

Peer Review File

Manuscript Title: The first-principles phase diagram of monolayer nanoconfined water

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

The manuscript by Kapil et al. combines several state-of-the-art molecular simulation techniques to study the phase diagram of a water monolayer confined between two graphene sheets. The manuscript is significant both in the development/refinement of the computational methodology and in its conclusions. The two following main results are probably worth publishing in Nature: (1) This research provides convincing evidence of a step-wise sequence of first-order and a second-order phase transitions for the melting of a realistic 2D system, and (2) it predicts a superionic phase with high proton mobility occurring at moderate temperature and lateral pressure that can be easily achieved. The first prediction has important fundamental implications as it corroborates the general KTHNY theory for 2D materials, while the second result may have a significant technological impact. The proposed methodology is based on DFT calculations tested against QMC benchmarks and extended through the fitting of machine learning potentials. It is sound and at the highest standards of accuracy. The manuscript is very well written, and it may be enjoyed by the broader readership. For these reasons, I would be pleased to see this work published in Nature. However, I would like the authors to address the following issues:

- 1) QMC is used to calculate an effective confinement potential to model (on average) the water-graphene interaction. It should be discussed how realistic such confinement potential is to mimic the effect of confinement from a specific material, such as graphene. Even though graphene is rather hydrophobic, I would expect a certain amount of C-H directional interaction that may affect the structure and the dynamics of the water monolayer.
- 2) Whereas the effect of varying the confinement width has been in part discussed in a previous paper (PRL 2016), it should be discussed also in this work. I would expect it to have some impact on the structure, dynamics, and phase boundaries, especially for the hexatic and superionic phases.
- 3) PIMD simulations have been used to train the MLP, and the Gibbs free energy calculations for the solid phases consider nuclear quantum effects (NQE). It is, however, not clear to me to what extent NQEs have been considered in the calculations of the phase boundaries between crystalline and disordered phases and in the dynamic characterization of the hexatic and superionic phases.

A minor issue: in figure 3b the "gray region" is not clearly visible.

Referee #2 (Remarks to the Author):

This computational study reports a nearly-all-inclusive phase diagram of monolayer water between graphene layers and provides a comprehensive understanding of the phase-transition behaviour of confined water. The authors developed an accurate machine learning (ML) force field for 2D water in order to quickly map out the full phase diagram of monolayer water. Not only they reproduced low-pressure ice phases published before but also identified a hexatic-like phase previously simulated only based on empirical water potentials, and a new 2D superionic ice phase.

Novelties of this work:

Major novelties of this work include (1) a nearly-full phase diagram of monolayer water; (2) development of an ML potential of 2D water at the same level of accuracy as the density functional theory, (3) identification of the hexatic-like phase of 2D water, and (4) revealing a new 2D superionic phase for the first time from molecular dynamics and first-principle molecular dynamics simulations.

“Does the work provide the sort of striking new advance or clear and generic conceptual and methodological leap forward that would excite the immediate interest of very broad Nature readers?” The four major novelties, although very impressive, are still not quite meeting the high standard exemplified above. I would suggest this work be transferred to a Nature sister journal, Nature Physics, for the following reasons:

(1) Although the nearly-full and accurate phase diagram of monolayer water is very interesting, a large number of the ice phases have already been reported by several co-authors, in Phys. Rev. Lett. 116, 025501 (2016) “Two Dimensional Ice from First Principles: Structures and Phase Transitions”.

(2) For the development of the ML water potential, similar methodology has been published in the literature, for example, by Cheng et al., Nature Physics, 17, 1228 (2021) “Phase behaviours of superionic water at planetary conditions”. In that paper, the author Pickard is also a co-author of this manuscript.

(3) Regarding the hexatic phase of the confined water, a preprint has been published on arXiv in 2011, by Vilanova & Franzese, arXiv:1102.2864 (2011) “Structural and dynamical properties of nanoconfined supercooled water”. This preprint should be cited.

Additionally, in the Phys. Rev. E paper (Ref. 22) “Continuous melting through a hexatic phase in confined bilayer water”, the hexatic phase of bilayer water was reported for the first time. Although both previous work employed empirical water models, the conceptual advances have already been made by the researchers.

(4) The most novel result reported here is the discovery of a new 2D superionic phase from computer simulations. However, the closely related 3D superionic ice phases and the similar simulation methodology has been reported in the 2021 Nature Physics paper (17, 1228 (2021)) by one of the co-authors.

Over the past few years, the superionic ice phases have received extremely high interests from physics communities, evidenced by the following publications:

- 1) Nature Physics, 17, 1233 (2021) “Structure and properties of two superionic ice phases”;
- 2) Nature Physics, 15, 1065 (2019) “Multiple superionic states in helium–water Compounds”;
- 3) Nature Physics, 14, 297 (2018) “Experimental evidence for superionic water ice using shock

compression”.

The discovery of the new 2D superionic phase from the computer simulations, in this reviewer’s opinion, deserves a consideration for potential publication in Nature Physics as it provides the sort of striking new advance that would excite the immediate interest of physics communities.

I would however highly recommend this work for consideration of potential publication in Nature if any one of the monolayer ice phases illustrated in the phase diagram (Figure 1) can be detected from an experiment (excluding the square ice phase which has been reported in Nature in 2015 by an experimental group (Ref. 1)). The experimental observation, in conjunction with the comprehensive phase diagram of Figure 1, would provide the sort of striking new advance that would excite the immediate interest of very broad audience of Nature readers.

A few technical comments on the phase diagram of Figure 1

The present nearly-full phase diagram of Figure 1 needs more quantitative information for completeness.

(1) The phase boundary between the hexatic phase (e) and superionic phase (f) needs more quantitative description, like the use of the solid black lines with error bars for drawing the phase boundaries between (a), (b) and (c), and between (a) and (g).

(2) It would highly informative to find out at what temperature, a direct phase transition from the liquid water (g) to superionic ice phase (f) would occur. A more quantitative data is needed to show this important phase-transition behaviour beyond 600 K.

(3) Would a proton-disordered monolayer triangular ice phase emerge at high pressure beyond 4 GPa and at temperature of 290 K or 300 K? If so, it would be akin to the proton-disordered bilayer triangular ice phase shown in Figure 1 of Phys. Rev. Lett. 116, 085901 (2016). Such a comparative study would be highly informative.

Referee #3 (Remarks to the Author):

Review of “The first-principles phase diagram of monolayer nanoconfined water,” Venkat Kapil, Christoph Schran, Andrea Zen, Ji Chen, Chris J. Pickard, and Angelos Michaelides (#2021-10-16925).

In many ways, understanding the behavior of water at interfaces and in confinement is arguably more important than understanding bulk water (which is, itself, the subject of extensive, ongoing research). The wide range of surfaces with which water can interact, coupled with the diversity of structures that water can adopt leads to a wide variety of interesting, and often unexpected, phenomena. Thus, despite decades of research, new discoveries are reported almost every year. In this manuscript, the authors investigate the structure of a water monolayer confined between hydrophobic walls as a function of pressure and temperature. They use advanced simulation techniques that combine electronic structure calculations, statistical sampling, and machine learning to produce probably the most accurate calculations to date (considering the scope of the calculations). With this approach they confirm several previous results, resolve some existing

conflicts, and predict several new phenomena. A key aspect of this research is its potential to move the field beyond the dichotomy of the efficiency of classical molecular dynamics simulations versus the higher accuracy, but higher cost, of electronic structure calculations. While classical MD simulations have been, and will undoubtedly continue to be, a workhorse in water research, they also come with notable limitations, many of which are likely to be more problematic when water interacts with surfaces. Overall, I find the results, which should be of interest to a wide variety of researchers, convincing. If these (excellent) results on the phase diagram for monolayer, confined water were the only aspect of this report, it might be hard to justify their publication in Nature. However, when coupled with the advances in technique outlined in the manuscript, I believe they are suitable for publication in Nature.

I have only a few minor questions/issues that the authors should consider before publication.

1. Most of the ordered structures identified by the authors involve non-tetrahedral bonding arrangements. It seems likely to me that there are changes in the H-O-H angle in individual molecules that accompany these structures. For example, how much do the water molecules distort in the square and the pentagonal phases? I recall that there were some discrepancies between early structures predicted with rigid water models (e.g. Koga, et al., Phys Rev. Lett., 79 (1997) 5262) and later calculations with AIMD. Some discussion might be useful.
2. This work focuses on confined water. Do the authors believe that their approach will be similarly helpful for calculations on bulk water, including solutions, isotope effects, supercooled water, etc.? A sentence or two to give the readers some perspective would be nice.
3. In the discussion of the hexatic-like and superionic phases (pgs. 12 -13), the authors suggest that perhaps the higher pressures needed for this phase might be achieved experimentally inside “nanobubbles” that have been reported in the literature. Maybe, but it looks like only a few water molecules would fit inside these (i.e., not really enough to convincingly display a longer-range structure). Have the authors tried to estimate how quickly the lateral pressure falls below the regime for the high-pressure phases as the dimensions of the nanobubbles increase? This could help the readers understand the lateral sizes needed to contemplate such experiments.
4. There are several typos associated with calling out the figures in the main text. For example, on the first line on page 10, I think the small diffusion coefficient refers to figure 2d (not 2b). There are also several references to figure 2(r), while Figure 2 only has a) – e). On page 11, the 4th line from the bottom refers to figure 2(b), while I believe they mean figure 3(b).
5. For reference 23, the longer article on this topic by Kosterlitz and Thouless (J. Phys. C: Solid State Phys. 6 (1973) 1181) seems to be a better choice. The short letter (1972) L124 doesn't really discuss the two-step melting process.

Author Rebuttals to Initial Comments:

Referees' comments

Referee #1 (Remarks to the Author):

The manuscript by Kapil et al. combines several state-of-the-art molecular simulation techniques to study the phase diagram of a water monolayer confined between two graphene sheets. The manuscript is significant both in the development/refinement of the computational methodology and in its conclusions. The two following main results are probably worth publishing in Nature: (1) This research provides convincing evidence of a step-wise sequence of first-order and a second-order phase transitions for the melting of a realistic 2D system, and (2) it predicts a superionic phase with high proton mobility occurring at moderate temperature and lateral pressure that can be easily achieved. The first prediction has important fundamental implications as it corroborates the general KTHNY theory for 2D materials, while the second result may have a significant technological impact.

The proposed methodology is based on DFT calculations tested against QMC benchmarks and extended through the fitting of machine learning potentials. It is sound and at the highest standards of accuracy. The manuscript is very well written, and it may be enjoyed by the broader readership.

For these reasons, I would be pleased to see this work published in Nature.

We thank the reviewer for their positive assessment of the manuscript and for acknowledging the predictive accuracy of our approach.

However, I would like the authors to address the following issues:

1) QMC is used to calculate an effective confinement potential to model (on average) the water graphene interaction. It should be discussed how realistic such confinement potential is to mimic the effect of confinement from a specific material, such as graphene. Even though graphene is rather hydrophobic, I would expect a certain amount of C-H directional interaction that may affect the structure and the dynamics of the water monolayer.

We thank the reviewer for raising this issue. Our reference simulations performed with DFT (see supporting data files: V5.mp4 and V6.mp4), suggest a good agreement between our MLP simulations with a confining potential and the behavior of water with explicit graphene sheets (including explicit C..H interactions). We observe facile rotational dynamics and proton transfer for the hexatic and superionic phases, respectively. The DFT results suggest that, at finite temperature and pressure, the confining potential is able to qualitatively describe the phase-behavior of water with explicit C..H interactions.

To further understand how C..H interactions affect the low temperature and pressure part of the phase diagram, we have performed a “sensitivity analysis” of the parameters of the confining potential. To this end, we have calculated the change in the hexagonal-pentagonal

and pentagonal-rhombic transition pressures, along the coexistence lines, arising from changes in the parameters of the Morse potential. Specifically parameters corresponding to the following different orientations of a water molecule were considered:

1. Morse potential parameters corresponding to the QMC energy of a 0-leg water molecule [10.1021/acs.jpcllett.8b03679],
2. Morse potential parameters corresponding to the QMC energy of a 1-leg water molecule [10.1021/acs.jpcllett.8b03679],
3. Morse potential parameters corresponding to the QMC energy of a 2-leg water molecule [10.1021/acs.jpcllett.8b03679].

The changes in the free energy, and subsequently in the transition pressures, are calculated from preexisting trajectories using thermodynamic perturbation theory. As shown in the table below, across a wide range of temperatures the description of the confining potential leads to changes in the transition pressures that are smaller than the statistical uncertainties (see in the phase-diagram), suggesting that changes in the confinement potential to incorporate C..H interactions should lead to the same qualitative phase-diagram.

Potential	Change in the Hexagonal to Pentagonal transition pressure [Gpa] at			Change in the Pentagonal to Rhombic transition pressure [Gpa] at		
	20 K	60 K	120 K	20 K	100 K	200 K
0 Leg	0.000	0.000	0.000	0.008	0.006	0.001
1 Leg	0.003	0.001	0.010	0.022	0.165	0.030
2 Leg	0.001	0.001	0.005	0.116	0.087	0.016

To address the referee’s comment, we have added this analysis to the SI and included the following statement in the main text in the subsection entitled “The pressure-temperature phase diagram”

As shown in the SI (see section SI.E of the SI), our predictions are robust with respect to the choice of the confining potential, small ($\sim 0.5 \text{ \AA}$) changes in the confinement width, as well as finite-size effects.

2) Whereas the effect of varying the confinement width has been in part discussed in a previous paper (PRL 2016), it should be discussed also in this work. I would expect it to have some impact on the structure, dynamics, and phase boundaries, especially for the hexatic and superionic phases.

We thank the reviewer for raising this issue. To address this point we have again performed a sensitivity analysis of the confinement width for the hexagonal-pentagonal and

pentagonal-rhombic transitions. Below we report the changes in the transition pressures for a given change in the confinement width.

Change in width [\AA]	Change in the Hexagonal to Pentagonal transition pressure [GPa] at			Change in the Pentagonal to Rhombic transition pressure [GPa] at		
	20 K	60 K	120 K	20 K	100 K	200 K
0.1	0.000	0.000	0.003	0.045	0.034	0.011
0.2	0.001	0.001	0.006	0.090	0.067	0.021
0.5	0.003	0.002	0.015	0.226	0.168	0.053

Given that these changes are within statistical uncertainties (see phase-diagram) we expect the phase-diagram of monolayer water to exhibit the same qualitative behavior up to a width of 5.5 \AA .

Preliminary surveys for widths of 6 \AA indicate non-trivial changes in the phase behavior, i.e. the formation of bilayer phases at high pressures and temperatures. Since the focus of the current manuscript is monolayer water we feel that this goes beyond the scope of the current study. We hope to comprehensively address this question in the future; after sufficient careful validations with QMC and DFT have been performed within the approach presented in this work.

However, to address the referee's comment, we have added this analysis to the SI and included the following statements in the main text in the subsection entitled "The pressure-temperature phase diagram"

As shown in the SI (see section SI.E of the SI), our predictions are robust with respect to the choice of the confining potential, small ($\sim 0.5 \text{\AA}$) changes in the confinement width, as well as finite-size effects.

and in the section entitled "conclusions"

This work has been enabled by developments in high-level electronic structure theory – to guide the selection of an appropriate DFT functional – and a simple and efficient active learning scheme, which dramatically reduces the computational and human time required to train and validate a MLP across the full phase-diagram. The employed workflow can readily be applied to provide a rigorous description of nanoconfined water under other conditions (e.g. different confinement geometries and materials) as well as other classes of material.

3) PIMD simulations have been used to train the MLP, and the Gibbs free energy calculations for the solid phases consider nuclear quantum effects (NQE). It is, however, not clear to me to what extent NQEs have been considered in the calculations of the phase boundaries

between crystalline and disordered phases and in the dynamic characterization of the hexatic and superionic phases.

We thank the referee for pointing this out. We agree that the discussion on NQEs could have been clearer. This is, in part, also because an entire section on NQEs was mistakenly not included in the supporting information (in the previous submission). The referee is correct that structures in which NQEs were taken into consideration were included in the training data. However, the simulations reported in the manuscript were with classical nuclei. Although NQEs can sometimes prove important and interesting (and we have shown that in many studies), for the systems studied here, tests on parts of the phase diagram show that the changes in the phase boundaries due to NQEs are smaller than the uncertainties presented in the phase-diagram.

To address this we have (now) included the section in the SI that shows that the change in the phase boundary due to NQEs for the hexagonal, pentagonal and rhombic phases with the liquid are smaller than the uncertainties in the phase diagram. Similarly, NQEs do not seem to impact the hexatic to liquid phase transition. These results are unsurprising as NQEs are known to shift the melting temperature of hexagonal ice by around 10 K for bulk water, and by a similar amount for other high pressure ice phases, and are not expected to have a significant impact at 1 GPa and in the 400 - 500 K regime [10.1038/s41467-020-20821-w]. In light of these observations, we did not perform simulations with quantum nuclei to study the approximate quantum dynamics of the hexatic and the superionic phases, as we only anticipate quantitative differences in the diffusion behavior by a few tens of percentages [0.1038/s41567-021-01334-9].

In addition to the new section in the SI (see section S1.E of the SI), we have added the following statement in the main text in the subsection entitled “The pressure-temperature phase diagram”

We also show that nuclear quantum effects have only a small impact on the phase boundaries, and therefore for clarity, they are not taken into account in Fig. 1.

A minor issue: in figure 3b the "gray region" is not clearly visible.

We thank the referee for this suggestion. We made the necessary changes in Fig 3b.

Referee #2 (Remarks to the Author):

This computational study reports a nearly-all-inclusive phase diagram of monolayer water between graphene layers and provides a comprehensive understanding of the phase-transition behaviour of confined water. The authors developed an accurate machine learning (ML) force field for 2D water in order to quickly map out the full phase diagram of monolayer water. Not only they reproduced low-pressure ice phases published before but also identified a hexatic-like phase previously simulated only based on empirical water potentials, and a new 2D superionic ice phase.

Novelties of this work:

Major novelties of this work include (1) a nearly-full phase diagram of monolayer water; (2) development of an ML potential of 2D water at the same level of accuracy as the density functional theory, (3) identification of the hexatic-like phase of 2D water, and (4) revealing a new 2D superionic phase for the first time from molecular dynamics and first-principle molecular dynamics simulations.

“Does the work provide the sort of striking new advance or clear and generic conceptual and methodological leap forward that would excite the immediate interest of very broad Nature readers?” The four major novelties, although very impressive, are still not quite meeting the high standard exemplified above. I would suggest this work be transferred to a Nature sister journal, Nature Physics, for the following reasons:

First we would like to thank the referee for taking the time to read our manuscript and their overall very positive and thoughtful assessment -- specifically for their summary of the main findings and novelty of our work and acknowledging its relevance to the Physics community.

(1) Although the nearly-full and accurate phase diagram of monolayer water is very interesting, a large number of the ice phases have already been reported by several co-authors, in Phys. Rev. Lett. 116, 025501 (2016) “Two Dimensional Ice from First Principles: Structures and Phase Transitions”.

We thank the reviewer for pointing this out. In terms of the advance in understanding provided by the current manuscript over the 2016 PRL, we think there are a number of significant advances. Specifically, the paper 10.1103/PhysRevLett.116.025501

1. Only studied the phase diagram at 0 K without any treatment of thermal effects or dynamics
2. Did a rather limited structure search with relatively small unit cells and so did not identify all possible metastable phases e.g. the flat-rhombic phase.

In our work we have aimed to address the full temperature and pressure dependent phase behavior at a given confinement width and have addressed a number of issues such as the dynamical stability of phases, the solid to liquid phase transitions, (the origin of) a non-monotonic melting temperature dependence, entropically stabilized phases -- the hexatic and the superionic phases, corroboration of KTHNY theory, the onset of superionic behavior, a distinction of continuous and discontinuous phase transitions, and the presentation of clear experimental routes towards the measurement of the new phases. While some of the phases have been observed in previous studies, accounting for all physical effects, allows us to provide a comprehensive and clear answer on the phase-behavior of monolayer water, which can serve as a starting point for experiments and nano-engineering. We were excited about our 2016 PRL at the time but the sheer extent of the advance in understanding between then and now is one of the key reasons we believe this current manuscript is suitable for publication in Nature. We have modified the manuscript to more clearly highlight the new insights obtained in particular by rewriting large parts of the summary, introduction and conclusion.

(2) For the development of the ML water potential, similar methodology has been published in the literature, for example, by Cheng et al., Nature Physics, 17, 1228 (2021) “Phase behaviours of superionic water at planetary conditions”. In that paper, the author Pickard is also a co-author of this manuscript.

We thank the reviewer for this comment. We agree that there are similarities in the approaches used. However, aside from revealing new insights on a different set of systems, even in terms of methodology the current study represents an advance over the work by Cheng et al. Specifically,

1. We use quantum Monte Carlo to select the most appropriate density functional for a given system, which is subsequently used to train an ML potential. This makes our approach completely general -- agnostic to the system of interest or to the deficiencies of commonly used density functionals.
2. The use of an advanced active learning scheme considerably reduces the wall time and human labour required to train a potential. To elaborate, it took us just 14 days to train and validate the final potential (in contrast to several months). The efficiency of the active learning scheme also allowed us to perform a tight optimization of the potential (10 meV / molecule for energies and 100 meV / Å for forces, as against, around 42 / meV / molecule for energies and 750 meV / Å for forces in 10.1038/s41567-021-01334-9).

These advances dramatically reduce the human time and effort required for a “bottom up” study at the highest possible level of accuracy at DFT level for a general system using ML potentials.

To clarify these points, we have included the following lines in the section entitled “Conclusions”:

This work has been enabled by developments in high-level electronic structure theory – to guide the selection of an appropriate DFT functional – and a simple and efficient active learning scheme, which dramatically reduces the computational and human time required to train and validate a MLP across the full phase-diagram. The employed workflow can readily be applied to provide a rigorous description of nanoconfined water under other conditions (e.g. different confinement geometries and materials) as well as other classes of material.

(3) Regarding the hexatic phase of the confined water, a preprint has been published on arXiv in 2011, by Vilanova & Franzese, arXiv:1102.2864 (2011) “Structural and dynamical properties of nanoconfined supercooled water”. This preprint should be cited.

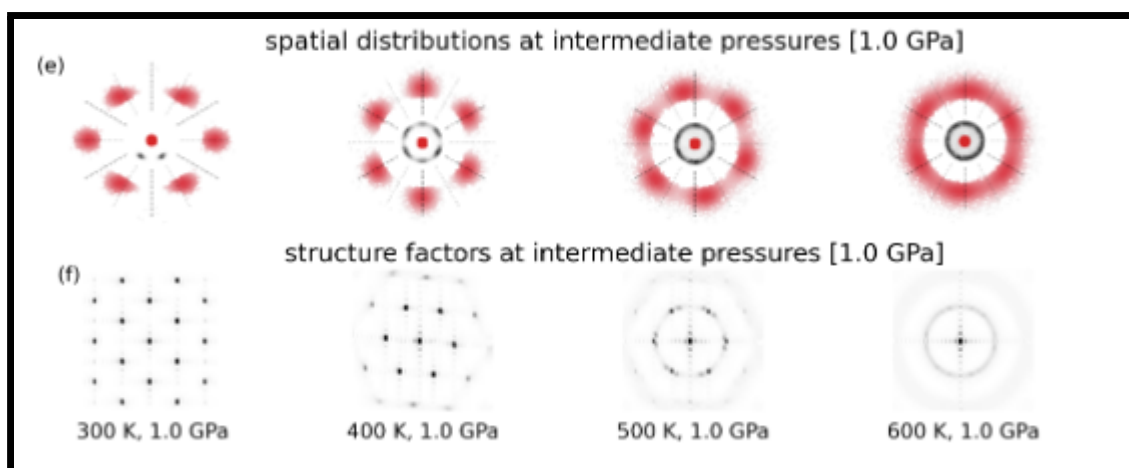
Additionally, in the Phys. Rev. E paper (Ref. 22) “Continuous melting through a hexatic phase in confined bilayer water”, the hexatic phase of bilayer water was reported for the first time. Although both previous work employed empirical water models, the conceptual advances have already been made by the researchers. More quantitative analysis of this issue with a better model (consider adding structure factor)

We thank the reviewer for this comment. We have now cited the arxiv preprint from Vilanova and Franzese. We believe that, on the hexatic phase, we have provided the following key advances:

1. Confirmation with a first-principles water model (and direct first-principles simulations with explicit graphene) of an hexatic phase in monolayer water.
2. Predictions with first principles accuracy about the temperature and pressure regime in which this phase can be observed experimentally under graphene confinement; conditions which turn out to be accessible experimentally.
3. A quantitative analysis of the hexatic phase, including calculation of the structure factor (see Fig 2), estimation of rotational relaxation constants accessible to NMR measurements, and the temperature dependent vibrational spectrum could facilitate the experimental identification of this phase and corroborate the KTHNY theory.

To highlight these advances

1. We have now included the structure factor (as suggested by the referee) in Fig 2 which shows clear features of the solid, hexatic and liquid phases and suitably modified the discussion of the hexatic phase.



2. We have also included the following statement in the subsection entitled “A phase distinct from solid and fluid at intermediate pressures”:

Although the hallmarks of an intermediate hexatic-like phase have been discussed qualitatively in previous forcefield studies [27], our first-principles level prediction in the intermediate pressure regime suggests that this phase can be realized experimentally in graphene confinement. We provide further support for this by simulating water between explicit graphene sheets at the reference first-principles level (see video V6 in SD and section S2.B of the SI), and observing hexatic behavior in agreement with the prediction of our MLP. Finally, to facilitate the identification of this phase we calculate the rotational relaxation time of water molecules and the temperature-dependent vibrational spectra, which can be compared with nuclear magnetic resonance and Raman spectroscopic measurements, respectively (see section S3 of the SI).

(4) The most novel result reported here is the discovery of a new 2D superionic phase from computer simulations. However, the closely related 3D superionic ice phases and the similar simulation methodology has been reported in the 2021 Nature Physics paper (17, 1228 (2021)) by one of the co-authors.

Over the past few years, the superionic ice phases have received extremely high interests from physics communities, evidenced by the following publications:

- 1) Nature Physics, 17, 1233 (2021) “Structure and properties of two superionic ice phases”;*
- 2) Nature Physics, 15, 1065 (2019) “Multiple superionic states in helium–water Compounds”;*
- 3) Nature Physics, 14, 297 (2018) “Experimental evidence for superionic water ice using shock compression”.*

The discovery of the new 2D superionic phase from the computer simulations, in this reviewer’s opinion, deserves a consideration for potential publication in Nature Physics as it

provides the sort of striking new advance that would excite the immediate interest of physics communities.

I would however highly recommend this work for consideration of potential publication in Nature if any one of the monolayer ice phases illustrated in the phase diagram (Figure 1) can be detected from an experiment (excluding the square ice phase which has been reported in Nature in 2015 by an experimental group (Ref. 1)). The experimental observation, in conjunction with the comprehensive phase diagram of Figure 1, would provide the sort of striking new advance that would excite the immediate interest of very broad audience of Nature readers.

We thank the reviewer for their comment. We agree that the existence of a superionic phase is fascinating and intriguing for the physics community and hence a number of papers on the properties or measurements of superionic ice have been published in Nature Physics.

We would, however, like to highlight that the computational discovery of a (reactive) superionic phase at accessible conditions in confinement is likely to have broad appeal outside the core (high pressure) physics community who have traditionally been most interested in superionic water. In particular, the existence for a superionic phase at mild conditions brings about a potential for its direct use in nanotechnological applications. Similarly, the high reactivity of this phase could be harnessed for water splitting in the energy sector or for facile chemical reactions with a high activation in bulk. A new means of probing superionic behavior of general materials (i.e. via confinement) could have direct implications for engineering. We believe that this aspect of our work – from both a fundamental and technological perspective – will be of interest also to engineers, materials scientists, chemists and physicists.

In conjunction with the other findings of our work, we think that it also appeals to many other fields. Confined water is omnipresent in biological systems and has in recent years been utilized for a multitude of nanofluidics and material science applications, such as water desalination and energy harvesting. At the same time, our findings appeal to geoscience and astrophysics, while revealing novel properties of the kind of every-day substance every reader can relate to.

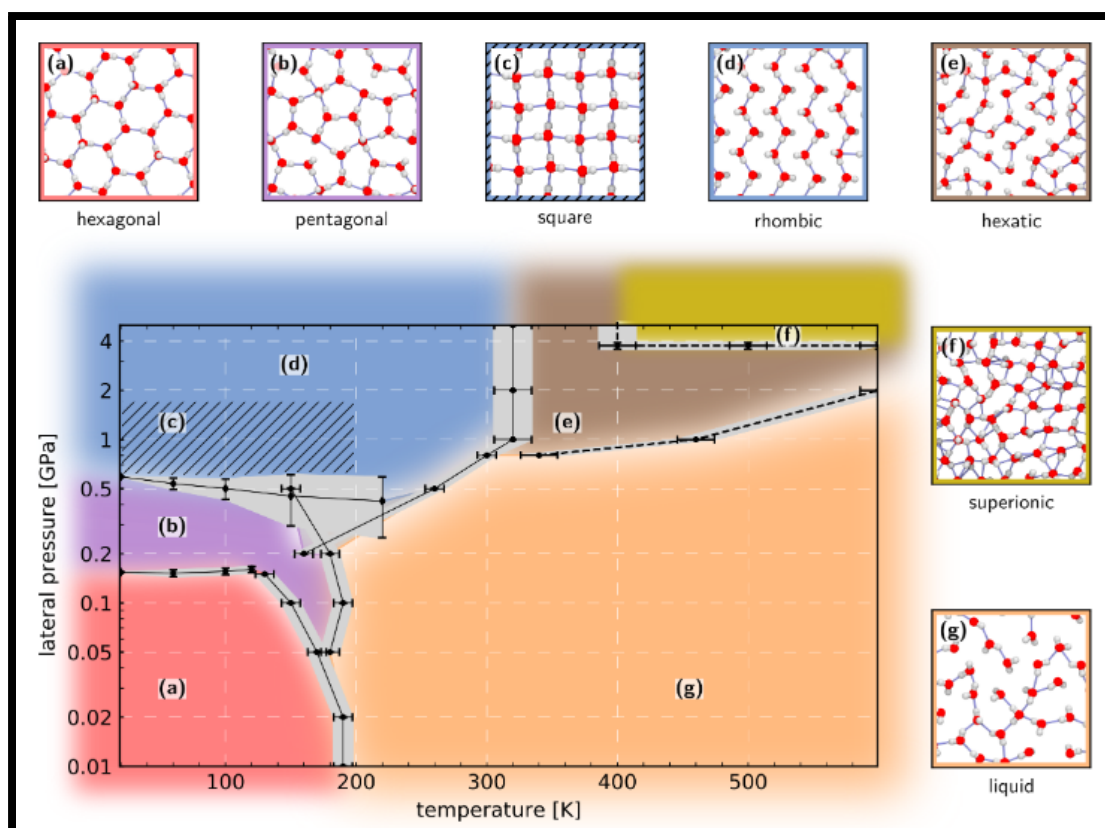
We agree with the referee that experimental observations of one of the phases predicted would be desirable. Whilst measurements are taking place and planned in two of the groups we are collaborating with, experiments in well-defined graphene nano-channels are challenging. Although there is already promising preliminary data on high ionic conductivity from one group it is likely to be some time before a convincing set of experiments is completed. It is precisely with future experimental verification in mind that we have put in effort to compute the experimental observables reported in the SI.

To make the broad appeal clearer, we have reformulated large parts of the introduction and conclusion to better reflect these aspects, and hope that in light of these changes the reviewer finds our work of interest to the broad audience of Nature.

A few technical comments on the phase diagram of Figure 1

(1) The present nearly-full phase diagram of Figure 1 needs more quantitative information for completeness. The phase boundary between the hexatic phase (e) and superionic phase (f) needs more quantitative description, like the use of the solid black lines with error bars for drawing the phase boundaries between (a), (b) and (c), and between (a) and (g).

We thank the referee for this suggestion. We have performed additional simulations at higher pressures and made the necessary changes to highlight the phase boundary of the superionic phase.



(2) It would highly informative to find out at what temperature, a direct phase transition from the liquid water (g) to superionic ice phase (f) would occur. A more quantitative data is needed to show this important phase-transition behaviour beyond 600 K.

We thank the referee for this suggestion. We have performed additional simulations up to 800 K for pressures up to 5 GPa and we did not observe a direct phase transition. In all cases we observed a continuous transition into a hexatic like phase which further transitioned continuously into the superionic phase. Going beyond this set of temperatures and pressures would require retraining the potential and more careful validations. However, to shed more

light onto the nature of the phase transition into the superionic phase, we have included a clear statement that monolayer water undergoes a continuous phase transition into the superionic phase.

As shown in Fig. 3(b), water “continuously” transforms to a phase with a specific ionic conductance above 0.1 S/cm, a commonly used threshold for characterizing a superionic conductor.

(3) Would a proton-disordered monolayer triangular ice phase emerge at high pressure beyond 4 GPa and at temperature of 290 K or 300 K? If so, it would be akin to the proton-disordered bilayer triangular ice phase shown in Figure 1 of Phys. Rev. Lett. 116, 085901 (2016). Such a comparative study would be highly informative.

We thank the referee for this suggestion. We have performed additional simulations up to 5 GPa in the suggested temperature range and we did not observe a proton disordered triangular phase. However, given that enthalpy (and free energy) differences between high pressure phases become very small (leading to the near degeneracy of the square phase with the rhombic phase), we do not nullify the existence of more (ordered or disordered) phases at higher pressures. However, a comprehensive exploration and description of these phases will require retraining the potential and performing validations at DFT and QMC level.

We have included the following statement in the section entitled “Conclusions”:

This work has been enabled by developments in high-level electronic structure theory – to guide the selection of an appropriate DFT functional – and a simple and efficient active learning scheme, which dramatically reduces the computational and human time required to train and validate a MLP across the full phase-diagram. The employed workflow can readily be applied to provide a rigorous description of nanoconfined water under other conditions (e.g. different confinement geometries and materials) as well as other classes of material.

Referee #3 (Remarks to the Author):

Review of “The first-principles phase diagram of monolayer nanoconfined water,” Venkat Kapil, Christoph Schran, Andrea Zen, Ji Chen, Chris J. Pickard, and Angelos Michaelides (#2021-10-16925).

In many ways, understanding the behavior of water at interfaces and in confinement is arguably more important than understanding bulk water (which is, itself, the subject of extensive, ongoing research). The wide range of surfaces with which water can interact, coupled with the diversity of structures that water can adopt leads to a wide variety of interesting, and often unexpected, phenomena. Thus, despite decades of research, new discoveries are reported almost every year. In this manuscript, the authors investigate the structure of a water monolayer confined between hydrophobic walls as a function of pressure and temperature. They use advanced simulation techniques that combine electronic structure calculations, statistical sampling, and machine learning to produce probably the most accurate calculations to date (considering the scope of the calculations). With this approach they confirm several previous results, resolve some existing conflicts, and predict several new phenomena. A key aspect of this research is its potential to move the field beyond the dichotomy of the efficiency of classical molecular dynamics simulations versus the higher accuracy, but higher cost, of electronic structure calculations. While classical MD simulations have been, and will undoubtedly continue to be, a workhorse in water research, they also come with notable limitations, many of which are likely to be more problematic when water interacts with surfaces. Overall, I find the results, which should be of interest to a wide variety of researchers, convincing. If these (excellent) results on the phase diagram for monolayer, confined water were the only aspect of this report, it might be hard to justify their publication in Nature. However, when coupled with the advances in technique outlined in the manuscript, I believe they are suitable for publication in Nature.

[We thank the referee for their very positive and thoughtful assessment of our work.](#)

I have only a few minor questions/issues that the authors should consider before publication.

1. Most of the ordered structures identified by the authors involve non-tetrahedral bonding arrangements. It seems likely to me that there are changes in the H-O-H angle in individual molecules that accompany these structures. For example, how much do the water molecules distort in the square and the pentagonal phases? I recall that there were some discrepancies between early structures predicted with rigid water models (e.g. Koga, et al., Phys Rev. Lett., 79 (1997) 5262) and later calculations with AIMD. Some discussion might be useful.

[We thank the referee for this suggestion. We have looked at the histogram of O-H bond lengths and H-O-H bond angles for the crystalline phases and found that all phases exhibit a number of possible bond lengths and angles with the exception of the square phase.](#)

polymorph	O--H bond length(s) [Å]	H--O--H bond angle(s) [°]
Hexagonal	0.98, 0.99, 1.01	103, 108
Pentagonal	0.98, 0.99, 1.00, 1.02	104, 105, 108, 109
Flat Rhombic	0.98, 1.00	102, 106
Square	0.98	104

Overall, we find that the hexagonal and pentagonal phases exhibit the longest O--H bond lengths and the largest distortions to the H--O--H bond angles. While the square phase exhibits a single bond length and bond angle. This observation is rather intriguing as empirical forcefields are generally unable to stabilize the monolayer hexagonal and pentagonal phases at finite temperature (most forcefields lead to either rhombic or square phases [10.1039/C9CP00849G]), while square phases have been ubiquitous in empirical force field studies. We have included the following statement in the subsection entitled “Extensive polymorph search enabled by a machine learning potential” and a discussion in the SI.

This structure is stabilized by a strong network of zig-zagging hydrogen bonds, which differs from the motifs present in flat-rhombic phases observed in empirical force-field studies. [10, 11]. We attribute the differences to the rigid water models employed in these studies that do not describe the complex hydrogen bond network arising from the full spectrum of O–H distances and H–O–H angles present in our structures (see section S1.C of the SI).

2. *This work focuses on confined water. Do the authors believe that their approach will be similarly helpful for calculations on bulk water, including solutions, isotope effects, supercooled water, etc.? A sentence or two to give the readers some perspective would be nice.*

We thank the reviewer for their suggestion. Indeed our approach is general and can be applied to study a wide array of systems at a predictive accuracy. To highlight this point, we have included the following lines in the section entitled “Conclusions”:

This work has been enabled by developments in high-level electronic structure theory – to guide the selection of an appropriate DFT functional – and a simple and efficient active learning scheme, which dramatically reduces the computational and human time required to train and validate a MLP across the full phase-diagram. The employed workflow can readily be applied to provide a rigorous description of nanoconfined water under other conditions (e.g. different confinement geometries and materials) as well as other classes of material.

3. In the discussion of the hexatic-like and superionic phases (pgs. 12 -13), the authors suggest that perhaps the higher pressures needed for this phase might be achieved experimentally inside “nanobubbles” that have been reported in the literature. Maybe, but it looks like only a few water molecules would fit inside these (i.e., not really enough to convincingly display a longer-range structure). Have the authors tried to estimate how quickly the lateral pressure falls below the regime for the high-pressure phases as the dimensions of the nanobubbles increase? This could help the readers understand the lateral sizes needed to contemplate such experiments.

We thank the reviewer for this suggestion. The paper [10.1021/acs.nanolett.5b02475](https://doi.org/10.1021/acs.nanolett.5b02475) suggests nanobubbles as large as tens of nanometers in diameter can be controllably formed using thermal treatment. A back of the envelope calculation suggests that a 10 nm radius nanobubble could accommodate over 5000 water molecules in two-dimensions, which should allow for long range order. In order to give the readers a sense of the lateral size of the nanobubbles we have included the statement in the subsection entitled “Anomalously high water dissociation leads to superionic behavior at high pressures”

Experiments already suggest that graphene sheets distorted through “nanobubbles” can exert pressures in the tens of GPa regime [20] over a length scale of tens of nanometers.

4. There are several typos associated with calling out the figures in the main text. For example, on the first line on page 10, I think the small diffusion coefficient refers to figure 2d (not 2b). There are also several references to figure 2(r), while Figure 2 only has a) – e). On page 11, the 4th line from the bottom refers to figure 2(b), while I believe they mean figure 3(b).

We thank the referee for pointing these out, and we apologize for the errors in referencing. We made the necessary changes.

5. For reference 23, the longer article on this topic by Kosterlitz and Thouless (*J. Phys. C: Solid State Phys.* 6 (1973) 1181) seems to be a better choice. The short letter (1972) L124 doesn't really discuss the two-step melting process.

We thank the referee for this suggestion. We made the necessary changes.

Reviewer Reports on the First Revision:

----- Referees' comments -----

Referee #1 (Remarks to the Author):

The authors performed new simulations and added significant information to the manuscript (in particular in the SI) to meet the criticism from the reviewers. The new section on nuclear quantum effects and the new calculations of the transition pressure between the hexatic and the superionic phases are especially useful. The latter in particular may aid the experimental verification of the simulation results.

The new results on confined water together with the technical novelties brought by this work make it in my opinion publishable in Nature.

Referee #2 (Remarks to the Author):

The authors made significant effort to illustrate the broad appeal of their comprehensive computational study and they did a very good job. They have also addressed all the technical comments well. I am particularly impressed by the promising preliminary data on high ionic conductivity from one of authors' collaborating experimental groups. Therefore, I would like to recommend publication of the paper in Nature.

Minor technical suggestions:

(1) The authors should also provide side views of all monolayer structures (a) – (g) in the Supporting Information. I am particularly curious whether the hexatic and superionic structures are planar (flat) or non-planar, given that the rhombic structure (d) is non-planar.

(2) It would be informative to add the metastable flat-rhombic region (with a different color) in the phase diagram, in an extended Figure 1, in the Supporting Information.

Referee #3 (Remarks to the Author):

I believe the authors have successfully addressed the comments from all the reviewers in their revised manuscript. I recommend publication in Nature.

I note that Referee #2 raised a number of good points concerning the novelty of this manuscript with respect to some previous work. Based on this, they make the case that Nature Physics might be a better place for the current manuscript. While I believe Nature Physics would be a fine choice for this work, I personally believe it is of sufficient novelty and general interest to warrant publication in Nature.

Author Rebuttals to First Revision:

Point-by-point response

The reviewers' comments are formatted in *italics and gray* color, followed by our response in black font.

----- Referees' comments -----

Referee #1 (Remarks to the Author):

The authors performed new simulations and added significant information to the manuscript (in particular in the SI) to meet the criticism from the reviewers. The new section on nuclear quantum effects and the new calculations of the transition pressure between the hexatic and the superionic phases are especially useful. The latter in particular may aid the experimental verification of the simulation results.

The new results on confined water together with the technical novelties brought by this work make it in my opinion publishable in Nature.

We thank the referee for their technical comments and their appraisal of the updated version of the manuscript. We would like to highlight that the tables and figures on the sensitivity of the phase diagram with respect to the confinement potential, confinement width, and quantum nuclear effects are now in extended data.

Referee #2 (Remarks to the Author):

The authors made significant effort to illustrate the broad appeal of their comprehensive computational study and they did a very good job. They have also addressed all the technical comments well. I am particularly impressed by the promising preliminary data on high ionic conductivity from one of authors' collaborating experimental groups. Therefore, I would like to recommend publication of the paper in Nature.

We thank the referee for their valuable comments on highlighting the novelty in the methodology introduced in this work, and for their technical comments on the high pressure part of the phase-diagram.

Minor technical suggestions:

(1) The authors should also provide side views of all monolayer structures (a) – (g) in the Supporting Information. I am particularly curious whether the hexatic and superionic structures are planar (flat) or non-planar, given that the rhombic structure (d) is non-planar.

We thank the referee for their suggestion. We have included the top and side views of the crystalline phases in the extended data. The side view of the hexatic and the superionic phases, within the confinement potential and explicit carbon atoms, are now also clearly

added to the videos. All the phases are planar as out-of-plane motion being limited to thermal fluctuations.

(2) It would be informative to add the metastable flat-rhombic region (with a different color) in the phase diagram, in an extended Figure 1, in the Supporting Information.

We thank the referee for their suggestion. In our current phase diagram we only display thermodynamically stable phases and do not show any metastable phases. The hatched area in the phase-diagram indicates degeneracy of the square and the flat-rhombic phases (as opposed to metastability of one of them). The phases (more specifically the hexagonal, pentagonal, square, rhombic and even the disordered liquid and hexatic ones) are metastable much beyond the region of thermodynamic stability. We feel that indicating the metastable regime for just one phase but not others would possibly serve to confuse the reader. Likewise adding more metastable phases to an extended SI version of Fig. 1 would produce an overly complicated figure which again would potentially confuse readers and distract the reader from the main focus of Fig 1– thermodynamic stability. While the suggestion is much appreciated, we have chosen to politely decline this request to prioritise clarity over detail, keeping in mind the multidisciplinary nature of the audience of this journal.

Referee #3 (Remarks to the Author):

I believe the authors have successfully addressed the comments from all the reviewers in their revised manuscript. I recommend publication in Nature.

I note that Referee #2 raised a number of good points concerning the novelty of this manuscript with respect to some previous work. Based on this, they make the case that Nature Physics might be a better place for the current manuscript. While I believe Nature Physics would be a fine choice for this work, I personally believe it is of sufficient novelty and general interest to warrant publication in Nature.

We thank the referee for their appraisal of our work.

----- End of comments -----