



Interpretation of
freezing nucleation
experiments

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Interpretation of freezing nucleation experiments: singular and stochastic; sites and surfaces

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Publications of recent years dealing with laboratory experiments of immersion freezing reveal uncertainties about the fundamentals of heterogeneous freezing nucleation. While it appears well accepted that there are two major factors that determine the process, namely fluctuations in the size and configuration of incipient embryos of the solid phase and the role of the substrate to aid embryo formation, views have been evolving about the relative importance of these two elements. The importance of specific surface sites is being established in a growing number of experiments and a number of approaches have been proposed to incorporate these results into model descriptions. Many of these models share a common conceptual basis yet diverge in the way random and deterministic factors are combined. The divergence can be traced to uncertainty about the permanence of nucleating sites, to the lack of detailed knowledge about what surface features constitute nucleating sites, and to the consequent need to rely on empirical or parametric formulas to define the population of sites of different effectiveness. The goal of this paper is to demonstrate that recent experiments and models, consistent with earlier work, point to the existence and primary role of permanent nucleating sites and to the continued need for empirically based formulations of heterogeneous freezing. The paper focuses on three identifiably separate but interrelated issues: (i) the combination of singular and stochastic factors, (ii) the role of specific surface sites, and (iii) the modeling of heterogeneous ice nucleation.

1 Introduction

This paper focuses on laboratory experiments of heterogeneous freezing nucleation. Many such experiments have been reported in recent literature. While disagreements about some of the fundamentals of the process continue to present problems, a considerable degree of commonality in the data can also be identified. The goal of this paper is to examine both sides of the situation.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



It is well known that heterogeneous nucleation of ice takes place at quite different temperatures depending on the chemical and physical properties of particles present in the water, or in contact with it. It is also fairly well established that the probability of nucleation increases in proportion to the total amount, more specifically the total surface area of the particles. On the other hand, still little is known about the specific surface properties that govern what conditions lead to ice nucleation and about the structure of the ice embryos which eventually become stable. Conceptual descriptions of heterogeneous nucleation center on two main factors: one factor specific to the interaction between the nucleating surface and the embryo of the new phase, the other due to random timing of the formation of a stable embryo. The first can be viewed as a static factor, the second as a dynamic one. The static factor is very complex because it involves details about what surface properties or anomalies serve as sites for embryo formation. In addition it has to incorporate details about how the sites are distributed among otherwise identical particles, and how particles are distributed among sample volumes of water in an experiment. The first of these difficulties is by far the most serious and is the fundamental reason why theoretical descriptions remain rough approximations.

The main elements of the dynamic factor can be envisaged in terms of the energy difference between the solid and liquid phases and the rate at which molecules are added to the embryo or detach from it. This view has been confirmed for homogeneous nucleation. Only rough estimates are available for defining the same parameters for a crystalline embryo on a substrate. Classical nucleation theory (CNT) is based on the foregoing description with two assumptions, namely that the embryos can be viewed similarly to liquid drops and that the interaction with the foreign surface can be characterized in terms of the contact angle between that surface and water. These assumptions are considered substitutes for more definitive parameters until those are identified.

In accord with the two types of factors discussed, emphasis in experimental studies is placed on measurements of the temperature-dependence and/or of the time-

dependence of nucleation. Interpretations of the experimental results face considerable difficulties in identifying the relative importance of the two factors. At the most basic level, the difficulty arises from the impossibility to fully decouple temperature and time in any practical experimental approach. This dilemma gave rise very early in the history of freezing nucleation studies to two separate ways of interpreting the same observations; one assigned primacy to time the other emphasized the temperature-dependent impacts of the impurities. The origins of this dichotomy – the stochastic and singular models – are reviewed in Appendix A.

This paper is an examination of how the singular and stochastic aspects of heterogeneous freezing nucleation are evidenced in experiments, the models that have been constructed to describe that behavior, and how the evidence leads to models that combine both aspects. While given experiments often direct attention to one or other factor due to the design of the experiment, the reported results are actually more complementary than contradictory and can be interpreted in a consistent way, leaning on the relatively small impact of time-dependent effects.

2 Singular vs. stochastic nucleation

The quantitative statement of the singular model starts with assigning a “characteristic temperature” to each nucleating site and expresses the abundance of sites of various characteristic temperatures in terms of differential and cumulative nucleus spectra (Vali, 1971; Murray et al., 2012). The stochastic model is quantitated as a first order reaction, with the principal parameter being the rate of nucleation as a function of temperature (e.g. Murray et al., 2012).

In order to reduce ambiguities, it is important to note that there are at least three levels of random contributions to freezing experiments with distributed samples. The basic one is that resulting from molecular fluctuations of the ice embryo. This is clearly a stochastic process. The allocation of ice nucleating particles (INPs) in the sub-samples, as for example from a water sample in which INPs are suspended and sub-

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sequently divided into drops, is expected to be random (not stochastic). A possible third level of randomness arises from the location of the nucleating sites on the surfaces of the INPs. The principal use of the term “stochastic” in this paper is to refer to the molecular fluctuations of the embryos. The two other processes mentioned are random events and do not involve time sequences.

2.1 Freezing rate vs. nucleation rate

The time-dependence expected in heterogeneous ice nucleation experiments depends on whether the singular or stochastic description is adopted. Predictions differ clearly for the two scenarios and the empirical results should dictate which of the two views is appropriate. However, many experiments do not contain tests of the critical measures, and, on the basis of features for which the two interpretations do not differ, arrive at conclusions not supported by the results of the specific experiment. Examination of experiments in this paper will focus on this issue and will do so with reliance on the distinction between “freezing rate” and “nucleation rate” as defined in the following paragraphs.

Freezing rate, R , is derived from observations of a number of externally identical sample units and is defined as the fraction of sample units freezing per unit time. It is a simple representation of observations and expresses the combined effects of the distribution of nucleating particles/sites within the sample units, the time dependence of nucleation and other possible factors deliberately introduced by experimental conditions. External parameters influencing the freezing rate are the sample volume and the time-temperature history to which the sample is exposed. Freezing rate is a valid expression of observations when the sample units are identical with respect to these external parameters and originate from the same bulk sample. Weighted averages of the freezing rate for sample units of different volumes but from the same bulk sample can also be constructed but will not be introduced here.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The freezing rate for N_0 samples at time t when N_F units have frozen and $N_L = (N_0 - N_F)$ have not yet frozen is defined¹ as:

$$R(t) = -\frac{1}{N_L(t)} \frac{dN_L}{dt} = \frac{1}{N_0 - N_F} \frac{dN_F}{dt}. \quad (1)$$

- 5 The negative sign is needed since dN_L is negative. It is also possible to write Eq. (1) in terms of the fraction of samples not frozen $g = N_L/N_0$, or in terms of the fractions frozen $f = N_F/N_0$:

$$R(t) = -\frac{1}{g(t)} \frac{dg}{dt} = \frac{1}{1-f} \frac{df}{dt}. \quad (2)$$

- 10 From Eq. (1), for $R = \text{const.}$, the well-known expressions follow:

$$\ln[N_L(t)/N_0] = -R \cdot t \quad \text{and} \quad N_L(t) = N_0 \exp(-R \cdot t). \quad (3)$$

These equations demonstrate an exponential decay in the number of unfrozen samples with time, at a rate defined by the constant R . However, as it will be shown, the condition
15 $R = \text{const.}$ is not realized empirically.

A change to temperature dependence is readily made for experiments in which the samples are cooled at a rate $w = dT/dt$ (a negative number):

$$R(t) = -w \cdot R^*(T) \quad \text{and} \quad R^*(T) = -\frac{1}{N_L(T)} \frac{dN_L}{dT}. \quad (4)$$

- 20 $R^*(T)$ can also be expressed in terms of f or g as above. In the simplest case, w is a constant but the definition applies equally well if w varies with time. It should be noted that $R^*(T)$ has dimensions of inverse temperature, while $R(t)$ has dimensions of inverse time.

¹List of symbols and acronyms is at the end of the text.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Nucleation rate, J , is the probability of nucleation per unit time for a population of identical ice embryos. This quantity is derived in classical nucleation theory (CNT) by considering the rate of addition of molecules to the embryo and the assumed shape of the embryo. From an experimental perspective, the nucleation rate for homogeneous nucleation with all sample units of identical volume, is equal to the freezing rate per unit volume of liquid:

$$J_{\text{hom}} = \frac{R_{\text{hom}}}{V}. \quad (5)$$

Similarly, nucleation rate for heterogeneous nucleation is best defined as the probability of nucleation per unit surface area of substrate. The main problem in applying this concept is how to envisage the existence, and how to ascertain empirically, identical embryos and the properties of the surface on which they form, so that the rate expression might be validly defined. The underlying problem is the lack of knowledge of what nucleating sites are and the absence of empirical methods of identification of those sites. In the strictest sense, the nucleation rate could be determined with identical nucleating sites located in separate sample units (drops), or with a single site which can be repeatedly tested at identical conditions. Many authors extend the definition using the assumption that any part of the surface has an equal likelihood of containing a nucleating site or has the same probability distribution of nucleating sites of different effectiveness. The conversion from freezing rate is, in principle, via the expression

$$J = \frac{R}{A} \quad (6)$$

but application of Eq. (6) is only justified if the conditions mentioned are fulfilled. That is, it is necessary to ensure that all sample units (drops) contain the same amount of substrate surface. This is achievable in practice. However, the validity of the assumption of uniform surface properties with respect to the probability of nucleation is debatable and will be discussed in a later section. In contrast with that, the working assumption for this article is that sites are specific locations with relatively stable characteristics.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



where $k(T)$ is the differential spectrum and $K(T)$ is the cumulative spectrum. As can be seen, the only formal difference between the right-hand formula in Eq. (4) and (8) is the inclusion of drop volume V . The essential difference is in the meaning attached to the nucleus spectra. The differential spectrum expresses the interpretation that the observed freezing rate is determined by the number of sites becoming active in the temperature interval considered. The cumulative spectrum is the frequency distribution per unit volume of water of particles causing nucleation at temperatures higher than T .

The fact that Eqs. (4) and (8) differ only by a factor V^{-1} shows that for experiments with continuous cooling the temperature-dependent freezing rate $R^*(T)$ is a measure of the differential nucleus concentration: $R^*(T) \propto k(T)$. This expression of nucleating ability does not assume that each site is located on a separate particle, neither is it necessary for valid evaluation of the spectra by experiment that each sample volume contain only one INP. Overlap and multiple INPs per drop are accounted for statistically in the derivation of Eq. (8), as shown in V71. In practice, if the overlap leads to a saturation effect, dilution of the sample can eliminate that problem.

It is possible to change from a volume to a surface reference in Eqs. (8) and (9). The functions $k(T)$ and $K(T)$ then refer to the number of sites becoming active at T per unit surface area of the INPs in the bulk sample. With known sizes of the particles, the spectra can express the surface density of sites, called “ice-active surface site density (IASSD)” in Connolly et al. (2009) and “ice nucleation surface site (INAS) density” in Hoose and Möhler (2012). The expressions by which these quantities are derived are variants of Eq. (9) with $A \cdot n_s$ equated to the cumulative spectrum $K(T) \cdot V$, that is the Poisson probability of encountering a site with activity above the given temperature.

The underlying concept in the use of nucleus spectra to characterize freezing nucleation is that INPs contain sites, each of which can be assigned a characteristic temperature T^c , and that it is the abundance of the sites with different values of T^c that is the crucial parameter for determining the potential of some material to promote ice nucleation. This is the “static” factor referred to earlier.

2.3 The VS66 model

Time-dependence introduced by the fluctuating growth of embryos is incorporated in the concept of nucleation rate and has to be accounted for in any model. The singular model and the definition of nucleus spectra in Eqs. (8) and (9) do not include this dynamic factor. An extension of the singular model by Vali and Stansbury (1966, VS66) is a qualitative formulation of the combined static and dynamic factors. Early support for the VS66 model was given by Okamoto and Yamada (1970) with observations of the solidification of liquid indium droplets. As will be presented in later parts of this article, essentially all available empirical data are consistent with this model.

Following Fletcher (1958), the view taken in VS66 was that nucleating sites can be described by a nucleation rate function $J(T)$ anchored to a characteristic temperature T^c specific to that site. The freezing temperature of a given drop is determined, with small random variations about it, by the nucleus with the highest characteristic temperature found in the drop. This model is illustrated schematically in Fig. 1c. The function $J(T)$ is shown for four nucleating sites having characteristic temperatures T_i^c etc. These values correspond to the temperatures at which J takes on an arbitrary value conveniently taken as $J(T^c) = 1 \text{ s}^{-1}$. Here the nucleation rate J is taken to have dimension of inverse time as it refers to a single entity and not to the volume or surface area of the nucleating material. For simplicity, Fig. 1 shows $J(T)$ as independent of T^c but this assumption could be replaced by more complex ones without altering the essence of the model. For comparison, Fig. 1a shows the simplest stochastic assumption that the single $J(T)$ function is valid over the whole range of observations (well beyond the values of the ordinate in this graph) and for all sample units. Figure 1b is a depiction of the basic form of the singular assumption for the same four sites as in Fig. 1c.

The key results in support of the VS66 model are the observations that, if cooling of a population of drops from the same sample of water is interrupted for a period of time and the temperature is held constant, the number of freezing events during that period is just a fraction of all the samples still unfrozen, and that the freezing

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



rate decreases after cooling stops. As shown in Vali (1994, V94), if a short period of warming is introduced before holding the temperature fixed, the freezing rate drops to zero. Neither the stochastic nor the singular models provide an adequate explanation for these observations.

5 According to VS66, the temperature at which nucleation is observed to take place in any particular experiment will differ from T_i^c depending on the rate of cooling and on chance. Conversely, T_i^c cannot be determined exactly from a single realization of freezing. However, the observed freezing temperature in a given experiment provides a good approximation to its value. This is so, because $J(T)$ rises over many orders
10 of magnitude over a narrow range of temperatures. For a population of sample units, the difference between the empirical $k(T)$ and the more fundamental $k(T^c)$ is relatively small. Furthermore, the difference is dependent on w , the rate of cooling of the sample. According to V94, $k(T) = k(T^c \pm \Delta T)$ and $\Delta T < 1^\circ\text{C}$ for a reasonable range of w values. On the average, ΔT approaches zero if the cooling rate is high because less time is
15 available for nucleation to take place at a temperature higher than the characteristic temperature as it may happen if the rate of cooling is slow; this leads to lower average freezing temperatures for higher cooling rates.

For a population of sample units held simultaneously at the same temperature T , the number of freezing events is limited due to the fact that sample units which happen to
20 contain a most effective nucleating site with $T_i^c = T - \Delta T$ will have an increasingly lower probability to become active due to the fact that the nucleation rate decreases rapidly for increasingly positive values of ΔT . The increase in the number of potential sites at a somewhat lower temperature is insufficient to offset the much lower value of J for those sites at T .

25 As described in the foregoing, VS66 is a qualitative formulation. The only explicit requirement for it to be meaningful is that the spread in T_i^c values for the population of sites available on a substrate be larger than the range of temperatures over which $J(T_i^c)$ covers all practically relevant values. A quantitative definition of the limits of validity of the model has not yet been attempted.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3 Observations of heterogeneous immersion freezing

A number of selected publications are summarized in what follows in order to seek out what common factors can be identified. To accomplish this, reported results were utilized in the simplest possible form. The experiments reviewed are grouped into two major groups: those that involved repeated freezing of the sample units and those with single tests of numerous sample units. Freezing rates, as defined in Eqs. (1) and (4), were extracted from the published data and are summarized in Fig. 2a and b. The data are not normalized by volume or surface area except for those experiments which involved measurements with the same setup for different concentrations of the INPs. Because much of the data was derived from graphs in the published articles, the accuracy of the plots in Fig. 2 is limited. The values entered in Table 1 for ω and ε are also approximate; these were derived by linear fits to the major portions of each data set. No probable error ranges were considered. The plots and derived values are sufficient for the purposes of this article and certainly do not reflect adequately the actual precision of the measurements.

3.1 Experiments with repeated freezing cycles

Repeated freezing of the same sample at a specific test temperature is a powerful and direct way for observing what consequences arise from the fluctuating and probabilistic nature of nucleation. Ideally the sample would contain only one nucleating site and that site would be perfectly stable. Clearly, these conditions cannot be rigorously realized. Additionally, an inherent uncertainty exists in these experiments since setting $t = 0$ when the sample reaches the test temperature ignores the time spent while the sample is brought from 0°C to the test temperature. No definitive way has been found for making corrections for this. Additional uncertainty arises from the temperature gradients in the sample during stabilization.

Two kinds of experiments fall in this group; those using a single test temperature, with the time until freezing as the measured variable, and those in which the sample

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



is cooled until freezing takes place and the temperature of freezing is the observed variable. Interesting differences arise from these two approaches. The main one is that experiments at constant temperatures are restricted by practical considerations to measurements of times-to-freezing that are orders of magnitude longer than the times available at given temperatures during constant cooling, and so the range of values for the measured rate constants are quite different. Large sample sizes (numbers of repetitions) can mitigate this difference.

3.1.1 Experiments with single samples at fixed temperatures – measurements of time-to-freeze

The definition of nucleation rate as a probability of freezing per unit time, when applied to heterogeneous nucleation, has to be considered in reference to a large number of identical nucleation sites, as stated earlier. With current knowledge about what constitutes a site that condition cannot be fully realized. An alternative approach, at least in principle, is to observe the frequency distribution of the time until freezing in many repetitions with the same sample at the same temperature. Making that measurement at different temperatures with the same sample can lead to the function $J(T)$.

Perhaps the earliest attempt to perform experiments of this type was that of Johnson (1948). Measurements were made with drops suspended on filaments inside a large cooled chamber. Drop temperatures could not be well stabilized with this apparatus so the only result that can be extracted from the observations is that at temperatures ranging from -15°C to -35°C several minutes to over an hour passed before freezing. A total of 50 observations were made. Bayardelle (1954) argued against the stochastic interpretation based on results with the repeated freezing of drops maintained at a mercury–oil interface but did not have sufficient data to draw further conclusions.

Vonnegut and Baldwin (1984, VB84) used an automated apparatus for repeated immersion of a sample into a temperature-controlled bath. The water sample was at the bottom of a U-shaped glass tube and had silver iodide particles in it. Freezing was detected by the change in conductivity of the sample. The range of times-to-freezing

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



it more likely that all freezing events initiate on the same site. Experiments were performed at -7.6°C , -8.0°C and -8.5°C . The observed times-to-freezing extended up to 3 h. In order to evaluate R , the initial 1000 s were ignored because fewer events were observed over that period than expected from a backward extrapolation of the exponential function derived for later times; this was ascribed by the authors to temperature lags in the sample. Accepting the decay rates fitted to the main segments of the data, the rate constants determined in these experiments were (as read from the published graphs) $R = 3.1 \times 10^{-4}$, 4.9×10^{-4} and $8.1 \times 10^{-4} \text{ s}^{-1}$ for -7.6°C , -8.0°C and -8.5°C . These values yield $\omega = 1.12$ and $\varepsilon \approx 3$. Measured values of R are smaller than those of VB84 by factors of roughly 10^4 , probably due to the fact that the amount of silver iodide used in the two experiments were quite different.

3.1.2 Experiments with single samples and steady cooling – measurements of freezing temperatures

In the experiments of Seeley and Seidler (2001a, 2001b; Se01a and Se01b) a drop of water of 0.01 cm^3 in volume was supported on a prepared glass surface. Cooling was at $-3^{\circ}\text{C min}^{-1}$ and 100–200 cycles of freezing and melting were performed for each sample. The drops were coated by various aliphatic alcohols. In Se01a, the temperature to which the samples were heated between cooling runs was varied in order to gain insight into the preactivation mechanism of the crystalline films but that aspect of the experiments in not dealt with here. Freezing rates were derived by equating the fraction of runs in which the sample remained unfrozen at a given temperature with what the unfrozen fraction would be within a large number of identical samples tested simultaneously. Apparent randomness of the observed freezing temperatures with time for four of the six series of reported measurements provided justification for that assumption. In two runs, those with the most active coatings, the freezing temperatures showed a gradual decrease with time, so for these samples the freezing rates cannot be validly deduced in a direct way. For the four steady series, freezing temperatures were in the

range -6°C to -12°C and the freezing rates for these are included in Fig. 2a and in Table 1.

Using the same apparatus as in He01, experiments with steady cooling were performed by Heneghan et al. (2002; He02). The sample held in a tube was cooled at a steady rate of $\alpha = -1^{\circ}\text{C min}^{-1}$ in hundreds of repeated cycles. Results are reported for two series of experiments, one with pure water, the other with a silver iodide crystal immersed in the sample. The randomness of the time series of freezing temperatures was supported by various statistical tests. The fraction of runs in which the sample remained unfrozen at a given temperature was equated to what the unfrozen fraction would be within a large number of identical samples tested simultaneously. The distilled water and the silver iodide samples exhibited identical temperature-dependence in spite of a nearly 8°C difference in the actual freezing temperatures observed. For this paper, in order to make the data directly comparable among different experiments, the rate constants were re-computed from the published plot of the fraction frozen (Fig. 1. in He02). For this, Eq. (4) was applied with dg as the change in the fraction unfrozen between T and $(T + dT)$ and using $dt = dT/\alpha$. Values of R so obtained increase from $8 \times 10^{-4} \text{ s}^{-1}$ to 0.25 s^{-1} within the interval of -12°C to -14.5°C for distilled water and between -4.5°C to -7°C with the silver iodide crystal. The plots of the data in Fig. 2a lead to $\varepsilon = 5.8$. The R values here obtained and plotted in Fig. 2a are different from those reported in the paper.

Zobrist et al. (2007; Z07) described another study of the nucleating activity of aliphatic alcohol coatings. Water drops supported on glass or metal surfaces were covered with nonadecanol and subjected to repeated freezing cycles with cooling rates of $-10^{\circ}\text{C min}^{-1}$. Freezing rates were derived by counting the frequency of freezing events per discrete temperature intervals and normalized by the water-monolayer contact area. The authors showed that the observed freezing-rate vs. temperature function could be reconciled with CNT if the contact angle increased with decreasing temperatures. We will return to this point later. Data shown in Fig. 2a from this work was obtained by re-calculating the freezing rates from the number of freezing events re-

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ported in Table 1 of the paper and normalized by the square of the drop radius. From these data, $\varepsilon = 2.3$ for the larger drops and $\varepsilon = 3.8$ for the smaller drops.

Shaw et al. (2005; Sh05) performed repeated cycles of cooling and melting with a drop of water which had a small piece of volcanic ash placed either inside the drop or at its surface. Freezing temperatures were near -20°C with the particle immersed in the drop. Freezing temperatures varied within a range of $\sim 1^{\circ}\text{C}$ over 100 cycles. The very narrow range of freezing temperatures for immersion freezing (Fig. 3 in Sh05) make it difficult to extract a reliable $R^*(T)$ function, but appear to justify a rough estimate of $\varepsilon > 20$. With the particle at the drop surface, freezing temperatures were near -16°C for about 90% of the events with variations of $< 1^{\circ}\text{C}$. Scattered along the time sequences, exceptionally low freezing temperatures occurred in both series of tests in a fashion similar to that found in other experiments with repeated cycles of freezing.

Hoyle et al. (2011, Ho11) reported results for 8–10 freezing cycles with samples containing either volcanic ash particles or ATD (Arizona test dust). In the majority of cases, the range of variation in mean freezing temperatures for externally identical samples was greater than the variation in freezing temperatures for the individual samples. Depending on dust concentration and size, freezing temperatures varied between -8 and -20°C . Pinti et al. (2012, P12) performed experiments of cycles of freezing and melting with samples of $\sim 2500\ \mu\text{L}$ and with different clay mineral particles in them. Freezing temperatures ranged from -5°C to -25°C for individual samples. In twenty repetitions, fluctuations of $\sim 1^{\circ}\text{C}$ magnitude were observed in a number of cases, while other samples showed fluctuations of up to 8°C . Both of these experiments are consistent with the notion of specific sites, but the support is weak because the experiments were not designed to explore that point in depth.

Even though many sample drops were used in each experiment, the results shown in Vali (2008, V08) are of the same general type as others in this section since the freezing temperatures were recorded individually for each drop and were analyzed as separate sequences. Deviations from the mean temperature for each drop were used to determine the freezing rate for a soil sample that had freezing temperatures in the

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



chamber or formed by condensation within the chamber are the main approaches. Ideally, for purposes of evaluating the data, all drops in a given test would be the same size and would contain the same nucleant(s), but this is frequently unachievable. Reducing and controlling deviations from those requirements pose significant experimental challenges and accounting for spreads in those variables usually involves some uncertainties.

The majority of experiments with populations of sample drops examine the temperature dependence of freezing, either by sequences of tests at discrete temperatures or with steady cooling. In the first case, the observations can be evaluated in terms of $R(t)$ from Eq. (1) or (2), or as $R^*(T)$ from Eq. (4) if the rate of cooling is known. Even if a time-dependent freezing rate $R(t)$ is derived, the connection to nucleation rate is more questionable for these experiments than for those with single samples, since there are many different INPs involved and the homogeneity among the particles is not always assured. All of these experiments share the problem of how to account for the time period during cooling to the test temperature, i.e. the time-temperature history of the sample.

Additionally, in a smaller number of experiments, the time evolution of the sample was studied at fixed temperatures or with varying cooling rates. In the following, findings from experiments focusing on temperature-dependence are summarized first, then those examining time-dependence are reviewed.

3.2.1 Experiments with variable temperatures

Independently whether discrete test temperatures were used or steady cooling was applied, the results for this group of experiments are all presented in terms of $R^*(T)$ and are plotted in Fig. 2b. Where cumulative spectra were published, those have been differentiated and are given in Fig. 2b as concentrations, or site densities per degree temperature interval. For exponential spectra the values of ω and of ε are the same for the cumulative and differential spectra.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Following many earlier studies, freezing rates were determined in V94 and V08 for millimeter-sized drops placed on a hydrophobic solid surface and cooled at a constant rate. Samples of distilled water and soil suspensions were investigated. The composition of the INPs in the distilled water was not examined and the soil samples were not classified by size. For distilled water, freezing rates were found to increase exponentially with decreasing temperatures between -15°C and -25°C . The measurements yielded $\omega = 0.6$ and $\varepsilon = 1.8$. For a soil suspension, $\omega = 0.3$ and $\varepsilon = 1.4$ represent the data reasonably well even though the exponential approximation for this sample is poorer. Some of the samples produced complex spectra with pronounced peaks and valleys.

Water-in-oil emulsions and differential scanning calorimeters (DSC) have been widely used, for homogeneous nucleation studies at first and with suspended particles more recently. Since the water droplets are not of uniform size, their size distribution is convolved with the shape of the exotherm and the thermal properties of the instrument. Nonetheless, the fraction of sample volume frozen as a function of time can be deduced. Marcolli et al. (2007) reported on such tests with two different size fractions of ATD. Taking into account the size distribution of the particles, the particle surface area per drop was calculated. Random allocation of the particles was assumed and the number of particles per drop was taken to be proportional to drop volume. Freezing was observed to occur between -15°C and -30°C . Freezing rate per unit surface area was deduced using a variant of Eq. (4). The results did not match the predictions of a stochastic model. Instead, particles were assigned unique temperature-dependent properties using contact angle as a proxy, either by assuming each particle to be characterized by a single value of the contact angle, or by assuming a distribution of sites of different effectiveness. These two assumptions led to very similar results and reproduced the observations with about the same degree of precision.

Using a microfluidic apparatus, Stan et al. (2009, St09) measured the nucleation frequency for droplets of $100\ \mu\text{m}$ diameter cooled almost instantaneously ($-100^{\circ}\text{C s}^{-1}$) from above 0°C to the test temperature and then in a series of equally rapid small

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



steps to yet lower temperatures. Results for homogeneous nucleation were close to previous data. With silver iodide particles added to the droplets, freezing temperatures were between -10°C and -18°C . Freezing rates derived from these measurements (Fig. 9a in St09) are shown in Fig. 2b. Over the first four-degree interval, where the rate increases rapidly, $\omega = 1.7$ and $\varepsilon = 5.5$. These values are close to those of VB84. At lower temperatures the freezing rates increased more slowly; the same pattern was reported in V08.

In the experiments of Lüönd et al. (2010, L10) droplets were produced by condensation onto size-selected kaolinite particles and then introduced into the Zurich Ice Nucleation Chamber (ZINC). Freezing took place in the temperature range between -30°C and -35°C . One additional experiment was conducted with silver iodide particles for which freezing occurred between -8°C and -20°C . The fraction of droplets frozen with different final temperatures in the chamber was the primary data product. The curves shown in Fig. 2b were derived from the published graphs for $200\ \mu\text{m}$ kaolinite particles and for silver iodide. The slope of the silver iodide curve is significantly less than for the data of S09 and VB84. Results were shown to be compatible with a distribution of active sites (α -pdf model) on the particle surfaces; more will be said about this later.

Murray et al. (2011, Mu11) employed a technique in which drops of aqueous suspensions of particulates are dispersed onto a glass surface, cooled at controlled rates and observed optically to detect freezing. Drop volumes ranged from $\sim 10^{-6}$ to $10^{-4}\ \mu\text{L}$. With kaolinite particles, freezing temperatures were in the range -27°C to -35°C . Tests were conducted to examine the dependence of freezing rates on the concentration of particles and on cooling rate. Freezing rate was shown to scale with the surface area of the particles and depend negligibly on cooling rate. Hence, a unique freezing rate function was used to represent all the data. The data shown in Fig. 2b represent results for sample set (ν) from Fig. 1 of the publication. The slope of this line is $\omega = 1.1$ which yields $\varepsilon = 3.0$. As seen in Fig. 5 of Mu11, this particular data set is quite representative of the composite of all results obtained.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



A large body of experiments have been performed with the Leipzig Aerosol Cloud Interaction Simulator (LACIS). These experiments consist of forming cloud droplets on particles of controlled size and composition, passing the cloud through a chamber held at a fixed temperature and determining by optical means the fraction of droplets frozen. This approach has the advantage of assuring a near-perfect one particle to one ice crystal correspondence. Niedermeier et al. (2010, 2011a, b; N10, N11a and N11b) report on experiments using size-sorted ATD particles with various coatings, and similar tests with pure water droplets. Freezing temperatures were in the range -28°C to -40°C ; those lower than -37.5°C were attributed to homogeneous freezing. For the pure mineral, the freezing rate increased gradually between -28°C and -36°C and 10...60% of the droplets were frozen at -36°C . Only at -40°C did the frozen fraction reach 100%. For these experiments, the data shown in Table 1 and in Fig. 2b were obtained by differentiating the reported fractions frozen. For ATD, the slope of the line is $\omega \approx 0.34$, so that $\varepsilon \approx 1.4$.

Hartmann et al. (2013, H13) used the LACIS facility to study the ice nucleating abilities of *Pseudomonas syringea* bacteria, and fragments of those bacteria from the commercial Snowmax product. Freezing temperatures as high as -6°C were detected so that this data set extended significantly the range that has been obtained with mineral particles (preceding paragraph). Significant increases in the fraction of frozen drops exiting the chamber were found to end at -10°C with only about 20% of the drops frozen. This was interpreted as being due to lack of activity in the remaining particles. Even so, measurements were obtained over two orders of magnitude of the frozen fraction. For inclusion of these data in Fig. 2b, freezing rates were calculated from the published values of the frozen fraction (from Fig. 3 of Ha13, for 800 nm size fraction) scaled to unity at the maximum observed at -10°C . This analysis results in $\omega \approx 2.4$, so that $\varepsilon \approx 12$. These values agree with the slope of the line fitted to data for two different sizes of particles in Fig. 7 of the paper, as well as the value of B quoted in their Eq. (9). Earlier tests for the same material (Snowmax) by Wood et al. (2002) produced similar results, with the frozen fraction rising from near zero at -6°C to near unity by -9°C .

The mass concentration of Snowmax was less than a tenth of that used by Ha13 and the suspension was tested directly, not aerosolized and size sorted.

Experiments performed in the AIDA (Aerosol Interaction and Dynamics in the Atmosphere) chamber produced a substantial body of data on the nucleating abilities of various materials and on the mechanisms of ice nucleation. Niemand et al. (2012, Nm12) tested five desert dust samples and found that data from all could be described reasonably well by a single $n_s = f(T)$ function of exponential form, although the scatter about the best fit amounted to over an order of magnitude. These data (from Fig. 6 and Eq. 5 of the paper) yield $\omega = 0.52$ and $\varepsilon = 1.8$, valid for the temperature range -13°C to -28°C . This range is extended in Hoose and Möhler (2012, Fig. 13) to near -10°C to -35°C and the data are approximated by a line with $\omega = 0.63$ and $\varepsilon = 1.9$. The survey in Hoose and Möhler (2012) also includes results for various other minerals, bioaerosol, bacteria and soot.

In experiments with steady cooling of samples containing 0.01, 0.1 and 1.0 wt% of ATD, WP13 obtained the data shown in Fig. 2b. The plotted data were derived from the published Fig. 5 with the freezing rates adjusted to the same mass concentration of ATD. As the three segments of the data show, the freezing rate scaled with concentration. The plot yields $\omega = 0.6$ and $\varepsilon = 1.8$.

3.2.2 Observations of time-dependence

While time dependence is a factor in all the experimental methods already discussed, two other types of measurements are of special relevance in this regard: (i) observing the evolution of the frozen fraction with time at a constant temperature for populations of externally identical sample units, and (ii) varying the rate of cooling for such samples. Experiments of these types have been reported in the recent literature by Mu11, Broadley et al. (2012, B12), W12 and WP13.

A test of the distinction between freezing rate and nucleation rate can be found in the influence of cooling rate. Brewer and Palmer (1951) reported no detectable change in freezing temperatures with a tenfold change in the rate of cooling. A lowering of

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the freezing temperatures with increased cooling rate was reported in VS66 and V94: by changing from cooling rate w_1 to w_2 an offset in freezing temperatures equal to $0.3 \cdot \ln(w_1/w_2)$ was measured. Slower cooling rate leads to higher freezing temperatures by allowing more time for embryos to reach stable sizes.

Some hint, but no clear dependence of the freezing rate on the rate of cooling was detected in the experiments of Mu11; the rate of cooling ranged from $-1^\circ\text{C min}^{-1}$ to $-10^\circ\text{C min}^{-1}$. Using the same technique but with a suspension of illite rather than kaolinite, Broadley et al. (2012, B12) noted a definite shift for samples with high concentrations of the mineral, while no change was seen with low concentrations. For the high-concentration samples, a factor 6 increase in cooling rate led to 1°C to 2°C colder freezing temperatures. These samples of higher site density had steeper spectra (increases in the fraction frozen) and froze at temperatures about 4°C higher than the samples that showed no dependence on cooling rate.

With a very extensive data set for ATD and with the cooling rate varied from $-0.01^\circ\text{C min}^{-1}$ to $-5^\circ\text{C min}^{-1}$ WP13 found the effect to be about 0.7°C for a factor 10 change in cooling rate; a result that is quite close to that given by V94.

Hiranuma et al. (2013) show data for illite in the temperature range -28°C to -33°C for two rates of cooling in the AIDA chamber. After accounting for sedimentation of the crystals, a shift was found toward colder temperatures by about 1°C for a factor 8 increase in the rate of cooling. This change is also fairly close to that given in V94.

For experiments in which time-to-freezing was observed at fixed temperatures, the critical measure is whether the number of samples that remain unfrozen tends to zero with time as the stochastic model predicts, or significant numbers remain unfrozen. Results in V94 clearly support the second alternative, as did results shown in Fig. 5 of Vonnegut (1948). Results shown in Fig. 3 of Mu11 show a decrease in freezing rate with time for one temperature but not for others (each set was obtained with a different set of drops). Longer residence time at the test temperature was found to increase the frozen fraction in the experiments of Welti et al. (2012) and for most temperatures the increase leveled off. That result suggests that even after extended time periods there

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



would have been only a limited fraction of the particles producing freezing. WP13 show data for two experiments, one of which extended to 16 h; the rate of freezing clearly slowed with time in both runs. Only about a third of the sample drops froze after 16 h, even though all drops of the same sample would have frozen with a few degrees more cooling. In all, the evidence clearly points to the correctness of the results in V94 and WP13.

4 Interpretations of freezing rates

4.1 Summary of observations

The summary of observed freezing rates in Table 1 and in Fig. 2 focuses on the rate of change of the freezing rate with temperature, expressed by the slope ω , and the factor ε increase per degree of decrease in temperature. Absolute values of the freezing rates are influenced by additional parameters like sample volume and the amount of INPs suspended or in contact with the sample drop but the slope is independent of these.

A number of patterns can be noted in Fig. 2 and Table 1:

1. There is a paucity of data in Fig. 2a for temperatures below -25°C .
2. While freezing rate increases nearly exponentially with decreasing temperatures, deviations from the linear increase in Fig. 2 are quite frequent. Without full analyses of errors it is hard to weigh the potential sources of the deviations. Complex shapes of the rate functions do not contradict any fundamental law. Because of these variations in the shapes of the $R(t)$ and $R^*(T)$ plots, the ω and ε values are imprecise representations of the data.
3. The value of ω varies from experiment to experiment but the range of variations is limited to within a factor of ten. This narrow range is a purely empirical result at this time.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4. Plots of data for $R(t)$ in Fig. 2a tend to be steeper than those for $R^*(T)$ in Fig. 2b.
5. There is no clear trend in the slopes of the lines with temperature, though there is an indication for lines to be flatter in Fig. 2b at lower temperatures.
6. Significant differences are observed even among experiments with the same nucleating substance (silver iodide, ATD and others).
7. Different experimental approaches produce comparable results.
8. In a number of experiments (e.g. Z07, WP13) the freezing rate was shown to scale with the concentration of the suspended particles. For given size-distribution of the INPs, scaling the freezing rate by mass and by surface area produces equivalent results.
9. All the observed slopes are smaller (less negative) than for homogeneous freezing.

4.2 CNT with adjustable parameters

Difficulties were encountered in reconciling CNT with a number of empirical results. This led authors to introduce somewhat arbitrary temperature-dependent variations in selected parameters of the nucleation rate expression in CNT in order to achieve a fit.

Stoyanova et al. (1994, S94) used three different regimes with different pairs of constants in the CNT rate equation in order to match the results of their measurements. The composite function so created was specific to that one set of experimental results and was not expected to have general validity for other materials.

Zobrist et al. (2007) found that in order to bring CNT into agreement with their observations of nucleation by a monolayer coating required the contact angle to vary linearly from large values at lower temperatures to smaller values closer to the melting point. They argued that this could arise from adjustments in the monolayer leading to better fits to the ice lattice at higher temperatures.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Marcolli et al. (2007, Ma07) found the best fit to their observations with ATD suspensions could be achieved by assuming that the contact angle varies from site to site and that the number of sites increases in a specific way with increasing contact angle. They viewed this solution as a proxy for factors not clearly identified. Following the same approach, Welti et al. (2012, W12) found a good fit to their data with the CNT rate equation combined with the assumption that the contact angle has a log-normal distribution (α -pdf) for different particles and hence for different droplets in the cloud within the chamber.

The “soccer ball” model proposed by Niedermeier et al. (2011a, N11a) applies CNT with a prescribed variation of the contact angle. It is assumed that each sample drop contains one particle, each particle is divided into an assigned number of smooth patches, and the patches possess a contact angle randomly selected from a frequency distribution with adjustable parameters. This solution allowed various scenarios to be explored and depending on the constants chosen it was shown to match the predictions of either the singular or the stochastic models. It isn’t clear whether the authors envisaged the patches to possess the assigned properties as permanent, or at least durable features, or the random assignment was meant to imply a random occurrence that would manifest itself differently in any one of a series of repeated tests. A modified version of the model (Niedermeier et al., 2013) assigns the same contact angle to all sites on a particle, the number of sites per particle is fixed, and all particles are assumed to be identical. This model is conceptually very similar to the α -pdf model.

Yet another way to specify the distribution of nucleating sites in sample drops is the CHES model (stoCHastic modEl of similar and poiSSon distributed ice nuclei) developed by Hartmann et al. (2013). All INPs – in this case fragments of bacteria – were assumed identical and the number of INPs per drops was determined from a Poisson distribution. The probability of freezing was determined as in Eq. (9) with the concentration of sites in a drop given as the product of the number of sites, their area, nucleation rate and time. The nucleation rate was assumed to be an exponential function of temperature with parameters retrieved from the observed freeing rates.

4.3 Empirical approaches

The fundamental direction taken in empirical models is to emphasize the static factor and to define the number of nucleation sites directly in terms of the temperature at which freezing is initiated by the site. Time-dependence (the dynamic factor) is either assumed to be negligible or is incorporated with additional parameters.

Going beyond the definition of nucleus spectra (Sect. 2.2), the so-called time dependent freezing rate (TDFR) formulation was developed in V94. Two steps were introduced to account for time-dependent effects. One accounts for the dependence of freezing temperatures on the rate of cooling, as already indicated in Sect. 3.2.2. The second step expresses the number of freezing events when cooling is stopped relative to the freezing rate observed at the same temperature while cooling. The two parameters for the time-dependent effects may turn out to be constants but more data are needed with different materials and a range of temperatures of measurements to ascertain that. Both the cooling-rate dependence and the additional freezing after cooling stops are relatively small effects in comparison to the strong temperature dependence found for almost all types of INPs. Nonetheless, accounting for these properties of freezing nucleation rounds out the conceptual framework for that process and evidences how the combination of static and dynamic factors work.

The observed spectra in all these different forms are functions of temperature in addition to the formulas needed to describe the partition of INPs among the sample units. Many spectra approximate exponential functions of temperature (VS66, V71, B12, H13, and others) but significantly different forms have been observed for some samples. There is no a priori reason to anticipate one functional form or another. Connolly et al. (2009, C09) used linear and quadratic equations to describe the cumulative number of sites per unit surface area of different dust particles. The formulation of Barahona (2012) used the sum of several functions to define the activity spectrum.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5 Discussion

Two issues that reflect directly on the interpretation of freezing nucleation data require further discussion. First, the evaluation of the slopes of the $\ln(R)$ vs. T plots in Fig. 2. Second, the use of CNT in recent papers.

5.1 CNT predictions of ω

For homogeneous nucleation, reasonable agreement between theory and observation has been found by several authors (Krämer et al., 1999; Stockel et al., 2005; Stan et al., 2009; Murray et al., 2010). Even so, the different data sets correspond to different ω values in the range from 3 to 4.5 and ε values from 20 to 100. The lines shown for homogeneous nucleation in Fig. 2 bracket this range.

Adoption of the expressions for homogeneous nucleation to the heterogeneous case in forms that can be evaluated empirically has been attempted in many ways, as already discussed. Here the focus is only on the parameter ω . The line shown in Fig. 2 for heterogeneous nucleation follows the formulation given in Fletcher (1958). This treatment is for the nucleation rate per unit surface area and the function is anchored to a characteristic temperature of a site. The characteristic temperature is defined as the value at which $J(T^c) = 1 \text{ cm}^{-2} \text{ s}^{-1}$. From this formulation one can derive the slope of the $J(T)$ functions at T^c . For a particle of $0.1 \mu\text{m}$ equivalent diameter

$$\omega = -\frac{d(\ln J)}{dT} \approx -\frac{46}{T^c}. \quad (10)$$

Using constants as given in Fletcher (1958) and corrected in Fletcher (1969) for $T^c = -10^\circ\text{C}$ the result is $\omega = 4.6$ and $\varepsilon = 100$. Somewhat oddly, if the temperature-dependence of the interfacial energy over a small range is ignored, Eq. (10) predicts a steeper slope at higher temperatures. Inclusion of the factor that accounts for the contact angle between the substrate and the ice embryo in the CNT rate equation reduces ω and brings it closer to the range of observations. However, since less effective

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



substrates are expected to correspond to larger contact angles, greater reduction in ω (shallower slope) would be expected for lower temperatures. Values of ω close to zero would be expected as the homogeneous nucleation threshold is approached, so the trend that results from Eq. (10) is not reversed but accentuated.

Another way to examine the predictions of ω from CNT is from the temperature dependence of the frequently cited equation for $J(T)$, as for example Eq. (11) in Murray et al. (2012). Keeping the contact angle fixed, and neglecting the temperature dependence of thermodynamic parameters, the value of ω is found to decrease by a factor of about 240 between -5°C and -35°C . Some support may be seen in Fig. 2 for shallower slopes toward lower temperatures but the pattern is far from being as strong as predicted.

Experiments (Sect. 3.1.1) in which time-to-freezing was observed for a single sample (VB84, WV84 He01 and He02) could yield direct measurements of the rate constant in Eq. (3). Other tests with single samples but with steady cooling (Sect. 3.1.2) provide less direct measurements of the rate constant but these too are close to being free of the dilemma of having to distinguish between freezing due to a single site or several. How well results can indeed be assigned to a single, stable site is difficult to judge mainly due to the paucity of data. That these measurements yielded the steepest lines in Fig. 2 ($\omega \geq 1.5$) is perhaps significant. On the other hand, it is very difficult to rule out temporal changes of the substrate that affect the sites. An interesting finding is that identical values of ω result from the measurements of VB84 with silver iodide and of WV84 with distilled water. The same match was found by He02 for laboratory distilled water with and without the inclusion of a silver iodide crystal in the sample. The observed freezing temperatures in both cases differed by roughly 8°C . It may possible to reconcile this with CNT but only with some forced assumptions. In all, some caution is warranted with respect to these results.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5.2 Expressions for site concentrations

In most publications, the observed fractions of frozen samples are related to the concentration of INPs of different effectiveness via the Poisson distribution. The various formulas used to express this in the literature are equivalent to Eq. (9) in Sect. 2.2. That equation, from V71, has $K(T)$ equal to the probability that a sample unit will contain at least one INP active at temperatures higher than T . Equation (9) is for the number concentration per unit volume of water, but similar expressions can be written in terms of the concentration per total surface area of the INPs, or number of INPs, or other statistically uniform parameter for all sample units. For example one can substitute $n_s(T) \cdot A$ for $K(T) \cdot V$ so that

$$f(T) = \frac{N_F(T)}{N_0} = 1 - \exp[-n_s(T) \cdot A] \quad (11)$$

Of course, Eq. (11) is based on the singular model. In many publications, Eq. (11) is changed to a form that appears to link it to the stochastic model by equating $n_s(T)$ to $J_s(T) \cdot t$ with $J_s(T)$ as the nucleation rate per unit surface area:

$$f(T) = \frac{N_F(T)}{N_0} = 1 - \exp[-J_s(T) \cdot A \cdot t] \quad (12)$$

However, time is fixed by the experimental arrangement in most cases. With $t = \text{constant}$, $J \cdot t$ expresses the probability of a site being found in a sample unit, just as $n_s(T)$ or $K(T)$ does, so the stochastic element reduces to one relating to the random occurrence of a site somewhere on the surface of the INP within a sample unit, not the randomness of possibly encountering a given type of site within the sample unit. That is the same step as the one that distinguishes freezing rate from nucleation rate, as discussed in Sect. 2.

In effect, use of Eq. (12) is an assumption against the existence of quasi-permanent sites. If empirical results are interpreted using Eq. (12) the implication is that uniform

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



surface properties are being assumed to prevail and the nucleation rate so deduced refers to the probability of identical sites existing on the surface and become active spontaneously. Since individual samples (drops) freeze at different temperatures even with externally identical content of INPs (composition and size) using Eq. (12) would imply that while the surface in each drop is uniform, the surfaces in each drop are different in some significant way. This seems to be a difficult proposition to maintain, but cannot be disproven with available data. It is highly desirable to attempt critical tests in future investigations.

In contrast, continuing with the view that specific sites exist, it can be stated that if N_F is measured as a function of temperature and not as a function of time, the product in the exponent of Eq. (11) should be viewed as an expression of the number of active sites present in the sample and not as a random development realized once. Thus, the most appropriate description of laboratory results, and hence the best basis for constructing predictive models for ice nucleation in the atmosphere or in other systems starts with the measured freezing rate interpreted as the probability of freezing, directly determined by the abundance of freezing nuclei. Hence, nucleus spectra rather than nucleation rates are the best representations of experimental results. Perhaps the strongest argument for this is that freezing nucleation is a much stronger function of temperature, a static factor, than of time, the dynamic factor. The other reason for this approach is that CNT does not have much predictive power for heterogeneous freezing and evaluations of the constants in the CNT formulations have not led to any significant insights. The situation may change when the factors governing freezing nucleation become well enough understood that the nucleation rate can be expressed in terms of variables that reflect the specific properties of the substrate with variables that can be empirically confirmed and with a model superior to the spherical cap assumption.

An important corollary to the aforesaid is that focus should be on the frequency, or surface density of nucleating sites of different effectiveness. That appears to be the most meaningful characterization of the substrate being evaluated. Knowledge of the sizes of INPs involved in a test is now routinely available. In light of this, it is preferable

to interpret observations as freezing rate normalized by unit area and to deduce from that the density of active sites as a function of temperature. This latter approach has already been adopted in Hoose and Möhler (2012), Murray et al. (2012), and others.

It is also worth noting that Eq. (10) expresses activity as the cumulative number above given temperatures, i.e. as cumulative spectra. With sufficient sample size, the differential spectra, $k(T)$ or equivalent per unit area, can be determined; these spectra contain more information about the frequency distributions of sites. If the spectra are exponential in form the difference is minimal, but there are indications in Fig. 2 that several data sets may have more complex spectra.

Time-dependence need not be ignored when evaluating nucleus spectra. While more tests are clearly needed, available evidence is consistent with the VS66 -V94 model, i.e. positive deviations from the characteristic temperature for longer available times near that temperature. The magnitude of effect can be expected to depend on the rate of rise of the $K(T)$ function (i.e. the value of $k(T)$), not on the slope of the nucleation rate function as it would be in the stochastic description. The two are not equal, as has been already seen.

5.3 Evidence for sites

It was argued in the preceding section that the evidence points away from uniform probabilities of embryo formation across surfaces and in the direction of the existence of specific sites probably associated with surface irregularities. Cracks, dislocations, steps, spiral faults, impurities, etc. have been suggested as potential sites. Some additional considerations about sites are included here.

While the link to freezing nucleation is not definitive, the importance of specific sites for deposition nucleation was shown quite clearly by linking them to topographic features on the crystal surfaces (Bryant et al., 1959; Fukuta and Mason, 1963) and by the repeated appearance of ice crystals on specific locations on the substrate (Anderson and Hallett, 1976). Since deposition is thought to be initiated by the formation

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of a minute amount of liquid followed by freezing, perhaps these observations can be taken as significant also for freezing nucleation.

It was shown in V94 that freezing temperatures observed in one run were highly correlated with those observed in a subsequent run (correlation coefficient of 0.98) while a simulated random selection had a correlation coefficient near zero. This is in clear contradiction with all drops having the same probability of freezing, i.e. a violation of the assumption for a stochastic treatment applied to the collection of drops. Conversely, evidence points to the fact that the drops did not contain identical nucleating sites even though all were drawn from the same bulk preparation. It is possible that different substances or sizes were included in each drop but that is a rather unlikely proposition considering the large sample size involved.

The fact that both V08 and WP13 diagnosed fluctuations much smaller than the range covered by the freezing temperatures of the different drops in the sample validates the concept of nucleating sites with nearly permanent characteristic temperatures and puts bounds on the range of variations expected in particular instances about that value. Wilson and Haymet (2012) reviewed a number of experiments and arrived at the same conclusion.

Normalization by surface area allows data obtained with particles of different sizes to be combined. Success in deriving compatible values from experiments with different particle sizes (e.g. Z07, WP13) is good evidence for the dependence of heterogeneous nucleation on the sites located on substrate surface. Li et al. (2012) came to the same conclusion based on experiments with water drops on silicone surfaces. However, the proportionality to surface area does not provide any distinction between specific sites being randomly distributed on the surface or all parts of the surface having equal probability of having embryos form on it.

Exceptional changes well outside the range of freezing temperatures observed over most of the test series (Sect. 3.1) have been associated with various tentative explanations. Sh05 mentions possible movement of the particle on the surface of the drop, or movement of the drop on the supporting surface between tests. In V08 a number of

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



other possibilities are listed, such as some interference with the ordering of an embryo on the site responsible for most of the events and another site of lower characteristic temperature becoming the source of nucleation. Clearly, these observations need further exploration.

5 The experiments with monolayer coatings deserve special consideration. In Se01a, Se01b and Z07 the results were interpreted in terms of nucleation rates and CNT, thereby implying a stochastic process with nucleation expected to have the same probability at any point on the monolayer surface. A small number of exceptional (non-random) patterns were also present in these sequences and some samples exhibited
10 clear trends. These can be viewed as indications of specific sites in the same sense as in the preceding paragraph. Pre-activation of the coatings was reported to be required before showing nearly stable nucleating properties, indicating that the monolayers are not simple, smooth surfaces but need some sort of ordering by ice crystals. The monolayer coating is not rigid but undergoes changes as the temperature is lowered
15 according to Ochshorn and Cantrell (2006).

Simulations of ice nucleation have also drawn attention to the role of specific surface irregularities as possible sites by showing that smooth surfaces are less likely to have embryos form on them (Hu and Michaelides, 2007; Croteau et al., 2010). On the
20 other hand, the observations of Gurganus et al. (2011) appear to indicate no preferred location for nucleation underneath drops placed on a silicon surface.

6 Conclusions

The main points made in this paper are summarized below. The list contains items that are closely interrelated and may not be fully meaningful individually.

1. The interpretation of freezing nucleation experiments is simplified if the results
25 are expressed in terms of freezing rate, which is a simple empirical expression of the results. Further meanings can be derived from the freezing rate depending on what assumptions are made concerning the details of embryo formation.

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2. The debate between stochastic and singular descriptions of freezing nucleation among populations of externally identical sample units is no longer productive. Most recent publications attest to the dominance of static factors. The V71, α -pdf, soccer-ball, multicomponent-stochastic, and other similar models are basically the same. These models, in common, describe the frequency distribution of sites of different effectiveness in the exponent of Eq. (11) with constants derived from observations.
3. Evidence points to nucleation sites being stable features with respect to their effectiveness expressed as the temperature at which nucleation becomes highly likely. The sites are considered only quasi-permanent because they do undergo gradual or abrupt changes and are influenced by memory effects, but such changes are rare. While support for this statement is relatively strong, the evidence is not conclusive and the question needs further study.
4. Extensions of the singular description are needed to account for time-dependent adjustments; these are known to be of relatively small magnitude but their exact form is not yet well established. Little research has been done to find adequate methods for implementing such adjustments.
5. Nucleation rate, $J(t)$, on given sites has not become accessible by direct measurement.
6. The need to modify the CNT formula for nucleation rate with empirical temperature-dependent parameters underscores the weakness of support for the use of the CNT nucleation rate expression.
7. Time-dependence has been shown to be weak, so that in the interpretation of freezing experiment aimed at characterizing the INPs it can be set aside without significant degradation of the results.
8. The temperature dependence of experimental results is most usefully expressed in terms of the differential spectra $k(T)$ of Eq. (9) or $n_s(T)/dT$ derived from



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Eq. (11). There is progress toward being able to characterize likely site densities on different materials and thus gain some predictive capacity of freezing rates for given scenarios of sample volume and INP content. The reviews of Murray et al. (2012) and of Hoose and Möhler (2012) provide a survey of these results. Laboratory techniques have advanced greatly for performing the required experiments. Theoretical underpinning for these advances will require much more detailed knowledge about the nature of nucleating sites.

9. The patterns seen in Fig. 2 and discussed in Sect. 4.1 are largely unexplored and unexplained at this time. A relatively narrow range of slopes is also seen in the analysis of Murray et al. (2012; Fig. 18) except at the temperatures closest to 0°C. It is to be expected that further studies of this regularity will lead to better understanding of freezing nucleation.

Appendix A

A brief summary of the origins of the stochastic and singular models are reviewed here in order to provide a historical perspective and to help illuminate the differences in viewpoint that have been a source of controversy over several decades.

Bigg (1953) used a time-dependent freezing rate description for a population of drops, and his approach was identified as a stochastic description by Marshall (1960). The model formulated by Levine (1950) and by Langham and Mason (1958) was named the singular description by Vali and Stansbury (1966, VS66), adopting a phrase from Dorsey (1948)².

²Dorsey (1948) referred to the location where freezing originates in a sample – whether homogeneous or heterogeneous – as a singularity.

each drop freezing at the temperature corresponding to the particle with the highest characteristic temperature.

Brewer and Palmer (1951) repeated Rau's experiments with an automated apparatus specifically designed to check on the claim made by Rau that freezing temperature can be lowered to -72°C in some cases by many cycles of freezing and thawing. They showed that this was an artifact in Rau's work due to alcohol vapors seeping into the system. With up to 500 cycles of observations, Brewer and Palmer found that the freezing temperature remained constant within 1°C and often within 0.25°C for drops of about 0.01 cm^3 in volume. Changing the rate of cooling over a factor of ten did not affect the freezing temperature either. Brewer and Palmer obtained data for only a few drops; the freezing temperatures of these were in the range -15°C to -20°C . In their conclusions they agree with the main claims of Rau, namely that the freezing of a sample is "due to the presence of freezing nuclei each of which acts at its own characteristic temperature", and that "there is a whole spectrum of such nuclei".

The view expressed by Dorsey, Rau and Brewer and Palmer is what became known as the singular model.

A2 Early evidence for stochastic freezing

The dependence of nucleation on time was clearly seen in the experiments of Vonnegut (1948). Water drops were placed on a metal plate and brought to a steady temperature in the range -14°C to -18°C . The number of frozen drops increased rapidly over the first few minutes then continued at gradually slower rates. Slight decreases in temperature corresponded to much faster rates of freezing of the drops. Vonnegut interpreted the observations as a measurement of nucleation rates.

Bigg (1953) introduced the description of the freezing of a number of small volumes of water in terms of a probability per unit time. He showed experimental results that demonstrated the dependence of the mean freezing temperature on volume and on

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the rate of cooling. This result can be stated as

$$T_m = 2.3 \left[\log \frac{V}{V_o} + \log \frac{w_o}{w} \right] - 16.9 \quad (\text{A1})$$

where T_m is the mean freezing temperature in $^{\circ}\text{C}$, V is the volume of the samples in cm^3 , w is the rate of cooling in $^{\circ}\text{C min}^{-1}$; the constants are $V_o = 1 \text{ cm}^3$ and $w_o = 1 ^{\circ}\text{C min}^{-1}$. The range of values for V were roughly six orders of magnitude (the majority of data from a smaller range of factor 50) and one order of magnitude for w . Bigg also showed that Eq. (A1) is consistent with a freezing probability per unit time that is proportional to an exponential function of supercooling (temperature in $^{\circ}\text{C}$):

$$\frac{1}{N_L} \frac{dN_L}{dt} = b e^{-aT} \quad (\text{A2})$$

where N_L is the number of drops not yet frozen at T and a and b are constants. Since this relationship does not contain any dependence on the prior history of the sample it can be properly identified as a representation of a stochastic process, and Marshall (1960) attached that designation to the theory. The most important result that led Bigg to Eq. (A2) was the observed dependence of freezing temperatures on volume as expressed in Eq. (A1). Dependence on cooling rate provided an independent check on the result: a factor 10 decrease in cooling rate led to a 2°C higher value of T_m while Eq. (A1) predicts 2.3°C . Based on Eqs. (A2) and (A1), the fraction $f(T)$ of a population of drops frozen when cooled at a steady rate of w can be written as

$$f(T) = \exp \left(- \exp \left(\ln \frac{bV}{aw} - aT \right) \right) \quad (\text{A3})$$

The observed shape of the frequency distribution of freezing events, normalized to a common volume according to Eq. (A1) was shown by Bigg to be in agreement with Eq. (A3).

Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

The linear dependence of the mean (or median) freezing temperature on the logarithm of drop volume was confirmed by Langham and Mason (1958) in a repeat of Bigg's experiments. They have also shown that the temperatures vary depending on the source (purity) of the water. The logarithmic dependence on droplet size was shown to also hold for highly purified water that froze at considerably lower temperatures (-35°C to -42°C). On that basis Langham and Mason argued that Bigg's measurements represented heterogeneous freezing. Furthermore, they showed that the logarithmic dependence on volume can also result from the drops containing a random selection of particles whose activity is an exponential function of temperature, similarly to atmospheric particles tested in cloud chambers. Somewhat misleadingly, Pruppacher and Klett (1997; pages 349–351) gloss over the fact that that logarithmic volume dependence is consistent with the singular model only for an exponential form of the number vs. activity function and is not a general result. This simplification led to a number of erroneous statements in later literature.

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Interpretation of freezing nucleation experiments

G. Vali

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


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Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Interpretation of
freezing nucleation
experiments**

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Interpretation of freezing nucleation experiments

G. Vali

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Vali, G.: Freezing rate due to heterogeneous nucleation, *J. Atmos. Sci.*, 51, 1843–1856, 1994.
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Interpretation of freezing nucleation experiments

G. Vali

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)
**Table A1.** Nomenclature.

A	surface area of substrate in a water drop
f	fraction of number of samples frozen
g	fraction of number of samples not frozen
$J(t)$	nucleation rate [s^{-1}] or [$\text{s}^{-1} \text{cm}^{-2}$]
$k(T)dT$	number per unit volume of sites active between T and $T + dT$
$K(T)$	number per unit volume of sites active above T
$n_s(T)$	number of sites per unit surface area
N_F	number of samples frozen
N_L	number of samples not frozen
N_0	total number of samples in an experiment
$R(t)$	freezing rate per unit time [s^{-1}]; Eq. (4)
$R'(t)$	freezing rate per temperature interval
t	time in seconds
T	temperature [$^{\circ}\text{C}$]
T°	characteristic temperature for a nucleating site [$^{\circ}\text{C}$]
V	volume of water drop (sample unit)
w	cooling rate
ω	slope, defined in Eq. (7)
ε	factor increase per degree, defined in Eq. (7)
ATD	Arizona test dust
CNT	classical nucleation theory
INP	ice nucleating particle – designates a particle that has been diagnosed or is expected to initiate ice by a site on its surface

Interpretation of freezing nucleation experiments

G. Vali

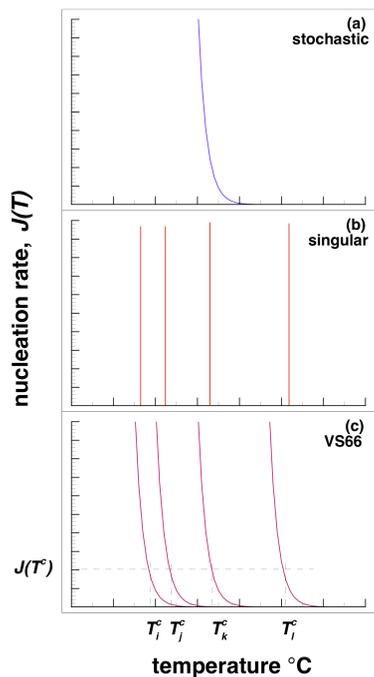


Fig. 1. Schematic representation of the assumptions made about nucleation rate in the **(a)** stochastic, **(b)** singular, and **(c)** VS66 models.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interpretation of freezing nucleation experiments

G. Vali

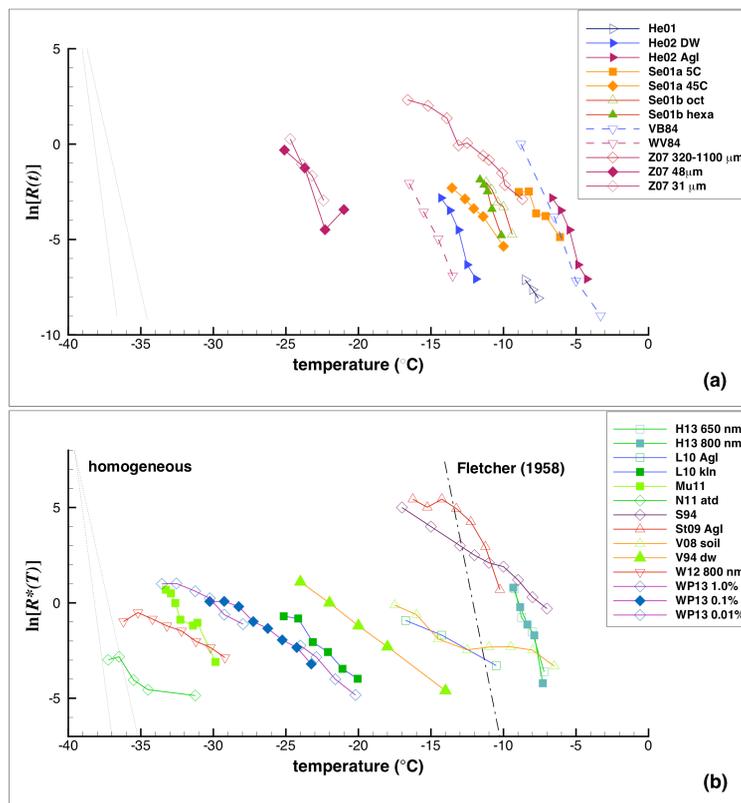


Fig. 2. Measured freezing rates in different experiments. The legend identifies the sources using the abbreviations defined in the text and in Table 1. Upper panel shows data for freezing rate per unit time $R(t)$, while the lower panel collects data for the freezing rate per unit temperature interval $R^*(T)$. The number of data points has been reduced in all cases for the sake of clarity.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion