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# Pore-scale simulation of entrapped non-aqueous phase liquid dissolution

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## Abstract

We investigated the dissolution of non-aqueous phase liquids (NAPLs) in a three-dimensional random sphere-pack medium using a pore-scale modeling approach to advance fundamental understanding and connect rigorously to microscale processes. Residual NAPL distributions were generated using a morphological approach and the entrapped non-wetting phase was quantitatively characterized by calculating volume, orientation, interfacial area, and shape of isolated NAPL regions. With a detailed aqueous-phase flow field obtained by a multiple-relaxation time lattice Boltzmann approach, we solved the advective–diffusive equation in the pore space using a high-resolution, adaptive-stencil finite-volume scheme and an operator-splitting algorithm. We show good agreement between the mass transfer rates predicted in the computational approach and previously published experimental observations. The pore-scale simulations presented in this work provide the first three-dimensional comparison to the considerable experimental work that has been performed to derive constitutive relations to quantify mass transfer from a residual NAPL to a flowing aqueous phase.

*Keywords:* NAPL; Dissolution; Mass transfer; Lattice Boltzmann

## 1. Introduction

Since many subsurface systems are contaminated with non-aqueous phase liquids (NAPLs), dissolution of an immobile NAPL to a mobile aqueous phase is a process of primary importance. Because of this, NAPL dissolution has been actively studied over the last 15 years using macroscale experimental [2–4,19,27,54,63–66], microscale experimental [6,18,32,36,40,56,68,79], pore-network modeling [15,16,23,31,32,81,83], and other microscale modeling approaches [35,42]. The results of this significant body of work are a maturation in our level of understanding of factors that affect this process. Even in light of this level of knowledge, only a partial connection between microscale processes and macroscale observations has been made, and macroscale models remain grounded in empirical representations of rather limited sets of experimental observations.

The situation that we desire is a firm connection between microscale, or pore-scale, fluid distributions and transport phenomena and macroscale, or porous medium continuum scale, and mesoscale systems that are often of concern in practice. Ideally, rigorous models can be derived at the microscale and upscaled to larger scales to provide such a connection. The existence of such a complete theory would provide a means to understand NAPL dissolution on a fundamental level, to evaluate the dominant factors that control the process, and to identify both explanatory and predictive models of the process at the given scale of concern. Considerable work remains to be accomplished to achieve this level of knowledge. A knowledge base

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## Notation

*Roman letters*

| | |
|---|---|
| $A$ | area of the downstream external face of a boundary $\Gamma$ ($L^2$) |
| $A_n$ | NAPL surface area ($L^2$) |
| $a_n$ | specific NAPL surface area $a_n = A_n/V$ ($L^{-1}$) |
| $a_{na}$ | specific interfacial area of NAPL–aqueous phase interface ($L^{-1}$) |
| $a_{ns}$ | specific interfacial area of NAPL–solid phase interface ($L^{-1}$) |
| $C$ | local aqueous phase solute concentration ($M\,L^{-3}$) |
| $C_a$ | macroscale solute concentration ($M\,L^{-3}$) |
| $C_s$ | solubility concentration of NAPL species in the aqueous phase ($M\,L^{-3}$) |
| $c$ | centroid of a 3D digital object $c = (\bar{x}, \bar{y}, \bar{z})$ (L) |
| $D_{ax}$ | dispersion along the flow direction $x$ ($L^2\,T^{-1}$) |
| $D_m$ | molecular diffusion coefficient in the aqueous phase ($L^2\,T^{-1}$) |
| $d_g$ | mean grain size diameter (L) |
| $d_i$ | grain diameter for which $i$% of particles are smaller than $d_i$ (L) |
| $d_M$ | diameter of a "median" sand grain as defined by USDA (L) |
| $\boldsymbol{e}_i$ | discrete velocity vector at $i$ direction used in the lattice Boltzmann models |
| $\boldsymbol{F}$ | vector of external driving forces |
| $\boldsymbol{f}(\boldsymbol{x}, t)$ | distribution functions of fluid particles in location $\mathbf{x}$ and time $t$ |
| $\boldsymbol{f}^{(eq)}(\boldsymbol{x}, t)$ | equilibrium distribution functions of fluid particles in location $\mathbf{x}$ and time $t$ |
| $g(x, y, z)$ | indicator function representing whether a voxel $(x, y, z)$ belongs to an object of interest |
| $\boldsymbol{h}$ | vector of acceleration coefficients due to external forces |
| $\mathbf{I}$ | identity matrix |
| $I_n$ | inertial matrix |
| $K_l$ | lumped mass-transfer coefficient ($T^{-1}$) |
| $k_l$ | mass transfer rate coefficient ($L\,T^{-1}$) |
| $l_{1,2,3}$ | major/minor/intermediate length of a disconnected blob (L) |
| $M$ | three-term minmod function |
| $N_b$ | number of NAPL blobs |
| $N_s$ | number of spheres |
| $\mathbf{n}$ | outward unit normal vector |
| $p$ | voxel in a 3D digital image |
| $q_x$ | Darcy velocity in the macroscopic flow direction $x$ ($L\,T^{-1}$) |
| $S$ | sphere object |
| $\mathsf{S}$ | collision matrix used in the lattice Boltzmann models |
| $S_x$ | all the translates of a sphere $S$ |
| $s_n$ | NAPL saturation |
| $s_r$ | residual NAPL saturation |
| $u$ | microscale aqueous phase velocity in the direction $x$ ($L\,T^{-1}$) |
| $u_a$ | mean pore velocity of the aqueous phase in the flow direction $x$ ($L\,T^{-1}$) |
| $U_i$ | uniformity index $U_i = d_{60}/d_{10}$ |
| $V$ | volume of a spatial domain ($L^3$) |
| $V_d$ | volume of a sphere with mean particle diameter $d_g$ ($L^3$) |
| $V_e$ | volume of the smallest enclosing sphere of a 3D object ($L^3$) |
| $V_o$ | volume of a 3D object ($L^3$) |
| $\mathbf{v}$ | microscale aqueous phase velocity vector $\boldsymbol{v} = (u, v, w)$ ($L\,T^{-1}$) |
| $v$ | microscale aqueous phase velocity in the direction $y$ ($L\,T^{-1}$) |
| $w$ | microscale aqueous phase velocity in the direction $z$ ($L\,T^{-1}$) |
| $X$ | geometric object |
| $\mathbf{x}$ | position vector $\boldsymbol{x} = (x, y, z)$ (L) |
| $x, y, z$ | spatial coordinates (L) |
| $\bar{x}, \bar{y}, \bar{z}$ | central position of a 3D object (L) |

*Greek letters*

| | |
|---|---|
| $\alpha_l$ | longitudinal dispersivity (L) |
| $\beta_i$ | fitting parameters |
| $\Gamma$ | boundary of domain of interest |
| $\Gamma_e$ | external portion of $\Gamma$ |
| $\Gamma_i$ | internal portion of $\Gamma$ |
| $\theta_n$ | volumetric fraction of the NAPL, $\theta_n = s_n\phi$ |
| $\theta_{n0}$ | initial volumetric fraction of the NAPL |
| $\lambda$ | Courant–Friedrichs–Lewy number |
| $\mu_{i,j,k}$ | $(i + j + k)$ order moment of a 3D digital object |
| $\nu$ | kinematic viscosity ($L^2\,T^{-1}$) |
| $\rho$ | fluid density ($M\,L^{-3}$) |
| $\tau$ | single relaxation time used in the lattice Boltzmann models |
| $\phi$ | porosity |
| $\Psi$ | similarity measure of an object to a sphere |
| $\Omega$ | spatial domain |
| $\omega$ | weight coefficient |

*Dimensionless numbers*

| | |
|---|---|
| $Pe$ | Peclet number, $Pe = ReSc = u_a d_g/D_m$ |
| $Re$ | Reynolds number, $Re = u_a d_g/\nu_a$ |
| $Sc$ | Schmidt number, $Sc = \nu_a/D_m$ |
| $Sh$ | Sherwood number, $Sh = k_l d_g/D_m$ |
| $Sh'$ | modified Sherwood number, $Sh' = K_l d_g^2/D_m$ |
| $Sh'_h$ | $Sh'$ estimated for half of the domain size |
| $Sh'_t$ | $Sh'$ estimated for the entire domain |

*Subscripts and superscripts*

| | |
|---|---|
| a | aqueous-phase qualifier (subscript) |
| D | Dirichlet boundary qualifier (subscript) |