Responses to Referee #1's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript "Unexpected enhancement of new particle formation by lactic acid sulfate resulting from SO_3 loss in forested and agricultural regions" (Manuscript ID: egusphere-2025-4894). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #1's comments are summarized below:

Referee Comments:

The manuscript by Wang et al. presents a comprehensive theoretical investigation into the formation mechanism of lactic acid sulfate (LAS) and its unexpected role in enhancing sulfuric acid-ammonia (SA-A) driven new particle formation (NPF). The combination of quantum chemical calculations and ACDC kinetic modeling provides molecular-level insights into the catalytic effects of SA and H_2O on LAS formation and the role of LAS in enhancing SA-A nucleation. This study advances our molecular-level mechanistic understanding of how organosulfates influence nucleation events. The manuscript is well-structured and clearly written. Therefore, I recommend publication of this manuscript after consideration of the following comments.

Response: We would like to thank the reviewer for the positive and valuable comments, and we have revised our manuscript accordingly.

Specific Comments:

Comment 1:

In the Introduction (Lines 52-53), the rationale for specifically investigating the enhancement of the SA-A system is introduced somewhat abruptly. The transition to this focus would be strengthened by briefly outlining the existing evidence or theoretical basis that suggests such an enhancement is plausible and significant.

Response: Thank you for your valuable comments. To better transition to the focus on the ternary nucleation process driven by SA-A, relevant existing studies and theoretical foundations have been added in the introduction, emphasizing the plausibility and significance of this enhancement effect, thereby providing a clearer rationale for investigating the enhancement of the SA-A system. According to the reviewer's suggestion, in Lines 52-55 Page 2 of the revised manuscript, the

sentence of "In response to this, several studies have explored the role of ternary nucleation driven by SA-A, which involves a broader array of atmospheric species, including ammonia (NH_3) (Li et al., 2020b; Yin et al., 2021a), organic amines (Li et al., 2017; Li et al., 2018a), organic and inorganic acids (Wang et al., 2011; Liu et al., 2018), and highly oxidized multifunctional compounds (HOMs) (Liu et al., 2021a; Liu et al., 2019a; Ning and Zhang, 2022; Yin et al., 2021b; Zhang et al., 2018)." has been changed as "Then plenty of low weight molecular organic acids such as glycolic acid (Zhang et al., 2017), malonic acid (Zhang et al., 2018) and pyruvic acid (Tsona Tchinda et al., 2022) also exhibit enhancement effects on ternary nucleation driven by SA-A nucleation system through catalytic mechanisms.".

Comment 2:

The acronym "SA-A" (where "A" stands for ammonia) is inconsistent with the use of "NH_3" throughout the text. This can be confusing for readers. For improved readability, please adopt a single, consistent acronym.

Response: Thanks for the suggestion of the reviewer. We apologize for the misunderstanding about ammonia. As the suggestion of the reviewer, the name of ammonia have been corrected. Specifically, ammonia has been labeled as "ammonia (A)" when they are first used. Besides, when they are used again, ammonia has been labeled as "A". The specific revisions are as follows:

(a) In Line 45 Page 2 of the revised manuscript, the "ammonia (NH_3)" has been changed as "ammonia (A)".

(b) In Line 82 Page 3 of the revised manuscript, the "ammonia" has been changed as "A".

Comment 3:

In Section 2.1, regarding the search for the global minimum configuration of the $(SA)_x(A)_y(LAS)_z$ clusters (when $y = 3$, $x + z = 3$), it is unclear whether the sampling of 4000 initial configurations is sufficient to adequately explore the complex conformational space.

Response: Thanks for your valuable comments. Indeed, a multi-path searching approach is utilized to explore the stable structures of $(LAS)_x(SA)_y(A)_z$ (where $0 \leq y \leq x + z \leq 3$). For each global minimum cluster of $(LAS)_x(SA)_y(A)_z$ (where $0 \leq y \leq x + z \leq 3$), n different searching pathways were considered to ensure a thorough exploration of the complex conformational space. Specifically, a single monomer is incorporated to form a larger cluster on top of the existing smaller ones. For instance, in the process of searching for the stable structure of $(SA)_2 \cdot (A)$ clusters, two search

pathways exist: (SA)·(A) + SA and (SA)$_2$ + A. Similarly, in the search for the stable structure of (LAS)·(SA)·(A) clusters, three pathways are considered: (SA)·(A) + LAS, (SA)·(LAS) + A and (LAS)·(A) + SA. Additionally, we apologize for the incorrect range of *n* values previously used. Upon reviewing all the search pathways, we confirm that the correct range for *n* is $1 \leq n \leq 3$, rather than n = 2 to 4. Consequently, the sentence of "a diverse set of initial structures $n \times 1000$ ($1 < n \leq 4$) were randomly produced." has been changed as "a diverse set of initial structures $n \times 1000$ ($1 \leq n \leq 3$) were randomly produced." in Line 115 on Page 5 of the revised manuscript.

Comment 4:

The computational details, such as the definition of boundary clusters and the coagulation sink in the ACDC simulations, should be more thoroughly described in the main text or supplementary information to ensure reproducibility.

Response: Thank you for your valuable comments. According to your suggestion, boundary conditions and the coagulation sink in the ACDC simulations have been added in Lines 155-160 Page 6 of the revised manuscript, which has been organized as "Sensitivity tests were conducted by varying the condensation sink (Cs) from $6 \times 10^{-4} \sim 6 \times 10^{-2}$ s^{-1}, indicating that the Cs exerted minimal influence on the main conclusions (Fig. S11). Therefore, the Cs was set to a representative value of 2.6×10^{-3} for all subsequent calculations (Liu et al., 2021). Additionally, (LAS)$_4$(A)$_3$, (LAS)$_4$(A)$_4$, (LAS)$_2$(SA)$_2$(A)$_3$, (LAS)$_2$(SA)$_2$(A)$_4$, (LAS)(SA)$_3$(A)$_3$, (LAS)(SA)$_3$(A)$_4$, (SA)$_4$(A)$_3$ and (SA)$_4$(A)$_4$ clusters are acting as boundary clusters for LAS-SA-A system.".

Comment 5:

Line 210, please explain the reason for introducing lactic acid sulfuric anhydride (LASA). A clarification on its chemical relationship and distinction to LAS would be helpful for readers to follow the viewpoint.

Response: Thank you for your valuable comments. Following your suggestion, the distinctions between lactic acid sulfate (LAS) and lactic acid sulfuric anhydride (LASA) have been clarified. Both LAS and LASA are products of the reaction between SO$_3$ and lactic acid (LA). LAS is generated via esterification of the hydroxyl group of LA with SO$_3$, whereas LASA is formed through cycloaddition of the carboxyl group of LA, as illustrated by the potential energy surfaces in Fig. S1. Based on this, the detailed introduction of LASA has been clarified and added in Lines 215-216 Page 8 of the revised manuscript, which has been organized as "LASA, the product from the reaction

between SO$_3$ and the carboxyl group of LA, Fig. S1".

Comment 6:

In Section 3.2.3, please clarify how "LAS contribution" is quantitatively calculated. Specifically, is it determined by the fraction of outgrowing clusters that contain at least one LAS molecule? A brief description of the calculation methodology is needed.

Response: Thank you for your valuable comments. According to your suggestion, regarding the calculation of the final outgoing fluxes of LAS in the ACDC simulations have been added in Lines 160-161 Page 6 of the revised manuscript, which has been organized as "Also, the details of the contribution of LAS to SA-A nucleation was estimated in the first part of the Supplement".

To further elaborate on the computational procedures, we have included the specific outgoing fluxes of LAS in the ACDC simulations in the supplementary material, organized as follows: "To quantify the contribution of LAS to SA-A nucleation, we analyzed the steady-state cluster formation fluxes (J) output by ACDC. The LAS-related nucleation fraction at a given temperature was defined as the ratio of the total formation flux of all nucleated clusters containing at least one LAS molecule to the total nucleation flux from all pathways. Specifically,

$$f_{\text{LAS}}(T) = \frac{\sum J_{\text{out}}(C_i | C_i \in C_{\text{LAS}})}{\sum J_{\text{out}}(C_i)} \tag{S1}$$

where $J_{\text{out}}(C_i)$ denotes the outgoing flux of cluster C_i that meets the nucleation criterion (size/composition threshold), and C_{LAS} represents the set of all nucleated clusters containing one or more LAS molecules. This metric directly reflects the proportion of new particles formed through LAS-involved pathways under steady-state conditions." .

Comment 7:

In Section 3.2.3, the authors state that LAS contributions are more pronounced in forested and agricultural regions. It would be helpful to clarify why these regions exhibit higher LAS relevance compared to urban or industrial areas.

Response: Thank you for your valuable comments. The influence of LAS on sulfuric acid-ammonia (SA-A)-driven new particle formation (NPF) show that, under elevated SA concentrations, such as those commonly observed in urban or industrial environments, the dominant effect of SA suppresses the nucleation-promoting role of LAS, thereby substantially diminishing its contribution to nucleation. In contrast, in forested and agricultural regions characterized by relatively low SA

concentrations and more abundant sources of LAS, LAS exhibits a markedly stronger nucleation-promoting effect within the sulfuric SA-A system. Accordingly, we infer that in forested and agricultural regions, which are typically characterized by low SA concentrations, LAS plays a pronounced role in promoting SA-A nucleation. The corresponding explanations can be mainly attributed to two aspects.

(a) The enhancement factor R in the SA-A-based system is strongly influenced by the concentrations of both SA and LAS. To illustrate this dependence, Fig. S10 shows R as functions of [SA] and [LAS] under the conditions of [A] = 10^9 molecules·cm^{-3} and T = 278.15 K. As depicted in Fig. S10, the R increases as the [SA] decreases. At low [SA] (10^5 molecules·cm^{-3}), the R value reaches its maximum of 1.32×10^7 fold at [LAS] = 10^6 molecules·cm^{-3}. In contrast, at high [SA] (10^7 molecules·cm^{-3}), the influence of [LAS] on R is markedly reduced, resulting in a 1.54 fold increase in R at [LAS] = 10^6 molecules·cm^{-3}. Based on the above analysis, in Lines 322-324 Page 12 of the revised manuscript, the discussion of why agricultural-developed and forested areas exhibit higher LAS relevance compared to urban or industrial areas, which has been added and organized as "In contrast, environments with typically high SA concentrations, such as urban and industrial areas, promote SA-A self-aggregation nucleation, thereby diminishing the relative contribution of LAS (Fig. S10)."
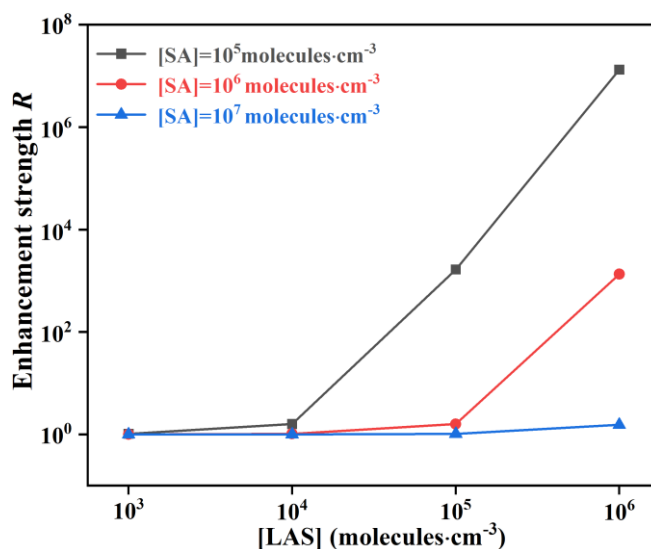
Fig. S10 Enhancement factor R as functions of [SA] and [LAS] at [A] = 10^9 molecules·cm^{-3} and 278.15 K.

(b) During formation of LAS via the reaction of SO_3 with LA strongly competes with SA formation. To further evaluate the competitive interactions between LAS and SA molecules, another

set of ACDC simulations was conducted, considering different ratios of the concentrations of LAS and SA ([LAS]/[SA]) and varying the total concentration of LAS and SA. Fig. S12 shows particle formation rates (J, cm$^{-3} \cdot$s^{-1}) with varying ratios of [LAS]:[SA] at 278.15 K under different concentrations ((a)10^7 molecules·cm^{-3}, (b)10^9 molecules·cm^{-3} and (c)10^{11} molecules·cm^{-3}). The specific revisions are as follows:
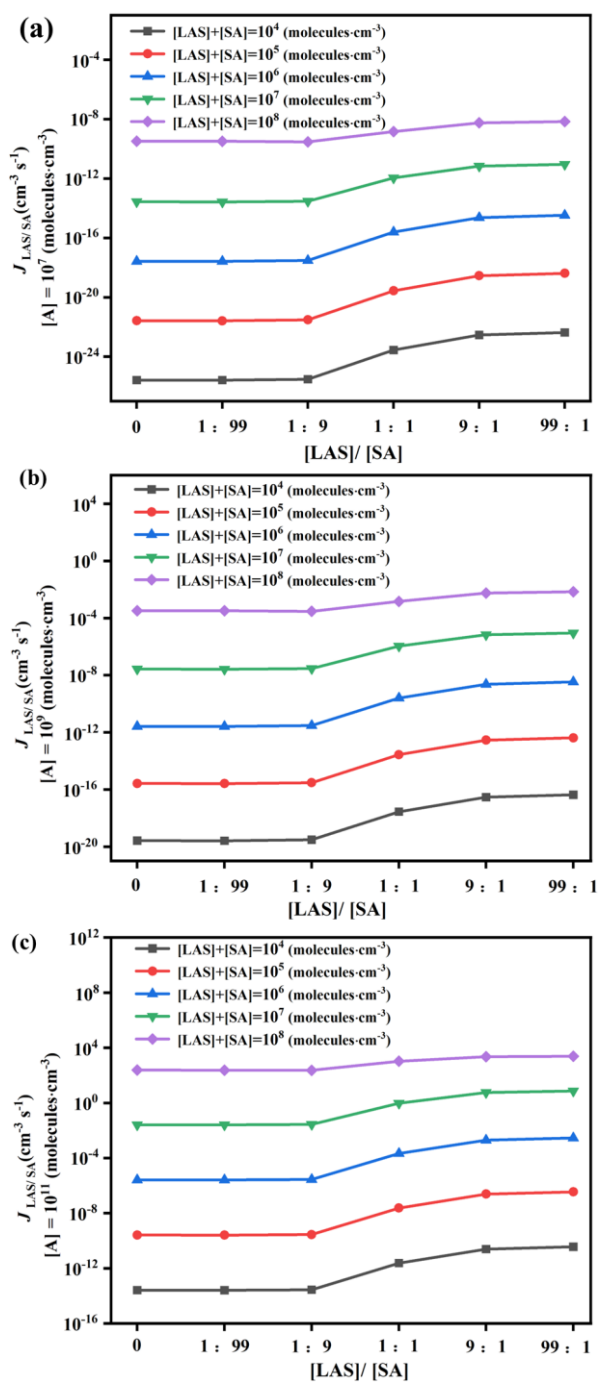
Fig. S12 Particle formation rates (J, cm$^{-3} \cdot$s^{-1}) with varying ratios of [LAS]:[SA] at 278.15 K under different concentrations ((a)10^7 molecules·cm^{-3}, (b)10^9 molecules·cm^{-3}, (c)10^{11} molecules·cm^{-3}). [LAS] + [SA] = 10^4-10^8

molecules·cm^{-3}

The corresponding revision has been added and organized as "The observed concentration dependence indicates that the LAS-driven nucleation process becomes particularly significant in environments with moderate to high LAS concentrations and relatively low SA levels. Therefore, in the LAS-SA-A ternary nucleation system, LAS is likely to function as an "acid" molecule, exhibiting a competitive effect. To evaluate the competitive interactions between LAS and SA molecules, another set of ACDC simulations was conducted, considering different ratios of the concentrations of LAS and SA ([LAS]/[SA]) and varying the total concentration of LAS and SA. Fig. S12 shows the variation of $J_{LAS/SA}$ with the total concentrations of SA and LAS at A concentrations of 10^7, 10^9, and 10^{11} molecules·cm^{-3}.

As shown in Fig. S12(a), at lower atmospheric concentration of A (10^7 molecules·cm^{-3}), the formation rate $J_{LAS/SA}$ increases with the substitution percentage. At a 50% substitution rate ([LAS]:[SA] = 1:1), $J_{LAS/SA}$ sharply increases to 1.46×10^{-9} cm^{-3}·s^{-1}, which is larger by 1-2 orders of magnitude than the value at unsubstituted condition. At a 99% substitution rate ([LAS]:[SA] = 99:1), $J_{LAS/SA}$ reaches its maximum value of 6.99×10^{-9} cm^{-3}·s^{-1}, which is 1-3 orders of magnitude greater than the value under non-substituted conditions. These results indicate that, at lower atmospheric concentrations of A, the enhancing effect of LAS on the SA-A group particle formation rate increases with the substitution percentage. At intermediate (10^9 molecules·cm^{-3}) and higher concentrations (10^{11} molecules·cm^{-3}) of atmospheric A, the $J_{LAS/SA}$ at a 99% substitution rate ([LAS]:[SA] = 99:1) reaches its maximum value (Fig. S12(b) and Fig. S12(c)). Compared to the $J_{LAS/SA}$ under non-substituted conditions, the value at a 99% substitution rate is increased by one order of magnitude. In contrast, urban and industrial environments, which typically have high SA concentrations, favor SA-A self-aggregation nucleation, thereby reducing the relative contribution of LAS. Thus, in regions characterized by high T, low [SA], high [A] and high [LAS], especially in agricultural-developed areas and forested areas, the LAS contribution to SA-A aerosol nucleation can be substantial." in the supplementary material.

Comment 8:

Line 398 and Line 17: "particle formation rates can increase by up to 10^8-fold", if this value is provided in the SI, please indicate where it can be found.

Response: Thanks for your valuable comments. We apologize for not clearly citing the source of

this data in the previous version of the manuscript. According to the reviewer's suggestion, the specific data indicating that particle formation rates can increase by up to 10^8-fold has been clarified in the revised manuscript. The supporting data can be directly viewed in Fig. S5(b).

Comment 9:

Some minor mistakes are shown in the manuscript, e.g., Line 64: "PM10"; Line 100: "nucleation and particle formation (NPF)"; Line 267: "exits the system"; Line 348: "negative negative ΔG values"; Line 64: "whereas in the LAS-SA-A system" and so on. Please totally and carefully recheck the whole manuscript and correct all the mistakes.

Response: Thanks to the reviewer's insightful comment, we are sorry for the trouble we have caused by oversight. In order to improve the accuracy of the expression, the corresponding main revision has been made as follows:

(a) In Line 62 Page 3 of the revised manuscript, "PM10" has been changed as "PM_{10}".

(b) In Line 98 Page 4 of the revised manuscript, "nucleation and particle formation (NPF)" has been changed as "new particle formation (NPF)".

(c) In Line 272 Page 10 of the revised manuscript, "exits the system" has been changed as "exit the system".

(d) In Line 360 Page 13 of the revised manuscript, "negative negative ΔG values" has been changed as "negative ΔG values".

(f) In Line 369 Page 13 of the revised manuscript, "whereas in the LAS-SA-A system" has been changed as "whereas in the LA-SA-A system".