Response to Reviewer #1

This study by Zhang et al. addresses the problem of relatively uniform (1-10 nm h-1) nanoparticle growth rate observations across different environments and conditions, which was recently formulated and investigated by Stolzenburg and co-workers (Stolzenburg et al., 2023, 2025). Zhang et al. uses a multi-layer model of multiphase chemistry (KM3C) to investigate if temperature-dependent diffusion limitations and volatility-shifts of the condensable vapors can explain as to why nanoparticle grow at comparable speeds at cold and warm temperatures. While the application of a better multiphase chemistry model to this puzzle is of great value and the authors seem to find a better agreement of their model with the slow growth observations at high temperatures, the manuscript, in its current form clearly overstates the achievement of this work. In fact, the references to previous studies are not put into the correct context, and therefore the manuscript cannot be published without major revisions clarifying what are the novel aspects in this work and how exactly the application of the KM3C model changes our previous understanding of the process.

Response: We thank Reviewer #1 for taking the effort to review our manuscript. We highly appreciate the comments, questions, and suggestions aimed at improving the study and its presentation. Some of the comments and suggestions, however, seem to arise from misperceptions of our study and related earlier publications as detailed 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.

In the manuscript under review (Zhang et al. 2026), we perform an independent analysis of high-quality measurement data sets collected by the research team that has formed around the CERN CLOUD experiment to address secondary organic aerosol (SOA) formation and nanoparticle growth in the atmosphere. Over the past decades, this team has performed very valuable laboratory chamber experiments and field measurements. Recent publications and presentations, however, have repeatedly emphasized that the measurement data are not in agreement with theory and model predictions. They highlighted incomplete mass closure, a remaining significant gap in the understanding of nanoparticle growth processes, and a puzzling mystery why the measured initial growth rates exhibit rather weak dependence on the condensable vapor concentration (e.g., Stolzenburg et al. 2025, Cai et al. 2026, and references therein). In response to the reviewer's concerns, we will clarify these aspects and improve the manuscript as detailed below.

Major comments:

* It is important to acknowledge in the text that there is a fundamental difference between a purely kinetic approach and the volatility-basis-set (VBS) based growth modeling (Stolzenburg et al., 2022), with the latter being able to capture most observations under the condition that the full volatility distribution is known (through e.g., combination of different mass spectrometers). The problem statement of Stolzenburg et al. (2025) is rather, as to why at high temperatures (summer-time) in ambient data, the VBS-based approach predicts higher growth rates than measured.

The high VBS distribution is a result of higher organic emissions and enhanced autoxidation, with the latter already demonstrated by Stolzenburg et al. (2018) and Praske et al. (2018). The manuscript currently reads (I am convinced that this wasn't the intention of the authors), such as the full experimental coverage of the OOM distribution and the shift in volatility at low temperatures, which promotes the condensation of moderately oxygenated organics, is the result of the KM3C model. However, this puzzle has been already solved and there are several passages in the manuscript which do not convey this information or point towards the real problem addressed here, that is the slower than expected growth at high temperatures.

Response: Multiple studies published in the past years highlight a gap in our understanding of nanoparticle growth rates, both on the side of slower-than-expected and higher-than-expected growth rates, using words like "surprising" and "puzzling mystery" (e.g., Cai et al., 2026). For example, Stolzenburg et al. (2025) state:

1. Abstract: "... recent studies have shown that growth rates of nanoparticles derived from particle size distribution measurements show surprisingly little dependency on potentially condensable vapors observed in the gas phase."
2. Introduction: "We demonstrate that modeled GRs are often too low due to an incomplete coverage of gas-phase OOMs, which is especially important at colder temperatures. Most importantly, we also report cases where the modeled GRs exceed the observed GRs. While it is easier to invoke "undetected" vapors to explain predictions that are too low, explaining why observed condensable vapors do not drive growth is a taller challenge. These cases are exemplars illustrating the problem of the surprisingly limited GR variation observed both at single sites (20,21) and across continental observations (4)."
3. Conclusion: "We showed that mass closure between nanoparticle growth rates predicted from gas-phase measurements and growth rates inferred from the particle number size distribution is still incomplete for a variety of settings."

We agree that the main remaining problem presented in Stolzenburg et al. (2025) is why their VBS-based approach predicts higher summer-time ambient growth rates than measured. Furthermore, Stolzenburg et al. (2025) only display kinetic limit-type modeling approaches for the CERN-CLOUD chamber data (Fig. 1, Fig. 3c) and not the successful modeling results of Stolzenburg et al. (2018, Fig. 3) and Stolzenburg et al. (2022, Fig. 6). Thus, the figures in Stolzenburg et al. (2025) indicate disagreement between measurement and model results for the reported summer-time field measurements as well as for low- and high-temperature chamber experiments. Our study presents a kinetic modeling approach that can describe all growth rate data presented in Stolzenburg et al. (2025), including laboratory and field measurements. We see the contribution of our paper in the consolidation of openly available data with a single kinetic model, to explain why nanoparticle growth rates observed in the atmosphere are fairly uniform and appear less dependent on condensable organic vapor concentrations than anticipated. The model allows us to not only describe the data, but also understand the buffering of nanoparticle growth rates by counteracting chemical and physical effects.

1. 21-23: The growth rates in Stolzenburg et al. (2018) were perfectly described by their model, which considered the volatility shifts at different temperatures (see Fig. 2 E,F and Fig. 3 in their work). Moreover, Mohr et al. (2019), Qiao et al. (2021), Dada et al. (2023) and more recently Cai et al. (2026) (all for ambient data) and Dada et al. (2023) (for more complex organic mixtures in a chamber experiment) provided closure between nanoparticle growth rates and modeled condensational growth using a volatility-basis-set (without diffusion limitations) for most conditions.

Response: We highly appreciate the contributions of Mohr et al. (2019), Qiao et al. (2021), Dada et al. (2023), and Cai et al. (2026) to the scientific investigation of nanoparticle growth rates. We note, however, that Mohr et al. (2019) show several instances in which the model overestimates the observed growth rates (by more than a factor of 4). We have now included an additional statement referring to these studies:

> l. 23-26 – "Computational models utilizing volatility basis sets (VBS; Donahue et al., 2006, 2011; Bhattacharyya et al., 2025) were found to reproduce observations under a variety of conditions, while under- or over-predicting nanoparticle growth rates measured in other instances (Stolzenburg et al.,

2018; Mohr et al., 2019; Qiao et al., 2021; Stolzenburg et al., 2022; Dada et al., 2023; Cai et al., 2026)."

Our study mostly focuses on the results presented in Stolzenburg et al. (2025), for which data are available. Cai et al. (2026) is a very recent study that dealt with different aspects of new particle formation (i.e., how the "NCG term can accelerate the growth of a population of particles compared to a single particle") and did not address how particle-phase diffusion may affect nanoparticle growth. Taking the feedback of the reviewer into account, we now more strongly highlight the main novelty of our modeling approach, i.e. the effect of particle-phase diffusion, as outlined below. We also adjusted the title of our manuscript to be more specific about the novel aspects:

Title – "Buffering of atmospheric nanoparticle growth by temperature-dependent shifts in molecular composition, volatility and diffusivity"

2. 81-87: The main challenge in this puzzle is not explaining the CLOUD data, as Stolzenburg et al. (2018) were able to do this. The main challenge is why a diffusion limitation is needed for ambient data and not for CLOUD data to achieve closure, as the Stolzenburg (2018) data at high temperatures can be perfectly explained from VBS-based condensation with no diffusion-limitations. In that sense, the main value of Fig.2 are the shaded areas which show the differences between a diffusion-limited case and a non-diffusion-limited case. And here we exactly see the difference between CLOUD and ambient data: For 3-7 nm (the most robust region in terms of GR determination), the experimental results at warm temperatures are all at the upper end of the yellow band (so imply a diffusivity of only 10-15 cm2 s-1) and therefore - in line with Stolzenburg (2018) - there seems to be no need to imply diffusivity constraints for warm temperatures (in contrast to the ambient data). The authors need to address this ambiguity in a revised version of the manuscript.

Response: We thank the reviewer for their perspective on the value of our work. What the reviewer calls "ambiguity" is what we consider as a matter of natural variability and avenue for further research. Molecular composition, diffusivity and growth rates may differ between atmospheric nanoparticles formed from a wide variety of organic precursors in a natural boreal forest environment with daytime photochemistry (Hyytiälä) and nanoparticles formed in a particular set of laboratory chamber experiments investigating the dark ozonolysis of the single monoterpene α-pinene (CERN-CLOUD), even if temperature and concentration of oxidized organic vapors are similar. We address this now directly in the manuscript:

l. 144-151 – "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. Furthermore, sunlight and atmospheric photochemistry may promote condensed-phase reactions that can enhance the formation of more highly oxygenated compounds, dimers, oligomers, and other accretion products. Such condensed-phase reaction products with high molecular mass and low volatility can influence particle composition, viscosity, and diffusivity without being reflected in gas-phase measurements of condensable organic vapor concentrations and volatility distributions (Mehra et al., 2020; Maben and Ziemann, 2023; Kenseth et al., 2023; Kang et al., 2026)."

In the revised manuscript, we added a figure with model outcomes for different diffusivities (Fig. S3), showing that the Hyytiälä spring data is not very sensitive to changes in diffusivity above 10^{-18} cm^2 s^{-1} and that KM3C still fits the data within the experimental error margins using a diffusivity of 10^{-18} cm^2 s^{-1}. Thus, there is no need for large differences in viscosity and diffusivity to describe both spring and summer data.

l. 74-75 – "We find that the sensitivity to particle phase state and diffusivity is less pronounced in the springtime scenario (Fig. S3), and KM3C captures the spring data within experimental errors also at a diffusivity of 10^{-18} cm^2 s^{-1} (dashed blue line)."

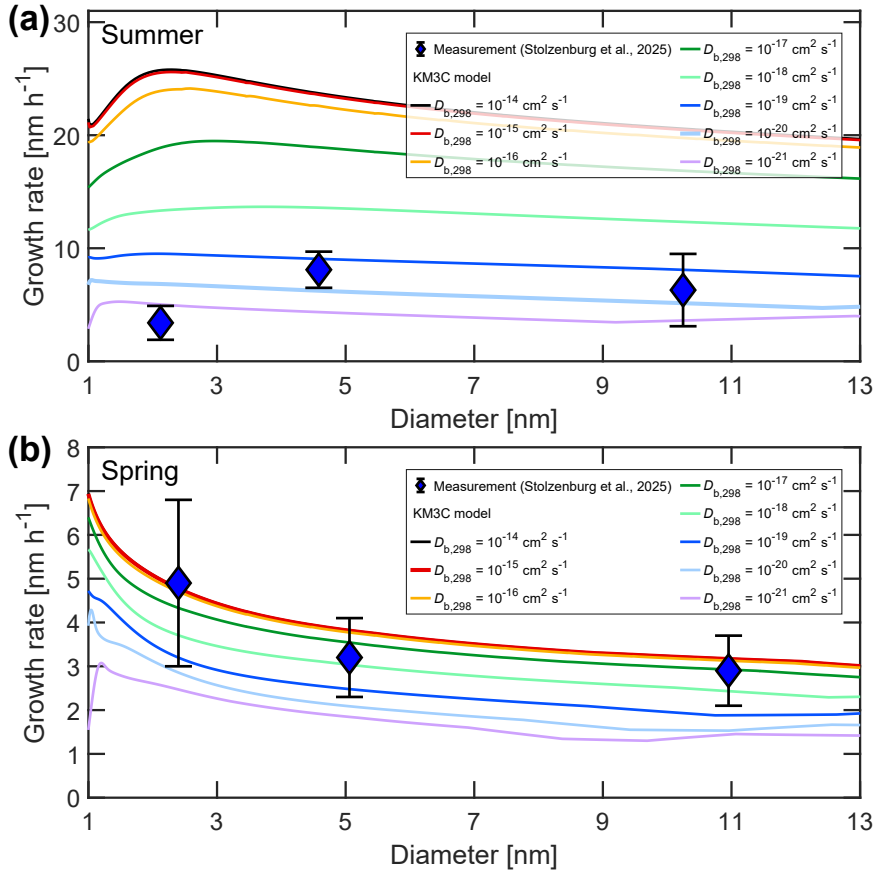

Figure S3: Observed (blue diamond markers and error bars) and KM3C-modelled (solid lines) atmospheric nanoparticle growth rates at a boreal forest site (Hyytiälä, Finland) in **(a)** summer and **(b)** spring, respectively. A range of diffusivities ($D_{b,298} = 10^{-21}$ – 10^{-14} cm^2 s^{-1}) shown with different colors is utilized in KM3C simulations.

We now also discuss that the model agrees better with the 25°C, 3-7 nm CERN CLOUD chamber data using high diffusivities as pointed out by the reviewer:

l. 135-142 – "As illustrated in Fig. 2, the growth rates observed at high temperature in the CERN CLOUD chamber experiments of α-pinene ozonolysis under dark conditions (25°C, yellow bands and data points) are best reproduced assuming relatively low diffusivity for particles smaller than 3 nm (Fig. 2a) and higher diffusivity for larger nanoparticles (Fig. 2b). In contrast, reproducing the boreal summertime field observations requires low diffusivity for the entire size range up to 11 nm (Fig. 1a). These differences in diffusivity can be plausibly attributed to differences in particle composition and chemical aging. As shown in Fig. S2, smaller particles contain higher proportions of organic compounds with low intrinsic volatility (ELVOC/ULVOC), while the uptake and partitioning of relatively more volatile compounds (SVOC/LVOC) tend to reduce the viscosity and increase the diffusivity of larger particles."

To validate the applied diffusivity coefficients, we now present semi-empirical relations between diffusion coeffi-

cients and vapor pressures yielding diffusivities in the range of 10^{-20} - 10^{-18} cm^2 s^{-1} or lower. The parameterizations are described in detail in the revised Supplementary Materials (Sect. S7). In the main text of the revised manuscript, we added the following:

l. 95-105 – "To obtain quantitative estimates of these effects, we employ semi-empirical parameterizations of SOA diffusivity established by Li et al. (2020) and Kang et al. (2026), which relate glass transition temperatures, viscosities and self-diffusion coefficients to the volatilities of organic compounds (Sect. S7). Inserting these parameterizations in KM3C, we can calculate diffusivities for each particle layer as a function of chemical composition and time (Kang et al., 2026). As detailed in Fig. S4, the model simulations following Li et al. (2020) predict glassy solid nanoparticle phase states with glass transition temperatures (T_g) well above 300 K and diffusivities smaller than 10^{-20} cm^2 s^{-1} throughout the investigated growth events in summer and spring. Plasticizer effects of water and sulfate were taken into account (Sect. S7; Koop et al., 2011; Dette and Koop, 2015), but did not alter the modeling results substantially. The model simulations following Kang et al. (2026) in Fig. S5 predict time-dependent and radially inhomogenous semi-solid phase states with diffusivities that are initially lower in summer than in spring, and of comparable magnitude overall (10^{-20} to 10^{-18} cm^2 s^{-1}). In both scenarios, the diffusivity increases over time as the particles grow by condensation of relatively more volatile compounds (Figs. S4, S5)."

l. 112-116 – "Overall, the available data and parameterizations suggest that nanoparticle formation and growth by condensation of low-volatile organic vapors indeed yields nanoparticles with high viscosity and low diffusivity. Despite the remaining uncertainties in predicting these molecular properties, our model results demonstrate that kinetic limitations related to particle-phase diffusivity of condensable organic vapors offer a plausible, coherent, and quantitative explanation for previously unexplained observations."

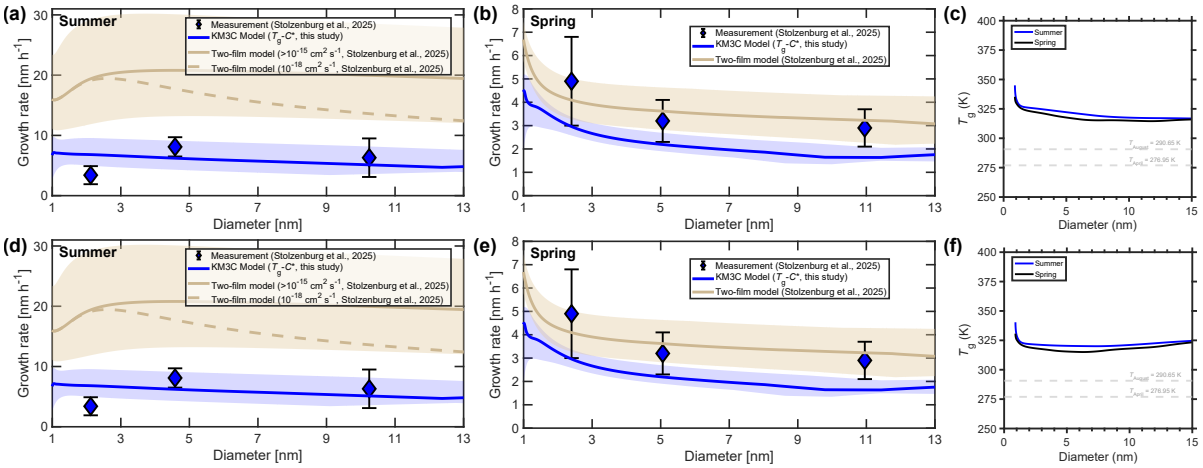

Figure S4: Observed (blue diamond markers and error bars) and modelled atmospheric nanoparticle growth rates in field experiments (Hyytiälä, Finland) in summer **(a, d)** and spring **(b, e)**, respectively. Brown line and shading represent a two-film model (Stolzenburg et al., 2025). Blue line and shading represent the KM3C model in which diffusivity is estimated following Li et al. (2020). Panels **(c)** and **(f)** show the predicted average glass transition temperature (T_g) as a function of particle size. In all the simulations shown here, T_g depression as a function of nanoparticle size following Mahant et al. (2024) is considered. In panels **(a-c)**, the water content of the SOA-H_2SO_4-water mixture is calculated using Raoult's law. In panels **(d-f)**, the water content of the mixture is calculated using an effective hygroscopicity parameter κ of approximately 0.01 as reported by Mikhailov et al. (2013) for the hygroscopic growth of ambient SOA under subsaturated conditions (RH $\sim$ 50%).

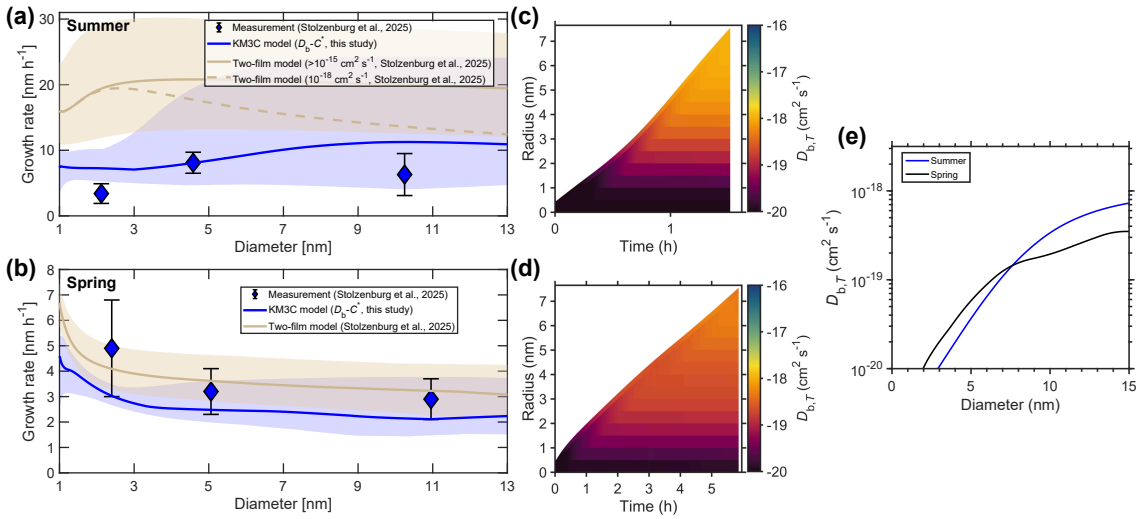

Figure S5: Observed (blue diamond markers and error bars) and modelled atmospheric nanoparticle growth rates in field experiments (Hyytiälä, Finland) in **(a)** summer and **(b)** spring, respectively. Brown line and shading represent a two-film model (Stolzenburg et al., 2025). Blue line and shading represent KM3C in this study and diffusivity is estimated following Kang et al. (2026). Panels **(c)** and **(d)** show the radial profiles of diffusivity as a function of time in summer and spring, respectively. Panel **(e)** shows the predicted average diffusivity as a function of particle size.

3. 89-91: Related to the above: "Thus, we included organic vapors measured by proton-transfer reaction time-of-flight mass spectrometry (PTR3) and integrated the Clausius-Clapeyron equation in KM3C to describe the temperature-dependent volatility distribution of organic vapors". This was exactly done by Stolzenburg et al. (2018) (see Fig. 1 of their work) and they achieved closure with this approach across all temperatures and without any diffusion-limitations. It is not the novelty of this work, which is noted in the SI but never in the main text.

Response: We agree that Stolzenburg et al. (2018) deserve full credit for using both instruments and providing the measurement data. As this may not have been clear enough in our original formulation, we added another reference to their work to the sentence in question.

> l. 125-127 – "Thus, we included organic vapors measured by proton-transfer reaction time-of-flight mass spectrometry (PTR3; Stolzenburg et al., 2018) and integrated the Clausius-Clapeyron equation in KM3C to describe the temperature-dependent volatility distribution of organic vapors (Supplementary Information, Sect. S1)."

We now also point out that Stolzenburg et al. (2022) showed the relative contributions of vapors measured with NO_3^--CIMS and PTR3 to nanoparticle growth in a CERN CLOUD experiment:

> l. 129-131 – "In accordance with the VBS modeling approach of Stolzenburg et al. (2022), our kinetic model calculations confirm that comprehensive measurement techniques and data are needed to cover the full range and variability of condensable organic vapors."

4. 93-95: The requirement for a full coverage of the volatility distribution and therefore the measurement of moderately oxygenated organics at lower temperatures have been previously stated by other work: Mohr et al. (2019) used iodide CIMS, which covers the moderately oxygenated organics well (Riva et al., 2019), Stolzenburg et al. (2018, 2025) and Dada et al. (2023) used a combination of different ionization schemes to obtain that coverage.

These studies (and the once mentioned above) should be referenced and the statement put this manuscript better into perspective.

Response: We agree with the reviewer that this is not a novel finding of our work, but rather a confirmation of the high value of developing and applying a variety of complementary experimental techniques and modeling approaches. For clarification, we have added the following sentence:

> l. 132-134 – "As shown by Riva et al. (2019); Mohr et al. (2019); Dada et al. (2023), full coverage of condensable organic vapors by mass spectrometry requires suitable instrumentation and ionization techniques as the sensitivity towards compounds with different degrees of oxygenation can vary strongly."

Moreover, we removed a half-sentence from our conclusions that had re-iterated the importance of combining NO3-CIMS and PTR3 data to fully cover the volatility distribution. Nevertheless, we still find it important and appropriate to address this aspect in our manuscript because truncated volatility distributions are widely used in conjunction with kinetic-limit modeling approaches. For example, Stolzenburg et al. (2025) plot the growth rates observed in chamber experiments and field measurements against NO3-CIMS data and the corresponding kinetic limit in their Fig. 1. In their Fig. 3c, they use different data ("sum of all volatility bins in supersaturation") for a similar analysis, without specifying whether these include PTR3 or other data. Such approaches do not represent the experimental data well, perform worse than two-layer and multilayer kinetic modeling approaches as shown in Stolzenburg et al. (2018), Dada et al. (2023), and our study, and give the impression that the nanoparticle growth rates are in fundamental disagreement with model predictions.

5. 114-118: Again here: The purely kinetic approach (condensing all measured OOMs kinetically) did not provide any insights into this behavior, the full VBS approach however could already explain most of these observations, except for the points at high temperature (high OOM) well below the kinetic line.

Response: We now make clearer that the high OOMs concentration dependence displayed in Fig. 1 of Stolzenburg et al. (2025) is the result of their kinetic-limit approach, and not their two-film model.

> l. 177-179 – "The tilt and flattening of the high OOMs concentration dependence by kinetic-limit lines introduced in earlier studies (Stolzenburg et al., 2018, 2025) towards the weak OOMs concentration dependence indicated by KM3C can be attributed to the following key factors:"

6. 3: While I agree with the conceptual statement of Fig. 3, the solid black lines as a fit to three CLOUD experiments at different temperatures would already have been possible for Stolzenburg et al. (2025). The real difference is – as outline above extensively – not the CLOUD data but the ambient data and therefore I do not see the benefit of a line obtained from the data where diffusion limitation was not needed to be included. I would keep the Figure as a conceptual picture and add it to Fig. 4 with the two think black errors being label "volatility shift" and "diffusion limitations" or something along those lines.

Response: We disagree with this comment and suggestion. Evaluating what might have been possible in Stolzenburg et al. (2025) falls outside the scope of our study. Figures showing growth rates plotted against a subset of condensable vapors together with the corresponding kinetic-limit line are widely used in recent publications and conference presentations (e.g., in Stolzenburg et al. 2018, 2025; Mohr et al. 2019; Dada et al. 2023). These plots illustrate that growth rates are not just governed by condensation at the kinetic limit, but also influenced by other factors that reduce the apparent dependence on condensable vapor concentration. Our Fig. 3 presents

a modification of this widely used approach, in which we show how the apparently weak concentration dependence can be plausibly explained, which is conceptually illustrated in Fig. 4. In Fig. 3, however, this is not just illustrated conceptually but demonstrated by data points and a fit line obtained by proper numerical simulations with a kinetic model that is able to reproduce the concentration dependence of the CERN CLOUD chamber data as well as the growth rates observed in Hyytiälä. We are not aware of any other publication that had presented such a straightforward explanation underpinned by agreement between measurement data and model results. In the revised manuscript, we highlight the field data points successfully described by the KM3C model based on available measurement data (star-shaped markers in Fig. 3) and modified the text accordingly:

> l. 169-171 – "The field measurement data points and their weak dependence on ambient temperature and measured OOMs concentration do not follow the kinetic-limit line (black dashed) to which they had been related in the recent study of Stolzenburg et al. (2025) highlighting incomplete mass closure of atmospheric nanoparticle growth."

> Fig. 3 caption – "The two cases studied in Fig. 1 are highlighted with star-shaped markers."

* It is not clear currently if the K3MC model outperforms the two-film model with respect to the growth rate prediction at warmer temperatures. In fact, the manuscript currently shows not the correct comparison. In a revised version the authors need to address the following points:

1. 1 shows the VBS-based modeling result from Stolzenburg et al. (2025) with the ±1 bin uncertainty on the VBS distribution and not the results from the model including the diffusion-limitations within the two-film model (yellow shaded area in Stolzenburg et al., 2025). This should be included as well. The relevant data can be found in the data repository published together with Stolzenburg et al. (2025).

Response: Thank you for the suggestion. In the revised manuscript (Fig. 1), we have included the sensitivity study for particle-phase diffusion limitation as reported by Stolzenburg et al. (2025) using their two-layer model with a diffusion coefficient of 10^{-18} cm^2 s^{-1} as suggested by the reviewer, and modified the text accordingly.

> l. 45-50 – "As shown in Fig. 1a and reported by Stolzenburg et al. (2025), nanoparticle growth rates observed in the boreal forest summer (blue markers) were substantially lower than those predicted with a two-film model (Zaveri et al., 2014) assuming quasi-liquid particles with high diffusivity ($>10^{-15}$ cm^2 s^{-1}, solid brown line and shading). In their modeling approach, Stolzenburg et al. (2025) considered uncertainties and variations related to condensable vapor concentration measurements, activity coefficients, decomposition reactions, and reduced diffusivity (10^{-18} cm^2 s^{-1}, dashed brown line), but they did not reach agreement with the measurement results and highlighted incomplete mass closure."

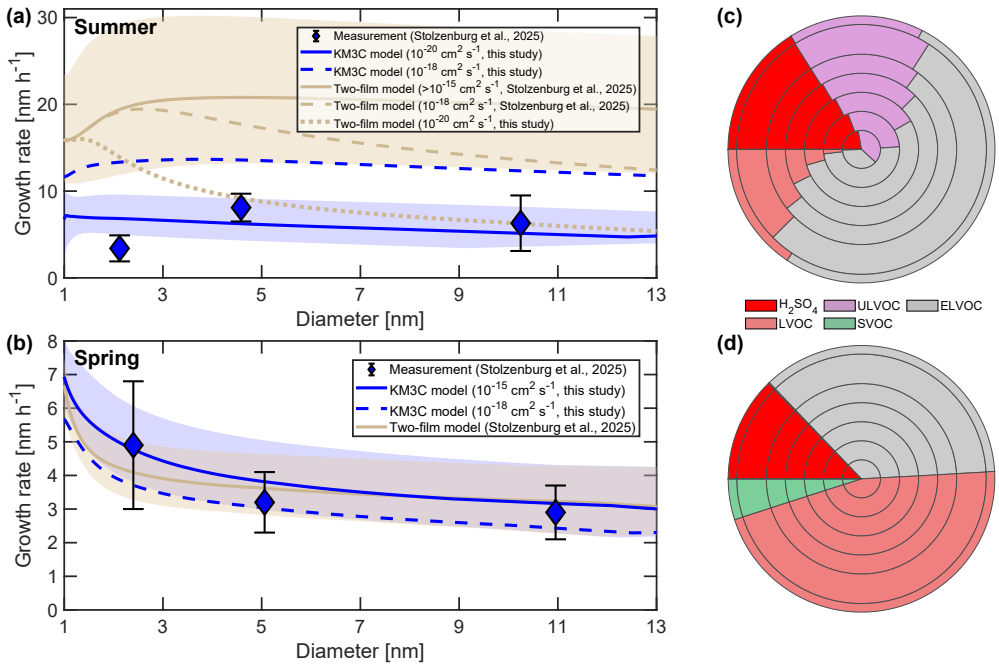

Figure 1: Atmospheric nanoparticle growth observed in field measurements. Blue diamond markers and error bars represent arithmetic mean values and standard deviations of growth rates measured in **(a)** summer and **(b)** spring at a boreal forest site (Hyytiälä, Finland; Gonzalez Carracedo et al. (2022)). KM3C captures the observations assuming low diffusivity (10^{-20} cm^2 s^{-1}) in summer **(a)** and high diffusivity (10^{-15} cm^2 s^{-1}) in spring **(b)**. With the high and intermediate diffusivities assumed by Stolzenburg et al. (2025), the two film model matches the observations in spring but not in summer ($>10^{-15}$ cm^2 s^{-1}, solid line; 10^{-18} cm^2 s^{-1}, dashed line). Inserting the same low diffusivity as in KM3C (10^{-20} cm^2 s^{-1}), the two-film model can also match the summertime observations data for particles larger than 4 nm (dotted line). Note that all diffusivities listed for KM3C represent values at 298 K that are adjusted for temperature with $E_{a,dif} = 40$ kJ mol^{-1} in the model, while diffusivities in the two-film model are kept at their nominal values. Radial concentration profiles of sulfuric acid (H_2SO_4) and organic compounds with different volatilities (ULVOC, ELVOC, LVOC, SVOC) calculated by KM3C show that the growing particles (7 nm) are well-mixed and contain larger proportions of more volatile compounds (LVOC/SVOC) in spring **(d)**. In summer **(c)**, however, the growing particles contain larger proportions of less volatile compounds (ULVOC/ELVOC) and exhibit differential concentration gradients, which reflect kinetic limitations of mass transport ~~that were not captured by the two-film model~~.

2. In addition, the diffusion coefficient assumed here for summer-time is 10-20 cm2 s-1, while Stolzenburg et al. (2025) used only 10-18 cm2 s-1 (I needed to look into the published code for producing their respective figure, as it is, indeed, not mentioned in the text). It is therefore not clear if the agreement is due to the even lower assumed diffusivity or due to the model choice.

Response: We thank the reviewer for this suggestion. We downloaded the model and ran the script used to generate Fig. 3 in Stolzenburg et al. (2025) with a diffusion coefficient of 10^{-20} cm^2 s^{-1}. As shown in Fig. 1, the low diffusion coefficient leads to much better agreement with the data, but the model continues to overestimate the particle growth rate during the early stage of nanoparticle growth. Moreover, we included model simulations with KM3C using a diffusion coefficient of 10^{-18} cm^2 s^{-1} and added the following sentence in the main text:

> l. 54-57 – "Using the same diffusivity in a two-film model, we obtained closure for larger particles sizes, but not below 3 nm (brown dotted line), which indicates that details of interfacial mass transport, molecular diffusion, and differential concentration gradients as resolved in KM3C are relevant for the kinetics of atmospheric nanoparticle growth."

3. One major determinant to decide if the model simulates the behavior during growth is the agreement of the size-dependency of the modeled versus measured growth rates. Here, it seems that the KM3C approach is stronger, as diffusion limitations do not only appear at larger sizes. This is a strong point of the manuscript and therefore I would love if the authors can elaborate on the difference of this prediction in more detail (one possibility I could think of is showing Fig. 1 c-d type plots for different sizes).

Response: Many thanks for the suggestion. In the revised version of the supplement, we included the radial concentration profiles for nanoparticles at diameters of 1.5 nm, 3 nm, and 7 nm for the Hyytiälä summer and spring scenarios (Fig. S2). In the main text, we added the following description:

> l. 65-69 – "An analysis of the temporal evolution of particle growth, composition and concentration gradients shows that the particle core largely retains the initial composition dominated by relatively less volatile vapors (ELVOC, ULVOC) when diffusivity is low (Fig. S2, panels a-c). In a sensitivity test with high diffusivity and otherwise unchanged conditions, relatively more volatile vapors (SVOC, LVOC) are readily taken up and well-mixed throughout the particle (Fig. S2, panels d-f)."

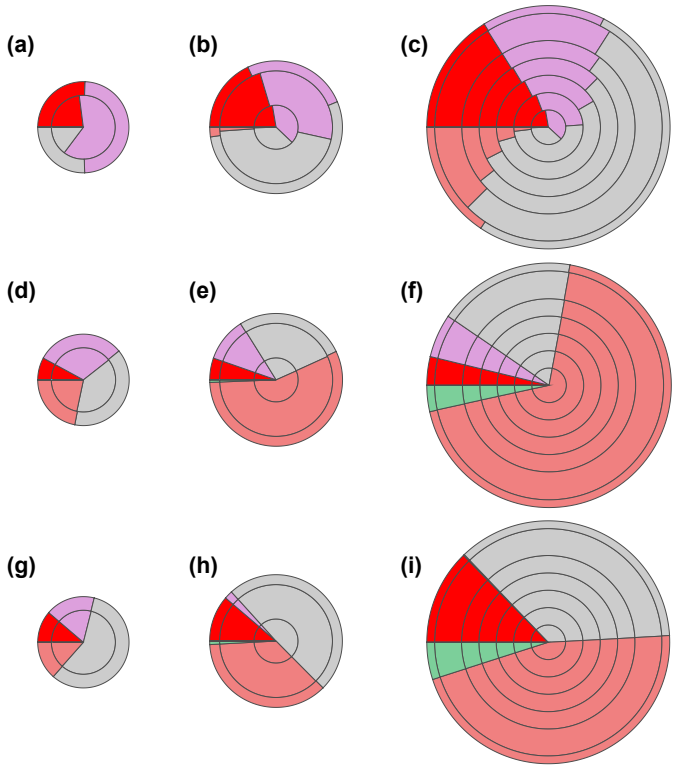

Figure S2: Radial concentration profiles for nanoparticles at diameters of 1.5 nm, 3 nm, and 7 nm for **(a-c)** the summer case with lower diffusivity ($D_{b,298}$ = 10^{-20} cm^2 s^{-1}), **(d-f)** the summer case with higher diffusivity ($D_{b,298}$ = 10^{-15} cm^2 s^{-1}) and **(g-i)** the spring case with higher diffusivity ($D_{b,298}$ = 10^{-15} cm^2 s^{-1}), respectively.

References

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Response to Reviewer #2

Zhang et al. analyze data from field measurements and chamber studies to investigate why atmospheric particle growth rates are often lower than those predicted by traditional kinetic models. They propose that nanoparticles may exist in a highly viscous phase state, resulting in limited surface-to-bulk transport and consequently reduced particle growth rates. Under this assumption, the model can successfully reproduce observations from previous field campaigns and chamber experiments. The manuscript is written very clearly and the presentation quality is outstanding.

Response: We thank Reviewer #2 for their time and effort to review our manuscript, and we highly appreciate the thorough and overall positive evaluation. Individual concerns, comments, questions, 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.

However, I have several major concerns regarding this work as detailed below. First, several previous studies have suggested that nanoparticles are likely to be liquid-like rather than highly viscous, which appears inconsistent with the central assumption of the manuscript. Only with indication from the modeling without experimental/observational evidence, it is hard to believe that particles would adopt a lower viscous phase state under low T. The authors do not account for coagulation nor particle wall loss, despite their potential influence on particle growth rates. These issues need to be addressed.

Response: As detailed below, we have utilized semi-empirical parameterizations of Li et al. and Kang et al. to demonstrate that SOA nanoparticles can indeed be expected exhibit high viscosity and low diffusivity under the conditions investigated in this study. Coagulation would accelerate particle growth, and wall loss could cause artifacts in the measurement of particle size distributions and condensable vapor concentrations. We have no reason to assume that the high-quality measurement data reported by Stolzenburg et al. (2025) would be subject to artifacts beyond their uncertainty estimates. For the field measurement data, Stolzenburg et al. (2025) reported "little influence of inter- and intramodal coagulation as well as diffusion-driven growth on the derived GR values making them easily comparable to our simple monodisperse growth model". For the chamber measurement data, Stolzenburg et al. (2018) reported that the "apparent growth rate of the particle size distribution does not necessarily represent the growth caused by pure condensation, as it omits coagulation and, in chamber experiments, wall losses, which both alter the particle size-distribution (6). Therefore, a systematic uncertainty of the method is estimated to be 50% (7)." Performing measurement data analyses that go deeper than the studies from the measurement data are taken would go beyond the scope of our current study, but may be addressed in follow-up studies including coagulation in KM3C provided that the necessary experimental parameters are available. This has been clarified in the revised text of our manuscript as follows.

> l. 216-220 – "Another process affecting nanoparticle growth is coagulation, which can increase measured growth rates (Cai et al., 2021, 2026). Coagulation was not explicitly treated in this study, as Stolzenburg et al. (2025) reported little influence of coagulation for the investigated field data, while Stolzenburg et al. (2018) included it into their uncertainty estimates for the investigated chamber data."

- The authors estimate extremely low diffusion coefficients (10-15 – 10-20 cm2 s-1; please show/list bulk diffusivity at different T for ambient and chamber conditions) and suggest that this is due to nanoparticles being highly viscous and nearly glassy. This is contradicting to previous work by several groups that indicate that nanoparticles should be liquid-like. a-pinene SOA formed in CLOUD was found to be viscous semisolid under low temperature

(Jarvinen et al., ACP, 16, 4423–4438, 2016); this study showed that particle viscosity is lower at lower T, which is consistent with numerous other literatures showing that particles would be more viscous under low temperature. In general, particles at room temperature are expected to be liquid for diameters below 20 nm (Cheng et al. Nat. Commun., 6, 5923, 2015). Similarly, another study has demonstrated that as SOA diameters decrease below 100 nm their glass transition temperatures decrease significantly leading to lower viscosities (Petters & Kasparoglu, Sci. Rep., 10:15170, 2020). Even if the bulk is glassy, it may have a highly mobile surface layer which is a few nanometers thick (Tian et al. Appl. Phys. Rev. 9, 011316, 2022). The fractional Stokes-Einstein relation implies that 10-20 cm2 s-1 is unlikely at higher temperature. For ambient PM in Hyytiala, bounce measurements have also indicated that small nanoparticles are less likely to bounce compared to larger particles indicating that nanoparticles are more liquid-like (Virtanen et al. Atmos. Chem. Phys., 11, 8759–8766, 2011). I understand the authors argument that more SVOC would be condensed at lower T, but it is hard to believe this effect would overwhelm temperature effect on phase state. The authors could calculate Tg based on volatility distributions presented in Fig. S3 using Tg parameterizations (even then, Tg might be suppressed for small particles).

Response: We thank the reviewer for giving us the opportunity to clarify key questions, some of which are still open and subject of ongoing investigations beyond the scope of this work. We adjusted the title of our manuscript to clarify and highlight the aspects on which our study is focused, and we extend the discussion of particle phase state and utilize state-of-the-art parameterizations to estimate molecular diffusivities as follows:

> Title – "Buffering of atmospheric nanoparticle growth by temperature-dependent shifts in molecular composition, volatility and diffusivity"

> l. 76-77 – "The diffusion properties of complex SOA mixtures have not yet been constrained with high precision, but the occurrence of different phase states and diffusivities of SOA nanoparticles in the investigated growth events is consistent with earlier studies."

> l. 83-85 – "At elevated temperatures, organic compounds need higher molecular masses and oxygen contents to reach low-enough vapor pressures for condensing and partitioning largely into the particle phase (Donahue et al., 2011; Shiraiwa et al., 2014; Bilde et al., 2015; Li et al., 2016)."

The parameterizations following Li et al. (2020) and Kang et al. (2026) are described in detail in the revised Supplementary Materials (Sect. S7). In the main text of the revised manuscript, we now added the following discussion:

> l. 95-105 – "To obtain quantitative estimates of these effects, we employ semi-empirical parameterizations of SOA diffusivity established by Li et al. (2020) and Kang et al. (2026), which relate glass transition temperatures, viscosities and self-diffusion coefficients to the volatilities of organic compounds (Sect. S7). Inserting these parameterizations in KM3C, we can calculate diffusivities for each particle layer as a function of chemical composition and time (Kang et al., 2026). As detailed in Fig. S4, the model simulations following Li et al. (2020) predict glassy solid nanoparticle phase states with glass transition temperatures (T_g) well above 300 K and diffusivities smaller than 10^{-20} cm^2 s^{-1} throughout the investigated growth events in summer and spring. Plasticizer effects of water and sulfate were taken into account (Sect. S7; Koop et al., 2011; Dette and Koop, 2015), but did not alter the modeling results substantially. The model simulations following Kang et al. (2026) in Fig. S5 predict time-dependent and radially inhomogenous semi-solid phase states with diffusivities that are initially lower in summer than in spring, and of comparable magnitude overall (10^{-20} to 10^{-18}

$cm^2\ s^{-1}$). In both scenarios, the diffusivity increases over time as the particles grow by condensation of relatively more volatile compounds (Figs. S4, S5)."

We are aware of earlier studies addressing nanosize effects on particle phase state, and we build on the results reported by Mahant et al. (2024) from which we derive ΔT_g estimates in the range of 40-50 K for the particle sizes investigated in this study. Coupled with the parameterization of Li et al. (2020), this shift is not expected to lower T_g below ambient temperatures because very high T_g values are associated with the predominantly ultra-low and extremely-low volatility compounds condensing onto nanoparticles in the investigated growth events. This information has been added to the revised manuscript as follows:

l. 105-109 – "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."

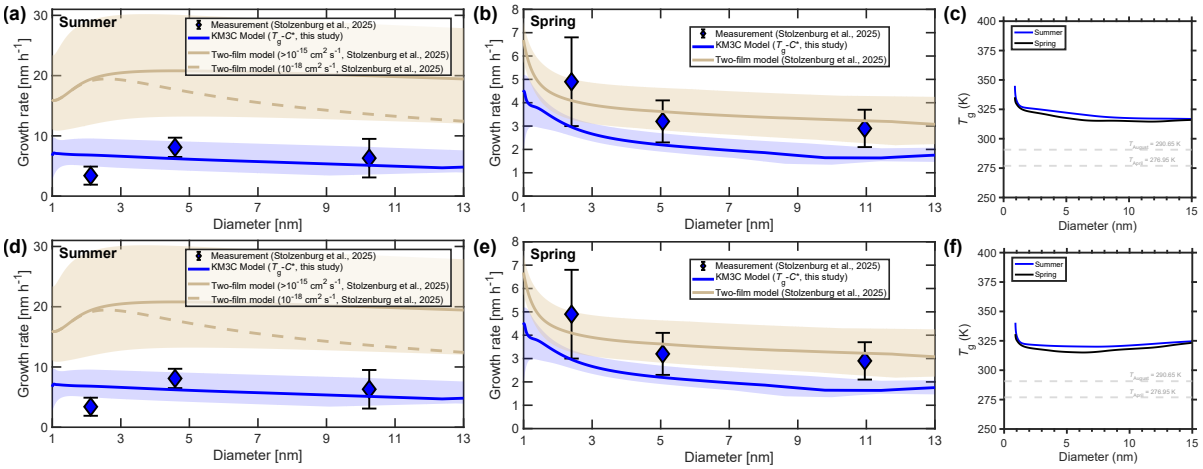

Figure S4: Observed (blue diamond markers and error bars) and modelled atmospheric nanoparticle growth rates in field experiments (Hyytiälä, Finland) in summer **(a, d)** and spring **(b, e)**, respectively. Brown line and shading represent a two-film model (Stolzenburg et al., 2025). Blue line and shading represent the KM3C model in which diffusivity is estimated following Li et al. (2020). Panels **(c)** and **(f)** show the predicted average glass transition temperature (T_g) as a function of particle size. In all the simulations shown here, T_g depression as a function of nanoparticle size following Mahant et al. (2024) is considered. In panels **(a-c)**, the water content of the SOA-H_2SO_4-water mixture is calculated using Raoult's law. In panels **(d-f)**, the water content of the mixture is calculated using an effective hygroscopicity parameter κ of approximately 0.01 as reported by Mikhailov et al. (2013) for the hygroscopic growth of ambient SOA under subsaturated conditions (RH $\sim$ 50%).

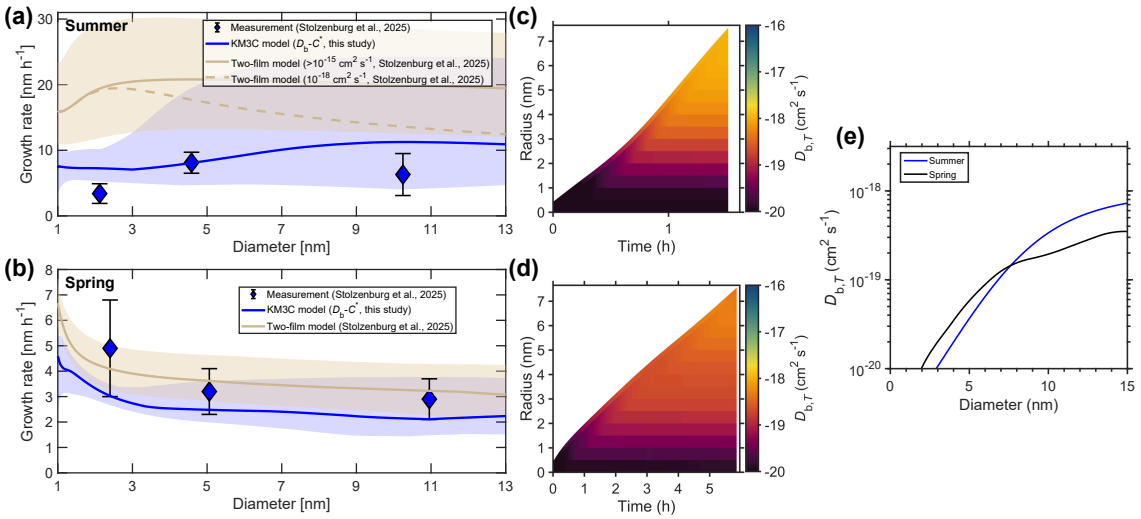

Figure S5: Observed (blue diamond markers and error bars) and modelled atmospheric nanoparticle growth rates in field experiments (Hyytiälä, Finland) in **(a)** summer and **(b)** spring, respectively. Brown line and shading represent a two-film model (Stolzenburg et al., 2025). Blue line and shading represent KM3C in this study and diffusivity is estimated following Kang et al. (2026). Panels **(c)** and **(d)** show the radial profiles of diffusivity as a function of time in summer and spring, respectively. Panel **(e)** shows the predicted average diffusivity as a function of particle size.

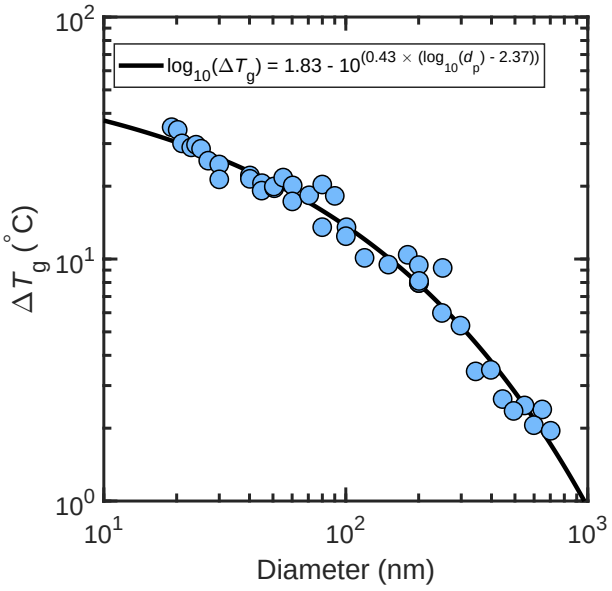

Figure S6: Glass transition temperature depression as a function of nanoparticle diameter. Black solid line represents fitting an exponential function to experimental data (blue circular markers) digitized from Mahant et al. (2024).

In the revised manuscript, we mention potential effects of enhanced mobility or quasi-liquid layers at the surface of glassy organic aerosol particles, which go beyond the scope of this study but warrant further investigation in follow-up studies:

l. 109-111 – "Additional effects such as enhanced mobility in the surface layers of solid particles (quasi-liquid layers) warrant further investigation in follow-up studies (McNeill et al., 2006; Stevenson and Wolynes, 2008; Tian et al., 2022)."

On the other hand, particle-phase chemistry has the potential to further increase viscosity and decrease diffusivity in nanoparticles, which is now also more explicitly pointed out in the extended discussion:

> l. 146-151 – "Furthermore, sunlight and atmospheric photochemistry may promote condensed-phase reactions that can enhance the formation of more highly oxygenated compounds, dimers, oligomers, and other accretion products. Such condensed-phase reaction products with high molecular mass and low volatility can influence particle composition, viscosity, and diffusivity without being reflected in gas-phase measurements of condensable organic vapor concentrations and volatility distributions (Mehra et al., 2020; Maben and Ziemann, 2023; Kenseth et al., 2023; Kang et al., 2026)."

We added a new table in the revised Supplementary Materials (Table S2) detailing the bulk diffusion coefficients used in this study:

Table S2: Diffusion coefficients used in this study at different temperatures for simulating nanoparticle growth in field and CERN CLOUD chamber studies.

	T (°C)	$D_{\mathrm{b},T}$ ($\mathrm{cm^2\,s^{-1}}$)		
		$D_{\mathrm{b},298} = 1 \times 10^{-15}$ ($\mathrm{cm^2\,s^{-1}}$)	$D_{\mathrm{b},298} = 1 \times 10^{-18}$ ($\mathrm{cm^2\,s^{-1}}$)	$D_{\mathrm{b},298} = 1 \times 10^{-20}$ ($\mathrm{cm^2\,s^{-1}}$)
Field	17.5 (summer)	-	6.59×10^{-19}	6.59×10^{-21}
	3.8 (spring)	2.91×10^{-16}	2.91×10^{-19}	-
CERN CLOUD chamber	-25	3.87×10^{-17}	3.87×10^{-20}	3.87×10^{-22}
	5	3.13×10^{-16}	3.13×10^{-19}	3.13×10^{-21}
	25	1×10^{-15}	1×10^{-18}	1×10^{-20}

Given these studies, it is questionable that the bulk diffusivity is 10-20 cm2 s-1 at higher T while Db is higher at 10-15 cm2 s-1 at lower T; Db would be lower for summer compared to spring even though temperature difference is 13 degree C (it would be helpful to compare Tg in both seasons if they could provide estimates; otherwise are there any measurements indicating difference in bounce behavior, chemical composition, or volatility distributions?). Without any additional experimental measurements or constraints, they may rather indicate that the model might be missing some critical processes (coagulation, wall loss, etc.) that might lead to this conclusion. Overall, I feel that experimental measurements of phase state/viscosity/bulk diffusivity would be necessary to solidify their results, given that the conclusion appears to be inconsistent with previous studies in many regards.

Response: We agree that uncertainties remain regarding the phase state and diffusivity of atmospheric nanoparticles and added the following statement in the revised manuscript:

> l. 113-116 – "Despite the remaining uncertainties in predicting these molecular properties, our model results clearly demonstrate that kinetic limitations related to particle-phase diffusivity of condensable organic vapors can offer a plausible, coherent, and quantitative explanation for previously unexplained observations."

In original manuscript, we had already called for measurements of particle phase state and diffusivity:

> l. 225-228 – "To further constrain key parameters and enhance the mechanistic understanding and predictability of nanoparticle growth under varying atmospheric conditions, we suggest to perform

further laboratory experiments and field observations in which particle phase state and diffusivity are determined alongside condensable vapor concentrations."

Following the suggestions of the reviewer, we added diagrams showing the evolution of T_g and D_b over time, as shown above in Figs. S4 and S5. Moreover, we emphasize which other effects may be involved and warrant further investigation:

l. 152-155 – "Our model currently assigns identical self-diffusion coefficients to the many different organic compounds lumped into each bin of decadic volatility basis sets (VBS). We note, however, that molecules in the same VBS bin may exhibit different properties such as diffusivity, effective volatility or desorption lifetime, based on their molecular structure and functionalities, even if they exhibit similar intrinsic volatilities."

l. 216-223 – "Another process affecting nanoparticle growth is coagulation, which can increase measured growth rates (Cai et al., 2021, 2026). Coagulation was not explicitly treated in this study, as Stolzenburg et al. (2025) reported little influence of coagulation for the investigated field data, while Stolzenburg et al. (2018) included it into their uncertainty estimates for the investigated chamber data. Moreover, the analysis and description of nanoparticle growth rates in atmospheric air masses can be influenced by differences between Lagrangian and Eulerian perspectives in the analysis and modeling of condensable vapor concentrations and aerosol particle size distributions. Such effects were not taken into account here but will be investigated in follow-up studies combining KM3C with regional and global 3D models of atmospheric transport and chemistry."

- I understand that ksb parameter is critical; could other unresolved miscroscopic surface processes or thermodynamics (activity coefficient or solubility?) play a role that is not treated for this parameter?

In line with previous modeling by Stolzenburg et al. (2018), we assume ideal solution behavior. Activity coefficients less than unity could make a difference for SVOC/LVOC species that do not condense at the kinetic limit. We added a statement about mixing and matrix effects to the manuscript:

l. 155-157 – "Furthermore, the properties of organic aerosol mixtures may deviate from linear combinations of properties of individual species. Fully resolving SOA nanoparticle growth may thus require a detailed accounting of specific molecular identities and their corresponding matrix interactions."

- The authors only treat condensation of SVOCs and do not consider coagulation and the impact that this may have on growth rates. Coagulation is an essential process in nanoparticle growth (Vehkamäki & Riipinen, Chem. Soc. Rev., 41, 5160-5173, 2012.) which may increase growth rates of nanoparticles significantly which might also depend on particle phase state (Nguyen et al. Environ. Sci.: Atmos., 2026, 6, 152). If the model does not treat coagulation, can you at least estimate (quantitatively if possible) or discuss the impact of coagulation on the results?

Response: In the current study, we do not consider coagulation, in line with previous investigations and model simulations building on the same data (Stolzenburg et al., 2018, 2022, 2025). Stolzenburg et al. (2025) state in their paper that "meteorological conditions are stable during regional NPF events and the pre-existing sink, as well as the overall nucleation rates, are moderate, resulting in little influence of inter- and intramodal coagulation as

well as diffusion-driven growth on the derived GR values making them easily comparable to our simple monodisperse growth model". In Stolzenburg et al. (2018), the effect of the omission of coagulation are accounted into a systematic uncertainty of 50 %.

- Coagulation could also lead to an apparent decrease in growth rates if nanoparticles are being scavenged by larger background particles. For chamber experiments there may also be losses of nanoparticles to chamber walls. Have the authors considered these mechanisms to explain the apparent low growth rates and could the omission of these mechanisms from their model be the reason for the apparent low diffusion coefficients that they estimate in their work?

Response: All simulations carried out for this work prescribe the gas-phase concentrations of condensable vapors at fixed, time-dependent values based on measurements. In line with related earlier studies Stolzenburg et al. (2018, 2025), particle coagulation and wall losses are thus not expected to have effects that would go beyond the reported uncertainties of measurement and model results.

- It is unclear how the growth rates are calculated in both the experimental measurements and in the model. Could this be clarified? Do the growth rates change over time?

Response: The measured growth rates are taken from Stolzenburg et al. (2025), who give a detailed description about the calculation of their growth rates in Stolzenburg et al. (2018) and Stolzenburg et al. (2025). In brief, for the Hyytiälä field measurements, "growth rates were estimated with the appearance time and maximum concentration methods (Stolzenburg et al., 2023). Only measurements with an agreement within a factor of 2 between maximum concentration and appearance time method are used for the in-depth analysis". For the CLOUD experiment, growth rate was estimated by the appearance-time method. Specifically, the maximum concentration method defines the representative time (t) as when the particle number concentration within a specific size bin peaks (Kulmala et al., 2013), typically determined by fitting a Gaussian function to each size channel's signal. The resulting time shift as a function of particle size reflects particle growth. The appearance time method uses the time (t_m) when the concentration reaches a specific percentage ($m\%$) of its maximum during an new particle formation event (Lehtipalo et al., 2014).

With regard to simulated growth rates, we have added the following information to the Supplementary Material of the revised manuscript (Sect. S6):

> SI l. 107-112 – "In both, KM3C used in this study and the two-film model used in Stolzenburg et al. (2025), the diameter growth rate of the particle (GR = dd_p/dt) was calculated from the $d_p(t)$ trajectory of a monodisperse particle population. The growth rate within a size interval is determined from the time required for a monodisperse particle to grow from one end of the size interval to the other:"

$$GR_{1.5\text{–}3\,\mathrm{nm}} = \frac{\Delta d_p}{\Delta t_{1.5\text{–}3\,\mathrm{nm}}} = \frac{1.5\,\mathrm{nm}}{\Delta t_{1.5\text{–}3\,\mathrm{nm}}}$$

$$GR_{3\text{–}7\,\mathrm{nm}} = \frac{\Delta d_p}{\Delta t_{3\text{–}7\,\mathrm{nm}}} = \frac{4\,\mathrm{nm}}{\Delta t_{3\text{–}7\,\mathrm{nm}}}$$

- How did you consider particle and vapor wall loss in modeling CLOUD chamber studies? These processes might

be temperature dependent (or not?). Do wall loss impact modeled or measured growth rates?

Response: As described above, all simulations carried out for this work prescribe the gas-phase concentrations of condensable vapors based on measurements. Thus, particles can be treated independently and the particle number concentration, and thus particle losses, have no effect on the modeling result. Particle and vapor wall losses were considered in the measurements of growth rates and gas phase OOMs concentration as described in Stolzenburg et al. (2018), which we would like to quote here:

(1) For particle wall losses: "Particle growth rate measurements were performed with the appearance time method." "However, this apparent growth rate of the particle size distribution does not necessarily represent the growth caused by pure condensation, as it omits coagulation and, in chamber experiments, wall losses, which both alter the particle size-distribution. Therefore, a systematic uncertainty of the method is estimated to be 50% (Lehtipalo et al., 2014)."

(2) For vapor wall losses: (2.1) To estimate the concentration of a HOM species measured by nitrate-CI-APi-ToF (NO3-CIMS), "sampling line losses SL_{HOM_i} are estimated assuming laminar flow diffusional losses in the sampling lines with a diffusion coefficient of HOMs scaling with the molecular mass M_i of the compound via $D[\mathrm{cm^2 s^{-1}}] = 0.31 \times M_i^{-1/3}$ at 278 K, determined from wall loss measurements in the CLOUD chamber. As the sampling lines of the nitrate-CI are thermally insulated, for other experiment temperatures $D \propto (T/278\mathrm{K})^{1.75}$ is assumed." (2.2) To estimate oxidized organics using PTR3-ToF (PTR3), Stolzenburg et al. (2018) applied a temperature dependent loss-correction for the sampling line losses, "which is split up into three sections: losses at the sampling line within the CLOUD chamber at chamber temperature T, as well as losses occurring at the sampling line outside the chamber at room temperature (as it was not thermally insulated) and losses within the PTR3 instrument heated to 37 °C."

- What is surface coverage during the simulation? Given very long desorption lifetime shown in Fig. S6, the coverage seems to be close to 1 (correct?). In this case, would you need to consider multilayer adsorption?

Response: Here we list the average surface coverages in the simulations of summer (both high diffusivity and low diffusivity) and spring cases over the size intervals of d = 1.5-3 nm and 3-7 nm. Even in the low diffusivity case, the surface coverage is much less than 1, therefore, a multilayer adsorption scheme is not needed in this study. We plan to look further into this topic in future studies.

	Size intervals	Surface coverage
Summer ($D_b = 10^{-20}$ cm^2 s^{-1})	1.5–3 nm	2.3×10^{-3}
	3–7 nm	1.3×10^{-3}
Summer ($D_b = 10^{-15}$ cm^2 s^{-1})	1.5–3 nm	3.0×10^{-4}
	3–7 nm	1.4×10^{-4}
Spring ($D_b = 10^{-15}$ cm^2 s^{-1})	1.5–3 nm	9.9×10^{-5}
	3–7 nm	4.6×10^{-5}

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