

Interactive comment on “Kinetic Controlled Glass Transition Measurement of Organic Aerosol Thin Films Using Broadband Dielectric Spectroscopy” by Yue Zhang et al.

Anonymous Referee #1

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Zhang et al. present a new experimental setup measuring glass transition temperature (T_g) using dielectric spectroscopy of thin films. Aerosol particles are deposited on an interdigitated electrode device using an electrostatic precipitator, eventually forming a thin film. The authors propose a new data analysis approach using the broadband dielectric spectroscopy data to determine T_g . The advantage of the technique compared to more traditional calorimetric techniques is that it needs considerably less material, hence it may open the possibility to measure ambient aerosol. Clearly, that makes the paper important and well suited to be published in AMT. The authors use two surrogates for secondary organic aerosol (SOA) to demonstrate that their technique yields glass transition temperatures comparable to reference methods. Both are pure

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compounds (glycerol and citric acid), no simple mixture nor an aqueous solution was investigated.

However, as one of the two tests (citric acid) show quite substantial deviation in measured T_g (307 K) compared to what is measured with calorimetric techniques (281–285 K) -when the data are analyzed using the new technique - there is little evidence (namely, only the glycerol data) that the technique will actually work for ambient or laboratory SOA particles. As there are ample data available for pure compound SOA surrogates, aqueous SOA surrogates, as well as for simple mixtures [e.g. Lienhard et al., 2012; Dette et al., 2015; Dette and Koop, 2015], I think it is essential to perform measurements on more pure component surrogates, at least one mixture and – if possible – also an aqueous surrogate to characterize the experimental setup. As it is now, the paper does not allow the reader to judge whether the technique is actually feasible or needs further improvements before being applied to samples of unknown T_g .

Detailed comments:

1 Introduction:

I suggest add a paragraph explaining that one important property needed to understand kinetic limitations in gaseous uptake or loss of compounds in atmospheric aerosol particles is the diffusivity of this compound in the condensed phase. Measuring T_g of ambient SOA will indicate that below/at this temperature kinetic limitations will occur, but it does not give immediate quantitative insight.

Technical comment: Page 3, line 60: “nucleate” seems not the right wording here, better use “become activated” or similar.

2 Experimental Setup:

One information missing is how much aerosol mass is needed for producing the film on the device. At least the area of the device and the approximate film thickness should

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be given. Even better, if the authors can provide the mass concentration in the aerosol flow prior to the precipitator and the time needed to accumulate for forming the film on the device.

3 Data analysis:

I do not see the advantage of not adding the information of the SI into the main text. Please. Incorporate it including the raw data of Fig. S1 into section 3.1.

I also find section 3.2 difficult to read as a non-expert. How does the discussion here connect to the issues of determining “fragility” [e.g. Angell, 2002]? I am not convinced that the glass community agrees that the intercept shown in Fig. 4 is the “true” glass transition.

Fig. 4: The caption needs to say which material is shown. Or, is this just a sketch to show the idea? Instead of “given cooling rate” in the legend, the actual cooling rate should be provided. There are no error bars shown for the data points: Are these actually the measurements, or some points arbitrarily taken from the fits? You need to provide more detail here.

4 Results and discussion:

First, there is more data available in the literature to compare your data with: for glycerol see for example Lienhard et al. (2012). Citric acid has been measured by Lienhard et al. [2012] as well and by Dette et al. [2014].

Second, in Fig. 5 you determined T_g of citric acid as 305-315 K, whereas in Table 1 you write 307 \pm 5 K. Please check.

Obviously, Fig. 5 shows a very significant difference when comparing the “classical” determination ($\tau = 100$ s) for T_g (281 K) and your new method (305-315 K). As the former agrees with the calorimetric measurements of numerous experiments in the literature, whereas the latter show significant deviation, you definitely need more evidence than provided to support the new method. At present, the reader will conclude

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that the new method is not reliable.

Concerning the influence of cooling rates, I recommend to the authors to make use of the detailed study of Simatos et al. [1996], do an additional experiment using sorbitol or fructose with the setup, and compare the results with those of Simatos et al. [1996].

References:

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