Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Insights into the morphology of multicomponent organic/inorganic aerosols from molecular dynamics simulations" *by* Katerina S. Karadima et al.

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(1) *The topics of particle morphology, salting-out effects of ions on organic compounds and liquid–liquid phase separation in multicomponent aerosol particles are of great interest in the field of aerosol science and atmospheric chemistry and physics. Karadima et al. performed a series of molecular dynamics simulations of nanometer-sized particles using ammonium and sulfate ions as well as water molecules as inorganic components combined with organic components of different functionalities and hydrophilicities. They describe the observed morphologies, including the prevalent feature of phase separation and the propensity of hydrophobic organic compounds to diffuse to*

the particle surface layer as a function of system composition at different water contents. This concise article discusses interesting insights about the internal structures of nanoparticles. It is very well written and accompanied by an appropriate set of high quality figures and tables. I found only a few minor issues that are suggested to be addressed by the authors. These are listed in the following.

We thank the reviewer for the comments and suggestions. Our responses (in regular font) and corresponding changes to the manuscript are given after each comment (in italics).

General comments

(2) *On page 8, lines 4, it is stated that the E-AIM model was used to estimate the equilibrium RH for the particles studied. As far as I understand, the reported RH is equivalent to the computed water activity in the particles, which was determined here by the mole fractions of water, ammonium and sulfate ions (were the organics considered in the calculation?).*

The reviewer is correct; the reported RH is indeed equivalent to the predicted water activity in the particles. The values shown now in Tables 1 and 2 do not include the organics in the calculation. This is now explained using a footnote in the tables and the text. We repeated the RH estimation considering the hydrophilic organics in E-AIM assuming an ideal solution. The effect in most cases was a change of the RH by 1-2 percent. The highest effect was at the low RH simulations like Case 20 in which the RH changes from 40 to 31 percent. We have also estimated the RH using the concentration of the water molecules in the gas phase. In all cases this value was just a few percent different than the value based on particle thermodynamics. In some cases the RH calculation based on the number of water molecules is quite uncertain because there are only a few such molecules in the simulation cell. This information has also been added to the paper.

(3) *Therefore, the approximate RH values, reported in Table 1 and the text, represent the equilibrium RH of macroscopic (bulk) solutions of the considered compositions, but most likely not that of nanometer-sized particles. At the particle diameter scale of this study, the Kelvin effect is non-negligible (a factor of about 1.3 - 1.6 here scaling the water activity) due the large surface area to volume ratio, which should be considered with the Köhler equation to determine the appropriate equilibrium RH. As a consequence, 40 percecnt RH may actually be about 55 to 60 percent in equilibrium with these particles and the higher (bulk equilibrium) RH values reported may represent water vapor supersaturation conditions when the Kelvin effect is considered. Ideally, the equilibrium RH would be computed from the simulated gas phase water vapor mixing ratio in the simulation domain; however, I understand that for the chosen small domain size, there is hardly a single water molecule in the gas phase, which renders that approach inadequate. The authors should address this issue by either adjusting the reported RH or by clearly stating that the values are a reference referring to bulk equilibrium conditions and not to nanoparticles.*

The reported values refer to the bulk equilibrium conditions and this is now clearly stated in Section 2.3 and Tables 1 and 2. The estimation of the magnitude of the Kelvin effect in these particles is quite uncertain given that in a lot of the investigated systems (e.g., pinonic acid) the organic acts as a surfactant. As a result, the magnitude of the Kelvin effect, depending on the assumed surface tension, can be as high as the reviewer suggests, but also much lower just a few percent. The estimated RH values based on the concentration of the water molecules in the gas phase suggest though that the Kelvin effect (based on the simulation itself) is small and increases the reported values by only a few percent. We now stress this uncertainty of the estimated RH in the revised manuscript. Please note that this uncertainty in the RH does not affect the major conclusions of the paper.

(4) *Repeatability of the simulated structures. Most of the simulation results were obtained by considering a 10 ns time period at the end of a simulation, after allowing*

particle formation, diffusion and relaxation. While this seems to be an adequate procedure, some of the structures observed, especially cases like the one shown in Fig. 7 or Fig. 11d,g, raise questions about the repeatability of these structures (i) when the initialization of the simulation is changed (which is briefly discussed in Section 3.6.2) or (ii) whether such structures are long-lasting equilibrium or rather transient, metastable configurations.

Most of the systems were discussed in the paper were simulated twice. This includes the systems mentioned by the reviewer (shown in Figures 7 and 11). The repeated simulations started from different initial system configurations (different atoms positions and initial velocities). The differences in the final particle morphologies were minor. For example, for the particle shown in Figure 7 (n-eicosane, ammonium sulfate and water), the second simulation resulted once more in three inorganic regions and one extended alkane phase. It is interesting that the two simulations reached this structure following different paths; initially the corresponding particles had a different number of inorganic regions but then these merged to the three regions. For the particles shown in Figure 11d and Figure 11g (n-triancontane, CPA, ammonium sulfate, and water) the final complex structures were also very similar. We have added a detailed discussion of the repeatability of our simulated structures starting from different initial conditions in the revised paper. We have also added pictures of the resulting particles in the SI.

(5) *In the case shown in Fig. 7, one could imagine that the true thermodynamic equilibrium configuration (lowest Gibbs energy state) would favor merging of the three distinct aqueous inorganic phases into a single, larger aqueous inorganic phase of smaller surface area, phase-separated from the eicosane-rich phase. Have repeated simulations always resulted in three distance-separated aqueous phases (each of which of similar composition) in the case of this system? Also, would it be possible that the three aqueous ion-rich phases would merge on a substantially longer (but reasonable) time scale, say ms to seconds time rather than the 60 or 100 ns simulated. In other words, how sure are the authors that the simulation results are reflecting stable thermody-*

namic equilibrium configurations? Considerations of the limited simulation time scale and the procedure followed for initializing the simulations may then also be discussed in the context of the structures IIa vs. IIb shown in Table 2. An extended discussion on such aspects and potential implications for larger particle sizes (tens to hundreds of nm diameter) would be of interest to the community.

We also expected the formation of a single region, but in our simulations for this system we got twice the same three regions. In both simulated systems, the hydrophilic regions were quite far away so as not to interact due to the intermediate hydrophobic region. Starting from the moment of the particle formation the system's potential energy decreased gradually and reached a plateau at the middle of the simulation period as the particle was approaching the final configuration. The system's energy fluctuated (plus or minus 2 percent) around this low energy value for the second half of the simulation period. The difference of the potential energy between the two final configurations in the repeated simulations of this system was less than 1 percent. Of course, given the duration of our simulations we cannot guarantee that the three aqueous structures will not merge at much longer timescales. Please note that while the presence of these three regions even at short timescales is intriguing, the main characteristic of these particles is not the exact number of the hydrophilic regions, but that fact that the particles are inhomogeneous and phase separated. We did simulate a few systems (e.g., systems 14 and 25, the particle of simulation 25 is shown in Figure 11d) twice as long and we did not observe any changes in the particle morphology. System 14 is one of the structures of type II mentioned by the referee. The above discussion has been added to the revised manuscript.

Specific comments

(6) *Page 2, lines 20 - 22: Consideration of the effect of organic coatings/films/phases on the formation of cloud droplets have also been central topics in key studies by Ruehl et al. (2014; 2016) and Ovadnevaite et al. (2017).*

We have added the Ruehl et al. (2014) and Ovadnevaite et al. (2017) references and corresponding discussion to the Introduction.

(7) *Page 3, line 1: "surface partitioning" is bulk–surface partitioning meant?*

Yes. It is clarified now in the revised text.

(8) *Page 3, lines 12 - 19: In addition to the cited experimental studies, the application of thermodynamic equilibrium models have also provided valuable insights into the factors of organic–inorganic interactions and composition ranges of liquid–liquid phase separation, e.g. the works by Zuend et al. (2010), Zuend and Seinfeld (2012), Renbaum-Wolff et al. (2016), Pye et al. (2018). Conclusions from such studies for the mixing in (non-nanoscale) aerosols are in agreement with the statement made in the last paragraph of Section 4 in this article. The authors may want to extend the discussion on Pages 3 and 21 considering those studies.*

This is a good point. A discussion of the above publications has been added in the Introduction but also in the Conclusions.

(9) *Page 4, line 2: "theoretical and kinetic models". What do you mean by theoretical; are you referring to thermodynamic models? The latter are not more or less "theoretical" than kinetic models.*

We have rephrased this rather confusing sentence.

(10) *Page 4, line 29: phrasing: "liquid either glassy"*

We have followed the reviewer's suggestion.

(11) *Page 5, line 21: spelling: carboxyl (not carboxylic)*

The typo has been corrected.

(12) *Page 16, line 12: I think "Fig. 11d-e" should be Fig. 10d-e.*

The figure number was corrected.

(13) *Page 17, lines 1-4: Fig. 11 should be Fig. 10 in all instances there.*

The figure numbers were corrected.

(14) *Page 20, line 9: correct phrasing of "salt aqueous solutions".*

We have rephrased this.

(15) *Page 20, line 15: in this comparison with experimental studies, especially regarding a potential size effect on phase separation, it would be useful to further discuss the simulation results compared to the experimental findings under different particle drying rates by Veghte et al. (2013) and by Altaf and Freedman (2017).*

We have followed the reviewer's suggestion and added the corresponding discussion.

(16) *Fig. S23 of the Supplement is neither discussed/mentioned in the main text nor the supplement text.*

Figure S23 is now mentioned in Section 3.5.2.