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Computer simulations of fluid flow over catalytic surfaces for water splitting

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ABSTRACT

Interfacial phenomena arising at solid/fluid interfaces depend upon the nanoscale structural and dynamical properties of the system. The presence of active sites on the solid surface that can bind with reactants in the fluid enables the investigation of reaction kinetics and its effect on multi-scale transport processes. We develop a coarse-grained particle-based model of the flow of reactants over a solid surface composed of close packed particles with embedded active sites. We investigate the role of the adsorption of the reactants onto these sites on the transport phenomena via the coarse-grained molecular dynamics technique. Our objective is to understand the role of nanoscale interfacial phenomena on the structural and dynamical properties of the system through the measurement of diffusion coefficients, velocity profiles, radial distribution functions, and mean residence times. We have investigated these properties as a function of the active site density, coarse graining effects and interaction strengths. Our results can potentially be used for future studies on multi-scale phenomena driven by reaction kinetics at solid/fluid interfaces, such as artificial photosynthesis cells.

1. Introduction

Fundamental insight into the interfacial phenomena at solid–fluid interfaces in photocatalytic systems are paramount for the development of new sustainable renewal energy technologies, such as fuel cells. One area of growing promise is artificial photosynthesis where light is used in conjunction with dye sensitized semiconductor films to generate electricity for hydrogen production [1]. An accurate representation of the interfacial behavior of this system must include the formation of transition metal complexes in the film and the membrane material where the oxidation to hydrogen occurs. A common example of photocatalysis is the water splitting reaction utilizing a titanium dioxide surface doped with transition metals [2]. Beyond photocatalysis, solid–fluid interface research is highly prevalent in applications related to electrochemistry, corrosion and wetting [3]. The broad spectrum of applications is captured by the numerous investigations on the fluid properties near surfaces of varying chemistry and morphology. Hence, an investigation of the reactants flowing over a surface with active sites must encompass the role of the reactant concentration, the active site density, and the chemical nature of the various species.

We are interested in understanding the role of molecular scale interfacial phenomena at a catalytic reactive surface on the bulk transport phenomena. This setup could be envisioned as a catalyst on a solid support, and the reactions with the fluid via the adsorption and desorption of the reactants. The yield of these processes depends upon parameters such as the concentration of the catalytic or active sites on the support, the density of the reactants, and the chemistry of the reactants and the active sites. Fundamental insight into the effect of each of these key factors on the efficacy of the process requires characterization of the molecular scale interfacial phenomena and bulk transport properties at the solid–fluid interfaces. Fluid flow over solid surfaces is a multi-scale problem where observations on the microscopic level will influence macroscopic properties that can be measured in the laboratory.

In this paper, we develop characterization methods that will serve in the future to investigate the flow of the reactants over a support with active sites, and model the interaction of the reactants with the active support through the process of adsorption. The flow of the reactants is induced via forcing along a specific dimension. The support surface has active sites that are uniformly distributed, and can induce the adsorption of the reactants due to favorable screened electrostatic interactions. We treat the active site as a metal ion. Earlier studies have demonstrated the adsorption of an ion onto a metal ion due to polarization effects, and analyzed the transport phenomena for the flow over a charged surface [4,5]. Our approach provides fundamental insight into the

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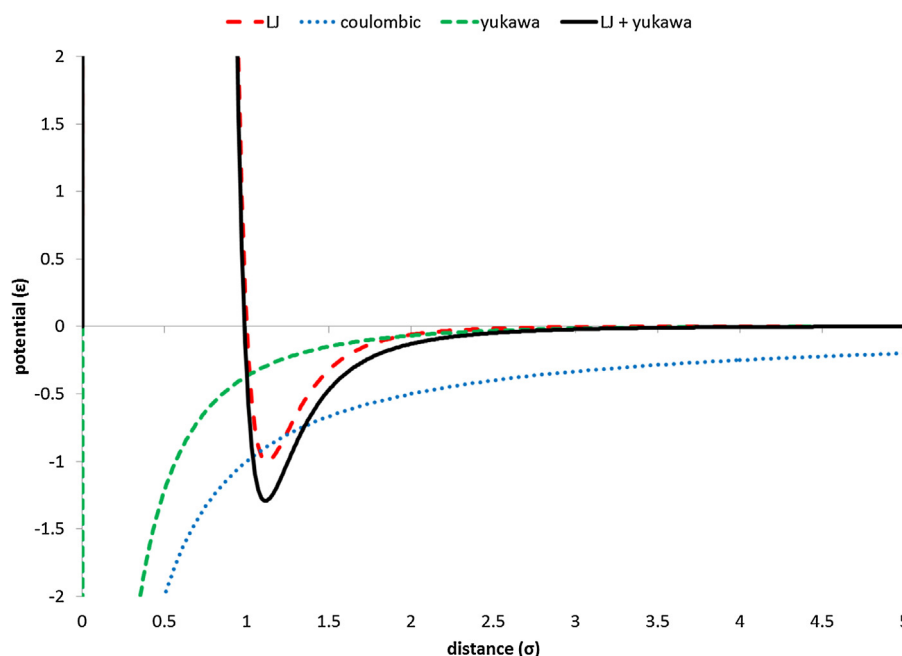 *E-mail address:* meenakshi.dutt@rutgers.edu (M. Dutt).

Fig. 1. Plot of the Lennard–Jones (LJ) potential with ($\sigma = 1$ and $\varepsilon = 1$) and the screened Coulombic potential (for a pair of oppositely charged monovalent ion, Yukawa potential with screened length of 1), and a combined LJ and Yukawa potential.

effect of adsorption on the transport properties as a function of the active site concentration, screened Coulombic potential strength, and the level of coarse graining. We characterize the dynamical and structural properties of the system using particle trajectory data to compute the velocity profiles, diffusion coefficients, radial distribution functions, and residence times.

The aforementioned characterizations can be extended to the investigations of other systems with analogous interfacial behavior, encompassing fluid flow over a reactive surface. Physical properties such as velocity profiles and diffusion coefficients can be used to compare with experimental measurements to relate to the continuum behavior of bulk fluid flowing over reactive surfaces. We have introduced a novel characterization of the interfacial reaction kinetics through the calculations of residence times of the reactants at the active sites. All the characterization codes that are discussed in this paper have been designed to analyze general solid–fluid interfaces.

2. Methods

The particle dynamics can be modeled by using classical molecular dynamics (MD) simulations [6]. The equation of motion for each bead i is given by $\mathbf{F}_i = m_i \mathbf{a}_i$ where $\mathbf{F}_i$ is the force acting on bead i, m_i is the mass and $\mathbf{a}_i$ is the acceleration of the bead i. The force can be expressed as the gradient of the potential energy U by the relations $\mathbf{F}_i = -\nabla_i U$. The dynamics of each bead i can be determined by the following equations $-\nabla_i U = m_i \mathbf{a}_i = m_i(d^2\mathbf{r}_i/dt^2) = m_i(d\mathbf{v}_i/dt)$ and $\mathbf{v}_i = d\mathbf{r}_i/dt$, where $\mathbf{r}_i$ and $\mathbf{v}_i$ are the position and velocity vectors of bead i, respectively. The equations of motion will be integrated using the Velocity Verlet method [7] which has greater stability, time reversibility and preserves the symplectic form on the phase space compared to the Euler method [8]. The position $\mathbf{r}_i$ and velocity $\mathbf{v}_i$ of a bead i using the Velocity Verlet algorithm are calculated as follows: $\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + (1/2)(\mathbf{a}_i(t) + \mathbf{a}_i(t + \Delta t))\Delta t$ and $\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + (1/2)\mathbf{a}_i(t)\Delta t^2$, where $\mathbf{r}_i(t)$, $\mathbf{r}_i(t + \Delta t)$, $\mathbf{v}_i(t)$ and $\mathbf{v}_i(t + \Delta t)$ are respectively the position and velocity vectors at time t and $t + \Delta t$ (Δt is the integration time step). The MD simulations will sample the canonical ensemble and will be

run using the open source parallelized MD program called Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [9].

In this study, the dual prerequisites for multiscale dynamics resolution and the frequent independent sampling of system configurations will be addressed through the adoption of coarse-grained representations of the components in the system. A coarse-grained representation of a chemical entity models a group of atoms as a single bead at a larger scale by reducing the internal degrees of freedom. The concept of coarse-graining stems from renormalization group theory [10] where a methodical process of smoothening out the degrees of freedom to attain a larger scale at which the coarse-grained interactions operate [11]. The coarse-grained interactions between the beads are determined by pair potentials which capture the excluded volume effect and the long range screened electrostatic interactions.

The short-range repulsion due to excluded volume effects between two beads is modeled by the shifted-truncated 12-6 Lennard–Jones potential (LJ) [12] given by:

$$U_{\text{rep}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - 4\varepsilon\left[\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^{6}\right] \qquad (1)$$

The ε and σ parameters are characteristic to each pair of beads and r is the distance between the pair. For this study, we set $\varepsilon = 1$ and $\sigma = 1$ with the potential cut-off distance $r_c = 2^{1/6}\sigma$. In Fig. 1, we compare the 12-6 LJ potential form with its purely repulsive shifted-truncated form.

Long range screened Coulombic interactions are considered to dominate the interaction between the active sites on the support and the reactants, and was modeled by the Yukawa potential [13] given in Eq. (2):

$$U_{\text{scp}} = A\frac{e^{-kr}}{r} \qquad (2)$$

The parameter $A = q_1 q_2 / 4\pi\varepsilon\varepsilon_0$ is the strength of the electrostatic interaction between two point charges q_1 and q_2 in a medium of dielectric constant ε. The parameter k is the inverse Debye screening length in a solvent medium that depends upon the counterion concentration [14]. The Yukawa potential has been shifted