Probing tuneable phase behaviour of soft solids for solid-state refrigeration through molecular simulations

Dr Claire L. Hobday (Claire.hobday@ed.ac.uk**)**
Dr Antonia Mey (antonia.mey@ed.ac.uk**)**

Heating and cooling processes use 53 % of the UK's annual energy consumption, employing environmentally damaging hydrofluorocarbon refrigerant gases.[1] Such compounds are being phased down in both the US and EU, due to their devastating environmental effect, requiring more efficient, environmentally friendly materials as replacements.[2] Barocaloric materials are one potential solution. The barocaloric effect is the change in temperature of a solid when an external force is applied to a material, resulting in a structural rearrangement (phase transition).[3] For these materials to realise their potential, a fundamental understanding of what makes a material "barocaloric" must be identified.

The number of barocaloric materials reported is limited to a few broad ranging materials such as: polymers, graphene, magnetic alloys, and recently a soft solid, neopentyl glycol. Knowing that both simple inorganic solids and organic polymers can display barocaloric effects, it is conceivable that there must exist many more barocaloric materials. A class of materials called organic ionic plastic crystals (OIPCs), are comprised completely of ions, which at room temperature are solids with significant disorder in the crystal lattice. This disorder comes from the rotational, translational and conformational motions which allows them to flow under stress and increases their conductivity.[4] It is these properties that make OIPCs desirable solid-state electrolytes that can be used in batteries, fuel cells and solar cells. These previously explored properties are conducive as potential candidates for barocaloric solid-state refrigerants; however, little is known how to maximise their ionic conductivity, ability to flow and phase change.

High-pressure crystallography is a powerful structural technique, providing experimental crystal structure as a function of pressure. However, the technique has two downsides. The first is that the crystal structure model is a time and space average, reducing the information we understand about the dynamics of the crystal structure. Secondly, when an OIPC goes through a phase change, we are presented with a before and after and do not have any information of the phase transition pathway. Therefore, this project will also rely on molecular simulation. We will use conventional molecular simulations and enhanced sampling to generate conformations with which we will train a machine learning model.[5] Sampling from the latent space of this model will allow the efficient exploration of phase space and allowing for phase diagram mapping. To avoid retraining for each new material we want to study, we will use transfer learning techniques to minimise simulations needed.

This project will directly help pave the way for cheaper, greener refrigeration. The development of soft-solid barocaloric materials as refrigerants will: (1) Reduce the greenhouse gases emissions within the refrigeration industry. (2) Create solid-state materials which can be disposed/recycled more easily than gases. (3) Improve efficiency of the heat transfer, which will reduce energy demands.

1. S. Pezzutto et al. *Sustainability,* 2022, **14**, 2667. https://doi.org/10.3390/su14052667
2. UN Treaty Collection, Kigali, 2016. https://treaties.un.org/doc/Publication/MTDSG/Volume%20II/Chapter%20XXVII/XXVII-2-f.en.pdf
3. P. Lloveras; J.L. Tamarit *MRS Energy & Sustainability,* 2021*,* **8,** 3. https://doi.org/10.1557/s43581-020-00002-4
4. J. Timmermans *J. Phys. Chem. Solids,* 1961, **18**, 1 https://doi.org/10.1016/0022-3697(61)90076-2
5. E. P. L. van Nieuwenburg et al. *Nature Physics*, 2017 **13** 435 https://doi.org/10.1038/nphys4037