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Review

The Dynamics of Per- and Polyfluoroalkyl Substances (PFAS) at Interfaces in Porous Media: A Computational Roadmap from Nanoscale Molecular Dynamics Simulation to Macroscale Modeling

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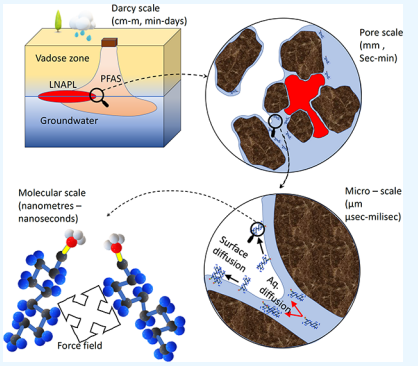
ABSTRACT: Managing and remediating perfluoroalkyl and polyfluoroalkyl substance (PFAS) contaminated sites remains challenging. The major reasons are the complexity of geological media, partly unknown dynamics of the PFAS in different phases and at fluid−fluid and fluid−solid interfaces, and the presence of cocontaminants such as nonaqueous phase liquids (NAPLs). Critical knowledge gaps exist in understanding the behavior and fate of PFAS in vadose and saturated zones and in other porous media such as concrete and asphalt. The complexity of PFAS−surface interactions warrants the use of advanced characterization and computational tools to understand and quantify nanoscale behavior of the molecules. This can then be upscaled to the microscale to develop a constitutive relationship, in particular to distinguish between surface and bulk diffusion. The dominance of surface diffusion compared to bulk diffusion results in the solutocapillary Marangoni effect, which has not been considered while investigating the fate of PFAS. Without a deep understanding of these phenomena, derivation of constitutive relationships is challenging. The current Darcy scale mass-transfer models use constitutive relationships derived from either experiments or field measurements, which makes their applicability potentially limited. Here we review current efforts and propose a roadmap for developing Darcy scale transport equations for PFAS. We find that this needs to be based on systematic upscaling of both experimental and computational studies from nano- to microscales. We highlight recent efforts to undertake molecular dynamics simulations on problems with similar levels of complexity and explore the feasibility of conducting nanoscale simulations on PFAS dynamics at the interface of fluid pairs.



1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS), also known as "forever chemicals", are man-made chemicals that have been increasingly detected in various environmental settings since the early 2000s. These have a typical molecular representative, C_nF_{2n+1}-R.[1] Based on the total number of carbons, the U.S. EPA categorizes PFAS into long-chain (≥8C) and short-chain compounds (≤7C).[2,3] PFAS are widely applied in various industries (clothing, cosmetics, fire extinguishers, textiles, packaging, household products, pesticides, etc.).[1,4] PFAS are usually solid at room temperature and partially dissolve in water (longer carbon chains have lower solubility). Despite a wide range reported in the literature for the PFAS solubility in water (550−9500 mg/L),[1,5,6] during use and in the environment PFAS are typically measured at much lower concentrations, such as μg/L (or μg/kg) in soils and water,[7] and regulatory compliance concentrations can be much lower.[8]

PFAS movement in subsurface environments can be retarded relative to water flow due to several processes.[9,10] PFAS exhibit surfactant-related properties and are much more surface active than hydrocarbon surfactants because of the substitution of fluorine atoms for hydrogen atoms. In general, low concentrations of PFAS can mix with polar liquids to reduce surface tension.[4,10,11] Some of their unique properties include hydrophobicity, oleophobicity, and high chemical and thermal stability. In general, PFAS have a special molecular structure consisting of a hydrophobic fluoroalkyl chain (repellent to both oil and water liquids) at one end and a hydrophilic functional group (attracted to aqueous liquids) at the other.[1,12] These characteristics (e.g., perfluorinated carbon chain length, functionality, and polarity) strongly impact the environmental concentrations of PFAS in the soil and groundwater. Moreover, light nonaqueous phase liquids (LNAPLs) such as petroleum products affect the mobility

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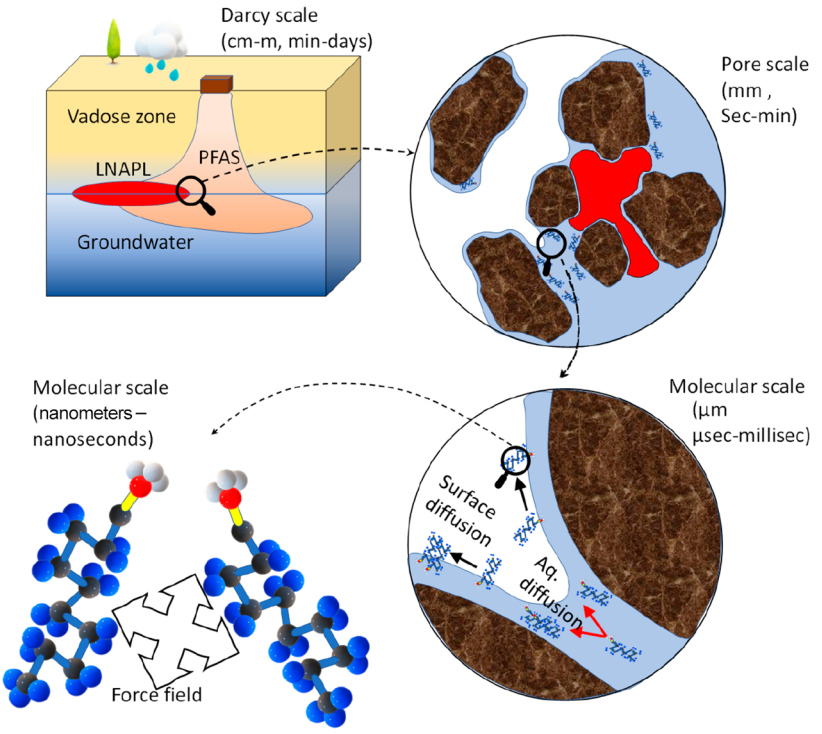

Figure 1. Transport of PFAS in the presence of contaminants such as LNAPL in the subsurface is a multiscale phenomenon. Here the difference between the surface and bulk diffusion in thin films results in spatial and temporal changes of the surface tensions and hence the specific surface area solutocapillary effect.[32,33]

and retardation of PFAS in the subsurface.[1,13] The colocation of PFAS and LNAPL is quite common at large fuel storage facilities and airports—whereby fuels and PFAS liquids would have been used for fire-fighting training and during incidents.[11]

PFAS contamination in the vadose zone has been a source of groundwater contamination for years. This indicates that PFAS contamination sites with little or no control of PFAS release from soils (e.g., mobilization of PFAS in contaminated soil, soil washing, phytoremediation, and immobilization[14]) can continue as a source of groundwater contamination long after production or disposal activities have ceased. This allows PFAS to have a long-term, long-range transport to the surrounding and deep soil–groundwater systems.[10,15,16] The soil and subsurface environments are the geological media commonly affected by PFAS, primarily because of the disposal of PFAS-containing waste materials, application of PFAS-containing biosolids, and the use of PFAS-based aqueous film-forming foams (AFFFs) for fire-training and fire suppression activities.[14−16]

The behavior of PFAS at interfaces is critical for effective remediation. The remediation of PFAS can be prolonged and is very costly. Replacing conventional methods with new, lower-cost methods is on many industry agendas. Because of the extent and threat of PFAS plumes in groundwater, active pumping and above ground treatment have been common—with attempts made to reduce water volumes and maximize PFAS recovery. Cost-effective destruction of PFAS is actively pursued.[14] The treatment of PFAS-contaminated soils is often undertaken by mobilization (e.g., soil washing) or immobilization strategies. PFAS immobilization in soils aims to sequester PFAS in soils using geo-sorbents with strong sorption capacity.[15,17] The purpose is to minimize PFAS mobility in soils and reduce their bioavailability to the surrounding biota.[15,18] Clay minerals, such as kaolinite and montmorillonite, are promising adsorbents for PFAS removal due to their high affinity to contaminants, widespread availability, low cost, and eco-friendly properties.[3] Likewise, activated and powdered carbon sorbents can be very effective at retaining PFAS in soils and seem to be effective over longer time periods.[19] Concrete and asphalt sealants are being strongly considered.[20,21] Again, selection of the best adsorbent and sealants and their optimization require quantification of the adsorption/sealant mechanism relative to PFAS behavior at the interface with the adsorbents[12,18] and sealants.[21]

The number of studies investigating the fate and transport of PFAS in subsurface environments and in associated infrastructure such as concrete and asphalt materials,[20−22] as well as the effects of PFAS properties and geological and porous media factors (e.g., soil and water chemistry and media textures and structures) on these transport processes, have increased considerably in recent years.[1,4,11,23] However, fundamental studies quantifying the interfacial behavior of PFAS remain lacking.

This gap is a critical obstacle to developing representative constitutive relationships at a Darcy scale (essential for modeling contaminated sites and the feasibility of remediation efforts), which are then applicable at the field scale. In contrast with conventional solute mass transport models (which consider a dilute solute concentration as a passive scalar), PFAS affects the equilibrium state of the fluids. We explore the need and value of molecular dynamics (MD) simulations of the PFAS effect (concentration, type of molecules, etc.) on a two-phase interface to parametrize altered surface tension and wettability from molecule statistics (e.g., stress field) as a function of PFAS concentration. We envisage that it would be possible to interlink MD simulations and the continuum (Navier–Stokes) equations through surface tension parametrized forcing terms (constitutive relationships) and

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characterize surface diffusion at the interface. Experimental and computational studies from nano- to microscales are required to derive bulk parameters (such as a retardation factor and effective diffusion) and constitutive relationships, which are based on a systematic upscaling. Here a strategy and roadmap are outlined to clarify and address the challenge of advancing linkages from nano- to macroscales.

2. CHALLENGES IN CHARACTERIZING PFAS DYNAMICS

2.1. Overview. The fate and transport of PFAS in subsurface environments and other porous media are controlled by various processes, including adsorption to the solid−water interface,[24] adsorption to the air−water interface (in the unsaturated media),[25] and partitioning to NAPL or adsorption to NAPL−water interfaces in NAPL-contaminated source zones.[10] Mechanisms affecting PFAS dynamics include electrostatic interaction, hydrophobic interaction, hydrogen bonding, and ligand exchange.[16,26,27]

The amphiphilic and oleophobic characteristics of PFAS make it difficult to accurately predict their sorption and transport in porous media based on surface and solution conditions. For example, when attempting to correlate PFAS sorption with the bulk properties of soil/sediment, such as an organic fraction, protein content, anion or cation exchange capacity, and mineral type, the covariation of these properties in the sorbent has been shown to lead to confounding results.[12,17] Additionally, the complexity of PFAS molecular interaction at fluid interfaces challenges experimentation, characterization, and the computational tools that might reveal molecular scale behaviors.[12,15] Efforts are needed for a fundamental understanding of interactions, surface chemical features, and fluid−fluid behaviors embedded within computational platforms required to assess feasible experimental designs and to assist with upscaling.[28] Based on the fundamental understanding, quantitative models for PFAS dynamics are expected via correlating with specific soil properties, interfacial parameters, PFAS chemical structures, and solution chemistry. There is no clear understanding of these phenomena without the molecular study of the processes.[15,17]

A great challenge in characterizing PFAS dynamics is its behavior at the interface of fluid pairs. An example here is PFAS retention processes that may occur in NAPL-contaminated source zones, including partitioning into NAPL and adsorption at the NAPL−water−soil interface.[29,30] The impact of NAPL on the sorption of PFAS to solids (soil, concrete, or asphalt in this context) depends on chain length, molecular structure, counterion, and the concentration of PFAS. The orientation of perfluorocarbon molecules positioned at the NAPL/water interface is not clear because the oleophobic property of the PFAS limits their partitioning into the hydrocarbon phase. Hence, altering NAPL saturation is expected to affect the retardation of PFAS, as the area of the NAPL/water interface changes for entrapped NAPL ganglia.[31]

2.2. Solutocapillary Marangoni Effect. Figure 1 depicts the scales at which the PFAS dynamics in the subsurface and porous media might be interconnected and addressed. At the microscale, different diffusive transport mechanisms (surface and bulk) are schematically distinguished at the interfaces and inside a thin film of the liquid phase. Indeed, this important phenomenon, which has not been thoroughly discussed in the PFAS literature, means the PFAS molecules at, e.g., air−water interfaces (and other pairs) may also move along the interfaces by repulsive/attractive molecular forces (surface diffusion).

Diffusion of adsorbed hydrocarbon surfactants at air−water interfaces has been reported in the surface science literature.[34,35] The magnitude of the surface diffusivity of hydrocarbon surfactants at air−water interfaces is close to that of aqueous diffusivity. However, unlike the flux due to aqueous diffusion, surface diffusion does not scale with the film thickness which means the surface diffusion flux does not decrease in thinner water films.[36] Furthermore, for PFAS molecules, especially those with longer carbon chains and greater interfacial activity, the adsorbed mass at the air−water interfaces may represent the majority of their mass in a thin water film. This may be even more pronounced when the thickness of the water films is down to <100 nm. Therefore, surface diffusion along the air−water interfaces is likely to become the dominant mass-transfer process for PFAS in thin water films.[25,36]

We note here that a change in the abundance of PFAS molecules at the interface also temporally and spatially changes the surface tension which results in changes to contact angles and again to the interfacial area (i.e., PFAS are not passive scalars[37]). To the best of our knowledge, surface diffusion along the interfaces has been overlooked in the literature of PFAS transport in the vadose zone.[36] We believe this phenomenon, which is called the solutocapillary Marangoni (solutal Marangoni) effect,[32,33] can be significant for PFAS dynamics. Given that the solutal Marangoni effect/flow occurs under interfacial tension gradients, such an effect is expected in the presence of PFAS, being highly surface active. This has been measured directly at the air−water interface for fluoro surfactants in dynamic conditions,[35,38] whereas at the NAPL−water interface, this is expected for many PFAS due to their lipophilic nature, as it can dissolve (and thus transfer) into both aqueous and LNAPL phases, creating an interfacial gradient, causing Marangoni effect/flow. Furthermore, where the temperature might vary such as in shallow soils or concrete/asphalt surfaces, LNAPL−water interfaces will vary, which may induce solutal Marangoni convection, leading to further changes in PFAS behavior.

Theoretical studies and numerical simulations have been used to systematically upscale some interlinked transport phenomena in two-phase systems from a microscale to a macroscale. For instance, a macroscopic model has been developed to express seepage velocity as contributions of interfacial tension and inertia.[39] The mass and momentum upscaled equations were obtained, and generalized Darcy-like dominant and viscous coupling terms were presented.[40] A closed expression for the average pressure difference (referred to as the capillary pressure at a macroscale) has been proposed.[41]

However, the complex behavior of PFAS challenges such upscaling approaches. The quantitative constitutive relationships are purely based on empirical studies (and disconnected from theoretical upscaling) and have limited applicability. Interscale systematic studies on multiphase PFAS adsorption and transport are extremely limited.[1] This is an important gap, as upscaling the knowledge from a nanoscale to Darcy scale would require comprehensive studies on different characteristics of the PFAS dynamics, as depicted in Figure 2. Upscaling the knowledge to develop widely applicable constitutive relationships also requires the quantitative studies to be systematically verified against measurements at the same scales.

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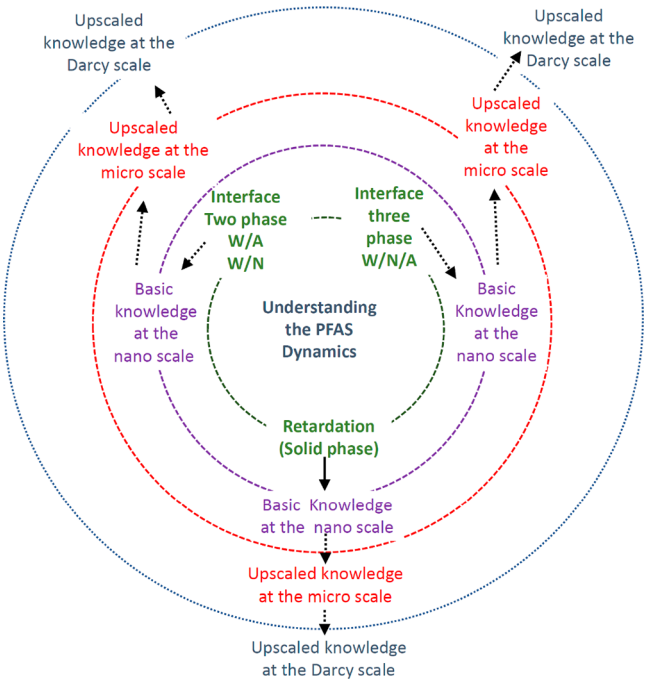

Figure 2. Interconnected scales of the PFAS dynamics characteristics that need to be developed to construct a systematically upscaled model for field applications. Solid arrow (solid phase) indicates where systematic upscaling has shown advances. Dotted arrows indicate areas where advances seem required. W, N, and A stand for the water (aqueous), NAPL (DNAPL and LNAPL), and air (gaseous) phase, respectively.

In the following sections we discuss the level of quantitative modeling science on PFAS dynamics at each scale and highlight the discontinuity in the upscaling.

3. NANOSCALE MOLECULAR DYNAMICS

3.1. Overview and Potential. As depicted in Figure 1, biochemo−physical phenomena typically involve many different time and length scales. At the finest scale (nano), the time ranges from tens of femtoseconds (bond vibrations) to microseconds and even seconds for some surface-active compounds, especially at fluid−fluid interfaces. The length scale ranges from a few Angstroms on the atomic level to the size of a complex molecule such as a folded protein (1−100 nm).[42,43]

Molecular dynamics (MD) simulations have become one of the most powerful tools for scientists, requiring increased confidence in interpreting experimental results. These simulations mimic molecular interactions at a very small scale through representing the atomic structure of the molecules. A key component in MD simulation is the representation of the molecular mechanics force field, which is constrained by quantum mechanical calculations and targeted measurements and experiments. A typical force field incorporates terms that capture electrostatic (Coulombic) interactions between atoms, springlike terms that model the preferred length of each covalent bond, and terms capturing several other types of interatomic interactions. Such force fields are inherently approximate. To design and interpret data from targeted experiments, increasingly linked molecular simulations are being undertaken, due to effective simulation speeds, precision, accessibility, and cost.[44−47]

Different methods are normally employed to describe the dynamics and interactions of molecules depending on the length and time scale of the process of interest. Methods based on quantum mechanics provide the most accurate results; however, they are computationally expensive, and thus they are limited to short time scales (a few tens of picoseconds (ps)) and small length scales (nanometers), involving relatively few atoms.[47] In many problems, such a detailed representation may not be required, and less refined models of atoms and representation of the force fields (short-range and long-range electrostatic interactions) may be applied.[46]

In general, molecular simulation methods include density functional theory (DFT), hybrid quantum and classical MD,[44] ab initio molecular dynamics (AIMD),[48] and coarse-grained molecular dynamics.[45,49] AIMD is the most detailed MD technique to solve the quantum Schrödinger equation. The effect of the electrons is considered implicitly. This method is very accurate but computationally intensive and, hence, is appropriate for systems containing 100−1000 atoms within a time duration of 1−100 ps. The approach is capable of investigating the phenomena containing a chemical reaction, charge transfer, and electron excitation and hence is beyond the complexity required for understanding PFAS dynamics.[44,47,50]

In contrast to AIMD, for classic MD simulations, electronic structures are not directly considered, while atomic-level resolution is retained. Solving Newton's equation of motion for a system of atoms and/or molecules forms the central task of classical MD, just as solving the Schrödinger equation is the central tenant of quantum mechanics. Classic MD potentially extends the simulation range to a few thousand atoms on the nanosecond time scale, by applying Newton's equation of motion to describe the time evolution of any particles (atoms, molecules, or radicals) for a set of initial conditions. Once the trajectories and velocities of individual atoms and/or molecules, subjected to interatomic and/or intermolecular forces, are obtained by MD, the system's macroscopic behaviors and properties might also be determined (upscaling). The disadvantage, however, is that in a classical MD simulation the subatomic electronic structure and dynamics are not computed, so inherently quantum-mechanical events, such as chemical reactions (i.e., chemical bond breaking and formation), photoinduced processes, and charge transfer are excluded.[50]

To ensure numerical stability, the time steps in an MD simulation must be short, typically only a few femtoseconds (10^{-15} s) each. Most of the events of biochemical interest take place on time scales of nanoseconds, microseconds, or longer. A typical simulation thus involves millions or billions of time steps. This fact, combined with the millions of interatomic interactions typically evaluated during a single time step, causes simulations to be considerably computationally demanding, even with existing advanced computational infrastructure.[45]

Focusing on PFAS, several interaction mechanisms are involved in contaminant adsorption on the adsorbent and the interface of the fluids; the most well-known are van der Waals forces, electrostatic interactions, and hydrogen bonding.[28] The classical MD simulations reveal the mechanisms underlying these processes. For that reason, classical MD gained attention in recent years among molecular researchers in this field[28] and has been shown to be affordable for systems containing the maximum number of 10^6 atoms and time duration of 1000 ns. As we will discuss later, this means in a typical simulation box

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thousands of water or sorbent molecules may exist. The number of PFAS molecules is usually limited to a few to mimic their low concentrations.

Various commercial and open source codes are available (and have been partially used) for classical MD simulation of PFAS dynamics. Among them, LAMMPS,[51] COMSOL,[52] and GROMACS[53] have also widely been used in other disciplines for studying similar problems. However, as discussed later, the application of MD for PFAS is limited and is mainly focused on the adsorption to solid surfaces.

3.2. Example of MD Simulation of PFAS Adsorption to Solids. MD simulations were used to investigate the interaction of PFAS with clay minerals. In these studies, the MD simulations for PFAS sorption on clays corroborated the mechanisms suggested by the experimental results and assisted in identifying the PFAS binding sites.[3,12,17,54,55]

Recently, the LAMMPS simulation tool[51] was used to model an average surface coverage of 1.5 molecules/nm^2 of PFAS. With a time step of 0.1 fs, 20 million timesteps were calculated. As described earlier, a key component in MD simulation is to have the right force field describing the experimentally verified interaction between molecules. This relies on the PFAS molecules being accurately constructed and characterized at an atomic scale to generate the underlying electrostatic potential maps of molecules and consequently calculate the correct forces based on the force field. In this study (and in many others), the interatomic interactions among the adsorbent (clay) molecules and PFAS were described via the optimized potentials for the liquid simulations (OPLS) force field.[12]

In another study, the adsorption of three PFAS molecules with different chain lengths was simulated.[3] The simulation box (with a periodic boundary condition) had a size of about 5.18 × 5.39 × 12.6 nm. The CLAYFF force field was used for clay and Na^+ atoms (to initially neutralize the solution), and the OPLS-AA force field was used for PFAS and the SPC/E for water molecules.[3]

Luft et al. simulated the sorption of medium- and long-tail PFAS to clay.[54] All simulations with the clay surfaces were conducted with GROMACS.[53] The clay surface was parametrized with CLAYFF. PFAS molecules were parametrized with Gaussian-1633 to generate the underlying electrostatic potential maps of each molecule.[54]

Classical MD simulations were also used to predict the partitioning of PFAS to smectite clay. Simulations were run using LAMMPS, and interatomic interactions were modeled using the CLAYFF model for clay atoms. Similar to previous studies, the OPLS-AA model for PFAS molecules and the SPC/E model for water molecules were applied.[55]

MD simulations of the adsorption, interfacial structure, and dynamics of 16 short- and long-chain PFAS molecules at the water-saturated mesopores of kaolinite clay were conducted.[56] The LAMMPS simulation package was applied. For the adsorbent, the force fields were obtained from the CLAYFF. The interactions of the water and PFAS molecules were modeled with the flexible SPC63 interaction potential and AMBER force field, respectively. To construct the PFAS molecules, the partial charges for the atoms in all four different PFAS molecules were computed using the AM1-BCC charge generation scheme.[56]

Monte Carlo molecular simulation of PFAS interacting with graphite in an aqueous medium has also been reported.[57] In contrast with the deterministic approaches discussed thus far, the Monte Carlo simulation method is employed to calculate the equilibrium statistical properties. Statistics on the molecule positions and orientations are collected for each accepted new configuration.[57]

Together, the MD studies discussed in this section expand the fundamental knowledge of PFAS adsorption to clay minerals. The studies address the effect of various ambient parameters on the adsorption magnitude and mechanism. For instance, the effect of salinity, structure of the PFAS molecules, and coordinating cation types are characterized.[55] Distinct adsorption mechanisms on different surfaces have also been revealed.[3] One important finding was the difference between local and bulk (aqueous) diffusion coefficients,[3,12] which is expected to also occur at fluid interfaces (Marangoni effect). Overall, the studies have advanced the mechanistic understanding of PFAS−smectite interactions and provided new insights into developing fate and transport models and the development of adsorbents and remediation techniques.

3.3. Lack of MD Simulation of PFAS at the Interface. The behavior of molecules and ions at the interface of two fluids has been one of the challenging questions over the past century and involves more complex physics than adsorption to a solid phase.[58] A classic example is the use of surfactants to attract dissolved ions to the interfaces in both solvent-based and solvent-free separation processes.[59] Many industrial problems include nanoscale molecular and atomic dynamics at the interface. For example, the transfer of rare metal ions from aqueous to organic phases underlies the process of solvent extraction for separation and recovery. Another example is the reprocessing of spent nuclear fuel and nuclear waste, which has received attention both experimentally and computationally (through MD simulations). However, the mechanism of transport under these conditions remains under investigation.[42,49]

Studies on the interfacial dynamics of molecules at fluid interfaces, in the presence of LNAPLs, seem rare. One (to some extent) relevant study is the adsorption of radionuclides to an alkane interface.[42,59] Another study focused on organic phosphorus adsorption at the diaspore−water interface.[44] However, no studies of nanoscale MD for PFAS molecules were identified, probably due to the lack of experimental work that can support the optimization required for verification of the molecular scale force fields.

4. UPSCALING FROM MOLECULAR SCALE BEHAVIOR

4.1. Microscale Marangoni Effects. As depicted in Figure 1, the microscale models can inherit the knowledge from molecular scale behavior and interaction of the molecules to develop constitutive relationship, in particular to distinguish between surface and bulk diffusion.

The authors did not come across any microscale study of PFAS dynamics in porous media with such a systematic approach. Furthermore, independent microscale studies of PFAS resembling porous media analogues of soil−water−NAPL interfaces are not numerous. Excluding industrial studies on microfabricated structures,[60] the only study identified looked at pore scale PFAS dynamics in porous media.[36] The pore-scale model mimicked PFAS adsorption at bulk capillary and thin-water-film air−water interfaces. Here we note that pore scale models do not directly resolve the two-phase Stokes flow equation.[61]

We propose the following two steps to study the Marangoni effect with the existence of PFAS dissolved in groundwater. The first step is to perform MD simulations of a nanometer

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droplet on a flat hydrophilic mineral substrate. These simulations can have two configurations: a droplet of LNAPL surrounded by groundwater and a water droplet surrounded by LNAPL. These simulations are expected to determine surface tension and wettability from molecular statistics, such as Bakker's equation[62] on the simulated stress components. The result of these MD simulations will offer a validation between the MD simulations and the continuum Navier−Stokes equations (fluid mass balance and momentum balance for LNAPL and groundwater) with a surface-tension-parametrized force term. The two-phase Navier−Stokes equations can be computed using lattice Boltzmann methods[63] or the volume of fluid methods.[64]

The second step is to conduct MD simulations of the effect of PFAS on the established two-phase interface in the first step. These simulations should parametrize the altered surface tension and wettability from molecule statistics (e.g., stress field) as a function of PFAS concentration, which should be validated with respect to the continuum two-phase Navier−Stokes equations. In addition, the migration of PFAS molecules should be analyzed to formulate the corresponding mass-transfer processes between bulk capillary water and thin water films (including advection, aqueous diffusion, and surface diffusion along air−water interfaces), through applying semiempirical constitutive relationships which were derived through curve fittings to existing field-scale data sets in the literature.[36]

4.2. Darcy (Macro)scale Modeling. At a Darcy scale, modeling of PFAS transport processes in porous media includes advection, dispersion, diffusion, and partitioning processes. Partitioning processes might include (but are not limited to) (i) adsorption to air−water interfaces, (ii) partitioning or volatilization to air,[65] (iii) partitioning (absorption) to NAPL trapped in source zones, and (iv) adsorption to NAPL−water interfaces in NAPL-contaminated source zones.[10] Measurements (laboratory and field scale) are used to characterize the named processes for modeling purposes (e.g., changes in the interfacial tensions of the fluids pairs and hence the mobilities[66]).

The authors did not find any systematic study on upscaling the dynamics of PFAS from the nano- and microscale to a Darcy scale. Hence, the resulting Darcy models in the literature are highly dependent on the conditions of the laboratory, pilot, and field studies to characterize the transport phenomena. As PFAS molecules show complex behavior at the nanoscale, any Darcy scale model derived based on existing data sets and measurements may produce misleading information in variant cases.[15,18,56] For instance, a very common simplifying assumption used in Darcy scale models is that intermolecular interactions are negligible at fluid−fluid interfaces.[67,68] Such an assumption is usually justified through an empirical relationship between surface excess and the bulk solution concentration of PFAS.[13] However, it is known that surface active compounds (experimental data only available for non-PFAS long-chain hydrocarbon surfactants) at fluid−fluid interfaces behave uniquely and often show thermodynamically counter-intuitive behavior during mass transfer.[42,69,70] Such information cannot be captured through the macroscale experiments performed to build an empirical relationship. Thus, simplifications used in Darcy scale models such as negligible intermolecular interactions at the fluid−fluid interface will likely lead to less reliable characterization of the transport phenomena.

In general, empirical models fitted to measurements are rate limited mass transfer models.[71,72] The central focus in all these models is to characterize the distribution coefficient (retardation) of the PFAS molecules for their interfacial and solid phase adsorptions.[1] As a classic example of PFAS dynamics in a two-phase (air−water) system, the transport and retention of PFAS in the subsurface was modeled through a 3D advection−dispersion equation coupled with adsorption at the solid surfaces and air−water interfaces.[73]

Studies on the Darcy scale dynamics of PFAS in the presence of NAPLs are scarce. Among the few models, a multiprocess retention model is proposed to account for potential additional sources of retardation for PFAS transport in source zones. These included volatilization, adsorption at air−water interfaces, partitioning to trapped NAPL, and adsorption at NAPL−water interfaces. Data collected from the literature were used to determine measured or estimated values for the relevant distribution coefficients and hence the retardation factors.[10] The authors did not find any Darcy scale model in which multiphase transport of air/water/LNAPL is linked to the consequences of the PFAS existence.[30]

4.3. Upscaling Experiments. In the literature, currently there are a number of studies for nanoscale interaction of PFAS at air−liquid[74] and solid−liquid interfaces.[75] These studies present interesting observations and can guide the development of nanoscaled transport modeling and clearly indicate the need for consideration of the Marangoni effect. For instance, Sekine et al. investigated the adsorption kinetics of perfluorononanoate surfactant at the air−water interfaces in dynamic conditions employing Neutron reflectivity.[35] They further utilized laser Doppler velocimetry to understand the expansion of dynamic bubble surfaces in the presence of perfluorononanoate. The authors found that the dynamic surface excess of perfluorononanoate surfactant was in good agreement with the diffusion-controlled adsorption model, and the surface expansion of the perfluorononanoate surfactant solution showed significant correlation with the Marangoni effect. Such investigations are of high significance but have not been upscaled from the model system to real world situations and are sparse at the fluid−fluid interface scale.

The Marangoni effect at the air−water interface is commonly measured using a pendent drop method with a high-speed camera, where a drop (with solute) is released onto a reservoir filled with water, and its trajectory and flow pattern on the air−water interface are measured and analyzed with a high-speed camera.[34] In a similar manner, at fluid−fluid interfaces, an immiscible liquid drop (often called lens) is formed at the water surface creating a fluid−fluid interface (for LNAPLs), and the change in the lens size and movement is analyzed to determine the Marangoni effect in its various forms.[32] These experiments provide detailed fundamental information about the role of the Marangoni effect under controlled laboratory conditions. However, measurements following these procedures often cannot be simply upscaled to allow nanomicro-Darcy scale transport modeling of PFAS.

To measure the behavior of PFAS in real-world scenarios, column experiments are applied where the effect of mass of adsorbed species (i.e., PFAS) in saturated[77] and unsaturated conditions[29] is determined. However, these experiments provide averaged information across a variety of interactions that are interlinked, acting together to drive the net transport of PFAS in porous media. At this scale, effectively, only empirical models can be developed from such experiments

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with assumptions that cannot capture the Marangoni effect.[10,78,79] Micromodel studies provide a possible way to study microscopic transport scenarios. Micromodels can focus on transport phenomena at the pore scale level, and these models can provide valuable insights into water/LNAPL/soil phase displacement (or transport) at the macroscopic level. However, PFAS studies using micromodels are limited.[80] In building a roadmap for PFAS information available for closely related systems, studies that include other surface-active substances in multiphase systems can be utilized.

Key micromodel studies have been undertaken to investigate the multiphase displacement dynamics during the enhanced oil recovery (EOR) process, where chemical and surfactant flooding is common in order to increase oil recovery yield.[80] This multiphase system has water/LNAPL/solid or water/LNAPL/air interfaces, common to those of PFAS in porous media. Further, EOR often uses surfactants, so outcomes and approaches developed for EOR investigations provide a basis to support fundamental PFAS investigations of a transport model or for planning upscaled experiments. Commonly, in micromodel studies of EOR, a porous model system is engineered and fabricated, and water, LNAPL, and/or solution with solutes are injected into the porous micromodel (which can be made up of model minerals[80]). Often, digital images are captured and analyzed to show transport effects and to gain insights into the Marangoni effect.[81] Additionally, hydrodynamic interfacial instability patterns (including the Marangoni effect/flow) at fluid−fluid interfaces can be measured employing a Hele−Shaw cell.[82] Further, its observation can be correlated with finite element simulations to build a relationship between experimentally and computationally obtained information.[83]

To upscale the transport model, quantitative information is needed that can be used to develop efficient nano-, micro-, and macro- (Darcy) scale models. For verification of these models, the Marangoni number (Ma - a dimensionless number that characterizes the Marangoni effect) can be used

$$Ma = \frac{\Delta\sigma L_m}{\mu D} \quad (1)$$

Here, $\Delta\sigma$ is the change in the interfacial tension $[MT^{-2}]$ (due to a solute concentration) along the characteristic length L_m; μ is the dynamic viscosity $[ML^{-1}T^{-1}]$; and D is the diffusion coefficient $[L^2T^{-1}]$.[84] The Marangoni number concept is applicable to studies across scales[33,85−87] and thus adaptable to quantitative studies of the PFAS interaction in multiphase systems for the development of transport model systems.

5. CONCLUSIONS

Managing and remediating PFAS-contaminated sites and porous materials remain challenging. Critical knowledge gaps exist on the behavior and fate of PFAS in vadose and saturated zones in the field and in other porous media such as concrete and asphalt. Partitioning and movement of PFAS between and within multiple (air, water, NAPL, solid) phases is particularly complicated by the surfactant and surface-active properties of PFAS. In addition to the adsorption to the soil and solid surfaces, a critical behavior of PFAS molecules because of their unusual properties is their surface and bulk diffusion at the interface of fluid pairs. In thin fluid films, this results in an yet unquantified solutocapillary behavior at the nano- and microscales.

The complexity of porous media and the presence of LNAPLs further challenge the success of remedial options and can compromise remediation efficiency. The colocation of PFAS and petroleum hydrocarbons is common at oil fields, refineries, large fuel storage facilities, and airports. Such facilities are where PFAS liquids have been used in fire-fighting foams, for training, and with LNAPL releases. The global scale and spread of such incidents (and hence usage of a PFAS-contaminating subsurface) are significant.[88] Despite its occurrence, the dynamics of PFAS is an unknown function of the multiphase multicomponent dynamics of LNAPLs in the subsurface, which by itself has been shown to be challenging to characterize. Migration, disturbance, and changes of LNAPL plumes due to active remediation and natural source zone depletion increase the complexities even more.[30,89,90]

Representing these behaviors requires the establishment of quantitative modules that allow development of constitutive relationships at a Darcy scale, which are then applicable at the field scale. This is seen to be feasible through systematic upscaling of both experimental and computational studies from nano- to microscales. Indeed, similar to the momentum field for which the Darcy law has been amended by further terms for special cases (e.g., Darcy−Forchheimer[91] and Darcy Brinkman[92] for inertia and friction, respectively), it might be possible to include terms in the Darcy scale mass transport equation. Where NAPLs also coexist (including DNAPLs[27,93]), this is particularly challenging, but such occurrences are common and warrant investigation. Here a strategy and roadmap are outlined to clarify and address the challenges of advancing linkages from nano- to macroscales.

Based on the discussion related to Figure 2, a critical gap is to characterize the Marangoni effect with the existence of PFAS dissolved in groundwater. We proposed a two-step approach. The first step is to perform MD simulations of a nanometer droplet (LNAPL in the presence of water) on a flat hydrophilic mineral substrate. These simulations are expected to determine the statistical characteristics of the system at rest. The second step is to conduct MD simulations of the PFAS effect (concentration, type of molecules, etc.) on the established two-phase interface in the first step. These simulations would parametrize the altered surface tension and wettability from molecule statistics (e.g., stress field) as a function of PFAS concentration. It would then be potentially possible to interlink the MD simulations and the continuum (Navier−Stokes) equations through surface-tension-parametrized forcing terms (constitutive relationships) and characterize surface diffusion at the interface. Various two-phase flow simulation methods would need to be evaluated (e.g., pore network, lattice Boltzmann, front tracking method, volume of fluid, level set method, phase field method).[94]

The insight and knowledge obtained through such a two-step approach potentially would provide modified microscale flow and solute mass governing equations in which the solute mass (PFAS) behaves as an active scalar at the interface where the surface tension would become a function of the PFAS concentration. This would be a critical step toward upscaling and developing Darcy scale governing equations and models to be applicable to field problems.[95]

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Notes

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