Uncertainty Quantification in a Reacting Electrochemical Microchannel Flow Model

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ABSTRACT

We describe a technique for modeling electrochemical microchannel flows including the propagation of uncertainty from model parameters and boundary conditions to the model predictions. The approach uses a pseudo-spectral stochastic construction with a polynomial chaos (PC) representation for parameters and field quantities. Using a Galerkin approach, the governing equations are reformulated into equations for the coefficients in the PC expansion. The implementation of the resulting uncertainty propagation schemes is illustrated in the context of microfluidic applications, including a homogeneous protein-labeling reaction as well as two-dimensional electrochemical flow.

Keywords: Microchannel, Polynomial Chaos, Uncertainty, Stochastic, Simulation

1 INTRODUCTION

Mathematical models used to simulate physical systems usually contain several input parameters. In particular, simulations of electrophoretic phenomena in microchannel flow require knowledge of species mobilities, viscosity, equilibrium constants, reaction rate parameters, and other physical and environmental parameters [1]. These parameters are typically not known exactly due to experimental measurement uncertainties. Therefore, computational predictions will have some uncertainty, associated with the uncertainties in the input parameters. In order to make valid comparisons between experimental and computational data, a careful analysis of uncertainty must be performed.

In the current work, a spectral stochastic uncertainty quantification method [2] is applied to reacting electrochemical microchannel flows. This method introduces a new stochastic dimension for each uncertain parameter, and uses polynomial chaos (PC) representations [3] to describe the dependence of model parameters and flow quantities on these dimensions. These expansions are introduced into the governing equations, which in the present work describe the evolution of an electrokinetically driven multi-component mixture in a microchannel. The physical model accounts for species advection, electromigration, diffusion, and includes a mixed finite-rate, partial-equilibrium formulation for the chemical reactions. In particular, "fast" electrolyte reactions are described by associated equilibrium constraints, while the remaining "slow" reactions are modeled with finite-rate kinetics.

After introducing the PC representations into the governing equations, a pseudo-spectral approach is used to determine evolution equations for the coefficients in the expansion. The pseudo-spectral approach relies on a straightforward Galerkin scheme for linear and quadratic terms, and on approximate projections for other nonlinear terms. The resulting system is more complex than the corresponding deterministic model, requiring more computational effort. On the other hand, it is potentially more efficient than Monte-Carlo (MC) simulations. Moreover, the pseudo-spectral PC approach readily provides sensitivity information and the contribution to total uncertainty by each of the model parameters.

First we outline the formulation and implementation of the stochastic uncertainty quantification method for the microchannel model. Since previous papers [4], [5] addressed the uncertainty quantification of the momentum solution in detail, we will focus mainly on the species transport equations. The methodology is then applied to model protein labeling reactions in homogeneous systems as well as two-dimensional microchannel flows.

2 FORMULATION

2.1 Governing Equations

The formulation includes the continuity and momentum equations for incompressible 2D flow in a rectangular microchannel. The flow is electrokinetically pumped with an electrostatic field in the x-direction. We assume a thin double layer, and an associated slip boundary condition for the streamwise velocity at the wall. We use an empirical relationship for the zeta-potential (ζ) in terms of pH and molarity [6]. Species concentrations evolve according to bulk convection, electromigration, diffusion, and reaction source terms. We assume an aqueous potassium phosphate buffer with the three equilibrium constants (K_1,K_2,K_3) in order of increasing pKa. The solution also contains a model "unlabeled

protein" U and a dye D, which react with a known irreversible pH-dependent labeling rate $k_L = k_L(pH)$ to give a "labeled protein" L. These model proteins are assumed to be electrically neutral. Based on [7], we integrate the transport equations for the two conserved scalars, $\theta_{\mathrm{K}} = [\mathrm{K}^+]$, and

$$\theta_P = [\mathrm{H_3PO_4}] + [\mathrm{H_2PO_4^-}] + [\mathrm{HPO_4^{2-}}] + [\mathrm{PO_4^{3-}}] \quad (1)$$

The concentrations of the individual components of θ_P can then be calculated as $c_i = \alpha_i \theta_P$ where the α_i are a function of $[\mathrm{H}^+]$ and K_i only:

$$\alpha_{\mathrm{H_3PO_4}} = \frac{[\mathrm{H}^+]^3}{[\mathrm{H}^+]^3 + K_1[\mathrm{H}^+]^2 + K_1K_2[\mathrm{H}^+] + K_1K_2K_3} \quad (2)$$

$$\alpha_{\mathrm{H_2PO_4^-}} = \frac{K_1[\mathrm{H}^+]^2}{[\mathrm{H}^+]^3 + K_1[\mathrm{H}^+]^2 + K_1K_2[\mathrm{H}^+] + K_1K_2K_3} \quad (3)$$

$$\alpha_{\mathrm{HPO_4^{2-}}} = \frac{K_1K_2[\mathrm{H}^+]}{[\mathrm{H}^+]^3 + K_1[\mathrm{H}^+]^2 + K_1K_2[\mathrm{H}^+] + K_1K_2K_3} \quad (4)$$

$$\alpha_{\mathrm{PO_4^{3-}}} = \frac{K_1K_2K_3}{[\mathrm{H}^+]^3 + K_1[\mathrm{H}^+]^2 + K_1K_2[\mathrm{H}^+] + K_1K_2K_3} \quad (5)$$

The concentrations of H^+ and OH^- are obtained from the electroneutrality condition and the equilibrium of $\mathrm{H_2O}$.

Finally, allowing for concentration field gradients, a Helmholtz equation is inverted to determine the electric potential, ϕ, and consequently the electrostatic field strength.

2.2 Stochastic Formulation

The Stochastic uncertainty quantification method considers the uncertainty in model parameters by expanding the probability density function (PDF) of these parameters in terms of the PC system [2]. For example, the species diffusivity D can be written as

$$D = \sum_{k=0}^{P} D_k \Psi_k \quad (6)$$

where the Ψ_k are the PC basis functions and the scalar coefficients D_k are the mode strengths. If just one parameter is uncertain in the model, then the PC basis functions are functions of the gaussian variable ξ [3]

$$\Psi_0 = 1,\ \Psi_1 = \xi,\ \Psi_2 = \xi^2 - 1,\ \Psi_3 = \xi^3 - 3\xi,\ \ldots \quad (7)$$

and P corresponds to the highest order polynomial used in the expansion. Given the orthogonality of the basis functions, the coefficients D_k can be calculated from

$$D_k = \frac{< \Psi_k D >}{< \Psi_k^2 >} \quad (8)$$

where the expectation is defined as

$$\langle f \rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(\xi) \exp\left(-\frac{\xi^2}{2}\right) d\xi \quad (9)$$

Note that the expectations $< \Psi_k >= 0$ for $k > 0$. Therefore the coefficient D_0 represents the mean value of D, whereas the higher order modes represent the variation, or uncertainty, around this mean. For a model with N uncertain parameters, an N-dimensional stochastic space is considered, and the Ψ_k are generalized orthogonal polynomials in the gaussian variables ξ_i, $i = 1, \ldots, N$.

The solution variables are expanded similarly to the input parameters. The PC expansions are then introduced into the governing equations in order to determine the evolution of unknown coefficients. For instance, consider the transport equation for the species concentration c

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\boldsymbol{u}) = \nabla \cdot (D \nabla c) + \hat{w} \quad (10)$$

where $\boldsymbol{u}$ is the total convective velocity (bulk + electromigration) and $\hat{w}$ the chemical source term. Substituting the appropriate PC expansions in equation (10), multiplying by Ψ_k, and taking the expectation gives

$$\frac{\partial c_k}{\partial t} + \sum_{i=0}^{P}\sum_{j=0}^{P} C_{ijk} \nabla \cdot (c_i \boldsymbol{u}_j) = \sum_{i=0}^{P}\sum_{j=0}^{P} C_{ijk} \nabla \cdot (D_i \nabla c_j) + \hat{w}_k \quad (11)$$

with $C_{ijk} \equiv \langle \Psi_i \Psi_j \Psi_k \rangle / \langle \Psi_k \Psi_k \rangle$. Equations (11) are then integrated to determine c_k, $k = 0, \ldots, P$.

2.3 Implementation

The computational domain is discretized using a cartesian mesh with uniform cell size Δx and Δy in the x and y direction respectively. The velocities are defined on the cell faces, but the pressure and species concentrations are defined at the cell centers. Spatial derivatives are calculated using 2^{nd} order central differences and the time integration uses a 4^{th} order Runge-Kutta method.

For the momentum equations, we use a stochastic projection method, which results in an efficient solution of the stochastic momentum equations at a cost of essentially $P + 1$ deterministic solutions [5].

The integration of equation (11) to obtain the concentrations [U], [D], [L], $[\mathrm{K}^+]$, and θ_P is straightforward. The individual concentrations of the phosphoric acid ions and $[\mathrm{H}^+]$ are obtained from the electroneutrality condition. This results in a set of non-linear algebraic relations between $P+1$ stochastic modes. This coupled non-linear system is solved at each point in the domain with a Newton iteration scheme, using the solution from the previous time step as initial guess.

3 MICROCHANNEL FLOW

3.1 0D Labeling Reaction

Figure 1 shows the time evolution of the concentrations of the unlabeled and labeled protein in a homogeneous system with a potassium phosphate buffer of pH = 8.25. In this problem, the dye D is assumed to be present in abundance so that the source term for the labeled protein in equation 10 can be written as

$$\hat{w}_L = k_L[\mathrm{U}] \tag{12}$$

with the following expression for the reaction rate

$$k_L \quad = \quad k_L^0 + d_L e^{-(p\mathrm{H}-p\mathrm{H}_0)^2/\delta_{p\mathrm{H}}^2} \tag{13}$$

where $k_L^0 = 0.25 \times 10^{-3} sec^{-1}$, $d_L = 2.15\ sec^{-1}$, $p\mathrm{H}_0 = 9.25$, and $\delta_{p\mathrm{H}} = 0.85$. For this simulation, a standard

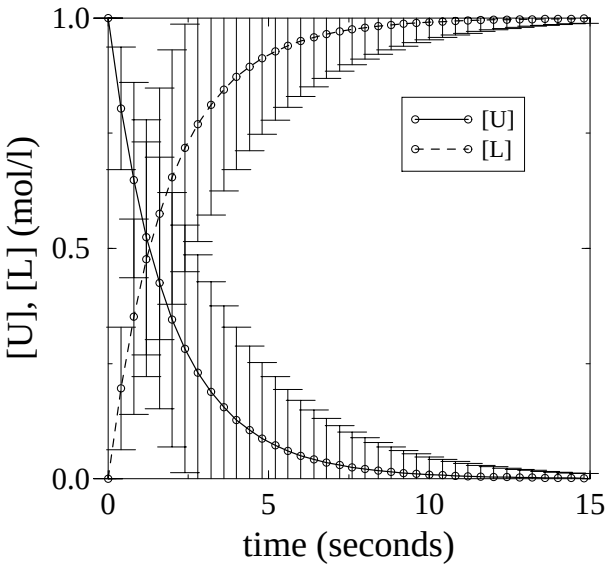

Figure 1: Evolution of U and L concentrations in a homogeneous system. The uncertainty is indicated by $\pm 3\sigma$ "error bars".

deviation of 1% was assumed for all parameters in the rate expression (13), as well as for the electrolyte dissociation constants. Third order PC expansions were used. The resulting uncertainty in the protein concentrations is indicated in figure 1 with "error bars" that span the $\pm 3\sigma$ range. Clearly, uncertainty in the input parameters causes large uncertainties in the simulated concentrations. At the point where [U] = 0.5, a standard deviation of 1% in the parameter $p\mathrm{H}_0$ is magnified about 16 times in the standard deviation of [U].

Figure 2 shows the probability density function of [U] at various points in time. When the mean value of [U] is sufficiently far away from 0, this PDF has a gaussian shape. However, for mean values of [U] closer to 0, the

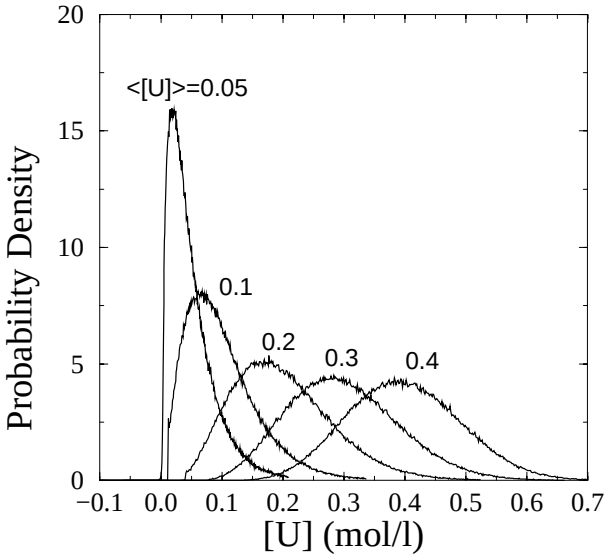

Figure 2: PDF of the unlabeled protein at various points in time, for the system of figure 1.

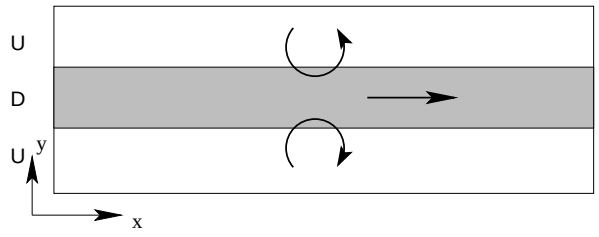

Figure 3: Protein labeling in a 1 cm by 100 μm microchannel. A recirculation zone is created by reversal of the ζ-potential between $x = 2.5$ mm and $x = 6.5$ mm. Parallel streams of U and D are mixed to produce L.

PDF becomes narrower and more skewed. This reflects the physical system behavior where all unlabeled protein reacts away, but its concentration can not be negative.

3.2 2D Microchannel

The configuration of the 2D microchannel is shown in figure 3. The channel is 1 cm long in x and 100 μm wide in y. At the inlet, parallel streams of unlabeled protein and dye are fed in. The buffer solution has a pH of 7.25. A uniform electrostatic field of 1 kV/cm is applied in the x direction. Between $x = 2.5$ mm and $x = 6.5$ mm, the wall properties are altered such that the ζ-potential in this zone is the opposite of the ζ-potential elsewhere in the domain. This ζ-potential reversal creates a recirculation zone, which mixes U and D. With a finite concentration of dye, the reaction source term is written as

$$\hat{w}_L = k_L[\mathrm{U}][\mathrm{D}] \tag{14}$$

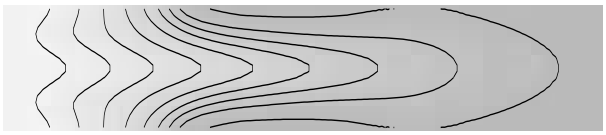

Figure 4: Mean concentration of L at $t = 2$ sec. The contour values increase from left to right in steps of 0.02 mol/l with a minimum value of 0.01 mol/l. The full computational domain is shown.

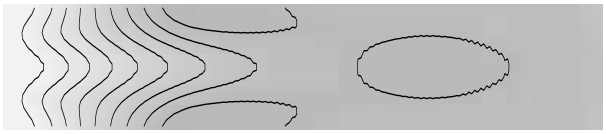

Figure 5: Standard deviation in [L] at $t = 2$ sec. The contour values increase from left to right in steps of 2.9×10^{-4} mol/l with a minimum value of 1.4×10^{-4} mol/l.

The reaction rate is again given by equation (13), with $k_L^0 = 0.25\ mol.l^{-1}.sec^{-1}$, $d_L = 2.15\ mol.l^{-1}.sec^{-1}$, $p\mathrm{H}_0 = 7.40$, and $\delta_{p\mathrm{H}} = 0.85$. In this calculation, there were three uncertain parameters: $p\mathrm{H}_0$ in equation (13), the electric field strength E, and the diffusivity D_U of the unlabeled protein. Again, each of these parameters had a standard deviation of 1%, and third order PC expansions were used.

Figure 4 shows a contour plot of the mean concentration of the labeled protein after 2 sec, at which point the flow has reached steady state. The standard deviation in the labeled protein concentration that results from the uncertainty in the input parameters is shown in figure 5, also at $t = 2$ sec. The uncertainty in the labeled protein concentration rises rapidly in the beginning of the domain, but then levels off as most of the unlabeled protein and dye have reacted away.

Figure 6 further details this standard deviation, along a slice normal to the streamwise direction at $x = 3.5$ mm. The graph shows the individual contributions of the three uncertain parameters to the uncertainty in [L]. Since the parameter $p\mathrm{H}_0$ directly affects the labeling reaction rate, it has a large contribution to the uncertainty. The diffusivity and electric field strength have a smaller, but still significant, contribution.

4 CONCLUSIONS

In this work, a stochastic uncertainty quantification method was developed and applied to simulations of homogeneous reacting systems as well as 2D microchannel flows. The method enables the user to propagate uncertainty from model inputs to simulation results. The method also provides quantitative estimates of the contributions of individual parameters to the overall uncertainty in simulation results.

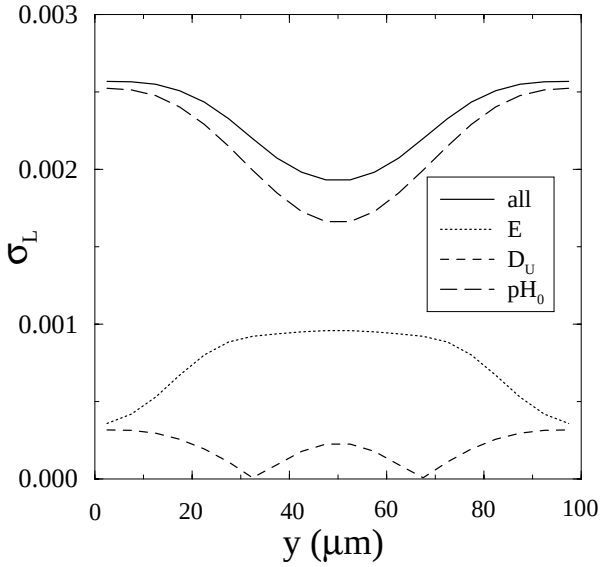

Figure 6: Contribution of individual parameters to the standard deviation of the labeled protein at $x = 3.5$ mm and $t = 2$ sec. The curve labeled "all" shows the total effect of all uncertain parameters combined.

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