

Generic force fields for ionic liquids



Florian Dommert^{a,*}, Katharina Wendler^b, Baofu Qiao^a, Luigi Delle Site^{c,*}, Christian Holm^{a,*}

^a Institut für Computerphysik, Universität Stuttgart, Allmandring 3, D-70569 Stuttgart, Germany

^b Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

^c Institut für Mathematik, Freie Universität Berlin, Arnimallee 6, D-14195 Berlin, Germany

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ABSTRACT

Ionic liquids have been intensively studied during the last decade, but many questions still remain unresolved. From the computational side there is the lack of good transferable force fields for molecular simulations that would allow accurate theoretical predictions and interpretations of the properties of ionic liquids. Within this article a method is described that allows for the derivation of partial charges for ionic liquids since they play a particular important role, particularly for a liquid that consists entirely of ions. Our partial charges are carefully determined in such a way that they incorporate in an average way the influence of polarization effects of the neighboring ions in a bulk situation thereby reducing the total ionic charge to values less than one. When combined with our recently introduced method for the optimization of the short-range interactions [1] we have a well described route to develop generic force fields for ionic liquids. In this article we describe our results for the partial charges for the three imidazolium based liquids [MMIM]⁺, [EMIM]⁺, and [BMIM]⁺ for three different anions.

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1. Introduction

Ionic liquids (ILs) have attracted a considerable amount of attention from various branches of industry and research due to their variety and tuneability [2–6]. Classical molecular dynamics (MD) simulations are a suitable tool to study ionic liquids (ILs), but they rely on the availability of an accurate force field (FF) that models the molecular interaction in an effective and computationally very efficient manner. Although a large number of FFs have been developed for ILs [7], many of them are not transferable or do not correctly describe dynamic properties [8,9]. There are still exceptions, such as the FF for [C_nMIM][Tf₂N] [10], which is transferable within arbitrary chain length and accurately describes thermodynamic and dynamic properties [10,11]. However, these exceptions are rare, and it is nontrivial to extend the procedure to other anions.

Transferability is an important aspect, because the number of ILs is huge and parametrizing a separate FF for every IL is too time-consuming. In order to solve this problem, we have developed a multi-scale approach that transfers the electronic structure information about an IL gained on the quantum-mechanical level of theory to classical theory and maps the interaction into suitable potentials [1,12–18]. It has been proven by experiment [19,20] that the method gives physical consistent results between the different levels of theory, such as an accurate modeling of the dipole moments and charge reduction, which can also be related to the values of the refractive index of the IL. The information about the bulk IL is gained from electronic density

functional theory (DFT) studies benchmarked against higher levels of theory which has been proven as a suitable method. Refs. [21–29] present only a small selection out of numerous successful studies.

In the present article we combine our results that we have obtained in the past for different imidazolium-based ILs [17,18,30] and present a technique to derive a transferable set of partial charges which are the basis for developing an accurate IL FF. The article is organized as follows. We start with a general description of the method for calculating the partial charge. We then show that small variations of the charge do not strongly impact the properties of the IL. This finally allows us to suggest a generic partial charge model for imidazolium-based ionic liquids.

2. Partial charges from the bulk phase

Partial charges for classical IL force fields have been derived in many different ways. They differ in many aspects and even a short appraisal would go beyond the scope of this article. For this reason we want to refer the reader to a corresponding review [7,31,32], while here we will briefly report only relevant aspects of the method that is applied in the current work. Further details can be found elsewhere [1,7,14–18].

One major problem in FF parametrization is the mapping of the forces to a simple mathematical model that can be easily calculated by a computer. Under optimal conditions we can derive all necessary parameters for pair interactions from high-level ab initio quantum calculations. If no multi-body forces are present the FF parameters should be applicable to the whole state space. Usually these conditions are not met. Instead experimental knowledge has to be invoked to adapt the parameters to specific state points and to test their validity, which is a computationally very demanding task.

* Corresponding authors.

An important part of the FF is the assignment of partial charges located at each atom site. The standard approach to derive them relies on single ion calculations. This method completely neglects the effects of polarization, which are very important for the liquid phase. ILs are strongly polarizable and many FFs, such as CLaP [33–36] are mainly based on single-ion calculations without involving dynamic properties in the parametrization process. Therefore they do not describe the detailed dynamics of the system correctly, although they may capture statistical (static) properties in a satisfactory way [7–9]. In order to remove this deficiency, we use the Blöchl method [14,37] for the calculation of the partial charges from ab initio calculations of a bulk system; this allows us to describe the mean polarization of the liquid, though only in an implicit way. [1,17,18,38].

A characteristic feature of the partial charges q^{eff} is that they sum up to a reduced ionic net-charge $q^{\text{net,eff}}$. This concept has been introduced for polyelectrolytes some time ago [39] and many FFs are already based on this concept [40–44], but its precise meaning had not been addressed systematically for ILs, nor did one have a good method for determining which partial charges should be changed. A good argument for this global charge reduction is given through the MDEC theory [38,45,46], which describes polarization in FF with static partial charges on a mean-field level. The reduction of the net-charge q^{net} is a measure for the mean polarization and it is even experimentally accessible via the refractive index $n^2 = \epsilon_\infty$ with $\epsilon_\infty = 1/(q^{\text{net,eff}})^2$ [17,20] and NMR measurements [19]. Actually, the effect of mean polarization and effective charge distribution can be formally decoupled:

$$E_{ij}^{\text{Coul.}} = \frac{1}{4\pi\epsilon_0} \frac{q_i^{\text{eff}} q_j^{\text{eff}}}{r_{ij}} \quad (1)$$

$$= \frac{1}{\epsilon_\infty} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (2)$$

where $E_{ij}^{\text{Coul.}}$ is the electrostatic interaction between the atoms i and j , which are separated by a distance r_{ij} . This means, that the charge distributions q should not differ for different cation–anion combinations, but only the effective interaction influenced by ϵ_∞ . We should stress at this point that our method of obtaining Blöchl partial charges from bulk takes, in addition to the MDEC theory, local polarization effects into account, since we do not globally scale our partial charges down, but construct a consistent set of partial charges that represents the ionic polarization properties of the IL [14,16–18].

One important property of the derived partial charges immediately follows. On the one hand $q^{\text{net,eff}}$ is related to n , but on the other hand n depends on the temperature T . This implies that the charge reduction is also temperature dependent, which is expected, because polarization is temperature dependent as well. Fortunately, the refractive index behaves essentially as a constant within the temperature window, where the IL is liquid, and the partial charges behave correspondingly. In the next section, we will also show that small changes of the partial charges only have negligible effects on the system properties allowing us to approximate our derived charge distribution by a static set of charges, which include a mean description of polarization.

Eqs. (1) and (2) show that either q^{eff} or q combined with ϵ_∞ can be used to calculate the electrostatic forces, but care has to be taken about which set is used to calculate certain properties.

In previous publications we have shown that the cationic charge distributions obtained with Blöchl's method [14,37] do not significantly differ if [EMIM]⁺ is combined with the counterions [SCN][−], [DCA][−], or [Cl][−] [14,16,17]. Now the partial charges for [BMIM]⁺-based ILs that are schematically depicted in Fig. 1, have also been calculated, because appropriate trajectories became accessible [18,30].

An overview of the so far calculated ILs is given in Table 1 [13–18]. The net charge varies from 0.56 to 0.71 e , but only differences up to 0.04 e arise within a family containing the same anion.

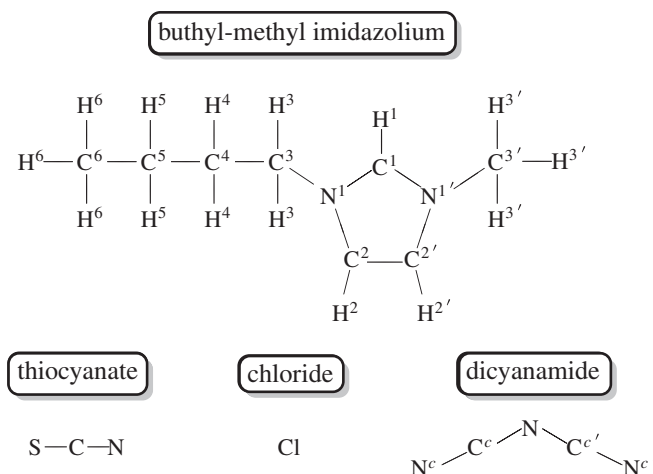


Fig. 1. Nomenclature scheme for the [BMIM]⁺ cation and the [SCN][−], [Cl][−], and [DCA][−] anions.

It has also been extensively studied and discussed [7,16–18] that the variation of the charge distribution q , as well as q^{eff} , is rather similar for the different ions with different ILs. As an example, the different charge distributions for the anions combined with [EMIM]⁺ and [BMIM]⁺ are shown in Fig. 2.

The variations are small suggesting that a generic model can be constructed by averaging over the different results. Since we expect that rounding errors are introduced, the pure averages will have to be slightly changed in order to assure charge neutrality for ion pairs. Thus the question how far the properties of the model are influenced, if the partial charges are only slightly changed, has to be investigated. Although these questions were already addressed by previous studies on [EMIM][DCA], [47], the models are quite different, and thus a general conclusion cannot be drawn. In the next section, we will study the impact of small charge alterations in order to pave the way for the construction of a generic set of partial charges.

3. Influence of small charge variations

To this end we have studied different electrostatic models based on the charge assignment method of Blöchl (CAB) for the IL [EMIM][DCA] [17,18]. The nomenclatures for the ions follow the same scheme as for [BMIM]⁺ and [DCA][−] in Fig. 1.

Two FFs based on the CLaP parametrization were constructed by inserting two different sets of partial charges. One set, aCAB, contains a ring with asymmetrically charged carbon and nitrogen atoms, while CAB contains a symmetrically charged ring. The partial charges of [EMIM]⁺ are summarized in Table 2. Finally the dihedral parameters have been adapted to the new set of charges as described previously in Ref. [1]. In Fig. 3, the distributions of the cationic dipole moments with respect to the center of mass are shown which were derived from Car–Parrinello Molecular Dynamics (CPMD) snapshots [17]. It shows the improvement of the modeling of the dipole moment, achieved by the symmetric ring of CAB.

The two different FFs, CAB and aCAB, are now applied to study the structural properties, density ρ , radial distribution functions $g(r)$, the

Table 1
Net charges q_{net} of some imidazolium based ionic liquids derived with the Blöchl method.

	q_{net}/e		
	[SCN]	[Cl]	[DCA]
[MMIM]		0.63	
[EMIM]	0.56	0.61	0.67
[BMIM]	0.60	0.62	0.71

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