Dr. Thorsten Bartels-Rausch
Co-Editor of Atmospheric Chemistry and Physics

Dear Dr. Bartels-Rausch,

Given below are our responses to the comments provided by the reviewers of our manuscript. For clarity, the referee comments or questions are in black text, and are preceded by bracketed, italicized numbers (e.g. *[1]*). Our (authors') responses are in in blue text below each comment or question with matching italicized numbers (e.g. *[A1]*). The revised text according to each referees' comment or question is in green text below each authors' response, with corresponding page and line numbers in the original manuscript (e.g. *[R1, page 1 lines 1-2]*). We thank the reviews for their time and care reading our manuscript and for their helpful comments and questions.

Sincerely,

Allan Bertram
Professor of Chemistry
University of British Columbia

Anonymous Referee #1

Summary:
The authors present measured diffusivities of tracers in three proxies for secondary organic aerosols. They have compared their observations with predictions based on the Stokes-Einstein relation. From their measurement data, they have presented parameters for a fractional Stokes-Einstein relation. They have also compared their observations with observations in literature and predictions from Stokes-Einstein relation and their model for a fractional Stokes-Einstein relation. The experiments seem properly done and are simply and clearly explained. Their data are also simply and clearly presented. There are however a few questions I would like answered:

Major comments:
[1] There is a comparison between their developed fractional Stokes-Einstein relation and the Stokes-Einstein relation. Price et al. (2016) already presented a fractional S-E relation. A comparison of their outcome with this model was not made. Do we really need a new fractional S-E relation when that from Price et al. already exists? How does Price et al.'s compare to your model and your observations? What does C in the fractional relation represent?
[A1] Regarding the first part of this comment, the fractional Stokes-Einstein relation from Price et al. 2016 was derived using only diffusion data of sucrose in sucrose-water matrices. The new fractional Stokes-Einstein relation was derived using diffusion data of several large organic molecules in several types of organic water-matrices. To address the referee's comments, in the revised manuscript we will add a direct comparison between the new fractional Stokes-Einstein relation, and the fractional Stokes-Einstein relation derived by Price et al. (2016).

Regarding the second part of this comment, the C in the fractional Stokes-Einstein relation is related to ξ and the crossover viscosity (η_c), specifically, $C=\eta_c^{\xi}/\eta_c$. The crossover viscosity is the viscosity at which the Stokes-Einstein relation and the fractional Stokes-Einstein relation predict the same diffusion coefficient. Based on the data in Fig. 3 we have chosen $\eta_c = 10^{-3}$ Pa s.

For clarity we have decided to re-write the fractional Stokes-Einstein relation to eliminate the variable C. An alternative way to write the fractional Stokes-Einstein relation is:

$$D = D_c\left(\frac{\eta_c}{\eta}\right)^{\xi}$$

where ξ is the same empirical parameter as in the previous version of the fractional relation, η_c is the crossover viscosity, and D_c is the crossover diffusion coefficient. The crossover viscosity corresponds to the viscosity at which the system changes from one that follows the Stokes-Einstein relation to one that follows the fractional Stokes-Einstein relation. The crossover diffusion coefficient corresponds to the diffusion coefficient at η_c (which can be calculated with the Stokes-Einstein relation). The following changes were made to the text and all references to the variable C have been removed.

[R1, page 9 line 3] This is in close agreement with the findings of Price et al. (2016) who showed that the diffusion of sucrose in a sucrose-water matrix could be modelled using a fractional Stokes-Einstein relation with ξ = 0.90 over a large range in viscosity. The new fractional Stokes-Einstein relation, which builds on the work of Price et al. (2016), was derived using diffusion data of several large organic molecules in several types of organic water-matrices, and thus demonstrates a broader utility of the fractional Stokes-Einstein relation.

[R1, page 8 line 23] Building on that work, the data in Fig. 3a were fit to the following fractional Stokes-Einstein relation:

$$\cancel{D = C\frac{kT}{6\pi\eta^{t}R_H}}\, D = \left(\frac{\eta_c}{\eta}\right)^{\xi}$$

where ~~t and C are~~ ξ is an empirical fit parameter,~~s.~~ η_c is the crossover viscosity, and D_c is the crossover diffusion coefficient. The crossover viscosity is the viscosity at which the Stokes-Einstein relation and the fractional Stokes-Einstein relation predict the same diffusion coefficient. Based on the data in Fig. 3 we have chosen $\eta_c = 10^{-3}$ Pa s. The crossover diffusion coefficient corresponds to the diffusion coefficient at η_c (which can be calculated with the Stokes-Einstein relation). The value of ξ is determined as the slope of the dashed line in Fig. 3a. ~~When fitting Eq. 3 to the data, we used the additional constraint that log (D) – log (kT/6πRH) equals 3 when the viscosity is 10-3 Pa s, which is equivalent to assuming the Stokes-Einstein relation is valid at a viscosity of 10-3 Pa s (roughly the viscosity of water).~~ The best fit to the data (represented by the dashed line in Fig. 3a) resulted in a ~~t~~ξ value of 0.93~~ and a C value of 1.66~~.

[2] What saturated salts were used in setting the relative humidity and what is the water activity over those salts used? This can be presented as part of the SI.
[A2] A new table has been added to the SI (Table S1) which lists the salts used and the relative humidity of the air space measured above each salt.

[3] Crystallization in the droplets: was there a control sample without the tracers? How does the occurrence of crystallization at the low water activity in droplets without tracers compare to droplets with the tracers? A statement of how the tracers impact the behaviour of the test solution should be made.
[A3] We did not condition a control sample without fluorescent organic molecules to experimental a_w in order to determine the effect of the tracer on the crystallization of the droplets. However, pure solutions (of the organic matrix molecules and water studied here) can exist as supersaturated droplets at the same water activities as studied here without crystallizing. We know this because droplets in the metastable supersaturated (non-crystalline) phase are required to generate the viscosity data given by the literature viscosity sources. Furthermore, since the concentrations of the tracers in the droplets were so low, the

tracers are not expected to change the driving force for crystallization in the droplets. The following has been added to the text.

[R3, page 5 line 6] We did not condition droplets without fluorescent organic molecules to determine the effect of the tracer molecules on crystallization. However, previous studies have shown that droplets with the compositions and range of a_w values studied here can exist in the metastable liquid state if heterogeneous nucleation by surfaces is reduced. Furthermore, since the concentration of the tracers in the droplets were so low, the tracers are not expected to change the driving force for crystallization in the droplets.

Minor comments:

[4] Please include a "," after following on line 8, page 3

[R4, page 3 line 8] In the following, we expand on the previous studies with sucrose matrices…

[5] Please include a "," before "we account..." on line 12, page 7

[R5, page 7 line 12] By plotting log (D) – log ($kT/6\pi R_H$), we account for differences in hydrodynamic radii…

[6] Please include a "," after "In Fig 3a on line 30, page 7

[R6, page 7 line 30] In Fig. 3a, we have combined the results from the current study…

[7] Please change "t" as the symbol for the fractional parameter in the fractional S-E relation; "t" has been used elsewhere in the paper to represent time.

[A7] We have replaced the variable "t" with the symbol "ξ" for the exponent in the fractional Stokes-Einstein relation.

Anonymous Referee #2

Summary:

In this work the authors present measurements of the diffusion coefficients of a fluorescent organic tracer in secondary organic aerosol proxy compounds (citric acid, sorbitol, and a sucrose-citric acid mixture). They compare their measured diffusion coefficients with the predicted diffusion coefficients by the Stokes-Einstein relation. From this comparison they propose a parameterization of a fractional Stokes Einstein relation. The suggested fractional Stokes-Einstein relation seems to be a better model for predicting diffusion coefficients in SOA proxies, for the range of viscosities studied. The comparison is made as well for earlier work. The writing is clear and the data is presented in a comprehensive and clear way. This work is of a great interest for the atmospheric science community and it is definitely suitable for publication in ACP. I would raise only few minor comments.

Comments:

[8] How dependent of the nature of the diffusing molecule are the parameters t and C? In the experiments the diffusing molecule was rhodamine 6D, which is quite a large molecule. How would the parameters change for smaller molecules?

[A8] A strong relationship between the size of the diffusing molecule and the parameter t (now ξ in this work) is suggested by Price et al. (2016), who report values of t for both sucrose and water molecules diffusing in a sucrose-water matrix. Here we focus on providing a fractional Stokes-Einstein relation that is applicable to cases where the size of the diffusing molecule is equal to or larger than the organic molecule in the matrix. For this case, a strong relationship between the size of the diffusing molecule or the nature of the diffusing molecule was not observed. Ongoing work in our laboratory is exploring the

relationship between t and the size of the diffusing molecule when the size of the diffusing molecule is smaller than the organic molecule in the matrix. We have changed “organic molecules” to “large organic molecules” in the title, and added the following text to the manuscript.

[R8, page 9 line 3] For the case of large diffusing molecules such as those included in this work (i.e. the radius of the diffusing molecule is equal to or larger than the radius of the organic molecules in the matrix), we do not observe a strong dependence of ξ on the size or nature of the diffusing molecule. For smaller molecules, ξ is expected to change significantly. For example, Price et al. (2016) showed that ξ = 0.57 for the diffusion of water in a sucrose-water matrix, and Pollack (1981) showed that ξ = 0.63 for diffusion of xenon in a sucrose-water matrix. The development of a relationship between ξ and the size of small diffusing molecules is beyond the scope of this work.

[9] Line 21, page 1.“...measured diffusion coefficients over eight orders in magnitude...”. Diffusion coefficients of what? I would write “diffusion of coefficient of organic compounds” or something similar.
[A9] The text has been modified as follows.
[R9, page 1 line 21] We measured diffusion coefficients of large organic molecules over eight orders in magnitude in proxies of SOA.

[10] I would include in the abstract how the diffusion coefficients were measured (fluorescence, rhodamine 6G...).
[A10] The description of the measurement technique has been added to the abstract.
[R10, page 1 line 22]). However, the accuracy of this relation for predicting diffusion in SOA remains uncertain. We measured diffusion coefficients over eight orders in magnitude in proxies of SOA including citric acid, sorbitol, and a sucrose-citric acid mixture. Diffusion coefficients of two fluorescent organic molecules, rhodamine 6G and cresyl violet, were measured using rectangular fluorescence recovery after photobleaching (rFRAP).

[11] Is the photobleaching affecting the temperature of the films?
[A11] The photobleaching is not expected to affect the temperature of the thin films in such a way that measured diffusion coefficients would be affected. The following text has been added to the manuscript.

[R11, page 5 line 21] The energy absorbed by the thin film during photobleaching is not expected to affect measured diffusion coefficients. Although local heating may occur during photobleaching, the thermal diffusivity in the samples is orders of magnitude greater than the molecular diffusivity, and the heat resulting from photobleaching will dissipate to the surroundings on a timescale much faster than the diffusion of molecules will occur (Chenyakin et al., 2017). Measurements as a function of photobleaching size and power are consistent with this expectation (Chenyakin et al., 2017; Ullman et al., 2019).

Anonymous Referee #3

Summary:
The manuscript submitted to Atmospheric Chemistry and Physics titled “Predictions of diffusion rates of organic molecules in secondary organic aerosols using the Stokes-Einstein and fractional Stokes-Einstein relations” by Evoy et al. presents diffusion coefficients, D, and viscosity, η, of fluorescent dyes in organic compounds, which are proxies of secondary organic aerosol (SOA) material. Using their data and data from previous studies, they test the applicability of the Stokes-Einstein (SE) relation. The authors find that although the SE relation is fairly accurate within their experimental uncertainty, a better fit could be made

using a fractional Stokes-Einstein (FSE) relationship, with 2 fit parameters to adjust the linear relationship between ln D versus ln η. The authors compare the SE and FSE relation in terms of mixing times, τ, calculated for particles 200 nm in diameter as a function of latitude and pressure levels in the atmosphere. The authors conclude that when η is high, τ and D calculated using the FSE are up to 10 times shorter. Overall, this manuscript adds to the growing database of D and η for many atmospherically relevant compounds and proxies. The methods are accurate and the error analysis is justified. Finally, the results and implications are presented clearly. I will add that this manuscript was a pleasure to read and review. There is one major comment about how previous literature is described by the authors. A few minor comments must also be addressed before I can recommend publication. Page and line numbers are indicated below, and all references are taken from the manuscript.

Major Comments:

[12] p. 2, l. 13-17: The authors use these sentences to claim importance of SOA growth, mass, chemical reactivity and photochemical reactivity. These statements are valid but for a limited range of conditions. The authors should state what range of D or η these are actually valid, or readers not in the field may be misled. Specific examples should be given here to reveal to the reader when diffusion limitations significantly affect atmospheric processes such as SOA growth or photochemical reactions and when they do not. This paragraph can be extended to discuss these details. I will only discuss a few references below, and implore the authors to recheck all cited previous publications here for the conditions of D and equilibrium timescales, τ, that are important for SOA formation and (photo)chemical reaction.

- Shiraiwa and Seinfeld (2012): Measurements in this manuscript are for10−15−10−6cm2s−1. However, Shiraiwa and Seinfeld (2012) show that values of τ are unchanging when D is varied between about10−15−10−5cm2s−1. This says to me that changes in D are not important at all to τ for their observations, and thus not important to SOA growth. It can be important for a lower range of D and a specific particle size, however these details are not included in the manuscript. This should change in the introduction.
- Zaveri et al. (2018): In Figs. 4 and 5 of Zaveri et al. (2018), size changes for SOAparticles ≥ 200nm in diameter could be successfully modeled using both liquid-like and semi-solid scenarios. This would lead to the conclusion that, changing D and τ for 200 nm particles shown in Fig. 5 of this submitted manuscript would not make any difference to SOA size or mass. This is contrary to what they write.
- Hinks et al. (2016): How does viscosity change light absorption and quantum yield of a photochemical reaction rate? Excitation reaction R1 in Hinks et al. (2016) is not altered by changing D. Therefore, the statement that “photochemistry” depends on D is incorrect. However, chemical reactions R2-R4 could be diffusion limited. These details should be stated, otherwise this statement can mislead readers.

[A12] To address the referee’s comments, we have qualified many statements in the text relating to the importance of diffusion for predicting SOA growth, reactivity, and the long-range transport of pollutants. References relating to photochemistry have been removed. The reference relating to predictions of SOA mass has also been removed. The following illustrates the modifications made to the text.

[R12, page 2 line 13] ~~For example, predictions of SOA mass, which has major implications for climate and air quality, can vary by an order of magnitude when the molecular diffusion rate of organic molecules in SOA is varied in models (Shiraiwa and Seinfeld, 2012).~~

[R12, page 2 line 15] For example, predictions of SOA particle size, which has implications for climate and visibility,~~ also~~ varies significantly in simulations as the diffusion rate of organic molecules is varied from 10^{-17} to 10^{-19} m^2 s^{-1} (Zaveri et al., 2014~~, 2018~~)

[R12, page 2 line 17] Lifetimes of polyaromatic hydrocarbons (PAHs) in an SOA particle increase as the bulk diffusion coefficient of PAHs decreases from 10^{-16} m^2 s^{-1} at a relative humidity of 50% to 10^{-18} m^2 s^{-1} under dry conditions (Zhou et al., 2019). Shrivastava et al. (2017) have shown that including shielding by a viscous organic aerosol coating (equivalent to a bulk diffusion limitation) results in better model predictions of observed concentrations of PAHs.

[R12, page 2 line 17] Reactivity ~~and photochemistry~~ in SOA can also depend on diffusion rates of organic molecules (Davies and Wilson, 2015; ~~Hinks et al., 2016;~~ Lakey et al., 2016; Li et al., 2015; ~~Lignell et al., 2014;~~ Liu et al., 2018; Shiraiwa et al., 2011; Zhang et al., 2018; Zhou et al., 2013). For the cases discussed above, diffusion of organic molecules within SOA becomes a rate-limiting step only when diffusion rates are small.

Minor Comments

[13] p. 1, l. 20-21: The authors did not measure D. They measured the change inflorescence intensity over time. D was derived from fitting their florescence intensity measurements, and then fitting again their fitted parameter (r2+4Dt) over time (p. 6, l. 9 and 15). Please search for all instances of the phrase "measured diffusion coefficients" or similar and rephrase.

[A13] We have either replaced the phrase "measured diffusion coefficients" with "determined diffusion coefficients," "experimental diffusion coefficients," or else have deleted the word "measured" throughout the manuscript.

[14] p. 1, l. 27-28: The authors make the claim that differences in D between the SE and FSE relation can be important for predicting SOA particle size and chemical reaction rates. SOA size or reaction rates were not measured or modeled in this manuscript and so this sentence misleads readers. This is more of an introductory sentence than a consequence determined by their results. This sentence should be included in the beginning of the abstract and reworded for clarity.

[A14] This sentence has been moved to the beginning of the abstract and reworded.

[R14, page 1 line 18] ~~These differences~~Diffusion can be important for predicting growth, evaporation, and reaction rates of SOA under certain atmospheric conditions.~~in the middle and upper part of the troposphere.~~

[15] p. 1, l. 28-29: This sentence is a very unusual way to end an abstract. What I read here is that the diffusion results are important when diffusion is important. This is a very weak sentence and suffers circular reasoning. Please rephrase.

[A15] The final sentence of the abstract has been modified as follows.

[R15, page 1 line 28] These results also have implications for other areas where organic water-matrices are important, such as in food sciences and the preservation of biomolecules.~~diffusion of organic molecules within organic-water matrices is important.~~

[16] p. 6. l. 8 and Equation 2: I am confused about how the fitting was done, likely because of Fig. S6. Was a time evolving surface fit (2-D) performed? Was the data first averaged as in Fig. S6, and then fit in 1-D? Please briefly clarify what was actually fit in the text.

[A16] Equation 2 was fit to the full images (128x128 pixels following downsizing) to determine the diffusion coefficients. Figure S6 is included only to allow the reader to visualize the fit of the equation to the data. The text has been modified in two places to clarify.

[R16, page 6 line 8] The entire images (128x128 pixels following downsizing) collected during a rFRAP experiment were fit to Eq. (2) using a Matlab script...

[R16, page 6 line 20] Figure S6 is given only to visualize the fit of the equation to the data, and the cross-sectional fit was not used to determine diffusion coefficients. As mentioned above, the entire images (128x128 pixels following downsizing) were used to determine diffusion coefficients.

[17] Figure S6: I question why averaging over the y-direction was used here. The corners of the bleached rectangle should "round" as time progresses (Fig. S4e), and the spot then appears more like a circle. Therefore, can averaging over the y-direction really be called a cross-section? Would the authors agree that showing a measured 2-D surface intensity plot and modeled lines of constant intensity would be more beneficial to understand the measurements and fit?
[A17] Averaging over the width of the bleach in the y direction was done to demonstrate to the reader, using Fig. S6, that the bleach depth is initially roughly 30% and decreased over time as diffusion of fluorescent molecules occurred. We believe this is easier to visualize using an intensity profile rather than a surface intensity plot.

[18] p. 8, l. 17-18: I am pleased that the authors have not oversold themselves here and used words like "suggest" and "may". Throughout their manuscript, their data and analysis has been worded very well.
[A18] No changes have been made in terms of the wording of the data and analysis. Qualifying words such as "suggest" and "may" have been maintained.

[19] p. 9, l. 1-3: Is this too obvious? More fitting parameters will always give a better fit. Is a quantitative metric to evaluate whether or not the data are consistent with a certain model? As it is written, the authors want the reader to look at the residuals in Fig. 3b) and c) and come to the same qualitative reasoning. I would recommend a simple chi-squared test to give quantitative evidence and strengthen their claim.
[A19] A reduced chi-squared test has been used to strengthen the claim that the data are more consistent with the fractional Stokes-Einstein relation compared to the Stokes-Einstein relation. The following has been added to the text.
[R19, page 9 line 1] Beyond the sum-of-squared residuals test we have performed a reduced chi-squared (χ^2) test which takes into account the extra fitting variable present in the fractional Stokes-Einstein relation. Assuming a variance of 0.25, the reduced χ^2 value is 1.24 for the Stokes-Einstein relation and is 0.67 for the fractional Stokes-Einstein relation.

[20] Figure 3a and Eqn 3: When the authors fit to the FSE relation, did they consider a weighted fit to the uncertainties? I could imagine some data points by different authors are more certain than others. Please state in the manuscript if the fit was weighted with any uncertainties.
[A20] The fit to the data in Figure 3a given in Equation 3 was not weighted with any uncertainties. This is in part because precise uncertainties were not given in all literature sources. The text has been updated to reflect that the data were not weighted using uncertainties.
[R20, page 8 line 29] Each data point was weighted equally when performing the fitting.

[21] From the journal website, "Authors are required to provide a statement on how their underlying research data can be accessed. This must be placed as the section "Data availability" at the end of the manuscript before the acknowledgements." Please fulfill this data policy requirement.
[A20] The following statement has been added to the manuscript.
[R20, page 11 line 3] Underlying data and related material for this paper are located in the Supplement.