

Empirical function for homogeneous water nucleation rates

Judith Wölk and Reinhard Strey^{a)}

Institut für Physikalische Chemie, Universität zu Köln, Luxemburger Strasse 116, D-50939 Köln, Germany

Christopher H. Heath and Barbara E. Wyslouzil

Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

(Received 15 April 2002; accepted 13 June 2002)

Very recently, Wölk and Strey [J. Phys. Chem. B **105**, 11683 (2001)] presented empirical temperature correction functions for calculating homogeneous nucleation rates J of H₂O and D₂O ($1 < J/\text{cm}^{-3} \text{s}^{-1} < 10^{20}$) from classical nucleation theory over an extended range of temperature T ($200 < T/K < 310$) and supersaturations S ($5 < S < 200$). Here, we critically test the correction functions to the Becker–Döring nucleation rate equation J_{BD} against an extensive set of experimental data, and find that the equations distinctly improve the agreement between theory and experiment for very little extra work. The success of the corrected nucleation rate functions is surprising, given that they were developed based on experimental nucleation rates measured in a nucleation pulse chamber over a limited nucleation rate range $10^5 < J/\text{cm}^{-3} \text{s}^{-1} < 10^{10}$, supersaturation range $6 < S < 22$, and temperature range $220 < T/K < 260$. © 2002 American Institute of Physics. [DOI: 10.1063/1.1498465]

I. INTRODUCTION

Nucleation and condensation of water is of considerable interest in several natural and industrial processes. In steam turbines, for example, it is important to calculate the onset of nucleation inside a turbine to prevent efficiency losses. To make accurate predictions, we need a thorough understanding of the condensation process, i.e., the nucleation and growth of water droplets. A large number of experimental^{1–12} and theoretical^{13–17} studies have been performed to understand the physics of water nucleation and, in general, none of the theories can quantitatively predict all of the experimental observations. Our goal here is to use the available data to demonstrate that a simple empirical modification to the Becker–Döring nucleation rate expression yields a robust function for predicting water nucleation rates over broad ranges of temperature and supersaturation.

Experimental studies of homogeneous nucleation date back to 1897, when Wilson made the first quantitative study of water nucleation.¹⁸ Since then, the homogeneous nucleation of water has been repeatedly studied with different experimental techniques including expansion cloud chambers,^{5–7,10} diffusion cloud chambers,^{2,4} the nucleation pulse chamber,^{3,12,19} a pulse-expansion wave tube,^{20,21} shock tubes,^{22,23} and supersonic nozzles.^{24–29} The data are reported either in terms of the critical supersaturations required to induce condensation in the apparatus or, more recently, in terms of the actual nucleation rates. When critical supersaturations are reported, estimates for the nucleation rates can often be deduced from models of the nucleation and growth processes occurring in the apparatus. Table I summarizes the data available for the two water isotopes that we use in this paper. We have restricted ourselves to data from the past 30

years, because it is rarely clear how to accurately extract nucleation rates from the earlier work. A more extensive listing of the water nucleation literature is available in Heist and He³⁰ for data between 1968 and 1992, and in Pound³¹ for data prior to 1968.

II. EMPIRICAL CORRECTION FUNCTION

The need for a correction function is evident in Fig. 1, where we compare the homogeneous nucleation rates for H₂O, measured by Wölk and Strey¹ in the nucleation pulse chamber, with the predictions of classical nucleation theory (dashed lines). The Becker–Döring nucleation rate J_{BD} is calculated using¹³

$$J_{\text{BD}} = \sqrt{\frac{2\sigma}{\pi m}} v_m \left(\frac{p_v}{kT}\right)^2 \exp\left\{\frac{-16\pi v_m^2 \sigma^3}{3(kT)^3 (\ln S)^2}\right\}. \quad (1)$$

In Eq. (1), $S = p_v/p_e$ is the supersaturation, p_v and p_e are the actual and the equilibrium vapor pressures, k is the Boltzmann constant, T is the temperature, and σ , v_m , and m are the surface tension of the critical cluster, the molecular volume, and mass of the water molecule, respectively.

Although the agreement between theory and experiment in this temperature range is actually quite reasonable, it is already clear that the temperature dependence of the classical theory is incorrect. Applying classical theory outside this experimental window will, therefore, result in increasingly larger discrepancies. Using the data in Fig. 1, Wölk and Strey developed a two-parameter correction function to the classical nucleation rate expression. They assumed that in general the nucleation rate J can be written as

$$J = K \exp(-\Delta G^*/kT), \quad (2)$$

^{a)} Author to whom correspondence should be addressed. Electronic mail: rstrey@uni-koeln.de

TABLE I. Techniques used to study light and heavy water nucleation. The measurement ranges (nucleation rate J , temperature T , supersaturation S) are given in comparison.

Technique	$J/\text{cm}^{-3}\text{s}^{-1}$	T/K	S	Reference
TDCC ^a	~ 1	280–330	2–4	Heist and Reiss (2)
ECC ^b	$10^2\text{--}10^6$	230–290	4–13	Miller <i>et al.</i> (10,11)
ECC	$10^6\text{--}10^8$	260	7–8	Dobbins <i>et al.</i> (6)
TPEC ^c	$10^5\text{--}10^9$	275–300	6–15	Wagner and Strey (12)
NPC ^d	$10^5\text{--}10^{10}$	220–260	6–23	Viisanen <i>et al.</i> (3,19)
NPC	$10^5\text{--}10^{10}$	220–260	6–25	Wölk and Strey (1)
PEWT ^e	$10^8\text{--}10^{11}$	230–250	8–18	Luijten <i>et al.</i> (21)
ST ^f	$10^7\text{--}10^9$	200–260	10–17	Peters and Paikers (23)
SN ^g	10^{17}	190–240	40–190	Heath <i>et al.</i> (35,36)
SSN ^h	$4 \cdot 10^{15}\text{--}6 \cdot 10^{15}$	230	29–32	Streletzky <i>et al.</i> (39)
SN	...	235–295	7–100	Stein and Moses (26,28)
ST	$\sim 10^{10}$	230–255	8–17	Lee (38)

^aThermal diffusion cloud chamber.

^bExpansion cloud chamber.

^cTwo-piston expansion chamber.

^dNucleation pulse chamber.

^ePulse-expansion wave tube.

^fShock tube.

^gSupersonic nozzle.

^hShaped supersonic nozzle.

where K is the kinetic prefactor and ΔG^* is the formation free energy of a critical cluster. Normalizing the experimental nucleation rate by the corresponding theoretical rate suggests that the ratio $J_{\text{exp}}/J_{\text{theor}}$ should be a linear function of the inverse temperature ($1/T$), since

$$\ln \frac{J_{\text{exp}}}{J_{\text{theor}}} = \ln \frac{K_{\text{exp}}}{K_{\text{theor}}} + \frac{\Delta G_{\text{theor}}^* - \Delta G_{\text{exp}}^*}{kT} \quad (3)$$

Experimental nucleation rates for n - and i -propanol³² and the homologous series of n -alcohols³³ have already been analyzed in this fashion. It was observed that the experimental nucleation rates depend less strongly on temperature than predicted by classical nucleation theory. One might note that if $K_{\text{exp}}=K_{\text{theor}}$, then $\ln(J_{\text{exp}}/J_{\text{theor}})$ is the difference in free energy (in units of kT) between the experimental critical cluster and that predicted by theory. From a scaling analysis of density functional theory in relation to classical nucleation

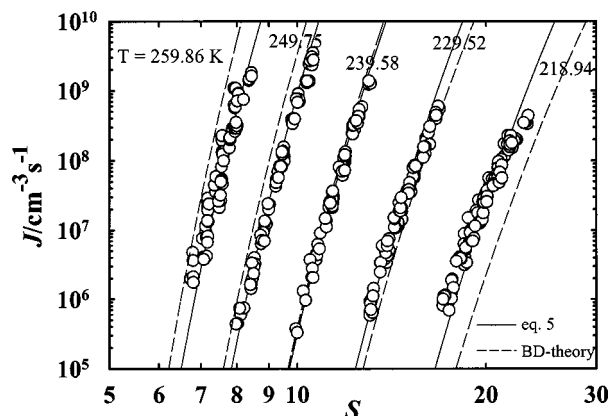


FIG. 1. The isothermal homogeneous nucleation rates for H_2O measured by Wölk and Strey (Ref. 1) (circles) are compared to the predictions of classical nucleation theory (dashed lines), Eq. (1), and the empirical nucleation rate function for H_2O Eq. (5) (solid lines).

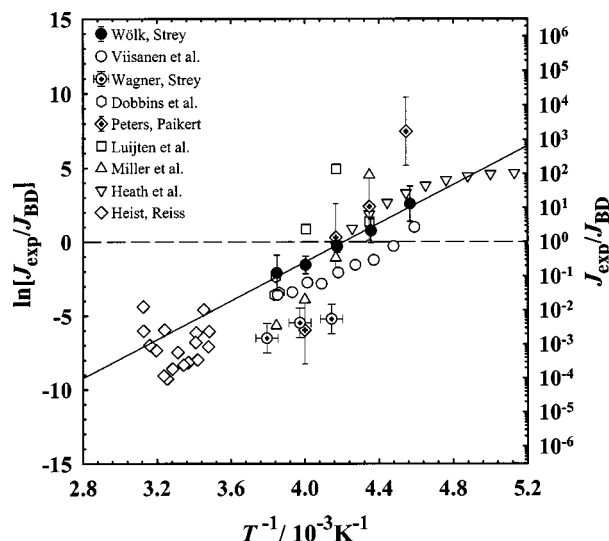


FIG. 2. When the H_2O rate data in Fig. 1 are normalized by J_{BD} , they are a linear function of $1/T$. The data reported by other research groups follow the extrapolated temperature dependence rather well (Refs. 2, 3, 6, 10, 11, 19–21, 35, 36).

theory, McGraw and Laaksonen arrived at the conclusion that the difference should be a temperature function only,³⁴ in agreement with our experimentally motivated approach.

To see whether this linear relationship holds for the H_2O nucleation rates, all of the experimental rates shown in Fig. 1 were divided by the corresponding value of J_{BD} . The filled circles in Fig. 2 represent the mean value of the ratio $J_{\text{exp}}/J_{\text{BD}}$ at the mean nucleation temperature. The error bars represent one standard deviation from the mean. The data follow the expected linear trend, and the solid line is the fit of the data to the functional form

$$\ln \frac{J_{\text{exp}}}{J_{\text{BD}}} = A + B \frac{1}{T}, \quad (4)$$

where $A = \ln(K_{\text{exp}}/K_{\text{BD}}) + (\Delta S_{\text{BD}}^* - \Delta S_{\text{exp}}^*)/k$ and $B = (\Delta H_{\text{BD}}^* - \Delta H_{\text{exp}}^*)/k$. In Fig. 2 the dashed line represents complete agreement between theory and experiment. For H_2O , Wölk and Strey found $A = -27.56$ and $B = 6.5 \times 10^3$ K. Because A and B are constants, the size of the critical cluster will not be affected by the correction function, even though ΔG^* has changed. Rewriting Eq. (4) yields the empirical correlation for water

$$J_{\text{H}_2\text{O}} = J_{\text{BD}} \exp \left(-27.56 + \frac{6.5 \times 10^3}{T} \right). \quad (5)$$

The solid lines in Fig. 1 are calculated using Eq. (5), and the corrected predictions now agree with the experimental nucleation rates to within experimental error.

III. FURTHER EXPERIMENTAL OBSERVATIONS

We can now test this correlation against the results of other groups. The earlier data of Viisanen *et al.*,^{3,19} the open circles in Fig. 2, were measured using the same nucleation pulse chamber as Wölk and Strey and, therefore, cover the same range of nucleation rates and temperature. Although they are not shown, we estimate that the error bars on the

Viisanen data are at least as large as those of Wölk and Strey, and would generally overlap the error bars of the filled circles. Regressing the Viisanen data set yields a very similar value for the slope of the temperature correction ($B = 5.8 \times 10^3$ K), and the value of A ($A = -26.54$) is only 4% lower.

Early measurements by Wagner and Strey¹² in a two-piston expansion chamber yielded nucleation rates for water starting from three different initial chamber temperatures ($T_0 = 3$ °C, 13.2 °C, 24.5 °C), but due to the operating characteristics only nonisothermal J - S curves were obtained. However, the nucleation temperature for each T_0 varied only about ± 3 K. To calculate the ratio $J_{\text{exp}}/J_{\text{BD}}$ needed for the comparison in this paper their lowest nucleation rates for $T_0 = 3$ °C and 13.2 °C were not taken into account, because they show a kink in the J versus S plot (indicating possible contamination). In Fig. 2 we included the mean values of their inverse nucleation temperatures and the mean values of the $J_{\text{exp}}/J_{\text{BD}}$ ratio (circle with a cross in the middle) and estimated the comparatively large error. Although these early measurements are three orders of magnitude lower than the actual Wölk and Strey data, they show the same temperature dependence.

Four other data sets also cover the same temperature range as the nucleation pulse chamber. Already in 1977, Dobbins *et al.*⁶ measured comparable nucleation rates of $J \sim 10^7$ cm⁻³s⁻¹ using a much simpler expansion chamber, and their data (hexagons in Fig. 2) show remarkable agreement with the more extensive nucleation pulse chamber results. The data of Peters and Paikert²³ (diamonds with a cross in the middle) are measured in a shock tube where $10^7 < J/\text{cm}^{-3}\text{s}^{-1} < 10^9$. The authors only reported onset pressures and temperatures, so we used an experimental nucleation rate of $J = 10^8$ cm⁻³s⁻¹ and included the error bars for ± 1 order of magnitude. The squares are the data of Luijten *et al.*^{20,21} measured with a pulse-expansion wave tube. For 230 K ($1/T = 4.35 \times 10^{-3}$ 1/K) and 250 K ($1/T = 4.00 \times 10^{-3}$ 1/K) their results are consistent with the others. Only the measurements at 240 K ($1/T = 4.17 \times 10^{-3}$ 1/K), where helium is the carrier gas, deviate significantly. We note that Viisanen *et al.*'s³ measurements in the nucleation pulse chamber found that the water nucleation rate is insensitive to the nature of the carrier gas. Finally, the data of Miller *et al.*^{10,11} (upward-facing triangles) were measured using a larger expansion chamber and their nucleation rates are 3–4 orders of magnitude lower than the nucleation pulse chamber results. The data of Peters and Paikert and Miller *et al.* both have a somewhat stronger temperature dependence, but again the agreement with the correlation is quite reasonable. Furthermore, both data sets confirm that classical theory does an excellent job of predicting the nucleation rate when $T = 240$ K.

Figure 2 also incorporates the onset measurements for condensation of H₂O in a supersonic nozzle.^{35,36} Modeling shows that the peak nucleation rates found in the gently diverging Laval nozzles for either isotope of water are close to 10^{17} cm⁻³s⁻¹, and that the peak rates occur close to the onset of condensation. We therefore picked 10 points from the supersaturation–temperature correlation for the onset of H₂O condensation presented by Heath and set

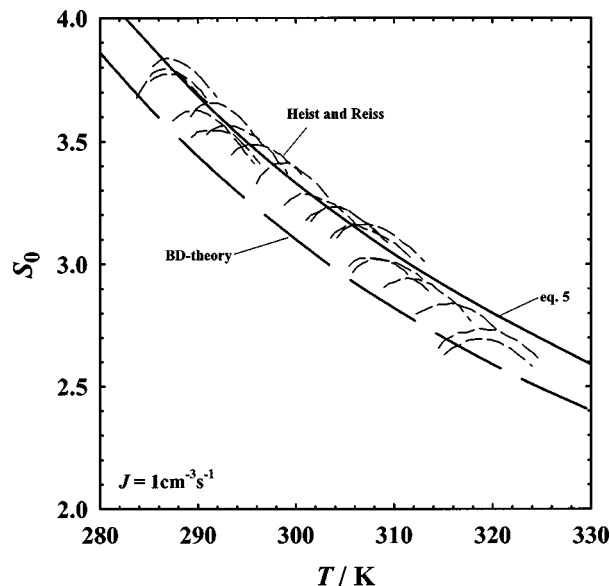


FIG. 3. The empirical correlation predicts the critical supersaturation data measured in the expansion cloud chamber by Heist and Reiss (Ref. 2) to within 2%. In contrast, the values predicted by the Becker–Döring equation are about 8% below the measured values.

$J = 10^{17}$ cm⁻³s⁻¹. These are the downward-facing triangles in Fig. 2. Again, most of the data lie closer to the line described by Eq. (5) than to the predictions of classical theory.

Finally, the diamonds correspond to the water nucleation data of Heist and Reiss.² From their variation of the critical supersaturation of water vapor at an experimental nucleation rate of $J = 1$ cm⁻³s⁻¹ (Fig. 3 in Ref. 2), we read off the maximum experimental supersaturation and the corresponding temperature and then calculated the theoretical nucleation rates. The scatter in these data (diamonds) is due in part to the difficulty in determining S and T from their figure, as well as to the fact that the experimental nucleation rate was probably not always exactly 1 cm⁻³s⁻¹. Given that their nucleation rates are 6 to 8 orders of magnitude lower and the temperatures are 20–50 K higher than those in the nucleation pulse chamber, the agreement with the regression line is rather good.

To demonstrate the improvement afforded by using the new correlation, Fig. 3 illustrates the diffusion cloud chamber data as originally reported by Heist and Reiss.²

The thin dashed lines are the supersaturation–temperature curves that correspond to the individual experiments and a nucleation rate of $J = 1$ cm⁻³s⁻¹. The envelope of these curves represents the measured temperature dependence of the critical supersaturation. The lower dashed line is the critical supersaturation predicted using the classical nucleation theory [Eq. (1)] assuming $J = 1$ cm⁻³s⁻¹, while the upper solid line is that predicted including the correction function. Obviously Eq. (5) provides a substantial improvement over the classical theory.

Wölk and Strey also derived the temperature-dependent correction function for D₂O¹ and that the empirical nucleation rate equation for D₂O is given by

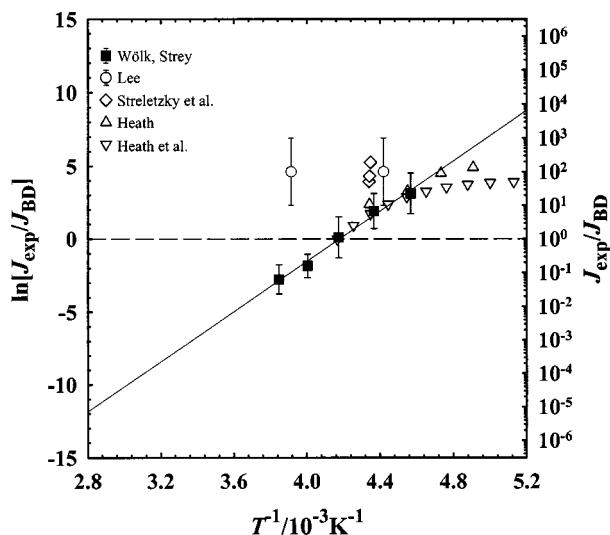


FIG. 4. The normalized data for D₂O, although sparser, also show a linear dependence on $1/T$ (Refs. 1, 35, 36, 38, 39).

$$J_{\text{D}_2\text{O}} = J_{\text{BD}} \exp\left(-35.98 + \frac{8.6 \times 10^3}{T}\right). \quad (6)$$

As illustrated in Fig. 4, far fewer data are available for D₂O than for H₂O.

The earliest data are those of Flood and Tronstad,³⁷ who measured critical onsets in an expansion cloud chamber. Without reasonable estimates for the nucleation rate we cannot incorporate their data into Fig. 4. In 1977, Lee³⁸ reported onset data for D₂O condensation in a shock tube and stated that no match onset with a model incorporating nucleation and growth, he had to adjust the classical nucleation rate upward by 1–3 orders of magnitude. Since individual values of the adjustment factor $\Gamma = J_{\text{exp}}/J_{\text{BD}}$ are not reported, we used $\Gamma = 2$ and included error bars of ± 1 order of magnitude. The two data points shown (open circles) span the range of temperatures for this experiment and, although not in quantitative agreement, they illustrate the qualitative information that can be obtained from these early experiments.

Nucleation rate measurements and modeling estimates are also starting to become available for D₂O from supersonic nozzle experiments. Streletzky *et al.*³⁹ (diamonds) measured nucleation rates near $T = 230$ K in a shaped supersonic nozzle that decouples nucleation from droplet growth. Because nucleation in the shaped nozzle is controlled by the wall profile, these rates are lower than the peak rates found in a conventional nozzle. Heath³⁵ derived peak nucleation rates (upward-facing triangles) as a function of supersaturation and temperature by modeling condensation in a conventional nozzle. Finally, we treated the D₂O onset data of Heath^{35,36} in the same way as the H₂O data in Fig. 2, and these are given by the downward-facing triangles in Fig. 4. In the region of overlapping temperature the conventional nozzle results are in excellent agreement with the Wölk and Strey data, and even the shaped nozzle results are reasonable.

In Fig. 5 we test the low temperature limit of Eqs. (5) and (6) more directly, by comparing the critical supersatura-

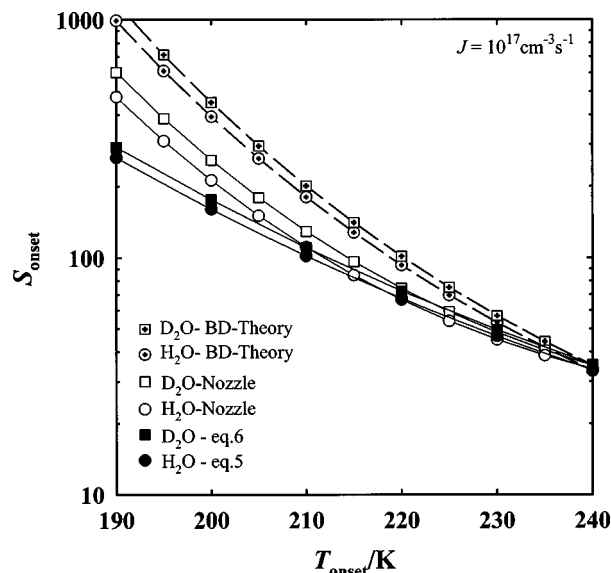


FIG. 5. The critical supersaturations predicted by the Becker–Döring equation for the onset of condensation in a supersonic nozzle for H₂O and D₂O deviate rapidly from the measurements of Heath *et al.* (Refs. 35, 36) as T decreases. The agreement between the data and the predictions of the empirical correlations is rather good down to about 210 K. Possible reasons for the deviations observed at lower temperatures are discussed in the text.

tion curves for the onset of H₂O and D₂O condensation in a conventional supersonic nozzle to those predicted by classical theory and the empirical functions.

As expected, near 240 K the data, the predictions of classical theory, and those of Eqs. (5) and (6) all coincide. As the temperature decreases, the critical supersaturations predicted by classical theory deviate rapidly from the measurements. In contrast, the predictions of the empirical functions do quite well down to about 210 or 215 K. As temperature decreases further, classical nucleation theory predicts that the critical nucleus contains fewer than 5 molecules. Thus, the assumptions inherent in the classical theory become systematically worse, and even the improved equations underestimate the onset supersaturation or, equivalently, overestimate the nucleation rates. These trends will be examined further in a forthcoming paper.⁴⁰

Finally, we compare the available nucleation rate data for D₂O directly in Fig. 6. The open squares are the measured nucleation rates for D₂O from Wölk and Strey (NPC)¹ and the solid lines are the nucleation rates calculated with the empirical correlation. Again, the agreement is within experimental error. In addition, this plot contains the very recent results of supersonic nozzle experiments [full squares—Heath (SN),^{35,36} squares with a cross in the middle—Streletzky *et al.* (SSN)].³⁹ Again, the conventional nozzle results are inferred from modeling the pressure profile measurements, while the shaped nozzle results are deduced from analyzing pressure trace data and measuring the number density of the aerosol using small angle neutron scattering (SANS). Because the experimental temperatures from the nozzle experiments are lower ($200 < T/K < 230$) than the nucleation pulse chamber data ($220 < T/K < 260$), while both the nucleation rates (nozzle: $10^{15} < J/\text{cm}^{-3} \text{s}^{-1} < 10^{18}$; nucleation pulse chamber: $10^5 < J/\text{cm}^{-3} \text{s}^{-1} < 10^{10}$) and supersatura-

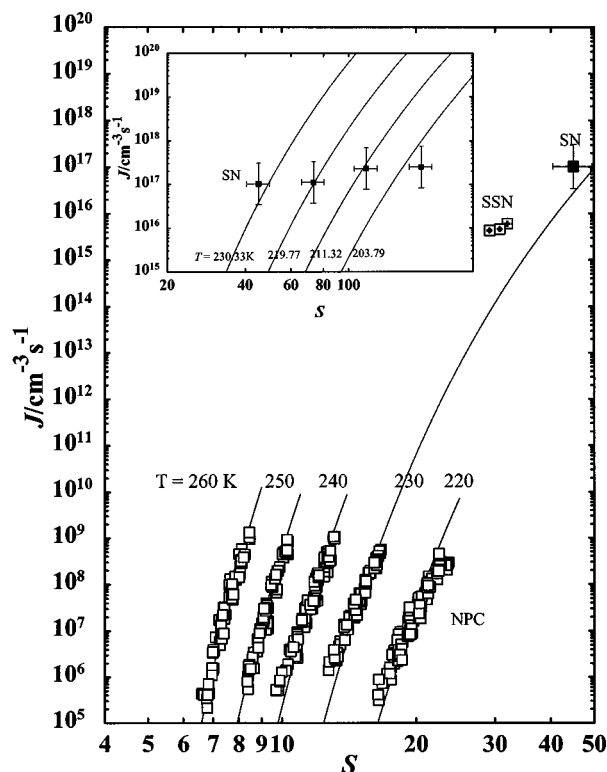


FIG. 6. The isothermal nucleation rate data for D_2O of Wölk and Strey (NPC) (Ref. 1) are in excellent agreement with the empirical correlations for this substance, Eq. (6). The ability of this correlation to predict nucleation rates up to 8 orders of magnitude higher (SN) (Refs. 35, 36) (SNN) (Ref. 39), at significantly higher supersaturations and lower temperatures is very encouraging.

rations (nozzle: $30 < S < 200$; nucleation pulse chamber: $5 < S < 30$) are much higher, a direct comparison is difficult. The empirical correlation makes it possible to calculate nucleation rates for the whole experimental range and connect the experimental results. As illustrated in Fig. 6 there is remarkably good agreement between the D_2O nozzle experiments and the nucleation rates measured with the nucleation pulse chamber. Only as the temperature drops below 210 K does Eq. (6) begin to fail.

IV. FURTHER DISCUSSION

The deviations between experimental measurements and classical nucleation theory are not a special property of water. Rather similar deviations have been seen for alcohols^{32,33} and n-nonane.⁴¹ Recently, Uchtmann *et al.*⁴² showed that for diffusion cloud chamber data, S_{BD}/S_{exp} appears to be a universal function of ΔT for a wide range of substances, including exotic substances like sulphur and cesium. Here, ΔT is the difference between the experimental temperature and that temperature at which classical theory and experiment agree completely. In Fig. 7 we present their data (open symbols and crosses) together with the predictions of our H_2O correlation in the temperature range of the nucleation pulse chamber (filled circles).

The general observation is that theory overestimates the supersaturation when $\Delta T < 0$ and underestimates the supersaturation when $\Delta T > 0$. When $-20 < \Delta T/K < 20$, we find

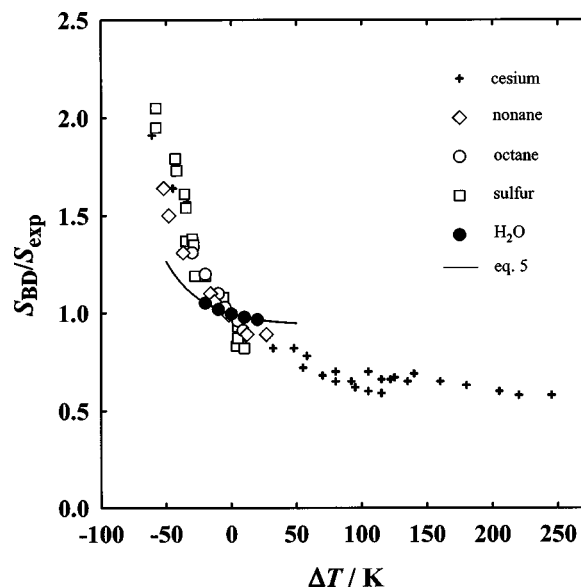


FIG. 7. The temperature dependence of the supersaturation at constant nucleation rate follows a consistent trend once both have been normalized to the values where classical theory and experiment agree exactly. The open symbols measured by Uchtmann *et al.* (Ref. 42) are in qualitative agreement with the results for water (filled circles) measured by Wölk and Strey (NPC) (Ref. 1).

quantitative agreement between H_2O and the nonpolar substances measured by Uchtmann *et al.* Extending the calculation to a wider temperature range (line) shows a growing deviation between the data sets, although the overall trend is similar. The demonstration in Fig. 7 that such different substances exhibit the same qualitative behavior reinforces the fact that there are flaws in classical nucleation theory. In light of the simplistic assumptions inherent in the approach, it is tempting to ask, aren't there other theories that describe nucleation more accurately? At present the answer is no. Up to now all theoretical approaches that have an improved temperature dependence still differ from the experimental nucleation rates by many orders of magnitude¹ or contain molecular quantities that make them less suited for practical use. Examples for such modifications are the self-consistent approach by Reiss, Kegel, and Katz,⁴³ the density functional approach by Oxtoby,⁴⁴ and the gradient approach by Granasy.⁴⁵

Density functional theory calculations, however, shed light on the origin of the general flaw discussed above. From density functional theory (DFT) calculations on Lennard-Jones fluids, Zeng and Oxtoby⁴⁶ found that classical nucleation theory correctly predicts the supersaturation dependence, an observation strongly supported by Figs. 1 and 6. Furthermore, these authors found that the classical rate goes from being orders of magnitude too low at low temperatures to being too high at high temperatures. Again, this is the trend we observe experimentally (cf. Fig. 1). In a recent review article, Oxtoby⁴⁷ explained the physical reason behind the observed deficiencies of the classical theory in terms of two mutually compensating effects:

Two physical features of nucleation are omitted by classical theory: the surface free energy of a small nucleus

should depend on curvature, and the nucleation barrier should vanish at the spinodal (the point where the vapor phase becomes thermodynamically unstable). The first feature should lower the nucleation rate relative to the classical prediction (see explanation (A) below), while the second should increase it (B). The two errors accidentally cancel at some temperature (often within the experimentally accessible region) but together give rise to the systematically incorrect temperature dependence of classical theory.

According to Oxtoby,⁴⁸ one should remove the word “surface” from the first sentence in the paragraph cited above⁴⁷ in order to understand the experimentally observed difference from classical theory.

In classical nucleation theory, the free energy is written as the sum of a bulk term and a surface term. In DFT, this separation does not exist (there is no separation of a “bulk” from a “surface” term), and only a single critical nucleus free energy is calculated. If, however, one wants to modify the classical theory, and one assumes that the bulk term is curvature independent, the surface free energy is the only quantity that depends on the radius. Furthermore, if the experimentally determined nucleation rates are lower than those predicted by classical theory, then the experimental free energy is higher than that given by classical theory. To correct the classical predictions, the surface tension would have to be increased over the planar surface tension. This is the case at high T and larger nuclei, and is the first flaw in classical theory (marked by (A) in the citation above).

As conjectured by Oxtoby,⁴⁸ even for reasonably large clusters, a molecule near the surface of the cluster does not feel attractive forces from a full half-plane of other molecules (as it would at a planar interface) but from a reduced number because of the local curvature. This effect reduces the magnitude of the negative (attractive) contribution to the cluster free energy and thus raises the total free energy of the nucleus. If this effect is attributed to and taken care of by adjusting the surface free energy, an increased surface free energy results. Thus, the resulting form for the dependence of surface free energy on radius (fitting the classical model to a more accurate theory or to experiments) is for it to begin by increasing from the planar value as the droplet shrinks (due to the curvature effect).

At the other extreme of very deep quenches into the two-phase region, a second inadequacy of the classical theory (point B above) is that it does not recognize the presence of a spinodal, where the nucleation barrier vanishes. If one wants to include this vanishing into a corrected classical model, it is necessary to make the surface tension to go to zero at sufficiently large undercoolings. Inevitably, in approaching the spinodal the classical theory will predict nucleation barriers that are too high and, correspondingly, nucleation rates that are too low. This is the situation that is usually observed experimentally (and also correctly predicted by DFT) in the low temperature region.

The scenario for the curvature dependence of the surface tension that would make classical theory work is that the surface tension starts out with the planar value, increases with decreasing size, reaches a maximum, and then approaches zero at very small clusters (due to the spinodal

effect). As the critical cluster size changes, the surface tension must, therefore, reach the planar value at some intermediate size (temperature and supersaturation) and, at this point, classical nucleation theory will coincidentally work. Where this crossover takes place depends on temperature in a way that cannot be predicted *a priori*, but for water it is close to 240 K.

Thus, the experimental results of Wölk and Strey¹ suggest that the spinodal effect dominates at low temperatures and the curvature effect at high, and that density functional theory makes the qualitatively correct prediction. Finally, we note that the right-hand side of Eq. (4) (or the bracket in Eqs. (5) and (6)) corresponds to the $D(T)$ function envisioned by McGraw and Laaksonen,³⁴ and, thus, experimentally the functional form is given by

$$D(T) = A + B/T. \quad (7)$$

V. CONCLUSIONS

The observed empirical correlations have several important consequences. First, if one assumes that the prefactor K of the classical nucleation theory is essentially correct, the correction function quantifies how much the work of formation of the nucleus needs to be revised as a function of temperature. Second, because supersaturation dependence of the rates, i.e., the slope of the experimental nucleation rate curve and the prediction by classical nucleation theory are essentially the same, an extrapolation of the correction function to high nucleation rates as observed in supersonic nozzles is possible. The quantitative agreement between the nucleation pulse chamber and supersonic nozzle results supports this. Finally, the applicability of our correction function to data far outside the actual measuring range suggests that the empirical correction function to the classical nucleation theory may safely be used to calculate homogeneous nucleation rates over extended ranges of J , S , and T . This is a feature of interest to many natural and industrial processes.

ACKNOWLEDGMENTS

The authors thank Professor D. Oxtoby for illuminating discussions. This work was supported by grants from the National Science Foundation (CHE-0097896 and INT-0089897) and the DAAD.

¹J. Wölk and R. Strey, *J. Phys. Chem.* **105**, 11683 (2001).

²R. Heist and H. Reiss, *J. Chem. Phys.* **59**, 865 (1973).

³Y. Viisanen, R. Strey, and H. Reiss, *J. Chem. Phys.* **99**, 4680 (1993).

⁴J. L. Katz and B. J. Ostermier, *J. Chem. Phys.* **47**, 478 (1967).

⁵E. F. Allard and J. L. Kassner, Jr., *J. Chem. Phys.* **42**, 1401 (1965).

⁶R. A. Dobbins, T. I. Eklund, and R. Tjoa, “The direct measurement of the nucleation rate constants,” in *Condensation in High Speed Flows*, edited by A. A. Pouring (ASME, Am. Soc. Mech. Eng. NY, New York, 1977), pp. 43–58.

⁷M. Volmer and H. Flood, *Z. Phys. Chem. Abt. A* **190**, 273 (1934).

⁸A. Sander and G. Damköhler, *Naturwissenschaften* **31**, 460 (1943).

⁹P. Wegener and G. Lundquist, *J. Appl. Phys.* **22**, 233 (1951).

¹⁰R. Miller, Ph.D. thesis, University of Rola, Missouri (1976).

¹¹R. Miller, R. J. Anderson, J. L. Kassner, Jr., and D. E. Hagen, *J. Chem. Phys.* **78**, 3204 (1983).

¹²P. E. Wagner and R. Strey, *J. Phys. Chem.* **85**, 2694 (1981).

¹³R. Becker and W. Döring, *Ann. Phys. (Leipzig)* **24**, 719 (1935).

- ¹⁴M. Volmer, *Kinetik der Phasenbildung* (Theodor Steinkopf, Dresden and Leipzig, 1939).
- ¹⁵W. G. Courtney, *J. Chem. Phys.* **35**, 2249 (1961).
- ¹⁶L. Gránásy, *J. Phys. Chem.* **100**, 10768 (1996).
- ¹⁷S. M. Kathmann, G. K. Schenter, and B. C. Garrett, *J. Chem. Phys.* **116**, 5046 (2002).
- ¹⁸C. R. T. Wilson, *Philos. Trans. R. Soc. London, Ser. A* **189**, 265 (1897).
- ¹⁹Y. Viisanen, R. Strey, and H. Reiss, *J. Chem. Phys.* **112**, 8205 (2000).
- ²⁰C. C. M. Luijten, K. J. Bosschaart, and M. E. H. van Dongen, *J. Chem. Phys.* **106**, 8116 (1997).
- ²¹C. C. M. Luijten, "Nucleation of Droplet Growth at High Pressure," Ph.D. thesis, Eindhoven (1998).
- ²²F. Peters, *J. Phys. Chem.* **91**, 2487 (1987).
- ²³F. Peters and B. Paikert, *Exp. Fluids* **7**, 521 (1989).
- ²⁴P. P. Wegener, *J. Appl. Phys.* **25**, 1485 (1954).
- ²⁵P. P. Wegener and A. A. Pouring, *Phys. Fluids* **7**, 352 (1964).
- ²⁶G. D. Stein and C. A. Moses, *J. Colloid Interface Sci.* **39**, 504 (1972).
- ²⁷D. Barschdorff, *Phys. Fluids* **18**, 529 (1975).
- ²⁸C. A. Moses and G. D. Stein, *J. Fluids Eng.* **100**, 311 (1978).
- ²⁹B. E. Wyslouzil, C. H. Heath, G. Wilemski, and J. L. Cheung, *J. Chem. Phys.* **113**, 7317 (2000).
- ³⁰R. H. Heist and H. He, *J. Phys. Chem. Ref. Data* **23**, 781 (1994).
- ³¹G. M. Pound, *J. Phys. Chem. Ref. Data* **1**, 119 (1972).
- ³²A. Kacker and R. H. Heist, *J. Chem. Phys.* **82**, 2734 (1985).
- ³³R. Strey, P. E. Wagner, and T. Schmeling, *J. Chem. Phys.* **84**, 2325 (1986).
- ³⁴R. McGraw and A. Laaksonen, *Phys. Rev. Lett.* **76**, 2754 (1996).
- ³⁵C. H. Heath, "Binary Condensation in a Supersonic Nozzle," Ph.D. thesis, Worcester (2001).
- ³⁶C. H. Heath, K. A. Streletzky, B. E. Wyslouzil, J. Wölk, and R. Strey, *J. Chem. Phys.* (to be published).
- ³⁷H. Flood and L. Tronstad, *Z. Phys. Chem. Abt. A* **175**, 347 (1936).
- ³⁸C. F. Lee, "Condensation of H₂O and D₂O in Argon in the Centered Expansion Wave in Shock Tube," in *Condensation in High Speed Flows*, edited by A. A. Pouring (ASME, Am. Soc. Mech. Eng. NY, New York, 1977), pp. 83–96.
- ³⁹K. A. Streletzky, Y. Zvinevich, B. E. Wyslouzil, and R. Strey, *J. Chem. Phys.* **116**, 4058 (2002).
- ⁴⁰A. Khan, Master thesis, Worcester Polytechnic Institute, 2001; and to be published.
- ⁴¹C.-H. Hung, M. J. Krasnopoler, and J. Katz, *J. Chem. Phys.* **90**, 1856 (1989).
- ⁴²H. Uchtmann, S. Yu. Kazitsyna, F. Hensel, V. Zdimal, B. Triska, and J. Smolik, *J. Phys. Chem.* **105**, 11754 (2001).
- ⁴³H. Reiss, W. K. Kegel, and J. L. Katz, *Phys. Rev. Lett.* **78**, 4506 (1997).
- ⁴⁴D. W. Oxtoby, *J. Phys.: Condens. Matter* **4**, 7627 (1992).
- ⁴⁵L. Gránásy, *J. Chem. Phys.* **104**, 5188 (1996).
- ⁴⁶X. C. Zeng and D. W. Oxtoby, *J. Chem. Phys.* **94**, 4472 (1991).
- ⁴⁷D. W. Oxtoby, *Acc. Chem. Res.* **31**, 91 (1998).
- ⁴⁸D. W. Oxtoby, private communication (2002).