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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.

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We thank referee #1 for the favourable assessment of our manuscript.

ad 1.
We thank the referee for bringing this very relevant paper to our attention – we will acknowledge it both in the introduction and the methods section. We have also prepared a 2D density map of collision probability as a function of impact parameter and relative velocity in a similar style as in the reference mentioned above (see Fig. 1). This will replace the original plot showing individual collision probabilities as function of impact parameter at a certain relative velocity in the results section. The original plot, including

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the new data at 250 and 400 K (Fig. 2), will be moved to the appendix.

ad 2.
We agree with the referee – we mainly included this section because the Brownian coagulation model was used in the papers emphasising the discrepancy between experimental data and kinetic modelling of new particle formation (Kürten et al. (2014) and Lehtipalo et al. (2016)), but it was not explained in detail there. We will add the following "disclaimer" to the section: "It should be noted that the model of Brownian coagulation does not describe the correct transport physics of collisions of molecules in the gas phase."

ad 3 and 4.
We thank the referee for pointing out this limitation in our simulations and analyses. As the referee pointed out, temperature has a double effect on systems of colliding molecules: first, the Maxwell-Boltzmann distributions of relative velocities are different, and second, the rotational and vibrational motion of the molecules are different. In the calculation of collision coefficients from both the MD simulations as well as simpler models such as the Langevin approach, the first point can be addressed by carrying out the integration over the appropriate velocity distribution. However, the second point requires carrying out MD simulations at different temperature. In order to check the effect of temperature on the collision probabilities, we have rerun MD simulations with a subset of impact parameters with initial rotational and vibrational energies corresponding to 250 K and 400 K, as typical atmospheric processes will happen in this temperature range. These additional simulations indicate however that the differences in collision statistics at 250 K, 300 K, and 400 K, at a given relative velocity, are very small (see Fig. 2). We therefore used the collision probability distributions calculated at $T = 300$ K, obtained for more values of b, to compute the collision rate coefficients and enhancement factors for the temperature range $T = 250 - 400$ K. In this range, the collision rate coefficient is found to increase slightly with increasing temperature. The increase is smaller than in kinetic theory, where $\beta \sim T^{1/2}$ (see upper panel in Fig. 3).

The Langevin model also has an explicit temperature dependence in the Maxwell-Boltzmann distribution, as well as a temperature dependence of the intermolecular interaction parameter ε. To address this we have carried out additional PMF calculations for the H_2SO_4 pair at $T = 250$ and 400 K. The collision rate coefficient obtained from the Langevin model in this temperature range is found to decrease with increasing temperature (see upper panel in Fig. 3). This is due to the neglect of the anisotropy of the dipole-dipole interactions in the Langevin model: at higher temperatures, the effect of anisotropy becomes less important and therefore the model overestimates the collision rate less, compared to lower temperatures.

In the temperature range 250-400 K, the collision enhancement compared to kinetic theory decreases with temperature both for the MD simulations, and the Langevin model. At higher temperatures, the enhancement factor obtained from the Langevin model approaches the MD value, for reasons discussed above (see lower panel in Fig. 3). As we are interested in atmospheric new particle formation, we are not interested in temperatures outside of this range in the present work. We will add this discussion (including Fig. 3) to the manuscript and simulation details and Fig. 2 will be added to a new section in the appendix.

ad 4.
Regarding the very last comment on the effect of collision rate enhancement on new particle formation rates, we note that in cluster dynamics codes such as ACDC (McGrath et al., 2012) detailed balance is assumed, and therefore global changes to the collision rates obtained by application of an enhancement factor are compensated by the corresponding changes in evaporation rates. However, in complex systems, individually changing collision rates for reactions that are close to the kinetic limit can change the preferred pathway for cluster growth, leading to different cluster distributions and particle formation rates.

We will add the following paragraph to the conclusions. "However, before we can quantitatively assess the influence of collision rate enhancement on atmospherical new

particle formation rates obtained from cluster dynamics models (for example ACDC, McGrath et al., 2012), it is necessary to obtain the enhancement factors for all the relevant collisions between clusters of different sizes and composition, as the pathway for growth may change–a formidable task, even if only the simplest acid-base clusters were considered. Future work therefore should also be aimed at finding simple models for predicting approximate rate enhancements, based on just a few physico-chemical properties, such as molecular structures, dipole moments or charge distributions, of the interacting molecules and/or clusters."

Full figure captions:

Figure 1: Heat map of the collision probability of sulfuric acid molecules plotted as a function of impact parameter b and relative velocity v obtained from molecular dynamics simulation. The squared impact parameter equivalent to the hard-sphere collision area ($b^2 = (2R)^2$) and the squared critical impact parameter obtained from the Langevin capture model (Eq. (9)) are indicated by the dashed red and the white lines, respectively.

Figure 2: Collision probabilities of sulfuric acid molecules, as a function of the impact parameter squared, for different values of the relative velocity, obtained from molecular dynamics simulation at 300 K (solid coloured lines), at 250 K (coloured dots) and at 400 K (coloured dots). The step-like collision probabilities for a hard-sphere model ($b^2 = (2R)^2$), or obtained from the Langevin capture model (Eq. (9)), are indicated by the solid black, and dashed coloured lines, respectively.

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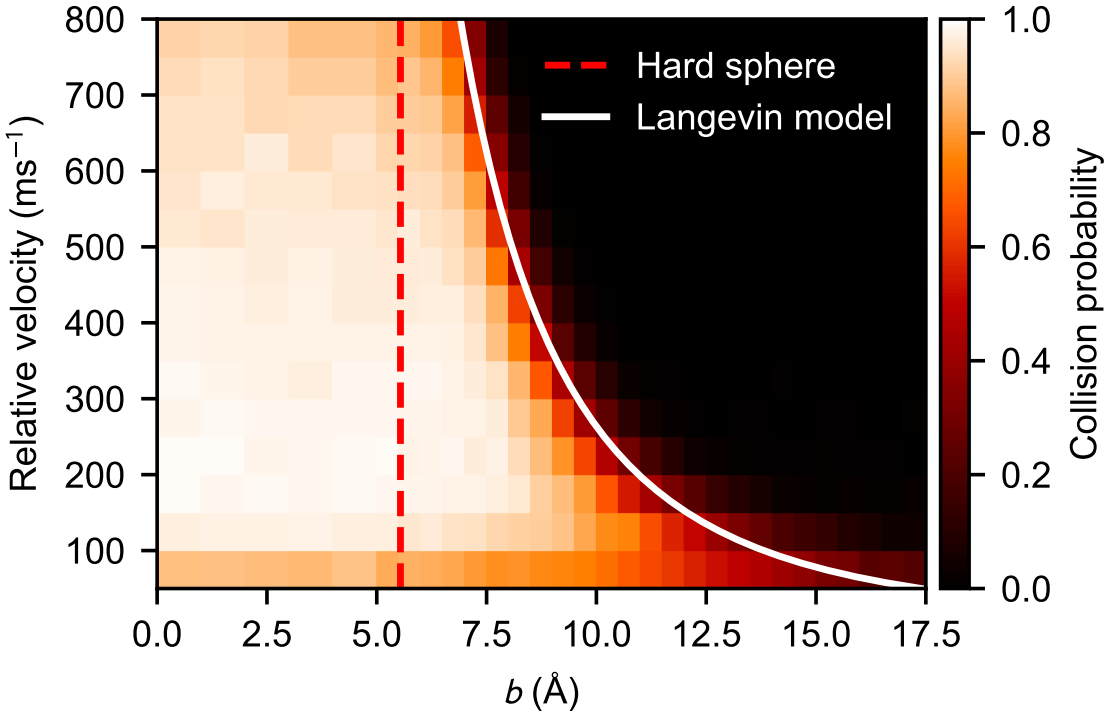

Fig. 1. Heat map of the collision probability of sulfuric acid molecules plotted as a function of impact parameter b and relative velocity v obtained from molecular dynamics simulation. The squared impact

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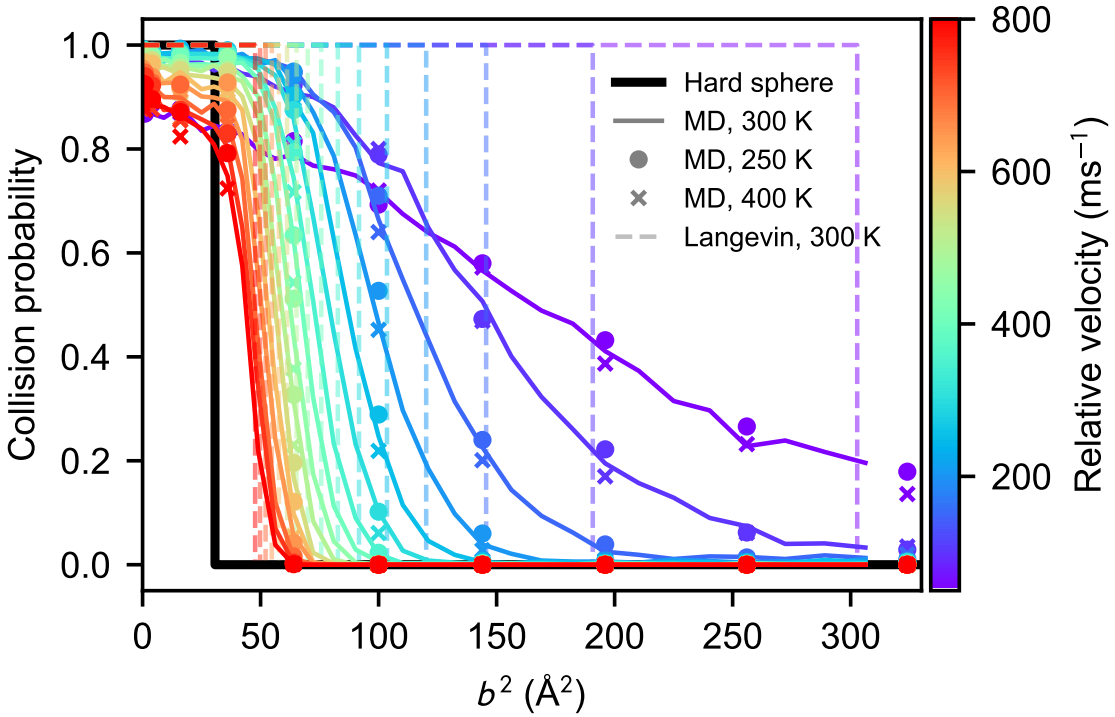

Fig. 2. Collision probabilities of sulfuric acid molecules, as a function of the impact parameter squared, for different values of the relative velocity, obtained from molecular dynamics simulation at 300 K (

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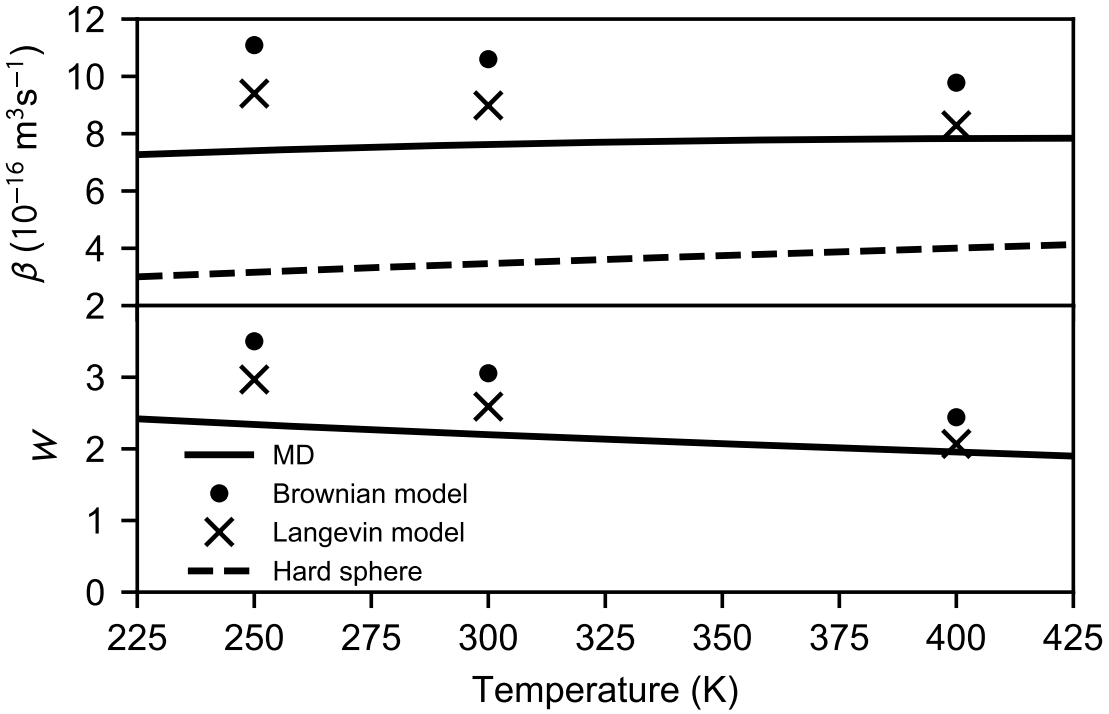

Fig. 3. Collision rate coefficient β (upper panel) and the enhancement factor W (lower panel) as a function of temperature calculated for the hard-sphere, MD, Langevin and Brownian approaches.

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