Modelling solid defects and impurities beyond the dilute limit with grand-canonical configurational ensembles

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The disordered occupancy of crystal sites in heavily defective materials, or in solid solutions, represents a challenge for computational materials science. The established approach to model the thermodynamics of site disorder in solids is the use of cluster expansion methods, where an approximate interaction potential, which is only a function of site occupancies, is used to efficiently evaluate energies in the configurational space. However, when other properties beyond thermodynamics are of interest, a different approach is needed. In this talk, I will first discuss strategies for the computational modelling of the NMR spectra of disordered solids via configurational ensembles. Obtaining NMR peaks via DFT calculations for all the configurations in a canonical ensemble, and then taking statistical averages, represents a useful approximation [1]. However, because relatively small supercell sizes must be used for this, the statistical representation suffers: not all possible chemical environments, in particular those representing compositional fluctuations, are represented in the canonical ensemble. I will show how a grand-canonical ensemble approach, recently implemented in our SOD (Site Occupancy Disorder) code [2], gives a much better description of compositional fluctuations and explains peaks in the NMR spectrum of the $La_2(Zr_{1-x}Sn_x)_2O_7$ pyrochlore solid solution that are missed in the canonical representation [3]. I will discuss strategies to minimise the large computational cost of these simulations, including ensemble truncation and machine-learning-aided predictions. I will also illustrate how grand-canonical ensembles can be generally useful in the simulation of disorder of defects and impurities, when one is forced to employ relatively small supercells.

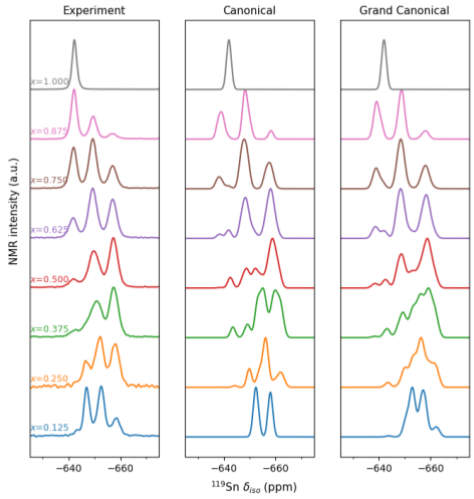

Figure 1: Experimental (left) and simulated NMR spectra for $La_2(Zr_{1-x}Sn_x)_2O_7$. The centre and right panels correspond to the spectra simulated using the canonical and grandcanonical ensembles, respectively.

Acknowledgments

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[1] Moran, R.F.; McKay, D.; Tornstrom, P.C.; Aziz, A.; Fernandes, A.; Grau-Crespo R.; Ashbrook, S.E., 2019. Ensemble-based modeling of the NMR spectra of solid solutions: cation disorder in $Y_2(Sn,Ti)_2O_7$. *Journal of the American Chemical Society*, *141*(44), pp.17838-17846.

[2] Grau-Crespo, R.; Hamad, S. Site-Occupancy Disorder (SOD) code: https://github.com/gcmt-group/sod. Release version 0.52 (2023)

[3] Grau-Crespo, R; Hamad, S.; Balestra, S.R.G.; Issa, R.; Sparks, T; Fernandes, A; Griffiths, B. L.; McKay, D.; Ashbrook, S.E.; In preparation.