Response to Reviewer #2

The authors have substantially improved the manuscript and have addressed most of my previous comments. I appreciate the additional discussion and responses regarding particle phase state, the inclusion of Tg suppression and diffusivity estimates, clarification of the growth rate calculations, and the information regarding the uncertainties due to coagulation and wall losses. The revised manuscript is clearer, and the authors have made a considerable effort to place their results in the context of previous literature. While I support publication of this study in ACP, I have two remaining major comments that were not addressed adequately.

Response: We thank Reviewer #2 for their time and effort to review our manuscript a second time. We appreciate the positive evaluation of the improvements to the manuscript. Individual remaining comments and suggestions are addressed in the following point-by-point responses, which are marked by blue font color and the label "Response" while the reviewer's comments are reproduced in black. Citations from the manuscript are displayed in indented paragraphs with changes highlighted in green font. Line numbers refer to the marked-up version of the revised manuscript.

The authors state that coagulation leads to a 50% systematic uncertainty in growth rates based on statements given in previous literature. This seems like a large uncertainty, but it is still unclear what the impact of this could be on their estimated bulk diffusivity. I would like to encourage them to perform a sensitivity study to check the impact on their calculated Db values.

Response: We would like to clarify that the 50% systematic uncertainty was assigned to the apparent particle growth rates derived from the appearance time method when comparing to the growth rates from pure condensation (Stolzenburg et al., 2018). This uncertainty is not only due to coagulation, but also from wall loss in the chamber experiments and potential evaporation. In response to the reviewer, we performed additional calculations that show that coagulation was likely negligible. Following Nguyen et al. (2026), we now calculate the self-coagulation timescale (τ_{scoa}).

$$\tau_{\mathrm{scoa}} = \frac{2}{K N_{\mathrm{p}}} \tag{S4}$$

where, N_{p} is the particle number concentration and K is the coagulation coefficient. We derive K from the formulas given in Nguyen et al. (2026) as a function of particle diameter, Brownian diffusivity of the particles, mean thermal velocity of the particles, and their coagulation efficiency (α). α represents the fraction of collisions that result in coagulation. For details on the calculation of K, please refer to Table S1 in Nguyen et al. (2026).

Calculation results are shown in Fig. S11 below. From the model scripts in Stolzenburg et al. (2025), we infer a particle number concentration N_{p} = 10^3 cm^{-3}. With this N_{p}, the estimated characteristic self-coagulation timescales (star-shaped markers) are much longer than the observation time of 6 hours (gray dashed line), irrespective of sensitivity tests with different particle sizes (shadings) and coagulation efficiencies (blue vs. black lines). Previous studies also suggested viscous particles might adopt a lower coagulation efficiency (Hou et al., 2020), which would further prolong the coagulation timescale. Scavenging of nanoparticles by larger particles outside the observed mode may occur, but these particles then do not contribute to nanoparticle growth rates measured by the appearance time method. Therefore, we think that the impact of coagulation in this study should be minor. More detailed impacts of coagulation on the diffusivity calculation and nanoparticle growth are beyond the scope of this study and will be investigated in follow-up studies. We added Fig. S11 and the following text in the supplement discussing the estimated self-coagulation timescale and now cite the paper by Nguyen et al. (2026) in the revised

manuscript:

l. 162-163 – "This also applies for the effects of coagulation and air mass history (Sect. S1; Hussein et al., 2009; Cai et al., 2021; Hakala et al., 2022; Nguyen et al., 2026; Cai et al., 2026)."

SI l. 42-55 – "Following Nguyen et al. (2026), we estimated the self-coagulation timescale (τ_{scoa}, Eq. S4) and show the results in Fig. S11.

$$\tau_{\mathrm{scoa}} = \frac{2}{K N_{\mathrm{p}}} \tag{S4}$$

where, N_{p} is the particle number concentration and K is the coagulation coefficient. We derive K from the formulas given in Nguyen et al. (2026) as a function of particle diameter, Brownian diffusivity, mean thermal velocity, and coagulation efficiency (α). For details on the calculation of K, please refer to Table S1 in Nguyen et al. (2026). At a particle number concentration of 10^3 cm^{-3} (Stolzenburg et al., 2025), characteristic self-coagulation timescales (star-shaped markers) are much longer than the observation time of 6 hours (gray dashed line), irrespective of particle size (shadings) and coagulation efficiency (blue vs. black lines). Previous studies also suggested viscous particles might adopt a lower coagulation efficiency (Hou et al., 2020), which would further prolong the coagulation timescale. Besides self-coagulation, scavenging of nanoparticles by larger particles may occur, but these particles then simply do not contribute to nanoparticle growth rates measured by the appearance time method. Therefore, we assume a negligible impact of coagulation in this study."

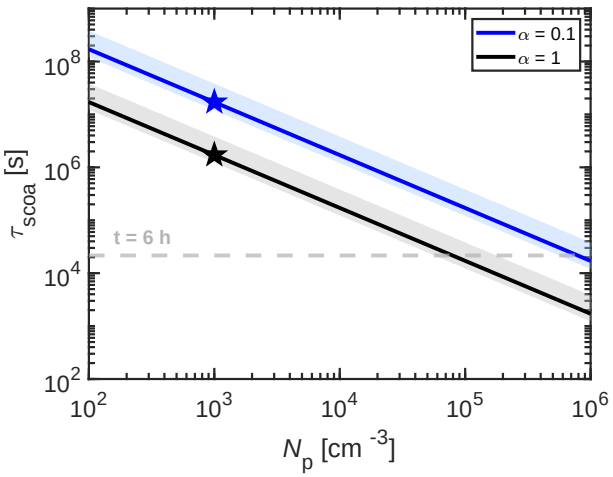

Figure S11: Characteristic self-coagulation timescale for monodisperse particles as a function of different particle number concentrations ($N_{\mathrm{p}} = 10^2$ - 10^6 cm^{-3}) at 5 nm (solid lines) and for the range of 1-10 nm (shadings), where the upper bound corresponds to 1 nm and the lower bound to 10 nm. Calculations were performed for coagulation efficiencies (α) of 0.1 (blue) and 1 (black). The star-shaped markers indicate a nanoparticle concentration level of 10^3 cm^{-3} as indicated by Stolzenburg et al. (2025) (DOI: 10.48436/9633r-zf904).

The comment on discrepancy with non-bounce and liquid-like behavior of freshly-nucleated nanoparticles was not addressed (Fig. 1 in Virtanen et al., Nature, 2010; Virtanen et al., ACP, 2011). These studies show that freshly-nucleated particles are initially liquid-like and then become more solid-like upon growth. This is opposite of what the authors estimate with modeling. How would you explain this difference? Figure S5e (smaller particles have lower Db) shows also an opposite trend compared to Tg suppression (smaller particles would have lower Tg, hence higher Db), but I suppose that the authors argument would be that this is due to evolution of chemical composition; but then, why Virtanen papers imply otherwise?

Response: Thank you very much for this renewed comment on a topic that is equally fascinating to us. First, we would like to re-iterate what was found in the cited studies. Virtanen et al. (2010) found biogenic SOA particles can adopt an amorphous solid state; however, the authors stated that "Bounce factor data for geometric mean diameter less than 30 nm cannot be determined reliably by our method; Therefore, newly nucleated sub-30-nm particles might well be in a solid state despite the apparently small bounce factor values". Virtanen et al. (2011) extended previously published results to diameters in the range of 17–30 nm. They found that "the smaller (diameters between 17 and 30 nm) particles having lower oxidation degree or containing higher amount of SO_4^{2-} bounced less than larger (diameters greater than 30 nm) particles indicating different material characteristics in the case of fresher sub 30 nm size particles". Thus, technically speaking, these two previous studies differ from the size range of interest in this study (<15 nm). Accordingly, the assumptions and findings of this study do not appear to contradict previous research.

In response to the reviewer's original comment, we had implemented an estimation of potential nanosize softening effects on the calculation of D_b via the $T_g - C^*$ parameterization in the first revised version of our manuscript based on recent experimental data of Mahant et al. (2024). As explained in Sect. S9, we found that the estimated softening effect balances the increase in T_g resulting from the condensation of very low-volatility species, leading to a near-constant D_b. Despite a T_g-shift of 40-50 K, the glass transition temperature did not fall below 300 K. To clarify and point out that there are still open questions to address in follow up studies, we have inserted additional references to the studies of Virtanen et al. (Nature 2010, ACP 2011) and a couple of sentences to the following paragraph of the revised manuscript:

> SI l. 253-261 – "To explore the potential influence of nanosize effects following Cheng et al. (2015), we combined the parameterization of Li et al. (2020) with data measured by Mahant et al. (2024) and find that glass transition temperatures decrease substantially ($\Delta T_g \sim 40 - 50$ K), but not below 300 K. As the nanoparticle size effect declines towards larger particle sizes (Fig. S6), condensation of higher volatile vapors offsets this change, leading to a near-constant T_g around 320 K. In contrast, Virtanen et al. (2010) and Virtanen et al. (2011) found an amorphous solid phase state for Finnish boreal forest aerosol particles. They reported that particle bounce decreased at the smallest diameters they investigated (17-30 nm), suggesting that these particles may not have been glassy. Thus, the relations between nanoparticle growth, phase state, and bounce as well as additional effects such as enhanced mobility in the surface layers of solid particles (quasi-liquid layers) warrant further investigation in follow-up studies."

The confusion may have arisen because the softening effect was not considered in the $D_b - C^*$ parameterization (Sect. S8.4 and Figure S5e). For this parameterization, that is not based on the glass transition temperature T_g, we have no means of estimating the softening effect, yet, but will work on this topic in future studies. We now clarify this in the paper:

> SI l. 239-240 – "An implementation of the particle size effect is not available for the $D_b - C^*$ parameterization at this moment and will be the topic of future studies."

With these two points remaining, I am still not fully convinced about Db = 1e-20 cm2 s-1, which seems still unrealistically small (are there any previous studies showing such low Db in any system involving organic compounds at relevant T and RH?). With this Db value, the mean squared displacement x = sqrt (2Dt) means that a molecule would move one angstrom by taking 5000 s; a single molecule hop spanning over an hour would mean that it could be below thermal fluctuation limits (considering the Debye frequency of 1e13 s-1) and the physical validity of bulk diffusion is questionable (it would be a stochastic event, rather than a thermodynamic flux).

Thus, the authors might be right about 1e-20 cm2 s-1, but I do not see strong evidence robustly supporting their argument. This low number appears to come out due to incompleteness, misrepresentation or some missing processes in the model. If they still claim this, I think that some other experimental validation, beyond model estimations based on growth rates, is necessary for validation (which may be beyond the scope of this work). Additionally, it would be great to have field observations of bounce behavior or viscosity measurements (or chemical composition or volatility measurements that may be used to estimate viscosity), implying that Db in summer would be lower than Db in spring (which is again beyond the scope of this study, but observational evidence would be eventually necessary).

Response: Numerous earlier studies have shown that under atmospheric conditions, organic aerosol particles, or compounds therein, can exist in an amorphous solid (glassy) state (e.g., Zobrist et al., 2008; Mikhailov et al., 2009; Virtanen et al., 2010; Koop et al., 2011; Renbaum-Wolff et al., 2013; Shiraiwa et al., 2017; Reid et al., 2018). Per definition, a glass has a viscosity of $>10^{12}$ Pa s, which per the Stokes-Einstein relation corresponds to a diffusivity coefficient on the order of 10^{-21} cm^2 s^{-1} and smaller. Considering the fractional Stokes-Einstein relation, we expect diffusivity coefficients $\sim10^{-20}$ cm^2 s^{-1} right at the border between glassy and viscous semi-solid. We thus find it very conceivable that such diffusivity coefficients are realistic for organic aerosol particles and that indeed these solid particles would show very little diffusional movement, as the reviewer points out. This is the main problem with detecting low diffusivity coefficients: the mixing timescale must match the observation timescale of a macroscopic sample. At 10^{-14} cm^2 s^{-1}, a 1 µm particle (visible under a microscope) has a mixing time scale between 1 h and 1 day (Shiraiwa et al., 2011). Thus, measurement of diffusivity coefficients in viscous organic matrices in previous studies were confined to the region $<10^4$ Pa s, with mixing timescales of seconds to minutes (Ullmann et al., 2019; Evoy et al., 2019; Kiland et al., 2019). Price et al. (2016) managed observation time scales of weeks, but were also looking at larger systems. We highly appreciate the available studies and suggest further investigations of slow diffusion in solid or semi-solid organic matrices, which will likely require new methodology and goes beyond the scope of this study.

We agree with the reviewer that diffusion may be non-Fickian below a certain D_b value, which is one of several reasons for the lower cut-off of diffusivity ($D_{b,298}$ = 10^{-20} cm^2 s^{-1}) we use. In the section "Conclusions and Outlook", we already call for additional targeted measurements to infer the effects of phase state on nanoparticle growth. Here, we further specify this statement:

> l. 164-170 – "To further constrain key parameters and enhance the mechanistic understanding and predictability of nanoparticle growth under varying atmospheric conditions, we suggest performing further laboratory experiments and field observations in which nanoparticle composition and phase state are determined alongside condensable vapor concentrations. Future work should quantify the distribution and gradients of organic compounds between and within aerosol particles across the relevant size range. For example, it may be possible to detect or infer radial concentration gradients in highly viscous particles (Huisman et al., 2025; Kang et al., 2026; Schervish et al., 2026) or detect deviations from the composition expected for the uninhibited growth of well-mixed, quasi-liquid particles (Lopez et al., 2025; Bhattacharyya et al., 2025)."

L146-151: regarding sunlight may promote particle-phase chemistry to increase viscosity: this was clearly shown by Baboomian et al.: Sunlight can convert atmospheric aerosols into a glassy solid state and modify their environmental impacts, Proc. Natl. Acad. Sci. USA, 119, e2208121119, 2022. You may cite this study here.

Response: Thank you for the suggestion. We have cited the study in the revised manuscript:

> l. 103-107 – "The molecular composition of SOA particles formed by dark ozonolysis of α-pinene

(CERN CLOUD) is likely not the same as for particles formed in summertime boreal forest air (Hyytiälä), which may be influenced by other volatile precursors (monoterpenes, sesquiterpenes; Hellén et al., 2018) and photo-oxidants including OH radicals (Baboomian et al., 2022). These differences in aerosol composition and chemical aging can plausibly lead to differences in particle-phase diffusivity (Sect. S5)."

After carefully addressing and implementing the suggestions of the two reviewers, we realized that the revised and extended manuscript exceeded the word limit specified for ACP Letters. We thus moved some of the details into the Supplementary Information, while keeping the key messages, information, and references in the main text. In the manuscript submitted for revision, we highlight the modified and shifted paragraphs with blue color.

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