

Response to Anonymous Referee #1:

We appreciate the reviewer's comments which are copied below. Our responses are given in bold fonts and line numbers refer to the manuscript currently under discussion.

In this paper the question is raised whether the number of droplets analyzed in experimental freezing studies is large enough to constrain uncertainties of experimental parameters sufficiently and how uncertainties in relative humidity, temperature, time, and surface area present in droplets affect interpretation of laboratory ice nucleation, corresponding ice nucleation parameterization and extrapolation to atmospherically relevant conditions. To do this, simulations of droplet freezing are carried out for recently published experimental freezing studies. The authors come to the conclusion that indeed the variation of heterogeneous surface present per sample often leads to strong uncertainties in J_{het} for the number of droplets investigated in experimental studies. However, in their analysis the authors explain all uncertainties in J_{het} by variations of ISA (ice nuclei surface area) per droplet and do not consider that a single J_{het} does not apply to a whole sample of INP when the sample composition is heterogeneous i.e. for multi component and inhomogeneous samples. In the introduction they state that J_{het} can be viewed as a material parameter, but did not specify that this is only the case for a homogeneous material or sample. In cases where their evaluation procedure derives a large value for the fit parameter σ_g , this condition is not fulfilled and their analysis leads to erroneous results when they apply a single J_{het} to the whole ISA present in a droplet. By using just one J_{het} , a non-linear slope $\ln J_{\text{het}}/T$ is ascribed to variations of surface area, while it is indeed caused by a variation of J_{het} . Therefore, they need to discuss for all studies whether it is justified to apply a single J_{het} and remove the ones for which this assumption is not fulfilled, which unfortunately will be the case for most datasets (the ones performed with ATD, K-feldspar, illite, and natural dusts). The assumption of a single J_{het} only seems to be valid for the kaolinite KGa-1b (see specific comments). Taking variations of J_{het} into account influences much of the conclusions drawn in this paper and make some even invalid. The implications of this study (Sections 3 – 5) need therefore to be reconsidered and rewritten. Such a revision is needed for publication in ACP.

We thank the reviewer for the evaluation of our manuscript. We would like to clarify some points raised by the reviewer when responding to this general comment:

First, as stated in general response, we do not assume a homogeneous sample. Our statement of J_{het} being material specific may have been confusing. We meant the J_{het} is particle-type specific. We use a single function of J_{het} for a single particle type, which is consistent with the concept of internally mixed ice nucleating components on the surface of particles (Broadley et al., 2012).

Second, accurate estimates of σ_g are not typically provided by previous studies, however when enough information is provided, as in Broadley et al. (2012) and Wright and Petters,

(2013), this parameter is well constrained. Contrary to this comment, it is undebatable that any surface area dependent nucleation description will be erroneous without correctly accounting for the variability of ISA in droplets. We have demonstrated this to be the case. The results of previous studies that assume identical ISA per droplet will suffer from incorrect surface area estimates.

Third, we have demonstrated that variability in ISA alone leads to a non-exponential decay of the experimentally derived unfrozen droplet fraction. ISA variability of components (i.e. variability of J_{het}) from droplet to droplet is therefore a challenged interpretation of immersion freezing. Currently, determining the ice nucleation ability of individual components on a particle's surface independent of a droplet freezing experiment is impossible. For now, the presence of different components or hypothesized active sites exhibiting different ice nucleation efficiencies for each droplet represents conceptual assumptions only. Instead, we encourage future studies to better measure and evaluate ISA and ISA variability in experiments, which are experimentally feasible. Clearly, any future studies that can observe and quantify ice active site properties independent of an ice nucleation experiment can also help to resolve this issue.

We agree with the reviewer that an exponential and non-exponential decay could imply a uniformity and diversity of these ice nucleating components in different droplets. However, uniformity and diversity of ISA in different droplets should be rigorously determined rather than assumed. We note that the Multiple Component Stochastic Model (MCSM) parameterizes droplet to droplet variability, by distributing ice active site on surfaces within droplets (Broadley et al., 2012). However, MCSM is applied assuming ISA is identical in each of the droplets as discussed in our general response. We suggest that future studies incorporate ISA measurements on a per droplet basis into new or modified mathematical frameworks. At present, active sites or multiple components exhibiting vastly different ice nucleation efficiencies from droplet to droplet and consequential variability in J_{het} remains an unproven or imposed concept, contrary to the reviewer's certainty that some particles of same type possess rare, but variable J_{het} , to significantly impact droplet to droplet variability.

Specific comments:

Page 13112, line 27: comparison with a second order rate constant is not very helpful and might be removed.

We agree with this point.

p. 13112, l. 24-28: "The heterogeneous ice nucleation rate coefficient, J_{het} , is a physically and experimentally defined parameter which gives the rate of nucleation events for given surface area and unit time. By definition, J_{het} is a material specific parameter, similar to a second order rate constant in gas-phase kinetics."

will be changed to

“The heterogeneous ice nucleation rate coefficient, J_{het} , is a physically and experimentally defined parameter which gives the rate of nucleation events for given surface area and unit time”.

Page 13114, lines 3-4: The singular hypothesis can be easily combined with a freezing point depression by determining a Δa_w .

We disagree with this statement. The singular hypothesis is an empirical description and, by definition, a function of temperature only. Therefore, it cannot account for any other physical observables such as solute concentration or water activity, a_w (e.g. Vali, 1971, Niedermeier et al., 2011; Rigg et al., 2013; Vali et al., 2015). Wex et al. (2014) parameterized f_{frz} data accounting for the freezing point depression using a temperature offset approach (also known as the lambda approach) following Koop and Zobrist (2009) and using a singular description, i.e. deriving $n_s(T, a_w)$. Thus, the authors introduced a new concept of active sites, that solutes in solution can alter a site’s ice nucleating capability. One study has tested the modified singular hypotheses accounting for time-dependent ice nucleation known as “ α -PDF” and “distribution of active sites”, and found that these were incapable of representing immersion freezing data in various aqueous solutions (Rigg et al., 2013).

p.13113, l. 29 - p. 13114, l. 9: “and the soccer ball model (Niedermeier et al., 2011), in which the latter assume that ice preferentially occurs on ice active sites located on the particle surface. According to the singular hypothesis, the number of active sites, $n_s(T)$, is dependent on T only. Furthermore, these parameterizations cannot describe the freezing point depression (e.g. Zuberi et al., 2002; Archuleta et al., 2005; Koop and Zobrist, 2009) and nucleation kinetics (in analogy of homogeneous ice nucleation) observed in immersion freezing experiments where the IN are immersed in aqueous solution droplets (Rigg et al., 2013; Knopf and Alpert, 2013). These limitations clearly support further analytical efforts to improve our understanding on the governing parameters of immersion freezing.”

Will be changed to

“and the soccer ball model (Niedermeier et al., 2011). For example, Rigg et al. (2013) showed that the single contact angle model, α -PDF model, active site model and singular description cannot describe the freezing point depression (e.g. Zuberi et al., 2002; Archuleta et al., 2005; Koop and Zobrist, 2009) and nucleation kinetics (in analogy of homogeneous ice nucleation) observed in immersion freezing experiments where the IN are immersed in aqueous solution droplets (Rigg et al., 2013; Knopf and Alpert, 2013). According to the singular hypothesis, the number of active sites, $n_s(T)$, is dependent on T only and neglect ice nucleation kinetics. Wex et al. (2014) parameterized f_{frz} data accounting for the freezing point depression using a temperature offset approach following Koop and Zobrist (2009) and using a singular description, i.e. deriving $n_s(T, a_w)$. However, the approach the authors used is solute

type dependent (Koop and Zobrist, 2009) and thus, may be cumbersome for atmospheric application where INPs can be associated with a wide variety of solutes. These limitations clearly support further analytical efforts to improve our understanding on the governing parameters of immersion freezing.”

Page 13116, lines 9 – 11: Lüönd et al. (2010) and Marcolli et al. (2007) do not assume that every droplet contains the same ISA. The citations have to be revised.

We thank the reviewer for pointing out this mistake and we will alter this sentence. Our main point was that the ISA in each individual droplet used is typically not measured or considered. Typically, average ISA is estimated and applied for all droplets (Broadley et al., 2012; Herbert et al., 2014).

p. 13116, l. 9-13: These sentences will be removed and the following new paragraph will be added. “An assumption typically made is that all droplets contain the same ISA, or $A_{tot}=A_g N_{ufz}$, where A_g is the ISA for all droplets (e.g. Niedermeier et al., 2010; Murray et al., 2011; Rigg et al., 2013). Using this assumption and assuming a continuous differential in Eq (1) leads to,

$$2) \frac{dN_{ufz}}{N_{ufz}} = -J_{het} A_g dt.$$

Integrating Eq (2) further results in the commonly used expression for the fraction of frozen droplets,

$$3) f_{frz} = \frac{N_{frz}}{N_{tot}} = 1 - e^{-J_{het} A_g t}.$$

The form of the expression given in Eq (3) is used in many studies although modified slightly when considering multiple components or contact angle distributions (e.g. Niedermeier et al., 2010; Murray et al., 2011; Broadley et al., 2012; Rigg et al., 2013), and when particle or droplet sizes are discretized or binned (e.g. Marcolli et al., 2007; Lüönd et al., 2010). The major weakness of this exponential form to describe f_{frz} lies entirely in the assumption it is based on, i.e. it is only valid if the ISA is exactly the same for all droplets considered. When taking into account individual droplet ISA for all droplets, this formulation is not valid. Thus, application of this formula to interpret ice nucleation studies, or use in mathematical frameworks, strictly speaking, is also invalid when ISA on a droplet per droplet basis is different.”

p. 13114, l. 20: We will add the sentence “Despite this assumption, advancement in accounting for particle size variability considering multiple charged particles in ice nucleation experiments has been made (Lüönd et al., 2010)”.

Page 13133, line 9: Such an increase due to surface roughness is not justified when one considers kaolinite particles with 300 nm diameters (e.g. Welti et al., 2009).

We have altered our model simulation by constraining the Fluka kaolinite ISA distribution in Wex et al. (2014) to the multiple charge distribution outlined in Wiedensohler and Fissan (1988). We have calculated the probability for particles having multiple charges as a function of particle diameter, $P(\ln D_p)$, at a constant electrical mobility diameter of 300 nm. The distribution $P(\ln D_p)$ is a probability density function from which particle diameters can be sampled in new simulations, IsoCFDC and IsoLACIS. We will include a new supplemental figure, Figure S1, which shows the result of sampling 833 particle diameters from this distribution. Individual particle surface area is calculated assuming spherical particles. Using this new ISA distribution, shown in Fig. S1, a lognormal distribution and parameters μ_g and σ_g are not required in IsoCFDC and IsoLACIS.

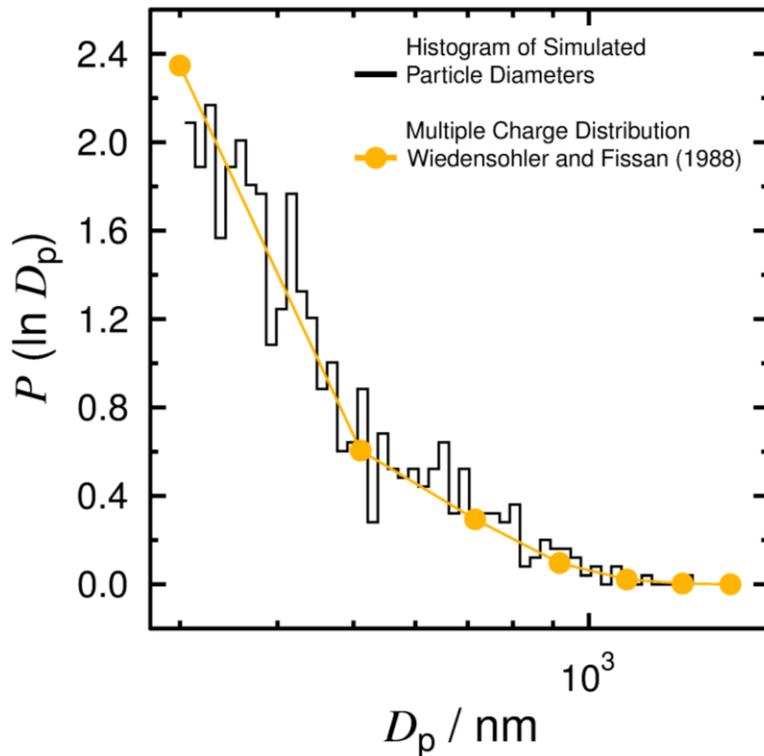


Figure S1: Probability density function, $P(\ln D_p)$, of multiple charged particles with respect to particle diameter, D_p , with a constant electrical mobility diameter equal to 300 nm. Orange circles at 300, 510, 720, 920, 1100, 1300 and 1500 nm represent particles with increasing multiple charges, i.e. 0, 1, 2, 3, 4, 5 and 6 extra charges, respectively. The histogram in black shows the frequency distribution of 833 randomly sampled D_p from $P(\ln D_p)$.

p. 13132, l. 27: "...tendency for greater surface area than assumed. Therefore, a distribution of particle surface area is expected and used in IsoCFDC and IsoLACIS with parameters $A_g = 6.2 \times 10^{-8} \text{ cm}^2$ and $\sigma_g = 8.2$. These values were fitted to experimentally derived f_{frz} ."

will be changed to

“...tendency for greater surface area than assumed. Additionally, particles of larger diameter, and thus larger surface area, may have the same electrical mobility due to the presence of multiple charges. Therefore, a distribution of particle surface area can be expected. Following Wiedensohler and Fissan (1988), the probability for particles having multiple charges as a function of particle diameter, $P(\ln D_p)$, at a constant electrical mobility diameter of 300 nm is shown in Fig. S1. The distribution $P(\ln D_p)$ is a probability density function from which particle diameters are sampled in simulations IsoCFDC and IsoLACIS. Individual sampled particle surface area is calculated assuming spherical particles.”

Experiments Iso1 – Iso4 shown in Figure 1a: This figure shows experiments from Herbert et al. (2014; Figs. 4b (KGa-1b, 16 droplets) and 7 (K-feldspar, 20 droplets). Herbert et al. state that K-feldspar is a multicomponent system and should therefore be represented by different J_{het} , not just one. They write: “For a uniform species the decay of liquid droplets over time will be exponential (as was the case for kaolinite KGa-1b in Fig. 4b), whereas a diverse species will result in a non-exponential decay. Inspection of the data in Fig. 7 shows that the decay of liquid droplets was not exponential, again consistent with a diverse population of INPs.” In the present analysis, the parameter σ_g is used to account for droplet to droplet variability. This seems to work as fitting procedure but has no physical meaning. The authors should discuss this. I suggest that they remove these data from the paper.

Please see our general comment and previous responses above regarding our approach of using a single averaged J_{het} and the hypothesized existence of J_{het} variability *between droplets*. The quote from Herbert et al. (2014) is only valid if the droplets contain the same ISA. We reiterate that variable droplet volumes, particle roughness, variability in particle numbers per droplets, etc... can all contribute to ISA variability and result in a non-exponential decay.

Our model shows that using too few droplets results in substantial uncertainty in experimentally derived f_{ufz} . In the case of Broadley et al. (2012) and Herbert et al. (2014), it is highly likely (5-95 percentiles) that if the authors had repeated their experiments with the same N_{tot} , measured values of f_{ufz} would lie within the shaded regions shown in Fig. 2A and C. Thus, a single measured decaying trajectory of f_{ufz} versus t may or may not be exponential simply by chance. In other words, the uncertainty is sufficiently large that one could draw a straight line or a line having greater curvature than what is expected between the percentile bounds. This is stated on p. 13123, l. 23-24 and p. 13124, l. 14-17. From this we conclude that there is too much uncertainty in the results of Broadley et al. (2012) and Herbert et al. (2014) to make a clear statement that illite or feldspar are externally mixed multicomponent systems as the authors define them. We have demonstrated that variability in ISA alone can fully explain the trajectories of f_{ufz} versus t , to such a degree that evoking (i.e. not measured) different ice nucleating components in different droplets is not necessary.

The σ_g parameter applied in our model is, in fact, physical, contrary to what is stated by the reviewer. As discussed above it is impossible to expect that every droplet prepared in an immersion freezing experiment possesses exactly the same ISA. Instead, actual values of ISA per droplet will deviate around an expected value, e.g. an average value and standard deviation. The parameters in our model, A_g and σ_g , are physical, observable, measurable, and reproducible. They are exactly the median and geometric standard deviation for a logarithmically distributed ISA. Logarithmic values are required because ISA can vary orders of magnitude and negative ISA values are impossible. Values of A_g and σ_g are accessible and can be known before an immersion freezing experiment is performed by measuring ISA in each droplet (e.g. Wright and Petters, 2013). Other parameters are N_{tot} and J_{het} , which are unquestionably physical and measurable.

p. 13116, l. 13: A new paragraph will start here which reads as follows: “The ISA in a single droplet is a measurable quantity with a corresponding measurement uncertainty. It is unlikely that every droplet prepared in an immersion freezing experiment has identical ISA. For the same particle type, there exists a systematic ISA uncertainty with respect to a particular droplet preparation technique. This systematic uncertainty is σ_g and can be determined by directly measuring ISA in a population of independently prepared droplets. Since the ISA variability cannot be resolved from....”

It should be noted that our approach using observables to describe immersion freezing is in contrast to the approaches used in other models, e.g. the multicomponent stochastic model, or MCSM, (Broadley et al., 2012; Herbert et al., 2014), the soccer ball model (Niedermeier et al., 2011), the singular (or deterministic) model (Vali, 1971; Connolly et al., 2009; Niemand et al. 2011), α -PDF model and the distribution of active sites model (Marcolli et al., 2007; Lüönd et al., 2010). The parameters in all of these models stem from fitted frozen fraction data and cannot be directly accessed in experiments. As an example, we demonstrate this for the MCSM (Broadley et al., 2012; Herbert et al., 2014) to describe immersion freezing by NX illite. For each i^{th} component on the surface of NX illite particles immersed in different droplets, $J_{het,i}$ is not known. It is fitted to the equation $\ln(J_{het,i}) = a_{NXillite}T + b_i$ that reproduces frozen fraction data, having parameters which are not experimentally accessible. In the MCSM, J_{het} is in principle a physically defined variable. However, it is incapable of being measured on a per active site basis. It follows that the ice nucleating ability of a surface component is conceptual by definition, not a physically, measurable quantity. It is only defined after it is fitted to the same ice nucleation experiment that it aims to reproduce.

We respectfully disagree with the reviewer that these data and model results should be removed. Please see our points in the general comment. A main goal of our study is to demonstrate to what degree variability of ISA is significant for analysis of ice nucleation data, i.e. when is the assumption that all droplets contain the same ISA is no longer valid. We conclude from our model results that quantification of the ISA distribution is necessary before deriving any solid conclusion about the presence of multiple components or active sites.

Furthermore, our model results yield three major contributions to advance our understanding of immersion freezing: 1) The model provides guidance for immersion freezing experiments by setting constraints on the minimum amount of droplets that need to be examined and trials required. This is demonstrated by using previous experimental data. The model outcome challenges us to make better measurements of ISA per droplet. 2) The model resolves commonly used, but yet unproven, assumptions that contribute to additional uncertainty. Removing these assumptions, or carefully evaluating their validity, will decrease the uncertainty in predicting immersion freezing for model implementation. 3) The simulations extend the validity of α_w based immersion freezing model, or the ABIFM (Knopf and Alpert, 2013). We show in Figs. 1-3 and 5-8 that the ABIFM can reproduce immersion freezing by mineral dust for many vastly different experiments and methods. By design, the ABIFM simultaneously accounts for immersion freezing in aqueous solution, independent of the nature of the solute.

p. 13145, l. 4-10: We will modify our conclusions in response to this comment to clarify. "These findings have significant implications for analysis and interpretation of immersion freezing data. We suggest that ice nucleation experiments and field studies focus on the effect of particle surface area and nucleation time for further validation of presented analyses and improvement of our predictive understanding of atmospheric ice formation. Laboratory derived J_{het} values can greatly aid in interpretation of atmospheric ice nucleation due to the fact that this parameter allows extrapolation to time scales and IN surface areas experienced in the atmosphere. A very simple stochastic..."

will be changed to

"Our findings concerning laboratory immersion freezing experiments emphasize the importance of setting constraints on the minimum number of droplets and experimental trials that need to be employed for improved characterization of ISA per droplet. The results presented here resolve commonly used assumptions that contribute to additional uncertainty in predicting immersion freezing data for model implementation. The simulations use ABIFM, shown to be valid for various INP types. We demonstrate that the ABIFM can reproduce immersion freezing by mineral dust for many vastly different experimental designs and measurement methods. Laboratory derived J_{het} values can aid in testing existing ABIFM parameterizations and formulating new ones. Their application to a very simple stochastic..."

Experiment IsoWR shown in Figure 1b: ATD is again a multicomponent system and should therefore be represented by different J_{het} , not just one. I suggest that this dataset is removed from the paper.

Please see also previous comments. We never claim that ATD is a single-component system. Wright and Petters (2013) clearly state that their droplets have variable ISA. Our model

simulations demonstrate that at a constant T , J_{het} can reproduce the results of Wright and Petters (2013) and that variability in ISA per droplet can explain the observed non-exponential dependence. Furthermore, the statistically derived uncertainty, based only on the number of droplets the authors employed in their experiments, can entirely explain the scatter in their data. Again, this representation of the experimental data is possible without invoking the concept that some droplets contain non-observable, rare ice nucleating sites. We believe that these results provide substantial evidence for our hypothesis and conclusions and, therefore, they should remain.

Experiments IsoBR and IsoHe2 shown in Figure 2: Broadley et al. (2012) use a multiple component stochastic model to describe their data (Murray et al., 2011). This model describes systems in which there is more than one nucleating species or type of nucleation site. Each nucleation site can be described by a single temperature dependent nucleation rate coefficient and the total absolute rate of freezing is a function of the distribution of nucleation sites. This seems to be the appropriate way to interpret the illite NX data. Assuming just one J_{het} does not seem to be justified. Moreover, Broadley et al. (2012) rule out different surface areas present in different droplets as a valid explanation for their experimental results: “One explanation is that different droplets may not have contained the same surface area, due to an inhomogeneous distribution of particles or particle sizes between droplets, which could have occurred during nebulisation. However, the surface area of NX illite in the droplets which nucleated in the first half of run 20 would have needed to be about seven times larger than the surface area in the droplets which nucleated in the second half if only one type of nucleation site was present, which seems unlikely. In addition, this did not appear to be the case when we applied the same experimental technique to ice nucleation by kaolinite (Murray et al., 2011b).” IsoHe2 was performed with K-feldspar which was considered by Herbert et al. (2014) as multicomponent sample, hence a single J_{het} is again not applicable. I suggest that these datasets are removed from the paper.

We disagree with the reviewer that the datasets and our model results should be removed. Please see general comment and comments above. The main argument made by the reviewer is that a multicomponent model ‘seems to be appropriate’ to explain the experimental data sets. As discussed above, the concept of the multicomponent model relies on unmeasurable parameters. In the future it may be proven correct or incorrect. Mathematical representation of experimental data is not sufficient proof of a new concept which is not physically founded. We feel that significant reduction of uncertainty calls for use of a physical model or theory using measurable parameters. For these reasons, it is well justified in questioning other interpretations of immersion freezing analyses.

In Table 3 of Broadley et al. (2012), it is clearly stated that “run 20” applies droplets in the size of 10-20 μm . This means that the volume of the droplets varied by a factor of 8 (see general comments). Considering this ISA variability, the non-exponential trajectory of $f_{\text{ufz}}(t)$ for NX illite can be entirely explained by ISA variability.

Experiments IsoDI1, IsoDI2, IsoDI3, Figure 3: These experiments were performed with illite NX, which is not a pure sample but contains only 60 – 69 % illite (Diehl et al., 2014 and references therein). Moreover, the large temperature range of freezing observed for illite NX suggests that a contact angle distribution has to be used to describe this sample as was done by Hiranuma et al. (2015) and a single Jhet is not applicable. The authors should discuss how this affects the fitting parameters derived for illite. I suggest that these datasets are removed from the paper.

We disagree with the reviewer that we should remove these data and model results from our manuscript for same reasons as given above. The main argument made by the reviewer is that freezing over a wide temperature range suggests that a contact angle distribution should be used. As discussed in our general comment, many components can exist on a particle surface with different efficiencies to nucleate ice. This can be parameterized by a contact angle distribution or any other mathematical framework. However, application of a suggestive or assumed concept, does not constitute a proven interpretation. Thus, questioning other interpretations of immersion freezing and compare those to our model results is justified.

We reiterate and emphasize that all of our model parameters are directly measureable without the need of ‘fitting to the data’. Diehl et al. (2014) did not provide sufficient information to derive or estimate variability in ISA, and thus some parameters must be fitted. However, we have clearly stated that there is too much experimental uncertainty due to the small number of measured droplets to better constrain ISA. The large statistical uncertainty is derived from small N_{tot} and, therefore, is independent from any chosen ISA or contact angle distribution. This means that an ISA distribution or a contact angle distribution will be equally uncertain not allowing to infer superiority of one approach over the other.

Spelling error: Page 13134, line 8: “s” has to be removed from “particles”.

This has been corrected.

Figure 3, Figure caption, second line: add “of” between “function” and “time”.

This has been corrected.

References:

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