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Modelling phase diagrams of crystalline ice structures - a comparison of force fields and density functional theory

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Solid water comprises the most abundant form of ice in the universe and is believed to have played an important role in catalysing the formation of those prebiotic molecules that were essential for the development of life on earth. Apart from amorphous structures solid water also appears in a plethora of ordered structures under different temperature and pressure conditions. The corresponding phase diagrams have been well studied in numerous experiments. On the other hand, despite 30 years of computer simulations of water, computer simulations of this phase diagram based on atomistic chemical interaction models are still challenged by accurately for hydrogen bonding and van-der-Waals interactions. The quantum mechanical interaction of electrons is at the heart of these interactions, but this is not explicitly included in well-established empirical force fields – which have commonly been parameterized for liquid water. Given this situation, it is an interesting question how recently developed density-functional theory (DFT) methods perform in comparison.

In this work, we focus on the well-known ordered crystalline ice structures (Ih, II, VIII, IX, XIII, XIV, XV), which capture a wide range of local coordination and thus bonding scenarios between individual molecules in solid water. For these structures, we calculate the corresponding (sub-part of the overall) phase diagram based on various different empirical force fields (SPC/E, TIP3P, TIP4P/2005, TIP4P/ice, q-TIP4P/F) and systematically compare to results of state-of-the-art DFT including an explicit account for van-der-Waals interactions. We start from the experimentally determined crystal structures and perform space-group-constrained structural relaxations individually for each different chemical interaction model. This yields the internal energy of the solid and allows us to calculate well-defined phononic properties by means of lattice dynamics. Using the quasi harmonic approximation allows us to compute the free energy contribution as an analytical function of the temperature and volume for a given potential. We will compare the so-obtained phase diagrams to available experimental data and discuss the influence of different bonding contributions within the investigated atomistic chemical interaction models –potentially also including a detailed analysis of the phononic band structure.

Significance statement

We present a systematic comparison of simulated phase diagrams of crystalline ices based on a variety of atomistic interaction models, ranging from commonly used force fields to recently developed density-functional theory methods and including a detailed account of vibrational properties. This scrutinizes different chemical bonding contributions in solid water.

Primary authors: Dr MEYER, Jörg (Theoretical Chemistry, Leiden Institute of Chemistry, Leiden University); Mr RASTI, Soroush (Theoretical Chemistry, Leiden Institute of Chemistry, Leiden University)

Presenter: Mr RASTI, Soroush (Theoretical Chemistry, Leiden Institute of Chemistry, Leiden University)

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