

How do external forces related to mass and charge affect the structures and dynamics of an ionic liquid?

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ABSTRACT

Ionic liquids (ILs) are novel promising materials widely used in various fields. Their structures and properties can be tuned by means of external perturbations, thus further broadening their applications. Herein, forces proportional to atomic mass (mass-related field) and atomic charge (electric field) are applied in molecular dynamics simulations to the IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide to investigate the origin of the resulting changes in structures and dynamics. The results show that both electric and mass-related fields cause the ion cages to expand and deform, eventually leading to their breakdown to produce a transformation of ILs from the cage structure to a channel-like structure, which results in faster self-diffusion of ions in the directions of the applied force and to a lesser extent other directions. Further comparison of electric and mass-related fields demonstrates that only the electric fields reorientate cations to produce a hydrodynamically favored conformation in the force direction, which shows faster diffusion. The *cis* isomer of the anion is preferred in the presence of the electric fields, whereas applying the forces proportional to mass does not change the anion conformer equilibrium significantly. The results presented in this work aid in the understanding of how ions adjust their structures to adapt to external perturbations and facilitate the application of ILs as electrolytes.

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I. INTRODUCTION

Ionic liquids (ILs) are an emerging class of functional liquids entirely composed of cations and anions, which have been widely applied in various fields due to their excellent physicochemical properties and “task-specific” characteristics.^{1–3} Applying external perturbations (electromagnetic fields, shear, nanoconfinement, etc.) to ILs can further tune their microscopic structures and properties to promote applications in variable-focus lenses,⁴ microwave-assisted synthesis and extraction,^{5,6} energy harvesting,^{7–10} and optical (electro-) chemical sensors and biosensors.^{11,12} ILs exhibit complex

microscopic interactions due to the asymmetric structures and large molecular volumes of their cations and/or anions.¹³ Therefore, probing and understanding their microscopic heterogeneous structures and behavior under external perturbations, although difficult, are important.

The effect that external electric fields (EEFs) have upon the microscopic structures and properties of ILs has attracted widespread attention of researchers. Previous experimental research has confirmed that a DC voltage can tune the wetting behavior of an IL droplet on a smooth fluoropolymer surface.¹⁴ The local electric fields on the surface of the electrode can affect the microstructures

of the ILs at the solid–liquid interface to produce an electric double-layer structure, which, for example, enables ILs to be used as an electrolyte in supercapacitors.^{2,15–17} Computational calculations can be beneficial to probe the microstructures of the electric double-layer or bulk ILs in EEFs at the molecular or atomistic level.^{18–21} Coarse-grained molecular dynamics (MD) simulations have shown that the native bulk structure of ILs is first disrupted from spatially heterogeneous to homogeneous and then reorganized into nematic-like order with increasing EEF strength arising from ion alignment in the direction of the EEF.¹⁸ At the same time, the ion mobility, self-diffusion coefficient,¹⁹ and electrical conductivity^{20,21} increase with increasing EEF strength due to ion cages expanding and deforming. However, the coarse-grained results are noisier and less accurate as significant thermostat effects arise in very high EEFs ($\sim 1 \text{ V } \text{\AA}^{-1}$) compared to all-atomistic (AA) models.²² AA MD simulations have been conducted to show that hydrophobic ILs can be strikingly changed to be hydrophilic in a strong EEF,²³ while ionic rotational and translational responses to EEFs lead to dipolar alignment and an increase in diffusivities. When an EEF is applied to a nanodroplet of ILs, the droplet deforms in shape and loses some of its cations (cation depletion phenomenon).²⁴ Further polarizable AA MD simulations confirm that the charge arms [a vector from the center of mass (COM) to the center of charge (COC) of an ion] of ions align with and stretch out along the EEFs.²⁵ Finally, in alternating electric fields, ILs have been shown to respond to much lower frequencies of the EEFs than smaller polar solvents, such as water.^{26–28}

The EEFs applied to ILs do not only interact with charged atoms to cause the deformation of molecular geometry and local order but also lead to a distortion of the electron distribution relative to the atomic nuclei to produce electric polarization. While polarizable force fields are generally a minimum requirement to investigate detailed structures and dynamics of species in electric fields using MD simulations,^{25,29,30} most of the aforementioned research works employed non-polarizable force fields that do not consider atomic polarization in response to the redistribution of the electron density. In addition, there are internal electrostatic forces from the intrinsic electric fields (IEFs) of ILs, which also need to be considered when we apply external forces to see how the balance between these two forces affects the ILs. We obtained interesting results in our previous work, but it was not possible to separate the direct effects of the EEF from those that come from the fact that the ions have been accelerated due to the application of a force. To separate these factors, MD simulations with Drude-particle polarizable AA force fields are employed to probe the structures and dynamics of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{C}_{1}\text{im}][\text{NTf}_2]$) in the presence of external forces proportional to atomic charge (EEFs) and atomic mass (external mass-related fields, EMFs) in this work to observe the similarities and differences between the two. The latter forces proportional to mass were applied in opposite directions for the cations and anions. This setup is unphysical insofar as neither the directionality nor the magnitude of interaction occurs in natural gravitational fields; thus, here, it serves only as a means to gain a deeper understanding of the effects of the EEFs. To study the ions, the distribution of dihedral angles, the charge arm, and the orientation of cations and anions in different EEFs and EMFs are analyzed and compared. The dynamical properties, including diffusion, reorientation, and

relaxation of dihedral angles of cations and anions, are also determined and discussed in detail.

II. THEORY AND METHODS

A. Computational methods

MD simulations were employed to investigate the structures and dynamics of $[\text{C}_4\text{C}_{1}\text{im}][\text{NTf}_2]$ (Fig. 1) under external forces related to atomic mass and charge. The force field used in this work is based upon the CL & P force field^{31–33} with polarizability added using Drude particles. The van der Waals (VDW) interaction parameters between different atoms were obtained from the Lorentz–Berthelot combining rules.³⁴ According to the reported polarizable methodology,³⁵ the polarizabilities³⁶ were added to most heavy atoms, while the polarizabilities of hydrogen and fluorine atoms were merged onto the polarizability of the atoms to which they are bonded. The mass of Drude particles (DPs) was set as $m_D = 0.4 \text{ amu}$, and the harmonic spring force constant between Drude cores (DCs) and DPs was set as $k_D = 4184 \text{ kJ mol}^{-1}$. The partial charges of the DPs were calculated using $q_D = \sqrt{k_D/\alpha}$,³⁷ and the charge of DCs (Fig. S1) was adjusted to ensure that the total charge of the DC and DP is equal to the charge of the nonpolarizable atom before adding DPs. The short-range dipole–dipole electrostatic interactions were damped using a Thole damping function^{35,38} with parameter $a = 2.6$.^{38–40}

All MD simulations were performed using the open-source package Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).⁴¹ The simulation box was initially composed of randomly packed 256 ion pairs using *ffttool*⁴² and *PACKMOL*⁴³ packages, and the polarizable input files for LAMMPS were built using the polarizer package.^{35,42} Periodic boundary conditions were applied to all the directions of the simulated box during the entire simulation. The cut-off for the Lennard-Jones interactions was set as $12 \text{ \AA}$. Long range Coulombic interactions were treated using the particle–particle–particle–mesh method with a relative accuracy of 1×10^{-6} . The SHAKE algorithm was used to maintain bonds terminating in hydrogen atoms at their equilibrium values.

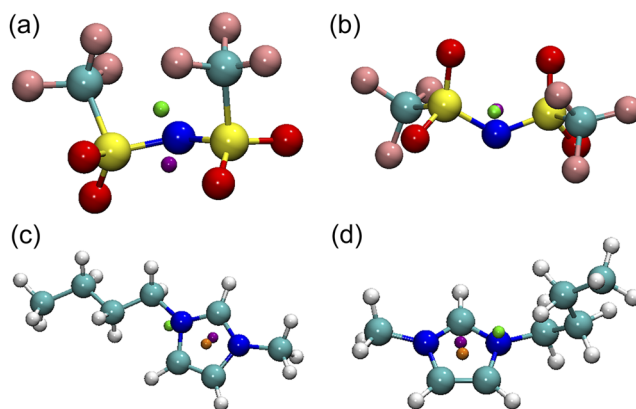


FIG. 1. Molecular structures of the anion with (a) *cis* and (b) *trans* conformers and cation with (c) stretched and (d) curled alkyl chains, where the orange, green, and purple balls represent the imidazolium ring's center, COM, and COC, respectively.

Newton's equations of motion are integrated using the well-known Velocity-Verlet algorithm with a time step of 0.5 fs. All DCs and DPs were thermostatted at $T = 300$ and 1 K by independent Nosé–Hoover thermostats with a relaxation time of 50 and 5 fs, respectively.

The initial conformation was minimized using a conjugate gradient minimization algorithm to eliminate overlapped atoms (1000 step), and then, the system was run for 2 ns in the NPT ensemble, after which the density of the system matches the experimental value well (Fig. S2). Following the NPT run, an equilibration run of 10 ns was performed in the NVT ensemble. After equilibration, in order to consider the interference of general thermostat to EEFs and EMFs, a modified thermostat that only considered the degrees of freedom perpendicular to the field was used to maintain the system temperature.^{25,44} At this point, a series of simulations were performed in which EEFs and EMFs of varying strengths were applied only along the z direction to run for 1 ns equilibration followed by a 10 ns run used to collect corresponding data every 500 fs for static structure analysis, while for dynamic correlation analysis, a 1 ns run was used with sampling every 1 fs.

The strengths of static EEFs applied in the $+z$ direction are from 0.01 to 0.50 V Å⁻¹, and the corresponding strengths of EMFs applied to the cation ($+z$ direction) and anion ($-z$ direction) to generate total forces on cations and anions equal to those of the static EEFs are listed in Table SI. In the following, we refer to the EMFs simply as the EMFs of 0.01, 0.05, 0.10, 0.20, 0.30, 0.40, and 0.50, i.e., by giving the field strength of the corresponding EEF. The structural properties and dynamics (correlation) were calculated with the TRAVIS package⁴⁵ and prealpha tool (source code, manual, and executable available under <https://github.com/FPhilippi/prealpha>), respectively. The structures were visualized with molecular graphics software Visual Molecular Dynamics (VMD).⁴⁶

B. Theory

During the simulation, the cations and anions exhibit random Brownian motion, and the 1D mean square displacements (MSDs) of ions can be defined as

$$\text{MSD} = \langle x^2(t) \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N |r_{\alpha,i}(t) - r_{\alpha,i}(0)|^2 \right\rangle, \quad (1)$$

where t is the moving time of the ion, r is the position of the ion, α is the Cartesian coordinates of the atoms or molecule COM, and N is the number of atoms or molecules.

The self-diffusion coefficient of the cation or anion can be calculated using the Einstein relation approach from the MSD as follows:

$$D = \frac{1}{2d_\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle x^2(t) \rangle, \quad (2)$$

where d_α is the dimensionality and $\langle \dots \rangle$ represents an average over the ensemble.

When applying external force in the z direction, the ions are accelerated to drift along in the z direction until the internal viscous drag from the surrounding ions is equal to the applied external force, which leads to the ions drifting at a constant velocity.^{8,25} The drift makes the MSDs of ions in the z direction present a nonlinear

trend with time, which means that Eq. (2) cannot be used to calculate the self-diffusivity coefficient of the cation or anion. Therefore, an effective self-diffusion coefficient considering a drift correction is defined as

$$D_{\text{eff}} = \frac{1}{2d_\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} (\langle x^2(t) \rangle - \langle x(t) \rangle^2), \quad (3)$$

where $\langle x(t) \rangle$ represents the ensemble mean displacement.

The reorientational correlation functions of the cations, anions, and charge arm^{25,47,48} are defined as⁴⁹

$$C_l(t) = \langle P_l[\mathbf{u}_i(t + t_0) \mathbf{u}_i(t)] \rangle, \quad (4)$$

where $\mathbf{u}_i(t)$ is a unit vector parallel to the internuclear axis of molecule i at time t . $P_l(\dots)$ denotes a Legendre polynomial of order l . In this work, the selected vectors are N–N (the N bonded to the butyl chain to the N bonded to the methyl group) in the cation, S–S in the anion, or charge arm in the cation and anion.

The intermolecular time autocorrelation function corresponding to *trans*–*cis* isomerization based on the two dihedral angles (C–S–N–S and S–N–S–C) in the [NTf₂][−] anion is defined as

$$C(t) = \frac{\langle (h(t_0 + t) - \langle h \rangle)(h(t_0) - \langle h \rangle) \rangle}{\langle (h(t_0) - \langle h \rangle)^2 \rangle}, \quad (5)$$

where the value of quantity h is 1 for *trans* conformers and 0 for *cis* conformers. The anion is defined to be the *trans* conformer when both dihedral angles C–S–N–S and S–N–S–C are between 0° and 150° or when both are between 210° and 360°. Otherwise, the anion is considered to be the *cis* conformer.

III. RESULTS AND DISCUSSION

This section comprises four subsections that focus on the molecular structures and dynamics of the ions in [C₄C₁im][NTf₂] under different EEFs and EMFs. First, the structures of the cations and anions in different EEFs and EMFs are presented and discussed to understand their distribution relative to the direction of the applied force. The anion [NTf₂][−] has two conformers, a *trans* and a *cis* isomer [Figs. 1(a) and 1(b)], and hence, the conformations of the anions are discussed in Subsec. III B to show the distribution and transformation of *trans* and *cis* conformers in different EEFs and EMFs. Then, the distribution and orientation of the charge arms in both cations and anions are calculated to show the change in the COM and COC of the cations and anions in different EEFs and EMFs. In Subsec. III D, the self-diffusion coefficients of the cations and anions are calculated in different EEFs and EMFs, and then, the effect of the structures of ions on their dynamics is discussed in detail.

It is worth noting that the strength of the applied EEFs and equivalent EMFs in this work is much higher than can reasonably be applied to ILs in most practical experiments; however, they are necessary here in order to see the effects of the forces within the simulations. Because of this, we are not attempting to replicate or simulate experiments directly but instead seeking insight

into how changing the distribution of external forces within an ion affects an IL.

A. Structures of cations and anions

1. Orientation of cations and anions

In this work, the charge related force (EEF) is applied to the individual atoms of the cations and anions of $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ in the $+z$ direction. Thus, the net force on the cations pulls them in the $+z$ direction, and the net force on the anions pulls them in the $-z$ direction. Likewise, the force proportional to atomic masses (EMF) is applied to the individual atoms of cations in the $+z$ direction, but for anions, the EMF is applied in the $-z$ direction to make the anions experience the force in the same direction as in the EEF. As mentioned above, we are aware that applying the forces proportional to mass in the opposite direction for the cations and anions is unphysical and that this does not occur in reality, but doing so allows us to gain a deeper understanding of the effects of the EEFs and EMFs on ILs. Crucially, we are thus able to distinguish between the effects of net force and polarization, which occur simultaneously in the EEFs.

When EEFs and EMFs are applied to the IL, the normal thermal movement of cations and anions is disrupted. In weak EEFs and EMFs, the orientation of cations and anions is subject to the IEFs in the IL and is random, as in zero field (Fig. 2). Figure 2(a) shows that EEFs of $0.05 \text{ V } \text{\AA}^{-1}$ or larger lead to the angle between the $+z$ direction and the N–N vector (the N bonded to the butyl chain to the N bonded to the methyl group) of the imidazolium ring to gradually reduce; the alignment tends to 0° as the applied field increases, which means that the imidazolium rings align nearly parallel to the EEF direction in a sufficiently strong field. In contrast, the angles between the $+z$ direction and the N–N vector of the imidazolium ring tend to 180° in the EMF, although to a lesser

extent than the effect in the EEF [Fig. 2(b)]. Hence, whether it is an EEF or an EMF, the cation always presents a most hydrodynamically favored profile to the direction of the force, which is beneficial to faster motion and diffusion. However, there is still a clear difference between the effects of the EEFs and EMFs on the orientation of the cations and the EEFs can more efficiently change the orientation of cations compared with the EMFs. Furthermore, the EEFs up to $0.50 \text{ V } \text{\AA}^{-1}$ lead to a continuous increase in the alignment [Fig. 2(a)], whereas the population of ions with the antiparallel alignment in Fig. 2(b) does not change significantly at $\text{EMF} > 0.20$.

The orientations of the anions in an EEF of $0.05 \text{ V } \text{\AA}^{-1}$ or larger [Fig. 2(c)] indicate that the probability of the angles (between the $+z$ direction and the S–S vector) at around 90° slightly increases, while for the EMFs, the probability of the angles at 0° and 180° shows a slight increase [Fig. 2(d)]. This indicates that the anions rotate to a small degree to give their most hydrodynamically favored profile to the direction of movement in the EMF, but in the EEFs, the anions present their large cross section in the direction of movement. This orientational change is to a lesser extent than the effect of EEFs and EMFs on cations. It is pertinent to note at this point that due to the shape of the anion and the change in the abundance of each conformer (Table I), depending upon the angle between the S–S vector and the direction of the force, the cross section the anion presents toward diffusion is very different. In the cation, the N–N vector is rigid and does not change with changes in its conformation, whereas there is a slight change in the position of the S atoms between the *cis* and *trans* conformers of the anion, which affects the S–S vector.²⁵ Therefore, these results discussing the orientation of a specific vector in the anions under EEFs and EMFs are affected by the conformation of the anion, which is discussed in Subsection III B 1 in detail.

To further investigate the reorientation of the cations and anions, the reorientational correlation functions of the N–N and S–S vectors under different EEFs and EMFs were calculated according to Eq. (4), and the results are shown in Fig. 3. In zero field, all $C_1(t)$ values decay to zero, which indicates that the cations and anions can decorrelate fully (i.e., the orientation of the ion is independent of its initial orientation) given enough time. For the S–S vector of the anions, the decay of $C_1(t)$ in all EEFs and EMFs reaches zero, but

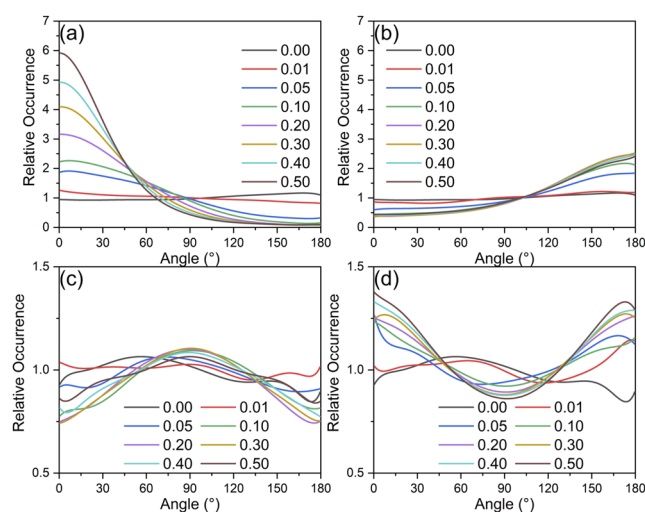


FIG. 2. Distribution of the angles between the $+z$ direction and the N–N vector (the N bonded to the butyl chain to the N bonded to the methyl group) in the cation in different EEFs (a) and EMFs (b) and the S–S vector in the anion in different EEFs (c) and EMFs (d).

TABLE I. Percentages of *trans* and *cis* under different EEFs and EMFs.

Strength	EEFs		EMFs	
	<i>trans</i> (%) ^a	<i>cis</i> (%) ^b	<i>trans</i> (%) ^a	<i>cis</i> (%) ^b
0.00	34.2	65.8	34.2	65.8
0.01	33.3	66.7	33.6	66.4
0.05	27.1	72.9	34.2	65.8
0.10	19.3	81.7	34.3	65.7
0.20	12.7	87.2	36.0	64.0
0.30	10.5	89.5	35.6	64.4
0.40	9.6	90.4	35.1	64.9
0.50	9.3	90.7	35.0	65.0

^a*trans*: 120° – 240° .

^b*cis*: 0° – 120° and 240° – 360° .

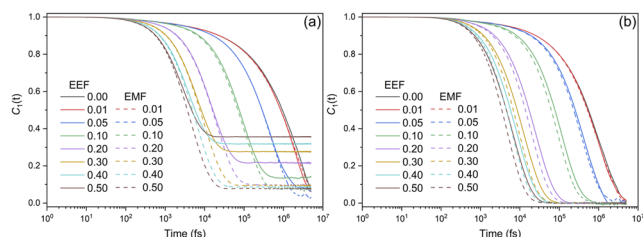


FIG. 3. Reorientational correlation functions $C_1(t)$ of the N–N (a) and S–S (b) vectors under different EEFs and EMFs.

the decay time of $C_1(t)$ decreases as the EEFs and EMFs increase. Figure 3(b) shows that the decay time of $C_1(t)$ in the EMFs is slightly quicker than that in the corresponding EEFs; however, there is no significant difference between the EEFs and EMFs with respect to the reorientation of the anions. This means that the reorientation of anions is similar for the case in EEFs and EMFs of the same strength, highlighting that the distribution of force in the anion does not affect the reorientation.

For the N–N vector of the cations, the decay of $C_1(t)$ follows the same trend, which decreases as the strength of the EEF and EMF increases. However, there is a significant difference between the EEF and EMF for the strength greater than 0.05. In both the EEFs and EMFs, $C_1(t)$ converges onto non-zero values, and the cations do not fully decorrelate. In the EMFs, it decays to about 0.08, indicating a slight correlation of the cations over long times. However, in the EEFs, this value is much higher and increases with the EEF strength. In combination with the results in Fig. 2(a), it can be determined that the cations are strongly aligned in the presence of EEFs with the N–N vector parallel to the direction of the field, and there is very

little variation in the angle despite the rapid reorientation. Conversely, in the EMFs, there is a rapid reorientation combined with a more random distribution [Fig. 4(d)] but with some orientation in the direction of travel [Fig. 2(b)].

Combining the results for the cations and anions, it can be found that the rapid reorientation is directly related to the magnitude of the force applied to the ion, and the distribution of this force does not influence this drastically. With regard to the correlation, the anion correlation is very similar in EEFs and EMFs of the same strength, indicating again that this is not affected by the distribution of a force, only the presence of a force. However, the correlation is different for the cation in EEFs and EMFs, indicating that the reorientation of this ion is sensitive to the type of perturbation applied to it.

Considering changes in the conformations of the individual ions, the cation of $[C_4C_1im][NTf_2]$ has a butyl chain, which can take curled or extended configurations, depending on the number of its C–C bonds that are in a *gauche* conformation.^{25,50} Figures 4(a) and 4(b) show that there are five peaks and shoulders centered at about 3.7, 4.5, 5.3, 5.6, and 6.1 Å for the length distribution between the center of the imidazolium ring (COR) and the terminal C atom in the butyl chain in zero field. The sequence of the intensity of the peaks and shoulders is $5.3 > 5.6 > 6.1 > 4.5 > 3.7$ Å, which means that more curled butyl chains exist in ILs in zero field. The weak EEFs and EMFs have almost no effect on the butyl chain, and the distributions remain as they are in zero field.

Increasing EEFs continuously increases the intensity of the peak at 6.1 Å and the shoulder at 5.6 Å. The intensity of the peak at 5.3 Å gradually reduces and transforms to a shoulder, eventually disappearing as the EEF increases further [Fig. 4(a)]. The intensity of the shoulder at 4.5 Å continuously reduces as the EEF increases, whereas the intensity of the shoulder at 3.7 Å only slightly decreases. This indicates that most cations adopt fully extended butyl chains in strong EEFs and the cation always extends its butyl chain to keep a most hydrodynamically favored profile to the direction of the EEFs as the EEF increases.

In the case of the increasing EMFs, Fig. 4(b) shows that as the EMF increases from 0 to 0.1, the intensity of the peak at 5.3 Å gradually reduces and the intensity of the peak at 6.1 Å increases. As the EMF further increases, the peak at 5.3 Å transforms to the shoulder and eventually disappears, whereas the intensity of the peak at 6.1 Å gradually decreases and transforms to the shoulder. Particularly, unlike the EEFs, when the EMF is greater than 0.20, the intensity of the shoulder at 5.6 Å does not increase as the EMFs increase, whereas the intensity of the shoulder at 3.7 and 4.5 Å continuously increases. A possible explanation for these observations would be that the peaks whose intensity increases correspond to hydrodynamically favored conformations. However, this would suggest that the most extended conformations in Fig. 4(b) (5.6 and 6.1 Å) are those that align with the drift direction, i.e., showing angles near 180° in Fig. 2(b). However, the corresponding combined distribution function (see Figs. S3 and S4 in the supplementary material) shows that this is not the case. Hence, it appears that the mechanism of action for the EMF here is equivalent to thermal motion, effectively perturbing the system away from the equilibrium conformer distribution. Hence, the peaks in Fig. 4(b) are “washed out” for the largest EMFs.

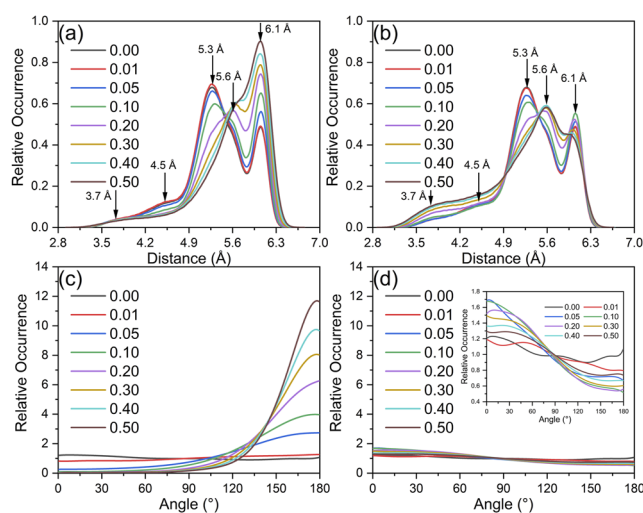


FIG. 4. Distribution of the length between the COR and the terminal C atom in the butyl chain in different EEFs (a) and EMFs (b) and distribution of the angles between the +z direction and the vector from the COR to the terminal C atom in the butyl chain in different EEFs (c) and EMFs (d).

Figures 4(c) and 4(d) present the distribution of the angles between the $+z$ direction and the vector from the COR to the terminal C atom of the butyl chain in different EEFs and EMFs. The angle distribution in weak EEFs and EMFs remains the same as that in zero field. As the EEFs increase [Fig. 4(c)], the butyl chain tends to align parallel to the direction and extends along the EEF direction. The increasing EMFs make butyl chains reorient in the same way to some degree; however, this is not as pronounced as in EEFs. These results indicate that the force being exerted upon the COM of cations does not efficiently change the orientation of the butyl chains. Therefore, the EEFs induce alignment with the direction of the external force, which is not the case for EMFs. Since no rotational force is applied to the cations directly, the change in the orientation is likely due to the motion of the ions in the opposite direction to each other and the distortion and alignment of the cations to reduce hydrodynamic drag.

Combining the orientation of the N–N vector (Figs. 2 and 4) and the vector from the center of the COR to the terminal C atom of the butyl chain, it can be further found that the cation assumes a beneficial hydrodynamic favored profile in the force direction under the EEFs. The above simple hydrodynamic effect is added by an addition of a direct rotational force on the cation. Hence, we deduce that the imidazolium ring makes the butyl chain to drift along the force direction under the EEFs, just like “tadpole swimming.” On the contrary, only the imidazolium ring in the most extended conformations in Fig. 4(b) (5.6 and 6.1 Å) follows the butyl chain to drift along the force direction under the EMFs.

2. Distribution of ions around cations and anions

As the ILs are solely composed of charged cations and anions, there are strong IEFs that compete with the applied external forces. In weak EEFs ($<0.02 \text{ V Å}^{-1}$), the EEFs are smaller than the IEFs of ILs, and the IEFs are dominant factors in ILs.⁵¹ The weak EEFs

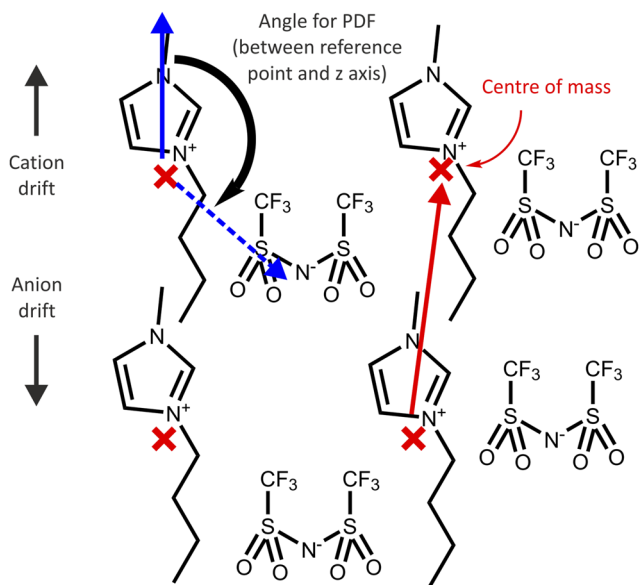


FIG. 5. Graphical representation of the channel-like structure formation (the cation is the reference).

only affect the structure of the individual cations or anions without changing the overall structure of the IL. Therefore, the distribution of cations and anions shows nearly the same trend as zero field, and this is confirmed by the COM radial distribution functions (RDFs) of cations and anions, cations and cations, and anions and anions (Figs. S5a, S5c, and S5e). Likewise, applied EMFs generated equal force to cations and anions as weak EEFs and do not affect the distribution of the cations and anions (Figs. S5b, S5d, and S5f).

When the EEFs and EMFs further increase, the IEFs of ILs are no longer dominant factors in ILs. The cations and anions are subject to the synergies of the IEFs with the EEFs or EMFs and move in opposite directions. Consequently, the structures of the IL become anisotropic. The motions of the ions result in the breakdown of ion cages and aggregation of the counterion to form a channel-like structure (Figs. 5–7 and Figs. S6–S9).

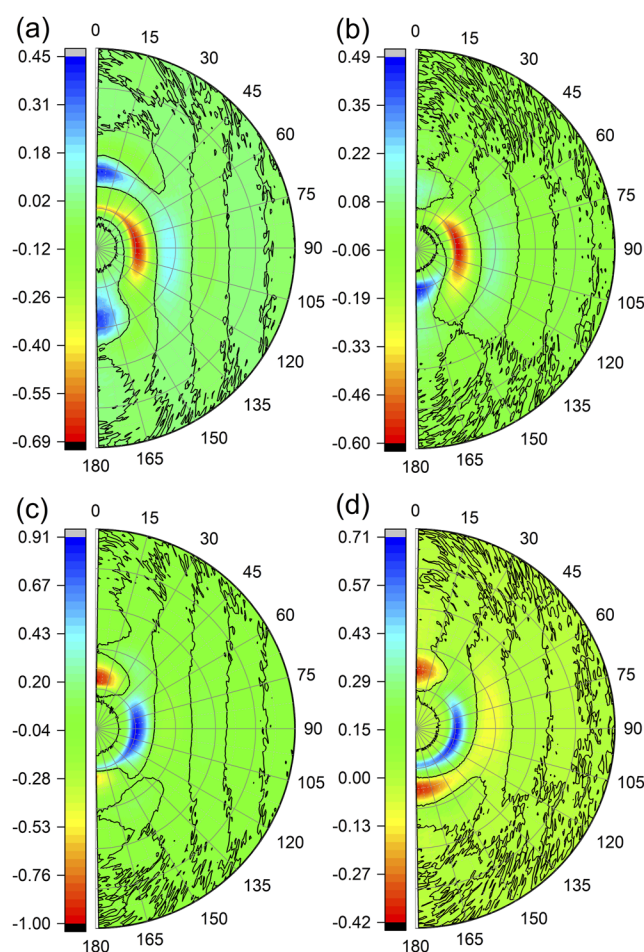


FIG. 6. PDFs for the ions around the cations (charge weighed) in an EEF of 0.5 V Å^{-1} (a) and equal EMF (b) and around the anions in an EEF of 0.5 V Å^{-1} (c) and equal EMF (d). The maximum radius, corresponding to the outer boundary of the half circles, is 25 Å in all cases, and the referenced vector is the $+z$ direction. The negative values of “cation surroundings” indicate a statistical excess of negative charge and vice versa. The “zero charge line” that separates these regions is drawn by the black line.

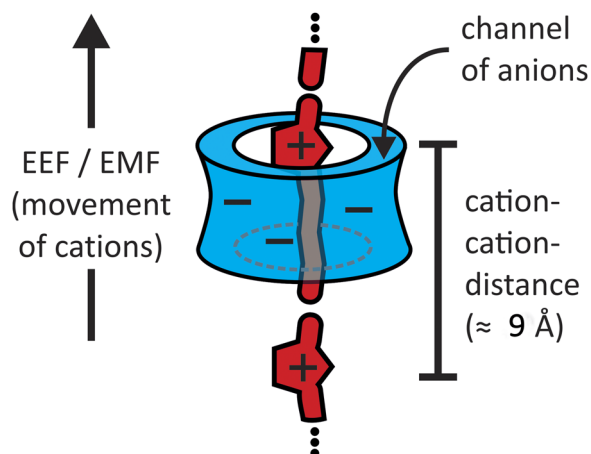


FIG. 7. Schematic representation of the channel-like structure (the cation is the reference ion).

At this point, the general COM RDF is no longer a good representation of these anisotropic systems as this requires an assumption of isotropy. Therefore, the resulting channel-like structures have been analyzed using combined distribution functions. All ions are represented by their COM. Taking the cation as an example, the cation in the upper left corner (Fig. 5) is arbitrarily chosen as a reference, with the direction of movement represented by the blue solid arrow. Starting from this reference point, the average density of the surroundings is calculated and displayed as a function of the position of the observed point. One such observed point relative to the reference molecule is distributed along the blue dashed arrow. The polar distribution functions (PDFs) are employed to illustrate the channel-like structure, and the average density of the surroundings is evaluated as a function of the angle between the $+z$ direction (i.e., the direction of drift movement of cations) and the dashed blue vector, as well as the length ("radius") of the dashed blue vector. If the cations align in the channel as indicated by the red bold arrow, then an increased cation density is observed at 0° and 180° .

The calculated PDFs for the ions around the cations and anions under an EEF of $0.5 \text{ V } \text{\AA}^{-1}$ and the corresponding EMF are presented in Fig. 6. It can be seen that the green region within a radius of $\sim 5 \text{ \AA}$ occurs because other ions are excluded from the van der Waals volume of the reference ion. For cations, the channel walls are formed by the shell of counter anions (red region of high density and excess negative charge), and the cations line up within these channel walls (blue regions of positive charge both in and opposite to the movement direction, red bold arrow in Fig. 5). Figure 6(a) shows that the cation-cation distance in the movement direction is $\sim 9 \text{ \AA}$ under an EEF of $0.5 \text{ V } \text{\AA}^{-1}$, whereas the cation-cation distance in the corresponding EMFs is $\sim 5 \text{ \AA}$ in Fig. 6(b). This can be attributed to more of the butyl chains of the cations in the EMF in a curled state, allowing them to pack closer together [Fig. 4(b)]. On the other hand, a more random orientation of cations [Figs. 2(b) and 4(d)] in the movement direction under the EMFs may promote the $\pi^+-\pi^+$ stacking

of imidazolium cations,⁵² also resulting in a shorter cation-cation distance.

For anions [Figs. 6(c) and 6(d)], the channel-like structure formation is similar. Under an EEF of $0.5 \text{ V } \text{\AA}^{-1}$, most S-S vectors are perpendicular to the direction of the EEF [Fig. 2(c)], which means that the anions line up with their shorter axis aligned with the direction of motion in the channel, and meanwhile, most anions are *cis* conformers (Table I) to produce a closer distance between each other compared with the *trans* conformers, thereby resulting in a closer anion-anion distance in the channel. Under the corresponding EMF, the anions including *trans* and *cis* conformers and the S-S vectors are along the direction of the EMFs [Fig. 2(d)], resulting in a longer axis aligned with the direction of motion in the channel. Thus, as shown in Figs. 6(c) and 6(d), the anions line up within the channel at a distance of $\sim 6 \text{ \AA}$ (red regions of negative charge both in and opposite to the movement direction) under an EEF of $0.5 \text{ V } \text{\AA}^{-1}$, but the anion-anion distance increases to $\sim 7.5 \text{ \AA}$ under the corresponding EMF. The visual cage structure and channel-like structure of ILs from simulations under an EEF of $0.5 \text{ V } \text{\AA}^{-1}$ are presented in Fig. S11.

Compared with the cage structure, the cations or anions moving in their channels along the directions of the EEFs or EMFs can reduce the cation-anion clashes because the counter ions are perpendicular to the movement direction. On the other hand, the specific orientation of cations and anions in the channel-like structure (Figs. 2, 4, and S10) can also reduce cation-anion clashes. Thus, the channel-like structure can produce a lower drag for cations and anions, resulting in faster diffusion of ions in the movement direction.

Unlike strong EEFs and EMFs, the effect of the weak EEFs and EMFs on the ILs is small and the ions remain in cage structures. Thus, the distribution of the ions around cations or anions is almost the same as zero field due to the dominant effect of the IEFs of ILs (Figs. S6–S9).⁵¹

The schematic representation of the channel-like structure for the reference cation is shown in Fig. 7. The cations (red) are surrounded by a channel of counter anions (blue) at a radius of $\sim 5 \text{ \AA}$ and angles of 60° – 110° [Figs. 6(a) and 6(b)]. The statistical increase in the average density both in (0°) and opposite (180°) to the movement direction at a distance of $\sim 9 \text{ \AA}$ in Fig. 6(a) can be interpreted as the cations lining up within the channel. Likewise, if the anion is chosen as a reference ion, the statistical increase in the average density in and opposite to the movement direction means that the anions line up within the channel [Figs. 6(b) and 6(d)]. Therefore, the formation of the channel-like structure indicates that the like-charged ions are positioned along the z direction, whereas the unlike-charged ions are perpendicular to the z direction (relative to the reference ion).

B. Conformation of anions

1. Distribution of dihedral angles in anions

The EEFs and EMFs can lead to changes in the relative proportions of the *trans* and *cis* conformers of the anion. The dihedral angle C-S-S-C of the anion is a good measure of its conformation. To show quantitatively the transformation between the *trans* and *cis* conformers, the relative percentages of each conformer under different EEFs and EMFs are presented in Table I. In zero field,

the percentage of the *trans* conformer is 34.2%. The percentage of the *trans* conformer greatly decreases from 34.2% to 9.3% as the EEFs increase from 0 to $0.50 \text{ V \AA}^{-1}$, which indicates that the anions undergo a *trans*–*cis* isomerization and are all nearly transformed to *cis* conformers. For the increasing EMFs, the percentage of the *cis* and *trans* conformers remains approximately constant, fluctuating only slightly.

The increasing EEFs interact directly with the anions to favor the *cis* conformer to lead to a clear *trans*–*cis* transformation. While the movement resulting from the net force in the EMFs does broaden the distribution, it does not change the ratio of the *cis* to *trans* conformers. When the EEFs and EMFs are not applied, the numbers of *cis* conformers in zero field are about twice those of *trans* conformers and the two conformers are in dynamic equilibrium. Once the EEFs are applied to the anions, the ratio of *cis* conformers to *trans* conformers non-linearly increases to about 9.8 (Fig. S12). Unlike the EEFs, the ratio only fluctuates slightly around 1.9 to keep dynamic equilibrium as the EMFs increase. Therefore, we can conclude that the shift in the equilibrium of the *trans*–*cis* isomerization occurs as a direct result of the polarizing nature of the EEFs.

It is noted that when the strength of EMFs is greater than 0.2, it is difficult to well define the *cis* and *trans* conformers.²⁵ However,

this does not affect the changing trend of the effect of EEFs and EMFs on *cis* and *trans* conformers. It could be conceived that the results are biased by a too high translational temperature, in particular in the *z* direction, which was not thermostatted. To eliminate the effect from the thermostats on the distribution of dihedral angles, the new temperature-grouped Nosé–Hoover (tgNH) thermostats^{53,54} subtracting the COM for the groups of all cations and anions were used to simulate the same systems under an EEF of $0.50 \text{ V \AA}^{-1}$ and corresponding EMF. The results presented in Fig. S13 show consistent results with Figs. S14h and S15h. This demonstrates that the observations we made are indeed not biased by violation of the equipartition theorem since the results at the highest EEF and EMF remain the same.

As shown in Fig. 8, in zero field, the peaks at 40° and 315° represent the *cis* conformers and the peak at 180° represents the *trans* conformers. In weak EEFs and EMFs, there is no great change in the proportions of *trans* and *cis* conformers of the anions. The intensities of the peaks at 40° and 315° increase, with a corresponding decline in the peak at 180° , with increasing EEFs [Fig. 8(a)] indicating an increase in the proportion of the anions residing in the *cis* conformation. In the case of the EMFs [Fig. 8(b)], while the intensity of the peak at 180° decreases with increasing EMFs, this is not compensated for by an increase in the intensities of the peaks at 40° and 315° . It should be pointed out that the broadened peaks do not mean the emergence of new conformers other than *cis* and *trans* but are an artifact of the classical potential.

2. Relaxation of dihedral angles in anions

Based on Eq. (5), the intermittent time autocorrelation functions $C(t)$ corresponding to *trans*–*cis* isomerization based on the two dihedral angles (C–S–N–S and S–N–S–C) in different EEFs and EMFs are calculated and presented in Fig. 9. All the $C(t)$ values decay to zero as the EEFs and EMFs increase. In weak EEFs and

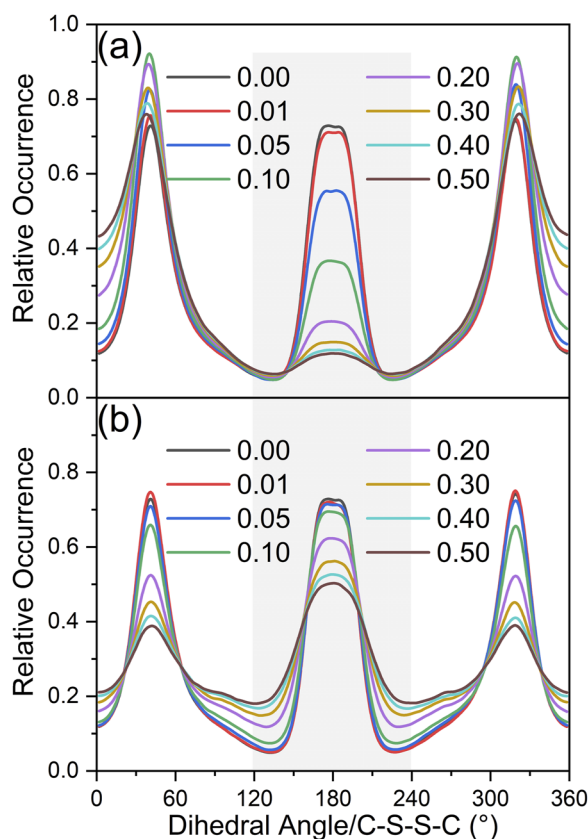


FIG. 8. Distribution of dihedral angles C–S–S–C in anions under different EEFs (a) and EMFs (b), where the shaded region from 120° to 240° represents *trans* conformers and others are *cis* conformers.

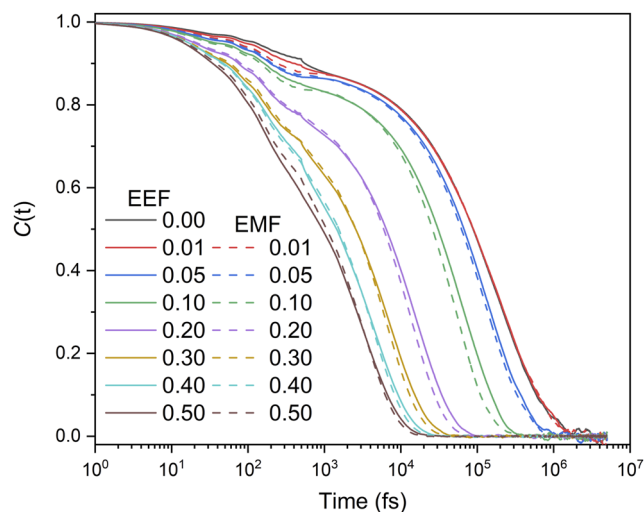


FIG. 9. Autocorrelation function $C(t)$ of dihedral angles for the *trans*–*cis* transformation in different EEFs and EMFs.

EMFs, the decay time of $C(t)$ is the same as that in zero field, and the rate of *trans*–*cis* transformation does not change.

As the EEFs and EMFs increase, the decreased decay time of $C(t)$ shows that faster *trans*–*cis* transformations occur possibly due to lower free energy activation barriers. Although $C(t)$ is almost the same in weak EEFs and EMFs, with increasing EEFs, the *trans*–*cis* transformation becomes slightly faster than that in equal EMFs. Therefore, although the share of the *cis* and *trans* conformers under EEFs and EMFs is different (Table I), the rate of *trans*–*cis* transformation is almost identical for EEFs and corresponding EMFs. Thus, in conclusion, the effects of the EEF can be separated into polarization and drag force. The shift of the equilibrium toward *cis* conformers is solely a result of the polarization, whereas the faster rate of interconversion between conformers is due to the presence of an accelerating force.

C. Charge arms of cations and anions

1. Distribution and orientation of charge arms

The calculated length and angle distribution of the charge arm (a vector from the COM to the COC of an ion) of the cations and anions are shown in Figs. 10 and 11 to probe the effect of the EEFs and EMFs on the COM and COC of the cation and anion. Compared with the COM RDFs and orientation of the cations and anions, the charge arms of the cations and anions are very sensitive to the EEFs and EMFs.

When applying the EEFs to the IL, the peak of the length distribution of the charge arm of the cation shifts to a greater length and the intensity of the peak slightly fluctuates [Fig. 10(a)], showing that increasing EEFs elongate the charge arms of the cations. Generally, the COC of the cation $[C_4C_1im]^+$ is near the COR regardless of the ion conformation, while the COM changes with the changing butyl chain (Fig. 1). With an extended butyl chain, the COM is further toward the terminal methyl group on the butyl chain, which produces a longer charge arm, while the COM shifts to above the plane of the imidazolium ring to produce the shorter charge arm

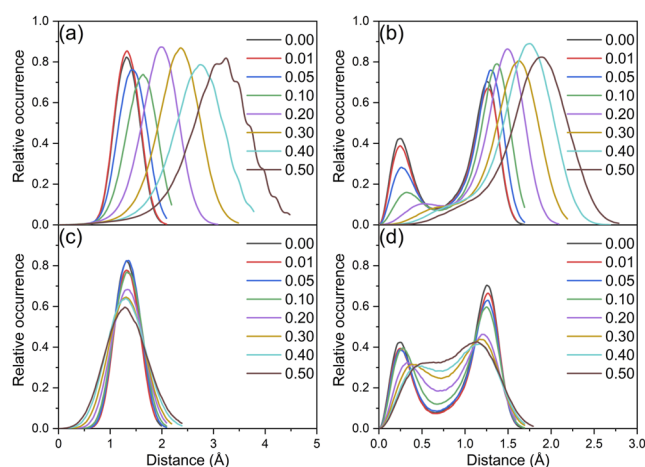


FIG. 10. Length distribution of charge arms in cations in different EEFs (a) and EMFs (c) and anions in different EEFs (b) and EMFs (d).

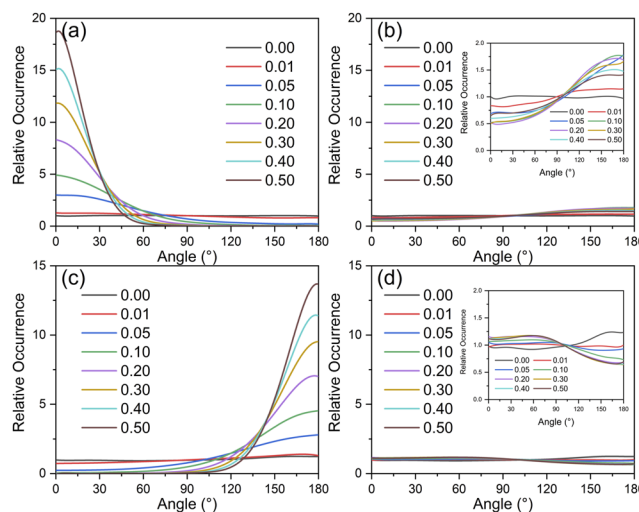


FIG. 11. Distribution of the angles between the +z direction and the charge arms in cations in different EEFs (a) and EMFs (b) and anions in different EEFs (c) and EMFs (d).

arm for a curled butyl chain. It is therefore not surprising that the effect of the EEF on the charge arms of the cations is in agreement with the distribution of the length between the COR and the terminal C.

Although the series of EMFs was designed to produce net forces equal to those of the EEFs, the peak of the charge arm does not shift as the EMFs increase, and only the intensity of the peak decreases to give a broader peak [Fig. 10(c)], which is consistent with the results in Fig. 4(b). Therefore, the extended butyl chain is a direct result of the EEF upon the COC of the cation.

The *trans* and *cis* conformers of the anion $[NTf_2]^-$ have different charge arms. The COC is always near the N atom for both conformers, but the COM is almost coincident with the COC in the *trans* conformer but shifts to closer to the center of the two CF_3 groups in the *cis* conformer, which means that the *cis* conformer presents a longer charge arm than the *trans* conformer (Fig. 1). In zero field, the two peaks of the charge arms correspond to *trans* (~ 0.3 Å) and *cis* (~ 1.3 Å) conformers [Figs. 10(b) and 10(d)]. With increasing EEFs, the peak corresponding to the *trans* conformer shifts to a greater distance and its intensity is gradually reduced until it eventually disappears. The second peak corresponding to the *cis* conformer shifts to a greater distance, and its intensity increases [Fig. 10(b)]. This is in agreement with previous analysis that the anion undergoes a *trans* to *cis* isomerization. The *cis* conformer gives the anion a larger charge arm that is preferred in the presence of strong EEFs, which is why most of the *trans* conformers are transformed to the *cis* conformer to adapt to the EEFs.²⁵ The pronounced polarization of the anion in strong EEFs is clearly visible as the peak position of the *cis* conformer shifts to charge arm values considerably longer than in the absence of an external field.

In comparison with the EEFs, the intensity of the first and second peaks in Fig. 10(d) is weakened to a lesser extent by the

weak EMFs. When the strength of the EMF is greater than 0.20, the intensities of the first and second peaks decrease, while the first peak shifts to a greater distance and the second peak shifts to a smaller distance. Thus, clear definitions of *cis* and *trans* conformers in the anion disappear due to an artifact of the classical potential. Comparison of Figs. 10(b) and 10(d) demonstrates again the polarizing effect of the EEFs, which is not present in the EMFs.

The EEFs and EMFs also alter the distribution of angles between the $+z$ direction and the charge arms in both cations and anions (Fig. 11). For weak EEFs and EMFs, the angles between the $+z$ direction and the charge arms in cations and anions remain the same as without an external field. Increasing EEFs lead to an angle of 0° between the $+z$ direction and the charge arms in cations, which means that the charge arms of the cations adjust themselves to be parallel to the applied EEFs [Fig. 11(a)]. In contrast, for increasing EMFs, the same vector angle only shows a slight increase around 180° , antiparallel to the direction of the applied EMFs [Fig. 11(b)]. For anions, the angles between the $+z$ direction and the charge arms tend to 180° under increasing EEFs, which shows that the charge arm is also parallel to the EEFs, however, in the opposite direction to the cation [Fig. 11(c)]. In EMFs, there is a slight increase between 0° and 75° [Fig. 11(d)] with increasing EMF strength, but this is not a significant change. The different conformation of the anion under EEFs and EMFs could be responsible for the different orientation of the charge arm in the anion. However, it must be pointed out that the changes in the orientation in the presence of EMFs are negligible compared to the changes in EEFs.

Although the applied EMFs cause changes in the length of the charge arms in cations and anions, the angles between the $+z$ direction and the charge arms are not strongly affected, whereas in EEFs, both the length and orientation of the charge arm are strongly affected. This phenomenon can be explained by considering the difference in where the forces from EEFs and EMFs act upon the charge arm. In EEFs, the electric field acts upon the COC, pulling (or pushing, depending on which ion) this in the direction of the electric field, while there is an inertial force upon the COM that acts to retard the motion of the ion. The competition between these two leads to an extension force on the charge arm along the electric field and a torque force on the charge arm toward the field lines. In the EMFs, both the force and inertia are incident upon the COM; therefore, there is no extension or torque upon the charge arm. Therefore, the reorientation of charge arms is a direct effect of an EEF. However, like the EEFs, the EMFs can produce the deformation and expansion of ion cages, which can promote the breakdown of ion cages and faster diffusion of ions (Sec. III D), meaning that the observed changes in the EMFs arise due to an increase in the motion of the ions.

PDFs have been constructed from the angle and length of the charge arm, which can intuitively show the influence of the EEFs and EMFs on these (Figs. S16–S19). Taking the $0.30 \text{ V } \text{\AA}^{-1}$ EEF and the corresponding EMF as examples (Fig. 12), this extension and orientation effect of the EEFs compared to that of the EMFs can be clearly seen. In the EEF, the cation and anion [Figs. 12(a) and 12(c), respectively] show a strong preference for stretched charge arms and alignment in and against the direction. However, in the EMF, there is a preference but not such a strong alignment.

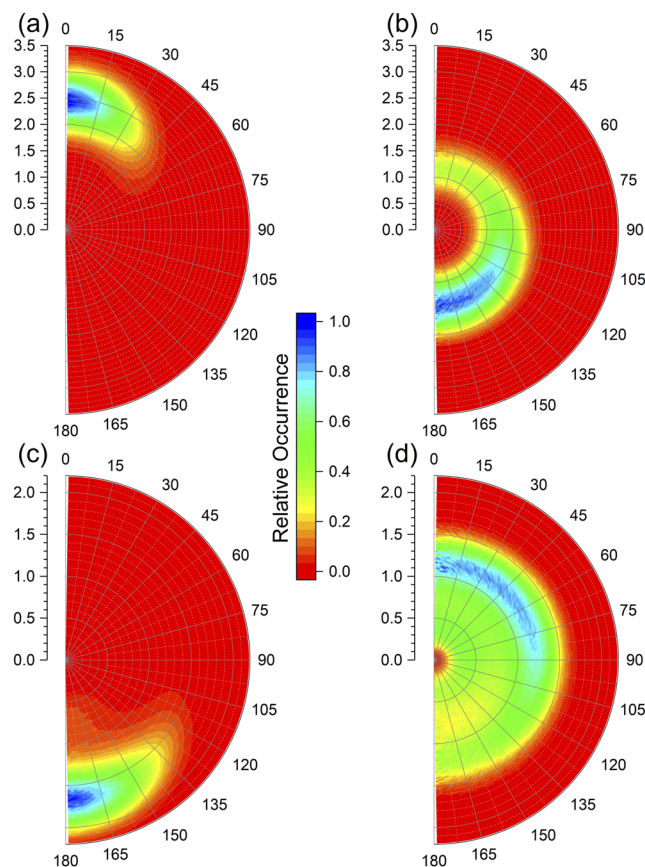


FIG. 12. PDFs of the charge arm in cations in an EEF of $0.30 \text{ V } \text{\AA}^{-1}$ (a) and equal EMF (b) and anions in an EEF of $0.30 \text{ V } \text{\AA}^{-1}$ EEF (c) and equal EMF (d). The referenced vector is the $+z$ direction, and the inner and outer rings correspond to the *trans* and *cis* conformers in anions, respectively.

2. Reorientation of charge arms

The reorientational autocorrelation functions $C_1(t)$ of the charge arms are presented in Fig. 13, calculated according to Eq. (4). In weak EEFs and EMFs, $C_1(t)$ can decay to zero and decorrelate fully, which is the same as that in zero field. For cations, the $C_1(t)$ values of the charge arms do not decay to zero when the EEF is greater than $0.05 \text{ V } \text{\AA}^{-1}$, and thus, the orientations of charge arms of the cation do not decorrelate fully. This is consistent with the results of the reorientation of the N–N vector of the cations, but the correlation of charge arms of cations is stronger than that of the N–N vector under the equal EEFs [Figs. 3(a) and 13(a)]. Under corresponding EMFs, the charge arms do not decorrelate fully, but all the $C_1(t)$ values of the charge arms decay to very close to zero, which is similar to the reorientation trend of the N–N vector [Figs. 3(a) and 13(b)].

In the case of anions, when the EEF is greater than $0.05 \text{ V } \text{\AA}^{-1}$, the decay of the $C_1(t)$ value of the charge arms cannot reach zero, which is different from the trend of the $C_1(t)$ value of the S–S vector in anions [Figs. 3(b) and 13(c)]. Although the S–S vector in anions can decorrelate fully, the charge arms do not exhibit the

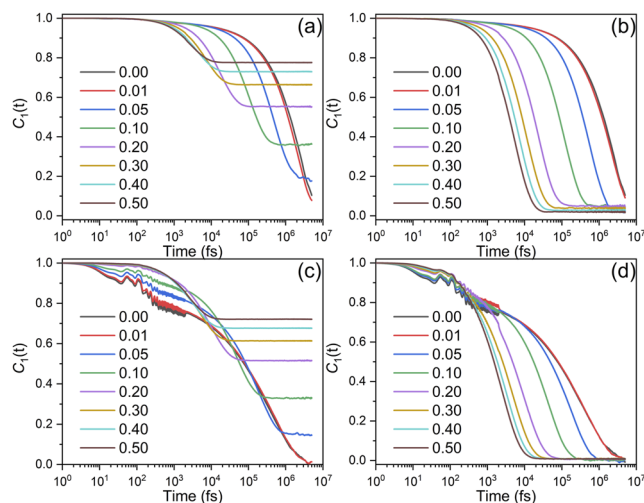


FIG. 13. Reorientational autocorrelation functions $C_1(t)$ of the charge arm in cations in different EEFs (a) and EMFs (b) and anions in different EEFs (c) and EMFs (d).

same results because even in an extremely strong EEF, where the anion must assume the *cis* conformer in the preferred orientation (Table I), it can still rotate around the z direction. Therefore, the S–S vector can decorrelate fully, while the charge arms cannot. The reason for this is that the S–S vector in the preferred orientation is perpendicular to the z direction, whereas the charge arm is parallel to the z direction. Under corresponding EMFs, the decay time of the $C_1(t)$ value of the charge arms decreases and the charge arms show faster reorientation, but all the $C_1(t)$ values can decay to zero and the charge arms of anions can decorrelate fully, which shows the same trend with the reorientation of the S–S vector [Figs. 3(b) and 13(d)].

Comparison of the $C_1(t)$ value of the charge arm in cations between the EEFs and EMFs shows that the EMFs can produce faster reorientation of the charge arm in cations, and the EEFs produce the stronger correlation of the charge arms of cations (Fig. 15 and Fig. S20). The $C_1(t)$ value of the charge arms of anions shows the same trends as the cations. These results are different from the trends of the $C_1(t)$ value of the N–N vectors of the cations and S–S vectors of the anions, which indicates the importance of the alkyl chains in cations and conformation of anions for the reorientation of the charge arms. Meanwhile, the slower reorientation in EEFs indicates that the charge arms are much more strongly coupled to the EEFs.

D. Diffusion of cations and anions

1. Diffusion parallel to the external force direction

In this work, an EEF is applied to the cations and anions of $[C_4C_{11}im][NTf_2]$ in the $+z$ direction. Thus, the net force on the cations pulls them in the $+z$ direction, and the net force on the anions pulls them in the $-z$ direction. Likewise, the mass-related force (EMF) is applied to cations in the $+z$ direction, but for anions, the EMF is applied in the $-z$ direction to make the anions experience the same net force as in the EEF. As mentioned above, we recognize

Table II. 1D effective diffusion coefficients (D_{eff}) of the cation and anion in the z direction.

Strength	$D_{\text{eff}} (\times 10^{-10} \text{ m}^2 \text{ s}^{-1})$			
	EEFs		EMFs	
	Cation	Anion	Cation	Anion
0.00	0.13	0.11	0.13	0.11
0.01	0.15	0.12	0.12	0.10
0.05	0.94	0.74	0.68	0.64
0.10	5.51	3.29	6.39	4.20
0.20	42.79	22.15	47.41	35.30
0.30	108.84	52.86	82.58	75.72
0.40	235.86	100.86	188.72	134.37
0.50 ^a	436.57	150.32	325.21	276.42

^aThe D_{eff} values of cations and anions using new temperature-grouped Nosé–Hoover (tgNH) thermostats are presented in Table SII.

that applying the forces proportional to mass in the opposite direction for the cations and anions is unphysical and that they do not occur like this in reality, but that doing this allows us to gain a deeper understanding of the effects of the EEFs and EMFs on ILs. When the external force is applied to the ILs, the ions are accelerated to move along the direction of net force.

Due to the external force, the ions drift along the force direction and the MSDs of ions parallel to the force direction present a non-linear trend with time (Figs. S21–S24). Therefore, drift correction must be considered when calculating the self-diffusion coefficient D . According to Eq. (3) and drift-corrected MSDs (Figs. S25–S28), the effective self-diffusion coefficient D_{eff} of cations and anions parallel to the net force (and thus drift) direction is calculated by fitting the slope, which should be ~ 1 in the diffusive regime in a log-log plot of MSD with respect to time,^{19,25,55} the results of which are listed in Table II.

In zero field, the D values of the cations and anions are equal to D_{eff} since there is no ion drift (random thermal motion). In weak EEFs ($< \sim 0.02 \text{ V } \text{\AA}^{-1}$) and corresponding EMFs, the EEFs and EMFs do not overcome the stronger IEFs of the IL that arise from Coulombic forces between its ions. The inherent random thermal motion of the cations and anions is not disturbed, and thus, the structure of the IL is almost unaffected (Figs. S5–S9). The cage structure of the IL does not expand or deform, and the movement of both cations and anions is subject to the IEFs of the IL (in the “cage/bound” region),^{19,25,56} producing the very small and equal drift velocity for EEFs and EMFs. Therefore, the D_{eff} values of the cations and anions are approximately equal to D in zero field despite exhibiting a very small drift velocity (Fig. 14 and Table SIII).

With the further increase in EEFs and EMFs, the D_{eff} values of the cations and anions are greater than D in zero field. The increasing EEFs and EMFs change the bulk structure of the IL (Fig. S4) and have an impact on its ion cages, resulting in the expansion and deformation of the ion cages. The expansion and deformation of the ion cages can weaken the cage potential well; thus, the ions can more easily overcome the activation energy to escape the ion cage and enter the “jump/free” region.^{19,25,56} In the “jump/free” region,

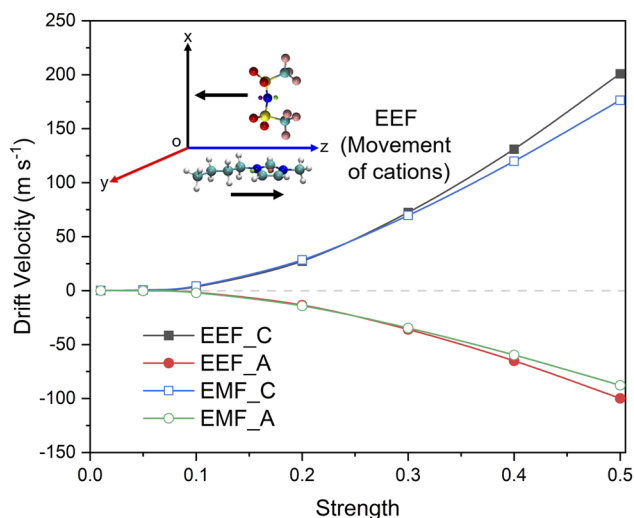


FIG. 14. Drift velocities of cations and anions in the z direction under different EEFs and EMFs, where the inset shows the movement of the anion (*cis* conformer) and cation (stretched alkyl chain) along the force direction. The drift velocities of cations and anions under an EEF of $0.50 \text{ V } \text{\AA}^{-1}$ and the corresponding EMF using tgNH thermostats are presented in Table SII.

the ions are no longer bound by any species in the IL and diffuse freely through the IL (“free” ions in Fig. 15), thereby producing a net drift. Hence, the D_{eff} values of the cations and anions parallel to the direction of the force increase as the EEFs and EMFs further increase.

When the increasing EEFs and EMFs are smaller than the IEFs of the IL, the expansion and deformation of the ion cages are subject to the synergy of the EEFs/EMFs and IEFs. Stronger EEFs and EMFs can cause greater deformation and expansion of the ion cage, which results in faster diffusion. Table II shows that the D_{eff} value of the cations and anions has an exceptional increase (~ 8 times) as the EEF increases from 0.10 to $0.20 \text{ V } \text{\AA}^{-1}$.

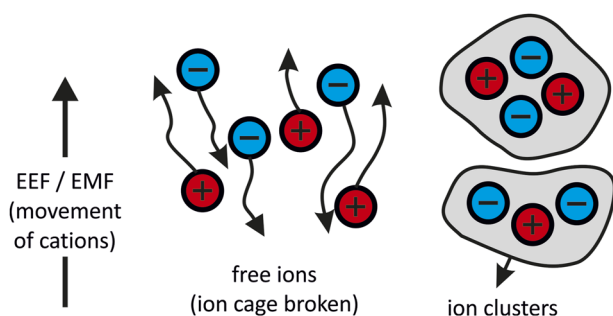


FIG. 15. Schematic representation of the difference between individually moving free ions (on the left, longer arrows indicate fast movement) and clustered ions (on the right). The clusters can be both neutral (top right corner) and charged (bottom right corner).

When the EEF increases beyond $0.20 \text{ V } \text{\AA}^{-1}$, D_{eff} only increases by ~ 2 times as the EEF increases by $0.1 \text{ V } \text{\AA}^{-1}$. There is no doubt that the breakdown of the ion cages and ion clusters contributes part of the increase in diffusion, but another reason may be the transformation of the structure of the IL from the cage structure to the channel-like structure (Figs. 5–7). Compared with the cage structure, the channel-like structure can provide more space to produce fewer clashes and less friction between ions. This is beneficial to the movement of ions, leading to faster diffusion and greater drift velocity. This large increase in the diffusive character of the ions may also be due to the release of “free” ions from ion clusters as a consequence of the breakdown of ion cages (Fig. 15) or a combination of both effects.

In Table II, the D_{eff} value of cations under the EEF is greater than that in the corresponding EMF, whereas the D_{eff} value of anions presents an opposite trend being slower in the EEF than the corresponding EMF. As discussed in Sec. III A 1, in the EEFs, the cation orients itself with the imidazole group parallel to the EEF, with the methyl group leading and the butyl chain extended behind it (inset in Fig. 14). This perfect combination of effects leads to a small cross section in the direction of diffusion for the cation (lower friction), which allows the cations to diffuse faster, whether it is a deformed and expanded cage structure or a channel-like structure. For the anions, most of these are in *cis* conformers (Fig. 8 and Table I) in EEFs and the alignment of the charge arm with the direction of the field leads to a large cross section in the direction of flow (greater friction), resulting in slower diffusion. Therefore, the EEF stretching the butyl chain and rotating the charge arm parallel to the electric field puts the cation into a favorable hydrodynamic conformation and orientation, which allows it to diffuse quickly, whereas for the anion, the EEF causes a *trans-cis* isomerization and rotation of the charge arm, which puts it into a less hydrodynamically favored conformation and orientation compared to the EMF. We speculate that the neutral and charged ion clusters (Fig. 15) may also contribute to the difference in the D_{eff} value of cations and anions under EEFs and EMFs, but it is very difficult to accurately clarify the effect of ion clusters on D_{eff} .^{57,58}

To confirm the D_{eff} results obtained in this work, the new tgNH thermostats^{53,54} that subtract the COM of the particles in the system were applied in all three dimensions to simulate the same systems in an EEF and an EMF of $0.50 \text{ V } \text{\AA}^{-1}$. The results (Table SII) are consistent with data in Table II. This shows that even when applying a thermostat in the z direction, the diffusion of cations still significantly increases, which indicates that the changes in dynamics presented here are free from unphysical thermal motion or artifacts arising from the violation of equipartition. For anions, this is not the case for the tgNH thermostat, so it is likely just an artifact of either the missing thermalization in the z direction or the violation of equipartition.

Figure 14 shows that the drift velocity changes linearly in weak EEFs, but the relationship between the drift velocity and EEF/EMF breaks down as the EEF/EMF further increases, which is consistent with previous work.^{19,25} The drift velocity of the cation in strong EEFs is greater than that in the corresponding EMF, which can be attributed to the hydrodynamically favored conformation of cations. The drift velocity of the anion in strong EEFs also presents a greater value compared with the corresponding EMFs, which is different

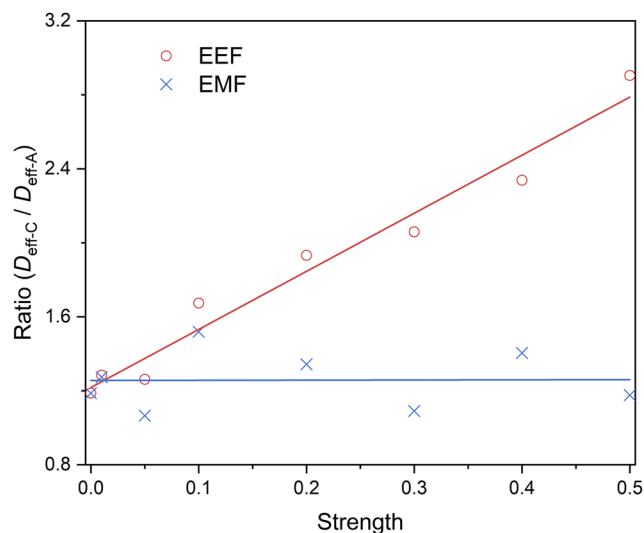


FIG. 16. Ratio of the self-diffusion coefficients of cations to those of anions in the z direction under different EEFs and EMFs, where the solid line represents linear fitting.

from the results of D_{eff} of the anion under EEFs and EMFs. One reason for this difference is the different configurations of anions under EEFs and EMFs, and the other reason we speculate is different behaviors of charged ion clusters (Fig. 15) under EEFs and EMFs.

The increase in the D_{eff} value of cations is greater than that of the anions with increasing EEFs, while for increasing EMFs, the increase in the D_{eff} value of anions and cations is approximately equal (Table II and Fig. 16). This appears to arise from the conformation and orientation in the EEFs, making it less hydrodynamic, but this is not sufficiently different from the change in the cation

conformation and orientation in the EEFs, making it more hydrodynamic. The change in the anion random orientation in the EMFs leads to a change in the observed ratios.

2. Diffusion perpendicular to the external force direction

To observe the effect of the EEFs and EMFs on the D value perpendicular to the external force direction (x and y directions), the D values of the cations and anions are calculated and listed in Table III according to Eq. (2) and corresponding MSDs (Figs. S28–S39). In weak EEFs and EMFs, like the D_{eff} values, the D values of cations and anions perpendicular to the external force direction are approximately equal to D in zero field. As the EEF and EMF further increase, the D value increases and is greater than that in zero field. This indicates that although the applied EEFs and EMFs produce no forces perpendicular to the external force direction, there is still an effect on the D value. However, the D values of the cations and anions perpendicular to the external force direction are slower than the D_{eff} values of cations and anions parallel to the external force. Hence, the increased diffusion perpendicular to the external force can be attributed to the expansion and deformation of ion cages, which is caused by both the applied EEFs and EMFs.¹⁹

The data presented in Table III show that there are differences in the D value of cations and anions under the EEFs and EMFs perpendicular to the external force direction. The D values of anions under the EEFs are lower than those under the EMFs, which is the opposite trend to the D_{eff} values of anions parallel to the external force direction, whereas for the cation, there are only slight differences. The calculated mean displacement of cations and anions indicates that there is no ion drift perpendicular to the external force direction (Figs. S40 and S41); hence, these differences are derived from the different structures of anions and cations under EEFs and EMFs. Compared with EMFs, the specific orientation of cations and anions under the EEF can increase the retardation of ions perpendicular to the external force direction. Thus, the D value

TABLE III. Self-diffusion coefficients (D) of the cation and anion in the x and y directions.

Strength	$D (\times 10^{-10} \text{ m}^2 \text{ s}^{-1})$											
	EEFs						EMFs					
	Cation			Anion			Cation			Anion		
	x	y	xy	x	y	xy	x	y	xy	x	y	xy
0.00	0.12	0.12	0.12	0.10	0.11	0.11	0.12	0.12	0.12	0.10	0.11	0.11
0.01	0.18	0.14	0.16	0.14	0.13	0.14	0.16	0.15	0.15	0.15	0.10	0.13
0.05	0.66	0.83	0.75	0.56	0.67	0.61	0.62	0.74	0.68	0.47	0.54	0.51
0.10	3.32	3.53	3.43	2.07	2.47	2.27	2.99	3.83	3.41	2.72	2.76	2.74
0.20	19.26	19.97	19.62	16.89	15.99	16.44	21.34	23.47	22.40	20.24	17.85	19.05
0.30	52.01	48.51	50.26	31.21	26.83	29.02	52.66	44.11	48.39	44.05	38.51	41.28
0.40	77.09	71.66	74.37	49.06	38.25	43.66	94.82	81.39	88.10	52.04	64.21	58.12
0.50 ^a	92.07	100.65	96.36	68.01	73.22	70.61	101.50	108.41	104.96	79.20	95.47	87.34

^aThe D values of cations and anions in x and y directions using tgNH thermostats are presented in Table S3.

of cations and anions under the EEF is smaller than that under the EMF.

IV. CONCLUSIONS

In summary, the structures and properties of the IL $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ under both EEFs and EMFs have been investigated by MD simulations employing a polarizable force field. EEFs were varied from 0 to $0.50 \text{ V } \text{\AA}^{-1}$, and the corresponding EMFs were constructed so as to produce equal net forces on the cations and anions. These external forces were applied to the IL $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ to probe the change in the static structures and dynamic properties of both cations and anions.

Weak EEFs ($< \sim 0.02 \text{ V } \text{\AA}^{-1}$) and corresponding EMFs have almost no effect on the static structures and dynamic properties of the ions compared to the case in zero field. Increasing the EEFs and EMFs above this threshold leads to the change in the structures and properties of the ILs. The ion cages expand and deform to decrease the energy for the ions to escape the cages ("cage/bound" region) and enter the "jump/free" region, producing greater diffusion and drift. Further breakdown of ion cages promotes a transformation of the ILs from a cage structure to a channel-like structure, which leads to a reduction in the collisions of ions and reduces drag for ions in the channel, leading to faster diffusion in the direction of the applied force. Hence, the self-diffusion of ions in the force direction is faster than that in other directions due to the anisotropy of expansion and deformation of ion cages in different directions.

Although the EEF and EMF produce equal net forces on the ions, the imidazolium rings and charge arms of the cations reorient parallel to the force direction with alkyl chains also extending under the EEF. This combination of effects leads to a hydrodynamically favored conformation of cations in the direction of diffusion, producing faster diffusion compared with the EMF. For anions, the EEF reorients the charge arms parallel to the force direction and causes a *trans-cis* isomerization. This combination leads to the anion presenting its less hydrodynamically favored profile to the direction of motion so that it does not increase its diffusion to the same extent as seen for cations in the same EEF. In the EMF, these conformational and orientational effects do not occur in the same way so that the increases in diffusion with the increasing EMF are approximately equal for both cations and anions.

From the results of applying both EEFs and EMFs, we can see that the application of the forces leads to the motion of the ions, and with stronger forces, the breakdown of the ion cage structure, in turn, leads to even greater diffusion of the ions. In the EMFs, this is accompanied by a small degree of hydrodynamically driven reorientation of the ions. In the EEFs, it is the differential forces on individual atoms of the ions that lead to direct torsional forces and a much greater degree of reorientation of the ions and alignment of the charge arms of the ions with the EEF, which, for the cation, presents the same cross section (albeit turned 180°) as the hydrodynamically favored orientation, but for the anion, it is opposite (i.e., at 90°) to this.

Overall, the results presented in this work deepen the understanding of the static structures and dynamic properties of ILs under external fields and begin to unravel the specific effects that an EEF has upon ions in an IL.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the strength of EEFs and EMFs, the drift velocity of the cation and anion in the z direction, the effective diffusion coefficients of the cation and anion in the z direction, the self-diffusion coefficients of the cation and anion in the x and y directions, the drift velocity of the cation and anion in the z direction under an EEF of $0.50 \text{ V } \text{\AA}^{-1}$ and the corresponding EMF using temperature-grouped Nosé–Hoover thermostats, the simulated and experimental densities of $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ at 300 K, the (drift-corrected) MSD of the cation and anion in z , x , and y directions, the COM radial distribution functions of cations and anions, cations and cations, and anions and anions, the mean displacement of the cations and anions in x and y directions, the PDFs for the charge arm in cations and anions, the 2D distribution of dihedral angles, the PDFs for the ions around the cations and anions, the cage structure and channel-like structure under an EEF of $0.50 \text{ V } \text{\AA}^{-1}$, the ratio of *cis* conformers to *trans* conformers in anions under different EEFs and EMFs, the distribution of the angles between the z direction and the vector from the center of the S–S line to the N atom in the anion under different EEFs and EMFs, the reorientational correlation functions of the charge arms, the combined distribution functions for simulations of the strongest EEF and EMF, and the input and log files of the prealpha tool.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

REFERENCES

- ¹T. Welton, *Biophys. Rev.* **10**, 691 (2018).
- ²S. Zhang *et al.*, *Chem. Rev.* **117**, 6755 (2017).
- ³N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.* **37**, 123 (2008).
- ⁴X. Hu *et al.*, *Soft Matter* **7**, 5941 (2011).
- ⁵W. Routray and V. Orsat, *Food Bioprocess Technol.* **5**, 409 (2012).

- ⁶R. Martínez-Palou, *Mol. Diversity* **14**, 3 (2010).
- ⁷Y. Guan *et al.*, *J. Phys. Chem. C* **123**, 6981 (2019).
- ⁸Y. Guan *et al.*, *J. Mater. Chem. A* **6**, 11941 (2018).
- ⁹X. He *et al.*, *J. Phys. D: Appl. Phys.* **50**, 465002 (2017).
- ¹⁰Q. Shao *et al.*, *J. Chem. Phys.* **144**, 124703 (2016).
- ¹¹S. V. Muginova *et al.*, *Anal. Sci.* **33**, 261 (2017).
- ¹²D. S. Silvester, *Analyst* **136**, 4871 (2011).
- ¹³Y.-L. Wang *et al.*, *Chem. Rev.* **120**, 5798 (2020).
- ¹⁴S. Millefiorini *et al.*, *J. Am. Chem. Soc.* **128**, 3098 (2006).
- ¹⁵S. Bi *et al.*, *Nat. Mater.* **19**, 552 (2020).
- ¹⁶R. Hayes, G. G. Warr, and R. Atkin, *Chem. Rev.* **115**, 6357 (2015).
- ¹⁷S. Perkin *et al.*, *Chem. Commun.* **47**, 6572 (2011).
- ¹⁸Y. Wang, *J. Phys. Chem. B* **113**, 11058 (2009).
- ¹⁹R. Shi and Y. Wang, *J. Phys. Chem. B* **117**, 5102 (2013).
- ²⁰X. Jiang, *J. Phys. Chem. C* **124**, 5817 (2020).
- ²¹J. W. Daily and M. M. Micci, *J. Chem. Phys.* **131**, 094501 (2009).
- ²²Y. Zhao *et al.*, *Mol. Simul.* **38**, 172 (2012).
- ²³M. Sha *et al.*, *Soft Matter* **7**, 4228 (2011).
- ²⁴M. M. Ahn *et al.*, *J. Mol. Liq.* **244**, 117 (2017).
- ²⁵R. Clark *et al.*, *J. Chem. Phys.* **151**, 164503 (2019).
- ²⁶N. J. English and D. A. Mooney, *Phys. Chem. Chem. Phys.* **11**, 9370 (2009).
- ²⁷N. J. English, D. A. Mooney, and S. O'Brien, *Mol. Phys.* **109**, 625 (2011).
- ²⁸S. Aparicio, M. Atilhan, and N. Pala, *J. Chem. Phys.* **139**, 224502 (2013).
- ²⁹D. Bedrov *et al.*, *Chem. Rev.* **119**, 7940 (2019).
- ³⁰N. J. English and C. J. Waldron, *Phys. Chem. Chem. Phys.* **17**, 12407 (2015).
- ³¹J. N. Canongia Lopes, J. Deschamps, and A. A. H. Pádua, *J. Phys. Chem. B* **108**, 2038 (2004).
- ³²J. N. Canongia Lopes, J. Deschamps, and A. A. H. Pádua, *J. Phys. Chem. B* **108**, 11250 (2004).
- ³³J. N. Canongia Lopes and A. A. H. Pádua, *J. Phys. Chem. B* **108**, 16893 (2004).
- ³⁴M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, 2nd ed. (Oxford University Press, 2017).
- ³⁵A. Dequidt, J. Devémy, and A. A. H. Pádua, *J. Chem. Inf. Model.* **56**, 260 (2016).
- ³⁶C. E. S. Bernardes *et al.*, *Phys. Chem. Chem. Phys.* **18**, 1665 (2016).
- ³⁷G. Lamoureux and B. Roux, *J. Chem. Phys.* **119**, 3025 (2003).
- ³⁸B. T. Thole, *Chem. Phys.* **59**, 341 (1981).
- ³⁹K. Goloviznina *et al.*, *J. Chem. Theory Comput.* **15**, 5858 (2019).
- ⁴⁰P. T. van Duijnen and M. Swart, *J. Phys. Chem. A* **102**, 2399 (1998).
- ⁴¹S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).
- ⁴²A. Padua, *agiliopadua/fftool*: Update, 2019.
- ⁴³L. Martínez *et al.*, *J. Comput. Chem.* **30**, 2157 (2009).
- ⁴⁴J. Petravic and J. Delhommelle, *J. Chem. Phys.* **118**, 7477 (2003).
- ⁴⁵M. Brehm *et al.*, *J. Chem. Phys.* **152**, 164105 (2020).
- ⁴⁶W. Humphrey, A. Dalke, and K. Schulten, *J. Mol. Graphics* **14**, 33 (1996).
- ⁴⁷P. Atkins, J. De Paula, and J. Keeler, *Atkins' Physical Chemistry*, 11th ed. (Oxford University Press, Oxford, UK, 2017).
- ⁴⁸H. Li *et al.*, *J. Chem. Phys.* **129**, 124507 (2008).
- ⁴⁹J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids: With Applications to Soft Matter*, 4th ed. (Academic Press, 2013).
- ⁵⁰T. Endo *et al.*, *J. Phys. Chem. B* **120**, 10336 (2016).
- ⁵¹S. Zhang *et al.*, *Chem. - Eur. J.* **18**, 11904 (2012).
- ⁵²F. Tang *et al.*, *Phys. Chem. Chem. Phys.* **19**, 2850 (2017).
- ⁵³K. Goloviznina *et al.*, *J. Chem. Theory Comput.* **17**, 1606 (2021).
- ⁵⁴C. Y. Son *et al.*, *J. Phys. Chem. Lett.* **10**, 7523 (2019).
- ⁵⁵E. J. Maginn *et al.*, *Living J. Comput. Mol. Sci.* **1**, 6324 (2018).
- ⁵⁶G. Feng *et al.*, *Phys. Rev. X* **9**, 021024 (2019).
- ⁵⁷A. Strate *et al.*, *Phys. Chem. Chem. Phys.* **22**, 6861 (2020).
- ⁵⁸S. Chen *et al.*, *Phys. Chem. Chem. Phys.* **16**, 5893 (2014).