

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

Anonymous Referee #1

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1 Synopsis

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

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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.

2 General comments

- Equilibrium relative humidity (RH) reported is not accounting for size effect. 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?). 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 % RH may actually be about ~55 to 60 % RH 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

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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.

- 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. 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 thermodynamic 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.

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3 Specific comments

1. 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).
2. Page 3, line 1: “surface partitioning” is bulk–surface partitioning meant?
3. 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.
4. 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.
5. Page 4, line 29: phrasing: “liquid either glassy”
6. Page 5, line 21: spelling: carboxyl (not carboxylic)
7. Page 16, line 12: I think “Fig. 11d-e” should be Fig. 10d-e.
8. Page 17, lines 1-4: Fig. 11 should be Fig. 10 in all instances there.
9. Page 20, line 9: correct phrasing of “salt aqueous solutions”.

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10. 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).
11. Fig. S23 of the Supplement is neither discussed/mentioned in the main text nor the supplement text.

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