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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Thermodynamics of homogeneous nucleation of ice particles in the polar summer mesosphere" *by* A. Y. Zasetsky et al.

A. Y. Zasetsky et al.

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The authors are grateful to both reviewers for their valuable comments that helped to improve the manuscript. Our detailed responses to all comments and questions are given below.

Responce to Referee #1

Minor comments: The suggested reference is now included. Also all suggested minor corrections have been introduced. We have also added all clarifications suggested by the Reviewer and expressed the critical radius in terms of molar values. As advised, the caption for Figure 2 (former Figure 3) has been changed to "Mass density". The citation style and other technical details have been corrected.

Question: Why is the density profile that symmetric on both sides of the interface? I

would expect a higher density in the amorphous cluster then in the vapour phase.

Answer: The density profile is computed as a function of the distance from cluster's center-of-mass, so it is symmetric.

Technical question: How you define the thickness of the diffuse interface to arrive at 10 A°?

Answer: The thickness is defined as the distance between points with the density of 5 and 95% in the profile.

Comment: Figure 4, X-axis label: It is more precise to denote it as thefree formation energy of an amorphous droplet. Please add in the caption, that this figure refers to Eq. (1). Please add the reference temperature in the figure caption. (Minor: Please consider for the final manuscript to eventually present the free formation energy in units of thermal energy kBT, i. e., in dimensionless form as G/(kBT).

Answer: Free formation energy has been added in the caption, as well as the reference to Equation 1 and the reference temperature T=120 K. As for the suggestion to present the free formation energy in units of thermal energy, we believe that it is important to keep the current units (J*10ˆ-18). These units were used by Rapp and Thomas (2006), the paper we often refer to in this work, to illustrate the free formation energy provided by the classical calculations.

Responce to Referee #2

1. Question: In section 2, the authors attempt to estimate particle number densities from measurements with ACE-FTS assuming a fixed particle radius of 60 nm. Clearly, this procedure is not appropriate and subject to severe errors because of several reasons. First of all, the authors should note that it is well known from ground based and satellite observations that radii of NLC particles show a strong variation from say 20 nm to 120 nm (e.g., Baumgarten et al., 2008; Karlsson and Rapp, 2006; von Savigny and Burrows, 2007). Hence, using a fixed radius of 60 nm could in the worst case

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result in an over-estimate (under-estimate) by a factor of 3(2) and hence a misinterpretation of the particle number density by a factor of 27(8) since the signal by ACE-FTS is proportional to ice volume. Secondly, any optical observation such as from ACE-FTS or Odin-OSIRIS or any other optical instrument can only provide information on the number density of the visible part of the particle size distribution. Since optical measurements depend on the third (ACE-FTS) to the sixth power (any instrument depending on light scattering rather than absorption) of the particle radius it is obvious that any particle number density retrieval will result in a severe under-estimate of the true number density since the smallest particles in the size distribution will basically not make any contribution to the optical signal. For the issue of nucleation and subsequent ice microphysics, however, it is really the total ice particle number density which is important since all nucleated particles will compete for the available water vapor. The total number density of ice particles, however, can only be obtained making use of in-situ techniques which rely, e.g., on measuring charges carried by the ice particles (e.g., Havnes et al., 1996; Mitchell et al., 2001). In line with my arguments above, such measurements typically imply ice number densities of order 10ˆ3-10ˆ4 particles/cmˆ3 rather than the few tens to hundred/cm3 implied in this manuscript. While the above comments are correct and definitely specify the possible range for uncertainties in every individual case, using the statistically significant dataset (more than 200 PMCs in this work) greatly diminishes such uncertainties.

Answer: Our approach of using the average ice particle radius of about 60 nm (calculated for bright PMCs at 60-70°N) to estimate the average PMC particle number density for more than 200 clouds yelds an average PMC ice number density of 20 to 130 cmˆ-3. This is actually in excellent agreement with the results from 10 years of ground-based lidar measurements of PMCs over ALOMAR in northern Norway (69°N, 16°E) reported by Baumgarten et al. (2008). In that work, the typical values for ice number density in PMCs are between 33 and 105 cmˆ-3. As the quality analysis of ACE-FTS PMC detections is not vital for this work, the entire Section 2 and Figure 1 have been removed from the manuscript. Instead, the following information has been

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added to the Introduction (last paragraph): "PMC particle number densities have also been calculated from ACE-FTS measurements of more than 200 clouds. These values vary between 20 and 130 cmˆ-3 and are in a good agreement with the findings of Baumgarten et al. (2008) based on 10 years of ground-based lidar measurements of PMCs over ALOMAR in northern Norway (69°N, 16°E). In the above work, the value for mesospheric ice number density was found to be between 33 and 105 cmˆ-3."

2. Question: I further note that using Odin/OSIRIS brightness measurements as a proxy for particle number density is impossible because brightness varies as number density times particle radius to the sixth power. Hence, minute changes of particle radius will result in dramatic changes of cloud brightness. Consequently, the apparent match of the two distributions shown in Figure 1 rather raise questions about the data sets. In any case, this comparison cannot demonstrate that the ACE-FTS observations are of high quality (which I don't doubt), but they show completely different things.

Answer: The authors agree that two satellite datasets shown in former Figure 1 should not have been compared that way. Consequently, Section 2 and Figure 1 have been removed.

3a. Question: The authors further use ACE-FTS temperature and water vapor observations in order to estimate saturation ratios in the summer mesopause environment. The authors should note that even with the very optimistic error estimates of ś8 K for temperature and ś10% for water vapor, they end up with an error of about 300% for the resulting saturation ratio.

Answer: The original manuscript already points this out on page 14505, lines 12-15: "We note that this is a very steep function of T and a relatively small uncertainty in the retrieved temperature, therefore, translates into large errors in the water vapor pressure". To further stress this point, as suggested by the reviewer, the information on uncertainties in the saturation ratio due to errors in T and H2O has now been added to the text.

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3b. Question: More to that, for a fixed temperature, the data shown in Figure 5 imply a variability in S by more than 2 orders of magnitude. Do the authors interpret this as real variability in water vapor or are these rather statistical fluctuations of the data? In any case, the presentation of these data needs a much more in-depth discussion than is presented here.

Answer: As the reviewer pointed out, small errors of <=10% in T and H2O result in up to 300% errors in the calculated saturation ratio. Similarly, natural variations in T and H2O in the upper mesosphere will result in about 2 orders of magnitude (or more) variability in the calculated saturation ratio. Thus the variability in S shown in Figure 4 (former Figure 5) can be attributed to a natural variability in T and H2O.

4a. Question: In section 4, the authors refer to their own unpublished work regarding molecular dynamics simulations of water clusters under mesospheric conditions. This is not acceptable. It is just these simulations which are critical for the contents of this manuscript. A detailed description of the simulations must be given here to give the reader the chance to judge about the basis of the presented results. This description should also contain a detailed discussion of the initial conditions of the simulations presented here. In the current version, the authors state that spherical liquid particles were then cut out and placed in a large simulation box.

Answer: The authors would rather disagree with the statement that "It is just these simulations which are critical for the contents of this manuscript". We believe that it is the thermodynamic estimates based on the experimental data that provide such a sound and logical picture of the sequence of transitions from supersaturated water vapor to crystalline ice at the mesospheric conditions in the absence of any condensation nuclei. The use of molecular dynamic (MD) simulations was necessary only (and only) to make quantitative estimates for the parameter Ks (Equation 1). As we state on page 14504 of the original manuscript, "The simulations were performed to obtain realistic density profiles for interfaces between water vapor and amorphous clusters." The molecular dynamic simulations are used to obtain the density profile of the condense

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phase-vapor interface in order to quantitatively characterize the rigidity coefficient, Ks, so that Equation 1 can be used without any adjustable parameters. All other parameters are experimental data and are readily accessible in the literature. At the same time we agree with the reviewer that referencing a published work on the MD simulations technique is important. Thus we have removed the reference to the unpublished work (which concerns with the computation of the surface excess of free energy for small water particles, and is not directly relevant to this work) and added a reference to recently published paper that describe the details of MD simulations technique (Zasetsky et al., 2007).

4b. Question: As I understand it with the limited information which is supplied at this point, this seems to imply that the simulations start at a point where liquid drops have already formed. This is really confusing since I thought that the initial formation of such particles/droplets from the gas phase is just what is to be studied. In any case, the authors should add significantly more information to avoid any such confusion.

Answer: Yes, the simulations started at the point where the liquid droplets are placed in the vapor. A direct simulation of vapor to water (or ice) nucleation by the MD method is impossible due to a very large time-length scale required at such low temperatures. Almost all simulation details were provided on Pages 14505-14504 of the original manuscript. The sampling time value of 100 ns was, however, missing. To correct this, we added: "...over the time period of 100 ns" on Page 14504.

5. Question: When discussing equation 1, I recommend that the authors quantitatively compare their results to corresponding results from CNT. Also, I strongly urge the authors to add detailed calculations of nucleation rates and not just include relative order of magnitude comparisons which are difficult to follow. In the end, the important question is really whether the here proposed mechanism can quantitatively explain observed particle number densities or if it can only make a small contribution.

Answer: A quantitative comparison between CNT and the Laaksonen and McGraw

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formulation for nucleation was provided in the following sentence on Page 14504 of the original manuscript: "relatively small reduction in the nucleation barrier height is enough to increase the nucleation rate J by 3 orders of magnitude in comparison to that of CNT, J/JCNT=˜2*10ˆ3, making the hypothesis of homogeneous nucleation of water vapor to amorphous particles in the mesosphere plausible". Thus, the quantitative comparison of our results with those given by CNT is about 2*10ˆ3. At the same time, calculations of the absolute nucleation rate are beyond the scope of the present study, as it would require the use (and the choice) of a kinetic model (which would contain adjustable parameters such as sticking probability etc.) to compute the kinetic prefactor.

6. Question: In their discussion of the new nucleation pathway, the authors repeatedly refer to laboratory data from Devlin and co-workers. While I am convinced that these are excellent lab-experiments, I wonder whether the findings from these papers can be applied to the conditions of particle formation at the polar summer mesopause. The ice clusters studied by Devlin et al. were created by an expansion of supersaturated air into a vacuum. Hence, ice nano-particles form on very short time scales (milliseconds) under extreme thermodynamic conditions with large super-saturations. In the polar mesosphere, on the other hand, we may rather assume that formation times are very different, presumably significantly longer than in the lab experiments. A corresponding discussion should be added to the text.

Answer: To the best of our knowledge, this is the only experimental data on water nano-sized particle at the conditions close to those in the mesosphere. Although the time scale of milliseconds is short it is not short enough to safely state that forming particles are solid (glassy) amorphous water. One can also expect the crystal to form. It is more important for our analysis that the experimental results of Devlin and Buch on the structure of water particles are in a good agreement with the estimates obtained by the Johari's approach. Thus the experimental results and thermodynamic calculations are consistent in this respect (the structure of particles).

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7. Question: When discussing equations 1 and 4, the authors should also clearly point out that they are using macroscopic properties like surface tensions for the description of microscopic entities. A critical discussion about the validity of this concept would be helpful.

Answer: We are not sure what microscopic entities the reviewer refers to. In our view, there are no microscopic entities here and the description is solely macroscopic. If the Reviewer's concern is about the result of simulations, the interface density is a macroscopic (observable) property of the particles. It is obtained by averaging molecular trajectories over the time period that is significantly longer than needed to obtain accurate statistics. Also, as advised by the Reviewer #1, equations 2-4 are now described in more detail with the critical radius (former Eq. 4) expressed in terms of molar values.

8a. Question: In section 6, the authors speculate about a cubic-hexagonal transition. They should note, however, that estimates by Murphy (2003) imply that the transition time is far too long to be of any relevance for mesospheric conditions. A corresponding short discussion should be added.

Answer: We believe that this issue has been addressed directly on Page 14508 of the original manuscript: "Cubic ice may be kinetically stable at the mesospheric conditions. In other words it may require very long time to transform into the stable hexagonal form and thus be a main component of PMCs at some conditions. However, to the best of our knowledge, any accurate visible, infrared, or microwave spectra for cubic ice (or any difference from hexagonal) have not yet been reported and, therefore, there have not been any successful attempts to distinguish cubic ice from hexagonal ice based on optical measurements. The kinetic aspects of ice freezing, which control the transition of amorphous-to-cubic and cubic-to-hexagonal ice, as well as the effect of impurities on the nucleation kinetics, require additional studies."

8b. Question: In the same direction, the authors should also correct their statement that Rapp and Thomas (2006) were assuming an ice formation from saturated water

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vapor to crystalline hexagonal ice. Rather, these authors refer to Murphys's studies and only consider cubic ice.

Answer: Corresponding changes have been made in the first paragraph of Section 6 (former Section 7): "This is rather different from the commonly discussed (but not yet confirmed) scenario of a direct transition of saturated water vapor to crystalline hexagonal ice (Murphy, 2003). The latter results suggest that the transition time is too long to be of any relevance for mesospheric conditions".

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14497, 2008.