

1P024

Smectic Phase Formation in Imidazolium-based Ionic Liquids with Long alkyl chain: the role of orientational dynamics

Hailong Peng¹, Hayato Shiba¹

¹ *Institute for Materials Research, Tohoku University, Japan*

[Abstract] We conduct molecular dynamics simulation on 1-methyl-3-alkylimidazolium hexafluorophosphate (C12mimPF6) ionic liquids using a united atom model. Temperature dependent dynamics including translational, orientational, and rotational dynamics are investigated, finding the orientational dynamics couples with shear viscosity while decouples with the others. We found a transition from isotropic phase to smectic phase in the supercooled liquids. The time scale for the formation of smectic phase roughly coincides with the characteristic time of the orientational relaxation, which is about hundreds of nanoseconds. A strong anisotropic behavior is found on the atomic dynamics and transport process in the smectic phase. As ionic liquids, especially those with long-alkyl chain can be easily supercooled, these findings would be of importance for unveiling the phase behavior and dynamics in a temperature range in the vicinity of room temperature.

[Introduction] Merits of ionic liquid (ILs) mostly come from the low melting temperatures, which is usually less than 100 Centigrade and could even below the room temperature. Before glass transition or crystallization, ILs with long-alkyl chain can be easily supercooled and exhibit tremendous metastable phase behavior, e.g. smectic A phase. Understanding formation of the metastable phases near the room temperature is important for the usage of ILs as solvent, extraction product and electrolyte.

Structural feature of the smectic phase displays as prepeaks in static structure factors at a length scale of about several nanometers, which can be observed in experiments via X-ray or neutron scattering. The detailed knowledge about this nano-structured phase, however, is difficult to access in experiments. Computer simulation is an adequate tool for the investigation of the nano-scale phase. The prediction of smectic phase in ILs is first made in computer simulation in a coarse-grained model [1]. For the dynamical and electrochemical properties of ILs, the coarse-grained model usually is inaccurate and even unable to describe. Thus, in order to understand the dynamic and electrochemical property of the nanostructured phase, an all-atom model or united-atom model is necessary. Due to the large time scale for the formation of the nanostructured phase, achievement of the smectic phase in atomic simulation level is usually very difficult. In this work, we utilized an atomic model with the atoms on the alkyl chain is united, successfully achieved the smectic phase by a long-time relaxation up to 1 micro second.

[Methods] Molecular dynamics simulation is conducted for 1-methyl-3-alkylimidazolium hexafluorophosphate ILs with 12 carbons in the alkyl chain. The force field is taken from Ref 2, with the structure and dynamic property the ILs verified. The simulated box contains 1000 ionic pairs. All the bonds and angles related to hydrogen is fixed by SHAKE algorithm. The Lennard-Jones pair-wise interaction is cut off at 1.2 nm. Long range correction for LJ interaction and the electrostatic interaction are calculated using particle-particle particle mesh solver with the accuracy 1e-6. We first equilibrate the system at high temperature, i.e. 800K, in order to get the random configurations. Then the system is cooled down to target temperatures in NPT ensemble, i.e. 700, 600, 540, 500, 460, 430, 400, 380, 360 K. Finally, we use microcanonical ensemble to collect data.

[Results and Discussion]

At high temperatures, the liquid structure is found to be isotropic and homogenous. Upon cooling down, a transition from the isotropic phase to smectic phase happens. The transformation time of the smectic phase roughly coincides with the relaxation time of orientational dynamics that is also the slowest relaxation process in ILs, e.g. comparing with translational, aromatic ring's rotational, and chain-length relaxation dynamics.

The transformation time is temperature dependent, and drastically increases with temperature decreasing. In the system investigated, we found the temperature where smectic phase formation time has the shortest time is at about 400 K. If at 360 K, the formation time of smectic phase is roughly one order of magnitude longer than at 400 K. We stress the importance of this point in computer simulation, as cooling rates in the simulation are usually ultra-fast. A too fast cooling rate in simulation could bypass the most facilitated smectic phase formation temperatures, making the smectic phase unachievable at low temperatures and the system will stay in meta-stable isotropic phase that would somethings not be sure in realistic experiments.

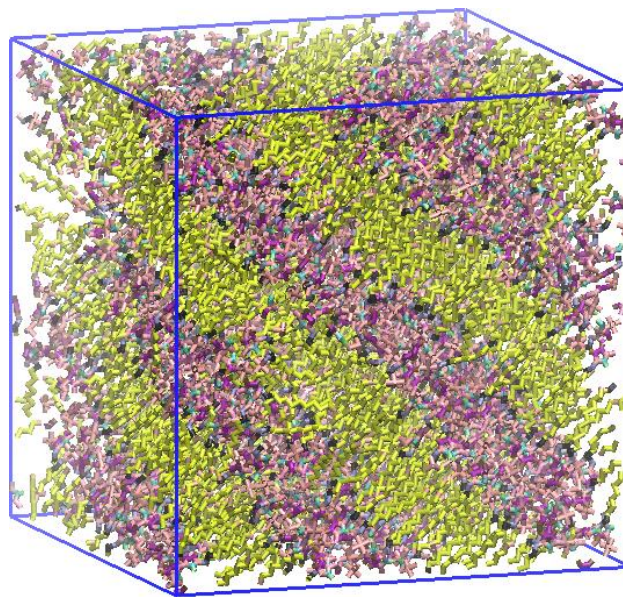


Fig. 1. Snapshot for the formed smectic phase at 380 K

The dynamical property of the smectic structure is also investigated in terms of self-intermediate scattering function and mean square displacement field. A strong anisotropic behavior is found for these properties. The motion of atoms in the normal direction of layers are constrained, while facilitated in the plane of layers.

[References]

- [1] Yanting Wang and Gregory A. Voth, *J. Am. Chem. Soc.* **127**, 12192 (2005).
- [2] Xiujuan Zhong, Zhiping Liu and Dapeng Cao, *J. Phys. Chem. B*, **115**, 10027 (2011).