

Interactive comment on “Heterogeneous freezing of water droplets containing kaolinite and montmorillonite particles” by B. J. Murray et al.

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Referee #1 stated the main issue in connections with this paper in a somewhat tentative way. I'd like to make the point more firmly. It is a question that has been debated for nearly half a century and remains a source of errors mostly because of mis-applied intuition and tradition. I am referring to describing heterogeneous ice nucleation as either stochastic or singular. And it all comes down to the interrelatedness of time and temperature in experiments and in models.

The main argument against the application of a stochastic description to heterogeneous ice nucleation is presented briefly, then the manifestation of that in the Murray et al. paper will be discussed.

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Envisaging the dynamic clustering of water molecules into an ice germ clearly leads to the recognition of stochastic fluctuations in the chance to reach critical size and hence to a definite time dependence of nucleation. Theory and experiment fully support this for homogeneous nucleation and it is inevitably a factor in heterogeneous nucleation as well. However, the evidence is also clear for the existence of nucleation sites with specific energy contributions to passing the barrier to formation of the stable phase. This is the physically plausible and accepted description of the role of nucleating substances. How to combine these two elements of the process into a model and to test that model with experiments is at the heart of the problem.

The results of experiments in which to some degree, if not fully, temperature and time were decoupled, led to the “modified singular” description (Vali and Stansbury 1966, Vali 1994, Vali 2008, and other references cited there). In essence, heterogeneous nucleation temperature in a volume of water is determined primarily by the characteristic temperature T_c of one or another site on the suspended impurities (singular description) and secondarily by random fluctuations about that value.

With nucleation on a foreign surface, stochasticity would result either from having a uniform surface or from having a very large number of identical sites uniformly distributed on the surfaces of even the smallest particles of that material. Neither is a realistic assumption. Empirical manifestations of stochastic heterogeneous nucleation would be that the likelihood of nucleation would rise in proportion to the surface area of the foreign material in the sample, that all identical samples (drops) would have an equal chance to freeze at any moment, and that sooner or later any volume of water containing some of the material would undergo nucleation. The first of these manifestations is shared equally by the singular model, the second and third are not. Therefore, the first does not constitute proof in either sense. The other two afford possible ways to testing stochasticity. It is the negative outcome of such tests that constitutes powerful evidence against the stochastic model for heterogeneous nucleation, while the same kinds of test for homogeneous nucleation provide positive support. At the same time it

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should be emphasized that experiments in which temperature is decreased at a steady rate cannot provide any proof for stochasticity unless a large number of repetitions are performed with a large number of macroscopically identical samples. That is so, because time and temperature are closely coupled and an increasing fraction of frozen drops, or other measures, can result from lapse of time or from activation on less active nuclei.

The results summarized in the foregoing are not as simple as they are made to sound here, but their essence is as stated. The references cited complete the picture. However, as the paper under discussion demonstrates, along with a number of other recent publications, those conclusions are not generally accepted, though it is fair to say that no contradictory evidence has been presented so far. It seems that the appeal of the stochastic description is hard to overshadow.

Specifically, on page 9704, lines 9-10, Murray et al. state that "... heterogeneous nucleation on kaolinite is a stochastic process ... supported later in the paper." That support appears to be that the probability of freezing scales with surface area for kaolin. As pointed out earlier that is also consistent with the singular model. Differently from kaolinite, freezing temperatures didn't change with the mass of suspended montmorillonite. In the last paragraph of page 9713 the authors propose that the two minerals have to be described by the two different models. That is surprising as there is no reason to think that nucleation has some inherently different mechanism on one mineral or another. Only qualitative differences can reasonably be expected.

The authors do not rationalize why different nucleation mechanism are at work for the two minerals. There is more than 6°C difference in the freezing temperatures reported for the two materials but both are well separated from the homogeneous freezing temperature for the higher particle concentrations. So, it is clear that nucleation is brought about by the impurities. How can then one material produce freezing depending on the amount of suspended particulate and the other not? According to Table 1, the amount of kaolinite had a ratio of 11.7 for the ratio of 20 in mass concentration (0.05 % to 1%),

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while the same ratio for montmorillonite is 22.2, close to what is expected. It is unclear what the 11.7 ratio means, but is consistent with having different size distributions for samples of different mass concentrations of kaolinite. Table 1 also reveals that there was roughly four times the surface area of montmorillonite (at 1% mass) than of kaolinite, i.e. particles on the average were smaller. None of this translates into a ready explanation of the different results for the two materials in terms of the density and quality of sites, i.e. the modified singular description, but it hints at the possibility that if the detailed size distributions of the particles were known perhaps clearer interpretations could be made of the results. Of course, just knowing the size distribution is not fully adequate since there is no assurance that the probability for a given type of site to occur will be the same, after generation of the powders by grinding or other means, for particles of all sizes.

While I clearly disagree with the interpretations of the measurements presented in this paper, those measurements reveal that the authors succeeded in developing a system that can produce important data on heterogeneous freezing nucleation.

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