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The Rate of Homogenous Nucleation of Ice in Supercooled Water

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Abstract

The homogeneous freezing of water is of fundamental importance to a number of fields, including that of cloud formation. However, there is considerable scatter in homogeneous nucleation rate coefficients reported in the literature. Using a cold stage droplet system designed to minimize uncertainties in temperature measurements, we examined the freezing of over fifteen hundred pure water droplets with diameters between 4 and 24 μm. Under the assumption that nucleation occurs within the bulk of the droplet, nucleation rate coefficients fall within the spread of literature data and are in good agreement with a subset of more recent measurements. To quantify the relative importance of surface and volume nucleation in our experiments, where droplets are supported by a hydrophobic surface and surrounded by oil, comparison of droplets with different surface area to volume ratios was performed. From our experiments it is shown that in droplets larger than 6 μm diameter (between 234.6 and 236.5 K), nucleation in the interior is more important than nucleation at the surface. At smaller sizes we cannot rule out a significant contribution of surface nucleation, and in order to further constrain surface nucleation experiments with smaller droplets are necessary. Nevertheless, in our experiments, it is dominantly volume nucleation controlling the observed nucleation rate.

1 Introduction

The homogeneous nucleation of ice in water is of fundamental importance for the glaciation of many clouds.[1-5] Ice formation in clouds, including homogeneous freezing of deeply supercooled clouds droplets, substantially alters their properties, dynamics and the formation of precipitation.[5,6] However, the rate at which water freezes homogenously is poorly constrained, with rate coefficients ranging over three orders of magnitude at around 236 K.[7,8] There is also significant disagreement on the temperature (T) dependence of the nucleation rate coefficient (J_V, cm^{-3} s^{-2}), with dln(J_V)/dT ranging from ~-2 to ~-4.5.[9,10] Cloud simulations show that predicted cloud properties are especially sensitive to uncertainty in the temperature dependence of the homogeneous nucleation rate coefficient.[5] Hence, accurate knowledge of the nucleation rate coefficient and its temperature dependence is important for accurately predicting the rate of ice formation in supercooled liquid clouds.[5] The primary cause of scatter in coefficients has been suggested by Riechers *et al.*[7] to stem from differences in the accuracies of reported temperature measurements, rather than the precision of individual temperature measurements (Riechers *et al.*[7] calibrated their experiments by observing a range of well-defined phase changes at temperatures ranging from 148.9 to 505.1 K in a variety of materials).

Another source of uncertainty in current estimations of homogeneous nucleation is that nucleation at the droplet surface (termed surface nucleation from here on) may be more important than nucleation in the bulk of a droplet (volume nucleation).[11-17] Surface nucleation may become more important in smaller droplets, in which the surface to volume ratio is larger. Analysis of droplet freezing data for a range of droplets sizes has suggested that for supercooled water droplets with water-air interfaces the size where the probability of surface and volume nucleation are equal is less than 10 μm diameter at around 235 - 237 K.[14,15] The rate of surface nucleation is likely to depend on the nature of the interface, hence it may depend on the presence of air, surfactants, oils, solid surfaces or charge. Regardless of the nature of the interface, it is important to quantify the relative contribution of surface and volume nucleation in any experiment where the objective is to study homogeneous nucleation of small droplets.

In this paper the freezing of sessile droplets ranging from 4 to 24 μm diameter (3.2 – 20.4 μm spherical equivalent diameter by volume) is quantified using a technique in which we pay special attention to reducing and quantifying the uncertainty in both the rate and the temperature of nucleation.

2 Methods

A cold stage droplet freezing instrument which has been previously used to investigate ice nucleation[8,18,19] was recently modified.[20-22] Briefly, the cold stage consisted of a small aluminum block attached to an optical microscope operating in transmission mode. The block was cooled via two embedded liquid nitrogen pipes, with temperature control provided by two embedded cartridge heaters controlled by a Eurotherm 2416 PID controller (Figure 1). Droplets were generated by the use of a nebulizer to create a mist which was then allowed to deposit onto a siliconized glass coverslip. To prevent droplet evaporation and Bergeron-Findeisen type mass transfer after freezing has commenced, droplets were covered with a layer of silicone oil before being transferred to the cold stage for experiments. The glass coverslip was positioned over a hole in the stage to allow light for microscopy; to minimize temperature gradients this hole was bridged by a square wafer of thermal management grade diamond (Element Six, TM180, 10 × 10 × 0.25 mm, 1800 $Wm^{-1}K^{-1}$). During the experiment the coverslip was isolated from the surrounding air using a Perspex shield, with the resulting air-space dried by a flow of dry nitrogen gas to prevent condensation during cooling. The stage was cooled rapidly (at 10 K min^{-1}) from above the laboratory dew point temperature (~285 K) to near the freezing temperature (~243 K), and then cooled more slowly (1 K min^{-1}) to below 233 K. This slow cooling, combined with the modifications to the cold stage (reduction of the stage thermal mass, embedding of N_2 cooling pipes into the stage, and use of a diamond window instead of a less thermally conductive sapphire window) minimized the temperature difference between the droplets and temperature probes. The accuracy of temperature measurements was also improved by replacing the thermocouple with a fast response platinum resistance thermometer (Fluke Corporation, USA, 5622-05 probes with manufacturers reported precision of ±0.04 K, recorded with a Fluke Corporation, USA, 1524 data logger with manufacturers reported accuracy of ±0.01 K, both calibrated against a Fluke Corporation, USA, 5608 secondary standard probe). The progress of each experiment was recorded using a digital camera at 5 frames per second, with freezing events identified visually. Droplet sizes were determined from the video by comparison with images of a micrometer scale taken using the same equipment and magnification. Droplet volumes and surface areas were calculated taking into account their capped spherical shape due to the water/substrate contact angle of 100°. The experiments discussed in this paper consider 1513 droplets in total, ranging from 3.8 to 23.8 µm diameter (3.2 – 20.4 µm spherical equivalent diameter by volume). Note that the diameters given throughout the manuscript are for the diameter of a droplet supported on the substrate, i.e. a capped sphere, unless otherwise stated.

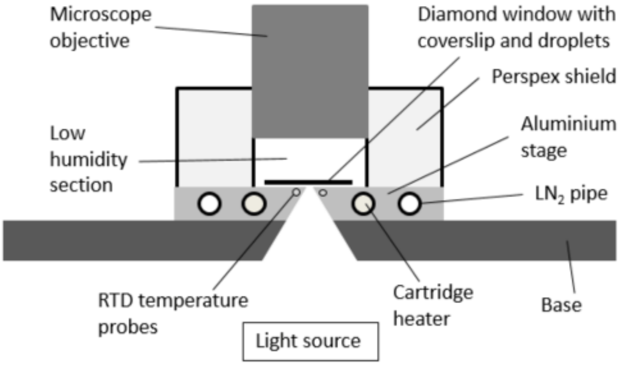

Figure 1. Schematic of the cold stage. The cold stage itself consists of a small aluminium block with heaters, liquid nitrogen pipes (LN_2) and temperature probes embedded into it. The droplet containing coverslip is placed on a diamond window, which bridges the hole in the stage that provides light for transmission microscopy. See section 2 for further details.

3 Results and discussion

3.1 Volume nucleation rate coefficients

The ice nucleation rate coefficient within pure water droplets can be related to observations of freezing via the Poisson distribution (a detailed derivation is provided in the Supporting Information):[23-25]

$$J_V(T) = \frac{-\ln\left(1-\frac{n_i}{n_L}\right)}{V(T)\Delta t} \quad (1)$$

Where $J_V(T)$ is the volume nucleation rate coefficient calculated from n_i droplets freezing from a population of n_L liquid droplets of mean volume $V(T)$ during the time period Δt. Over the narrow range of freezing temperatures typical to homogeneous experiments $J_V(T)$ can be empirically approximated with a log-linear function:[7,8]

$$J_V(T) = e^{aT+b} \quad (2)$$

where a and b are empirically fitted constants. In the calculation of nucleation rate coefficients there are a number of uncertainties, represented by 1σ error bars in the figures, which need to be taken into account: the accuracy of the time measurement (±0.1 s), the droplet size measurement and the conversion from the fraction frozen to nucleation rate via the Poisson distribution. The Poisson error is inversely related to the number of droplets which freeze in a time step, hence the error on the first and last few time steps tends to be larger. The methods used to estimate these uncertainties are detailed in the Supporting Information.

A number of homogeneous drop freezing experiments were performed and an example set of fraction frozen curves – the cumulative fraction of droplets frozen as a function of decreasing temperature – is shown in Figure 2a. The volume nucleation rate coefficients ($J_V(T)$, calculated using eq. 1) for this experiment are shown in Figure 2b and it is clear that the values of $J_V(T)$ for the different size bins are self-consistent. Volume nucleation rate coefficients for all four experiments are shown in Figure 3. It can be seen from Figure 3 that while the temperature dependence of $J_V(T)$ is consistent between experiments there are temperature offsets between experiments. This emphasizes the importance of temperature accuracy for determining the nucleation rate. In these experiments freezing of the entire population occurs over only 2 K, with the nucleation rate increasing by more than three orders of magnitude over this temperature range. Hence, relatively small uncertainties in temperature can result in large

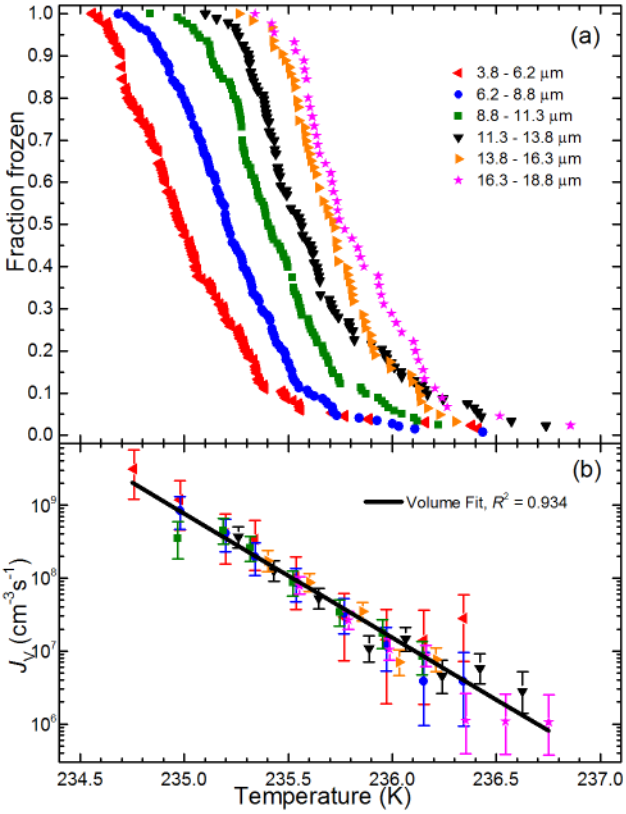

Figure 2. (a): Sample frozen fraction curves for Run 1, (b) Volume nucleation rate coefficients calculated for the freezing shown in (a). The frozen fraction of a size bin is defined as the cumulative number of frozen droplets divided by the starting number of droplets. A fit to the nucleation rate coefficients is provided ($\ln(J_V(T)) = -3.9126T + 939.916$, $R^2 = 0.934$, see Table 1 for fits to the other runs). Quoted droplet sizes are the diameters of the sessile droplets on the surface. Note that the higher time resolution of the freezing data in panel (a) can result in several freezing observations being grouped into each Δt period in panel (b).

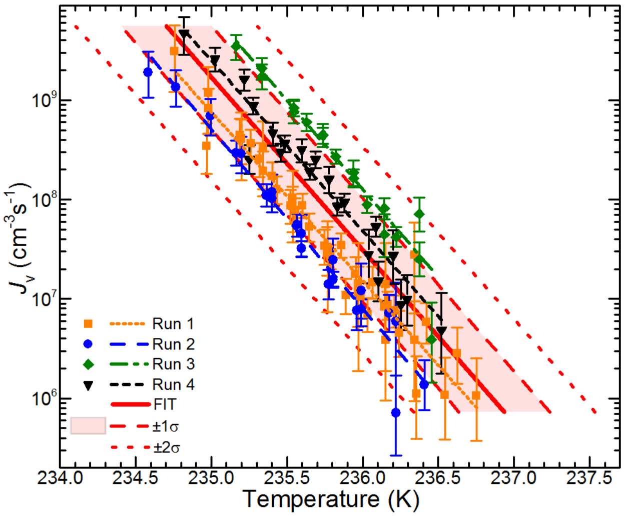

Figure 3. Experimental homogeneous volume nucleation rate coefficients from four experiments with a cooling rate of 1 K min^{-1}. The overall fit is shown in red ($\ln(J_V(T)) = -4.0106T + 963.706$), with a shaded area and dashed lines giving the 1σ standard deviation and dotted lines for the 2σ range. For each experiment a fit to eq. 2 has been performed (Table 1). The fitting process was by a least sum of squares, weighted by the uncertainty in the nucleation rate (see Supporting Information). The fit gives an R^2 value of 0.947.

Table 1. A summary of the experimental parameters.

Run	No. drops	Size range (μm dia.)	S.A. range (10^{-6} cm^2)	Vol. range (10^{-10} cm^3)	S.A. fit[a]; R^2	Vol. fit[b] R^2
1	581	3.8 – 18.8	0.5 – 12	0.2 – 22	$-3.5705T + 850.141$; 0.915	$-3.9126T + 939.916$; 0.934
2	307	3.8 – 23.8	0.5 – 19	0.2 – 44	$-3.2785T + 781.756$; 0.881	$-4.1547T + 996.412$; 0.956
3	304	3.9 – 10.6	0.5 – 3.8	0.2 – 3.9	$-3.7953T + 904.837$; 0.917	$-4.0975T + 985.669$; 0.922
4	321	3.9 – 10.6	0.5 – 3.8	0.2 – 3.9	$-3.6369T + 866.550$; 0.935	$-3.9517T + 950.296$; 0.943
Overall	1513	3.8 – 23.8	0.5 – 19	0.2 – 44	$-3.5826T + 853.706$; 0.920	$-4.0106T + 963.706$; 0.947

[a]See eq 4. [b]See eq 2.

uncertainties in the nucleation rate.[7] Given these uncertainties, an average fit with a standard deviation of ±0.3 K has been produced, giving $\ln(J_V(T)) = -4.0106T + 963.7063$ (red line in Figure 3).

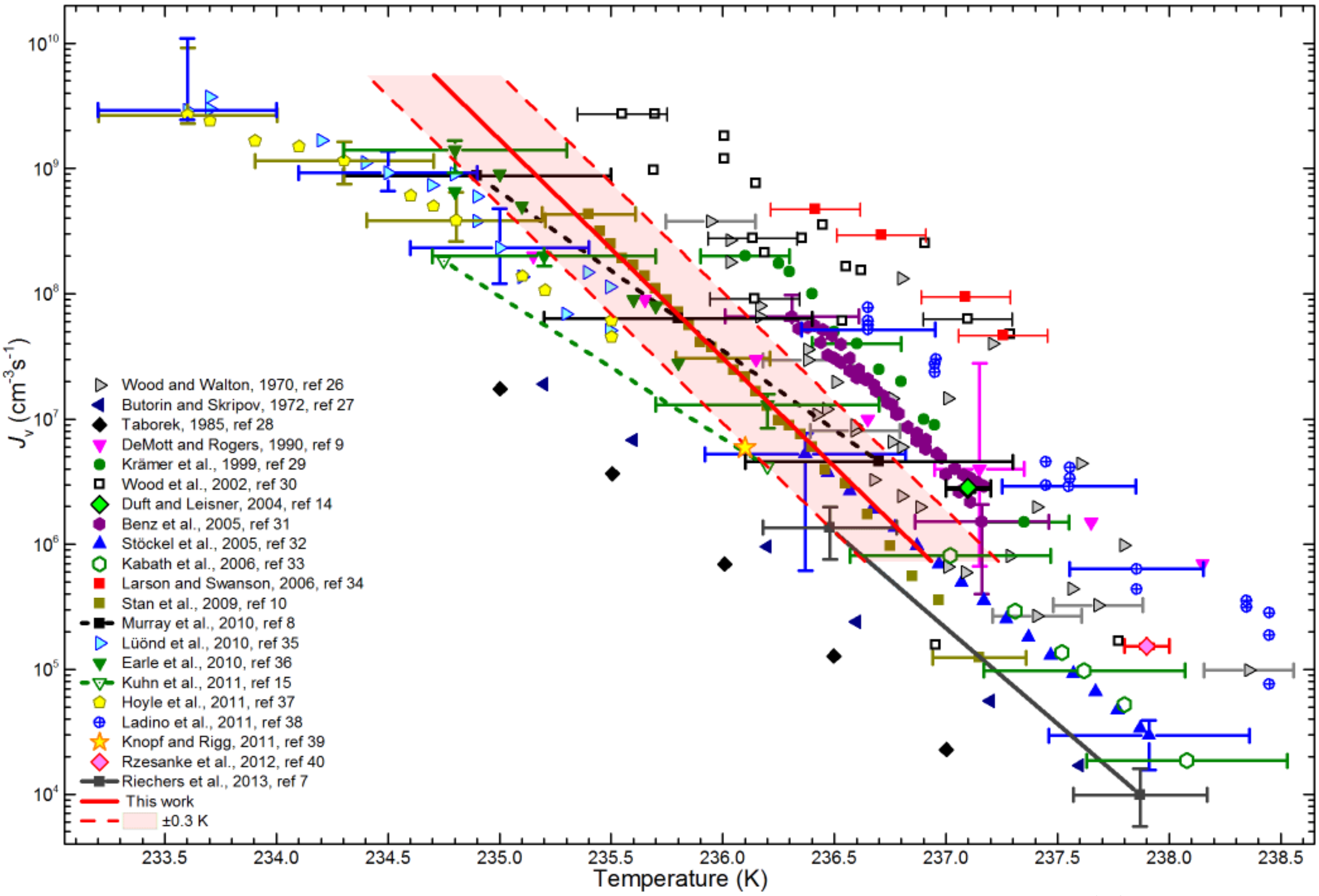

Figure 4. The new volume based nucleation rates in comparison with the literature data.[7-10,14,15,26-40] For clarity only a few sample error bars are provided for each dataset.

The parameterization, with 1σ standard deviation, of the new data is compared to the available literature data in Figure 4. The new dataset is in very close agreement with the data presented by Stöckel *et al.*,[32] Kabath *et al.*[33] and Stan *et al.*[10]. Within temperature uncertainty the new dataset agrees with the data of Murray *et al.*,[8] Earle *et al.*[36] and Riechers *et al.*[7], but with the remaining datasets the agreement is less good. As suggested by Riechers *et al.*[7] much of the spread in J_V values is likely due to the temperature uncertainty in the various measurements, but this is difficult to assess because the temperature accuracy is sometimes not reported and calibration methods are rarely provided.

While differences in absolute nucleation rate coefficients may be related to temperature uncertainties, differences in the reported temperature dependence must be related to some other factor than a systematic temperature offset. One issue is the treatment of broad droplet size distributions. For example, Murray *et al.*,[8] report values of $J_V(T)$ consistent with the new data but the temperature dependence is not as strong. The explanation for this is that Murray *et al.*[8] used a different method of determining average droplet volume. In the present study the mean droplet volume is recalculated as droplets freeze, whereas Murray *et al.*[8] used a constant median droplet volume for relatively broad size bins. The new method takes into account the fact that it is the largest droplets in a size bin which will tend to freeze first, resulting in a reduction of the mean droplet volume during the experiment. Not including this effect will result in calculated $J_V(T)$ values that are too small in the latter stages of the experiment. The slope of the new data from our study is in good agreement with the slope from Stan *et al.*[10] and Riechers *et al.*,[7] who studied nucleation with a very narrow size range of droplets. This suggests that the correct slope, $\mathrm{d}\ln(J_V)/\mathrm{d}T$, is at the steeper end of the range of literature estimates.

In summary, the new data presented here is in good agreement with a selection of the more modern data sets, but in general there is a lack of data at temperatures above about 238 K for nucleation rates smaller than 10^4 cm^{-3} s^{-1}. It has been suggested that nucleation rate coefficients as small as 1 cm^{-3} s^{-1} might start to produce significant quantities of ice crystals in some clouds.[5] Hence, there is a need to extend the measurements of homogeneous nucleation to warmer temperatures.

3.2 Surface nucleation rate coefficients

Considering the case where nucleation occurs only within the droplet surface layer (at the oil-water interface), a surface-based derivation similar to eq. 1 can be used:[11,14,15,41]

$$J_\mathrm{S}(T) = \frac{-\ln\left(1-\frac{n_\mathrm{i}}{n_\mathrm{L}}\right)}{s(T)\Delta t} \tag{3}$$

where s(T) is the droplet surface area and J_s(T) is the surface nucleation rate coefficient. Similarly to volume nucleation, surface nucleation can be empirically approximated with a log-linear expression, with c and d as empirical constants:

$$J_s(T) = \mathrm{e}^{cT+d} \tag{4}$$

The $J_s(T)$ values for each size bin from experiment 1 are shown in Figure 5. As in the case of $J_V(T)$ (Figure 2b) the data for the different size bins falls onto the same line. The R^2 goodness of fit parameter is slightly smaller than the equivalent $J_V(T)$ plot (0.915 vs. 0.934), but is still a reasonable fit. Hence, on this basis it is not possible to say that nucleation occurs dominantly at the surface of droplets or in their volume, although the volume based model does provide a better fit. In order to explore the potential role of surface nucleation further we now fit both surface and volume freezing to the data simultaneously.

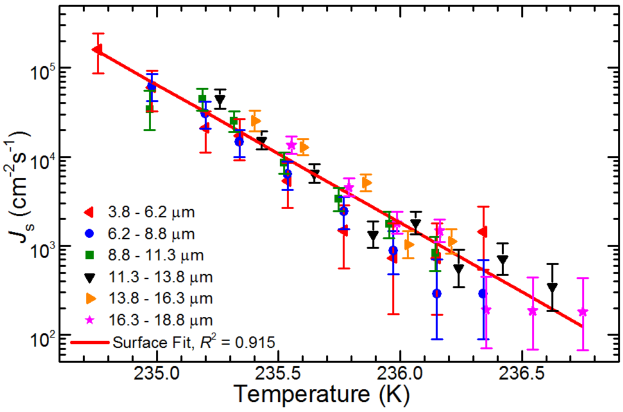

Figure 5. Surface nucleation rate coefficients calculated for Run 1. These values are determined from the fraction frozen curves shown in Figure 2a. The R^2 goodness parameter of the provided fit ($\ln(J_s(T)) = -3.5705T + 850.141$) is slightly smaller than the equivalent J_V plot (0.915 vs. 0.934, Figure 2b). The R^2 and fit parameters to all runs are provided in Table 1.

3.3 The combination of nucleation in the droplet surface and volume

The rate of freezing is a combination of both surface and volume terms. Therefore, the overall freezing rate $R(T)$ (units of s^{-1}) should be described as the sum of the freezing rates due to each component in the system:[11,14,15,19,23]

$$R(T) = J_s(T)s(T) + J_V(T)V(T) = \frac{-\ln\left(1-\frac{n_i}{n_L}\right)}{\Delta t} \tag{5}$$

By comparing different droplet sizes the contribution of surface and volume nucleation can, in principle, be determined.[15] For this, values of $R(T)$ was calculated using a, b, c and d (which define $J_V(T)$ and $J_s(T)$, see equations 2 and 4). The difference between the observed and calculated values of $R(T)$ was then minimized through a process of iteratively adjusting a, b, c and d for each individual run. Hence, each run produces independent values of $J_s(T)$ and $J_V(T)$.

Best fits (i.e. lowest total residuals; note that there were other local minima) to the experimental freezing rates are shown in Figure 6 a-d. In these figures, the experimentally derived freezing rates for each size bin in each experiment are shown as symbols and the fits to these using eq. 5 are shown as solid lines. In addition the contributions by surface and volume nucleation are shown for the smallest droplets, where surface freezing will be most important (it is not shown for the other droplet sizes for the sakes of clarity). The volume and surface nucleation rate coefficients derived from each run are compared with one another in Figure 7 (a and b) and summarized in Table 2. In panel c of Figure 7 the equivalent diameter $d_{eq}(T)$ is presented, which is the size of a spherical droplet at which the predicted number of freezing events due to surface and volume nucleation are equal, defined as:[11,14,15]

$$J_s(T)s(T) = J_V(T)V(T)$$

$$J_s(T) \cdot 4\pi\left(\frac{d_{eq}(T)}{2}\right)^2 = J_V(T) \cdot \frac{4}{3}\pi\left(\frac{d_{eq}(T)}{2}\right)^3$$

$$d_{eq}(T) = 6\frac{J_s(T)}{J_V(T)} \tag{6}$$

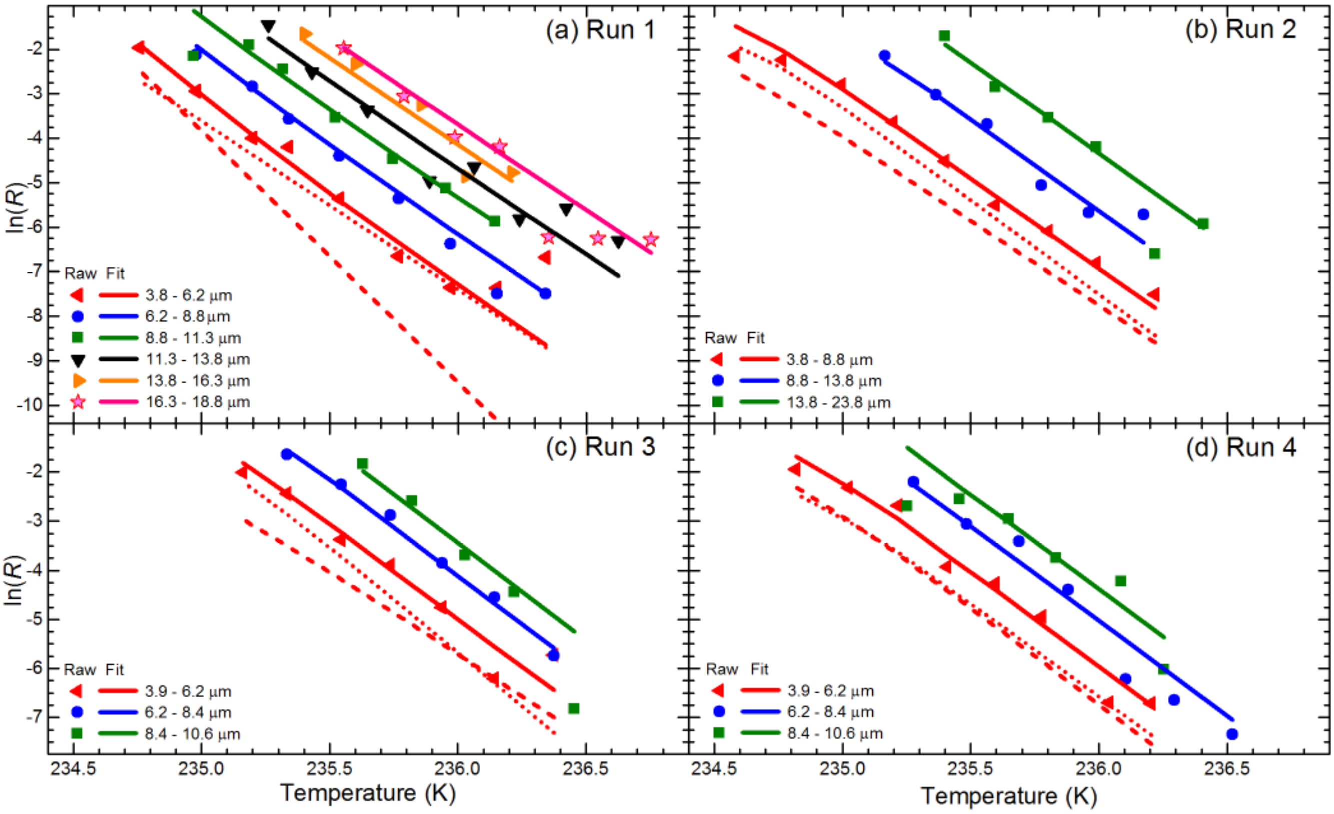

Figure 6. Size dependent fits to experimental freezing rates (R). The observed freezing rates (eq. 5) are shown as points, with the fitted freezing rates as solid lines. The balance between freezing due to the surface and volume for the smallest droplet size of each run is provided (Dotted lines: volume = $J_V(T)V(T)$, dashed lines: surface = $J_s(T)s(T)$). The fitted $J_V(T)$ and $J_s(T)$ for each experiment are presented in Figure 7.

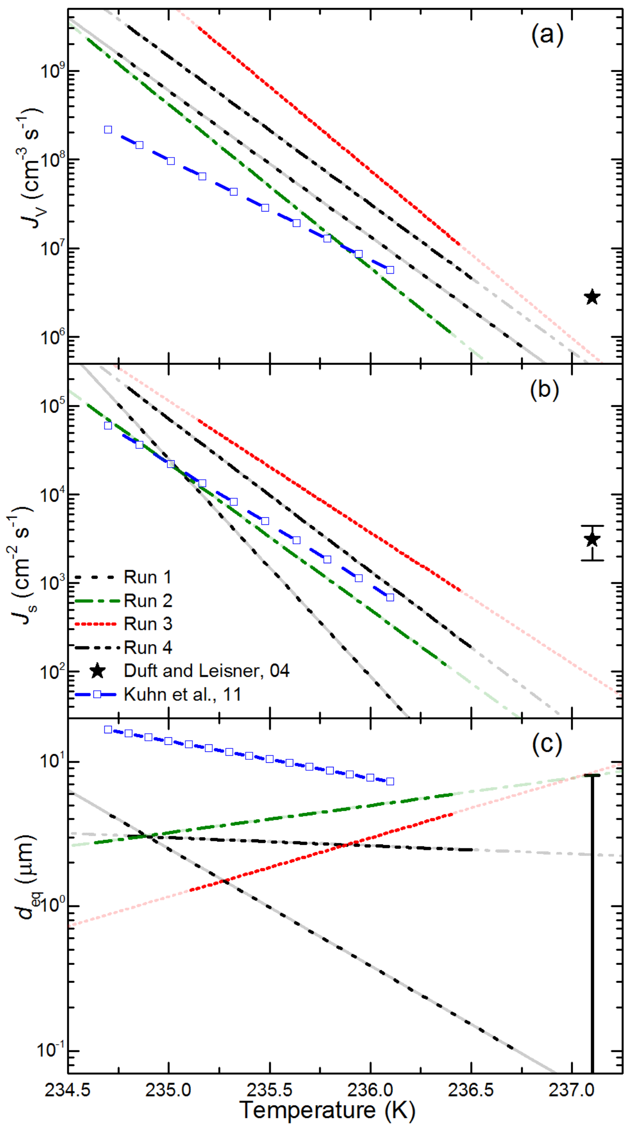

Figure 7. Volume (a) and surface (b) nucleation rate coefficients resulting from combined surface and volume nucleation fits (see Table 2). Panel (c) shows $d_{eq}(T)$, the diameter at which surface and volume freezing are equivalent (eq. 6). For comparison the parameterization of Kuhn *et al.*[15] and limiting data from Duft and Leisner[14] are shown. The data from Duft and Leisner[14] corresponds to 100 % of freezing due to the volume (panel a) or surface (panel b). For surface nucleation the data vary by a factor of 2.5, the range of which is given by error bars, and for volume nucleation the error is smaller than the data point. At 237.1 K all of the experiments give a calculated $d_{eq}(T)$ less than the ~8 µm limit from Duft and Leisner,[14] which is shown as a single error bar in panel c. The data are extrapolated beyond experimental temperature ranges, with temperatures outside this range denoted by fainter lines.

Table 2. A summary of ice nucleation parameterizations assuming freezing is due to the combination of the droplet surface and bulk volume.

Fit	No. Bins[a]	Bin widths (µm dia.)[a]	$\ln(J_s(T))$	$\ln(J_V(T))$	R^2	% surface nucl. at T_{50}[c]
Run 1	6	3.8 – 6.2	$-5.6506T+$ 1338.02	$-3.7891T+$ 910.638	0.925 (0.921; 0.914)[b]	37
		6.2 – 8.8				25
		8.8 – 11.3				14
		11.3 – 13.8				9
		13.8 – 16.3				5
		16.3 – 18.8				4
Run 2	3	3.8 – 8.8	$-3.8039T+$ 903.928	$-4.2378T+$ 1015.72	0.948 (0.935; 0.872)[b]	35
		8.8 – 13.8				20
		13.8 – 23.8				12
Run 3	3	3.9 – 6.2	$-3.4112T+$ 813.267	$-4.3522T+$ 1045.25	0.914 (0.905; 0.909)[b]	40
		6.2 – 8.4				37
		8.4 – 10.6				34
Run 4	3	3.9 – 6.2	$-3.9642T+$ 942.763	$-3.8332T+$ 921.894	0.935 (0.932; 0.929)[b]	48
		6.2 – 8.4				39
		8.4 – 10.6				33

[a]Droplets in each experiment are split into a number of size-bins to produce freezing rate datasets with different surface area to volume ratios. The runs have different size bins due to the differing droplet size distributions. [b]As eq. 5 defines the freezing rate rather than nucleation rate, R^2 values calculated for it are not directly comparable with those in Table 1.In the parentheses R^2 values for freezing rates assuming volume only and surface only nucleation respectively are provided for comparison. [c]T_{50} refers to the temperature at which 50 % of the droplets have frozen.

There are considerable differences between the estimates of $d_{eq}(T)$ from the four experiments in the present study, which results from the differences in fitted volume and surface nucleation rates coefficients. This highlights the uncertainty in quantifying the rate of surface nucleation. Nevertheless, it can be concluded from Figure 7c that between 234.5 and 236.5 K $d_{eq}(T)$ is most likely smaller than 6 µm, which is consistent with the limiting value estimated by Duft and Leisner,[14] but smaller than those reported by Kuhn *et al.*[15]. It should be noted that Duft and

Leisner[14] and Kuhn *et al.*[15] studied droplets suspended in gas, whereas our droplets were on a surface and surrounded by oil and may therefore not be directly comparable.

The differences in $d_{eq}(T)$ of each experiment, and especially for Run 1, are mainly due to differences in the temperature dependency of the calculated surface nucleation rate coefficients (Figure 7b). While the volume rate temperature dependencies are all similar ($d\ln J_V/dT$ ranging between -3.8 and -4.4 K^{-1}), the surface rate temperature dependencies are more variable (-3.4 to -5.7 K^{-1}). A reason for this inconsistency could be that surface nucleation is not significant and the minimization process produced parameterizations that best represent variability caused by other experimental factors and the probabilistic nature of freezing. Alternatively, surface nucleation may be less constrained by the data than the volume nucleation rate, for example due to the droplets not being small enough. In order to further constrain surface nucleation rate coefficients, one approach would be to perform experiments with a wider range of droplet sizes in which smaller droplets would define the rate of surface nucleation and larger droplets would define the rate of volume nucleation.

4 Conclusions

In summary, we present new measurements of the rate of homogeneous nucleation in pure supercooled water droplets. We used a cold stage instrument in which we paid special attention to minimizing and quantifying uncertainty in both the temperature and the rate coefficients. The resulting volume nucleation rate coefficients fall within the spread of literature data and are consistent with a subset of the more modern measurements. In addition, the temperature dependence of the volume nucleation rate coefficient ($d\ln(J_V)/dT$) is consistent with the steepest of those in the literature data.

We also analyzed our data for the contribution of surface versus volume nucleation. We found that volume nucleation is more probable than surface nucleation in droplets larger than ~6 µm (between 234.6 – 236.5 K, where measurements were made). This size is consistent with the limiting value derived by Duft and Leisner,[14] but smaller than the values quoted by Kuhn *et al.*.[15] However we used droplets on a substrate and covered in oil, whereas Kuhn *et al.*[15] used droplets suspended in gas and Duft and Leisner[14] used charged droplets suspended in gas. Surface nucleation may be susceptible to the exact nature of the interface, i.e. if it is air-water or oil-water, or if there is a charge residing at the interface. The volume nucleation rate coefficients presented in Figure 4 are a good approximation, although we note that the lower temperature end of this parameterization may be influenced by surface nucleation.

Ultimately, an improved knowledge of homogeneous nucleation is needed to describe ice formation in cloud models. Herbert *et al.*[5] recently showed that the temperature dependence of the nucleation rate coefficient is critical for determining the upper temperature limit where homogeneous nucleation becomes important in supercooled clouds. The steeper of the parameterizations of the nucleation rate coefficient tested by Herbert *et al.*[5] is consistent with the slope ($d\ln(J_V)/dT$) defined by our data. However, Herbert *et al.*[5] also show that homogeneous nucleation begins to become important at much smaller J_V values than most of the literature data extends, hence measurements at higher temperatures of smaller nucleation rates are needed. Measurements of larger rates, at lower temperatures, will also help to define a more accurate parameterization of the nucleation rate. In order to measure larger rates, either much smaller droplets will need to be sampled or droplet freezing will need to be done on shorter time scales. Such experiments might make use of new approaches such as a fast synchrotron technique which was recently used to probe nucleation rates between 227 and 232 K.[42] Advances are also being made in the calculation of nucleation rates from molecular models of water; although the absolute values deviate substantially from experimental values, they may be very useful in defining the temperature dependence of nucleation.[43] For smaller nucleation rates, either longer time periods or larger droplets must be sampled. In practice, these measurements are challenging for numerous reasons, not least that larger droplets have a higher probability of contamination and temperature accuracy and discrepancies between different instruments remains a major obstacle. Nevertheless, given the importance of the fundamental process of homogeneous nucleation of ice in water droplets, it is a challenge which should be addressed.

Associated content

Supporting Information Available: Supporting Methods: Derivation of nucleation rate coefficients, Fitting process, Estimation of uncertainties; Supporting Table: Fiducial ranges for Poisson statistics. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. J.D.A and B.J.M designed the experiments, which were performed by J.D.A and analyzed by J.D.A. and D.O'S. J.D.A. prepared the manuscript, with contributions from all co-authors.

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