

Author statement

We thank both referees reviewing this manuscript despite the ongoing COVID-19 crisis. An itemized response to the comments is listed below and the tracked-changes version can be found below.

Our responses correspond to direct edits made in the main text. Additions to the main text are in **red**.

Response to Reviewer #1

Summary Comments

The experimental work is great but the analysis is hard to follow and more detail is needed.

Response: We thank the referee for positive recommendation.

Questions:

1: Figs. 2 and 3: What is the dimensionless number D that appears in the plots? It's not defined anywhere. Is it D_A that's defined on line 155 or is it related to the diffusivity?

Response 1: Thank you for bringing to this typo to our attention. The dimensionless number D that appears in the plots of Fig. 2 and Fig. 3 is fragility parameter, D_A . The typos on the plots are corrected in the revised manuscript.

2: My main issue is that it's unclear to me what's going on in Fig. 5 (and Fig. 6 which is related). In Fig. 5, the contour lines are said to represent equilibration timescales. Obviously you are not just taking the inverse diffusivity at a given RH and T and multiplying that by the particle radius squared to get tau because you state that you did KM-GAP simulations to get these values. So my questions are:

2.1: What is the initial and final state (RH and T)?

2.2: What is the radius of the particle?

2.3: Why is tau defined in such an unconventional manner on line 173? Why is not just the e-folding time?

Response 2: The KM-GAP simulations are performed on an equidistant grid with $-90 < T < 90$ and $0 < RH < 100$ (as indicated on line 172) for a 100 nm particles, thus the radius of the particle is 50 nm. We preferred to $\pm 1\%$ variability in composition throughout the drop instead of e-folding time. We rewrote the sentence for clarification. The revised text on page 8 reads as follows:

"The model was initialized with T, RH on an equidistant grid with $-90 < T < 90^\circ\text{C}$ and $0 < RH < 100\%$ and 50 points in each dimension **for 100 nm diameter particles**. The time to reach equilibrium, τ , is defined when the variability in composition throughout the drop is $< \pm 1\%$. **This corresponds to 4.6 traditional e-folding times. For τ equals one e-folding time, the particle interior is still solid, which will interfere with the dimer relaxation. The non-traditional choice for τ is thus motivated by the need to defining a timescale where the particle composition has become nearly uniform throughout the semisolid domain.**

3: The third paragraph in the discussion that begins "The central tenet ...". Have you proven this hypothesis? You state it then quickly say that it's supported by the phase diagram model. But it's a

very complicated hypothesis and you don't explain how your results prove it. Conceptually, what would it even look like if the hypothesis was not true?

Response 3: The central tenet of this study is the hypothesis that a phase diagram model that involves a water/organic binary mixing rule of the glass transition temperature, a glass transition temperature scaled viscosity fragility parameterization, and a water uptake parameterization connects the four common state spaces used to characterize the amorphous state: glass transition temperature vs. water weight fraction, viscosity vs. temperature, viscosity vs. RH at constant temperature, and viscosity isopleths as function of temperature and RH. **The model prediction and the synthesis of data from a wide range of sources are in good agreement, as shown in Figs. S1 and Figs. 2-4.** This suggests that the hypothesized simple phase diagram model can provide a self-consistent description of the four state spaces.

Typos:

Line 267: "attempted by unsuccessful"

Line 280: "timescale evaluate along"

Figure 5 caption: "timescale"

Figure 6 caption: no units on the numbers that are listed in the caption.

Figure 6 y-axis: "1k" and "100m"

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-768>, 2020.

Response typos: We revised the caption of Figure 6 as follows on page 11: "Figure 6. Time to reach equilibrium viscosity along the viscosity isopleth shown in Figure 5. The shading corresponds to the range $5 \times 10^6 \text{ Pa s}$ to $4.8 \times 10^7 \text{ Pa s}$ (sucrose, blue shaded area) and $5 \times 10^6 \text{ Pa s}$ to $3.8 \times 10^7 \text{ Pa s}$ (citric acid, red shaded area).

The typos are corrected in the revised manuscript.

Line 267: "Sucrose measurements at even colder temperature were **attempted but they were unsuccessful as** no dimer coalescence was observed."

Line 280: "Figure 6 shows the modeled equilibration timescale evaluation along the viscosity isopleths characterized by the DCIC experiments."

Figure 5 caption: "timescale"

Figure 6 caption: no units on the numbers that are listed in the caption. (fixed on figure)

Figure 6 y-axis: "1k" and "100m" (fixed on figure)

Response to Reviewer #2

Summary Comments (Referee 2)

Review of “Toward closure between predicted and observed particle viscosity over a wide range of temperature and relative humidity” by Kasparoglu et al. This paper compares measured viscosities for sucrose and citric acid particles with predicted viscosities based on a semiempirical model. This comparison is needed to test the accuracy of the semiempirical model for predicting viscosity of atmospheric aerosols. In general, closure is observed between the measured viscosities and predicted viscosities, although additional tests of the semiempirical model are needed, as pointed out by the authors.

Since viscosity of atmospheric aerosols is related to several important atmospheric processes (e.g. ice nucleation, gas-particle partitioning, and heterogeneous chemistry), this paper is appropriate for ACP. The paper is rigorous, insightful, and provides an underpinning for future predictions of viscosity in atmospheric models. The paper is clearly written, and the scientific quality of this paper is in the top 10 % of the field.

I recommend this paper for publication in ACP, after the authors have adequately addressed the comments below.

Response: We thank the referee for positive recommendation.

Comments:

1. Page 4. Lines 95 – 98. The dimer, coagulation, isolation, and coalescence (DCIC) method was used to determine coalescence relaxation of dimers consisting of polyethylene monomers and sucrose or citric acid monomers. Coalescence relaxation times were then converted to viscosities using the Frenkel sintering theory. However, Frenkel sintering theory is developed for two dimers of identical composition, which is not the case in the current study. The application on Frenkel sintering theory does not seem appropriate for the current study. The authors need to justify the use Frenkel sintering theory for interpretation of coalescence relaxation times of two different monomers.

Response 1:

“Dimer particles are composed of a polyethylene monomer and either a sucrose or citric acid monomer particle. Rothfuss and Petters (2017) showed that dimer particles composed of sucrose and sodium dodecyl sulfate relax into a sphere at T and RH like those observed in sucrose–sucrose dimer particles. Thus, it is assumed that the relaxation measured from sucrose–polyethylene and citric acid polyethylene dimer particles approximates that sucrose–sucrose, and citric acid–citric acid dimer particles. Measurements reported later in this work compare well with literature data, this lending further support to this approach. Polyethylene particles were generated using an evaporation-condensation system that is described in Tandon et al. (2019) and Rothfuss et al. (2019).”

2. Table 1. Surface tensions of 0.065 and 0.08 J/m² were used for citric acid and sucrose, respectively. I assume that the surface tensions are dependent on water content. Was this taken into account when calculating viscosities?

Response 2:

Surface tension values used in the conversion are identical to those used in Marsh et al. (2018).

The dependence of surface tension on water content was not considered. The mass fractions of sucrose and citric acid at the 10⁷ Pa s viscosity transition are 0.88±0.11 and 0.95±0.06, respectively. The variability of the solute mass fractions at the transition points is small and the solution molarity

approaches the upper end of available surface tension measurements (Petters and Petters, 2016). Furthermore, the influence of surface tension on the retrieved relaxation T/RH is much smaller than other measurement errors (Marsh et al., 2018). Thus, ignoring the dependence of surface tension on water content does not influence our conclusions.

3. Page 6, line 146. “The effect of particle curvature on water content is not considered”. Is it reasonable to ignore the curvature effect?

Response 3:

The effect of particle curvature on water content is not considered. This leads to a slight overestimate in the calculated water content. The maximum difference between RH and a_w for 100 nm particles is ~2% in absolute RH units (RH = 40% instead of 42%). The difference depends on the hygroscopicity of the compound and solution/air interfacial tension of drop. The effect is not considered for simplicity. A treatment of the phase diagram model including the effect of curvature and particle size are provided in Petters and Kasparoglu (2020).

4. What is the uncertainties in the viscosity values listed in Table 2?

Response 4: Temperature and RH corresponding to shape factors $\xi = 1.5$, $\xi = 2.5$, and $\xi = 3.5$ and the associated viscosities are summarized in Table 2. Uncertainty in the reported viscosity stems from assumed surface tension and a long list of potential experimental errors (sizing errors, flow rates, temperature and dewpoint measurement, and concentration variability) and how they propagate through the data reduction process. In Table 2 we report uncertainty in terms of T and RH at the midpoint viscosity ($\xi = 2.5$). The uncertainty is typically dominated by RH. Typical error bars correspond to at least ± 1 order of magnitude in viscosity, with larger uncertainties at colder temperatures.

5. The authors refer to Figures 1, 2, etc. in the supporting information. Should this be Figures S1, S2, etc.

Response 5: Thank you for pointing out this detail. The journal made a last-minute change to figure numbering and we have forgotten to change the labels embedded in the text. This has been corrected.