Anonymous Referee #1

This manuscript uses poke-flow measurements to determine the viscosity of organic-rich urban $PM_{2.5}$ collected from Seoul and Beijing in the autumn. They find that the viscosities of the filter extract samples are comparable to or higher than laboratory model systems (sucrose/ammonium sulfate/water, and citric acid/ammonium sulfate/water). The two biggest drawbacks in this study are that the droplets created from filter extracts are not necessarily representative of the original aerosol morphology and the poke-flow technique was limited to an RH regime lower than during sample collection. However, these limitations are discussed and clear within the manuscript, and these measurements provide important context for the viscosities of laboratory model systems as compared to field-collected material. Overall, I believe this manuscript will be suitable for publication after the authors address the following comments.

Response: Listed below are our point-by-point responses to the comments of the reviewer of our manuscript. For clarity, the referee comments are reproduced in black with bracketed numbers (e.g., [1]), and the authors' responses are provided in red with matching numbers (e.g., [A1]). We thank both reviewers for their careful reading of the manuscript and for their constructive and helpful suggestions.

Specific Comments:

[1] Line 176, 178, 182: The language of single liquid and two-liquid I think can be confusing here since these are complex field samples, I would recommend changing to "single-phase liquid" and "two-phase liquid" or LLPS.

[A1] We thank the reviewer for this helpful comment. To improve clarity, we have replaced "single liquid" and "two-liquid" with "single-phase liquid" and "two-phase liquid (LLPS)" throughout the manuscript, including in Sects. 3.2 and 4.

[2] Figure 1: Are the scales for 60% and 20% the same as the scales for 85%? In addition, if feasible I think it would be helpful for the scale to remain consistent between samples for all of the 85% and below samples. It appears that the 95% samples are all at the same scale, so I think it would be helpful to visualize the relative changes in size across samples.

[A2] We thank the reviewer for this helpful suggestion. To make it clearer, we have included the explanation in the figure caption as:

> "Optical images obtained during RH decrease for (a) Seoul and (b) Beijing $PM_{2.5}$ droplets showing phase separation, as RH decreases from ~95 % to 85, 60, and 20 %. Upon dehydration, particles transition from a homogeneous single-phase liquid to a core-shell morphology, illustrating separation of organic and inorganic components driven by water

> loss. The images at ~95 % RH are shown at the same scale, while those at ~85 % RH and lower are presented at a consistent scale to facilitate comparison between samples. The scale bar represents 20 μm. Seoul (10/15) and Beijing (10/14) samples have already been reported by Song et al. (2025) and are included here for completeness of discussion."

[3] Line 219: The particles are semi-solid under the conditions of poke-flow, but during collection the RH was generally much higher. This is touched on at later points but please also include a discussion of what that could indicate for these samples here.

[A3] We thank the reviewer for this important suggestion. We agree that the contrast between the ambient RH during sample collection and the experimentally accessible RH range in the poke-and-flow measurements deserves explicit discussion in Section 3.3. We have added the following text after the first sentence of that section (Lines 266–274):

> "Although the poke-and-flow experiments were conducted under drier conditions (RH < ~45 %) than the mean ambient RH during sampling (Seoul: 69 ± 12 %; Beijing: 54 ± 13 %), direct quantitative viscosity constraints at higher RH could not be obtained, as the droplets behaved as low-viscosity liquids above ~45 % RH and relaxed too rapidly to yield a resolvable $\tau_{(exp,\ flow)}$. Nevertheless, comparison with sucrose–AS–H_2O systems (Fig. 5) indicates that semisolid behavior may still occur during at least episodic portions of the sampling period, particularly for the Beijing samples and during lower-RH periods in Seoul. These results, therefore, suggest that semisolid behavior of urban $PM_{2.5}$ cannot be ruled out even under the RH ambient conditions observed during the sampling period, particularly during drier episodes, and that viscosity measurements at higher RH remain an important target for future work."

[4] Line 235: Please add citations for why you are assigning 10^8 as the lower limit of viscosity for these particles and indicate if this is based on any physical or chemical properties.

[A4] The assignment of ~10^8 Pa·s as a conservative lower-bound viscosity when no restorative flow is observed within the experimental timescale (> ~2 h) is a well-established convention in the aerosol viscosity literature using the poke-and-flow technique (Renbaum-Wolff et al., 2013b; Grayson et al., 2015; Jeong et al., 2022; Gerrebos et al., 2024). The relevant citations have been added to the revised manuscript (Line 291)."

References:

- Gerrebos, N. G. A., Zaks, J., Gregson, F. K. A., Walton-Raaby, M., Meeres, H., Zigg, I., Zandberg, W. F., and Bertram, A. K.: High viscosity and two phases observed over a range of relative humidities in biomass burning organic aerosol from Canadian wildfires, Environ. Sci. Technol., 58, 21716–21728, https://doi.org/10.1021/acs.est.4c09148, 2024
- Grayson, J. W., Song, M., Sellier, M., and Bertram, A. K.: Validation of the poke-flow technique combined with simulations of fluid flow for determining viscosities in samples

with small volumes and high viscosities, Atmos. Meas. Tech., 8, 2463–2472, https://doi.org/10.5194/amt-8-2463-2015, 2015.

- Jeong, R., Lilek, J., Zuend, A., Xu, R., Chan, M. N., Kim, D., Moon, H. G., and Song, M.: Viscosity and physical state of sucrose mixed with ammonium sulfate droplets, Atmos. Chem. Phys., 22, 8805–8817, https://doi.org/10.5194/acp-22-8805-2022, 2022.
- Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity, Proc. Natl. Acad. Sci. U.S.A., 110, 8014–8019, https://doi.org/10.1073/pnas.1219548110, 2013b.

[5] Figure 3: Similar to Figure 1, please adjust these images if at all possible to make the scale bars consistent between samples.

[A5] As suggested, we have adjusted the images in Fig. 3 so that the scale bars are as consistent as possible across samples. This facilitates direct visual comparison of hole-closure dynamics and particle morphology across the different $PM_{2.5}$ samples.

[6] Figure 4: Same thing as Figures 1 and 3, please adjust the scaling. Additionally, is there a reason why the brightness is so different for Beijing 10/14 0 s vs after 1–2 hours? I think it is probably clear there is no change in morphology, but the difference in brightness makes it more challenging to tell.

[A6] To address the comment, we have adjusted the images in Fig. 4 to make the scale bars as consistent as possible between samples. Regarding the brightness difference in the Beijing 10/14 panels: this arises from slight changes in illumination and focus conditions between the needle-insertion frame (t = 0 sec) and the subsequent frames acquired during the 1–2 h waiting period.

[7] Figure 5: Please indicate what experimental techniques were used to determine viscosities for the other studies included here.

[A7] We thank the reviewer for this suggestion. We have updated the caption of Figure 5 to specify the measurement technique used in each cited study. The revised caption now reads:

> "RH-dependent viscosities of Beijing and Seoul $PM_{2.5}$ droplets compared with sucrose–AS–H_2O and citric acid (CA)–AS–H_2O systems from previous studies (Jeong et al., 2022; Tong et al., 2022; Sheldon et al., 2023). Viscosities in the previous studies were determined using the poke-and-flow technique (Jeong et al., 2022), a dual optical tweezer system (Tong et al., 2022), and the droplet coalescence method (Sheldon et al., 2023)."

Technical Corrections:

[8] Line 166: “deducing” should be changed to deducting, subtracting, or another synonym. The same applies to Line 20 in the Supplementary Information.

[A8] Thank you for the correction. “deducing” has been replaced with “subtracting” in both the main manuscript and in the Supplementary Information.

Anonymous Referee #2

The manuscript by Ullah et al. presents measurements of the dynamic viscosity of aerosol particles generated from washing off filter samples of urban particulate matter ($PM_{2.5}$) collected in two megacities in Asia. Aerosol viscosities were determined using a combination of poke-and-flow experiments and fluid dynamic simulations. In addition, the authors report observations of liquid–liquid phase separation (LLPS) and other phase transitions during controlled dehumidification cycles from approximately 100% RH to 0% RH. The dataset is valuable, particularly given the scarcity of viscosity measurements for real atmospheric particles. In my opinion, this novelty outweighs the relatively small number of filter samples and the limited number of droplets analyzed per sample, even though this limitation should be more clearly discussed. Overall, the subject of the paper aligns well with the scope of the journal, and the manuscript is clearly written.

Response: Listed below are our point-by-point responses to the comments of the reviewer of our manuscript. For clarity, the referee comments are reproduced in black with bracketed numbers (e.g., [1]), and the authors' responses are provided in red with matching numbers (e.g., [A1]). We thank both reviewers for their careful reading of the manuscript and for their constructive and helpful suggestions.

General Comments:

[1] Sect. 2.1: It would be helpful to add some more information on the method used to wash off the filters. How did you ensure that all the organic and inorganic material was washed off the filter and was nebulized onto your glass slides for LLPS and viscosity analysis?

[A1] We thank the reviewer for this helpful comment. The filter extraction procedure was described in detail in Sect. S2. To improve clarity in the main text, we have revised the sentence (Lines 107–109):

> "For the morphology and viscosity experiments, $PM_{2.5}$ material was recovered from each filter using a 1:1 (v/v) methanol–water extraction procedure designed to capture both hydrophilic and hydrophobic species, as detailed in Sect. S1."

[2] Sect. 2.3: The explanation of how the microscope images were combined with fluid dynamic simulations deserves a more detailed discussion in the main text, as this is the focus of the results presented in this manuscript. Some important details are covered in the Supporting Information (Section S3) but flipping back and forth between the main text and the SI makes the reading difficult. See my specific comments below.

[A2] We thank the reviewer for this constructive comment. To improve readability and avoid the need to refer back and forth between the main text and the Supporting Information, we have created a new section (Sect. 2.4, *"Fluid-dynamic simulations"*) in the revised manuscript. The content previously included in Sect. S3 (Input parameters for COMSOL simulations) has been moved to this new section. The revised section now provides a self-contained description of how the optical images were analyzed and linked to the fluid-dynamic simulations, including the key input parameters (slip length, surface tension, contact angle, and density) and their bounds.

[3] The study contains a very limited number of samples, which make generalizations of observed trends on atmospheric PM2.5 difficult. While this limitation is acknowledged in parts of the manuscript (Sect. 3.3), it would be good to emphasis this in both abstract and conclusion. It could be helpful to indicate the number of droplets analyzed in terms of viscosity and LLPS for each filter sample and add this information to Table 1. E.g., for the Beijing filter sample of 10/03 I can only find 2 viscosity data points in Fig. 2, which renders a comparison with the other samples very challenging.

[A3] We thank the reviewer for raising this important point, which we fully agree with. Below, we address each part of the comment in turn.

Abstract:

As suggested, we added the following sentence to the abstract:

> "Although based on a limited number of filter samples and analyzed droplets, these findings offer a foundation for future, more extensive viscosity studies of urban aerosols."

Conclusion:

We have also revised the conclusion to note this limitation explicitly and to state that additional measurements on a larger number of samples will be needed to assess the broader atmospheric representativeness of the observed trends. We added the following sentence to the conclusion:

> "However, these conclusions are based on a limited number of filter samples and droplets, and future studies extending measurements across additional seasons, compositions, and particle sizes will be essential for further constraining the role of aerosol viscosity in urban atmospheric processes."

Number of droplets analyzed for LLPS and viscosity for each sample

To improve transparency, we have now added a new column to Table 2 reporting the number of droplets analyzed for each sample. In addition, the relevant methodological details have been clarified in Sect. 2.3, where we now specify the droplet numbers used for the viscosity measurements.

[4] Sect. 3.2: Can the authors provide more quantitative information on the separation relative humidity, i.e., the RH at which liquid-liquid phase separation was observed in your particles? Are the observed 1- vs. 2 liquid phases consistent with the O:C ratio of the organic material and the OIR of the samples and trends discussed in literature that the occurrence of LLPS is impacted by these parameters, i.e., O:C ratio and OIR.

[A4] Regarding the separation RH, LLPS was consistently in the RH range of approximately ~85–95 % RH in all six samples during dehydration. We note that precisely identifying the LLPS onset in ambient $PM_{2.5}$ droplets was inherently challenging due to their complex, multicomponent composition, which produces gradual morphological changes compared with laboratory proxy systems. This point has been addressed in the main text (Lines 220–221).

For the O:C and OIR, the occurrence of LLPS in all six samples was qualitatively consistent with their O:C ratios (0.45–0.52), which fall below the ~0.56 threshold commonly associated with LLPS in mixed organic–inorganic particles (Song et al., 2012; You et al., 2013). A quantitative analysis of compositional dependence was not feasible given the narrow O:C range across samples and the limited sample number, and is beyond the scope of this study. This point has been clarified in the main text (Lines 223–227).

References:

- 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, 19801–19801, https://doi.org/10.1029/2012gl052807, 2012.
- You, Y., Renbaum-Wolff, L., and Bertram, A. K.: Liquid–liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride, Atmos. Chem. Phys., 13, 11723–11734, https://doi.org/10.5194/acp-13-11723-2013, 2013.

Specific Comments:

[5] L24: Change "to non-flowing behavior" to "phase state"

[A5] As suggested, we have changed to “phase state”.

[6] L24: I would tune down "compositionally constrained" a bit, and/or explain more clearly that you provide overall mass fraction of organic material and inorganic material (your Fig. S2), but no detailed chemical composition.

[A6] We thank the reviewer for this helpful comment. The phrase has been revised to reflect the nature of compositional characterization more accurately. The sentence now reads (Lines 23–25):

> “These results indicate that organic-rich urban $PM_{2.5}$ can exhibit highly viscous, semisolid to solid phase states, and they provide quantitative, field-based viscosity estimates constrained by the bulk organic and inorganic mass fractions of urban aerosols.”

[7] L34: Replace "cloud nucleation" by "cloud formation"

[A7] “cloud nucleation” has been replaced with “cloud formation”.

[8] L36: Delete "within the regional and global".

[A8] It has been deleted in the revised manuscript.

[9] L35-37: Can the authors provide a specific example of which parameterizations are currently inaccurate?

[A9] Thank you for the comment. We have revised the sentence as follows (Lines 37–40):

> "This limitation fundamentally undermines the accurate parametrization of urban aerosol impacts in atmospheric models, for example, by violating the liquid-phase assumptions underlying gas–particle partitioning schemes and heterogeneous reactive uptake coefficients (Shiraiwa and Seinfeld, 2012; Gržinić et al., 2015)."

References:

- Gržinčić, G., Bartels-Rausch, T., Berkemeier, T., Türler, A., and Ammann, M.: Viscosity controls humidity dependence of N_2O_5 uptake to citric acid aerosol, Atmos. Chem. Phys., 15, 13615–13625, https://doi.org/10.5194/acp-15-13615-2015, 2015
- Shiraiwa, M. and Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophys. Res. Lett., 39, L24801, https://doi.org/10.1029/2012GL054008, 2012.

[10] L41: Replace "inorganic species" by "inorganic salts" and delete "sea salt". Alternatively delete "trace metals", as this would be part of the inorganic material.

[A10] We have revised the sentence (Line 43–45).

> "$PM_{2.5}$ typically consists of organic aerosols (OA), inorganic salts, trace metals, mineral dust, and elemental or black carbon (EC or BC)."

[11] L50: Change to: "... of PM2.5, particle phase state, described in terms of dynamic viscosity is particularly important for controlling particle reactivity. Viscosity describes..."

[A11] The suggested revision has been revised as:

> "Among the physical properties affected by the chemical complexity and atmospheric evolution of $PM_{2.5}$, particle phase state, described in terms of dynamic viscosity, is particularly important for controlling particle reactivity. Viscosity describes the internal resistance of a material to flow or deform, quantifying molecular mobility within the condensed phase." (Lines 52–55)

[12] L51: Write as "to flow or deform".

[A12] The phrase has been updated to “to flow or deform” as suggested.

[13] L52: Write as "aerosols with dynamic viscosities"

[A13] The phrase has been revised to “aerosols with dynamic viscosities”.

[14] L53: Add "are considered as amorphous semisolids"

[A14] The phrase “are considered as amorphous semisolids” has been added for the viscosity range 10^2 to 10^{12} Pa·s, consistent with the physicochemical literature on aerosol phase classification.

[15] L54: Add "are considered as amorphous solids" and change to: "Viscosity dictates how rapidly molecules..."

[A15] Both changes have been incorporated. The revised sentence reads (Lines 56–59):

> “….aerosols with dynamic viscosities below 10^2 Pa·s behave as liquids, those between 10^2 and 10^{12} Pa·s are considered as amorphous semisolids, and particles exceeding 10^{12} Pa·s are considered as amorphous solids (Koop et al., 2011; Zobrist et al., 2011). A highly viscous particle restricts internal diffusion and slows multiphase chemistry…...”

[16] L56: Change to "liquid-like"

[A16] The term has been changed to “liquid-like” as suggested.

[17] L59: The cited reference of Freedman 2017 discusses liquid-liquid phase separation and should be removed here.

[A17] It has been removed from Line 62 and retained only where LLPS is discussed.

[18] L64: Add reference: (Baboomian et al., 2022)

[A18] The reference Baboomian et al. (2022) has been added (Line 68). The full citation is:

- Baboomian, V. J., Gu, Y., Shi, Y., Crescenzo, G. V., Montoya-Aguilera, J., Nizkorodov, S. A., and Grassian, V. H.: Sunlight can convert atmospheric aerosols into a glassy solid state and modify their environmental impacts, Proc. Natl. Acad. Sci. U.S.A., 119, e2113272119, https://doi.org/10.1073/pnas.2113272119, 2022.

[19] L84: "using optical microscopy". Please globally change "optical microscopy" to "light microscopy" throughout manuscript.

[A19] We thank the reviewer for this suggestion. After careful consideration, we have chosen to retain the term “optical microscopy” throughout the manuscript. This term is consistently used in the aerosol phase-state and morphology literature upon which the present study builds (Ciobanu et al., 2009; Song et al., 2012, 2013, 2022, 2025; Renbaum-Wolff et al., 2013b; You et al., 2013; Grayson et al., 2015; Jeong et al., 2022; Gerrebos et al., 2024), and changing the terminology could introduce inconsistency with the cited works and potentially confuse readers familiar with that literature. Both “optical microscopy” and “light microscopy” are acceptable and widely used terms for the same technique; we therefore prefer to retain the established convention used by the broader aerosol community.

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, 10966–10978, https://doi.org/10.1021/jp905054d, 2009.
- Gerrebos, N. G. A., Zaks, J., Gregson, F. K. A., Walton-Raaby, M., Meeres, H., Zigg, I., Zandberg, W. F., and Bertram, A. K.: High viscosity and two phases observed over a range of relative humidities in biomass burning organic aerosol from Canadian wildfires, Environ. Sci. Technol., 58, 21716–21728, https://doi.org/10.1021/acs.est.4c09148, 2024.
- Grayson, J. W., Song, M., Sellier, M., and Bertram, A. K.: Validation of the poke-flow technique combined with simulations of fluid flow for determining viscosities in samples with small volumes and high viscosities, Atmos. Meas. Tech., 8, 2463–2472, https://doi.org/10.5194/amt-8-2463-2015, 2015.
- Jeong, R., Lilek, J., Zuend, A., Xu, R., Chan, M. N., Kim, D., Moon, H. G., and Song, M.: Viscosity and physical state of sucrose mixed with ammonium sulfate droplets, Atmos. Chem. Phys., 22, 8805–8817, https://doi.org/10.5194/acp-22-8805-2022, 2022.
- Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity, Proc. Natl. Acad. Sci. U.S.A., 110, 8014–8019, https://doi.org/10.1073/pnas.1219548110, 2013b.
- Song, M., 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.org/10.1039/c3fd00049d, 2013.
- 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, 19801–19801, https://doi.org/10.1029/2012gl052807, 2012.
- Song, M., Li, Y., Seong, C., Yang, H., Jang, K.-S., Wu, Z., Lee, J. Y., Matsuki, A., and Ahn, J.: Direct observation of liquid–liquid phase separation and core–shell morphology of PM2.5 collected from three Northeast Asian cities and implications for N2O5 hydrolysis, ACS ES&T Air, 2, 1079–1088, https://doi.org/10.1021/acsestair.5c00043, 2025.

- Song, M., Jeong, R., Kim, D., Qiu, Y., Meng, X., Wu, Z., Zuend, A., Ha, Y., Kim, C., Kim, H., Gaikwad, S., Jang, K.-S., Lee, J. Y., and Ahn, J.: Comparison of phase states of PM2.5 over megacities, Seoul and Beijing, and their implications for particle size distribution, Environ. Sci. Technol., 56, 17581–17590, https://doi.org/10.1021/acs.est.2c06377, 2022.
- You, Y., Renbaum-Wolff, L., and Bertram, A. K.: Liquid–liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride, Atmos. Chem. Phys., 13, 11723–11734, https://doi.org/10.5194/acp-13-11723-2013, 2013.

[20] L100: Please add details how collected filters were stored.

[A20] Additional detail on filter storage has been added to the revised manuscript (Lines 104–107):

> "After collection, filters were individually sealed in aluminum foil, placed in zip-lock bags, and stored at ~255 K to minimize evaporative loss of semi-volatile compounds and microbial degradation. All morphology and viscosity experiments were conducted within ~1 month of collection to limit changes in $PM_{2.5}$ chemical and physical properties."

[21] L110: When the droplets are equilibrated at 100% RH, do you not condense a lot of water onto your glass slide, as you are essentially at bulk water saturation?

[A21] We thank the reviewer for this perceptive comment. On the hydrophobic substrate used in this study, water tends to condense as isolated, discrete droplets rather than as a continuous bulk film, even at RH approaching close to ~100 %. The $PM_{2.5}$ sample droplets (~20–100 μm) are visually distinguishable from any small, condensed water droplets that may form on the substrate surface, and no bulk water film that would interfere with the optical observations was observed during our experiments.

[22] L114: Please add information on model and manufacturer of the RH sensor used.

[A22] We have included the information on the RH sensor (Sensirion, SHT C3, Switzerland) used in this study in the revised manuscript.

[23] L116: Please change to: "N2 and H2O-saturated vapor"

[A23] The text has been revised to read "N_2 and H_2O-saturated vapor" in the revised manuscript.

[24] L119: Do not capitalize "flow", consistent with use on e.g., L120.

[A24] We have corrected it in the manuscript.

[25] L121: Please also add the reference to Renbaum-Wolff et al. (2013)

[A25] The reference Renbaum-Wolff et al. (2013b) has been added at Line 128.

[26] L122: Are your droplets really 20-40 µm in diameter? Based on your scale bar in Fig. 1 it appears that some of your droplets were considerably larger than 40 µm.

[A26] As we described, the droplet size range of 20–40 µm refers specifically to the droplets used for viscosity measurements in the poke-and-flow experiments (Sect. 2.3). The larger droplets visible in Figure 1 were used for LLPS and morphology observations only (Sect. 2.2). This distinction has been clarified in the revised manuscript to avoid confusion (Lines 129–132).

> "In this technique, a micrometer-scale droplet (~20–40 µm in diameter) is mechanically deformed by a fine needle; the subsequent relaxation of the deformed shape is governed by the competition between surface tension (restoring force) and viscous resistance, allowing viscosity to be quantified from the observed relaxation timescale in combination with fluid-dynamics simulations."

[27] L123: "...in the flow-cell." After this statement it would be good to provide some brief explanation of the poke-flow technique. You have some of this on L130-132, but I feel that it would be helpful to get some of this description earlier to better follow the description in your Sect. 2.3.

[A27] To address the suggestion from the reviewer, a brief introductory description of the poke-and-flow principle has been added immediately after Line 128 (before the detailed procedural description) to provide context for the reader as follows:

> "In this technique, a micrometer-scale droplet (~20–40 µm in diameter) is mechanically deformed by a fine needle; the subsequent relaxation of the deformed shape is governed by the competition between surface tension (restoring force) and viscous resistance, allowing viscosity to be quantified from the observed relaxation timescale in combination with fluid-dynamics simulations."

[28] L128: "to identify the critical RH for particle cracking." Does this mean that the particle is glassy? Please clarify.

[A28] We thank the reviewer for this insightful comment. Upon careful revision, we found that the sentence referring to the "critical RH for particle cracking" was not well aligned with the context of the discussion. It has therefore been removed to improve clarity and the overall flow of the manuscript.

[29] L134: "in the absence of..." Do you mean that the flow time could not be experimentally measured? Please elaborate and explain.

[A29] To make it clearer, the text has been revised accordingly (Lines 144–146)

> "At RH > ~50 %, the $PM_{2.5}$ droplets behaved as low-viscosity liquids and hole closure occurred too quickly to be captured within the imaging frame rate; therefore, $\tau_{(exp,\ flow)}$ could not be determined under these conditions."

[30] L135: delete "high"

[A30] The word "high" has been deleted from the revised manuscript.

[31] L136: Please indicate version number of COMSOL and the modules used for your analysis.

[A31] We have included the information (Lines 148–150):

> "Viscosities were determined from $\tau_{(exp,\ flow)}$ using finite-element fluid flow simulations in COMSOL Multiphysics (version 5.5), employing the Laminar Flow interface to model viscous droplet flow and the Moving Mesh interface to account for deformation of the droplet geometry during relaxation…."

[32] L139: Please add: "In the simulations, the dynamic viscosity..."

[A32] We have revised the text accordingly.

[33] L140: Please provide details within what uncertainty the experimental and simulated flow times had to match along with a reasoning for it.

[A33] We thank the reviewer for this helpful comment. The manuscript has been revised accordingly, and the description has been updated to be consistent with our previous study (Song et al., 2016)

> "For each particle for which flow was observed, the dynamic viscosity was iteratively adjusted until $\tau_{(model,\ flow)}$ agreed with $\tau_{(exp,\ flow)}$ to within ~1 % (Song et al., 2016)." (Lines 155–156)

Reference:

- Song, M., Liu, P., Hanna, S. J., Zaveri, R. A., Potter, K. J., You, Y., Martin, S. T., and Bertram, A. K.: Relative humidity-dependent viscosity of secondary organic material from toluene photo-oxidation and possible implications for organic particulate matter over megacities, Atmos. Chem. Phys., 16, 8817–8830, https://doi.org/10.5194/acp-16-8817-2016, 2016

[34] L141: Please add details to the text how this "lower-bound viscosity" was determined.

[A34] This has been addressed in the response to Comment [A4] of Referee #1, where the basis for assigning ~10^8 Pa·s as the lower-bound viscosity is described in detail. We have modified the text to clarify this point in the revised manuscript (Lines 173–176):

> "At low RH, droplets exhibited brittle cracking without relaxation, indicating non-flowing behavior. If no recovery occurred over 2 h, a lower-bound viscosity of ~1×10^8 Pa·s was assigned, following established practice in poke-and-flow studies (Renbaum-Wolff et al., 2013b; Jeong et al., 2022; Gerrebos et al., 2024; Gerrebos et al., 2025)."

References:

- Gerrebos, N. G. A., Zaks, J., Gregson, F. K. A., Walton-Raaby, M., Meeres, H., Zigg, I., Zandberg, W. F., and Bertram, A. K.: High viscosity and two phases observed over a range of relative humidities in biomass burning organic aerosol from Canadian wildfires, Environ. Sci. Technol., 58, 21716–21728, https://doi.org/10.1021/acs.est.4c09148, 2024
- Grayson, J. W., Song, M., Sellier, M., and Bertram, A. K.: Validation of the poke-flow technique combined with simulations of fluid flow for determining viscosities in samples with small volumes and high viscosities, Atmos. Meas. Tech., 8, 2463–2472, https://doi.org/10.5194/amt-8-2463-2015, 2015.
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[35] L182: Can the authors quantify what fraction of their phase separated samples adopted a core-shell morphology and what fraction had other morphologies?

[A35] The precise fraction of droplets adopting a core–shell morphology versus other two-phase morphologies could not be quantified on a hydrophobic substrate, as the phase-behavior observations were conducted to document representative morphological evolution during dehydration.

[36] L199: Add: "viscous amorphous semisolids"

[A36] The phrase "viscous amorphous semisolids" has been added at Line 241 of the revised manuscript.

[37] Fig. 1: – Consider deleting "likely" from labels of red arrows. – Caption and figure: Please consistently provide spacing between numeric value and percentage symbol or not, e.g., "90%" vs.

"90 %". Please check ACP house-style.

[A37] As suggested, we have deleted “likely” from the figure. Regarding spacing: the manuscript and figures have been revised to consistently follow ACP house style, using a space between the numeric value and the percentage symbol throughout.

[38] L216: Based on your Fig. 2, "RH < 45%" would be more appropriate, also on L19.

[A38] We agree with the reviewer’s observation. We have accordingly revised the text at Line 89, 268, and the abstract (Line 19) from “RH < ~40 %” to “RH < ~45 %” to better reflect the actual data range.

[39] Fig. 2: Y-axis label: Please fix units to read "Pa·s"

[A39] The *y*-axis label has been corrected to read “Viscosity (Pa·s)” using the interpunct (·) dot as per standard SI convention and ACP style.

[40] Fig. 3: – What is the difference between "after poking" and "post poking"? Would it not make sense to use one label for this, as all images were captured after retracting the needle from the particle. – Why is there a "T" symbol in the "after poking" and a "τ" symbol in the "post poking" column. Also, for the former units of "s" are missing.

[A40] We agree with your comment and have revised the figure to use post-poking consistently. The time labels have also been clarified: the first frame corresponds to the image taken immediately after needle retraction (t = 0 sec), whereas the later frame corresponds to $\tau_{(exp,\ flow)}$, defined as the time at which the inner-hole diameter decreases to 50 % of its initial value. In addition, the missing unit has been added.

[41] Fig. 4: See comments of Fig. 4. Fig. 5 appears blurry, please replace with a high-resolution version of that figure.

[A41] Figure has been replaced with a high-resolution version.

[42] L267: Can you clarify what you mean with "phase-resolved chemical imaging"?

[A42] We have revised the sentences to clarify in the revised manuscript (Line 322–326):

> "Our conclusions are based on a limited number of filters and droplets, and the experiments were conducted on micrometer-sized extracted droplets on a substrate, which may not fully represent submicron ambient particles. Future studies extending viscosity measurements to a larger number of samples across different seasons and to smaller, atmospherically relevant particle sizes would further constrain the phase behavior of urban $PM_{2.5}$ under real atmospheric conditions.”

[43] L279: How often have 1 vs. 2 vs. 3 phases been observed?

[A43] We thank the reviewer for this comment. In all six samples, single-phase liquid morphology was consistently observed at ~95 % RH, two-phase liquid (LLPS) morphology was observed in all droplets by ~85 % RH, and three-phase morphologies (two liquid phases coexisting with a solid-like inclusion) were frequently observed at ~60 % RH. At lower RH (~20 %), non-flowing morphologies were observed in all analyzed droplets. Because the microscopy observations were conducted to document representative RH-driven phase behavior rather than to statistically classify every individual droplet, a systematic quantitative count of the frequency of each phase type across all droplets was not performed.

Comments to Supporting Information:

[44] L11: Change to 2 tables.

[A44] The information is updated accordingly.

[45] L13: Add "measured by a β-ray continuous ambient".

[A45] It has been added.

[46] L19: delete blank line

[A46] The blank line has been deleted.

[47] L29: Please provide information on why a 1:1 methanol-water solution was used for filter extraction.

[A47] We thank the reviewer for this comment. A methanol–water mixture is commonly used for extracting $PM_{2.5}$ components from filters for chemical analysis, as it efficiently recovers both hydrophilic inorganic constituents and hydrophobic organic species across a wide range of polarities (Choi et al., 2017; An et al., 2019; Kim et al., 2025). This has been noted in the revised Supporting Information.

References:

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[48] L39: Please provide a brief explanation of what the slip length is and how it affects your COMSOL simulations. The upper and lower limit of the slip length of 5 nm and 10 µm denote a wide range of possible values. What was the final slip length value chosen for your simulations, so that the simulated and modeled flow times matched. Was the slip length value the same for all simulations or is this a free parameter and why? Could the range of possible slip length values be narrowed down? How? According to your statement on L56-59, the wide range of possible slip length values leads to the large uncertainty of the viscosity estimates.

[A48] We address each question in turn and have added a brief explanation of slip length to the revised Sect. 2.4 of the manuscript.

What is slip length, and how does it affect the COMSOL simulations?

The slip length is a parameter characterizing the degree of velocity slip at the fluid–solid interface, representing the extrapolated distance below the solid surface at which the fluid velocity profile would reach zero under the Navier slip boundary condition. A slip length of zero corresponds to the classical no-slip condition, whereas a larger slip length indicates reduced interfacial friction. In the COMSOL simulations, a larger slip length leads to faster simulated hole closure, and therefore requires a higher inferred viscosity to reproduce a given $\tau_{(exp,\ flow)}$. This definition has been added to the revised Sect. 2.4 (Lines: 158–162)

> “The slip length, which characterizes the degree of velocity slip at the fluid–solid interface, was bounded between 5 nm and 10 µm based on literature values for fluid–solid interactions at hydrophobic surfaces (Schnell, 1956; Churaev et al., 1984; Watanabe et al., 1999; Baudry et al., 2001; Cheng and Giordano, 2002; Tretheway and Meinhart, 2002; Jin et al., 2004; Joseph and Tabeling, 2005; Choi and Kim, 2006; Zhu et al., 2012; Li et al., 2014).”

What were the slip length values used, and were they the same for all simulations?

The slip length was not a free-fitting parameter. The lower limit (5 nm) was applied consistently in all lower-bound viscosity calculations, and the upper limit (10 µm) was applied consistently in all upper-bound viscosity calculations, following the approach of previous poke-and-flow studies using the same substrate and experimental configuration (Renbaum-Wolff et al., 2013b; Song et al., 2015; Grayson et al., 2015).

Why was the range 5 nm to 10 µm chosen, and could it be narrowed?

These bounds span the full range of slip lengths reported in the literature for fluid–solid interactions at hydrophobic interfaces (Schnell, 1956; Churaev et al., 1984; Watanabe et al., 1999; Baudry et al., 2001; Cheng and Giordano, 2002; Tretheway and Meinhart, 2002; Jin et al., 2004; Joseph and Tabeling, 2005; Choi and Kim, 2006; Zhu et al., 2012; Li et al., 2014). Because the exact slip length for our $PM_{2.5}$ extract–substrate system cannot be independently determined, this broad range was intentionally adopted to ensure that all plausible viscosity values are captured within the reported bounds. This conservative approach is identical to that used in previous poke-and-flow studies (Song et al., 2015; Grayson et al., 2015).

Does the wide slip length range contribute to the large viscosity uncertainty?

Yes. The slip length is the dominant contributor to the approximately two-order-of-magnitude uncertainty in the derived viscosities, consistent with previous poke-and-flow studies (Renbaum-Wolff et al., 2013b; Song et al., 2015; Grayson et al., 2015).

References:

- Baudry, J., Charlaix, E., Tonck, A., and Mazuyer, D.: Experimental evidence for a large slip effect at a nonwetting fluid–solid interface, Langmuir, 17, 5232–5236, https://doi.org/10.1021/la0009994, 2001.
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- Watanabe, K., Udagawa, Y., and Udagawa, H.: Drag reduction of Newtonian fluid in a circular pipe with a highly water-repellent wall, J. Fluid Mech., 381, 225–238, https://doi.org/10.1017/S0022112098003747, 1999.
- Zhu, L., Neto, C., and Attard, P.: Reliable measurements of interfacial slip by colloid probe atomic force microscopy. III. Shear-rate-dependent slip, Langmuir, 28, 3465–3473, 2012.

[49] L44-46: For the lower bound of viscosity the lower bounds of material density and contact angle were used. What was the slip length value and the contact angle value used to determine the lower bound viscosity values?

[A49] We thank the reviewer for seeking clarification. The parameter sets used for the lower- and upper-bound viscosity calculations have been explicitly listed in the revised Table 1, which now clearly distinguishes the parameter combinations applied in each case.

[50] L46-48: For the upper bound of viscosity the upper bounds of material density and contact angle were used. What was the slip length value and the contact angle value used to determine the upper bound viscosity values?

[A50] Please see the response [A49] above.

[51] L48: Add "highly concentrated aqueous solutions"

[A51] The text has been updated to read (Line 164–165):

“the upper bound applied values for supersaturated ammonium sulfate (AS) …..”

[52] L53: Please provide details how the contact angle was determined.

[A52] Contact angles were measured from side-view optical images of representative droplets (~1 µL) on the hydrophobic substrate, following the procedure described in Grayson et al. (2015). The angle at the droplet–substrate interface was measured on both the left and right sides of each droplet using ImageJ, and the average value was used. The measured contact angles ranged from 30° to 75° across the analyzed droplets, reflecting variability in droplet size and composition, and these bounds were used as the range for this parameter in the COMSOL simulations (Table 1). We have now clarified this procedure in Sect. 2.4 of the revised manuscript.

Reference:

- Grayson, J. W., Song, M., Sellier, M., and Bertram, A. K.: Validation of the poke-flow technique combined with simulations of fluid flow for determining viscosities in samples with small volumes and high viscosities, Atmos. Meas. Tech., 8, 2463–2472, https://doi.org/10.5194/amt-8-2463-2015, 2015.

[53] L54-55: How good is the assumption of a perfect torus geometry and what is the uncertainty in determining the size of the hole from your microscopy images? For example, when I look at your Fig. 3a at 33% RH, the inner hole after poking has a highly aspherical shape. How is this taken into account in your COMSOL simulations? How does the shape of the hole affect your COMSOL simulations and ultimately your viscosity estimates? Some of this information should be discussed in the main text.

[A53] We thank the reviewer for this perceptive and technically important comment. The reviewer is correct that the inner hole formed after poking is often not perfectly circular (as visible in Fig. 3a at 33% RH). We have addressed this point in both the main text and SI:

Handling of non-circular holes. Rather than using a single linear diameter, the perimeter of the hole was traced in each frame from the optical image, and the enclosed area A was calculated. An equivalent circular diameter, $d = (4A/\pi)^{½}$, was then used both to define $\tau_{(exp,\ flow)}$ (the time to reach 50% of the initial equivalent diameter) and to specify the initial torus geometry in the COMSOL simulations. This approach reduces the influence of asphericity on the analysis. The following clarification has been added to both the main text (Lines 153–155):

> "Since the inner hole could exhibit irregular, non-axisymmetric shapes, its perimeter was traced from the optical images, the enclosed area was calculated, and an equivalent circular diameter ($d = (4A/\pi)^{½}$) was used to define the initial torus geometry and $\tau_{(exp,\ flow)}$."

Uncertainty from the torus geometry assumption. The COMSOL model assumes an idealized axisymmetric torus geometry, which is a simplification. However, sensitivity analyses in previous studies have shown that modest deviations in the initial hole geometry have a smaller effect on the inferred viscosity than the uncertainty propagated from the slip length, density, surface tension, and contact angle (Grayson et al., 2015). The dominant source of uncertainty, therefore, remains the spread in those input parameters (~two orders of magnitude), as described in Sect. 2.4.

[54] L69: Remove "," after than

[A54] The comma after "than" has been removed.

[55] L70: Add "forming the OA matrix"

[A55] The phrase "forming the OA matrix" has been added at Line 48 of the revised SI.

[56] L75: Add "surrounding OA matrix"

[A56] The text has been updated to include "surrounding OA matrix" as suggested at Line 53.

[57] L77: How is the radius of the matrix molecules determined?

[A57] The hydrodynamic radius of the matrix molecule (r_{matrix} = 0.44 nm) was not measured directly in this work. This value is taken from Evoy et al. (2020), where it was derived from molecular weight and liquid-density data for sucrose, a common surrogate for the organic aerosol matrix. The use of this value is consistent with previous aerosol viscosity studies that applied the fractional Stokes–Einstein approach (Maclean et al., 2021; Kiland et al., 2023). A clarifying sentence has been added to the SI (Line 55–56).

References:

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- Maclean, A. M., Li, Y., Crescenzo, G. V., Smith, N. R., Karydis, V. A., Tsimpidi, A. P., Butenhoff, C. L., Faiola, C. L., Lelieveld, J., Nizkorodov, S. A., Shiraiwa, M., and Bertram, A. K.: Global Distribution of the Phase State and Mixing Times within Secondary Organic Aerosol Particles in the Troposphere Based on Room-Temperature Viscosity Measurements, ACS Earth Space Chem., 5, 3458–3473, https://doi.org/10.1021/acsearthspacechem.1c00296, 2021.

[58] Fig. S1: – Turn blue font in caption to black font. – Looking at the blue pentagon symbols at ~30% RH, there is an enormous spread between the two data points, i.e., different droplets from the same filter (10/15). Can the authors provide some reasoning for this spread in flow time and hence also viscosity (Fig. 2)? Is this due to different composition of the individual droplets generated from the same filter extract? This should be discussed in the main text.

[A58] Thank you for the correction. The caption font has been corrected to black throughout.

For the spread in flow time for Seoul 10/15 at ~30 % RH, we note that although the droplets were generated from the same filter extract, variability in $\tau_{(exp, flow)}$ between individual droplets can arise from several factors. These include heterogeneity in the local phase state and water distribution within individual droplets upon dehydration, supersaturation of inorganic salts that may occur at different RH thresholds in different droplets, and minor experimental factors such as local impurities or differences in droplet size and morphology. Such variability is expected to be most pronounced at intermediate RH (~20–45 %), where viscosity is highly sensitive to small changes in water content and phase state. A brief discussion has been added to the revised main text (as noted below).

> "The observed spread in $\tau_{(exp,\ flow)}$ between individual droplets from the same filter extract likely reflects variability in local phase state upon dehydration, differences in the RH threshold at which inorganic salts become supersaturated, and minor experimental factors such as droplet size heterogeneity, all of which can strongly influence viscosity at intermediate RH." (Lines 275–278)