Modelling the interplay between vibrations and disorder in crystalline materials

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Predictions of materials stability are of paramount importance for computational materials design, and should account not only for the internal energy, but also for entropic effects at finite temperature [1]. In crystalline materials, the entropic effects arise mainly from thermal vibrations and configurational disorder. In many cases, such as for order-disorder phase transitions and solid solutions, it is commonly assumed that the configurational entropy alone can describe stability. Here, however, we will show that the interplay between the configurational disorder and thermal vibrations can have a large impact on phase stability, including miscibility gaps and order-disorder phase transition temperatures, and that machine learning force fields (MLFFs) are the key to include these effects at tractable computational costs.

In the first case, we consider hybrid organic-inorganic materials, which have recently emerged as high-performance ferroelectric and piezoelectric materials. These materials typically feature temperature driven order-disorder (ferroelectric-to-paraelectric) phase transitions above which the spontaneous polarisation and piezoelectric performance is lost [2]. Thus, predictions of phase diagrams are necessary to design materials with high performance at room temperature. To tackle this challenge, we first develop a disorder model for the hybrid piezoelectric material, $TMCMCdCl_3$ (TMCM: trimethylchloromethyl ammonia), trained on density functional theory (DFT) calculations and show that it is necessary to include vibrational effects to obtain reasonable agreement with experimental phase transition temperatures [3]. However, important differences between models and experiments are observed. To remedy this difference and motivated by the importance of vibrational effects, we further study the dynamics in $TMCMCdCl_3$ using MLFF molecular dynamics simulations and reveal the influence of orientational dynamics of dipolar organic molecules on the phase transitions, including the presence of an unexpected type of orientational defects [4].

In the second case, we show how MLFFs more generally can accelerate predictions of vibrational effects in disordered materials. Configurational disorder is commonly modelled using the cluster expansion method, and to incorporate vibrational effects hundreds of lattice dynamics calculations are needed, resulting in a high computational cost. Here, we show that vibrational entropy can be included by training an MLFF on the geometry optimisation trajectories already available when constructing a cluster expansion model for a solid solution. This MLFF can be used to make accurate lattice dynamics calculations at low cost, and it is shown to lead to predictions of compositional phase diagrams in better agreement with experiments (Fig. 1) [5].

These results pave the way for inclusion of finite temperature effects at a tractable cost in computational materials design.

References

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Figures

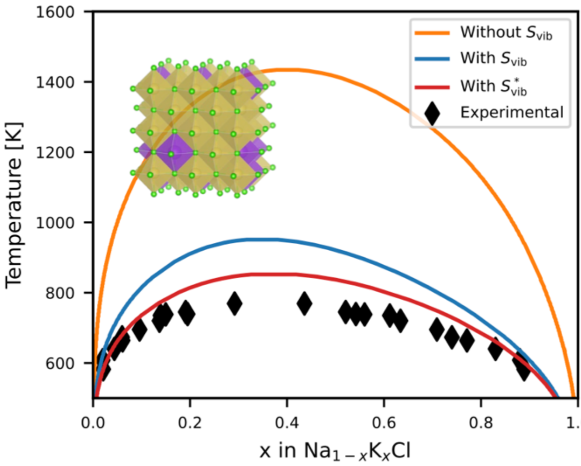

Figure 1. Predicted miscibility gap in the $Na_{1-x}K_xCl$ solid solution with and without inclusion of vibrational entropy calculated from lattice dynamics with MLFFs. The asterisk corresponds to end-members computed with DFT to improve accuracy of the final model. Inclusion of vibrational entropy significantly improves agreement with experiment [5].