NOVELTIES IN ICE NUCLEATION TERMINOLOGY

G. VALI[1], P.J. DEMOTT[2], O. MÖHLER[3] and T.F. WHALE[4]

[1]Department of Atmospheric Science, University of Wyoming, Laramie, WY, USA (Retired-Emeritus).

[2]Department of Atmospheric Science, Colorado State University, Fort Collins, CO, USA.

[3]Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany.

[4]School of Earth and Environment, University of Leeds, Leeds, UK.

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INTRODUCTION

A revision of the Nucleation Terminology of 1985 was put forth in Atmospheric Chemistry and Physics (**15**, 10263, 2015; VDMW15), focussed on ice nucleation. For some of the terms dealt with in VDMW15, in connection with heterogeneous ice nucleation, additional explanations are offered here with a grouping by the degree of novelty involved. The goal is to promote the acceptance of the terms and to motivate discussion about the principles involved.

MOST NOVEL, MOST CONTROVERSIAL

1. **Site nucleation rate (4.7.2)**[1]. This term is suggested as a clear indication for the probability of nucleation on a site of given characteristics. In principle this is the most fundamental measure for heterogeneous nucleation. This is the quantity that is derived from CNT[2] where the physical parameters defining the site are specified.

   Site nucleation rate has been given the symbol J_{site}, but it is the same as designated as J_{T_c} in Vali (2008). Empirically, different sites are diagnosed by their freezing temperatures and this temperature can be taken as being a first estimate of the characteristic temperature of the site (in terms of the VS66 model); hence the equivalence of J_{site} and J_{T_c}.

   What is new with this definition is the focus on site-specific nucleation, i.e. recognizing that the value derived from CNT, or determined from experiment, is specific to a sub-set of potential sites in a sample. The emphasis on site-specificity is necessary in order to distinguish it from nucleation rate in homogeneous nucleation, and from the assumed cases of infinite number of sites of identical potential for nucleation under given conditions. Here, we stress that the fact that when a large spread of freezing temperatures, say more than 5°C, is observed in an experiment, that spread can safely be assumed to be due to difference in effectiveness of sites and not a statistical spread associated with a single value of the rate coefficient. The 5°C spread is quite conservative, as current evidence points to an even smaller value, more like 1-2°C (Vali 2008; Wright and Petters *et al.* 2013). These estimates are inferred from repeated observations of the freezing tempeartures of the same drop, which is dilute enough

[1]These numbers refers to the paragraph on the topic in VDMW15

[2]The symbols and acronyms given in VDMW15 are used in this communication. They are listed in Table 1 of VFMW15.

to minimize the probability of containing more than one INP and more than one site. A narrow range of freezing temperatures for a population of drops (such as reported in Wex *et al.* 2015) may also arise with high numbers of INPs that carry identical sites so a site nucleation rate may also be inferred from that data. However, the proof for the identical configuration of sites, or for the lack of alteration of single sites in repeated freezing tests, should, ideally, have independent confirmation. Such independent confirmation is not feasible with current methods, so inferences for J_{site} from either method are the best estimates that can be obtained.

2. **Stochastic description (4.8.1)**. The main novelty, or clarification in this case, is to emphasize that the stochastic description means assuming that there are a very large number of locations (sites) on the surface of the nucleating material with the same probability of having a critical embryo form on it. When freezing temperatures in an experiment are observed to extend over a range ΔT and the results are assumed to arise from a single nucleation rate function J, it follows that the range of appreciable values of J also extend over the same ΔT. For ΔT greater than 1-2^{o}C, this contradicts the expectation from homogeneous nucleation and from relevant experiments (not detailed here) that the J function is a very steep function of temperature. In a number of papers the data are reconciled with theory on the basis of multiple J functions representing a variety in nucleating ability(cf. Section 4.8.2 in VDMW15)

3. **Freezing rate (4.6)**. (Some authors use "extensive nucleation rate" for the same concept.) This term is a straightforward representation of the results of freezing experiments with multiple sample units. The distinction between freezing rate, R, and nucleation rate J, is worth emphasizing since assuming the two to be the same implies the acceptance of a stochastic description, and in many papers is then identified as an application of CNT. However, use of the first order reaction equation $rate = (1/N)(\delta N/\delta T)$ to describe the rate at which freezing is observed for number of sample units is, strictly speaking the freezing rate $R(T)$. Interpretation of this rate as the nucleation rate $J(T)$ is only valid (as in homogeneous nucleation) if all sample units are identical. For heterogeneous nucleation that can only be satisfied if the INP content of all sample units is exactly the same, with the same surface characteristics. This condition is very demanding and in view of the complexities of surfaces can't be fulfilled with simple measures of laboratory procedures. Neither is there any simple inference from the observations of $rate$ that the condition of uniformity is fulfilled or not. Thus, using $rate = J(T)$ and then using CNT to interpret the observations is very difficult to justify.

IN WIDESPREAD USE

1. **INP – ice nucleating particle, and its variants like INM (4.1)**. The main change with this term is to replace the use of ice nucleus, IN, in order to recognize that the reference is in the vast majority of cases is, in fact, to the particle that carries the ice nucleating site, not to the embryo which is really the ice nucleus. Variants of the term, such as INM has also seen fairly extensive use to refer to ice nucleating macromolecules. In that case too, the site is a minor part of the entity, so referring to as INM is more informative.

2. **Modes of heterogenous ice nucleation (4.4)**. Reference to "modes" to distinguish between freezing and deposition nucleation has been well established in the literature. What is somewhat new in comparison with the 1985 definitions is the lack of emphasis on condensation-freezing and a much reduced focus on contact nucleation. This is due to the lack of clear evidence that these pathways are fundamentally different from immersion freezing. Both are freezing events initiated by an INP within supercooled water. Freezing within pores appears

to be consistent with observations that were previously interpreted as deposition (Marcolli 2014).

OUTSTANDING

Entries in this list represent newer, less settled or less known designations and concepts. Publications of recent years reveal that there are many important questions concerning these processes, which, by turn, are also of potential relevance to the processes believed to be better understood.

1. **Contact nucleation (4.4.2)**. Also called, although with subtle differences **surface nucleation or edge nucleation**. Literature support is fairly strong, though not extensive, for preferential nucleation with the ice nucleating surface, INS, when located at the outer boundary of a water drop, i.e. at the water-air-INS interface. This situation may arise, to take an atmospheric example, as a result of a collision between an INP and a water drop. In the laboratory, a variety of arrangements has been used to create the water-air-INS interface (*e.g.* Ladino *et al.* 2013; Niehaus *et al.* 2014; Gurganus *et al.* 2014; Yang *et al.* 2015; Nagare *et al.* 2016). It isn't yet clear if a distinction needs to be made between the cases in which the drops are supercooled at the moment of collision and cases in which the particle remains at the surface following collision at some earlier time (termed "adhesion freezing" in Nagare et al. 2016). A difference has been reported depending on the INP being located inside or outside the drop, i.e. mostly in the liquid or mostly in the air. The dynamic effect of a collision, or the preconditioning of the INP prior to collision are other potential sources for influencing the outcome. Further clarification will have to be awaited to narrow the evidence on these modes of ice nucleation. These processes may have practical impacts, specially in cloud glaciation, and are intriguing processes whose clarification can provide important insights to nucleation.

2. **Dynamic effects**. A moving water-substrate interface has long been associated with freezing on shaking and other similar phenomena. Few reproducible and quantitative experiments have been performed, so that knowledge of these dynamic effects in not much beyond anecdotal. Movement associated with electrowetting has been shown to lead to enhanced nucleation in Yang *et al.* 2015. As mentioned in the previous paragraph, contact nucleation may also involve a dynamic effect.

CONCLUSIONS

The study of ice nucleation is progressing at a rapid pace. This is clearly reflected in the state of flux that is evident in the nomenclature of heterogeneous ice nucleation. Many concepts are being reviewed, revised and brought into question by new evidence. All this puts special demands on communicating ideas and describing results carefully and unambiguously. Any set of definitions – terminology – will undergo both gradual acceptance and continuous revision. This paper is just a marker in that process.

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