Understanding superionic conductivity in disordered systems using machine learning potential molecular dynamics and Monte Carlo sampling

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The competition between order and disorder in materials leads to a wide variety of materials functionalities such as electronic, ionic, and thermal conductivity/insulation and catalytic activity. However, because of the huge number of degrees of freedom in disordered systems, successes in theory-driven design of such functionalities have been rather limited. In this research project, we tackled this problem through a combination of first-principles calculation and machine learning.

For disordered crystalline systems, we employed our abICS (ab Initio Configuration Sampling) framework for deriving an on-lattice neural network model from first-principles calculations [1] and used that to perform replica-exchange Monte Carlo sampling. One system that we have been examining is heavily Sc-doped $BaZrO_3$, which is known as a promising perovskite proton conductor for solid oxide fuel cells [2]. The oxygen vacancy is known to be the active site for the hydration reaction, which is the key reaction to introduce protons into the system. However, it is yet unclear which of the three types of vacancy environments, $Sc-V_O-Sc$, $Sc-V_O-Zr$, or $Zr-V_O-Zr$, are responsible for the hydration behavior. Using abICS, we have clarified that the former two are active sites for hydration, while the $Zr-V_O-Zr$ site seldom exists under normal thermodynamic conditions and contributes little to the hydration reaction [3].

In the case of amorphous systems, we considered the use of the neural network potential (NNP) approach originally proposed by Behler and Parinello [4]. Although the neural network potential methodology seems to be a well-established approach at this point, we have found that it is quite a challenge to apply to many-component glass systems. This is because the NNP requires that the training set sufficiently covers the thermodynamically relevant configuration space, which will be huge for many-component glasses. We observe regularly that NNP molecular dynamics (MD) calculations 'fall apart' and exhibit completely unphysical structures after it wonders into regions of previously unlearned configuration space. To tackle this issue, we have been trying an active learning cycle approach where we

take structures from the NNP-MD trajectory, perform DFT calculations on those structures, add them to the training set, and run the NNP-MD again with the new NNP. As shown in Fig. 1 for the AgI-As$_2$Se$_3$ superionic mixed glass system, increasing the number of cycles leads to improvement in the NNP predictions, although we have not been able to fully converge the low energy structures yet.

We have also been examining the feasibility of training on DFT data using high-cost functionals such as the HSE06 hybrid. Since it is not feasible to obtain a long enough MD trajectory to use as the training set with HSE06, we first performed first-principles MD using the relatively low-cost GGA functional. Afterwards, we took a subset of the structures (~1500 structures) and recalculated them using HSE06, which were then used as the training set in NNP training. This approach was applied to amorphous GeO$_2$, and we were able to obtain structure factors in excellent agreement with experiment (Fig. 2). This shows that NNP technology is promising for realizing long-time and large-scale MD simulations with the accuracy of high precision (and high cost) electronic structure methods.
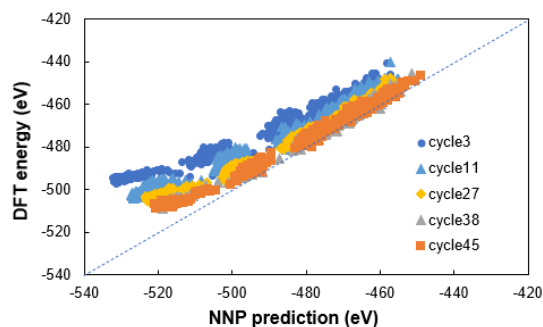

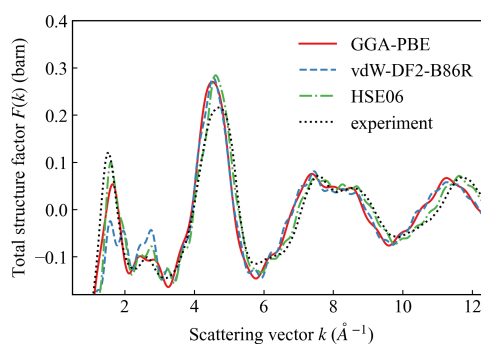Fig. 1: Improvement of NNP accuracy with active learning iterations for AgI-As$_2$Se$_3$

Fig. 2: Total structure factors from NNPs trained on various functionals and compared to experiment.

References

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