

# Chemically active domains of liquids

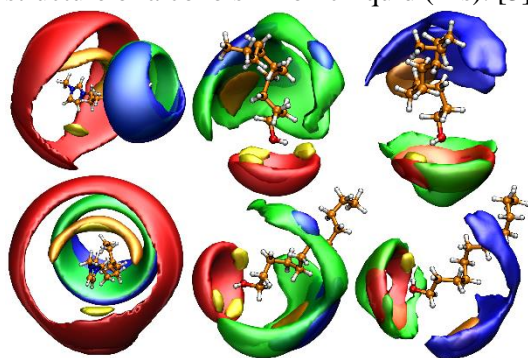
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Choosing the right solvent is important for the successful outcome of many reactions, therefore, an understanding on the molecular level behavior of the given liquid itself is mandatory if the full potential of the solvent should be reached. This is particularly the case if the liquid is actively participating in the reaction, not only as a solvent, but also as a catalyst. In this talk, we discuss liquids that are examples of such complex processes and we show how we analyze their behavior [1]. The catalytically active mixtures of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) - which is one of the more stabilizing solvents for spin centers serves as such an example. [2]

In another example, we elaborate on the structure of alcohols in ionic liquid (ILs). [3]



**Figure 1: From Ref [3]: Spatial distribution functions of cation (left), alcohol (long side chain cation: middle; short side chain: right). Cation: red; anion: orange; side chain: green; OH: yellow; side chain alcohol: blue.**

Structure-directing or template effects have been invoked several times for ILs to explain the different outcome in material synthesis. The successful imprinting of the ILs' order in the alignment of the alcohol molecules in these simple model systems (Fig. 1) shows that the micro-heterogeneous structure of ILs can indeed be applied to arrange reaction substrates in a predetermined fashion, opening new possibilities for explaining or enhancing the selectivity in chemical reactions in ILs.

In electrolyte systems, the association of the ions to form ion pairs or other, low charge aggregates is a long discussed issue, since it can affect the manner and the extent of conduction by changing the number of charged species in the solution. Thus, we will cover ion pairing in ionic liquids [4] considering the bulk but also the interface gas-liquid. The charge of the ions is often assumed to  $\pm 1$ . Although this seems trivial, but due to a combination of polarization and charge transfer effects between the ions these charges are decreased in their absolute values.[5] The derivation and application of a polarizable force field in order to describe the  $\text{TiO}_2$ -IL interface [6] playing a role in solar cell applications can account for those effects. Connected to this is structural diffusion. [7] We will also elaborate on voids in liquids to deepen our understanding of complicated liquids. [1]

## References

- [1] M. Brehm, B. Kirchner, *J. Chem. Inf. Model.*, (2011), 51 (8), 2007-2023; M. Brehm, H. Weber, M. Thomas, O. Hollóczki, B. Kirchner, *ChemPhysChem* (2015), 16, 3271-3277; S. Gehrke, R. Macchieraldo, B. Kirchner, *PCCP*, submitted; J. Ingenmey, J. Blasius, G. Marchelli, A. Riegel, B. Kirchner, *J. Chem. Eng. Data* 2019, 64 (1), 255-261; M. von Domaros, E. Perlt, J. Ingenmey, G. Marchelli, B. Kirchner, *SoftwareX* (2018), 7, 356-359; M. Brüssel, E. Perlt, S. B. C. Lehmann, M. von Domaros, B. Kirchner, *J. Chem. Phys.*, (2011), 135 (19), 194113
- [2] O. Hollóczki, A. Berkessel, J. Mars, M. Mezger, A. Wiebe, S. R. Waldvogel, B. Kirchner, *ACS Catal.* 2017, 7, 1846-1852. DOI: 10.1021/acscatal.6b03090
- [3] R. Elfgen, O. Hollóczki, B. Kirchner, *Acc. Chem. Res.* (2017), 50, 2949-295
- [4] B. Kirchner, F. Malberg, D. S. Firaha, O. Hollóczki, *J. Phys.: Condens. Matter*, (2015), 27, 463002; O. Hollóczki, F. Malberg, T. Welton, B. Kirchner, *Phys. Chem. Chem. Phys.* (2014), 16, 16880; F. Malberg, O. Hollóczki, M. Thomas, B. Kirchner, *Struct. Chem.* (2015), 26, 1343
- [5] T. Cremer, et al., *Chem. Eur. J.*, (2010), 16, 9018; N. Taccardi, I. Niedermaier, F. Maier, H.-P. Steinrück, and P. Wasserscheid, *Chem. Eur. J.* 2012, 18, 8288; Richard M. Fogarty et al., DOI: 10.1039/c7fd00155j; S. Kossmann, J. Thar, B. Kirchner PA. Hunt, T. and Welton, *J. Chem. Phys.* (2006), 124, 174506
- [6] H. Weber, M. Salanne, B. Kirchner, *J. Phys. Chem. C*, (2015), 119 25260; H. Weber, T. Bredow, B. Kirchner, *J. Phys. Chem. C*, (2015), 119, 15137; M. Salanne, B. Rotenberg, S. Jahn, R. Vuilleumier, C. Simon, P. Madden, *Theor. Chem. Acc.* (2012), 131, 1143; D. Corradini, D. Dambournet, M. Salanne, *M. Sci. Rep.* (2015), 5, 1155
- [7] R. Elfgen, et al., *Z. Anorg. Allg. Chem.* (2017) 643, 41; B. Kirchner, A. P. Seitsonen, *Inorg. Chem.*, (2007), 46, 2751; E. Perlt, M. von Domaros, B. Kirchner, R. Ludwig, F. Weinhold, *Sci. Rep.* 2017, 7, 10244; J. Ingenmey, S. Gehrke, B. Kirchner, *ChemSusChem* (2018), 11, 1900-1910; O. Hollóczki *ACS Sustainable Chem. Eng.*, DOI: 10.1021/acssuschemeng.8b05668