Nuclear quantum effects in compressed hydrogen and deuterium from path integral molecular dynamics

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Keywords: hydrogen, PIMD, phase transition

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As the lightest element on the periodic table, hydrogen can exhibit very strong isotope effects. One example of such an effect is seen in high pressure experiments on hydrogen and deuterium, where there are large differences in certain phase boundaries between the two isotopes. This is particularly evident in the broken symmetry phase I-II transition[1] and the molecular to atomic liquid-liquid transition[2]. Interestingly, the melting curve does not exhibit any isotope effect, even though it lies between these two mass-sensitive transitions.

When these phase transitions are modeled the effect of particle mass is often neglected and thus nuclear quantum effects are not considered. However, the difference in zero point energy between the two molecules is critical when discussing isotope effects and thus the nuclei must be treated as quantum particles if we are to model these phase boundaries accurately. Path integral molecular dynamics (PIMD) provides an avenue for incorporating nuclear quantum effects into molecular dynamics simulations. For this, nuclei are represented as semi-classical ring polymers using the path integral formulation of quantum statistical mechanics. We used PIMD to probe the phase diagram of H_2 and D_2, in combination with a novel machine learning interatomic potential for the phase I-II and melting transitions, and with density functional theory for the liquid-liquid transition. Here we present the results, along with a comparison to experiment.

Acknowledgments: This work was supported by the ERC grant HECATE. Computing resources were provided by EPSRC via the UKCP consortium.

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