Review of Molecular dynamics study on the liquid-liquid contact angle in liquid-liquid phase separated aerosols

In the manuscript titled *Molecular dynamics study on the liquid-liquid contact angle in liquid-liquid phase separated aerosols* Zhang et. al. present MD-simulation-based calculations of the liquid-liquid contact angles in partially engulfed liquid-liquid phase separated (LLPS) aerosol. Indeed, the particle morphology, as well as the partitioning of components can drastically impact aerosol growth kinetics, therefore knowing the morphology of nanoparticles, whose size falls below the experimentally accessible size range is important and timely. The choice of molecular dynamics as a method to estimate contact angles and particle morphology is also appropriate. Therefore the paper could represent a significant contribution to our understanding of LLPS aerosol, however, to be publishable in ACP, some major concerns need to be addressed.

I. Major revision items:

I.1) In its current format the paper provides detailed a phenomenological description of the impact of temperature, concentration of multiple atmospherically relevant components (salts, water, organic acids and alkanes), and retrieval method on the contact angle in LLPS droplets. However, it only marginally mentions atmospheric impacts and does not provide any quantitative analysis of how these results affect main properties needed to describe growth kinetics or aerosol thermodynamics. I believe that ACP's focus is on atmospheric science and therefore a direct link between the MD data and for instance estimated growth timescales, water uptake kinetics, Kohler curves etc. would significantly improve the fit of this manuscript to the journal's scope. Please add model calculations (e.g. gas to particle partitioning) that link the phenomenological description to atmospheric impacts.

I.2) I am concerned about the use of two relatively outdated coarse grained potentials. The OPLS-UA appears to be justified for aqueous system, and indeed it has the SPC/E water which is atomistic, even though it is known to have some discrepancies which might impact current calculations. In particular the liquid phase tends to retain unphysical planar molecular structures which may impact the surface tension calculations and the interfacial structure between the polar and the non-polar phases. The Martini forcefield, on the other hand, is extremely problematic: its water representation consists of a bead which collectively represents 4 water molecules, which definitely impacts pressure tensors as well as interfacial structures. Further, as the authors also realise it shows artificial phase separation and really low surface tension values (much below the experimental value), which is expected due to the number of water beads' impact on the pressure tensors. Based on the limitations of both models, I suggest the authors to remove the Martini forcefield and compare the OPLS-UA with a more up-to-date atomistic potential (e.g. OPLS-AA with SPC/E, CHARMM or AMBER with TIP4P or TIP5P).

II. Minor revision items:

II.1) Please add more information about the MD simulations in the methods section of the main text. (Temperatures, type of thermostat, barostat if applicable, type of long-range treatment, software used, length of equilibration and production, how was equilibration monitored, how were the systems prepared).

II.2) The geometrical contact angle retrieval method used in this manuscript heavily relies on the assumption that the droplets assume a spherical cap geometry, which is known to be false for droplets with radii inferior to 7 nm, as the amplitude of capillary wave fluctuations that perturb all fluid interfaces becomes comparable to the droplet radius below such cutoff diameters. Please present the temporal evolution of a sphericity metric for both partial droplets to justify the validity of the spherical cap approximation.

II.3) Depending on how the systems were prepared, sessile droplet-style contact angle simulations can be easily trapped in metastable states (e.g. when water droplets on solid surfaces are initiated from a cubic water slab or perfectly spherical droplet is placed on top of the surface). The theoretically correct way to prepare such systems is to allow the two phases to collide and assume their equilibrium shape within the simulation. State how the systems were prepared and how thermodynamic equilibrium was ensured. Present (at least in supporting information) the time evolution of the droplet morphology (contact angle) at least for the slowest evolving system (likely the largest number of atoms with the lowest temperature)

II.4) Please comment on how relevant the chosen particle size (up to 20 nm) for real atmospheric particles is.

II.5) In Section 3.4 the authors state that water-organic interface is « a plate ». Can you support this statement by snapshots from the simulations zooming on the interfacial zone?

II.6) Comparison of the simulated surface tensions (Figure 8) with earlier MD-data obtained with identical potentials is not necessary. It could be moved to the SI as consistency check, if the authors wish to present it.

III. Editorial comments:

III.1) line 117: were consisted —> consisted

III.2) line 202: under the same temperature condition would read better as at the same temperature.

III.3) line 206 mechanisms of temperature and water content would read better as effects/ impacts of temperature and water content.

III.4) line 232 is presented —> is present

III.5) line 250 mass centre —> centre of mass

III.6.) In the left panel of Figure 6 the periodic image of the aqueous droplet clearly comes from incorrect treatment of periodic boundaries by the visualisation software and should be removed.

III.7) line 519 adsorption coefficient —> absorption coefficient