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Towards NMR driven structural modelling of oxide glasses

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Solid State NMR and Molecular Dynamics (MD) simulations are two techniques that have clearly proven to be very powerful and versatile for studying the structure of glassy materials. On one hand, the strength of NMR relies on the strong correlation between the NMR parameters and the short- to medium-range structure of the probed nucleus. In the last decade, this is has greatly benefited from the wealth of advanced methodologies that have been devised for determining very precise NMR parameters.[1] On the other hand, MD is the reference technique employed to build atomistic structural models, generally comprising hundreds to millions of atoms. However, for many years, the comparison between these two major techniques was limited to the populations of the structural motifs building the glass network, provided that an interpretation of the NMR spectra has already be made. In glass, such an interpretation remains difficult because of the inhomogeneous broadening caused by a continuous distribution of NMR parameters arising from both the chemical and topological disorder (which increase with the number of constituents).

The introduction of the DFT GIPAW method which is specifically devised for periodic systems has led to the concept of first-principles modelling of Solid state NMR spectra.[2–4] Through spin-effective Hamiltonian simulations built with the computed NMR parameters, a direct comparison between the experimental NMR spectra and their experimental counterparts is feasible. Because of the efficiency of GIPAW codes together with the increase of the computational power available, systems up to 1000 atoms can now be investigated. The use of MD instead of cluster models can be crucial as MD can better account for correlations between structural parameters and long-range interactions. With the MD-GIPAW method, key questions regarding the glass structure can be addressed, such as i) the extent of structural disordering and how it is reflected into the measured NMR parameter distributions,[5] and ii) the relationships between local structural features and NMR parameters.[6]

As examples of this methodology, investigations of the structure of silicate, aluminosilicate and borosilicate glasses will be presented. This approach will be shown to be a decisive interpretative tool for deeper understanding of the spectral behaviour of the different cations (Al, Si, B, Na, Ca) or anions (O) in multicomponent glasses. Recent extensions for predicting spin lattice relaxation of quadrupolar ions from first-principles will be reported as well.[7] Finally, integration of the NMR data in the generation process of structural models, i.e. in an active manner to drive the modelling process, will be discussed.

References

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