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# Developing a Coarse-Grained Model for 1-Alkyl-3-methyl-imidazolium Chloride Ionic Liquids

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8  Developing Coarse-grained Model for 1-Alkyl-3-methyl-imidazolium Chloride

9  Ionic Liquids

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17  **ABSTRACT:** Due to sluggish dynamic and complex electrostatic potential networks of ionic

18  liquids, establishing a reasonable and efficient coarse-grained model is very important for a large

19  system with enough simulation time. In this work, novel coarse-grained models of 1-n-alkyl-3-

methylimidazolium chloride [C$_n$mim][Cl] (n=4, 6, 8) have been developed from the united atom model of ionic liquids. There are two mapping strategies for the ionic liquids coarse graining, one is that the imidazolium cations ([C$_n$mim]$^+$ (4, 6, 8)) and Cl$^-$ anion are represented as single coarse-grained bead as ionic model. The other is a pair of ionic liquids mapped to one bead as molecular model. It was found that both of two coarse-grained models could give good description of structures and thermodynamic properties for ionic liquids. Moreover, because of [1]reducing freedom of coarse-grained model a correction was established for self-diffusion coefficients which could be reproduced effectively of the results as united atom force field. Notably, the ionic model improves the calculation efficiency up to 9.5 times compared with united atom force field under the same simulation conditions due to electrostatic potentials in ionic model are indicated highly importance on coarse-grained model for ionic liquids. In summary, the coarse-grained models could provide a theoretical basis for large-scale ionic liquids systems.

**KEYWORDS:** Ionic liquids, Molecular dynamics, Coarse-grained model

# 1 Introduction

Ionic liquids (ILs) have attracted considerable attention due to their unique physical properties including wide electrochemical window, low melting point, low vapor pressure, high thermal stability conductivity, designable structure and low toxicity[1-4]. It gains potential groundbreaking developments in catalysis, separation, electrochemistry, material science and life

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1  science[5-8]. Commonly, ILs are composed of a large organic cation and a small anion[9-11].

2  Therefore, the theoretical researches in molecular level on ILs are crucial for their practical

3  application. In this regards, the molecular simulation is quite lively and has been made important

4  progress.

5  Molecular simulation is a method based on inter-molecular interactions to study the kinetic

6  and thermodynamic properties of molecular systems. The classical molecular dynamics (MD)

7  simulation as one of the methods which are based on molecular mechanics can effectively

8  observe and explain the interaction of ILs[12-16]. MD simulation uses atoms as the basic simulation

9  unit, and the charges, interactions, bonds, angles, and the dihedrals of each atom are

10  characterized by a force field, the quality of which is the main factor affecting the accuracy of

11  MD simulation. Currently, the most commonly used force field is the all atom (AA) force fields

12  which can accurately simulate micro-level system behaviors and structures[17-19].

13  Due to the complex structures and particular properties of ILs, it is difficult to simulate a

14  realistic and large-scale system by AA force field . Therefore, simulations of coarse-grained

15  (CG) models is an effective alternative to overcome the limitation of AA force fields. Molecular

16  level understanding on large scale could be investigated by constructing CG models, which

17  therefore could become one of the most powerful tools to investigate ILs.  Several atoms are set

18  as one "bead" or "particle" in CG models, while the parameters are generally obtained from all

19  atom molecular dynamics. In earlier work on CG models, Liu *et al.*[20] developed a CG model

20  called united atom (UA) force field for imidazolium-based ILs. The CG beads are defined

21  according to the difference of location of the atom in imidazole cations. UA force field has now

22  become one of the most widely used and most accurate CG model for the study in addition to the

1    AA force field. Recently, Patnaik *el al.*[21] set up a UA force field of octane which they treat each

2    of the methylene and methyl groups as a new bead. The effect of the model details on the

3    computed value of the condensation coefficient was explored by comparing the AA and the UA

4    force fields. It was found to predict shorter residence times in the first coordination shell of bulk

5    octane molecules on UA force field. As well as, the condensation coefficient of octane was

6    probed at five different temperatures using MD simulation.  They found the condensation

7    coefficient of octane independent of the liquid temperature within the studied temperature range.

8    Kyrychenko *et al.*[22] uses a UA force field simulated for poly(vinyl alcohol) with its polymer

9    chain length from 220 up to 1540 repeating units. They indicated that the size of the poly (vinyl

10   alcohol) polymer plays a crucial role in providing water protecting effects for the silver

11   nanoparticles core.

12        Another widely used CG representation is the MARTINI model which is used in simulation

13   of biomolecules, lipids and amino acids[23-25]. In recent works, Tieleman et al.[26] reported the

14   clusters of different anchors in lipid membranes by using the MARTINI force field. This work is

15   crucial for the correct reproduction of the expected biophysical behavior of peripheral membrane

16   proteins at the membrane-water interface. Schmalhorst *et al*. [27] researched the ability to

17   accurately represent molecular forces between saccharides by applying the MATINI force field

18   for biological macromolecules. Moreover, Sun and Zhou first proposed a CG model by using the

19   MARTINI force field of ILs with Nafion[28]. They used a simple three-site model to represent 1-

20   butyl-3-methylimidazolium tetrafluoroborate ([$C_4$mim][$BF_4$]) ILs which respectively represent

21   [$BF_4$]$^-$ anion and two segments on [$C_4$mim]$^+$ cation. For Nafion, in each monomer, hydrophobic

22   backbone is represented by four apolar beads and side chain is represented by apolar bead and

23   charged bead. CG simulation results of bulk [$C_4$mim][$BF_4$] show good agreement with AA

1    simulation results and experimental data. ILs cluster formation inside Nafion was revealed by

2    this CG model.

3        Recently, a multiscale coarse-grained (MS-CG) model had been presented by Wang *et al.* [29].

4    For the MS-CG model, [C$_2$mim][NO$_3$] ILs have been grouped into 5 CG sites. The anion and the

5    aromatic ring in the cation have been separately considered as one CG bead, because they are

6    both almost rigid bodies. Due to the methyl group and the two methylene groups are rotationally

7    symmetric to their principal axes, they have been seen as three CG beads, respectively. This

8    model for ILs exhibits very good transferability in different systems at various temperatures and

9    is suitable for investigating their microscopic structural properties. In the following years, they

10   developed an effective force coarse-grained (EF-CG) model[30]. The side chain length of the

11   [C$_n$mim][NO$_3$] ILs is increased to twelve. This model is similar to the MS-CG model which the

12   entire nitrate anion, the imidazole ring, single methyl group and the terminal methyl group on the

13   side chain as a CG bead, respectively. The ethyl group adjacent to the terminal methyl group as a

14   CG bead. And the others ethyl groups are denoted as a type of CG beads. They explored the

15   effects of various cation side chain length in ILs by using the EF-CG model and revealed

16   features of the system that were difficult to use ordinary AA simulations. Simulations with EF-

17   CG model show that, with long side-chain length, neutral tail groups of cations aggregate to form

18   spatially heterogeneous domains, while the charged head groups and anions tend to distribute

19   uniformly because of the strong electrostatic interactions. At present, more and more research

20   works and apply fields focus on CG models development. Pfaendtne *et al.*[31] discussed the

21   interactions of human serum albumin with different ILs. They systematically predict differences

22   in the dynamics of proteins solvated in ILs-water mixtures versus pure water systems by

23   applying a CG model. And they demonstrated that the presence of ILs changes the distribution of

1  intermolecular distances among several ligands, indicating that the protein structure swells in the

2  presence of certain ILs, consistent with experimental evidence. Balasubramanian *et al.*[32]

3  proposed a CG model to investigate the self-assembly of benzene-1, 3, 5-tricarboxamide class of

4  compounds in nonpolar solvents. Clare *et al.*[33] set up a CG model for water by using K-means

5  algorithm in which they used several water molecules as one CG bead. Through the study of a

6  simple mixture between water and 1-pentanol, they found a four-water bead model has the

7  optimal balance between computational efficiency and structural properties.

8      To the best of our knowledge, most researches developed CG model of ILs that CG beads

9  are divided according to different sites for a cation or anion. In this work, in order to explore a

10  novel CG model of imidazole-based ILs for fitting large-scale and long-time simulation, we

11  make an attempt on development of CG model using single ion and one ion pair. We

12  investigated the accuracy and efficiency of much bigger CG model in ILs. 150 pairs of ILs are

13  used to develope model and extent the CG model to simulate 5000 pairs of ILs.

14      The contents of this paper are organized as follows: in Section 2, we present the details of

15  our newly developed CG model for a series of imidazolium based ILs, as well as the simulation

16  methods. In section 3, we propose that the model was able to predict reasonable ILs properties.

17  CG simulations were used to study micro-structures and dynamics properties of [$C_n$mim]Cl (n=4,

18  6, 8). Radial distribution functions, densities, mean square displacements and self-diffusion

19  coefficients were analysed and compared the results of the UA simulation and experiments. In

20  section 4, the main conclusions of this paper are summarized.

21  **2 Model and Method**

## 2.1 Model

The force field model is the basis for understanding the thermodynamic and dynamic properties of ILs in MD simulation research. It is essential to understand microstructures and interactions of ILs systems to select or design reasonable model for a variety of applications of ILs. In this study, a CG model of 1-n-alkyl-3-methylimidazolium chlorine ([$C_n$mim]Cl, (n=4, 6, 8)) ILs was developed based on UA force field by Liu *et al.*[34] In UA force field three H atoms on the ring (H4 and H5 in Fig. 1a) which are different from those on the alkyl groups are regarded. Since methyl (-CH3) and methylene (-CH2) in the alkyl groups can be treated as united atom. Therefore CN2, CN3, CT2 and CT3 are defined in UA force field. Among them, CN2 and CN3 stand for the united atom of methylene and methyl groups attached to the imidazolium ring, respectively. Similarly, CT2 and CT3 are those which do not attach to the ring. These atoms in UA force field are illustrated in Fig. 1a. On this foundation, two different mapping schemes of CG model were proposed in describing the [$C_n$mim]Cl (n=4, 6, 8).

It is well known that the electrostatic potential plays an important role in ILs. In recent years, many researchers found that electrostatic potential provides the most important contribution for explaining the macroscopic physical properties and understanding the molecular dynamics and microstructure of ILs. Blanco-Diaz *et al.*[35] reported the structure of ions for 1-butyl-3-methylimidazolium bis(trifluorometilsulfonil) imide ([$C_4$mim][$TF_2N$]). They found that electrostatic potential plays an important role in the shear viscosity for imidazolium based ILs, because the reduction in viscosity is in proportion to the reduction in the number of electrostatic potential. Weber *et al.*[36] found the equilibrium solubility of acetaminophen in 1-ethyl-3-methylimidazolium acetate to be very large due to electrostatic potential exist between

1    acetaminophen and acetate. In summary, electrostatic potential has a significant influence on the

2    physical properties of imidazolium based ILs. Moreover,  Youngs *et al.*[37,38] researched

3    intermolecular potentials for dimethylimidazolium chloride. They have probed that local

4    electrostatic is important in determining the crystal packing by investigating the charge

5    distribution in the cation and the effects of anion polarization. Therefore, to retain the effect of

6    electrostatic potential in the imidazolium based ILs, the $[C_n mim]^+$ (4, 6, 8) cations and $Cl^-$ anions

7    are represented as one single bead in first mapping model (CM I), as shown in Fig. 1b.

8    Another mapping model (CM II) is that mapped a pair of ILs to one bead. The idea of ion

9    pair coexisting with free ions was first proposed by Bjerrum[39]. Ion pair is an especially intriguing

10   issue in ILs. The speciation and scale of ion pair in ILs have an important effect on the physical

11   and chemical properties of ILs and recognition of the structure of ion pairs in solution is

12   essential. Ion pair in ILs was used in an extremely wide variety of applications, e.g. electrolytes

13   for electrochemical purposes, or tunable media for synthesis. Moreover, the ion cluster that

14   composed of multiple ion pairs are studied on both theoretical[40, 41] and computer simulations[42, 43]

15   in ILs. For instance, Bhar-gava *et al.*[44] performed MD simulations of 1-alkyl-3-

16   methylimidazolium bromine aqueous solutions, indicated that the cluster size increases and

17   number of cluster decreases with increased chain length. Wang *et al.*[45] investigated the cluster

18   shape of pH responsive ILs by modifying the pH of the system, and a reversible transition

19   between spherical micelles and vesicles with the change of solution pH value was observed. Liu

20   *et al.*[46] simulated a series of systems of imidazolium based ILs with a small amount of water,

21   they compared the microstructures of water in ILs-water systems and found that water is more

22   aggregated in $[C_4 mim][Tf_2 N]-H_2 O$ system to form clusters. To sum up, ion pair in ILs is a

23   heuristic construct. However, there is a lack of definition of the ion pair scale. In this model,

1    based on one ion pair, the effects of the minimum scale ion pair on the physicochemical

2    properties of ILs in simulation are investigated. Schematic representations of the CM II model of

3    [C$_4$mim]Cl are provided in Fig. 1c.

4    **2.2 Coarse-grained Method**

5    **2.2.1 CM I Model for [C$_4$mim]Cl**

6    In our work, the idea of model establishment is based on UA force field. A large number of

7    interactions in UA force field were statistically averaged to obtain fewer interactions in CG

8    model. The details of atoms description are neglected and fewer interactions sites to represent the

9    motion process on the larger-scale are used. For the CM I model, the method we utilized are as

10   follows:

11   (1) Firstly, 150 pairs of [C$_4$mim]Cl ILs in a cube simulate box with a size of 36.64×36.64×36.64

12   Å$^3$ on UA force field were simulated. The starting configurations of all the systems were

13   generated using the PACKMOL package. A cutoff distance was set to 12 Å and tail corrections

14   to energy and pressure were applied. Coulomb interactions were treated by the particle-particle

15   particle mesh Ewald method using an accuracy of 10$^{-4}$. Nose-Hoover thermostat and barostat

16   were used for three temperatures (298 K, 348 K, 398 K) and 1.0 atm. All angles and bonds

17   involving hydrogen were constrained by the SHAKE algorithm with a tolerance of 10$^{-6}$. The

18   neighbor lists were set with a distance of 2 Å and updated every 5 steps. At each temperature,

19   simulations of 2 ns were performed in the isothermal-isobaric (NPT) ensemble, then the value of

20   the last 2 ps is statistically averaged as density value. Afterwards, canonical ensemble (NVT)

21   simulations at the same temperature for 2 ns were allowed to equilibrate. After the equilibration,

22   10000 configurations and trajectory of approximately 20 ns was obtained and transport

1    properties were calculated in the NVT ensemble. The trajectory of the last conformation was

2    used as the target conformation of the CG models in this work.

3    (2) Secondly, the target RDFs could be obtained by performing the last 20 ns NVT ensembles

4    simulation on UA force field. RDFs can be used to characterize the microscopic structure of ILs

5    which represents the distance-dependent relative probability of observing a given site relative to

6    some center sites, as following:

7
$$g_i(r) = \frac{\rho_i(r)}{\rho_0(r)} \exp(-\frac{U_i(r) - U}{kT})$$
(1)

8        Where $r$ is the radial distance, $\rho_i(r)$ is the probability of appearance within a distance of $r$

9    for molecular $i$, $U_i(r)$ is the energy for the molecular $i$, $k$ is the Boltzmann constant,

10   $k = 1.38066 \times 10^{-23}$ J/$K$, and $T$ is the system temperature.

11   (3) Next, the Iterative Boltzmann Inversion (IBI)[47, 48] method is used to make sure that the

12   effective pair potentials are agreed between the pair correlation functions at the UA and CG

13   levels. The *Eq 2.* is used to iterate the potential energy, which is to modify the potential energy

14   $U_i^{j+1}(r)$ by using the RDF ($g_i^j(r)$) where $j$ represents the current iteration. The fitting process

15   ended until the iterative result is less than the $f_{target}$ of $10^{-4}$.

16
$$U_i^{j+1}(r) = U_i^j(r) + k_B T \ln \frac{g_i^j(r)}{g_t(r)}$$
(2)

17
$$f_{target} = \sum_{r=1}^{cutoff} \omega(r)(g_i(r) - g_t(r))^2$$
$$\omega(r) = \exp(-r)$$
(3)

1  (4) Finally, force values created by using linear interpolation of potential energy.

$$F = \frac{dU(r)}{dr} \tag{4}$$

3  Here, potential parameters of table form was established that contains of potential energy

4  and force values as a function of distance. Using this table as a potential energy parameter for

5  CG model, the CG simulation was carried out. Potential energy and force parameters of

6  [C$_4$mim]Cl were presented in supporting information. We use the same method to build the CM I

7  model for [C$_6$mim]Cl and [C$_8$mim]Cl ILs systems. We further assume that the total charge of all

8  atoms in the cation is the charge of the cation bead. Similarly, the charge of anion bead is the

9  charge in anion. In this way, the charges of bead for cation and anion are set to $\pm0.8e$ according

10  the UA force field from Liu et al.[20].

11

12  **2.2.2 CM II Model for [C$_4$mim]Cl**

13  As we know, it is difficult to define an ion pair in pure IL systems, because one cation is

14  surrounded by many anions. However, from the microscopic point of view a possible way to

15  look at ion pair in pure ILs is to define it via distance and time scale. Hence, a searching

16  algorithm was utilized in this work. The searching algorithm could find the most optimal

17  grouping for ILs and determine the coordinates for the location of the CG beads. Searching

18  process of the CM II model for 150 pairs of [C$_4$mim]Cl ILs is as follows by Lammps package

19  and Python program:

20  (1) Firstly, simulations of 2 ns were performed in the NPT and NVT ensemble in UA force field,

21  respectively. Then 20 ns simulations to equilibrate the system in NVT ensemble using Lammps

1  package, as well as 5000 conformations were obtained. The trajectory of the last conformation is

2  used as the initial conformation of the CM II model.

3  (2) Secondly, all cations and anions of initial conformation for [C$_4$mim]Cl were labeled by ID

4  number and two lists ( list p and list q) of cations and anions were established according to the

5  order of their ID number;

6  (3) Thirdly, the center of mass of the cations and anions of each conformation was obtained and

7  the distances (s(r)) between cations and anions was calculated by Euclidean distance for each

8  cations in list p ;

9
$$s(r) = \sqrt{\left|x_{i1}^2 - x_{j1}^2\right| + \left|x_{i2}^2 - x_{j2}^2\right| + ... + \left|x_{in}^2 - x_{jn}^2\right|}$$

10
$$i = (x_{i1}, x_{i2}, ... x_{in}), j = (x_{j1}, x_{j2}, ... x_{jn}) \tag{5}$$

11  Where $i$ and $j$ is the location of the center of mass of cations and anions, respectively.

12  (4) Next, sorting the distance between cations and anions and compare with the first peak value

13  of RDF in UA simulation, the nearest anion to be matched as a pair if $0 < s(r) < g(r)_{peak\ value}$, and

14  the paired anion was deleted in the list q;

15  (5) Then, the steps 3-4 were circulated for each cation in the list p, the nearest anion except list q

16  is found to be matched with the cation if the corresponding anion have been matched with other

17  cation;

18  (6) Finally, the above processes were repeated until all anions and cations are matched with a

19  pair.

20      Every pair of [C$_4$mim]Cl should be seen as a CG bead in the CM II model. In the same way,

21  the [C$_6$mim]Cl and [C$_8$mim]Cl systems were also matched according to the above searching

1 method. The center of mass of location of each pair of ILs were calculated as the initial position

2 of the CM II model. In the same way as CM I model, the same method was used to create a table

3 as a potential energy parameter for CM II modelThe charge of the CG bead was seen as

4 electrical neutral and the CG simulation were carried out.

5 **2.3 Coarse-grained Simulation Details**

6     All CG simulations were performed using the molecular dynamics simulation software

7 package LAMMPS[49]. Periodic boundary conditions are applied to [$C_n$mim]Cl (n=4, 6, 8) systems

8 and physical quantities are calculated from systems with different sizes of 150 and 5000 ILs

9 pairs. The simulations for ILs systems were carried out at three different temperatures298K,

10 348K and 398K. A time step of 2.0 fs was used to integrate the equation of motions. All

11 simulations are evolved using the Nose–Hoover thermostat and barostat. The neighbor lists were

12 set with a distance of 0.2 nm and updated every 5 steps. The potential parameters of table form

13 contains of potential energy and force values for 3 pairs of center of mass between anions and

14 cations that was used to calculate each ILs systems. Similar to UA simulation, the systems were

15 allowed to equilibrate with 2 ns NPT ensemble and 2 ns NVT ensemble before collecting data in

16 20 ns NVT long equilibrium simulations. For the analysis of transport properties we have saved

17 the last 2 ns of simulation for a total of 5000 configurations, at each temperature and system.

18 **3 Results and Discussion**

19 **3.1 Radial Distribution Functions**

20     The structural properties were compared by RDFs in this work. RDFs provide the

21 probability distribution between a specific atom and another surrounded atom, which provides

significant insight of microscopic structure. Hence, it is essential to compare the RDFs from the UA and CG model. For ILs, the RDFs have been calculated for cation-anion, anion-anion, cation-cation. The locations between cations and anions have been described by their centers of mass.

In Fig. 2, the RDFs for cation-anion, cation-cation and anion-anion were shown for [C$_n$mim]Cl (n=4, 6, 8) at 298K from UA force field, CM I model and CM II model. Fig. 2a and Fig. 2b shown that the highest maximum is observed for the cation-anion RDF for [C$_4$mim]Cl on UA force field and CM I model, it appears at a distance of 4.2 Å. Moreover, it is obvious that pair-pair RDF from CM II model and cation-cation RDF from UA force field approximately coincide, the first peak value exist at around 6.7 Å. In Fig. 2c and Fig. 2d, for cation-anion RDF and anion-anion RDF of [C$_6$mim]Cl, the first peak value respectively appeared at the same location at 4 Å and 6 Å as well as they have the same intensity. In Fig. 2e and Fig. 2f, the pair-pair RDF frm the CM II model shows a higher and narrower peak compared with the result from UA force field for cation-anion of [C$_8$mim]Cl. In addition, the cation-cation RDF of [C$_8$mim]Cl from the CM I model appears a smaller peak value at a short distance. This is due to increase of the side chain, the interaction sites for CM II model deviate from the center of mass of cation for [C$_8$mim]Cl. Therefore, for RDF of [C$_8$mim][Cl], the result from CM II model have a difference compared to UA force field. Hence, for the ionic liquids with shorter side chains, the structural properties on CM I and CM II model are much closer to the UA force field.

In Fig. 3, the relationship between RDFs with the alkyl chain length from UA force field and the CM I model was investigated. Comparison of cation-anion RDF of [C$_n$mim]Cl (n=4, 6, 8) ILs between UA force field and CM I model is in Fig. 3a. There is a decrease in the intensity

1    of the first peak with increase in chain length on the cation. On comparing these RDF among

2    [C$_n$mim]Cl (n=4, 6, 8) ILs systems, the same location  for first peak both on the CM I model and

3    UA force field can be noticed. It is revealed that first sharp peaks at about 4 Å and broader

4    second peak at distance larger than 10 Å. The second peak shifts to further distances with the

5    increased alkyl side chain of cation which implying that first and second peaks were the first and

6    second coordination shells of anions around a cation. This result is consistent with that of

7    [C$_n$mim][Br] (n=4, 5, 6) reported by Yeganegi *et al.* [50]. From Fig. 3b, we note the presence of

8    two main peaks in the cation–cation RDF on CM I model and UA force field, which is typical of

9    imidazolium based cation for ILs. The intensity of the first and second peak were decreased with

10   the increased chain length, which indicated this arrangement is more structured in cations with

11   shorter chain lengths. The calculated RDF of anion-anion for [C$_n$mim][Cl] (n=4, 6, 8)

12   correlations were presented in Fig. 3c. Differences from the cation-anion RDF and the cation-

13   cation RDF, first peak value on UA force field increased with the increased alkyl side chain of

14   cation. In addition, there are two peaks different from other ILs systems in the [C$_8$mim]Cl system

15   on CM I model. It shows that the anion in the long side chain of the imidazolium based ILs is

16   gathered at a relatively short distance. Above all, decrease in the intensity of the first peak with

17   increase in chain length on the cation in CM I model. That indicated a lower interaction between

18   ILs in CM I model.

19   **3.2 Density**

20       For CG model, density is an important parameter to verify whether the model is

21   reasonable. In this work, the density value of [C$_n$mim]Cl (n = 4, 6, 8) was calculated using UA

1    force field, CM I model and CM II model at 298K, as shown in Table 1. The absolute relative

2    deviations ($\Delta\rho$) were calculated

$$\Delta\rho = \left|\frac{\rho_{CM} - \rho_{UA}}{\rho_{UA}}\right| \times 100\%$$

3                                                                                      (6)

4        From Table 1, we note the maximum deviation between UA fore field and CG model is

5    3.83% for CM I model, 5.21% for CM II model. In addition, the density decreases gradually as

6    the length of the chain increases on both two CG models. On the contrary of CM II model, the

7    error of density increases as the length of the chain increases for the CM I model. Therefore, CM

8    I model is more suitable for short side chain systems and CM II model is more accurate in a

9    system with long side chains.

10       To further test the CG model, a correlation function between density and the carbon atom

11   number of [$C_n$mim]Cl (n = 4, 6, 8) was proposed here by fitting our simulated data given by:

12                                $$\rho_{UA} = 1.164 - 0.0218n$$

13                                $$\rho_{CMI} = 1.164 - 0.0205n$$

14                                $$\rho_{CMII} = 1.057 - 0.0088n$$                        (7)

15       Where $\rho$ is the density of [$C_n$mim]Cl (n=4, 6, 8), and n is the carbon number of the alkyl

16   group in [$C_n$mim]$^+$.

17       In Fig. 4, it was found that the density of the ILs were in good agreement with the UA

18   simulation. It is probably because CM I model regards the anion and cation as spheres, however,

19   the shape is changed into an ellipsoid with the increased side chain. The same conclusion was

1    reported previously by Wilkes and co-workers[51]. The predictive capability showed that the CM I

2    model is reasonable in our work.

3    **3.3 Coefficient of Thermal Expansion**

4    Based on the results of density of CM I and CM II model, we investigated the thermophysical

5    properties in further. In Table 2, we found the density on UA force field is very similar to the

6    experiment at 313K, 333K and 348K that illustrate the accuracy of UA simulation[52]. Therefore,

7    we compare the results of density for CM I and CM II model to the UA force field at three

8    different temperatures. We could found the density decreased with the increase of the length of

9    the alkyl chain at 313 K, 333 K and 348 K from UA force field, CM I and CM II model. The

10   error of density frm CM I, and CM II models and UA force field increased with the increased of

11   temperature. Since the CM I and CM II model are based on the result of UA force field at 298K.

12   Therefore, the result may appear great deviation when the temperature is much higher than

13   298K. Next the coefficient of thermal expansion from the CM I and CM II models were

14   simulated by Eq .8
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) = -(\frac{\partial \ln \rho}{\partial T})$$
(8)

15   Where $\rho$ is the density of [$C_n$mim]Cl (n=4, 6, 8), and $T$ is the temperature of simulation.

16   The results of coefficient of thermal expansion from the CM I and CM II models have been

17   summarized in Table 2. The coefficient of thermal expansion is basically a scale for the response

18   of a system's volume to temperature as well as closely related to density. Hence, thermal

19   expansion coefficient was calculate for the system that density error is less than 3.6%. The small

20   α value gets less sensitive in the volume of the systems versus a change of temperature. As

21   shown in table 2 the coefficients of thermal expansion in the system of [$C_4$mim]Cl and

[C$_6$mim]Cl decrease with the increased of temperature from both CM I and CM II models. **3.4**

**Self-diffusivity Coefficient**

Apart from thermodynamic property, the transport property is highly sensitive to force field. The diffusion property of ILs is the key factor of the correctness of the force field. The self-diffusivity coefficient of the ILs can be obtained by mean square displacement (MSD). It can not only reflect the short-range interaction between anions and cations, but also reveal electrostatic interactions. It was determined by calculating the slope of the MSD of the molecules versus time over a sufficiently long period of time. The self-diffusion coefficient $D_i$ was calculated by the Einstein relation

$$D_i = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\left\langle\left[\vec{r_i}(t) - \vec{r_i}(0)\right]^2\right\rangle \qquad (9)$$

Where in the $< >$ is the ensemble averaged mean square displacement of the centers of mass of the anions or cations. $\vec{r_i}$ is the vector coordinate of atom $i$.

Owing to ILs tardiness in MD simulation, reliable value was obtained by a long MD simulation in this work. Proper equilibration and trajectory averaging are required to observe the trends in the MSD curves for different ILs. UA force field, CM I model and CM II model were used in several simulations of 10 ns in NVT ensemble for 5000 pairs of [C$_n$mim]Cl (n=4, 6, 8) and the self-diffusion coefficient were calculated in the last 2ns under different temperatures, respectively. Self-diffusion coefficient of the cations (D$^+$) and anions (D$^-$) for three types of ILs at 298 K, 313K and 348 K were summarized in Table 3 on CM I model. It is obvious that the self-diffusion ability of ions increases with the extension of the alkyl chain length. Meanwhile,

1    the self-diffusion coefficient decreases with the increase of the temperatures. Because of the

2    increase of the alkyl chain, van Der Waals interaction and hydrogen bond interaction in the ILs

3    decrease.

4      For CM II model, we also investigated dependence of the self-diffusion coefficients on the

5    length of alkyl chain for $[C_n mim][Cl]$ (n=4, 6, 8) at 298K. In Table 4, compared with the UA

6    simulation values, the ratios of the self-diffusion coefficients in CM I model between the cations

7    and anions $D^+/D^-$ increased from 1.14 to 1.54 at 298K. The self-diffusion coefficients of ILs

8    pairs in CM II increased to $2.04 \times 10^{-3} cm^2 / s$ when length of alkyl chain increased from 4 to 8.

9    The self-diffusion coefficients in CM I and CM II model are 3 and 4 orders of magnitude higher

10    than UA force field, respectively. It is obvious that the self-diffusion coefficients become larger

11    and larger with the increase of the CG level. Hence, to solve this problem of larger self-diffusion

12    coefficient on CG model, a new method is applied to deal with the self-diffusion coefficient. The

13    correction for self-diffusion coefficients ( $D_\delta$ ) are as follows:

$$D_\delta = \frac{a}{n_{cation} \times D_{CM}^{\frac{1}{a}}}$$

14

$$a = 3n_{ILs} - 6 \tag{10}$$

15

16      Where $n_{ILs}$ is the total numbers of atoms for ILs on UA force field, and $a$ is the degree of

17    freedom of ILs. The parameters in the Eq. 10 are shown in Table 5.

18      As shown in Table 6, the self-diffusion coefficient can be obtained with the same order of

19    magnitude as the result from UA simulation using this method. Meanwhile, the self-diffusion

1   coefficient of the UA force field, CM I model and CM II model increases with the increase of the

2   length of the alkyl chain at 298 K. Table 6 shows that the deviation increases with the increase of

3   side chain between the results of the correction for self-diffusion coefficients on CM I and CM II

4   model and the results of UA simulation. Hence, the correction for self-diffusion coefficients is

5   more effective for ionic liquid with a shorter side chain. Compared with Sun et al.[53], the self-

6   diffusion coefficients are nearly several orders of magnitude larger than those from the UA force

7   field. The correction of self-diffusion coefficients in this work, the difference in order of

8   magnitudes has been overcome. It is notably that in application fields requiring high accuracy in

9   diffusion properties, especially electrochemistry, the error could not be ignored.

10      The MSD of UA force field and CM I model for $[C_6mim]Cl$ was presented at T=298K in

11  Fig. 5. It can be seen that, when cations in 0 to 1.5 ns under UA force field, MSD increases very

12  fast, but the rate decreases gradually, which indicatesthat the cations movement is larger than

13  anions, and the intensity decrease gradually. However, MSD increases linearly with the increase

14  of time after 1.5 ns, which means the cations motion tends to be stable. Meanwhile, the MSD of

15  the anions and cations in the CM I model showed a linear variation, indicating that the

16  establishment of the CG model can promote the stability of ILs.

## 17  4 Conclusions

18      In this work, a CG model with two mapping strategies was developed for imidazolium-

19  based ILs systems and MD simulations of ILs were carried out. It is worthy that the CM I and

20  CM II models provide a new method for larger scale simulation of ILs with a short side chain.

21  The CM II model has been established for the first time that the ILs is regarded as one bead, it

22  can also reflect on structure, density and diffusion property for ILs with short side chain. To

1    retain the effect of electrostatic potential in ILs, the $[C_nmim]^+$ (4, 6, 8) cations and $Cl^-$ anion are

2    represented as one single bead in the CM I model, and a pair of ILs mapped to one bead in CM II

3    model. Two mapping schemes can effectively improve the efficiency. CM I model and CM II

4    model are respectively 7-10 times and 4-7 times faster than the UA force field. Based on the

5    simulation of the RDF, the micro-structure between anions and cations could be investigated.

6    The results showed that the RDF of the center of masses of cation-anion in the CM I model and

7    the pair-pair RDF in the CM II model for $[C_nmim]Cl$ (n<=6) were in good agreement with the

8    results from UA force field.  As well as compare with UA force field, the intensity of the peak

9    value decreases with the increased chain length for the cation in CM I model. That indicated a

10   lower interaction between ILs in CM I model. The density and diffusion property of the pure ILs

11   systems were obtained using MD simulations. The density error within 3.83% contrasted with

12   the UA force field and CM I model. For CM II model, the maximum deviation of density is 5.2%

13   and the error decreased with the increase of side chain. In this work, the same order of magnitude

14   of the self-diffusion coefficients for UA force field could be obtained using a self-diffusion

15   coefficients correction for CM I model and CM II model. This correction helps to solve the

16   problem of increasing the diffusion performance of ILs on CG model, and it is effective to be

17   used in large scale simulations for ILs. Generally, CM I model is more excellent than CM II

18   model since electrostatic potential are highly important in ILs, how much the presence of charge

19   transfer influences both microscopic structures and macroscopic properties of ILs with respect to

20   ion pair should be evaluated in CG model.

21       Therefore, it is worth gaining insight into microscopic detail and correlating these data

22   with macroscopic direct experimental data avoiding the application of simple model.

23   Consequently, the CG model of ILs is an important factor that affects the calculation and

prediction of molecular dynamics simulation, these models would provide a theoretical basis for ILs systems. The CG model we developed provides a method for larger scale simulation of ILs. The future work will be focused on the improvement of the efficiency and accuracy of the CG models. **Acknowledgment**

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1    **Table and Figure Captions**

2    **Table 1.** The density of the UA force field, CM I and CM II model for [$C_n$mim]Cl (n=4, 6, 8)

3    under 298K.

4    **Table 2.** The density and coefficient of thermal expansion of the UA force field, CM l model for

5    [$C_n$mim]Cl (n=4, 6, 8) under different temperatures.

6    **Table 3.** Self-diffusion coefficients ($10^{-12}$m$^2$/s) between UA force field and CG model under

7    298K.

8    **Table 4.** Self-diffusion coefficients ($10^{-12}$m$^2$/s) on CMI model at three types of temperatures.

9    **Table 5.** Parameters of correction for self-diffusion coefficients.

10   **Table 6.** The correction for self-diffusion coefficients ($10^{-12}$ m$^2$/s) for CM model under 298K.

11   **Figure 1.** Schematic structure of [$C_4$mim]Cl ionic liquid in (a) UA force field, (b) CM I model,

12   (c) CM II model.

13   **Figure 2.** Radial distribution functions g(r) for center of mass of cation-anion (black), cation-

14   cation (red) anion-anion (blue) and pair-pair (green): (a) [$C_4$mim]Cl on UA force field, (b)

15   [$C_4$mim]Cl on CG model, (c) [$C_6$mim]Cl on UA force field, (d) [$C_6$mim]Cl on CG model, (e)

16   [$C_8$mim]Cl on UA force field, (f) [$C_8$mim]Cl on CG model.

17   **Figure 3.** Radial distribution functions g(r) for [$C_4$mim]Cl (black), [$C_6$mim]Cl (red) and

18   [$C_8$mim]Cl (blue) at 298K: (a) cation-anion, (b) cation-cation, (c) anion-anion on UA force field

19   ( solid line) and CM I model (dotted line).

20   **Figure 4.** The relationship between density of [$C_n$mim][Cl] (n=4, 6, 8) and chain length.

21   **Figure 5.** Mean square displacements for [$C_6$mim][Cl] on different force fields: (a) UA force

22   field, (b) CM I model.

1  **Table 1.** The density of the UA force field, CM I and CM II model for [C$_n$mim]Cl (n=4, 6, 8)
2  under 298K

| ILs | $\rho_{UA}$ (g/cm$^3$) | $\rho_{CMI}$ (g/cm$^3$) | Δ(ρ) (%) | $\rho_{CMII}$ (g/cm$^3$) | Δ(ρ) (%) |
|---|---|---|---|---|---|
| [C$_4$mim][Cl] | 1.079 | 1.078 | 0.09 | 1.024 | 5.21 |
| [C$_6$mim][Cl] | 1.031 | 1.049 | 1.75 | 0.999 | 3.24 |
| [C$_8$mim][Cl] | 0.992 | 0.954 | 3.83 | 0.989 | 0.32 |

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6  **Table 2.** The density and coefficient of thermal expansion of the experiment, UA force field, CM
7  I and CM II model for [C$_n$mim]Cl (n=4, 6, 8) under different temperatures.

| T (K) | $\rho_{exp}^{52}$ (g/cm$^3$) | $\rho_{UA}$ (g/cm$^3$) | $\rho_{CMI}$ (g/cm$^3$) | $\rho_{CMII}$ (g/cm$^3$) | $\Delta\rho_{CMI}$ (%) | $\Delta\rho_{CMII}$ (%) | $\alpha_{CMI}$ 10$^{-3}$/K | $\alpha_{CMII}$ 10$^{-3}$/K |
|---|---|---|---|---|---|---|---|---|
| | | | | [C$_4$mim][Cl] | | | | |
| 313 | 1.06 | 1.070 | 1.054 | 1.049 | 1.493 | 1.962 | 1.501 | 1.608 |
| 333 | 1.06 | 1.062 | 1.025 | 1.024 | 3.484 | 3.578 | 1.395 | 1.206 |
| 348 | - | 1.055 | 1.004 | 0.986 | 4.834 | 6.540 | - | - |
| | | | | [C$_6$mim][Cl] | | | | |
| 313 | 1.02 | 1.022 | 1.024 | 0.996 | 0.195 | 2.544 | 1.608 | 0.201 |
| 333 | 1.01 | 1.012 | 0.992 | 0.971 | 1.996 | 4.051 | 1.587 | - |
| 348 | 1.03 | 1.004 | 0.971 | 0.949 | 3.286 | 5.478 | 1.426 | - |
| | | | | [C$_8$mim][Cl] | | | | |
| 313 | 0.99 | 0.989 | 0.933 | 0.968 | 5.765 | 2.123 | - | 1.431 |
| 333 | 0.99 | 0.979 | 0.905 | 0.941 | 7.562 | 3.882 | - | - |
| 348 | 0.98 | 0.972 | 0.882 | 0.912 | 9.281 | 6.173 | - | - |

8

9  **Table 3.** Self-diffusion coefficients (10$^{-12}$m$^2$/s) on CMI model at three types of temperatures.

| Temperature | D$^+$ | D$^-$ | D$^+$/D$^-$ |
|---|---|---|---|
| | [C$_4$mim]Cl | | |
| 298K | 9721 | 8525 | 1.14 |
| 313K | 11562 | 11416 | 1.01 |

| | | | |
|---|---|---|---|
| 348K | 13953 | 14233 | 0.98 |

[C$_6$mim]Cl

| | | | |
|---|---|---|---|
| 298K | 16886 | 10595 | 1.59 |
| 313K | 18542 | 14929 | 1.24 |
| 348K | 25166 | 20549 | 1.22 |

[C$_8$mim]Cl

| | | | |
|---|---|---|---|
| 298K | 23232 | 15017 | 1.54 |
| 313K | 22841 | 15883 | 1.43 |
| 348K | 27732 | 25029 | 1.11 |

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4 **Table 4.** Self-diffusion coefficients ($10^{-12}$m$^2$/s) between UA force field and CG model under 298K.

| ILs | UA | | | CM I | | | CM II |
|---|---|---|---|---|---|---|---|
| | D$^+$ | D$^-$ | D$^+$/D$^-$ | D$^+$ | D$^-$ | D$^+$/D$^-$ | D$^{pair}$ |
| [C$_4$mim][Cl] | 2.405 | 1.368 | 1.758 | 9721 | 8525 | 1.14 | 20334.02 |
| [C$_6$mim][Cl] | 3.159 | 1.818 | 1.738 | 16886 | 10595 | 1.59 | 22316.08 |
| [C$_8$mim][Cl] | 3.729 | 2.075 | 1.797 | 23232 | 15017 | 1.54 | 20482.75 |

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6

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**Table 5.** Parameters of correction for self-diffusion coefficients

| ILs | $n_{carbon}$ | $n_{cation}$ | $n_{ILs}$ | a |
|---|---|---|---|---|
| [C$_4$mim]Cl | 8 | 13 | 14 | 36 |
| [C$_6$mim]Cl | 10 | 15 | 16 | 42 |
| [C$_8$mim]Cl | 12 | 17 | 18 | 48 |

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**Table 6.** The correction for self-diffusion coefficients ($10^{-12}$ m$^2$/s) for CM model under 298K

| ILs | UA | CM | CM-IM |
|---|---|---|---|
| | | $D^+$ | |
| [C$_4$mim]Cl | 2.405 | 7412.711 | 2.145 |
| [C$_6$mim]Cl | 3.159 | 8673.242 | 2.220 |
| [C$_8$mim]Cl | 3.729 | 13005.160 | 2.289 |
| | | $D^-$ | |
| [C$_4$mim]Cl | 1.368 | $5.943 \times 10^3$ | 2.153 |
| [C$_6$mim]Cl | 1.818 | $5.051 \times 10^3$ | 2.245 |
| [C$_8$mim]Cl | 2.075 | $6.946 \times 10^3$ | 2.310 |
| | | $D^{pair}$ | |
| [C$_4$mim]Cl | - | $2.033 \times 10^4$ | 2.102 |
| [C$_6$mim]Cl | - | $2.232 \times 10^4$ | 2.206 |
| [C$_8$mim]Cl | - | $2.048 \times 10^4$ | 2.295 |

9