Review of «The impact of aerosol mixing state on immersion freezing: Insights from classical nucleation theory and particle-resolved simulations» by Tang et al.

The paper presents an analysis of the effects of aerosol mixing state on ice formation by comparing internally and externally mixed monodisperse particle populations with equal ice-nucleating surface areas. In a theoretical section, the authors derive the mathematical expressions used for this comparison and examine their sensitivity to key parameters. The mixing-state-dependent formulation of ice formation is then implemented in a simulation framework, and the agreement between the analytical predictions and the numerical results is evaluated. The topic is relevant for researchers in the field of ice nucleation, and the results are presented with mathematical rigor and considerable depth of detail.

General comments:

There are several parts in the paper where the reader must work through an algebra heavy presentation to extract the underlying physical concept. Adding an interpretation paragraph after major derivations stating *why* something is the case or *what the math means* would make the paper more accessible without sacrificing rigor. Some suggestions where physical concepts could be brought forward are included below.

To better guide the reader, it should be stated more explicitly in the introduction that the study presents a mathematical framework developed under controlled and idealized assumptions, rather than a direct physical representation of the real atmosphere. The level of idealization, underlying assumptions, and inherent limitations should be clearly articulated and consolidated in the introduction instead of being dispersed throughout the manuscript. In addition, the authors should specify the types of models or data analyses in which the derived analytical expressions could be meaningfully applied.

The central finding, that internal mixtures yield higher frozen fractions than external mixtures rests on the critical assumption that the total ice nucleating surface is identical in both cases. The extent to which this assumption can be considered generally applicable should be discussed in greater detail. In the real atmosphere, changes in mixing state are typically accompanied by processes such as coating and coagulation, which alter both the available ice-nucleating surface area and the particle size distribution. These coupled effects may limit the direct transferability of the theoretical result to atmospheric conditions and deserve further consideration

Specific comments:

Line 10, 81, 450: Clarify in what aspect the simulation goes beyond a numerical realization of the theory which allow to confirm/ verify the theory.

Line13-14: To illustrate how important it is to consider the mixing state for modelling, it would be helpful to estimate the influence of the mixing state in relation to the variation in the number of particles containing ice-active species on a temperature spectrum of the INP concentration. It could be expected that the variation in particle concentration would outweigh the influence of the mixing state on the INP concentration as a function of temperature.

Introduction: Summarize the findings of each cited study in one sentence each. It is not helpful for the reader to have 10 different references provided to support one fact without having pointed out what each of them contribute.

Line 69: Instead of putting the singular description out of scope, it can be said that because both CNT and INAS have the same exponential form shown below, Theorem 1 holds for both. In the given function, x changes the distribution of ice nucleating surface area.

$$N_{ice}(x) = \left[1 - \exp\left(\frac{-c}{x}\right)\right] \cdot x \cdot N_P$$

For CNT: $c = SJt$, for INAS: $c = Sn_s$. Basically, ϕ in your notation can be replaced by the surface site density n_s.

Consider discussing the soccer ball model by Niedermeier et al., 2011 and their findings in context of internal or external mixed INP and time dependence.

Line 71-72: support this claim with an example and a citation.

Line 73: Provide an example how a quantitative investigation could look like. Explain why size or mass dependent experiments that determine the frozen fraction as function of exposed surface area wouldn't provide the needed data. You cite Broadley et al., 2012 on line 172. Are their data not covering the question on the mixing state effect on the frozen fraction?

Line 76: Necessarily aging or coating causes these effects. Provide an atmospheric example in which mixing state changes, but surface area is conserved.

Line 104: Describe how the surface coverage can be determined from the particle morphology.

Line 115, 120: Why is Eq. 9 not just a substitution but considered simpler than Eq. 7?

Line 126, 141-144: Explain why it is stressed that the following analysis is only valid for monodisperse particle populations. Brefly discuss what the expected impact of a polydisperse distribution is, for example, based on Eq. 9. Would it go beyond replacing $S_p$by the average $\overline{S_p}$?

Sec. 3.1. Eq. (12)-(15): The paper presents the algebra but never explains that the geometric mean appears for internal mixtures because a mixed particle remains unfrozen only when no surface component nucleates ice. Given independent nucleation events, the corresponding probabilities of not freezing multiply. Raising each term to the power of its surface fraction accounts for proportional surface coverage.

Line 166-167: It is difficult to understand what is meant by "droplets containing multi and single species" in the context of internal mixing. Provide a physical explanation to clarify this relationship.

Line 173-174: The internal vs. external mixture difference is fundamentally a geometric mean vs. arithmetic mean problem. For any set of positive, not all equal numbers the arithmetic mean is always greater than the geometric mean and the difference between them increases as the variability increases. This could be highlighted more. It confirms Theorem 1.

Line 175: Relate the statement to the difference in geometric mean vs. arithmetic mean.

Line 207: Explain the situations in which these combinations are relevant.

Figure 3: consider repeating the scenario conditions in the caption.

Line 212: Define “uncertainty” or for consistency use “sensitivity” instead.

Sec. 3.2. Eq. (16)-(19): Taylor expansions are given but the physical picture explaining the different regimes could be expanded: When nucleation rates are very low, freezing is a rare event regardless of species and most particles don’t freeze. How the species are distributed doesn’t matter. When nucleation rates are very high, most particles freeze regardless of mixing state. The mixing state only becomes important when the good species is efficient enough to cause freezing, but the bad species is not, creating a population where external mixing leaves many particles unfrozen.

Line 232: Is the significant sensitivity what is marked as red 20% line in Figs. 3, 4, 5?

Line 250: Provide an estimation of how relevant the error in the frozen fraction from the mixing state is for calculating the INP concentration compared to the uncertainty regarding the quantity and nucleation rate of the INP species.

Line 314: According to the previous section there is no insoluble components. Mention in the text why the effect of solutes has not been tested, especially as the ABIFM can specifically consider them.

Line 326: The notation changes from before where P was used for probability and N_p for particles and π as a number (line 217). Consider using the same notation for all parts of the paper.

Line 327: Explain how the condition of sufficient water is defined and if water uptake on insoluble particles is simulated.

Line 388: Explain the χ index in the text and point to Appendix F.

Line 389: Explain why this aspect cannot be analysed using the framework.

Line 402: Clarify why it is important to note that the population is not monodisperse.

Figure 9: At what time of the simulation are the frozen fraction compared?

Line 457: Quantify the minimum number of computational particles required to suppress sampling noise for low frozen fractions.

Line 481-482: The same argument presented on line 176-181 applies to (b) vs. (c). Explain why nevertheless Theorem 1 is not applicable when comparing the particle population of (c) to (a) instead of bin wise comparison. A plot demonstrating the failure of Theorem 1 would be helpful.

Appendix D, Eq. D8-D9: Explain that $\mathcal{K}$ is constant because it depends only on the total surface area of each species, not on how that area is distributed among particles.

Appendix D, Eq. D15-D20: The Lagrange multiplier method is correct but a bit overkill. It could be replaced by the inequality of the arithmetic and geometric mean:

For a fixed product, the sum is minimized when all terms are equal.

$$\frac{1}{N_p}\sum_{j=1}^{N_p} P_{\mathrm{unf},j} \geq \left(\prod_{j=1}^{N_p} P_{\mathrm{unf},j}\right)^{1/N_p} = \mathcal{K}^{1/N_p}$$

with equality iff $P_{\mathrm{unf},1} = \cdots = P_{\mathrm{unf},N_p}$. Thus, the minimum possible unfrozen fraction (maximum frozen fraction) requires equal freezing probabilities of all particles.

Appendix D, Eq. D28-D36: Add some interpretation or an example explaining that the index-heavy algebra shows that exchanging equal amounts of inefficient with efficient species between particles preserves each species' total surface area and each particle's total surface area. Making one particle more efficient and the other less efficient increases the sum of their probabilities not to freeze. The new configuration has a higher unfrozen fraction (a lower frozen fraction) than the original. The external mixture therefore must be the least efficient mixing state.

Technical corrections:

Line 76: correct sentence structure

Line 85, and other places: It could be argued that it is not the particle that freezes in immersion freezing but the droplet. Consider specifying “freezing of a droplet” or “ice nucleation on the surface of a particle” where practical.

Line 119 is a repetition of line 117.

Line 119: Clarify why the cooling rate and duration must be controlled. Do you mean they must be “known”?

Line 135: To include all restrictions mentioned on line127, “monodisperse INP” could be replaced with “this scenario”.

Line157, Appendix A2, B: As “mode” and “species” seem to refer to the same thing, consider using only “species”.

Line 183: ...in unfrozen droplets, producing more ice.

Line 204: How are the ϕ identified as “typical”? Better “exemplary”

Line 344: ... are as follows

Line 422 is a repetition of line 420.

Line 508: specify “error” as “overprediction”

Line 580: do you mean “described” instead of “decreased”

Line 589: Clarify what simulation. At the point in the paper the appendix A is mentioned the simulation is not introduced. Do you mean calculation?

Line 596: reformulate. In the limits $\Delta t \to 0$ and $\Delta h \to \infty$, the unfrozen probability $P_{\mathrm{unf}}(0, t)$ is given by the time integral of λ:

Line 956: Pöschl

References:

Niedermeier, D., Shaw, R. A., Hartmann, S., Wex, H., Clauss, T., Voigtländer, J., and Stratmann, F.: Heterogeneous ice nucleation: exploring the transition from stochastic to singular freezing behavior, Atmos. Chem. Phys., 11, 8767–8775, https://doi.org/10.5194/acp-11-8767-2011, 2011.