

**We appreciate the authors' efforts putting this manuscript together, which proposes Adsorption Nucleation Theory (ANT) as a unifying theory of pore condensation and freezing (PCF), adsorption, and deposition nucleation. However, we want to point out that in certain portions of the manuscript, PCF is misrepresented.**

**On lines 76–86, PCF is correctly summarized as involving pore filling followed by immersion or homogeneous freezing of the pore water and ice growth out of the pores. But on the next lines (86–91), it insinuates that the foundation of this framework is based on molecular simulations in David et al. (2019), which is not the case. Instead, PCF describes pore filling with the Kelvin equation, ice nucleation with classical nucleation theory (CNT) parameterizations based on experimentally determined homogeneous ice nucleation rates, and ice growth again based on the Kelvin equation (Marcolli, 2014; 2020; David et al., 2019; 2020; Marcolli et al., 2021). In David et al. (2019), molecular simulations are used to show that (i) ice does not nucleate on the substrate, which was tailored to mimic the silica surface, (ii) ice also does not grow out of a single ice-filled pore with a diameter of 3 nm, but (iii) that ice is growing out of closely-spaced 3 nm pores.**

Thank you for pointing out the inaccuracy in our description of PCF, we will correct this in the revised manuscript.

**As in PCF ice nucleation occurs in pores, it is very different from deposition nucleation and ANT, which both rely on an ice-nucleating surface as the location of ice nucleation. Therefore, the claim to unify PCF and deposition nucleation under a theory based on ANT cannot be kept unless PCF is strongly distorted. For PCF in its right description, the question posed in the title has therefore to be answered with “no”. We think a title change is appropriate to reflect this.**

Pores are physical entities, which means that the only difference between the interior pore surface and the exterior surface of an INP is geometry. The basis of ANT is a combination of the FHH adsorption theory and the Kelvin effect. Pore geometry induces an inverse Kelvin effect, which can be accounted for in the ANT framework, as we have shown in Laaksonen and Malila (2021) (subsection 10.7.1). In both cases, our simulations show that ice nucleation proceeds by adsorption of liquid like water onto the surface that then freezes to ice, starting from the surface. We therefore believe that the title of our paper is quite appropriate.

**Moreover, it is incorrect that in David et al. (2019) droplet emulsion experiments were used to show that ice nucleation rates are high enough to occur in the small volumes of pore water (as stated on line 85). Instead, we use slurry experiments (and not emulsion freezing experiments) in David et al. (2020) to show that the pores in the mesoporous silica particles are wide enough to hold ice. Marcolli (2020) discusses in more detail the role of homogeneous nucleation rates. There, it is also shown that the water volume just needs to be large enough to hold the critical ice embryo for water to freeze when temperatures fall below about 230 K.**

We will correct the description on line 85. The pore volume vs. critical cluster size calculated using CNT is at best circumstantial evidence for homogeneous nucleation and does not prove that the freezing inside pores always happens in the “bulk” of the water instead of starting from the pore surface.

**On lines 420–422, the authors write that PCF involves pore filling as a prerequisite for ice nucleation. This statement might be a misinterpretation of David et al. (2019), where ice nucleation in the cylindrical pores of mesoporous silica particles is investigated. The filling of cylin-**

**drical pores is occurring almost instantaneously when RH is above a threshold value. Therefore, these pores are either completely filled or empty. Yet, pores with other shapes like conical pores and wedges fill gradually as discussed in Marcolli (2020). For such pores, ice nucleation occurs when the water volume is large enough to hold a critical ice embryo. Moreover, it occurs irrespective of whether the surface is ice nucleating when temperatures are below about 230 K.**

We will correct the statement on lines 420-422. We agree that at  $T < 230$  K, if the freezing does not start from the interior pore surface, then it will occur homogeneously. However, our simulations indicate that at least in the graphene-water system, freezing starts from surface. Both the original and the control simulations (performed with different MD/MC ratios) clearly show that freezing begins in the layer adjacent to the surface and not in the bulk. Figure 5 and Appendix Figure A3 follow the time evolution of the frozen fraction within the first three layers adjacent to the graphene surface. Before freezing onset transitional ice clusters appear and melt in the bulk of the adsorbed water, while it is only the ice embryo anchored to the surface that can grow beyond the critical size and result in the freezing of the whole adsorbed layer within the simulation time. This is a qualitative indicator that heterogeneous freezing at the surface is energetically favorable compared to the homogeneous process. Additionally, the fact that the hemispherical pore does not nucleate ice despite of the condensation rate being similar as observed for the cylindrical pore indicates the importance of the surface. The volume of the two pores is comparable and both can accommodate critical embryos of homogeneous freezing in the bulk however, it is only the cylindrical pore, with the bottom of the pore being smooth and having an area that is sufficient for the formation of a critical embryo that promotes freezing, indicating that heterogeneous freezing is favored over homogeneous freezing in the studied systems.

Moreover we point out that the statement “the pore is either filled or empty” only makes sense if the temporal resolution of the observation is known. The temporal resolution of the simulations is on the order of picoseconds, therefore they are able to resolve process that appears to be instantaneous in experiments.

**PCF was introduced to explain measured ice nucleation data as e.g. in Marcolli (2014) and in Marcolli et al. (2021). In the latter, the requirements for ice nucleation on soot particles were established taking the primary particle size, overlap, soot contact angle, and soot aggregate size into account. This soot PCF framework can explain why some types of soot nucleate ice while others do not. Specifically, it predicts that soot particles with a contact angle of  $90^\circ$  do not nucleate ice below water saturation because, according to the Kelvin equation, there is no capillary condensation in pores for contact angles of  $90^\circ$  or higher. Conversely, the graphitic surface in the present study shows an unrealistically high water adsorption of several monolayers for  $RH_w < 100$  % despite its contact angle of  $90^\circ$ . A reason for this strong water adsorption might be that the simulation was carried out at a supersaturation of 300 %  $RH_i$  or  $S_i = 300$  % (lines 145–146). A high saturation ratio of 250 %  $RH_i$  was also used for the simulation with mW water shown in Fig. 3 of David et al. (2019) to speed up the simulation. Nevertheless, the simulation in David et al. does not indicate significant water adsorption on the flat silica surface although its contact angle of  $64^\circ$  is clearly below the one of the graphitic surface and the simulation time was much longer (300 ns compared to 10 ns in the present study).**

We would like to point out that the capillary condensation equations used for calculating pore filling may be inaccurate at small pore sizes (Kruc and Jaroniec, 1997). As noted above, we have shown

that the ANT equations can be used to predict pore filling RH (Laaksonen and Malila, 2021), accounting explicitly for the molecular interactions (described using the FHH parameters) between the water meniscus and the pore walls. With large pores, our approach gives identical results to the capillary condensation calculations, but not when the pore radii are only a few nm. For example, assuming the FHH parameters for carbon of  $A = 12$ .  $B = 1.93$  (Laaksonen et al., 2020) and contact angle of 90 degrees, we calculate that a hemispherical pore with a radius of 2.6 nm is filled at an RH of 89% at room temperature.

We acknowledge that the supersaturation of 300% used in the simulation is exaggerated and does not model atmospheric conditions. Similarly to the simulations shown in David et. al. (2019), where two supersaturation values are used (250% and 300%), we adapt this value to increase the speed of the simulation by increasing the driving force. We stress that we cannot convert the instantaneous vapor pressures (numbers of molecule in the vapor phase) to relative humidity in this simulations because, exactly due to the exaggerated driving force, the vapor phase is not expected to be equilibrium with the adsorbed layer at all steps of the simulation. This means we cannot unambiguously determine the structure of the adsorbed layer as a function of equilibrium relative humidity, therefore it is not meaningful to state that we reach several molecular layers thick adsorbed layer at  $RH < 100\%$ .

While acknowledging the above caveat of using exaggerated vapor pressure to speed up the simulations, we do not believe that it leads to unphysical adsorption and that adsorption on a molecularly flat graphite surface is not expected to happen. First of all, experimental evidence from HREEL spectroscopy of water adsorbed on monolayer graphene shows that at room temperature not only water adsorbs on the surface but even chemisorption and C-H bond formation are expected (Poltano et. al., 2011). An SFG study that finds pre-ordering of water near graphite and relates it with the potential IN activity of graphene (Singla et. al., 2017). Quantum chemical calculations also yield negative adsorption energies for the water/graphene system (Ma et. al. 2011). Atomistic molecular dynamics simulations of water adsorbed on the surface of graphene (Gordillo&Martí, 2008) and graphite (Gordillo&Martí, 2008) predict adsorption energies on the order of -30 kJ/mol.

In David et. al. (2019) the authors relate the IN activity of the silica surface to the extent of premelting: *“Recent experiments (59) quantitatively confirm the simulations prediction (30) of the fraction of water that is premelted in silica pores as a function of temperature. We have demonstrated, using thermodynamics and nucleation theory, that surfaces that induce premelting (as is the case of silica) cannot heterogeneously nucleate ice from the liquid phase (31).”* (David et. al. (2019)). We note that while amorphous silica might induce premelting, graphene has an ordering effect on the surface water molecules which makes premelting unlikely. This has been seen from sum frequency generation spectroscopy (Singla et. al. ,2017) as well as atomistic molecular dynamics simulations (Gordillo&Martí, 2008), and quantum chemistry (Leenaerts et. al., 2009, Sanfelix et. al., 2003 ), the latter supporting that hexagonal ordered monolayers are the most stable configuration at the graphene surface. Therefore the fact the amorphous silica does not nucleate ice due to pre-melting does not rule out the that graphene will adsorb water and promote heterogeneous ice nucleation. And the observation that in our simulations, freezing starts from the surface, already indicates that graphene does not induce premelting.

**Moreover, experiments with the non-porous particles do not show any deposition nucleation (David et al., 2019). The question therefore arises why the water adsorption is so high in the simulations with a graphite slab (non-porous) and monatomic water despite the high contact angle of 90°.**

The experiments of DeMott et al. (1999), Mahrt et al. (2018) and Nichman et al. (2019) show that non-porous soot nucleates ice at rather high ice supersaturation, but still below water saturation at temperatures below 230 K.

**Another point that sheds doubt on the meaning and relevance of the simulation results shown in Lbadaoui-Darvas et al. is that the graphitic surface proved to be an efficient ice-nucleating agent in immersion mode in molecular simulations with mW water (Lupi and Molinero, 2014; Lupi et al., 2014). Yet, experiments have shown that soot is a poor INP in immersion mode or even ice nucleation inactive (Hoose and Möhler, 2012; Kanji et al. 2020). We wonder why the authors chose a graphitic surface for their study, although the mW water model is known to overpredict the ice nucleation activity of the graphitic surface in immersion mode (Qiu et al., 2018). The high water adsorption together with the false prediction of IN activity may explain the ability of the mW water to nucleate ice on a flat graphitic surface. Yet, these simulations do not represent real physical processes occurring in or on soot particles.**

As acknowledged before in the response as well as in the manuscript, we are aware of the caveats of the water model as well as of the lack of testing and validation for adsorption studies. The overprediction of freezing on graphene using the mW potential is due to the model's inability to reproduce the contact angle of water and the free energy of the ice-graphite interface simultaneously. This caveat is intrinsic to the resolution of the model and arises from the lack of rotational degrees of freedom, therefore only atomistic potentials could resolve the issue.

Unfortunately, the only MD program package (LAMMPS) that can be used to perform hybrid GCMC/MD simulations does not allow for parallelisation of this particular simulation type if the adsorbate is a truly polyatomic molecule. Atomistic simulations in this case would come at absurdly high computational cost due to the fact that freezing is a rare event and it can be observed from unbiased simulations only at the best IN surfaces (AgI, kaolinite). The potential parameters used in the simulation were chosen because they represent the best available compromise in terms of computational cost and accuracy.

In any case, we do not expect to obtain quantitative information relevant to real graphitic surfaces from the coarse grained simulations. Even if the water model overpredicts freezing on graphite, our aim in this manuscript is not to make quantitative predictions of ice nucleation on porous and non-porous graphitic surfaces, but rather to reveal the mechanisms of ice nucleation and their similarities/dissimilarities in the two cases. We believe that for this purpose, the systems we have chosen for our simulations are completely adequate. It is also clarified in the text that the surfaces used in the GCMC/MD simulations do not represent real graphene and we refrain from using these simulations to predict any quantitative data. Quantitative data (interaction energies) are only obtained from atomistic MD simulations.

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