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Systematic comparison of force fields for molecular dynamic simulation of Au(111)/Ionic liquid interfaces

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ABSTRACT

Selecting the most suitable force field is a key to meaningful molecular dynamics (MD) simulation. To select the appropriate gold force field to model the Au(111)/ionic liquid interface, a systematic comparison of four different widely used force fields of gold and a typical carbon force field has been studied by MD simulations with constant potential method. We calculated the ion adsorption behavior and differential capacitance of interfaces between the gold electrode and ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([PYR][TFSI]) in comparison with the experimental results and showed the effects on the solid-liquid interfaces from the van der Waals interaction, image force effect and cumulative ions. Based on the comparison between the results of simulations and experiments, we recommend two types of force fields to properly model the Au(111)/ionic liquid interfaces.

1. Introduction

Room-temperature ionic liquids (RTILs) are promising electrolytes because of their remarkable advantages, such as low volatility, wide electrochemical windows, and designable properties [1–3]. Beyond that, they have been used in various applications including energy storage, electrocatalysis, electrowetting, and electronic gating [4–7]. The interfacial structures of RTILs at solid-liquid interfaces determine the performance of such applications. Therefore, many studies have investigated fluid-solid interfaces with ILs. Among these, gold electrodes are commonly employed due to gold's high electrical conductivity, chemical stability, and compatibility with conventional microfabrication procedures [8,9]. Relevant experimental studies have been carried out to investigate gold/RTILs interfaces in order to reveal the mechanism of the electric double layer (EDL) formation. For example, Atkin et al. [10] used atomic force microscopy (AFM) to reveal that there is a multilayered structure at electrified gold/RTILs interface and ion arrangements change as a function of potential, which suggested the RTILs interface can be shaped by the electrode potential and ions structure. Later, Mao et al. [11] obtained high quality AFM force curves to prove the existence of charged interior layers and neutral exterior layers. Gebbie et al. [12] employed a surface force apparatus (SFA) to investigate the electric screen of ionic liquids at charged gold and mica surfaces. Their results showed that both Stern and diffuse layers are formed to screen the charged surfaces and the diffuse double layer consists of dissociated cations and anions. In addition, neutron or X-ray reflectometry and surface tunneling microscopy are further methods found in studies of solid/RTILs interfaces [13–17].

In addition to experimental research, there are many theoretical works and simulations investigating gold/RTIL interfaces. Using molecular dynamics (MD) simulations, Sha et al. [18] reported the change of ion structure on gold electrode surface for different applied voltages. They also calculated the interaction energy of gold-ions and binding energy of cation-anion, which are difficult to extract directly from experimental data. Ferreira et al. [19] used MD simulations to investigate the orientation of ions on the solid surface and found the orientations of cations are more dependent on the interface instead of the anions. Furthermore, Nikitina et al. [20]

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combined MD simulations and quantum mechanical theory to study the electron transfer reaction at the gold/RTIL interface. They found a higher energy barrier that impedes the charged reactants from approaching the gold surface, which influences the electron transfer. In these simulations, the accuracy of the force fields plays a crucial role in determining the amount of ions adsorption, molecular orientation, energy barrier, and so on. However, so far most MD studies used different gold force fields to investigate the interface of gold/RTILs and the validation of the applicability of the force fields is usually ignored before modeling. Meanwhile, there are several kinds of force fields developed for gold, thus it is necessary to make systematic comparisons between them to reveal the suitable one for modeling gold/RTILs interfaces.

In the present work, we used MD simulations to compare four different types of often-used force fields of gold with a typical carbon force field systematically, using the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([PYR][TFSI]) as the electrolyte. We investigated the electro-adsorption behavior and differential capacitance of Au(111)/RTILs interface and attributed the interfacial phenomena to van der Waals interaction, image force effects, and cumulative ions.

2. Simulation details

2.1. Simulation methods

The simulation unit cell is shown in Fig. 1. Ionic liquids were enclosed between two electrodes with a size of 5.488 × 5.488 nm^2. Electrodes are modeled as Au (111) single-crystal surfaces and graphene sheets. The distance between positive electrode and negative electrode is 8.232 nm and the electrodes are fixed during the simulation, which should be wide enough to ensure that the RTILs in the central portion of the system are bulk-like (see Fig. S1). The expectation that [PYR][TFSI] in the central portion of the system are bulk-like is corroborated by the observation that, beyond positions ~3.0 nm from the electrode surface, the ionic space charge density is practically zero (i.e., both cations and anions are distributed homogeneously) and the electrical potential profile is flat (see Fig. S2 and Fig. S3). Detailed number of the ionic liquids and electrode atoms are gathered in Table S1 for all studied systems. The equal potential was maintained on the electrode surfaces and located at a plane across the center of surface atoms. This method was able to take the electronic polarizability of the electrode surfaces into account, for instance, a local redistribution of charges on the electrode surface due to interaction with RTILs. This approach has been verified by previous work [21,22], and it was shown that this method is much more realistic comparing to assigning a uniform and constant partial on each electrode atom when simulating supercapacitors based on RTILs. The number of ion pairs was tuned to guarantee the electrolyte density in the center of channel was in accord with the bulk. Long-range Coulomb interactions were quantified by using the particle mesh Ewald (PME) method [23] with a correlation for slab-geometry [24]. An FFT grid spacing of 0.1143 nm and cubic interpolation for charge distribution were used to compute the electrostatic interactions in the reciprocal space. A cutoff length of 1.2 nm was used in the calculation of electrostatic interactions in the real space. The non-electrostatic interactions were computed by direct summation with a cutoff length of 1.2 nm. LJ interactions between different atoms were calculated using Lorentz-Berthelot mixing rules. Simulations were performed in the NVT ensemble using a customized MD code Gromacs [25], with a time step of 2 fs The ensemble temperature was maintained at 338 K using the Nose-Hoover thermostat. All configurations were first run by annealing from 800 K to 338 K for 20 ns, and then an 80 ns production run was performed for analysis.

2.2. Force fields

For the gold electrode surface, we choose four highly cited gold force fields that all used in modeling gold electrode. In this work, the form of the force fields adopts 12-6 Lennard-Jones potential, where r_{ij} is the distance and ε_{ij} is the potential well describing the interaction intensity between atom i and atom j.

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

2.2.1. Face-centered cubic metals (FCCM) force field

The face-centered cubic metals force field [26] was parameterized for simulating the surface and interface of face-centered cubic metals, such as Au, Ag, Al, and Cu. It was developed to simulate the interface between metals and organic, inorganic, and biological

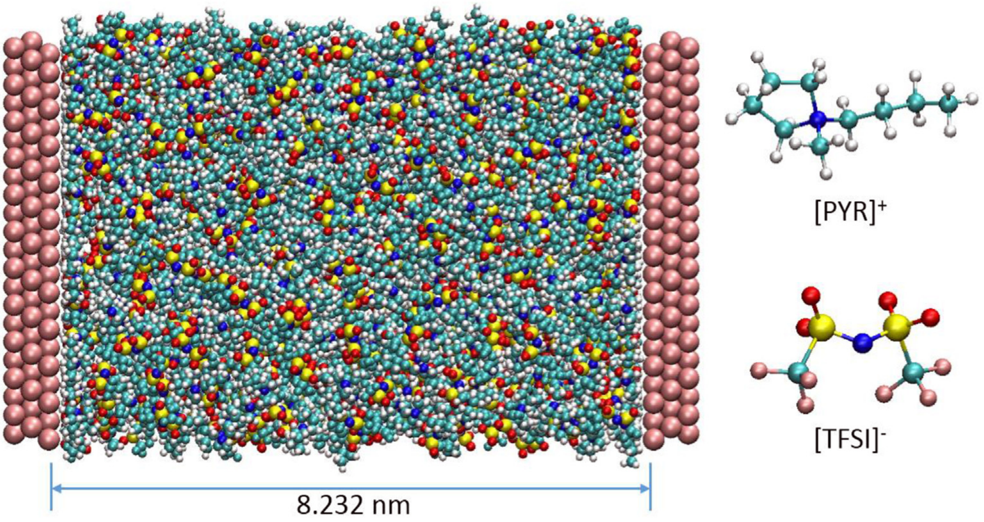

Fig. 1. a) The schematic configuration of the simulation unit cell. b) All-atoms molecular structure of [PYR][TFSI].