

Reviewer #1

This manuscript compared the simulations of new particle formation rate from sulfuric acid (H_2SO_4) and dimethylamine (DMA) by different molecular cluster kinetics modeling under various conditions (e.g., different T and CS) and aims to find applicable parameterizations for 3-D NPF modeling in Beijing. The provided results indicated that: ACDC_DB, an ACDC derived parameterization, incorporated into WRF-Chem/R2D-VBS model can effectively reproduce particle formation rates and PNSDs evolution for both winter and summer in Beijing. The content of this paper is useful for developing parameterizations aiming at predicting or simulating NPF in urban areas. The manuscript is well written and the topic fits the scope of Atmos. Chem. Phys. I recommend publication of this manuscript after responding the following comments.

Response: We sincerely thank for the reviewer's careful review of our manuscript and the positive comments.

Specific comments:

The authors should clarify the advantage or difference of the parameterizations developed using ACDC to the one used in Dynamic_Sim. On the words, why the authors developed ACDC based parameterizations rather than making iteration on the base of Dynamic_Sim in L173-176 and in the introduction part. Moreover, except for making comparison with Dynamic_Sim, what's the consideration of setting the ACDC_BC coupling with three simplifications?

Response: In 3-D modeling, calculating detailed real-time nucleation dynamics for arbitrary chemical systems can impose a substantial computational burden, presenting a significant challenge for direct implementation (Yazgi and Olenius, 2023). Practical approaches for integrating NPF mechanisms into 3-D models generally follow two strategies: 1) simplifying the processes to derive explicit mathematical expressions, such as Dynamic_Sim, or 2) utilizing precomputed look-up tables generated from other box-model simulations, such as ACDC-derived parameterizations. Therefore, the primary difference between Dynamic_Sim and ACDC-derived parameterizations lies in the manner of their integration into the 3-D model.

Beyond that, a key difference between the main ACDC-derived parameterization ACDC_DB and Dynamic_Sim lies in their ability to accurately represent cluster dynamics and, consequently, particle formation rates under different atmospheric conditions. Our results suggest that simplifying the cluster dynamic processes in Dynamic_Sim may introduce biases compared to the comprehensive treatment (Figure 2), resulting in an overestimation for Dynamic_Sim in $J_{1,4}$ prediction relative to ACDC_DB under high temperature ($> \sim 300$ K) and low CS conditions ($< \sim 3 \times 10^{-3} \text{ s}^{-1}$) (Figure 1).

Based on our previous study (Li et al., 2023), removing the three inherent assumptions in Dynamic_Sim would escalate the computational demand by over several orders of magnitude. Consequently, we chose the alternative approach of employing ACDC-derived look-up tables for probing the impacts of simplifications and subsequent comparison and selection of SA-DMA nucleation parameterization. We have added relevant explanations to line 191-195 in the revised manuscript. The

purpose of establishing an ACDC-derived parameterization that simultaneously couples three simplifications is to elucidate the differences between ACDC_DB and Dynamic_Sim. Our results (Figure S1) indicate that the discrepancies between the two arise from only the three simplifications in cluster dynamics and the thermodynamics of the initial cluster, while other dynamic processes remain consistent.

The look-up table approach has its limitation due to the ignorance of the explicit interactions of clusters with gas phase precursors and pre-existing particles. The author should add some discussion about the disadvantage of the applied look-up table approach and discuss about the possible conditions that may lead to the biased simulation results.

Response: We appreciate the reviewer's suggestions, which can help to improve the quality of our manuscript. We agree that the explicit interactions among gaseous precursors, clusters, and pre-existing particles are simplified when using a look-up table approach, though it is commonly used in 3-D modeling. Additional analysis and discussion on the potential impacts of this simplification have been added to the *CONCLUSIONS and DISCUSSIONS* sections. Olenius and Roldin (2022) provided insights on the potential impact of gas-cluster-aerosol dynamics on NPF simulation using chemical transport models. Among various standard treatments of gas-cluster-aerosol dynamics in chemical transport modeling, they highlighted the assumption of instantaneous steady-state nucleation at every model time step as a potential source of bias. In response to this, we conducted a reliability assessment of steady-state nucleation in our WRF-Chem/R2D-VBS simulations. We evaluated the validity of the steady-state nucleation assumption by considering the system's e-folding time (time for clusters to reach $(1-1/e)$ of their terminal concentration, following Li et al., (2023)). Specifically, we deemed the assumption reasonable if, under certain atmospheric conditions, the system's e-folding time is less than the simulation time step (300 s).

As shown in Figure S14, results indicates that the e-folding time does not show a significant correlation with $J_{1.4}$. Under the majority of atmospheric conditions (77.3%), the nucleating system's e-folding time is less than 300 s. Instances where the e-folding time exceeds 300 s are primarily observed in winter clean conditions characterized by low temperature ($T < \sim 270$ K), low condensation sink ($CS < \sim 0.003$ s⁻¹), and low precursor concentrations ($SA < \sim 10^6$ cm⁻³). These findings align with the observations of Olenius and Roldin (2022). It's important to emphasize that this e-folding time represents the duration required for the system to transition from having only precursor molecules to reaching near-equilibrium concentrations of various clusters. In reality, cluster concentrations generally do not start from zero. Therefore, the calculated e-folding time serves as an upper limit estimate. Given the predominance of atmospheric conditions where the e-folding time falls within or below the simulation time step of 300 s, consequently, the steady-state treatment is generally deemed reasonable for our WRF-Chem/R2D-VBS simulations.

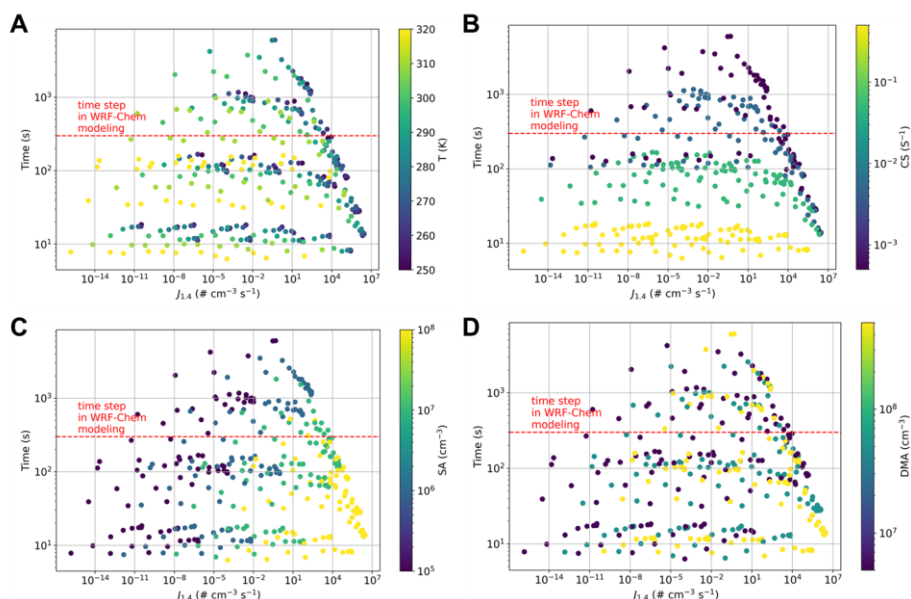


Figure S14. The variation of e-folding time with $J_{1.4}$ correlated with temperature (A), CS (B), SA concentration (C), and DMA concentration (D). The data points were calculated using a more sparse sequence of input parameters (T : 250, 260, 270, 280, 290, 300, 310, 320 (K); CS: 5.00×10^{-4} , 5.00×10^{-3} , 5.00×10^{-2} , 5.00×10^{-1} (s^{-1}); SA: 1.00×10^5 , 1.00×10^6 , 1.00×10^7 , 1.00×10^8 (cm^{-3}); DMA: 5.00×10^6 , 5.00×10^7 , 5.00×10^8 (cm^{-3})) compared to those shown in Table S1.

We further investigated another common treatment that may introduce bias: neglecting cluster formation in consuming precursor during nucleation. Our examination focused on assessing the proportion of precursor consumption by cluster formation relative to precursor concentrations. As shown in Figure S15 and S16, we found that this proportion increases with $J_{1.4}$ for both SA and DMA. Under the majority of atmospheric conditions (82.0% for DMA and 57% for SA), proportions are below 10%. Proportions exceed 10% are predominantly observed in scenarios also characterized by low temperature ($T < \sim 270$ K) and low condensation sink ($CS < \sim 0.003$ s^{-1}), but with high deference in concentrations between DMA and SA. Specifically, elevated SA concentrations, which lead to significant DMA consumption through cluster formation, and vice versa, contribute to scenarios where precursor consumption by cluster formation exceeds 10%. It's noteworthy that our calculation of precursor consumption by cluster formation starts from zero cluster concentration. Also, in the real atmosphere, cluster concentrations are generally nonzero, leading to another upper limit estimate. Therefore, based on our analysis, it can be inferred that cluster formation may not introduce significant bias into NPF simulations under typical atmospheric conditions. We have added this additional analysis and discussion of the potential impacts of these common treatments in NPF simulations to line 717-731 in the revised manuscript and the supporting information.

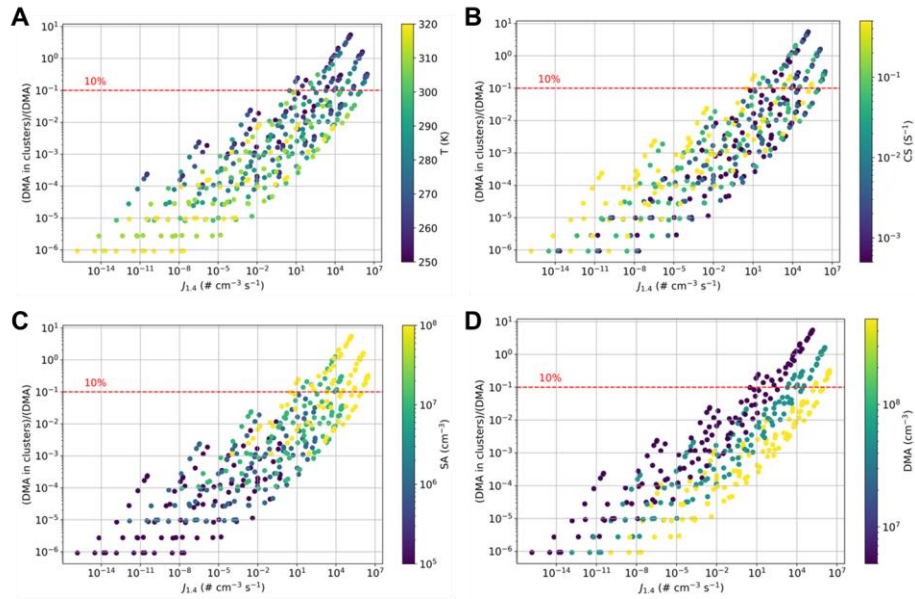


Figure S15. The variation of proportion of DMA consumption by cluster formation relative to precursor concentrations with $J_{1,4}$, correlated with temperature (A), CS (B), SA concentration (C), and DMA concentration (D). The input variables are consistent with Figure S14.

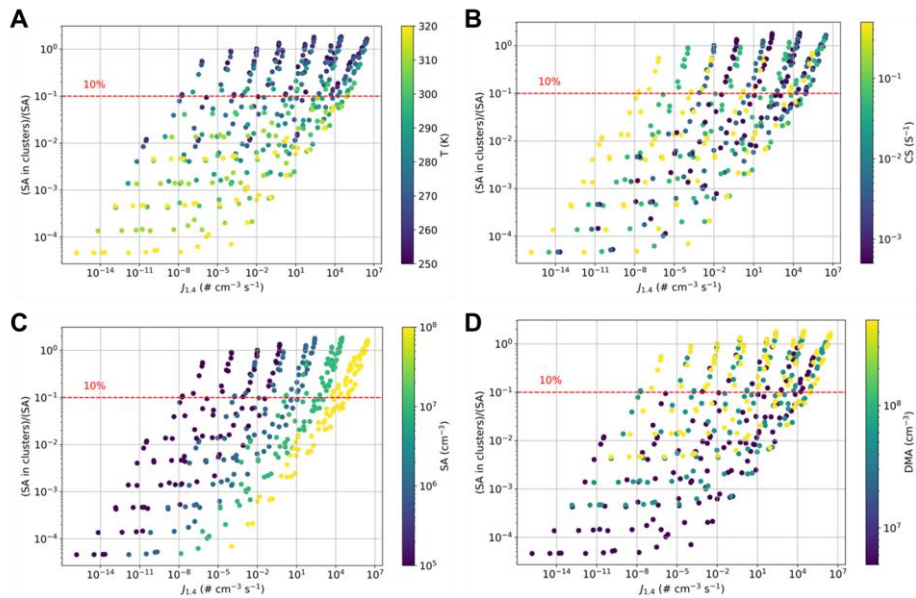


Figure S16. The variation of proportion of SA consumption by cluster formation relative to precursor concentrations with $J_{1,4}$, correlated with temperature (A), CS (B), SA concentration (C), and DMA concentration (D). The input variables are consistent with Figure S14.

In Figure S8, it seems to me that ACDC_RM_SF0.5 overestimate the formation rate by a factor of 2 at 293K, please check the simulation results or discuss the possible reasons. Would this influence the 3D model simulations during summer, leading to the overestimation of $J_{1,4}$? Moreover, Figure S8 also indicated that ACDC_DB and

Dynamic_Sim overestimate the formation rate more at 293K compared with at 278K, would this be the reason of the overestimation during summer?

Response: Figure S8 compares box-model simulations from three main parameterizations, ACDC_DB, Dynamic_Sim, and ACDC_RM_SF0.5, with the well-controlled CLOUD chamber experiments. The results reveal that under the conditions of 278 K, all three parameterizations are consistent with the CLOUD chamber experiments. This alignment mirrors our 3-D simulation for winter Beijing (Figure 5A), which also corresponds to a similar temperature (~274.7 K). However, at 293 K, while ACDC_DB and Dynamic_Sim remain close to the observations, ACDC_RM_SF0.5 substantially overestimates the particle formation rate by more than an order of magnitude. Additionally, our summer simulation for Beijing, illustrated in Figure 6A, demonstrates that ACDC_RM_SF0.5 significantly overestimates particle formation rates compared to those derived from in situ observations at ~298.2 K. Hence, the patterns shown in Figure S8, Figure 5A, and Figure 6A are actually consistent. The inability of ACDC_RM_SF0.5 to accurately simulate particle formation rates at high temperatures can be attributed to its inappropriate representation of cluster thermodynamics as explained in line 468-491 in the revised manuscript.

In Figure S8, we used the average DMA concentration for the box-model simulation, whereas the DMA concentration for each data point from Xiao et al. (2021) might differ slightly. Here, we re-simulated these cases using ACDC_DB with the precursor concentrations corresponding to each particle formation rate from Xiao et al. (2021). As shown in Figure S9A, the simulations at both 278 K and 293 K generally align with the experimental values from Xiao et al. (2021) within a factor of two. The box-model simulations at 293 K tend to slightly overestimate the particle formation rates. This discrepancy may arise because the CLOUD chamber measured particles with a diameter of 1.7 nm, while our simulations modeled the formation of particles with a diameter of 1.4 nm, which may be slightly higher (Almeida et al. 2013). According to the modified Kerminen-Kulmala equation (Lehtinen et al., 2007), the difference between the formation rates of 1.4-nm and 1.7-nm particles should be related to the growth rate of clusters. In the SA-DMA nucleation system, SA-DMA clusters with different molecular ratios are the main materials for growth. We further compared the differences in SA-DMA cluster concentrations at two temperatures. As shown in Figure S9B, (SA)₁(DMA)₁ has the highest concentration among all SA-DMA clusters and is likely the most critical cluster contributing to growth, consistent with previous studies (Almeida et al. 2013; Cai et al. 2023). Notably, the concentration of (SA)₁(DMA)₁ cluster at 278 K is about an order of magnitude higher than that at 293 K. Therefore, this will result in the particle formation rate of 1.4-nm particles at 278 K being closer to the particle formation rate of 1.7-nm particles in the CLOUD chamber compared to that at 293 K. In Figure 6A, the particle formation rate derived from the 3-D simulation using ACDC_DB is higher than the observed rate, likely due to the slight overestimation of the SA concentration during this period (Table S2). We have added these additional analysis and discussion to line 511-515 in the revised manuscript.

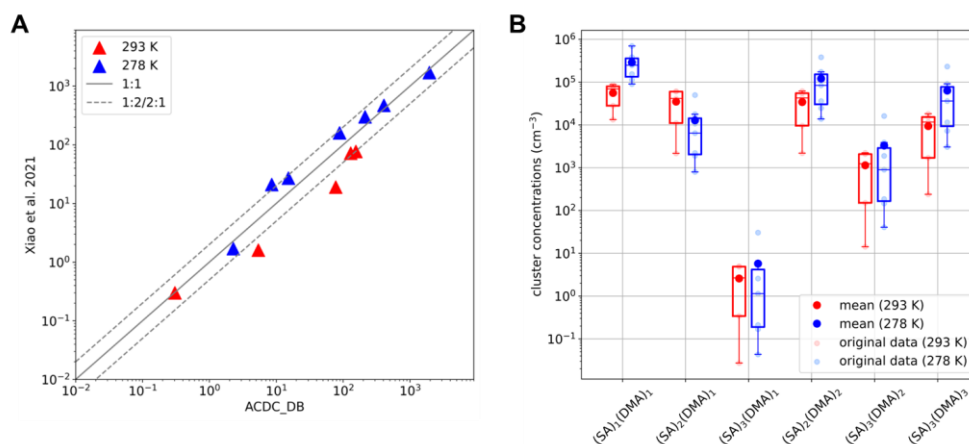


Figure S9. Comparison of measured $J_{1.7}$ from Xiao et al. 2021 and simulated $J_{1.4}$ using ACDC_DB with corresponding DMA concentrations in experiments (A), and the comparison of cluster concentrations at 293 K and 278 K (B).

Technical comments:

L90-91: check the reference

Response: The revisions have been made accordingly.

Lines 465 and 482: “ACDC_RM” should be “ACDC_RM_SF0.5”

Response: The revisions have been made accordingly.

Line 476-478 and other parts in section 3.1: I suggest using “overestimate” and “underestimate” instead of “applicable” and “suitable”, since the discussion in section 3.1 is the evaluation of different simplifications on the molded $J_{1.4}$ for ACDC_RM and ACDC_DB.

Response: We agree with the reviewer that “overestimate” and “underestimate” is better. The revisions have been made accordingly.

Line 525: Replace the comma of ‘ACDC_RM show higher concentrations,’ with period.

Response: The revisions have been made accordingly.

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