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

Anonymous Referee #2

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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.

For a volume that corresponds to 1 atm and 320K 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?

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 a NVT simulations with no gas-phase molecules for these "low" pressures (and is more often used in such studies).

Is acid deprotonation neglected in these simulations?

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.

Jungwirth, P., Tobias, D.J., 2000. Surface Effects on Aqueous Ionic Solvation: A Molecular Dynamics Simulation Study of NaCl at the Air/Water Interface from Infinite Dilution to Saturation. J. Phys. Chem. B 104, 7702–7706. https://doi.org/10.1021/jp000941y

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).

Malila, J., & Prisle, N. L. (2018). A monolayer partitioning scheme for droplets of surfactant solutions. Journal of Advances in Modeling Earth Systems, 10. https://doi.org/10.1029/2018MS001456

Garland, E.R., Rosen, E.P., Clarke, L.I., Baer, T., 2008. Structure of submonolayer oleic acid coverages on inorganic aerosol particles: evidence of island formation. Physical Chemistry Chemical Physics 10, 3156–3161. https://doi.org/10.1039/B718013F

Ye, J., Gordon, C.A., Chan, A.W.H., 2016. Enhancement in Secondary Organic Aerosol Formation in the Presence of Preexisting Organic Particle. Environ. Sci. Technol. 50, 3572–3579. https://doi.org/10.1021/acs.est.5b05512

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