Our response to referee 2’s comments are in red

Anonymous Referee #2

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There are growing interests on effects of amorphous (semi-)solid state of organic aerosols on various atmospheric processes such as gas uptake, chemical aging, and CCN & IN activation. This study focuses on ice nucleation ability of glassy aerosols under cirrus conditions. The experiments conducted using the AIDA chamber were designed nicely, executed well, and the obtained results sound reasonable. The results have important implications on cloud formation in the upper troposphere and they are certainly interesting for atmospheric science community. I recommend publication in ACP but some points need to be clarified as below and I encourage authors to improve the presentation quality of paper.

Major Comments:

1. The authors missed to include semi-solid state at L6 in page 8996. The authors discuss only liquid vs. solid (glassy), but not effects of semi-solid. The viscosity of particle changes continuously from 10ˆ-3 Pa s (liquid like water) to 10ˆ12 Pa s (glass) when temperature approaches to Tg, but not abruptly at Tg. In this sense, the particle what you call “liquid” might be actually not liquid but already semi-solid (10ˆ2 – 10ˆ12 Pa s; viscous, gel-like, rubbery) because temperature is close to Tg. The authors should discuss the potential effects of high viscosity (or low diffusivity).

We have used the term “ultra viscous” rather than semi-solid, but we agree that the term semi-solid is more appropriate so we have changed such instances to semi-solid. We have also added semi-solid to L6 P8996 (of the original). We have already provided discussion of the effects of high viscosity when referring to the ‘iso-humid’ experiments shown in figure 9.

2. It is helpful to include quantitative information such as timescale of homogeneous mixing or bulk diffusion coefficient in glassy aerosols to show how slow is the rate of bulk diffusion in section 2.1.

To address this comment and that of the other reviewer, we have estimated the viscosity of the aerosol during the expansion experiments shown in Fig 9 using an approach previously described by Murray et al. (ERL, 2008) in a study of glass formation and crystallisation in citric acid solutions. For both the experiments shown in Fig 9 we have displayed the time to diffuse 85 nm as a colour map overlaid on the RH_i time series in panels a1 and b1.

The paragraph in section 3.3 has been modified to:

"There are several potential explanations for the nucleation of ice above RH_g but below the homogeneous nucleation threshold. Firstly, at the temperatures at which this behaviour was observed, and also at those found in the upper troposphere, the absolute amount of water vapour for a given relative humidity is much smaller than at room temperature. For this reason, the aerosol may take longer to liquefy than the 10s – 100s of seconds found in experiments performed using glassy sucrose droplets at room temperature {Tong, 2011 #303}. This would also be supported by the observations of Zobrist et al. {, 2011 #291}, who found that sucrose viscosities increased strongly with decreasing temperature. In the presented iso-humid experiments the aerosol could therefore have persisted in the glassy state for the duration of the experiments, allowing them to be available for heterogeneous ice nucleation. To further investigate this possibility, we have estimated the viscosity of the aerosol during the expansion experiments shown in Figure 9 using an approach used my Murray {Murray, ERL, 2008; murray, ACP, 2008} to understand glass formation and crystallisation in citric acid droplets. The super-Arrhenius dependency of viscosity with temperature (η_T) above the glass transition temperature (T_g) at an RH_i can be approximated by the Williams-Landel-Ferry (WLF) equation:

$$\log \eta_T = \log \eta_{T_g} \left(\frac{17.44[T - T_g]}{51.6 + [T - T_g]} \right) \tag{2}$$

Where viscosity is in cP and T is the chamber gas temperature. The numerical values are typical for glass forming systems {Debenedetti, book}. The molecular diffusion coefficient for the water molecules in the aerosol was then estimated based on the viscosity (converted to Pa s) using the Stokes-Einstein equation:

$$D_{\mathrm{H_2O}} = \frac{kT}{6\pi \eta_T r_{\mathrm{H_2O}}} \tag{3}$$

Where k is the Boltzmann constant and r_{H2O} is the hydrodynamic radius of water (0.94 Å; {Murray, erl, 2008}). Finally, we estimated the time, t, for a water molecule to diffuse a root mean distance (x_i) of 85 nm (the average radius of the aerosols used in this study, see Fig 2) using the estimated diffusion coefficients:

$$t = \frac{x_i^2}{6 D_{\mathrm{H_2O}}} \tag{4}$$

For both the experiments shown in Fig 9 we have displayed the time to diffuse 85 nm as a colour map overlaid on the RH_i time series in panels a1 and b1. From this it can be seen that at even the highest humidities reached in the two experiments, the time to diffuse 85 nm is estimated at days, much longer than the duration of the experiments, suggesting that the aerosols would not have had time to liquefy."

3. Figure 8 shows that fraction frozen is very low (maximum 0.003). Why is it so low? Can you really argue that ice nucleation ability is general for glassy aerosol from this low fraction frozen? It might be possible that 0.3% particles have just some special properties (active surface sites, non-spherical, larger size etc.) and how can you exclude these possibilities and attribute to glassy state?

We addressed a similar comment from referee 1 and have already made some changes to clarify our point. The nucleation of a small fraction of particles in an aerosol is common to all the aerosols we tested. Only a few particles in an aerosol of glassy particles have the ability to nucleate ice. Our results indicate that this is a general property of dispersions of glassy aerosol particles.

I found that the results of levoglucosan are not included in Figure 8. Are there any reasons?

At lower temperatures there is less water vapour available so ice crystals do not grow as large on the experimental timescales at AIDA. This prevents the application of a size threshold to the WELAS data to infer N_{ice} by excluding background aerosol. For this reason we do not show f_{ice} or n_s for experiments below 198 K (e.g. the lowest temperature levoglucosan experiment). We state in the text (line 14/15, p. 8989):

"At lower temperatures ice particles do not grow as large because of the lower absolute humidity. Consequently for experiments which took place below ~200 K it was not possible to apply a size threshold to distinguish ice crystals from the larger of the background aerosol particles."

To make this clearer we have also added now added to the Figure 8 caption – "At temperatures below 198 K, the ice crystals were too small to allow N_{ice} to be inferred accurately from the WELAS data using a size threshold, preventing the calculation of f_{ice} for those experiments."

4. The authors argue that Kelvin effect is secondary importance, which implies particle size may not affect ice nucleation ability. Have you tried to conduct experiments with different particle size distribution to confirm it? I am wondering because size is the most important factor for CCN activation.

We argued that the Kelvin effect was of secondary important for the aerosol particle solute concentration rather than having implications for ice nucleation. We have not studied ice nucleation by particles of different sizes. We agree that this is an important area for future study.

5. I recommend authors to improve figure quality. Some figures are very difficult to read and difficult to catch the points. Please use larger fonts in Figures 5, 6, 7, and 9. The fonts used in the current figure are too small to see in a print out. Please include legends in Figure 10.

We agree that some of the figures are difficult to read. We have increased font size in a number of the figures.

6. Table 2 is not included in the manuscript even it is referred at L22 in page 9006.

This table has now been added. It was in the final proof we saw before publication on ACPD.

Minor comments:

P8994, L4: “100s nm” should be “100 nm”

Changed to ~100 nm

P8999, L11: What do you mean “amorphous deliquescence”? I have never heard ofthis word.

We have used the terminology defined by Mikhailov et al. (2009) who define the term amorphous deliquescence:

> “Overall, the transformation of (semi-)solid amorphous particles (glassy, rubbery, gel-like, or ultra-viscous) into liquid aqueous solution droplets by uptake of water vapor (combined humidification and liquefaction) can be regarded as a deliquescence transition (“amorphous deliquescence”).”

Since neither referee knew this term we have modified the sentence to read: “Aerosol particles in expansions that start close to but still below T_g’ may take up water, which serves as a plasticiser, and liquefy on crossing RH_g. This solid-to-liquid transition is also known as amorphous deliquescence {Mikhailov, 2009 #259}) and may occur before ice can nucleate heterogeneously.”

P9026, caption of Fig. 4: “panel bshow” should be “panel b show” Corrected