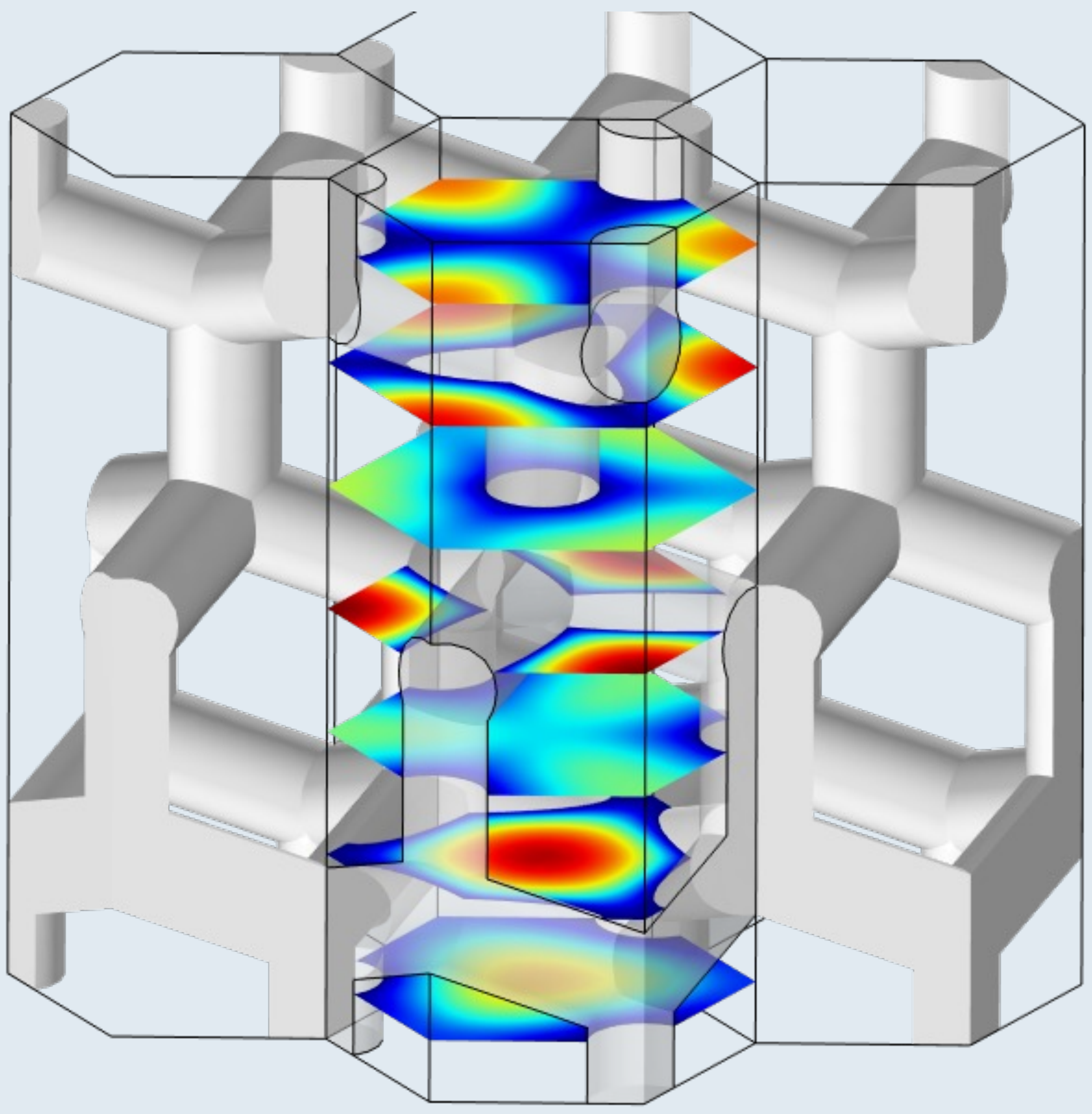

Are 3D Printable Triple Periodic Minimal Surfaces Optimal Geometries For The Stationary Phase In LC?

The two zone moment analysis method (TZMA) is proposed for the evaluation of the effective longitudinal diffusion in discontinuous and bi-continuous chromatographic beds.

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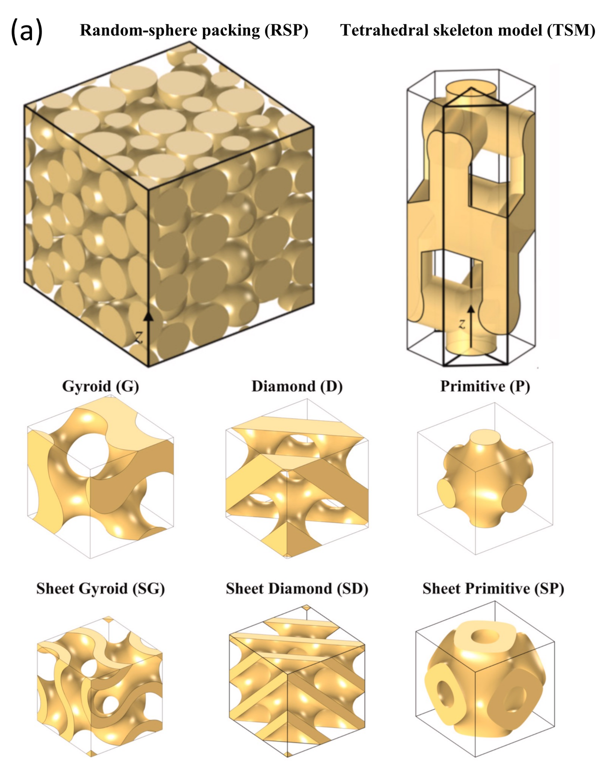
Abstract

The band broadening in chromatographic beds is governed by analyte advection and diffusion, which occur at different rates inside and outside the mesoporous solid zones of the bed. The presence of the retentive zone creates a micro-environment affecting diffusion rates and consequently all three terms (A, B, C) of the plate height equation. Understanding local diffusion rates is essential to improve the quality of the solid support and packing. The most experimentally accessible physical quantity is the longitudinal diffusion coefficient D_{eff}, which can be derived from the TZMA method, by solving the steady-state b-field transport equations in the unit lattice cell. This approach is computationally efficient compared to CFD/DNS, Stochastic Lagrangian (SL), and Lattice-Boltzmann (LB) methods. Here, the TZMA, previously used for discontinuous packings, is extended to bi-continuous media to model monolithic columns, where solutes traverse both mobile and stationary zones.



(b)

$$\nabla^2 b_m(\boldsymbol{x}) = 0 \quad \forall \boldsymbol{x} \in \Omega_m$$

$$\nabla^2 b_s(\boldsymbol{x}) = 0 \quad \forall \boldsymbol{x} \in \Omega_s$$

$$b_m = b_s \quad \forall \boldsymbol{x} \in \Gamma_{ms}$$

$$-\nabla b_m \cdot \boldsymbol{n}^{ms} + n_z^{ms}\Big|_{\boldsymbol{x}\in\Gamma_{ms}} = \alpha_{\text{part}}\left(-\nabla b_s \cdot \boldsymbol{n}^{ms} + n_z^{ms}\right)\Big|_{\boldsymbol{x}\in\Gamma_{ms}}$$

$$\nabla^2 b_m^0(\boldsymbol{x}) = 0 \quad \forall \boldsymbol{x} \in \Omega_m$$

$$-\nabla b_m^0 \cdot \boldsymbol{n}^{ms} + n_z^{ms}\Big|_{\boldsymbol{x}\in\Gamma_{ms}} = 0$$

$$\nabla^2 b_s^\infty(\boldsymbol{x}) = 0 \quad \forall \boldsymbol{x} \in \Omega_s$$

$$-\nabla b_s^\infty \cdot \boldsymbol{n}^{sm} + n_z^{sm}\Big|_{\boldsymbol{x}\in\Gamma_{ms}} = 0$$

FIGURE 1. (a) Geometries adopted for modelling the unit-cell of the stationary phase: random packings of spheres (RSP), TSM, TPMS monoliths. (b) Stationary diffusion equations of the b-fields with related boundary conditions. Periodic boundary conditions must be also taken into consideration.

Methodology

In chromatography, the effective longitudinal diffusivity, representing the B-term band broadening, significantly impacts the total band broadening, contributing about one-third to half of the near the van Deemter curve minimum. Two models initially developed for discontinuous packings are extended to bi-continuous media. These models are based on approximate and accurate descriptions of the effective diffusion factors γ_m and γ_s emerging from the TZMA approach. D_{eff} is computed by solving the diffusion equations for the b-fields with periodic boundary conditions using the Coefficient Form PDE package. Several ordered packing structures, such as random spheres (RSP), the tetrahedral skeleton model (TSM), and triple periodic minimal surfaces (TPMS) monoliths are examined.

Results

Figure 2a compares the γ_{eff} between discontinuous and bi-continuous RSP. While connectivity has a minimal impact for practical values of k'', the differences in the asymptotic values are noticeable and important to derive well-posed analytical models describing the behavior of γ_{eff} in the whole range of k'' values.

Figures 2b-c present experimental data of γ_{eff} versus k'' for different monolithic silica columns, along with predictions from an approximate model based on numerical simulation analysis. These insights suggest that strut-based TPMS models are more suitable than sheet-based models for describing monolithic silica columns.

$$\gamma_{\text{eff}} = \frac{D_{\text{eff}}}{D_m} = \frac{1}{\varepsilon(1+k'')}\left[\frac{\varepsilon\gamma_m^0 + \left(1-\varepsilon\gamma_m^0+\varepsilon\gamma_m^\infty\beta_0\right)\alpha_{\text{part}}}{1+\beta_0\alpha_{\text{part}}}\right] + \frac{1}{\varepsilon(1+k'')}\left[\frac{(1-\varepsilon\gamma_m^\infty)\beta_0\alpha_{\text{part}}^2}{1+\beta_0\alpha_{\text{part}}}\right]$$

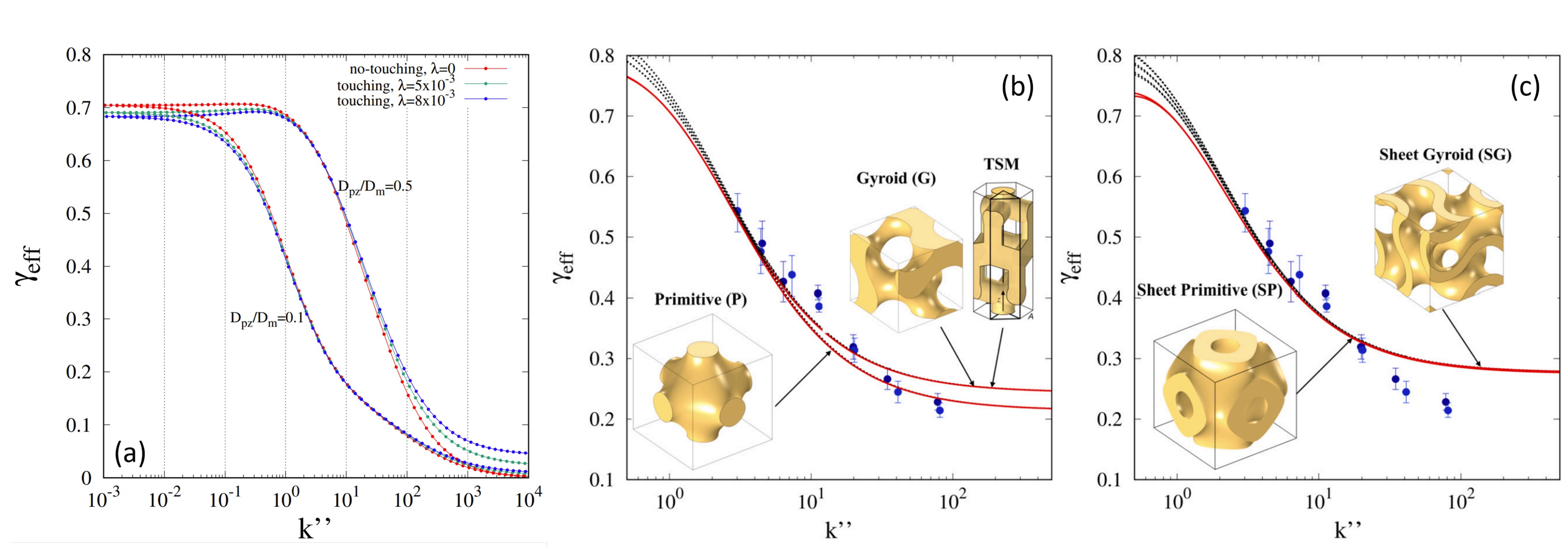


FIGURE 2. (a) Analysis of the random packings. Comparison between non-touching and touching spheres. (b)-(c) Analysis of monolithic silica columns: blue points represent experimental data[4], while red curves show the predictions of the approximate model. Curves for Gyroid G and TSM are not distinguishable.

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Excerpt from the Proceedings of the COMSOL Conference 2024 Florence