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Comment on acp-2021-488

Anonymous Referee #1

Referee comment on "Molecular-scale description of interfacial mass transfer in phase-separated aqueous secondary organic aerosol" by Mária Lbadaoui-Darvas et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-488-RC1, 2021

The present paper aims at obtaining microscopic understanding of water uptake into inhomogeneous aerosols. I understand the importance of this topics, and the questions posed in Introduction and summarized in Conclusions are very interesting.
The authors adopted the steered MD to calculate free energy profiles. While the steered MD is proven to yield accurate and equivalent results of other methods based on equilibrium sampling in principle, the statistical accuracy should be carefully evaluated to confirm the convergence. My only and fundamental concern in this paper is related to the accuracy or the reliability of the results.

In the free energy profiles in Figure 2, I have some issues assessing the results. The following are the questions about the accuracy, and I wish the authors to address these questions.

* Free energy profiles should take asymptotic values in both ends of vapor and water phases. (Otherwise, the system size is not sufficient.) The calculated profiles do not seem to show the asymptotic values. Is this behavior acceptable?
* The difference in the asymptotic values should be consistent with the equilibrium vapor pressure of water. The author should confirm that the values are at least consistent with the vapor pressure in a semi-quantitative sense.
* The free energy profile in the water phase should be consistent with the density profile of water. This should be a consequence that the bulk water and the tagged water are identical.
In relation to this issue, the structure of Delta G profile in the water phase (s = 0 ~ 2 nm) is hard to understand. I might suspect that this is a kind of artifact?

I have also some questions about the usage of intrinsic surface analysis.

* Since the system in this paper contains two interfaces, water-hpca and hpca-vapor, there are two ways to define the intrinsic coordinate. Which interface was used to define the z coordinate? Does the choice affect the result of the profile?

* What is the merit of using the intrinsic coordinate in the present system? As far as I understand, the intrinsic coordinate results in an apparent layering structure of density profile, since it removes corrugation. However, Figure 2 does not show such apparent layering structure at 300 K. (Some structure is discernible at 200 K (Figure 2b), but I guess that liquid water at 200 K may not be realistic...)

Decomposing the free energy into energetic (enthalpic) and entropic contributions is known to be more challenging than the calculation of free energy itself. Usually, the decomposition requires more statistical sampling than the free energy calculation in one order of magnitude. Therefore, unless the authors confirm the statistical accuracy of the free energy, I could not evaluate the results of decomposition at present. The careful discussion on the accuracy of free energy calculation is required.