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Sigurbjörnsson, Ómar F.; Signorell, Ruth 

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Volume versus surface nucleation in freezing aerosols

Ómar F. Sigurbjörnsson and Ruth Signorell*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

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The present study puts an end to the ongoing controversy regarding volume versus surface nucleation in freezing aerosols: Our study on nanosized aerosol particles demonstrates that current state of the art measurements of droplet ensembles cannot distinguish between the two mechanisms. The reasons are inherent experimental uncertainties as well as approximations used to analyze the kinetics. The combination of both can lead to uncertainties in the rate constants of two orders of magnitude, with important consequences for the modeling of atmospheric processes.

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The mechanism behind homogeneous nucleation and crystallization in submicron aerosol droplets is as topical an issue as it is controversial [1–11]. The interest in phase transitions in finite-size systems encompasses aspects of both applied and fundamental sciences. To name but one example, the crystallization kinetics of supercooled submicron water droplets and nitric acid dihydrate aerosols turns out to be important for the formation of clouds in our atmosphere, thus influencing our climate by various physical-chemical processes. The determination of corresponding crystallization rates has been the subject of numerous laboratory investigations [7,8,11–17]. By their reanalysis of some of these data Tabazadeh and co-workers [1–3] have sparked a controversy regarding particle crystallization by homogeneous nucleation [1–11]: Are the kinetics determined by volume nucleation or by surface nucleation; i.e., is the freezing rate proportional to the volume or to the surface area of the particle? Although experimental evidence for surface crystallization in thin films has been reported [18], so far no experimental study has been able to unambiguously prove the importance of surface nucleation in small molecularly structured aerosol particles. The reason lies in the major experimental difficulties to observe crystallization processes in *unsupported nanosized* aerosol particles under well defined experimental conditions. Particles collected on a substrate cannot provide reliable information because the interaction of the substrate with the particles surface can strongly influence surface nucleation processes. The observation of crystallization processes in single free-falling or single levitated aerosol particles is currently restricted to much larger, micron-sized particles [7,8,16], where homogeneous freezing rates are found proportional to the volume. Hence for these particles surface nucleation is negligible, and not surprisingly so given their high volume-to-surface ratio.

For single aerosol particles in the nm-size range, small enough that surface nucleation might become important, levitation and sensitive detection of crystallization processes is currently impossible. Investigations in this size range must still rely on particle ensembles, generated either in super-

sonic expansions [12,19] or in aerosol chambers [11,13–15], to determine freezing rates by electron diffraction or infrared spectroscopy. Most of these studies have interpreted the experimental data in terms of volume freezing, but after reanalyzing some of these data Tabazadeh and co-workers have challenged this interpretation. Their conclusion that nucleation takes place preferentially at the surface rather than throughout the volume [1–3] has revived the current dispute regarding the issue. In all these studies of particle ensembles the apparent dominance of volume or surface nucleation was deduced from fitting experimental nucleation rates. Their derivation implied various approximations to account for the distribution of particle sizes in the freezing process, but very little if any attention has been paid to the influence of these approximations on the results. The discussion of experimental uncertainties and their effects has remained likewise incomplete.

The present constitutes the first study to clarify the role of those factors in deciding the issue of volume versus surface nucleation on the basis of aerosol ensembles measurements. For the current state of the art for such measurements, our study puts an end to the ongoing debate and provides a clear evaluation of the accuracy of experimental nucleation rate constants. For that purpose, we combine a proper analysis of the crystallization dynamics of a particle ensemble with systematic experimental studies on freezing fluoroform (CHF₃) droplets. With distinct band shapes for its supercooled liquid and crystalline state CHF₃ is an ideal model system to study fundamental aspects of particle freezing *in situ*, noninvasively, and with good time resolution by rapid-scan Fourier transform infrared (FTIR) spectroscopy. Various CHF₃ aerosols with mean radii between 20 and 700 nm were generated by bath gas cooling in our aerosol chamber at a temperature of 78 K (see Refs. [20,21], and references therein). Prior to droplet formation the precooled cell (78 K) was filled with He bath gas, thermally equilibrating with the cell within minutes. The droplets were then formed by rapid injection of a CHF₃/He gas mixture (100–10⁵ ppm CHF₃ in He) into the cold He bath gas (pressures 200–1000 mbar). The rapid cooling leads to supersaturation of the CHF₃/He gas mixture and subsequent condensation into supercooled liquid droplets. The progressive crystallization of the droplet ensembles—bulk CHF₃ freezes at 118 K—was monitored *in situ* by rapid-scan FTIR spectroscopy with a time resolution of 30 ms and a spectral resolution of 1 cm⁻¹. As illustrated in Fig. 1 the

*Present address: Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1; FAX: +1 604 822 2847; signorell@chem.ubc.ca

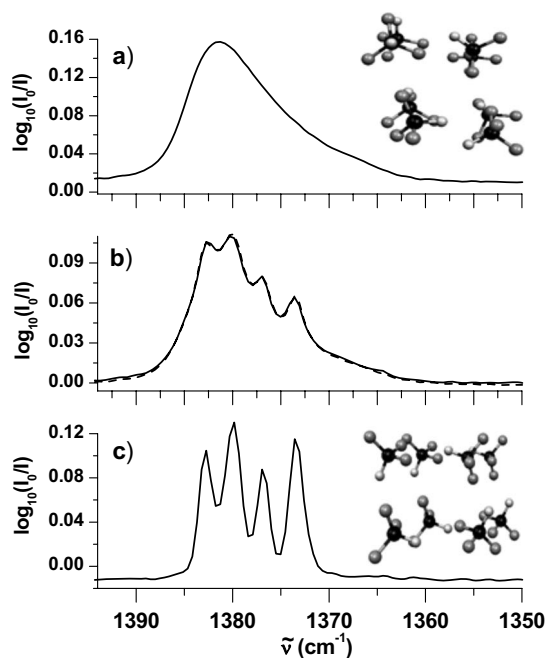


FIG. 1. Experimental infrared spectra of freezing nanosized fluoroform aerosol particles. (a) Initially formed supercooled liquid droplets. The molecules in these droplets do not show any long-range order [26]. (b) Intermediate spectrum. Eighteen percent of the whole droplet ensemble is frozen at this time. The dashed line represents a linear combination of spectrum *a* and spectrum *c*. (c) Crystalline aerosol particles after crystallization is complete. The band structure arises from the long-range order of the molecules in this phase [27].

supercooled liquid state of CHF₃ (trace *a*) is readily distinguished from the crystalline state (trace *c*) by very characteristic IR band shapes [22]. This allows us to determine the time evolution of the average volume fraction of unfrozen particles $\bar{P}_{\text{exp}}(t)$ (see below) with high accuracy from the linear decomposition of the time-dependent FTIR spectra into their liquid and crystalline components. As an example trace *b* shows an intermediate spectrum in the region of the ν_4 vibration of CHF₃ (full line) together with its reconstruction (dashed line) as a linear combination of liquid and crystalline spectra. The match is almost perfect. The ability to observe the progressive crystallization of the particle ensembles up to completion together with the high time resolution of the rapid-scan FTIR provides us with a uniquely complete experimental data set for the investigation of particle freezing mechanisms.

According to classical nucleation theory the freezing process of a *single* aerosol droplet is governed by a first order rate equation (Refs. [23,24], and references therein)

$$\frac{-d \ln P(x,t)}{dt} = J_V(T)V(x) + J_S(T)S(x). \quad (1)$$

$P(x,t)$ is the probability that the particle is still unfrozen at time t [$P(x,0)=1$]. $x=\ln(r/u)$ is the logarithm of the particle radius r in units of $u=1$ nm. $J_V(T)$ and $J_S(T)$ are the volume nucleation rate and the surface nucleation rate, respectively.

$V(x)=(4/3)\pi e^{3x}$ and $S(x)=4\pi e^{2x}$ are the particle volume and the particle surface area, respectively. T is the temperature. Equation (1) includes both volume and surface contribution to nucleation. If freezing is exclusively a volume process the surface term equals zero and vice versa. Even though Eq. (1) is only valid for a single droplet, it has been used in previous investigations to describe droplet ensembles simply by replacing the droplet's volume and surface area *ad hoc* with their respective mean values \bar{V} and \bar{S} .

$$\frac{-d \ln \bar{P}(t)}{dt} = J_V(T)\bar{V} + J_S(T)\bar{S}. \quad (2)$$

The solution to Eq. (2) is

$$\bar{P}(t) = e^{-[J_V(T)\bar{V} + J_S(T)\bar{S}]t}. \quad (3)$$

$\bar{P}(t)$ is the average volume fraction of droplets that are still unfrozen at time t [$\bar{P}(0)=1$]. With \bar{V} and \bar{S} estimated or determined from the droplet size distribution using various approximations [1,2,11–15,19] the volume nucleation rate J_V and the surface nucleation rate J_S have been determined by nonlinear least-squares fits of $\bar{P}(t)$ to the experimentally determined average volume fraction of unfrozen droplets $\bar{P}_{\text{exp}}(t)$. Such fits have provided the basis to decide whether or not surface nucleation is important.

The following demonstrates that Eq. (3) represents a very crude approximation to the correct treatment of the crystallization kinetics of a droplet ensemble. In particular, we show that it becomes impossible to distinguish between volume and surface nucleation, and that the approximation strongly affects experimental nucleation rate constants. In contrast to a single particle the crystallization kinetics of a particle ensemble no longer follows a simple first order rate law. The correct treatment yields

$$\bar{P}(t) = \frac{\int f(x,t)V(x)e^{-[J_V(T)V(x) + J_S(T)S(x)]t} dx}{\int f(x,t)V(x) dx}. \quad (4)$$

$f(x,t)$ is the size distribution of the droplet ensemble. Note that the volume-weighted size distribution $f(x,t)V(x)$ appears because $\bar{P}_{\text{exp}}(t)$ is derived from measurements that are proportional to the volume. Figure 2 compares the full treatment of Eq. (4) with the approximation given in Eq. (3) for a model case. The squares show an artificial data set calculated with the correct expression in Eq. (4) for $J_V=1.2 \times 10^9 \text{ cm}^{-3} \text{ s}^{-1}$ (typical value found for CHF₃ droplets, see below) and $J_S=0$ (no surface nucleation). For $f(x,t)$ we used a lognormal distribution with a typical time dependence experimentally found for CHF₃ droplets (see below). The squares in Fig. 2 thus mimic an experimental data set for which only volume nucleation is important. To calculate \bar{V} and \bar{S} [Eq. (3)] two classes of approximations are typically used in the literature: (i) A monodisperse aerosol with radius \bar{r} , $\bar{V}=\frac{4}{3}\pi \bar{r}^3$, and $\bar{S}=4\pi \bar{r}^2$. We calculate \bar{r} as the volume-weighted mean radius $\bar{r}=\int f(x,t)r(x)V(x)dx/\int f(x,t)V(x)dx$

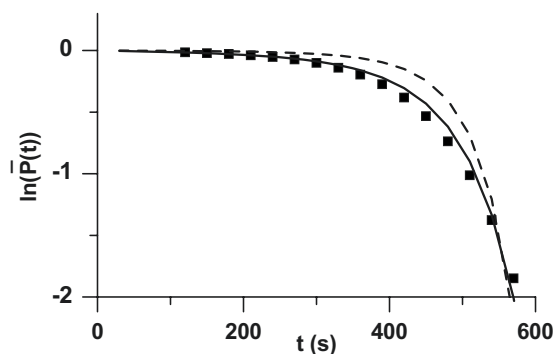


FIG. 2. The logarithm of the fraction of unfrozen aerosol droplets $[\ln \bar{P}(t)]$ is depicted as a function of time t . Squares: Synthetic data set calculated from Eq. (4) for pure volume nucleation (i.e., $J_S=0$). Dashed line: Fit to the squares using the approximations described in the text [Eq. (3)] under the assumption of pure volume nucleation (constraint $J_S=0$). Full line: Fit to the squares using the approximations described in the text under the assumption of pure surface nucleation (constraint $J_V=0$).

(sometimes even cruder approximations have been used). (ii) An aerosol with a volume-weighted mean volume $\bar{V} = \int f(x,t)V(x)^2 dx / \int f(x,t)V(x) dx$ and a volume-weighted mean surface $\bar{S} = \int f(x,t)S(x)V(x) dx / \int f(x,t)V(x) dx$. The lines in Fig. 2 represent fits to the artificial data set using the approximate Eq. (3). Case (ii) was used to calculate \bar{V} and \bar{S} , but the same qualitative results are also found for case (i). The dashed line shows a fit for which only J_V was refined and J_S was fixed to zero. The full line represents a fit for which only J_S was refined and J_V was fixed to zero.

Equation (3) is completely misleading when used to differentiate between volume and surface nucleation in the freezing of aerosols. The fit results in Fig. 2 would lead to the conclusion that the freezing of the model particle ensemble was dominated by surface nucleation even though the data points describe pure volume nucleation only. This evident contradiction makes it abundantly clear that the approximations implicit in Eq. (3) are far too crude to distinguish between the two processes. Hence we must conclude that the reanalysis of data in Refs. [1–3] cannot provide any support for the dominance of surface nucleation claimed by the authors. A second important conclusion refers to the values of the rate constants previously determined using Eq. (3) or similar approximations [1,2,11–15,19]. Compared with the true values, such approximations can lead to deviations of the rate constants of one order of magnitude. To account for this effect published rate constants should be quoted with an uncertainty of a factor of 10.

With the correct ensemble average [Eq. (4)] it should, in principle, be possible to determine from an experimental data set whether volume or surface nucleation is the dominant process. The major problem here, however, is the experimental uncertainties associated with such ensemble measurements in aerosol chambers. To clarify this aspect we have performed systematic studies of freezing CHF_3 droplet ensembles with mean radii ranging from 20 to 700 nm. In particular, this includes the size range, for which surface phenomena might be important. In addition, sample gas concen-

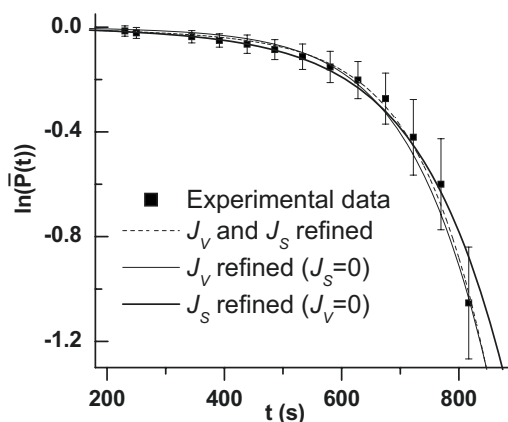


FIG. 3. The logarithm of the fraction of unfrozen aerosol droplets $[\ln \bar{P}(t)]$ is depicted as a function of time t . Squares: Experimental data points. Dashed line: Fit under the assumption that both volume and surface nucleation contribute. Thin line: Fit for pure volume nucleation (constraint $J_S=0$). Thick line: Fit for pure surface nucleation (constraint $J_V=0$).

tration, sample gas pressure, and bath gas pressure were systematically varied. The squares in Fig. 3 represent a typical experimental data set with error bars to indicate estimated uncertainties. The three traces represent weighted nonlinear fits to the experimental data using Eq. (4), with different constraints: pure volume nucleation ($J_S=0$, thin line), pure surface nucleation ($J_V=0$, thick line), and a combination of both (no constraint, dashed line). The droplet size distribution $f(x,t)$ —in particular, its temporal evolution—is a major unknown in this type of measurement. Arguments for an increase, decrease, and no change of the mean radius with time have been put forward [11,13–15], while thorough studies of growth mechanisms of liquid aerosol particles have been performed only recently (see Ref. [25], and references therein). For the data used for Fig. 3 we have observed an increase of the mean particle radius with time and determined $f(x,t)$ from Mie fits to the infrared spectra assuming lognormal functional forms for the size distributions at different times. Figure 3 illustrates for a particular experiment how typical experimental uncertainties associated with ensemble measurements in aerosol chambers make it impossible to distinguish between the two nucleation mechanisms. Within error bars we find the same qualitative result for all experimental conditions and particle sizes (20–700 nm) we have investigated, which provides further evidence against claims of experimental support for surface nucleation [1,2]. The highly nonlinear error propagation greatly amplifies the uncertainties of experimental data: From our systematic studies we must conclude that at present, nucleation rates for particle ensembles cannot be more accurately determined than to within about one order of magnitude, even with the proper ensemble average [Eq. (4)]. Since the two mechanisms cannot be experimentally distinguished, Table I quotes both rate constants, J_V (for $J_S=0$) and J_S (for $J_V=0$), for the freezing kinetics of CHF_3 aerosols at 78 K.

The present results are the first clear proof that it is impossible to distinguish between volume and surface nucleation by current state of the art measurements of freezing

TABLE I. Pure volume nucleation rate J_V (for $J_S=0$) and pure surface nucleation rate J_S (for $J_V=0$) of freezing fluoroform aerosol droplets (size range 20–700 nm) at a temperature of 78 K.

$J_V/\text{cm}^{-3} \text{ s}^{-1}$	$10^8 - 10^{10}$
$J_S/\text{cm}^{-2} \text{ s}^{-1}$	$10^3 - 10^5$

submicron to nm-sized aerosol droplet ensembles. This finding is consistent with the comments in Refs. [6,7,9,10], but contradicts the claims put forward in Refs. [1,2,5]. The problem arises from two sources: experimental uncertainties associated with those measurements and approximations commonly used to determine the kinetics. While the latter can be avoided with a proper ensemble average [Eq. (4)], the former are inherent to the experimental techniques currently avail-

able. Both sources contribute about a factor of 10 each to the relative uncertainty of published experimental nucleation rates. As long as neither the dominance of volume nucleation nor any influence of surface nucleation can be proven by ensemble measurements, both rate constants, J_V and J_S , should be specified to characterize the freezing kinetics of aerosol particle ensembles. These general results must be taken into account as uncertainties in the current modeling of aerosol nucleation processes in the atmosphere until the nucleation mechanism is clarified and more accurate rate constants become available.

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