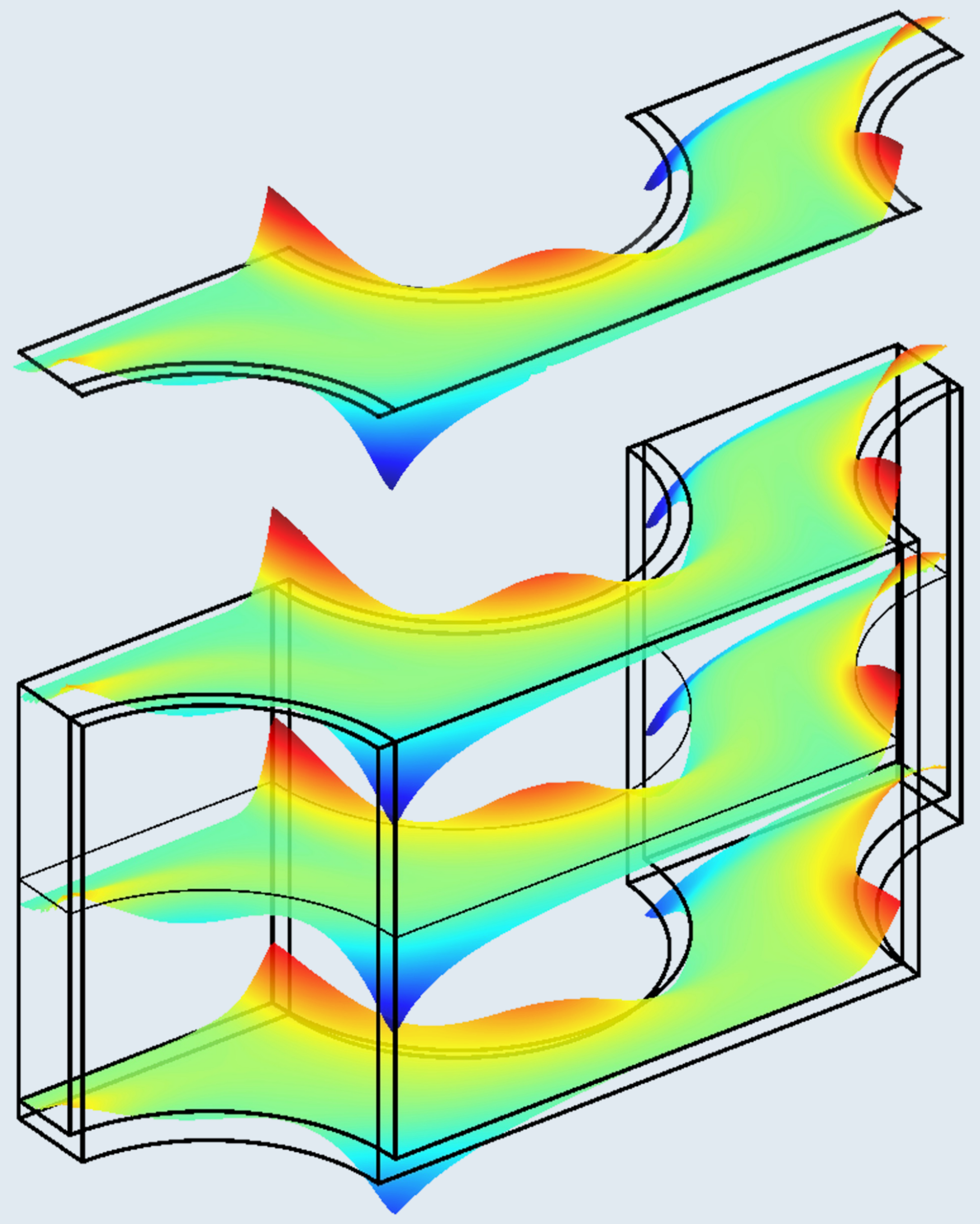

A General COMSOL® Tool For Predicting Separation Efficiency Of Hydrodynamic Chromatographic Columns

The Exact Moment Approach (EMA) is used to predict, without any fitting parameters, the plate height curves in micropillar array columns performed by hydrodynamic chromatography. EMA allows an analysis of how pillar height and interpillar distance affect separation performance.

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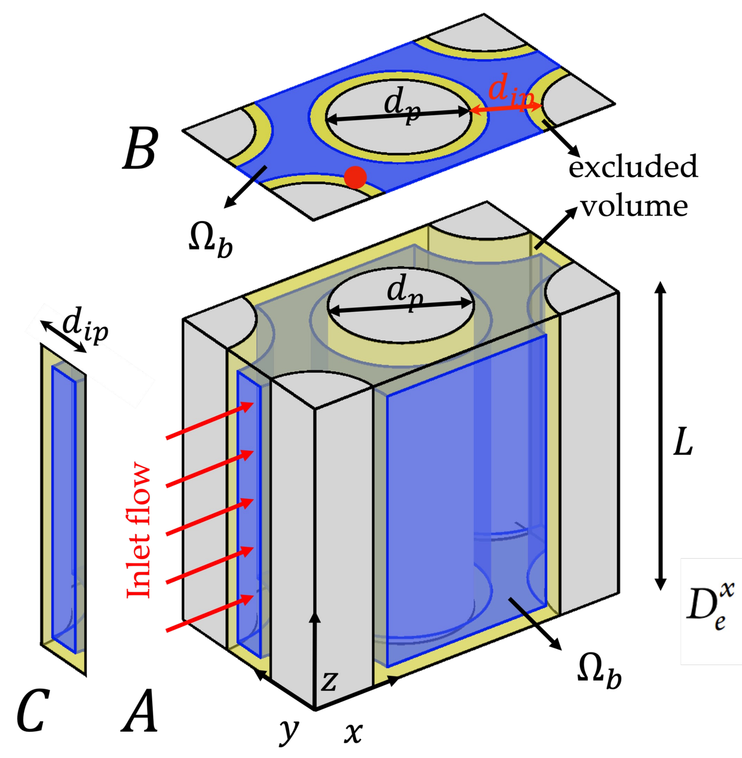
Introduction

The COMSOL® tool, implementing the EMA equations, developed for micropillar array columns can be easily extended and generalized to any geometry representing the unit-periodic cell, the repetition of which allows the entire chromatographic column to be reproduced/modeled.

The device, used here to show the tool, was experimentally realized by Op de Beeck et al.,[2] and plate height curves were provided for four different particles, namely, a low MW tracer (fluorescein isothiocyanate FITC) and three polystyrene bead samples with diameters d_b = 100, 200, 500 nm.

For a tracer particle (FITC) the fluid dynamic domain Ω coincides with the transport domain. However, for a finite-sized particle of diameter d_b, the effective accessible volume (Ω_b) is smaller due to steric effect. As d_b increases, more volume is excluded, leading to a higher effective velocity because larger low-velocity regions become inaccessible.



$$\mathcal{L}[w_0] = -\boldsymbol{v}\cdot\nabla w_0 + D_b\nabla^2 w_0 = 0$$
$$(\boldsymbol{v}w_0 - D_b\nabla w_0)\cdot\boldsymbol{n}|_{\partial\Omega_b} = 0$$
$$U_e^x = \int_{\Omega_b}(v^x w_0 - D_b\partial_x w_0)d\boldsymbol{x}$$
$$\mathcal{L}[w_0 b] = w_0(U_e^x - v^x) + 2D_b\partial_x w_0$$
$$(\boldsymbol{v}w_0 b - D_b\nabla(w_0 b) + D_b w_0\boldsymbol{e}_x)\cdot\boldsymbol{n}|_{\partial\Omega_b} = 0$$
$$D_e^x = D_b + \int_{\Omega_b}((v^x - U_e^x)w_0 b - D_b\partial_x(w_0 b))d\boldsymbol{x}$$

FIGURE 1. (A) 3D periodic unit cell. (B) 2D horizontal (x,y) cross-section (domain adopted for 2D simulations). (C) Rectangular open channel (width d_{ip}, height L). The blue and yellow regions highlight the portion of the fluid domain accessible to a finite-sized particle and the excluded volume, respectively.

Methodology

A micropillar array column is modeled by exploiting the periodic conditions of the geometry. The fluid velocity field v(x) can be obtained from solving the Stokes problem in the entire fluid domain Ω, with no-slip conditions at the walls (lateral surface of the pillars and top/bottom walls) and periodic boundary conditions at the edges of the periodic unit-cell. The EMA allows us to estimate the transient and asymptotic values of the effective axial velocity U_e^x and the axial dispersion coefficient D_e^x, for both point-sized and finite-sized particles, solving, together with the velocity field, the Stationary-coupled equations for the particle pdf and the b-field, implemented as PDE coefficient form with periodic boundary conditions.[1]

Results

The huge advantage is that the transport equations for the local moments need to be solved exclusively on the periodic unit-cell, the repetition of which allows the entire chromatographic column to be reproduced. Figure 2 shows the behavior of the rescaled axial velocity U_e^x/U and the rescaled axial dispersion coefficient D_e^x/D_b for point-sized FITC and finite-sized particles, as a function of the particle Peclet number $Pe_b = Ud_p/D_b$. 2D data underestimate both U_e^x and D_e^x because they do not account for the presence of the top/bottom walls. Despite the simplifying assumptions made, 3D numerical results predicts quite accurately the experimental plate height curves $H = 2\, D_e^x / U_e^x$ vs U obtained by Op de Beeck et al.[2], as shown in Figure 2C for all the four different particles. It is worth noting that no fitting parameters are present.

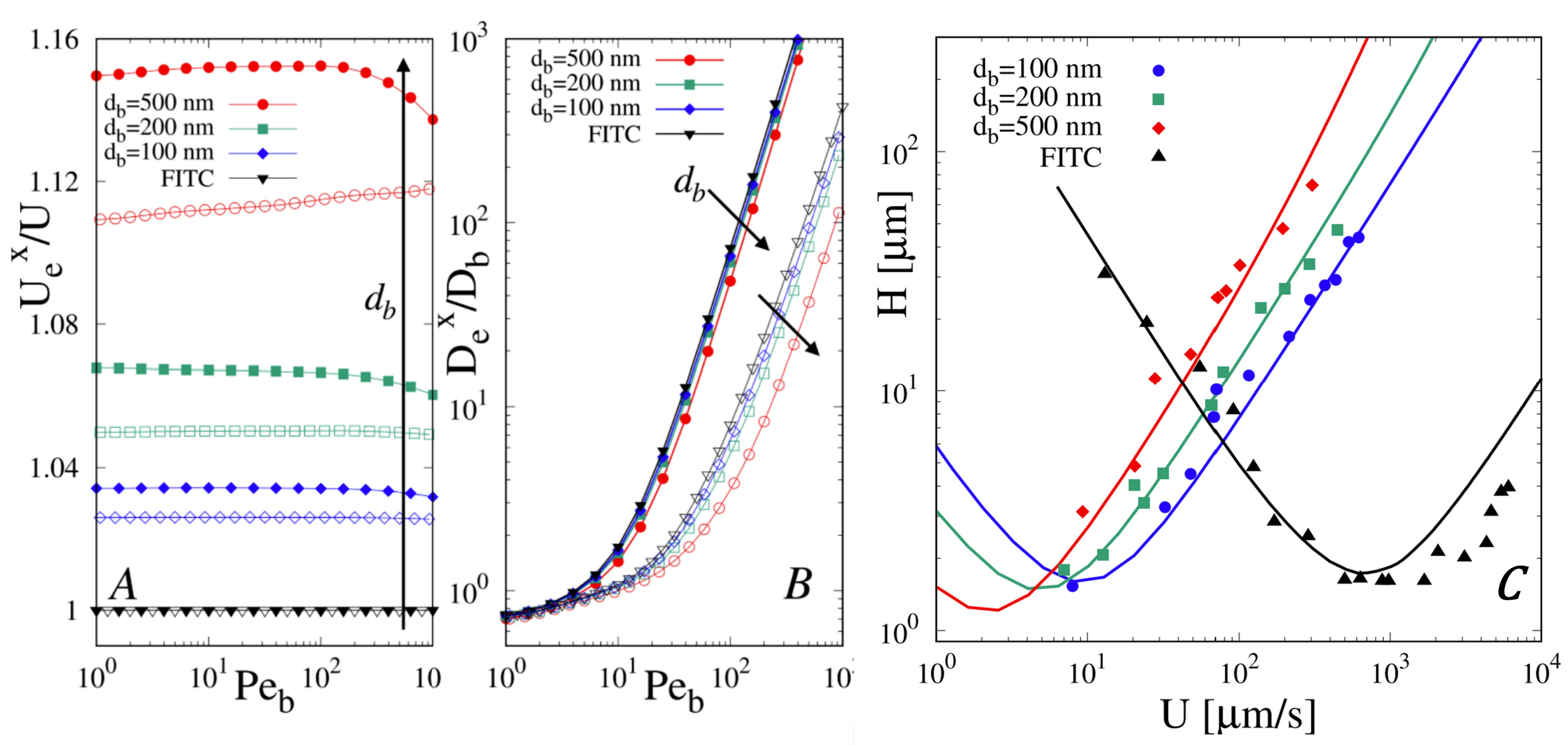


FIGURE 2. U_e^x/U (A) and D_e^x/D_b (B) vs $Pe_b = Ud_p/D_b$ for d_b=0 (tracer FITC) and d_b =100, 200, and 500 nm. Full points: 3D numerical results. Open points: 2D numerical results. Device geometry: d_b =0.5 μm, L=12 μm, d_{ip}=2.5 μm, ε=0.6. (C) Prediction of experimental plate height curves $H=2\, D_e^x / U_e^x$ vs U (points from Op de Beeck et al.[2]) from 3D numerical simulations (continuous lines).

REFERENCES

1. Venditti, C., Moussa, A., Desmet, G., and Adrover, A.,“An In-Depth Investigation of Micropillar Array Columns for the Separation of Finite-Sized Particles by Hydrodynamic Chromatography”. Analytical Chemistry, 2024.
2. De Beeck, J. O., De Malsche, W., Vangelooven, J., Gardeniers, H., & Desmet, G., “Hydrodynamic chromatography of polystyrene microparticles in micropillar array columns”. Journal of Chromatography A, 1217(39), 6077-6084, 2010.

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