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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces" *by* Roope Halonen et al.

Anonymous Referee #2

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General Comments:

The authors calculate the collision rate of two sulfuric acid (SA) molecules in gas phase using atomistic molecular dynamics (MD) instead of the traditional hard sphere kinetic gas theory that is based on the diameter of sulfuric acid derived from its bulk liquid density. They benchmark two force fields for SA against ab initio results and conclude that an OPLS all-atom force field is better suited for the MD simulations. They find that the traditional kinetic gas theory underestimates the collision coefficient of two SA molecules by a factor of 2.2 compared to the MD simulations at 300 K. This discrepancy is consistent with empirical scaling used to match experimental new particle formation

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Discussion paper

(NPF) rates and with those from theoretical ones employing hard sphere kinetics. They also explore other simpler models for calculating collision coefficients such as Brownian coagulation and Langevin dynamics. They find that both simpler models perform better than hard sphere kinetics and that their accuracy depends on the velocity of the colliding sulfuric acid molecules.

The work is promising in that it charts a new way to incorporate accurate collision rates into NPF rate calculations. The collision rate corrections for other species involved in sulfate aerosol formation are presumably larger than those for sulfuric acid, making this work particularly important. However, the authors need to address one critical point before the manuscript's acceptance for publication. They have previously employed their Atmospheric Cluster Dynamics Code (ACDC) to calculate NPF rates for various sulfate aerosol systems.[McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., KurtelÌĄn, T., Kulmala, M., and VehkamaÌĽki, H.: Atmospheric Cluster Dynamics Code: a Flexible Method for Solution of the Birth–Death Equations, Atmos. Chem. Phys., 12, 2345–2355, https://doi.org/10.5194/acp-12-2345-2012, http://www.atmos-chem-phys.net/12/2345/2012/, 2012.] ACDC uses collision rates from hard sphere kinetics and evaporation rates from quantum mechanically derived Gibbs free energies to calculate the population of clusters and NPF rates. It would be appropriate for the authors to demonstrate how the cluster populations and NPF would change using collision rates from atomistic MD simulations. Such a comparison will also put the current work in the greater context of calculating NPFs which is the ultimate goal of studies like the current one.

Specific Comments:

1. Page 1, line 19: Define "impact parameter"

2. Page 2, line 8-10: The following statement is important enough to warrant a more detailed discussion. "In fact, it has recently been found that collision coefficients obtained in this way had to be scaled by a factor 2.3–2.7 to predict kinetically limited

nucleation rates in agreement with experiment, for a system containing sulfuric acid, dimethylamine and water (KuÌĹrten et al., 2014; Lehtipalo et al., 2016; KuÌĹrten et al., 2018).

3. Page 2, line 11: Define “capture rate constant” and how it differs from “collision rate constant”. If collision and capture rates are the same for the purposes of this work, the authors should stick with one or the other for the sake of clarity.

4. Page 3, Section 2.1: What are the exact forms of the Ding and Loukonen/OPLS force fields? What terms are included? Which one is more flexible? Including this information will be instructive to the reader.

5. Page 4, Figure 1: The authors should label the different hydrogen bonds in the figure to facilitate cross-referencing with the d[O. . .H] lines in Table 1.

6. Page 4, Table 1: It is curious that the authors benchmark the two force fields against a 2012 paper while more recent and more rigorous computational results should be available. The authors should reference other high quality works on the sulfuric acid dimer and justify their choice to use the 2012 paper as a benchmark.

7. Page 4, Table 1: It is curious why the authors use eV units for their $\Delta\Delta$E values while the most commonly used unit is kcal mol-1.

8. Page 8, line 16: “diameters of 49-127nm” seems incorrect. Perhaps the units are wrong.

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