Dear editor and referee 1,

We sincerely thank referee 1 for their valuable feedback and corrections, which have helped to improve our manuscript. In the following, we provide point-by-point responses to general and specific comments. Referee comments are given in ***bold italic***, while responses are given in roman (non-bold, non-italic). Excerpts from the revised manuscript to support our responses are written in yellow highlight. The line and page number to which a response refers to, is indicated by (L### P#).

We hope that the revisions in the manuscript and our accompanying responses prove sufficient, rendering our manuscript suitable for publication in *Atmospheric Chemistry and Physics*.

We look forward to hearing from you at your earliest convenience and thank you for considering out manuscript for publication.

Best regards,

Huan Yang

Referee 1 comments

General comments

In this work, the authors developed an 'analytical interacting hard sphere' model based on an effective molecule-cluster potential using Hamaker's approach. This model is verified by comparison with point particle molecular dynamics and atomistic MD simulations. Overall, I enjoy reading this work, especially the discussion on relevant time scales, which I believe helps clarify confusions on the cluster formation process. However, I'm a bit doubtful about the applicability of the proposed methods and how much difference it makes compared to current approaches of calculating enhancement factors. The manuscript can be published after the following comments have been addressed.

We thank the referee for their overall positive assessment of our manuscript. Specifically, their praise for the relevant time scales section is appreciated as the time scale analysis results in a rational strategy for defining a "collision-sticking" event in the molecular dynamics sense. We understand that the referee has doubts about the necessity of the proposed models. We would like to clarify this point. The model introduces two extensions to the central field approach. The first, obtaining cluster-monomer interaction potentials from monomer-monomer potentials using Hamaker's approach, ensures that we do not have to obtain cluster-monomer potentials for each specific cluster through often costly and complex computational calculations. While the second extension, introducing a second collision criterion based on the sum of hard-sphere radii of the collision partners, doesn't produce a significant difference compared to the traditional central field approach for the acid-base systems studied here, it does lead to significant differences for other systems such as water and carbon dioxide (as is discussed in the main text P12&13 L330-340). These systems will be more closely examined in a follow-up paper.

Specific comments

In the discussion of the enhancement factor, I'd like to see comparisons with previous works (such as the work by Sceats). By doing so the readers can have a quantitively understanding of the difference between the current work and previous ones and decide whether to implement proposed model.

We thank the reviewer for the suggestion. Sceats [J. Colloid Interface Sci. 129, 1, 105 (1989)] provides a straightforward equation to determine the collision rate enhancement $1/W_{ij}(\infty)$ for interacting hard spheres in the free molecular limit,

$$W_{ij}(\infty) = \left(\frac{R_i + R_j}{R_T}\right)^2 exp\left(\frac{V_{ij}(R_T)}{k_B T}\right),$$

Where $R_i + R_j$ is the sum of hard-sphere radii, $V_{ij}(r)$ the effective interaction potential, k_B the Boltzmann constant and T the temperature. R_T is the distance at which the free energy profile $F(r)$ exhibits a maximum which results from the competing contributions of the attractive interaction potential, and the asymptotic decrease in free energy due to entropic contributions, $F(r) = V_{ij}(r) - k_B T \ln r^2$.

In our work, we have first calculated the interaction potential for "monomer-monomer" interactions from metadynamics simulations with an atomistic OPLS force field. These interactions were then fitted with a 12-6 Lennard-Jones potential. The effective monomer-cluster interactions in our interacting hard-sphere model were then obtained using Hamaker's approach and the Lennard-Jones parameters of the "monomer-monomer" interaction. In principle, a direct comparison of our work to Sceats' result is possible. However, we must note that due to the Boltzmann factor in eq. (9) of Sceats' paper, the resulting enhancement factor will critically depend on the accuracy of $F(r = R_T)$. E.g., an error of $k_B T$ in the value of $V_{ij}(R_T)$ would translate to an error of a factor 2 in the enhancement factor. For our test, we have also carried out additional free energy calculations, using Umbrella Sampling, to obtain more accurate free energy profiles for the atomistic "monomer-monomer" systems at these intermediate distances, which did not affect the Lennard-Jones parameters of the fitted interactions.

The collision rate enhancement factors obtained from our interacting hard-sphere model, collision MD simulations, and Sceats' formula, for collisions of H_2SO_4, and $(CH_3)_2NH$, respectively, with clusters $[HSO_4^- \cdot (CH_3)_2NH_2^+]_n$, are shown in Fig. 1. The MD and interacting hard sphere model data is the same as in Fig. 9 of the main paper. While the agreement between our model and the atomistic collision MD is acceptable, the enhancement factors obtained from applying Sceats' formula to the fitted interactions using Hamaker's approach in Eq. 13 in the main paper are significantly smaller over the entire range of cluster sizes. However, if we apply Sceats' formula directly to the interaction potentials obtained from the free energy calculation using the atomistic model for $n = 1$ (orange points in Fig. 1), we find good agreement with the atomistic collision MD results.

We conclude that calculating the collision rate enhancement using the central field approach in the interacting hard-sphere model is less sensitive to differences in the interaction potentials, compared to Sceats' formula, which only considers the strength of the interaction at the position of the free energy barrier. We believe that it is not necessary to include this discussion in the main paper, but we will explore this topic further in a future publication.
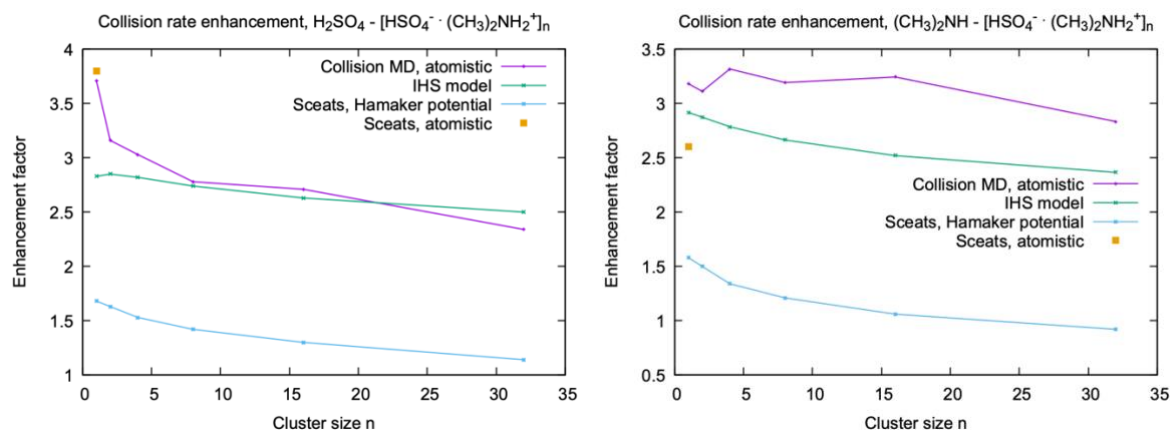
Figure 1: Collision rate enhancement factor comparison for collisions between H_2SO_4, and $[HSO_4^- \cdot (CH_3)_2NH_2^+]_n$ clusters (left), and $(CH_3)_2NH$ and $[HSO_4^- \cdot (CH_3)_2NH_2^+]_n$ clusters (right).

Although from the text one can figure out how to apply the proposed model, it is better if a step by step procedure is given in the supplementary information, specifying at each step what technique is used and what quantities are calculated.

We thank the reviewer for the suggestion. This will certainly help other researchers to apply the interacting hard-sphere model. We have added a step-by-step procedure of the entire workflow in the Supplementary Materials.

If one intends to do calculations for collision rates involving (SA)₁(DMA)₁ or other atmospherically relevant clusters, is it necessary calculate the interactions parameters with MD simulations? If this is the case, the applicability of the model is somewhat restricted.

Thanks for noting this point. Calculating the interaction parameters with MD simulations is not obligatory. Our model requires the values of monomer-monomer interaction parameters to derive the effective monomer-cluster interaction potential. The latter is then used in the analytical framework to compute monomer-cluster collision rate coefficient for arbitrarily sized clusters. In our manuscript, the monomer-monomer interaction parameters were computed from atomistic simulations, but in principle, one can use any Lennard-Jones 12-6 potential parameters directly taken from literature if the values are available.

The following changes have been made in the manuscript to demonstrate these points:

We note that, though in the current manuscript the monomer-monomer interaction parameters were obtained from the PMF calculated by atomistic simulations, they could in principle be taken directly from literature values, if available. (P10 L259)

Here, the underlying monomer–monomer interaction parameters were obtained from fitting Lennard-Jones potential to the monomer–monomer potential of mean force calculated from atomistic simulations, but we note that the monomer-monomer interaction parameters could also be obtained by other methods, or taken directly from literature values, if available. (P22 L516)

How to proceed with the model if the clusters are heterogeneous containing several types of 'monomers'?
The model can be conveniently extended to multi-component clusters containing several types of "monomers". The effective monomer-cluster potential derived from Hamaker's approach (Eq. 13 in the main text) is essentially a sum over the individual contributions of the monomer-monomer potentials. Therefore, for multi-component clusters, Eq. 13 can be used in a similar fashion, and the corresponding multi-component monomer-cluster potential is

$$-\frac{4}{(r^2 - R_c^2)^3} \sum_{i=1}^{\text{monomer type}} n_{c,i} \varepsilon_i \sigma_i^6,$$

where $n_{c,i}$ is the number of monomers of type i in the cluster, and ε_i and σ_i are the interaction parameters between a monomer of type i in the cluster and the free monomer colliding with the cluster.

The following changes have been made in the manuscript to clarify these points:

In Eq. 13, the effective monomer-cluster potential is essentially a sum over all individual contributions of the monomer-monomer potentials, which has two implications: First, the monomer-monomer potentials have to be pairwise in order that their individual contributions are additive. Hence, this approach is not suitable for non-pairwise interactions. Second, the approach can be conveniently extended to multi-component clusters containing several types of monomers. By using Eq. 13 in a similar manner, the corresponding multi-component monomer-cluster potential is $-4 \sum_i n_{c,i} \varepsilon_i \sigma_i^6 / \left(r^2 - R_c^2 \right)^3$, where $n_{c,i}$ is the number of monomers of type i in the cluster, and ε_i and σ_i are the interaction parameters between a monomer of type i in the cluster and the free monomer colliding with the cluster. (P7 L180)

Line 391: Some citations on the vibrational coupling between vapor molecules and clusters can be added here. For readers with no formal training in physical chemistry, this does not seem to be common knowledge.
We agree with the referee that we should be mindful of readers with no background in physical chemistry. As such, we have clarified the sentence.

We first differentiate the two types of monomer–cluster interactions influencing the cluster formation process: 1) the vibration and diffusion of a condensable vapor monomer on the cluster surface immediately after a collision, which, if successful, drives the cluster formation while storing excess energy due to bond formation (hydrogen bonds in this study), and 2) collisions between background carrier gas and the cluster, dissipating the excess energy and equilibrating/thermalizing the nascent cluster. (P16 L403)

Technical comments
In Fig. 4a, the horizontal white line in the middle should be removed.
The origin of the white line is that the graph is comprised of two separate data sets, for low ($v_0 < 1000 \text{ ms}^{-1}$) and high ($v_0 > 1000 \text{ ms}^{-1}$) relative velocities. We have removed the line in the revised figure and added a clarification in the figure caption:

Figure 4. Collision probability and critical impact parameter. Collision probability $P_c(b, v_0)$ from atomistic collision MD simulation and analytical critical impact parameters b_c (solid lines) for the collision of (A) H_2SO_4 and $[HSO_4^- \cdot (CH_3)_2NH_3^+]_1$, and (B) H_2SO_4 and $[HSO_4^- \cdot (CH_3)_2NH_3^+]_{16}$ at 300 K. In panel (A), data points were obtained for impact parameter intervals of 1 Å, and 0.2 Å, below, and above, $v_0 < 1000 \text{ m/s}$ respectively. For

the analytical monomer–cluster critical impact parameter in panel (B), the effective monomer–cluster interaction potential was obtained using Eq. 13. The dotted line represents the sum of the hard sphere radii of the collision partners, obtained by assuming bulk density and spherical shape. (P14 Figure 4)

Line 383: Revise this sentence. 'When considering the quantum mechanical nature of the system, some high frequency intramolecular vibrations possess no, or at least significantly less, energy than $k_B T/2$ at finite temperature.'
We have revised the sentence as follows:

Last, it is likely that the cluster dissociation process is unphysically enhanced due to the fact that in the classical atomistic model employed, each vibrational mode possesses $k_B T/2$ energy on average, while in a quantum-mechanical description of the same system, some high-frequency degrees of freedom would remain "frozen" at atmospherically relevant temperatures. (P16 L393)