region, and because our method reduces significantly the electroneutrality error in this region, the concentrations are also much better resolved.

Finally recall that the linearised version of (12) is well-posed only if  $\psi \neq 0$ . Figure 2 shows that this is indeed the case in our examples. Note that there are natural physically relevant situations where this hypothesis is not satisfied. For example this happens when the background species have valences of opposite sign and whose mobilities are approximately equal. We hope to consider this case in a future work.

## 7 Concluding remarks

We have shown above how our methodology, which was applied in [9,10] to Stokes problem, can also be used to improve existing solvers of microfluid systems. The results show that our approach give clearly better results than the standard approach. It is also remarkable that implementing our method did not require a very big effort. Indeed starting from an existing code it was relatively straightforward to modify it for the present purposes. Moreover the



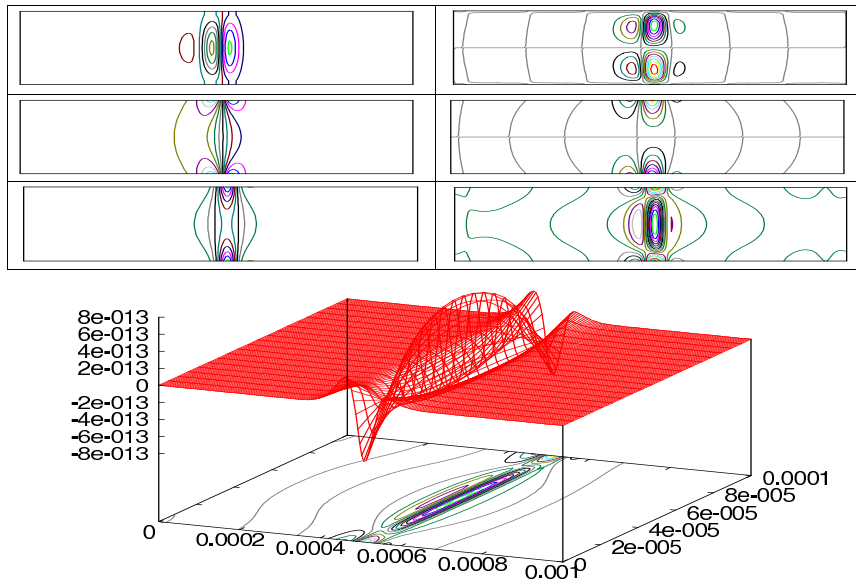


Fig. 1. From top-left to bottom-right: instantaneous iso-contours for  $\phi_x$ ,  $\phi_y$ ,  $u_1$ ,  $u_2$ ,  $p$  and  $\rho^e$ . Bottom figure shows iso-contours of  $c^3$ .

computational cost of solving the augmented system was about the same as the initial system.

In the present paper we did not discuss using the information contained in auxiliary variables so it seems the computation of these quantities did not serve for any useful purpose. However, since the auxiliary variables should be identically zero in exact solution these could be used as error indicators in adaptive numerical schemes. In [9] we indicated how this could be implemented, but we have not explored systematically this aspect.

There are also other physical models with algebraic constraints like the electroneutrality assumption. As an example we may cite the combustion problems where the conservation of mass leads to an algebraic constraint for mass fractions [14]. However, it is important to point out that our approach is not restricted to microfluidic systems or flow problems in general, but can be useful in the analysis of rather arbitrary overdetermined systems.

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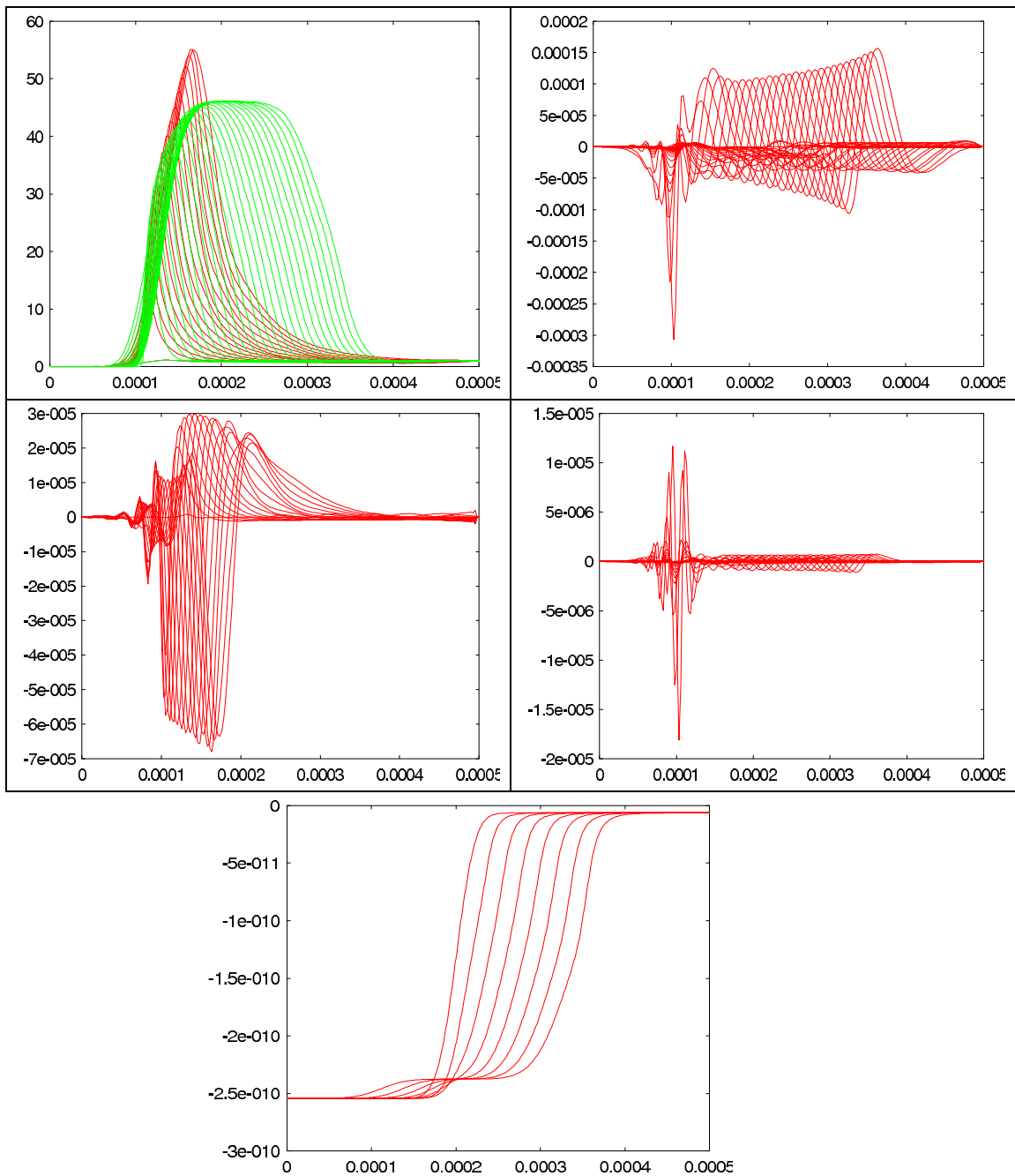


Fig. 2. Evolution of  $c^3$  (top-left) with the initial (6) and augmented (12) systems along the centerline of the channel for an applied electric field of  $100kV/m$  and  $\gamma = 50$ . Top-right picture shows the evolution of  $\tilde{y}^2$ . Middle left (resp. right):  $\rho^e$  with (6) (resp. with (12)). Bottom picture shows that  $\psi$  remains nonzero.

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