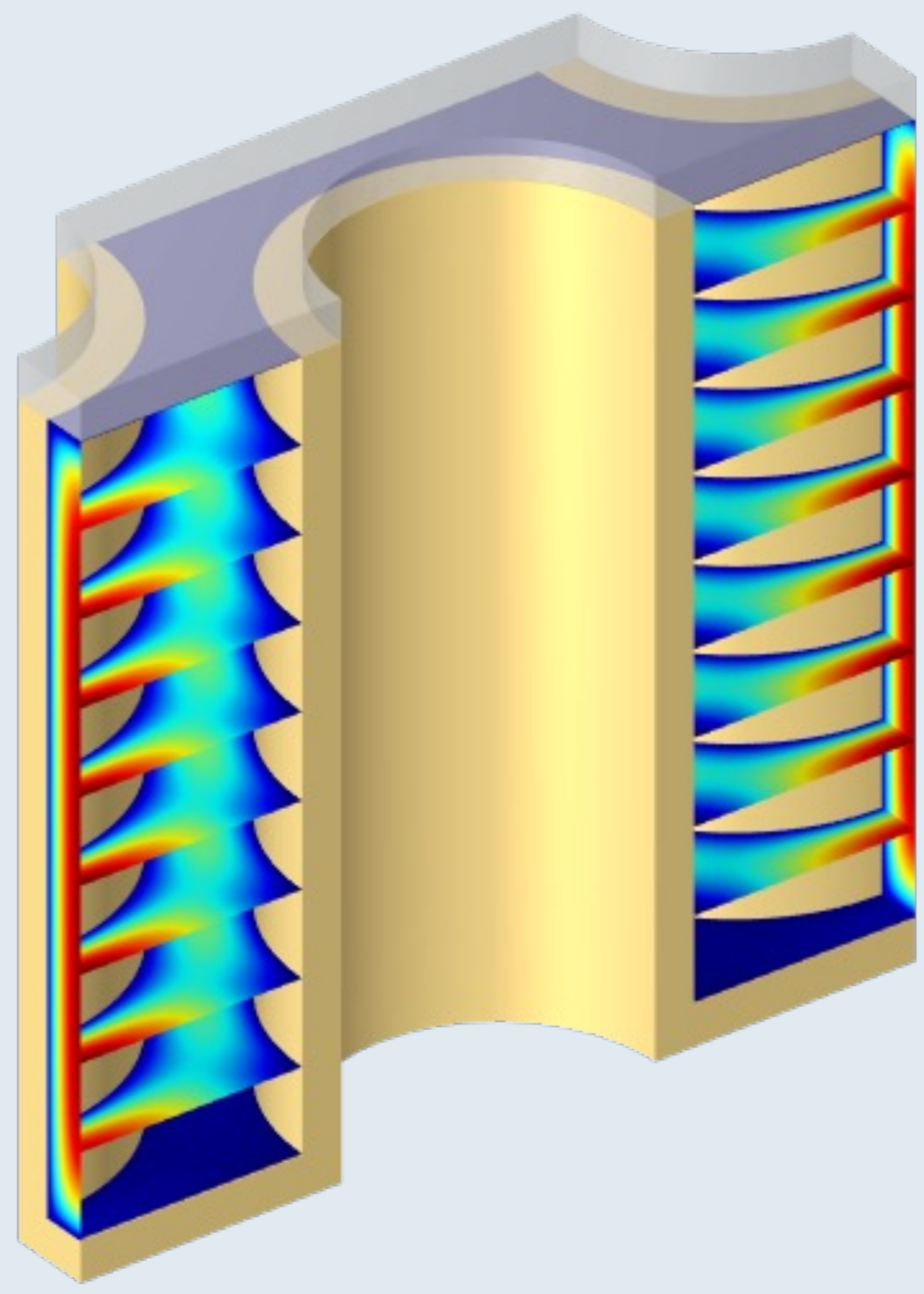


Moments Analysis for Predicting Effective Transport Parameters in Chromatographic Columns: a General Tool with a Simple, Multipurpose Implementation in COMSOL Multiphysics®

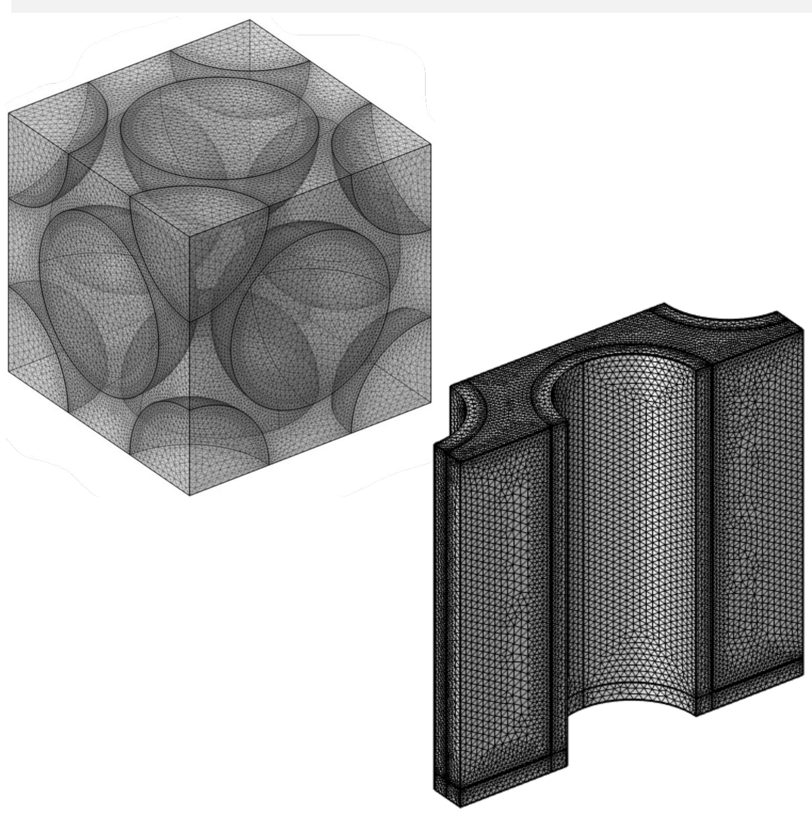
A robust and computationally efficient homogenization approach is proposed to investigate the temporal evolution and asymptotic properties of the effective velocity vector and dispersion tensor in Hydrodynamic Chromatographic Columns (HDC) and Liquid Chromatography (LC).

C. Lauriola, C. Venditti, A. Adrover
Dipartimento di Ingegneria Chimica Materiali Ambiente, Sapienza, Rome, Italy.

Introduction

The effective transport parameters (effective velocity and dispersion tensor) are essential quantities to analyze and optimize the efficiency of devices in Hydrodynamic Chromatography, as well as in Liquid Chromatography.

If the hierarchical porous media can be represented as the periodic repetition of a unit lattice cell, the method proposed only requires the solution of the time-dependent advection-diffusion equations for the zeroth order and first-order exact local moments, exclusively on the unit cell. This implies an enormous reduction of computational efforts and a significant improvement of the accuracy of the results when compared to the direct numerical simulation (DNS) approaches which require flow domains that are long enough to achieve steady-state conditions, and hence often cover tens to hundreds of unit cells.



$$\partial_t P_m^{(q)}(\boldsymbol{\xi},t) = D_m \nabla^2 P_m^{(q)} - \mathbf{v}\cdot\nabla P_m^{(q)} + q\left[v^1 P_m^{(q-1)} - 2D_m\,\partial_{\xi,1}P_m^{(q-1)}\right] + q(q-1)D_m P_m^{(q-2)},\quad \boldsymbol{\xi}\in\Omega_m$$

$$\partial_t P_s^{(q)}(\boldsymbol{\xi},t) = D_s \nabla^2 P_s^{(q)} - 2\,q\,D_s\,\partial_{\xi,1}P_s^{(q-1)} + q(q-1)D_s P_s^{(q-2)},\quad \boldsymbol{\xi}\in\Omega_s$$

$$\left(-D_m\nabla P_m^{(q)}\right)\cdot\mathbf{n}_{ms}\big|_{\bar{\boldsymbol{\xi}}} = -\left(q\,D_m P_m^{(q-1)}\right)(\mathbf{e}_1\cdot\mathbf{n}_{ms}) + K_t\left(k_p P_m^{(q)} - P_s^{(q)}\right)\big|_{\bar{\boldsymbol{\xi}}}$$

$$\left(-D_s\nabla P_s^{(q)}\right)\cdot\mathbf{n}_{ms}\big|_{\bar{\boldsymbol{\xi}}} = -\left(q\,D_s P_s^{(q-1)}\right)(\mathbf{e}_1\cdot\mathbf{n}_{ms}) + K_t\left(k_p P_m^{(q)} - P_s^{(q)}\right)\big|_{\bar{\boldsymbol{\xi}}}$$

$$\mathcal{V}^1(t) = \int_{\Omega_m}\left[v^1 P_m^{(0)} - D_m\,\partial_{\xi,1}P_m^{(0)}\right]d\boldsymbol{\xi} + \int_{\Omega_s} -D_s\,\partial_{\xi,1}P_s^{(0)}\,d\boldsymbol{\xi}$$

$$\mathcal{D}^{1,1}(t) = \int_{\Omega_m}\left[\left(v^1-\mathcal{V}^1\right)P_m^{(1)} - D_m\,\partial_{\xi,1}P_m^{(1)} + D_m P_m^{(0)}\right]d\boldsymbol{\xi} + \int_{\Omega_s}\left[-\mathcal{V}^1 P_s^{(1)} - D_s\,\partial_{\xi,1}P_s^{(1)} + D_s P_s^{(0)}\right]d\boldsymbol{\xi}$$

FIGURE 1. Mesh adopted for the perfectly ordered array of micro-porous spheres in a face-centered cubic arrangement and for the µ pillar array column unit periodic cell.

Methodology

In hierarchical porous media there are at least two phases: a fluid (mobile) macro-porous phase and a micro-porous adsorbing stationary phase.

The velocity field can be obtained from the solution of the Stokes problem in creeping flow condition, enforcing periodic boundary conditions. The time-dependent coupled transport equations for the local moments and the stationary equations for the b-fields can be efficiently implemented and solved with Coefficient Form PDE physics interface.

Different types of hierarchical porous media have been analyzed to assess the reliability of the proposed method, comparing its prediction with DNS and experimental results, in both transient and asymptotic conditions.

Results

Figure 2A shows numerical results obtained by exact moment analysis in excellent agreement with DNS results (colored points) for a perfectly ordered array of micro-porous spheres in a face-centered cubic arrangement for different values of the zone retention factor. Figure 2B compares experimental data and experimental results for different porous shell thickness of a micropillar array column. Figure 2C displays transient numerical results stemming from the exact moment analysis, also in excellent agreement with DNS results (black point) for circular pillars. Figure 2D shows the contour plots of the concentration fields into the two phases and solute distributions for increasing values of $D_s = \gamma\, D_m$. The distribution is far from assuming a Gaussian shape, even though the dispersion coefficient $D_{x,x}(t)$ has nearly reached its asymptotic value $D_{x,x}^{\infty}$. Transient analysis is crucial to ensure that the solute band approaches a Gaussian shape, in order to correctly estimate the bandwidth and henceforth the plate height curve.

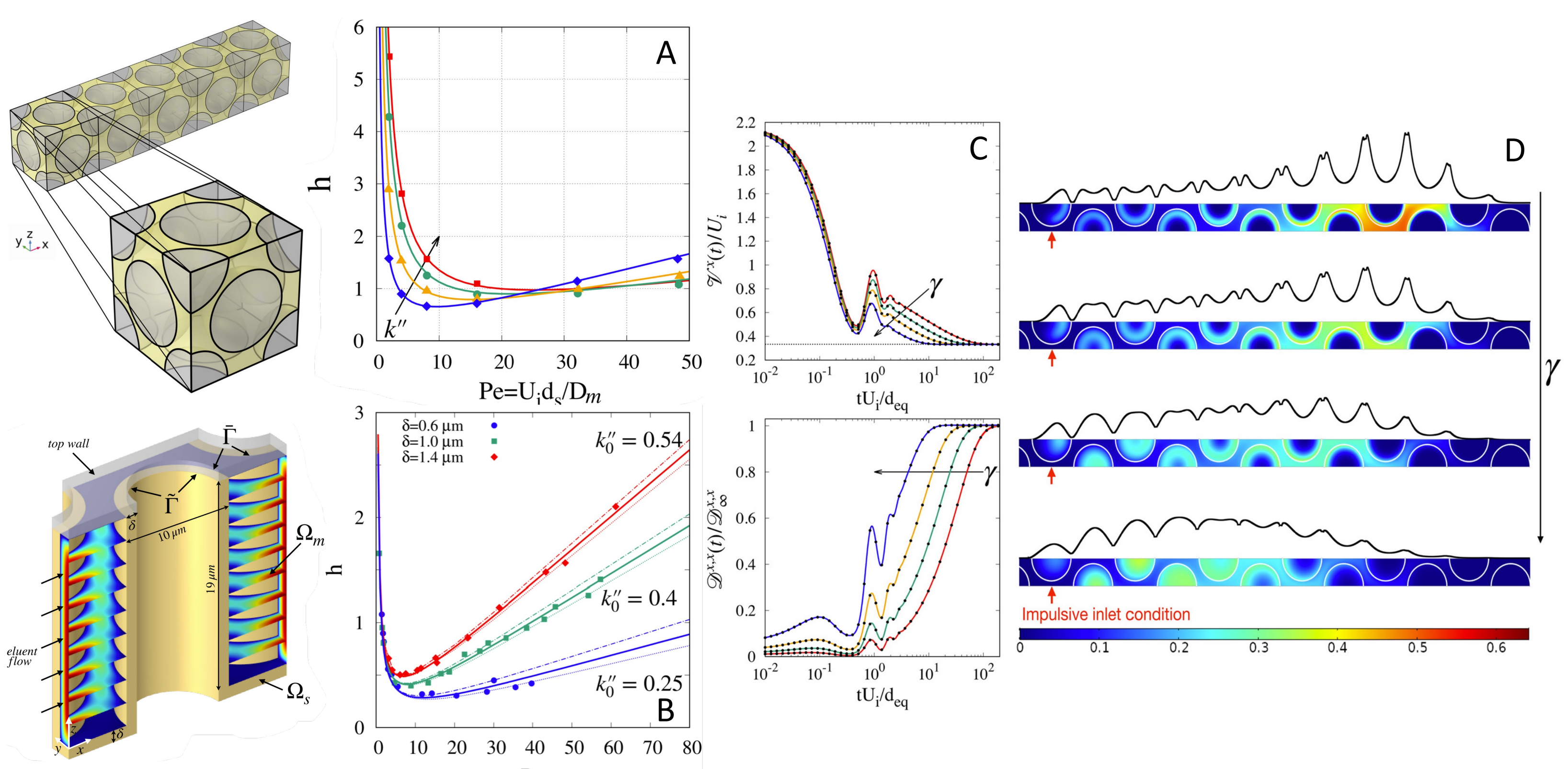


FIGURE 2. (A) h vs Pe for D_s=0.3D_m, Kt→∞ and different values of zone retention factor k''=2,6,12,18. Arrow indicates increasing values of k'' .Results obtained from exact-moment analysis (continuous lines) and DNS results from Matheuse et al. [3] (colored points) (B) Comparison between model predictions and experimental data [4] for h vs. Pe in the non-retentive case. Different curves correspond to different values of the porous-shell thickness δ=0.6,1,1.4µm. (C) Transient behaviour of $V_x(t)/U_i$ and $D_{x,x}(t)/D_{x,x}^{\infty}$ vs $\tau=tU_i/d_{eq}$ at $Pe=U_i d_{eq}/D_m$=50 for the circular pillar array column with macro-porosity ε=0.4, zone retention factor k''=2 and neglegible mass transfer resistance at the interface, Kt→∞. Arrows indicate increasing values of $D_s=\gamma D_m$, with γ=0.05,0.1,0.2,0.5. Continuous lines and points are the results obtained by exact-moment analysis and DNS, respectively. (D) Contour plots of the concentration fields and solute distribution at τ = 10 and Pe = 50, for increasing values of γ=0.05,0.1,0.2,0.5.

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UNIVERSITÀ DI ROMA

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