AN OPTICAL STUDY OF THE CRITICAL
BEHAVIOUR OF CHF₃

By

MICHAEL PAUL STEIN

B.Sc., The University of Manitoba, 1983

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
DEPARTMENT OF PHYSICS

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1986
© Michael Paul Stein, 1986
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of PHYSICS

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date APRIL 29, 1986
To the memory of my grandmother, Clara Stein,

and my grandfather, Ross McNaught
The coexistence curve for CHF$_3$, measured in the reduced temperature range $4 \times 10^{-6} < -t < 3.5 \times 10^{-2}$ by focal plane interference methods, has been analyzed in terms of the correction to scaling prediction

\[
\frac{\rho_\lambda - \rho_v}{\rho_c} = B_0 |t|^\beta (1 + B_1 |t|^\Delta + B_2 |t|^{2\Delta})
\]

to yield values of the critical exponent $\beta$, the critical temperature $T_c$, and the amplitudes $B_0$, $B_1$ and $B_2$. An image plane interference technique has been employed in the reduced temperature range $1.7 \times 10^{-5} < t < 2 \times 10^{-4}$ to obtain pressure-density isotherms for CHF$_3$. These isotherms are used to determine a value of the critical exponent $\gamma$ defined by the compressibility power law expression

\[
\kappa_T = \Gamma_0 |t|^{-\gamma}.
\]
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>.................................................................</td>
<td>iii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>.................................................................</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>.................................................................</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>.................................................................</td>
<td>vii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>.................................................................</td>
<td>viii</td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>.................................................................</td>
</tr>
<tr>
<td>2</td>
<td>THEORY</td>
<td>.................................................................</td>
</tr>
<tr>
<td>2.1</td>
<td>Introduction to Theories of Phase Transitions</td>
<td>.................................................................</td>
</tr>
<tr>
<td>2.2</td>
<td>Classical Theories</td>
<td>.................................................................</td>
</tr>
<tr>
<td>2.3</td>
<td>Modern Theories</td>
<td>.................................................................</td>
</tr>
<tr>
<td>3</td>
<td>OPTICS</td>
<td>.................................................................</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>.................................................................</td>
</tr>
<tr>
<td>3.2</td>
<td>Fraunhofer Diffraction</td>
<td>.................................................................</td>
</tr>
<tr>
<td>3.3</td>
<td>Image Plane Interference</td>
<td>.................................................................</td>
</tr>
<tr>
<td>3.4</td>
<td>The Lorentz-Lorenz Relationship</td>
<td>.................................................................</td>
</tr>
<tr>
<td>4</td>
<td>THE EXPERIMENT</td>
<td>.................................................................</td>
</tr>
<tr>
<td>4.1</td>
<td>The Cell</td>
<td>.................................................................</td>
</tr>
<tr>
<td>4.2</td>
<td>Temperature Control</td>
<td>.................................................................</td>
</tr>
<tr>
<td>4.3</td>
<td>Experimental Procedure</td>
<td>.................................................................</td>
</tr>
<tr>
<td>Chapter</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>RESULTS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Fraunhofer Diffraction Pattern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Image Plane Pattern</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>CONCLUSION</td>
<td></td>
<td></td>
</tr>
<tr>
<td>REFERENCES</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Experimental and theoretical values of the critical exponents $\alpha$, $\beta$, $\gamma$ and $\delta$</td>
<td>20</td>
</tr>
<tr>
<td>Fig.</td>
<td>Description</td>
</tr>
<tr>
<td>------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>The pure fluid phase diagram</td>
</tr>
<tr>
<td>2.</td>
<td>Some possible paths on the phase diagram</td>
</tr>
<tr>
<td>3.</td>
<td>Ideal gas isotherms</td>
</tr>
<tr>
<td>4.</td>
<td>Van der Waals isotherms</td>
</tr>
<tr>
<td>5.</td>
<td>Density profiles of a pure fluid in the earth's gravitational field</td>
</tr>
<tr>
<td>6.</td>
<td>The Fraunhofer diffraction pattern</td>
</tr>
<tr>
<td>7.</td>
<td>The optical set-up</td>
</tr>
<tr>
<td>8.</td>
<td>The cell</td>
</tr>
<tr>
<td>9.</td>
<td>The temperature control circuit</td>
</tr>
<tr>
<td>10.</td>
<td>The pulse-width modulation circuit used to control the bath temperature</td>
</tr>
<tr>
<td>11.</td>
<td>Fringe pattern samples</td>
</tr>
<tr>
<td>12.</td>
<td>Log-log plot of order parameter, ((\rho_L - \rho_v)/\rho_c), versus reduced temperature, (t = (T - T^\circ)/T^\circ)</td>
</tr>
<tr>
<td>13.</td>
<td>Sensitive log-log plot of ((\rho_L - \rho_v)/\rho_c</td>
</tr>
<tr>
<td>14.</td>
<td>Plot of (P_o - P) versus reduced temperature, (t = (T - T^\circ)/T^\circ)</td>
</tr>
<tr>
<td>15.</td>
<td>Plot of isothermal compressibility, (\kappa_T), versus reduced temperature, (t = (T - T^\circ)/T^\circ)</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

It has been a pleasure to work in the critical phenomena lab at UBC. I am very grateful to Dr. David Balzarini for this opportunity and for his supervision of my work on this project.

Friends have helped a great deal. Among them, I would like to thank Barbara Frisken, my dance partner; Nick Mortimer, my draftsman; and Tony "Spud" Noble, my auto mechanic. I offer a special thanks to my colleague John de Bruyn, who has allowed me to tap his knowledge and experience in the lab. His assistance and encouragement were invaluable.

I appreciatively acknowledge financial support received from the Natural Sciences and Engineering Research Council of Canada.

Thanks also to Dr. Birger Bergersen for helpful comments and criticisms, to Mark Halpern for cutting and pasting, and to Antoinette Tse, who typed this manuscript.

Finally, I wish to thank my parents, Paul and Helen, and my sister, Shannon. Their unfailing support of my work has been of great benefit to me.
Chapter 1
INTRODUCTION

This thesis describes two optical experiments that were performed to study the liquid-vapour phase transition in the pure fluid CHF$_3$. In the first experiment, the subcritical temperature dependence of the difference in liquid and vapour densities, $\rho_L - \rho_V$, was determined from an analysis of a Fraunhofer diffraction pattern produced by a collimated laser beam that traversed a thin CHF$_3$ sample cell. In the second experiment, the sample cell was placed in one arm of a Mach-Zehnder interferometer; the resultant interference pattern, recorded as the sample was heated through $T_c$, was used to obtain pressure-density isotherms. These in turn yielded the temperature dependence of the isothermal compressibility, $\kappa_T$, along the critical isochore. Near $T_c$, both quantities, $\rho_L - \rho_V$ and $\kappa_T$, are expected to obey power laws:

$$\rho_L - \rho_V \sim |t|^\beta$$

$$\kappa_T = \frac{L(d\rho)}{\rho(dP)} \sim |t|^{-\gamma},$$

where $t = (T - T_c)/T_c$ is the reduced temperature. The parameters $\beta$ and $\gamma$ are critical exponents which are predicted to be universal for all pure fluids and, in fact, for other types of systems as well. A major objective of the two experiments was to determine values for $\beta$ and $\gamma$. 
The measurement of these and other critical exponents is particularly
difficult in pure fluids, for which the critical region is known to be very
small; i.e., the power law behaviour expressed in Eqs. (1.1) and (1.2)
appears to hold only for $|t| < 10^{-5}$. Furthermore, significant density
gradients near the critical point make conventional pressure-volume methods
awkward and unreliable. Optical interference methods, on the other hand,
when used in conjunction with a stable and precise temperature control
system, are particularly well-suited to making high precision measurements in
the critical region of pure fluids. The deflection of individual light rays
traversing a thin sample is sufficiently small that each ray probes a region
of essentially constant density.

The second major goal of this work was to investigate the existence of
corrections to Eqs. (1.1) and (1.2) that are expected when measurements are
made outside the asymptotic critical region. Current theories predict that,
as the distance from $T_c$ is increased, it is necessary to modify the power law
dependences of thermodynamic quantities by the addition of so-called
correction-to-scaling terms. A detailed analysis of the Fraunhofer
diffraction data was performed in an attempt to confirm and measure the
departure from power law behaviour exhibited by the density difference
$\rho_L - \rho_v$.

The remainder of this introduction is devoted to a historical survey
which will help to illustrate how the experiments of this thesis fit into the
overall picture of critical phenomena.

Research in the field of critical phenomena was triggered in the late
1860's by the experimental work of Thomas Andrews, who found that
liquid-vapour coexistence in CO₂ is not observed above a critical temperature $T_c \approx 32°C$. A theoretical explanation of this phenomenon was proposed by van der Waals in 1873. Van der Waals derived an equation of state that described various aspects of the liquid-vapour phase transition in a pure fluid. The shapes of isotherms and the coexistence curve were predicted, as was the critical region behaviour of certain thermodynamic properties. The van der Waals theory is discussed in Sec. 2.2.

Similar developments took place in the field of ferromagnetism. The existence in iron of a critical temperature above which spontaneous magnetization did not occur was first reported by Hopkinson in 1890, and thoroughly investigated by Curie in 1895. In 1907, Weiss formulated a theory to account for the effect. In many respects, the Weiss theory was analogous to that of van der Waals. In fact, they are both characteristic examples of large class of theories known as classical or mean field theories of critical phenomena. Such theories have been devised for a variety of systems exhibiting phase transitions and, when first developed, they appeared to be in approximate agreement with the limited and somewhat crude experimental results available at the time. Of particular importance was van der Waals' law of corresponding states — the first formal statement concerning the universal features that pervade the study of critical phenomena.

With the advent of more numerous and sophisticated experiments, however, it gradually became apparent in the early decades of the twentieth century that the predictions of classical theories were not in quantitative agreement with experimental results. The most convincing evidence of discrepancies between theory and experiment came in 1945 from Guggenheim's
detailed study of the coexistence curves of various pure fluids. Guggenheim obtained a value of $\beta = 1/3$ which clearly disagreed with the classical value $\beta = 1/2$. The classical theories presented some important qualitative concepts — particularly that of universality — but lacked some fundamental ingredients. Attempts to modify or extend these theories did not succeed. A new and more complete type of theory was required for a realistic explanation of critical phenomena.

The first steps towards a new approach were studies of the Ising model. Developed in 1925, the Ising model was initially intended to describe ferromagnetic systems. It has since turned out to be an extremely important model, applicable to a variety of systems, including antiferromagnets, lattice gases and DNA molecules. In its simplest form, the Ising model consists of a lattice of spins, each spin interacting with its nearest neighbour; the coupling energy is of constant magnitude, its sign depending on whether adjacent spins are parallel or antiparallel. The one-dimensional Ising model shows no phase transition, but the two-dimensional version, solved analytically by Onsager in 1944, does predict a phase transition. While an analytic solution to the three-dimensional case has not been found, there are continuing efforts to refine numerical solutions to the problem. In particular, there has been considerable success in calculating 3-D Ising model critical exponents which, it turns out, are in better agreement with experimental results than classical exponents.

Developments in modern theories pertaining to pure fluids started in 1952 when Lee and Yang proved that the lattice gas model is mathematically
isomorphic to the Ising model. More recently, it has been shown that pure fluids, binary fluids, lattice gases and Ising-like spin systems all belong to the same universality class; i.e., they each exhibit critical behaviour that may be treated by the same mathematical techniques, with the same results obtained for each type of system.

Further significant theoretical developments were introduced with Widom's scaling theory (1965) and Kadanoff's application of scaling theory to spin systems (1966). In 1971, Wilson formulated the renormalization group approach, a powerful mathematical technique that is used to calculate properties of systems near the critical point. The basic concepts behind these contemporary theories are outlined in Sec. 2.3.

There have been equally substantial improvements in experimental methods used to study phase transitions. As explained earlier, the common goal is to make precise measurements as near to the critical point as possible. For studies of pure fluids, it has been necessary to find alternatives to the conventional pressure-volume measurements which become exceedingly difficult in the critical region. Buoyant spheres were used by Maass in 1938 to study the density distribution in CO₂. In 1952, Habgood and Schneider obtained similar information for Xe using a radioactive tracer. More recently Pittman et al used a sample cell containing two small parallel plate capacitors to make dielectric constant measurements in ³He and a ³He - ⁴He mixture. Pestak and Chan have used this capacitance method, with a four-capacitor cell, to make high precision measurements in N₂ and Ne. They obtained values of β, γ and correction terms that are in good agreement with current theories. Yet another approach is the light
scattering method used by Guttinger and Cannell\textsuperscript{16} in 1981 to investigate corrections to scaling in Xe.

Among the most elegant and accurate means of investigating critical point behaviour are methods using optical interference techniques. Lorentzen\textsuperscript{17} was the first to try this approach when, in 1953, he examined the critical region density distribution of carbon dioxide by measuring the diffraction of parallel beams of light passing through a prismatic sample vessel. In 1954, Palmer\textsuperscript{18} used a Schlieren optical system and a sample cell with plane parallel windows to study CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{6} and Xe. High precision interferometric measurements similar to those described in this thesis were first performed by Wilcox and Balzarini\textsuperscript{19,20} in 1968 to study the critical region properties of xenon. These techniques have since been used by Balzarini and Ohrn\textsuperscript{21} to measure in SF\textsubscript{6} a temperature dependence in the effective value of $\beta$, thus demonstrating the need for corrections to scaling, and by Hocken and Moldover\textsuperscript{22} to investigate Xe, SF\textsubscript{6} and CO\textsubscript{2} sufficiently close to their critical points to obtain values of $\beta$ consistent with theoretical results. In 1983, Balzarini and Mouritsen\textsuperscript{23} used the same interference methods to examine universal ratios of correction amplitudes in Xe.

While the existence of corrections to scaling is now well-established, more data must be collected in order to make an unambiguous evaluation of the predicted quantitative nature of these corrections. Studies such as the one presented here should help to make such an evaluation possible.
Chapter 2
THEORY

2.1. Introduction to Phase Transitions

A pure fluid system is one consisting of only one type of molecule. Its state may be defined by the thermodynamic variables pressure $P$, density $\rho$, and temperature $T$. Depending on the values of these variables, the fluid can exist in any one of three possible phases: vapour, liquid or solid.

The relationship between a particular fluid's phases and the variables $P$, $\rho$ and $T$ may be illustrated by a phase diagram. The phase diagram of a typical pure fluid is shown in Fig. 1(a). The three phases are separated by lines called coexistence curves. Along these curves, two phases coexist in equilibrium. At the point A, the triple point, all three phases coexist. The point C, at which the liquid-vapour coexistence curve terminates, is called the critical point. The values of pressure, density and temperature at this point are termed critical and are denoted by $P_c$, $\rho_c$ and $T_c$. The role of the critical point will be discussed later.

The liquid and vapour phases of a pure fluid may also be examined in the pressure density plane, as in Fig. 1(b). The solid line is the liquid-vapour coexistence curve. The dashed lines are isotherms — lines of constant temperature. The critical isotherm, $T = T_c$, is the one which is tangent to the top of the coexistence curve. The region inside the coexistence curve is thermodynamically unstable. A fluid cannot exist, in equilibrium, in a state lying in this region, say at point G with density $\rho_G$ and pressure $P_G$. Rather, it will separate out into vapour and liquid phases
Fig. 1. The pure fluid phase diagram.

(a) Pressure-temperature plane

(b) Pressure-density plane
of densities $\rho_v$ and $\rho_\lambda$. In the region outside the coexistence curve, there is no distinction made between liquid and vapour. The labels "liquid" and "vapour" in Fig. 1(b) refer only to the phase densities corresponding to the two sides of the coexistence curve. While it is possible, as will be shown, to take a system from state D to state E by traversing the coexistence curve and, hence, undergoing a phase transition, the same result may be attained by a process which circumvents the coexistence curve so that no phase transition occurs. For this reason, the system is considered to exist off the coexistence curve simply as a homogeneous fluid.

As an example of a liquid–vapour phase transition, consider the process depicted in the phase diagram of Fig. 2(a). The system starts at point J with pressure $P_o$ and density $\rho_J$. Increasing the temperature, with the pressure held constant, takes the system to the coexistence curve, where phase separation occurs; i.e., the fluid separates into phases of density $\rho_v$ and $\rho_\lambda$, corresponding to the points labelled K. At this stage, heat may be added to the system isothermally until all of the liquid boils away. This heat is referred to as the latent heat of the transition. Finally, if the temperature is increased further, the system moves toward point L as a homogeneous fluid.

Another possible path on the phase diagram is shown in Fig. 2(b). Starting at point M with density $\rho_M$ and pressure $P_M$, the temperature is decreased, at constant density, until the coexistence curve is reached at N, and the system separates into vapour and liquid phases with densities $\rho_v = \rho_M$ and $\rho_\lambda$. As the temperature is further reduced, the system moves down the sides of the coexistence curve, with the average density, $\rho_M$, remaining
Fig. 2. Some possible paths on the phase diagram.

(a) A first order transition

(b) A first order transition

(c) A second order transition
It is often useful to study phase transitions by looking at the behaviour of a particular quantity called the order parameter. As the name suggests, the value of this quantity is a numerical measure of the amount and kind of ordering associated with a particular state of a system. For pure fluid systems, the order parameter is defined to be the difference in liquid and vapour densities divided by the critical density, \( \frac{\rho_l - \rho_v}{\rho_c} \). In the two examples described above, the order parameter is discontinuous across the coexistence curve: its value is zero when the system first reaches the coexistence curve, but non-zero as soon as phase separation takes place. Such processes, for which the order parameter jumps discontinuously from zero, are known as first order phase transitions. They are also characterized by a latent heat of transition.

Now consider the path shown in Fig. 2(c). It is essentially the same process as the one in Fig. 2(b), except that the system starts with density equal to the critical density \( \rho_c \). The temperature is lowered, with density fixed, until the coexistence curve is reached at the critical point \( C \), where \( T = T_c \) and \( P = P_c \) and the order parameter is zero. Here, unlike the previous two examples, there is no jump in the value of the order parameter. As the temperature is lowered from \( T_c \), phase separation occurs and \( \frac{\rho_l - \rho_v}{\rho_c} \) grows continuously from zero. Processes of this type are called second order transitions and are characterized by an order parameter that is continuous through the transition. As well, they have no associated latent heat. The experiment described in this thesis deals with a second order phase
transition in a pure fluid. The discussion from this point on will focus on transitions of this type.

A major objective in the field of critical phenomena is to study the behaviour of thermodynamic properties as close as possible to the critical point. It is in this region, the critical region, that classical theories tend to break down. And, as will be seen, the success of modern theories is determined largely by their ability to quantitatively predict the way in which thermodynamic properties approach the critical point. Furthermore, since the ultimate test of any theory is experiment, considerable efforts are being made by experimentalists to devise methods of probing systems very near their critical points.

A conventional means of characterizing the critical region behaviour of a system is via critical exponents. As $T$ approaches $T_c$, most thermodynamic quantities are expected to exhibit a power law dependence on temperature or other state variable. For example, the order parameter for a pure fluid may be expressed near $T_c$ as

$$\frac{\rho_L - \rho_v}{\rho_c} \sim |t|^\beta$$  \hspace{1cm} (2.1)

where $\beta$ is the associated critical exponent and $t = (T - T_c)/T_c$ is the reduced temperature. Other pure fluid properties expected to show critical power law behaviour include the following:

$$c_v = T (\frac{\partial S}{\partial T})_V \sim |t|^{-\gamma},$$  \hspace{1cm} (2.2)
for $\rho = \rho_c$ ($t > 0$) or on the coexistence curve ($t < 0$);

$$\kappa_T = \rho \left( \frac{\partial \rho}{\partial T} \right)_T \sim |t|^{-\gamma}, \quad (2.3)$$

for $\rho = \rho_c$ ($t > 0$) or on the coexistence curve ($t < 0$);

$$\frac{\rho - \rho_c}{\rho_c} \sim \left( \frac{P - P_c}{P_c} \right)^{1/\delta}, \quad (2.4)$$

for $t = 0$. In the above relations, $\alpha$, $\gamma$ and $\delta$ are the critical exponents associated with the specific heat at constant volume, $C_v$, the isothermal compressibility, $\kappa_T$, and the reduced density, $(\rho - \rho_c)/\rho_c$. The variables $S$ and $V$ refer to entropy and volume.

Critical exponents may be defined analogously for systems other than the pure fluid. In a ferromagnetic system, for example, $\beta$ is defined by

$$m(T) \sim (-t)^\beta$$

where the magnetization $m(T)$ is the order parameter for such a system.

As will be demonstrated in the following sections, critical exponents play a vital role in the field of critical phenomena. Much work is being done to develop theories that predict their values and experiments that measure their values. Since they emerge from theories as universal constants, it is of particular interest to examine the critical exponents of different thermodynamic systems (e.g., pure fluids, ferromagnets, binary
fluids, liquid crystals, etc.) as well as of a variety of materials for each type of system. Such comparisons should indicate the extent to which the critical exponents are, in fact, universal.

2.2 Classical Theories

Classical or mean field theories of phase transitions generally fail in making quantitative predictions that are in agreement with experimental results near a phase transition. Nevertheless, it is instructive to examine such theories since they do illustrate many fundamental aspects of critical phenomena, and often serve as a starting point for more complex theories. The following is a brief survey of some of the classical theories that pertain to pure fluid systems.

The simplest model used to describe a pure fluid is the ideal gas. Defined to consist of non-interacting point particles, the ideal gas obeys the empirical equation of state

\[ P = \rho \, k_B \, T. \]  

(2.5)

Here \( k_B \) is the Boltzmann constant and \( \rho \) is the number of particles per unit volume. Ideal gas isotherms, as shown in Fig. 3, are straight lines which intersect the origin of the pressure-density coordinate system. The ideal gas law predicts no phase transitions and is really only useful for dilute gases. As the density increases, the interactions and finite size of particles cannot be neglected.

In 1873, van der Waals\(^1\) formulated the first equation of state that is
Fig. 3. Ideal gas isotherms \((T_1 < T_2 < T_3)\).
applicable to both vapour and liquid phases, and exhibits a second order phase transition. The van der Waals equation of state may be developed by making the following refinements to the ideal gas law. To begin with, the pressure of a real gas is slightly less than that of an ideal gas, by an amount proportional to the square of the density of particles. As well, the particles of a real gas are of finite size, unlike the point particles of an ideal gas. Hence, the volume of a real gas will tend to a finite volume as the pressure is increased, not to zero as predicted by the ideal gas law. With these modifications, van der Waals obtained the equation of state

\[(P + a \rho^2)(\frac{1}{\rho} - b) = k_B T\]  

(2.6)

where \(a \rho^2\) is the pressure correction due to particle interactions and \(b^{-1}\) is the high pressure limit of the density. The constants \(a\) and \(b\) are characteristic of a given material and may be determined experimentally.

Fig. 4(a) shows some typical van der Waals isotherms. For \(T > T_c\), the isotherms have the expected shape. For \(T < T_c\), however, there is a region (indicated by dashes) on each isotherm with negative slope. Thus, the compressibility is negative in these regions. If a system is to be in a mechanically stable state, though, its compressibility must be positive: positive pressure increments must produce positive density increments. To make the van der Waals isotherms more physical, a modification known as the Maxwell construction\(^{24}\) is employed. This technique is based on the principle
Fig. 4. Van der Waals isotherms.

(a) Van der Waals isotherms

(b) Van der Waals isotherms with the Maxwell construction
that, for liquid-vapour coexistence, the Gibbs free energy of the two phases must be the same. As illustrated in Fig. 4(b), a portion of each isotherm below $T_c$ is replaced by a horizontal line segment, resulting in a more realistic phase diagram, with the same basic features as the phase diagram of a real gas (cf. Fig. 1(b)). Hence, with the Maxwell construction, the van der Waals equation of state predicts liquid-vapour coexistence terminating with a second order transition.

The critical values of pressure, density and temperature may be obtained from the equation of state, and from the conditions that, at the critical point, the critical isotherm has both a vanishing slope and a point of inflection:

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T = T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T = T_c} = 0$$

One obtains

$$P_c = \frac{a}{27 b^2}$$

$$k_B T_c = \frac{8a}{27b} \quad (2.7)$$

$$\rho_c = \frac{1}{3b}.$$
In terms of the dimensionless parameters $\tilde{P} = P/P_c$, $\tilde{\rho} = \rho/\rho_c$ and $\tilde{T} = T/T_c$, the van der Waals equation of state may be written as

$$\left( \tilde{P} + 3\tilde{\rho}^2 \right) \left( \frac{3}{\tilde{\rho}^\prime} - 1 \right) = 8\tilde{T}. \tag{2.8}$$

The striking feature of Eq. (2.8) is that it is independent of the material-dependent quantities $a$ and $b$. In other words, the van der Waals equation, cast in this form, may be interpreted to be universal. In principle, one needs only to know $P_c$, $\rho_c$ and $T_c$ for any material to determine its equation of state. Furthermore, Eqs. (2.7) may be combined to yield a universal relation for the critical parameters:

$$\frac{P_c}{k_B T_c \rho_c} = \frac{3}{8}. \tag{2.9}$$

Such universal predictions are manifestations of the law of corresponding states, postulated by van der Waals in 1880. It states that all classical fluids, described in terms of reduced parameters such as $\tilde{P}$, $\tilde{\rho}$ and $\tilde{T}$, obey an identical equation of state

$$\tilde{P} = f(\tilde{\rho}, \tilde{T})$$

where $f$ is a universal function. While the law is not entirely corroborated experimentally, it has played a key role in advancing the understanding of the critical behaviour of various systems.
A more stringent test of the van der Waals theory is to see what values it predicts for the various critical exponents. For example, consider the critical exponent $\gamma$, defined in Eq. (2.3). From the equation of state, Eq. (2.6), the isothermal compressibility is found to be

$$\kappa_T = \frac{\rho(1 - bp)}{3abp^2 - 2ap + k_B T + bP}.$$  \hspace{1cm} (2.10)

The temperature dependence of $\kappa_T$ near the critical point may be found by setting $P = P_c$ and $\rho = \rho_c$ to yield

$$\kappa_T \sim \frac{2}{T - T_c} \sim t^{-1}.$$  \hspace{1cm} (2.11)

Thus, the van der Waals equation predicts $\gamma = 1$. Experimental results confirm that the compressibility does, in fact, diverge at the critical point, but with $1.2 < \gamma < 1.4$. The other exponents may be calculated in a similar fashion. The results are listed in Table 1, together with values determined by experiment, and values predicted by a modern theory known as the renormalization group, which is discussed in Sec. 2.3.

<table>
<thead>
<tr>
<th>critical exponent</th>
<th>experimental value</th>
<th>mean field theory</th>
<th>$\text{RG}^{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0 - 0.2</td>
<td>0</td>
<td>0.110</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.3 - 0.4</td>
<td>1/2</td>
<td>0.325 - 0.328</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.2 - 1.4</td>
<td>1</td>
<td>1.237 - 1.241</td>
</tr>
<tr>
<td>$\delta$</td>
<td>4 - 5</td>
<td>3</td>
<td>4.82</td>
</tr>
</tbody>
</table>
There are numerous other classical theories, each with its own equation of state. Typical examples are the Dieterici equation

\[ \frac{a_1 \rho}{k_B T} \left( 1 - b_1 \rho \right) = \rho k_B T \]

and the Berthelot equation

\[ (P + a_2 \rho^2 / k_B T)(1 - b_2 \rho) = \rho k_B T \]

where \( a_1, b_1, a_2 \) and \( b_2 \) are experimental constants like \( a \) and \( b \) in van der Waals' equation.

Another equation of state is obtained by making the so-called virial expansion in density:

\[ P = k_B T \left[ \rho + B(T)\rho^2 + C(T)\rho^3 + \ldots \right]. \]

The temperature-dependent coefficients \( B \) and \( C \) are called the second and third virial coefficients, and may be calculated from the intermolecular potential. For example, \( B(T) = b - a/k_B T \) for the van der Waals equation of state. Conversely, an experimental determination of the virial coefficients can be used to obtain information about the intermolecular forces of a particular system.
All such classical theories are the same as the van der Waals theory in terms of their predictions for the values of critical exponents. The inadequacy of these theories became apparent in the early 1900's when careful measurements were first performed on pure fluid systems. In 1945, Guggenheim obtained the universal coexistence curve equation

\[
\frac{\rho_L - \rho_V}{\rho_c} = 3.5 \left( \frac{T_c - T}{T_c} \right)^{1/3}
\]

(2.12)

from liquid-vapour coexistence data of a variety of fluids. This result provided some evidence for van der Waals' law of corresponding states. At the same time, however, Guggenheim's value of \( \beta = 1/3 \) indicated that classical theories could not be relied upon to predict values of critical exponents. Since then, experimental results have fully confirmed that the classical critical exponents are incorrect. A more realistic analysis of critical phenomena has required the development of modern theories of phase transitions. While no attempt will be made to give a detailed discussion of these theories, the following section will outline their basic approach.

2.3 \textbf{Modern Theories}

How does one accurately describe the behaviour of a macroscopic thermodynamic system? This, in principle, is a formidable task. Such a system consists of on the order of \( 10^{23} \) particles. The state of each particle is determined by the values of six degrees of freedom — three for position and three for momentum — making the total number of degrees of
freedom for the system enormous. It is clear that simplifications of some sort are required in order to make any progress. Furthermore, it is reasonable to expect that the nature of the simplifications made will ultimately determine the extent to which a particular theory succeeds in making realistic predictions.

The basic assumption made by classical theories of critical phenomena is that interactions in a system are limited to those between each particle and an average field due to all other particles; long range fluctuations and correlations among particles are neglected. Despite this coarse approximation, classical or mean field theories are remarkably successful: they provide a reasonably accurate description of a variety of systems, while avoiding entirely the problem of $10^{23}$ or so degrees of freedom.

Nevertheless, it is evident that a satisfactory understanding of critical phenomena cannot be gained from classical theories alone. To be valid, a theory must provide a quantitative description of what happens when a system is taken arbitrarily close to its critical point. In particular, such a theory should yield values of critical exponents that agree with those found by experiment and, as demonstrated in the previous section, classical theories fail in this respect. The reason for this failure lies in the fact that the approximations made by classical theories break down in the critical region. To see why this happens, consider the density fluctuations in a pure fluid. Far from $T_c$, the single phase present is extremely stable and density fluctuations are small. Classical theories work in this region. As $T_c$ is approached, however, the energy difference between liquid and vapour phases diminishes and the compressibility of the system diverges. It becomes more
probable that regions of higher or lower than average density will form. The closer the system gets to \( T_c \), the larger the extent of these coherent regions of independent density fluctuations. Eventually they become large enough to scatter visible light, causing an effect known as critical opalescence. This effect is not predicted classically since, as mentioned above, classical theories ignore fluctuations and expect the properties of a macroscopic system to correspond directly with the properties of small groups of particles. This assumption must be replaced with a more realistic one if the critical behaviour of systems is to be fully understood.

To deal with these aspects of critical phenomena, modern theories introduce a thermodynamic quantity, the correlation length \( \xi \), that is a measure of the extent of fluctuations in a system. In other words, the thermodynamic properties of a system, in a particular state, will not appear to change provided that they are not measured over a scale smaller than \( \xi \).

The correlation length is a state variable. Far from \( T_c \), \( \xi \) is typically on the order of inter-particle spacing. Close to \( T_c \), \( \xi \) is expected to diverge according to the power law

\[
\xi \sim |t|^{-\nu}.
\]  

The exponent \( \nu \) is another critical exponent, one that does not emerge from classical theories since they do not account for fluctuations. Modern theories predict \( \nu \approx 0.63 \), a value that is in good agreement with experimental results.

The first theory to effectively incorporate the concepts of
fluctuations and correlation length was developed by Widom in 1965. Widom's so-called scaling theory is based on the principle that thermodynamic quantities are homogeneous functions of their distance from the critical point; i.e., as a system approaches its critical point, the associated thermodynamic properties change their scale but not their functional form. Among the predictions made by this theory are the universal critical behaviour of various classes of systems and critical region power law dependences of thermodynamic quantities. Also predicted are a number of useful relationships between the critical exponents. For example:

\[ \alpha + \gamma + 2\beta = 2 \]

\[ \alpha + \beta(\delta + 1) = 2. \]

In fact, according to the theory, all of the critical exponents may be expressed in terms of two fundamental parameters.

The principle of scaling underlies most of the contemporary theories of critical phenomena. In 1966, Kadanoff applied scaling theory to Ising-like spin systems by describing the spin lattice in terms of interacting spin blocks. A block of spins replaces the individual spins as the basic unit of interaction, an average spin being associated with each block. As the critical temperature is approached, and the correlation length increases, the block size is also increased, in such a way that the relevant thermodynamic quantities rescale without changing their functional form. Increasing the block size in this manner is equivalent to reducing the
effective correlation length, or moving away from the critical point. With this procedure, the critical region may be examined mathematically by iteratively reducing the large number of degrees of freedom per unit correlation length.

A general and mathematically complete theory of critical phenomena known as the renormalization group (RG) was formulated by Wilson\textsuperscript{11} in 1971. In simple terms, this theory incorporates the concept of scaling and, as in the Kadanoff picture, provides a practical method for analyzing critical behaviour by systematically reducing the number of relevant degrees of freedom in a system near its critical point. Universality is predicted by demonstrating that critical region behaviour depends only on the dimensionality of the system and the order parameter, and not on the details of the interaction Hamiltonian. The qualitative features of phase transitions are explained in terms of system dimensionality and cooperative degrees of freedom. Perhaps of greatest importance, the RG approach has proved to be an extremely successful technique for calculating realistic values of critical exponents.

Another significant feature of RG theory is that, as shown by Wegner\textsuperscript{26}, it predicts deviations from simple power law behaviour in measurements made away from the critical point. Such corrections arise because while the critical point value of the correlation length is predicted by scaling theory to be infinite, experiments are necessarily performed at finite distances from the critical point. The resulting departure from power law behaviour is seen in the RG predicted functional form of a thermodynamic variable $f(t)$,
where \( \lambda \) is the critical exponent associated with \( f(t) \). The exponents \( \Delta_1 \) and \( \Delta_2 \) are expected to be universal, as are certain ratios of the amplitudes \( a_1 \), \( a_2 \), \ldots . For the case of the pure fluid coexistence curve, Eq. (2.14) becomes

\[
f(t) = A |t|^{-\lambda} (1 + a_1 |t|^{\Delta_1} + a_2 |t|^{\Delta_2} + \ldots ),
\]

where \( \lambda \) is the critical exponent associated with \( f(t) \). The exponents \( \Delta_1 \) and \( \Delta_2 \) are expected to be universal, as are certain ratios of the amplitudes \( a_1 \), \( a_2 \), \ldots . For the case of the pure fluid coexistence curve, Eq. (2.14) becomes

\[
\frac{\rho \lambda - \rho_v}{\rho_c} = B_0 |t|^{\beta} (1 + B_1 |t|^\Delta + B_2 |t|^{2\Delta} + \ldots ).
\]  

Similarly, the isothermal compressibility \( \kappa_T \) takes the form

\[
\kappa_T = \Gamma_0 |t|^{-\gamma} (1 + \Gamma_1 |t|^\Delta + \Gamma_2 |t|^{2\Delta} + \ldots ).
\]

It is a major objective of current critical phenomena experiments, including those presented in this thesis, to obtain sufficiently high precision data that the status of corrections-to-scaling predictions may be accurately assessed.
3.1 Introduction

This chapter describes the optical methods used to study the critical behaviour of the pure fluid sample. There were two interferometric techniques used, each one providing information about different aspects of the transition. In the first method, discussed in Sec. 3.2, a Fraunhofer diffraction pattern created by the sample was used to determine the critical exponent $\beta$. Sec. 3.3 describes an optical technique used to obtain the critical exponent $\gamma$. In this case, the sample was placed in one arm of a Mach-Zehnder interferometer. The Lorentz-Lorenz relationship is discussed in Sec. 3.4.

Both of the optical methods used are based on the following properties of a pure fluid sample having an average density equal to the critical density. At a given temperature, the sample exhibits a height-dependent density profile $\rho(z)$ due to the effect of the earth's gravitational field. Typical examples of $\rho(z)$ are illustrated in Fig. 5. In Figs. 5(c) and 5(d) the sample is in the one phase region ($t > 0$). In Figs. 5(a) and 5(b) the temperature is below the critical temperature ($t < 0$); the discontinuity in $\rho(z)$ at $z = z_o$ occurs at the interface separating the liquid and vapour phases. If the average density of the sample is in fact equal to the critical density, the height $z_o$ at which the maximum density gradient occurs will be approximately temperature-independent. The shape of the density profile changes as the distance from $T_c$ is varied, but at any given
Fig. 5. Density profiles of a pure fluid in the earth's gravitational field.

(a) $t << 0$

(b) $t < 0$

(c) $t > 0$

(d) $t >> 0$
temperature \( p(z) \) is assumed to be antisymmetric about the height \( z_0 \). Hence, \( dp/dz \) is symmetric about \( z_0 \). As \( p(z) \) changes with temperature, so does the refractive index \( n(z) \), in accordance with the Lorentz-Lorenz relationship (Eq. (3.5)). This temperature dependence of the refractive index may be exploited to obtain information about the liquid-vapour phase transition. In particular, the optical methods described below have proved to be effective in examining the transition very near \( T_c \), at least for \( |t| \gtrsim 10^{-6} \).

3.2 Fraunhofer Diffraction

To understand how a pure fluid sample can produce a Fraunhofer diffraction pattern, consider the arrangement shown in Fig. 6. A plane wave beam of laser light strikes the sample with normal incidence. Using Snell's law, it is found that a light ray traversing the sample is deflected according to

\[
\frac{d\theta}{dx} = -\frac{1}{n(z)} \frac{dn}{dz},
\]

where \( x \) is the horizontal distance in the cell. If the sample thickness \( L_o \) is sufficiently small that the ray is not bent appreciably before emerging from the sample, the deflection angle \( \theta_1 \) may be written as

\[
\theta_1 = \left[-\frac{L_o}{n(z)} \frac{dn}{dz}\right]_{z=z_1},
\]

(3.2)
where $z_i$ is the incident height. At the cell boundary, a further refraction takes place. Snell's law may be used to find the exit angle

$$\theta_o = n\theta_i = \left[-L_o \frac{dn}{dz}\right]_{z = z_i} \quad (3.3)$$

The refractive index $n$ is relative to that of air, and the small angle approximation $\sin \theta_i \approx \theta_i$ has been made.

Hence, a horizontally incident ray leaves the cell at angle $\theta_o$ given by Eq. (3.3). A ray $R_o$ passing through the region of the cell where the density gradient is a maximum is bent through a maximum angle $\theta_m$. Since $dn/dz$ is symmetric about $z_o$, for each ray $R^+$ that traverses the cell above $z_o$, there is a ray $R^-$ that traverses the cell in a region below $z_o$ with the same density gradient. Rays $R^+$ and $R^-$ emerge from the cell parallel to each other, as shown in Fig. 6. The entire beam may be decomposed into such pairs of rays. Because of the varying density distribution, rays $R^+$ and $R^-$ will have travelled unequal optical path lengths. If they are superimposed in the back focal plane of an objective lens, they will produce an interference spot. The intensity of this spot depends upon the phase difference of the two rays, which in turn is a function of their distance from $z_o$. If all such ray pairs are considered, the result is a Fraunhofer diffraction pattern produced in the focal plane $F$ of lens $L_1$. The pattern will consist of a vertical strip of bright and dark interference spots.

For the case $t < 0$, the discontinuity in $\rho(z)$ at the liquid–vapour interface ($z = z_o$) produces an additional phase difference in each pair of
rays $R^+$ and $R^-$. If $N$ is the number of interference fringes at a given
temperature $T < T_c$, the difference in liquid and vapour refractive indices is
given by

$$n_l - n_v = \frac{N \lambda}{L_o}$$

(3.4)

where $\lambda$ is the laser wavelength and $L_o$ is the cell thickness. Thus, the
order parameter for the system, $(\rho_l - \rho_v)/\rho_c$, may be obtained by measuring $N$
as a function of temperature and relating refractive index to density with
the Lorentz-Lorenz relationship. It was in this manner that $\beta$ was determined
for the CHF$_3$ sample.

The optical setup used is shown in Fig. 7. The light source was a
helium-neon laser ($\lambda = 6.328 \times 10^{-7}$ m). The beam was attenuated by a
polarizer. A microscope objective, $L_2$, focussed the beam onto a 10 micron
pinhole $P$ which, in turn, was positioned at the focal point of a converging
lens, $L_3$. An essentially plane wave beam was thus generated.

The sample cell, filled to the critical density and placed within the
temperature control system, was positioned in the path of the laser beam,
with the cell windows perpendicular to the beam. The Fraunhofer diffraction
pattern produced in the focal plane $F$ of lens $L_1$ was recorded continuously on
photographic film as the cell temperature was increased in steps from several
degrees below $T_c$ to a final temperature above $T_c$. The details of the
experimental procedure are outlined in Sec. 4.3.
He-Ne laser

Reference beam blocked at B, for Fraunhofer diffraction experiment.
3.3 Image Plane Interference

As described earlier, the density of a pure fluid varies considerably with height near the critical temperature. Thus, at a given temperature, light rays that traverse the sample will travel optical paths of varying lengths. Rays crossing the lower region of the sample, where the density and refractive index are greater, are retarded relative to rays that cross the upper region of the sample. If these rays are then combined with the rays of an undisturbed reference beam, the resulting interference pattern, seen in the image plane of a converging lens, directly maps the refractive index of the sample as a function of position. Since the refractive index is a maximum at the bottom of the cell and decreases monotonically with height, each fringe in the vertical direction represents a change in optical thickness of one wavelength. From an analysis of the fringe spacing, it is possible to determine the temperature dependence of the compressibility along the critical isochore. This, in turn, yields a value of the critical exponent \( \gamma \). The details of this analysis are given in Sec. 5.2.

The effects discussed above were achieved by placing the sample cell in one arm of a Mach-Zehnder interferometer. Fig. 7 illustrates the arrangement of the optical apparatus that was used. A plane wave laser beam was generated as described in the previous section. The beam was split at \( B_1 \), with one portion traversing the CHF₃ sample before recombining with the reference portion at \( B_2 \). The lens \( L_1 \) placed behind \( B_2 \) formed a combined image of the exit plane of the sample at position 0 and the reference beam at some position 0'. A series of horizontal fringes was observed in the image plane I of the lens \( L_1 \), with maxima occurring at points where the phase
difference of the two beams was an integral multiple of \(2\pi\). The fringe pattern was recorded continuously as a function of temperature. A description of the data collection procedure is given in Sec. 4.3. The data for this experiment, and the Fraunhofer diffraction experiment, are presented and analysed in Chapter 5.

3.4 The Lorentz-Lorenz Relationship

What was actually measured by these experiments was the refractive index or the difference of refractive indices. To convert refractive indices to densities, the Lorentz-Lorenz relationship was used. Derived independently by Lorentz and Lorenz in 1880, it may be expressed as

\[
\rho L = \frac{n^2 - 1}{n^2 + 2},
\]  

(3.5)

where \(n\) is the refractive index, \(\rho\) is the density and \(L\) is the Lorentz-Lorenz function. For many applications, it is sufficient to assume that \(L\) is a constant. This assumption is known to be valid for a homogeneous medium in which the correlation length \(\xi\) that characterizes the extent of density fluctuations is negligible compared to the wavelength \(\lambda\) of the incident light. As explained earlier, though, a pure fluid in the vicinity of its critical point does not satisfy the above condition: the characteristic size of density fluctuations becomes large when the system is near \(T_c\). Nevertheless, there is some evidence to suggest that the approximation of constant \(L\) may still be reasonable in the critical region.
In particular, Larsen, Mountain and Zwanzig\textsuperscript{27} use a theoretical argument to conclude that, when $\lambda$ and $\xi$ are of the same order of magnitude, $L$ deviates from its off-critical value by approximately 0.02%. The experimental results of Burton and Balzarini\textsuperscript{28} indicate that, for $C_2H_6$, $L$ varies by less than 0.1% in the critical region.

Under the assumption of constant $L$, the Lorentz-Lorenz equation may be expanded about the critical density $\rho_c$ in a Taylor series

$$n(\rho) = n_c + a_1(n_c - 1)\left[\frac{\rho - \rho_c}{\rho} + a_2\left(\frac{\rho - \rho_c}{\rho_c}\right)^2 + \ldots\right]$$

where

$$a_1 = \frac{(n_c + 1)(n_c^2 + 2)}{6n_c}$$

$$a_2 = \frac{(n_c^2 - 1)(3n_c^2 - 2)}{12n_c^2}.$$

For the purposes of this experiment, it was sufficient to neglect second and higher order terms, and the expression

$$n(\rho) - n_c = a_1(n_c - 1)\left(\frac{\rho - \rho_c}{\rho_c}\right)$$

was used to relate refractive index to density.
Chapter 4

THE EXPERIMENT

4.1 The Sample Cell

The material studied in both experiments was a 98% pure sample of trifluoromethane, CHF$_3$, commonly known as fluoroform. It was chosen because it is a pure fluid with a second order phase transition that had not been previously investigated by an experiment of this type. The fact that it is polar makes CHF$_3$ even more interesting, as most critical behaviour studies of pure fluids have been limited to non-polar materials. Furthermore, it has properties that made it a particularly convenient sample to use. It is optically transparent and thus suitable for an experiment that optically probed changes in refractive index. It has a relatively low critical temperature ($T_c \approx 26^\circ$C). Temperatures in this neighbourhood were not difficult to reach and maintain with the temperature control system used in the experiment. Finally, it was relatively easy to design and construct a vessel capable of holding CHF$_3$ under pressures in the range of its critical pressure ($P_c \approx 5 \times 10^4$ Pa).

The vessel used to contain the CHF$_3$ sample was the aluminum cell shown in Fig. 8. Two sapphire windows, 2.54 cm in diameter and 0.635 cm thick, were situated parallel to each other on either side of the central hole, separated by a gap of 1.84 mm. The gap size was determined by subtracting the total window thickness from the distance between the outer window faces. Indium wire, 0.76 mm in diameter, was used to form a seal between the cell and the windows. Aluminum flanges clamped the windows to the cell, with
Figure 8. The Cell.
gaskets serving as a cushion between the windows and the flanges. The ten cap-head screws on each flange were tightened progressively to 0.8 Nm with a torque wrench.

The cell was filled as follows. The sample entered the cell via a small hole that connected the sample space between the sapphire windows to a larger, tapped hole at the top of the cell. A stainless steel needle valve, inserted in the tapped hole, was used to seal and unseal the small hole during the filling procedure.

Once the cell was cleaned, assembled and free of leaks, it was attached, via the needle valve, to a gas handling system. The cell and the gas delivery lines were evacuated by 48 hours of pumping with a diffusion pump and then flushed out with CHF$_3$, contained under pressure in a cylinder. A meniscus appeared as the CHF$_3$ entered the cell, which was at room temperature. After several flushes, the cell was filled slowly until the meniscus was just above the midpoint of the cell windows. The critical density was recognized as the density for which the meniscus remained stationary (before disappearing) as the sample was heated through its critical temperature. With the cell slightly overfilled, small amounts of CHF$_3$ were bled out through the needle valve. After each bleeding, the motion of the meniscus was observed while the cell was immersed in a temperature-controlled water bath that was slowly heated through $T_c$. This procedure was repeated until there was no discernable motion of the meniscus, at which point the cell was removed from the gas handling system.
4.2 Temperature Control

An important requirement of most phase transition experiments is stable and precise temperature control of the system being studied, particularly in the vicinity of the critical region. This section outlines the procedure and equipment with which temperature control was achieved in these experiments.

The sample cell was situated inside three containers, each insulated from the other by a 5 cm thick layer of styrofoam. The innermost container was a solid aluminum "block" through which had been bored a hole of the same diameter as that of the cell. With the cell placed inside the block, good thermal contact was maintained between the two pieces. Insulated heating wire was wrapped and glued around the outside of the block. The heating wire had a resistance of about 6 ohms. Two Fenwal thermistors were epoxied inside hollow copper screws which, in turn, were inserted into holes tapped in the block. A Hewlett-Packard model 2804A quartz thermometer probe was placed in a hole in the top of the block. Apiezon N grease was applied to the quartz thermometer probe and thermistor screws to improve their thermal contact with the block.

Next, the aluminum block was encased in a layer of styrofoam and inserted into the second container, an aluminum "box". Machined in the interior of the 1.5 cm-thick walls of the box was a channel system through which a temperature-controlled water-antifreeze mixture could circulate. This box was covered with styrofoam and placed inside the third and outermost container, a plywood box. Appropriate holes were cut in the containers and
styrofoam to allow for the unobstructed passage of a laser beam through the sample cell during the experiment.

The primary means of temperature control consisted of an electronic feedback system that regulated the temperature of the inner aluminum block. The electronic circuit is shown in Fig. 9. The control thermistor in the block was balanced against a decade resistance box in a Wheatstone bridge. The error signal was amplified by a Hewlett-Packard 419A DC nullimeter and fed into a Kepco OPS 7-2 power supply. The feedback produced a combined proportional and integral control which powered the heater on the inner block.

During the course of the experiment, the temperature was changed in a series of sweeps and waiting periods that systematically took the sample cell from an initial temperature several degrees below $T_c$, through $T_c$, to a final temperature above $T_c$. A ten-turn, 1 ohm variable potentiometer divided resistors $R_1$ and $R_2$ in the Wheatstone bridge. An electric motor drove a gear system that turned the potentiometer; when the motor was on, an imbalance in the bridge was created in a continuous and steady fashion. The rate at which the temperature changed was determined by the motor speed, which could be varied, and by the resistances of the bridge arms $R_1$ and $R_2$, which could be set at identical values of 30 ohms, 100 ohms, 300 ohms or 1000 ohms. A Commodore Pet computer was interfaced with the motor and programmed to turn the motor on and off for desired lengths of time. The waiting periods, when the motor was off, allowed the cell to reach thermal equilibrium after a temperature change.
Fig. 9. The temperature control circuit.
A secondary level of temperature control was also incorporated. A temperature-controlled water-antifreeze mixture was circulated via foam-insulated hoses through the channels in the walls of the aluminum box. A modified Forma model 2095 circulator, able to heat and refrigerate, pumped the bath mixture through the system. The temperature of the bath mixture was regulated in the following manner. Cell and bath temperatures were monitored by separate thermistors, one in contact with the inner aluminum block, the other with the aluminum box. These thermistors served as balancing resistance arms in a Wheatstone bridge. The error signal from the bridge was amplified and fed into the pulse-width modulation circuit shown in Fig. 10. This circuit controlled the bath temperature by alternately switching on, for appropriate time periods, the Forma circulator's heater and refrigerator. The circuit was adjusted to maintain the bath temperature at approximately 0.5°C below that of the cell. The bath temperature was stable to ± 0.005°C.

The cell temperature was monitored with the quartz thermometer, which was previously calibrated against the triple point of water using a Jarrett water triple-point cell. The quartz thermometer had a resolution of 0.0001°C. Its output was continuously recorded by a chart recorder.

With the control system described above, it was possible to hold the sample cell temperature stable to ± 0.0001°C for a period of days.

4.3 Experimental Procedure

The data collection for the Fraunhofer diffraction pattern experiment took place as follows. With the sample cell filled and in place in the temperature control system, the cell and optical apparatus were aligned on an
Fig. 10. The pulse-width modulation circuit used to control the bath temperature.
optical bench as described in Sec. 3.2. A motor and gear assembly was used to advance the film in a 35 mm camera body. The camera was positioned so that the film, exposed to the diffraction pattern through a narrow vertical slit, was in the focal plane of lens $L_1$ (Fig. 7). With the camera motor running, it was possible to obtain a continuous record of the focal plane diffraction pattern as the sample was taken through its phase transition.

An initial wait of several hours allowed the sample to reach thermal equilibrium at a temperature about 10°C below $T_c$ ($t = -3 \times 10^{-2}$). At this point, the experimental room was darkened and the camera motor was turned on. Film was transported across the camera slit at a rate of 3 cm/hour. The Commodore Pet computer changed the cell temperature by switching on and off, for desired lengths of time, the motor that drove the variable potentiometer in the control bridge. Temperature was increased towards $T_c$ in steps; a waiting period after each step allowed the sample to equilibrate. The waiting times varied from several minutes to two hours, depending on the distance from $T_c$ and on the size of the previous temperature increment. The size of the temperature steps was systematically decreased so that there was roughly an equal number of data points for each decade of reduced temperature that was covered. For example, for $t = -10^{-2}$, 0.1°C steps were taken; for $t = -10^{-5}$, 0.001°C steps were taken.

To minimize thermal and optical disturbances, the experimental area was vacated during most of the data collection period. The camera was reloaded with new film approximately every 24 hours. The Fraunhofer diffraction pattern data used for analysis was collected over a period of eight days. Several preliminary runs were conducted to obtain an estimate
for $T_c$ and to determine an appropriate beam intensity and suitable sweeping rates.

The procedure for the image plane experiment was identical to that of the focal plane experiment, except that the camera was positioned with the film in the image plane of lens $L_1$. Data was collected over a four-day period for temperatures in the range $1.7 \times 10^{-5} < t < 2 \times 10^{-4}$. 
5.1 Fraunhofer Diffraction Pattern

The Fraunhofer diffraction pattern data, collected in the two-phase region over a temperature range of $4 \times 10^{-6} < |t| < 3.5 \times 10^{-2}$, were evaluated by examining the fringe pattern that was continuously recorded on film. Samples of the film are shown in Figs. 11(a) and 11(b). A vertical slice at any point on the film represents the Fraunhofer diffraction pattern at a particular temperature. Regions where the fringe pattern changes, with new fringes appearing at the top edge of the film, indicate temperature sweeps. Once the sample reached equilibrium after a temperature change, the fringe pattern remained essentially constant until the next temperature step. Intermittent problems with electronics hindered the stability of temperature control at times, causing fluctuations such as those seen in Fig. 11(b). The chart recorder output of the quartz thermometer readings was used to assign values of temperature to each region of equilibrium. The vertical bars on the film are due to a light emitting diode that was momentarily turned on between temperature steps; these bars aided temperature identification on the fringe pattern.

At any given subcritical temperature, there was a certain number of fringes $N$ that were "missing" due to the infinite refractive index gradient at the liquid-vapour interface. The number $N$ decreased as the critical point was approached and the difference in liquid and vapour indices, $n_\lambda - n_v$,
Figure 11. Fringe pattern samples.

(a) Fraunhofer diffraction pattern \((t = -10^{-3})\)

(b) Fraunhofer diffraction pattern \((t = 0)\)

(c) Image plane pattern \((t = -2 \times 10^{-5})\)

(d) Image plane pattern \((t = 3 \times 10^{-5})\)
diminished. By the time the sample was taken through its phase transition into the one phase region, the last missing fringe appeared. This fringe, the zeroth fringe, represents the light that was most refracted at any given temperature.

A value of N was measured for each of 91 subcritical temperatures. Fringe number was converted to refractive index difference using Eq. (3.4),

\[ n_\lambda - n_v = \frac{NK}{L_o}, \tag{3.4} \]

where \( \lambda \) is the laser wavelength and \( L_o \) is the cell thickness. In turn, the order parameter, \( (\rho_\lambda - \rho_v)/\rho_c \), was related to \( n_\lambda - n_v \) via the approximate form of the Lorentz-Lorenz relationship, Eq. (3.6), to obtain

\[ n_\lambda - n_v = a_1(n_c - 1)(\frac{\rho_\lambda - \rho_v}{\rho_c}). \tag{5.1} \]

Eqs. (3.4) and (5.1) were then combined to yield

\[ \frac{\rho_\lambda - \rho_v}{\rho_c} = \frac{\lambda N}{a_1(n_c - 1)L_o} = 1.67 \times 10^{-3} \text{ N}, \tag{5.2} \]

where the following values of constants were used:

\[ \lambda = 6.328 \times 10^{-7} \text{ m} \]
\( n_c = 1.196 \)
\( a_1 = \frac{(n_c + 1)(n_c^2 + 2)}{6n_c} = 1.05 \)
\( L_o = 1.84 \times 10^{-3} \) m.

Since no tabulated value of \( n_c \) for CHF\(_3\) was available, the value listed above is an estimate that was obtained from the following calculation. The density of CHF\(_3\) at \( T_1 = 173.15 \) K is known to be \( \rho_1 = 1.520 \) g/cm\(^3\), and the refractive index at \( T_2 = 199.85 \) K is known to be \( n_2 = 1.215 \). As well, \( \rho_c = 0.516 \) g/cm\(^3\) and \( T_c = 298.95 \) K. A corresponding states expression of the form

\[
\frac{\rho - \rho_c}{\rho_c} = K_o \left( \frac{T_c - T}{T_c} \right)^{1/3}
\] (5.3)

was assumed for the reduced density (cf. Eq. (2.12)). The values of \( \rho_1, T_1, \rho_c, \) and \( T_c \) were substituted into Eq. (5.3) to determine the constant \( K_o \), with the result \( K_o = 2.6 \), so that

\[
\frac{\rho - \rho_c}{\rho_c} = 2.6 \left( \frac{T_c - T}{T_c} \right)^{1/3}
\] (5.4)

Eq. (5.4) was then used to find \( \rho_2 = 0.564 \) g/cm\(^3\) at \( T_2 \). Substitution of \( n_2 \) and \( \rho_2 \) into the Lorentz-Lorenz relationship, Eq. (3.5), yielded a value of the Lorentz-Lorenz coefficient \( L = 0.243 \) cm\(^3\)/g. Finally, this value of \( L \),
assumed to be constant (see Sec. 3.4) and the value of $\rho_c$ were substituted into Eq. (3.5) to give the result $n_c \approx 1.196$.

The coexistence curve data are shown in Fig. 12, which is a plot of $\log [(\rho_\lambda - \rho_v)/\rho_c]$ versus $\log |t|$. If the order parameter obeyed a simple power law, the data would fall on a straight line of slope $\beta$. The curve is nearly linear but close inspection reveals a slight curvature. The departure from power law behaviour may be examined in greater detail in the sensitive plot shown in Fig. 13. This graph shows the same data with $\log [(\rho_\lambda - \rho_v)/\rho_c |t|^{0.327}]$ versus $\log |t|$. The value of $T_c$ used was obtained from a fitting procedure described below. In this graph, the leading power law dependence on temperature has been divided out, so that a straight horizontal line would indicate power law dependence of the order parameter. This may be the case for data point in the region $5 \times 10^{-6} < |t| < 10^{-4}$. Those points in the region $10^{-4} < |t| < 5 \times 10^{-2}$, however, clearly deviate from power law behaviour and it is evident that corrections to scaling must be considered to interpret the data properly.

No error bars have been plotted with the data. Points at the right of the graph are insensitive to errors in measurement and the choice of $T_c$. These factors become important as $T_c$ is approached. The scatter of the points is a good representation of the size of error bars on the points.

A multi-parameter non-linear least-squares fitting routine was executed by computer to fit the functional form of the order parameter predicted by corrections to scaling theory,
Fig. 12. Log-log plot of order parameter, \((\rho_x - \rho_y)/\rho_c\), versus reduced temperature, \(t = (T - T_c)/T_c\).
Fig. 13. Sensitive log-log plot of \((\rho_{\perp} - \rho_v) / \rho_c |t|^{0.327}\)

versus reduced temperature, \(t = (T - T_c) / T_c\).
\[
\frac{\rho_2 - \rho_V}{\rho_c} = B_0 |t|^\beta \left( 1 + B_1 |t|^\Delta + B_2 |t|^{2\Delta} \right),
\]

(5.5)

to the experimental data. Initially, a three-parameter fit was made, with both correction terms neglected \((B_1 = B_2 = 0)\). This yielded the results

\[\beta = 0.342 \pm 0.001.\]
\[T_c = 298.9506 \pm 0.0002 \text{ K}\]
\[B_0 = 1.644 \pm 0.004.\]

The fit exhibited a systematic deviation from the data and gave a value of \(\beta\) that is not in good agreement with the accepted RG value, \(\beta = 0.327\), thereby confirming that the data is not well-described by a simple power law. An improvement was seen in a four-parameter fit in which only the second correction term was neglected \((B_2 = 0)\) and \(\Delta\) was fixed to its RG value, \(\Delta = 0.5\). This fit gave the results:

\[\beta = 0.330 \pm 0.001\]
\[T_c = 298.9499 \pm 0.0001 \text{ K}\]
\[B_0 = 1.50 \pm 0.01\]
\[B_1 = 0.31 \pm 0.02.\]

The best value of \(\beta\) was obtained from a five-parameter fit with \(\Delta = 0.5\) and both correction terms included:
\[ \beta = 0.327 \pm 0.002 \]
\[ T_c = 298.9497 \pm 0.0001 \text{ K} \]
\[ B_0 = 1.47 \pm 0.03 \]
\[ B_1 = 0.5 \pm 0.1 \]
\[ B_2 = -0.4 \pm 0.3. \]

This fit is indicated by the solid line of Fig. 13.

As well, a fit made with \( T_c \) and \( \beta \) fixed at their accepted values, yielded a value of \( \Delta = 0.48 \pm 0.13 \), consistent with the RG prediction of \( \Delta = 0.5 \).

Finally, an attempt to fit the data with \( B_0, B_1, B_2, \beta, T_c \) and \( \Delta \) all free parameters gave erroneous results, indicating that the precision of the data was not sufficient to perform a meaningful six-parameter fit.

5.2 Image Plane Pattern

The films obtained from the Mach-Zehnder image plane experiment were used to plot supercritical isotherms of CHF\(_3\), which, in turn, were used to estimate the value of \( \gamma \), the critical exponent associated with the compressibility, \( \kappa_T \). Data were collected in the one-phase region \( 1.7 \times 10^{-5} < t < 2 \times 10^{-4} \) with steps of \( \Delta t = 10^{-5} \).

Samples of the film obtained from the experiment are shown in Figs. 11(c) and 11(d). The fringe pattern maps the optical thickness of the sample as a function of position, with each successive fringe indicating a change in optical thickness of one wavelength at a particular height in the
sample. For every positive increment in temperature, the sample became more homogeneous and the refractive index changed more slowly across the vertical length of the cell, causing the fringes to branch out from the central region of the film.

Isotherms were extracted in the following manner. For each of 15 supercritical temperatures, the distance z' of each interference fringe minimum from the undeflected zeroth fringe (interference maximum) was measured using a travelling microscope. These distances were converted to pressure via the relation

\[ P_0 - P = \frac{\rho_c g z'}{M} \]  

(5.6)

where \( \rho_c \) is the critical density, \( g \) is the acceleration due to gravity, \( M \) is a magnification factor due to lens \( L_1 \) (Fig. 7) and \( P_0 \) is the undetermined reference pressure at the centre of the cell. Eq. (5.6) was obtained by calculating, at a given distance \( z = z'/M \) above the centre of the cell, the pressure \( P \) due to the weight of the sample above \( z \). Fringe number was related to density using Eq. (5.2). Three typical CHF\(_3\) isotherms are plotted in Fig. 14.

The maximum value of \( \left| \frac{\partial \rho}{\partial P} \right| \) was found for each isotherm in order to calculate values of \( \kappa_T \) along the critical isochore. The one-phase critical region temperature dependence of the compressibility is illustrated in the \( \log \kappa_T \) versus \( \log |t| \) plot of Fig. 15. A least-squares fit of the power law \( \kappa_T = \Gamma_0 |t|^{-\gamma} \) to this data yielded a value of \( \gamma = 1.26 \pm 0.05 \), which is in
Fig. 14. Plot of $P_0 - P$ versus reduced temperature, $t = (T - T_c)/T_c$.

- $T - T_c$ (°C):
  - 0.0051
  - 0.0179
  - 0.0267
Fig. 15. Plot of isothermal compressibility, $\kappa_T$, versus reduced temperature, $t = (T - T_c)/T_c$. 
agreement with the RG value $\gamma = 1.24$. The result is also consistent with other experimentally measured values of $\gamma$.

There was not a sufficient number of data points to investigate corrections to scaling associated with $\kappa_T$. 
Chapter 6

CONCLUSION

Two optical interference methods were employed to study the second order phase transition in the pure fluid CHF$_3$. In the first experiment, a Fraunhofer diffraction technique was utilized to determine the difference in liquid and vapour refractive indices along the coexistence curve for the reduced temperature range $4 \times 10^{-6} < -t < 3.5 \times 10^{-2}$. Refractive index difference was related to the pure fluid order parameter, $(\rho_l - \rho_v)/\rho_c$, by means of the Lorentz-Lorenz relationship. A multi-parameter fit to the data of the corrections to scaling expression

$$\frac{\rho_l - \rho_v}{\rho_c} = B_0 |t|^\beta (1 + B_1 |t|^\Delta + B_2 |t|^{2\Delta})$$

gave a value of $\beta = 0.327 \pm 0.002$, in agreement with the predicted renormalization group value for this critical exponent. The existence of corrections to scaling was confirmed and values of the correction amplitudes were obtained from the fit.

In the second experiment, a Mach-Zehnder interference pattern, produced over the reduced temperature range $1.7 \times 10^{-5} < t < 2 \times 10^{-4}$, mapped pressure as a function of height in the sample. From an analysis of this pattern, pressure-density isotherms were obtained and used to determine the critical behaviour of the isothermal compressibility, $\kappa_T$, along the critical isochore. The expected power law, $\kappa_T = \Gamma_0 |t|^{-\gamma}$, was fit to the data with the
result $\gamma = 1.26 \pm 0.05$, which is consistent with the accepted renormalization group prediction for the critical exponent $\gamma$. 
REFERENCES


2. C. Domb, Physics Today 21, 23 (1968).


29. The computer program was written by John de Bruyn and will appear in his Ph.D. thesis. The program utilizes the fitting routine NL2SNO supplied by the UBC computing centre.