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Testing the Limits of the Cryogenic Nucleation Pulse Chamber

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CRYOGENIC NUCLEATION PULSE CHAMBER



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Chapter 1

Introduction

1.1 Nucleation phenomena

Aerosol formation is an important process in both nature and technology. It affects the formation of clouds as well as the functionality of plane turbines and the production of nanomaterials. It is therefore of great interest to develop a more thorough understanding of how aerosols are formed. Aerosols are formed in three stages: formation, growth, and aging.

Formation of aerosols, or nucleation, occurs as the initial step in first-order phase transitions. Through rapid change of external conditions such as pressure or temperature, the previously stable phase becomes metastable. If the phase transition is hindered due to a high activation energy or the properties of the new phase, the metastable phase can continue to exist for a significant amount of time. Within that metastable phase, small clusters of the new, stable, phase will be formed and grow until the phase transition is complete. These small clusters are called nuclei, and the process of their formation in a first-order phase transition is called nucleation.

One has to distinguish between two different types of nucleation, the heterogeneous and the homogeneous nucleation. In heterogeneous nucleation, a foreign seed particle is present in the system, which significantly reduces the kinetic inhibition by supplying a surface on which nucleation can take place and allowing for a much faster growth of new phase clusters. In homogeneous nucleation, no such seed particle is present, the clusters of the new phase form solely through random density fluctuations within the vapor phase, which makes it a slower process. Almost all naturally occurring nucleation phenomena are heterogeneous processes, such as the

formation of clouds through condensation of water onto atmospheric aerosol particles. Fig. 1.1 shows the growth rate of a droplet over time. At first, the clusters are

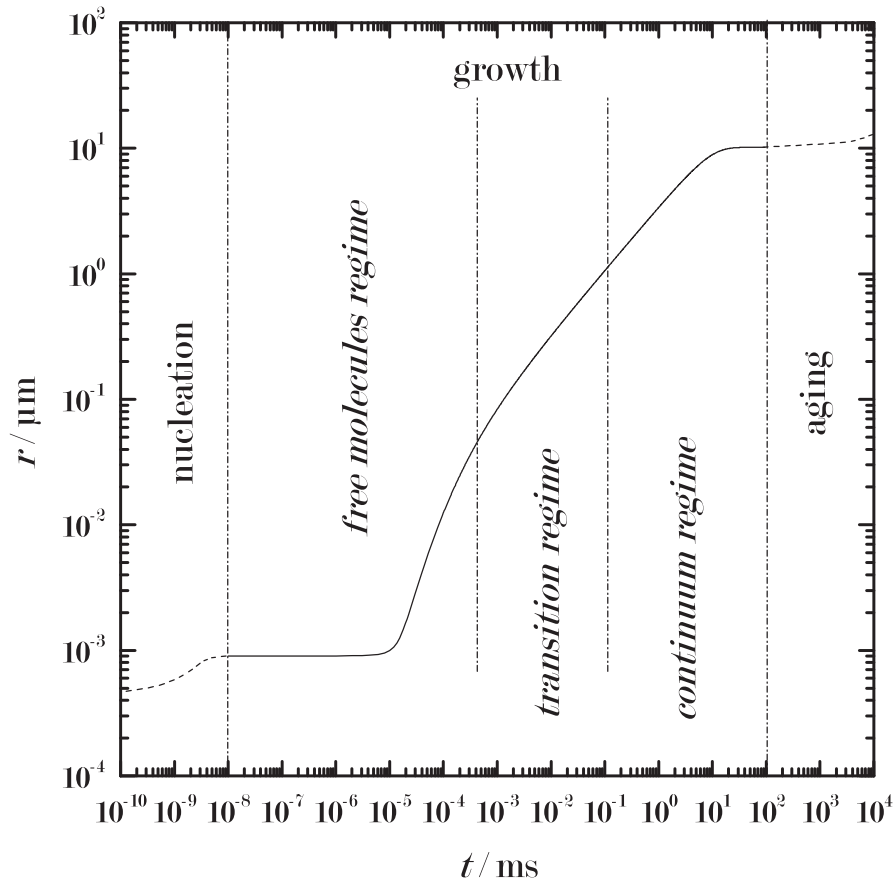


Figure 1.1: Particle radius as a function of time with the different growth regimes highlighted. Redrawn from [1].

so small (less than 20 nm diameter) that they can be treated as gas molecules, and their growth is determined by the kinetics of the gas phase (free molecule regime). From a diameter of about 400 nm, the growth becomes determined solely by the diffusion of vapor onto the droplet (continuum regime). For droplet sizes between those two extremes, the growth rate is determined by a combination of both factors, with the diffusion-controlled contribution becoming more important as the cluster grows (transition regime). The growth process is completed when the vapor pressure of the condensable gas becomes equal to the equilibrium vapor pressure. After the growth process is complete, aging processes such as Ostwald ripening and coagulation occur.



1.2 Literature overview

Homogeneous nucleation has been studied extensively in both experiments [2–10] and theoretical models [11–17] to understand the basic first step before going on to study the more complex heterogeneous nucleation process.

Over the years, a variety of experimental apparatuses have been used to measure vapor-liquid nucleation rates J , which are defined as the number of particles formed per unit of time and volume [18]. Nucleation is induced by creating a supersaturated vapor phase through various means. The supersaturation S is defined as the ratio of the actual vapor pressure inside the system to the equilibrium vapor pressure of the same substance under identical conditions. The first such apparatus was the cloud chamber built by *Wilson* [19] in 1897. Other methods include supersonic nozzles [20], wave tubes [21] or nucleation pulse chambers [2, 22], in which a gas is expanded very quickly, diffusion cloud chambers [23], in which the required supersaturation is achieved by keeping the gas between two metal plates at different temperatures, and laminar flow diffusion chambers [24] in which a gas mixture flows from a warm reservoir into a cooler section of a pipe.

Nucleation rates can only be measured when the nucleation and growth stages can be separated from each other. This is achieved by different means in the various experimental setups. For example, the nucleation pulse chamber creates a short pressure pulse after which the gas phase is recompressed so that the supersaturation drops below the critical level again. Nucleation and growth can be decoupled when the pulse length is short compared to the time it takes the nuclei to grow.

Each experimental setup can only measure nucleation rates within a narrow range of 3-4 orders of magnitude, limited by the accuracy of the detection system and the supersaturations which can be achieved in it. Overall, nucleation rates from $J = 10^{-3} \text{ cm}^{-3} \text{ s}^{-1}$ to $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$ are accessible in experimental studies. Fig. 1.2 shows the nucleation rate ranges which can be achieved in the various experimental setups. The nucleation pulse chamber, which will be used in this work, can measure nucleation rates from $J = 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ to $10^9 \text{ cm}^{-3} \text{ s}^{-1}$.

In addition to the experimental results, various theories of nucleation were developed. The first such theory is the classical nucleation theory (CNT) developed by *Becker* and *Döring* [15], based on thermodynamic observations by *Gibbs* [26] and previous works by *Vollmer* and *Weber* [18, 27] and by *Farkas* [28]. CNT treats nuclei as small, incompressible spherical objects with the properties of the macroscopic

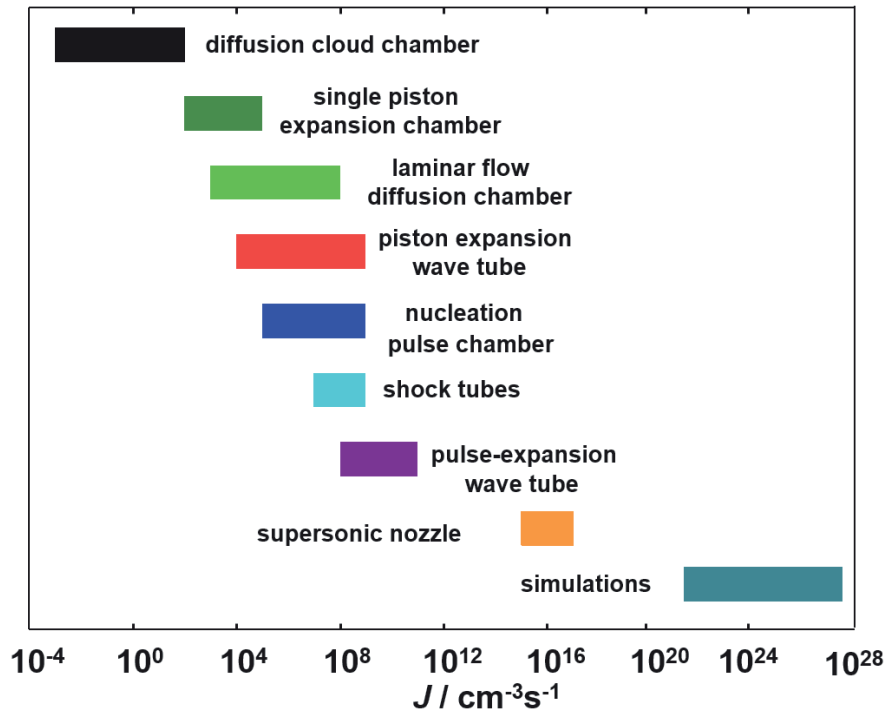


Figure 1.2: Overview over the nucleation rate ranges which can be measured in the different experimental setups. Redrawn from [25].

phase (capillarity approximation. Since then, various additions have been made to CNT, most notable those of *Girshick* and *Chiu* [16] and of *Reiss, Kegel* and *Katz* [17]. More recent theories include the Extended Modified Liquid Drop-Dynamic Nucleation Theory (EMLD-DNT) [11,12] and the Mean-Field Kinetic Nucleation Theory (MKNT) [14].

The density functional theory developed by *Oxtoby* and *Evans* [29], based on earlier works by *Cahn* and *Hilliard* [30], describes the thermodynamic potential as a functional of the inhomogeneous density distribution along the radius of the cluster. In this theory, the barrier to nucleation disappears when the spinodal is reached, while CNT predicts a finite barrier to nucleation even at the spinodal, which is physically inconsistent.

A trend that all substances have in common is that the classical nucleation theory predicts a stronger temperature dependence of nucleation rates than can be found in experimental results. To correct for the incorrect temperature trend, empirical correction functions such as the ones by *Wölk et al.* for water and D_2O can be used [31].



The third aspect of nucleation research are computer simulations. By using Monte-Carlo [32–34] (MC) or molecular dynamics (MD) simulations, the dynamics of nucleation can be observed, which is not possible in any of the experimental apparatuses used to measure nucleation rates since the particles involved have diameters of a few nanometers at most. However, since both methods are based on interactions between molecules, such simulations are only possible for molecules with well-known interaction potentials. For noble gases and nitrogen Lennard-Jones potentials can be used to describe the interactions between particles [35], an approach that fails for more complicated molecules such as water and the alcohols. This is unfortunate, since these substances are well-suited for experimental investigations, which are more complicated with argon and nitrogen.

The first attempts to qualitatively measure the growth of droplets dates to *Owe Berg* and *George* [36] in 1968, who used a high-speed camera to measure droplet growth in a cloud expansion chamber. In 1969 *Cohen* [37] developed an experimental setup which formed the basis of many future droplet growth experiments. He used light scattering at an observation angle of 90° to detect the droplets and was able to measure growth dependent scattering curves in a cloud diffusion chamber. The first quantitative measurement of droplet growth was carried out by *Vietti* and *Schuster* in 1973 [38, 39] in an expansion cloud chamber built by *Allard* and *Kassner* [40]. They correlated the experimental light scattering curves, which show the intensity as a function of time, with a calculated scattering curve of intensity as a function of radius. The theory which describes the scattering of light by spherical particles was published by *Mie* in 1908 [41]. In 1974, *Wagner* [42] published growth rates of latex droplets for various particle numbers, supersaturations and observation angles, and found only small deviations between the experimental and theoretical curves. *Fladerer* measured growth rates of water clusters in 1998 [1] and argon in 2002 [43]. He also found good agreement between the experimental growth rates and the growth theory, in this case the growth theory by *Fuchs* and *Sutugin* [44, 45].

Additional growth rate measurements have been carried out on atmospheric aerosols. In atmospheric measurements, the systems are far more complex, containing multiple substances and particles that become partially or fully oxidized as they grow. Those measurements are carried out both at external locations of interest [46, 47], and in controlled laboratory environments like the CLOUD experiment at CERN [48] or the plant atmosphere chamber in Jülich [49].

The first theoretical description of droplet growth was published by *Maxwell* [50] in 1877, describing the mass and heat flow to and from an individual droplet. Various other theoretical descriptions of droplet growth have been developed since then. A summary of the available literature was published by *Fuchs* in 1959 [51], and another by *Wagner* in 1982 [52]. *Vesala et al.* [53] published a summary of the theories on binary growth in 1997.

1.3 Overview of available data

1.3.1 Water

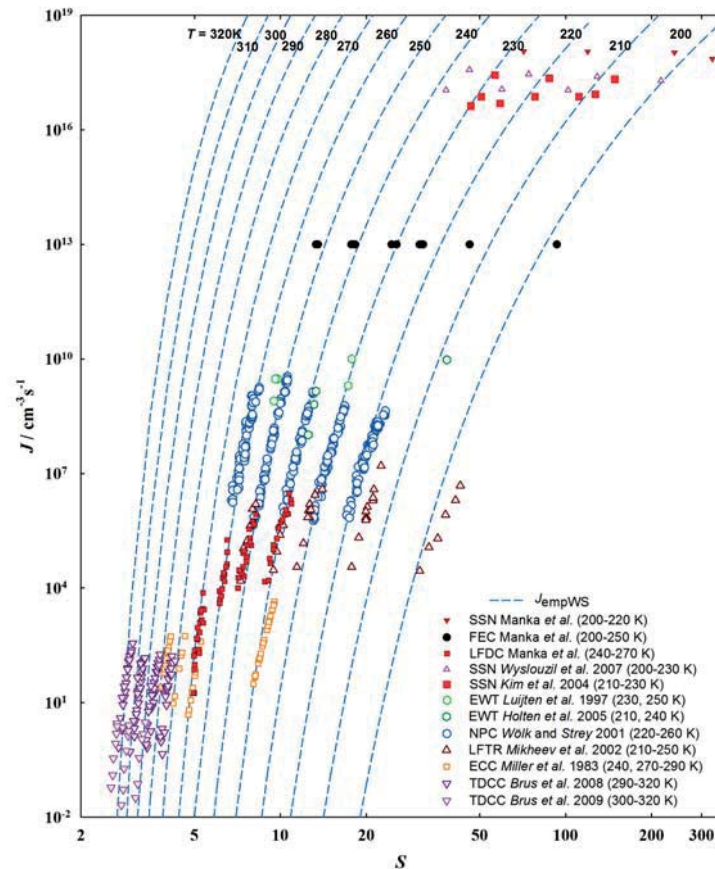


Figure 1.3: Nucleation rates of water measured in various experiments [54–65] compared with the empirical correction function by *Wolk* and *Strey*. Slightly modified from [54].

For water, a huge amount of literature data is available, both onsets and nucleation rates. The most interesting data set for this work is that measured by *Wolk* and *Strey* [55] in the room temperature nucleation pulse chamber. The design of the



cryogenic nucleation pulse chamber is based on the room temperature nucleation pulse chamber, and it is expected to produce nucleation rates in the same range. The nucleation rates by *Wölk* and *Strey* were found to show very good agreement with the classical nucleation theory, with complete agreement between experiment and theory at 240 K, and an incorrect temperature dependence at the other temperatures. An empirical correction function was fitted to the data to correct for the too strong temperature dependence, and the correction function was able to describe nucleation rates from other experiments over a wide range of nucleation rates, as shown in Fig. 1.3. Most of the available literature nucleation rates lie on, or close to, the nucleation rate modified with the empirical correction function.

1.3.2 Argon

A major problem in measuring the nucleation rates of argon clusters is that the growth of the clusters is extremely fast, so it is currently not possible to separate the nucleation and growth stages. However, it is still possible to determine the onset of nucleation, the point at which the first clusters of the liquid phase appear within the system.

Several groups have measured nucleation onsets of argon in various experimental setups. There is also one set of simulated nucleation rates by *Wedekind* [73]. The results by *Wu et al* [67] and *Sinha et al* [69], both measured in supersonic nozzles, lie at lower temperatures for a given pressure than the data from the nucleation pulse chamber. This is to be expected, since supersonic nozzles can push the system further into the metastable region. *Stein's* results [68], also measured in a supersonic nozzle, lie at higher temperatures and do not agree with the other supersonic nozzle results, which indicates heterogeneous contamination in *Stein's* data. The results by *Matthew* and *Steinwandel* [72] and the lower-pressure results of *Zahoransky et al* from 1995 [71] lie close to the binodal, which indicates heterogeneous contamination. At higher pressures, the 1995 results by *Zahoransky et al* as well as those from 1999 [70] agree well with the nucleation pulse chamber data, which is consistent with expectations, since *Zahoransky et al's* results were measured in a shock tube, which has similar nucleation rates to the nucleation pulse chamber. The simulated nucleation rates by *Wedekind* [73] lie at even higher nucleation rates than the data from the supersonic nozzle, therefore their position at even lower pressure for a fixed temperature is also consistent with expectations.

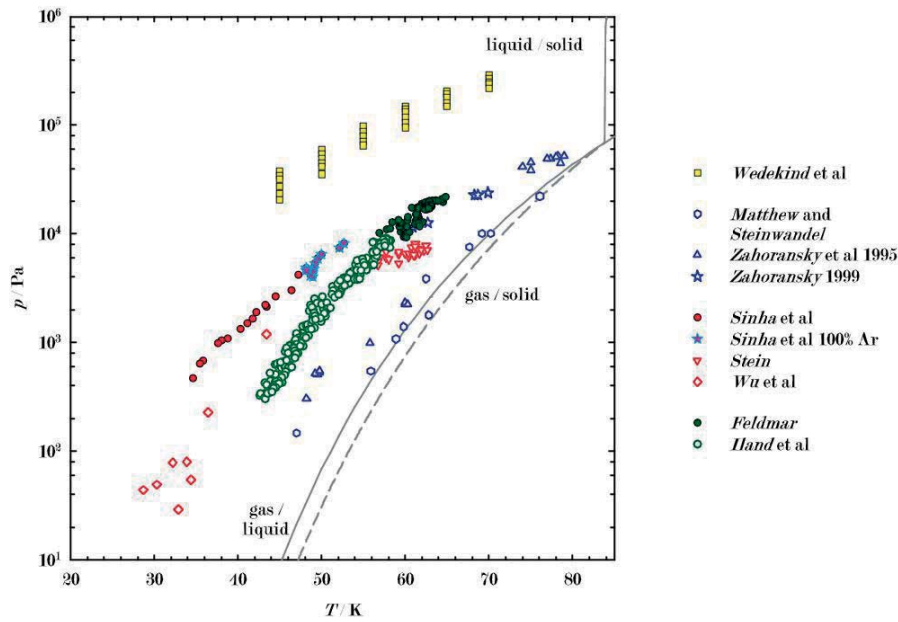


Figure 1.4: Overview of the available nucleation onset data for argon. The dashed line is the gaseous-solid boundary; the solid lines are the liquid-solid boundary and the gaseous-liquid boundary, extrapolated past the triple point. open and filled green circles are results from the cryogenic nucleation pulse chamber by *Iland et al* [2] and *Feldmar* [66], diamonds are results by *Wu et al* [67], inverted triangles by *Stein* [68], red circles are by *Sinha et al* [69], red stars with blue borders are also results by *Sinha et al*, but measured with pure argon without a carrier gas. Blue stars are results by *Zahoransky* in 1999 [70], blue triangles are by *Zahoransky* in 1995 [71], blue open circles are results by *Matthew and Steinwandel* [72]. Yellow Squares are simulated nucleation rates by *Wedekind* [73].

1.3.3 Nucleation onsets of nitrogen

A major problem in measuring the nucleation rates of nitrogen clusters is that the growth of the clusters is extremely fast, so it is currently not possible to separate the nucleation and growth stages. However, it is still possible to determine the onset of nucleation, the point at which the first clusters of the liquid phase appear within the system. Fig.1.5 shows the currently available nitrogen onset results. The results from the supersonic nozzle lie at lower temperatures and pressures than the data from the nucleation pulse chamber and the shock tubes. This is to be expected, since supersonic nozzles can push the system further into the metastable region. The nucleation pulse chamber data and the shock tube data of *Zahoransky* [10] show onsets at similar pressures and temperatures, since both devices achieve similar expansions. The results by *Matthew and Steinwandel* are very close to the binodal, which indicates heterogeneous contamination of the system. Unfortunately,

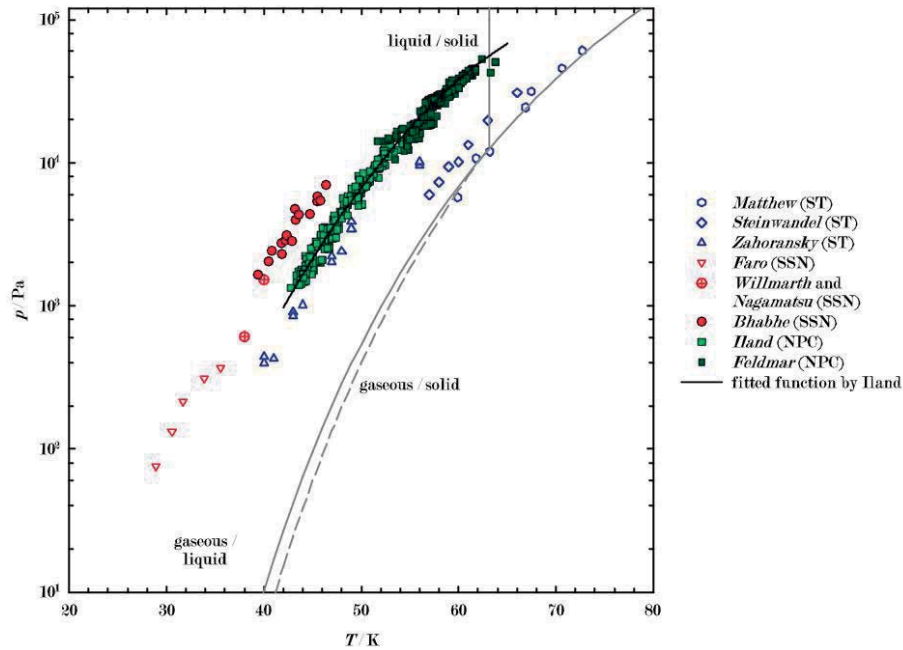


Figure 1.5: Overview of the available nucleation onset data for nitrogen. The dashed line is the gaseous-solid boundary; the solid lines are the liquid-solid boundary and the gaseous-liquid boundary, extrapolated past the triple point. Light and dark green squares are results from the cryogenic nucleation pulse chamber, measured by *Iland* [3] and *Feldmar*. Inverted triangles are results by *Faro et al* [6], filled circles by *Bhabhe et al* [7], crossed circles by *Willmarth and Nagamatsu* [8], hexagons by *Matthew* [74], diamonds by *Steinwandel* [9] and triangles by *Zahoransky* [10]

cryogenic measurements are very susceptible to such contamination. It was found in a previous work in the cryogenic nucleation pulse chamber that even $\sim 10 \text{ cm}^3$ of air in a 10 l gas mixture was enough to cause heterogeneous nucleation.

1.3.4 Growth rates

Growth rates of water and argon were measured by *Fladerer* [1, 43] in the room temperature and the cryogenic nucleation pulse chamber. He found that, despite the failure of the classical nucleation theory, the growth of the nuclei is described very accurately by the *Fuchs–Sutugin* [44, 45] growth theory. Fig. 1.6 shows the experimental growth rates for argon and water in comparison with the growth theory. Argon nuclei grow much faster than water nuclei, as indicated by the time scale in (b) which is ten times as long as in (a).

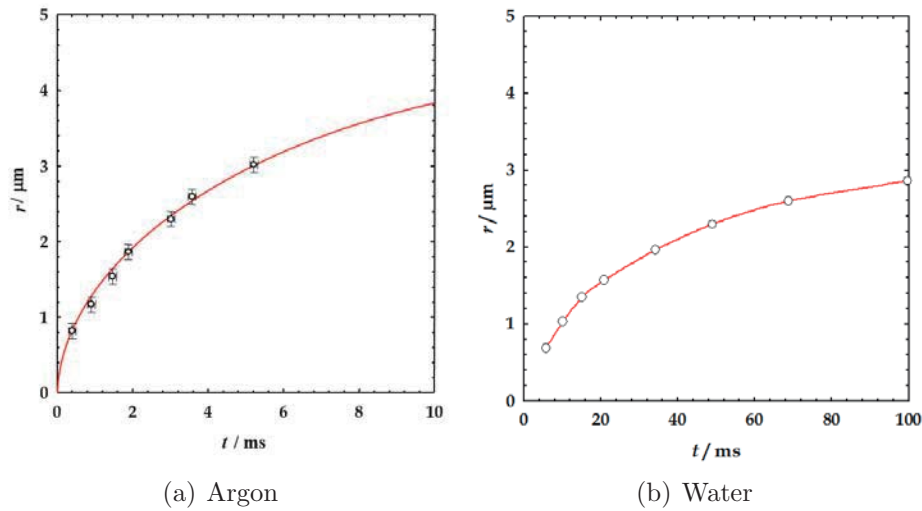


Figure 1.6: Experimental growth rates of argon and water (circles) in comparison with the *Fuchs-Sutugin* growth theory. [1, 43]

1.4 Task description

One of the main issues when attempting to measure homogeneous nucleation rates in the cryogenic nucleation pulse chamber has always been the extremely fast growth of argon and nitrogen nuclei, which made it impossible to separate nucleation and growth with the shortest achievable pulse length of 4 ms.

The first aim of this work was to convert the cryogenic chamber for room temperature measurements to find out whether it is possible to measure nucleation rates at these temperatures. The nucleation rates and critical nucleus sizes were to be compared with the classical theory and literature data. Water with helium as a carrier gas was chosen as a test system, because it is a well-characterized substance and there is a large amount of literature data available for comparison, most importantly a set of results which lies in the same range of nucleation rates as the cryogenic chamber was expected to show.

In a second step, the methodology for measuring nucleation rates at room temperature was to be transferred to the cryogenic experiment in another attempt to measure nucleation rates of argon.

Additionally, homogeneous nucleation onsets of nitrogen were to be measured and their scattered light signals used to determine the growth rate of nitrogen droplets at several temperatures. The quality of the onset data was to be tested by comparing it with older nucleation onset results from the cryogenic nucleation pulse chamber.