

We thank both reviewers for the thorough revision of the paper and for the useful suggestions. Below we discuss the changes made in the manuscript in response to the reviewer comments.

Answers to the comments of reviewer 1.

“I think it should be stressed that the terminology/definition of deposition ice nucleation is historically macroscopically defined (before the application of in situ microscopy and MD simulations). For many current experimental techniques, this still has validity. Though on a molecular level this may not be true. Following the conventional definition, it is “deposition ice nucleation” and not “deposition freezing”. Liquid (macroscopic) water freezes, but deposition ice nucleation does not involve (following convention) bulk liquid water. If the authors by purpose mix these two definitions and generate a novel terminology, since they observe deposition ice nucleation to originate from a liquid-like water cluster, then this has to be discussed. However, this seems not to be the case since this term is readily used. Also, I would not challenge the conventional definition based on one simulation study only. Hence, “deposition freezing” should be exchanged for deposition ice nucleation throughout the manuscript.”

We agree that using a more conservative and coherent terminology is beneficial for the paper and we have changed all instances of “deposition freezing” to “deposition ice nucleation”

“The other issue regarding terminology is to call the water clusters “droplets”, “dropletwise”, etc. I see that the authors struggle with this issue as well, trying also “nanodroplets” or “nanophase”. In this community droplets are usually defined to be 10s of micron in size. The “nanodroplets” forming inside the pore are about 2 nm or smaller. Typically, we call those entities clusters. It may not even be clear if this cluster size possesses bulk-liquid water properties (surface tension, etc.)? I am also not entirely sure how to name those condensed nanometer-sized islands of water but naming those “droplets” is unfortunate and ambiguous. Liquid-like or ice-like water clusters may be an idea. Maybe “nanodroplets” works to convey the idea but I feel this is not ideal either.”

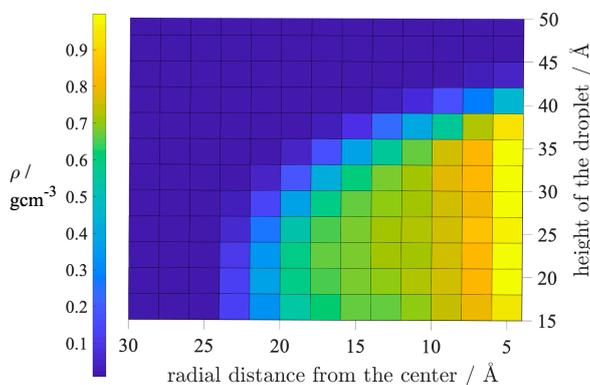


Figure 1: The radial mass density distribution of a simulated water droplet (from unpublished work of the authors).

We agree that the water aggregates observed before condensation are presumably too small to be called droplets and in order to clearly differentiate from other uses of the word droplet in aerosol science (e.g. cloud droplet) we adapt the term “nanodroplet”, however “dropletwise adsorption” is a standard term used for non filmwise adsorption, and has been used to describe ANT based droplet nucleation on non completely wettable surfaces in previous publications (Laaksonen, Malila and Nenes 2020: <https://acp.copernicus.org/preprints/acp-2020-202/acp-2020-202.pdf>), therefore we prefer to keep it for the description of the adsorption mechanism and the structure of the adsorbed layer. However, we have added a phrase to define “dropletwise adsorption” as “adsorption that proceeds through the formation of aqueous nanodroplets on the surface that merge into multilayer film at higher supersaturations.” We refrain from using the term “clusters” in order to avoid confusion with the terminology of new particle formation that typically refers to non-stabilised molecular aggregates with diameters lower than 1 nm

as clusters. We justify the choice of using the term “nanodroplets” by sharing results from atomistic simulations of water nanodroplets on flat graphene having around 1000 molecules, that correspond approximately to the size of the droplets in the dropletwise phase of these simulations. The percentage of surface molecules determined by selective surface analysis (PYTIM) reaches 50% of the total number of molecules but the density within the droplet reaches its bulk value, as seen in the figure above. This analysis suggests that the water droplets are clearly different from macroscopic droplets used on the surface to bulk ratio, but they cannot be called clusters, which have a well defined bulk that reaches the density of the corresponding macroscopic phase.

“From the abstract and introduction, one would expect some analysis using ANT, i.e., deriving ice nucleation rates, etc. However, this study makes the case that ANT can be applied to deposition ice nucleation based on the simulation results. As written, this fact may not be so clear, and the overall confidence is only supported by this study looking at one idealized substrate. Maybe in some instances the text could convey a more exploratory study. I do not disagree with the authors; I suggest being a bit more conservative. Especially when reading the model methods. Many caveats are discussed (which I appreciate, and this does not minimize the impact of the study) but it feels a bit counter (i.e., weaker) to the introduction. This is maybe something the authors could consider.”

We have considered the concerns raised by the reviewer and made the following modifications to clarify that the presented results are to be viewed as a case study that evidences the potential to extend ANT for ice and droplet nucleation:

1. Abstract: “We put forward the plausibility of” was changed as follows: "Based on the results of our case study, we put forward the plausibility
2. Abstract: “but the input parameters are also potentially transferable across phase states of the nucleating phase.” was changed to “but the input parameters are also potentially transferable across phase states of the nucleating phase at least for the case of the graphite/water model system.” to clarify that our study does not necessarily imply general extension of ANT to deposition ice nucleation.
3. Introduction: “In this work we address all of the above three crucial points using atomistic and coarse-grained molecular simulations.” was changed to “In this work we address all of the above three crucial points using atomistic and coarse-grained molecular simulations, with aims i) of providing novel insights into the so much debated mechanism of deposition freezing; and ii) of demonstrating that adsorption and deposition ice nucleation are sufficiently similar in terms of mechanism and thermodynamics for ANT to be used as a collective framework to describe both of them.”
4. Conclusions: “We also demonstrated the potential that deposition freezing can be described by ANT developed for droplet nucleation” was changed to “We also demonstrated the potential that deposition ice nucleation on the model graphite/water system can be described by ANT with the parameters developed for droplet nucleation” to convey the idea that at this stage results are system specific.

Specific comments:

Line 22: The authors could cite here the recent review by (Knopf and Alpert, 2023).

The requested citation was added

Line 30: I doubt that (DeMott et al., 2010) discuss in detail nucleation theory and rates relevant for this paper and they do not discuss specifically deposition ice nucleation. Other literature would be needed in this place.

The reference was corrected, the revised manuscript refers to recent reviews on ice nucleation: Hoose et. al. 2012, Kanji et. al. 2017, Welti et. al. 2014

Line 37: “... adsorbed water can exist...”

The sentence was rephrased according to the suggestion

Line 40: At this point it is not clear what you mean by “whereas other locations that collect pre-critical clusters might have an opposite effect.” Why do they have an opposing effect?

The reason for this is that certain active sites might collect water due to the inverse Kelvin effect but have geometries that do not allow the formation of pre-critical ice clusters, as it was seen for the hemispherical pore geometry in our simulations. To clarify this in the text we have added the following phrase: “*whereas other locations that collect pre-critical clusters might have an opposite effect, for instance because their geometry disfavors the formation of pre-critical ice embryos (Bi et. al. 2017).*”

Line 47: Here it suddenly switches to immersion freezing. I recommend keeping the focus on deposition ice nucleation throughout the introduction. Also, I am not sure if I agree with this statement. When CNT is expressed in terms of water activity, intrinsic parameters like contact angle, interfaces, etc. are considered. See, e.g., the work by Knopf and Barahona groups. In fact (Knopf and Alpert, 2023) show that deposition ice nucleation may be well described using water activity as for the case of homogeneous ice nucleation and immersion freezing.

We understand that the molecular simulations cited in this section were conducted in immersion mode, however we cannot refer to work on deposition ice nucleation because ours is the first such study, safe for the simulations presented in David. et. al. 2019. We clarify this in the revised version and we argue that pre-critical enhancement or suppression of ice formation is presumably equally important in any ice nucleation mode. Further we clarify - both here and in the revised manuscript - that while surface specific properties can be treated by different versions of CNT (e.g.: the soccerball model by Niedermeyer or the activity based formulation), even these cannot take into account pre-critical enhancement or suppression or freezing, because the original theory considers ice nucleation as a single step process with no assumption about surface-water interactions before the critical nucleus formation.

Line 55-57: Missing words, empty brackets?

Missing citations were added.

Line 73-75: As mentioned above, considering water activity in CNT descriptions might account for these issues (Knopf and Alpert, 2023; Koop et al., 2000; Barahona, 2015, 2014; Knopf and Alpert, 2023).

Citations for models treating surface water interactions were added, but we maintain that CNT is inherently unable to account for pre-critical stages of ice nucleation.

Line 81: Period missing?

This is addressed in the next point.

Line 81-86: A long sentence, maybe too long. Also, this statement is too general. Careful literature review will show that there are several studies (some employ nanoscale resolution) which do not corroborate PCF occurring in observed deposition ice nucleation experiments, e.g. (Wang et al., 2016). I would avoid “in reality” and write “... ‘freezing’ could be pore condensation...”.

The sentence was divided into smaller sentences and rephrased to avoid declaring PCF as the only plausible mechanism of deposition freezing, what is implied by the expression “in reality”.

Line 112: It is crucial to conduct atomistic and coarse-grained molecular simulations as discussed in (Knopf and Alpert, 2023) and shown in (Roudsari et al., 2022). They can yield different results while atomistic simulations are likely the preferred method, if feasible.

The requested sentence was added to the manuscript.

Line 127: What do you mean by energetic background? This is not a thermodynamic expression. Maybe just state the parameters you assess?

The expression has been changed to “*interaction energies that drive adsorption and deposition ice nucleation*”

Line 146-147: Could you please elaborate here. The target vapor pressure corresponds to the adsorption layer structure”? At such high vapor pressure, one would have multiple layers of water? I assume, this is what you want?”

The statement has been rephrased as follows: “*The target vapor pressure is not to be confused with the instantaneous vapor pressure in the simulation box, it is strictly the vapor pressure that corresponds to the value expected in the fully converged simulation (i.e. at multilayer coverage).*”

Line 159: What do you mean by “deterministic dynamics”?

By deterministic dynamics, we mean standard Newtonian dynamics of classical simulations. We stress the importance of this condition by adding the following note in the manuscript: “*Note that it is important to ensure that the spatial dynamics in the system are not driven by stochastic changes introduced by the Monte Carlo sampling, otherwise it is impossible to estimate time dependent properties from the simulation.*”

Answers to the comments of reviewer 2.

Specific comments:

The atomistic simulations of the graphite/water interface, used to determine the FHH parameters employ the TIP5P water potential. While TIP5P overall predicts structural and thermodynamic properties of water and ice quite well, it does underestimate the density difference between water and ice Ih [see e.g. Vega et al., J. Phys.: Cond. Matter 7, S3283–S3288 (2005)]. Do you believe that using a water model yielding more realistic differences in density between liquid and ice phases, in conjunction with the fixed definition of the layer thickness, could lead to systematic differences in the average interaction energies obtained, in addition to possible differences in interaction energies resulting from the different water model?

The difference between the bulk density of water and Ih is 0.015 gcm^{-3} and 0.07 gcm^{-3} for TIP5P and TIP4P/ice. This appears to be large enough to non-negligibly alter interaction energies. However, given that these are differences between the mean bulk densities, they can be used as proxies to predict the dependence of interaction energies on the water model choice only in the bulk, where the impact of the vicinity of the surfaces on the density profiles especially of the liquid phase is negligible. In our systems, seen from the density profile of liquid water (Figure B1.) this is expected to occur below layer 3. As we state in the manuscript, in the particular case of graphene/water systems “*The interaction energy of both water and ice decays rapidly with the distance from the solid surface, only the first two molecular layers give a non-negligible contribution to the overall adsorption energy.*” therefore we do not expect that the bulk density difference can be directly related to potential differences in the interaction energy across different water models.

It could on the other hand be useful for future studies to compare the density profiles of different water models near the surface and provide depth-dependent estimate of the sensitivity of interaction energies to the choice of the water model. However, such a study requires a number of simulations and potentially the use of different surfaces, and it goes far beyond the scope of this work.

I would encourage the authors to review their variable names and formulae. Throughout the manuscript, sub- or superscripts in variables that do not denote indices are set in italics (e.g. A_{FHH} , k_B , σ_{OC} , V_{filled} , N_{ice} , etc.). These sub- and superscripts should be changed to roman font. In addition, several variable names appear unnecessarily long or convoluted to me (e.g., in eq. 2, the number of carbon atoms “NC” could be n_{NC}) and the number of water molecules in i -th adsorbed layer, “ NW_{Li} ” could simply be “ N_i ”, so that the mean interaction energy per unit area in the i -th adsorbed layer could simply be denoted “ E_i ”.

We have reviewed the variable names according to these suggestions, however NC and NW were kept. Instances of denoting the number of water molecules as N_{tot} or N_{wat} were also changed to NW.

Technical corrections: We appreciate for pointing out technical issues. We addressed each of them as requested in the manuscript. For those where we feel that additional explanation of the changes made in the manuscript is need, we provide a detailed explanation below the comment.

l.14: *not only the extension ... is possible -> not only is the extension ... possible*

l. 39: *clusters , -> clusters,*

l.55: *implemented regional -> implemented into regional*

l.57: *two broken references*

l.69: ... with direct links to the molecular-scale interactions...
l.139: ... a graphite slab with a hemispherical or cylindrical pore consisting...
l.164: numerically->numerically
l.171: remove comma after carbon
l.176: remove spurious "because"
l.178: any estimating -> estimating any
l.194: units missing for σ_{OC}^{LJ} (I assume nm)

The correct unit (nm) was added.

l.206: space missing before reference.
Figure 2 caption: describe arrows and label water and graphite in panel (a). Shaded areas mentioned in the caption not visible in panel (b).

In panel a) the arrows were labelled E_1 , E_{HB} and $E_{2/3}$ to indicate the interaction energy component that they represent, graphite and water were labelled. In panel b) the shaded areas are now shown with the same color coding as used in Figure 6.

l.230: increase of adsorbed water molecules
l.231: re-format reference
Figure 3: "b)" is missing in the figure. A period is missing at the end of the first sentence in the caption. Carbon atoms are not mentioned in the caption.

The figure was corrected, panel b) is now correctly labelled and we indicate that carbon atoms (alike liquid-like water molecules) are shown in white.

l.299: steepness -> slope?
Figure 4: "teal" and "blue" curves are very hard to distinguish; please change one of the two colors! "gray" curve appears black to me, especially as the graph has a gray background. Period at the end of the first sentence of the caption is missing. "adsobing" -> adsorbing. "out-of-pore nucleation" -> ice growing out of the pore?

The colors were corrected, now the results for the hemispherical pore are shown in yellow colour. V_{filled} in the axis label of panel b) was changed to V_f consistently with the overall simplification of the variable names. Out-of-pore nucleation was not changed, as out-of-pore nucleation is an established term (Page and Sear PRL, 2006).

Figure 5: panels (a) and (b) in the actual figure are not references in the caption. Instead, the caption references a "top" and "bottom" panel, which are both part of panel (a) in the actual figure. The content of panel (b) is not explained at all in the figure caption, but it is referenced in the main text...

The caption was corrected and N_{tot} in the axis label of panel a) was changed to NW for consistency

l.327: shifted towards the left -> shifted to smaller time values?
l.345 remove "makes"
l.355 "and a A_{FHH} " -> and A_{FHH}
l.360 broken reference
l.381: missing math environment $3k_B T/2$
l.385/fig 6: in the text, E_i has the unit of energy (kJ/mol), in the figure the unit of energy/area (kJ/mol/nm²). Please fix this.

Correctly, the interaction energies calculated are normalised by the surface area, the mistake was corrected in the text.

l.386: missing math environment $k_B T$
Figure 6: caption: add explanation that "LnS" denotes the interaction between the surface and the n-th adsorbed

layer in the graphs. add information that the means and standard deviations(?) (in parantheses) of the distributions are also shown as insets on the graphs of the distributions. Check whether the unit of energy/surface area is the correct one for E_i (see l.385 in the main text)

L1S, L2S... were changed to L1, L2... for consistency and the revised caption explains that they refer to layer 1, layer 2 etc. We also describe the meaning of the insets: mean interaction energy and standard deviation (in brackets). Energy units were corrected in the manuscript text.

l.393: missing space after 30°

l.399: ice made up TIP5P water molecules -> the ice phases of the TIP5P water model?

l.401: box plots obtained from the time series... -> box plots of the distribution...

Figure 7: caption: box plots of the time series... -> box plots of the distribution...

l.425: “the potential that deposition freezing can be described” -> “that deposition freezing can/could be described”