

Interactive comment on “Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP): linking condensation, evaporation and chemical reactions of organics, oxidants and water” by M. Shiraiwa et al.

M. Shiraiwa et al.

m.shiraiwa@mpic.de

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Referee General Comment:

This manuscript describes development of a kinetic model simulating gas and particle phase mass transport and chemical reactions. Developing such a model is timely and the manuscript is for the most part easy to follow. I have, however, a number of suggestions / concerns that should be addressed before the manuscript can be considered for publication in ACP; The new model represents substantial scientific progress in terms

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of methods used to understand and interpret microphysical processes in atmospheric aerosol particles. Hence, the paper is well suited for publication in Atmospheric Chemistry and Physics but should first address adequately the following comments.

Response:

We thank Anonymous Referee #2 for the review and the very positive evaluation of our manuscript. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee Comment 1:

Abstract, line 10-11. The authors suggest an unlimited number of species, chemical reactions, and physical processes can be treated. As the number of species, reactions, etc. increase the computational cost must increase. The authors should give some indication how computationally expensive it is to carry out these calculations and discuss whether it is really practical to include a large or unlimited number of species.

Response:

The computational time for simulating the system presented in this study was less than one minute using Matlab software on a standard desktop computer. Of course the computational cost will increase if very large numbers of species and reactions are included. We will clarify this point in the abstract of the revised manuscript.

Referee Comment 2:

When discussing the water condensation work, the authors state that they have confirmed that the accommodation coefficient of water at 270K is close to unity (see Abstract and Conclusions). This sounds like they have made an original contribution to our understanding of water accommodation. However, Winkler et al. (2006) have already come to this conclusion by comparing their experimental data with theory for droplet growth. The authors could do a better job of giving proper credit to the work of

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Winkler et al. (2006) while more clearly indicating their own contribution.

Response:

Indeed Winkler et al (2006) already showed that the accommodation coefficient is close to unity, but the actual value is still under discussion (Kolb et al. 2010). Winkler et al. (2006) used a continuum model of gas phase diffusion and condensation, which does not resolve microscopic information such as the desorption and surface residence times of water molecules. To the best of our knowledge, earlier studies have not provided a direct, quantitative link between molecular dynamic simulations and laboratory observations through a single model resolving both the molecular processes at the surface and the macroscopic growth of particles. In this sense, we think that the presented model calculations help to confirm the earlier findings of Winkler et al. (2006) and contribute to the understanding of water accommodation. We will clarify this in the main text and cite Winkler et al (2006) not only in the main text but also in the abstract and conclusions of the revised manuscript.

Referee Comment 3:

Page 33706, line 24-26. Here the authors are assuming a desorption lifetime of water based on molecular dynamic simulations that is uncertain. How sensitive are the calculations to this number? Because of the uncertainty associated with the desorption lifetime used, if the calculations are sensitive to this number, then I think it is too strong to conclude that the authors have confirmed that the mass accommodation of water is close to unity.

Response:

We agree that MD simulations have uncertainties. We did sensitivity studies varying desorption lifetime of water in the range of 10^{-12} – 1 s, and found that the growth curve is insensitive to τ_d as long as it is below 10^{-7} s. We will add the following sentence to the revised manuscript.

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“A sensitivity study on $\tau_{d,w}$ showed that the growth curve is insensitive to $\tau_{d,w}$ as long as it is less than 10^{-7} s.”

Referee Comment 4:

In the case of DOP evaporation, the desorption lifetime of DOP is assumed to be 10^{-6} s; however, the basis of this assumption is not stated nor is any citation given. Later the authors indicate that the desorption lifetime showed practically no effect. How much did the authors vary the desorption lifetime in their calculations? This information should be included.

Response:

We varied $\tau_{d,DOP}$ in the range of 10^{-12} – 1 s and saw practically no effect. As DOP molecules are larger and heavier than H₂O molecules, we assumed that the surface residence time of DOP is longer than the one of H₂O inferred from molecular dynamics simulations ($\tau_{d,DOP} = 10^{-6}$ s vs. $\tau_{d,H_2O} = \sim 10^{-11}$ s). We will add this information in the revised manuscript.

Referee Comment 5:

The authors could consider adding a shaded region to the modeling figures to represent some measure of the uncertainty associated with model results.

Response:

Thanks for the suggestion. For water condensation the variation of growth curve associated with different accommodation coefficients give the sensitivity of the model. As this paper is basically the model development and demonstration paper, we would rather not add further details to Fig. 3 (organic evaporation) and Fig. 4 (oleic acid ozonolysis). We intend to perform comprehensive systematic sensitivity studies and will provide uncertainty estimates in the follow-up studies.

Referee Comment 6:

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In the modeling of oleic acid ozonolysis, the bulk diffusion coefficient of oleic acid was 1.88×10^{-7} cm²/s. In the previous KM-SUB model, the bulk diffusion coefficient of oleic acid used in fitting the experimental data was 10⁻¹⁰ cm²/s, three orders of magnitude slower than the current model parameter. How do the two models compare when the same model parameters were used?

Response:

In the KM-SUB paper 10⁻¹⁰ cm² s⁻¹ was assumed. After work of Shiraiwa et al. (2011), we know bulk diffusivity can be well estimated using the Stokes-Einstein equation if its viscosity is known. The refinement of D_b did not affect the simulation results because oleic acid ozonolysis is limited by accommodation. We will add the following sentence in the revised manuscript.

“Note that in our earlier studies D_b for oleic acid was assumed to 10⁻¹⁰ cm² s⁻¹ (Pfrang et al., 2010; Shiraiwa et al., 2010), but here we provide a better estimate of 1.9×10^{-7} cm² s⁻¹.”

Referee Comment 7:

One of the novelties of the new KM-GAP model is that it considers gas-particle partitioning of reaction products. For ozonolysis of oleic acid, evaporation of nonanal appears to decrease the particle size. Is there any experimental evidence in the literature to support or contradict this conclusion? Are the results from Katrib et al. 2005 and Sage et al. 2009 consistent with the calculations?

Response:

Katrib et al. (2005) observed the evaporation of nonanal upon oleic acid ozonolysis. As they did not quantify it, we cannot directly compare with this study. Sage et al. (2009) observed that only 1.5% of the original oleic acid mass was lost by volatilization of the reaction product nonanal within a reaction time of several hours (KM-GAP + Ziemann data suggests ~20%). The discrepancy might be due to additional, previously

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unrecognised secondary chemistry involving the carbon backbone or heterogeneous uptake of nonanal to the particle (Sage et al., 2009), which are not considered in this study. These processes could be implemented in KM-GAP if kinetic parameters for secondary reactions system would become available. We will add below sentences in the revised manuscript.

“Sage et al. (2009) observed that only 1.5% of the original oleic acid mass was lost by volatilization of the reaction product nonanal within a reaction time of several hours. The discrepancy might be due to additional secondary chemistry involving the carbon backbone or heterogeneous uptake of nonanal to the particle, which are not considered in this study. These processes can be implemented in KM-GAP when the relevant kinetic parameters of secondary reactions can be determined or estimated, which is a target for follow-up studies but goes beyond the scope of this study introducing the new model approach.”

Referee Comment 8:

The authors have chosen to model two single-component systems (condensation of water onto Ag nanoparticles, evaporation of DOP) that can be predicted with simple theory (such as droplet growth theory). For these systems the authors could do a better job of highlighting the benefits of their complex model compared with simple theory. Alternatively, the authors may want to model a more complex system (in addition to oleic acid ozonolysis) to illustrate the novelty of the KM-GAP model.

Response:

Thanks for the suggestion. A follow-up study on water condensation including comparison with simple theory is currently under way. More complex systems with multiple different species, reactions, and phase states go beyond the scope of the present study (model description and applicability) but will be investigated in further follow-up studies.

Referee Comment 9:

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On page 33693, line 5, the authors state “all steps of mass transport and chemical reaction from the gas phase to the particle core are considered,” which is consistent with the rest of the text and figures. In the following paragraph (lines 11-13), however, when describing Figure 1, layers beyond the near-surface bulk are not included. The strata beyond the near surface bulk layer should be added here.

Response:

Thanks for pointing it out. We will correct it in the revised manuscript.

Referee Comment 10:

Figure 5 caption reads (a) ozone, (b) oleic acid, (b) nonanal, and (d) non-volatile products. This should read (a) ozone, (b) oleic acid, (c) nonanal, and (d) non-volatile products.

Response:

Thanks for pointing it out. We will correct it in the revised manuscript.

References:

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Sage, A. M., Weitkamp, E. A., Robinson, A. L. and Donahue, N. M.: Reactivity of oleic acid in organic particles: changes in oxidant uptake and reaction stoichiometry with particle oxidation, *Phys Chem Chem Phys*, 11, 7951-7962, 2009.

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