

Locality and Fluctuations: Trends in Imidazolium-Based Ionic Liquids and Beyond

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ABSTRACT: Three different imidazolium-based ionic liquids, 1,3-dimethylimidazolium chloride, 1-ethyl-3-methylimidazolium thiocyanate, and 1-ethyl-3-methylimidazolium dicyanamide, are investigated by Car–Parrinello simulations. A common behavior, such as a broad electric dipole moment distribution of the ions and a related high degree of locality, is found to characterize all these systems. Going beyond imidazolium-based systems, we found that even for the protic ionic liquid monomethyl ammonium nitrate, the same features hold. These results represent a strong support to the hypothesis of rattling ions in long-living ion cages proposed in the last years.

1. INTRODUCTION

Ionic liquids (ILs) are defined as low-melting salts being often liquid at room temperature. Due to their unique physicochemical properties, ILs have gained immense interest.^{1,2} For instance, they offer tailor-made high-potential solutions in chemical reactions as catalysts,³ in separation processes due to their adaptable solubility,⁴ or being ionic, as electrolytes.⁵ Moreover, ILs dissolve cellulose and permit to reshape and process the most abundant organic raw material using less energy and chemicals and increasing the processes sustainability.⁶ Chemically, ILs are designed and synthesized by combining two ions; however, a reasonable accurate prediction of newly formed ILs' properties, employing basic theoretical principles, is often not possible, as the underlying physics is not yet fully understood.⁷ Current theoretical approaches and (above all) large-scale simulation methods, being based mostly on empirical models, can provide only a rather limited capability of predictions of properties and a partial interpretation of experimental data.^{8,9} Thus, there is a vivid interest in elucidating the governing interactions, Coulomb and van der Waals forces¹⁰ as well as hydrogen bonding^{11–18} and their subtle interplay. As for any molecular liquid, this interplay is expressed by the connection between the local scale, i.e., how a molecule reacts to its immediate surrounding in the short time, and the global mesoscopic scale, i.e., the bonding network or diffusion properties which typically occur on a larger scale.^{9,19} In this context, for this work we intend to identify basic universal physical principles for (at least a class of) ILs. To this aim, we study a series of imidazolium-based ILs, 1,3-dimethylimidazolium chloride (MMIM Cl), 1-ethyl-3-methylimidazolium thiocyanate (EMIM SCN), and 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA) as well as the protic IL monomethyl ammonium nitrate (MMAN) (see Figure 1) using state of the art electronic structure methods and proceed to a systematic comparison among them. In previous work on MMIM Cl,¹⁹ the electric dipole moment distribution was found to be very much

spread, indicating a strong degree of fluctuation, but the electrostatic properties were rather local. Further studies confirmed the strong electrostatic screening (theoretical,^{9,10,20,21} experimental²²). The natural question arising is whether this behavior is due to any peculiar chemical structure of the ions or may be a sign of a more general behavior. Here, we show that these properties are common to several ionic liquids, and thus, they may represent a “true ionic liquid” signature.²²

2. COMPUTATIONAL DETAILS

This study makes use of some of the largest ab initio simulations of ILs ensuring sampling and equilibration so far not reached. We used the Car–Parrinello approach implemented in the CPMD code^{23,24} with the BLYP functional.^{25,26} We employ Troullier–Martins pseudopotentials, derived using the BLYP functional, and an empirical dispersion correction,²⁷ which has been accurately tested in previous work.²⁸ Further checks were done for this work by studying three one-ion pair clusters and comparing structures and geometries with those obtained by high-level quantum chemical methods. For the MMAN ion pairs, we used instead the DCACP-BP pseudopotentials,²⁹ which were tested accurately for this system in previous work.¹⁴ The simulations were started from a snapshot of a classical MD simulation, and the equilibration time was chosen to be 5 ps unless otherwise specified. A short overview of the systems is given below: (1) 8 ion pairs EMIM SCN, 400 K, (12.64 Å)³, 67.66 ps; (2) 32 ion pairs EMIM SCN, 400 K, (20.06 Å)³, 6.24 ps (started from an ab initio trajectory¹¹ snapshot); (3) 48 ion pairs EMIM SCN, 400 K, (22.97 Å)³, 1.0 ps (0.5 ps equilibration); (4) 8 ion pairs EMIM DCA, 400 K, (13.11 Å)³, 63.50 ps; (5) 30 ion pairs EMIM DCA, 400 K, (20.37 Å)³, 43.85 ps; (6) 64 ion pairs EMIM DCA, 400 K, (26.23 Å)³, 4.5 ps (0.5 ps equilibration); (7) 8 ion pairs MMAN,

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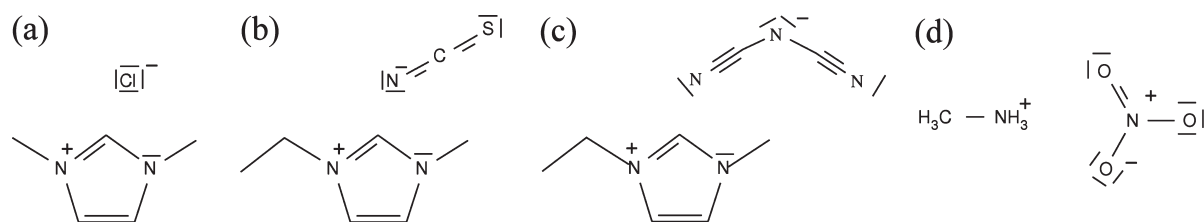


Figure 1. Presentation of one mesomeric structure of (a) MMIM Cl, (b) EMIM SCN, (c) EMIM DCA, and (d) MMAN.

400 K, $(10.19 \text{ \AA})^3$, 84.02 ps; (8) 48 MMAN ion pairs where 100 snapshots were randomly selected for analysis from the trajectory of ref 14; (9) 8 ion pairs MMIM Cl, 425 K, $(11.62 \text{ \AA})^3$, 79.66 ps. The latter was done with the same setup as the corresponding larger system of 30 MMIM Cl pairs.¹⁹ The two larger systems of 48 ion pairs of EMIM SCN and 64 ion pairs of EMIM DCA were used here as preliminary tests to indicate possible size effects on the distributions of the dipoles and on the correlations studied. The large computational effort required allows only for short simulations, and technically, it is important to justify why one may use a short equilibration time in this context. The starting configurations obtained from the equilibration by classical simulations gave interatomic forces which were smaller than 0.003 au after the first step of the quantum calculation. This implied that the starting configuration provided a reasonable overall liquid structure and that the equilibration time chosen (0.5 ps) was sufficient to equilibrate the local electronic degrees of freedom. As a further test, we considered 10 uncorrelated classical configurations to sample statistically the liquid structure found in the classical molecular dynamics (MD). After performing a wave function optimization, the largest force acting on an atom was below 0.004 au for each of them. In a similar study of ionic liquids in literature, a much larger value of 0.1 au was taken for identifying equilibrated (at quantum level) configurations obtained from classical samples.³⁰ The resulting electron densities were used to calculate dipoles and their distributions; we found the same results obtained for smaller systems. Since we did not consider quantities linked directly to the dynamic properties of the system (for which a long equilibration is mandatory), the technical set up used for these larger calculations was sufficient to represent a preliminary test. The dipole moments were calculated using the maximally localized Wannier analysis^{31,32} every 500th time step. In general, density functional theory (DFT) and Wannier center-based dipole moments were found to be consistent with experimental values for single molecules in the gas phase.^{33,34} For 100 snapshots per system, the Blöchl analysis was done as in ref 9.

3. RESULTS AND DISCUSSION

3.1. Molecular Dipole Moment As Physical Indicator.

In general, the electric dipole moment of an ion (denoted as dipole in the following), contrary to that of a neutral molecule, is not defined uniquely, as it depends on the arbitrary choice of the origin with respect to which it is calculated. This implies that the absolute value of ionic dipoles does not have a physical quantitative meaning but, defined in a consistent way for all systems, can be employed for a systematic comparison among different ions to identify some generic trends. Here, the dipole moment of imidazolium ions is calculated with respect to the geometric center of the five ring atoms (COR), the dipole moment of all

other ions with respect to the geometric center of all atoms (COG). However, our findings are largely independent of such a choice. Molecular dipoles in ILs are also not experimentally measurable, however, they represent a powerful tool for a theoretical interpretation of the system properties. In fact, the ion dipole moment is an indicator for charge displacement as well as (being a vector) local molecular packing. It sums up electronic and steric influences and describes the interplay of charge and shape; hence, it represents an accurate descriptor for the variation of the ion's electrostatic properties upon local liquid configurational changes. Moreover, the evaluation of dipole correlations along the whole system provides information about the effective range of electronic interactions.

3.2. Fluctuations. Figure 2 reports the dipole distributions of anions and cations for all the systems considered. In general, the distributions are broader compared to those of nonionic liquids, such as liquid water.³³ The MMIM and EMIM cation dipole distributions have about the same mean value with a strongly pronounced spread in all three cases essentially independent of the counterion. For the chemically more different anions of the imidazolium ILs, a trend emerges: given the size of each specific anion, the spread of the distributions is also very pronounced and rises as the size and polarizability of anions increase. In fact, a larger size can imply a larger number of both conformational degrees of freedom (e.g., internal vibrations and local motion of the side chain) and electronic degrees of freedom (i.e., possibility of polarization). We may conclude that all these imidazolium systems are characterized by large electrostatic fluctuations and that the difference between the imidazolium systems is dictated mostly by the nature of the anion and not so much by the chemical specificity of MMIM or EMIM. Going beyond imidazolium-based systems to the protic IL MMAN, we have found that this general trend still holds although in reverse order, i.e., the anion has a broader dipole distribution than the cation, which can be motivated by the larger van der Waals volume of the anion. Interestingly, the gas-phase polarizability of the nitrate anion is significantly lower than the ones of the SCN or DCA anions, but the nitrate dipole distribution has a larger spread. This suggests that, in general, all these systems are characterized by strong electrostatic fluctuations. The natural question arising at this point is what the origin of these fluctuations is: Are they the product of bulk density fluctuations on a large length scale, or are they the result of very local but largely diverse molecular packing?

A comparison with the results obtained with classical flexible models shows that the spread of the dipole distribution of the quantum chemical calculations is 50% larger than that of the classical studies. Furthermore in quantum chemical calculations, the ions dipole moment distributions of a gas-phase ion pair are also broad. The spread is larger compared to the liquid phase. This is mainly due to the large number of ion pair configurations associated with strong mutual polarization. The results above

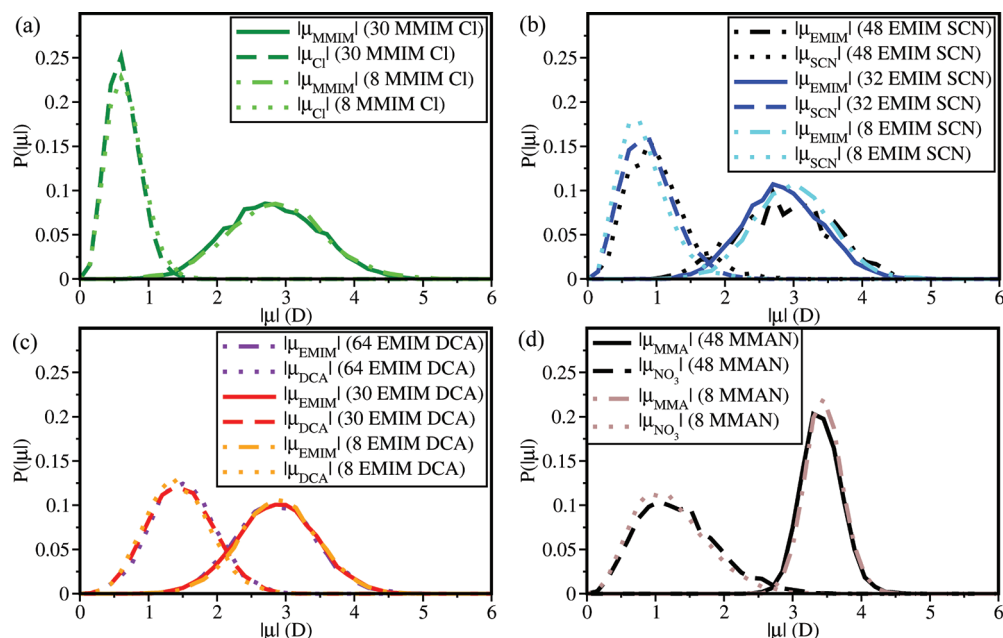


Figure 2. Dipole moment distributions for large and small (≥ 30 and 8 ion pairs, respectively) IL systems of (a) MMIM Cl, (b) EMIM SCN, (c) EMIM DCA, and (d) MMAN.

indicate that while, in general, the large spread seems intrinsic to ILs and their electronic properties, the actual dipole moment distributions are very sensitive to the specific ions environment. The decisive interactions are characterized by a certain range that needs to be quantified.

In the next section, we address this point by comparing various correlation functions and by comparing large systems with smaller systems of eight ion pairs.

3.3. Locality. Figure 2 reports the dipole distributions for both the large systems considered and their thermodynamical equivalent systems of eight ion pairs. It is remarkable that the ion dipole moment distributions of the large systems and the eight ion pair systems are the same in all cases. A possible scenario emerging from this comparison is that an ion is influenced only by its immediate neighbors in the short time and seems to not experience perturbations from the long-range behavior of the liquid. Indeed, the counterions in the first shell overcompensate the charge of an ion, thus, showing overscreening.^{20,35,36} This result would strongly support the idea of ions rattling in a long-living ion cage proposed in literature.^{14,37–40} The statement above is certainly true for the simulations done here. However, at this stage, it should not be taken as a general claim but only as an indication of a possible trend. In fact, the box sizes of the systems providing a statistically significant set of reliable data (i.e., ion pairs < 48) are truncated at distances well short of those where the radial distribution functions go to unity. It is, however, rather encouraging that short simulation tests on larger systems (48 ion pairs EMIM SCN and 64 ion pairs EMIM DCA), which do not suffer from the limitation above, confirm all the conclusions reached here. To further check the idea of locality, we test the range of extension of three types of electrostatic interactions: monopole–monopole, monopole–dipole, and dipole–dipole. The interionic radial distribution functions would not capture the electrostatic effects, as they are dominated by excluded volume interactions. To obtain the monopole interactions between ions, we fit a set of partial charges on the atom centers that give a best

Table 1. Cation Charges in Units of e Obtained via Blöchl Analysis⁹

system	MMIM Cl	EMIM SCN	EMIM DCA	MMAN
≥ 30	0.63 ± 0.15	0.56 ± 0.25	0.67 ± 0.21	0.55 ± 0.29
8	0.64 ± 0.16	0.56 ± 0.25	0.70 ± 0.19	0.56 ± 0.27

fit to the multipole moments of the bulk ion configurations in Fourier space via the Blöchl method.^{9,41} Surprisingly enough, we find for all investigated systems, ionic charges considerably less than one, in the range 0.55–0.7 in units of the elementary charge e , see Table 1. Force fields with ad hoc reduced ionic charges,^{21,37,42} treating this just as another free parameter in the force field description, have been partially successful to reproduce dynamical quantities of ILs besides the static ones. In this context, our results suggest that the charge reduction may be a real physical effect as proposed by experiments.⁴³ For instance for EMIM DCA, the reduced charges correspond to an electronic dielectric constant $\epsilon_{\text{el}} = (q/q_{\text{eff}})^2 \approx 2.2$, which is in agreement with the experimental refraction index $n = (\epsilon_{\text{el}})^{1/2} \approx 1.5$.⁴⁴ Moreover, the cation charges in the large and the small systems obtained via this analysis are the same within the standard deviation in all cases, demonstrating that this charge reduction effect takes place over a range of only a few angstroms. Thus, eight ion pairs are sufficient to reproduce the effective monopole structure of each ion. For the monopole–dipole correlation, we consider the angular distribution between the dipole of an ion and the vector from the ion's center of reference to another ion's center of charge (COC), e.g., taking one cation per time as reference: $\cos \Phi = \mu_{\text{cat}}^{\text{ref}} \cdot \mathbf{r}_{\text{cat}}^{\text{shell}} / |\mu_{\text{cat}}^{\text{ref}}| |\mathbf{r}_{\text{cat}}^{\text{shell}}|$; $\mu_{\text{cat}}^{\text{ref}}$ is the dipole of the reference cation, while $\mathbf{r}_{\text{cat}}^{\text{shell}}$ is the vector from the COR of the reference ion to the COC of cations in the i th radial bin ($i = 1$: below 5 Å, $i = 2$: 5–7 Å, $i = 3$: 7–9 Å, $i = 4$: above 9 Å). All possible distributions were calculated: $\mu_{\text{an}} - \mathbf{r}_{\text{an}}$, $\mu_{\text{an}} - \mathbf{r}_{\text{cat}}$, $\mu_{\text{cat}} - \mathbf{r}_{\text{an}}$, and $\mu_{\text{cat}} - \mathbf{r}_{\text{cat}}$. Similarly, all possible dipole–dipole angular distributions as $\mu_{\text{an}} - \mu_{\text{an}}$, $\mu_{\text{cat}} - \mu_{\text{an}}$, and $\mu_{\text{cat}} - \mu_{\text{cat}}$ were

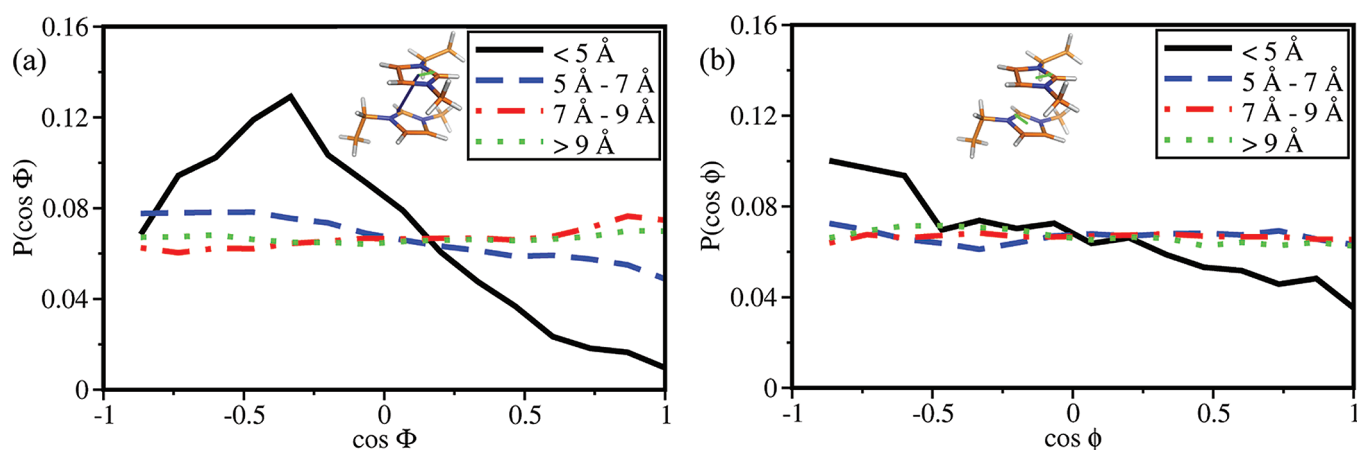


Figure 3. Angular probability distribution of (a) $\cos \Phi$ (charge–dipole) and (b) $\cos \phi$ (dipole–dipole) of cations separated by distances below 5 Å (black), from 5–7 Å (blue), 7–9 Å (red), or above 9 Å (green) in the 30 EMIM DCA system.

studied as in ref 19, e.g.: $\cos \phi = \mu_{\text{cat}}^{\text{ref}} \cdot \mu_{\text{cat}}^{\text{shell}} / |\mu_{\text{cat}}^{\text{ref}}| \cdot |\mu_{\text{cat}}^{\text{shell}}|$ in which $\mu_{\text{cat}}^{\text{shell}}$ is the dipole of cations in the i th radial bin. As examples, $\mu_{\text{cat}} - \mathbf{r}_{\text{cat}}$ and $\mu_{\text{cat}} - \mu_{\text{cat}}$ of the 30 EMIM DCA system are given in Figure 3. Basically, the dipole of a cation correlates only in the very immediate neighborhood with both the direction to the COC and the dipole of cations, while displaying no preferential alignment beyond this short range. All other distributions give the same qualitative picture. For the cation–anion and the anion–anion dipole–dipole angular distributions, only a negligible preferential order is observed even in the first radial bin, while the correlations of the dipoles and the COC directions decay slower. In any case at distances above 8 Å, there is no preferential alignment in any of the distributions. Given the diversity in the chemical structure of the ions of each system and the fact that the short simulation tests on larger systems confirm the results, we are tempted to propose that the locality and the fluctuations may be a general characteristic of, at least, a large class of ILs. The question arising at this point is what happens at the local level that produces these pronounced fluctuations? We can provide some hints for the imidazolium-based case.

We have found that the dipole moment distribution of ions depends neither on the overall numbers of close cations or anions nor on the magnitude of dipole moments of adjacent ions. However, there are some geometries¹⁵ that may, at least in part, clarify the molecular origin of the dipole fluctuations. We have identified two counterbalancing aspects: ring stacking that lowers dipole moments and hydrogen bonding that increases them.^{45,46} Although the complexity is much higher and probably involves several other balancing effects, a basic qualitative explanation of locality and fluctuations is given by the fact that as ions move between environments that are hydrogen bonding dominated to those which are ring stacking dominated (and vice versa), the dipoles change from larger to smaller values (and vice versa) leading to a broad distribution.

4. CONCLUSIONS

We have studied a series of imidazolium-based ILs and, for comparison, one protic IL of different chemical nature. For all systems, we find that static electrostatic properties are the result of two main aspects: locality and fluctuations. Basic considerations about the physics of these systems lead us to propose that these two aspects may actually be a more general signature for a larger class of ILs. Despite the fact that properties of electrolytes

are governed mainly by long-range electrostatic interactions, we found that the electrostatic interactions in the ILs investigated by us were reduced and very local, yet dominated by large fluctuations. In general, one expects screening in a liquid consisting of ions. However, it is not obvious that this takes place on a range comparable to the molecular size. Our results can be useful for a rational design of further molecules and for providing building criteria for large-scale theoretical and simulation methods. Likely, the high locality and charge reduction are the reasons of the success of classical force fields with empirically reduced ion charges^{21,37,42} in describing bulk properties.

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REFERENCES

- (1) Pádua, A. A. H.; Costa Gomes, M. F.; Canongia Lopes, J. N. A. *Acc. Chem. Res.* **2007**, *40*, 1087–1096.
- (2) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- (3) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Hoboken, NJ, 2007.
- (4) Werner, S.; Haumann, M.; Wasserscheid, P. *Annu. Rev. Chem. Biomol. Eng.* **2010**, *1*, 203–230.
- (5) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621–629.
- (6) Pinkert, A.; Marsh, K. N.; Pang, S.; Staiger, M. P. *Chem. Rev.* **2009**, *109*, 6712–6728.
- (7) Kirchner, B. *Top. Curr. Chem.* **2009**, *290*, 213–262.
- (8) Dommert, F.; Schmidt, J.; Krekeler, C.; Zhao, Y. Y.; Berger, R.; Delle Site, L.; Holm, C. *J. Mol. Liq.* **2010**, *152*, 2–8.
- (9) Schmidt, J.; Krekeler, C.; Dommert, F.; Zhao, Y.; Berger, R.; Delle Site, L.; Holm, C. *J. Phys. Chem. B* **2010**, *114*, 6150–6155.

- (10) Zahn, S.; Uhlig, F.; Thar, J.; Spickermann, C.; Kirchner, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 3639–3641.
- (11) Thar, J.; Brehm, M.; Seitsonen, A. P.; Kirchner, B. *J. Phys. Chem. B* **2009**, *113*, 15129–15132.
- (12) Tsuzuki, S.; Tokuda, H.; Mikami, M. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4780–4780.
- (13) Lehmann, S. B. C.; Roatsch, M.; Schöppke, M.; Kirchner, B. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7473–7486.
- (14) Zahn, S.; Thar, J.; Kirchner, B. *J. Chem. Phys.* **2010**, *132*, 124506–124506.
- (15) Qiao, B.; Krekeler, C.; Berger, R.; Delle Site, L.; Holm, C. *J. Phys. Chem. B* **2008**, *112*, 1743–1751.
- (16) Dommert, F.; Schmidt, J.; Qiao, B.; Zhao, Y.; Krekeler, C.; Delle Site, L.; Berger, R.; Holm, C. *J. Chem. Phys.* **2008**, *129*, 224501.
- (17) Stark, A. *Top. Curr. Chem.* **2009**, *290*, 41–81.
- (18) Fumino, K.; Wulf, A.; Ludwig, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 3830–3834.
- (19) Krekeler, C.; Dommert, F.; Schmidt, J.; Zhao, Y. Y.; Holm, C.; Berger, R.; Delle Site, L. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1817–1821.
- (20) Lynden-Bell, R. M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1733–1740.
- (21) Youngs, T. G. A.; Hardacre, C. *ChemPhysChem* **2008**, *9*, 1548–1558.
- (22) Hallett, J. P.; Liotta, C. L.; Ranieri, G.; Welton, T. *J. Org. Chem.* **2009**, *74*, 1864–1868.
- (23) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
- (24) CPMD; IBM and Max-Planck Institut, Stuttgart: Stuttgart, Germany; <http://www.cpmid.org/>.
- (25) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3098.
- (26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (27) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (28) Zahn, S.; Kirchner, B. *J. Phys. Chem. A* **2008**, *112*, 8430–8435.
- (29) Lin, I.-C.; Röthlisberger, U. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2730–2730.
- (30) Bagno, A.; D’Amico, F.; Saielli, G. *ChemPhysChem* **2007**, *8*, 873–881.
- (31) Wannier, G. H. *Phys. Rev.* **1937**, *52*, 191–197.
- (32) Marzari, N.; Vanderbilt, D. *Phys. Rev. B* **1997**, 12847–12847.
- (33) Silvestrelli, P. L.; Parrinello, M. *Phys. Rev. Lett.* **1999**, *82*, 3308–3308.
- (34) Kirchner, B.; Hutter, J. *J. Chem. Phys.* **2004**, *121*, 5133–5142.
- (35) Kornyshev, A. A. *J. Phys. Chem. B* **2007**, *111*, 5545–5557.
- (36) Fedorov, M. V.; Kornyshev, A. A. *J. Phys. Chem. B* **2008**, *112*, 11868–11872.
- (37) Morrow, T. I.; Maginn, E. J. *J. Phys. Chem. B* **2002**, *106*, 12807–12813.
- (38) Del Popolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108*, 1744–1752.
- (39) Turton, D. A.; Hunger, J.; Stoppa, A.; Hefter, G.; Thoman, A.; Walther, M.; Buchner, R.; Wynne, K. *J. Am. Chem. Soc.* **2009**, *131*, 11140–11146.
- (40) Méndez-Morales, T.; Carrete, J.; Cabeza, O.; Gallego, L. J.; Varela, L. M. *J. Phys. Chem. B* **2011**, *115*, 6995–7008.
- (41) Blöchl, P. E. *J. Chem. Phys.* **1995**, *103*, 7422–7422.
- (42) Bhargava, B. L.; Balasubramanian, S. *J. Phys. Chem. B* **2007**, *111*, 4477–4487.
- (43) Cremer, T.; Kolbeck, C.; Lovelock, K. R. J.; Paape, N.; Wölfel, R.; Schulz, P. S.; Wasserscheid, P.; Weber, H.; Thar, J.; Kirchner, B.; Maier, F.; Steinrück, H.-P. *Chem.—Eur. J.* **2010**, *16*, 9018–9033.
- (44) Fröba, A. P.; Kremer, H.; Leipertz, A. *J. Phys. Chem. B* **2008**, *112*, 12420–12430.
- (45) Zahn, S.; Wendler, K.; Delle Site, L.; Kirchner, B. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15083–15093.
- (46) Wendler, K.; Dommert, F.; Zhao, Y. Y.; Berger, R.; Holm, C.; Delle Site, L. *Faraday Discuss.* **2011**, DOI: 10.1039/C1FD00051A.