

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2020-1329

Anonymous Referee #2

Referee comment on "Energetic analysis of succinic acid in water droplets: insight into the size-dependent solubility of atmospheric nanoparticles" by Chuchu Chen et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-1329-RC2>, 2021

Chen et al. report results of a comprehensive study of the bulk/surface partitioning and its energetics of aqueous succinic acid solution nano-droplets using MD simulations. The authors use established methods to obtain the potential of mean force (PMF) experienced by a succinic acid molecule along a reaction coordinate across the liquid-vacuum interface and discuss the effects of curvature on the energetics.

The study is carefully conducted and sound, and the results are interesting from a molecular perspective. However, given the scope of ACP, the authors should reflect more thoroughly on relevance of this work in the atmospheric context. This is important particularly in the light of earlier investigations (especially Werner et al. 2016 which the authors cite) that found the direct changes in CCN activity due to the surface composition in this system to be rather insignificant. It therefore remains to put the current results better into an atmospheric context and emphasize their relevance. Furthermore, the readability and the language of the manuscript needs to be reviewed and improved, and key concepts clarified throughout the manuscript, where possible.

I therefore feel that this manuscript requires major revision before it can be published within ACP, and elaborate further on these comments in the following:

General comments:

- A more elaborate and specific discussion about the relevance for atmospheric chemistry and physics is missing especially in Abstract, Introduction and Conclusions, given the placement in this journal. How are the simulations of nanometer-sized droplets relevant in the atmosphere? What is the relevance of the studied system (i.e. succinic acid)? What implications might the observed phenomena have and can they be generalized to

a larger set of atmospherically relevant compounds? Can the authors please put their results in a larger context to link the physical chemistry results of their work to atmospheric processes? Where will these results lead?

- Furthermore, a brief discussion on the applicability, strengths and weaknesses for this type of molecular dynamics simulations in addressing the problem of atmospheric phase state would be appropriate under Results and Discussion.

Specific comments:

- Please simplify the last sentence of the abstract: "Meanwhile, structural analyses, however, ..." (remove "Meanwhile"?)
- Introduction: "compositions" -> "compounds"?
- Throughout the manuscript: Please check the use of tenses ("was" vs. "has been" vs. "is").
- L 4: remove "area"?
- L 36: Which "observed phenomenon" do you mean? Please specify.
- L 39: "Higher relative humidity" than what? Please specify. Please also clarify the the connection to the following sentence starting with "And Cheng et al. (2015)...". Please clarify what exactly you would like to say with these two sentences.
- L 43: "is dependent" -> "depends"
- L 55: Werner et al. 2016 also state that "... this direct effect of the aqueous surface composition on the CCN activation is very small...". Please re-phrase.
- L 58: "organic composition solvation" -> "organic compound solvation"
- L 59: "surrogate" of what?
- Top of page 4: I have concerns about the restraining potential (top of page 4) preventing water molecules to evaporate: Droplets of such small sizes undergo relatively strong deforming fluctuations which would be dampened by the artificial potential if the allowed radius is too small. How do the authors exclude this to be significant for the interfacial structure? From own MD simulations we obtain the radius fluctuation's amplitude to be $\sqrt{(\Delta r)^2} \sim 0.15$ nm for a droplet of average radius $\langle r \rangle = 4$ nm at a temperature of $T = 280$ K. Can the authors confirm this and put the result in relation to the width of the restraining potential?
- L 107: How is the thickness of the spherical shell determined? Please add the unit of Δr .
- Eq. 5: Why not just refer to Eq. 3 which is identical?
- Eq. 4: The shape of the harmonic umbrella potential has already been defined in Eq. 1, it is sufficient to mention that the radial distance from the droplet center is replaced by the distance from the slab center perpendicular to the surface with corresponding spacings along the reaction coordinate and refer to Eq. 1.
- Fig. 1: There are numbers missing on the r-axis of the figure - I can only guess that the tick marks are at -1 and 1 nm, respectively?
- Fig. 1: Where exactly is the succinic acid molecule when it is in the PMF minimum at the interface? Is it "on top" of the water molecule's instantaneous surface (in the sense of Willard & Chandler, J. Phys. Chem. B, 2010) or fully hydrated?
- L 140 ff: what does it mean to "statistically" calculate or average? Please revise or remove.
- L 143: I assume that Eq. 7 was fitted to the density profiles and not the other way around?
- L 150: Could the authors more precisely describe "minimum at the surface region"? It would be interesting to know whether or not the succinic acid molecule is fully hydrated in this "surface state" or if it rather lies "on top" of the instantaneous liquid surface, see

earlier comments on Fig. 1.

- L 155: ΔG_{sb} is a PMF difference and I would rather say the difference is larger for the droplets, the current phrasing depends on the reference.
- L 161: It might not be immediately clear to the reader what is "smaller"/"larger", the negative number or the difference. Maybe it would help to say "more/less negative"?
- L 177: "weaken" -> "weakened"
- 3a: both ΔG_{ba} and ΔG_{sb} are r-dependent. At what r were the values in Fig. 3a obtained?
- In the droplet case, the coordinate r is defined radially outwards from the COM of the droplet. In the PMF plots, the origin is moved to the interface. Is this still consistent with Eq. 3? Or are these different r's?
- L 180: Please rewrite "This result shows that different from thin slabs:" – do you mean "This results shows that nanodroplets behave differently from thin slabs."?
- L 194: The "slight jump in the internal PMF", is this the barrier-like bump located around $r = -0.5$ nm? Please rephrase for clarity. I'm also not quite sure what the "internal" PMF is.
- L 196: Do you mean "behavior" instead of "performance"?
- L 198: Please clarify what you mean by "more active molecule interactions..."
- L 206: What is the difference between "internal bulk" and "bulk"? Do the authors want to point out the difference between surface propensity of flat vs curved surfaces and isn't the bulk of the solution always bulk? If the latter is not the case, please precisely define "bulk" and "internal bulk".
- L 215: Constant with what? Slab thickness?
- L 233: As far as I understand, Wang et al. 2019 discuss capillary waves in slab simulations rather than droplets? Could the authors please elaborate on this point and/or provide a suitable reference, e.g. one of those referred to in the discussion of Wang et al. 2019?
- L 409-412: Please clarify how the uncertainty estimates presented in Fig. 5 are calculated. In particular, one would expect the uncertainties of the MOL-SOL contribution to be larger than SOL-SOL given the statistics (see especially Fig. 5c)?