Homogeneous condensation in n-pentanol/helium mixtures in a nucleation pulse expansion wave tube

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Summary

Homogeneous condensation, the process of droplet formation in the absence of foreign particles, occurs when in a vapour the supersaturation ratio exceeds some critical value. Dropwise condensation consists of two stages: nucleation and droplet growth. Nucleation is the formation of critical clusters, which is followed by droplet growth. Two theories predicting the nucleation rate are the classical nucleation theory and the semi-phenomenological theory by Kalikmanov and Van Dongen.

Nucleation rate data available from different experimental methods still show considerable scatter. Therefore, joint experiments were instigated. These experiments consist of measurements of nucleation rates in n-pentanol/helium mixtures at selected conditions.

In a nucleation pulse expansion wave tube, a pulse like pressure history is generated by means of a local widening in the tube. The experiment is designed in such a way that significant nucleation occurs only during this nucleation pulse. Because the time duration of the pulse is very short, all nuclei formed are approximately of the same size. The nuclei will grow to macroscopic droplets which can be detected optically. From the measurements, the nucleation rates can be calculated.

Nucleation rate data were obtained for temperatures between 240 K and 260 K, at nucleation pressures near 1 bar. The supersaturation ratios for these series ranged from about 11 at the lowest temperatures up to about 27 for the highest temperatures.

Comparison of the nucleation data with the classical nucleation theory and the theory by Kalikmanov and Van Dongen, lead us to the preliminary conclusion that the second theory gives slightly better results. In contradiction to results found by other experimentalists, no temperature trend was observed on comparing experimental to theoretical results.

The nucleation data obtained for n-pentanol/helium show considerable scatter. Efforts to diminish this scatter proved not to be successful. It is most probable that the scatter is caused by the error in the nucleation temperature and/or the initial vapour pressure.

The experimental growth patterns were generally situated in the transition regime between Knudsen growth and continuum growth. Therefore, these growth curves may serve as data source for future investigations of different transition models in droplet growth.
Chapter 1

Introduction

Condensation, the formation of liquid droplets out of a vapour, is a commonly observed phenomenon. For example, one may think of the formation of fog: due to a sudden temperature drop in a humid atmosphere, droplets are formed. A second example is found in the transport of natural gas through pipelines: sudden pressure drops will cause the temperature of the gas to drop as well. This can result in condensation of vapour components present in the gas. Generally, this is an undesired situation, since droplets can obstruct the gas flow through pipes and valves.

Cooling of a gas-vapour mixture leads to a thermodynamic non-equilibrium state, in which the vapour pressure is higher than the saturated vapour pressure at the same temperature. The supersaturation ratio, defined as the vapour pressure divided by the saturated pressure, becomes larger than unity. In order to return to an equilibrium state, some of the vapour condensates into droplets, thus lowering the vapour pressure and thereby the supersaturation ratio. One can distinguish two stages during the condensation process. First, microscopic clusters of molecules are formed. This stage is known as the nucleation stage. The rate at which stable nuclei are formed is termed the nucleation rate $J$. In the second stage, the nuclei grow to macroscopic droplets. This is referred to as the droplet growth stage. Nucleation can take place in an environment with or without foreign particles, such as dust or ions. In the presence of foreign particles, which act as condensation nuclei, the nucleation is heterogeneous. When no foreign particles are present, homogeneous nucleation occurs. In this study we will concentrate on the latter.

Homogeneous nucleation has been the subject of quantitative experimental investigations for a hundred years now. At present, data from different nucleation experiments still show considerable scatter. Tests of theoretical predictions by comparison with experimental data are therefore often difficult. There are several reasons for the occurrence of this scatter. First of all, different experimental methods were used to generate the data. Secondly, different compounds were used in the experiments. A third explanation is that different experimental conditions were considered. And finally, different values of physico-chemical parameters were used so far, both in the evaluations of experiments and in theoretical predictions.

The participants of the Nucleation Conference in Prague, June 1995, concluded that joint experiments were urgently needed. These experiments should consist of measurements of nucleation rates in one particularly chosen vapour-carrier gas mixture at selected condi-
tions. Moreover, every participant should use the same set of physico-chemical parameters, both in evaluation and comparison with theory. Thus, the last three reasons mentioned for scatter in nucleation data are eliminated. One objective of these joint experiments is to generate definitive data in a sufficient range of nucleation rates. Another is to compare and verify the different experimental methods. It will also be possible to test the various nucleation theories more thoroughly than before. The first results of the joint experiments will be presented at the International Conference on Nucleation and Atmospheric Aerosols in Helsinki in August 1996.

The compound chosen for these experiments is n-pentanol (C₅H₁₁OH), since there is much data available on the properties of this compound. The pentanol is taken from the same lot for all experiments. The carrier gas is Helium (purity 99.999%). The experimental conditions are chosen such that nucleation takes place at a total pressure of 100 kPa and at the temperatures 240, 250 and 260 K.

In chapter 2 we will discuss two models for homogeneous nucleation. In general, nucleation models differ mainly by different models for the Gibbs free energy of formation of a cluster of $n$ molecules, $\Delta G_n$. The first theory that will be presented is the classical nucleation theory (CNT). This theory depends on the capillarity approximation, that is the assumption that microscopic clusters, consisting of only tens of molecules, have the same properties as macroscopic droplets. These clusters are no macroscopic systems, however: it is necessary to consider curvature effects on the properties of the clusters. The second theory described in chapter 2 is a semi-phenomenological theory, in which curvature effects are taken into account by taking the microscopic surface tension to be radius dependent.

In a laboratory, condensation can be studied by a fast expansion of a gas-vapour mixture. When the expansion is fast enough, the change of the thermodynamic state develops adiabatically and temperature falls with pressure. The vapour will become supersaturated, and homogeneous nucleation will start. All experiments described in this report are performed with a nucleation pulse expansion wave tube, often referred to as shock tube. In this tube, the gas-vapour mixture is subjected to a proper pressure history, resulting in a pulse-like supersaturation history at the endwall of the tube. Nuclei are formed only during this pulse. The time duration of the nucleation pulse is short, compared to the duration of the growth stage. Therefore, all droplets formed have approximately the same size. The macroscopic droplets can be detected optically, with a technique that allows us to determine the droplet radius as a function of time and the number density of the droplets. From this information, the droplet growth rate and the nucleation rate can be obtained. The experimental setup of the shock tube is described in chapter 3.

The results of the experiments performed within the scope of the joint nucleation experiments are presented in chapter 4. Discussion and conclusions follow in chapter 5.
Chapter 2

Nucleation Theory

In this chapter, two models for the nucleation process in supersaturated mixtures of an inert gas and a vapour will be discussed. The aim of any nucleation theory is to predict the rate of formation of stable nuclei, the so-called nucleation rate $J$. The classical nucleation theory, developed by Becker and Döring [1] and Zeldovich [2], is outlined in section 2.1. In section 2.2 the nucleation model of Kalikmanov and Van Dongen [3] is presented. This theory is one of the group of semi-phenomenological theories. The treatment of these nucleation models is largely taken from an earlier report by Muitjens [4].

2.1 Classical Nucleation Theory

The nucleation process is a kinetic process. Due to density fluctuations, clusters of vapour molecules are formed. Clusters consisting of $n$ molecules are referred to as $n$-clusters or $n$-mers, and molecules are referred to as monomers. In the kinetic process cluster-cluster interactions are neglected, only cluster-monomer reactions are considered. Schematically, this is shown in figure 2.1. So, it is the collision of an $n$-cluster with a monomer, that makes an $n$-cluster transite into an $(n+1)$-cluster. Evaporation of a molecule decreases the cluster size from $n$ to $(n-1)$. The clusters are assumed to be spherical.

![Figure 2.1: Kinetic processes](image)

Figure 2.1: Kinetic processes: $C_n$ condensation rate, $E_n$ evaporation rate, $J_n$ net rate of clusters transiting from $n$ to $n+1$. 

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The rate of change in number density \( \rho_n \) of \( n \)-clusters is given by the difference of the rates of \( n \)- and \( (n + 1) \)-cluster formation:

\[
\frac{d\rho_n}{dt} = J_{n-1} - J_n, \tag{2.1}
\]

where

\[
J_n = C_n \rho_n - E_{n+1} \rho_{n+1}. \tag{2.2}
\]

The condensation rate \( C_n \) is the collision frequency of vapour molecules with the cluster, multiplied by the probability that a vapour molecule will stick to the cluster, the mass accommodation coefficient \( \alpha_n \):

\[
C_n = \alpha_n \rho_0 n^{2/3} \rho_1 (kT/2\pi m)^{1/2}, \tag{2.3}
\]

where \( \rho_0 \) is the surface of one molecule, \( k \) is Boltzmann's constant, \( T \) is the temperature and \( m \) is the molecular mass of the vapour component. From here on, \( \alpha_n \) is taken to be unity. In equilibrium, the cluster concentration \( \rho_n^e \) is time independent and \( J_n = 0 \). This leads to the detailed balance relation

\[
E_{n+1} = C_n^e \rho_n^e / \rho_{n+1}^e, \tag{2.4}
\]

where \( C_n^e \) is the collision frequency in the equilibrium state, and \( \rho_n^e \) is the number density of \( n \)-clusters in the equilibrium state

\[
\rho_n^e = \rho_1 \exp(-\Delta G_n^e/kT). \tag{2.5}
\]

Here, \( \Delta G_n^e \) is the Gibbs free energy of formation of an \( n \)-cluster at the equilibrium state. The solutions of the equations (2.1) and (2.2) reach a steady state within a characteristic time of the order of 1 \( \mu s \) or less [5]. Most of the homogeneous condensation processes occur on much larger time scales. Therefore, only the steady state is of interest to us and it yields a constant \( J \) independent of \( n \). From (2.2) and (2.4) it follows that

\[
\frac{J}{C_n^e \rho_n^e} = \frac{C_n \rho_n}{C_n^e \rho_n^e} - \frac{\rho_{n+1}^e}{\rho_{n+1}^e}. \tag{2.6}
\]

The last two expressions show that two problems remain to be solved. First, the equilibrium state has to be defined and second, the Gibbs free energy of formation of an \( n \)-cluster in the equilibrium state has to be determined.

For the equilibrium state, two methods are reported in literature. In the first method, the equilibrium is assumed to be a constraint equilibrium, which would exist at the same temperature and supersaturation. It is referred to as the classical approach. The second method is the kinetic approach, which was developed by Katz and Wiedersich [6]. Here the equilibrium state is taken to be the actual vapour-liquid equilibrium at the same temperature, \( S = 1 \). This can be done since the evaporation rate is a function of temperature
and cluster size only, i.e., the right hand side of (2.4) does not depend on the particular equilibrium model.

In both approaches, the vapour-droplet system is described by a spherical liquid volume, the vapour phase surrounding the droplet, and the surface dividing the two phases. The vapour is assumed to be an ideal gas and the liquid is taken incompressible, with a constant molecular volume \( v^l \). The total pressure of the vapour and the inert gas component is \( p \), the temperature is \( T \), and the partial vapour pressure is \( p_v \). It can be shown [5] that for a spherical droplet with radius \( r \) and a macroscopic surface tension \( \sigma \), the Gibbs free energy of formation is equal to the Helmholtz free energy \( \Delta F \):

\[
\Delta G_n = \Delta F = -nkT \ln S + \sigma n^{2/3} a_0. \tag{2.7}
\]

\( S \) is the supersaturation ratio defined by

\[
S = \frac{p_v}{p_{vs}(T)}, \tag{2.8}
\]

with \( p_{vs} \) the saturation vapour pressure. The first term at the right hand side of (2.7) is a bulk term, the second is a surface term. The bulk term depends linearly on the number of molecules \( n \) in the droplet. The surface term denotes the energy that is needed to form the surface of the droplet.

When the supersaturation ratio is smaller than or equal to unity, \( \Delta G_n \) is always positive and stable droplets can not be formed. An equilibrium Boltzmann distribution will exist due to statistical density fluctuations. But for saturation ratios larger than unity, expression (2.7) has a negative and a positive term, leading to an energy barrier for droplet formation. The Gibbs free energy of formation of a cluster reaches a maximum value \( \Delta G^* \) at the critical cluster size \( n^* \), corresponding to the critical radius \( r^* \). These critical values can be calculated from (2.7) with \( \frac{\partial \Delta G}{\partial n} = 0 \):

\[
\begin{align*}
n^* &= \frac{4\pi(r^*)^3}{3v^l}, \tag{2.9} \\
r^* &= \frac{2\sigma v^l}{kT \ln S}, \tag{2.10} \\
\Delta G^* &= \frac{1}{3} \sigma 4\pi (r^*)^2, \tag{2.11}
\end{align*}
\]

where \( \sigma \) is the macroscopic surface tension and \( v^l \) the molecular volume. Clusters smaller than the critical size tend to evaporate due to the positive slope of \( \Delta G \). Inversely, clusters larger than the critical cluster size tend to grow due to the negative slope of \( \Delta G \).
Taking the properties, e.g. the surface tension, of the droplet as macroscopic (the capillarity approximation), we found an expression for $\Delta G_n$ for a given thermodynamic state. Combining this with a chosen equilibrium state by either the classical or kinetic approach, we obtain an expression for the nucleation rate.

We will now proceed according to the classical approach. For the constraint equilibrium the partial vapour pressure is equal to the supersaturated vapour pressure, hence with (2.3) $C_n = C_n^*$. The cluster equilibrium number density is found by substituting expression (2.7) in expression (2.5),

$$\rho_n^* = \rho_1 \exp \left( n \ln S - \frac{\sigma n^{2/3} a_0}{kT} \right)$$

The formation of a cluster is assumed to have a negligible effect on the number density of vapour molecules. So, the concentration of single vapour molecules is taken to be very large and equal to the equilibrium state value, $\rho_1^* = \rho_1$. From this and expression (2.6) the nucleation rate can be found [5]:

$$J = Z_{n^*} C_{n^*} \rho_{n^*}$$

The Zeldovich factor, $Z_{n^*} = \left( \frac{-\sigma^2 \Delta G / \partial n^2}{2\pi kT} \right)_{n^*}$ is introduced to correct for $\rho_n$ being less than $\rho_n^*$ and for the probability of supercritical clusters to re-evaporate. From expressions (2.7) and (2.9) it follows that:

$$Z_{n^*} = \frac{1}{3 \sqrt{\pi kT (n^*)^{2/3}}}$$

Substituting the expressions for $Z_{n^*}$ (2.14), $C_{n^*}$ (2.3), and $\rho_{n^*}$ (2.12) together with (2.9) and (2.11), in (2.13) yields:

$$J = (p_v/kT)^2 \left( \frac{2\sigma m}{\pi} \right)^{1/2} \frac{1}{\rho_1} \exp \left( -\frac{16\pi \sigma^3 m^2}{3k^3 T^3 \rho_1^2 \ln^2 S} \right)$$

Here, $\rho_1$ is the liquid mass density, and we used $m/\rho_1 = v'$. As one can see, only macroscopic quantities are needed to calculate the nucleation rate according to the CNT.

A drawback to the classical approach, is that the constraint equilibrium is an unstable state. As we have seen, the Gibbs free energy of formation of a cluster $\Delta G$ has a maximum. Consequently, the number density of droplets $\rho_n^*$ (2.12) has a minimum, so that for $n$ approaching infinity, the number density also approaches infinity. This is physically impossible, since we only have a limited number of molecules. Therefore, the constraint equilibrium state can only exist by introducing so-called Maxwell demons: large clusters are removed from the system, separated into single molecules and returned to the system.
Now we return to the kinetic approach [6]. Since the saturation ratio is equal to unity, the Gibbs free energy of formation of an $n$-cluster only contains the surface term,

$$\Delta G = a_0 n^{2/3} \sigma,$$

and the equilibrium number density of an $n$-cluster is given by

$$\rho_n^* = \rho_1^* \exp(-a_0 n^{2/3} \sigma/kT).$$

(2.17)

We can rewrite this as:

$$\rho_n^* = \rho_1^* \exp(-\sigma A_n/kT),$$

(2.18)

with $A_n = a_0 n^{2/3}$ the surface area of an $n$-cluster. We now introduce [6] $C_n \rho_n^* S^n$ as $\exp(H(n))$, which with (2.17) results in

$$H(n) = n \ln S + n^{2/3} \frac{\sigma a_0}{kT} + \ln(C_n \rho_1^*).$$

(2.19)

Without the last term on the right hand side, expression (2.19) is identical to the expression for $\Delta G(n)$ for the classical approach (2.7). From (2.6), (2.17) and (2.19) we can find an expression for the nucleation rate [6]:

$$J = \sqrt{\frac{H''}{2\pi}} C_{n^*} S^{n^*} \rho_{n^*}^*.$$  

(2.20)

Here, $n^*$ is the solution of $H'(n) = 0$ and $' = \frac{\partial}{\partial n}$. The contribution of $\ln(C_n)$ in (2.20) to $H''$ is negligible [7]. The final expression for $J$ according to the kinetic approach is a factor $S$ smaller compared to the expression for the classical approach (2.15). This is a relatively small difference in view of the many orders of magnitude difference when compared to other models.

### 2.2 Semi-phenomenological Nucleation Theory

There is one major drawback to the classical (kinetic) nucleation theory. Microscopic quantities as the surface tension are not known for a small cluster. Therefore, the macroscopic properties are used in this theory. For the surface tension, the macroscopic value over a flat surface is used. In the semi-phenomenological model of Kalikmanov and Van Dongen [3], the Gibbs free energy of formation of an $n$-cluster is found by applying Fisher’s droplet model [8] and combining it with a microscopic surface tension [9]. This model for $\Delta G$ is inserted into the kinetic approach of Katz.

Fisher’s droplet model is a microscopic treatment of a substance in the vapour phase. The vapour, a real gas, is assumed to be an ideal collection of clusters of different sizes. So, Dalton’s law can be applied to find a relation between cluster number densities and the vapour pressure,

$$\frac{p_{vs}}{kT} = \sum_{n=1}^{\infty} \rho_n^*.$$  

(2.21)

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Here, we immediately applied the kinetic approach where the vapour pressure is the saturated vapour pressure at temperature $T$. The overall vapour density is given by

$$\rho_{vs} = \sum_{n=1}^{\infty} n \rho_n^c.$$  \hspace{1cm} (2.22)

Fisher’s droplet model leads us to an expression for $\rho_n^c$:

$$\rho_n^c = q_0 n^{-\tau} \exp(-\sigma_{micro} A_n / kT),$$  \hspace{1cm} (2.23)

where the parameter $\tau$ accounts for the rotational and vibrational degrees of freedom that an $n$-cluster has compared to the bulk liquid, and $q_0$ for the translational degrees of freedom. Furthermore, in the microscopic surface tension $\sigma_{micro}$ effects of curvature are incorporated [9]:

$$\sigma_{micro} = \sigma (1 + \alpha_\sigma n^{-1/3}),$$  \hspace{1cm} (2.24)

where $\sigma$ is the macroscopic surface tension. In comparison to expression (2.18), expression (2.23) contains three additional unknown parameters: $q_0$, $\tau$ and $\alpha_\sigma$. These parameters can be determined using experimental data available in literature. By extrapolating Fisher’s droplet model to the critical point and substituting the critical properties of the vapour component, $T_c$, $p_c$ and $\rho_c$, in the expressions (2.21) and (2.22), two equations are found from which $\tau$ and $q_0$ can be determined:

$$\frac{p_c}{kT_c} = q_0 \zeta(\tau),$$  \hspace{1cm} (2.25)

$$\rho_c = q_0 \zeta(\tau - 1),$$  \hspace{1cm} (2.26)

where $\zeta$ is the Riemann zeta function. The parameter $\alpha_\sigma$ follows from the known value of the saturated vapour pressure at the temperature $T$ and expressions (2.21) and (2.23):

$$\frac{p_{vs}(T)}{kT} = \sum_{n=1}^{\infty} q_0 n^{-\tau} \exp(-\sigma_{0T} (1 + \alpha_\sigma n^{-1/3}) n^{2/3}).$$  \hspace{1cm} (2.27)

Applying the kinetic approach, the final result for the nucleation rate $J$ is given by

$$J = \frac{1}{3} \sqrt{\frac{\sigma q_0}{\pi kT} (1 + \alpha_\sigma (n^*)^{-1/3}) + \frac{9}{2\pi} (\tau - \frac{2}{3}) (n^*)^{-2/3}} \times \frac{p_c q_0}{\sqrt{2\pi m kT}} S_{n^*} q_0 (n^*)^{-\tau} \times \exp(-\sigma_{0T} (1 + \alpha_\sigma (n^*)^{-1/3})(n^*)^{2/3}),$$  \hspace{1cm} (2.28)

where $n^*$ is the real root of

$$- n \ln S + \frac{2 \sigma q_0}{3 kT} n^{2/3} + \frac{1 \sigma q_0}{3 kT} \alpha_\sigma n^{1/3} + \tau - \frac{2}{3} = 0$$  \hspace{1cm} (2.29)
In their paper, Kalikmanov and van Dongen compared the predicted nucleation rates of various theories to nucleation rate data reported in literature for various vapour components. Overall, the best agreement was found applying the theoretical model outlined above.

When comparing the theoretical nucleation rates (2.15) and (2.28) with experimentally measured nucleation rates, it is useful to introduce the factor $\Gamma$, which is the ratio of the experimental and theoretical nucleation rates:

$$\Gamma = \frac{J_{\text{exp}}}{J_{\text{theory}}}.$$  \hspace{1cm} (2.30)

The factor $\Gamma$ is plotted as a function of the temperature $T$. 
Chapter 3

Experimental Setup

3.1 Introduction

As already remarked in chapter 1, a fast expansion is an excellent means to create a superaturated state. When the expansion is fast enough, the change of the thermodynamic state develops adiabatically and temperature falls with pressure. Since the equilibrium density of a vapour depends strongly on temperature, a supersaturated state can be reached during the expansion.

One way to achieve a controllable and fast expansion, is to make use of the expansion wave that travels in the opposite direction of the shock wave in a shock tube. The temperature after the expansion can be controlled by varying the pressure ratio between the high pressure section (HPS) and the low pressure section (LPS) of the tube. When the molar fraction of pentanol is known (which is not assumed to change during the expansion), the value of the supersaturation ratio $S$ after the expansion is also a known quantity.

By introducing a small local widening in the low pressure section of the tube, a pulse-like variation of $S$ can be obtained. Since nucleation rates depend strongly on supersaturation, the only significant nucleation will take place during the pulse. After the pulse, however, $S$ still exceeds unity, so that the nuclei formed will grow to optically detectable sizes. Information on the nucleation rate can now be obtained by simply "counting" the droplets per unit volume and dividing by the duration of the nucleation pulse. Since the pulse duration is very short, compared to the duration of the growth stage, all droplets formed have approximately the same size. This has the advantage, that information can be obtained on the droplet radius as a function of time, i.e. the droplet growth rate. The principle of the nucleation pulse is described in section 3.2. The technique of optical detection will be the subject of section 3.3.

In addition to the nucleation and droplet growth rates, the thermodynamic state at which these quantities are measured is important. The state of a binary mixture of gases is characterized by the temperature $T$, the total pressure $p$ and the molar vapour fraction $y_v$. The determination of these quantities is subject of section 3.4.

A description of the experimental procedure is given in section 3.5. In section 3.6, an error estimation of the nucleation experiments is presented.
3.2 Shocktube

A schematic representation of the nucleation pulse shock tube can be seen in figure 3.1. It is a modification of the expansion shock tube developed by Peters [13].

The mixing circuit is connected to the HPS of the tube by valves $V_7$ and $V_8$. The vapour is let into the tube through valves $V_1$ and $V_5$. These connect the vessel, containing pentanol vapour over a small amount of liquid pentanol, and the tube.

![Figure 3.1: Schematic representation of the nucleation pulse shock tube setup.](image)

<table>
<thead>
<tr>
<th>HPS</th>
<th>high pressure section</th>
<th>$V_1,\ldots,8$ valves</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPS</td>
<td>low pressure section</td>
<td>TP: turbo molecular vacuum pump</td>
</tr>
<tr>
<td>MS</td>
<td>membrane section</td>
<td>RP: rotation vacuum pump</td>
</tr>
<tr>
<td>PM</td>
<td>photomultiplier</td>
<td>$p_d$: static pressure transducer (Druck PDCR81)</td>
</tr>
<tr>
<td>PD</td>
<td>photodiode</td>
<td>$p_e$: dyn. pressure transducer (Kistler 603B)</td>
</tr>
<tr>
<td>L</td>
<td>lens</td>
<td>$p_k$: static pressure transducer (Edwards 600AB)</td>
</tr>
<tr>
<td>MP</td>
<td>mixing pump</td>
<td></td>
</tr>
</tbody>
</table>

The vapour inlet/vacuum pump section contains a complex system of valves. This has a simple explanation. Pentanol works as a solvent on the lubrication of the bearings of the turbo molecular vacuum pump. It is essential, therefore, that the tube is largely cleared from pentanol, before the turbo molecular pump is connected to the tube. To this end, a separately connected rotation pump is used.
At time zero, the membrane is heated by a hot ribbon and opens in approximately 100 \( \mu \)s \([11]\). A shock wave travels into the LPS, and an expansion wave travels in the opposite direction. The shock wave reflects at the local widening as another small expansion, followed by a small recompression as it reaches the end of the widening. In figure 3.2 a schematic \((x,T)\)-diagram of the propagating waves is presented, along with a schematic drawing of the tube, and the development of the pressure at the HPS endwall of the tube.

![Schematic diagram](image)

Figure 3.2: Schematic \((x,T)\)-diagram of the wave propagation in the shock tube.

The pressure dip due to the local widening, which is in fact the nucleation pulse, is typically 0.3 ms in time. This can be varied by mounting a widening of different length into the tube. After typically 13 ms the shock wave, that has reflected at the LPS endwall of the tube, arrives at the HPS endwall and brings the experiment to an end. The mentioned times hold for experiments where helium was used as carrier gas. When for example nitrogen is used, these characteristic times are larger due to a smaller sound speed \( c \).

The gasdynamic aspects of the setup are described in detail by Looijmans \([11]\).

### 3.3 Optical setup

The optical setup used for the determination of droplet concentrations and droplet sizes during the nucleation experiments, is shown in figure 3.3. A laser beam (wavelength 514.2 nm) passes the HPS through two small windows in the side wall of the tube, at about 5 mm from the endwall. In this way, the velocity of the gas at the point of detection can be neglected during the experiments, whereas detection still takes place outside the thermal boundary layer at the endwall. The transmitted beam is sent through a thick
The light of the laser beam is scattered by the droplets that are formed inside the tube during a nucleation experiment. The size of the droplets as a function of time is obtained by recording the intensity of the light, scattered within a small solid angle of the direction perpendicular to the incident beam (90°-scattering). For particles with sizes of the order of the wavelength of light (hundreds of nanometers), the Mie theory describes the intensity scattered by spherical particles as a function of scattering angle, index of refraction $m$ and dimensionless radius $2\pi r/\lambda$ ($\lambda$ being the wavelength of the incident light). Details of this theory can be found in references [11, 14]. A typical Mie-pattern is plotted in figure 3.4.

In our optical setup, the recorded intensity of the scattered light has, to a very high degree of accuracy, the same form, but now as a function of the square root of time. Measured peaks can be identified with the theoretical ones and so, knowing the wavelength and index of refraction, the droplet radius can be obtained as a function of time very accurately. In principle, this can be done for $r$ being a continuous function of time. It is sufficient, however, only to consider the peak tops in order to determine the growth rate.

When droplets are formed, the transmitted beam is attenuated. The droplet concentration can be derived from the amount of attenuation, according to the law of Lambert-Beer [11]. There is also some (undesired) forward scattered light included in the transmitted signal. Contributions of forward scattered light to the signal are estimated in section 3.6.
Here, a remark has to be made about the detection limits of the scattering setup. The lower limit is constituted by the recognizability of the Mie-peaks (thus by the signal-to-noise ratio). The upper limit is formed by the saturation limit of the measuring device (photomultiplier + acquisition system). Consequently, the measurable droplet concentrations are all within a range of about a factor $10^4$ (nucleation rates have been measured varying from $3 \cdot 10^{13}$ m$^{-3}$s$^{-1}$ up to $1 \cdot 10^{17}$ m$^{-3}$s$^{-1}$).

3.4 Thermodynamic state

The static pressure before the expansion is measured by means of a Druck PDCR81 pressure transducer. The pressure during the expansion and the subsequent measuring time is recorded using a Kistler 603B pressure transducer.

The initial temperature $T_0$ is measured with a thermocouple (Keithley 871A), in thermal contact with the wall of the HPS. It is assumed that the wall temperature equals the gas temperature inside the HPS. The temperature during the experiment is calculated under the assumption that the changes of the thermodynamic state are adiabatic in the core of the shock tube:

$$\frac{T}{T_0} = \left(\frac{p}{p_0}\right)^\alpha.$$  \hspace{1cm} (3.1)

In case of an ideal gas, i.e. helium, expression (3.1) is an isentropic relation where $\alpha$ is given by $\alpha = \frac{2}{\gamma} - 1$, with $\gamma$ the ratio of specific heats: $\gamma = \frac{C_p}{C_v}$.

The next quantity to measure, is the mixture composition. The most straightforward method is the following. The molar density of the vapour is calculated from the initial vapour pressure with the ideal gas law, and is assumed not to change when the other
component (the gas) is added. The total molar density is calculated from the total pressure of the mixture with the ideal gas law, since helium can be considered an ideal gas at the pressures of interest (up to 2 bar). The vapour fraction is now equal to the ratio of the two densities. An important observation has to be made here. When the vapour is let into the tube, some of the vapour is adsorbed on the walls of the tube. As the adsorption process takes some time to equilibrate (typically three quarters of an hour), leakage of ambient air into the system becomes important. The measured vapour pressure has to be corrected for the leakage. The leakage rate of the HPS, including the vapour inlet section and the mixing circuit, has been established to be $1.5 \cdot 10^{-2}$ Pa/min.

3.5 Experimental procedure

An experiment starts with mounting a membrane in the membrane section (see figure 3.1). The thickness of the membrane is chosen such that the membrane can withstand the initial pressure difference between HPS and LPS, whereas it is also thin enough to open easily when heated by the hot ribbon. The LPS is evacuated until the pressure is below 1 Pa. The HPS is brought below $10^{-3}$ Pa, using a turbo molecular vacuum pump (TP). Pumping is continued for one hour, in order to clear the HPS section of the tube of residual gas and foreign particles, which could act as condensation nuclei. During this evacuation, valves $V_1, V_2, V_7$ and $V_8$ are open, the others remain closed.

In the time that has passed since the last experiment, air may have leaked into the pentanol vessel. Therefore, the vapour is removed from the vessel using a rotation pump (RP) by opening valve $V_4$. After approximately one minute, valve $V_4$ is closed again, and the liquid pentanol vaporizes until the pressure in the vessel equals the saturation vapour pressure of pentanol.

Now, valve $V_2$ is closed, ending the evacuation of the HPS. The pentanol vapour is slowly let into the tube by opening valve $V_5$ very carefully. When a desired vapour pressure is reached, the valve is closed again. At first, the vapour pressure in the tube decreases, due to adsorption of vapour on the walls. After typically 45 minutes the adsorption process reaches an equilibrium, and the vapour pressure of the pentanol is recorded with pressure transducer $p_a$. After that, valve $V_1$ is closed, separating the vapour inlet section from the HPS. Through valve $V_6$, the gas component, helium, is added to the mixture in the HPS. Simultaneously, the LPS is pressurized, keeping in mind the maximal pressure difference the membrane can withstand. In order to prevent weakening of the membrane by bowing back and forth, the LPS pressure is always kept lower than the HPS pressure. In this way, undesired premature rupture of the membrane is prevented.

When the pressure in the HPS has reached its desired value, the mixing pump is put on for a quarter of an hour, in order to homogenize the gas/vapour mixture. During this time, the laser is turned on in order to let the beam stabilize before the experiment starts. Then, the mixing circuit is isolated from the HPS by closing valves $V_7$ and $V_8$.

The tube is now prepared for the experiment. The initial pressure and temperature of the HPS and the initial pressure of the LPS are recorded. The dynamic pressure transducer
(Kistler 603B, in combination with a Kistler 5001 charge amplifier) is put in its operating state. This is done just now to prevent its output signal from drifting. A pulse is sent through the heating ribbon in the membrane chamber, the membrane bursts and the experiment starts.

During the experiment, four signals are recorded: the dynamic pressure, the intensities of the reference beam and the transmitted beam (both by means of a photodiode) and the intensity of the light scattered under 90° (see section 3.3). These signals are recorded with a sampling rate of 32 kHz into a LeCroy waveform recorder, which is triggered by the dynamic pressure signal falling below a threshold value. Typical results are described in chapter 4.

3.6 Error analysis

In this section, the experimental uncertainties involved in the nucleation experiments are analyzed. The aim of our experiments is to determine the relationship \( J = J(S, T) \). Therefore, it is necessary to know the experimental uncertainties of these quantities.

The nucleation temperature is calculated from the initial static pressure, the nucleation pressure and the initial temperature. The dominant error is caused by the determination of the nucleation pressure. The dynamic pressure transducer was calibrated twice: before and after the experiments. The difference between these calibrations resulted in a relative uncertainty of 0.7% in the determination of the nucleation pressure. The absolute uncertainty of the initial temperature is 0.1 K, and the uncertainty of the initial pressure is 0.1%. A detailed analysis shows that the resulting absolute uncertainty in the condensation temperature is 0.7 K.

The nucleation vapour pressure \( P_v \) is calculated according to the method described in section 3.4, and its accuracy is 0.7%. The saturated vapour pressure \( P_{vs} \) is calculated according to the expression found by Schmeling and Strey [15]. The uncertainty in the saturation vapour pressure is caused by the uncertainty in the condensation temperature, and is determined to be as large as 9%. Since the supersaturation ratio is the ratio of the vapour pressure and the saturation vapour pressure, the effect of the uncertainty in \( P_{vs} \) on the accuracy of the supersaturation ratio is dominant, and the uncertainty of \( S \) is also 9%.

Now we proceed with estimating the accuracy of the nucleation rate \( J \). The nucleation rate is the ratio of the droplet number density and the time duration of the nucleation pulse. The duration of the nucleation pulse can be determined within an accuracy of 10%. The error that the forward scattered light induces in the droplet number density is equal to:

\[
\frac{P_s}{P_0 - P_b} = \frac{P_s P_b}{P_0 P_b P_0 - P_b}.
\]

where \( P_0 \) is the power of the undisturbed transmitted beam, \( P_b \) is the power of the attenuated beam and \( P_s \) is the power of the forward scattered light. An estimation of the
contribution of the forward scattering to the transmitted signal was found by Smolders [16]:

$$\frac{P_s}{P_b} = n_d L \pi r^2 \frac{i_0(\alpha, m)}{\alpha^2} \theta^{\text{det}}.$$  \hspace{1cm} (3.3)

Here, \(n_d\) is the droplet number density, \(L\) is the length of the measuring volume, \(r\) is the droplet radius, \(m\) is the refractive index and \(\theta^{\text{det}}\) is the angle of detection. The variable \(\alpha\) is the dimensionless radius, mentioned in section 3.3: \(\alpha = 2\pi r/\lambda\). The function \(i_0(\alpha, m)\) is the scattering function [17].

![Diagram of the path of the transmitted light beam](image)

Figure 3.5: A representation of the path of the transmitted beam. The scattering angle is 0.024 rad. The length of the measuring volume is 36 mm.

A representation of the path of the transmitted light beam is given in figure 3.5. The detection angle is determined by \(\theta^{\text{det}} = \phi_{L_3}/2f\), where \(\phi_{L_3}\) is the diameter of lens \(L_3\) and \(f\) is the focal length of lens \(L_2\). This provides us with the value \(\theta^{\text{det}} = 0.024\) rad, since \(f = 25\) cm and \(\phi_{L_3} = 12\) mm. The length of the measuring volume is 36 mm. When the droplets are of the size belonging to the second Mie-peak, \(r = 0.31\) \(\mu m\). For the third Mie-peak, the droplet radius is \(r = 0.47\) \(\mu m\). With typical experimental droplet concentrations \(n_d < 3 \cdot 10^{13} m^{-3}\), expression (3.3) yields ratios of \(\frac{P_s}{P_b} < 2 \cdot 10^{-3}\) (second Mie-peak) and \(\frac{P_s}{P_b} < 1 \cdot 10^{-2}\) (third Mie-peak). The maximum permitted attenuation is 10% of the total transmitted intensity, in order to satisfy the criterion of no multiple scattering (inherent to the Mie-theory). Therefore, the last factor on the right hand side of expression (3.2) is of the order of 10. Consequently, the error in the droplet concentration is 2% of the droplet concentration for the second Mie-peak. For the third Mie-peak, the error in the droplet concentration is 10%. The error rises with increasing droplet radius. At the seventh Mie-peak, the error is as high as 60% (\(r = 1.0\) \(\mu m\)). In view of the orders of magnitude scale that is commonly used in work on nucleation, an error of about 15% in nucleation rates can be considered small. For nucleation rates determined for droplet radii larger than 0.47 \(\mu m\),
the total error becomes larger than 15%. The only way to diminish the effect of forward scattering, is to decrease the detection angle. Using a pinhole of 2 mm diameter, instead of lens L3, decreases the ratio $\frac{P_a}{P_b}$ by a factor 0.03. Consequently, the error at the seventh Mie-peak would be 2%, instead of 60%, for the droplet concentration. The total error in the nucleation rate would then be 10%, since the error in the duration of the nucleation pulse becomes dominant.
Chapter 4

Experimental Results

4.1 Introduction

In the previous chapter we discussed the experimental techniques applied to measure homogeneous nucleation rates. This chapter deals with experimental results obtained with n-pentanol/helium mixtures. In section 4.2 a typical experiment is described. The nucleation rates found are presented in section 4.3. We shall compare these results with the classical model and the semi-phenomenological model of Kalikmanov and Van Dongen, described in chapter 2. The droplet growth stage is discussed in section 4.4.

4.2 A typical experiment

This section describes the results of a typical experiment performed in the shock tube using a n-pentanol/helium mixture. A typical pressure history at the endwall of the HPS is shown in figure 4.1, together with a numerical simulation. The numerical method used,

![Figure 4.1: The experimental (solid line) and simulated (dashed line) pressure history at the endwall of the HPS.](image)
is the one-dimensional Random Choice Method (RCM). Details of this method can be found in references [18, 19].

First, we will discuss the experimental pressure signal. The initial HPS pressure is 1.490 bar and the condensation pressure is 1.056 bar. At $t = 1.2$ ms, the first expansion starts. The reflection of the shock wave at the widening results in the nucleation pulse, starting at $t = 1.8$ ms. The bumps in the pressure signal at $t = 4.5$ ms and $t = 7.5$ ms are caused by reflections of the first expansion wave at the widening. At $t = 13.6$ ms the shock reflection at the endwall of the LPS arrives at the HPS endwall, ending the experiment.

The minimum pressure plateau of the nucleation pulse of the experiment is not strictly horizontal. This is probably caused by imperfect bursting of the membrane. The membranes used all could withstand a maximum pressure difference of 1-2 bar. The actual initial pressure difference between HPS and LPS was approximately 0.5 bar. Using a thinner membrane might be a solution. Unfortunately, no thinner membranes were available, so the membrane could not be chosen more critically.

Experiment and simulation show similar pressure profiles. As time proceeds, a slight difference between simulation and experiment occurs. This is probably due to the fact that wall friction plays a role in the experiment, while this effect is not taken into account in the RCM simulation. After 13.6 ms, the pressure signals start to deviate. This is caused by different boundary conditions at the LPS end of the shock tube in experiment and simulation.

![Figure 4.2: The transmitted light signal. The shock reflection can be recognized as a sudden decrease in the signal.](image)

The intensity of the transmitted light beam is shown in figure 4.2. The shock reflection causes the transmitted signal to decrease suddenly, as the droplet density is increased by the compression. Not all transmitted signals are as smooth as the signal in figure 4.2. In some experiments the droplet density is much lower, resulting in less attenuation of
the transmitted beam. The signal-to-noise ratios in these experiments are much lower. However, the droplet concentration can be determined, even if the signal-to-noise ratio of the transmitted signal is extremely low, provided that the scattered light signal has well defined peaks. This can be done by comparing the absolute heights of the Mie-peaks to the peaks in a reference experiment. The ratio of the intensity of the highest detectable peak to that of the reference peak is taken and multiplied by the droplet concentration in the reference experiment. After a correction due to the intensity of the incident beam, which differs slightly from one experiment to another, the droplet concentration is obtained for the other experiments.

Figure 4.3: The scattered light signal, theoretical (a) and measured (b). At $t = 13.6$ ms, the shock reflection ends the experiment.

The scattered light signal and the theoretical Mie-pattern are plotted in figure 4.3. Equivalent peaks are marked with the same number. The droplet radius is determined as a function of time, by comparing the measured peak positions with the theoretical ones, as explained in section 3.3. The intensity of the fifth experimental peak exceeds the saturation
limit of the measuring device. After 13.6 ms the shock wave stops the condensation process. The existing droplets start to evaporate, due to the temperature increase after the shock wave. Consequently, the scattered light signal shows the Mie-pattern in reverse direction. Here, the increased droplet density, caused by the compression, enlarges the signal as a whole. Therefore, the extrema after the shock have higher values.

Some experiments showed a scattered light signal as plotted in figure 4.4. At first, the increase of the signal proceeds as in a usual Mie-pattern. Then, the signal abruptly changes in slope, showing an approximately linear increase, followed by a decrease as the shock wave causes the droplets to evaporate again. It is very probable that this deviant signal is caused by depletion of the pentanol vapour. If too many nuclei are formed, the amount of pentanol needed to allow them to grow to detectable sizes is larger than the amount present in the vapour. If more pentanol is added, even more nuclei will be formed, so this is not a solution. As we experienced, there is an optimal amount of vapour for every nucleation temperature. Inserting this amount will give a good chance of obtaining a successful experiment.

At 240 K and 250 K, this optimal amount was easily found by trial and error. At 260 K, however, the droplets grow extremely fast (the few successful experiments showed approximately eight Mie-peaks), so the depletion can be complete even before the scattering exceeds the noise in the scattering signal. Therefore, it is impossible to make a distinction between experiments with too little vapour (resulting in too few detectable droplets), and experiments with too much vapour (resulting in no detectable droplets at all). Finally, we found the optimal amount by simultaneously increasing the nucleation temperature and the vapour amount in small steps, starting at 255 K.

There is yet another difficulty in trying to perform successful experiments. Since the supersaturation ratio depends strongly on temperature, even small deviations of the nucle-
ation temperature resulted in too high or too low nucleation rates. At 240 and 250 K this was not a problem. Here, two out of three experiments were succesful. Experimenting at 260 K, however, was extremely unpredictable. Only one in ten experiments was succesful.

4.3 Nucleation

In this section the experimental nucleation rates are presented and compared with the classical nucleation theory and the theory by Kalikmanov and Van Dongen. In figure 4.5 the nucleation rates are plotted as a function of the n-pentanol supersaturation ratio $S$ for the nucleation temperatures 240, 250 and 260 K. The supersaturation ratio required for a certain nucleation rate varies with temperature. For example, for a nucleation rate of $3 \times 10^{15}$ m$^{-3}$s$^{-1}$, the supersaturation ratios needed at the respective temperatures 240, 250 and 260 K, are roughly 24, 17 and 12.

![Figure 4.5: The experimental nucleation rate $J$ plotted as a function of the supersaturation ratio $S$. The results of experiments at different nucleation temperatures are indicated with different markers. The results of the classical nucleation theory are plotted as solid curves.](image)

The theoretical nucleation rates according to the classical nucleation theory are also shown in figure 4.5. A significant difference of about three orders of magnitude is found between experiment and theory.

The nucleation temperatures were approximately the indicated temperatures. In reality, the temperature in the nucleation pulse differed from the desired value by at most two degrees. This scatter in temperature partly causes the scatter in figure 4.5. In order to diminish this effect, a correction factor $\Delta \ln S$ is introduced:

$$\Delta \ln S = \Delta T \cdot \frac{\partial \ln S}{\partial T} |_J,$$

(4.1)
where $\Delta T$ is the deviation from the desired nucleation temperature. This correction causes a point in the $J$-$S$ plane to shift in the $S$ direction. The derivative in the equation is calculated on the basis of the classical nucleation theory, and it reads:

$$\frac{\Delta \ln S}{\ln S} = -\frac{3 \Delta T}{2 T}.$$  \hspace{1cm} (4.2)

The corrected nucleation data are plotted in figure 4.6. Apparently, the correction factor does not diminish the scatter significantly. Therefore, a more sophisticated correction is tried. According to the classical nucleation theory (see section 2.1), the nucleation rate shows the following behaviour:

$$J = J_0 \exp(A\phi(T)),$$  \hspace{1cm} (4.3)

with $A = -\frac{16\pi m^2}{3k^2}$ and $\phi = \frac{\sigma^2}{\rho \Gamma^2 \ln \frac{T}{S}}$. The prefactor $J_0$ is weakly dependent on $T$, but this effect is negligible compared to the effect variations of $T$ have on the factor $\exp(A\phi)$. Although the classical theory is not necessarily correct, we assume that the behaviour of the nucleation rate is governed by the factor $\exp(A\phi)$. In other words: $\Gamma$ is constant in $J_{exp} = \Gamma J_{theory}$, and consequently:

$$J_{exp} = \Gamma J_0 \exp(A\phi_{exp}).$$  \hspace{1cm} (4.4)

We now want to find the nucleation rate $J_{ref}$ we would have measured if the expansion had been slightly smaller or larger, starting from the same initial total pressure $p$, initial vapour pressure $p_{v,0}$ and initial temperature $T_0$, resulting in the exact desired nucleation temperature $T_{ref}$ ($T_{ref}$ being 240, 250 or 260 K):

$$J_{ref} = \Gamma J_0 \exp(A\phi_{ref}).$$  \hspace{1cm} (4.5)
The correction factor for the nucleation rate is defined as:

$$\Delta \ln J \equiv \ln J_{\text{ref}} - \ln J_{\text{exp}}, \quad (4.6)$$

from which we find with (4.4) and (4.5)

$$\Delta \ln J = A(\phi_{\text{ref}} - \phi_{\text{exp}}) = A \frac{\partial \phi}{\partial T} |_{p_{v,0}} \Delta T. \quad (4.7)$$

The derivative in this equation can be found by using the chain rule. The correction of the supersaturation ratio $S$ is found with an expression, similar to expression (4.2):

$$\Delta \ln S = \Delta T \cdot \frac{\partial \ln S}{\partial T} |_{p_{v,0}}, \quad (4.8)$$

As we discussed in section 3.4, the supersaturation ratio $S$ is calculated according to:

$$S = \frac{p_v(T, p_{v,0})}{p_{\text{vs}}(T)} = \frac{p_{v,0} \left( \frac{p(T)}{p_0} \right)}{p_{\text{vs}}(T)} = \frac{p_{v,0} \left( \frac{T}{T_0} \right)^{\frac{\gamma}{\gamma-1}}}{p_{\text{vs}}(T)}, \quad (4.9)$$

From expression (4.7) through (4.9) and the expressions for the temperature dependent physico-chemical parameters $\sigma$, $\rho_1$ and $p_{\text{vs}}$, the corrected values of $J$ and $S$ can be obtained. These values are plotted in figure 4.7. Again, the correction diminishes the scatter in the nucleation data somewhat, but not considerably better than the correction we used earlier.

Comparing the results for the two correction methods, we can conclude that the complicated second method does not give significantly better results than the first correction method. We must therefore conclude that the scatter in the results are not caused by the
scatter in nucleation temperatures. Most probably, it is the error in $T_{\text{exp}}$ and/or $p_{v,0}$ that is responsible.

In figure 4.8, the results of the nucleation rates are shown for all successful experiments. The results are given in terms of the factor $\Gamma$, being the ratio of experimental and theoretical values of the nucleation rates, as a function of the nucleation temperature. For the theoretical nucleation rates, both the classical nucleation rates and the nucleation rates according to the semi-phenomenological theory are used. Again, there is a considerable spreading in the measurements. For both models, the spreading in $\Gamma$ is about two orders of magnitude. The ratio $\Gamma$, calculated according to the classical nucleation theory, differs from unity by about three orders of magnitude. For the results concerning the semi-phenomenological theory, this difference is about two orders of magnitude. Therefore, the semi-phenomenological model seems to give slightly better results. This is a preliminary conclusion, however, since the results according to both theories show overlap.

![Figure 4.8: The experimental nucleation rates in terms of $\Gamma$, plotted as a function of the nucleation temperature. The theoretical models used are the classical nucleation theory and the theory by Kalikmanov and Van Dongen.](image-url)
4.4 Droplet growth

In this section the droplet growth stage is discussed. According to the droplet growth model by Gyarmathy [20], the droplet growth stage can be divided into four regimes: the Knudsen regime, the transitional regime, the continuum regime and the depletion regime. This is schematically shown in figure 4.9, where the square of the droplet radius $r$ is plotted against time.

![Schematic droplet growth curve](image)

Figure 4.9: Schematic droplet growth curve.

The first regime is the Knudsen regime, where the droplet size is small compared to the molecular mean free path $l$. This region is characterized by $K_n > 10$, with $K_n$ the Knudsen number, defined by $K_n = \frac{l}{2r}$. Here, the Knudsen growth law applies, i.e. the increase of droplet radius is proportional to time:

$$dr \propto dt.$$

In the continuum regime $K_n < \frac{1}{100}$. Here, the quadratic growth law is valid, i.e. the increase of droplet radius squared is proportional to time:

$$dr^2 \propto dt.$$

The transitional regime connects the Knudsen regime and the continuum regime for $10 < K_n < \frac{1}{100}$. Finally, in the last regime of the growth stage, the vapour is depleting, and eventually the droplet radius does not increase with time anymore. Obviously, it is possible that depletion starts before the droplets grow to sizes corresponding to the continuum regime.

An experimental growth curve is plotted in figure 4.10. The molecular mean free path of n-pentanol molecules in helium at atmospheric conditions is $l = 1.7 \cdot 10^{-8}$m. Now, $K_n > 10$
when $r < 1 \text{ nm}$. The smallest detectable droplets have $r = 0.16 \mu m$, so the Knudsen regime can not be distinguished in our experiments. The continuum regime starts at $K_n < \frac{1}{100}$.

![Figure 4.10: Experimental droplet growth curve.](image)

when $r > 0.8 \mu m$. Since the maximum droplet radius measured at temperatures lower than 255 K is $r = 0.75 \mu m$, these experiments provide information about the transitional regime only. Vapour depletion is found in experiments with relatively high nucleation rates. In the experiment shown in figure 4.10, the transitional regime ends at approximately $t = 8 \text{ ms}$, when the vapour depletion starts.

In the experiments performed at nucleation temperatures near 260 K, the droplets are able to grow up to $r = 1 \mu m$, so from these experiments information about the continuum regime can be found.

The droplet growth data, obtained with the n-pentanol/helium experiments, can be compared with the various existing growth models. This is an interesting subject for future studies.
Chapter 5

Conclusions

This work has dealt with experiments, performed within the scope of joint experiments, concerning the nucleation of n-pentanol vapour in helium. The experiments were carried out in a nucleation pulse expansion wave tube. The nucleation pressure was 1 bar, the nucleation temperatures were 240, 250 and 260 K.

Comparison of the nucleation data with the classical nucleation theory and the semi-phenomenological theory by Kalikmanov and Van Dongen, lead us to the preliminary conclusion that the second model gives slightly better results. Nucleation data, produced by other participants of the joint experiments, might give more insight on this subject. In contradiction to results found by other experimentalists, no temperature trend was observed on comparing experimental to theoretical nucleation rates.

A serious point of concern is the accuracy of the determination of the supersaturation ratio and the nucleation rate.

For the supersaturation, the effect of the uncertainty of the saturation vapour pressure, caused by the uncertainty in the nucleation temperature, is dominant, and gives an uncertainty of 9% in the supersaturation ratio. Since the uncertainty of the nucleation temperature is caused by the uncertainty of the dynamic pressure, a possible solution of this problem might be to calibrate the dynamic pressure transducer more frequently.

The accuracy for determining the nucleation rate is influenced by forward scattered light contributing to the transmitted signal. The error in the nucleation rate, caused by this effect can range from 2% at the droplet radius belonging to the second Mie-peak, to 60% at the seventh Mie-peak. For future experiments, it is advisable to use a pinhole, instead of the lens L3 in the optical setup, since this lowers the detection angle for forward scattering considerably.

The nucleation data obtained with the experiments show considerable scatter. Efforts to diminish this scatter, by correcting the supersaturation ratio and/or the nucleation rate for small deviations in nucleation temperature, proved not to be successful: only a slight improvement was obtained. Therefore, it is most probable that the scatter in the results is caused by the error in \(T_{exp}\) and/or \(p_{v,0}\).

The experimental growth patterns were generally situated in the transition regime between Knudsen growth and continuum growth. Therefore, these growth curves may serve as data source for future investigations of different transition models in droplet growth.
Bibliography


