

We thank the referees for carefully reading our manuscript and for their helpful comments! Listed below are our responses to the comments from the referees of our manuscript. For clarity and visual distinction, the referee comments or questions are listed here in black and are preceded by bracketed, italicized numbers (e.g. [1]). Author's responses are offset in blue below each referee statement with matching numbers (e.g. [A1]).

## Response to Referee #1

Summary: The authors investigate liquid-liquid phase separation (LLPS) of  $\alpha$ -pinene and  $\beta$ -caryophyllene ozonolysis particles, as well as other atmospherically relevant organic particles. The different types of particles with different O:C ratios were studied under different relative humidity conditions. Results show that LLPS occurred to the single component organic particles with O:C smaller than 0.44, and for two-component organic particles with O:C smaller than 0.67. Overall, the results from this study present potential to improve current understanding of atmospherically relevant aerosol particles and with some revisions as noted below this should be publishable in Atmospheric Chemistry and Physics.

### General Comments of Referee #1

[1] The different types of particles with varying O:C show LLPS, the morphology (e.g. core-shell, engulf-coated, inclusions) of particles associated with different O:C ratios should be discussed more in details.

[A1] Thank you for the comment. Different morphologies of core-shell, partially engulfed, and inclusions in the particles on the hydrophobic substrate were observed after LLPS occurred for RH increasing. These morphologies were also observed in the previous studies (Kwamena et al., 2010; Reid et al., 2011; Song et al., 2012a, b; 2013). The different morphologies of phase-separated particles deposited on the hydrophobic substrate can be explained by phase separation mechanisms, and variations in the volume ratio, chemical compositions, and spreading coefficients rather than the O:C ratios. Particles of  $\beta$ -nocaryophyllonic acid had inclusions after LLPS occurred, while other particles had a core-shell morphology after LLPS. Only one particle type ( $\beta$ -caryophyllonic acid/ $\beta$ -nocaryophyllonic acid) was observed both core-shell and partially engulfed morphology with increasing RH (Fig. S1). To address the referee's comment, we will discuss the morphologies in Sect 3.2 and present the morphologies of all particles studied in Tables S1 and S2. In addition, we will replace to the clearer optical images for  $\beta$ -caryophyllonic acid,  $\beta$ -nocaryophyllonic acid,  $\beta$ -nocaryophyllinic acid, pinonaldehyde and pinic acid (Figs. 1 and 2). Also, we will add an example of optical images for core-shell and partially engulfed morphologies of particles of  $\beta$ -caryophyllonic acid/ $\beta$ -nocaryophyllonic acid in Fig. S1. As the morphologies of the particles will be discussed more details in the revised manuscript, we will change the title of the manuscript to "Liquid-liquid phase separation and morphologies in organic particles consisting

of  $\alpha$ -pinene and  $\beta$ -caryophyllene ozonolysis products and mixtures with commercially-available organic compounds”.

40 “Interestingly, particles showed different morphologies of core-shell, partially engulfed, and inclusions  
after LLPS occurred for RH increasing. These different morphologies have been also observed previously  
(Kwamena et al., 2010; Reid et al., 2011; Song et al., 2012a, 2013). The different morphologies could be  
resulted from variations in the phase separation mechanisms, volume ratios and different functional  
groups (dicarboxylic acid vs carboxylic acid and ketone) which can result in different interfacial energies  
and spreading coefficients (Kwamena et al., 2010; Reid et al., 2011; Song et al., 2013; Stewart et al.,  
45 2015, Gorkowski et al. 2020).”

#### References:

- Kwamena, N. O. A., Buajarern, J., and Reid, J. P.: Equilibrium morphology of mixed organic/inorganic/aqueous aerosol droplets: Investigating the effect of relative humidity and surfactants,  
50 J. Phys. Chem. A., 114, 5787–5795, doi:10.1021/Jp1003648, 2010.
- Reid, J. P., Dennis-Smith, B. J., Kwamena, N.-O. A., Miles, R. E. H., Hanford, K. L., and Homer, C. J.: The morphology of aerosol particles consisting of hydrophobic and hydrophilic phases: hydrocarbons, alcohols and fatty acids as the hydrophobic component, Phys. Chem. Chem. Phys., 13, 15559–15572, doi:10.1039/C1CP21510H,doi:10.1039/C1CP21510H, 2011.
- 55 Song, M., Marcolli, C., Krieger, U. K., Zuend, A. and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmos. Chem. Phys., 12, 2691–2712, doi:10.5194/acp-12-2691-2012, 2012a.
- Song, M. J., Marcolli, C., Krieger, U. K., Lienhard, D. M., and Peter, T.: Morphologies of mixed organic/inorganic/aqueous aerosol droplets, Faraday Discuss., 165, 289–316,  
60 <https://doi.10.1039/C3fd00049d>, 2013
- Stewart, D. J., Cai, C., Nayler, J., Preston, T. C., Reid, J. P., Krieger, U. K., Marcolli, C. and Zhang, Y. H.: Liquid-liquid phase separation in mixed organic/inorganic single aqueous aerosol droplets, J. Phys. Chem. A, 119(18), 4177–4190, doi:10.1021/acs.jpca.5b01658, 2015.
- Gorkowski, K., Donahue, N. M. and Sullivan, R. C.: Aerosol Optical Tweezers Constrain the Morphology  
65 Evolution of Liquid-Liquid Phase-Separated Atmospheric Particles, Chem, 6(1), 204–220, doi:10.1016/j.chempr.2019.10.018, 2020.

[2] The figures show large size particles  $\sim 80$  to  $100 \mu\text{m}$ , do smaller size particles ( $30 \mu\text{m}$ ) present same result in this study?

70 [A2] The result for LLPS in the organic particles was consistent within the size range of  $\sim 30$  -  $\sim 100 \mu\text{m}$  in this study. To address the referee’s comment, this information will be added to the revised manuscript (Sect. 3.1).

“These results for LLPS occurrence in the organic particles was consistent within the studied size ranges (~30-100  $\mu\text{m}$  in diameter).”

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[3] Author expected the inner phase of the particle mainly consist of water and outer phase consisted mainly of organic. Would it be possible to use spectroscopy to confirm the chemical composition of the particle in different phases (e.g. core and shell)?

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[A3] Raman spectroscopy could be used to confirm the chemical composition of the phases, but this technique was not available for the current study. We assume that the inner phase is mainly water and the outer phase is mainly organics because the amount of the inner phase reduced in size as the RH was decreased. This assumption, which is most likely valid, has also been used in several other studies (Renbaum-Wolff et al., 2016; Song et al. 2017, 2018; Ham et al. 2019). The surface tension of water and the surface tensions of organics are consistent with this assumption (Jasper, 1972). To address the referee’s comment, we will add the following to the revised manuscript (Sect. 3.1).

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“We expect that the inner phase consisted mainly of water while the outer phase consisted mainly of organic molecules because the amount of the inner phase reduced in size as the RH was decreased (Renbaum-Wolff et al., 2016; Song et al., 2017, 2018). This assumption has also been reported in several other studies (Renbaum-Wolff et al., 2016; Song et al. 2017, 2018; Ham et al. 2019). The surface tension of water and the surface tensions of organics are consistent with this assumption (Jasper, 1972).

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#### References:

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Ham, S., Babar, Z. Bin, Lee, J., Lim, H. and Song, M.: Liquid-liquid phase separation in secondary organic aerosol particles produced from  $\alpha$ -pinene ozonolysis and  $\alpha$ -pinene photo-oxidation with/without ammonia, *Atmos. Chem. Phys.*, 19(14), 9321–9331, doi:10.5194/acp-2019-19, 2019.

Jasper, J. J.: The surface tension of pure liquid compounds, *J. Phys. And Chem. Ref. Data*, vol 1, 841-1009, Doi: <http://dx.doi.org/10.1063/1.3253106>, 1972.

100

Renbaum-Wolff, L., Song, M., Marcolli, C., Zhang, Y., Liu, P. F., Grayson, J. W., Geiger, F. M., Martin, S. T. and Bertram, A. K.: Observations and implications of liquid-liquid phase separation at high relative humidities in secondary organic material produced by  $\alpha$ -pinene ozonolysis without inorganic salts, *Atmos. Chem. Phys.*, 16(12), 7969–7979, doi:10.5194/acp-16-7969-2016, 2016.

105

Song, M., Liu, P., Martin, S. T. and Bertram, A. K.: Liquid-liquid phase separation in particles containing secondary organic material free of inorganic salts, *Atmos. Chem. Phys.*, 17, 11261–11271, doi:10.5194/acp-17-11261-2017, 2017.

Song, M., Ham, S., Andrews, R. J., You, Y. and Bertram, A. K.: Liquid-liquid phase separation in organic particles containing one and two organic species: importance of the average O:C, *Atmos. Chem. Phys.*, doi:10.5194/acp-18-12075-2018, 2018.

110 [4] The inclusions present in different types of particles, which is very interesting and this occurred frequently in one-component particles. What are these inclusions and how does these inclusions form? Is this something correlated to O:C ratio?

115 [A4] The numerous small inclusions indicate onset of phase separation and are related to the mechanism of spinodal decomposition. Spinodal decomposition occurs with small inclusions within whole volume since there is no energy barrier to this type of phase transition (Ciobanu et al., 2009). The numerous small inclusions appeared and then coalesced on moistening resulting in inner and outer phases. The occurrence of LLPS was clearly correlated with O:C as shown in Fig. 3.

#### References:

120 Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U. and Peter, T.: Liquid-liquid phase separation in mixed organic/inorganic aerosol particles, *J. Phys. Chem. A*, 113(41), 10966–10978, doi:10.1021/jp905054d, 2009.

#### Specific comments of Referee #1

125 [5] Line117: Does RH continuous decrease/increase? If so, how do you know if the particles reach to the equilibrium and the optical images is representative for that specific RH?

130 [A5] At the beginning of LLPS experiments, the SOA particles were equilibrated at ~100% RH for 15-20 min. Then, RH in the flow-cell was continuously decreased and increased with ramp rates of 0.1 - 0.2 % RH min<sup>-1</sup>. We did not observe a dependence of LLPS and non-LLPS on the RH ramp rate. Previous studies of Song et al. (2017) and Ham et al. (2019), they used two RH rate: if LLPS was not observed, RH decreasing and increasing rates were 0.5–1.0% RH min<sup>-1</sup>, and if LLPS was observed, they used 0.1–0.5% RH min<sup>-1</sup>. In this case, they also did not observe a dependence of LLPS and non-LLPS on the different RH ramp rate. In the current study, we use a slower range of ramp rates. Moverover, particle  
135 size did not change at a specific RH.

#### References:

140 Song, M., Liu, P., Martin, S. T. and Bertram, A. K.: Liquid-liquid phase separation in particles containing secondary organic material free of inorganic salts, *Atmos. Chem. Phys.*, 17, 11261–11271, doi:10.5194/acp-17-11261-2017, 2017.

Ham, S., Babar, Z. Bin, Lee, J., Lim, H. and Song, M.: Liquid-liquid phase separation in secondary organic aerosol particles produced from  $\alpha$ -pinene ozonolysis and  $\alpha$ -pinene photo-oxidation with/without ammonia, *Atmos. Chem. Phys.*, 19(14), 9321–9331, doi:10.5194/acp-2019-19, 2019.

145 [6] Line 120: Particle diameter of 30–100  $\mu\text{m}$  seems like a big range, is this aerodynamic diameter or the diameter after impaction? Why does author choose those sizes to study and how relevant comparing the particle sizes in the atmosphere?

[A6] This is a good question! In this study, supermicrometer-sized particles (30-100  $\mu\text{m}$ ) were used since this is an optimum size to reach good quality images using the optical microscope equipped with a long working distance objective. We did not observe a size dependence for the LLPS within the size ranges studied. So far, there is no study investigated size effects for LLPS in organic particles free of inorganic salts. However, using organic/inorganic aerosol particles, Krieger et al. (2012) and You et al. (2014) reported that the separation relative humidity is not significantly depended on the micrometer-sized particles. Altaf et al. (2016), and Altaf and Freedman (2017) showed that LLPS was independent of size down to  $\sim 50$  nm when a slow drying rate was used. These results can support that the phase separation behaviour with the supermicron particles provides organic particles that dominated the aerosols in the accumulation mode in large parts of the troposphere.

#### References:

160 Altaf, M. B., Zuend, A. and Freedman, M. A.: Role of nucleation mechanism on the size dependent morphology of organic aerosol, *Chem. Commun.*, 52(59), 9220–9223, doi:10.1039/c6cc03826c, 2016.

Altaf, M. B. and Freedman, M. A.: Effect of Drying Rate on Aerosol Particle Morphology, *J. Phys. Chem. Lett.*, 8(15), 3613–3618, doi:10.1021/acs.jpcclett.7b01327, 2017.

165 Krieger, U. K., Marcolli, C. and Reid, J. P.: Exploring the complexity of aerosol particle properties and processes using single particle techniques, *Chem. Soc. Rev.*, 41(19), 6631–6662, doi:10.1039/C2CS35082C, 2012.

You, Y., Smith, M. L., Song, M., Martin, S. T. and Bertram, A. K.: Liquid-liquid phase separation in atmospherically relevant particles consisting of organic species and inorganic salts, *Int. Rev. Phys. Chem.*, 33(1), 43–77, doi:10.1080/0144235X.2014.890786, 2014.

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[7] Line 125: What caused other different types of particles not presenting LLPS?

[A7] We showed that the oxygen-to-carbon elemental (O:C) ratio of the organic compounds is an important parameter to predict occurrence of LLPS and absence of LLPS. In single-component organic particles, LLPS almost always occurred when the O:C was  $\leq 0.44$ , but did not occur when the O:C was  $> 0.44$ . In two-component organic particles, LLPS almost always occurred when the average was O:C  $\leq 0.67$ , but never occurred when the average O:C was  $> 0.67$ .

[8] Line 131:  $\beta$ -caryophyllinic acid and  $\beta$ -nocaryophyllonic acid has same O:C ratio but have very different behavior on LLPS, can author explain why?

180 [A8] Both particles of  $\beta$ -caryophyllinic acid and  $\beta$ -nocaryophyllonic acid occurred LLPS. Particles of  $\beta$ -caryophyllinic acid occurred LLPS by a mechanism of spinodal decomposition while particles of  $\beta$ -

nocaryophyllonic acid occurred LLPS by a mechanism of nucleation and growth. Due to the different phase separation mechanisms, the two particles exhibited different morphologies. Regarding the particle morphologies, please see response to [A1].

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[9] Line 133: From Figure 1g, the pinic acid at 95.6% RH also present engulf coated morphology, which is not included in discussion. In Figure 1, b, d, and e all exhibit inclusions inside the particle, what are these inclusions and how do they form?

[A9] Thank you for the comment. To clarify the morphologies, we will replace to better optical images of Fig. 1. Particles of pinic acid have core-shell morphology rather than engulf coated morphology on a hydrophobic substrate. We expect that the inclusions with a core-shell morphology consisted mainly of water as discussed above in [A3]. Such morphology with inclusions has been observed (Ciobanu et al., 2009; Song et al., 2012a, 2013)

195 References:

Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U. and Peter, T.: Liquid-liquid phase separation in mixed organic/inorganic aerosol particles, *J. Phys. Chem. A*, 113(41), 10966–10978, doi:10.1021/jp905054d, 2009.

200 Song, M., Marcolli, C., Krieger, U. K., Zuend, A. and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, *Atmos. Chem. Phys.*, 12, 2691–2712, doi:10.5194/acp-12-2691-2012, 2012a.

Song, M. J., Marcolli, C., Krieger, U. K., Lienhard, D. M., and Peter, T.: Morphologies of mixed organic/inorganic/aqueous aerosol droplets, *Faraday Discuss.*, 165, 289–316, <https://doi.10.1039/C3fd00049d>, 2013

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[10] Line 136: if the inner phase is considered as water and the outer phase are organic, do authors have data to support this statement? Most of the organic compounds are hydrophobic and wouldn't the outside organic layer prevent the water evaporation at lower RH?

[A10] Please see response to [A3] above. We did not observe significant water evaporation of organic layer at certain RH.

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[11] Figure 1f, the pinonaldehyde particles at 94.1% RH show multiple phase, looks like three layers, is that an artifact from microcopy image or that is real?

[A11] It is an optical artifact in Fig. 1f. In the revised manuscript, we will replace to the clearer images for a pinonaldehyde particle.

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220 [12] Figure 3, how many particles have been examined for each point? Do these particles have similar size? Previous study shows the size-dependent LLPS in atmospheric systems, which suggest smaller particles are likely present homogenous and large particles are likely to present LLPS. Could different sizes of particles in this study be a factor affect the results.

[A12] In Fig. 3, each data point is included 4~5 particles within the size range of 30 to 100  $\mu\text{m}$ . We will add this information in the revised manuscript (Sect. 2.3 and Fig. 3 caption). We did not observe a size-dependent within this size range. A more detailed response is in [A2].

225 [13] Line 185: It is very interesting to see the different mixture particles present LLPS at different RH, especially these two-component particles show LLPS at much lower RH. Can author explain what cause this? Is this can be triggered by high O:C ratio or large molecular weight of mixture particles?

230 [A13] This is a good question! As shown in Fig. 3b, the value of the  $\text{LLPS}_{\text{lower}}$  tends to decrease as the O:C ratio increases. However, organic functional groups could also be an important parameter for LLPS that still need to be studied. To address the referee's comments, we will add the following discussion (Sect. 4):

235 “In addition to the O:C ratio, the types of organic functional groups present in the molecules are also likely important for LLPS (Song et al., 2012b) because different functional groups lead to different strengths of intermolecular interactions with water. Further studies are needed to elucidate the effect of functional groups on the occurrence of LLPS in organic particles.”

#### References:

240 Song, M., Marcolli, C., Krieger, U. K., Zuend, A. and Peter, T.: Liquid-liquid phase separation in aerosol particles: Dependence on O:C, organic functionalities, and compositional complexity, *Geophys. Res. Lett.*, 39, L19801, doi:10.1029/2012GL052807, 2012b.