Taming Disorder in Solid Materials

Exploring how experiment and theory can combine
to understand and characterise disordered materials

Calman Learning Centre, Durham University, 12–13 Dec 2023

Scientific committee

Paul Hodgkinson (Durham University, CCP-NC)
Frédéric Blanc (Liverpool University, CCP-NC)
David Quigley (Warwick University, CCP5)
Vasily Oganesyan (University of East Anglia, CCP5)
and advised by Stewart Clark (Durham University, CCP9)

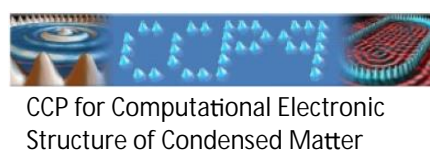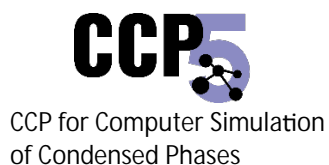## Local organisers

Paul Hodgkinson, Karen Johnston

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Programme
Talk abstracts (in order of presentation)
Poster abstracts (please follow this numbering when putting up posters)

Meeting sponsors

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Tuesday, 12 December

from **12:15**   Registration (Ground floor, Calman Learning Centre) and buffet lunch (Top floor). *Poster presenters to put posters up at arrival.*

Session 1
Chair: David Quigley (Univ. Warwick)

13:30   Welcome

13:35   **Andrew Goodwin** (Univ. Oxford)
Session Introduction + *New approaches for interpreting diffuse scattering: from single crystals to amorphous solids*

14:15   **Samuli Ollila** (VTT Technical Research Centre of Finland)
NMRlipids project delivers quality evaluated membrane simulations for data-driven applications

14:45   **Elena Patyukova** (Univ. Liverpool)
Structural disorder in inorganic crystalline materials: a comprehensive analysis

15:15   Refreshments and Poster Session 1 (Top floor)

Session 2
Chair: Paul Hodgkinson (Univ. Durham)

16:15   **Ricardo Grau-Crespo** (Univ. Reading)
Session Introduction + *Modelling the NMR spectra of solid solutions: canonical and grand-canonical ensembles, DFT and machine learning*

16:55   Frédéric Blanc (Univ. Liverpool)
Disorder and oxide ion diffusion mechanism in melilite: An NMR viewpoint

17:25   **Manuel Cordova** (EPFL)

Atomic-level structure determination of amorphous molecular solids by NMR

19:30   Conference dinner. Hatfield College dining room.
Please remember to bring your conference badge.

Wednesday, 13 December

Session 3:
Chair: Frédéric Blanc (Univ. Liverpool)

9:00   **Thibault Charpentier** (Univ. Paris-Saclay)

Session Introduction + *Boosting NMR-Driven Reverse Monte Carlo Simulations of Glasses with Machine Learning*

9:40   **Kim Jelfs** (Imperial College, London)

Session Introduction + *Computational Modelling of Amorphous Microporous Materials*

10:20   **Andrew Morris** (Univ. Birmingham)

Combining ss-NMR with XAS and first principles calculations to build and verify finite temperature amorphous models

10:50   Refreshments and Poster Session 2 (Top floor)

Session 4
Chair: Vasily Oganesyan (Univ. East Anglia)

11:50   **Nicholas Hine** (Univ. Warwick)

Calculation of Absorption and Emission Spectra in Explicit Solvent using Large-Scale DFT and Machine Learned Interatomic Potentials

12:20   **Yaroslav Khimyak** (Univ. East Anglia)

Understanding phase transitions and nature of disorder in pharmaceutical materials: polymorphs, co-crystals and nano-confined systems

12:50   **Karen Johnston** (Univ. Durham)

Probing Structural Subtleties in Anti-Perovskite Solid Electrolytes

13:20   Meeting close followed by buffet lunch. *Posters to be removed.*

New approaches for interpreting diffuse scattering: from single crystals to amorphous solids

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The presence of structural disorder in a material means that its diffraction patterns will contain a diffuse scattering component. The degree of structure in this diffuse scattering is characteristic of the extent of correlations within the disorder from which it arises. Interpretation of diffuse scattering patterns is one of the most challenging aspects of modern crystallography, and yet is key to providing important structural insight for systems with correlated disorder. This talk will summarise a handful of recent developments in the field that offer mechanisms for improving the quality and ease of interpretation of diffuse scattering. Key examples will be the methodologies of 3D-ΔPDF measurements for single crystals [1,2], the use of electron diffraction to access related data even from polycrystalline samples [3], and the application of hybrid reverse Monte Carlo (HRMC) analysis to generate realistic atomistic models of amorphous materials by combining the complementary sensitivities of experiment and interatomic potentials [4,5].

[1] T. Weber & A. Simonov, *Z. Kristallogr.* **227**, 238-247 (2012)

[2] E. G. Meekel, E. M. Schmidt, L. J. Cameron, A. D. Dharma, H. J. Windsor, S. G. Duyker, A. Minelli, T. Pope, G. Orazio Lepore, B. Slater, C. J. Kepert & A. L. Goodwin, *Science* **379**, 357-361 (2023)

[3] E. M. Schmidt, P. B. Klar, Y. Krysiak, P. Svora, A. L. Goodwin & L. Palatinus, *Nat. Commun.* **14**, 6512 (2023)

[4] G. Opletal, T. Petersen, B. O'Malley, I. Snook, D. G. McCulloch, N. A. Marks & I. Yavovsky, *Mol. Simul.* **28**, 927-937 (2002)

[5] T. C. Nicholas, A. E. Stones, A. Patel, F. M. Michel, R. J. Reeder, D. G. A. L. Aarts, V. L. Deringer & A. L. Goodwin, *Nat. Chem.* (2023, advance article) doi:10.1038/s41557-023-01339-2

NMRlipids project delivers quality evaluated membrane simulations for data-driven applications

O. H. Samuli Ollila[1,2*] and NMRlipids open collaboration

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Cellular membrane lipid composition is implicated in diseases and major biological functions in cells, but membranes are difficult to study experimentally due to their intrinsic disorder and complex phase behaviour. Molecular dynamics (MD) simulations have been useful in understanding membrane systems, but they require significant computational resources and often suffer from inaccuracies in model parameters. Applications of data-driven and machine learning methods, currently revolutionizing many fields, are limited to membrane systems due to the lack of suitable training sets. In the NMRlipids project (http://nmrlipids.blogspot.com/), we are tackling these issues by combining solid state NMR and X-ray scattering experiments with MD simulations using open collaboration approach. We evaluate the quality of simulation models against experimental data, and then use the best performing simulation models to interpret experiments. By this combination, we have elucidated, for example, charged small molecule binding to membranes[1] and lipid-protein interactions[2]. On the other hand, we have collected MD simulation data contributed via open collaboration into the NMRlipids Databank, which provides programmatic access to hundreds of MD simulation trajectories (https://nmrlipids.github.io/). The NMRlipids Databank enables wide range of novel data-driven and machine learning applications to understand lipid membranes. For example, we have analyzed how anisotropic diffusion of water and cholesterol flip–flop rates depend on membrane properties, and trained a machine learning model that predicts multi-component membrane properties.[3] Furthermore, the NMRlipids Databank performs automatic quality evaluation and ranking of MD simulations against experiments, which can be used to select best models for specific applications or to improve simulation models. We are currently extending similar approaches also to other than membrane systems[4].

1. Nencini and O. H. S. Ollila *J. Phys. Chem. B* 2022, 126, 36, 6955–6963 (https://doi.org/10.1021/acs.jpcb.2c05024)
2. Bacle et al. J. Am. Chem. Soc. 2021, 143, 13701–13709 (https://doi.org/10.1021/jacs.1c05549)
3. Kiirikki et al. https://doi.org/10.26434/chemrxiv-2023-jrpwm
4. Nencini et al. https://doi.org/10.26434/chemrxiv-2023-684br

Structural disorder in inorganic crystalline materials: a comprehensive analysis

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It is an interesting fact that approximately 50% of entries in the Inorganic Crystal Structure Database (ICSD) [1] exhibit some form of structural disorder. While ordered crystalline materials have been extensively researched, disordered materials remain less understood in terms of their stability and structure-property relationships. A deeper comprehension of structural disorder would allow using it as a tool for designing novel materials with tailored properties.

This work aims to provide a thorough analysis of structurally disordered materials within the ICSD, leveraging data extracted from cif files. To achieve this, we derive a new classification of structurally disordered crystalline materials which allows us to introduce a range of qualitative and quantitative measures of structural disorder. In particular, we derive much more accurate expressions for calculation of mixing and configurational entropy from cif files when existed in the literature [2,3]. We also perform statistical analysis of the experimental data on disordered compounds in the ICSD to draw insight about general trends or disorder distribution.

1. Zagorac, D., Mueller, H., Ruehl, S., Zagorac, J. & Rehme, S., Recent developments in the Inorganic Crystal Structure Database: theoretical crystal structure data and related features. Appl. Cryst. 52 (2019), 918-925; DOI: 10.1107/S160057671900997X
2. Kaussler, C. & Kieslich, G. CrystIT: complexity and configurational entropy of crystal structures via information theory. J. Appl. Cryst. 54 (2021), 306–316; DOI: 10.1107/S1600576720016386
3. Krivovichev, S., Krivovichev, et al, Structural and chemical complexity of minerals: an update, Mineralogical Magazine 86 (2022), 183-204; DOI: 10.1180/mgm.2022.23

Modelling the NMR spectra of solid solutions: canonical and grand-canonical ensembles, DFT and machine learning

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The disordered occupancy of crystal sites in solid solutions or heavily defective materials 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 discuss strategies for the computational modelling of the NMR spectra of solid solutions 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 first 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 prediction of NMR peaks. I will also discuss how grand-canonical ensembles can be more generally useful in the simulation of disorder from first principles, where one is forced to employ relatively small supercells.

1. 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 Y2 (Sn, Ti) 2O7. *Journal of the American Chemical Society*, *141*(44), pp.17838-17846.
2. https://github.com/gcmt-group/sod. Release version 0.51.
3. Grau-Crespo, R; Hamad, S; Balestra, S.R.G.; Issa, R.; Sparks, T; McKay, D.; Ashbrook, S.E.; In preparation (2023).

Li ion diffusion in disordered materials as seen by NMR

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The development of all-solid-state batteries requires solids with extraordinarily high (overall) ionic conductivities reaching or even exceeding those typically met in the liquid state. To understand the basic guidelines determining fast ion transport in solids we need to characterize model substance whose ion transport properties benefit from several key properties. Such properties may include (i) overall structural disorder in the bulk and interfacial regions [1a,1b], (ii) site disorder in partially occupied sub-lattices [1c,1d], (iii) the influence of lattice dynamics on cation hopping [1e] as well as (iv) dimensionality effects (1D, 2D) [1f]. The latter are usually met in materials with spatially confined diffusion pathways such as $RbSn_2F_5$ [2a], β-Li_3PS_4 [2b] and in Li-ion conductors inspired by natural hectorite-type structures [2c]. Results from recent studies performed in our lab will be presented and discussed, special emphasis is put on materials with structural disorder in both the bulk regions or, in the case of nanostructured ceramics, in their interfacial areas.

[1] a) L. Schweiger, et al., J. Am. Chem. Soc. 144, 9597 (2022); b) M. Gombotz, et al., Solid State Ionics 369, 115726 (2021); c) W. Schmidt, et al., Chem. Mater. 27, 1740 (2015); d) K. Hogrefe, et al., J. Am. Chem. Soc. 144, 1795 (2022); e) I. Hanghofer, et al., Chem. Mater. 31, 4591 (2019); f) M. Gombotz, et al., Phil. Trans. R. Soc. A 379, 20200434 (2021).

[2] a) M. Gombotz, et al., Phys. Chem. Chem. Phys. 21, 1872 (2019); b) D. Prutsch, et al., Chem. Mater. 30, 7575 (2018); c) C. Hiebl, et al., Chem. Mater. 32, 7445 (2020).

Atomic-level structure determination of amorphous molecular solids by NMR

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4. Early Chemical Development, Pharmaceutical Sciences, R&D, AstraZeneca, Macclesfield, UK

5. Early Product Development and Manufacturing, Pharmaceutical Sciences, R&D, AstraZeneca, Macclesfield, UK

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Structure determination of amorphous materials remains challenging, owing to the disorder inherent to these materials. Nuclear magnetic resonance (NMR) powder crystallography is a powerful method to determine the structure of molecular solids, but disorder leads to a high degree of overlap between measured signals, and prevents the unambiguous identification of a single modeled periodic structure as representative of the whole material. Here, we determine the atomic-level ensemble structure of the amorphous form of the drug AZD4625 by combining solid-state NMR experiments with molecular dynamics (MD) simulations and machine-learned chemical shifts. By considering the combined shifts of all ^{1}H and ^{13}C atomic sites in the molecule, we determine the structure of the amorphous form by identifying an ensemble of local molecular environments that are in agreement with experiment. We then extract and analyze preferred conformations and intermolecular interactions in the amorphous sample in terms of the stabilization of the amorphous form of the drug. The method presented here is generally applicable to any amorphous molecular solid.

Boosting NMR-Driven Reverse Monte Carlo Simulations of Glasses with Machine Learning

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As glass has become ubiquitous in our lives, in 2022, it was proclaimed by The United Nations as the International Year of Glass. Due to the lack of long-range order, glass is often referred to as amorphous, and its structure remains challenging to study. In this respect, solid-state NMR has established itself as one of the most powerful spectroscopy thanks to the wealth of techniques that it offers.[1] However, the acquired information is limited to short- (structural motifs building the glass network) to medium- (connectivity or proximity between these motifs) range order: it cannot allow the construction of complete 3D structural models. To this end, Molecular Dynamics (MD) is an effective technique for studying the atomic structure and structure-properties in glasses.[2] Thanks to recent advances in DFT calculations, NMR can now be effectively combined with MD to help interpret the experimental data, for example, to decipher the origin of the spectral broadening arising from the geometrical and chemical disorder inherent to the vitreous state.[3]

To incorporate NMR information into MD simulations, we have recently developed a Reverse Monte Carlo (RMC) approach that couples MD force fields, neutron and NMR data. RMC modeling [4] aims at generating structural models that best reproduce experimental data; its principle is based on random displacements of atoms using a Metropolis-Hastings algorithm. This approach will be described and illustrated using two examples: i) the construction of aluminosilicate glasses models with a constrained population of tetrahedral SiO_4 $Q^{(n)}(mAl)$ units as determined by J-coupling NMR experiments; ii) the construction of borate glasses with 6-membered rings, structural features that are still debated in these glass compositions. The combination with Machine Learning to compute the NMR properties[5] will be highlighted as a promising approach to predict NMR spectra for models containing thousands of atoms.

1. M. Edén, *J. of Magn. Reson Open* 16-17, 100112 (**2023**)
2. A. Pedone, M. Bertani, L. Brugnoli, A. Pallini, *J. of Non-Cryst. Solids X* 15, 100115 (**2022**)
3. T. Charpentier, M.C. Menziani, A. Pedone, *RSC Adv*. 3, 10550-10578 (**2013**); Y. Ishii Y, M. Salanne, T. Charpentier, K. Shiraki, K. Kasahara, N. Ohtori, *J Phys Chem C*. 120, 24370-24381 (**2016**)
4. R.L McGreevy, P Zetterström, J. of Non-Cryst. Solids 293–295, 297-303 (**2001**)
5. Z. Chaker, M. Salanne, J.-M. Delaye, T. Charpentier *Phys Chem Chem Phys*. 21, 21709-21725 (**2019**)

Computational Modelling of Amorphous Microporous Materials

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Amorphous microporous materials have potential for application as membranes for chemical separations, a technology that would require up to 90% less energy than distillation. Examples of these materials are amorphous microporous polymers and amorphous Metal—Organic Frameworks (*a*MOFs). The former can be directly processed from solutions (linear polymers like PIMs) or shaped into film through interfacial polymerisation (networked polymers), while the latter can be shaped into bulk morphologies through melt-quenching or ball-milling. However, due to their lack of structural long-range order, these materials are much more challenging to characterise compared to their crystalline counterparts, making their structure-property relationships difficult to discover. Molecular simulations can provide structural models for these materials and, in this way, help rationalise their behaviour though atomistic level understanding of their structure and derive design rules to direct future experimental efforts.

Using a computational approach developed for the structure prediction of organic polymers, we investigated the bulk structure of several porous polymers and amorphous MOFs. Notably, the approach used does not require any experimentally derived data to use as a target property for the structure construction and refinement, giving us the possibility to predict the structure of hypothetical amorphous microporous materials that have not been synthesised yet in the lab. This structure prediction approach opens the possibility to outline design rules for porous polymers and *a*MOFs, allowing us to suggest new promising candidates with properties tailored for specific applications.

Combining ss-NMR with XAS and first principles calculations to build and verify finite temperature amorphous models

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Structure determination (the process of uncovering the atomic arrangement of a material), is impeded, both experimentally and computationally, by disorder. Using molecular dynamics it is surely trivial to generate a model of a disordered solid. The problem comes in *verifying* the model against experiment, especially as the ubiquitous X-ray diffraction is no help.

The lack of a verifiable atomic model presents a huge challenge when designing functional amorphous materials. Such materials may be characterised through their local atomic environments using, in this example, solid-state NMR and XAS. By combining these two spectroscopy methods to inform the sampling of configurations from *ab initio* molecular dynamics we devise and, crucially, *validate* our amorphous model. We choose amorphous alumina to illustrate the approach due to its wide range of technological uses.[1] Our model matches well with both types of experimental spectra. We show how the disordered local environments match to the NMR chemical shift, and, finally, how the model may be used to understand the underlying electronic properties of a material.
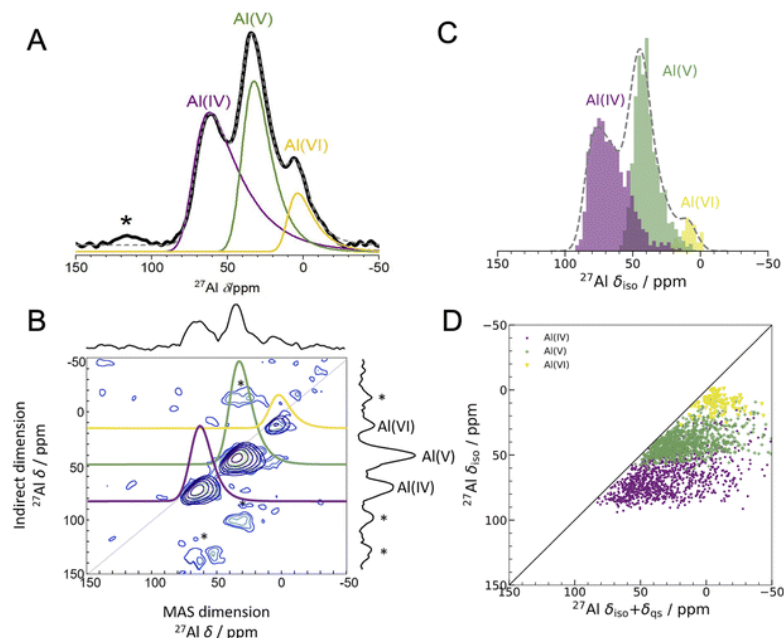
Experimental 1D NMR (A) and MQMAS (B) of am-Al_2O_3 compared to DFT-calculated isotropic chemical shifts (C) Comparison of δ_{iso} and $\delta_{iso} + \delta_{qs}$ from DFT-calculated NMR (D).

[1]. A. F. Harper, S. P. Emge, P. C. M. M. Magusin, C. P. Grey, A. J. Morris, *Chem. Sci.*, **14** (5) , 1155-1167 (2022) DOI: 10.1039/D2SC04035B

Calculation of Absorption and Emission Spectra in Explicit Solvent using Large-Scale DFT and Machine Learned Interatomic Potentials

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Theoretical spectroscopy calculations in explicit solvent require a challenging combination of high-accuracy electronic structure, large system sizes, and well-sampled molecular dynamics on the timescale of solvent reorganisations. Linear-Scaling TD-DFT approaches to LR-TDDFT can scale to thousands of atoms, but ab initio sampling is still unfeasible. Here we employ Machine-Learned Interatomic Potentials to approximate the DFT ground and LR-TDDFT excited states for clusters of solvent surrounding three isomers of a prototype sunscreen, methyl anthranilate. We demonstrate use of ESTEEM to train accurate MLIPs capable of accelerated MD in both ground and excited states. We can then sample configurations from the ground or excited nuclear ensembles, evaluate vertical transition energies, and predict absorption/emission peaks, solvatochromic shifts, Stokes' shifts and lineshapes in explicit solvent. MAE's are typically below 10nm: a dramatic improvement on implicit solvent approaches, and we can rigorously test the accuracy of the MLIP by comparing its cluster energies directly to DFT/TD-DFT. We further extend the approach by introducing Active Learning protocols based on error estimation through a committee of MLIP calculators to accelerate the learning of excitation energies.
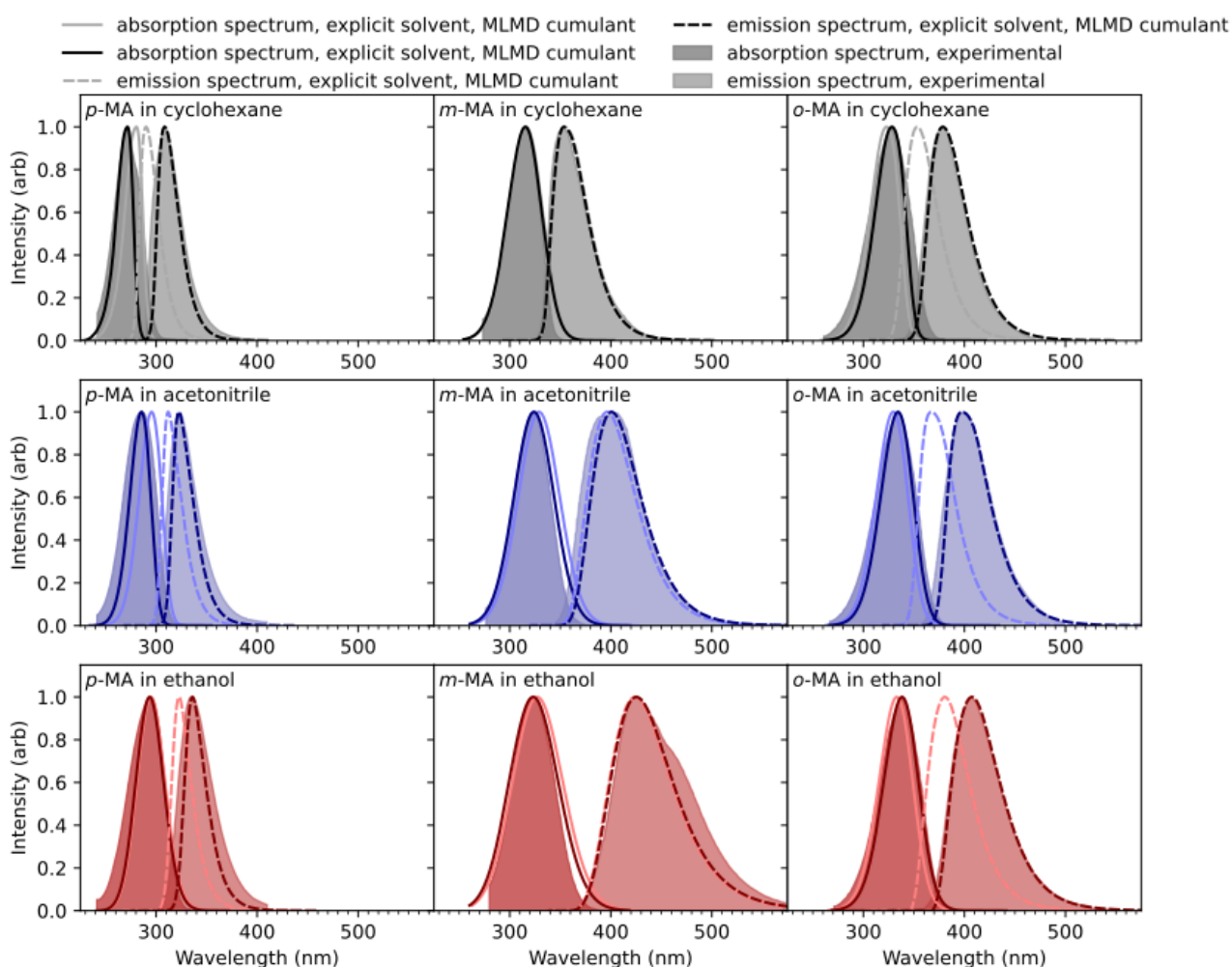
Understanding phase transitions and nature of disorder in pharmaceutical materials: polymorphs, co-crystals and nano-confined systems

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Understanding the phase transitions of pharmaceutical organic solids is of increasing importance from both academic and industrial perspective. The combined analysis of structure and dynamics of bulk and confined pharmaceuticals, as well as understanding the role of molecular mobility and disorder in directing phase transitions present considerable experimental and computational challenges. Solid-state NMR spectroscopy is well placed to probe both structure and dynamics of the molecules as bulk and confined nanocrystals due to its sensitivity to intermolecular interactions across different length scales and dynamic regimes. Using examples of pharmaceuticals with diverse polymorphism (flufenamic acid [1] and tolbutamide [2]), cocrystals (carbamazepine-tartaric acid [3], flufenamic acid-nicotinamide) and confined systems [1, 2, 4] this work will focus on identifying different structural and dynamics domains and transformations between such states.

The local environments of tolbutamide (TB) solid forms both in bulk and as encapsulated nanocrystals [2] were studied using solid-state NMR spectroscopy and relaxation measurements (^{1}H T_1, ^{1}H $T_{1\rho}$ and ^{13}C $T_{1\rho}$). Significant differences in the dynamics of TB forms I^L and I^H, which differ only in the conformation of aliphatic tail are explained using a combination of solid-state NMR, dielectric spectroscopy and MD simulations. The nature of the structural and dynamic disorder of the nanoporous organic cocrystal carbamazepine-tartaric acid was probed through complementary solid-state NMR, X-ray diffraction, and broadband dielectric spectroscopy experiments combined with molecular dynamics simulations [3]. The tartaric acid molecules present in the channel-like cocrystalline architecture show both translational and rotational dynamic disorder. We identified two different diffusion regimes of tartaric acid by dielectric spectroscopy and MD simulations, offering a very detailed picture of the nature of disordered in this channel-co-crystal [3]. We have also probed the formation of ordered/disordered domains in confined pharmaceuticals linking these with the hydration levels and storage conditions [1, 4].

1. K. P. Nartowski *et al*., *Angew. Chem*., 2016, 55, 8904-8908.
2. K. P. Nartowski *et al* ., *Mol. Pharm*, 2018, 15, 4926-4932.
3. L. Roca-Paixao *et al*., *Cryst. Growth Des*. 2023, 23, 120-133.
4. M. Nowak *et al*., *Int. J. Pharm*, 2023, 645, 123403.

Probing Structural Subtleties in Anti-Perovskite Solid Electrolytes

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The rechargeable lithium-ion (Li-ion) battery is considered the technology of choice for energy storage in a wide array of portable electronic devices. However, its application is limited by its use of liquid electrolytes, which are known to pose a serious fire and safety risk. All-solid-state Li-ion batteries are attracting considerable attention as possible alternatives to conventional liquid electrolyte-based devices as they present a viable opportunity for increased energy density and safety. In recent years, a number of candidate materials have been explored as possible solid electrolytes, including garnets, Li-stuffed garnets, Li-rich anti-perovskites (LiRAPs) and thio-LISICONs. In particular, the LiRAPs, including $Li_{3-x}OH_xCl$, have generated considerable interest, based on their reported ionic conductivities (~10^{-3} S cm^{-1}).[1,2] However, until recently, their lithium and proton transport capabilities as a function of composition were not fully understood. Hence, current research efforts have focused on the synthesis and structural characterisation of $Li_{3-x}OH_xCl$ using a combination of *ab initio* molecular dynamics, high-resolution powder diffraction and variable-temperature ^1H, ^2H and ^7Li solid-state NMR spectroscopy.

We will demonstrate that Li-ion transport is highly correlated with the proton and Li-ion vacancy concentrations. In particular, we will show that the Li ions are free to move throughout the structure, whilst the protons are restricted to solely rotation of the OH$^-$ groups. Based on these findings, and the strong correlation between long-range Li-ion transport and OH$^-$ rotation, we have proposed a new Li-ion hopping mechanism, which suggests that the Li-rich anti-perovskite system is an excellent candidate electrolyte for all-solid-state batteries.[3] However, to fully understand the mechanism for conduction, multiple, complementary characterisation techniques are needed.

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Poster Abstracts

1. Disorder and Oxide Ion Diffusion Mechanism in Melilite: An NMR Viewpoint

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Layered tetrahedral network melilite is a promising structural family of fast ion conductors that exhibits the flexibility required to accommodate interstitial oxide anions leading to excellent ionic transport properties at moderate temperatures.[1] Here, we present a combined experimental and computational MAS NMR approach which aims at elucidating the local configurational disorder and oxide ion diffusion mechanism in a key member of this structural family possessing the $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ composition.[2] ^{17}O and ^{71}Ga MAS NMR spectra display complex spectral line shapes that could be accurately predicted using a computational ensemble-based approach to model site disorder across multiple cationic and anionic sites, thereby enabling the assignment of bridging/non-bridging oxygens and the identification of distinct gallium coordination environments. The ^{17}O and ^{71}Ga MAS NMR spectra of $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ display additional features not observed for the parent $LaSrGa_3O_7$ phase which are attributed to interstitial oxide ions incorporated upon cation doping and stabilised by the formation of five-coordinate Ga centres conferring framework flexibility. ^{17}O high temperature (HT) MAS NMR experiments capture exchange within the bridging oxygens at 130 °C and reveal coalescence of all oxygen signals in $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ at approximately 300 °C, indicative of the participation of both interstitial and framework oxide ions in the transport process. These results, further supported by the coalescence of the ^{71}Ga resonances in the ^{71}Ga HT MAS NMR spectra of $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$, unequivocally provide evidence for the conduction mechanism in this melilite phase and highlight the potential of MAS NMR spectroscopy to enhance the understanding of ionic motion in solid electrolytes.
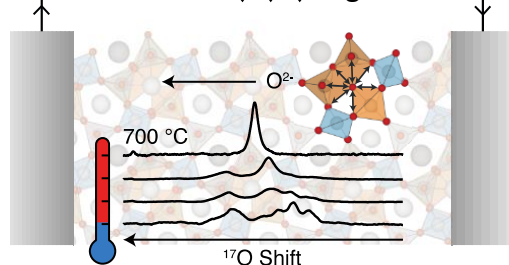
High temperature ^{17}O MAS NMR spectra reveal oxide ions diffusion in disordered oxides

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2. NMR crystallographic characterisation of mixed-metal aluminogallophosphate frameworks materials

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Microporous phosphate-based zeotypes have been investigated for various applications including as catalysts, catalyst supports, and guest storage/release systems. Many useful properties such as Lewis or Bronsted acidity and redox behaviour can be introduced by doping the framework with other species. Even the framework structures that are accessible can depend on their compositions.

Our recent work has involved characterisation of both aluminophosphates and gallophosphates through an NMR crystallographic approach, with a particular focus on the chabazite-type (CHA) system AlPO-34 and GaPO-34, as these are useful model systems in many experiments. However, as is so often the case, even these "model" systems show surprising complexity. The organic templates in AlPO-34 display microsecond timescale dynamics,[1] GaPO-34[2] has a complex gel aging process that can lead to the alternative phase, GaPO-34A with shorter aging times,[3,4] and calcination of GaPO-34 can (with 1-methylimidazolium as the template) proceed via an intermediate dehydrofluorination step.[5] The lessons learned from characterising and understanding these model systems have allowed us to prepare and characterise mixed-metal γ-(Al,Ga)$_2$O$_3$ oxide precursors[6] and convert these to "AlGaPOs".[7] Here, we present characterisation of the AlGaPO-34 solid solution, including combining NMR spectroscopy and DFT calculations to quantify and rationalise the non-random distribution of Al and Ga within the framework and understand the different orientations of the 1-methylimidazolium template molecules.

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7. Manuscript in preparation

3. What can NMR tell us about local structure disorder in electroceramics? A tale of two perovskite oxides.

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Two examples of the combination of solid-state ^{23}Na NMR and DFT calculations aimed to study local structure disorder and its relation to functional properties in perovskite oxides will be discussed **(Fig. 1)**. In the first example, I will cover the characterization of local structure disorder in (100-x)(Na$_{1/2}$,Bi$_{1/2}$)TiO$_3$ – x BaTiO$_3$ (NBT-BT) relaxor ferroelectrics for piezoelectric applications. I will highlight the relation between compositional disorder and tilting of oxygen octahedra, as unravelled by DFT computations of ^{23}Na EFG tensors, and discuss its role in the composition-driven ferroelectric-to-relaxor transition observed for this disordered perovskite oxide.[1]

The second example deals with solid-solutions of NaNbO$_3$ as promising antiferroelectric materials for high energy density capacitors. A peculiar relation is found between the distribution of ^{23}Na chemical shift and electric field gradient upon SrSnO$_3$ chemical substitution, which is elucidated with insight from DFT models encompassing site-occupation disorder. This analysis reveals that a more disordered, albeit less distorted ^{23}Na local environment correlates with the stabilization of an antiferroelectric state, and hence helps explain the increased ease for the corresponding ferroelectric-to-antiferroelectric transition in modified materials. [2]
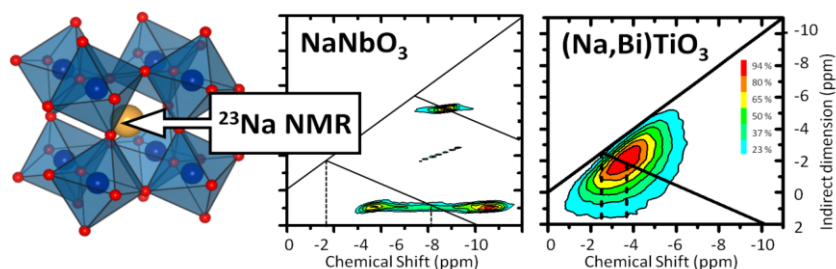

Fig. 1: ^{23}Na 3QMAS NMR spectra allows one to disentangle the distribution of NMR parameters for functional perovskite oxides; their structural origin is revealed with aid of DFT computations.

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M.H. Zhang, N. Hadaeghi, S. Egert, H. Ding, H. Zhang, P. B. Groszewicz, G. Buntkowsky, A. Klein, J. Koruza

4. Dynamic Aspects of Crystals

Calculating thermal diffuse scattering: a coarse-grained approach

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Keywords: diffuse scattering, framework, dynamics

In recent years, there has been a wealth of interest in framework materials such as metal-organic frameworks which show structured diffuse scattering. Structured diffuse scattering contains information about static and dynamic correlations within a crystal. There exist several approaches of attributing the signals to these two contributions: density functional theory, temperature dependence and inelastic scattering (IXS and INS). These methods can be time-consuming and difficult to carry out.

This work describes a faster alternative. This approximate, coarse-grained approach aims to reproduce the form of thermal diffuse scattering without an in-depth understanding of the underlying physics. Low energy modes tend to contribute the most to thermal diffuse scattering. For framework materials, these modes tend to be associated with parallel motions of atoms at the nodes. This is true for inorganic solids (ZnCN2, H2O) [1,2] as well as molecular systems [3] and metal-organic frameworks [4]. With this in mind, one can coarse-grain a framework by replacing the linkers with springs. This should generally capture the low-frequency modes associated with the framework and thus its corresponding thermal diffuse scattering. This method, that only requires a structure as an input, should allow researchers to calculate the underlying diffuse scattering of their framework material and help them in assigning static and dynamic correlations.
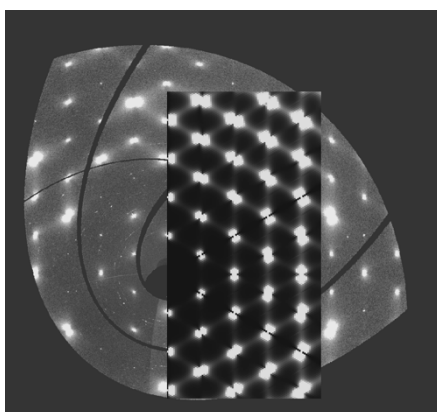
Figure 1. Measured and calculated (overlayed) thermal diffuse scattering for NH$_4$Zn(HCO$_2$)$_3$. The shape of the thermal diffuse scattering is captured whilst systematic absences are not.

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5. TAMING DISORDER IN PHARMACEUTICAL SOLIDS

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Amorphous materials generally have very different physical properties to crystalline forms, which poses a potentially major issue in developing active pharmaceutical ingredients (APIs). The higher free energy associated with amorphous materials can cause physical instability, leading to unwanted crystallisation. On the other hand, the higher solubility of amorphous forms compared to crystalline materials can be highly desirable, especially for APIs with poor aqueous solubility.

Although solid-state NMR spectroscopy can be readily applied to amorphous materials, the spatial disorder results in broad, often undistinctive line shapes that limit the usefulness of traditional "NMR crystallography". 2D experiments can significantly reduce the overlap of individual resonances. Our goal is to use solid-state 2D NMR spectra to distinguish between alternative structural models of amorphous solids and identify different chemical environments e.g., tautomers.

The major challenges of predicting NMR spectra from disordered materials are firstly in producing models of disordered materials, and secondly computing chemical shifts for large, disordered models. A protocol has been developed that uses molecular dynamics (MD) simulation to generate models of amorphous structures, while the second challenge has been addressed using a machine learning algorithm (ShiftML2[1]) to predict chemical shifts from snapshots of the MD simulations. Distinct 2D NMR spectra are predicted for amorphous forms containing different tautomers.

Obtaining experimental ^{13}C correlation data has proved challenging to date, despite the use of high-field and DNP techniques, but useful data has been acquired using ^{1}H correlation experiments. The prospects for experimentally characterising amorphous APIs using solid-state NMR will be discussed. Broadly speaking, we aim to use MD simulations to study molecular environments that can also be compared to more straightforward NMR experiments such as 1D ^{13}C, $^{13}C/^{1}H$ correlation, $^{1}H/^{1}H$ correlation and ^{15}N. We show how MD simulations can be used to identify molecular environments and how these change with time.

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6. Axial–Equatorial Halide Ordering in Layered Hybrid Perovskites from Isotropic–Anisotropic [207]Pb NMR

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Mixed-halide 2D perovskites are promising coatings for tandem 3D perovskite solar cells due to their resistance to photoinduced spatial halide segregation. Halide ordering has been proposed as the underlying mechanism for suppressed halide mobility, but this is challenging to study at the level of single octahedra. [207]Pb NMR can be used to probe the atomic-scale structure of lead–halide materials, but although the isotropic [207]Pb shift is sensitive to halide stoichiometry, it cannot distinguish configurational isomers.

Here, we use 2D isotropic–anisotropic correlation [207]Pb NMR to distinguish the $[PbX_6]$ configurations in mixed iodide–bromide 3D $FAPb(Br_{1-x}I_x)_3$ perovskites and 2D $BA_2Pb(Br_{1-x}I_x)_4$ perovskites based on formamidinium (FA^+) and butylammonium (BA^+), respectively. To extract structural information from the [207]Pb NMR, we used relativistic DFT calculations. However, reproducing the experimental [207]Pb chemical shift anisotropy for the 2D perovskites required us to use two different shift–shielding regressions for the in-plane and out-of-plane directions. Overall, we find that iodide preferentially occupies the axial site in BA-based 2D perovskites, which may explain the suppressed halide mobility.
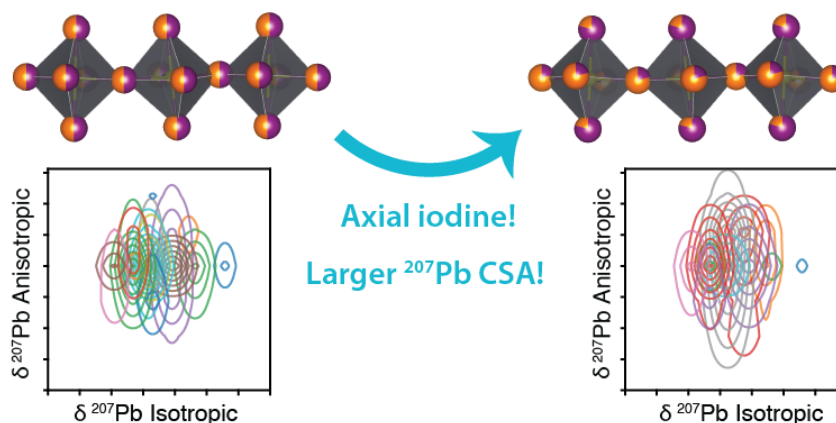
Figure 1: Axial–equatorial halide ordering in 2D perovskites determined by the [207]Pb CSA.

7. Exploring the Stability and Disorder in the Polymorphs of L-Cysteine through Density Functional Theory and Vibrational Spectroscopy

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Static and dynamic density functional calculations are reported for the four known polymorphs of L-Cysteine. Static calculations are used to explore the relative free energies (within the harmonic approximation) of the polymorphs as a function of pressure. An important feature of the structural differences between the polymorphs is shown to be the dihedral angle of the C-C-S-H bond. It is shown that by varying this angle it is possible to move between hydrogen bonding motifs S-H...S and S-H...O in all four polymorphs. The energetics for dihedral angle rotation are explored and the barriers for rotation between the hydrogen bonding motifs have been calculated for each polymorph. Two possible models for the experimental disorder observed in Form I at room temperature are explored using both static and dynamic methods; a domain disorder model, where the disorder is localised, and a dispersed disorder model, where the disorder is randomly distributed throughout the crystal. Molecular dynamics calculations show transitions between the two hydrogen bonding motifs occurring in the dispersed disorder model at 300 K and 350 K. In addition, molecular dynamics calculations of Form IV also showed the onset of hydrogen bond disorder at 300 K. Calculations of the predicted infrared and terahertz absorption are performed for both the static and dynamic simulations and the results compared with experiment to understand the influence of disorder on the observed spectra.

8. Modelling CsCd(NO$_2$)$_3$ as an analogue of octahedral spin ice

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Octahedral spin ices have been targeted as novel platforms for frustrated interactions [1]. CsCd(NO$_2$)$_3$ serves a structural analogue to these spin ices, with NO^{2-} directions in place of Ising spins. However, NO^{2-} does not only have a pointing direction but a planar rotation as well. In this work, we were interested to see whether the planar rotation of NO^{2-} contributed to the observed disorder in the material. Simulated annealing with the Metropolis Monte Carlo algorithm was used to generate supercells that were then used for simulated x-ray and neutron single crystal diffraction. Calculated diffuse scattering patterns showed faint and additional diffuse features in neutron and x-ray diffraction respectively not present in experiment. This suggests other sources of disorder in CsCd(NO$_2$)$_3$ apart from the planar rotation of NO^{2-} molecules.

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9. Modelling Amorphous Metal-Oxide Films Using Ab-Initio Molecular Dynamics

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The capacity retention of rechargeable battery electrodes can be improved by applying inert coating materials such as alumina or zirconia. When such thin films are synthesised at low temperatures, they are typically amorphous. This creates challenges for characterisation, as the atomic structure is poorly defined and difficult to infer from experiment. We investigate the atomic structure by using ab-initio molecular dynamics (AIMD) to generate a range of amorphous models using the melt-quench method with different initial conditions. Whilst the use of Density-Functional Theory (DFT) limits the size of the simulation cell, we combine multiple MD trajectories to create each model, thereby increasing the sampling. This approach is designed to include as many atoms as possible in the model to capture the disorder of the material, whilst being tractable for DFT. The model which best matches experimentally determined structural parameters is selected. We can then calcluate electronic density of states (eDoS), NMR, and XAS spectra, which can be compared to experimental data in order to validate the model.[1]

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10. Entropy differences in barocaloric materials for environmentally friendly refrigeration

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Conventional vapour-compression cooling techniques are inefficient and environmentally damaging. Hydrohaloalkane refrigerants are greenhouse gases and ozone depleters, while cooling processes that use them comprise about 20% of global energy consumption and yield 10% of carbon emissions. A promising alternative is solid-state cooling using barocaloric materials [1]. These materials can be switched between high- and low-entropy states – analogous to the vapour and liquid phases of conventional refrigerants – by applying pressure, and can thus be used as the basis of a refrigeration cycle. Since both phases are solid, these materials cannot escape into the atmosphere; moreover, they are non-toxic and cheap, and have greater cooling efficiency. Order-disorder phase transitions in crystals are an ideal source of barocaloric functionality because they are so easily reversible. These transitions occur in compounds with a wide range of chemistry, from organic molecular crystals to complex ions to coordination frameworks [2]. This chemical diversity is highly promising for materials discovery, as shown by the many materials whose barocaloric properties have been discovered over the past decade; it similarly offers many compositional parameters that can be varied to tune these materials' properties. But such a wide chemical space also means that *ad hoc* exploration is a highly inefficient way to find new barocalorics; instead, a better understanding is needed of the atomic origins of this functionality, so that new materials can be designed rather than simply discovered.

Such an understanding begins with an explanation of the origin of the large entropy change: the problem we tackle here. We present case studies of three different types of material: molecular-ionic salts such as the ferrielectric ammonium sulfate [3,4]; molecular plastic crystals such as adamantane [5]; and coordination framework materials such as the family of hybrid perovskites [6]. We complement traditional diffraction studies of long-range order with pair distribution function analysis of local structure; quasielastic and inelastic neutron scattering measurements of atomic dynamics; and modelling using both density-functional theory and classical potentials. In each case, we show that, although these materials are widely understood in terms of *configurational* entropy, a significant proportion of their entropy is in fact due to low-frequency *vibrational* modes. We demonstrate how such modes arise from these materials' structure, and suggest how this principle can be used to design new barocaloric materials with improved properties.

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11. Unravelling zeolite structures: NMR crystallographic approach to obtain insights into aluminium distribution in zeolites

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The precise location of aluminium within zeolite frameworks is a critical factor influencing catalytic performance, making its structure's accurate determination imperative. Traditional diffraction-based techniques are commonly used for structural analysis, but the presence of static disorder in terms of aluminium sites can challenge the reliability of diffraction results. As an alternative, solid-state Nuclear Magnetic Resonance (NMR) spectroscopy serves as a valuable tool for validating zeolite structures. However, NMR interpretation in zeolites can be intricate, with limited chemical shift dispersion and similar chemical environments. We incorporate theoretical modeling techniques to harness the full potential of NMR in validating zeolite structures. Leveraging Soprano, a Python-based script, we construct a diverse library of potential structural configurations within the zeolite framework, guided by pre-defined structural constraints. Subsequently, we employ GIPAW Density Functional Theory (DFT) calculations on this library to predict NMR parameters. This integrated approach enables systematic correlations between the theoretical model and experimental NMR data, offering an advanced understanding of zeolite structures and their influence on catalytic performance.

12. Structural Studies of Fluorine-Doped Lithium-Rich Anti-Perovskite Solid Electrolytes for All-Solid-State Batteries

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All-solid-state batteries (ASSBs) have the potential to improve the safety and performance of current Li-ion battery technology [1], which are unable to deliver the performance, safety and cost requirements of next-generation energy storage devices [2]. Fast ion conductors in the solid-state are a fundamental requirement for the ASSB concept. Consequently, the development of inorganic solid electrolyte materials forms the foundation of modern battery research [3]. Lithium-rich anti-perovskites (LiRAPs) are a promising class of solid electrolyte material owing to their high ionic conductivities (10^{-3} S cm^{-1}), wide electrochemical stability window, stability against Li metal, and tuneable crystal structure, which may be manipulated through chemical substitution (i.e., doping) to enhance ion transport mechanisms [4]. The hydrated LiRAP Li_2OHCl is known to undergo an orthorhombic to cubic phase transition at ~35 °C, which correlates with a significant increase in ionic conductivity. It has been shown that the cubic phase of Li_2OHCl may also be formed by the substitution of OH$^-$ for F$^-$, forming the solid solution $Li_2(OH)_{(1-x)}F_xCl$ [5].

A recurring issue within the study of LiRAPs is a lack of comprehensive structural characterisation and analysis, leading to speculation over their true composition. To the best of our knowledge, the structural changes of LiRAPs in the $Li_2(OH)_{(1-x)}FxCl$ series have not been investigated in any great detail experimentally. Therefore, a prerequisite to fully understanding the structure-functionality relationships in these materials is a thorough structural analysis through combination of complementary analytical techniques. Here, we present our recent X-ray powder diffraction (XRPD) and multinuclear (^1H, ^2H, ^7Li, ^{19}F, ^{35}Cl) solid-state NMR (SSNMR) results in conjunction with our first-principles DFT calculations, which are aiding us in unravelling the structure-property relationships in $Li_2(OH)_{(1-x)}F_xCl$ solid electrolytes. Our recent results indicate the true composition of $Li_2(OH)_{(1-x)}F_xCl$ materials differs from what has been previously reported. We also demonstrate that the synthetic conditions play a key role in the precise composition of the samples synthesised.

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13. Orgdisord: a Python code to tackle disorder in molecular crystals

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Disordered structures currently make up about 25% of the entire Cambridge Structural Database, with the proportion of disordered structures added each year increasing from 12% to 38% since 1980 [1]. Understanding disorder in molecular crystals is therefore both necessary and timely. However, it is an inherently challenging concept to address in computational modelling where finite, ordered unit cells are required. One approach that is used to account for disorder is that of the supercell ensemble, as has previously been used to model site-disorder in periodic structures [2]. Here, we report on our new software package, *orgdisord*, created to aid in the computer modelling of disordered molecular crystals using the supercell ensemble approach. *Orgdisord* can be used via a simple command-line interface, based on an input CIF file to (i) enumerate all possible ordered structures given a supercell size and shape, (ii) merge symmetrically equivalent structures, recording their degeneracy, and (iii) compute thermodynamically averaged properties within the canonical ensemble, e.g. free energies and simulated NMR spectra.

As an alternative to generating the full symmetry-reduced ensemble, our code can also output large random supercells that can be optionally constrained by the occupancies of the disorder components. With the advent of efficient machine-learning models to compute properties such as chemical shifts such large supercells can now be feasible to compute. I will demonstrate the use of *orgdisord* with the ensemble method, assessing the size of the supercell needed to reach convergence by comparing ensemble-averaged NMR spectra, predicted using ShiftML2, to those computed for large random supercells.

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14. Structure and composition of the alumina-silica gel formed upon enhanced carbonation of end-of-life concrete from solid-state NMR spectroscopy

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Portland cement production is responsible for about 7% of the anthropogenic CO_2 emissions where the major part stems from the calcination of chalk ($CaCO_3$) being the principal raw material. Recent research has shown that cement fines of concrete after its service life can be re-carbonated under aqueous or semi-dry conditions, sequestering nearly the same amount of process CO_2 as released from the cement production, i.e., ~40 g CO_2 per 100 g of end-of-life concrete fines can be bound again as $CaCO_3$ [1]. The principal product of aqueous carbonation is $CaCO_3$ along with an amorphous alumina-silica gel. It has recently been shown that this product can be used again as a highly reactive pozzolan in new composite cements [2], thereby contributing to a circular utilization of cement materials.

The favourable pozzolanic properties of the carbonated end-of-life cement fines are largely related to the alumina-silica gel, and this presentation focusses on the establishment of a structural model for this Al-Si gel based on solid-state ^{23}Na, ^{27}Al and ^{29}Si and NMR experiments. ^{29}Si NMR spectra of the Al-Si gel generally show a broad resonance from -80 to -120 ppm, indicating the presence of different types of $Q^n(mAl)$ silicate species. From the analysis of carbonated cement pastes including different types af supplementary cementitious materials (e.g., fly ash and slags) by ^{29}Si MAS and $^{29}Si\{^1H\}$ CP/MAS NMR, it has been possible to establish a deconvolution procedure for the ^{29}Si NMR spectra that accounts for different types of $Q^n(mAl)$ species. The model includes only Al in tetrahedral coordination, as $Al(-O-Si)_4$ sites, and suggests that the AlO_4 units are likely distributed in the alumino-silicate network in a quasi-heterogeneous manner, forming highly-polymerized clusters with high Al/Si ratio and depolymerized regions with low Al/Si ratio. The validity of the model is supported by comparing the Al/Si ratios determined by the model with Al/Si ratios estimated for the alumina-silica gel from mass balance calculations for six blended cement pastes carbonated for 6 hours.

1. M. Zajac, J. Skocek, J. Skibsted, M. Ben Haha, CO_2 mineralization of demolished concrete wastes into a supplementary cementitious material – a new CCU approach for the cement industry, *RILEM Tech. Lett*. **6** (2021) 53–60.
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15. Solid-state NMR investigation of an order-disorder molecular ferroelectric phase transition

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Ferroelectric materials have many applications in the electronics industry from capacitors to data-storage. These materials undergo a phase transition upon heating to a paraelectric phase which can be of the order-disorder type, whereby the molecular substituents become disordered at high temperature. If the disorder is extreme enough, in the case of plastic crystals for instance, then the nature of the molecular dynamics at this high temperature is often not decipherable solely from X-ray diffraction data. Solid-state NMR experiments can be used to provide evidence to interpret fast molecular motions which are averaged out in an X-ray experiment.[1]

Herein, we present the results of NMR and PXRD experiments for a potentially ferroelectric material with a high temperature paraelectric plastic phase, $(S\text{-CTA})_2\text{CdCl}_4$ (CTA = 3-chloro-2-hydroxypropyltrimethylammonium). The unit cell and basic structural model were solved from high temperature PXRD data however the systematic absences could not provide an exact space group. Static ^{1}H NMR spectra were measured through the phase transition temperature. The peak shape was used to rationalise the expected molecular dynamics which in turn supported our chosen space group. Investigations to model the molecular dynamics more accurately are ongoing.
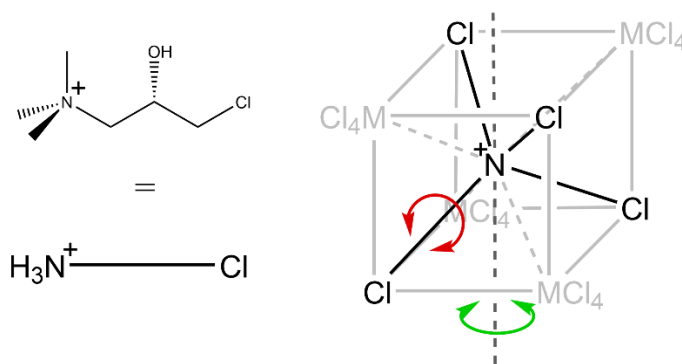

Figure 1 – Tetrahedral site symmetry of the CTA molecule in $(S\text{-CTA})_2\text{CdCl}_4$ at high temperature. Static ^{1}H NMR experiments determined which axis the rotational disorder occurs about.

1. S. Sturniolo, H. M. Wickins and P. Hodgkinson, *J. Chem. Phys.*, **158**, 244502 (2023)

16. The effect of disorder in multi-component covalent organic frameworks

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Covalent organic frameworks (COFs) are crystalline extended solids with permanent porosity constructed from organic building blocks. By virtue of the near infinite number of organic units and diversity of topologies formed, they are a powerful platform for synthetic tunablility for targeted functionality [1]. To introduce complexity and increase functionality into COFs, the number of monomers used in the synthesis can be increased. For most multi-monomer COFs, the monomers form an ordered structure. However, recently, solid solutions of COFs have been synthesised where monomers of different lengths are disorder within the structure (Fig 1a) [2]. This demonstrates the potential for monomer ratio to be used as a parameter to continuously tune the properties of these emerging materials. But disorder can be far random and linkers of different lengths may arrange themselves in a correlated fashion to alleviate strain, only allowing two linkers of the same type around each vertex (Fig 1c). The distribution of monomers on the lattice could influence the COF's properties, but it is unknown how the arrangement effects the properties, or whether it is controllable.
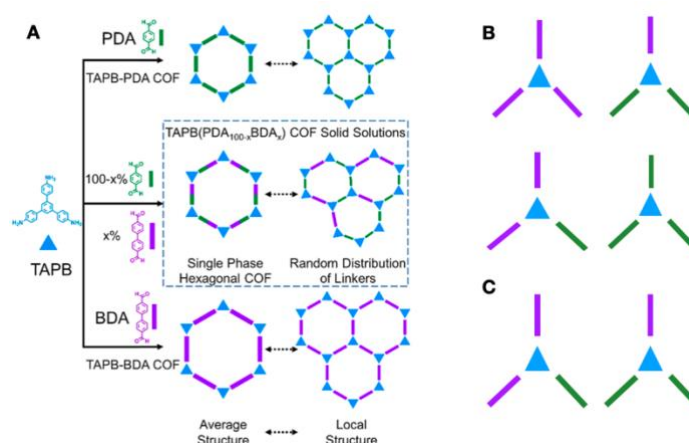

Figure 1: (a) COF Solid solution reported by Li et al. reproduced from Ref. [2]. The possible arrangement of linear linkers around the tritopic node if they were (b) statistically distributed or (c) distributed in a correlated fashion.

In this study, we use simple models to computationally investigate the effect of both random and correlated disorder on the pore size and shape of COFs formed from monomers of different lengths [3]. We find that the different linker lengths have a negligible effect on the pore size and shape when the ratio between the linker lengths is small, and a more significant effect for larger differences. These findings may have implications in using multi-component COFs for their porous applications as the distribution of the linkers affects the extent to which the pore size and shape can be selectively tuned for. Outside of porosity, the distribution of linkers in COFs can impact other properties such as electronic and optical properties. The process outlined in this study can help create atomistic models for further property prediction of disordered COFs, elucidating a disorder/property relationship, which is often too computationally expensive to explore with traditional techniques.

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[3] Wolpert *et al.*, Chem. Commun. 2023, **59**, 6909-6912