

Title: Disorder and exotic phases in ammonia hydrates at high pressure : navigating the phase diagram with machine-learning potentials.

Keywords: Advanced simulation methods: machine-learning interatomic potentials, path-integral molecular dynamics, accelerated sampling. Ammonia Hydrates. Hydrogen bonding. Extreme conditions.

Scientific description

The detailed understanding of the high-pressure behavior of ammonia hydrates is a major challenge for planetary physics, as they are found in the composition of giant planets the solar system such as Neptune and Uranus. These mixtures present a variety of solid phases, some of which exhibit exotic properties such as plasticity or superionicity, as well as diverse forms of disorder (orientational and substitutional disorder as well as partial auto-ionization, that all strongly impact the hydrogen-bond network). Though the phase diagram of ammonia hydrates is relatively well-known experimentally, theoretical studies remain scarce as they pose huge simulation challenges that we propose to address by combining machine-learning (ML) interatomic potentials with accelerated sampling methods for free-energy calculations, as well as path-integral molecular dynamics (PIMD) to tackle nuclear quantum effects (that is, all effects beyond classical statistical physics).

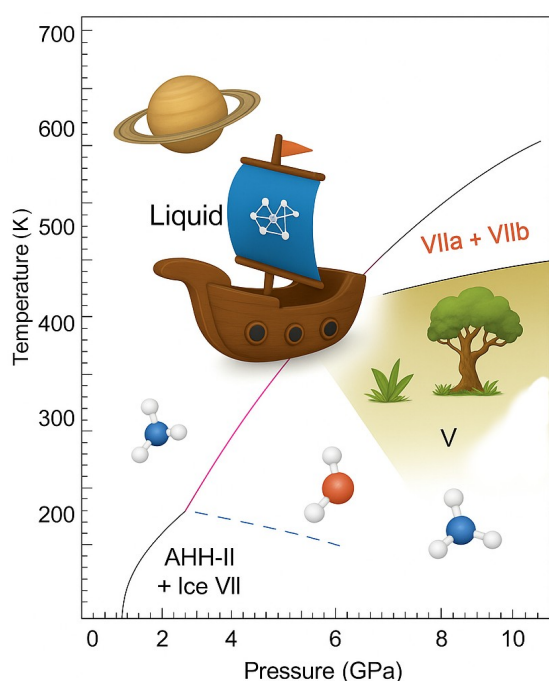


Figure : Navigating the high pressure phase diagram of ammonia di-hydrate (ADH). Image generated by IA based on the experimental phase diagram obtained by our collaborators (F. Datchi, S. Ninet, IMPMC, SU) during L. Andriambarijaona's PhD thesis (2021, full-text available on-line).

Experiments have shown that pressurized water-ammonia mixtures can exist in different stable phases with precise proportions of water and ammonia, the most stables are hemi-hydrates (AHH, $\text{H}_2\text{O}:[\text{NH}_3]_2$), mono-hydrates (AMH, $\text{H}_2\text{O}:\text{NH}_3$), and di-hydrates (ADH, $[\text{H}_2\text{O}]_2:\text{NH}_3$). The associated phase diagrams are extremely rich (see the figure for the case of ADH), they suggest various unusual phenomena such as the existence of plastic phases, auto-ionization processes ($\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$), and even super-ionicity, associated with high protonic conduction at very high pressures. However, microscopic understanding of these mechanisms is still incomplete and atomic-scale simulations face significant methodological difficulties. Indeed, the description of ionic species requires a quantum-mechanical treatment of the electronic structure, for instance using density functional theory (DFT) simulations, but the heavy computational cost of DFT does not allow for the simulation of large systems (approx. 10^4 atoms) over long times (few ns), as is necessary to characterize disordered systems. In addition, in

some conditions where the experiments are not able to fully characterize the crystal structure, accelerated sampling methods should be used to compare the free energy of different structures and determine their relative stability. Finally, as hydrogen plays a crucial role in the structure and dynamical properties of these compounds, nuclear quantum effects have an impact and should be included via path integral approaches (PIMD). This combination of techniques is highly challenging, and though we already obtained promising results on some well-characterized phases [1,2], methodological developments are still needed to tackle the most exotic properties of ammonia hydrates.

In practice, this internship aims at adapting and implementing advanced sampling methods to compute free-energy differences between competing candidate crystal structures (such as thermodynamic integration or alchemical transformations [3,4]), with interatomic interactions described via machine-learning potentials trained on DFT data (ML potentials will be built and run using the efficient FeNNol library [5] mainly developed by T. Plé). These developments will then be applied to explore the phase diagram of ADH between 300 and 600K, a region where the microscopic interpretation of the available experimental data is currently an object of active research.

[1] N. Avallone, S. Huppert et al, *Phys. Rev. Lett.* 133, 106102 (2024). [2] C. Liu et al. *Nature Comm.* 8, 1065 (2017).
[3] B. Cheng and M. Ceriotti, *Phys.Rev B* 97, 054102 (2018). [4] L. Lagardère et al, *J. Chem. Theory Comput.* 20, 11, 4481(2024). [5] T Plé, et al, *J. Chem. Phys.* 161, 042502 (2024).

Techniques/methods in use:

Molecular Dynamics. Machine-learning: training and active learning for interatomic potentials. Feynman path-integrals. Thermodynamic integration.

All of these advanced methods are currently being employed in the group and the applicant will benefit of an in-use introduction to them.

Applicant skills: Good background in statistical physics (classical and quantum). A taste for numerical simulation and extraction of relevant physical information from the numerical data. A propensity for programming is beneficial.

Industrial partnership: No

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Possibility for a Doctoral thesis: Yes (no secured funding but different possibilities to obtain one)