Predicting Thermophysical Properties of Halide Salts Using On-the-Fly Machine-Learned Interatomic Potentials Across Multiple Exchange-Correlation Functionals

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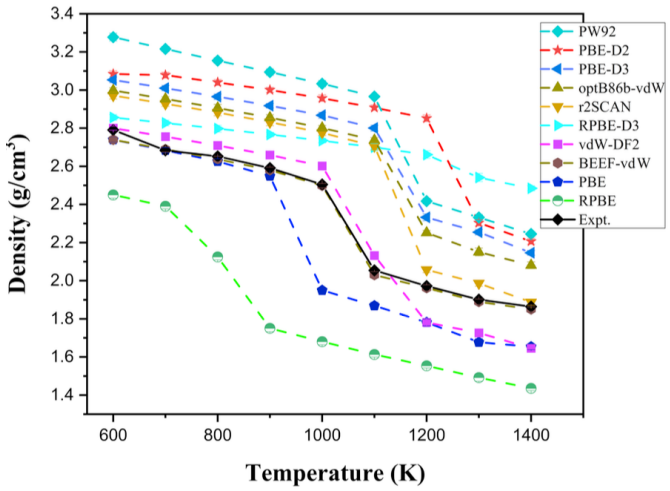
Molten salts are pivotal materials for emerging carbon-free energy technologies, yet accurate prediction of their thermophysical properties using quantum-mechanical methods remains computationally demanding at large length and time scales, while the choice of exchange-correlation (XC) functional critically governs predictive accuracy. Here, we train machine-learning force fields (MLFFs), using an on-the-fly active-learning scheme implemented in the Vienna Ab initio Simulation Package (VASP), to investigate the thermophysical properties of NaBr, KCl, and AgCl, representing alkali- and transition-metal halides, across their solid and liquid phases. We systematically benchmark ten XC functionals for NaBr over 600-1400 K and test the transferability of the best-performing functional to KCl (700-1200 K) and AgCl (500-900 K). These MLFFs enable prediction of densities and ionic diffusion coefficients at length and time scales beyond ab initio simulations, while capturing the first-order solid-liquid transition.

The BEEF-vdW functional accurately predicts the optimized lattice constants of NaBr and KCl, consequently reproducing experimental solid- and liquid-phase densities, with Na^+ and Br^- self-diffusion coefficients in molten NaBr agreeing with experiment within ~4% (Alcaraz et al., 2014). Conversely, BEEF-vdW inaccurately predicts the density of AgCl owing to an inaccurate lattice constant, whereas PBE-D3 yields excellent density agreement (~5% deviation) across both phases. Figure 1 illustrates the temperature-dependent density variation obtained across these systems. This work establishes a foundation for high-throughput generation of molten-salt thermophysical property databases using general machine-learning potentials, and shows that a functional's accuracy for alkali halides cannot be assumed to transfer to transition-metal halides.



Temperature-dependent density variation of NaBr using MLIPs for each exchange-correlation functional

Alcaraz, F. Demmel, and J. Trullas, Journal of Chemical Physics 141, 244502 (2014).