

Review: "Immersion freezing of water and aqueous ammonium sulphate droplets initiated by Humic Like Substances as a function of water activity" by Y. J. Rigg et al.

### **General comments:**

This contribution addresses the efficiency of immersion freezing on surrogates of humic like substances as a function of temperature and water activity. The authors conducted a series of freezing experiments and provide an intercomparison of the applicability of five different models to parameterise the data of each experiment.

The experimental results are interesting however the interpretation of the results and model analysis can be improved as pointed out below.

Overall the authors reuse already established approaches and to a large extent confirm previous results. The progress in understanding of immersion freezing in solution droplets is therefore only incremental and the need for the performed analysis should be motivated better.

### **Specific comments:**

4922, Line 20: Could it be that the initial particles consist of aggregates which break apart during sonication? Is this what is called "dissolution"?

4925, Line 21: Does the nucleation rate given here represent median hom. freezing temperatures of this specific experiment?

4925, Line 24: In your experimental data no obvious change for  $a_w < 1$  can be seen in comparison to  $a_w = 1$ . I would expect the conversion to a glassy state to influence ice nucleation on HULIS. Can you provide an explanation for the absence of a change in the ice nucleation efficiency?

4926, Line 2-7: Does the constant supercooling from the melting point ( $T_m - T_f \cong \text{const.}$ ) indicate that the change in  $T_f$  as function of  $a_w$  is only due to a change in the bulk water structure and there is no change in the lowering of the nucleation energy due to the IN? Additional discussion could be of interest also in regard to the next comment.

4926, Line 17-19: Contradicting to the suggestion that only  $a_w$  is needed to describe immersion freezing in solution droplets, Reischel and Vali (1975) reported experimental results where they observed varying interactions of solute and IN in dependence of their nature.

4930, Line 2: There is a more recent publication by Smith and Kay (2012), including an updated fit curve of the diffusivity based on additional data. Accordingly the surface tension given in Zobrist et al., 2007 should be revisited.

4930, Line 24 ff: Can you provide a physical explanation why a temperature dependence of the contact angle could be expected? The calculated temperature dependence of the contact angle is highly dependent (to the power of 3) on the chosen temperature dependence of the surface tension. Therefore it can be suspected that the derived change in contact angle is an artefact due to the uncertainty in the surface tension. As a

sensitivity test: How would the temperature dependence of the surface tension change if the contact angle would be held constant. Would this lead to an unphysical temperature dependence of the surface tension?

Depending on the author's response, the  $\alpha(T)$  approach might have to be declared a parameterisation with limited physical meaning.

4931, Line 13: Is there experimental evidence that the temperature dependence of contact angle is size independent for a large range of particle sizes (or at least the atmospherically relevant cases)?

4933, Line 1-9: Does the fact that the nucleation rate is constant with changing  $a_w$  indicate that there is no effect on the IN by the solute (see previous comments)?

4933, Line 10-16: The close fit of the  $\alpha(T)$  approach to the data is not surprising.

Especially by using a different parameterisation for each  $a_w$ -dependent  $f$  curve. It only indicates that it is possible to compensate deviations of CNT assuming a constant  $\alpha$  (probably due to uncertainties in the temperature dependence of the surface tension and diffusion energy) by introducing a new parameter in the form of a temperature dependence of the contact angle.

4933, Line 17-30 ff.: This discussion is not elaborative enough. Of course the nucleation rate is independent of the frozen fraction as it describes the nucleation probability on the IN surface area immersed in one droplet at a certain temperature.

The "commonly applied nucleation descriptions" were made to investigate the distribution of properties on the IN surfaces, in an ensemble of droplets. Their primary application is to investigate the underlying physics of ice nucleation and not to parameterise. The different approaches (single- $\alpha$ ,  $\alpha$ -pdf, active sites and deterministic) must be applied to the entire dataset (for one IN-species) simultaneously to judge how well one or the other model is able to describe the nucleation process in a physical way. The interesting questions the authors could address using their dataset are:

1. How well can  $a_w$  be implemented in CNT based models (using their parameterisations).
2. How well do the different physical model approaches perform in comparison to the two data sets.

For that the different models need to be applied once to all the LEO data and once to all the PP data to obtain two sets of parameters for each model.

4934, Line 14-19: As the authors point out in the discussion of the single- $\alpha$  model the log-normal distribution of contact angles can converge to a delta function at its extreme. In consideration of this fact, additional explanation is needed to clarify the statement of a bias due to the extension of the function from 0 to 180°. Also looking at the contact angle distributions provided in the supplementary Fig. 2 and 3 the probability of contact angles of 0 or 180° seem to be too small to be of any importance.

4935, Line 12-18: The performance of the single- $\alpha$  model (the steepness of slope) is strongly related to the temperature dependence of the used surface tension. This could be discussed.

4938, Line 8-27: Based on the comparison of the models which were applied to each  $a_w$  experiment separately and yields the result that, the more free fit parameters a model contains, the better the fit to the data, the authors express doubt of the usefulness of such descriptions. As pointed out above the comparison of the five models could be improved by applying them to the whole range of the experimental data and thereby testing their performance taking into account  $a_w$ . The discussion should be changed depending on these results.

To highlight the applicability of the  $\alpha(T)$  approach, a physical explanation for the change of contact angle with temperature is necessary.

It could be mentioned what other studies (Lüönd et al., 2010; Welte et al., 2012) using the same models to investigate the size and time dependence of immersion freezing concluded on the applicability of the different approaches to describe these features.

4939, Line 3-5: The fact that the necessary super cooling with respect to the melting point  $T_m - T_f$  remains nearly constant seems to contradict the hypothesis of an interaction of the solute with the IN surface (Reischel and Vali, 1975).

4940, Line 5: Lüönd et al., 2010 could be cited as additional reference for the size dependence of immersion freezing temperatures.

4940, Line 10: Welte et al., 2012 could be cited for the time dependence of immersion freezing.

4940, Line 15: It would be interesting for the reader to which differences you are referring. Aging effects, coatings?

4940, Line 16-23: Fitting a contact angle distribution or active site density assumes that these are particle properties which do not depend on ambient parameters. Therefore it is generally not true that such results are only valid for the experimental dataset from which they are obtained.

Also from the  $\alpha - pdf$ , single- $\alpha$  and active site model it is possible to calculate (apparent) nucleation rates at a given temperature (cf. Welte et al., 2012). The line of argumentation in this section should be adapted accordingly.

As mentioned above the authors should explain in more depth how the  $\alpha(T)$  approach is usable to gain “physical explanation” and for “exploiting the underlying physics”.

4941, Line 10-11: If the immersion freezing mechanism is independent of the nature of solute in combination with any IN is an unanswered question. Reischel and Vali (1975) reported that this is not so simple.

Supplement: The curves shown in Fig. 2 and 3 for the active site surface density look very different in comparison to the curves reported in Marcolli et al. 2007, Lüönd et al., 2010 or Welte et al., 2012 for this model.

### **Technical corrections:**

4919, Line 19, 20, 21: you could use the acronym “IN” for ice nucleus here. In addition it is the ice that nucleates on the IN and not the IN who nucleates ice. Consider to reformulate the definitions accordingly.

4921, Line 5: There are no “temperatures colder than heterogeneous ice nucleation” there are temperatures where homogeneous nucleation becomes more efficient than heterogeneous nucleation. Reformulate.

4928, Line 4: “r” might not be the best choice for a variable for the cooling rate as it is usually used as variable for the particle radius. I propose to use “ $\gamma$ ”.

4928, Line 17: ...temperature decrease  $> 10\text{K}$ ...

Fig.1: Experimental data for hom.  $\tilde{T}$  would be of interest to compare.

## References:

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, *Atmos. Chem. Phys.*, 7, 5081–5091, 2007.

Lüönd, F., Stetzer, O., Welti, A., and Lohmann, U.: Experimental study on the ice nucleation ability of size selected kaolinite particles in the immersion mode, *J. Geophys. Res.*, 115, D14201, 2010.

Reischel, M. and Vali, G.: Freezing nucleation in aqueous electrolytes, *Tellus*, 27 (4), 414 – 427, 1975.

Smith, R.S. and Kay, B.D.: Breaking through the Glass Ceiling: Recent Experimental Approaches to Probe the Properties of Supercooled Liquids near the Glass Transition, *J. Phys. Chem. Lett.* 3 (6), 725-730, 2012.

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Zobrist, B., Koop, T., Luo, B. P., Marcolli, C., and Peter, T.: Heterogeneous ice nucleation rate coefficient of water droplets coated by a nonadecanol monolayer, *J. Phys. Chem. C*, 111, 2149–2155, 2007.