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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) *This manuscript describes the morphology of mixed organic-inorganic nanoparticles under different composition regimes and environmental conditions (particularly RH) according to molecular dynamics simulations. The methods draw heavily upon a previously peer-reviewed paper by the first author (from 2017). The manuscript is written clearly and presents a concise summary of the diverse morphologies that can result from their prescribed conditions. The material is relevant for the ACP community and merits publication after the following comments have been addressed, many of which will likely not affect the conclusions.*

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Discussion paper

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

(2) *For a volume that corresponds to 1 atm and 320 K for the system sizes studied, should there not be about 3 to 9 water vapor molecules per 100 M molecules (N2 or O2) for the RHs described?*

The estimate of the reviewer is correct. Based on this we reexamined the partitioning of the water molecules between the gas and particulate phases focusing on the water molecules that were found near the particle surface. These molecules were included in the particulate water initially. We have corrected this in Table 1 and changed the average number of water molecules in the two phases accordingly. A brief discussion of this point has been added to the revised paper.

(3) *Is a vapor phase necessary at all? While NPT at 1 atm better reflect experimental and ambient conditions, the barostat used provides isotropic dimension rescaling (i.e., volume rescaling). When simulating a condensed-phase surrounded by "gas", this rescaling should have little effect on the condensed phase as the gas-gas and gas surface interactions are infrequent over the simulation timescales used in this work (approximately 1 collision per 10 ns?). The condensed-phase properties are therefore maintained primarily by the force field parameterizations, and similar results should be obtained with NVT simulations with no gas-phase molecules for these "low" pressures (and is more often used in such studies).*

We agree with the reviewer that for the reasons mentioned the effect of the gas phase in these simulations is probably of secondary importance. However, it is not negligible. The frequency of collisions for example for system 1 was 2 collisions per 10 picoseconds (much higher than the estimated value above). Apart from the force field choice, the statistical ensemble choice is also important for a MD simulation. The NPT statistical ensemble used allows more precise condensed–phase density calculations.

The NVT statistical ensemble is usually chosen when the simulation focuses on conformational properties in vacuum without periodic boundary conditions. The periodic boundary conditions are essential for the electrostatic energy calculations in our simulations. The above discussion has been added to the paper.

(4) *Is acid deprotonation neglected in these simulations?*

The organic acids used in the investigated systems are quite weak, so their deprotonation has been neglected. This is now explained in the manuscript.

(5) *While SPC/E is commonly used, other researchers have previously found polarizable force fields for water to be important for determining distributions of sodium and chloride ions in a system with an air/water interface (Jungwirth and Tobias, 2000). Some mention should probably be made especially for interpreting the morphology from the organic-inorganic-water system?*

SPC/E is a simple model with low computational cost, which includes a term for the polarization energy. We believe that a polarizable force field for water would not result in different morphologies in our cases. The distributions of sulfate and ammonium ions inside the simulated particles are in agreement with those reported by Jungwirth and collaborators (Gopalakrishnan et al., 2005; Jungwirth et al., 2005), who have used polarizable models for ammonium sulfate aqueous solutions. The repulsion of all the ions from the surface region, the ammonium slight preference for the surface, and the increased concentrations of ions near the core reported in the corresponding studies are also observed in our study. Following the reviewer's suggestion, we have added a brief discussion of this topic.

Gopalakrishnan, S., Jungwirth, P., Tobias, D. J. and Allen, H. C.: Air-liquid interfaces of aqueous solutions containing ammonium and sulfate: Spectroscopic and molecular dynamics studies, J. Phys. Chem. B, 109, 8861–8872, 2005.

Jungwirth, P., Rosenfeld, D. and Buch, V.: A possible new molecular mechanism of thundercloud electrification, Atmos. Res., 76, 190–205, 2005.

(6) *While difficult to generalize these findings at this stage, one conclusion put forth is that the diversity in heterogeneities can result but are currently not well-represented by chemical transport models. On this point, sometimes it is unclear what are surprising findings from this work vs. what was known previously (from experiment or MD simulation). The phase separation of organics by O:C is discussed by the authors, but the dependence of bulk-surface partitioning of mildly soluble species on concentration and composition is of course known (e.g., also demonstrated in molecular simulation by Hede et al. 2011 cited by the authors), and is anticipated by the Gibbs adsorption isotherm (and more recently by a finite volume model - Malila and Prisle 2018). Phase separation among immiscible organics have been investigated by Ye et al. (2016). Organic islands have been found in experiments (Garland et al. 2008) and in simulation (Hede et al. 2011). Also, aspherical droplets due to water-organic interactions have previously been reported in several papers by Zachariah and co-workers (including that already cited by the authors in the introduction).?*

Our comment here was related to chemical transport models that assume that all or at least all the secondary organics in the particles dissolve in the aqueous phase. The reviewer is correct that there has been a lot of work in previous experimental and theoretical studies, but this work has not found its way yet to most chemical transport models. This is now explained better in the revised paper. While parts of our work are in agreement with existing experimental results (this is encouraging) and other theoretical studies using rather different approaches, this is one of the first efforts trying to examine relative realistic atmospheric particle compositions and multiple organic compounds. This approach promises to synthesize the previous studies which had more limited scope. The most surprising result of our work is probably the structure of the particles containing multiple organics. The discussion in Section 4 was extended so as to include the above points.

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