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Interactive comment on "Viscous organic aerosol particles in the upper troposphere: diffusivity-controlled water uptake and ice nucleation?" *by* D. M. Lienhard et al.

D. M. Lienhard et al.

ulrich.krieger@env.ethz.ch

The authors would like to thank Referee #2 for finding our paper a "refreshing investigation", the comments and queries. We address the reviewer's comments in our response given below. We will incorporate corresponding changes and clarifications in a revised version of the manuscript.

Referee #2: Page 24478: line: "The numerical model subdivides the particle into up to several thousand individual shells and solves the non-linear diffusion equation in spherical coordinates while accounting for the concentration dependence of the

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water diffusion coefficient, i.e. accounting for the plasticizing effect of water . . .". I'm curious as to what this means, physically, when say a 900nm particle is split into a few thousands shells? I presume this has been covered in previous papers but what effects do a "sub molecular" representation mean for modelling the diffusion process? Is it because the numerics indicate a tangential behaviour for equilibration times when resolution is continually increased?

Authors' response: The reviewer is absolutely correct: a "sub molecular" representation causes numerical problems, because the flux through an infinitesimal thin layer becomes arbitrarily large. Hence, we use minimal width to avoid this problem. In Lienhard et al. (2014) we write: "... The number of new shells is calculated such that the widths of the new shells correspond to the diffusion length of water in 1 s but with a minimum width of the molecular dimension of water of about 0.3 nm.". We will add the following sentence to the revised manuscript: "The number of shells and the time steps are adjusted dynamically to provide numerical stability. **The minimum width of the shells are kept larger than the molecular dimension of water of about 0.3 nm.**"

Referee #2: On the same page:"the diffusion coefficients of the solutes are expected to be much slower than water and are not accounted for." Does this mean the solute is assumed not to diffuse with water? In other words, if you assume a system with symmetric diffusion coefficients, this would effectively result from assuming an ideal binary system within a Fickian framework. If you are not assuming this, presumably non-ideality is accounted for? I guess the easier way to answer this, is, what is the assumed diffusion coefficient for the solute with significant amounts of water?

Authors' response: Yes, we consider the water to diffuse through a matrix in which the solutes diffusivities are so small that the solutes can be considered static. This assumption may not hold at high humidity and high temperature, but there, the water

diffusivity is too fast to be measured in our setup anyway, see Fig. 2. Data on solute diffusivity in semi-solid SOA are very rare. They cannot simply be inferred from the Stokes-Einstein relationship as it may not be valid under these conditions. However, Abramson et al. (2013) estimated from their evaporation experiments a diffusion constant of $2.5 \cdot 10^{-17} cm^2 \cdots^{-1}$ for pyrene in alpha-pinene SOA at room temperature. If we compare this to our data for water diffusion we see that water has a diffusion constant about 6 orders of magnitude faster, which justifies our assumption.

Referee #2: Section 3. Do the authors expect any semi-volatile loss from the alpha-pinene aerosol when extracting diffusion coefficients of water? I'm just curious as to the use of these inferred diffusion coefficients in an atmospheric simulation somehow has an inherent effect from such a process?

Authors' response: We assume that any possible loss has occurred already with the collection of the SOA material on the filter. We measured the evaporation of 3-MBTCA as one of the products of alpha-pinene oxidation and calculated vapor pressures from the evaporation rates, see Fig. A6. At 286 K a pure MBTCA particle (of roughly the same size) shrank by 6 nm in 600 hours, which is much longer than the duration of the experiments described in this paper. Hence, the evaporative loss of a compounds similar in vapor pressure to 3-MBTCA can be safely neglected in our experiments.

Referee #2: In the abstract the authors note that: "condensed-phase water diffusivity is unlikely to have significant consequences on the direct climatic effects of SOA particles under tropospheric conditions." In the general atmospheric simulations, it isn't clear in the text whether size distribution dynamics are accounted for. Despite the hypothesis that, at the single particle level, time-scales are significantly reduced to remove the "importance" of diffusion, isn't there a potential effect on size distributions from a non-instantaneous equilibration below cloud? Is this accounted for? I would

expect a parcel model with the diffusion model accounted for to be quite expensive, perhaps I am wrong. The results from this model would also likely be sensitive to a range of initialisation conditions including assumed history of water uptake, size distribution, inorganic core and up draft?.

Authors' response: We agree with the reviewer that initialization conditions are indeed important, however, we consider the examples shown in the paper as rather conservative. Concerning size distribution dynamics: this is an interesting point. They would certainly occur and be of some importance for particular cold conditions (for example in high velocity updrafts at the cold point tropopause in the tropics). However, for all other conditions, based on the results shown, we expect them to be very small. A parcel model would answer this question but that is beyond the scope of this paper.

References:

Abramson, E. et al., *Phys. Chem. Chem. Phys.*, **15**, 2983 (2013).

Lienhard, D. M. et al., *Phys. Chem. Chem. Phys.*, **16**, 16677 (2014).

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