To the Graduate Council:

I am submitting herewith a dissertation written by Charles William Alvord entitled “Radiation Effects on Metastable States of Superheated Water.” I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Nuclear Engineering.

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(Original signatures are on file with official student records.)
Radiation Effects on Metastable States of Superheated Water

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Charles William Alvord
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Acknowledgements

"A watched pot never boils."

Old proverb

The journey that ends here was begun in 1994. I first retook undergraduate Quantum Mechanics at UT in the spring of 1994 to see if I recalled enough of the stuff to take on a Physics Ph.D. Many twists and turns later, including abandoning the Ph.D. altogether for a few years, restarting as a Nuclear Engineer, and getting a Masters in 2003, I find myself facing not being a student for the first time in more than a decade. My 14 year old daughter has never known me not to be a student, and my 17 year old son probably cannot remember a time when I wasn’t one.

The double entendre of the proverb above (probably only funny to me, and one or two members of my committee) is appropriate. The presentation of my dissertation appears to be a metastable event: determined by physical law but otherwise subject to stochastic behavior. I am sure there are a number of observers who saw no sign that the end was ever going to be reached. I am indebted to their patience. I am sure many of those observers represent forces and heat without which it would not have happened. All along the road I have been lucky to have the support of many people who made the work easier.

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As I mentioned at the start of this section, I have been a student almost all of the time I have been a parent. Over this time I have had a chance to work out just what kind of a parent I am, and what kind of a parent I should be. I know I need more patience. I know of no parent who comes through the process without feeling the same way. I was not a very challenging kid, and I think my parents and I agree I took it easy on them. Nevertheless, I think they have been rather patiently waiting for this day to come, and encouraging all along the way. Their love and belief in me is all I could hope for, and they are both examples of the parenting style I hope someday to achieve.

Finally, three people have walked every inch of this road with me. Anna, Miles and Hilary, it is wrong to say I did this for you. Were I to say it, you might well reply with “thanks but no thanks” and deservedly so. The degree has long since stopped being about anything that might benefit you, and was more of a personal quest for me. I thank all three of you for your patience with me while I did it. There is no way to express here what that means to me, and this is not the place. You three are my world and I think I am the luckiest.
Abstract

Radiation Effects on Metastable States of Superheated Water covers theory, application, and experimentation into the behavior of water at temperatures above the boiling point. The backgrounds of Positron Emission Tomography target design, bubble chambers, and superheat measurements are presented. The quantitative theory of metastable liquids and their characteristic waiting time is discussed. Energetics of bubble formation from two different perspectives are included. Finally, the design of an apparatus for measuring liquid superheats in the presence of radiation is covered in some detail, including several design iterations, first measurements made on the apparatus, and techniques for data reduction.
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1.0 Introduction

1.1 Background and relevance to PET

Positron Emission Tomography (PET) is a nuclear medicine imaging technology utilizing coincidence detection of 511 keV annihilation photons. Detection of annihilations rather than single photons removes the need for collimation of the gamma rays, increasing the available information, and thereby improving sensitivity and resolution. The core technological principles of this imaging technique (coincidence detection, attenuation correction and an image reconstruction using filtered backprojection) were first developed by Phelps and coworkers in 1974.\(^1\) Human imaging using these techniques was first published in 1976.\(^2,3\)

As important as the imaging methods and equipment are, they do not represent a complete technology for biological imaging. Molecular probes that illuminate biologically significant processes also needed to be developed. In 1978 Fowler, Wolf and coworkers at Brookhaven National Laboratory developed a glucose analog labeled with Fluorine-18 (2-deoxy-2-fluoro-D-glucose or \([^{18}\text{F}]\text{FDG}\)\(^4\). The first images of this tracer in the human brain were obtained the next year\(^5\). \([^{18}\text{F}]\text{FDG}\) is a remarkably versatile marker of biological processes. Glucose metabolism is altered in a variety of neurological disorders, in heart disease, and most significantly in most cancers.

A primary limitation on the use of \([^{18}\text{F}]\) is that it is not easily produced or distributed. It has a half-life of 109.8 minutes, necessitating production of the isotope in the city or region of the patient, and on the day of injection. In order to produce the \([^{18}\text{F}]\text{FDG}\) required for clinical imaging, compact commercial particle accelerators and compact targets for the production of \([^{18}\text{F}]\) had to be developed. Fluorine-18 remains the most widely used PET radioisotope, owing in no small part to the broad utility of \([^{18}\text{F}]\text{FDG}\), and also to the long (relative to other positron emitters) half
life. The most common precursor form of the isotope for synthesis is aqueous $[^{18}\text{F}]$fluoride ion, produced on small accelerators via proton bombardment of $[^{18}\text{O}]$ enriched water.

### 1.2 Water isotope targets – history and design

The development of $[^{18}\text{O}]$ enriched water targets for $[^{18}\text{F}]$ production, both in the academic and commercial realm, has a rich history. In 1983 Bruce Wieland and Al Wolf demonstrated that small volume enriched water targets could be used to produce aqueous $[^{18}\text{F}]$. This was controversial at the time, and conventional wisdom was that other reactions on un-enriched materials were the only technically and commercially viable approach. However, with this early success many other researchers reported similar targets. Most of the work over the next 5 years focused on variations on the same target, using small volumes (<1 ml), operating at low-pressures (<3 atm.), and presumably using some form of natural convection. Various target materials including titanium, silver, nickel-plated copper, and stainless steel were used. The techniques used in design and operation of the targets reached some stability. Using a variety of designs many researchers were able to obtain 500 mCi of useful $[^{18}\text{F}]$fluoride ion routinely in a 1 hour bombardment. From the mid-80s to the mid-90s, efforts continued on target designs, primarily aimed at increasing output. By the mid-90s the state of the art was approximately 1 Ci/hour/target. Overwhelmingly, these designs were still natural convection/phase change targets, volumes were now in excess of 1 ml, and the target body materials had settled on silver and titanium.

Eventually the community (commercial and academic target designers) began to investigate heat transport in the targets and ways to keep liquid density high while removing heat. The stated goal in some cases was to avoid phase change by forced circulation of the water or beam sweeping methods. In other cases, heroic efforts were undertaken to keep all of the water in the vapor phase. The importance of keeping water in a single phase in targets remains controversial. Steinbach and co-workers have shown in an elegantly simple paper that phase change even at modest
beam powers is nearly unavoidable, and contributes to the heat transport for liquid targets\textsuperscript{23}. The existence of phase change in typical water targets was partially confirmed by computational methods in 1998\textsuperscript{24}. In 2000, Alvord and Ruggles experimentally confirmed the existence of a stable vapor jet originating at the base of the entrance window (see Figure 1). Ruggles performed control volume calculations based on original forensic observations of the oxidation patches inside a commercial water target\textsuperscript{25}, and partially confirmed the behavior from a mock up of jet flow in a similar water volume\textsuperscript{26}.

Alvord measured the pressure rise in a silver water target holder with external process water cooling and under bombardment. The expansion volume above the liquid space in the target was well known. The pressure rise was a fairly precise measure of the amount of vapor generated in the target. The calculations modeled the flow of heat throughout the system, first from the proton

Figure 1 - Control volume vapor jet model
beam into the water via bulk heating from ionization, then conversion into vaporization of the water, condensation of the vapor on the inside walls of the target through film condensation, conduction of heat through the target walls to the process water surface, and finally film coefficients and temperature drops into the process water itself.

Good correlation between reasonable engineering values for film condensation and film coefficients at the outside walls of the system and the amount of vapor generated validated at least in part the stable vapor jet model. The validation of this model caused CTI to redesign targets to have a variable depth profile with height. This gave very good target performance and is the standard design element in all Siemens liquid target designs today. However attempts at making the target exactly as deep as the model predicts do not perform as anticipated. There is still evidence that unmodeled and unexpected density reduction and conversion to vapor are happening in some regions of the target.

This vapor jet provides, through shear forces, high velocity upflow of the liquid volume the protons stop in. The model holds that the heated region (control volume L in the figure) supplies vapor to the vapor jet region (control volume S in the figure) via film evaporation. This model also assumes most of the liquid volume is at saturation conditions, and finds that the top of the control volume L is superheated to 22 K above saturation. The mass transport normal to the interface between control volumes L and S to resupply film vaporization at the boundary is insufficient to avoid bulk nucleation. From Ruggles’ conclusion:

The time to traverse from jet bottom to jet top is 0.016 seconds, resulting in liquid superheat of 22 degrees Celsius when the jet velocity of 1.0 m/s is used. The liquid normal velocity is 0.0065 m/s, which gives a residence time of 0.23 seconds and a superheat value over 300 degrees Celsius. The vertical transport of the liquid motivated by the vapor jet is key to limiting fluid element residence times in the region of energy deposition. (my bold italics)

Further in the conclusion Ruggles states:

This (22 K superheat) is a modest level of superheat typical of that required to initiate vapor generation on a conventional heater surface where nucleation sites exist. Values of liquid
superheat of order 100 degrees Celsius are typically required to initiate boiling in bulk water. However, the amount of superheat required to initiate boiling in bulk water can be reduced if the water contains impurities or is being subjected to radiation.

Without the modeled upflow the liquid water in this region would reach temperatures above the critical point, and would certainly nucleate in the bulk. The vapor jet volume estimated in the original internal report was later confirmed in a published study of pressure rise of the enclosed target headspace under bombardment\textsuperscript{27}.

Some expansion and updating of that theory is warranted here. The original model assumed that 400 watts were deposited uniformly on an 8 mm diameter circular area. Given a 1.2 mm deep volume heating zone in the liquid water, this results in a beam power density of $6.63 \times 10^9$ W/m$^3$. The resulting transport time from jet bottom to jet top was 0.016 seconds in the 400 watt model. Since the calculations were originally performed, the operating current has risen to 60 uA, corresponding to 660 W. Moreover, the proton beam intensity is not uniform, but is a roughly Gaussian profile in both horizontal and vertical dimensions. This means that the central 4 mm diameter spot is subject to power densities closer to $3 \times 10^{10}$ W/m$^3$, or about a factor of 5 higher. The water in upflow due to vapor shear will have attained some superheat (on the order of 5 K) before entering this center hot spot. Assuming velocities in the system are as calculated before (water velocity is about 0.5 meters/second), then the transport time through this smaller zone is about 8 msec. The heating rate for water in this small volume is about 7700 K/sec, and the superheat just in this region is then 61 K. Added to the 5 K superheat entering the region, and the exiting flow can be expected to be 66 K above saturation, or at 318ºC.

Silver had been settled on as the target body material of choice by commercial manufacturers from the early 90’s. However, oxidation of the silver and entrainment of particulates of the target body plus soluble oxides led to reduced performance of targets as beam powers increased. The use of more oxidation resistant materials such as tantalum became necessary\textsuperscript{28}. However the lower thermal conductivity of tantalum placed additional restrictions on the target designer to keep up with the ever-increasing power requirements of the targets. Given the experience of the new
materials such as tantalum and a partially validated model for the relative volumes in each phase of the targets, it has been possible to design a new generation of targets capable now of production at rates 10 times those of the first enriched water targets\textsuperscript{29}.

The widespread commercial utility of the new high-power water targets notwithstanding, there remain challenges and opportunities for the designer of commercial water targets. The cost of enriched water is still between $40 and $100/gram, and the targets utilize 2-3 grams per bombardment. For a large commercial supplier the annual enriched water costs are in the millions of dollars. Reduction of the water inventory in a target by a few percent has significant financial impact and justifies a reasonably large investment in engineering of more water-efficient targets.

The designs in place still utilize a larger inventory of water than the minimum thickness one would calculate using the vapor-jet model. There appear to be more subtle phase change or density reduction phenomena in the targets that have yet to be fully understood. It can be shown that, at saturation temperatures, the likelihood of bubbles being formed in the bulk is insufficient to generate noticeable density reduction. However there is some superheating of the liquid region that is in upflow due to shear forces, reducing the size of a critical nucleus (one which will grow and survive without further energy input). The theory of radiation assisted nucleation has not been applied to the superheated water and particular radiations of interest here, nor have correlating measurements at elevated pressure and temperature and in the radiation field been carried out. The aim of this work is to gain some understanding of these phenomena and improve design of the targets through this understanding.

1.3 Summary of this work

A number of particle interactions and energy loss mechanisms are at work in the bombardment of water by protons. First, the various energy loss mechanisms in water will be discussed at a basic physics level. This will enable a discussion on the microstructure of particle tracks, historically first seen in a number of media including cloud chambers, photographic emulsions and bubble
chambers, and investigated and modeled to this day in terms of biological effects. Some exploration of the time history of particle tracks, including the non-equilibrium energy spectrum and equilibration times will be given. The discussion of energy loss and particle tracks will conclude with a definition of the energy terms useful in nucleation threshold calculations.

Fundamental thermodynamics will be covered with an eye to understanding the mechanisms of bulk nucleation on a sub-micron scale. The attainable superheats of pure substances, specifically water, will be developed theoretically. The theory of metastable liquids, including the characteristic times of a metastable state will be reviewed, along with experimental techniques and theories of cavitation thresholds. Coverage of these two concepts (microstructure of radiation interaction with matter and metastable state thermodynamics) will comprise the theoretical part of this exercise.

The development and first test of an apparatus for experimentally probing water of different types of pretreatment (such as previously proton bombarded and unbombarded), temperatures, pressures and under prompt bombardment by different forms of radiation will be presented. These results are correlated with theory to the extent possible. Through a validated theory of nucleation in water by various radiations at elevated pressures and temperatures, the effect of irradiation on net density/buoyancy and the thermal transport in the target can be calculated with confidence. A coherent picture of the probability of nucleation and boiling in the bulk, especially in the liquid upflow region, and its effect on target performance will be developed. Lower limits of desired operating pressure can be established, and are different, at least in some cases, than if cavitation in the bulk were neglected. Suggestions for appropriate operating modes and design criteria will be discussed in the conclusions.

The novel concepts explored and presented in this work are:

1. Integration of an existing body of nucleation theory to the applied literature on thermalhydraulics of liquid isotope targets;
2. Partial integration of two different bodies of literature on nucleation – from metastable (superheated) liquids and subcooled nucleation under tension;

3. The development of an automated system for measurement of characteristic metastable time constants of superheated liquid, portable enough to probe the changes in time constants when the apparatus is subjected to various forms of radiation;

4. First measurement of metastable characteristic times for pure water at elevated pressure and up to 60 K superheat;

5. The development and extension of a body of knowledge within the Nuclear Engineering Department at the University of Tennessee that is useful in a number of technologies currently being worked on in and around the university.
2.0 Energy loss

2.1 Interaction of energetic particles with matter

Protons lose energy as they pass through water by interacting with atomic electrons and, to a lesser extent, with nuclei. Proton-atom interactions (and for that matter electron-atom interactions as well) can further be classified into inelastic and elastic events. Inelastic nuclear reactions, resulting in a change of Z or A number, are important from an isotope production standpoint but do not contribute significantly to the energy loss picture. Typical cross sections for these reactions are many orders of magnitude below those for ionization and excitation. Brehmstrahlung, another inelastic nuclear process, does contribute somewhat to the energy loss picture, but at a level below 1% of the other inelastic processes. Nuclear reactions will not be discussed further except as a source of energetic neutrons.

Inelastic interactions of charged particles with atoms (ionizations and excitations) are the primary energy loss mechanism for protons (and other charged particles) down to about 10x the ionization threshold (a few hundred eV). Moreover, ionizations generate secondary electrons. The secondary electrons also lose energy through ionization, excitation, and elastic scattering off atoms. The equations governing the interactions of secondary electrons with atomic electrons differ from those for protons due only to mass and charge differences.

Elastic scattering of charged particles (both protons and secondary electrons) by atomic electrons and nuclei is also important. As the charged particle reaches the end of the track and is below the ionization threshold for water, elastic scattering of the particles is the only energy loss mechanism. Even several orders of magnitude above the ionization threshold, elastic scattering is the dominant mechanism. The elastic scattering cross section for protons on water exceeds excitation and ionization for proton energies below about 40 keV\textsuperscript{30}. The LET for electrons or protons when elastic scattering dominates is much lower than the LET at the Bragg peak, where
ionization dominates. However, because energy is coupled to the nucleus, this interaction can result in generating a very high LET secondary track, which is of particular interest when modeling nucleation. The various modes of charged particle energy loss/scattering are outlined in Figure 2.

Elastic scattering of neutrons by nuclei is also very important in this treatment. Neutrons are generated in an F-18 target from the isotope production reaction, O-18(p,n)F-18. The neutrons are generated with energies up to the proton energy minus the Q-value for this reaction, or about 8 MeV for an 11 MeV proton beam. The neutron scattering cross section (potential scattering) is relatively energy independent and a strong effect at epithermal and thermal neutron energies. Meanwhile the neutrons are also capable of delivering a large amount of energy to a nucleus, resulting in a very high LET particle.

In the next section, the fundamental equations of charged particle scattering will be developed. Limits on the size and energy density of hot centers for bulk nucleation will be defined in later sections. These limits require an understanding of density of energy deposition in areas of high LET, as well as some microstructure of that energy deposition. The physics of energy loss will enable the development of a flux per unit volume of sufficiently hot centers. The energy loss depends on the maximum energy transfer that is kinematically allowed, which is developed in the following section. Following that section, the flux rate of neutrons, cross section for neutron-nucleus interactions, and size and energy per unit volume of the resulting ions will be developed. In the last section of this chapter, the same quantities will be developed for direct proton nucleus interactions.

2.2 Ionization and excitation Losses – Rutherford, Bohr, Born and Bethe

Inelastic ionization and excitation losses are the predominant energy loss mechanism for charged particles for energies above the ionization threshold. For sufficiently energetic particles,
interaction with the electron can be approximated by interaction with an electron at rest. For this approximation to be valid, the incident particle velocity should be much larger than the electron velocity. The classical treatment of the interaction of two charged particles, one initially at rest, was done by Rutherford. In the center of mass frame, both charged particles are subject to Coulomb forces at the origin and will describe a hyperbolic orbit, regardless of whether the forces are attractive or repulsive. Angular momentum is conserved and identical in any non-rotating frame. It is determined by the impact parameter x, which is the distance between the two particle trajectories in the center of mass frame if they did not interact (straight line trajectories). In the center of mass frame, the finite angular momentum of each particle determines the recoil angle and eccentricity of the hyperbolic orbit. The impact parameter and the deflection angle in the center of mass are related as

\[ x = \frac{Zze^2}{M_0V^2} \cot \frac{\Theta}{2} \]  

(1)

where \( Z \) and \( z \) are the charges of the particles, \( V \) is the velocity of the incident particle in the laboratory frame, \( \Theta \) is the deflection angle in the center of mass frame, and \( M_0 \) is the reduced mass,

\[ M_0 = \frac{M_1M_2}{M_1+M_2} \]  

(2)

where \( M_1 \) and \( M_2 \) are the masses of the two particles being considered. In order for the units to be dimensionally consistent, this equation is only valid in c.g.s. units. Although this expression for the reduced mass has complete symmetry between particles, for purposes of the rest of this treatment \( M_1 \) is the incident particle mass, and \( M_2 \) is the mass of the particle initially at rest in the lab system.

Although there is no energy exchange in the center of mass system, in the lab system there is and the expression for the impact parameter above can be used to relate it to the energy.
Incident proton/ion/electron

Elastic atomic collisions
- Cross section: small until at energies below Born threshold
- WKB approximation
- Resulting particles: molecules at low (thermal and epithermal) energy
- Important for protons and electrons at low energies, not for energy loss, but structure

Inelastic electron collisions
- Hard Reactions
  - Cross section: moderate
  - Resulting particles: electrons
  - Always ionizing
  - Described by the Bethe-Bloch equation
  - Covered in Section 2.2 of this work

- Soft Reactions
  - Cross section: large
  - Significant below the Born threshold
  - Resulting particles: electrons, excited atoms and molecules
  - Includes ionizations, excitations
  - Rudd model for ionizations

Inelastic nuclear collisions
- Nuclear Reactions
  - Cross section: extremely small
  - Resulting particles: n, alpha, etc.

Brehmstrahlung
- Cross section: small
- Resulting particles: molecules at low (thermal and epithermal) energy, gammas

Figure 2 - Taxonomy of proton reactions
imparted to $M_2$. The differential Rutherford cross section can be expressed as

$$d\sigma = 2\pi x \, dx = \frac{2\pi Z^2 z^2 e^4}{M_2 V^2} \frac{dQ}{Q^2}$$

where $Q$ is the energy exchanged between incident and struck particles. Note that interactions in which large energy is transferred are unlikely owing to the $1/Q^2$ form of the differential cross section.

Bohr used the classical Rutherford scattering cross section to model the energy loss per unit path length of charged particles traversing matter. Bohr only took electrons into account. This is justified on several accounts. For one, the nuclear potential is screened by the electrons until within a few angstroms. Moreover, although the Rutherford scattering cross section for a given nucleus is higher than that for an individual electron by a factor of $Z^2$ owing to the charge of the nucleus, it is lower by a factor of approximately $0.511/(2^*Z*938)$ because of the difference in the masses of electrons and nuclei. The overall Rutherford cross section difference between electrons and nuclei of proton number $Z$ is then

$$\frac{0.511 \cdot Z^2}{2 \cdot Z \cdot 938} = 2.72 \times 10^{-3} \cdot Z$$

(4)

This number is much less than 1 for all physically realistic values of $Z$.

Knowing the cross section in terms of the energy transfer allows calculation of the expectation value of energy transfer to atomic electrons. This is

$$\sigma_{\text{stopping}} = \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q d\sigma$$

$$= \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q \frac{2\pi z^2 e^4}{m_e V^2} \frac{dQ}{Q^2}$$

$$= \int_{Q_{\text{min}}}^{Q_{\text{max}}} \frac{2\pi z^2 e^4}{Q m_e V^2} dQ$$

$$= \frac{2\pi z^2 e^4}{m_e V^2} \ln \frac{Q_{\text{max}}}{Q_{\text{min}}}$$

(5)
where \( m_e \) is the mass of the electron, and \( z \) is the charge of the bombarding particle. In order to be dimensionally consistent, the units used must be c.g.s. This expression has units of energy * area. In order to obtain energy loss per unit distance, it must be multiplied by the electron density, which is simply the atomic density times the \( Z \) number. The classical Bohr energy loss equation is

\[
\frac{-dE}{dx} = \frac{2\pi z^2 e^4}{m_e V^2} NZ \ln \frac{Q_{\text{max}}}{Q_{\text{min}}}
\]  

This form is essentially the same for all energy loss calculations of heavy charged particles passing through matter. Energy loss is proportional to electron number density, and inversely proportional to energy outside of the logarithm. Energy loss is also proportional to the square of the charge of the bombarding particle. Inside there is usually a log term, and it has as its argument a ratio of energies.

One way that various energy loss equations differ is on the forms used for the maximum and minimum energy transferred. The greatest difficulty arises from the latter. Classical kinematics allows us to establish the maximum energy transferred (this is covered in the next section). However, if the minimum energy transferred is allowed to be vanishingly small, this expression diverges. Bohr solved the problem by assuming a cutoff energy transfer associated with a maximum interaction time between the incident particle and the atomic electrons. The interaction time was also related to the impact parameter \( x \). If the interaction time was large with respect to the natural frequency that a non-displaced electron would oscillate in response to external forces, then it could not be treated as free. So for long interaction times, which correspond to large impact parameters and small energy transfers, no ionization could take place. The final form of Bohr’s classical energy loss formula is

\[
\frac{-dE}{dx} = \frac{4\pi z^2 e^4}{m_e V^2} NZ \ln \frac{1.123m_e V^3 M}{2\pi^2 ze^2 (M + m_e)}
\]
where \( \nu \) is a mean characteristic frequency of oscillation for all electrons in the atom in question and \( M \) is the mass of the incident particle.

There are weaknesses in the classical theory of energy loss. The minimum energy transfer is well below the ionization and excitation levels of the atom, at odds with quantum mechanics. This causes over-prediction of the energy loss. The quantum theory of scattering from a coulomb potential was developed by Born. The Born Approximation states that the incident particle velocity is large with respect to the K-electron velocity for the atoms in the medium. The threshold for this approximation

\[
\beta \approx \frac{Z}{137}
\]

is known as the Born threshold. The Born thresholds for the interactions of interest in this problem are tabulated in Table 1.

Clearly the validity of the Born Approximation, at least in the case of protons on oxygen, is severely limited. The assumption that the incident and scattered particles can be approximated by a plane wave is particularly unhelpful for low energy proton elastic scattering as might be seen with non-negligible frequency at the track end. However, electron and proton scattering on hydrogen nuclei and electron scattering on oxygen nuclei are well treated by the plane wave approximation for all energies of interest in this work.

Building on the Plane Wave Born Approximation, Bethe developed a quantum mechanical

**Table 1 - Born thresholds**

<table>
<thead>
<tr>
<th>Incident particle</th>
<th>Rest mass</th>
<th>Target nucleus ( Z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>511 keV/c^2</td>
<td>H 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27 eV/c^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.74 keV/c^2</td>
</tr>
<tr>
<td>Proton</td>
<td>938 MeV/c^2</td>
<td>H 18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 keV/c^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.20 MeV/c^2</td>
</tr>
</tbody>
</table>
treatment of ionization cross sections that remains a sufficiently powerful and simple tool for calculation of the LET for any particle. In his derivation, which takes into account interaction not only with the potential of the atom but also all the wave functions of the individual electrons, he shows that the minimum energy transfer can be replaced by the average ionization potential, which is an average of the binding energies of all the atomic electrons. The Bethe-Bloch equation for energy loss takes the form

\[ \frac{-dE}{dx} = \frac{4\pi e^4 z^2}{mv^2} NZ \ln \left( \frac{2mv^2}{I} \right) \] (9)

where \( e \) is elementary charge, \( z \) is the effective charge of the incident particle, \( m \) is the electron mass, \( v \) is the incident particle velocity, \( N \) is the density of the target particles, \( Z \) is the charge of the target nucleus, and \( I \) is the average ionization potential of the atom. The equation only applies if c.g.s. units are used owing to the specific dimensionality of charge in cgs units. The term effective charge refers to the fact that the incident ion, especially as it slows, can be less than fully ionized. The ionization potentials are typically tabulated in eV, so it is appropriate to convert the numerator of the natural log argument to eV as well. This formulation is valid down to approximately 10x the effective ionization potential of the material being bombarded. The adjusted ionization potential has been determined by Janni\textsuperscript{32} for both hydrogen and oxygen through an exhaustive survey of the literature on these experimental values. Janni uses 18.3 eV for hydrogen and 98.5 eV for oxygen. Once the ionization potentials are known for a given element, the ionization potential for the compound (water in our case) is derived using the Bragg rule for additivity:

\[ n \ln I_{adj} = \sum_i N_i Z_i \ln I_{adj-i} \] (10)

where \( n \) is the total electron density, \( N_i \) is the atomic density of each atom, and \( Z_i \) is the atomic number of each atom. Using the Bragg rule we obtain 70.34 eV, so the Bethe-Bloch equation is valid to about 700 eV. Further refinements are needed for relativistic particles, and are included
in more detailed forms of the Bethe equation. However the protons entering this problem are at only 15% of the speed of light, and all other particles are sub-relativistic as well. Relativistic corrections are therefore insignificant. Using this, and given a maximum energy transfer, one can quickly and roughly estimate energy loss per unit path length, or LET, for any of the particles considered herein.

2.3 Maximum energy transfer

In order to bound the energies, and therefore the LETs considered, it is important to estimate the maximum energy transfer for a number of free particle collisions that could happen in the target. Inelastic collisions will always result in recoil energies that are less than the elastic collisions. The kinematics of nonrelativistic elastic collisions are worked out in many texts\textsuperscript{33}. The laboratory velocity of a particle after collision that was initially at rest in the laboratory frame is

\[ V_2 = 2V \frac{M_0}{M_2} \cos \varphi \]  

where \( V_2 \) is the recoiling particle velocity, \( V \) is the bombarding particle velocity, \( M_2 \) is the target particle mass, and \( \varphi \) is the recoil angle in the laboratory frame. The recoil velocity is maximized when the recoil angle \( \varphi \) is 0. So the maximum velocity of a struck particle is

\[ V_2 = 2V \frac{M_0}{M_2} \]  

The maximum kinetic energy is

\[ T_{\text{max}} = \frac{1}{2} M_2 V_2^2 \]

\[ = \frac{1}{2} M_2 \left( \frac{2V M_0}{M_2} \right)^2 \]

\[ = 2V^2 \frac{M_0^2}{M_2} \]  

\[ = 2V^2 \frac{M_0}{M_2} \]  

\[ = 2V^2 \]  

\[ = 2V \]  

\[ = V \]  

17
The incident particle energy is

\[ T = \frac{1}{2} M_1 V^2 \]

or

\[ V^2 = \frac{2T}{M_1} \]  

(14)

Substituting to get \( T_{\text{max}} \) in terms of \( T \) yields

\[ T_{\text{max}} = 2 \frac{2T M_0^2}{M_1 M_2} \]

\[ = \frac{4M_1 M_2}{(M_1 + M_2)^2} T \]  

(15)

Using this equation, a table of estimated maximum energies can be generated (Table 2). For the maximum energy cases, one can also use the Bethe range-energy equation (or computational methods like SRIM) to estimate the maximum LET that will be seen in the resulting recoil particle track.

The LET calculations in Table 2 are calculated using SRIM 2003\textsuperscript{34}, which essentially employs versions of equation (9) plus elastic scattering to calculate stopping and range, and energy imparted to recoils. The notable reactions from the perspective of generating high-LET particles are elastic scattering of protons on O-18 atoms, and elastic scattering of neutrons on O-18 atoms. The max LET of a recoiling O-18 atom in water is at the maximum energy of 2.2 MeV. Similarly, the maximum LET noted for O-18 recoiling from a neutron event is at the maximum energy as well.

In addition to the clearly significant proton-oxygen and neutron-oxygen scattering, there are four other reactions of note. Proton-proton (elastic scattering of protons by hydrogen nuclei), and neutron-proton (elastic scattering of neutrons by hydrogen nuclei) are second-order processes, resulting in low energy proton tracks at a rate \( \ll 1 \) per incident proton. They will not be addressed further in this analysis. In the same sense, electron-electron reactions do not
Table 2 - Reactions, maximum energy transfers and resulting LETs

<table>
<thead>
<tr>
<th>Incident Particle</th>
<th>Max energy (MeV)</th>
<th>Rest mass (MeV)</th>
<th>Rest mass (MeV)</th>
<th>% transfer</th>
<th>Max resulting energy (MeV)</th>
<th>Max LET at or below max energy (MeV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton</td>
<td>11.0</td>
<td>938</td>
<td>938</td>
<td>100%</td>
<td>11.0</td>
<td>900</td>
</tr>
<tr>
<td>Electron</td>
<td>0.024</td>
<td>0.511</td>
<td>0.511</td>
<td>0.22%</td>
<td>0.024</td>
<td>N/A</td>
</tr>
<tr>
<td>Neutron</td>
<td>7.4</td>
<td>935</td>
<td>935</td>
<td>100%</td>
<td>7.4</td>
<td>900</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Target Particle</th>
<th>Proton</th>
<th>Electron</th>
<th>$^{18}$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max energy (MeV)</td>
<td>11.0</td>
<td>0.024</td>
<td>7.4</td>
</tr>
<tr>
<td>Rest mass (MeV)</td>
<td>938</td>
<td>0.511</td>
<td>16,854</td>
</tr>
<tr>
<td>Rest mass (MeV)</td>
<td>938</td>
<td>0.511</td>
<td>16,854</td>
</tr>
<tr>
<td>% transfer</td>
<td>100%</td>
<td>0.22%</td>
<td>20.0%</td>
</tr>
<tr>
<td>Max resulting energy (MeV)</td>
<td>11.0</td>
<td>0.024</td>
<td>2.20</td>
</tr>
<tr>
<td>Max LET at or below max energy (MeV/cm)</td>
<td>900</td>
<td>800</td>
<td>10,300</td>
</tr>
<tr>
<td>N/A</td>
<td>800</td>
<td>N/A</td>
<td>8,000</td>
</tr>
<tr>
<td>19.9%</td>
<td>N/A</td>
<td>1.47</td>
<td></td>
</tr>
</tbody>
</table>

Contribute significantly to microstructure of the type that would result in significant thermal spikes, and so only secondary electrons (directly from scattering of primary protons or elastically scattered atoms) will be accounted for.

The important high-LET events to account for are as follows:

1. The Bragg peak of the primary proton;
2. Energetic secondary electrons of significant LET (>100 MeV/cm in their Bragg peak);
3. Oxygen atoms scattered elastically by protons;
4. Oxygen atoms scattered elastically by neutrons.

The calculations of elastic scattering cross sections will be left to a later section. However the incident protons and the resulting particles from elastic scattering will lose energy primarily
through ionizations and excitations through mechanisms described in this section. Energetic secondary electrons will depend on the mechanics of this process as well.

## 2.4 Secondary electron spectra and fluence

The Bethe energy loss equation still does not take into account dielectric and screening effects that become important at low energy. Although some analytical models have been developed, the total ionization cross section at low energies is typically calculated by a fit to existing data. One such model is the Rudd model\(^3\).\(^5\)

However, even the Rudd model does not include the electron capture and loss processes that take place at low energy, nor excitation of the water molecules or other atomic species in the irradiated water. At proton energies around 100 keV in water, the total cross section for electron capture is within an order of magnitude of the ionization and excitation cross sections. This reduces the net charge of the protons as they slow.

Uehara et al.\(^3\)\(^6\) have calculated the important processes for proton energy loss in water vapor. Ionization of the water by protons and by hydrogen atoms has been calculated and compared to experimental data, with good correlation down to 1 keV. Excitation of water vapor by both particles has been treated in the same way, and again fit is good down to 1 keV. Finally, coupling between the two species (protons and hydrogen atoms) via electron capture by protons and electron loss by hydrogen were calculated.

When all of the above processes are taken into account, proton ionization of water remains the dominant process above 1 MeV. Note that the maximum energy transfer from a proton or hydrogen atom to an electron is .22%, so this would result in an electron energy of 24 keV at most. The resulting electron LET would be on the order of 120 MeV/cm\(^3\).\(^7\) Although this energy is clearly too small to create a thermal spike sufficient to nucleate in non-superheated water, it will be shown later that it is sufficient to induce nucleation in metastable water. It is appropriate to cut off calculations of rate and energy of secondary electrons, then, at 1 MeV proton energies. That

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\(^7\) For example, see references on energy loss in water.

---
being said, a rough estimate of the number of secondary electrons produced is the total energy lost by the proton (11 MeV) divided by the maximum energy transfer of 24 keV. This is 458 separate secondary electrons.

### 2.5 General elastic scattering of charged species

High-LET oxygen nuclei are created through two processes. One is elastic scattering of protons by nuclei. The basic classical development of a cross section for scattering of any charged particle by a nucleus, taking into account the screening of the nucleus by the atomic electrons, has been covered by Everhart\(^{38}\). The potential energy function is based on Coulombic repulsion of the bombarding ion and the nucleus of the atom, with an additional screening function to account for neutralization of the nuclear charge at large distances.

\[
V(r) = \frac{zZe^2}{r^2} F\left(\frac{r}{r_s}\right)
\]

(16)

Everhart’s screening function was exponential. As of 2001, the commonly used screening function was\(^{30,39}\)

\[
F\left(\frac{r}{r_s}\right) = 0.10 e^{-0.3r/r_s} + 0.55 e^{-1.2r/r_s} + 0.10 e^{-0.3r/r_s}
\]

(17)

The value of \(r_s\) then controls the shape of the screening function, and is called the screening radius. This is as developed by Thomas-Fermi\(^{12}\)

\[
r_s = 0.88534r_B \left( \frac{z^{2/3} + Z^{2/3}}{2} \right)^{1/2}
\]

(18)

This machinery was used by Mott and Massey\(^{40}\) to develop a classical scattering angle vs. impact parameter. This is found from

\[
\theta = \pi - 2 \int_{r_{\text{min}}}^{\infty} \frac{P}{\sqrt{1 - V(r)/T_{\text{cm}} - p^2/r^2}} dr
\]

(19)

where \(r_{\text{min}}\) is the distance of closest approach and is given by taking the root of
SRIM uses these same calculations for scattering of charged particles off of atoms in gases, liquids and solids. The primary difference is the ZBL screening function used, which is

\[ F\left(\frac{r}{r_s}\right) = 0.1818e^{-3.1\frac{r}{r_s}} + 0.5099e^{-0.9423\frac{r}{r_s}} + 0.2802e^{-0.4029\frac{r}{r_s}} + 0.02817e^{-0.2016\frac{r}{r_s}} \]  

(21)

The ZBL screening radius is also slightly different. Because of the ease of use of SRIM, it was used to provide Monte Carlo data generated for oxygen recoils in water.

Water was selected as a target material in SRIM from the standard library of materials. Density was not adjusted for higher temperature. Proton energy was 11 MeV. The ability to track every collision was enabled. All collisions are written to an output file called “collision.txt”. 10,000 protons were run in any one batch to keep the size of this file manageable. The file was then searched for hydrogen and oxygen recoils of any energy. The locations of the recoils were sorted into 20 depth groups (0.0075 cm thick), and 100 energy groups (80 eV wide). The highest energy group was 8 keV and above. This was repeated 5 times for a total of 50,000 incident protons. The total number of oxygen recoils of any energy was 628,239, or about 13 oxygen recoils per proton. But 411,786 of these (65.5%) were recoils in the first energy bin (less than 80 eV). Only 1909 oxygen recoils had energies above 7.2 keV, representing 0.30% of all oxygen recoils or 0.038 recoils per proton.

### 2.6 Elastic scattering of neutrons by oxygen nuclei

The elastic scattering of neutrons is dominated over a large range of energies by potential scattering\(^{41}\). This is simply hard sphere classical scattering of the nuclear potential. It is approximated by

\[ \sigma = 4\pi R^2 \]

\[ R \equiv 1.25 \times 10^{-13} A^{\frac{1}{3}} \text{cm} \]

(22)
Using this form, the potential scattering is 1.346 barn, and is independent of energy.

The experimental elastic cross section for neutrons on oxygen has been published for a number of neutron energies. Moreover, a semi-empirical fit of the existing data to the various measurements (Evaluated Nuclear Data File or ENDF) has been calculated and is available on the web. Using ENDF, it is clear that the potential scattering evaluated above is below the actual potential scattering cross section of roughly 3.85 barns. A plot of the ENDF function over an energy range from $10^{-5}$ eV to 100 MeV is shown in Figure 3.

For the energies above 100 keV where the maximum energy transfer of the neutron to the oxygen nucleus is expected to result in the highest LET, the cross section has a lot of fine structure. However relative to the other reactions in the target, this reaction is highly unlikely. For the purposes of estimating an upper limit of the potential of neutrons to sponsor nucleations, an energy independent cross section of 3.85 barns will be used.

---

**Figure 3 - ENDF cross section for neutron scattering on Oxygen**
2.7 A coarse spectrum of radiations in the target water

It is possible using the electron information from SRIM, elastic recoil information also from SRIM, neutron data from earlier work, and O-18 recoil calculations based on potential scattering to determine the various charged species in the target pet proton, and the energy each particle imparts in the maximum condition (at its individual track end). These numbers are tabulated in Table 3.

What becomes clear is for a maximum LET under 900 MeV/cm there are over 400 individual small track ends or localized depositions of energy from the original proton, numerous secondary electrons, and a handful of O-18 recoils from the protons. There is another handful (approximately 4 per original proton) of elastic oxygen recoils from the proton track that have an LET above 900, but less than 8000 MeV/cm. Finally, all of the highest LET events are rather unlikely. O-18 recoils from the primary proton, or from neutrons in the target environment, total only .0382 events per primary proton. In all cases, localization is in a volume of a few microns.

In terms of total energy deposited in a sphere of diameter 2 microns, there are over 400 events per proton that deposit about 200 keV (or about 0.032 picojoules). There are about 4 events that deposit 10 times that amount, or 2 MeV (.320 picojoules) in the same 2 micron volume.

Estimating that all the O-18 recoils from protons above 7.2 keV are at the maximum energy transfer of 2.2 MeV (which is extremely optimistic) there are about 0.038 events per proton over 2 MeV deposited.

Table 3 - Frequency of different reactions for each proton

<table>
<thead>
<tr>
<th>Particle</th>
<th>Low E (eV)</th>
<th>High E (eV)</th>
<th>LET (MeV/cm)</th>
<th>number per neutron</th>
<th>number per proton</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>proton</td>
<td>0</td>
<td>11,000,000</td>
<td>843</td>
<td>1.00000</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>electron</td>
<td>0</td>
<td>24,000</td>
<td>800</td>
<td>approx 450</td>
<td>SRIM</td>
<td></td>
</tr>
<tr>
<td>O-18 recoils</td>
<td>0</td>
<td>80</td>
<td>&lt;600</td>
<td>8.24000</td>
<td>SRIM</td>
<td></td>
</tr>
<tr>
<td>O-18 recoils</td>
<td>80</td>
<td>7,200</td>
<td>1550</td>
<td>4.28200</td>
<td>SRIM</td>
<td></td>
</tr>
<tr>
<td>O-18 recoils</td>
<td>7,200</td>
<td>2,200,000</td>
<td>10,300</td>
<td>0.03800</td>
<td>SRIM</td>
<td></td>
</tr>
<tr>
<td>neutrons</td>
<td>7.200</td>
<td>2,200,000</td>
<td>10,300</td>
<td>0.00160</td>
<td>Measured</td>
<td></td>
</tr>
<tr>
<td>O-18 recoils</td>
<td>0</td>
<td>1,470,000</td>
<td>8000</td>
<td>0.129</td>
<td>0.00021</td>
<td>Potential scattering</td>
</tr>
</tbody>
</table>
The most intensely bombarded region is also subject to the most superheat in the existing vapor jet model. It is approximately 1 mm deep by 1 cm height and width. This 0.1 cc volume has $3.75 \times 10^{14}$ protons per second entering. The flux rate of energetic regions for the various energies is listed in Table 4.

**Table 4 - Volumetric flux rate of events classified by energy**

<table>
<thead>
<tr>
<th>Energy</th>
<th>Flux rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MeV)</td>
<td>(cm$^3$sec$^{-1}$)</td>
</tr>
<tr>
<td>≤0.200</td>
<td>$1.5 \times 10^{19}$</td>
</tr>
<tr>
<td>0.200 to 2.0</td>
<td>$1.5 \times 10^{18}$</td>
</tr>
<tr>
<td>≥2.0</td>
<td>$1.4 \times 10^{14}$</td>
</tr>
</tbody>
</table>
3.0 Particle tracks

3.1 Background on bubble chambers, previous work

Initial experiments on nucleation of radiation in liquids were performed by Donald Glaser\textsuperscript{43} starting in the 1950s. His experiments with the bubble chamber led to a Nobel Prize in Physics in 1960. He wanted the radiation to introduce the only instability in an otherwise stable liquid (initially diethyl ether). In order to do this he dropped the pressure in tanks of varying liquids from above saturation pressure to below rapidly. When this was done he saw stability in the absence of radiation for periods of seconds. The time between rapid depressurization and boiling followed a Poisson distribution, and he surmised that external radiations were the triggering mechanism for these events.

Bubble chambers are almost exclusively operated in this way, with mechanical or ultrasonic methods used to drop the pressure rapidly to pressures well below the saturation pressure. In enriched water targets we operate at high pressures to raise temperature gradients at the walls and remove heat more quickly. In the present treatment the bubble chamber theory is used but modifications are made to refer to external pressures.

3.2 Track structure

The energy loss picture outlined in the Bethe equation is a smooth one. However the physics leading to that equation is clearly based on individual scattering events. The Bethe equation relies upon an assumption called the “continuous slowing down” approximation. However, the observable fine structure of radiation tracks in solids, gels and bubble chambers confirms that the energy loss is anything but smooth.

A nomenclature for the various structures in a particle track (known as track entities) has emerged over time. The various track entities are classified qualitatively by their shapes, but
quantitatively by the amount of energy deposited and their distance scales.\textsuperscript{44} A “spur” is the most common track entity, and represents a secondary electron track of 6 to 100 eV energy. A “blob” is a quasi-spherical distribution of ionizations created by a more energetic secondary particle, usually in the range of 100 eV to 500 eV. The highest energy track entities are “short tracks” which have a distinct and fairly linear trajectory away from the main track, and correspond to secondaries of 500 to 5000 eV.

The track of a charged particle is also divided into 2 regions in the direction transverse to the primary particle velocity. The core is a region filled with the energy deposition of the spurs. The range of these electrons and the radius of the core for an 11 MeV proton is between 1 and 2 nanometers. The penumbra contains tracks all the way up to the energy of short tracks, and is of a dimension on the level of microns in diameter.

3.3 Track development and time structure

The formation of a radiation track has several distinct time regimes. Three are worth mentioning in the context of this work. The first phase is the transport of the primary particle to the end of its track, sometimes referred to as the stopping time. By using kinetic energy and range data from SRIM, the stopping time for an 11 MeV proton in water can be calculated. It is $4.5 \times 10^{-11}$ seconds.

The second phase to consider is the transport of all of the secondary particles. These are formed much faster than the transport of the initial ion, along the lines of $10^{-16}$ seconds. In essence, they are part of the initial, unthermalized track formation.

The third phase is the thermalization of the core. It turns out that the concept of separated penumbras or cores is somewhat inappropriate. A 1 cm diameter area in the target is bombarded with $4.77 \times 10^{14}$ protons per second. This 1 cm diameter area is $2.5 \times 10^{7}$ times larger than a 2 micron core. Even assuming some ideal packing density of tracks, any given core would be re-irradiated $1.91 \times 10^{7}$ times per second, or every 52 ns.
West (following Seitz) observes that the time required to lose heat from a sensitive volume is calculated as

\[ t(r) \leq \frac{r^2}{4D} \]  

(23)

where \( r \) is the radius of the bubble or sensitive volume in meters, and \( D \) is the thermal diffusivity.

For a 2 micron core (also interestingly the approximate dimension of a bubble nucleus as shown in following chapters), the characteristic time is 1.45 µs. In that time, based on the 52 ns between overlapping irradiations calculated above, 28 additional protons will have passed through the volume resulting in overlapping cores being generated before thermalization of the first core has taken place.

Because of thermalization times out to the microsecond range, individual thermal spikes are not anticipated as one might see in a classical bubble chamber experiment. Nevertheless, nonequilibrium localized energy distributions of water molecules and ionized species will be created at the rate of between \( 10^{14} \) and \( 10^{18} \) cm\(^{-3} \) sec\(^{-1} \). The additional energy in these localized regions cannot be thought of in thermal terms. Moreover any one of the spurs is not sufficiently energetic to cause nucleation in a classical view of a uniform liquid. However as will be seen in following chapters, spurs, and parts of blobs and short tracks have a physical size on the order of a vapor nucleus that is large enough to grow and evolve into a second stable phase. And metastable liquids are sufficiently ready to nucleate that the case can be made that even these small amounts of energy deposition can carry pre-embryonic vapor nuclei into the region where they will grow to become macroscopic bubbles.
4.0 Nucleation theory in metastable liquids

4.1 Overview

The thermodynamics that we are interested in are single phase systems that are pushed into the creation of a second phase by the addition of energy via energetic particles. Before developing this non-equilibrium picture, we will first review equilibrium conditions of stable two-phase systems, and unstable or better, metastable systems. In metastable fluid systems, the system is composed of a single phase, but this phase is thermodynamically less favorable than another phase of the same system. We will also develop the absolute limit of stability of a single phase. At this limit (minimum entropy, the spinodal point) the second phase will be created due to any local, microscopic fluctuation of density.

If one follows the isothermic line for any equation of state in PV space, one will see a section of that line inside the vapor dome where \( \frac{\partial P}{\partial V} \) is positive. This is a physically unstable condition.

Pressure (and the energy density) in any volume of the fluid increases if that volume increases. If this volume is in equilibrium with a reservoir (the surrounding fluid) at the same pressure and temperature, then the volume will do PV work on its surroundings and expand. This has the effect then of a non-restorative force at the boundary of the volume, and the fluid will continue to move to a lower density unless and until \( \frac{\partial P}{\partial V} \) becomes negative again. However for a liquid at temperatures above the boiling point, there are regions on the isotherm that do have a negative slope. These are metastable regions. The threshold of total instability is the point where \( \frac{\partial P}{\partial V} \) =0, and is referred to as the spinodal point. A PV curve for water is shown in Figure 4.
A metastable state can be characterized by its characteristic duration. Intrinsically stable states, by definition, can remain in that state indefinitely. Intrinsically unstable states, by definition, can not exist for any period of time. Metastable states have a finite, non-zero characteristic time.

The characteristic time of a metastable state is determined by the comparison of the size of typical energy fluctuations in the single phase to the energy required to create a sustainable nucleus of the preferred phase. This comparison, in turn, leads to a flux rate of nuclei, and that to a characteristic time. Addition of energy to the system via energetic particles is manifested in additional critical nuclei, and a change in the flux rate. Because the survival time of the state is tied to this flux rate, bombardment of the single metastable phase will change the characteristic time.

### 4.2 Equilibrium conditions of a two-phase system

Equilibrium arguments proceed from conservation of energy (the first law of thermodynamics), mass and volume, and maximization of entropy at equilibrium (the second law of
thermodynamics). We consider a single fixed volume, isolated system, divided into two subsystems. Each subsystem represents one phase of the material. Energy and mass can flow between the systems freely, and the boundary between the phases can move. State variables such as temperature, pressure, etc. may be different initially between the phases. The state variables for each phase are denoted by a superscript I or II.

\[ U^I, T^I, P^I, V^I, N^I \quad \text{and} \quad U^{II}, T^{II}, P^{II}, V^{II}, N^{II} \]

Conservation of mass, energy and volume indicate that

\[
N = N^I + N^{II} \\
U = U^I + U^{II} \\
V = V^I + V^{II}
\]

And therefore for any change in the system

\[
dN^I = -dN^{II} \\
dU^I = -dU^{II} \quad \text{(25)} \\
dV^I = -dV^{II}
\]

Entropy is not conserved. However, it is extensive. Therefore

\[
dS = dS^I + dS^{II} \quad \text{(26)}
\]

The change in entropy of either subsystem is

\[
dS^I = \left( \frac{\partial S^I}{\partial U^I} \right)_{V^I, N^I} dU^I + \left( \frac{\partial S^I}{\partial V^I} \right)_{U^I, N^I} dV^I + \left( \frac{\partial S^I}{\partial N^I} \right)_{V^I, U^I} dN^I \\
= \frac{1}{T^I} dU^I + \frac{P^I}{T^I} dV^I - \mu^I dN^I \quad \text{(27)}
\]

31
where $\mu^i$ is the chemical potential of each phase, and employing in the second step Maxwell identities. Summing the two entropies and using the conservation of mass, volume and energy above,

$$dS = dS^I + dS^II = \left(\frac{1}{T^I} - \frac{1}{T^{II}}\right) dU^I + \left(\frac{P^I}{T^I} - \frac{P^{II}}{T^{II}}\right) dV^I - \left(\frac{\mu^I}{T^I} - \frac{\mu^{II}}{T^{II}}\right) dN^I$$ \hspace{1cm} (28)

At equilibrium, by the second law, $dS$ must be zero for any incremental change in energy, volume or mass. Therefore,

$$T^I = T^{II}$$

$$P^I = P^{II}$$

$$\mu^I = \mu^{II}$$ \hspace{1cm} (29)

for vapor-liquid equilibria. These useful equilibrium conditions will be used from here forward.

The internal energy for any system or component is

$$U = TS - PV + \mu N$$ \hspace{1cm} (30)

In the equilibrium version of the pressurized water system we are describing, temperature and (as long as there is no vapor bubble yet) pressure are constant. It is useful to work with the Gibbs free energy when the problem has fixed temperature and pressure. We have

$$G \equiv U + PV - TS$$ \hspace{1cm} (31)

However for a closed system the energy balance is

$$\frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt}$$ \hspace{1cm} (32)

For no heat added, and constant pressure, this reduces to

$$\frac{dU}{dt} = -\frac{d}{dt}(PV)$$ \hspace{1cm} (33)

So taking the time derivative of Gibbs free energy one has
\[
\frac{dG}{dt} = \frac{dU}{dt} + \frac{d}{dt}(PV) - \frac{d}{dt}(TS) \\
= -\frac{d}{dt}(PV) + \frac{d}{dt}(PV) - \frac{d}{dt}(TS) \\
= -T \frac{dS}{dt}
\]  

(34)

The second law of thermodynamics holds that entropy change is zero at equilibrium (entropy is maximized) so,

\[
\frac{dG}{dt} = 0
\]

(35)

Moreover, since entropy is maximized, Gibbs free energy is at a minimum, or

\[
d^2G > 0
\]

(36)

This essential stability criterion, that Gibbs free energy is minimized, leads to two other stability criteria\(^45\). They are the thermal stability criterion

\[
C_v > 0
\]

(37)

And the mechanical stability criterion

\[
\left. \frac{\partial P}{\partial V} \right|_T < 0
\]

(38)

This is simply a restatement of the qualitative stability limits described at the beginning of this chapter.

### 4.2.1 Spinodal limits of water

The spinodal limits of a fluid can be calculated directly using whatever equation of state is selected as the most appropriate. Two will be presented here. The Redlich-Kwong equation of state is:
\[ P = \frac{RT}{v-b} - \frac{aT^{-\gamma}}{v(v+b)} \quad (39) \]

where \( a \) and \( b \) are the van der Waals constants for the material in question. The expressions for the Redlich-Kwong spinodal limit have been derived by Debenedetti. They are parameterized in reduced density, \( \rho_r = \rho / \rho_{\text{crit}} \). They are

\[
T_r = 1.1804 \left[ \rho_r \left( 2 + 0.2599 \rho_r \right) \left( \frac{1 - 0.2599 \rho_r}{1 + 0.2599 \rho_r} \right)^2 \right]^{\frac{1}{\gamma}} \quad (40)
\]

and

\[
P_r = 3.5412 \left[ \frac{\rho_r^\gamma}{2 + 0.2599 \rho_r} \right]^{\frac{\gamma}{\gamma-1}} \left( \frac{1 + 0.2599 \rho_r}{1 - 0.2599 \rho_r} \right)^{\frac{\gamma-1}{\gamma}} \times \left( \frac{1 - 0.5874 \rho_r}{1 + 0.5874 \rho_r} \right) \quad (41)
\]

The Peng-Robinson equation of state is

\[
P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (42)
\]

where \( a \) in this case is defined as

\[
a = a_c \left[ 1 + K \left( 1 - T_r^{\frac{1}{\gamma}} \right) \right]^2 = \alpha(T_r)a_c \quad (43)
\]

and

\[
K = 0.37464 + 1.54226 \omega - 0.2699 \omega^2 \quad (44)
\]

where \( a_c \) is the value of the van der Waals constant \( a \) at the critical point, and \( T_r \) is the reduced temperature \( (T/T_{\text{crit}}) \). The acentric factor, \( \omega \), is characteristic of the molecule, and represents the deviation of that molecule from sphericity. The \( \omega \) for water is 0.344, and \( K \) for water is 0.8732.
The expressions for the Peng-Robinson spinodal limit are easier to calculate using the reduced specific volume, \( v_r = v/v_{\text{crit}} \). The expression for the reduced temperature is

\[
T_r = \frac{2Z_c \alpha a_r \left( \left( v_r^2 - b_r^2 \right) \left( v_r - b_r \right) \right)}{\left[ v_r (v_r + b_r) + b_r \left( v_r - b_r \right) \right]^2}
\]

(45)

where

\[
Z_c = \frac{P_c v_c}{R T_c} = 0.2345
\]

(46)

is the critical compressibility of water,

\[
a_r = \frac{0.45724}{Z_c^2}
\]

(47)

is the reduced value for \( a \), and

\[
b_r = \frac{0.07780}{Z_c}
\]

(48)

is the reduced value for \( b \).

Terms containing \( T \) can be collected on one side, and for every value of \( v_r \) the matching value of \( T_r \) can be found through iterative methods. (There is a closed solution, although it was not employed in the calculations below.) Once \( T_r \) is known, \( P_r \) is calculated from the equation of state.

\[
P_r = \frac{T_r}{Z_c \left( v_r - b_r \right)} - \frac{\alpha (T_r) a_r}{v_r^2 + 2b_r v_r - b_r^2}
\]

(49)

The Redlich-Kwong and Peng-Robinson spinodal curves are compared with the binodal curve (see Table 5 and Figure 5). Note that the tolerable amount of superheat (temperature difference between the saturation temperature or boiling point at a given pressure, and the spinodal limit)
Table 5 - Stability limits of water for various pressures and EOS

<table>
<thead>
<tr>
<th>Press. (psia)</th>
<th>Temp. (C)</th>
<th>Press. (psia)</th>
<th>Temp. (C)</th>
<th>Press. (psia)</th>
<th>Temp. (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>100.0</td>
<td>12.74</td>
<td>283.40</td>
<td>46.79</td>
<td>339</td>
</tr>
<tr>
<td>100</td>
<td>164.1</td>
<td>100.01</td>
<td>285.13</td>
<td>161.67</td>
<td>340</td>
</tr>
<tr>
<td>300</td>
<td>214.2</td>
<td>296.50</td>
<td>289.07</td>
<td>275.28</td>
<td>341</td>
</tr>
<tr>
<td>600</td>
<td>252.4</td>
<td>610.99</td>
<td>295.59</td>
<td>387.60</td>
<td>342</td>
</tr>
<tr>
<td>3208</td>
<td>374.0</td>
<td></td>
<td></td>
<td>498.62</td>
<td>343</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>608.35</td>
<td>344</td>
</tr>
</tbody>
</table>

The foregoing thermodynamics are for steady state conditions, and presume no local, time-varying fluctuation of energy. This model, then, does not offer any description of how the preferred state is created, over what time scales, and in what conditions. In practice, liquids in the metastable state can remain in that state for a limited amount of time before undergoing a transition into the energetically favored state. The characteristic time for such a transition is developed below, first for the case where no external radiation sponsors nucleation. The topic of additional (higher) nucleation rates due to external radiation is addressed later.

The following theory of homogeneous nucleation in superheated liquids is covered by several authors. Real fluids, whether metastable or not, are not composed of a bulk phase of homogeneous and uniform density. Rather, there are always local variations in density, and in the liquid phase these variations can reach and go below vapor densities on some microscopic scale. The reason that a large number of these local variations (called embryos) do not grow into a stable second phase (macroscopic bubbles) is that there are stability limits on their growth.

The minimum reversible work required to form an embryo of \( n \) molecules is

\[
W_{\text{rev}} = \sigma A + (P_{\text{ext}} - P_{\text{int}})V + n(\mu_{\text{int}} - \mu_{\text{ext}})
\]

(50)
where $A$ is the surface area of the embryo and $V$ is the volume of the embryo. Including expressions for these one finds

$$W_{rev} = 4\pi r^2 \sigma + \frac{4\pi r^3}{3} (P_{ext} - P_{int}) + n(\mu_{int} - \mu_{ext})$$  \hspace{1cm} (51)$$

For an embryo in equilibrium with the bulk, several additional conditions are placed. Temperature inside and outside the embryo are identical, as are chemical potentials. In that case the reversible energy reduces to

$$W_{rev} = 4\pi r^2 \sigma + \frac{4\pi r^3}{3} (P_{ext} - P_{int})$$  \hspace{1cm} (52)$$

Pressures should be equal between the phases, but this is not the case with a bubble in equilibrium with the bulk. There exists a force balance between surface tension and the external pressures, which work to collapse the bubble, and internal pressure which works to expand the bubble. This balance of forces is referred to as the Seitz condition.
For some finite internal pressure greater than the pressure in the bulk, this energy is positive for small radii, but becomes negative for larger radii. The case for water at saturation conditions at 300 psia (2.07 MPa) and a variety of embryo internal pressures is plotted in Figure 6. The three curves represent embryos with internal pressures at 10, 20, and 30 kPa above the bulk/saturation pressure.

Clearly for a given internal pressure there is a critical radius above which the bubble will grow and survive, and below which the bubble will collapse in upon itself. At that critical radius, the first derivative of energy with respect to radius vanishes.

Returning now to the mechanical equilibrium case, where the vapor/liquid boundary is force balanced, the pressure forces are easy to calculate. They are simply pressure times area:

$$\vec{F}_{\text{pint}} = P_{\text{int}} 4\pi r^2 \hat{r}$$

(53)

Similarly,

$$\vec{F}_{\text{pext}} = -P_{\text{ext}} 4\pi r^2 \hat{r}$$

(54)

where signs are kept in line with forces acting in the positive r direction. It is a little more complex to calculate the surface tension forces. Surface tension is a reduction in the energy of the surface proportional to surface area. Therefore,

$$dE = -\sigma dA$$

(55)

Working to reconstitute all forces in terms of r,

$$dE = -\sigma dA = -\sigma \frac{dA}{dr} dr$$

$$\frac{dA}{dr} = \frac{d}{dr} 4\pi r^2 = 8\pi r$$

$$dE = -\sigma 8\pi r dr$$

(56)

and expressing in units of force,
At any radius, these forces are balanced or the bubble grows or shrinks. For equilibrium,

\[
\frac{dE}{dr} = F_{st} = -\sigma 8\pi r \hat{r} \tag{57}
\]

This can be rewritten more simply in terms of pressures by dividing through by \( r \). Then the surface tension becomes the basis of another pressure term, and for a static bubble

\[
P_{\text{int}} - P_{\text{ext}} = \frac{2\sigma}{r} = 0 \tag{59}
\]

or

\[
P_{\text{int}} - P_{\text{ext}} = \frac{2\sigma}{r} \tag{60}
\]
If the left hand side of this equation is greater than zero, the bubble grows. This is the expression for the Seitz condition. The same condition can be derived by taking the derivative of $W$ with respect to radius, and setting it equal to zero.

Applying the Seitz condition to the energy of embryo formation (equation (52)) provides

$$W_{rev} = 4\pi r^2 \sigma + \frac{4\pi r^3}{3}(P_{ext} - P_{int})$$

$$= 4\pi r^2 \sigma + \frac{4\pi r^3}{3}\left(-\frac{2\sigma}{r}\right)$$

$$= 4\pi r^2 \sigma \left(1 - \frac{2}{3}\right)$$

$$= \frac{4\pi r^2 \sigma}{3}$$

$$= W_{crit}$$

(61)

This is the minimum energy required to create a critical nucleus of the given size that is in mechanical and thermal equilibrium with the bulk phase. It describes the locus of maxima of the curves in the preceding graph.

Starting with the full, non-equilibrium picture of equation (51), Debenedetti expands the energy around the critical nucleus radius to get the following form of the minimum energy

$$W_{rev} = \frac{4\pi (r_{crit})^2 \sigma}{3} - 4\pi \sigma (r - r_{crit})^2 \left[1 - \frac{1}{3}\left(1 - \frac{P_{ext}}{P_{vap}}\right)\right]$$

$$= \frac{4\pi (r_{crit})^2 \sigma}{3} \left[1 - 3B \left(\frac{r - r_{crit}}{r_{crit}}\right)^2\right]$$

(62)

$$= W_{crit} \left[1 - 3B \left(\frac{r - r_{crit}}{r_{crit}}\right)^2\right]$$

where
Unless otherwise specified, this is the minimum energy expression that will be used herein.

If the embryo is in unstable equilibrium with the superheated bulk, the pressure inside the embryo can be approximated by the saturation vapor pressure associated with the superheat temperature. In the equation above, \( P_{\text{crit}} \) can be replaced by \( P_{\text{vap}} \), and \( r_{\text{crit}} \) can be calculated via the Seitz condition. Rewriting the Seitz condition we have

\[
r_{\text{crit}} = \frac{2\sigma}{P_{\text{vap}} - P_{\text{ext}}} \tag{64}
\]

and

\[
W_{\text{rev}} = \frac{4\pi}{3} \left( \frac{r_{\text{crit}}}{2\sigma} \right)^2 \left[ 1 - 3B \left( \frac{r - r_{\text{crit}}}{r_{\text{crit}}} \right)^2 \right] \\
= \frac{4\pi\sigma}{3} \left( \frac{2\sigma}{P_{\text{vap}} - P_{\text{ext}}} \right)^2 \left[ 1 - 3B \left( \frac{r - r_{\text{crit}}}{r_{\text{crit}}} \right)^2 \right] \\
= \frac{16\pi\sigma^3}{3 \left( P_{\text{vap}} - P_{\text{ext}} \right)^2} \left[ 1 - 3B \left( \frac{r - r_{\text{crit}}}{r_{\text{crit}}} \right)^2 \right] \tag{65}
\]

This expression can be rewritten in terms of the number of molecules in the embryo. However, simply replacing \( r \) and \( r_{\text{crit}} \) with expressions for \( n \) and \( n_{\text{crit}} \) makes for a rather messy parameterization on the variable \( n \). It helps to rewrite the radial part of equation (65)

\[
\frac{r - r_{\text{crit}}}{r_{\text{crit}}} = \frac{r}{r_{\text{crit}}} - 1 \tag{66}
\]

The number of molecules and the radius are related by

\[
n = \frac{4}{3} \pi r^3 \cdot \rho \tag{67}
\]
where \( \rho \) is the density of molecules in a saturated vapor at equilibrium conditions. Then equation (66) becomes

\[
\frac{r - r_{\text{crit}}}{r_{\text{crit}}} = \left( \frac{n}{n_{\text{crit}}} \right)^{\frac{1}{3}} - 1 \tag{68}
\]

To remove the 1/3 power from the right hand side, one may perform a Taylor expansion of that term for \( n \) close to \( n_{\text{crit}} \). The first three terms are

\[
\left( \frac{n}{n_{\text{crit}}} \right)^{\frac{1}{3}} \equiv \left( \frac{n_{\text{crit}}}{n_{\text{crit}}} \right)^{\frac{1}{3}} + \frac{1}{3} \left( \frac{n - n_{\text{crit}}}{n_{\text{crit}}} \right) - \frac{2}{18} \left( \frac{n - n_{\text{crit}}}{n_{\text{crit}}} \right)^2 \tag{69}
\]

since

\[
\frac{n - n_{\text{crit}}}{n_{\text{crit}}} \ll 1 \tag{70}
\]

Even the third term is insignificant and the substitution then becomes

\[
\frac{r - r_{\text{crit}}}{r_{\text{crit}}} = \left( \frac{n}{n_{\text{crit}}} \right)^{\frac{1}{3}} - 1 \equiv 1 + \frac{1}{3} \left( \frac{n - n_{\text{crit}}}{n_{\text{crit}}} \right) - 1 \tag{71}
\]

The reversible work of embryo formation for an embryo near critical size is

\[
W_{\text{rev}}(n) = \frac{16\pi\sigma^3}{3(P_{\text{vap}} - P_{\text{ext}})} \left[ 1 - \frac{B}{3} \left( \frac{n - n_{\text{crit}}}{n_{\text{crit}}} \right)^2 \right] \tag{72}
\]
4.2.2 Alternate models of vapor nucleus energy of formation

The reversible energy of nucleus formation described above is far from the only established model. In particular, the model ignores some of the detailed terms that may be important in some regimes of liquid behavior. One model used by West (after Riepe and Hahn) is to calculate the various energy terms required to form a bubble of the critical radius from the liquid.

In this model there are five terms. The first is the surface energy stored at a vapor/water interface. This is simply the area of the outside of the bubble, times the surface tension. The second is the work done to expand against the externally imposed pressure field to the given radius, and is the volume of the bubble times the pressure. Third is the enthalpy of evaporation of the vapor filling the bubble. These terms are static energy terms, and do not depend on the rate of expansion of the bubble. West (whose mathematical model is aimed explicitly at the situation where the external pressure is large and negative, and where the incident particle flux is so low that each reaction event is caused by the energy deposited by one particle only) includes two other terms for the acceleration and viscous losses of the displaced liquid assuming that the bubble expands at radial velocity in a time determined in part by the cooling of the liquid through conduction, referred to as the relaxation time, \( \tau \). The equations for the terms (named \( W_1 \) through \( W_5 \)) are tabulated below.

\[
egin{align*}
W_1 &= 4\pi r^2 \sigma \\
W_2 &= \frac{4}{3} \pi r^3 P_{\text{ext}} \\
W_3 &= \frac{4}{3} \pi r^3 \rho H \\
W_4 &= 32\pi D^2 \rho_l r \\
W_5 &= 64\pi \eta D r
\end{align*}
\]

where \( \sigma \) is the surface tension, \( \rho \) is the vapor density, \( H \) is the mass heat of vaporization, \( D \) is the thermal diffusivity \( (k/\rho C_p) \), \( \rho_l \) is the liquid density, and \( \eta \) is the viscosity.
This model generates a rather large term $W_3$ for the pressures encountered in a water target. This $W_3$ is in turn dominated by the $PV$ work required to expand the vapor bubble against the surrounding liquid. In that the systems probed here are severely superheated, the theory that follows will use the Debenedetti energy of formation. The theory of that energy picture is that the vapor nuclei are born of thermal fluctuations of the fluid. Therefore the $PV$ work needed to create that void is provided by the momentary assembly of energetic particles in a substantially less dense microvolume.

The data along the lines of study of West, Riepe and Hahn support the fuller view of the total energetics required for embryo formation but in systems that are not deeply penetrant into the superheated region. The Debenedetti energy formulation appears to have experimental justification for deeply superheated systems. The current work will not illuminate which models are more appropriate in the intermediate superheat case. However, the apparatus and methods developed in the latter part of this work may be well suited to probing where the two models overlap well.

### 4.2.3 Number density of critical and near critical nuclei

Returning to the energy of formation used by Debenedetti, the population of vapor nuclei in thermal equilibrium with the bulk is determined by Boltzmann statistics, and the number distribution will follow the conventional form of

$$N(n) = N_{tot} \exp \left( - \frac{W_{rev}(n)}{kT} \right)$$

$$= N_{tot} \exp \left( - \frac{16\pi \sigma^3}{3kT(P_{vap} - P_{ext})^2} \left[ 1 - \frac{B}{3} \left( \frac{n - n_{crit}}{n_{crit}} \right)^2 \right] \right)$$

where $N_{tot}$ is the total number of molecules in the system. The argument of the exponent is very large negative for the kinds of temperatures and pressures that are of interest in fluoride targets. Therefore it is convenient to split the expression in the following form
For example at a pressure of 300 psia (2.068 MPa), and a superheat temperature of 96 K above saturation (583 K vs. saturation temperature of 487 K), the vapor pressure (and the pressure inside a critical nucleus) is 9.87 MPa, or 7.80 MPa higher than the bulk. Even at these extreme conditions, the ratio of the energy of the nucleus to $kT$ is 1027, and the first exponential function above evaluates to approximately $10^{-446}$. So critical nuclei, even at a superheat temperature of 96 K, are extremely unfavored from an energetic standpoint.

However, the shape of the second exponential function is of interest. It is plotted for the 96 K superheat at 300 psia case (Figure 7). It represents a rarefaction of states right at the critical nucleus, reflecting the preference for embryos just smaller than critical size to shrink, and embryos just larger than critical size to grow. Using the Seitz condition, the critical radius can be fixed at 7.9 nanometers for the example above, and filled with a vapor at saturation conditions this gives a critical vapor nucleus with only 3864 water molecules. It is interesting to observe that

![Figure 7 - Number density of vapor nuclei](image-url)
a nucleus with just 250 fewer molecules associated with it is almost three times more likely than the critical nucleus itself. Increase the distance from critical to 500 molecules, and that embryo is roughly 70 times more likely to exist.

There are some important things to observe about the populations of nearly critical vapor nuclei in a metastable liquid near the superheat limit, especially with respect to externally imposed, highly local energy additions such as ionizing radiation. If through fluctuation or the imposition of energy from outside the system, a barely subcritical embryo is created, the physics of the situation demands that it eventually shrink and be extinguished. The picture is one where the critical embryo that does grow into a macroscopic nucleus emerges from a much larger population of nearly sub-critical nuclei that exist in the metastable fluid at all times.

These barely sub-critical nuclei are very close to the critical nucleus energetically. The embryo described above (500 molecules smaller than the critical nucleus) has a reversible energy of formation only $3.40 \times 10^{-20}$ J or 0.212 eV less than the critical nucleus. To raise this nucleus to the critical energy, one needs to deposit about 0.266 MeV/cm in the vicinity of the embryo. This is interestingly just the energy of a typical secondary electron or spur, of which >400 are created per proton track. Of course at the distance scale of nanometers discussed here, the concept of LET breaks down somewhat. However, there are clearly a relatively large number of sub-critical embryo candidates in a metastable liquid under irradiation, and these candidates have a good chance of being supplied the necessary energy to achieve critical status and sponsor bulk nucleation.

We return now to the development of the theory of stability kinetics for metastable liquids without radiation. The population of sub-critical nuclei described above is the breeding ground for nucleation of liquids. Ignoring the addition of energy by radiation for now, the embryos make the leap by adding the appropriate number of vapor molecules to the embryo to go above the critical size. The rate that this happens will be proportional to the density of embryos, the surface area of the embryos, and the flux rate of molecules. It can be shown that this takes the form
\[ J = \frac{\beta}{\sum_{2}^{\Lambda} (N(n)A(n))^{-1}} \]  

where \( J \) is the flux rate of nuclei in units of \( \text{(volume}^{-1}\text{time}^{-1}) \), \( N(n) \) is the number density outlined above, and \( A \) is the embryonic surface area. \( \beta \) is the evaporation/condensation rate at a vapor/liquid interface, and can be approximated by

\[ \beta = \frac{P}{\sqrt{2\pi mkT}} \]  

The sum is performed over a range of embryos starting with two molecules up to a sufficiently large number, \( \Lambda \), and in any case greater than the critical embryo size. This can be converted to an integral over the radius of the embryos. Because of the steep drop in the number of embryos at the critical radius, the argument of this integral is very much like the surface area times a delta function at the critical radius. The expression for \( J \) becomes

\[ J = \beta A(r_c) N(r_c) Z \]  

where \( Z \), the Zeldovich factor has been added to adjust for the fact that the concentration of critical nuclei is less than that which is calculated in the expression for \( N \). \( Z \) is

\[ Z = \sqrt{\frac{\sigma kT}{B}} \cdot \frac{1}{P_{vap} A(r_c)} \]  

The equilibrium vapor pressure based on the temperature of the metastable liquid (referred to herein as \( P_{vap} \)) is higher than the pressure the superheated system is subject to, and is also not the true pressure of the vapor inside a vapor nucleus. The correction for this effect is referred to as the Poynting factor. It is

\[ \delta = 1 - \frac{P_{vap} v}{kT} \]  

where \( v \) is the specific volume of the vapor.
When the Poynting factor is included, the expression for the flux rate of critical nuclei becomes

\[ J = \rho \sqrt{\frac{2\sigma}{\pi m B}} \exp \left[ -\frac{16\pi}{3kT} \frac{\sigma^3}{\delta^2 (P_{vap} - P_{crit})^2} \right] \]  

(81)

This flux rate can be used to determine the characteristic survival time of a given volume of metastable liquid, and is the basis for comparison of theory and experimental data.

Like the partition function, this expression has an extremely strong dependence on surface tension. The onset of bulk nucleation is determined in no small part by this dependence. However, the surface tension of liquids is a difficult measurement at ambient conditions and this difficulty becomes compounded near the critical point, where surface tension drops rapidly to zero. Figure 8 is a comparison of several sources of surface tension data. The solid diamonds represent steam table data from Perry’s Chemical Engineer’s Handbook. The solid triangles are calculated, using the correlation

\[ \sigma(T) = 132.674 \frac{\text{dyne}}{\text{cm}} \left( 1 - \frac{T}{T_{crit}} \right)^{0.995} \]  

(82)

This form has the benefit that it is parameterized on temperature for easy calculation. However Skripov points out that well measured surface tensions diverge from the scaling laws used to produce the first two curves. They offer an alternate empirical fit to data that gives significantly lower values for the surface tension especially at temperatures near the critical point. The Skripov model is

\[ \frac{\sigma(T_r)}{\sigma_{0.6}} = \sum_{m=1}^{5} \beta_m (1 - T_r)^m \]  

(83)

where \( T_r \) is the reduced temperature, \( T/T_{crit} \). \( \sigma_{0.6} \) is the surface tension measured at \( T_r = 0.6 \), and the \( \beta_m \) are as listed in Table 6.
Note that the Skripov empirical model results in surface tensions near one half of the value one would obtain with the parameterized form contained in the Perry’s handbook. It is also very close to the measured steam table data as the critical point is approached. When these surface tension data are used in the expression of the flux rate of critical nuclei, a better match to measured superheat limits is obtained. For this reason, the Skripov model was used.

Using the Skripov surface tension model, the flux rate of critical nuclei can be calculated. Figure 9 is a graph of the log of J versus temperature for water at several pressures. The log of J is a more useful quantity to plot than J itself, since the expression covers many decades. Consider the case of water at 1 atmosphere. At 308ºC the log of J is 21.8, or $6.31 \times 10^{21}$ embryos will be formed per cubic centimeter per second. Even a nanoliter of water could stand no more than a femtosecond. However by reducing the temperature from 24ºC to 284ºC, which is still 184ºC above boiling, the log of J assumes a value of -152.7 or $J = 2 \times 10^{-46} \text{ cm}^{-3} \text{ sec}^{-1}$. Presume that one could prepare a sample of pure, mote-free water, equivalent in size to the earth’s oceans $(1.3 \times 10^{24} \text{ cm}^3)$ in a container without walls or nucleation sites of any kind, including no external radiation such as cosmic rays. This expression predicts that in the known life of the universe (highest estimates are around 20 billion years, or $6.3 \times 10^{17}$ seconds), $1.6 \times 10^{-4}$ nuclei would
Table 6 - Surface tension constants for water

<table>
<thead>
<tr>
<th>m</th>
<th>$\beta_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.149</td>
</tr>
<tr>
<td>2</td>
<td>8.69</td>
</tr>
<tr>
<td>3</td>
<td>-26.46</td>
</tr>
<tr>
<td>4</td>
<td>44.49</td>
</tr>
<tr>
<td>5</td>
<td>-28.67</td>
</tr>
</tbody>
</table>

have been created in that volume. For all practical purposes, a log J of -40 corresponds to a probability of zero.

The flux rate of critical nuclei converges to one value at the critical temperature, regardless of pressure, as it should. This is the number density of water molecules times the evaporation rate at the liquid/vapor interface, and represents the fact that all molecules become critical embryos at that point. As temperature is reduced, the flux rate drops steeply. It is interesting to note that the concept of the spinodal limit does not enter into this picture. The spinodal limit does not take time dependence into account. However the kinetic model allows that even when the physics demands that the liquid nucleate, there is a characteristic time for the necessary fluctuations to sponsor nucleation to occur.

### 4.3 Bubble formation due to ionizing radiation

The scenarios for the extremes of nucleation behavior in the previous section are understood to be highly idealized. In practice, solutions undergo phase change at the temperature and pressure prescribed by the equations of state. The required embryo for nucleation can be formed in ways other than normal thermal fluctuations in the liquid. Microscopic rough features at the surfaces of the liquid enclosure can trap small bubbles of gas, or can provide accumulations of surface energy sufficient to result in an embryo above the critical size. Dust particles or other suspended material in the liquid can have the same effect. And for almost any laboratory on earth there are also the effects of cosmic radiation. Ionizing particles passing through the liquid deposit energy locally, and can add energy to an embryo that is below the critical radius and
energy, taking it above the critical threshold which will allow it to grow into a macroscopic second phase.

Experiments designed to measure the superheat limit on liquids have to take these effects into account. The liquids are filtered, distilled, and degassed. The containers are made of clean glass or other smooth materials and care is taken to minimize surface defects. It is more difficult to avoid cosmic radiation. In fact, cosmic radiation is the predominant effect in artifacts on superheat measurements. A description of superheat measurement technique and taxonomy of methods is left to a later section. However, J can be measured indirectly. Real data give graphs like the one shown in Figure 10 (for illustration, not actual data).

The curve marked theoretical would be the flux rate J as calculated using known properties of the liquid, such as surface tension, vapor pressure, etc. As compared to the earlier plots of J for water, the vertical scale is expanded and a smaller range of J is plotted for just this region of
interest. In practice, experimentally measured values for J using state of the art techniques fall along this theoretical line or within a few tenths of a degree of it. However at some smaller levels of J theory and experiment diverge. As the temperature is lowered, the characteristic stable time of the volume in question in the apparatus cannot be achieved.

The experimental values of J in this region typically take on the shape of the theoretical J curve, suggesting that a nucleation source with much the same surface tension and pressure dependence of the theoretical one is at work. Because of the large population of just slightly sub-critical embryos known to be in the liquid at temperatures above boiling, it is probable that these are the source of the experimental artifact, and represent embryos that have been boosted above critical energy by interaction of cosmic rays with the apparatus. This is borne out by further experiment. Skripov\textsuperscript{53} measured attainable superheat in diethyl ether in the presence and

![Figure 10 - Critical embryo flux rate with and without radiation (other than background)](image-url)
absence of a Co-60 gamma ray source and got results that very much look like the curves presented above. The data with radiation shows an additional increase in $J$ of about a decade.

Because of the effects outlined above, the metastable fluid experimental literature makes reference to the typical nucleation rates achievable by different types of apparatus. These range from bubble chambers, which can reach a $J$ of $10^2 \text{ cm}^{-3} \text{ sec}^{-1}$, to pulsed heating methods, which can reach a $J$ of $10^{18} \text{ cm}^{-3} \text{ sec}^{-1}$.

With some understanding now of the theoretical and experimental limits on superheating of water at elevated pressure, a summary of these various limits is presented in Figure 11. All data is plotted versus reduced pressure and reduced temperature. An estimation of the spinodal limits using Redlich-Kwong and Peng-Robinson equations of state are presented, as well as the binodal curve for water. Lines describing the threshold of log $J = 2$ and log $J = 20$ are plotted, where $J$ has the units of $\text{ cm}^{-3} \text{ sec}^{-1}$. Finally, real superheat measurements on water are shown. The data from Chukanov$^{54}$ are from a bubble chamber. The data from Pavlov$^{55}$ are from a pulsed

![Figure 11 - Summary of superheat limits for water](image)

53
The typical operating pressure of a PET enriched water target is about 600 psia, or a reduced pressure of 0.187. A good estimate of the achievable superheat limit appears to be a reduced temperature of 0.91, or about 317°C. This is a superheat of 65°C over the boiling point at that pressure. This corresponds very closely to the estimate of superheat derived from the vapor jet model in the introduction.

Of interest in the operation of water targets is the characteristic time for a superheated volume within the target away from the walls. In this sense, J values, rather than the attainable superheat, are meaningful. The central superheated volume referred to in the vapor-jet model of operation is 0.015 ml (2 mm radius, 1.2 mm deep). The transport time is .008 seconds. In order that spontaneous bulk nucleations not take place in this volume, the flux rate should be below 8.3 x 10^3 cm^-3 sec^-1. This is a measurable flux rate. Particularly, the effect of the various radiations in the target on this flux rate can be probed in an appropriate apparatus.
5.0 Experimental work

5.1 Development of an apparatus

Avedesian\textsuperscript{56} offers an excellent summary of the various experimental methods used in measurement of nucleation limits in liquids as of 1985. He classifies methods into two broad categories: liquids in contact with solids, and liquids in contact with immiscible liquids. The latter category includes the earliest measurements of superheat limits, performed by Dufour in 1861. In these measurements, referred to as bubble column measurements, a droplet of water was introduced into a heated column of oil that was denser than water. A thermal gradient was set up in the oil. As the bubble rose through the oil, the temperature increased until the droplet violently exploded. The superheat temperature limit could be determined by the location in the tube where the explosion happened.

Within immiscible liquids methods there are two sub-categories of measurement: isobaric heating and isothermal decompression. These correspond to moving from the stable to the metastable region along lines of constant pressure and temperature respectively. Both methods have associated systematic errors that are controllable and quantifiable. The main limitation of immiscible fluids methods from the standpoint of the present work is the type of data generated. The output of the measurement is a superheat limit at a given pressure rather than the waiting time characteristic that varies over a temperature range. The effect in isotope targets that is of interest is a dynamic one, and so a method that determines the waiting time was needed. Moreover, the effect of radiation on the system is easily seen when two waiting time curves (with and without radiation) are plotted on the same axes. For these reasons, immiscible fluids methods were ruled out for these experiments.

The other primary category of measurement methods, liquids in contact with solids, is further categorized into pulse heating methods and capillary tube methods. Both of these methods
involve the added difficulties associated with nucleation sites provided by the surface flaws of the solid in question. However methods have been identified to control and quantify systematic errors in these methods as well. Since 1985 this method has been developed more fully, and is currently very sensitive\textsuperscript{57,58}. These modern methods simultaneously show nucleation at surface flaws that nevertheless reach near theoretical superheat limits. The pulse heating method was considered, but the ability to do those measurements at elevated pressure and in a radiation field appeared to be very difficult to carry out. In particular, the sensitive volume in pulse heating methods is difficult to quantify and in any case very small. Since the interest in developing this apparatus is eventually to bombard the test volume with a known flux of neutrons or other radiation, it is necessary to maximize and quantify the sensitive volume.

Capillary tube methods also have a long history and some of the earliest water superheat measurements were done in capillaries, notably by Briggs\textsuperscript{59}. Like the immiscible liquid methods, capillary tube methods can be further categorized into isobaric heating and isothermal decompression. The Briggs method, dropping a capillary into a heated liquid, is an isobaric heating method. A modified version of this method, using a sealed and pressurized capillary, was the first apparatus attempted, and is described in later parts of this section.

The experimental method that was finally selected is an isothermal decompression capillary tube apparatus. Liquid/solid isothermal decompression methods include bubble chambers like the one developed by Glaser. The Skripov group at the Ural Polytechnic Institute started using immiscible fluid methods to probe liquid superheat limits in 1961\textsuperscript{60}. Eventually a capillary tube version was the primary apparatus used by Skripov and colleagues\textsuperscript{61-65}. This method affords the possibility of relatively large superheated volumes. In particular, this method has been shown to provide the best and most detailed picture of radiation effect on nucleation phenomena in a variety of superheated liquids.

The best description of the Russian apparatus is offered by Baidakov. The temperature of a glass capillary was controlled by mounting in a copper block. The glass was connected to tubing
for loading and unloading of the liquid under test through Kovar braze joints. The capillary tube was rapidly depressurized through the motion of a metal bellows connected to the system. For reasons not made clear in the paper, the capillary is in an inverted U shape. It is not obvious how vapor generated at nucleation was cleared from the apparatus. The authors do note that to avoid temperature errors associated with adiabatic depressurization, a two stage depressurization routine was utilized.

The authors also note that the starting time for any particular measurement is somewhat indeterminate. During the vent down of the system, the liquid under test is below the boiling pressure but well above the pressure of measurement for some fractions of a second up to a few seconds. Baidakov analyzed wait time histograms and concluded that for their apparatus the delay time was approximately 0.5 sec. Correspondingly, events in under that time had to be excluded from their statistics.

As mentioned above, the first attempt at an apparatus in the current work was closely modeled on Briggs. Briggs method involved the momentary (about 4-8 seconds) immersion of glass tubes containing water in an oil bath at various oil bath temperatures. The superheat limit was determined as the temperature at which the water was ejected from the capillary by vaporization within the several second immersion. It does not appear immersion time was controlled very precisely, or if so, it was not reported. Briggs obtained a variety of superheat limit temperatures from 200 to 274ºC. In light of the kinetic theory of nucleation, it can be concluded that Briggs’ measurements involve two observables, the characteristic waiting time, $\tau$, and the spinodal limit at that pressure. This accounts in part for the spread in temperature limits in his measurements. He also notes differences in the various tubes he used. Much of this may come from the fact that they were hand drawn.

Briggs’ measurements were performed manually, and generating enough data points to enable a determination of $\tau$ would require automation. Moreover, the ability to have more uniform glass characteristics was desired. The apparatus constructed as part of this work utilized the same
type of heating oil (Briggs used Dow Corning 702, Dow Corning 703 was used for these experiments; vapor pressures are insignificantly different). In the present case, it was heated on a heat plate equipped with a magnetic stirrer (see Figure 12). The glass capillaries were made out of multiple loops (3 or 4 turns) of approximately 2" diameter of fused silica capillary tubing (Polymicro Technologies, Phoenix, AZ), commonly used for High Pressure Gas Chromatography. This material has the advantage of having a very precisely controlled inner diameter, very thin walls (to reduce temperature and timing errors), and is easy to wrap into small coils. It is rated to 400°C, which is well over the temperatures expected in the experiment. It is proof tested to pressures up to 100 kpsi.

This coil was connected to a pneumatically driven cylinder (Bimba Manufacturing, Monee, IL) positioned over the oil bath to allow the coil to be immersed in the oil bath in less than 1 second. The coil was connected to a pump, valves and a pressure transducer to facilitate the loading of

Figure 12 - First iteration of a metastable measurement apparatus
liquid water, pressurization, and detection of nucleation by the pressure shockwave some time after immersion. The coil would be lifted after nucleation, vented to ambient pressure, refilled with a new sample of test liquid, and the process repeated.

There were several important findings in the development of this early apparatus. Experience with Dow Corning diffusion pump oil was gained. Briggs states that the oil “evaporates very slowly even at 270ºC.” That statement is subject to challenge, or at least some qualification. Even at 230ºC the oil produces a noticeable amount of vapor, and the heat plate was unable to provide sufficient heating to reach higher temperatures. The first experiments were also useful in identifying inexpensive automation equipment and generating automation routines which were used in subsequent generations of the experiment.

The capillary tubing used at first ended up being unsuitable for the task. Some data were taken, but usually very early in the service life of the tubing (10-20 immersions) the tube ruptured. The liquid was then automatically dispensed into the hot oil (repeatedly). This caused a rather messy release of energy and matter as the vaporizing liquid performed PV work against the diffusion pump oil. It appears that the winding diameter used (2-4") was too tight for the fused silica, causing unacceptable residual stress and flaws in the inner walls. Knowing of the other methods, notably the isothermal decompression methods used in the Russian literature, a second generation apparatus was developed.

5.2 Materials and methods

5.2.1 Initial specifications

Concrete specifications were developed for the second generation apparatus. They are based on the operating pressure of water targets, and thermophysical characteristics of water as outlined above. We know that the pressures of interest for isotope targets are 15 to 600 psia. We also believe from the literature that the practical limit for $J \approx 10^{-1} - 10^2 \text{ cm}^{-3} \text{ sec}^{-1}$. Using kinetic nucleation theory we then know that we will need to take the temperatures of the water at
pressures of interest to 280 to 310 ºC. Meanwhile, in order to suppress cavitation during loading of the tube, pressure should exceed the binodal at 310 ºC (which is 1431 psia). This led to the following Primary Design Specifications:

- 15 to 1500 psia
- 280 to 320 ºC
- Waiting times of 1 to 600 sec
- 20 ul of heated/sensitive water volume

### 5.2.2 Overall layout

The apparatus consists of a vertically oriented glass tube surrounded by a heated and agitated oil bath. Figure 13 is an illustration of this apparatus in cross section. An immersion heater (Watlow, St. Louis, MO, pn # RBN291S-1) is suspended from the lid of the oil enclosure, and is

![Figure 13 - Cross section of the isothermal decompression apparatus](image-url)
coiled in such a way as to maximize distance of the heated section from the glass in the center and to be as close to the bottom of the oil bath as possible. A baffle, suspended from the lid, surrounds the glass tube. An agitator screw is connected to a gearmotor (Globe Motors, Dayton, OH, pn #317A104-8) suspended from the lid. The oil (as in the first apparatus, Dow Corning 703) moves through a combination of convective and mechanical forces up the outside annulus of the oil bath, through the holes in the baffle at the top of the bath, down the center annulus around the glass, and over the heater. In this way it is expected that the oil is as well mixed as possible when it contacts the glass for the most uniform heating. The thermocouple (Omega, Stamford, CT, pn #KMQXL-062U-24) used to control oil bath temperature is immersed in the oil, suspended from the lid, as close to the glass as possible, and about halfway along the heated section of the glass. The heater and thermocouple are connected in a control loop with a temperature controller and a zero crossing SCR power controller (Omega, pn #3251 and pn# SCR19Z-12-040) to provide the smoothest possible temperature profile. The temperature controller is an autotuning PID controller.

The entire oil bath is suspended in a stainless steel support housing. The support housing is folded in on four sides and a lip near the top of the outer diameter of the oil bath simply rests on the folded edges. In this way heat losses through contact are minimized. The area between the support housing and the oil bath is filled with residential fiberglass insulation (Owens Corning) to minimize convective losses on the outside of the oil bath. The plumbing schematic is shown in Figure 14.

The enclosure/oil bath assembly is shown in cross section. Water is supplied to the bottom of the glass tube from an HPLC pump (Eldex Laboratories, Napa, Ca., pn #A-120-S). This pump was selected for the correct match of flow rate and pressure regime. HPLC pumps are fixed displacement, short stroke piston pumps, equipped with high purity check valves at the upstream and downstream ends of the moving piston. The inlet of this pump is connected to a 500 ml supply bottle via 1/8 o.d. polyethylene tubing. The outlet is connected to the glass tube via 1/16" o.d. PolyEtherEtherKetone (PEEK) tubing.
The PEEK tubing is connected to the glass tube at both ends by two similar stainless steel manifolds. The manifolds contain O-rings that make a circumferential seal around the glass tube, and another set of O-rings that make a circumferential seal around a 1/16” o.d. stainless steel tube. The stainless steel tube has a brass tab soldered onto it. The brass and solder do not come in contact with water, but are used to hold the tube and the O-ring in place via a single 6-32 screw. Finally, the stainless steel tube is connected to the PEEK tube using a 1/16” stainless steel compression fitting (Swagelok, Solon, OH, pn #SS-100-6). In the bottom configuration, the stainless steel manifold also accommodates an O-ring that seals the glass tube to the base of the oil bath.

Above the glass tube there is an expansion volume for the vaporizing liquid. A pressure transducer (Omega, pn #PX603-2KG5V) monitors the pressure in that volume. The expansion volume and transducer are connected to the common port of a pneumatically actuated high pressure chromatography injection valve (Valco/Vici, Houston, TX, pn #AC4W, V1) with 1/16” o.d.
PEEK tubing. The normally closed leg of that valve is connected to a high pressure adjustable check valve (Upchurch/Idex, Oak Harbor, WA, pn #P880, V2). The outlet of the check valve drains to a waste vial.

The normally open leg of V1 connects to a manifold via a needle valve (Nupro, Solon, OH, pn #SS-SS1-A, V3). The function of this valve is to control the bleed rate of the primary expansion volume. The needle valve communicates directly with a secondary expansion chamber (Swagelok, pn #304L-HDF4-500) whose function is to provide a ballast to allow rapid equilibration of the headspace with a measurement pressure. The secondary expansion volume is connected via solenoid valves (GEMS/Precision Dynamics, Plainville, CT, pn #A20_1-1-SB-24VDC, V4 and V5) to a regulated argon supply and to atmosphere for the pressurization and depressurization of this ballast. Figure 15 is a photograph of the apparatus in the fume hood in Lab II at Siemens Molecular Imaging where the experiments were performed.

5.2.3 Operational procedure

At the beginning of any test the glass tube is filled with liquid water and at a pressure above the binodal curve for the temperature of the oil bath (selected at 1431 psi for all temperatures of interest). The check valve (V2) is preset for a pressure above the binodal curve. The isolation valve, V1, is switched to connect the top of the test section to the check valve. The HPLC pump is run for enough time to clear the tube of any vapor bubbles. The Argon regulator pressure is set to the desired measurement (superheat) pressure, and the ballast volume is allowed to pressurize to the regulator pressure. The temperature controller is set for the desired measurement temperature and the oil is allowed to heat and stabilize.

Starting from this condition, the isolation valve is switched to connect the test section to the ballast through the needle valve. The pressure as read on the transducer is monitored, and when the pressure reaches the desired measurement pressure the isolation valve is switched back to the check valve and a clock is started. Cavitation will cause a pressure spike, and at a predetermined amount above the measurement pressure, the spike is registered, the clock is
stopped, and the time to phase change recorded. Then the HPLC pump is restarted to purge water out of the check valve and the system returns to the condition required before the next pulse. This cycle is repeated approximately 100 times if possible to accumulate reasonable statistics to establish a Poisson distribution of waiting times and determine a reasonably stable average.

All of the operational steps are automated by way of a Visual Basic application and automation system. The automation system is a Labjack U12 USB data acquisition system (Labjack, Lakewood, CO). It includes 8 analog inputs with 12 bit resolution, 2 analog outputs, 0-5 VDC, 10 bit resolution, and 16 digital IO points. The Visual Basic application, named Pop, was designed as part of this work. It has a graphical interface that allows individual control of the valves and pumps in the system, a constantly updating screen view of pressure and temperature, configuration fields for automated running, and progress bars and other display information to allow the operator to understand what is happening during an automated data collection episode.
Figure 16 shows a screen shot from the user interface. The code is attached as Appendix A. A segment of a typical output file is attached as Appendix B.

### 5.2.4 Detailed design specifications and design review

Based on the top-level specifications, the layout of the equipment and the desired operational profile, detailed design specifications were developed. A design review was held with the dissertation committee, presenting basic design calculations and rationale for selecting the equipment used. The topics presented were size of the sensitive volume, pressure constraints (including sizing of the expansion volume), temperature constraints (including various cooling issues with the vaporizing/expanding test liquid), heater and insulation design, and general safety issues.

![Figure 16 - Screen shot of Pop application](image-url)
5.2.4.1 Selection of the size of test section

The equipment is intended at some point to be able to probe the effect of various radiation fields on the test liquid in the metastable state. Therefore, the volume should be minimized as much as possible to reduce the effects of cosmic rays, while still being large enough to have a reasonable chance of interactions with the radiation being investigated in a time on the order of seconds. Neutrons, having a low interaction probability, will be used to estimate the reaction rate in the test volume.

As stated above, the potential scattering elastic cross section of neutrons on a nucleus of atomic number $A$ is

$$
\sigma = 4\pi R^2
$$

$$
R = 1.25 \times 10^{-13} A^{1/3} \text{cm}
$$

For O-18 ($A=18$) the cross section is 1.348 barns. This cross section is energy independent. Although the measured and evaluated cross section is closer to 3.8 barns for a large range of energies, it does fall off at higher energies as would be likely in the area of the target. In order to be conservative the lower number is used. The glass tube has a 0.5 mm inner diameter. The reaction probability over a 0.5 mm depth is $2.25 \times 10^{-3}$ reactions/neutron. Presume that the neutron source used is the target of an Eclipse cyclotron being irradiated with 60 uA. It is known through Alice code simulations and direct measurements that the production rate for 60 microamps is $6 \times 10^{11}$ neutrons per second. Neglecting scattering and using only $1/r^2$ flux reduction, one can assume $4.77 \times 10^6$ neutrons/sec-cm$^2$ at 1 meter. This is a practical distance, since the target on the Eclipse is approximately 1 meter above the floor. The heated section is designed to be approximately 10 mm long (depending on the height of the oil filled in the system. This means the flux rate would pass through a sensitive area of 0.5 cm$^2$ (10 cm x 0.05 cm). Using this area and flux rate, one can expect 5366 reactions per second in the sensitive volume (regardless of the amount of energy transferred). Since the metastable times accessible by this
apparatus will also be on the order of seconds, it is concluded that the volume is sufficiently large to probe the interesting radiation fields for these experiments.

5.2.4.2 Pressure constraints

As stated above, the overall system maximum design pressure is 1500 psia. Each component must be evaluated for this design pressure. Parker rates their O-rings for 1500 psi if their design criteria are used for the seal glands. They were used in these designs. There is an assumed safety factor in the Parker calculations, and no additional safety factor was used here.

Conventional HPLC pumps (such as the Eldex used herein) run at 100 - 5000 psi. The only restriction on the pump used is that its maximum pump pressure must be derated for larger strokes (equivalent to higher flow rates). The Upchurch back pressure regulator that was selected is adjustable from 600 to 1500 psi. The Valco/Vici HPLC injection valve selected was rated at 2000 psi.

In addition to the off-the-shelf components, one must evaluate for various mechanical stresses in the fabricated components of the apparatus. In particular, evaluations were performed for the possibility of pushing the o-ring fittings off of the ends of the tube, rupture of the glass cylinder, and pressure rises during cavitation. In the latter case both extremes of performance needed to be evaluated, that is, will the pulses be both detectable and survivable.

To evaluate the strength of the glass tubing, one can use the Barlow Formula

\[ P = \frac{2t \times S}{D} \]  

(85)

where \( t \) is wall thickness, \( S \) is tensile strength, \( D \) is outside diameter, and \( P \) is pressure rating.

Simax borosilicate glass (Kavalier, Sazava, Czech Republic) was selected for the tube material. The tensile strength of Simax is 35 – 100 MPa (5,075 – 14,500 psi). The variation is due to uneven stresses in as-drawn glass. Originally the finished parts were to be annealed. However, during procurement of the glass it was discovered that it was difficult to maintain dimensional stability and anneal, so the glass was bought as-is. In either case, for the purposes of a rupture
calculation, the lower bound of 5,075 psi should be used. As above, the Simax stock tubing selected was 5 mm o.d., 0.5 mm i.d. Converting to inches to be in the same units as the tensile strength values, the thickness (t) is 0.089", and the outside diameter (D) is 0.197". The pressure rating of this tubing should be 4585 psi at a minimum. This gives the tubing component a safety factor of 3.06.

The next critical component to be evaluated is the screw used to hold the O-ring fixture to the bottom and top of the oil bath, which also confines the glass tube. The yield of this screw in tension would be caused by forces acting at the outside diameter of the O-ring gland. This is 0.285", which gives an area of .064 sq. in. or a force of 95.7 pounds at 1500 psi. The original design called for a single #4-40 screw. The .00604 sq. in. cross sectional area of that screw at the base of the threads gives 15,728 psi stress. The screw selected was a stainless steel screw, and the yield point for stainless steel is about 35 kpsi. This gives a safety factor for tensile stresses only of 2.22.

However, one must also calculate the yield of screw in bending. The closest the screw can be placed to the point where pressure is acting (tube centerline) is about .375” away. Applying 95.7 pounds of force at that radius gives 35.6 in-lb of torque at the center of the smallest cross sectional area of the screw. The stress at the base of the screw is 675 kpsi, well above the yield stress. The conclusion was that the design needed 2 each of the #4-40 screws on opposite sides of the tubing centerline, which both eliminated bending stresses and made the design doubly redundant.

Finally, the bounds of the pulse sizes anticipated must be evaluated and the design of the apparatus must accommodate them. Steam generated at cavitation has to compress into the argon filled headspace. Using once again the design parameters for the glass test section (10 cm glass column - .5 mm i.d.) the sensitive volume is calculated to be 17.6 µl. In a liquid state at ambient temperature this is about 1 mmole of water. (At all other temperatures it is somewhat less, so this is a conservative amount for the sake of safety estimates).
First, looking at the smallest anticipated pulses to be detected, one should select the lower pressure boundary for operation. At 1 atmosphere, a 0.5 ml headspace will have $2.23 \times 10^{-5}$ moles of ideal gas (argon). If the cavitation forces all of the vapor into that same 0.5 ml volume as an ideal gas, the same space now has $1.02 \times 10^{-3}$ moles in 0.5 ml. This should give a pressure of 45.7 atmospheres or 672 psi, and the pulse is detectable. In reality, the steam will condense as it comes in contact with surfaces outside the test section that are colder than the test section; still the pulse is expected to be substantial.

At the other operational extreme of 40 atmospheres (approximately 600 psia), 0.5 ml headspace will have $8.92 \times 10^{-4}$ moles of ideal gas (argon). If, as before, one forces all of the vapor generated in the test section into the headspace as an ideal gas one would have $1.89 \times 10^{-3}$ moles in 0.5 ml. This is equivalent to 84.7 atmospheres or 1246 psi. Again, condensation would serve to limit this to some degree. However, in this case the pulse remains detectable, and more importantly, the equipment survives the pulse, since it is designed for 1500 psi. In practice, besides condensation acting to limit the pulse size, the check valve/back pressure regulator also acts as a safety device, since the cavitation happens when V1 has connected the test section with the check valve.

5.2.4.3 Temperature constraints

The design goal stated above is a maximum temperature of 320 ºC. Most of the materials are metals that are very capable of withstanding this temperature. However, the seals are elastomer seals. The only material identified that was suited to these temperatures is Kalrez 4079, which is rated for 316 ºC. There were no risk mediations stated at the design review for this safety factor less than one, other than that the commissioning tests would reveal whatever the safety factor was, if any. In the notes below on commissioning, these limitations will be discussed further.

The oil vapor pressure is 0.2 atmospheres at 320 ºC. It has a boiling point at 396 ºC, and undergoes spontaneous ignition above 440 ºC. There are also practical considerations with this
high a vapor pressure, which have been alluded to above and which will be detailed a little further below.

In addition to material survivability, one must evaluate for heat losses and insulation design of the vessel, heater sizing and temperature, temperature gradients in the test section, and cooling of the water. In the latter case these can be further subdivided into evaporative cooling and stabilization time considerations, since the column will have just undergone a conversion of internal energy to PV work, and quasiadiabatic cooling of the water during depressurization, which has been addressed by using a multi-stage depressurization in the prior literature.

Turning to the topic of heat losses from the total assembly, a primary heat loss mode is evaporation of the diffusion pump oil from holes and gaps in the enclosure. The oil bath is essentially an open container, with holes and penetrations for the glass tube, the thermocouple, the agitator, and the immersion heater. Taken together these gaps were sized to be about 0.75 square centimeters. This is simplified to a circular hole geometry for purposes of calculation, and the modeled hole is 1 cm in diameter. Assume that the volume above the hole to height of 1 cm swept every 3 seconds, which corresponds to a very slight breeze. (In fact, the oil bath was set up and run in a chemical fume hood because the large amount of oil vapor produced. This produced something rather stronger than a slight breeze.) If the volume is filled every 3 seconds with 0.2 atmosphere vapor pressure of oil, this is equivalent to a 53 W loss.

Convection of room air on the outside of the assembly is another heat loss mode that was modeled. At the fume hood, sash velocity is maintained at or above 100 fpm. This gives a Reynolds number of 3600. Using the McAdams relation (which estimates heat loss from spheres in a flowing gas)$^{67}$

$$\frac{hd}{k_f} = Nu = 0.37 \left( \frac{u_d d}{V_f} \right)^{0.6}$$  \hspace{1cm} (86)
where \( u_w \) is the velocity far upstream of the assembly, \( h \) is the heat transfer coefficient, and \( d \) is the diameter of the sphere. This gives 140 W of losses on the outside of the assembly.

A third heat loss mechanism is radiation from the outside of the oil bath assembly. At the maximum temperature of 320ºC and assuming a perfect blackbody (emissivity of 1), radiation is 0.56 W/sq cm or 396 W. This has the risk of being the dominant heat loss mechanism. For that reason and the convective losses, the R29 insulation was used on the circumference of the assembly. The R29 should be able to support a temperature difference of 275K for the surface area of the outer circumference conducting less than 1 watt. The lid and base of the oil enclosure remain uninsulated simply due to the difficulty of doing so in a usable form. Considering those accommodations, the losses are anticipated to be on the order of 250 W.

The calculations above enable appropriate sizing of the immersion heater. The heater is a Watrod RBN291S-1, 500 W, 8mm dia, 55.9 cm length, 3.6 W/cm\(^2\) flexible immersion heater. This is 2x the maximum power required. A larger heater would threaten to have too short a duty cycle, and would be prone to temperature ripple in the system. A smaller heater, if the losses were not evaluated well enough, would risk not being able to reach the maximum temperature needed.

Given that the oil bath itself will be able to hold the temperature needed, consideration must be given to the heat inputs and outputs and time characteristics of the glass tube and water assembly itself. Conduction of heat out of the ends of the water column must be modeled as a steady state loss. Figure 17 is a graphic depiction of the simplified column geometry. Knowing that the water section is 0.5 mm diameter, and approximately one inch (2.2 cm) long, it will have to sustain a 295 K drop to ends that are roughly at room temperature. (This is a conservative estimate. In fact, the ends were suspended in blowing air but were much warmer than 25 C). The water in the column will be somewhere between a superheat temperature of 300ºC and 25ºC at the ends, so a thermal conductivity at 200ºC can be selected, somewhat arbitrarily. This value from steam tables is 0.0374 W/mK. Therefore,
Conduction through a still column of water out both ends of the geometry should give a loss of about 3.5 mW based on this temperature difference.

The next heat loss path is conduction through the glass tube itself. The tube is 5 mm diameter, and the drop to 25ºC (a temperature difference of 295 K) is approximately one inch (2.2 cm long). Simax borosilicate glass has a thermal conductivity of 1.2 W/mK.

\[
P = \frac{kA \Delta T}{l}
\]

\[
= \frac{0.664 \text{W/mK} \cdot (2.5 \times 10^{-4} m)^2 \pi \cdot 295 K}{2.2 \times 10^{-2} m}
\]

\[
= 1.75 \text{ mW}
\]

\[
(87)
\]

\[
P = \frac{1.2 \text{W/mK} \cdot (2.5 \times 10^{-3} m)^2 \pi \cdot 295 K}{2.2 \times 10^{-2} m}
\]

\[
= .316 \text{ W}
\]

\[
(88)
\]

Figure 17 - Heat flows in the glass tube
Modeling the ends of the tube as a solid rod, the total losses from both ends are twice this amount, or 0.632 W. The total steady-state losses from the column filled with water are then 0.635 W, and are clearly dominated by conduction through the ends of the glass tube. The conductivity of the heat flow path into the cylindrical tube geometry in the hot zone is calculated below, and is compared to this loss to come up with a total systematic steady-state temperature error.

The thermal resistance of the path that heat takes into the volume is calculated by simplifying the geometry such that the conduction path length is simply the wall thickness of the cylinder, and the cross-sectional area is heated zone length times cross-section circumference of the mid-wall. If the oil bath is at the measured temperature, then the potential is that the water could be cooler by a steady-state difference determined by this conductivity and the losses calculated above. Therefore,

\[ \Delta T = \frac{lP}{kA} \]

\[ = \frac{2.25 \times 10^{-3} \text{m} \cdot 0.635 \text{W}}{1.2 \text{W/mK} \cdot 0.1 \text{m} \cdot \pi \cdot 1.25 \times 10^{-3} \text{m}} \]

\[ = 3.03 \text{K} \quad (89) \]

There is the potential for a systematic error in the water temperature as much as 3 K in this apparatus. This is a conservative estimate, and the errors can be controlled somewhat by insulating the ends of the tubes.

The same conduction path is important in the non-steady state temperature behavior of water that has just been loaded into the hot zone from a 25 °C environment. The heat capacity of that water is 4.184 J/cc-K. The heated zone is 0.017 cc, and the heat required to bring this water to 320 °C is 21 J. Similarly, heat will be removed rapidly from the system when the superheated water does nucleate. Over all of the expected measurement conditions, the highest heat of vaporization for water is at 100 °C = 2.25 x 10^6 J/kg. Multiply this by 1.7 x 10^{-5} kg of water and the heat removed is 38 J.
The stabilization times associated with measurements then can be roughly estimated from the power that needs to be driven across the junction. Assume that the total of 38 J lost during vaporization is all taken from the inner wall of the glass tube. Then as room temperature water is loaded into the system, $21 + 38 = 59$ J needs to be conducted into the center region of the glass tube. Assume that the temperature difference is initially 295 K. Taking the same calculation used to determine a maximum systematic temperature error above, we have

\[
P = \frac{kA \Delta T}{l} = \frac{1.2 W/mK \cdot 0.1 m \cdot \pi \cdot 1.25 \times 10^{-3} m \cdot 295 K}{2.25 \times 10^{-3} m} = 61.8 W = 61.8 J/s
\]

Based on this calculation the heat required to be conducted into the system will do so in times on the order of a second. Of course this is a simplification on several levels. The temperature difference will rapidly approach zero, slowing as less and less heat is conducted. However as a rough estimate, a stabilization time of 10 seconds before depressurization should be sufficient to have the liquid reach the desired measurement temperature. This kind of time is reasonably attainable in an automated experimental apparatus.

5.2.5 Adiabatic cooling

The argon/steam mixture in the headspace above the liquid is vented out of the system through a control valve to reach the desired pressure. Both the gas and liquid are depressurized rapidly enough that they will experience adiabatic cooling, followed by a reheat to the stable temperature. Estimates of the temperature errors and methods for correcting for those are developed below. Skripov mentions experimental methods in his isothermic decompression experiments designed to control this error. Primarily, depressurization to a pressure near the measurement temperature was followed by an additional equilibration time, before a second, small depressurization took the
system to the final measurement state. In the case of water at the temperatures and pressures here, a two stage decompression is not needed, as shown below.

5.2.5.1 Cooling of gas in headspace

Adiabatic processes involve changes of temperature and pressure with no change in entropy. Therefore

\[
dS = \left( \frac{\partial S}{\partial T} \right)_p dT + \left( \frac{\partial S}{\partial P} \right)_T dP = 0
\]  

(91)

Using the identity for the constant pressure heat capacity

\[
\left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}
\]

(92)

the expression becomes

\[
\frac{C_p}{T} dT = - \left( \frac{\partial S}{\partial P} \right)_T dP
\]

(93)

Using the following Maxwell identity

\[
\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p
\]

(94)

the expression becomes

\[
\frac{C_p}{T} dT = \left( \frac{\partial v}{\partial T} \right)_p dP
\]

(95)

This is a generalized expression for temperature/pressure relationships that take place adiabatically (along lines of constant entropy). Treating the gas/vapor in the headspace as an ideal gas, this expression can be further simplified. Rearranging the ideal gas law as an expression for \( v \),
the expression for adiabatic change reduces to

$$C_p \frac{dT}{T} = R \frac{dP}{P}$$  \hspace{1cm} (97)

Integrating both sides over a range from \(T_1, P_1\) to \(T_2, P_2\), one obtains

$$\ln \left( \frac{T_2}{T_1} \right) = \frac{R}{C_p} \ln \left( \frac{P_2}{P_1} \right)$$  \hspace{1cm} (98)

Taking the exponent of both sides leads to

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{R/C_p}$$  \hspace{1cm} (99)

The headspace is going to be filled with argon, primarily. The constant pressure heat capacity for an ideal monatomic gas is \(5/2\ R\). So one has

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{0.4}$$  \hspace{1cm} (100)

If pressure dropped from 1400 psi to 300, and the starting temperature was 373K, the end temperature would be 201K, or a drop of 172K. The thermal conductivity of Argon is 0.072 W/mK at 20 bar, and a column of argon of the dimensions in the apparatus would support the full temperature difference of 172K at 0.11 mW power conducting through the gas column. This loss is less than 10% of other steady-state losses in the system, and can be neglected.

### 5.2.5.2 Cooling of liquid under study

The cooling of the liquid itself can not be modeled as an ideal gas. Returning to equation (95),
The partial derivative of molar volume with respect to temperature is dependent on pressure. To trace the appropriate adiabat in the pressurized water system, an Excel spreadsheet model of the Peng-Robinson equation of state was used. Isotherms in P-V space for every degree Kelvin between 273K and 647K were calculated. Pressure from the equation of state was calculated for specific molar volumes starting at $2.95 \times 10^{-5}$ m$^3$/mole, and increasing in steps of 0.6% increases until $5.50 \times 10^{-5}$ m$^3$/mole. Using this data, isobars in v-T space 25 psia apart from 300 to 1400 psia were interpolated, deriving a temperature for every specific volume in the same steps covered above. From that data it is possible to calculate $dV/dT$ at constant P using the discrete steps in the table for any specific volume and pressure.

Using the $dV/dT$ data, equation (95) was solved iteratively. Starting at a pressure of 1400 psia, $dP$ was always set to -25 psia, $dT$ was solved for and applied, and the equation solved again at the new pressure, volume and temperature. The result is plotted in Figure 18.

As anticipated, the adiabat has a slightly steeper negative slope relative to the 295ºC isotherm on which it originates. However, the difference is so minor as to be impossible to see on the printed graph. At 300 psi, the water has cooled from 568.00 K to 567.86 K, or a change of 0.14K.

### 5.2.6 Glass fatigue

Control and minimization of flaws in the glass surface is a, if not the, primary concern in the design of an apparatus for measurement of metastability limits. Experience with the first generation device, the Briggs paper, and much of the other literature in the area support this claim. Flaws support nucleation at reduced temperature and can lead to catastrophic failure of the pressure vessel. However it has been shown that many typical laboratory glasses are corroded in particular by water and water vapor at elevated temperatures and stresses. The corrosion mechanism is related to the concentration of sodium in the glass. Hydrogen ions from the water vapor replace sodium ions in the glass, liberating hydroxyl radicals to attack the
glass locally. It was shown that the failure growth rate was related to the rate of sodium ion diffusion in the glass. Therefore, the best glasses for the task are going to be very low in sodium concentration. Failure rates related to chemical action are further accelerated by stress locations in the glass. Annealing of the glass appears to limit the failure mechanism.

Simax is a heat resistant borosilicate glass with low (4.2%) sodium (and potassium) content. It has been shown to be particularly resistant to water, water vapor and boiling aqueous alkali solutions at elevated temperatures\(^\text{71}\). For this reason, Simax capillary tubes were selected for this application. The tubes were not annealed to maintain dimensions for the o-ring seals at the ends of the tubes. There was no chemical preparation of the tubes other than cleaning with a range or organic solvents followed by flushing with HPLC grade water.

### 5.2.7 Safety

Several safety concerns had to be evaluated with respect to the operation of the device. Primary among these was the potential release of energy if the tube ruptures. (This is based on the experience of the first fused silica capillary tube experiments.) Two terms are calculated: the

![Figure 18 - Adiabatic cooling of water](image-url)
energy of converting the water at saturation to steam, based on heat of vaporization, and the PV work performed by the expanding steam. The prior calculation for the first value (to determine temperature errors) was based on water properties at 200ºC. However, for purposes of energy release, the water/steam properties at saturation at 1500 psi will be used. The heat of vaporization of 17 ul of water at that pressure is 25.6 J. The PV work to expand that steam against a 14.7 psi reservoir is another 2.86 J, for a total energy release of 28.46 J. It is primarily the mechanical energy (PV) that is of concern. A small firecracker is commonly associated with about 30 J of mechanical energy released. The explosion risk is easily mediated by keeping the entire assembly in a fume hood enclosure.

Personal Protective Equipment (PPE) of a lab coat and safety glasses were always used during experiments. If handling of the heated parts of the apparatus was necessary, heat resistant gloves (also known as mill gloves) rated for 700ºF were used.

Spills of the diffusion pump oil were considered, especially because of the burn risk associated with the oil at maximum temperature, and the small safety factor of the O-ring seals used to contain the oil. The apparatus was set inside a simple disposable oil roasting pan to keep spilled oil confined. In order not to damage any components by local overheating, the automation system keeps the stirrer agitating until the system has cooled to 100ºC.

Most of the system operates at 24 VDC, however there is 110 AC voltage, notably on the terminals of the immersion heater, which sticks above the top surface of the oil enclosure. These connections are insulated with heat shrink tubing and electrical tape. The system is completely de-energized and cooled before handling.

5.2.8 Commissioning

The pressure transducer was calibrated using a NIST traceable test gauge (Wika) and argon overpressure connected to the arrangement of valves that comprise the volume above the tube. The tube was replaced with a Swagelok 1/16" compression plug. The results of pressure measurements after the calibration had been performed are shown in Figure 19. The line
Figure 19 - Pressure calibration

represents a perfect calibration, and diamonds are the actual data. The standard deviation of the 11 points is 1.45 psi. Although the calibration was not carried out over the full range of anticipated operation, it was calibrated over all the pressures that were used for measurements. Moreover, the linearity of the transducer is guaranteed by the manufacturer.

A graph of the pressure error better illustrates how well calibrated the system was (Figure 20). The calibration point at a test gauge pressure of 393.7 psia appears to be an outlier and could have been a transcription error. If that point is removed there is also a visual non-linearity or positive biased error at higher pressures. All the measurements taken below happened to be at around 170 to 180 psia. For those measurements, it appears that an accuracy of 1.4 psia, based on the standard deviation, can be assumed. Note that the transducer is a 2000 psi, 5V full scale unit, and that the analog input channel is a 0-10V, 12 bit channel. This gives 2.4 mV per bit, which is equivalent to about .96 psi on the transducer. With the selected electronics, accuracy is not expected to be better than 1 psia.
With the pressure transducer calibrated, it was possible to evaluate and develop ballast handling methods and settings for the needle valve that gave reasonable depressurize times. In order to have measurements in line with the timing capabilities of the apparatus, measurements should not have to be done much faster than the known thermal equilibration times of 10 seconds. However, accumulating 100 data points if the wait time for each is on the order of 1000 seconds would be too difficult to do, at least in the early phases of experimentation, where it was expected the apparatus would always be monitored. Therefore, a goal for the pressure equilibration time of 10 seconds was chosen.

The ballast tests were performed at 250 psi. The ballast was prefilled with argon at 250 psi. Over a number of vent downs from >1400 psi, it was determined that no needle valve was needed. It remained in the system, but was turned full open. The small bore tubing going to the valve acted as a more than sufficient flow reducer. An initial run of 10 pressurize/depressurize cycles was performed. Depressurize times slowly crept up over the 10 runs from 11.7 to 14.8 seconds. The ballast renormalization cycle (where the vent and pressurize valves were cycled)
was changed to give a 0.3 second vent, followed by a 10 second repressurize from the bottle. The 10 runs were repeated and a constant 10 second average bleed down time was achieved.

In order to shorten bleed down times a little further, larger bore tubing leading to the needle valve was added. It was subsequently discovered that with the same ballast equilibration times but attempting to run at atmospheric pressure, the best pressure that could be reached within 10 seconds of bleed down was 170 psi. Clearly droplets of water in the small bore tubing simply limit the performance of the device at low pressure, presenting too much of a pressure drop. For all the data taken, no pressure source was hooked up to the ballast, effectively rendering the pressure valve (V5) another vent valve.

The temperature probe and readout electronics were then calibrated. A NIST traceable test probe was used for oil temperature. The plot of temperature as displayed on screen (after calibration) and that read by the traceable probe is shown in Figure 21. The diamonds are actual data and the line represents a perfect calibration. The standard deviation of 19 separate point pairs is 1.63 K. As with the pressure signal, resolution is expected to be on the order of 1 K due

![Figure 21 - Temperature calibration curve](image-url)
to the 12 bit analog input.

A second graph (Figure 22) shows the behavior of the oil bath temperature with time as the setpoint is changed using the application Pop and the analog output of the Labjack. The line is the setpoint setting, and the meter and onscreen readings are the squares and diamonds respectively. At the top of the operating range one can observe that the temperature failed to converge to the setpoint. The autotuning function of the PID controller had been turned off, and the proportional band was set too high. At 10:50 the autotuning was turned back on, and the temperature converged within a few minutes.

Because of the sensitive nature of the physics of metastable states approaching the spinodal limit, it would have been preferable to reach the design goal of temperature control within a +/- 0.2 K band. A better analog input device with more bits (preferably 16) would be extremely valuable as an upgrade to the apparatus for future use. As it is, variation of characteristic time with temperature will be shown. However for the deepest penetration towards the spinodal limit,

![Figure 22 - System warmup characteristics](image)

Figure 22 - System warmup characteristics
the equipment is currently insufficient.

5.3 Results

The first tests of the fully commissioned apparatus were performed in January, 2008. Several practical issues became apparent. The motor and stirrer combination suffered from several problems. The motor made (and still makes) various noises as it is operating. The audibly different mechanical sounds are most noticeable at high temperatures (>250°C). This raised the worry that tolerances of the gears in the gearhead were being affected by the oil temperature. The gearhead specification states that the gear parts are all metal. However there is no temperature rating given for the gearhead. In the end it was determined that it was mechanically reasonable to protect the motor further by mounting it on one inch standoffs and making a three piece extension for the agitator. Furthermore, the agitator had a habit of coming off the motor shaft during operation, presumably driven in no small part by expansion of the agitator away from the shaft. Implementing these two extensions appears to have addressed the problem with detachment of the agitator during operation, although the gear noise issues do remain.

The second and more troubling aspect of commissioning in January was seal failures at the ends of the glass tube. The Kalrez seals used for their temperature resistance are compatible with silicone oils such as the Dow Corning diffusion pump oil used. However, after several seal failures, always of the water or steam to air seals, the specifications were reinvestigated and it was found that Kalrez is incompatible with steam. This forced a redesign to move the water or steam to air seals further away from the heated zone, and to replace the Kalrez with Buna N, which has a lower temperature rating but is compatible with water. This was accomplished by the fashioning of extension collars. One of these collars is shown in Figure 23.

The extension collar can be seen in the center of the picture. It has a cut-out that allows the viewing of the top of the glass tube from outside the enclosure, which ended up being a fortuitous aspect during the real experiments. Other aspects of the design that can be seen in this view are the O-ring block with tabbed stainless tubing coming out of the top, the Swagelok union to the
PEEK tubing, the ends of the immersion heater, the thermocouple laying across the top of the enclosure and going into the oil, and a bent copper housing or shield around the standoffs that the motor was mounted on, in order to minimize evaporation of diffusion pump oil.

Even this iteration was not capable of surviving more than 10 or 20 cycles of pressure at 250ºC. The original cut-out extenders fitted to the glass tubing were too large in inner diameter, and O-rings would eventually be extruded through the gap, which was dimensioned to be .005” to .010” larger than the glass tube. When a pair were made that only had .001” to .003” diametrical clearance around the glass tube at nominal diameter, reliability improved. In practice, not all tubes could be used because some were now larger than the i.d. of the finished extender collars.

The first reasonably long (> 10 cycles) experimental data were taken on April 25, 2008. In all cases that follow, the pressure indicated for the measurements (bleed down pressure) was 180 psia. However the algorithm in Pop left the pressure at 177 psi. All the water used was HPLC water, without degassing or filtering.

Pressure, temperature and time since stabilization are recorded by the application Pop every 0.1 seconds. A buffer fills with this data up to 20 samples. Every 2 seconds the first data point in the
Figure 24 - A typical vaporization of a metastable state, or Pop

set is written to another array that records the long-term performance of the system. The graph shows a classic metastable event. Pressure is steady at 173.6 psi for more than 17 seconds. Over about 0.5 seconds the pressure increases to 187 psi, then recoils as some of the ejected steam condenses once it is out of the heated zone. This is recorded as a Pop at 17.1 seconds.

Several different regimes of metastable phenomena were noticeable during the experiments. A typical cavitation graph is shown in Figure 24.

There are two regimes that are not counted as valid metastable vaporizations. One regime is a slow increase in pressure that is fairly linear with time, without a distinct pressure spike of less than 1 second duration. These events are referred to as “creeps” in my notes. A typical creep is shown in Figure 25.

Creeps were taken out of the data by hand by examining each graph individually. Eventually it became easiest to just note creeps as they were being recorded. Any time that a creep was occurring, it was possible to observe refluxing of a liquid vapor mixture through the sight portion of the top of the glass tube. The assumption is that a creep represents a vaporization that happened before the clock started, and that the slow rise in pressure is additional liquid slowly
being transported into the heated zone and being vaporized, primarily from elastic recompression of plastic tubing in the system.

A second phenomenon is a noticeable nucleation before reaching stable pressure. These events are referred to as “blips.” Because the pressure is updated several times onscreen even during the depressurization, it is possible to see when the pressure increases rather than decreasing. Some intelligence was written into Pop to catch these events, but some were only caught by watching the depressurization carefully. Again, like creeps, blips resulted in a visibly different refluxing state when the top section of Simax tube was viewed. Blips were also taken out of the final data.

A third phenomenon is the timeout. The application Pop is designed not to stay in an infinite loop if the liquid never has a nucleation event that is detectable. This seemed like a good feature before the ability to visually confirm liquid or vapor in the tube was developed. However the timeout feature only serves to reduce data at very long times if the test section is truly in the liquid phase. In this first set of data, there were no timeouts.

Figure 25 - An invalid passing of the pressure threshold, or Creep
When the data set is cleaned of blips and creeps, the resulting real pops can be graphed. Such a graph is shown Figure 26, for a temperature of 255ºC and a pressure of 177 psi.

These are 50 different recorded pulses. These pulses were recorded in 5 different experiments, all with the same Simax tube. Eventually, the tube could not be depressurized without a premature vaporization. The assumption was at that point that some damage or flaw had occurred on the inner surface of the tube that was sponsoring nucleation. The experiments were stopped at this point.

As can be seen, more than half of the pulses are in the first 5 seconds. Between 15 and 20 pulses lasted 5 to 20 seconds. One pulse was recorded after 27 seconds, one after 46 seconds, and one after 176 seconds (off the graph). This is clearly Poisson statistics behavior.

The wait times for this data set were histogrammed. The time bin size was adjusted to give 8 bins of equal time spacing. The resulting histogram is shown in Figure 27. Error bars are set at...
+/- $\sqrt{n}$ for each bin. An exponential characteristic was fit to the data between 2.5 and 20 seconds, excluding the very short and very long events. The characteristic time determined from this exponential fit (shown as the smooth curve) is 5.31 seconds. This corresponds to a log $J$ value (for 17 ul) of 1.04. The temperature error, based mainly on analog controls resolution, is +/- 2ºC. The time error, based mainly on the inability to probe nucleations of less than 1 sec characteristic time with any repeatability, is set at +/-1 second. For an average waiting time of 5 seconds, this corresponds to a time error of 20%, or an error in log $J$ of +/- .079.

It is notable that the 0-2.5 second time bin has fewer data points in it than the characteristic time would predict. However blips and creeps appear to include real metastable vaporization events that just happened too quickly for the apparatus to record them. Understood this way, the low number of events in the first bin is explainable. Similarly, the number of events in the last bin, which represents several bins in actuality, is understandably a little high.

---

**Figure 27 - Characteristic time curve at 255ºC**
A similar set of data was taken at the same pressure (177 psi) and 5 degrees cooler (250ºC). It is histogrammed in Figure 28. The data set includes 21 validated pops (cleaned of blips and creeps) taken in 4 sets of experiments with 3 different Simax glass tubes. During the 250ºC runs, the tube lifetime was much shorter than in the 255ºC runs. Typically tubes lasted 20 cycles or so before becoming damaged enough to result in 10 or more blips in a row.

Setting the time bins to 15 seconds wide accommodated most of the data into 8 bins. A fit to an exponential of this data (excluding times over 120 seconds) was also performed, and yielded a characteristic time of 23.0 seconds. This corresponds to a log J value (for 17 ul) of 0.307. The temperature error is as above. The time error for an average waiting time of 23 seconds is about 4%, or an error in log J of +/- .018. It is notable that the lowest bin (0-15 seconds) does not have a number of events significantly under the fit value. This is seemingly due to the fact that the time window is so much larger, and a smaller proportion of real events are under one second and therefore recorded as blips.

Figure 28 - Characteristic time curve at 250ºC
This data set also produced some impressively long metastable states. Four of the 21 pulses that were not recorded as timeouts came after 100 seconds in the superheated state. One of them came after 357 seconds. Most notably, there were 9 valid timeouts. The timeout of a given load of the tube was set to 400 seconds for all experiments. The second and third tube both produced valid timeouts. At 177 psia the boiling point of water is 189°C. The oil bath temperature of 250°C reflects 61°C of superheat. The timeout function in the experimental software introduces an artifact to the data. It is possible if more runs could have been accumulated at 250°C and longer timeout times (e.g. 1000 seconds) that the estimated average waiting time could have been larger.

5.4 Discussion

The two established data points from the previous runs are shown in Figure 29, alongside theoretical J values for 100 and 300 psia water. Note that the combination of the 17 ul volume and 1 second resolution on measurements limits the accessible J values to something like 2. However with a more crisp automation of depressurization, plus better timing resolution on the pulses and better handling of so called blips, the accessible J values could be moved towards 3, which is the reported state of the art for isothermal decompression bubble chamber methods. Overall, the experimental errors are suitably small to allow experimental separation of phenomena over significantly different regimes. Put simply, the data points at 250 and 255°C are separable, distinct, and follow the same trends that other experimenters have seen with other materials.

Several experimental observations should be noted. The typical pattern of individual tube performance is one of fairly random performance (long and short metastable pulses in no particular order) followed by a sharp decline in performance that seems irreversible. However during the 250°C studies, the third tube that was used had the bulk of its timeout runs after the first 20 cycles.
This final tube was eventually taken to 255 and 260ºC, and eventually yielded apparent degradation much like other tubes. Some months after the data above were taken, that same tube was taken up to pressure and temperature again for a brief demonstration. It had been stored all of that time in water at ambient temperature and pressure. It was expected to perform poorly but at least demonstrate nucleation phenomena. Surprisingly, it was able to give fairly long metastable states, perhaps demonstrating some method for recovering good performance. It is possible that this represents the dissolution of gas bubbles trapped on microscopic flaws back into the bulk liquid.

It is also important to note that there were no special precautions taken with the water, or preparation of the parts, other than cleaning with lint free wipers. The entire data taken here may have been part of an aging period required to run all metal flakes and flaws out of the system, especially since most of the metastable periods over 400 seconds came at the end of the experiments. The variability of the data from tube to tube and over time suggest that much more
could be done to understand, control and improve variation. It is encouraging that with very few
controls on material state of preparation of water, reasonably good data could be taken.
6.0 Conclusion

Considering the long metastable times in these experiments for water not under bombardment, at superheats of 60 K or more, it may be reasonable to expect that bulk nucleation in the upflow region of a commercial water target is suppressed for some meaningful fraction of that region. Especially considering that no special care was taken in preparing the metal parts, glassware or water in this experiment, it is also reasonable to suppose that motes and flaws in the water inside an operating target may not induce nucleation in the bulk. At the very least, it is unwise to assume they do induce nucleation to the extent of preventing superheated regions. The quantitative picture of what parts of the target bulk nucleate when and under what conditions has not emerged. However it is clearer now that the target water’s tolerance for superheating, which affects the void fractions and other important characteristics of the target under bombardment, is worthy of further investigation.

That being said, the calculations required to undertake this experiment point to an energetic fluid picture plus an enormous background of small energetic spikes in the water that are seemingly custom made to induce nucleation, especially with respect to the size and minimum energy required. This further points to the need to make more measurements in well controlled conditions to completely develop the physics behind the performance of water targets.

6.1 Relevance to other liquid/particle interactions

The physics and apparatus developed in this work have utility outside of PET isotope target design as well. Production of isotopes for nuclear medicine and other uses requires the operation of encapsulated, molten metal targets at the multi-kilowatt level. Metastable fluid theory and radiation assisted nucleation have not been analyzed or published for these materials or power regimes. Farther away from the superheated state, bubble detectors for neutron monitoring still operate in a metastable region, albeit one with less thermal energy being pumped into local density fluctuations. This work may be applicable to some compositions of those detectors.
Finally, neutron spallation targets such as the recirculating mercury target at the Spallation Neutron Source operate in subcooled states. However, this work also may be helpful in understanding operational limits and the effect of some subspectrum of radiations on that target.
7.0 Future work

7.1 Upgrades to this equipment

There are several easy and potentially important studies and upgrades to the equipment that should render it more useful for future experiments. The first fixes would be to repackage it for slightly easier transport, fasten the lid of the oil chamber to the main enclosure, and several other mechanical niceties. In order to vent more quickly and in a repeatable interval, the manifold of tubing above the heated zone should be enlarged in diameter. Finally, the control electronics should be upgraded to achieve +/- 0.2 K temperature control and faster timing of pulses.

As mentioned above, no special care was taken to prepare the hardware and in particular the glassware. The Simax tubes could be annealed, but would probably change dimension if the annealing is not done very carefully. There may be chemical treatments that would further prepare the inside surface with less flaws. (In particular, in light of some of the research on glass fatigue, anything that could be done to selectively deplete the inside surface of the glass of sodium seems to be worth doing for extended life.) Microfiltration of the liquid downstream of the positive displacement pump, which is a potential source of metal particles, was mentioned during the design review but never implemented. It seems to still be a worthy experimental control.

Finally, some basic tests using this newly commissioned equipment with the improvements mentioned above are indicated. Degassing of the water, filtration of the water, and aging of tubes in situ all should be studied for their relative importance in the stability of the data obtained. In particular, the repeatability of measurements from one tube to the next has not been demonstrated, and the effect of individual tubes should be quantified or bounded as much as possible.
7.2 Measurement with radiation

It will not be possible to perform measurements of water with the exact same spectrum and intensity of radiations that a proton target sees. In particular the primary radiation, the 11 MeV protons, cannot be introduced in the water under test. However, both neutrons and positrons can be introduced in a quantifiable and useful way. In particular, the apparatus is compact enough to go into the cyclotron vault of any number of PET cyclotrons worldwide. The exact spectrum and intensity of neutrons seen by the target can be introduced to the heated test section, and is an experiment that would be very valuable to PET cyclotron target designers.

Similarly, the two data points arising out of this work appear to support Baidakov’s assertion that cosmic rays and other terrestrial sources of radiation increase the J value measured at a given temperature above the theoretically predicted value. It would be very interesting to do measurements at the same temperatures and pressures in a normal lab and in an environment that is as free of radiation as possible (e.g. an underground, contamination free space). This should enable a very full picture of the effect of different radiations on the metastable phenomena, which would be at the heart of a cohesive mechanics for calculating target performance.

7.3 New target designs

This work has led to important insights into the behavior of water in a pressurized metastable environment. However, the work has not yet been applied to actual target designs. It is important to complete the work outline in the sections above before application is attempted. It is still rather unclear what the anticipated time characteristic of pressurized water metastable states are. The flow rates and dimensions and residence times of the current model require modeling of these metastable states down to the millisecond level. Provided the apparatus and theory can be improved to that level, the application of a model update to PET isotope target design would be extremely compelling.
References


33 See, for example R. D. Evans, The Atomic Nucleus, (Krieger Publishing Company, Malabar, Florida 1955). The starting equation in the derivation that follows this reference can be found as equation 29 of Appendix B.


37 Electron stopping in water down to 1 keV electron energy is available from the NIST website, ESTAR program. http://physics.nist.gov/PhysRefData/Star/Text/ESTAR.html


43 D.A. Glaser, Nobel Lecture, Stockholm, December 12, 1960


66 Parker has online design modeling software called inPhorm.  http://www.parker.com


71 http://www.pegasus-glass.com/simax.asp
Appendices
Appendix A – Visual Basic Code

What follows is the Microsoft Visual Basic 6.0 (SP6) form file for Pop!, the application used to collect and store metastable data. The form file includes all the descriptions of the layout of the window, plus all of the internal operation and data handling.

VERSION 5.00
Object = "{E46BCC02-8469-11D5-B00B-00008654A834}#1.0#0"; "ljackuwx.ocx"
Object = "{F9043C88-F6F2-101A-A3C9-08002B2F49FB}#1.2#0"; "COMDLG32.OCX"
Object = "{831FDD16-0C5C-11D2-A9FC-0000F8754DA1}#2.0#0"; "MSCOMCTL.OCX"
Begin VB.Form Form1
  Appearance = 0  'Flat
  BackColor = &H00FFFFC0&
  Caption = "Pop! - The Metastable Limit Measurement Tool"
  ClientHeight = 7470
  ClientLeft = 60
  ClientTop = 450
  ClientWidth = 9435
  BeginProperty Font
    Name = "Tahoma"
    Size = 8.25
    Charset = 0
    Weight = 400
    Underline = 0  'False
    Italic = 0  'False
    Strikethrough = 0  'False
  EndProperty
  LinkTopic = "Form1"
  ScaleHeight = 7470
  ScaleWidth = 9435
  StartUpPosition = 3  'Windows Default
Begin VB.CommandButton Command9
  Caption = "0.1 sec cycle"
  BeginProperty Font
    Name = "Tahoma"
    Size = 9.75
    Charset = 0
    Weight = 700
    Underline = 0  'False
    Italic = 0  'False
    Strikethrough = 0  'False
  EndProperty
  Height = 495
  Left = 3000
  TabIndex = 31
  Top = 2160
  Width = 1695
End
Appearance      =   0  'Flat
BackColor       =   &H00FFFFC0&
BorderStyle     =   0  'None
BeginProperty Font
   Name            =   "Tahoma"
   Size            =   14.25
   CharSet         =   0
   Weight          =   400
   Underline       =   0   'False
   Italic          =   0   'False
   Strikethrough   =   0   'False
EndProperty
ForeColor       =   &H00008000&
Height          =   375
Left            =   360
TabIndex        =   25
Text            =   "Text3"
Top             =   240
Width           =   1815
End
Begin VB.TextBox Text17
   Appearance      =   0  'Flat
   BackColor       =   &H00FFFFC0&
   BorderStyle     =   0  'None
   BeginProperty Font
      Name            =   "Tahoma"
      Size            =   14.25
      CharSet         =   0
      Weight          =   400
      Underline       =   0   'False
      Italic          =   0   'False
      Strikethrough   =   0   'False
   EndProperty
   ForeColor       =   &H00008000&
   Height          =   375
   Left            =   360
   TabIndex        =   24
   Text            =   "Text17"
   Top             =   840
   Width           =   1815
End
Begin VB.TextBox Text16
   BackColor       =   &H00FFFFC0&
   BorderStyle     =   0  'None
   Height          =   255
   Left            =   120
   TabIndex        =   23
   Top             =   6840
   Width           =   2895
End
Begin VB.TextBox Text15
   BackColor       =   &H00FFFFC0&
   BorderStyle     =   0  'None
   Height          =   255
   Left            =   120
   Top             =   6840
   Width           =   2895
End
DialogTitle = "Open a file or accept default..."

Begin VB.TextBox Text12
    Height = 285
    Left = 8400
    TabIndex = 17
    Text = "10"
    Top = 2760
    Width = 495
End

Begin VB.TextBox Text11
    Appearance = 0 'Flat
    BackColor = &H00FFFFC0&
    BorderStyle = 0 'None
    Height = 255
    Left = 6480
    TabIndex = 16
    Text = "Pulse size"
    Top = 2760
    Width = 1695
End

Begin VB.TextBox Text10
    Height = 285
    Left = 8400
    TabIndex = 15
    Text = "30"
    Top = 3240
    Width = 495
End

Begin VB.TextBox Text9
    Height = 285
    Left = 8400
    TabIndex = 14
    Text = "300"
    Top = 2280
    Width = 495
End

Begin VB.TextBox Text8
    Appearance = 0 'Flat
    BackColor = &H00FFFFC0&
    BorderStyle = 0 'None
    Height = 255
    Left = 6480
    TabIndex = 13
    Text = "Wait for pulse time"
    Top = 3240
    Width = 1695
End

Begin VB.TextBox Text7
    Appearance = 0 'Flat
    BackColor = &H00FFFFC0&
    BorderStyle = 0 'None
    Height = 255
    Left = 6480
    TabIndex = 12
Pressure threshold
Text = "Off"
Top = 3000
Width = 375
End

Begin VB.CommandButton Command5
Caption = "Vent valve"
BeginProperty Font
    Name = "Tahoma"
    Size = 9.75
    CharSet = 0
    Weight = 700
    Underline = 0 'False
    Italic = 0 'False
    Strikethrough = 0 'False
EndProperty
Height = 495
Left = 360
TabIndex = 7
Top = 2160
Width = 1695
End

Begin VB.CommandButton Command3
Caption = "Pressure valve"
BeginProperty Font
    Name = "Tahoma"
    Size = 9.75
    CharSet = 0
    Weight = 700
    Underline = 0 'False
    Italic = 0 'False
    Strikethrough = 0 'False
EndProperty
Height = 495
Left = 360
TabIndex = 6
Top = 2880
Width = 1695
End

Begin VB.Timer Timer1
Interval = 200
Left = 8160
Top = 6840
End

Begin VB.CommandButton Command4
Caption = "Stop"
BeginProperty Font
    Name = "Tahoma"
    Size = 8.25
    CharSet = 0
    Weight = 700
    Underline = 0 'False
    Italic = 0 'False
    Strikethrough = 0 'False
EndProperty
Height = 495
Private Sub Command9_Click()
    idnum = -1#
End
Private Sub Form_Load()
    tset = 20#
End Sub

Private Sub Form_Close()
    Close filename
End Sub
Private Sub Command1_Click()
    idnum = -1#
    If Text1.Text = "Off" Then
        dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 0, 1, 0)
        Text1.Text = "On"
    Else
        dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 0, 1, 1)
        Text1.Text = "Off"
    End If
End Sub

Private Sub Command2_Click()
    idnum = -1#
    If Text2.Text = "Off" Then
        dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 3, 1, 0)
        Text2.Text = "On"
    Else
        dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 3, 1, 1)
        Text2.Text = "Off"
    End If
End Sub

Private Sub Command3_Click()
    idnum = -1#
    If Text4.Text = "Off" Then
        dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 1, 1, 0)
        Text4.Text = "On"
    Else
        dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 1, 1, 1)
        Text4.Text = "Off"
    End If
End Sub

Private Sub Command4_Click()
    If stoprun = False Then stoprun = True
Private Sub Command5_Click()
    idnum = -1#
    If Text5.Text = "Off" Then
        dummy = Ljackuxxl.EDigitalOutX(idnum, 0, 2, 1, 0)
        Text5.Text = "On"
    Else
        dummy = Ljackuxxl.EDigitalOutX(idnum, 0, 2, 1, 1)
        Text5.Text = "Off"
    End If
End Sub

Private Sub Command6_Click()
    moveon = False
    If attemp = False Then
        Dialog.Show
        Do Until moveon = True
            pause (0.1)
            DoEvents
        Loop
        If Not continue Then Exit Sub
    End If
    CommonDialog1.DialogTitle = "Pick a file or accept the default..."
    CommonDialog1.DefaultExt = "txt"
    dumstr = Format(Now, "yyyymmddhhmm")
    filename = dumstr & ".txt"
    CommonDialog1.filename = filename
    CommonDialog1.InitDir = "C:\Documents and Settings\pcsetup\My Documents\Pop files"
    CommonDialog1.ShowOpen
    filename = CommonDialog1.filename
    Open filename For Output As #1
    dumstr = "***********************************************************"
    Print #1, dumstr
    dumstr = "Pop! - Application for controlling and recording metastable" water measurements - C.W.Alvord - November, 2007"
    Print #1, dumstr
    dumstr = "***********************************************************"
    Print #1, dumstr
    pthresh = Val(Text9.Text)
    waittime = Val(Text10.Text)
    pulsesize = Val(Text12.Text)
    cycles = Val(Text13.Text)
    stoprun = False
Command4.Visible = True
dumstr = "Pressure for measurement: " & Format(pthresh, "0") & " psi"
Print #1, dumstr
dumstr = "Temperature setpoint: " & Format(tset, "0.0") & " C"
Print #1, dumstr
dumstr = "Spike trigger: " & Format(pulsesize, "0") & " psi"
Print #1, dumstr
dumstr = "Timeout at: " & Format(waittime, "0") & " seconds"
Print #1, dumstr
dumstr = "Running for " & Format(cycles, "0") & " cycles"
Print #1, dumstr
'   Get to 1420 psi
'
ProgressBar1.Max = cycles + 1
ProgressBar1.Visible = True
ProgressBar1.Value = 0
For i = 1 To cycles
    ProgressBar1.Value = i
    Text16.Text = "Now on cycle number " & Format(i, "0") & " of " & Format(cycles, "0")
    Text16.Refresh
    dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 0, 1, 0)
    Text1.Text = "On"
    Text1.Refresh
    pause (1#)
    dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 3, 1, 0)
    Text2.Text = "On"
    Text2.Refresh
    Text6.Text = "Waiting for pressure to exceed 1420 psi..."
    Text6.Refresh
    If wait_for_pressure(1420, 1, 60) > 0# Then
        Text6.Text = "Reached > 1420 psi.  Now purging vapor..."
        Text6.Refresh
        pause (5#)
    Else
        Text6.Text = "Timeout"
        Text6.Refresh
    End If
    dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 3, 1, 1)
    Text2.Text = "Off"
    Text2.Refresh
    '   Bleed down to desired pressure
    '
    pause (3#)
    dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 0, 1, 1)
    Text1.Text = "Off"
    Text1.Refresh
    Text6.Text = "Bleeding down to " & Format(pthresh, "0") & " psi..."
    Text6.Refresh
    If wait_for_pressure(pthresh, -1, 30) > 0# Then
        dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 0, 1, 0)
        Text1.Text = "On"
        Text1.Refresh
        Text6.Text = "Pressure reached, flushing..."
        Text6.Refresh
    Else
        Text6.Text = "Timeout"
        Text6.Refresh
    End If
pause (1#)
pact = pnow
Text6.Text = "Stable at " & Format(pact, "0") & " psi"
Print #1, "Running cycle " & Format(i, "0")
Print #1, "Pulse trigger at " & Format(pact + pulsesize, "0.0") & " psi."
Else
Text6.Text = "Timeout."
Text6.Refresh
Print #1, "Cycle " & Format(i, "0") & " never bled down."
If stoprun = True Then Exit For
End If
ReDim pulsearr(3, Int(waittime / 2) + 200)
pulsedat = wait_for_pressure(pact + pulsesize, 1, waittime, True)
If pulsedat > 0# Then
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 3, 1, 1)
Text2.Text = "Off"
Text2.Refresh
dumstr = "Popped in " & Format(pulsedat, "0.0") & " seconds!"
Text6.Text = dumstr
Text6.Refresh
Print #1, dumstr
For j = 0 To k + 1 + 19
Print #1, Format(pulsearr(0, j), "0.0") & ", " & Format(pulsearr(1, j), "0.0") & ", " & Format(pulsearr(2, j), "0.0") & ", " & Format(tnow, "0.0")
Next j
Else
Text6.Text = "Timeout."
Text6.Refresh
Print #1, "Cycle " & Format(i, "0") & " never pulsed."
End If
'
'Secondary pressure vessel treatment
'
pause (2#)
dumstr = "Renormalizing pressure ballast..."
Text6.Text = dumstr
Text6.Refresh
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 2, 1, 0)
Text5.Text = "On"
Text5.Refresh
pause (0.3)
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 2, 1, 1)
Text5.Text = "Off"
Text5.Refresh
pause (0.3)
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 1, 1, 0)
Text4.Text = "On"
Text4.Refresh
pause (10)
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 1, 1, 1)
Text4.Text = "Off"
Text4.Refresh
If stoprun = True Then Exit For
Next i
ProgressBar1.Visible = False
Text16.Text ="
Text16.Refresh
Command4.Visible = False
End Sub

Private Sub Command7_Click()
  tset = Val(Text18.Text)
  dummy = Ljackuwx1.EAnalogOutX(idnum, 0, 0.01367 * tset + 0.73195, 0)
End Sub

Private Sub Command8_Click()
idnum = -1#
If Text20.Text = "Off" Then
  dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 4, 1, 0)
  Text20.Text = "On"
Else
  dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 4, 1, 1)
  Text20.Text = "Off"
End If
End Sub

Private Sub Timer1_Timer()
idnum = -1#
  dummy = Ljackuwx1.EAnalogInX(idnum, 0, 8, 2, overvoltage, voltage)
  pnow = voltage * 512.24 - 502.99
  dummy = Ljackuwx1.EAnalogInX(idnum, 0, 9, 2, overvoltage, voltage)
  tnow = voltage * 82.5 - 62.5
  Text3.Text = Format(pnow, "0.0") & " psia"
  Text3.Refresh
  Text17.Text = Format(tnow, "0.0") & " C"
  If Abs(tnow - tset) > 3 Then
    attemp = False
    Text17.ForeColor = &HC0&
  Else
    attemp = True
    Text17.ForeColor = &H8000&
  End If
  Text17.Refresh
  'Text4.Text = Format(voltage, "0.00") & " volts"
  'Text4.Refresh
  If tnow > 50# Then
    idnum = -1#
    dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 4, 1, 0)
    Text20.Text = "On"
  Else
    If tset > 50# Then
idnum = -1#
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 4, 1, 0)
Text20.Text = "On"
Else
    idnum = -1#
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 4, 1, 1)
    Text20.Text = "Off"
End If
End If

If pnow > 2500# Then
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 3, 1, 1)
Text2.Text = "Off"
dummy = Ljackuwx1.EDigitalOutX(idnum, 0, 0, 1, 0)
Text1.Text = "On"
End If

End Sub
Function wait_for_pressure(ByVal Threshold As Single, ByVal Direction As Integer, ByVal Timeout As Single, Optional ByVal filling As Boolean) As Single
If IsMissing(filling) Then filling = False
If filling Then
    k = 0
    l = 0
    ReDim smalldatarr(3, 20)
    ReDim smalldatbuf(3, 20)
    ProgressBar2.Min = 0
    ProgressBar2.Max = Int(Timeout)
    ProgressBar2.Value = 0
    ProgressBar2.Visible = True
End If
stoprun = False
nowtim = Timer
wait_for_pressure = -1#
Do Until stoprun = True
    DoEvents
    If filling Then
        smalldatarr(0, l) = Timer - nowtim
        smalldatarr(1, l) = pnow
        smalldatarr(2, l) = tnow
    End If
    If Direction > 0 Then
        If pnow > Threshold Then
            If filling Then
                For m = 0 To 19
                    pulsarr(0, k + m) = smalldatbuf(0, m)
pulsarr(1, k + m) = smalldatbuf(1, m)
pulsarr(2, k + m) = smalldatbuf(2, m)
                Next m
                For m = 0 To 1 - 1
                    pulsarr(0, k + 20 + m) = smalldatarr(0, m)
pulsarr(1, k + 20 + m) = smalldatarr(1, m)
pulsarr(2, k + 20 + m) = smalldatarr(2, m)
                Next m
            End If
        End If
    End If
End Do
End Function
Next m
End If
    wait_for_pressure = Timer - nowtim
Exit Do
End If
Else
    If pnow < Threshold Then
        wait_for_pressure = Timer - nowtim
        Exit Do
    End If
End If
If Timer - nowtim > Timeout Then
    wait_for_pressure = -1#
    Exit Do
End If
If filling Then
    testnum = Timer - nowtim
    If testnum < 0 Then testnum = 0
    ProgressBar2.Value = testnum
    Text15.Text = Format(Timer - nowtim, "0") & " of " & Format(waittime, "0") & " seconds completed."
    Text15.Refresh
If l = 19 Then
    pulsearr(0, k) = smalldatarr(0, 0)
pulsearr(1, k) = smalldatarr(1, 0)
pulsearr(2, k) = smalldatarr(2, 0)
k = k + 1
    For m = 0 To 19
        smalldatbuf(0, m) = smalldatarr(0, m)
        smalldatbuf(1, m) = smalldatarr(1, m)
        smalldatbuf(2, m) = smalldatarr(2, m)
    Next m
    ReDim smalldatarr(3, 20)
l = 0
Else
    l = l + 1
End If
End If
pause (0.1)
Loop
ProgressBar2.Visible = False
Text15.Text = ""
Text15.Refresh
End Function
Private Sub pause(ByVal secs As Single)
paustim = Timer
Do Until Timer - paustim > secs
DoEvents
Loop
End Sub
Appendix B – Typical output file excerpt

The first few pages of the output file from 12:19 p.m. on 25Apr08 are shown below. Immediately underneath the header are the user configured variables for the run. Primary data for each pulse cycle is recorded in the section immediately after the line “Running for 100 cycles.” Because there is the potential to bleed to a pressure slightly above or below the desired pressure, the pulse trigger value (actual pressure bled to plus pressure threshold) is recorded each time. After all the main data for the cycles is written, the mean and the variance are also calculated and written out. Finally, a dump of all pulse data is written for every pulse. Because of the size of this data, only the first pulse cycle and a section of the second one are copied here. Cycle data is a series of 3 element vectors, with the values separated by commas. The first value is time since stable pressure reached. The second value is pressure. The third value is temperature.

***********************************************************
Pop! - Application for controlling and recording metastable water measurements - C.W.Alvord - November, 2007
***********************************************************
Pressure for measurement: 180 psi
Temperature setpoint: 255.0 C
Spike trigger: 10 psi
Timeout at: 600 seconds
Running for 100 cycles
Running cycle 1
Pulse trigger at 183.6 psi.
Popped in 158.7 seconds!
Running cycle 2
Pulse trigger at 182.3 psi.
Popped in 48.9 seconds!
Running cycle 3
Pulse trigger at 182.3 psi.
Popped in 54.1 seconds!
Running cycle 4
Pulse trigger at 186.1 psi.
Popped in 43.7 seconds!
Running cycle 5
Pulse trigger at 189.8 psi.
Popped in 40.9 seconds!
Running cycle 6
Pulse trigger at 182.3 psi.
Cycle 6 never pulsed.
Running cycle 7
Pulse trigger at 183.6 psi.
Popped in 29.6 seconds!
Running cycle 8

121
Pulse trigger at 184.8 psi.
Popped in 37.5 seconds!
Running cycle 9
Pulse trigger at 184.8 psi.
Popped in 40.1 seconds!
Running cycle 10
Pulse trigger at 184.8 psi.
Popped in 36.8 seconds!
Running cycle 11
Pulse trigger at 184.8 psi.
Popped in 20.7 seconds!
Running cycle 12
Pulse trigger at 179.8 psi.
Popped in 15.6 seconds!
Running cycle 13
Pulse trigger at 178.6 psi.
Popped in 41.1 seconds!
Running cycle 14
Pulse trigger at 181.1 psi.
Popped in 41.8 seconds!
Running cycle 15
Pulse trigger at 181.1 psi.
Popped in 39.4 seconds!
Running cycle 16
Pulse trigger at 179.8 psi.
Popped in 38.2 seconds!
Running cycle 17
Pulse trigger at 181.1 psi.
Popped in 22.8 seconds!
Running cycle 18
Pulse trigger at 181.1 psi.
Popped in 23.1 seconds!
Running cycle 19
Pulse trigger at 182.3 psi.
Popped in 25.9 seconds!
Running cycle 20
Pulse trigger at 178.6 psi.
Popped in 25.7 seconds!
Running cycle 21
Pulse trigger at 179.8 psi.
Popped in 23.5 seconds!
Running cycle 22
Pulse trigger at 177.3 psi.
Popped in 28.2 seconds!
Running cycle 23
Pulse trigger at 182.3 psi.
Popped in 19.5 seconds!
Running cycle 24
Pulse trigger at 177.3 psi.
Popped in 1.9 seconds!
Running cycle 25
Pulse trigger at 196.1 psi.
Popped in 27.6 seconds!
Running cycle 26
Pulse trigger at 199.8 psi.
Popped in 23.5 seconds!
Running cycle 27
Pulse trigger at 187.3 psi.
Popped in 23.7 seconds!
Running cycle 28
Pulse trigger at 181.1 psi.
Popped in 25.0 seconds!
Running cycle 29
Pulse trigger at 184.8 psi.
Popped in 29.7 seconds!
Running cycle 30
Pulse trigger at 182.3 psi.
Popped in 17.1 seconds!
Running cycle 31
Pulse trigger at 181.1 psi.
Popped in 31.8 seconds!
Running cycle 32
Pulse trigger at 178.6 psi.
Popped in 6.7 seconds!
Running cycle 33
Pulse trigger at 181.1 psi.
Popped in 9.6 seconds!
Running cycle 34
Pulse trigger at 177.3 psi.
Popped in 6.4 seconds!
Running cycle 35
Pulse trigger at 182.3 psi.
Popped in 19.2 seconds!
Running cycle 36
Pulse trigger at 179.8 psi.
Popped in 19.2 seconds!
Running cycle 37
Pulse trigger at 177.3 psi.
Popped in 14.2 seconds!
Running cycle 38
Pulse trigger at 181.1 psi.
Popped in 14.3 seconds!
Running cycle 39
Pulse trigger at 176.1 psi.
Popped in 9.8 seconds!
Running cycle 40
Pulse trigger at 186.1 psi.
Popped in 21.4 seconds!
Running cycle 41
Pulse trigger at 183.6 psi.
Popped in 8.1 seconds!
Running cycle 42
Pulse trigger at 183.6 psi.
Popped in 19.7 seconds!
Running cycle 43
Pulse trigger at 179.8 psi.
Popped in 17.1 seconds!
Running cycle 44
Pulse trigger at 186.1 psi.
Popped in 20.1 seconds!
Running cycle 45
Pulse trigger at 179.8 psi.
Popped in 19.5 seconds!
Running cycle 46
Pulse trigger at 178.6 psi.
Popped in 1.9 seconds!
Running cycle 47
Pulse trigger at 182.3 psi.
Popped in 9.5 seconds!
Running cycle 48
Pulse trigger at 181.1 psi.
Cycle 48 never pulsed.
Running cycle 49
Pulse trigger at 176.1 psi.
Popped in 7.2 seconds!
Running cycle 50
Pulse trigger at 182.3 psi.
Popped in 7.8 seconds!
Running cycle 51
Pulse trigger at 176.1 psi.
Popped in 12.0 seconds!
Running cycle 52
Pulse trigger at 181.1 psi.
Popped in 9.8 seconds!
Running cycle 53
Pulse trigger at 182.3 psi.
Popped in 1.1 seconds!
Running cycle 54
Pulse trigger at 181.1 psi.
Popped in 9.1 seconds!
Running cycle 55
Pulse trigger at 178.6 psi.
Popped in 0.7 seconds!
Running cycle 56
Pulse trigger at 176.1 psi.
Popped in 7.6 seconds!
Running cycle 57
Pulse trigger at 174.8 psi.
Cycle 57 never pulsed.
Mean is 23.4 seconds.
Variance is 512.5 seconds.
Cycle number 1
0.0, 173.6, 253.8
2.3, 173.6, 253.8
4.7, 173.6, 254.0
7.2, 173.6, 253.8
9.6, 173.6, 253.8
12.0, 173.6, 253.8
14.4, 173.6, 253.6
16.8, 173.6, 253.8
19.2, 173.6, 253.8
21.6, 173.6, 253.8
24.0, 173.6, 253.8
26.4, 173.6, 253.8
28.9, 173.6, 253.8
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At this point a number of array rows filled only with zeroes have been omitted for brevity. The application writes out all of the array, which does not redimension, regardless of if it is filled or not.

Cycle number 2
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2.4, 172.3, 254.8
4.8, 172.3, 254.8
7.2, 172.3, 254.8
9.6, 172.3, 254.8
12.0, 172.3, 254.8
14.4, 172.3, 254.6
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| 48.9, 183.6, 254.8 |
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End of example
Vita

Charles William Alvord was born in Fullerton, California on November 25, 1961. He was raised in Menlo Park, California, where he graduated from Menlo Atherton High School in 1979. He went to the University of California, Berkeley, and graduated with a Major in Physics in 1984.

Charles was first employed after college with Varian Associates in Palo Alto, California as an Electron Gun Design Engineer. In 1990 he moved to CTI Cyclotron Systems in Berkeley, California as a Target Design Engineer. When CTI relocated their California facilities to the main office in Knoxville, Tennessee in October 1990, Bill moved to Knoxville. He attended the University of Tennessee while working, earning a Masters in Nuclear Engineering in 2004. He remains a full time employee of CTI (now Siemens). He is pursuing a Doctorate in Nuclear Engineering at the University of Tennessee.