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a molecular dynamics study

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Ionic Liquids in external electric and electromagnetic fields: a molecular

dynamics study

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Abstract

The non-thermal effects of external electric and electromagnetic fields in the microwave to far-infrared frequency range and at (r.m.s.) electric field intensities of 10^{-3} to 0.25 V/$\text{Å}_{r.m.s.}$ on neat salts of 1-3-dimethyl-imidazolium hexafluorophosphate ([dmim][PF$_6$]) and 1-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF$_6$]) have been investigated by means of non-equilibrium molecular dynamics simulation. Significant alterations in molecular mobility were found vis-à-vis zero-field conditions. Using Green-Kubo and transient time correlation function (TTCF) analysis, the electrical conductivity of these ionic liquids has been estimated. Results indicate that ionic liquids respond most significantly to frequencies much lower than those of smaller polar solvents such as water, although the mechanism of field response is almost exclusively translational.

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Introduction

Ionic liquids (here referred to as ionic liquids, or ILs) are organic salts in the liquid state, which offer considerable possibilities in the chemical process and allied industries due to their unique physical and chemical properties. They are excellent solvents for a wide variety of organic and inorganic substances, often bringing together otherwise immiscible reagents and, in many cases, maintaining or enhancing reaction rates, extents of reaction and selectivities. In addition, ILs are essentially non-volatile and provide an opportunity for replacing traditional organic solvents, thereby potentially reducing the emissions and energy requirements of unit operations used for separations. Those ILs which are liquids at room temperature ('room temperature' ILs), are of particular interest since they provide for more cost-effective handling and processing. Therefore, ILs are regarded as very promising 'green' solvents and, as such, the impetus for their introduction into existing processes is significant.[1,2]

From the earliest studies showing the utility of microwave fields in synthesis,[3,4] there has been significant growth in their application to a wide variety of reactions and processes, accelerated by advances in microwave technology.[5] For the case of ILs, their ionic nature, and, to a lesser extent, dipolar polarization, make them ideal candidates for use with microwave technology. One of the earliest investigations on microwaves in IL synthesis was in the solvent-free production of a series of 1-alkyl-3-methyl-imidazolium (AMIM) halides, by the reaction of 1-methylimidazole with alkyl halides/terminal dihalides using a household microwave oven.[6] In this work, improvements in reaction rates were observed. To date, the utility of microwave fields has been exploited in three areas of synthetic chemistry, namely in the synthesis of ILs themselves, as already mentioned, as an aid for heating dipolar substances and

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when ILs are used as solvents and reactants and as an aid in the processing of reactions carried out in the presence of ILs.[7]

Given the increasing importance of ILs, the use of electric and electromagnetic (e/m) fields to exploit their physical and catalytic properties further constitutes a valuable avenue of research. ILs possess important properties making them amenable to electric and e/m field processing, in particular their ionic nature, which offers many intriguing questions and potential applications. Enhancing the mass and heat transfer characteristics of ILs, and of other solvents in ILs, by e/m field exposure would result in smaller reactor volumes and improved, less expensive distillation and liquid-liquid extraction systems. Similarly, the use of microwave irradiation to improve the synthesis efficiency of ILs themselves, and for organic reactions therein, could potentially offer a means of process intensification in the chemical industry.[1] This would serve to maximize the use of resources by their efficient use, necessary for the long-term future of chemical and allied sectors.

This work builds on our earlier non-equilibrium molecular dynamics (MD) studies of the behavior of binary mixtures of water and ILs in external e/m fields.[8, 9] In those cases, the presence of water molecules led to the consideration of field-induced dipolar alignment as an important consideration in characterizing the response to the fields. In this work, we have chosen to investigate similar, imidazolium-based ionic liquids, specifically hexafluorophosphate ($[PF_6]^-$) salts of 1-3-dimethyl-imidazolium and 1-butyl-3-methyl-imidazolium - $[dmim]^+$ and $[bmim]^+$, respectively. This study seeks to study in more detail the molecular mechanisms of pure IL species' behavior in electric and e/m field conditions, which is dominated by induced translational motion for neat IL systems, given the absence of strongly dipolar species such as water. This work examines non-thermal field effects on IL properties, especially those

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determined by translational response, such as electrical conductivity and the variation of the *de facto* self-diffusivity with frequency, as well as the comparative field response of anions and cations, with simulations conducted over wide range of frequencies (2.45 GHz to 200 GHz) and e/m field intensities (10^{-3} to 0.25 V/$\text{Å}_{\text{r.m.s.}}$). Using Green-Kubo and transient time correlation function (TTCF) analysis, the electrical conductivity of these ionic liquids has been estimated, at lower applied electric field intensities than possible in previous molecular simulation studies (10^{-3}). A goal of this study is to provide insights into the optimization of the use of electric and e/m fields in processes involving ILs.

Methodology

There exist a large number of force-fields developed especially for ILs, where the trend has been toward a generic force-field model adaptable to a large number of possible IL variants.[10-12] In this work, we have employed the well documented and tested force-field of Lopes et al. for imidazolium salts,[10] which itself is based on the AMBER/OPLS[13, 14] force-fields, with the general form given by

$$E_{\text{tot}} = \sum_{i=1}^{N-1} \sum_{j>i}^{N} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{r_{ij}} \right\} +$$
$$\sum_{bonds} k_r \left(r - r_o \right)^2 + \sum_{angles} k_\theta \left(\theta - \theta_o \right)^2 + \tag{1}$$
$$\sum_{dihedrals} k \left[1 + \cos\left(n\phi - \delta \right) \right] + \sum_{improper} k_\varphi \left(\varphi - \varphi_o \right)^2$$

More recent work[15] has attempted to refine the force-field of Lopes et al.,[10] specifically the non-bonded contributions, in order to replicate more closely hydrogen bonding between cations and anions, as well as transport, including self-diffusion, coefficients. The most notable differences to the force-field of Lopes *et al.* is the inclusion of a reduced charge total on each ion (=/- 0.8*e*). Despite these differences,

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we have utilized the force-field of Lopes *et al*[10] for which we expect no qualitative

differences in behavior under the external fields applied in this work.

All simulations were conducted for 216 ion pairs, which for $[PF_6]^-$ salts of $[dmim]^+$

and $[bmim]^+$ systems corresponded to 4968 and 6912 ions respectively. van der

Waals interactions were treated by the twin range method,[16] with cut-off radii of 12

and 15Å, respectively. The smooth particle mesh Ewald method[17] was used to handle

long-range electrostatics. The screening parameters and number of wave vectors were

chosen so as to ensure that the relative error in the Ewald energy was less than 1×10^{-6};

in practice this lead to the product of the cut-off distance and screening parameter to

be approximately 3.2.

Initial structures were generated first by constructing a diamond lattice arrangement

of each IL, followed by relaxation under NPT conditions at 450K and 1 bar with

Melchionna's modified form of the Hoover barostat using isotropic cell fluctuations,[18]

for a period of up to 2 ns depending on the IL, using time-constants of 1 ps and 2 ps

for the thermal and pressure reservoirs, respectively. For all production runs (post

NPT relaxation), we employed the configurational thermostat of Braga and Travis[19, 20]

which has been applied recently to the calculation of conductivity within the TTCF

formalism.[21] We have found that this configurational-based thermostat gives rise

(with regard to the system under investigation here) to a conductivity that is 15%

higher than that determined using a kinetic-based Nosé-Hoover thermostat. This

arises because, in these non-equilibrium simulations, kinetic-based thermostats are

unable to distinguish between thermal motion and that flow which is induced by the

applied field (flow of anions and cations).

As the core purpose of this paper is to assess the influence of electric and e/m fields

(with varying field frequency and r.m.s. field intensity) on IL behavior, primarily in

terms of properties governed by translational response, it was decided to conduct all

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simulations at a single temperature. This temperature was chosen to be 450 K to ensure that reasonable sampling could be achieved within feasible simulation times of up to 5 ns. In addition, the choice of the cations and anion used in this work was based on the availability of well-tuned force-field models. Our goal is not an exhaustive study of electric and e/m field response over a wide range of temperatures and different types of IL cation and anion pairs, but rather a study of response of particular ILs to electric fields and to a spectrum of e/m field frequencies and intensities which may provide an insight into the behavior of a broader range of ionic liquid types. For example, a worthwhile study could consider the new ionic liquid cations and/or anions, including 'FAP' (tris(perfluoroalkyl)trifluorophosphate).[22,19][19]

Uniform electric and e/m fields were applied with the electric and magnetic components **E** and **B** in the *z*- and *y*- directions, *i.e.*, $\mathbf{E}(t) = E_{max}\cos(\omega t)\mathbf{k}$ or $\mathbf{E}(t) = \mathrm{E}_0\,\mathbf{k}$ (static case) and $\mathbf{B}(t) = B_{max}\cos(\omega t)\mathbf{j}$, or $\mathbf{B}(t) = 0\,\mathbf{k}$ for a static electric field[23, 24][20, 21]

$$m_i\ddot{\mathbf{r}}_i = \mathbf{f}_i + q_i\mathbf{E}(t) + q_i\mathbf{v}_i \times \mathbf{B}(t) \tag{2}$$

where q_i denotes the charge and $\mathbf{f}_i$ the force on site *i* due to the potential. Classical mechanics was considered valid to model the electric and e/m field absorption, since the experimental spectrum of ionic liquids is continuous. Fields of frequency $\nu =$ 2.45 to 200 GHz and of r.m.s. intensity from $E_{rms} = 0.001$ to 0.25 V/Å$_{r.m.s.}$ were studied, along with static electric fields of 0.001 V/Å. It has been found from equilibrium MD simulation that electric field intensities in condensed water phases are in the range of around 1.5 to 2.5 V/Å,[24][21] and the lowest field intensities investigated in this work is two orders of magnitude lower than those of previous MD studies of IL-water mixtures in e/m fields[8, 9] and close to the intensities available in experimental and industrial magnetrons.[25, 26][22, 23] In addition, the electric field force, qE, acting on the ions' centers-of-mass is ~0.1 % of the typical force magnitudes

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acting on them due to interactions with all other ions (determined from comparison of qE with center-of-mass forces in zero-field simulations) for the lowest field intensity applied (0.001 V/Å$_{r.m.s.}$). Meanwhile, qE (from eqn. 2) scales linearly with intensity, so that a 0.05 to 0.1 V/Å$_{r.m.s.}$ field corresponds to an electric force of between 5 and 10% of typical cohesive forces, and for the purpose of this work the criterion used for identification of the linear response régime was observed to be the point at which the applied field intensity resulted in an induced flow with a characteristic Reynold's number of <0.1. This is in line with previous simulation studies of non-thermal effects of static electric fields on molten NaCl,[27][24]. 2.45 GHz corresponds to the frequency of commercially available microwave reactors.[25, 26][22, 23] Field frequencies below this pose excessive computational demands since multiple field cycles are require to obtain statistically meaningful results. For example, a field of frequency of 2.45 GHz has a period of ~408 ps, requiring 3-5 ns of simulation to generate satisfactory statistics for results (cf. Results).

The external fields were applied in conjunction with a Nosé-Hoover NVT coupling with a relaxation time of 1 ps,[16] and are referred to as non-equilibrium NVT (NNVT) simulations.[23, 28][20, 25] These were performed in order to isolate athermal effects as much as possible from thermal effects. The electric (and e/m) fields induce anisotropic translational motion of the anions and cations, *i.e.*, in opposite directions (at any instant in time, cf. eqn. 1), but there is no net mass flow, so the temperature fixed by the Nosé-Hoover thermostat assumes that thermal motion is defined with respect to the overall center-of-mass velocity. A series of simulations were carried out at 450 K for up to 5 ns in fields of frequency 2.45, 10, 20 50, 100, 200 GHz with r.m.s. intensities from 0.001 to 0.25 V/Å$_{r.m.s.}$, as well as static fields with intensity of 0.001 V/Å, using the relaxed systems as starting configurations. Longer simulation times were required for lower field frequencies to ensure that an adequate number of

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field cycles for statistical sampling. These simulations were also of sufficient duration to investigate e/m field effects, as gauged by the development of Fickian diffusion within this time period. A reasonable number of cycles of the field can also be applied in this time (with a maximum period of ~408 ps for the 2.45 GHz field). Such a broad range of frequencies were chosen because the expected frequency response are different to that of water, as confirmed in our previous studies of IL-water mixtures: ILs respond to lower frequencies, owing to translational response and their greater mass vis-à-vis water molecules.[24][21] Equilibrium, zero-field simulations were also carried out for each system for 5 ns, as a basis for comparison to assessing the effects of the various field conditions.

For each simulation, the cation and anion self-diffusion coefficients were evaluated using the Einstein relation, along with the total system dipole (z-component), and percentage dipole alignment, which will be defined below. Also, the electrical conductivites, arising from translational motion in response to the fields, were estimated in the static fields using the TTCF approach,[29, 30][26, 27] and verified with respect to zero-field Green-Kubo analysis.[27, 31][24, 28]

Analysis

In order to rationalize the results of these simulations, it is useful to consider in the first instance the effect of electric and e/m fields on charged, dipolar bodies from a mechanistic perspective, although dielectric relaxation spectroscopy reveals that the response is essentially due to Ohmic loss attributable to translational motion in response to the applied field.[32][29] To confirm this in this study, it is however of use to define the dipolar alignment. The overall dipole moment $\mathbf{P}_s$ over a set N_s ions may be

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defined by summing the individual dipoles (defined with respect to their centers-of-mass)

$$\mathbf{P}_s = \sum_{i=1}^{N_s} \mathbf{p}_i \tag{3}$$

and the z-component of $\mathbf{P}_s$ vis-à-vis the overall magnitude taken as indicative of alignment. This definition was chosen because of the lack of dipole moment for $[PF_6]^-$ (as a result of individual dipole moments defined according to the ions' centre of mass) which leads to its purely translation (Ohmic) response to the applied fields. In addition, there is no centrally defined origin, being purely local for each ion, coinciding to each ion's centre of mass.

The proportional maximal alignment of a species, which we shall denote as α, may be determined from

$$\alpha = \left\langle \max |\mathbf{P}_s|_z \right\rangle / N_s \left\langle p_{0,s_z} \right\rangle \quad \alpha = \left\langle \max |\mathbf{P}_s| \right\rangle / N_s \left\langle p_{0,s} \right\rangle \tag{4}$$

i.e., as the time-average of the species' z-dipole extrema along + and – directions as a proportion of the maximum theoretical z-component alignment (for a sufficiently large number of sampled complete field cycles) vis-à-vis a hypothetical state of complete field alignment of each monomer's dipole vector for the entire species, taken as a time-average for our purposes.

For the translational response, the acceleration due to the field $a_E(t)\,\mathbf{k}$ (*i.e.*, acting along the + z-direction) is determined as a function of the force acting on ions' centers-of-mass and a retarding force due to friction. Provided that the Reynolds number, given by $\rho v a / \mu$, is less than around 0.1, in which limiting (translational) velocity is $\pm v_t\,\mathbf{k}$, the characteristic radius is a and the (mass) density of the medium

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is ρ, then laminar flow conditions prevail, and one may invoke Stoke's' law for the frictional force,[33][30] *i.e.*

$$\mathbf{a}_E(t) = \left[\left(qE_{max} \cos \omega t - 6\pi a \upsilon(t) \right) / m \right] \mathbf{k} \tag{5}$$

In the case of a static field, the cosine-dependence would not be present. In the case of this study, an (r.m.s.) electric field intensity of 0.001 V/Å$_{r.m.s.}$ led to laminar flow conditions, consistent with the linear-response régime (see 'Methodology'). At fields above 0.001 V/Å$_{r.m.s}$ the linear regime was not applicable. Here, $v(t)\,\mathbf{k}$ is the instantaneous velocity of the ion center-of-mass, which reaches 'terminal' values in either direction, $\pm v_t\,\mathbf{k}$. As mentioned previously, there is an anisotropic distribution of induced velocities at each instant of field application, with anions' and cations' induced velocities in opposite directions, without any overall mass flow in the system. In the case of a static electric field, this will lead to essentially constant induced flow of anions and cations in opposite directions, whereas in the e/m case, the field oscillates back and forth along the *z*-axis, leading to induced velocities changing direction in response to the field after a frictional lag time. Integrating eqn. 5 to obtain $v(t)$, assuming initial ions' centers-of-mass velocities of zero (or one which is certainly small in comparison to v_t), one obtains[34][31]

$$\mathbf{v}(t) = \left(qE_{max}/m \right) \left(1 / \left((B/m)^2 + \omega^2 \right) \right) \left(\frac{B}{m} \cos \omega t + \omega \sin \omega t \right) \mathbf{k} \tag{6}$$

where B denotes $6\pi\mu a$. For a static electric field, this (constant) velocity $v_t\,\mathbf{k}$ is given by $\left(qE_0/B \right)\,\mathbf{k}$. Integrating further to obtain the *z*-axis displacement of the center-of-mass vis-à-vis its initial position gives

$$\mathbf{z}(t) = \left(qE_{max}/m \right) \left(1 / \left((B/m)^2 + \omega^2 \right) \right) \left(\frac{B}{m} \frac{1}{\omega} \sin \omega t - \cos \omega t \right) \mathbf{k} \tag{7}$$

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or, for a static field, $\left(qE_0/B \right)t\,\mathbf{k}$.

This induced flow response is manifested in the definition of the electrical conductivity, σ. This was computed in the absence and presence of static fields to study the translational field response further. In both cases, the charge density $\mathbf{J}$ was defined over all ions as

$$\mathbf{J}(t) = \sum_{i=1}^{n} q_i \mathbf{v}_{\text{cm},i}(t) \tag{8}$$

Under zero-field conditions, the electrical conductivity may be computed from a Green-Kubo integral of the charge density's autocorrelation function[27, 31][24, 28]

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$$\sigma = \frac{1}{3Vk_{\text{B}}T} \int_0^{\infty} \left\langle \mathbf{J}(t) \cdot \mathbf{J}(0) \right\rangle \tag{9}$$

Using the TTCF approach in static electric fields, the electrical conductivity may also be estimated using[27][24]

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$$\sigma = \frac{1}{Vk_{\text{B}}T} \int_0^{\infty} \left\langle J_z(t) \cdot J_z(0) \right\rangle \tag{10}$$

where the correlation function has now been estimated from the *z*-component of the charge density directly from the non-equilibrium simulation. This approach has the distinct advantage that it may be used in direct non-equilibrium simulations in electric fields of arbitrarily high or low intensity.[27][24] In this study, the motivation is to study

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non-thermal field effects on systems in the linear-response régime close to experimentally and industrially available intensities: for 0.001 V/$\text{Å}_{\text{r.m.s.}}$, a direct estimate of σ from $\left\langle \mathbf{J}(t) \right\rangle / VE_0$ is highly unreliable due to a weak signal-to-noise ratio, which has also been found in previous attempts to estimate electrical conductivities directly at similar ranges of field intensity.[35][32]

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The Green-Kubo and TTCF correlation functions were sampled every 50 fs, following observation from previous studies that timescales for appreciable variation of charge density ACF's are in this range,[3128] and cubic spline interpolation used to compute intermediate points in constructing correlation functions.[3633] The validity of this method was checked by running a shorter simulation (0.25 ns) where the data was stored at half the intervals, so another 5 ps ACF was constructed but with double the number of points at half the time-spacing between discrete points. Upon application of spline interpolation, the results for the intermediate ACF points were the essentially identical. Correlation function lengths of 10, 20 and 50 ps were defined, based on 5 ns simulations, and all were found to give similar results for the electrical conductivity.

Equation Chapter 1 Section 1**Results and Discussion**

In order to ascertain the limited extent of dipolar orientation in terms of field response vis-à-vis translational motion, the z-component dipole alignment, α, from eqn. 4. Fig. 1 illustrates the relative extent and periodicity of dipole z-component alignment for both [dmim]$^+$ and [bmim]$^+$, respectively, under the same e/m field intensity, but with varying field frequency. Frequencies of 10, 50 and 200 GHz correspond to periods of 100, 20 and 5 ps, respectively, with this periodicity evident from this figure. Dipolar lag-times are of the order of 3-5 ps for very limited alignment. The dipole moments of [dmim]$^+$ and [bmim]$^+$ are centered narrowly about 0.87 D (±0.012 D) and 6.17 D (±0.043 D);[8, 9] the dipole moment of [bmim]$^+$ from the force-field of Bhargava et al.[15] was calculated to be only marginally lower than that of Lopes et al.[10] (5.84 ± 0.038 D). The difference in dipole moments between [dmim]$^+$ and [bmim]$^+$ is apparent from Fig. 1 in terms of the absolute magnitude of the z-component alignment. In order to quantify the extent of alignment, the maximal

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proportional alignment, α, given by equation (4) above, for [dmim]+ and [bmim]$^+$ at

two field intensities (0.1 and 0.25 V/Å$_{r.m.s.}$) is shown in Fig. 2. For both [dmim]$^+$ and

[bmim]$^+$, one may observe that dipole alignment is more pronounced at lower field

frequencies. This is more significant for [bmim]$^+$, which diminishes significantly at

field frequencies above 10 GHz. This frequency range for optimal dipolar alignment

is significantly lower than that of water in binary IL-water mixtures at similar

conditions to this study, as concluded in previous work.[8, 9] In this work, the higher

moments of inertia of the [dmim]$^+$ and [bmim]$^+$ species vis-à-vis water necessitates a

longer field period (i.e. lower frequency) to achieve the high levels of dipolar

alignment observed in Fig. 2 at low frequency.[8, 9]

In order to probe the translational response to the fields directly, the mobility of the

ions' centers-of-mass was assessed from self-diffusion coefficients (D) determined

using the Einstein relation (valid at long times)

$$2tD = \frac{1}{3}\left\langle \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right\rangle \tag{11}$$

where $\left\langle \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right\rangle$ is termed the ensemble-average mean-squared displacement

(MSD), with $\mathbf{r}_i(t)$ as the position of the centre-of-mass of the molecule at time t.[16]

The zero-field and NNVT simulations were performed for up to 5 ns each, so as to

ensure that the Fickian régime had been reached, a pre-requisite for obtaining

meaningful self-diffusion coefficients. As pointed out in previous work on liquid

water,[37][34] the MSD as computed under NNVT conditions are a reasonable

approximation to the self-diffusivity. Nevertheless, to verify this for the present study,

selected NNMD simulations (i.e. NVE with the field applied) were performed in fields and

the 'local' MSD time-derivatives (divided by six) for the period of the simulation where the

temperature was within 5% of 450 K were found to be within 20% or better of the NNPT

results presented here..

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Fig. 3 shows the MSD for cation and anion species under zero-field conditions. This includes results for [bmim][PF$_6$] for the force-fields of Lopes et al.[10] and, for comparison purposes, for that of Bhargava et al.[15] Diffusion coefficients for [bmim][PF$_6$] (reported in Table 2) are consistent with previous results.[15]

Figure 4 shows plots of the MSD of the centre-of-mass of anions and cations in (a) [dmim][PF$_6$] and (b) [bmim][PF6] ionic liquids at 2.45, 10 and 100 GHz for a field intensity of 0.1 V/Å$_{r.m.s.}$. It must be remembered that these *de facto* molecular mobilities are in the absence of any temperature rise and any effects are athermal in nature. As can be observed from Figure 4, diffusion is Fickian beyond ~200 ps (indicative of enhanced mobility under such field strengths) and beyond this region the diffusion coefficients were determined. The oscillation in the plot is most pronounced at 2.45 GHz (and 10 GHz), but appears to be damped at long times. In determining diffusion coefficients, care was taken to ensure that calculations incorporated a whole number of damped oscillations. Similarly, Fig. 5 illustrates the effect of r.m.s. field intensity on molecular mobility for both ionic liquids studied. As will be seen later, only field strengths above 0.05 V/Å$_{r.m.s.}$ witnessed an appreciable increase in diffusion within the time-scales of these simulations.

Self-diffusion coefficients, calculated from eqn. 11, are shown in Fig. 6 and reported in Tables 1 and 2. Here, these are plotted against the applied e/m field frequency for 0.1 and 0.25 V/Å$_{r.m.s.}$ (Fig. 5a), while those for [bmim][PF$_6$] are shown in (Fig. 6b). Also shown in these graphs are the self-diffusion coefficients for cations and anions under zero-field conditions. This highlights a number of results. Firstly, the imposition of e/m-fields results in self-diffusion coefficients for both cation and anion that are ~15 to ~50 times greater than the zero-field case (0.1 and 0.25 V/Å$_{r.m.s.}$, respectively), a dramatic translational response vis-à-vis induced dipolar rotational motion. This is consistent with eqns. 7 and 11, where increased mobility results from

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field-induced translational motion of the ions' centers-of-mass. Increasing field strength also correlates with an increase in cation and anion diffusion coefficients. Secondly, the mobilities of cation and anion are greatest under lower frequency conditions (2.45, 10 GHz), with the greatest dependence shown for the lower r.m.s. field strength. So, for 0.1 V/$\text{Å}_{r.m.s.}$, D reduces for $[dmim]^+$ by ~70% on going from 2.45 GHz to 200 GHz (slightly less for $[PF_6]^-$), while for 0.25 V/$\text{Å}_{r.m.s.}$, D for $[dmim]^+$ reduces by 14% (similar for ~~for~~ $[PF_6]^-$) over the same frequency range. This is consistent with the results shown in Figure 2, where the greatest dipole alignment was observed for lower e/m field frequencies, *i.e.*, those frequencies for which significant translational and, to a lesser extent, rotational effects occur. Finally, it should be noted that the difference in mobility between anions and cations under similar e/m field conditions is much lower than is the case for zero-field conditions, most likely a result of the disruption of the underlying ionic liquid hydrogen bonding network structure allowing much more free ion transport, i.e., a lower *de facto* viscosity (cf. eqns. 5-7).

The effect of r.m.s. field intensity on diffusion is shown in Fig 7, at a single field frequency of 2.45GHz. This figure shows that the (dramatic) onset of e/m field effects (at the frequency at which these ionic liquids are most susceptible to their action) takes place between 0.05 and 0.1 V/ $\text{Å}_{r.m.s.}$; a range of r.m.s. intensities that corresponds to the field electric force of 5-10% of the cohesive inter-molecular forces present in these systems.

In order to probe direct translational response further, time-evolution of the conductivity integrals via the Green-Kubo and TTCF approaches (cf. eqns. 9 and 10) is shown in Fig. 8. . In line with the work of Delhommelle et al.[27][24], we have carried out five non-equilibrium TTCF runs for each systems studied, taking each starting point from a long equilibrium trajectory, each 0.5 ns apart. The relatively high

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temperatures at which studies were conducted (namely 450K) ensure that there was little difference in computed conductivities between runs (<5%). Here, the conductivity results for 20 and 50 ps CF durations were equivalent, with optimal sampling statistics for the 20 ps CF's (*i.e.*, 250:1). Averaged over five independent simulation-s of 5ns each, the (Green-Kubo) electrical conductivities were found to be around 1.7 Sm^{-1} for [bmim][PF$_6$] and 1.9 Sm^{-1} for [dmim][PF$_6$], for the Lopes *et al.* force-field,[10] while a conductivity of ~5.7 Sm^{-1}, is observed for [bmim][PF$_6$] using the force-field of Bhargava *et al.*[15] While experimental values for conductivities at 450K are not available, it is worthwhile to present available data for [bmim][PF$_6$] which is presented by Suarez et al.[38][35] Here, a correlation for conductivity is present for temperatures up to 353K. At 353K, the conductivity of [bmim][PF$_6$] equals to 2.6 Sm^{-1}. However, if one tentatively extrapolates this to 450K, a conductivity of 20 Sm^{-1} is suggested. Taken together, it is reasonable to assume that the conductivity at 450K is closer to a value of 20 Sm^{-1} (even though it is obviously beyond the limits of the applicability). In this case, as we have seen for diffusion coefficients, the best agreement with experiment is achieved using the force-field of Bhargava *et al.*[15]

The TTCF results may also be seen to be essentially equivalent to the Green-Kubo results. This confirms the utility for use of the TTCF method for gauging properties in external fields of arbitrary intensity,[27][24] which is especially true for the relatively weak field used in this study (in comparison to typical force magnitudes acting in zero-field situations due to the force-field).

Conclusions

Non-equilibrium MD simulation of [dmim][PF$_6$] and [bmim][PF$_6$] ionic liquid systems have been conducted in the NNVT case, as a means of assessing and understanding the non-thermal effects of electric and e/m fields (in the microwave to

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far-infrared frequency) primarily on translational response, in the guise of molecular mobility and electrical conductivity. Results indicate that these ionic liquids responded most significantly to field frequencies of 2.45 GHz to 10 GHz for all measured properties including self-diffusion coefficients, and, less importantly, dipole alignment. This is in agreement with dielectric relaxation spectroscopy,[32][29] and confirms Ohmic loss as the dielectric relaxation mechanism. The use of the TTCF method to allow the more statistically robust estimation of the electrical conductivity at lower field intensities with a poor signal-to-noise ratio rather than by direct computation of $\langle \mathbf{J}(t) \rangle / V E_0$ leads to electrical conductivity results essentially in agreement with a Green-Kubo treatment. This work suggests that (non-equilibrium) classical molecular simulation offers a viable and potentially valuable way of assessing optimal e/m field design strategies for ionic liquid exposure in terms of solvent recovery, but these techniques could be applied to other exciting new areas, such as e/m field promotion of reaction rates.

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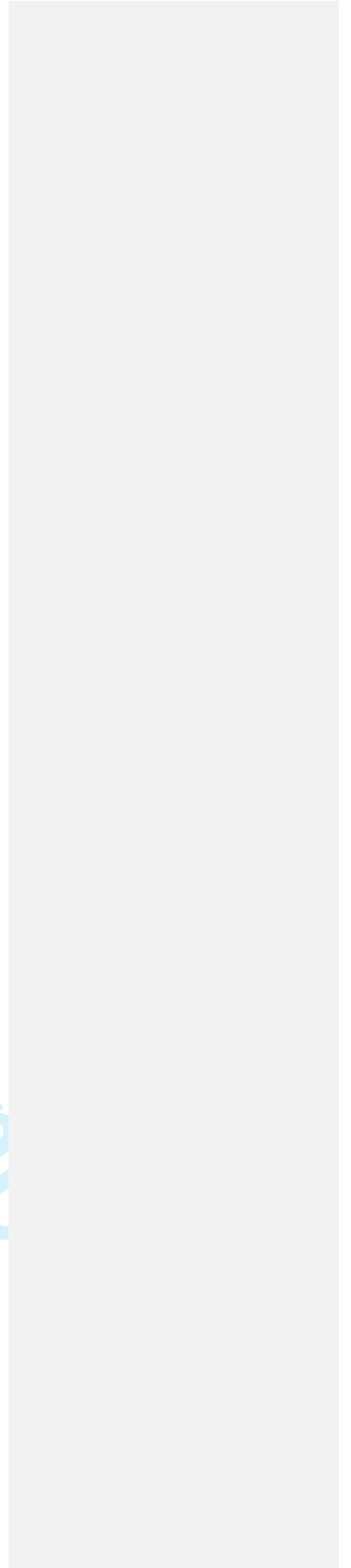
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Captions for the Tables

Table 1: Calculated self-diffusion co-efficient for [dmim]$^+$ and [PF$_6$]$^-$ under zero and

e/m field conditions.

Table 2: Calculated self-diffusion co-efficient for [bmim]$^+$ and [PF$_6$]$^-$ under zero and

e/m field conditions. Results (under zero-field conditions) are also reported

from simulations using the force-field of Bhargava et al.[15]

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Table 1

Conditions	$[dmim]^+$ $\times 10^{10}$ m^2 s^{-1}	$[PF_6]^-$ $\times 10^{10}$ m^2 s^{-1}
Zero-Field	0.81	0.51
0.1 V/Å		
2.45 GHz	14.50	11.02
10 GHz	18.12	12.05
20 GHz	16.11	12.04
50 GHz	14.11	7.86
100 GHz	9.39	6.46
200 GHz	4.81	4.81
0.25 V/Å$_{r.m.s.}$		
2.45 GHz	56.90	53.21
10 GHz	61.16	43.27
20 GHz	61.86	45.25
50 GHz	48.03	49.41
100 GHz	49.62	49.85
200 GHz	48.70	38.60

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Table 2

Conditions	[bmim] $\times 10^{10}$ m^2 s^{-1}	[PF$_6$]$^-$ $\times 10^{10}$ m^2 s^{-1}
Zero-Field	0.959 (3.125)	0.648 (2.990)
0.1 V/Å		
2.45 GHz	14.85	11.68
10 GHz	13.69	9.52
20 GHz	13.13	11.02
50 GHz	9.78	7.40
100 GHz	6.40	5.10
200 GHz	4.20	3.38
0.25 V/Å$_{r.m.s.}$		
2.45 GHz	59.48	48.82
10 GHz	60.39	54.35
20 GHz	60.17	54.91
50 GHz	50.17	54.15
100 GHz	37.30	44.87
200 GHz	34.46	33.68

Results of Bhargava *et al.* force-field[15] shown in brackets.

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Captions for the Figures

Figure 1: z-component ~~alignment~~ total dipole (in Debyes) of (a) [dmim]$^+$ and (b) [bmim]$^+$ under different field frequencies, namely 10, 50 and 200 GHz corresponding to periods of 100, 20 and 5 ps, respectively for r.m.s. field intensity of 0.25 V/Å$_{r.m.s.}$. For (a), 10 GHz and 200 GHz plots were offset by -100 and +100 D, respectively, for clarity, while for (b) 10 GHz and 200 GHz plots were offset by -1200 and +1200 D.

Figure 2: Maximal z-component alignment of (a) [dmim]$^+$ in [dmim][PF$_6$] and (b) [bmim]$^+$ in [bmim][PF$_6$] as a proportion of maximum possible alignment (see eqn. 6) for neat ionic liquid systems. The calculated dipole moments for isolated molecules using the force-fields in this study were 0.87 D and 6.71 D for [dmim]$^+$ and [bmim]$^+$, respectively.

Figure 3: Mean squared displacement under zero-field conditions for all model ionic liquid systems studied in this work (anion and cation), including [dmim]$^+$, [bmim]$^+$ and corresponding [PF$_6$]$^-$ species. (a) [dmim]$^+$ and [PF$_6$]$^-$ ions in [dmim][PF$_6$] and (b) [bmim]$^+$ and [PF$_6$]$^-$ ions in [bmim][PF$_6$]. Graphs for the [bmim][PF$_6$] are shown for both the force-field of Lopes *et al.*[10] and of Bhagarva *et al.*[15].

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Figure 4: Mean squared displacements of (a) [dmim]$^+$ and [PF$_6$]$^-$ ions in [dmim][PF$_6$] and (b) [bmim]$^+$ and [PF$_6$]$^-$ ions in [bmim][PF$_6$] at 0.1 V/ Å$_{r.m.s.}$ at three different field frequencies (2.45, 10 and 100 GHz).

Figure 5: Mean squared displacements of (a) [dmim]$^+$ and [PF$_6$]$^-$ ions in [dmim][PF$_6$] and (b) [bmim]$^+$ and [PF$_6$]$^-$ ions in [bmim][PF$_6$] at 2.45GHz at three different r.m.s. field intensities (0.05, 0.10 and 0.25 V/ Å$_{r.m.s.}$).

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Figure 6: Self-diffusion coefficient of (a) [dmim]$^+$ and [PF$_6$]$^-$ ions in [dmim][PF$_6$] and (b) [bmim]$^+$ and [PF$_6$]$^-$ ions in [bmim][PF$_6$] as a function of e/m field frequency at two different r.m.s field intensities (0.1 and 0.25 V/Å$_{r.m.s.}$). Zero-field diffusion coefficients for [dmim]$^+$ and [PF$_6$]$^-$ are plotted as horizontal lines for comparison.

Figure 7: Self-diffusion coefficient of (a) [dmim]$^+$ and [PF$_6$]$^-$ ions in [dmim][PF$_6$] and [bmim]$^+$ and [PF$_6$]$^-$ ions in [bmim][PF$_6$] as a function of r.m.s. field intensities (from 0.001 to 0.25 V/ Å$_{r.m.s.}$) at a field frequency of 2.45 GHz.

Figure 8: Development of the electrical conductivity, *i.e.*, time-evolution of eqns. 9 and 10, for (a) zero-field conditions (Green-Kubo) and (b) static-field (0.001 V/Å) conditions (TTCF). Results are shown for a typical 5ns simulation.
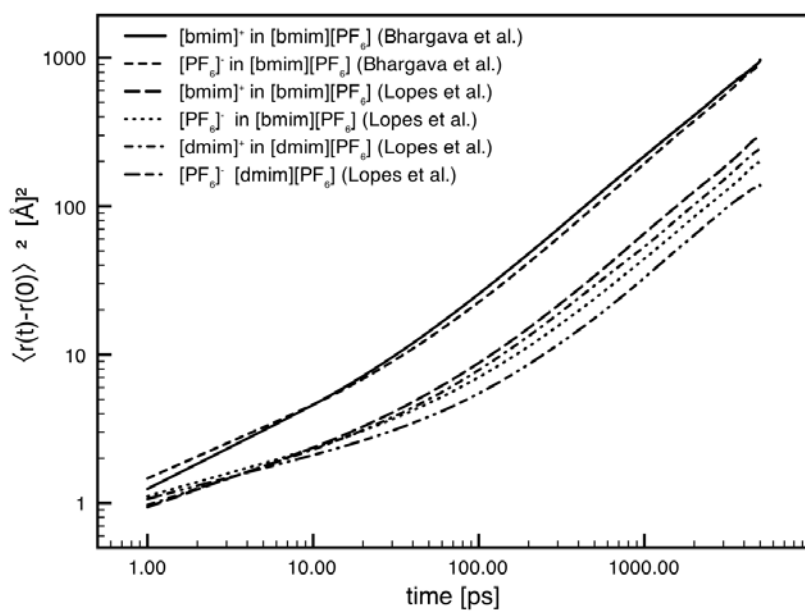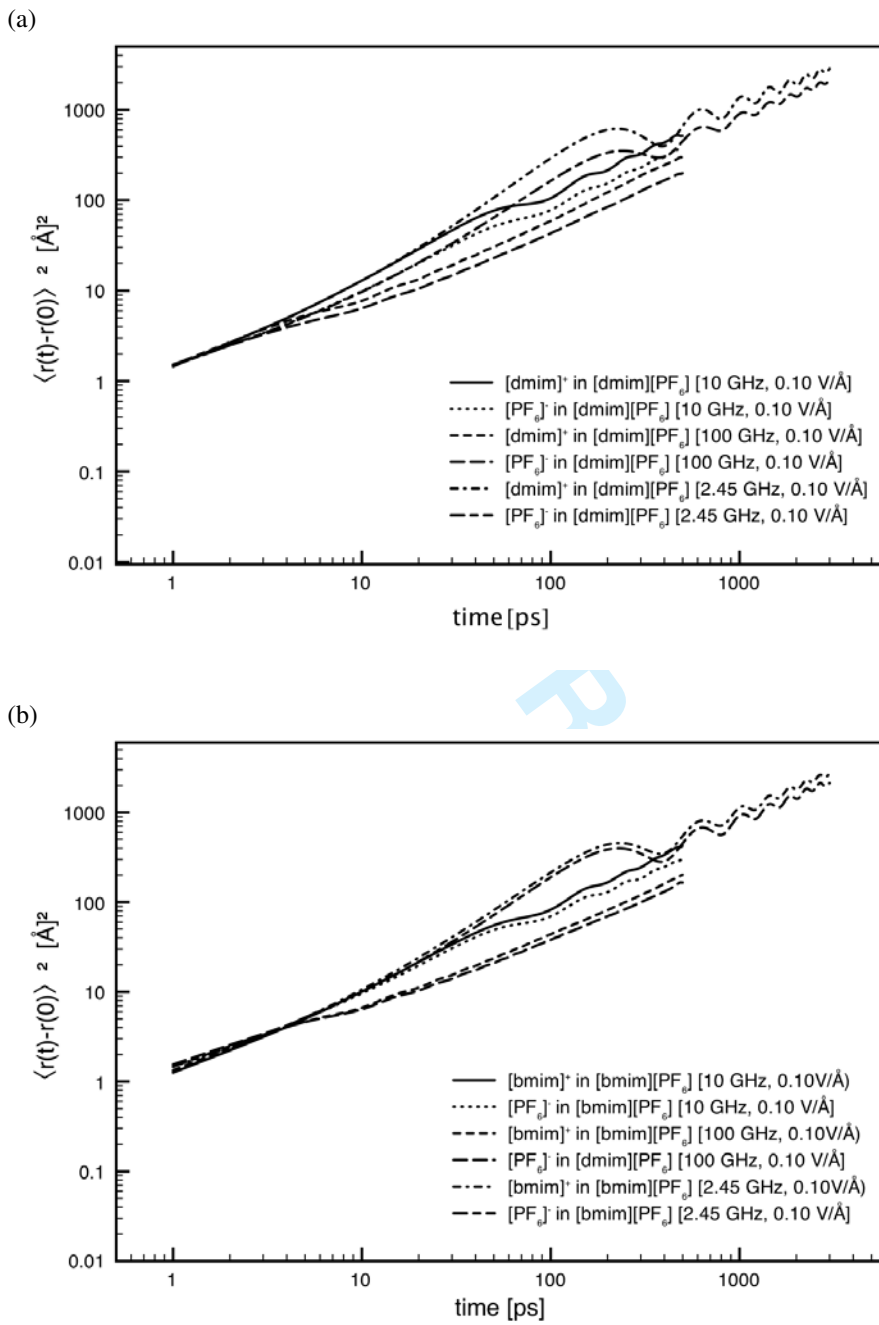
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Figure 1

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Figure 2

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Figure 4

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Figure 5

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Figure 7

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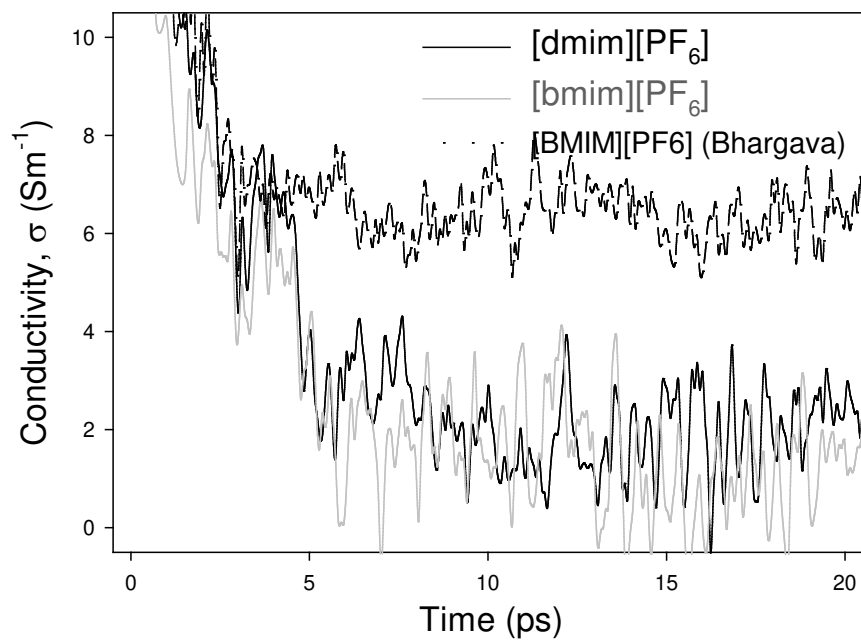47
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(a)

(b)

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Figure 8

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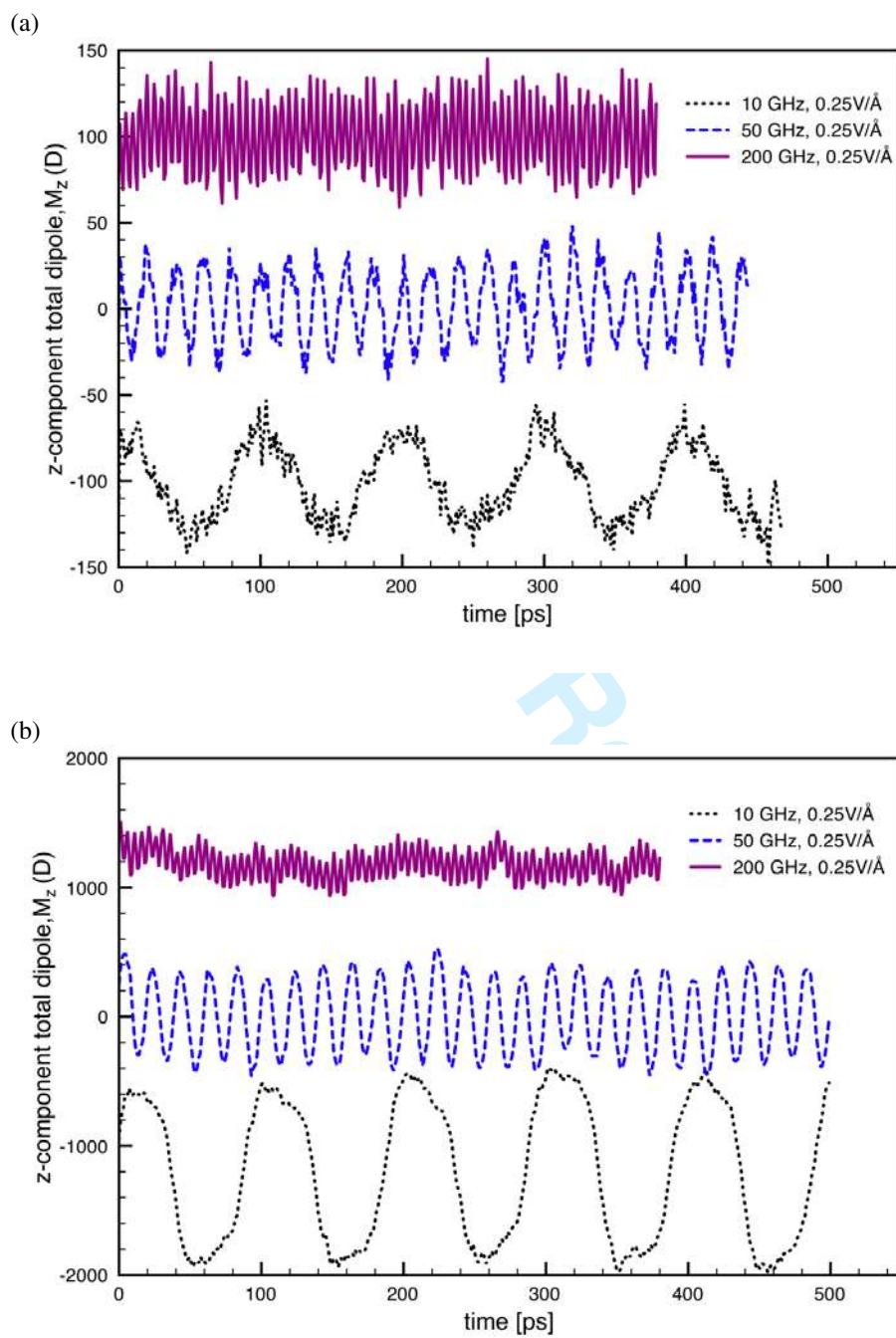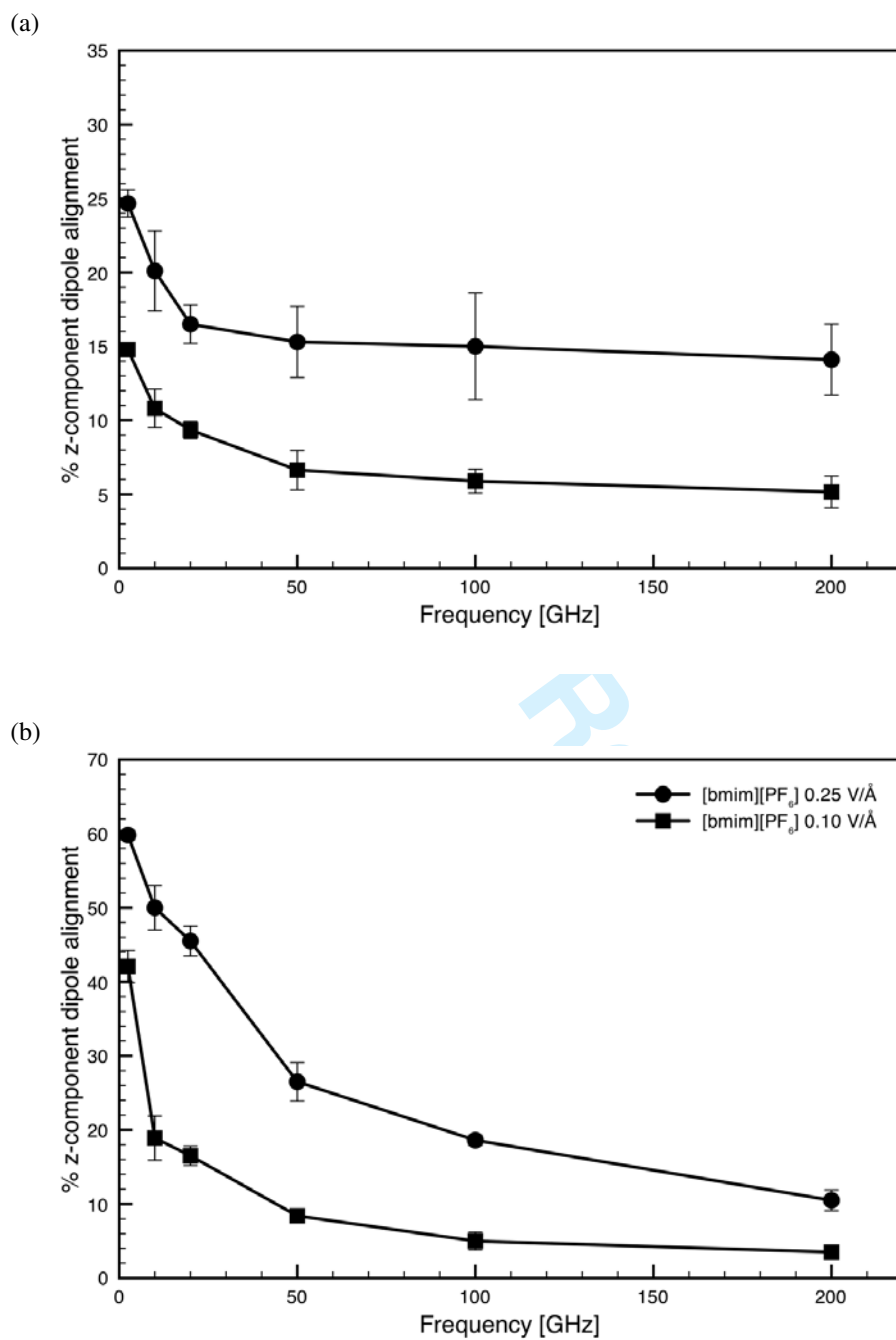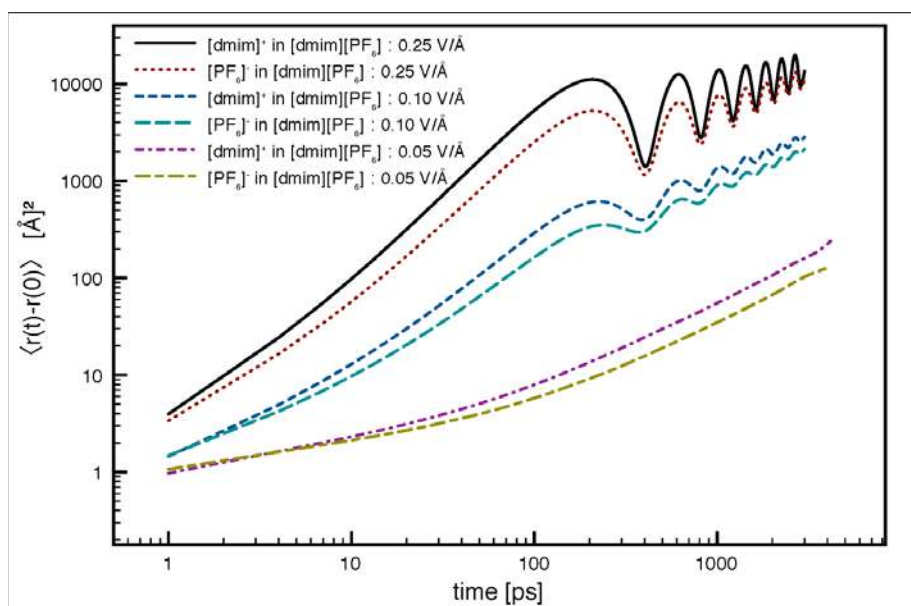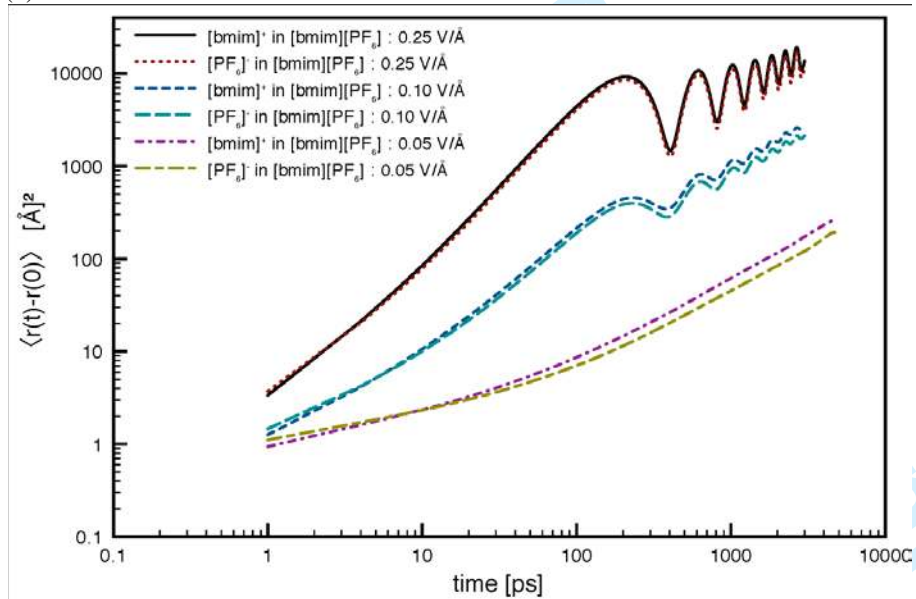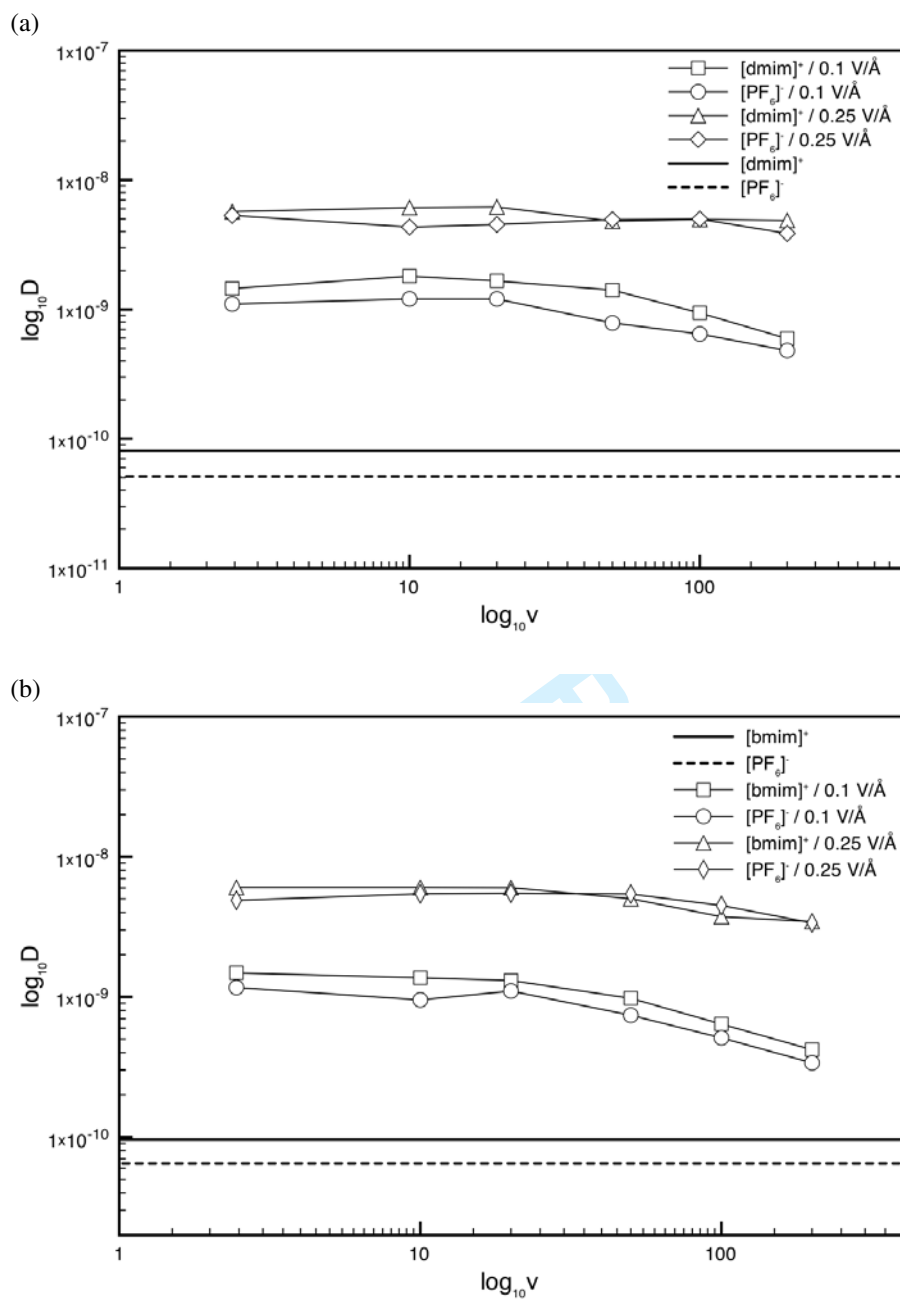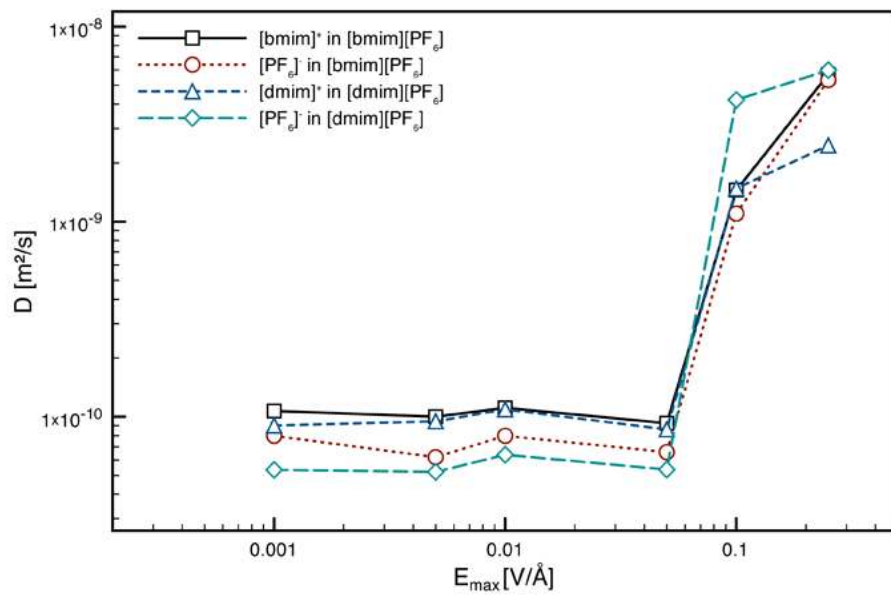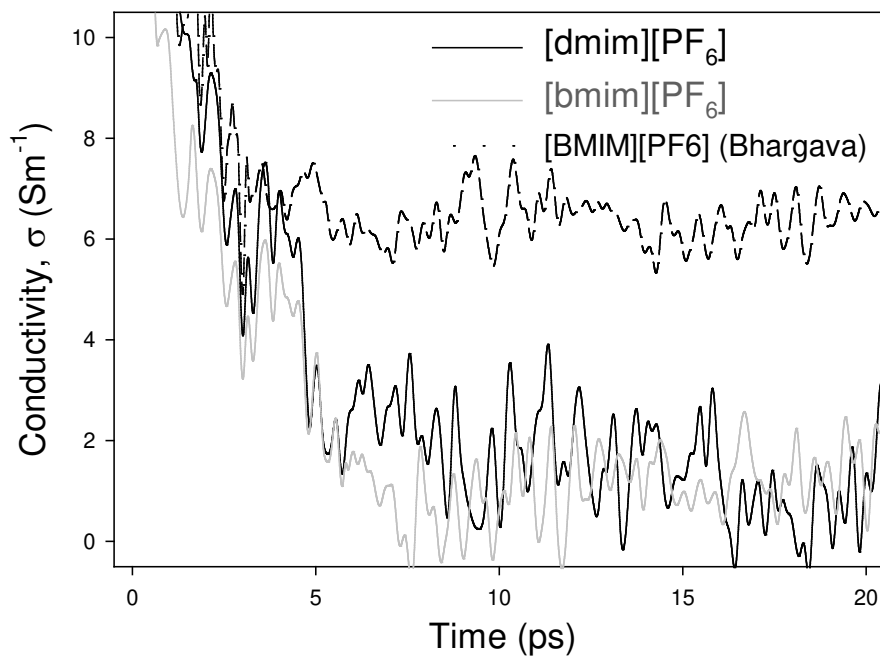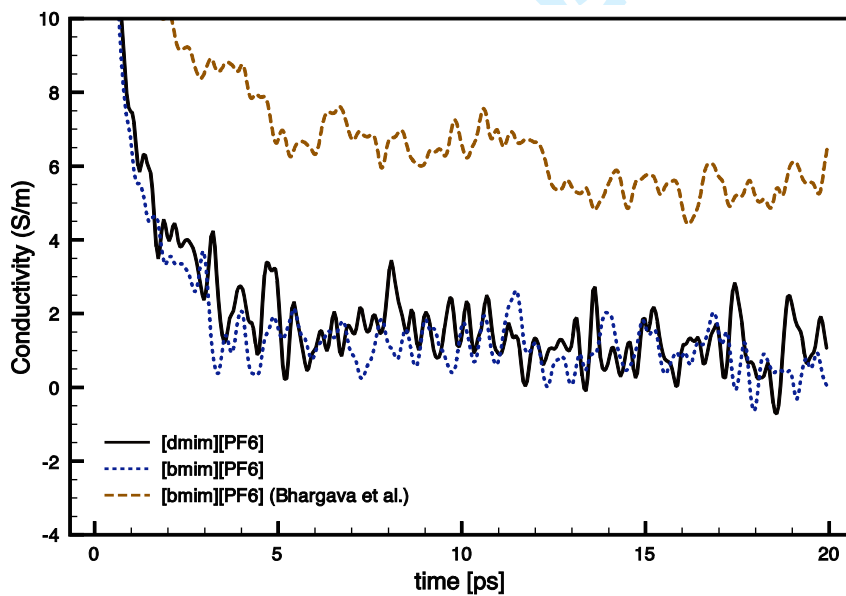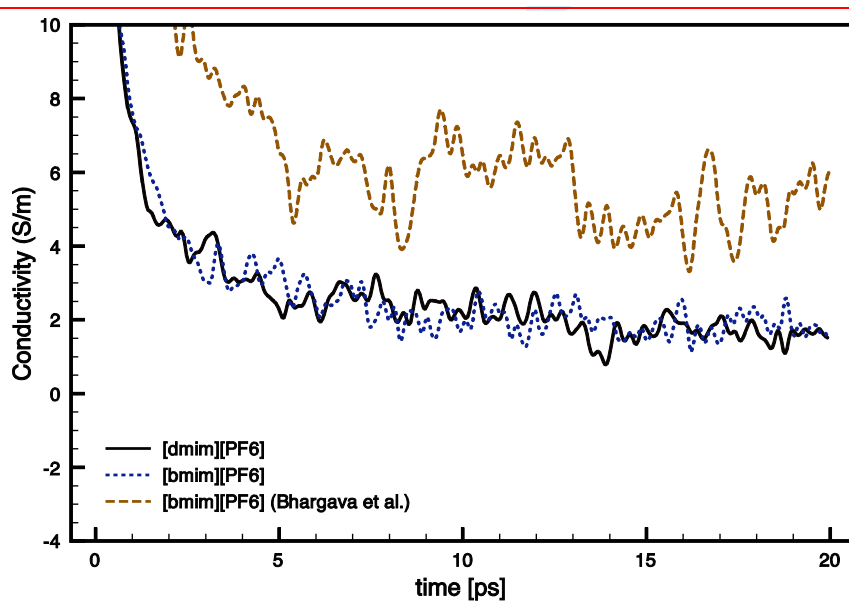
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Professor Jean-Pierre Hansen

Editor, Molecular Physics

26th October 2010

Re: Re-submission of Manuscript ID TMPH-2010-0292

Dear Professor Hansen

 Further to your e-mail dated August 28th 2010 (and my e-mail reply on 20th September 2010) regarding the aforementioned paper, namely,

Ionic Liquids in external electric and electromagnetic fields: a molecular dynamics study

Niall J. English[*], Damian A. Mooney[*] and Stephen O'Brien

please permit me to indicate the changes that we have applied in light of the comments made by referee 2 (forwarded in your e-mail of August 28th). I hope that these are satisfactory to the reviewer's and your requirements.

In order to make your re-review easier, I have reiterated each of the comments made by the reviewer and followed these by describing the changes applied to the paper. These are enumerated as follows:

1. *"I was surprised to see that the authors chose to define the thermal motion with respect to the overall center-of-mass velocity. While the authors are correct in stating that there is no net mass flow, the electric field will still induce the flow of cations and anions and this cannot be counted as thermal motion. The thermostat used by the authors artificially decreases the current and hence the conductivity since the current itself is identified as thermal motion by the thermostat. I would suggest to the authors to run a few tests using a thermostat free of this kind of assumption such as e.g. the configurational thermostat of Braga and Travis (JCP 123, 134101 - 2005), which has been recently applied to the calculation of conductivity within the transient-time correlation function formalism by Desgranges and Delhommelle (PRE 77, 027701 - 2008)"*

[*] Corresponding authors: niall.english@ucd.ie, damian.mooney@ucd.ie

We implemented the configurational (canonical-ensemble) thermostat of Braga and Travis for holonomic constraints, [K.P. Travis KP and C. Braga, J. Chem. Phys., 128, 014111 (2008)]. We have added this to the Methodology section with a short discussion of why this would be a superior thermostat method. We have also added the reference and renumbered all of them accordingly. It was found that the results for the electrical conductivity are up to 15% larger than previously, but little appreciable change was observed for the dipolar orientation or diffusion results. Therefore, Fig. 8 has been replaced accordingly (vide infra).

2. *"The definition of the overall dipole moment Ps over a set of Ns ions (Equation 3) is very confusing. Equation 3 can only be applied to ions with a non-zero dipole moment (it does not apply to the ion [PF6]⁻ considered in this work for instance) and the choice for the overall origin is not specified. Only the first non-zero moment of an electrostatic distribution is independent from the choice of an origin. For a set of ions, the overall dipole moment will depend on the choice of the origin. This needs to be addressed."*

We thank the referee for this insightful comment. We chose this definition because the lack of local dipole moment for [PF6]⁻ ions (according to our definition, w.r.t. the ions' individual centres of mass) leads to a purely translational (i.e., Ohmic) response in motion for each of these ions to the applied electric fields - thus our definition, which casts the [PF6]⁻ ions as non-dipolar, is entirely appropriate. The definition of the origin is a purely local one for each ion, and coincides with each ion's center of mass, to determine each ion's dipole vector. There is no central definition of an origin for the entire system. Remarks to this effect have been added to the paper.

3. *"The authors state that the z-component of Ps is indicative of alignment. However, in the definition of the proportional alignment of a species (Equation 4), the authors use the norm of Ps and not its z-component. This also needs to be addressed."*

Thank you for pointing that out. This is purely confusion in terms of symbols, and we apologise for this. We have specified the z-component, and have stated that the norm brackets refer here to the absolute value of the z-component.

4. *"There are many typos such as 'Reyonld's number' -> 'Reynolds' number' (page 7) or 'simulation sof' -> 'simulations of' (page 15)."*

Typos have been corrected and document re-read to eliminate others (where they might exist).

I trust that the above is to your satisfaction. Please do get back to me if there is anything else you require in advancing this paper.

With great respect

Damian A. Mooney

Senior Lecturer (US Associate Professor)