Molecular simulation study of dynamical properties of room temperature ionic liquids with carbon pieces

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Room temperature ionic liquids (RTILs) with dispersed carbon pieces exhibit distinctive physiochemical properties. To explore the molecular mechanism, RTILs/carbon pieces mixture was investigated by molecular dynamics (MD) simulation in this work. Rigid and flexible carbon pieces in the form of graphene with different thicknesses and carbon nanotubes in different sizes were dispersed in a representative RTIL 1-butyl-3-methyl-imidazolium dicyanamide ([Bmim][DCA]). This study demonstrated that the diffusion coefficients of RTILs in the presence of flexible carbons are similar to those of bulk RTILs at varying temperatures, which is in contrast to the decreased diffusion of RTILs in the presence of rigid carbons. In addition, interfacial ion number density at rigid carbon surfaces was higher than that at flexible ones, which is correlated with the accessible external surface area of carbon pieces. The life time of cation-anion pair in the presence of carbon pieces also exhibited a dependence on carbon flexibility. RTILs with dispersed rigid carbon pieces showed longer ion pair life time than those with flexible ones, in consistence with the observation in diffusion coefficients. This work highlights the necessity of including the carbon flexibility when performing MD simulation of RTILs in the presence of dispersed carbon pieces in order to obtain the reliable dynamical and interfacial structural properties.

room temperature ionic liquids, carbon pieces, flexibility, dynamical property, ion pair stability, interfacial structure

1　Introduction

Room-temperature ionic liquids (RTILs) have emerged as a new class of ionic materials, consisting of entirely ions but remaining in liquid state at room temperature [1–3]. Different combinations of cations and anions comprise a large number of RTILs with outstanding properties [4–6], such as low volatility, high thermal stability, and wide electrochemical windows. Based on these advantages, RTILs have been widely used for a variety of applications, such as lubricants [7,8], benign solvents [9], hypergolic propellants [10] and electrolytes of supercapacitors [11,12]. For example, the low energy density is the key limitation of utilizing aqueous electrolytes due to their narrow electrochemical windows (1–2 V) [13]. Whereas, RTILs electrolytes can sustain higher operating voltage (4–6 V) than the conventional aqueous electrolytes, thus greatly enhance the energy density of supercapacitors [14]. Moreover, ionic liquids are also potential energetic materials, which have been reported as hypergolic in the presence of oxidizers (e.g. H_2O_2) [15]. However, the utilization of ILs is limited by their high operating temperature [10], which can be lowered down to ambient condition by tuning their physicochemical proper-

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ties with graphene and carbon nanotubes (CNTs) as additives [16].

Graphene, a one atom thick layer of carbon atoms with a densely packed structure has attracted enormous attention of both experimental and theoretical researchers in recent years [17]. The unique mechanical, electronic, and thermal properties have made it an ideal material for various applications. For example, the graphite has been used as electrodes to enhance the performance of supercapacitors because of its high specific surface area and good electrical conductivity [18,19]. It has also been reported as a "lubricant" to decrease the viscosity of the system when dispersed in RTILs [20]. As another common carbon material, CNTs also receive great interests in a variety of technical fields including energy storage [21] and lubrication [22]. Thus, both graphene and CNTs can be used as additives to manipulate the bulk properties of solvents.

Recent researches have focused on dispersing the graphene and carbon nanotube in solvents such as water [23], ionic liquids [24,25] and other organic liquids [26], endowing the solvents with unique properties [16,23,24,27]. Aida and co-workers [24] found that the single-wall carbon nanotubes (SWCNTs) dispersed in RTILs generated gelatinous materials called "bucky gels" with good thermal stability, nonvolatility and high electrical conductivity, which can be used as electrodes in a fully plastic actuator by a simple layer-by-layer casting [28]. Then Shim *et al.* [27] reported that 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) could form stable structures inside different-sized CNTs due to the π-stacking interaction between the nanotubes and cations by molecular dynamics (MD) simulation. As mentioned above, the operating temperature of ILs is higher due to their high viscosities at low temperatures. McCrary *et al.* [16] successfully reduced the viscosity of RTIL, 1-butyl-3-methyl-imidazolium dicyanamide ([Bmim][DCA]) by adding carbon pieces, suggesting the altered dynamical properties of ionic liquids in the presence of carbon piece. However, it is still illusive to understand the molecular interaction between ILs and carbon pieces.

Although there have been experimental and theoretical studies on the RTILs/carbon pieces mixtures, the dynamical properties of RTILs with dispersed carbon pieces remain as a vast field to reclaim, especially at the microscopic level. There have been many studies investigating the dynamical properties of ionic liquids by MD simulation where all the computational results were in good consistence with experimental measurements, validating the reliability of MD simulation [29,30]. Through MD simulation, the influence of dispersed carbon pieces on the physicochemical properties of ILs can be explored. Moreover, the flexibility of carbon model used in simulations may be relevant to the properties of ILs, especially their dynamical properties, although the restricted diffusion of confined RTILs has been investigated in numerous studies by freezing the solid parts [31–33]. Motivated by the context described above, in this

work, we performed MD simulations to model a series of graphene and carbon nanotube pieces dispersed in IL [Bmim][DCA]. Here both rigid and flexible models of carbon pieces were used. It is known that the rigid models have been widely used in previously reported studies [23], whereas the flexible ones seem more realistic. The dissimilar effects of the flexibility of carbon models on dynamical properties and interfacial distributions of the ILs were elucidated. The use of rigid carbon leads to lower diffusion coefficient and longer ion pair life time compared with the flexible ones due to the concentrated ionic liquids at rigid carbon interfaces. Such significant discrepancies suggest that adopting realistic carbon model is of great importance when investigating the dynamical/interfacial properties of RTILs/carbon composite in molecular simulations.

2 Methodology

The all-atom force field used for [Bmim][DCA] and Van der Waals parameter for carbon atoms in the simulation were adapted from APPLE&P potential (Atomistic Polarizable Potential for Liquids, Electrolytes & Polymers) developed by Oleg Borodin [29]. Force field parameters of flexible graphene pieces and carbon nanotubes (CNTs) were taken from Wander *et al.*'s work [34]. All the bonds were constrained using the LINCS algorithm [35] during the simulation and a 1.1 nm cutoff was used for Van der Waals interactions. Long-range electrostatic interactions were processed using the particle-mesh Ewald (PME) method [36]. An IL box consisting of 940 ion pairs was equilibrated at 280, 290, 300, 310 and 320 K, respectively for 8 ns, followed by a 12-ns production run at 1 bar. The equilibrated RTIL box is approximately 7 nm in length at 300 K and 1 bar. Different carbon models used are shown in Scheme 1 and the simulation boxes containing RTILs and carbon pieces are shown in Scheme 2. In MD simulations, the rigid carbon model is defined as the model where only non-bonded interaction is included and the atoms are frozen at original positions throughout the simulation. On the contrary, for flexible carbon model, both bonded and non-bonded interaction between carbon atoms are taken into consideration and the position of each carbon atom will be updated every time step. To examine the effects of carbon additive concentrations, 1, 2 and 4 rigid/flexible graphene and CNTs were randomly placed in the box. In order to estimate the influence of layer number of the graphene and the size of CNTs, monolayer graphene, three-layer graphene, CNT(5,5) (0.67 nm in diameter) and CNT(10,10) (1.35 nm in diameter) with the length of approximately 2.1 nm were placed in the center of the RTIL box. MD simulations were conducted at temperatures ranging from 280–320 K and 1 bar. Periodic boundary condition (PBC) was applied in three dimensions. All simulations in this work were performed using MD package Gromacs [37]. The diffusion
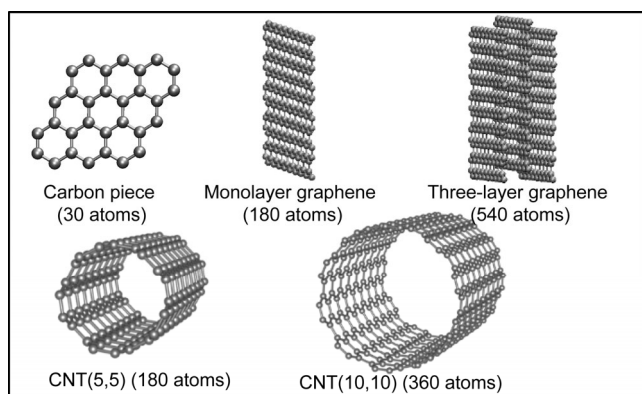
Scheme 1   Rigid/flexible carbon models including monolayer graphene, three-layer graphene, CNT(5,5) and CNT(10,10) used in MD simulations.
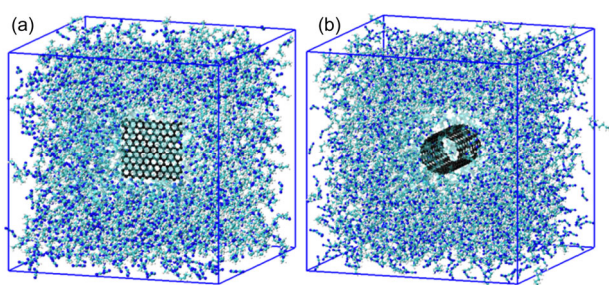
Scheme 2   Simulation boxes containing [Bmim][DCA] with one piece of monolayer graphene (a) and CNT(10,10) (b), respectively (color online).

coefficient was calculated according to the Einstein relation:

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left[r_i(t) - r_i(0) \right]^2 \right\rangle \tag{1}$$

3   Results and discussion

In order to obtain the impact of carbon additives on the dynamical property of ILs, the diffusion coefficients of ILs were calculated with 1, 2, 4 graphene pieces or CNTs at temperatures ranging from 280 to 320 K, respectively (Figure 1). Here we used flexible monolayer graphene piece containing 30 atoms and CNT(5,5). As shown in Figure 1, the diffusion coefficients increase with the increase of temperature in both ILs/graphene pieces and ILs/CNTs(5,5) mixture, consistent with previous experimental study [16]. When the mixture of ILs/graphene pieces is compared with the bulk ILs, it is found that the diffusion coefficients are almost identical with each other, which is most probably attributed to the low concentration of graphene in ILs and the unsteady carbon/IL interfaces, thus imposing almost no influence on dynamical properties of ILs compared with bulk ILs. Based on the previous studies [23], the presence of graphene or carbon nanotube will more or less affect the dynamical properties of solvents when the rigidity of carbon model is taken into account. Thus, both rigid and flexible
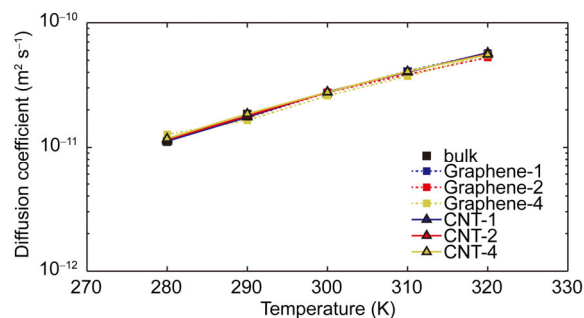

Figure 1   Diffusion coefficients of cation versus temperature and carbon concentration. The number 1, 2 and 4 refer to the number of graphene or CNT pieces in RTIL boxes (color online).

carbon models were used in the simulations.

The rigid carbon model has been widely used in many simulation studies, however, the flexibility of carbon should be taken into consideration when comparing the dynamical properties of ILs in the presence of rigid carbon pieces with those of flexible ones as shown in Figure 2. The diffusion coefficients of ILs were analyzed in the presence of monolayer/multilayer graphene and CNT(5,5)/(10,10) with or without flexibility. Compared with the bulk state, it is found that the use of either the flexible graphene or CNTs model does not obviously alter the diffusion properties of ILs, regardless of the layer number of graphene or the diameter of CNTs. In contrast, the use of the rigid model reduces the diffusion coefficients of ILs significantly, which also shows the dependence on the layer number of graphene and the diameters of CNTs, respectively. The higher the layer number of graphene or the larger the CNT diameter, the lower diffusion coefficient of ILs was observed. Such a tendency is correlated with the external surface area of carbon models used. For rigid models, the large exposed surface area to ILs leads to decreased diffusion coefficient, which is assumed to relate with the interfacial distribution of ILs on carbon surface. Thus we compared the total number density of ions near the flexible and rigid carbon pieces shown in Figure 3.

In order to gain the detailed distribution of ILs, we conducted a 2D density map analysis. It is obvious that the ion densities surrounding rigid graphene are higher than those near flexible ones, suggesting a dense ion packing on rigid surface and a relatively loose distribution of ions on flexible surface. Meanwhile, it is noticed that there are more regions occupied by highly accumulating ions near rigid three-layer graphene than those near rigid monolayer graphene. It can be attributed to the larger surface area of three-layer graphene compared with that of monolayer graphene, providing more sites for ions to reside on. On the contrary, the interfacial ion distribution near flexible graphene is not as dense as that near rigid ones and there is no obvious difference in ion density for rigid monolayer and multilayer graphene. Similar to the graphene sheets, the highly ordered ion distribution was observed near rigid CNTs. Comparing
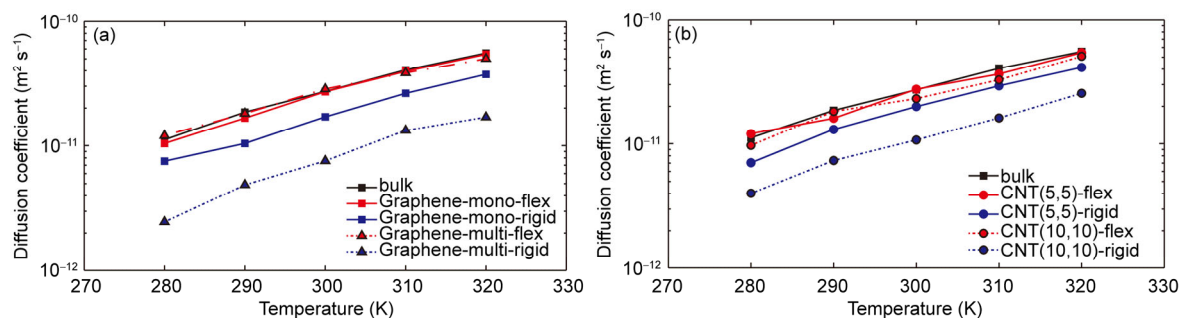
Figure 2 (a) Diffusion coefficients of cations in the presence of graphene versus temperature. Both monolayer and multilayer graphene with and without flexibility were analysed. (b) Diffusion coefficients of RTILs in the presence of CNTs versus temperature. Both CNT(5,5) and CNT(10,10) with and without flexibility were analysed (color online).
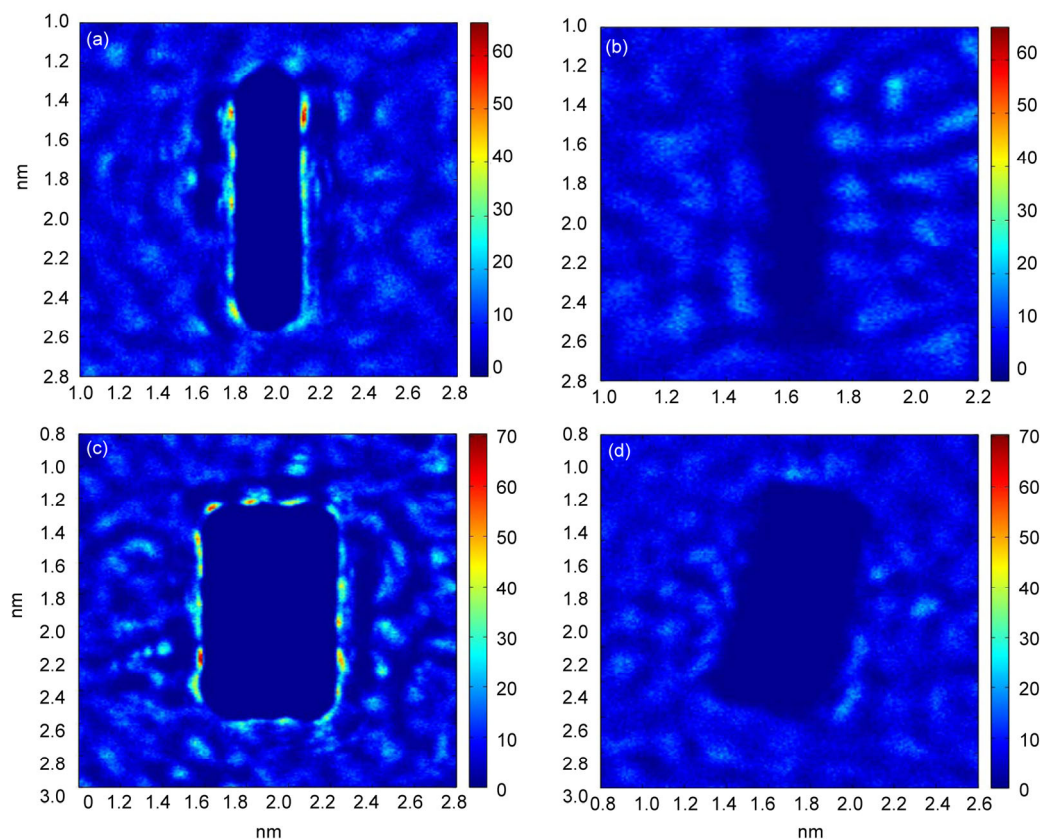

Figure 3 2D total ion number density (#/nm^3) maps in the presence of graphene with and without flexibility at 300 K. (a) Monolayer rigid graphene model; (b) monolayer flexible graphene model; (c) three-layer rigid graphene model; (d) three-layer flexible graphene model (color online).

CNT(5,5) with CNT(10,10) as shown in Figure 4, it is clear that the ILs accumulated on both external and internal surfaces of CNT(10,10), whereas only one dense IL layer was observed on the outer surface of CNT(5,5). Such phenomenon explains the differences between diffusion coefficients of ions near CNT(5,5) and CNT(10,10) shown in Figure 2(b). The larger exposed surface area of rigid CNT model attracted more ions to accumulate on, thus resulting in lower diffusion coefficients of RTILs. Near flexible CNTs, similarly, the ions are not as ordered as those near rigid ones and the ion number density is lower than that at rigid ones. An-

other interesting observation is the ion number densities near rigid CNT(10,10) are higher than those near smaller CNT(5,5), suggesting the denser packing of ions near larger-sized rigid CNT. However, it is not the fact when comparing flexible CNT(10,10) with flexible CNT(5,5), suggesting that the tendency observed in simulations using rigid carbon models may not be tenable, emphasizing the crucial role of flexibility of carbon models in simulations.

It has been demonstrated that the flexibility of carbon pieces including graphene or CNT dispersed in ILs does affect the dynamical property of ILs resulting from the dif-

ferent interfacial distributions on carbon surfaces. To gain more insights into the effects of structural flexibility of carbon pieces on cation-anion interactions, the ion pair stability of ILs in the presence of rigid or flexible carbon pieces was estimated by ion pair time correlation function developed by Kirchner and co-workers [38,39]:

$$C(t) \simeq \frac{\langle h(0)h(t) \rangle}{\langle h \rangle} \qquad (2)$$

where $h(t)$ is unity when the ion pair between cation and anion was formed, and zero otherwise. The angle bracket denotes the average of all ion pairs. Therefore, the $C(t)$ describes the probability that a particular ion pair is formed at time t, which is given to be 1 at time zero.

The $C(t)$ function of ILs in the presence of flexible graphene and CNTs at different concentrations were compared with bulk state as shown in Figure 5. It is clear that the $C(t)$ curves of ILs with and without the dispersing carbon materials are similar regardless of the concentration of carbon pieces, which agrees with the trend of diffusion coefficient shown in Figure 1. However, in contrast to the flexible model, when combined with rigid carbon pieces, the $C(t)$ of ILs decays more slowly than that of the bulk state. More specifically, the ion pair life time of ILs in the presence of rigid monolayer graphene model or rigid CNT(5,5) is longer than that with flexible multilayer graphene or CNT(10,10) (Figure 6), respectively, which is consistent with the trend

of diffusion coefficient observed in Figure 2. It is also found that these trends of $C(t)$ are in agreement with the interfacial ion distribution shown in Figures 3 and 4. The higher ion density at carbon surface, the slower decay of $C(t)$. Thus ion pairs of ILs in the presence of flexible carbon pieces dissociate faster than those in the presence of dispersed rigid ones.

It is necessary to point out that the ion pairs in the presence of rigid three-layer graphene exhibit the longer life time than those in the presence of rigid CNT(10,10), similar to the trend between the rigid monolayer graphene and rigid CNT(5,5). It is most probably because of the larger external surface area of three-layer graphene than CNT(10,10), especially the cross-section area of three-layer graphene providing more space for ion accumulation. Comparing monolayer graphene with CNT(5,5), the inner surface of CNT(5,5) is not accessible for ions due to its smaller diameter (0.67 nm), which greatly reduced the number of ions on its surfaces. All the ILs in the presence of flexible carbon pieces give rise to almost identical time correlation function to bulk ILs, on the contrary to the observation in the ones with rigid models.

4 Conclusions

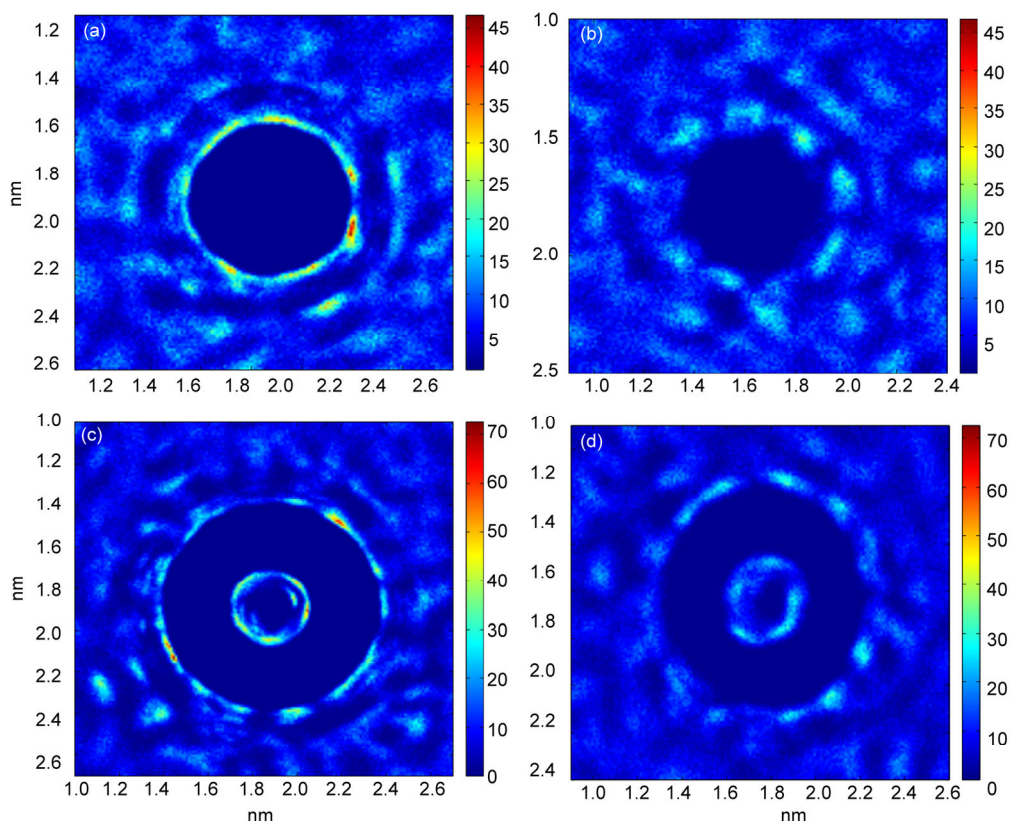This study illustrates the influences of structural flexibility

Figure 4 2D ion number density (#/nm³) maps near rigid and flexible CNTs at 300 K. (a) Rigid CNT(5,5) model; (b) flexible CNT(5,5) model; (c) rigid CNT(10,10) model; (d) flexible CNT(10,10) model (color online).
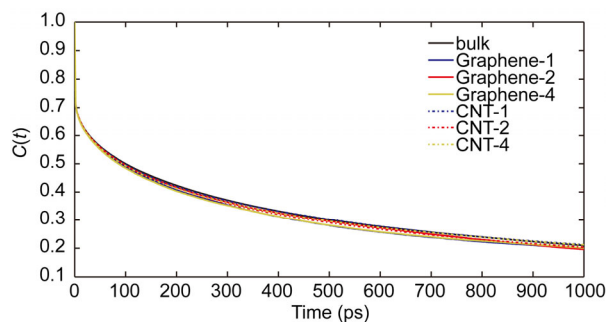
Figure 5 Time correlation functions $C(t)$ of the ion pair formed between cation [Bmim]$^+$ and anion [DCA]$^-$ with flexible carbon pieces at 300 K. 1, 2 and 4 refer to the number of graphene and CNT pieces dispersed in RTIL box (color online).
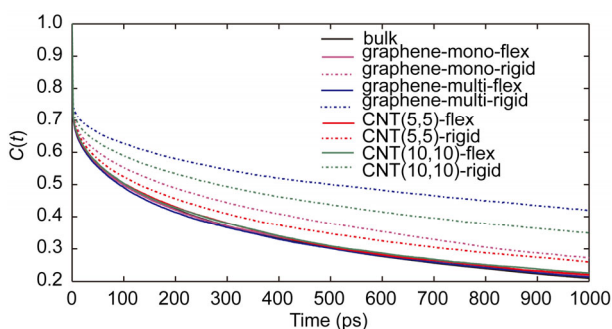

Figure 6 Time correlation functions $C(t)$ of the ion pair formed between cation [Bmim]$^+$ and anion [DCA]$^-$ at 300 K. The rigid and flexible monolayer/multilayer graphene and CNT(5,5)/(10,10) were analysed (color online).

of carbon pieces on the dynamical and interfacial structural properties of ILs by MD simulations. When flexibility of carbon pieces was taken into account, the diffusion coefficient of ILs is independent of the quantity of dispersed carbon pieces. However, comparing the diffusion coefficients of ILs in the presence of rigid and flexible carbon pieces, the diffusion of ILs with rigid carbon is slower than that with flexible ones. Interfacial ion distribution analysis reveals that there are more ions accumulating on rigid carbon surfaces, which increases with the external surface area of rigid carbon pieces. It was also observed that ion pairs of ILs in the presence of rigid carbon pieces have longer life time than those with flexible ones. Although rigid carbon model is commonly used in molecular simulation work, few studies report the impact of the structural flexibility of carbon on the dynamical and interfacial distribution behavior of ILs. By simulation, this work initially verifies that whether or not taking into account the flexibility of carbon pieces dispersed in ILs may give rise to significantly different dynamical properties of ILs. Therefore, it is noteworthy that the flexibility of carbon pieces may not be neglected when performing simulations of ILs with dispersed carbon. We also have to point out that such conclusion may only hold true at low concentration of carbon pieces or

when carbon pieces are extremely small compared with the ILs system. It is known that the solubility of carbon pieces is very low in ILs [16,40], high concentration of carbon pieces may result in precipitation. Thus it may be still acceptable to use rigid carbon models in the simulation when carbon material serves as a considerable part of the simulation system. One question may be proposed is whether the flexibility can affect the electric double layer (EDL) formation on carbon electrode surface, although there are many studies that investigated the diffusion of nanoconfined RTILs with a rigid model of the solid confinements [31–33]. Rouha *et al*. [41] found that the highly ordered layering of the RTILs was formed on flexible neutral graphene surfaces. However, without comparing with the results from rigid and charged carbon electrode, it is still hard to draw a conclusion that carbon flexibility will affect the EDL structure or not. Therefore, the in-depth investigation is still required on this aspect, such as how the flexibility can affect EDLs on carbon electrode surface and the effects of flexibility on the gas adsorption behavior of carbon adsorbents.

Conflict of interest   The authors declare that they have no conflict of interest.

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