

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

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Received and published: 9 May 2010

The new observations included in the reply by Murray and colleagues (ACPD 10, C2430) add very good material for continuing this debate about the applicability of a stochastic model to heterogeneous ice nucleation. I'll refer to this reply as M-REP and to the original paper under discussion as M-ORG

Indeed, experiments at constant temperatures constitute a good test of stochasticity. I reported on similar experiments in 1994 (J. Atmos. Sci., 51, 1843-1856, V94). The results of those experiments are qualitatively the same as those described in M-REP: the fraction of drops that remains unfrozen decreases with time and some drops are still unfrozen at the end of the period of time at constant temperature. The crucial difference between stochastic and singular character in such an experiment can be

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found by examining the rate (i.e. probability) of freezing per unit time  $1/n \cdot (dn_{liq}/dt)$ . Stochasticity would lead to a rate that is constant with time, while a decreasing rate with time is consistent with the modified singular description (cf. Fig 3 in V94).

Using rough numbers extracted from Fig. 1 in M-REP, it seems that the sample size in this experiment was 40 drops and each point in the graph represents the freezing of one additional drop. The rate of freezing, estimated as the inverse of the time interval between successive events, has two bursts of high values near 2800 and 3250 seconds, and low values past that. The number of points is insufficient to convincingly show either constancy or decrease. Clearly, more data will have to be examined .

As a minor issue, I want to reiterate my disagreement with the volume versus surface area dependence argument in M-ORG and in M-REP. Volume dependence arises in heterogeneous nucleation because when a bulk sample containing a suspension of particles is subdivided into drops of equal volumes, the average number of particles per drop scales with the volume of the drops. The probability of freezing due to the suspended particles is proportional to the number of particles per drop. It is also proportional to the total surface area of suspended material in the drops. It is proportional to the likelihood of finding a site active at a given temperature. Thus, the average freezing temperature, or the fraction frozen at a given temperature will vary in parallel with the amount of suspended material within a wide range of concentrations. That range is limited by saturation at the upper end, i.e. so much suspended material that dilution still leaves a high probability of finding an active site in every drop. At the low end, many drops will have no suspended particles at all, or none with active sites, so that many drops will freeze at or close to the homogeneous freezing temperature. It follows that dependence of freezing temperatures on total surface area is compatible with both the stochastic and the singular descriptions.

The new measurements in M-REP were made at 248 K with 0.23 wt% kaolinite. By the time 248 K was reached 5% of the sample drops were frozen. Interpolating between 0.1 wt% and 1 wt% data given in Fig. 1 of M-ORG, this fraction frozen was

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reached near 242 K. This difference may indicate a change in the properties of the kaolinite sample, either in size distribution or in surface properties. As argued before, the weight fraction, or even the BET surface area of suspended material is insufficient to uniquely characterize the nucleating potential of a powder. This is clearly important when comparing the results of different experiments.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 9695, 2010.

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