LA-UR-96- 2936

Title: **Nucleation and Condensation Model Development**

Author(s): **Herbert Fry, CST-6
John Lyman, CST-6
Dale Breshears, CST-6
David Zerkle, CST-6
Carl Wilson, CST-6
Cliff Hewitt, CST-6
David Gallegos, MST-6**

Submitted to: **DOE Office of Scientific and Technical Information (OSTI)**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ph*

MASTER

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Form No. 836 R5
ST 2629 10/91

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ll*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Nucleation and Condensation Model Development

Herbert Fry*, John Lyman, Dale Breshears, David Zerkle, Carl Wilson, Cliff Hewitt, and David Gallegos

Abstract

This is a final report of a one-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The purpose of this project was to bring to maturity a theoretical and experimental capability of the Laboratory to perform basic research in nucleation and condensation of water vapor. This report provides a general description of this capability and summarizes specific work in two areas: development and use of a combustive flow facility (CFF) to measure water monomer depletion in a supersonic nozzle and nucleation pulse experiments for investigation of transport effects on water droplet growth dynamics. The later work was performed in collaboration with Dr. Wehrner Strey in Göttingen, Germany. Preliminary water absorption data from the CFF experiment are presented. The nucleation pulse data is described along with an analysis that shows under the condition of the experiment the growth rate of water droplets is limited by monomer diffusion.

1 Background and Research Objectives

The prediction of the details of nucleation and condensation phenomena is important for many advanced technologies of interest to Los Alamos National Laboratory and the nation in general. In the semiconductor industry poorly understood particle creation due to nucleation and condensation processes hinder at least two steps in the production of large integrated circuits. While nanocrystalline materials have been shown to have interesting and useful properties, the methods of their production, which involve nucleation and condensation, have been difficult to scale up due to the lack of predictive modeling capability. In inertial confinement fusion the condensation of ablated material is thought to be important in the dynamics of the resulting implosion. In the paint industry the control of the size of metal oxide particles is important in creation of pigments. All of these technologies would benefit from the availability of a universal nucleation and condensation code.

*Principal investigator, e-mail: ha_fry@lanl.gov

Over the last decade we have developed a theoretical and experimental capability for the study of homogeneous nucleation and condensation kinetics in the support of several programmatic efforts. The purpose of this LDRD project was to apply this capability to the study of the homogeneous nucleation and condensation of water vapor with a goal of further benchmarking our modeling capability. During the course of the project it was recognized that an experimental capability in the laboratory of Dr. Reinhard Strey of the Max Planck Institute of Biophysical Chemistry, Göttingen, Germany, (MPBC) would complement our efforts. Dr. Strey made his laboratory available to us for two weeks in June and the results of that work are also presented in this report.

2. Importance to LANL's Science and Technology Base and National R&D Needs

This project supports Los Alamos core competencies in complex experimentation and measurement as well as theory, modeling, and high-performance computing. The disciplines of chemical engineering, chemical kinetics, computational fluid dynamics, advanced laser diagnostics, and super computing have been applied to nucleation and condensation science, resulting in a quantum leap in understanding of these phenomena.

3. Scientific Approach and Results to Date

The experimental methods developed in our laboratory are based on measuring the depletion of monomer as a function of position in a supersonic nozzle [1]. Figure 1 shows three nozzles that have been developed for nucleation and condensation studies. These nozzles provide a wide range of expansion conditions in which data can be produced for the benchmarking of our model.

Implementation of these nozzles requires that a pressure ratio of nearly 20 to 1 be maintained to insure proper supersonic flow. The large nozzle throat areas of several square centimeters result in considerable flow rate being required during supersonic flow. In the top two nozzles, referred to as the PRL CA nozzle and PRL CE nozzle, the flow rates and pressure ratios in constant area (CA) and constant expansion (CE) nozzles are obtained using a pulsed recirculating loop (PRL). In these experiments the supersonic flow is produced in pulsed mode for a 10 millisecond period [1,2]. The PRL uses a set of seven metal-bellows pumps, a large surge tank and a large supply tank, which allow for the system to provide a supersonic pulse once every 30 seconds. The bottom nozzle, which will be referred to as the combustive

flow facility constant expansion (CFF CE) nozzle, is implemented in continuous flow mode in which the nozzle is driven by a combustor and requires a high flow rate pumping system [3].

The three nozzle experiments and the nucleation pulse experiments described later in this report provide data from qualitatively different nucleation and condensation regimes. The challenge of developing a universal nucleation and condensation model is being able to describe the kinetics in all of these regimes adequately. Under some conditions of temperature, pressure and supersaturation ratio, a 20 percent change in water concentration can result in the nucleation rate changing by six orders of magnitude [1]. In the MPBC experiments, where the supersaturation is between 5 and 25 [4], the free energy barrier to droplet formation, which results from the instability of the small droplets with respect to the vapor and the bulk liquid, dominates the phenomenology. Under these conditions 10 to 10^4 droplets per cubic centimeter are produced in the one millisecond nucleation pulse, and then 5 to 100 milliseconds are required to deplete the concentration of vapor through condensation on these droplets. In striking contrast, in the PRL CA nozzle experiments, where supersaturations of over a million are attained in less than 10 microseconds, 10^{15} droplets per cubic centimeter are created and the vapor is completely depleted in under 30 microseconds. Under these conditions the nucleation and condensation phenomena are dominated by the kinetics of small droplet formation and the free energy barrier to droplet formation is irrelevant. The CFF CE nozzle experiments, which were the primary focus of this LDRD project, were designed to provide data in an intermediate regime.

Our nucleation and condensation model utilizes a chemical kinetics approach that has been successful in explaining the data from the PRL CA nozzle [1]. In this model the smaller droplets containing up to 100 monomer units are included explicitly and the dimerization reaction and the monomer addition and removal reactions are numerically integrated. To model the nozzle experiments, the one-dimensional flow equations are simultaneously integrated with the kinetics equations, which then provides the water monomer concentration as a function of position in the nozzle. This quantity is then compared to the experimental measurements. While this approach is adequate for the rapid supersonic expansions where very high supersaturations are attained, it is not adequate for the Strey nucleation-pulse experiments and the CFF CA nozzle experiments. This is because droplets containing considerably more than 100 monomer units are important.

The problem of describing the growth of large droplets was handled by incorporation of a moment formalism developed by McGraw [5]. This elegant formalism uses a set of differential equations involving the first four moments of the droplet size distribution to describe the growth dynamics of the larger droplets. This formalism was coupled to the explicit small droplet kinetics formalism existing in our model. Figure 2 provides three-

dimensional graphs of the time-dependent droplet-size distributions calculated with our model for the conditions of the PRL CE and CFF CE nozzle experiments. This figure demonstrates graphically how the CFF CE nozzle experiments are qualitatively similar to the traditional nucleation experiments where the nucleation and condensation stages are temporally separated. The model indicates that the CFF CE nozzle experiments should form relatively large droplets containing a few thousand monomers. Data from the as yet immature experiment would provide a good test of the large particle dynamics included as an important and untested part of our model. For this reason the majority of the limited resources for this project were put into obtaining data from this experiment.

In obtaining data from the CFF CE nozzle experiment and using it to benchmark our model, it was essential that an adequate understanding of the flow dynamics of the nozzle be obtained. A description of the apparatus [3] should help the understanding of the following discussions. There were two important differences between the combustive flow apparatus and the PRL apparatus used for the experiments described in [1]. First, the CFF CE nozzle was much longer. This is how the slower expansion rate is obtained, which results in the assumption of one-dimensional and isentropic flow being questionable. Second, the experiments are performed at elevated stagnation temperatures, which was also the only easily varied parameter. In the PRL apparatus it was easier to vary water mole fraction and stagnation pressure. This varying stagnation temperature brought into question the uniformity of the temperature in the flow produced by the operation of the combustor and the heat exchanger. Both of these issues were addressed using experimental measurements and computational fluid dynamics.

The CFF CE nozzle shown in Figure 1 was equipped with pressure transducers spaced at approximately every 4 cm downstream of the nozzle throat. It was found that the simple isentropic flow equations with an effective expansion angle taking into account boundary layer growth did not reproduce the static pressure measurement. This required that a full Navier-Stokes two-dimensional computational fluid dynamics (CFD) calculation be performed for the nozzle conditions. The static pressure along the nozzle wall resulting from this calculation could be compared to the laboratory measurements. Figure 3 shows that this analysis successfully calculated the measured static pressures. Also shown on a different scale is the stagnation pressure along the center line. The fact that the stagnation pressure is not constant as a function of position in the nozzle, indicates that the flow is irreversible and not isentropic. Incorporation of this irreversibility in the flow is essential for the proper analysis of the data provided by the experiment.

The temperature homogeneity of the flow was known to be an issue and during the construction of the system a simple baffle was placed between the heat exchanger and the

nozzle transition section. Seven thermocouples were placed in the transition piece and these indicated that the simple baffle was not working efficiently. While complex baffles could be designed that would adequately mix the flow, it was important that they also not introduce an unacceptable impedance in the flow that would disrupt overall operation of the apparatus. This was addressed by performing a full Navier-Stokes three-dimensional CFD calculation for both the old baffle and the new more complex baffle. The calculations indicated that the old baffle was ineffective and the new baffle would be effective and result in only a 20 Torr pressure drop during normal operation. The predictions of the CFD were verified by experimental measurements. Figure 4 shows the temperature measurements in the transition section with the old and new baffle. The temperature inhomogeneities have been reduced dramatically.

Infrared absorption measurements as function of position in the nozzle were obtained using a Digilab FTS-60 spectrometer which provides 0.1 cm^{-1} resolution. Due to several experimental difficulties we were limited to 0.5 cm^{-1} resolution for the experiments described in this report. Infrared absorption measurements were made across the nozzle at locations that corresponded to the pressure transducers used for static pressure measurements. These measurements were performed at six different initial temperatures with approximately the same water mole fraction of 0.032. The temperature was varied with constant mole fraction by adjustment of the natural-gas flow rate in the combustor and the water flow rate through a heat exchanger upstream of the nozzle. Data were obtained from approximately 350 K to 475 K, which was the range in which calculations indicated nucleation and condensation should change dramatically. Figure 5 shows examples of spectra obtained at the first four positions for two different temperatures. These spectra demonstrate that at the lower temperature the water spectrum becomes attenuated at the second position (E2) in the nozzle relative to the spectra obtained at a higher temperature. The attenuated spectrum indicates a high degree of condensation.

Figure 6 shows the initial attempt at testing the nucleation and condensation model. The fraction of monomer remaining was calculated from the measured spectra. The first step in this process was to obtain the pressure and temperature along the center line using a CFD calculation for the nozzle using measured initial conditions. Using these parameters synthetic spectra were calculated using line parameters from the HITRAN data base. These synthetic spectra were convoluted with the FTIR instrument line shape and compared to the observed spectra. The mole fraction of water was varied in this calculation until visual inspection indicated adequate agreement with the observed spectrum.

The modeling procedure used to predict the monomer fractions remaining required some modification from that described in [1] because the flow was not isentropic. Rather than simultaneously solving the flow and nucleation and condensation equations, special differential

relations for the velocity, temperature, and density were obtained for each set of specific experimental conditions. These relations were obtained by fitting the values calculated from the CFD calculations to polynomials in the nozzle position coordinate. The calculated flow variables produced by the kinetics model using these relations were then compared to the measured static pressures and the static temperature, velocity and density calculated with the CFD code. This tested that the kinetics model correctly treated the flow.

The preliminary results depicted in Figure 6 were obtained with no change in the model input parameters that were demonstrated to provide excellent agreement with the results obtained from the PRL CA nozzle [1]. It should be noted that all the model parameters are obtained or derived from quantities in the literature for bulk water, water vapor, and water droplets with no adjustment for our nucleation data. Clearly at this point the model agreement is not as good for the CFF CE nozzle experiments as for the PRL CA nozzle experiments. However, from the standpoint of nucleation rate experiments, where different measurements and calculations can disagree by orders of magnitude, it may be reasonable as a first attempt with no arbitrary adjustment of model parameters.

One part of the model that is known to have incorrect physics is the treatment of the growth of the larger clusters of water droplets. Presently, the model treats this growth with the moment-method formalism that assumes the particle growth rate is equal to the collisional rate with monomers, which is proportional to the cross sectional area of the particles. As the particles become larger, transport phenomena involving heat and mass will become important, which will greatly alter the real growth rate. These transport processes are not included in our model. These effects will work to slow down the growth rate and affect the time dependence of monomer depletion. Providing data to quantify this phenomena was the object of the nucleation pulse experiments at MPBC.

Dr. Reinhard Strey and coworkers at MPBC have developed a nucleation pulse method [4] for measuring the rate of nucleation in water vapor and similar materials. While this apparatus was built to measure nucleation rates, we recognized that the experiments could also provide information about the rate of growth of the water droplets, which was needed to make our model more accurate. Because of the potential usefulness of the results of experiments with the Göttingen apparatus, we proposed to Dr. Strey a collaborative set of experiments to determine the rate of particle growth for different conditions, and to determine the effects that control the rate of particle growth. Those experiments were performed during the first fifteen days of June 1995.

Figure 7 illustrates the nature of the nucleation pulse experiment and its use to determine nucleation rate. The method uses an expansion chamber wherein the pressure of a gas sample with a small amount of water is reduced rapidly to the point where homogeneous

nucleation begins to occur. The pressure (and consequently temperature) is then held constant for a short time (approximately 1 millisecond). At that point the temperature is increased by a slight recompression. This effectively stops nucleation. However, because the gas is still supersaturated, the existing nuclei continue to grow to the size where they can be detected by Mie scattering using a laser beam. As the particles grow monotonically in the size range 0.3 to 30 μm radius, the Mie-scattering signal provides a number of distinct resonances, which give the precise particle size at different times. This assumes that the size distribution is approximately monodisperse. The scattered light intensity at the first resonance determines the number of nuclei formed during the short nucleation period since the size at that time is well determined. The nucleation rate is then the number of particles produced divided by the nucleation time period.

Figure 7 also shows how we used the experiment to determine particle growth dynamics. After passing through the first resonance, the scattering signal passes through multiple peaks and valleys that allow for the determination of many particle-radius and time-data pairs. The particle sizes for different peaks and valleys are provided in the Figure. We found that a plot of the square of the radius so determined versus time forms a straight line. This is also plotted on the Figure. This linear dependence shows that

$$\frac{dr^2}{dt} = C$$

where C is a constant. Consequently,

$$\frac{dr}{dt} = \frac{C}{2r}$$

but because

$$V = \frac{4}{3}\pi r^3$$

and

$$\frac{dV}{dt} = 4\pi r^2 \frac{dr}{dt}$$

$$\frac{dV}{dt} = 2\pi C r = C' r$$

On the other hand, the dependence we assumed for the model was that the volume rate of change was proportional to the collision rate, which for uniform water monomer distribution gives a rate proportional to the cross-sectional area of the growing droplet, or

$$\frac{dV}{dt} = C'' r^2$$

The observed dependence is precisely what one would expect if transport phenomena were the rate-limiting process in particle growth.

To determine which of the two like transport phenomena, mass diffusion or condensation heat transport, was responsible for limiting the rate of droplet growth, experiments were performed at several temperatures (and hence different water concentrations) with four diluent gases (helium, nitrogen, argon, and xenon.) At the present time we have been able to analyze only a few of these experiments, which will be described below. Preliminary indications are that these experiments support the hypothesis that the rate-limiting process for particle growth was the time for water molecules to diffuse through the partially depleted region around the droplet.

The experiments chosen for analysis provide data at two different temperatures, with a variation in diluent species at constant water concentration. In Figure 8 we see the Mie-scattering traces for four different diluents at a single temperature and water mole fraction. The pressures for these experiments were also all about the same (390 Torr). The four traces cover about the same range of sizes. However, there is a dramatic difference in growth rate; the experiments with the heavier diluents exhibiting much slower growth. Figures 9 and 10 show that the water droplets grow with the same dependence (r^2 versus time is linear) as observed in Figure 7.

We have made some preliminary comparisons of these experiments with predictions of a diffusion model [6] for limiting the rate of droplet growth. The droplet growth has the correct dependence on time (Figures 9 and 10). The slopes of the data in those figures should be proportional to the binary diffusion coefficient for water vapor diffusing in the different diluents. The data and calculation procedures [6] show that the diffusion model does give the correct dependence on diffusion coefficient. The average deviation of the slopes in Figures 9 and 10 from those predicted by the diffusion model was less than 10 percent. Another possible restriction on the rate of droplet growth is the rate at which heat of condensation is conducted away from the droplets. We made a similar comparison of the slopes in Figures 9 and 10 with the thermal conductivity of the gases used in the experiments. The thermal conductivity did not have the right dependence on species. The average deviation of the slopes from the thermal conductivity was more than 250 percent.

The data provided by the nucleation pulse experiments indicate that our model will over predict the growth rate of particles larger than 0.5 micron radius. As the particles become smaller, the diffusion-limiting effect will become unimportant and the volume growth rate should become proportional to the radius squared instead of the radius. Whether this diffusion effect will be operative at the specific conditions of the CFF CE nozzle experiments as shown in Figure 6 will require more analysis of both the nucleation pulse and CCF CE nozzle data. Incorporation of this particle growth physics into our model will not be completely straightforward because it will require significant changes to the moment formalism. We are confident that this can be done. When it is done, data from this project will be used to test the validity of such a model.

References

1. H. Fry, H. Watanabe, N. Nereson, C. Wilson, D. Breshears, J. Romero, J. Lyman, and D. Pauley, "Kinetics of Water Vapor Condensation", in Los Alamos Report LA-12331-PR, pg 67.
2. H. Fry, D. Breshears, H. Watanabe, D. Pauley, and J. Lyman, "DARPA Condensation Studies", Los Alamos Report, LA-UR 92-1001 (1992).
3. E. C. Sams, P. J. Wantuck, D. K. Zerkle, and H. A. Fry, "A Laboratory Scale Supersonic Combustive Flow System", AIAA Paper No. 95-0485, presented at the 33rd Aerospace Sciences Meeting and Exhibit, Jan. 9-12, 1995, Reno, NV.
4. Y. Viisanen, R. Strey, and H. Reiss, "Homogeneous Nucleation Rates for Water," *J. Chem. Phys.* **99**, 4680 (1993).
5. McGraw and J. H. Saunders, "A Condensation Feedback Mechanism for Oscillatory Nucleation and Growth," *Aerosol. Sci. Technol.*, **3**(4), 367-80 (1984).
6. R. Strey, private communication, June 1995.
7. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, Inc., New York, 1954, pp 14-15.

**Pulsed Recirculating Loop
Constant Area (PRL CA)
Nozzle**

**Pulsed Recirculating Loop
Constant Expansion (PRL
CE) Nozzle**

**Combustive Flow Facility Constant Expansion
(CFF CE) nozzle**

Figure 1. The figure shows three nozzles. The first is a constant area nozzle because it has a precisely designed contour that provides a rapid expansion in the first 7 mm. The nozzle has a slight angle after this point that results in effectively constant area when the boundary layer growth is considered. The second nozzle is a constant expansion nozzle with a 4.5 degree angle and a 3.5 mm throat height. These first two nozzles are designed to be used in pulsed mode. The bottom CCF CE nozzle has a 5 mm throat and a 1 degree expansion angle. These nozzles provide dramatically different rates of expansion. One measure is in the distance required to attain Mach 3: the PRL CE nozzle - 7 mm, the PRL CE nozzle - 10 cm, and the CFF CE nozzle - 50 cm.

Figure 2. The figure demonstrates the nature of the nucleation and condensation model. In addition, it shows the qualitatively different nucleation and condensation regimes represented in the two nozzle experiments. The two graphs show the calculated droplet size distributions for the two constant-expansion nozzles shown in Figure 1. The graph on the left is a calculation simulating nucleation and condensation in the 4.5 degree constant-expansion nozzle used in the pulsed recirculating system. The graph on the right is a simulation for the 1 degree expansion nozzle used in the combustive flow facility. In both cases the horizontal axis represents bins of droplets for both the explicitly included individual droplets and those represented by the moment formalism (indicated by M on the axis). The vertical axis is the fraction of water monomer incorporated into the particular bin of droplets. The axis into the paper represents distance down the nozzle. For the graph on the left (the 4.5 degree nozzle) the total distance is approximately 5 cm and for the one on the right (the 1 degree nozzle) the distance is 50 cm. The time scales are 100 microseconds and 800 microseconds for the respective graphs. In the 4.5 degree nozzle the kinetics are dominated by the growth of small droplets (less than 100 monomer units) which are explicitly included in the model. In the 1 degree nozzle the moment formalism is required for a good description.

Figure 3. This figure shows the results of a flow analysis of the CFF CE nozzle. The horizontal axis is the distance downstream of the nozzle throat. The data points are obtained from pressure transducers in the wall of the nozzle placed approximately every 4 cm. The calculated lines are the result of a CFD calculation using the commercially available RAMPANT code sold by Fluent Inc. The static pressure trace agrees with the measured points within the error of the transducer output. It should be noted that the agreement is much better than that reported [3], which used the Fluent code also from Fluent Inc. Our work revealed a bug in the fluent code. The stagnation pressure decrease down the nozzle shows a significant deviation from isentropic flow.

Figure 4. The figure shows the output of selected thermocouples placed in the transition pipe between the heat exchanger and the nozzle entrance. Reference [3] provides a description of this apparatus. Data are shown for the combustor and heat exchanger operating at nearly the same conditions with the original baffle and the one designed during this project. Consistent with CFD calculations, the data show the increased efficiency of the new baffle.

Comparison of Spectra at Two Different Temperatures

Figure 5. The figure shows 0.5 cm^{-1} FTIR spectra obtained at different locations in the nozzle for two different temperature runs. The intensity of the peaks will decrease without condensation because the static pressure is decreasing and the instrument resolution is not sufficient to resolve the narrow lines resulting at low static pressure.

Fraction of Monomer Remaining versus Nozzle Position

Figure 6. The figure shows a plot of the monomer fraction remaining versus position in the nozzle. The measured points result from analysis of FTIR spectra like those shown in Figure 5. The calculated points are the results of our model as described in the text.

0601.565.Ar

Figure 7. The gray line, left axis, is the time dependence of the expansion-chamber pressure. The black line is the scattered-light signal. The arrows identify some of the points at which the droplet radius is known. The points, right axis, are the square of the droplet radius.

Scattering signals at 226 K for four diluents

Figure 8. Scattering signals for water fraction of 0.00188 at 226 K in four diluents. The time zero is the beginning of the lowest (nucleation) pressure in each experiment.

Cluster Growth at 226 K

Figure 9. Square of droplet radius versus time for three diluents at 236 K and 0.00416 water mole fraction. The points are from experiments like Figure 7 and the lines are fits to the points.

Cluster Growth at 236 K

Figure 10. Square of droplet radius versus time from the experiments in Figure 8.