Response to the comments of Anonymous Referee #1

Referee General Comment:

This manuscript explores the equilibrium timescale and mixing timescale of IVOC and LVOC with particles considering different phase states. The work combines the authors' previous KM-GAP model (Shiraiwa et al., 2012) with the authors' recent glass transition model (Shiraiwa et al., 2017; DeRieux et al. 2018) to understand the interplay among equilibrium timescale, temperature, relative humidity, and the glass transition temperature of the aerosols.

Besides the numerical results obtained from the model shown in Figure 1-5, the manuscript provides two more useful results: (1) when there is no diffusion limitation within the particle, the gases that have higher saturation mass concentrations will reach gas-particle equilibrium faster; (2) when there is strong diffusion limitation within the particle, gases that have lower volatility may reach gas-particle equilibrium (locally) faster than VOCs with higher volatility. One of the implications is that at a lower temperature (upper troposphere) or when dealing with highly viscous particles, the particle growth process may need to be treated kinetically.

The authors used a numerical model to obtain result #1 above, and it agrees with the findings in Liu et al. 2012 in which an analytical model was used. It is nice to see two different approaches come with the same results and can validate each other. On the other hand, result #2 is more interesting because it shows that local equilibrium could be reached relatively faster for low volatility species when the particle phase is highly viscous. The manuscript also illustrates some concepts that can be commonly misused by folks, such as the difference between equilibrium timescale and the mixing timescale. Because some of the results have been previously discussed in or can be easily inferred from other publications (Liu et al. 2012, Shiraiwa et al. 2011&2012), the novelty of the manuscript needs to be improved. I suggest that the author focus on result #2, which is novel, and use it to make further predictions regarding the physical and chemical processes of aerosols.

Response: We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. Following your constructive suggestions, in the revised manuscript, we add (1) a contour plot of τ_{eq} as a function of bulk diffusivity and volatility to illustrate under what conditions the fast local equilibrium may be achieved to highlight the result #2 you are interested; and (2) simulations for open systems and the results are compared with τ_{eq} in a closed system. We find partitioning of LVOC is very different in open and closed systems and the corresponding implications in SOA evolution in ambient air and chemical transport models are further broadened. As Referee #2 pointed, this publication essentially closes the loop between predicting phase state and calculating the gas/particle equilibration time. We believe after addition of above two aspects, the novelty of the revised manuscript is improved. Please see the detailed response below.

Referee Major Comment:

(1) For instance, what is the relationship between particle sizes and condensation/evaporation kinetics of gases with different volatility interacting with particles with various viscosity?

Response: Thanks for this helpful comment. In our ACPD manuscript, Figure 5 (Figure 6b and d in the revised manuscript) has shown the relationship between τ_{eq} and particle size for LVOC condensing on less viscous as well as highly viscous particles. In the revised manuscript, we add comparable calculation for SVOC (Fig. 6a, c). This issue has also been discussed in previous studies, e.g., Liu et al. (2013) and Mai et al. (2015). For example, Mai et al. (2015) presented τ_{eq} as a function of particle diameter and volatility, showing that τ_{eq} increases as the particle diameter increases or the volatility of the condensing species decreases when particles are liquid with partitioning limited by interfacial transport. When particles are highly viscous with bulk diffusion-limited partitioning, the time to reach full equilibrium depends on mixing timescale. The following discussions have been added in the revised manuscript:

Lines 259-263: "Previous studies have shown that τ_{eq} depends on particle size (Liu et al., 2013; Zaveri et al., 2014; Mai et al., 2015) and particle mass loadings (Shiraiwa and Seinfeld, 2012; Saleh et al., 2013). For further examination of these effects at different T, Figure 6 shows the dependence of τ_{eq} of SVOC (C^0 = 10 μg m^{-3}) and LVOC (C^0 = 0.1 μg m^{-3}) on the mass concentration and the diameter of pre-existing particles".

Lines 271-274: "When particles are less viscous at 298 K ($D_b = 10^{-11}$ cm^2 s^{-1}) τ_{eq} of SVOC is shorter than that of LVOC for the same particle size and mass loadings. When partitioning into highly viscous particles at 250 K ($D_b = 10^{-18}$ cm^2 s^{-1}), SVOC takes longer time than LVOC to reach equilibrium".

Lines 275-285: "Typical ambient organic mass concentrations in Beijing, Centreville in southeastern US, Amazon Basin, and Hyytiälä, Finland are indicated in Fig. 6. The particle phase state was observed to be mostly liquid in highly polluted episodes in Beijing (Liu et al., 2017), under typical atmospheric conditions in the southeastern US (Pajunoja et al., 2016), and under background conditions in Amazonia (Bateman et al., 2017). At these conditions τ_{eq} should be mostly less than 30 minutes (Fig. 6a, b). Particles were measured to be semi-solid or amorphous solid in clear days in Beijing (Liu et al., 2017), in Amazonia when influenced by anthropogenic emissions (Bateman et al., 2017), and the boreal forest in Finland (Virtanen et a., 2010). Under these conditions and also when particles are transported to the free troposphere, τ_{eq} can be longer than 1 hour especially in remote areas with low mass loadings (Fig. 6c, d)".

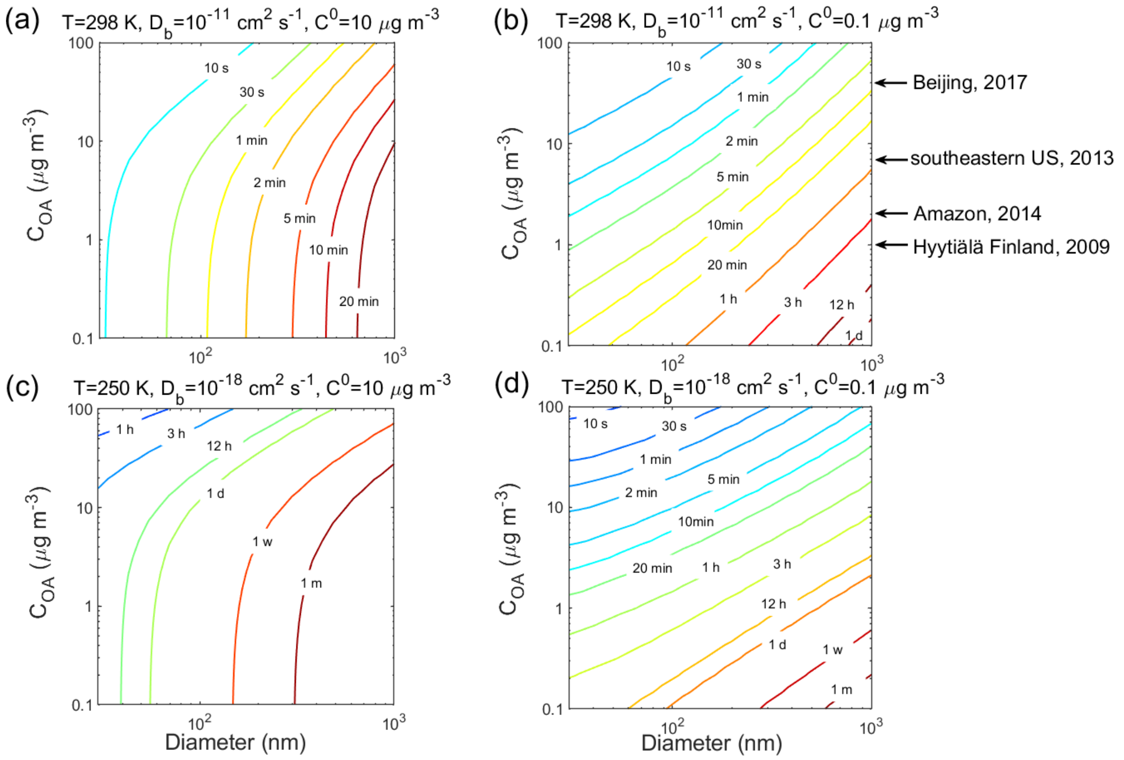

Figure 6. Equilibration timescale (τ_{eq}) for (a, c) SVOC (C^0 = 10 μg m^{-3}) and (b, d) LVOC (C^0 = 0.1 μg m^{-3}) as a function of particle diameter (nm) and mass concentration (μg m^{-3}) of pre-existing particles at 60% RH and T of (a-b) 298 K and (c-d) 250 K in the closed system. The glass transition temperature of pre-existing particles under dry conditions ($T_{g,org}$) is set to be 270 K, which leads to D_b of (a-b) 10^{-11} cm^2 s^{-1} and (c-d) 10^{-18} cm^2 s^{-1}. Ambient organic mass concentrations are indicated with arrows.

(2) I would also be curious to know what is the boundary criteria for result #2 to happen, i.e., how viscous would the particles have to be or how low the volatility of the VOC have to be in order to reach relatively fast local equilibrium? The author can also explore the effects of equilibrium partitioning when the gases can both partition in and react with the particle phase.

Response: This is a very interesting point. To address your question, we conducted additional simulations for τ_{eq} as a function of bulk diffusivity and volatility for both open and closed systems. The results of such simulations are shown in new Figure 4. The effect of particle-phase reactions on SOA partitioning is an important question, which is beyond the scope of this study. We plan to follow up on this issue in our future study. The following discussions have been added in the revised manuscript:

Lines 194-201: "We further computed τ_{eq} as a function of D_b and C^0 in the closed system. As shown in Fig. 4a, when D_b is higher than ~10^{-13} cm^2 s^{-1}, τ_{eq} is insensitive to bulk diffusivity but sensitive to volatility: decreasing volatility increases τ_{eq} in this regime. In the regime with D_b lower than ~10^{-13} cm^2 s^{-1} and C^0 higher than ~10 μg m^{-3}, τ_{eq} is controlled by bulk diffusivity: τ_{eq} increases from 30 s to longer than 1 year as D_b decreases from 10^{-13} cm^2 s^{-1} to 10^{-20} cm^2 s^{-1}. In the regime with D_b < ~10^{-13} cm^2 s^{-1}

and C^0 < ~10 μg m^{-3}, τ_{eq} depends on both diffusivity and volatility. Decreasing volatility would lead to shorter τ_{eq} due to an establishment of local equilibrium of LVOC".

Lines 221-225: "Figure 4b shows simulated evaporation timescales as a function of D_b and C^0 in an open system, which agrees very well with Fig. 3 in Liu et al. (2016). It shows that for less viscous particles τ_{eq} is limited by volatility, while for highly viscous particles τ_{eq} is insensitive to volatility and controlled by bulk diffusivity".

Lines 127-128: "Particle-phase reactions and their potential impacts on particle visocisty are also not considered in this study".

Lines 361-369: "Incorporation of the particle-phase formation of oligomers and other multifunctional high molar mass compounds can lead to a reduced bulk diffusivity (Pfrang et al., 2011; Hosny et al., 2016), which may prolong the equilibration timescales. Decomposition of highly oxidized molecules (e.g., organic hydroperoxides) in water may also affect gas-particle partitioning (Tong et al., 2016). Current simulations are focused on trace amount of SVOC or LVOC condensing on mono-dispersed particles with negligible particle growth. Potential phase transition in the course of particle growth/evaporation should also be incorporated in future simulations".

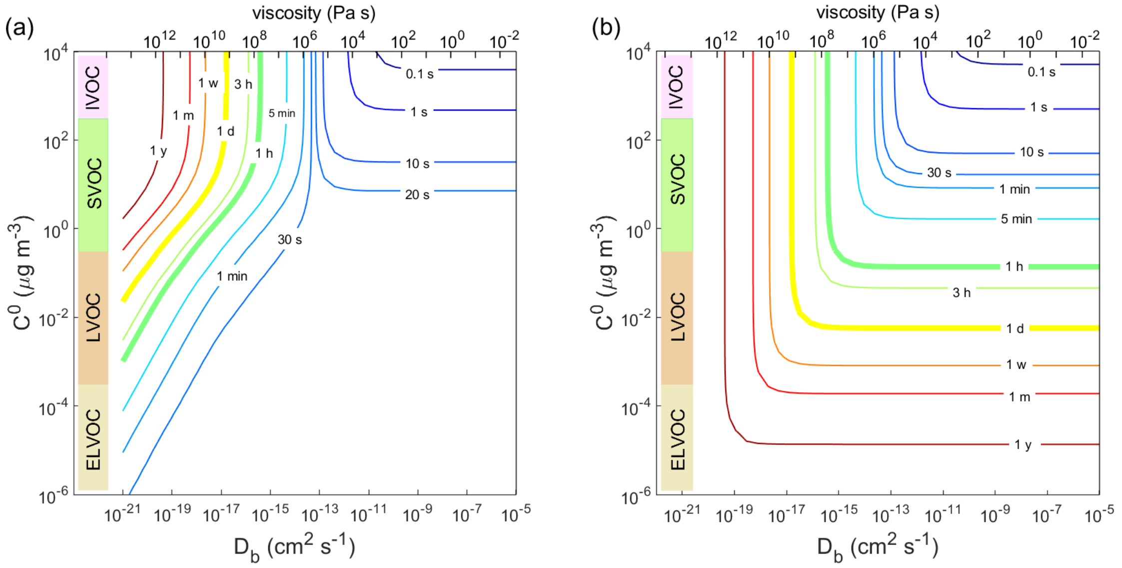

Figure 4. Contour plot of equilibration timescale (τ_{eq}) as a function of bulk diffusivity (D_b) and saturation mass concentration (C^0) for (a) condensation in the closed system and (b) evaporation in the open system. The initial mass concentration of pre-existing particles is set to be 20 μg m^{-3} with the number concentrations of 3 × 10^4 cm^{-3} and the initial particle diameter of 100 nm. Viscosity is calculated from the Stokes-Einstein equation assuming the effective molecular radius of 10^{-8} cm at T of 298 K.

(3) My other question is that most of the modeling results shown the manuscript assumed that the gas-particle is in a closed system. How realistic is the closed system in ambient environment? Would the ambient environment often be an open system for

evaporation kinetics?

Response: Thanks for this helpful comment. To address this question, we add simulations for an open system (Fig. 4b, S5, and S7) in the revised manuscript. The following discussions have been added in the revised manuscript.

Lines 202-208: "In an open system with fixed vapor concentration (Fig. S5), τ_{eq} of SVOC is slightly longer but on the same order of magnitude as τ_{eq} in the closed system, as relatively small amounts of SVOC need to condense to reach equilibrium. In contrast, τ_{eq} of LVOC in the open system become dramatically longer as LVOC continue to condense into the particle phase because of low volatility (Pankow, 1994). For further simulations we focus mainly on the closed system and the corresponding simulations for the open system are provided in the supplement".

Lines 221-225: "Figure 4b shows simulated evaporation timescales as a function of D_b and C^0 in an open system, which agrees very well with Fig. 3 in Liu et al. (2016). It shows that for less viscous particles τ_{eq} is limited by volatility, while for highly viscous particles τ_{eq} is insensitive to volatility and controlled by bulk diffusivity".

Lines 242-244: "The corresponding simulations of SVOC partitioning in the open system (Fig. S7) show a similar pattern as τ_{eq} in the closed system".

Lines 306-312: "The timescale of gas-particle partitioning can be different in closed or open systems especially for LVOC (Fig. 4, S7). The closed system simulations represent SOA partitioning in chamber experiments and in closed atmospheric air mass, which could be justified well within seconds-to-minutes timescales and possibly up to hours depending on meteorological conditions. The real atmosphere may be approximated better as an open system due to dilution and chemical production and loss especially at longer timescales".

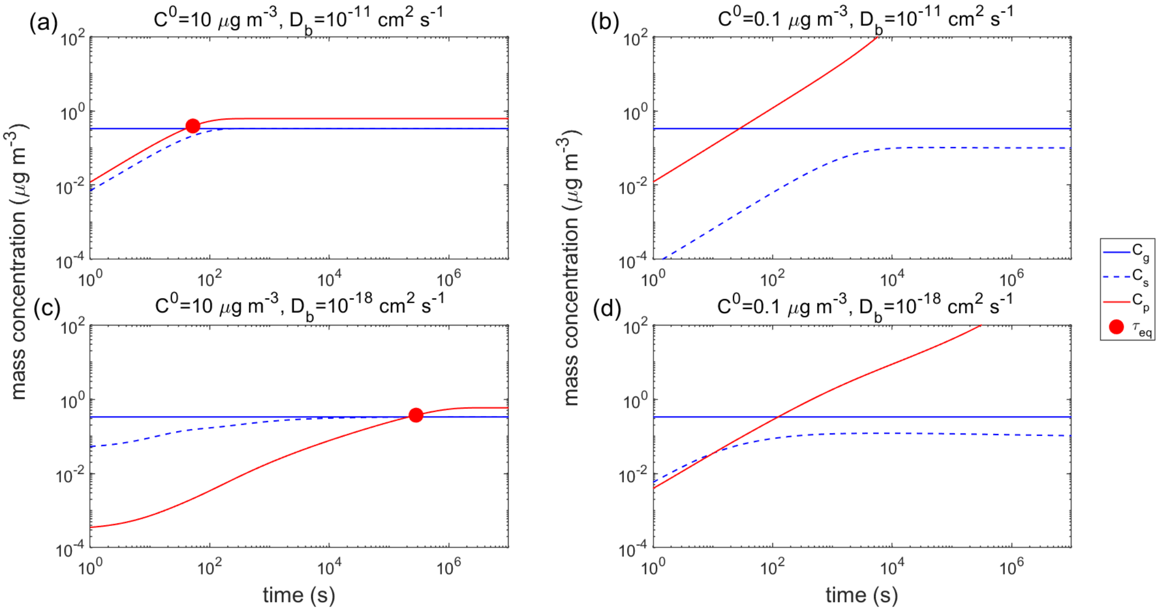

Figure S5. Temporal evolution of mass concentrations of the condensing compound Z in the gas phase (C_g), just above the particle surface (C_s), and in the particle phase (C_p) in the open system. τ_{eq} is marked with the red circle. RH = 60% and T is (a–b) 298 K and (c–d) 250 K. The C^0 of Z is (a, c) 10 μg m^{-3} and (b, d) 0.1 μg m^{-3}. The glass transition temperature of pre-existing particles under dry conditions ($T_{g,org}$) is set to be 270 K, which leads to D_b of (a–b) 10^{-11} cm^2 s^{-1} and (c–d) 10^{-18} cm^2 s^{-1}. The initial mass concentration of pre-existing particles is set to be 20 µg m^{-3} with the number concentrations of 3×10^4 cm^{-3} and the initial particle diameter of 100 nm.

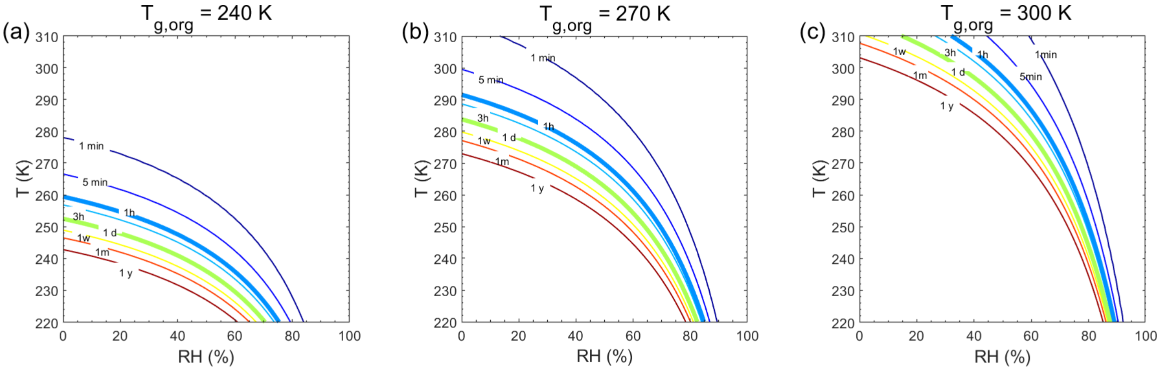

Figure S7. Equilibration timescale (τ_{eq}) as a function of temperature and relative humidity in the open system. The glass transition temperatures of pre-existing particles at dry conditions ($T_{g,org}$) are (a) 240 K, (b) 270 K, and (c) 300 K, respectively. The saturation mass concentration (C^0) of the condensing compound is 10 µg m^{-3} (SVOC). The mass concentration of pre-existing particles is set to be 20 µg m^{-3} with the number concentrations of 3×10^4 cm^{-3} and the initial particle diameter of 100 nm.

Referee Minor Comments:

The author should also include Price et al. 2015 in the reference list in line 115.

Reference: Shiraiwa et al. 2011: doi.org/10.1073/pnas.1103045108

Liu et al. 2012: doi.org/10.1080/02786826.2012.730163

Shiraiwa et al. 2012: doi.org/10.1029/2012GL054008

Price et al. 2015: doi.org/10.1039/C5SC00685F

Response: Price et al. (2015) has been included on Line 123 in the revised manuscript. Besides this, Liu et al. (2013) has been included on Lines 181, 259 and 357.

Liu, C., Shi, S., Weschler, C., Zhao, B. and Zhang, Y.: Analysis of the dynamic interaction between SVOCs and airborne particles, Aerosol Sci. Technol., 47, 125-136, https://doi.org/10.1080/02786826.2012.730163, 2013.