

外国語要旨

学位論文題目 Fragment based *ab initio* molecular dynamics simulation for predicting physicochemical properties of new functional liquids

氏名 Nahoko KUROKI

Chemical processes are unit operations with phase transition such as fluid transportation, separation extraction, and gas absorption that contribute to chemical engineering. Upon developing or designing chemical processes, it is necessary to understand states of matter and physicochemical properties. All matters exist as gases, liquids, or solids. The stable phase of the matters can be controlled by changing pressure and temperature conditions. Since gases and liquids including supercritical fluids are able to change their shapes by external forces, these states are called “fluids” and distinguished from the corresponding “solids”. With the high flowabilities, the fluids can often be mixed up with the other fluids, or even dissolve solids if suitable fluids are chosen. Thus, to understand the properties of fluids with proper molecular level insights is important in the fields of physical chemistry and chemical engineering. The purpose of this study is to develop novel simulation methods with high chemical accuracy and low computational cost for predicting static structures and transport properties of fluids in an *ab initio* manner. In this study, applicability of *ab initio* molecular dynamics simulation with Jensen’s effective fragment potential 2 (EFP2) were systematically investigated.

In chapter 1, the background of this study was reviewed from the view point of molecular theory. A set of theoretical methods to investigate intermolecular interactions of fluid proposed prior to this study was compactly reviewed.

In chapter 2, *ab initio* molecular orbital and EFP2 theories used in this study were explained in detail including the review of the history of molecular simulations.

In chapter 3, applicability of EFP2–MD simulation for investigating solution structure of ionic liquids (ILs) were discussed. ILs, which are defined as room temperature molten salts, are industrially important solvents for chemical reaction, extraction, and electrochemistry. However, guidelines to obtain novel chemical functions with ILs have not been well elucidated, since there had been no *ab initio* molecular dynamics simulation methods with low computational cost to perform fast enough molecular screening of candidate ILs. In this chapter, focusing on three ILs composed of 1,3-dimethylimidazolium cation and halogen anions ([C₁mim]Cl, [C₁mim]Br, [C₁mim]I), the applicability of EFP2–MD to predict the properties of ILs were investigated. Comparing previous

experimental observation and large-scale Car–Parrinello molecular dynamics (CPMD) simulation results, it was concluded that EFP2–MD has enough accuracy for predicting experimental ILs’ structures with at least 200 times lower computational cost compared with the CPMD.

In chapter 4, applicability of EFP2–MD simulation for predicting excess properties of mixed solvents were investigated. As discussed in the chapter 3 with the example of ILs, EFP2–MD secures its chemical accuracy by using multipole expansion to evaluate electrostatic interaction, which is the strongest physicochemical component of intermolecular interactions. However, it was not clarified whether EFP2–MD can evaluate short range interactions such as polarization energy with enough accuracy. The purpose of this chapter is to clarify the utilization of EFP2–MD not only for ILs but also for general organic mixed solvents. For this purpose, excess properties of water–methanol binary mixture, which is composed of weakly interacting neutral organic molecules, was evaluated with a set of EFP2–MD simulations. From the systematic simulations, it was concluded that EFP2–MD is capable of describing excess volume change with respect to the molar fraction of the mixed liquids in a semi quantitative manner.

In chapter 5, applicability of EFP2–MD simulation for predicting dynamic liquid properties including supercritical fluid phase was examined. Because of the dual, *i.e.* gases and liquids like nature, supercritical fluids can dissolve solutes that cannot be dissolved in usual organic solvents. Supercritical fluids are important, since they are expected to replace organic solvents which has been often used in the field of organic synthesis. To utilize supercritical fluids as functional liquids, it is necessary to understand their static/dynamic properties from the view point of molecular insights. Among various physicochemical properties, especially, the self–diffusion constant (particularly under extreme conditions involving high pressures and temperatures) is the most important one in the fields of chemical engineering and physical solution chemistry. In this chapter, focusing on highly compressed liquid NH_3 , of which critical temperature and pressure are 405.5 K and 111.3 atm, respectively, applicability of EFP2–MD to predict dynamic liquid properties (auto correlation functions and self–diffusion constants) was discussed. It was concluded that condensed phase properties including supercritical condition can be evaluated with sufficient accuracy with EFP2–MD compared with the corresponding experimental observations.

In chapter 6, concluding remarks were given. Future works inspired from the results were also presented. In this study, utilization of EFP2–MD to predict static/dynamic properties of fluids were investigated. It was concluded that liquid properties including mixtures or extreme conditions can be well predicted by EFP2–MD in high chemical accuracy with low computational cost.