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Transferable Coarse-Grained Models for Ionic Liquids

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Abstract: The effective force coarse-graining (EF-CG) method was applied to the imidazolium-based nitrate ionic liquids with various alkyl side-chain lengths. The nonbonded EF-CG forces for the ionic liquid with a short side chain were extended to generate the nonbonded forces for the ionic liquids with longer side chains. The EF-CG force fields for the ionic liquids exhibit very good transferability between different systems at various temperatures and are suitable for investigating the mesoscopic structural properties of this class of ionic liquids. The good additivity and ease of manipulation of the EF-CG force fields can allow for an inverse design methodology of ionic liquids at the coarse-grained level. With the EF-CG force field, the molecular dynamics (MD) simulation at a very large scale has been performed to check the significance of finite size effects on the structural properties. From these MD simulation results, it can be concluded that the finite size effect on the phenomenon of ionic liquid spatial heterogeneity (Wang, Y.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, *127*, 12192) is small and that this phenomenon is indeed a nanostructural behavior which leads to the experimentally observed mesoscopic heterogeneous structure of ionic liquids.

1. Introduction

Ionic liquids, also known as room-temperature molten salts, consist of bulky organic cations and/or anions. Because their melting temperatures are around room temperature, they may be used as liquids in industrial applications. In recent years, researchers have extended the possible applications of ionic liquids from solvents^{1,2} to other materials, such as lubricants,^{3,4} embalming fluids,⁵ fuel cells,⁶ biocatalysis,⁷ and energetic materials.⁸ These possible applications are bolstered by the fact that there are many ionic liquid candidates to be chosen from to meet different specific application requirements. Given a target application with a set of specific requirements, it would be valuable to select the best ionic liquid candidates using a computational design approach rather than experimentally testing every possible species one by one. Since ionic liquids can usually be considered as being constructed from smaller components, which can be enumerated, the systematic design of ionic liquids at a coarse-grained level,

where each component is treated as one or several coarse-grained (CG) sites, is one possible route to their computational design.

The multiscale coarse-graining (MS-CG) approach⁹ calculates the effective nonbonded CG forces between CG sites by a variational fitting to the total forces sampled from atomistic MD simulations. This approach has been successfully applied to ionic liquids,¹⁰ as well as some biomolecular^{9,11} and other liquid¹² systems. The MS-CG force fields accurately capture the atomistic local structures at the CG level. However, for the same underlying atomistic system, different MS-CG models must in principle be constructed for different temperatures. In addition, the effective forces cannot easily be transferred to other systems, which may be essential for the systematic computational design of ionic liquids at the CG level.

As an alternative to the general MS-CG approach, the effective force coarse-graining (EF-CG) method¹³ was designed to focus more on the transferability and additivity of the resulting CG force field by sacrificing some degree of structural accuracy. With the EF-CG approach, the effective forces between CG sites can be explicitly separated as different contributions from the collective electrostatic and

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van der Waals (VDW) interactions, respectively, and are generally more transferable between different temperatures and environments (e.g., surface and bulk). The EF-CG method works especially well for molecules which can be divided into CG sites with good symmetry. This condition is satisfied to some reasonable extent for many ionic liquids. In this study, the EF-CG approach is applied to the imidazolium-based nitrate ionic liquids with various alkyl side-chain lengths. It is shown that a set of effective forces constructed for a short-chain system can be extended to generate the effective force fields suitable for CG molecular dynamics (MD) simulations of the related ionic liquid systems with longer alkyl side chains.

An important structural feature of ionic liquids with an alkyl side chain is the spatial heterogeneity formed by the cationic alkyl tail aggregation.¹⁴ It was revealed by both the all-atom^{15,16} and CG^{14,17} MD simulations that, in a pure ionic liquid system, the nonpolar cationic tail groups tend to aggregate to form isolated tail domains, while the charged head groups and anions retain their local structures unchanged with various lengths of the side chains. The tail domains were also found to pass through a melting-like transition with increasing temperature.¹⁷ These phenomena were explained by the competition between the collective electrostatic and VDW interactions. In this paper, it will be shown that, despite the approximations made when constructing the EF-CG force fields, the spatial heterogeneity phenomenon is still captured at the CG level with satisfactory accuracy. Additionally, a CG MD simulation with the EF-CG model at a very large spatial scale is reported to connect the tail aggregation mechanism to experimentally observed liquid-crystal-like ionic liquid structures.^{18–21}

2. Methods

In this section, the EF-CG methodology and an order parameter quantifying the spatial heterogeneity are briefly reviewed. The construction and manipulation of the EF-CG force fields and the MD simulations at both the atomistic and CG levels are described in detail.

2.1. Effective Force Coarse-Graining Methodology. The EF-CG methodology¹³ aims to construct CG models with an enhanced degree of transferability. In order to accomplish this goal, the effective CG force fields should depend on thermodynamic and environmental conditions as little as possible. As a consequence, compared to the general MS-CG approach,²² the EF-CG methodology usually leads to CG models that have less accuracy in terms of their average local structures.

Before constructing the EF-CG force fields, an all-atom MD simulation at equilibrium must be performed. A coarse-graining strategy is then defined to group atoms together to form one or several CG sites for each molecule. With the atomic positions sampled during the all-atom MD simulation, the bonded coordinate Boltzmann distributions can be determined and fitted iteratively to obtain the bonded CG force fields,¹⁰ while the atomistic nonbonded forces between different atoms $\{\mathbf{f}_{ij}\}$ are also explicitly calculated. For a certain pair of CG sites I and J , all of the atomistic forces between these two sites are summed up and projected on

the direction of the unit vector $\hat{\mathbf{R}}_{IJ}$ connecting the center-of-masses of the two CG sites

$$F_{IJ}(R_{IJ}) = \sum_i \sum_j \mathbf{f}_{ij} \cdot \hat{\mathbf{R}}_{IJ} \quad (1)$$

where F_{IJ} is the effective force between CG sites I and J . The magnitude of this projected force F_{IJ} as a function of R is averaged over all pairs with the same type in all sampled MD configurations to obtain the final effective nonbonded EF-CG force between CG sites $\tilde{F}_{IJ}(R)$. Consequently, $\tilde{F}_{IJ}(R)$ is actually an ensemble-averaged effective force over the relative orientation Ω_{IJ} between CG sites I and J , with the probability distribution $P(\Omega_{IJ})$ sampled during the all-atom MD simulation:

$$\tilde{F}_{IJ}(R) = \int d\Omega \tilde{F}_{IJ}(R, \Omega) \quad (2)$$

Different types of atomistic forces, typically electrostatic and VDW interactions, can be calculated separately. The final effective CG forces are simply the sum of all different types of CG forces present in the system.

The effective electrostatic interactions are generally long-range, while the tabulated effective CG forces are usually required by MD simulation software to be short-ranged. It has been found that,¹³ for most systems, beyond a certain cutoff around 1 nm, the long-range interactions can be approximated by the electrostatic interactions of the net point charges on the CG sites, so that only the remaining effective short-range forces need be tabulated.

2.2. Heterogeneity Order Parameter. The degree of the spatial heterogeneity of the cationic tail groups in ionic liquids can be gauged by the height of the first peak of the tail–tail radial distribution function (RDF). However, it is more convenient if the spatial heterogeneity can be quantified by a single numerical value. In order to do this, a Gaussian-like *heterogeneity order parameter* (HOP)¹⁷ is defined for each site as

$$\hat{h}_i = \sum_j \exp(-r_{ij}^2/2\sigma^2) \quad (3)$$

where r_{ij} is the modulation of the vector $\mathbf{r}_i - \mathbf{r}_j$ corrected with the periodic boundary conditions, $\sigma = L/N^{1/3}$ with L the side length of the cubic simulation box and N the total number of the CG sites.

For one configuration, the HOP is computed by averaging over all N_s sites of interest (usually sites of the same type), such that

$$\hat{h} = \frac{1}{N_s} \sum_{i=1}^{N_s} \hat{h}_i \quad (4)$$

The HOP is defined so that it is topologically invariant with the absolute size of the simulation box. For a given topology, the HOP value exhibits finite size effect when very limited number of sites are present, but it approaches a constant value with increasing number of sites. The HOP values \hat{h}_0 for the ideally homogeneous systems with $N = n^3$, $n = 1, 2, 3, \dots$, in a cubic box were computed and listed

Table 1. Heterogeneity Order Parameter \hat{h}_0 (Equation 4) for Uniformly Distributed Systems with Different Number of Sites N_s

N_s	\hat{h}_0
1	1.0000
8	4.1464
27	10.8388
64	12.9513
125	15.3220
216	15.5285
343	15.7368
512	15.7431
729	15.7495
1000	15.7495
1728 and larger	15.7496

in Table 1. It can be seen that the HOP approaches a constant value of 15.7496 when $N \geq 729$.

In order to allow the HOP to have a value around zero when the sites distribute almost uniformly, a *reduced* HOP for each configuration is defined as

$$h = \hat{h} - \hat{h}_0 \quad (5)$$

The reduced HOP h allows one to see more clearly how far the structure deviates from the ideal uniform structure.

2.3. Molecular Dynamics Simulations. Without further theoretical development, the EF-CG method cannot decompose explicit many-body interactions into effective pairwise forces. In the case of ionic liquids, the current EF-CG approach is therefore not applicable to the electronically polarizable models, which are known to generate more accurate simulation results for some physical properties of certain species of ionic liquids.²³ Therefore, the atomistic nonpolarizable model was used to perform the all-atom MD simulations for the EMIM⁺/NO₃[−] system and to generate atomistic MD trajectories for the EF-CG approach. Except the electronic polarization parameters, the force field for the nonpolarizable model is the same as the polarizable model reported in refs 15 and 23.

The DL_POLY simulation package²⁴ was used to perform both the all-atom and CG MD simulations. After equilibration, the EMIM⁺/NO₃[−] system with 512 ion pairs first was simulated in a constant *NPT* all-atom MD simulation at $P = 1$ atm and $T = 400$ K for 1 ns, with a time step of 1 fs. The average side length of the cubic simulation box was determined from this *NPT* run to be $L = 50.03 \pm 0.08$ Å. A 1 ns constant *NVT* all-atom MD simulation with the side length of the simulation box fixed to be the above value L was then carried out. One configuration was recorded for every 1 ps (1000 MD steps), so totally 1000 configurations were saved. The EF-CG method was then applied to these configurations to obtain the EF-CG force field for EMIM⁺/NO₃[−], which was then extended without recalculation to generate the EF-CG force fields for the ionic liquid systems with longer alkyl side chains, as described in the next subsection.

With the various EF-CG force fields, the CG MD simulations were performed for ionic liquids with 512 ion pairs and varying different side-chain lengths at $T = 400$ K. After appropriate equilibration runs, the CG systems were

first simulated for 4 ns in a constant *NPT* MD ensemble, and then a 4 ns constant *NVT* MD simulation was performed to collect data. Note that CG simulation time corresponds to much longer atomistic simulation time, because dynamics of the CG systems are generally faster than those of the corresponding atomistic systems. Because the CG sites have heavier masses, the time step for the CG MD runs was set to the larger value of 4 fs. Totally 1000 configurations were sampled for each constant *NVT* CG MD run, with one configuration saved for every 1000 MD steps. The cutoffs for the effective VDW interactions and the real space part of the effective electrostatic interactions were both set to be 14 Å. In the *NVT* runs, the side length of the cubic simulation box was the average values obtained from the preceding *NPT* runs.

2.4. Transferable Coarse-Grained Model of Ionic Liquids. For imidazolium-based ionic liquid cations with an alkyl side chain, most of the positive charges are distributed close to the cationic ring. The net partial charges on the carbon groups, which are five sites or farther from the cationic ring, are so small that they can be effectively considered to be zero. Also, only imidazolium-based ionic liquids with a nitrate anion are studied in this paper. For convenience, the ionic liquid systems are denoted as C_n , where n is the number of carbon groups on the alkyl side chain. For example, EMIM⁺/NO₃[−] is denoted as C_2 , and HMIM⁺/NO₃[−] is denoted as C_6 . Because the structural properties of ionic liquid systems with an even number of carbon groups follow different rules than those for the ILs with odd numbers,²⁰ in the paper, only those with even numbers are investigated.

The atomistic partial charges and polarizable force fields for C_2 to C_{12} have been reported in ref 15. The CG strategy follows the previous one;¹⁰ the entire nitrate anion is coarse-grained as a single CG site D, the imidazole ring as CG site A, the single methyl group as CG site B, the terminal methyl group on the side chain as CG site E, and the ethyl group adjacent to site E as CG site C, and the other four ethyl groups are denoted as CG sites M1, M2, M3, and M4, ordered from the cationic ring to the terminal of the side chain.

For the ionic liquid systems with different side-chain lengths, the atomistic net partial charges on each CG group are slightly different. To unify the CG models, the atomistic net partial charges were averaged and adjusted so that they have the same values for systems with a side-chain length equal to or larger than C_6 . The net partial charges for C_2 were unchanged. The CG scheme for C_2 is shown in Figure 1, and the CG structures for C_2 to C_{12} systems are shown in Figure 2. The partial charges for the CG groups are also given in Figure 2. Since the partial charges for the CG model of C_4 cannot be unified, it is not directly related to the main focus of this study. Therefore, the study of the CG model for the C_4 system is not included in this paper.

The EF-CG approach was applied to C_2 with the effective VDW and electrostatic forces between CG sites computed separately. These force calculations have been reported in ref 13. The tails of the effective VDW forces approach 0 smoothly, and the middle to long-range parts of the effective

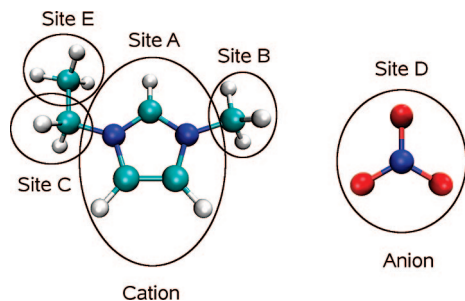


Figure 1. Coarse-graining scheme of EMIM⁺/NO₃⁻ (C₂) ionic liquid.

electrostatic forces are almost equal to the point charge forces, indicating that the EF-CG forces very weakly depend on the environment and thermal conditions. However, because of the multipole interactions, the short-range parts of the effective electrostatic forces are generally quite different from the point charge forces.

For atomic groups with the same atomic structure in different ionic liquid systems or in different positions in the same molecule, such as the CH₂ groups on the alkyl side chain, they should have very similar interactions at the CG level. If the difference caused by the orientation distributions, as shown in eq 2, is negligible, the effective VDW forces between these groups should be the same, and the long-range electrostatic forces should be proportional to their net partial charges. This has been verified by comparing the effective forces obtained for C₂ and C₆ systems (data not shown). Therefore, the effective forces for C₂ can be used as a set of general force fields to construct the CG force fields for imidazolium-based nitrate ionic liquids with arbitrarily long side chains.

The EF-CG force field for C₂ was first extended to construct the effective forces for C₆. The unified CG model for C₆ is shown in Figure 2. The effective VDW forces were copied from the C₂ system to the C₆ system for the CG groups with the same atomic structure, and CG sites M1, M2, M3, and M4 are the same as CG site C. For example, the effective VDW force between sites M1 and E in the C₆ system is the same as that between sites C and E in the C₂ system. The effective electrostatic forces were rescaled by the net partial charges on the CG sites. For example, the effective electrostatic force between CG sites M3 and A in the C₆ system is equal to that between CG sites C and A in the C₂ system multiplied by 0.1235. The total effective forces used to perform the CG MD simulations are the sum of the corresponding effective VDW forces and the modified effective electrostatic forces. For systems with longer side chains (C₈, C₁₀, and C₁₂), more CG sites C with zero partial charges were inserted between CG site C and E in the C₆ system, as shown in Figure 2. Since the effective electrostatic forces for CG sites C and E are all zero, their effective VDW forces are their total effective forces.

3. Results

The EF-CG force fields for ionic liquids with different side-chain lengths extended from C₂ were then used to perform CG MD simulations at *T* = 400 K. The absolute accuracy of these extended force fields was verified by comparing the CG MD simulation results for C₈ with those for the MD simulations with the atomistic polarizable model, which is known to be closer to the experimental results.²³ Besides the difference between the nonpolarizable and polarizable force fields, the modified partial charges for the unified CG

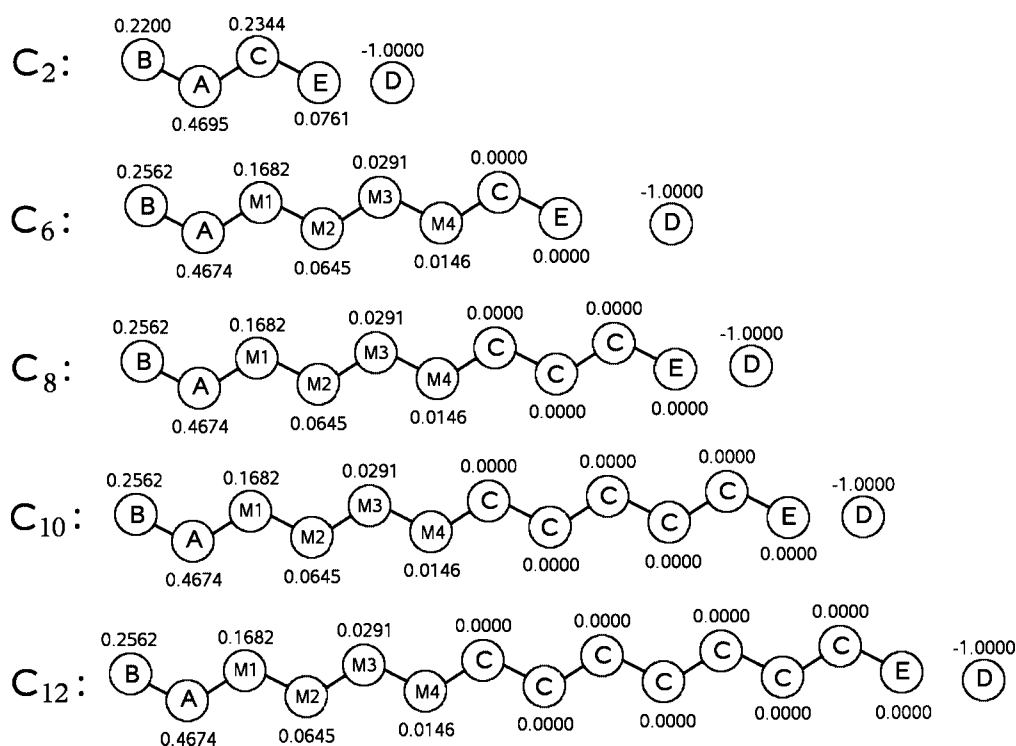


Figure 2. Coarse-grained molecular structures of the imidazolium-based nitrate ionic liquids with various side-chain lengths. The numbers shown on the coarse-grained sites are their effective partial charges.

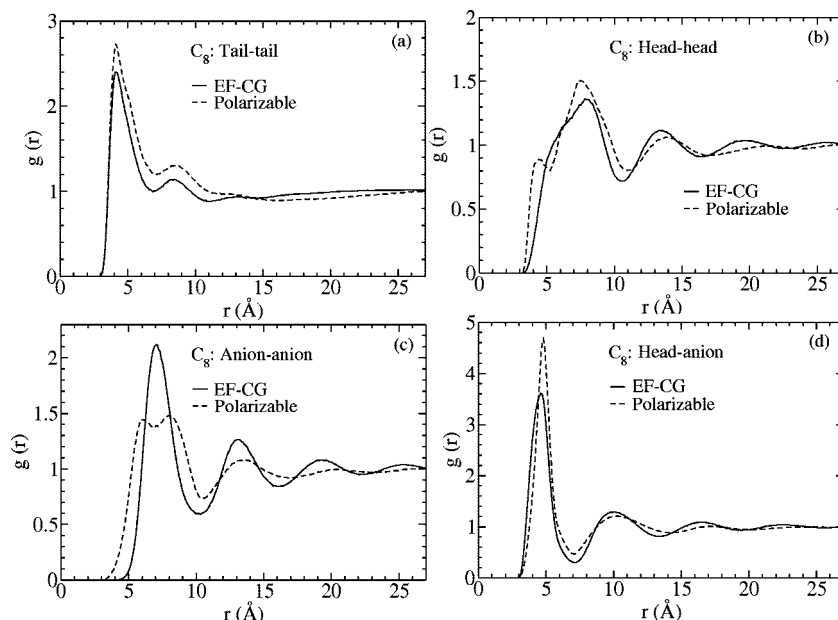


Figure 3. Comparison of radial distribution functions for the C_8 system with the atomistic polarizable model (dashed lines) and the EF-CG model (solid lines): (a) tail–tail (CG sites E–E); (b) head–head (CG sites A–A); (c) anion–anion (CG sites D–D); (d) head–anion (CG sites A–D). See Figure 2 for CG site definitions.

model and the slight difference in the orientation distributions also lead to errors for the CG MD simulations. Nevertheless, the results with the EF-CG model are still close enough to those with the all-atom polarizable model for the purpose of studying the general trends of the global behavior of ionic liquids.

All of the all-atom and CG MD simulations were equilibrated by annealing from $T = 1000$ K down to $T = 400$ K with a temperature interval of 100 K. At each temperature, a 10^6 -step constant NVT simulation was performed. The systems were then equilibrated at 400 K for a longer time. The systems were verified to be equilibrated at $T = 400$ K by observing that the ionic diffusion constants were nearly unchanged.

3.1. Validity of the Extended Coarse-Grained Force Fields. The results for the CG MD simulations of C_8 are compared with those for the all-atom MD simulations with the atomistic polarizable model previously reported in ref 15. The radial distribution functions (RDFs) between cationic head (CG site A), tail (CG site E), and anions (CG site D) are shown in Figure 3. It can be seen that, although there are some differences in these plots (primarily in the anion–anion structure), the RDFs for the CG MD simulations follow reasonably well those for the simulations with the atomistic polarizable model.

3.2. Thermodynamic and Structural Properties with the Coarse-Grained Models. With the atomistic polarizable model, it has been shown¹⁵ that the density of ionic liquids decreases with increasing side-chain length, which agrees with the experimental results.^{25–27} The densities of the ionic liquids with different side-chain lengths simulated by the EF-CG force fields at $T = 400$ K are shown in Figure 4, compared with those obtained with the atomistic polarizable model. For the C_2 system, the atomistic polarizable model gives a significantly higher density, because the electronic polarization effect leads the ions to a closer packed struc-

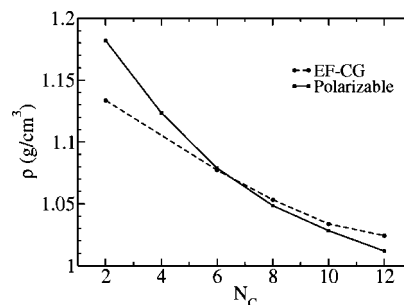


Figure 4. Average densities of the imidazolium-based nitrate ionic liquids with various side-chain lengths from both the atomistic polarizable models (solid line) and the EF-CG models (dashed line).

ture.²³ With increasing side-chain length, so that more nonpolar tail groups exist in the system, the polarization effect becomes more localized. Therefore, the density difference is much smaller for the ionic liquids with longer side chains. Despite the numerical differences, the CG model is able to reproduce the trend of decreasing density with increasing alkyl side-chain length.

The reduced HOPs obtained from the CG simulations are shown in Figure 5. With increasing side-chain length, the reduced HOPs for the cationic tail and head groups and for the anions all increase. The tail groups have larger HOPs than the head groups and anions, and the difference increases for the systems with longer side chains. This indicates that the tail groups aggregate more than the head groups and anions, and the tail aggregation is more pronounced for longer side-chain systems. This is consistent with the tail aggregation phenomenon revealed with both the MS-CG^{14,17} and atomistic polarizable¹⁵ models.

The RDFs between head groups, tail groups, and anions for different systems from the CG simulations are shown in Figure 6. The peak positions and the plot shapes are relatively

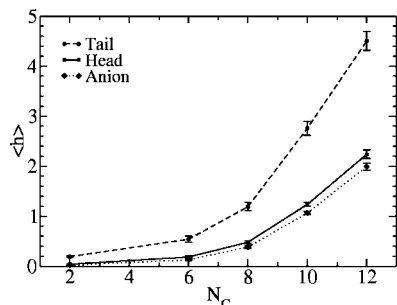


Figure 5. Reduced average heterogeneity order parameter (HOP) values $\langle h \rangle$ of the tail (CG site E), head (CG site A), and anion (CG site D) groups for the imidazolium-based nitrate ionic liquids with various side-chain lengths. See Figure 2 for CG site definitions.

unchanged, indicating that the local structures of these groups are retained for different systems. Because of the stronger tail aggregation of the tail groups, the first peak of the tail–tail RDFs increases with various side-chain lengths. The peaks of the RDFs between head groups and anions also increase with side-chain length, because systems become more heterogeneous with longer chains due to the tail aggregation phenomenon. This is also consistent with the all-atom simulation results with the polarizable model.¹⁵

From the above results, it can be concluded that, despite the differences in structural and thermodynamic properties, the transferable EF-CG ionic liquid model reproduces the spatial heterogeneity of ionic liquids studied to a satisfactory degree.

3.3. Mesoscopic Ionic Liquid Structure. Before the present work, the largest size MD simulation performed for studying the spatial heterogeneity of ionic liquids contained 512 ion pairs, with a cubic simulation box size of only several nanometers along its edges. As the simulations with a smaller system containing 64 ion pairs show quite different results

Table 2. Reduced Heterogeneity Order Parameters (Equations 4 and 5) Measured for C_{12} Systems Containing 512 and 4096 Ion Pairs, Respectively

	512 ion pairs	4096 ion pairs
tail groups	4.50 ± 0.19	4.19 ± 0.11
head groups	2.24 ± 0.08	2.10 ± 0.05
anions	2.00 ± 0.07	1.87 ± 0.05

from the 512 ion-pair system,¹⁵ a question is raised: is the system with 512 ion pairs large enough so that the observed microscopic spatial heterogeneity phenomenon due to tail aggregation is the real nanostructural behavior, or is the finite size simulation structure observed frustrated relative to the real structure having a larger characteristic length scale? The EF-CG model was therefore used to simulate a much larger system to study the change in structural properties. If the observed structure is a frustrated one, the larger system should show a significant structural change compared to the system with 512 ion pairs.

The EF-CG C_{12} system with 512 ion pairs was thereby duplicated in three dimensions to have a system with 4096 ion pairs. The corresponding all-atom ionic liquid system has a total of 217 088 atoms. After going through the same annealing steps as described above, a 1 ns constant *NPT* run yielded an average side length of the cubic simulation box of 127.8 Å, which is almost exactly twice of the box size of 63.8 Å for the C_{12} system with 512 ion pairs. Therefore, the CG MD simulations with the two sizes yield the same density. A subsequent 1 ns constant *NVT* run was carried out, with 1000 configurations evenly sampled. The time step of these runs was 4 fs.

The HOPs of the 512 and 4096 systems with the EF-CG force fields are compared in Table 2. Although the numbers are not the same, the ones for the system with 4096 ion pairs are only a little smaller than those for the system with 512

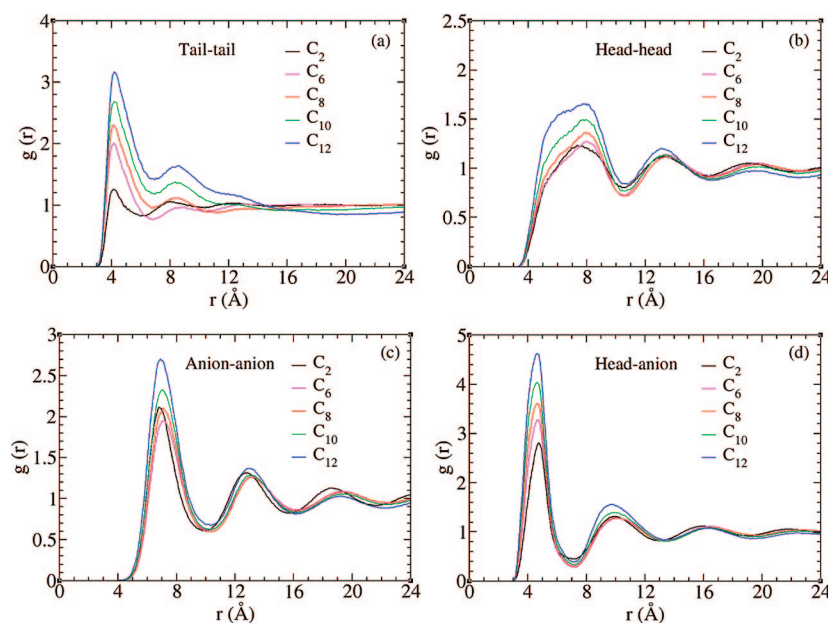


Figure 6. Radial distribution functions of (a) tail–tail (CG sites E–E), (b) head–head (CG sites A–A), (c) anion–anion (CG site D–D), and (d) head–anion (CG sites A–D) by the EF-CG models for imidazolium-based nitrate ionic liquids with various side-chain lengths. See Figure 2 for CG site definitions.

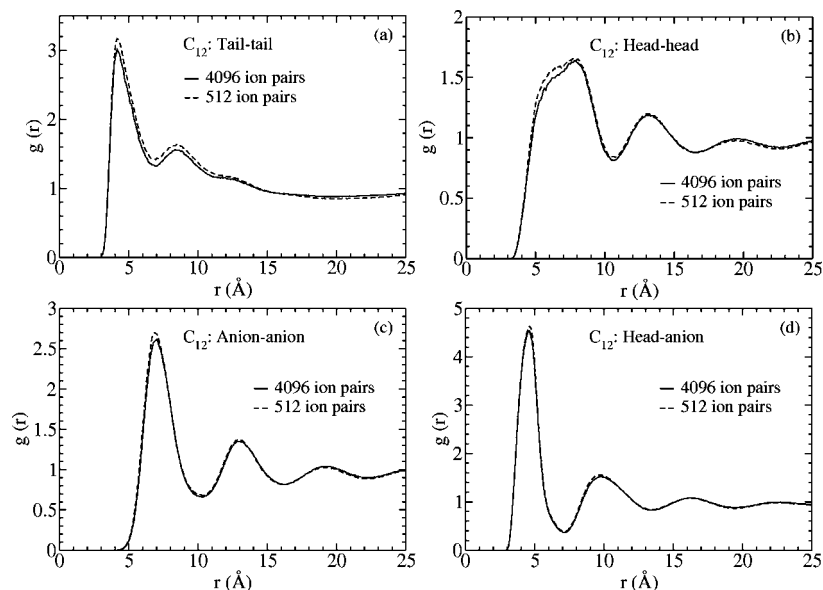


Figure 7. Radial distribution functions of (a) tail–tail (CG sites E–E), (b) head–head (CG sites A–A), (c) anion–anion (CG site D–D), and (d) head–anion (CG sites A–D) for C_{12} with 512 (dashed lines) and 4096 (solid lines) ion pairs by the EF-CG models. See Figure 2 for CG site definitions.

ion pairs. The RDFs of the two systems are compared in Figure 7. The only noticeable difference is that the peaks for the system with 4096 ion pairs are somewhat lower. From these results, it can be concluded that the C_{12} system with 512 ion pairs only has a slightly stronger tail aggregation than the one with 4096 ion pairs, and its finite size effect is not significant for the spatial heterogeneity phenomenon. It can be further anticipated that the observed structure will not change with increasing simulation size beyond 4096 ion pairs. Since the ionic liquid systems with longer side chains have a more significant finite size effect, the size of 512 ion pairs should also be large enough for the other systems investigated (C_2 – C_{10}).

4. Conclusions

By sacrificing some degree of accuracy in local liquid structure, the EF-CG method has been successfully applied here to imidazolium-based ionic liquids with varying alkyl side-chain lengths. In addition to the transferability in temperature shown in ref 13, the EF-CG method is also shown here to have good transferability and additivity between systems with various side-chain lengths. Therefore, a small set of effective CG force fields is adequate to represent a series of ionic liquids having different side-chain lengths. This will be of particular importance for building a library of ionic liquid interactions and for the systematic computational design of ionic liquids at the CG level.

For organic systems with large molecules, such as ionic liquids, the finite size effect can generally be significant due to the bulkiness of the underlying molecules. Testing the finite size effect of such systems at the CG level is convenient and efficient. The present EF-CG model for ionic liquids has, for example, been used to verify that the spatial heterogeneity in ionic liquids due to tail aggregation is truly a nanoscale phenomenon.^{14–17} Although the finite size effect is still noticeable, the ionic liquid systems with 512 ion pairs

were shown to be large enough for the qualitative study of such spatial heterogeneity in ionic liquids with alkyl side chains of C_{12} and shorter in length.

Although the current study has applied the EF-CG method to only the imidazolium-based/nitrate ionic liquids to build a set of transferable CG force fields, the method can be applied to other kinds of ionic liquids, as well as other organic molecular systems. Its extendibility, transferability, and additivity will prove to be important for the systematic computational design of these systems at a coarse-grained level.

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