OPTICAL STUDIES OF CRITICAL PHENOMENA IN FLUIDS

by

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Abstract

Accurate optical techniques were employed to study the behaviour of the binary liquid mixture n-heptane+nitrobenzene ($C_7H_{16} + C_6H_5NO_2$) and of the pure fluid 1,1-difluoroethylene ($C_2H_2F_2$) near their respective critical regions.

It is found that, in the region of reduced temperature, $t = (T_c - T)/T_c < 3 \times 10^{-4}$, the order parameter $\Delta \phi_H$ for the binary mixture follows a power law $\Delta \phi_H \approx t^\beta$, with a leading exponent $\beta = 0.367 \pm 0.006$, which is higher than the predicted theoretical value of $\beta = 0.326 \pm 0.002$. A careful study of the effect of refractive index gradients caused by the Earth's gravitational field, potential variation of the optical thickness of the sample cells due to wetting of the cell walls by one the phases, and the long thermal equilibration times of binary mixtures has failed to resolve the disagreement between $\beta$ measured on n-heptane+nitrobenzene and its theoretical value. A significant feature of this investigation is the novel application of an optical technique (the image plane technique) for studying critical phenomena in transparent binary liquids.

The Lorentz–Lorenz function, $\mathcal{L}$, of 1,1-difluoroethylene was measured in order to determine the fluid's density from its refractive index. The quantity $\mathcal{L}$ is found to vary by about 1.4% with density of the fluid, $\rho$, with a gentle maximum at a density slightly higher than the critical density, $\rho_c$. The density measurements were then used to construct the coexistence curve for this material.

The coexistence curve of $C_2H_2F_2$ was measured with the 'Lorentz–Lorenz' experiment and with a new apparatus combining two complementary optical methods, the prism cell technique and the focal plane technique, into one. The measurements carried out on $C_2H_2F_2$ in this thesis serve as a test of this apparatus. The order parameter data of $C_2H_2F_2$ are described accurately by a scaling power law in terms of the reduced temperature $t$, with the critical exponents at their theoretical values. The coexistence curve data taken simultaneously with the two combined techniques agree well with each over the whole range of temperature investigated.
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Chapter 1

Introduction

1.1 Features of critical phenomena

The work reported in this thesis is based on experiments investigating the so-called critical region of fluids. The main purpose of the experiments is to establish the correct shape of the coexistence curve of two kinds of fluid systems: a pure fluid and a binary liquid mixture. It seems worthwhile to give a brief description of the features which make critical phenomena interesting for physicists and to introduce the definition of some of the physical quantities used for the description of these phenomena.

As the temperature of a liquid in equilibrium with its own vapour is raised, the densities of the two phases approach one another. At a temperature called critical temperature, and usually indicated with $T_c$, the two densities coincide and above $T_c$ there is no longer a distinction between the two states of aggregation, but only one fluid in its gaseous state. As shown qualitatively in Fig. 1.1, the solid curve is the locus of points corresponding to the density of the vapour (part of the curve to the left of $p_c$) and the liquid (to the right of $p_c$) for phases at temperatures below $T_c$. Any thermodynamic change taking the system across the coexistence curve at any place different from $(p_c, T_c)$ is a first order phase transition. At the critical point $(p_c, T_c)$ there ceases to be a distinction between the vapour and liquid phases and a continuous transition between the phases occurs. This is usually referred to as a second order phase transition. A striking feature of this phenomenon is that one can bring the system from point A in the vapour state to point B in the liquid state without ever observing a discontinuity between the two phases. This
Figure 1.1: Qualitative coexistence curve of a pure fluid. Following the dashed line from point A to point B brings the fluid from the vapour state to the liquid state continuously, with the fluid always remaining in one phase.

would be achieved by following the dashed line joining point A to point B in Fig. 1.1. Another view of the critical point can be had through the \((P, T)\) diagram in Fig. 1.2, where \(P\) is the pressure in a closed vessel containing the phases, and \(T\) is the temperature. In this picture, the critical point C is the located at the end of a line of discontinuous, or first order, phase transitions between the vapour and liquid phases. The line from A to B illustrates another path that would take the system continuously from vapour to liquid.

This feature has attracted the interest of physicists for more than 130 years, starting with Thomas Andrews, the discoverer of the critical point. He noted in his 1870 paper on the critical point of \(\text{CO}_2\):

"As a direct result of his experiments, he [T. Andrews] concludes that the gaseous and liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas, to carbonic acid
Figure 1.2: Qualitative (and not to scale) pressure–temperature phase diagram of a pure fluid. The point C, at temperature $T_c$ and pressure $P_c$, is the critical point. Similarly to the phase diagram in Fig. 1.1, following the dashed line from point A to point B brings the fluid from the vapour state to the liquid state continuously, with the fluid always remaining in one phase. The thicker line represents here the coexistence curve and corresponds to the projection of the curve of Fig. 1.1 onto the $(P, T)$ plane.

as a perfect liquid, the transition may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes [1]."

As the critical temperature is approached from below, experiments show that the density difference between the two phases obeys a power law relation like the following, in the limit that $T \to T_c$:

$$\Delta \rho = \rho_L - \rho_v \approx (T_c - T)^\beta$$

(1.1)

The accurate determination of such power law and in particular of the exponent $\beta$ is one of the main results of the present work.

An arguably even more interesting feature of these phenomena is that they are not restricted to pure fluids. There is a common behaviour underlying what appear to be very different physical systems. The discovery of the
critical point of a pure fluid was soon followed by that of the critical point of a ferromagnet (Fe). The magnetization, $M$, of a piece of Fe vanishes above a certain critical temperature $T_c$, that has come to be known as Curie temperature [2]. Moreover, it is experimentally verified that as $T_c$ is approached from below the following power law holds:

$$M \approx (T_c - T)^eta$$

(1.2)

(where $T_c$ is now the Curie temperature) and the value of $\beta$ is the same found in the pure fluid case, within experimental error. The similarity of the shape of the experimental curves, which can be noticed in Figs. 1.3 and 1.4, albeit at different temperature ranges, is quite striking and suggests that there is more than just a coincidence to these events. Other examples of physical systems with critical points are: antiferromagnets, ferroelectrics, binary alloys, superconductors, superfluids.

One other example should be described since it one of the subjects of this thesis. Two different substances in their liquid state—a system known as a binary liquid mixture—display a critical behaviour, analogous to a pure fluid, through the phenomenon of mutual diffusion.
Given two liquids, called for convenience H and N, there can be a temperature, $T_c$, called the consolute temperature, below which the liquids separate in two phases, the lighter one above the heavier one, with a distinct meniscus between them. Above $T_c$, it becomes more energetically favourable for the system to be in one phase, thus diffusion occurs, the meniscus between the liquids blurs and eventually disappears, with the two species settling in one single liquid phase. The phase diagram in Fig. 1.5 represents qualitatively the coexistence curve of a binary liquid mixture, in terms of the concentration of one of the two species versus temperature.

Other physical quantities are found to behave similarly from one system to another in the neighbourhood of the critical point and to follow well-reproducible power laws. They are usually expressed in terms of the reduced temperature $t = (T_c - T)/T_c$ and they describe:

- the constant volume specific heat, $c_V$:

$$c_V = A_0^c |t|^{-\alpha} \quad (1.3)$$
Chapter 1. Introduction

One-phase region: liquids H and N completely miscible

Two-phase region: liquids H and N immiscible and coexisting

Figure 1.5: A typical qualitative coexistence curve of a binary liquid mixture.

- the isothermal compressibility $\kappa_T$ (or susceptibility $\chi_T$ in the ferromagnetic case):
  \[ \kappa_T = \Gamma_0^+ |t|^{-\gamma} \]  
  (1.4)

- the chemical potential, $\mu(\rho, T_c)$ along the critical isotherm:
  \[ \mu(\rho, T_c) - \mu_c = D_0 |\rho - \rho_c|^\delta \]  
  (1.5)

- the correlation length, $\xi$:
  \[ \xi = \xi_0^+ |t|^{-\nu} \]  
  (1.6)

beside the already mentioned density difference, $\Delta \rho$:

\[ \Delta \rho = B_0 |t|^\beta \]  
(1.7)

The latter quantity is more generally referred to as the order parameter. It is given by different quantities for different physical systems, such as $\Delta \rho$ for pure fluids and the magnetization, $M$, for ferromagnets. The exponents $\alpha$, $\beta$, $\gamma$, $\delta$, and $\nu$ are called critical exponents (other critical exponents will be encountered in Chapter 2) and $A_0^\pm$, $\Gamma_0^\pm$, $D_0$, $\xi_0^\pm$, and $B_0$ are known as critical
amplitudes. The $\pm$ sign in some of the amplitudes indicates quantities to be considered below (−) or above (+) $T_c$.

The power laws given by equations (1.3), (1.4), and (1.6) show that the specific heat, the compressibility and the correlation length are singular at the critical temperature. These singularities have proven to be very important in the development of the modern theory of critical phenomena.

As theoretical determinations of $\beta$ have become more precise, the need for precise and accurate measurements of $\beta$ have become increasingly more important. It is in this framework that the measurements reported in this thesis fit.

Fluids are particularly suited for the study of the critical region in that they do not present problems related to lattice structure imperfections or defects—a common occurrence in solids. Moreover, transparent fluids can be probed by optical methods which are in general quite accurate and "clean". One of the drawbacks of using fluids on Earth is the influence of the gravitational field, which can mask the phenomenon one is trying to observe. However, as it will be shown, the optical methods employed remain satisfactorily accurate despite gravitational effects.

1.2 Summary of work

1.2.1 Binary liquid mixture

Critical temperatures

The first datum needed to measure the coexistence curve of a binary liquid mixture (and of a pure fluid, for that matter) is the critical temperature of the system. Physical divergences prevent the experimenter from accessing the critical point directly. Thus, one can only take measurements in a neighbourhood of the critical point, termed the critical region, and then try to infer information about the physically inaccessible region by extrapolation from the available data. The critical temperature, $T_c$, is obtained in this fashion. The available literature on the subject suggests that different amounts of impurities are responsible for a variation in the critical temperature of a mixture. In particular, the critical temperature varies linearly with the amount of impurities in the system (see, for example, references [4], [5], and [6]). As data were taken from different samples of the same binary mixture, slightly different $T_c$s were found. These variations in $T_c$ were used to
assess the level of influence impurities might have had on the rest of the measurements. The critical temperature data available from the experiments of this work were analyzed in terms of the predictions on the behaviour of $T_c$ due to the presence of water and acetone as impurities in our samples.

**Coexistence curve**

In the binary liquid mixture experiment the coexistence curve was measured for the system $n$-heptane+nitrobenzene and in particular the value of the exponent, $\beta$, that characterizes it ($n$-heptane is a non-polar fluid, while nitrobenzene is strongly polar). The critical phenomena laboratory of UBC has applied its optical methods to the study of the critical region of binary mixtures before [7]. At the time of those studies, the value of $\beta$ found was in agreement with an older “trend” predicting $\beta = 1/3$ or slightly larger, but newer theoretical development in the field of phase transitions and critical phenomena, culminating in the early 1970s with Wilson’s renormalization group theory, would “dictate” a lower value of $\beta$. It seemed fit, therefore, to carry out a study on a binary liquid mixture system to obtain a more definitive experimental value for $\beta$.

As anticipated in section (1.1), optical techniques were employed for these measurements. These techniques have a history of successful results for the past thirty years [7, 8, 9] and will be described in detail later in the text. The method known as *focal plane technique* is the principal tool of investigation of the coexistence curve of a binary liquid mixture. The index of refraction difference between the two liquids was measured as a function of temperature and the critical exponent $\beta$ was obtained by fitting the theoretically predicted power law to the data. Also, it was possible to find the range of validity of equation (1.7) in terms of the reduced temperature $t$, and compare it the findings of other experimenters. Given the precision required to distinguish between a $1/3$ exponent and the slightly lower value of around 0.326 predicted by the modern theories, an improved experimental setup was made for these measurements. In particular, the thermal control was improved and samples with a longer optical path were employed, in order to reduce the error in the index of refraction measurements. The performance of the newly built thermostat was verified both in terms of its thermal gradients and its thermal stability with noticeably improved results with respect to the older apparatus. Using a thicker sample, to increase the optical path, considerably reduces the scatter in the coexistence curve data, thereby producing more reliable results.
An analysis of the possible sources of systematic errors needed to be carried out as thoroughly as feasible to ensure maximum accuracy of the collected data and of the final results. The effects influencing critical phenomena studies in binary liquid mixtures are:

- thermal gradients along the sample: this is an aspect of the apparatus that was improved upon by the construction of a new thermostat. The performance tests on the entity of vertical thermal gradients in the sample cell when it is placed in the thermostat suggest that thermal uniformity and stability conditions are within the tolerances for the required accuracy of these experiments.

- the Earth's gravitational field causing a vertical gradient in the index of refraction: to attempt observation of any gravitationally induced refractive index gradient, another optical interferometric technique, known as image plane technique, was employed possibly for the first time in this manner (no similar results were found in the literature). The results obtained are very helpful for the determination of the scale of these gradients and their influence on the final value of the critical exponent $\beta$.

- equilibration time at each temperature: it takes time for a system to reach equilibrium after the temperature is changed. Measurements should only be made after equilibration is achieved. The same technique employed to measure the effect of gravity could be used to study the equilibration time issue and rule out the possibility of this effect corrupting our data.

- wetting of the cell walls by the sample: if one of the two phases of a binary mixture wets the other phase as well as the wall of the cell that contains them, then the effective optical light path involved in light transmission through the cell is different from the nominal value given by the manufacturer. An estimate of the influence of this effect can be made by performing measurements with different nominal cell thicknesses.

- the relation between refractive index and concentration: this relation is needed to obtain the order parameter of the particular system studied. A reasonably complete search through the literature has provided information on the question of the relation between refractive index and
concentration of our binary mixture. The findings helped estimate the level of influence of this effect on the study of the coexistence curve reported.

The above influences on the observed critical phenomena were checked with a fine-toothed comb and analyzed with great care.

1.2.2 Pure fluid

Lorentz–Lorenz coefficient

The order parameter of preference for pure fluids is the density difference between the liquid and vapour phases. In the optical studies of this work, the order parameter has to be obtained from measurements of the difference in index of refraction between the phases, through the Lorentz–Lorenz relation, which relates the refractive index, \( n \), of a fluid to the fluid density, \( \rho \) [10]:

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

(1.8)

To be able to use it one must first determine the Lorentz–Lorenz coefficient \( \mathcal{L} \) by measuring the density, \( \rho \), and the refractive index, \( n \), of the pure fluid independently of one another and inserting them into equation (1.8). These measurements were obtained with another optical technique called the prism cell technique.

The pure fluid studied in this thesis is 1,1-difluoroethylene \( (C_2H_2F_2) \), whose critical temperature of around 30°C is accessible with relative ease. The measurements of \( \mathcal{L}_{C_2H_2F_2} \) as accurate as obtained in this work constitute a novel result, as a research in the literature has failed to reveal any other studies on the Lorentz–Lorenz function of this compound.

Coexistence curve

The prism cell technique was also used to study the coexistence curve of 1,1-difluoroethylene and analyze it in terms of the scaling relation (1.7) mentioned above in section 1.1.

The main expected difference between the coexistence curve of binary liquid mixtures and pure fluids is the extent of the asymptotic region, that is, the extent to which the scaling relation (1.7) is valid in terms of the reduced temperature, \( t \). While there is no theoretical estimate of the range of the
asymptotic region, experience seems to suggest that in pure fluids such a
relation holds true for a smaller range of \( t \) than for binary liquids. Beyond
that range, corrections to the simple power law relation must be added to
achieve a proper description of the coexistence curve.

Accurate coexistence curve data on both a binary liquid and a pure fluid
allow a careful study of the importance of correction terms in the inter­
pretation of the data as well as in the estimate of the value of the critical
exponent \( \beta \).

In general, gravity affects pure fluids at their critical point more than it
does binary fluids. This effect is quite evident when taking data with the
prism cell technique in a way that will be described in due course. Because
of this effect data cannot be reliably taken closer to the critical temperature
than about 25 mK or \( 10^{-4} \) in terms of \( t \). To obtain a more complete mea­
surement of the coexistence curve the focal plane technique was used as was
done for the binary liquid coexistence curve.

These complementary prism–cell and focal–plane measurements are car­
ried out in a single piece of apparatus, called \textit{combined cell}, in which both
kinds of measurements can be done simultaneously. This novel type of cell
circumvents the problem of having to use two different samples with possibly
different amounts of impurities in them, making data analysis and interpre­
tation easier and more reliable.

Ultimately, the two kinds of data can also be compared among each other
to assess the problem of wetting of the cell windows by the liquid phase of
the pure fluid. This effect could alter the effective length of the light path
in the cell and provide a source of systematic error in the data. Simulta­
neous measurements with the combined cell can verify the presence of some
measurable wetting.

1.3 Outline of the thesis

Beyond the present chapter, this thesis is organized as follows.

Chapter 2 is a summary of the \textit{status quo} of the theoretical work on crit­
ical phenomena, starting from the scaling ideas to the latest most accredited
Renormalization Group Theory results. Some more definitions of the quanti­
ties used, besides those already given in this chapter, are also introduced
in Chapter 2.

The main experimental features of the experimental techniques employed
for this work and which are common for both the binary liquid and the pure fluid experiments are described in Chapter 3. This chapter also has a description of the three optical techniques used in the experiments: the prism cell technique, the focal plane technique and the image plane technique.

The subject of Chapter 4 is the experiment on the binary liquid mixture $n$-heptane+nitrobenzene, including those details of the apparatus which differ from the common features introduced in Chapter 3, and a thorough analysis of the sources of systematic errors.

Chapter 5 presents the pure fluid experiment with sections on the Lorentz-Lorenz measurements and the measurements of the coexistence curve of 1,1-difluoroethylene.

Finally, Chapter 6 is a summary of the whole thesis with an evaluation of the results and their possible consequences.

The appendices contain interesting, relevant material which nevertheless would have unnecessarily encumbered the main text of this thesis.
Chapter 2

Theoretical background

2.1 Introduction

This chapter is dedicated to a description in broad strokes of the modern theory of critical phenomena and its principal results that are of interest for the present experimental work\(^1\).

I have deliberately elected not to write anything about what is normally known as the classical theory of critical phenomena\(^2\). Despite the importance of the historical development of the classical theories, it is the results of the modern theory that the experimental efforts are confronted with. I have therefore preferred to omit any mention of Van der Waals', Landau's or later, pre-scaling, theories, whose quantitative predictions of the critical exponents, for example, were not in agreement with experimental evidence. The classical results are only summarized in a table (Table 2.1).

Instead, the chapter is centred on the development of the idea of scaling and on an overview of renormalization group theory.

\(^1\)The notes in this chapter come from a variety of sources, the most significant of which are [11, 2, 13, 14, 15, 16, 17, 18].

\(^2\)In the theory of phase transitions and critical phenomena, the term "classical" is not used as against "quantal", but in opposition to the "modern" theory, which actually manages to produce more correct results.
2.2 Scaling

A successful theory of critical phenomena should be able to explain the universal character of the power laws that were exposed in section 1.1 and also to calculate the values of the critical exponents $\alpha, \beta, \gamma, \delta,$ and $\nu$ that govern those laws. The divergences in the specific heat, the isothermal susceptibility and the correlation length, in particular, should arise naturally from the theory. The scaling ideas that started to flourish in the mid '60s were the first theoretical effort capable of incorporating these singularities.

The so-called scaling hypothesis stems from the idea that the free energy, $f$, of a system with a second order phase transition can be thought of as the sum of a factor that behaves regularly at the critical temperature and another factor that contains the singular behaviour. The hypothesis is that the singular part of the free energy is a homogeneous function of the temperature and of one of the important fields. For critical phenomena in fluids the field of choice is usually the chemical potential of the substance, $\mu$. Therefore, one assumes that there exist two numbers, $a_\mu$ and $a_t$, such that for any positive $\lambda$, $f(\mu, t)$, with $t = (T_c - T)/T_c$ obeys the relation:

$$f_s(\lambda^{a_\mu} \mu, \lambda^{a_t} t) = \lambda f_s(\mu, t)$$  \hspace{1cm} (2.1)

where the subscript $s$ indicates the singular part of the free energy. From the properties of the homogeneous functions and their derivatives and the relation between the various thermodynamic functions and the derivatives of the free energy with respect to its variables, the critical exponents can be expressed in terms of the exponents $a_\mu$ and $a_t$ [16, 19]:

$$\alpha^\pm = 2 - \frac{1}{a_t}$$
$$\beta = \frac{1 - a_\mu}{a_t}$$
$$\gamma^\pm = \frac{2a_\mu - 1}{a_t}$$
$$\delta = \frac{a_\mu}{1 - a_\mu}$$

This 'singularity' story resembles the discovery of black holes, in reverse. There, the theory (Schwartzchild's solution to Einstein's equations) contained a singularity that turned out to be real in the form of black holes. Here, the measured, i.e., real, singularities had to be taken as a guide for a formulation of a complete theory.
The scaling equation (2.1) can be put in a form that makes it easier to obtain the power laws for the various thermodynamic quantities by choosing \( \lambda = t^{-1/\alpha} \). In this case

\[
f_s = t^{2-\alpha} f_s \left( 1, \frac{\mu}{|\Delta\rho|^{\delta}} \right)
\]

(2.2)

Another formulation of the scaling hypothesis is that all the singularities at the critical point stem from the divergence of the correlation length, \( \xi \) as a function of \( |T_c - T| \) and the conjecture that, at the critical point, \( \xi \) is the only relevant length of the problem. The correlation length is a measure of the range of the density fluctuations (in the fluid phenomena case). The scaling hypothesis then states that the details over small scales are not important to understand the physics of the phenomenon. From this picture, scaling relations can be obtained:

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

(2.3)

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

(2.4)

\[
\beta (\delta - 1) = \gamma
\]

(2.5)

Experimental data show that \( \xi \) diverges as a power law like

\[
\xi \approx |t|^\nu
\]

(2.6)

as \( |t| = |T_c - T|/T_c \) tends to zero. The correlation length is linked to the density–density correlation function \( G(r) \), which is used to describe the density fluctuations in the system. On quite general grounds it can be shown that \( G(r) \) decays exponentially for large distances, that is to say

\[
G(r) \sim e^{-r/\xi}
\]

(2.7)

as \( r \to \infty \). Since \( \xi \) becomes infinitely large at the critical point, while \( G(r) \) is still measured to decay to zero for large distances, it is reasonable to expect that the correlation function fall off as an inverse power law in the vicinity of the critical point:

\[
G_c(r) \sim r^{-d-2+\eta}
\]

(2.8)

for \( r \to \infty \), where \( d \) is the dimensionality of the system and \( \eta \) is another critical exponent.

Information on the correlation function can be obtained through light scattering experiments. The information comes from the intensity \( I(\theta) \) of
the light scattered at an angle, $\theta$, with respect to the forward direction. The scattering intensity $I(\theta)$ is determined by the fluctuations in the index of refraction, and therefore in the density, of the fluid and it is proportional to the quantity

$$I(\theta) \propto \hat{G}(k) = \int dr e^{ik \cdot r} G(r)$$  \hspace{1cm} (2.9)$$

where $k$ is the shift in the wave vector of the radiation. Equation (2.9) is the Fourier transform of the real space density-density correlation function $G(r)$. Through the fluctuation–compressibility relation [2]

$$I(0) \propto \int d^3r G(r) = \kappa_T$$  \hspace{1cm} (2.10)$$

the scattering intensity in the forward direction ($\theta = 0$) is proportional to the compressibility.

There is substantial evidence, therefore, that the increase in the density fluctuations, in the range of the density–density correlation function and the compressibility at and near the critical point are all interrelated. Consequently, it is plausible to expect that the critical exponents $\eta$ and $\nu$ be related to the thermodynamic exponents $\alpha$, $\beta$, $\gamma$, and $\delta$. One can use the fluctuation–susceptibility theorem to arrive at the scaling relation

$$\gamma = (2 - \eta)\nu$$  \hspace{1cm} (2.11)$$

There is a further relation that should be mentioned, which is the only relation involving the dimensionality of the system. Data show that the universal character of critical exponents holds only within so-called universality classes. The exponents appear to depend on the dimensionality of the system and on the symmetry of the order parameter. A universality class is identified by the the dimensionality $d$ of the system, by the rank, $n$, of the order parameter tensor of the system, and by the short or long range of the interactions. It is usually indicated by the symbol $[d, n]$. For example, fluid systems belong to the $[3, 1]$ universality class, since they are three–dimensional systems and their order parameter is a scalar, with short–range, van der Waals–like interactions. It is quite important, then, that a “proper” theory be able to account for a dimensionality dependence of the critical exponents. Without going into the details, from a dimensional analysis of the free energy emerges another exponent relation that goes by the name of “hyperscaling” relation:

$$d\nu = 2 - \alpha$$  \hspace{1cm} (2.12)$$
The scaling theory arrives at the important observation that at the critical point each physically important quantity has a natural size. When this size is accounted for the universal character of the phenomena emerges naturally from the theory. Furthermore, through the scaling theory and the scaling relations one can determine all the critical exponents from the knowledge of only two of them.

2.3 Models

Of course, one needs a way to calculate those two exponents, whichever they may be, to get the whole set and compare it with experimental results. One fundamental quantity from which the exponents can be obtained is the total free energy of the system (that is to say, the sum of the regular and the singular parts), which, as statistical mechanics teaches us, one can obtain from the partition function of the system, \( \mathcal{Z} \), once its Hamiltonian is known.

There are several theoretical models that serve this purpose in various ways, but there is one particular model that has inspired most of the other ones, which is the Ising model\(^4\) [20]. It is the simplest model of a many body system and, although it originated from the study of a ferromagnet, it can be used to represent a fluid.

In the Ising model the space is divided into a lattice of \( N \) cells of equal volume and identified by a single lattice point. Each lattice site represents a ‘particle’ of the system and in the ferromagnetic case an Ising ‘spin’, \( s_i \) (\( i = 1, \ldots, N \)), is associated with each lattice point, the spin variable taking either of two possible values, say \( \pm 1 \), to represent its microscopic state. To build a useful Hamiltonian function, interactions between spins must be included between nearest neighbours only, in the simplest formulation, and are represented by an interaction constant \( J \). The Ising Hamiltonian is

\[
\mathcal{H}_N \{ \{ s_i \} \} = -H \sum_{i=1}^{N} s_i - J \sum_{\langle i,j \rangle} s_i \cdot s_j
\]

where the second sum is meant to be over all, and only, nearest neighbour pair of spins and \( H \) is an external applied field (magnetic field in ferromagnets and pressure or chemical potential in fluids).

\(^4\)More correctly it should be referred to as the Lenz–Ising model.
Chapter 2. Theoretical background

It can be shown that the Ising model is isomorphic to the lattice gas model [21], the latter being a very crude but useful model of a fluid, where the continuous space is replaced by a lattice of sites. The fluid atoms or molecules are only allowed to sit at the lattice sites. The relation between the two models is realized by having, for example, the spin +1 state correspond to an empty lattice gas site and the −1 to an occupied one. The interaction potential between two occupied sites, i.e., between two fluid molecules is given by the quantity $u_{ij}$, such that

$$
 u_{ij} = \begin{cases} 
   \infty & \text{if } i = j \\
   -J & \text{if } i \neq j, \text{ } i \text{ and } j \text{ nearest neighbours} \\
   0 & \text{otherwise}
\end{cases}
$$

Having a Hamiltonian function like in equation (2.13), the partition function $Z_N$ is

$$
 Z_N = \text{Tr}_{s_i=\pm 1} e^{-\mathcal{H}_N/k_BT} 
$$

$k_B$ being Boltzmann’s constant and $T$ the absolute temperature. The free energy is then given by:

$$
 F = -k_BT \ln Z_N
$$

in the thermodynamic limit that the number of molecules, $N$, and the volume, $V$, of the system both tend to infinity in such a way that the ratio $N/V$ remains finite.

It is possible to solve exactly both the one dimensional and the two dimensional Ising models\textsuperscript{5}. However, for the three dimensional case only approximate solutions exist. One way to obtain numerical values of the critical exponents from a three dimensional Ising model is by the high-temperature series expansion [14].

The free energy is expanded as a function of the coupling parameter $J/k_BT$, which becomes small at high temperatures. Since the thermodynamic functions correspond to derivatives of the free energy, they will also be represented by series expansions in terms of that parameter. The critical exponents are then obtained by studying the ratios of the successive coefficients of the power series as a function of the reciprocal of the order of the

\textsuperscript{5}The exact solution of the 2-D Ising model by Lars Onsager in 1944, was one of the milestones of the development of the modern theories of critical phenomena (see, for example, reference [2], chapter 15).
Chapter 2. Theoretical background

coefficient ([14] and references therein). The high-temperature expansion method arrives at the following values of the critical exponents

$$\alpha \approx 0.105 \pm 0.010$$
$$\beta \approx 0.328 \pm 0.008$$
$$\gamma \approx 1.239 \pm 0.002$$
$$\nu \approx 0.632 \pm 0.002$$

2.4 Renormalization group theory

Renormalization group theory of critical phenomena is acclaimed as the most accurate in the description and understanding of the critical point features of universality and scaling and in the correct explanation of the origin of the critical exponents and the calculation of their values [22].

The theory is based on a transformation performed iteratively on the Hamiltonian of the system in order to reduce, or integrate out, the number of degrees of freedom required for the description of the critical point characteristics. The transformation in some way renormalizes the Hamiltonian at each step, hence the name of the theory⁶.

Relating back to the Ising model as a starting point, the typical Hamiltonian of a system exhibiting some kind of criticality depends on a number of parameters that are related to the relevant thermodynamic fields of the problem: temperature and external magnetic field in the ferromagnetic case or temperature and pressure in the case of a pure fluid. In the discussion that follows the magnetic case notation will be used, as it is often the case in the literature on the theory of critical phenomena.

The Hamiltonian usually appears in the partition function as an exponent of the form $-\mathcal{H}/k_BT$, it is therefore convenient to work with the quantity $\mathcal{H} = -\mathcal{H}/k_BT$, referred to as the reduced Hamiltonian:

$$\mathcal{H} = \mathcal{H}(K, h, C)$$ (2.17)

where the quantities $K$ and $h$ are respectively related to the temperature and external field in this way: $K = J/k_BT$ and $h = H/k_BT$, $J$ being the interaction amplitude of the Ising Hamiltonian. The parameter $C$ does not

⁶For the sake of exactness, since the inverse of such transformation does not exist, the algebraic structure of the set of transformations is a semigroup.
Chapter 2. Theoretical background

appear in equation (2.13), but it is used to simplify the mathematical treatment. It can be interpreted as the contribution to the free energy from the short wavelength degrees of freedom that are integrated out at each step of the renormalization transformation.

The common idea underlying renormalization group treatments is that of expressing the parameters describing the Hamiltonian in terms of some other, possibly simpler set of parameters, while keeping the physics of the problem unchanged. In the study of critical phenomena this is achieved by a process of coarse graining of the short–length–scale degrees of freedom in favour of the longer length–scales that appear to be the important ones as the critical point is approached, as was discussed in the previous section. In the process of coarse graining, the reduced Hamiltonian \( \tilde{\mathcal{H}}(K, h, C) \) is represented by a point in a space called space of Hamiltonians or parameter space. Knowledge of these parameters fully determines the free energy of the problem in the thermodynamic limit. Changing the temperature, \( T \), and magnetic field, \( H \) moves the point around in the parameter space. In the relatively simple example (at least conceptually) of a two–dimensional square lattice, one can see how the parameters get renormalized by a coarse graining operation. Referring to Fig. 2.1, the coarse–graining procedure can be carried out by dividing the lattice in blocks each containing a set of spins. Each block is represented by one value of the spin variable, chosen, for example, by the majority rule: if most of the spins in the block are +1, then the whole block spin will have value +1, and vice versa. The partition function is then calculated by taking the sum over the block spins instead of over all the original spins. From a lattice with spacing \( a \), after transforming once the new lattice has spacing \( 2a \), but to remain faithful to the original problem the transformed lengths are rescaled so that the new lattice spacing \( a' \) equals the original spacing. This entails that a generic distance \( r \) be rescaled to \( r' = r/2 \), in the particular case of Fig. 2.1. In general the length–rescaling will be \( r' = r/b^d \), where \( b \) is a coarse–graining factor, and \( d \) the dimensionality of the system.

In the general case, after a renormalization transformation \( \mathcal{R} \) is carried out, new couplings enter the picture, and the Hamiltonian will be:

\[
\tilde{\mathcal{H}}'(K', h', C', ... ) = \mathcal{R} \left( \tilde{\mathcal{H}}(K, h, C, ...) \right)
\]  

Hence, the space of Hamiltonians, in the most general case, is an infinite dimensional space, since each point in it represents a Hamiltonian that depends on an infinite number of parameters.
Figure 2.1: Coarse graining of a square lattice into block spins. The black circles are the original, unrenormalized spins, while the white circles correspond to the 'new' spins after a transformation $\mathcal{R}$ has been applied.

A fundamental role in the space of Hamiltonians is played by fixed points, $\tilde{\mathcal{H}}^*$, namely points that are invariant under renormalization:

$$\tilde{\mathcal{H}}^* = \mathcal{R}(\tilde{\mathcal{H}}^*)$$

(2.19)

From the rescaling of the lengths after each step of the transformation it follows that the correlation length also rescales as:

$$\xi(K', h', C', \ldots) = \xi(K, h, C, \ldots)/b$$

(2.20)

which at the fixed point implies that $\xi(K^*, h^*, C^*, \ldots) = \xi(K^*, h^*, C^*, \ldots)/b$, with $b > 1$. The last equality is valid for either $\xi^* = 0$ or $\xi^* = \infty$, the former is known as a trivial fixed point, while the latter is a nontrivial and more interesting fixed point. The divergence of the correlation length is the hallmark of the critical point, therefore it is reasonable to say that a (nontrivial) fixed point of a renormalization transformation represent a critical point.

The drawing in Fig. 2.2 is helpful in describing how the transformation $\mathcal{R}$ operates in the parameter space. A typical transformation $\mathcal{R}$ applied to the physical critical Hamiltonian ($\tilde{\mathcal{H}}^{(0)}$ in Fig. 2.2)—it can be imagined to be the critical Hamiltonian of Fe, for instance—yields a different renormalized Hamiltonian $\tilde{\mathcal{H}}^{(1)}$, which is also a critical Hamiltonian since the renormalized correlation length that was infinite at $\tilde{\mathcal{H}}^{(0)}$ is infinite at $\tilde{\mathcal{H}}^{(1)}$, too. This
Figure 2.2: Graphic representation of the space of Hamiltonians and the flows given by the renormalization group transformation $\mathcal{R}$ (taken from ([14])).

suggests that in general the physical Hamiltonian is not a fixed point of the parameter space, rather successive applications of $\mathcal{R}$ generates a trajectory of critical points in parameter space. It is plausible to expect that this 'renormalization trip' in parameter space will end at a fixed point, $\mathcal{H}^*$ of the space. In that case the critical Hamiltonian of Fe is said to lie on the stable critical manifold of the fixed point $\mathcal{H}^*$, that is to say the set of points in the space of Hamiltonians, which will flow to $\mathcal{H}^*$ under iterative renormalization transformations. Naturally, starting points different from the critical point of Fe, like those of water or $n$-heptane+nitrobenzene for example, could lie on the same manifold and therefore land at the same fixed point after renormalization. All the critical Hamiltonians that belong the stable critical manifold of the same fixed point are said to belong to the same universality class. Any perturbation causing the initial Hamiltonian to end up in the basin of attraction of a different fixed point is called relevant, otherwise is said to be irrelevant.

Under the reasonable assumption of smoothness of the generally nonlinear transformation $\mathcal{R}$, this can be expanded around a fixed point, considering then only linear terms. Based on the semigroup properties of the transformation $\mathcal{R}$, it can be shown that the free energy per unit volume as a function
Chapter 2. Theoretical background

of the linear scaling fields \( t, h, ..., g_j, ... \) transforms as follows:

\[
f(t, h, ..., g_j, ...) \approx b^{-dt} f \left( b^{\lambda_1} t, b^{\lambda_2}, ..., b^{\lambda_j} g_j, ... \right)
\]  \hspace{1cm} (2.21)

where \( b \) is a rescaling factor, \( d \) is the dimensionality of the system, \( l \) is the number of iterations of the linearized \( R \), and the \( \lambda \)s are constants that define the eigenvalues of the linearized transformation. By choosing \( b^{\lambda_1} = 1/t \), the general scaling result as in equation (2.2) is recovered:

\[
f(t, h, ..., g_j, ...) \approx t^{2-\alpha} f \left( 1, \frac{h}{t^\Delta}, ..., \frac{g_j}{t^{\phi_j}}, ... \right)
\]  \hspace{1cm} (2.22)

having set \( 2-\alpha = d/\lambda_1, \Delta = \lambda_2/\lambda_1, \) and \( \phi_j = \lambda_j/\lambda_1 \).

The terms like \( g_j/t^{\phi_j} \) play a particularly important role in the description of the critical region “not so close” to the critical point. If such terms correspond to irrelevant variables, \( \phi < 0 \) and the whole term will vanish as \( t = 0 \) is approached. If it is possible to expand the scaling function given by equation (2.22) in terms of these variables, for example, the order parameter for a pure fluid is described by

\[
\Delta \rho(T) = \rho_L - \rho_V = B_0 |t|^{\beta} (1 + b_{-\phi} t^{-\phi} + b_1 t + \cdots)
\]  \hspace{1cm} (2.23)

The universal exponent \( -\phi \) is normally called correction-to-scaling exponent and it is particularly significant since the magnitude of this term can interfere with a correct determination of the main critical exponent \( \beta \) [23]. It has been shown that equation (2.23) can be written as

\[
\Delta \rho(T) = B_0 |t|^{\beta} (1 + B_{-1} |t|^\Delta + B_{-2} |t|^{2\Delta} + \cdots)
\]  \hspace{1cm} (2.24)

which is the form of the order parameter with which the data of the experiments in this thesis will be confronted. In the work presented here, the correction-to-scaling terms play an important role and cannot be neglected if a correct analysis of the data has to be carried out. The experimental results will show how the need to include correction terms to the simple scaling law arises at different temperature ranges in binary liquid mixtures and in pure fluids.

To conclude, numerical values of the renormalization group theory critical exponent for a system can be calculated by using a microscopic model of the system. As we have seen, the three-dimensional Ising model in the form
Table 2.1: Theoretical values of the critical exponents. The results from the classical, mean field theories (MFT) are reported for comparison with the predictions of the modern theory.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0</td>
<td>0.105</td>
<td>0.109 ± 0.004</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1/2</td>
<td>0.328</td>
<td>0.3258 ± 0.0014</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1</td>
<td>1.239</td>
<td>1.2396 ± 0.0013</td>
</tr>
<tr>
<td>$\nu$</td>
<td>1/2</td>
<td>0.632</td>
<td>0.631 ± 0.013</td>
</tr>
</tbody>
</table>

of the lattice gas model has turned out to be a very good approximation of a fluid. The renormalization method values of the critical exponents for this model are summarized in table 2.1, where the scaling theory values and the ‘classical’ values of the mean field theories (MFT) are also reported for comparison.
Chapter 3

General experimental features

3.1 Introduction

There are common issues which must be addressed in order to carry out the experiments reported in this thesis. For example, the thermostats employed for the pure fluid experiments and for the binary liquid mixture experiments share some basic characteristics, although with slightly different geometries. Moreover, the optical techniques employed in the measurements are the same for the two kinds of experiment. This chapter is therefore a general description of the apparatus and techniques that produced the data for this thesis. The issue of the temperature control and measurement is dealt with in the first section. This is followed by a section describing the three optical techniques used in the experiments: the prism cell, the focal plane, and the image plane techniques.

Both metric and imperial units are used for the apparatus dimensions. The use of non-standard units is due to the standard dimensions of metal stock normally available in Canada.

3.2 Temperature control and measurement

An excellent control of the temperature and its precise measurement are important in critical phenomena experiments for several reasons. The thermodynamic anomalies at critical points of either pure fluids or binary liquid mixtures occur in a very narrow temperature region in a neighbourhood of the critical temperature, $T_c$. More precisely, in terms of the reduced
temperature, \( t = (T_c - T)/T_c \) the asymptotic critical region of pure fluids is typically observed for \( t < 10^{-4} \), whereas for binary liquid mixtures for \( t < 10^{-2} \) [28, 29, 30]. In other words, in critical phenomena occurring at roughly room temperature, like those studied for this thesis, experimental observations have to be made from as close as possible to \( T_c \) to about 0.03 K from \( T_c \) for pure fluids and to about 3 K for binary liquids. Naturally, the closer \( T_c \) can be approached, the more accurate, and scientifically useful a description of the critical region (and the more difficult to study it).

As the critical temperature is approached, the thermal equilibration time increases [31], and it is around 50 hours at our closest approaches to \( T_c \), that is to say at about \( \Delta T = T_c - T \approx 150 \, \mu \text{K} \). If equilibrium is not reached, one is not measuring the physical quantities in the appropriate conditions.

Temperature uniformity is also very important in these experiments to avoid thermal gradients in the sample fluids. Thermal gradients may induce measurable index of refraction gradients, which, as it will be discussed later (see “Results and discussion” section of chapter 4), constitute a source of systematic errors in the final measurements.

Therefore, successful experiments in critical phenomena depend crucially, among other things, on precise, accurate and stable temperature control. More quantitatively speaking, it is necessary to control the temperature within less than 1 mK for up to several days continuously.

### 3.2.1 Thermal control

Temperature control of the required stability and uniformity is achieved by means of a thermostat with two active thermal control stages. The sample cell is contained in the innermost stage of the thermostat (hatched region in Fig. 3.1). This stage is a copper or aluminum block fitting snugly in another massive block—also copper or aluminum. The latter block is wrapped in either heating wire or heating foils [32], through which electrical heating is delivered to the sample.

The inner stage is surrounded by a roughly 50-mm-thick layer of high density styrofoam to provide insulation (Styrofoam SM [33]). The thickness of the interlayer of styrofoam is arrived at through the heat conduction argument presented in appendix A. For the purposes described in this thesis the insulation provided by Styrofoam SM is very satisfactory and it circumvents the heat convection problem that air insulation alone would present.

Inner stage and styrofoam layer are contained in the second active heating
Chapter 3. General experimental features

Figure 3.1: Top view cross section of a typical multistage thermostat.
Chapter 3. General experimental features

stage of the thermostat, which is typically a copper cylinder with 3/8"-OD copper tubing soldered to the outside of it. Temperature regulated water is pumped through the copper tubing from tank of a water circulator [34] (we use distilled water to avoid growth of molds inside the circulator tank, hoses and tubing). The specified temperature control sensitivity of the circulator is ±0.02 K. The temperature of the water in the circulator tank was measured and found to be stable within ±0.01 K, however the water travels for a few meters at room temperature from the circulator to the thermostat and it is expected that the actual stability be within ±0.1 K. This constitutes the coarse stage of the thermal control and it is regulated at a temperature, \( T_{\text{coarse}} \), such that \( T_c - T_{\text{coarse}} \leq 1 \, K \).

The fine stage is the electrical heating applied to the inner cylinder. The principle on which the fine-tuned thermal control is based is the detection of the imbalance (or error) signal from a Wheatstone bridge. The electrical heating to the inner block is controlled by a negative feedback electronic system. A thermistor embedded in the metal senses its temperature and represents one arm of a resistive DC Wheatstone bridge, as illustrated in Fig. 3.2. The other three arms are two identical standard resistors (their typical tolerance is 2% and their temperature coefficient between 50 and 200 ppm/°C) and a decade resistance box (Time Electronics Ltd., model 1051, with a temperature coefficient of 100 pm/°C). The required temperature is set by a certain value of the decade box resistance. If this resistance is different from the thermistor’s value, i.e., the inner stage temperature, the Wheatstone bridge is imbalanced. The error signal from the bridge is fed into and amplified by a Hewlett-Packard nullmeter (model HP 419), whose output is input into an operational power supply (KEPCO model OPS 40–0.5 B) that controls the current applied to the heating wire or the heating foils of the inner block, which is, in turn, in thermal contact with the sample holder.

The whole thermostat is enclosed in a plywood box, lined with a 25-mm layer of high density styrofoam, of the same kind used between the outer and inner stages. During experimental measurements the only apertures of the box to the experiment room are through two small holes for the water hoses to and from the water circulator. Lastly, care has been taken not to have the experiment room temperature fluctuate too much, by keeping the door shut and the light off at all times.

The measured temperature of the inner stage of this two-stage thermostat is stable within 100 μK for several hours. A precise monitor of the temper-
Figure 3.2: Temperature control and monitor stages of the apparatus used for experiments on both pure fluids and binary liquids.
ature was carried out for the binary liquid experiment thermostat and the performance checks are reported in Chapter 4.

Windows in the plywood box, metal cylinders and styrofoam allow an expanded He–Ne laser beam to traverse the sample.

3.2.2 Temperature measurement

High precision and accuracy in the measurement of the temperature are of paramount importance in these experiments. Two types of thermometers were used: a Hewlett-Packard quartz thermometer and several semiconductor thermistors [35, 36].

Similarly to the circuit used for the control of the current to the electric heater in the thermostat (section 3.2.1), each thermistor for the temperature monitor is embedded in the inner block metal and is one of the arms of a DC Wheatstone bridge, the remaining arms being again two identical standard resistors and a decade resistor box. The bridge signal is the input of another Hewlett-Packard nullmeter and amplifier whose output is monitored on the meter’s front panel and on a chart recorder. The value of the decade resistor that nulls the bridge output voltage corresponds to the value of the thermistor resistance and, through the thermistor calibration equation, to the inner stage and sample temperature. The “temperature monitor” part of the circuitry is shown in Fig. 3.2.

The quartz thermometer probe is considerably bulkier than any of the thermistors used and does not provide as accurate a temperature measurement, especially for the data very close to the critical temperature. Some checks on the quartz thermometer reliability were done with the binary liquid experiment thermostat and are reported in Chapter 4. Therefore, once they are calibrated (see section 3.2.3), for which procedure the quartz thermometer is indeed very useful, only the thermistors are employed for reliable temperature measurements.

To ensure optimum thermal coupling between the inner block metal and the thermistors, the latter are glued, with high thermal conductivity epoxy [37] into copper bolts, which are, in turn, screwed into the metal. A further point in favour of the thermistors, is that the time they take to respond to the smallest temperature change occurring during the experiment is much shorter than that taken by the quartz thermometer.
3.2.3 Thermometer calibration

For maximum accuracy in our measurements both the quartz thermometer probes and the thermistors were calibrated at the triple point of pure water [38, 39, 40]. This is one of the fundamental defining fixed points of the International Practical Temperature Scale (IPTS–68) and its temperature has been assigned the value of +0.01 °C on the IPTS and of 273.16 K on the Kelvin thermodynamic scale.

Moreover, since the thermistors need to be calibrated at two temperatures, at least, in order to have a calibration equation for them, the quartz thermometer and a thermostat were used to calibrate the thermistors at different temperatures. More details on the calibration procedure are given in the binary liquid mixture experiment chapter (Chapter 4), where the newly built thermostat is described in depth.

3.3 Optical investigation techniques

The critical region of both pure fluids and binary liquid mixtures can be studied by observation of the optical properties of the fluid under investigation [9, 41, 42, 30, 43, 44, 45, 46, 47].

The order parameter for pure fluids is typically the mass density difference between the liquid and vapour phases of the fluids\(^1\), \(\Delta \rho = \rho_L - \rho_V\). We can therefore measure the index of refraction, \(n\), and then relate it to the density, \(\rho\), through the Lorentz–Lorenz (later referred to as LL) relation [10]:

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

(3.1)

Similarly, one of the accepted order parameters in binary liquid mixture studies is the concentration difference, \(\Delta X = X_L - X_U\), of one of the species between the two phases, lower (L) and upper (U). Thus, by measuring the index of refraction difference, \(\Delta n\), between the liquids, we have a measurement of \(\Delta X\) by the direct proportionality relation:

\[
\Delta n \propto \Delta X
\]  

(3.2)

\(^1\)Occasionally the molar volume difference is used as order parameter, but it produces a much less symmetric coexistence curve than the density difference, therefore the latter is preferred when the data is analysed for comparison with the Ising (lattice gas) model results [48].
derived from the LL relation applied to the two liquids under the assumption that index of refraction and density show no anomalies at the critical point and under the hypothesis of additivity of volumes upon mixing (appendix C has a derivation of relation (3.2)).

It should be emphasized that the degree of approximation of relation (3.2) could lead to systematic errors in the measurements of the coexistence curve of binary fluids. This issue is discussed more in depth in the chapter describing the binary liquid experiment (Chapter 4).

This section describes the three optical techniques used in the reported experiments. The prism cell technique is used for measuring both the LL coefficient, \( \mathcal{L} \), and the coexistence curve of pure fluids. The focal plane technique also is employed to measure the coexistence curve of pure fluids (but closer to the critical temperature than possible with the prism cell) as well as of binary mixtures. The image plane technique can be used to study the index of refraction, and hence the density and concentration profiles, both above and below the critical temperature.

### 3.3.1 Prism cell technique

One needs to determine the LL coefficient, \( \mathcal{L} \), appearing in relation (3.1) for any substance whose critical region is to be studied by means of its index of refraction behaviour in that region. The density, \( \rho \), and the refractive index, \( n \), of the fluid have to be measured independently of each other and used in equation (3.1) to obtain an experimental determination of \( \mathcal{L} \). This is realized by the prism cell experiment [49].

The fluid is introduced into a hollow, aluminum, prism–shaped cell, which is shown in the drawing in Fig. 3.3 and used in the setup shown schematically in Fig. 3.4. The cell walls (perpendicular to the plane of the page) are two sapphire windows that form an angle of about 20°. The cell is filled with the fluid to be studied and a spatial–filtered, expanded and collimated He–Ne laser beam passing through the cell emerges from it, bent through a certain angle, \( \theta \), with respect to the straight beam coming from the laser. The beam emerging from the cell is directed into an autocollimating telescope (Davidson model D275) by means of a movable mirror. The mirror is adjusted by a micrometer screw to bring the laser spot coming from each fluid phase to the crosshairs of the telescope eyepiece. There is then a one–to–one relation between the micrometer reading and the angle of refraction of the 632.8 nm He–Ne laser line through either the liquid or vapour phase. The microme-
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Figure 3.3: Illustration of the prism cell.

Figure 3.4: Schematics of the prism cell experimental principle and apparatus (not to scale).
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Figure 3.5: Data used to obtain a calibration of the micrometer scale on the movable mirror for the prism cell experiment.

To calibrate the adjustable mirror micrometer and hence be able to obtain an angle from its readings, a 50-lines/inch diffraction grating is inserted in the thermostat in place of the cell. Then, the position of the diffraction pattern maxima is read from the micrometer scale and plotted against the diffraction maxima angle calculated from the relation:

\[ d \sin \theta = N \lambda \]  \hspace{1cm} (3.3)

where \( d = 0.508 \pm 0.002 \text{ mm (1/50 inch)}, \lambda = 632.8 \text{ nm}, \text{ and } N = \pm 1, \pm 2, \ldots, \pm N_{\text{max}}, N_{\text{max}} \text{ being the highest visible maximum on either side of the central maximum}. \) A calibration equation is then found that relates the refractive angle \( \theta \) to the micrometer readings. As Fig. 3.5 shows, this relation is linear.

By measuring \( \theta \) and using Snell’s law applied to our particular optical system we are able to measure the refractive index, \( n_{\text{fluid}} \), as a function of the angle, \( \theta \),

\[ n_{\text{fluid}} = n_{\text{fluid}}(\theta) \]  \hspace{1cm} (3.4)
Figure 3.6: Effect of wedge angles of sapphire windows on the measurement of the refracted angle (not to scale).

at that particular density. The sapphire window surfaces are not perfectly parallel, but slightly wedged, which affects the determination of $n_{\text{fluid}}$ through equation (3.4), as illustrated in Fig. 3.6.

In the ideal case of perfectly parallel surfaces, equation (3.4) is explicitly:

$$n_{\text{fluid}} = n_{\text{air}} \frac{\sin(\alpha + \theta)}{\sin \alpha}$$  \hspace{1cm} (3.5)

where $\alpha$ is the prism angle measured at $(20.6885 \pm 0.0167)^\circ$. If the wedge angles, $\alpha_s$ and $\alpha_t$, of the straight and tilted window, respectively, are considered, then equation (3.5) becomes, to first order in $\alpha_s$ and $\alpha_t$:

$$n_{\text{fluid}} = \frac{n_a}{\sin \alpha} \left\{ \sin(\alpha + \theta) \pm \right.$$  
$$\left. \pm \alpha_s \left[ \cos(\alpha + \theta) - \frac{n_s}{n_a} \cos \alpha \right] \pm \right.$$  
$$\left. \pm \alpha_t \left[ \cos(\alpha + \theta) + \sqrt{\left( \frac{n_s}{n_a} \right)^2 - \sin^2(\alpha + \theta)} \right] \right\}$$  \hspace{1cm} (3.6)

where $\alpha_s = (0.0042 \pm 0.0035)^\circ$ and $\alpha_t = (0.0127 \pm 0.0035)^\circ$, $n_a = 1.000262194$ is the refractive index of air [50], and $n_s = 1.7660026$ the index of refraction of sapphire [51].

Then the density is decreased by bleeding some fluid from the cell and the measurement is repeated until the cell is empty.
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To measure the density of the fluid, \( \rho \), the volume, \( V \), and the mass, \( m_{\text{cell}} \), of the evacuated cell are measured first. The volume is measured by filling the cell with pure water, whose density can be precisely found out, and by weighing the water-filled cell. If the mass of the empty cell is known, the volume of the cell can be determined. The distortion of the volume of the cell with pressure is negligible for the pressures used in these experiments. The thermal expansion of the cell aluminum body in the range of temperatures of these measurements would cause a volume variation of 0.2 \%. The variation in the Lorentz-Lorenz data caused by such variation of the cell volume is less than the overall scatter in the data. The measured volume of the prism cell is \((12.066 \pm 0.003) \text{ cc}\).

Then, at each filling (or rather, emptying) stage, the cell-plus-fluid system is weighed on a precision chemical balance (sensitivity of 0.0003 g), thereby yielding the quantity:

\[
m = m_{\text{cell}} + m_{\text{fluid}} = m_{\text{cell}} + \rho_{\text{fluid}} V
\]  

and hence the density of the fluid is given by:

\[
\rho_{\text{fluid}} = \frac{m - m_{\text{cell}}}{V} \tag{3.8}
\]

The values of \( n_{\text{fluid}} \) and \( \rho_{\text{fluid}} \) from Equations (3.6) and (3.8) are used in relation (3.1) to yield values of the Lorentz-Lorenz function, \( \mathcal{L} \). This is usually plotted against the density \( \rho \), to study its behaviour in the range of densities expected to be investigated, for example, for the coexistence curve of the fluid.

To measure the coexistence curve with the prism cell technique, the sample in the cell is prepared at the critical density and the angles of refraction from the liquid and vapour phases are measured to yield the refractive index of the two phases at different temperatures. From the LL relation, \( \rho_V \) and \( \rho_L \) are then obtained, from which, in turn, the order parameter, \( \Delta \rho = \rho_L - \rho_V \), and the diameter, \( \rho_d = (\rho_L + \rho_V)/2 \), are determined.

3.3.2 Focal plane technique

The focal plane technique is one of the fundamental experimental techniques used by our laboratory to investigate the coexistence curve of either pure fluids or binary mixtures. It allows data to be taken closer to the critical temperature than the prism cell technique does.
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Figure 3.7: Illustration of the behaviour of the refractive index of a binary mixture as a function of cell height at $T < T_c$ (a), at $T_c$ (b), and $T > T_c$. Below $T_c$, $z_0$ marks the position of the meniscus between the two phases.
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This experimental method is based on the detection of variations that occur in the index of refraction profile of the liquid contained in a cell as its temperature varies. As indicated in Fig. 3.7a, when the temperature of the system is below \( T_c \), there is a step discontinuity in the index of refraction, as a function of height in the cell, at the meniscus between the two phases (either the vapour and liquid phases of a pure fluid or the two liquids of a binary mixture). As the temperature is raised above the critical temperature, a fraction of one phase transforms or diffuses into the other and \textit{vice versa}. As a result, the profile is no longer discontinuous, taking instead a sigmoidal shape, as illustrated in Fig. 3.7b, and 3.7c\(^2\).

Once again, the refractive index profile of the sample is probed using a coherent beam of light from a 632.8-nm He–Ne laser, space–filtered, expanded and collimated to a diameter of about 25 mm. Fig. 3.10 shows the configuration of the optical bench for both the focal plane and the image plane experiments. Light passing through the cell is bent due to the gradient of the refractive index \( n(z) \) in the sample by an angle \( \theta \) given by:

\[
\frac{d\theta}{dy} = - \frac{1}{n} \frac{dn}{dz}
\]

under our typical experimental conditions equation (3.9) can be integrated to yield the total deflection angle inside the cell

\[
\theta_i = - L \frac{dn}{n dz}
\]

where \( L \) is the cell thickness (appendix D explains briefly how this can happen through the application of Snell's law). After exiting the cell, the beam is again deflected according to Snell's law, so that, if \( \theta \) is the the angle of the beam leaving the cell with respect to the original direction

\[
\theta = - L \frac{dn}{n_{air} dz}
\]

Equation (3.11) gives the total bending angle of the light passing through a cell of thickness \( L \) at a height \( z \), where the refractive index profile has a gradient \( dn/dz \). Referring to Fig. 3.8, two rays encountering the sigmoidal

\(^2\)The refractive index profile at temperatures \( T \geq T_c \) is described by the “error function” \( erf(z) = \int_0^z \exp(-\zeta^2) d\zeta \), under the assumption that the profile is describable by an odd function of height with respect to the middle of the cell, that the profile is a step function before diffusion starts to occur, and that the system is unbounded.
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Figure 3.8: Formation of Fraunhofer diffraction pattern due to a non-uniform refractive index profile.

Figure 3.9: Geometrical illustration of the phase difference and the formation of the Fraunhofer diffraction pattern.
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profile at points with equal absolute value of the curvature (e.g., (+) and (−) in Fig. 3.8) are bent through equal angles. Those rays are then focused to the same point in the focal plane of a lens [7, 8, 9]. The difference in optical path length between ray (+) and ray (−) is given by,

$$\psi = \frac{2\pi}{\lambda} [L(n_- - n_+ + (z_- - z_+)n_{air}\sin\theta)]$$  \hspace{1cm} (3.12)

with $n_-$ and $n_+$ representing the index of refraction of the fluid at heights $z_-$ and $z_+$ in the sample, respectively. Combining equation (3.12) with (3.11), the optical path difference between the rays upon arriving at the focal plane of the lens can be re-written as

$$\psi = \frac{2\pi}{\lambda} \left[ L(n_- - n_+) - L(z_- - z_+) \left. \frac{dn}{dz} \right|_{\pm} \right]$$  \hspace{1cm} (3.13)

A Fraunhofer diffraction pattern\(^3\) then appears at the focal plane, with minima occurring at angles where $\psi$ is an odd multiple of $\pi$.

A geometrical description of the formation of the diffraction pattern is shown in Fig. 3.9, where $Ln(z)$ and $-L(\frac{dn}{dz})$ are plotted versus $z$. The quantity $L(n_- - n_+)$ corresponds to the area under the curve on the right hand side, between $z_+$ and $z_-$, while the quantity

$$L(z_- - z_+) \left. \frac{dn}{dz} \right|_{\pm}$$  \hspace{1cm} (3.14)

is equal to the area of the rectangle bounded by $z_+$ and $z_-$ and the lines $Ldn/dz = 0$ and $Ldn/dz = Ldn/dz|_{\pm}$. The difference between these two areas is equal to $(\lambda/2\pi)\psi$ and it is crosshatched in Fig. 3.9. Because the angle of refraction is proportional to $-L(\frac{dn}{dz})$, the angles corresponding to the minima of the Fraunhofer diffraction pattern can have the following explanation. Each time the crosshatched area in Fig. 3.9 increases by $2\pi$ another minimum is formed.

A camera fitted with a clock motor to allow continuous film transport is placed so that the plane of the film coincides with the focal plane of the lens.

The diffraction pattern is recorded on photographic film. The number of fringes, $N$, detected from the diffraction pattern at each run, that is, at

\(^3\)More accurately the diffraction fringes one observes in this setup are known as Gouy fringes, after the first observer of the formation of Fraunhofer fringes caused by an index of refraction gradient [52]
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Figure 3.10: Schematic diagram of the experimental optical setup.

Each temperature, is directly proportional to the difference in refractive index between the two phases, $\Delta n = n_1 - n_2$.

Therefore, a $\Delta n$–versus–temperature graph represents the coexistence curve of either the pure fluid or the binary mixture and it is suitable for an indirect measurement of the exponent $\beta$.

3.3.3 Image plane technique

In this technique the plane of the recording photographic film is placed on the image plane of the Fraunhofer lens also used in the focal plane technique, and the whole refractive index profile of the sample is imaged on the film. This is achieved by placing the thermostat and sample in one of the beams of a Mach–Zehnder interferometer (see, for example, [12]), the “sample beam”, while the other beam, the “reference beam”, travels through air. The situation is depicted in Fig. 3.10.
A He–Ne laser beam, approximately 25–mm in diameter, is prepared as in the focal plane technique and split by the first beam splitter, B₁, into the sample and reference beams. As shown in Fig. 3.7, the refractive index varies considerably with the cell height, when the temperature of the sample is in the neighbourhood of the critical temperature. The bottom part of the sample has a larger optical thickness, hence the light of the sample beam that traverses the bottom part of the sample is retarded more than the light passing through the top part.

Therefore, when the waves at P and P' are recombined at the beam splitter B₂ and imaged by means of the lens, horizontal interference fringes are observed at the image plane of the lens.

The index of refraction as a function of height is mapped this way. This technique is also very useful to study the sample equilibration time at a particular temperature.
Chapter 4

Binary liquid experiment

4.1 Introduction

This chapter describes the first of the two main experiments on which this thesis is based. Some of the data reported were taken with a thermostat that was built *ex novo* for the experiment. The details of critical phenomena in binary liquid mixtures are introduced in section 4.2, with the motivation for this experiment in section 4.3. Some details on the construction of the thermostat and preparation of the samples are given in section 4.4. Finally, the long section 4.5 describes the data that were taken, how they were analyzed, the results they produced and some considerations on the potential systematic errors encountered.

For the same reasons anticipated in the previous chapter’s introduction, both metric and imperial system units are used for the apparatus dimensions.

4.2 Criticality in binary liquids and order parameter

The liquid–liquid, or *binary liquid*, critical point is an example of critical behaviour in fluids that has been and still is studied both theoretically and experimentally [27, 53, 54, 55].

Referring to Fig. 4.1, a binary liquid is typically composed by two chemical compounds in their liquid state and the critical phenomenon in question is their mutual miscibility as the temperature is varied through the critical,
or *consolute*, temperature, $T_c$.

In the most common instance, binary fluids exist as two immiscible phases below $T_c$, while above such temperature the two liquids become completely miscible and only a single liquid phase exists. When the liquids are in the two phase region, a well-defined meniscus forms and is easily visible between the heavier liquid at the bottom of the sample cell and the lighter one floating on top of it. As the temperature is raised and brought above $T_c$, the meniscus becomes blurred until it eventually disappears leaving the two liquids completely mixed in one phase.

There do exist binary liquid systems which display an inverse behaviour, namely miscibility *below* the critical temperature and immiscibility above. They usually belong to the category of systems with two critical points, *lower* and *upper*, with the mixture having its two-phase region *between* the two critical temperatures. As depicted qualitatively in Fig. 4.2, these are called closed-loop systems, due to the aspect of their phase diagram [56]. The mixture studied in this thesis, however, is of the kind described in the text.

In the binary liquid experiment described in this thesis, the mixture $n$-heptane+nitrobenzene was studied [57], the former being lighter floats on the latter when the system is below its critical temperature of about 18.9°C.

If the two phases are called $U$ and $L$ as in Fig. 4.1, the order parameter of choice is usually the difference between the concentration of one of the
Figure 4.2: Illustrating a binary liquid mixture with two critical temperatures, $T_{c, upper}$ and $T_{c, lower}$. $\phi$ is the volume fraction of one of the species.

species, e.g., $n$-heptane, $\phi_H$, in phase $U$, and its concentration in phase $L$:

$$\Delta \phi_H = \phi_{H,U} - \phi_{H,L}$$ (4.1)

At this point the question arises: what kind of concentration is it best to choose as the order parameter? Mass fraction, volume fraction, mole fraction?

Although there does not seem to be a definite answer, the established trend is to consider the most appropriate order parameter the quantity that renders the coexistence curve more symmetric, to be able to compare experimental results with the lattice gas model predictions [48, 27].

Experience suggests that the volume fraction usually yields more symmetric coexistence curves. Moreover, the quantity that is usually measured in our binary liquid (and in the pure fluid for that matter) experiments is the index of refraction difference between the two phases, which turns out to be proportional to the volume concentration, as discussed below.

For these reasons, the volume fraction is the order parameter chosen in the binary liquid experiments reported in this thesis.
4.3 Motivation and expectations

The decision to measure the coexistence curve of a binary liquid mixture stems from the need to clarify earlier results on the critical exponent $\beta$ of binary mixtures from the early 1970s [58, 27].

It appears quite clearly from earlier literature [58, 27] that until the late 1970s or even early 1980s the typical accepted experimental values for the critical exponent $\beta$ describing the order parameter dependence on temperature in the case of binary mixtures was somewhat larger than the expected theoretical value for that exponent. In a compilation of experimental data on binary liquid mixtures, Stein and Allen [58] found that the data of the systems they analyzed were all consistent with the critical exponent $\beta = 0.34 \pm 0.01$.

The trend of other later experimental studies of coexistence curves of binary liquid mixtures seemed to be confirming the renormalization group theoretical result that the critical exponent $\beta$ should range between $0.325 < \beta < 0.327$ [27, 14, 24].

Following the relative uncertainty of the experimental results obtained on binary liquids, it was thought necessary to investigate this discrepancy further.

The optical methods employed by this laboratory are particularly suitable for the study of the critical region of both pure fluids [59, 60] and binary mixtures [7, 56], but they did not seem to have been used to their potential yet in previous studies (and there will certainly be room for improvement after the present work).

It seemed therefore fit to perform a study of the coexistence curve of the H+N binary liquid mixture with an improved thermal control system and reduced errors in the measurements so as to obtain a more precise value of the critical exponent $\beta$.

One would expect that, once re-measured, the value of $\beta$ would have a better-than-average probability of conforming to analogous "modern" measurements and therefore with the most accredited theoretical results. Surprisingly, as described below, this was not the case.
4.4 Experimental details

4.4.1 Thermostat

It is worthwhile distinguishing the thermostat employed for the more accurate data of this thesis from the typical thermostats used in the past for studies of critical phenomena on binary mixtures. Although it was built on the same principles of other thermostats—as described in the 'General Experimental Observations' chapter—its design has some improved features over older designs, which gives us confidence that a higher degree of accuracy is achieved in the measurements taken with it.

The main thermostat is made of three nested cylinders (Fig. 4.3): the cell holder, the electrical heating stage (the inner cylinder), and the water jacket (the outer cylinder).

We have chosen a cylindrical shape for the whole temperature control...
apparatus in order to achieve a more uniform heating of the sample all around. This is also an improvement on earlier thermostats, which had a parallelepipedal outer stage with cylindrical inner stage. In most cases, our sample cells have an elongated vertical shape, as can be observed in the picture of the sample cells in Appendix F.

The cell holder

The holder is a 160-mm tall copper cylinder with a 65 mm base diameter and it is split into two halves along its axis. Inside each half are milled out pockets to accommodate the sample cells of various shapes and sizes (see pictures in Appendix F) and also windows through which the laser beam used in our interferometer passes.

Special care was put into milling the faces of the two halves, since it is very important that the thermal contact between them be as good as possible, once again in an effort to achieve the most uniform heat distribution around the sample. The two halves are held together by six 1/4–20 stainless steel screws and the two face surfaces are coated with a thin layer of Thermal Compound (Thermal Compound, part no. 120-8, Wakefield Engineering Inc.).

Inner cylinder (electrical heating stage)

Next in the order of cylinders is the electrical heating stage, also referred to as inner cylinder. The purpose of this stage is to provide the fine-tuned temperature regulation of the thermostat to the sample.

The main body of the inner cylinder is a ‘monolith’ made from an approximately 230-mm long section of 4”-diameter copper rod. The cell holder fits snugly inside a hole machined along the axis of the inner cylinder, which also has windows milled out of its wall for the laser beam to pass.

The electrical heating of this stage is achieved by means of heating foils wrapped around the main body of the cylinder [32]. Current is supplied to the heating foils from the electronics in a way that is described in the ‘Thermal control’ section of the previous chapter.

Another component of the inner cylinder is its cap, also made of copper. Its purpose is to allow to completely enclose the cell holder inside the inner cylinder. In working conditions, the cell holder is contained in the inner
cylinder and it is surrounded by the same thickness of material both at the cylinder wall and at its ends.

The temperature is measured by both a quartz thermometer and a set of thermistors. Of the latter there are two in the inner cylinder cap and three in the bottom of the inner cylinder (one for the control circuit and two as temperature monitors). To ensure the temperature reading is accurate, the thermistors are glued into copper bolts, with high thermal conductivity epoxy [37], and the bolts are screwed into either the inner cylinder cap or the bottom of the inner cylinder.

**Outer cylinder (water jacket cylinder)**

The water-jacket cylinder is the first heating and thermal regulation stage and it will be referred to as the *outer cylinder*. It has a diameter of 190 mm and a height of 285 mm. The latter two dimensions are dictated by the need to minimize the effect of the temperature oscillations of the outer cylinder on the inner cylinder. In Appendix A, I have described how such dimensions of the outer cylinder are arrived at based on the characteristics of the water circulators and on the physical properties of the materials used. The outer cylinder is a rolled and welded 1/8"-thick piece of copper plate with two 1/2"-thick copper flanges soldered on ends. A lid, also 1/8"-thick, is screwed to the flanges. The water jacket is a 3/8" OD copper tubing soldered onto both the cylinder external surface and the lids. The third figure in Appendix E illustrates a side view of the external cylinder and the photographs in Appendix F show the final product. Windows are cut out of the wall of this cylinder in correspondence of the windows of the other cylinders.

As already mentioned, the entire unit, consisting of cell holder, inner cylinder, and outer cylinder is enclosed in a plywood box, which is thermally insulated from the room temperature by a styrofoam lining. The detailed technical drawings of the thermostat are reported in Appendix E.

### 4.4.2 Temperature uniformity

A test was performed to ensure that the possible vertical temperature gradient along the heater block was within tolerable margins. The heater block has two sets of heating foils, as illustrated in Fig. 4.4: one set is wrapped around the cap of the heater block only, $H_{\text{cap}}$ in Fig. 4.4, while the other,
$H_{body}$, envelopes the body of the block, providing a more symmetric distribution of heat to the cylinder than the cap heaters. The two sets of heaters can be connected in series or used independently, each one as the only source of heat to the block.

For the gradient test, heat was supplied to the block by providing current only to the cap heaters, thereby recreating a heating condition most prone to producing a large temperature gradient. Then, the temperature was measured with 4 different thermistors both at the top and at the bottom of the block. One of the thermistors measured consistently a much larger temperature difference between top and bottom than the other three and was not considered very reliable. It was later noticed that the decade resistance box associated with it did not give reproducible readings, possibly due to dirty contacts. From the remaining three thermistors, the worst temperature gradient measured was $2.4 \times 10^{-2}$ K/m. In the final arrangements used to take our measurements, heat was delivered to the block only via the body heaters, $H_{body}$, so that the heating power was more uniformly distributed on the cylinder wall and, in turn, on the sample cell. It seems reasonable to expect that thermal gradients in these conditions should be much smaller, all the other parameters being the same.
Chapter 4. Binary liquid experiment

4.4.3 Temperature stability

The temperature stability of the new thermostat was checked simply by monitoring the temperature of the heater block, as measured by the thermistors over a time span of up to two weeks. The result is reported in Fig. 4.5.

While the room temperature increased by about 1.3°C, the temperature measured by the thermistor remained stable within 0.5 mK. During the same two-week time span, the quartz thermometer measurements show an increase by about 4 mK. This is mainly due to the following factors. On the one hand, the thermometer probe itself is positioned in a well drilled through the centre of the heater block cap and partially into the top of the cell holder, it is therefore closer to the ambient than the thermistors are. Given the physical size of the probe, a stainless steel cylinder 25-mm long and 11 mm in diameter, it would have required substantial design modifications to place the probe elsewhere on the heater block. On the other hand, both due to its position and to its construction, the quartz thermometer probe has a worse thermal coupling to the block than the thermistors and for the same reason it represents a heat leak from the inner to the outer stage of the thermostat. Thirdly, the quartz thermometer electronics box, located in the
Figure 4.6: Temperature stability test with the quartz thermometer. The black diamonds represent the room temperature (left hand scale), the white ones the temperature measured by the quartz thermometer ($T_{QT}$).

experiment room, is subject to room temperature variations, which could lead to temperature misreadings. The link between the room temperature variation and the quartz thermometer readings appears clearly from the plot in Fig. 4.6. Some photographs of the thermostat and its various parts are reported in Appendix F.

4.4.4 Samples

As each part of the apparatus has to be assembled with great care to ensure maximum accuracy of the results, the preparation of the sample deserves particular attention. The two liquids must be present in the sample cell in the right proportions so that the mixture is at its critical concentration, if the critical region is to be studied accurately. As illustrated in Fig. 4.7, if the system is at a concentration $\phi_I$, different from the critical concentration, $\phi_c$, then, as the temperature is raised, the amount of one liquid, say the lower one, will decrease while the other increases, until at the coexistence curve, only one liquid will be present. In practical terms this implies that the meniscus between the two liquids will, in this case, travel to the bottom (to the top if we had started from $\phi_H$ in the diagram in Fig. 4.7) of the cell and we will lose track of it before the system reaches the consolute point.
Figure 4.7: A qualitative diagram of the coexistence curve of a binary liquid mixture. $\phi$ is the concentration (volume fraction) of one of the liquids.

For example, if the composition of the mixture is in error by about 2%, at best it will not be possible to get any closer to the critical temperature than a few mK, as shown in the graph of Fig. 4.8.

The liquids were purchased from Fisher Scientific with stated purity of 99% for nitrobenzene and 95% for $n$-heptane. They were distilled neat (the former under reduced pressure) and brought to a purity of better than 99.9%, as estimated by gas chromatography as well as NMR. A mixture was prepared in the proportions of 49.6 wt% $n$-heptane and 50.4 wt% nitrobenzene, as suggested by earlier studies [61] and the sample was prepared following a method devised and used by this laboratory in the past, with very good results [7].

The liquids in the above proportions are introduced in a pyrex glass manifold to which the sample quartz cell and a pyrex bulb are attached (Fig. 4.9). At first, the fluids are contained in the bulb and the manifold is connected to a vacuum pump. By repeatedly freezing, pumping, and thawing the fluids, the air is removed from the manifold and, eventually, the latter is flamed-
Chapter 4. Binary liquid experiment

Figure 4.8: The height, in the cell, of the meniscus between the two liquids as a function of temperature, for various concentration deviations from the critical concentration. Height "0" indicates the middle of the cell.

Figure 4.9: Illustration of the glass manifold used to prepare the binary liquid samples.
sealed off from the vacuum pump system. A drawback of the air–evacuation process is that it alters, however slightly, the composition of the mixture. Therefore, after this stage, the manifold is brought to a temperature $T > T_c$, at which the sample only has one phase, and part of the sample is transferred to the quartz cell. The whole manifold is then immersed in a bath at a temperature below, but very close to, $T_c$, and the formation of the meniscus separating the two phases is monitored by visual observation. Knowing the critical composition of the mixture in terms of weight fraction, the critical volume fraction is found (under the assumption that the mixing volume is negligible—see section 4.5.2) and therefore the expected position of the meniscus at the critical volume fraction is marked on the sample cell to aid visual observation. If it is observed that the meniscus does not form at the “critical mark”, part of the top, i.e., lighter, component is added or removed to bring the meniscus down or up, respectively. When we are satisfied that we have a critically filled sample, we flame-seal it off from the manifold. The samples are therefore prepared at the vapour pressure of the mixture.

Several different sample cells were prepared from the same manifold. In order to observe both the region far from the critical point and the near–critical region with relative ease, the sample cells were chosen to have light paths of 1, 2, 5, and 10 mm. (The tolerances of the light paths are 0.01 mm.) More precisely, from the description of the focal and image plane techniques, the number of fringes recorded at each temperature decreases as the critical temperature is approached, whereas the error made in counting the fringes is practically constant. Hence, in an effort to reduce the relative error on the fringe count on the data near the critical region, which are usually more significant, samples with longer light paths (5 and 10 mm) are used in that region. As data are taken farther and farther from critical, the number of fringes at each datum increases greatly for the same light path ($\simeq 300$ at $T_c - T \simeq 0.1$ K with the 10 mm cell). In the temperature region farther from $T_c$ the 2 and 1–mm light path sample cells are employed.

4.5 Results

The data for the study of the coexistence curve of the mixture $n$-heptane+nitrobenzene were taken over the course of several years with both the focal plane and the image plane techniques. While the former was used in the past to study other binary mixtures, the latter technique has been employed for
this sort of measurements for the first time. The image plane data were very useful in determining the importance of some potential sources of systematic errors.

4.5.1 Focal plane data for the order parameter

The collected coexistence curve data span 5 decades in terms of the reduced temperature $t$, from $t \approx 4 \times 10^{-7}$ to $t \approx 4 \times 10^{-2}$. From the consulted literature it would appear as though most experimenters do not extend their measurements as close to the critical temperature as in this work [30, 62, 53, 63, 64, 7, 41, 65, 29, 66].

Data taking in the binary mixture experiment is relatively slow, with the rate averaging at about one experimental point every two days. This is mostly due to the equilibration time required by the system to arrive at a steady concentration profile after a temperature change, especially for the data very close to the critical temperature. This point is treated in detail below in a separate subsection. The time line followed when taking data is shown in Fig. 4.10. The photograph is a typical set of fringes from a focal plane experimental run and it represents one experimental datum. The (not-to-scale) diagram in Fig. 4.10 indicates that the system is prepared at a temperature, $T_1$, below, but as close as possible to, $T_c$ and left there for several hours or days to allow it to reach equilibrium. The temperature is then increased to take the system above the critical temperature and let diffusion between the two species take place. As this happens, and as explained in Chapter 3, the Fraunhofer diffraction pattern generated by the He–Ne laser light interacting with the changing index of refraction profile is recorded on film, an example of which is in Fig. 4.10 [7]. The status of the system can be visually monitored to ensure that when the first, thicker fringe has been recorded on the film the datum has been taken and the temperature for the next one can be prepared. The system is then brought to a temperature, $T_2 < T_1$, and the procedure to take another point is repeated for as many data as are necessary to have a satisfactory coexistence curve. In the case of the mixture $n$-heptane+nitrobenzene, the data were taken so as to span the accessible range of temperatures of the mixture. The temperature range for this system is around 12.5°C and it is given by the difference between the critical consolute temperature and the freezing temperature of the species $n$-heptane.
Figure 4.10: Top: photograph of a typical focal plane film representing a datum taken at a particular temperature $T_1$, indicated in the bottom diagram. The number of fringes that can be counted from the top one down is proportional to the difference between the refractive indices of the two phases. Bottom: illustration of the time line followed during the datum shown above.
Figure 4.11: The coexistence curve for the binary mixture \( n \)-heptane+nitrobenzene plotted as the volume fraction \( \Delta \phi_H \) as a function of the reduced temperature (with the axes swapped as it is often done to plot coexistence curves). The inset is an enlargement of the critical region of the curve.

The coexistence curve as it is revealed by the data from six data sets is shown in Fig. 4.11. Naturally, it is only half of the whole coexistence curve, since it is a direct measure of the order parameter, \( \Delta \phi_H \), namely the difference in the volume fraction of one of the species (\( n \)-heptane) between the upper and lower phases. It is plotted as a function of the reduced temperature \( t \), instead of the absolute temperature \( T \), in order to be able to report data from several sets with slightly different critical temperatures. It will be discussed below how the different critical temperature “problem” arises.

It should be recalled from Chapter 2 that, in the vicinity of the critical temperature, the coexistence curve is supposed to be described by the simple scaling law:

\[
\Delta \phi = B_0 t^\beta
\]  

(4.2)

with \( t = (T_c - T)/T_c \). The ‘vicinity’ to \( T_c \), or \( t = 0 \)—the so-called asymptotic region—has generally been found to be the region with \( t < 10^{-2} \) for binary liquid mixtures [27]. Translating this to the particular case of \( n \)-
heptane+nitrobenzene, the region where the simple scaling law should be valid extends for about 3 degrees below $T_c$. It should be emphasized, however, that the asymptotic region is not known a priori, nor do we have a theoretical estimate of it. Moreover, in certain circumstances experiments on binary mixtures have indicated that the actual asymptotic region extends only to $t \approx 10^{-3}$ from the critical temperature [53, 67, 29]. In view of such findings, in the analysis of the present data a narrower asymptotic region $0 < t < 10^{-3}$ was chosen to find the critical temperature and the order parameter critical exponent $\beta$. Beyond the asymptotic region, corrections to scaling come into play:

$$\Delta \phi = B_0 t^\beta \left( 1 + B_1 t^{\Delta} + B_2 t^{2\Delta} + \cdots \right)$$  \hspace{1cm} (4.3)

Because it is physically inaccessible, the critical temperature $T_c$ must be inferred from the measured coexistence curve data. A first estimate of $T_c$ is gathered by plotting the raw data as $(\Delta \phi)^{1/\beta}$ versus $T$ in the (expected) asymptotic temperature range, where such a plot is linear. A linear fit to the data intercepts the horizontal axis at (a first estimate of) $T_c$. This value of the critical temperature is taken as an initial value for a nonlinear least square fit of relation (4.2) to the coexistence curve data. In the fit, $\beta$, $B_0$, and $T_c$ are used as free parameters. $T_c$ is only allowed to vary within the reasonable range suggested by a careful examination of the coexistence curve near the critical point. The best values of the parameters found by the nonlinear least square fit are given in table 4.1. As is apparent from the table, the fit obtained with $\beta$ set at $\beta = 0.326$ (the theoretical value) does not seem to represent the data as well as the one where $\beta$ is unconstrained. Moreover, the best value of the exponent is found to be higher than expected at $\beta = 0.367 \pm 0.002$. 

<table>
<thead>
<tr>
<th>Fit</th>
<th>Region</th>
<th>$B_0$</th>
<th>$\beta$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$t \lesssim 10^{-3}$</td>
<td>$1.34 \pm 0.01$</td>
<td>$(0.326)$</td>
<td>9.8</td>
</tr>
<tr>
<td>B</td>
<td>$t \lesssim 10^{-3}$</td>
<td>$1.91 \pm 0.04$</td>
<td>$0.367 \pm 0.002$</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Within each set of order parameter data the temperature was measured using the same thermistor, but different thermistors or other parts of the thermal control electronics were used in different sets. Moreover, as mentioned below in section 4.4.4, different samples were used to collect the body of data for this experiment.

Systematic experimental studies [4, 5] on the effect of water and acetone impurities in different binary liquid samples (methanol+cyclohexane) show that a percentage volume of water of about 0.1 in the mixture would alter the critical temperature by almost +4 K, while 0.5% of acetone gives an increase of about 2 K. No regular variation of the critical temperature with the different sample was found and the different absolute values measured are all within a fraction of a percent of one another. While it is reasonable to think that both water and acetone impurities are present in the samples (the glass manifolds are cleaned with both distilled water and acetone before making the samples as described in section 4.4.4), it is presumed that the amounts of those impurities do not differ much from one sample to the other.

For these reasons, the actual critical consolute temperature of n-heptane+nitrobenzene varied somewhat. While for each data set it can be determined to within less than 0.5 mK, its absolute value can only be given as \( T_c = 291.78 \text{ K} \pm 0.03\% (= 18.63\text{ C}) \).

Once a reasonably good estimate of \( T_c \) has been obtained, a log–log plot of the data in the full temperature range is useful to see if any correction-to-scaling terms would be needed, and whether they should be positive or negative, to interpret the data. Also, the slope of the data in the asymptotic region in the log–log plot corresponds to the critical exponent. A log–log plot for the data of Fig. 4.11 is reported in Fig. 4.12. The slightly decreasing slope at higher values of \( t \) indicates that some correction to the simple scaling law is needed and that it will have to have a negative coefficient. This can be seen by performing a nonlinear least square fit of the scaling law in relation (4.3) to the coexistence curve data in the whole range of temperature studied, by using the best values found in the asymptotic range for the critical temperature, \( T_c \), and the critical exponent, \( \beta \), and leaving the coefficient \( B_1 \) free, while the correction-to-scaling exponent \( \Delta \) is held fixed at its theoretical value of 0.54 [68, 69]. The line through the data in Fig. 4.11 corresponds to this fit and the parameters determined by the fit are reported in table 4.2, fit D.

A fit like C is useful in order to estimate how important correction terms would be in fitting the data. If the coefficient \( B'_0 \) and the exponent \( \beta \) of this
Figure 4.12: Log–log plot of the order parameter $\Delta \phi_H$ versus the reduced temperature $t$. The slope of the curve as $t$ tends to zero corresponds to the exponent $\beta$. A line with slope 0.326 is also drawn for comparison.

Table 4.2: Parameter values for a nonlinear least square best fit of $\Delta \phi = B_0't^{\beta}$, with $t' = (T - T_c)/T$ (fit C) and $\Delta \phi = B_0't^{\beta}(1 + B_1t^{\Delta} + B_2t^{2\Delta})$ (fits D, E, F) to the volume fraction data of Fig. 4.11. Quantities in brackets were held fixed during the fit.

<table>
<thead>
<tr>
<th>Fit</th>
<th>Region</th>
<th>$\beta$</th>
<th>$B'_0$, $B_0$</th>
<th>$B_1$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$t' \lesssim 10^{-3}$</td>
<td>$0.367 \pm 0.002$</td>
<td>$1.905 \pm 0.007$</td>
<td>$-0.96 \pm 0.03$</td>
<td>4.8</td>
</tr>
<tr>
<td>D</td>
<td>$t \lesssim 0.04$</td>
<td>$(0.367)$</td>
<td>$1.905 \pm 0.007$</td>
<td>$-0.96 \pm 0.03$</td>
<td>4.8</td>
</tr>
<tr>
<td>E</td>
<td>$t \lesssim 0.04$</td>
<td>$(0.326)$</td>
<td>$1.39 \pm 0.01$</td>
<td>$0.11 \pm 0.07$</td>
<td>18.4</td>
</tr>
<tr>
<td>F</td>
<td>$t \lesssim 0.04$</td>
<td>$0.361 \pm 0.002$</td>
<td>$1.82 \pm 0.03$</td>
<td>$-0.81 \pm 0.06$</td>
<td>4.3</td>
</tr>
</tbody>
</table>
fit were to differ appreciably from \( B_0 \) and \( \beta \) found through fit B, it would be plausible to suspect that correction terms would have to be considered. However, the values of the parameter found for fits B and C are the same within experimental error. It is evident from the best fit parameters of fits D, E, and F that the scaling law with correction terms works better on the data when \( \beta \) is the value found by the simple scaling law used in the asymptotic region (D) than when the theoretical value of \( \beta \) is imposed during the fit (E) or when the exponent is again treated as a free parameter in the fit (F).

A different way to perform the analysis of the data and arguably the ultimate verification of the importance of correction terms is achieved by plotting the data in a manner that separates the contribution of the corrections terms from the rest of the terms in the relation (4.3). The correction-term-sensitive form of equation (4.3) used is:

\[
\log\left(\frac{\Delta \phi_H}{t^\beta}\right) = \log B_0 + \log \left(1 + B_1 t^\Delta + \cdots\right)
\]

(4.4)

If no correction terms are needed to fit the data and the value of the critical exponent is 'correct', a plot of \( \log(\Delta \phi_H/t^\beta) \) versus \( \log t \), which I will refer to as sensitive plot, would distribute the data along a horizontal line. Departures from a zero-slope line would then indicate either an 'incorrect' value of \( \beta \) or the need of correction terms to fit the data (or both!). Fig. 4.13 is a sensitive plot of the coexistence data collected during the experiment with \( n \)-heptane+nitrobenzene, where the theoretical value of \( \beta = 0.326 \) was used. It is evident once again that a value of \( \beta \) larger than the theoretical value is necessary to 'flatten' the slope of the data. This type of graph can be used to perform a cross check on the values of the critical temperature \( T_c \) and \( \beta \) produced by a nonlinear least square fit to the raw coexistence data of Fig. 4.11. Starting from some 'good guesses' for \( T_c \) and \( \beta \), one can then vary each of them individually step-by-step until the data of the sensitive plot lies on a horizontal line. The critical temperature will only affect the data very close to \( t = 0 \), while changes in \( \beta \) will change the overall slope of the data. The values of the critical temperature and the critical exponent produced by the experiment will then be the values that make a zero-slope plot. Moreover, if after this stepwise analysis the data appear distributed along different slopes at different ranges of \( t \), this would be an indication that correction terms to the simple scaling law should be included in the fit.

The modern theory of critical phenomena being as widely accepted and successful as it is, it seemed worthwhile to try some fits to the data by using
Figure 4.13: Sensitive log–log plot, $\Delta \phi_H / t^\beta$ versus $t$, of the coexistence data on $n$-heptane+nitrobenzene. The value used for the critical exponent is $\beta = 0.326$. A sensitivity scale is also drawn in the graph to indicate the slope the data would preferentially take, were they plotted with the value of the exponent corresponding to the indicated slope. The size of the error bars is comparable to the data scatter.
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Table 4.3: Parameter values for a nonlinear least square best fit of \( \Delta \phi = B_0 t^\beta \left( 1 + B_1 t^\Delta + B_2 t^{2\Delta} \right) \) (fit G), \( \Delta \phi = B_0 t^\beta \left( 1 + B_1 t^\Delta + B_2 t^{1-\alpha} \right) \) (fit H), and \( \Delta \phi = B_0 t^\beta \left( 1 + B_1 t^\Delta + B_2' t^{2\beta} \right) \) (fit I) to the volume fraction data of Fig. 4.11. Quantities in brackets were held fixed during the fit.

<table>
<thead>
<tr>
<th>Fit</th>
<th>Region</th>
<th>( \beta )</th>
<th>( B_0 )</th>
<th>( B_1 )</th>
<th>( B_2, B_2', B_2'' )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>( t \leq 0.04 ) (0.326)</td>
<td>1.33 ± 0.01</td>
<td>1.5 ± 0.3</td>
<td>-7 ± 1</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>( t \leq 0.04 ) (0.326)</td>
<td>1.32 ± 0.01</td>
<td>2.3 ± 0.4</td>
<td>-6 ± 1</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>( t \leq 0.04 ) (0.326)</td>
<td>1.295 ± 0.015</td>
<td>7 ± 1</td>
<td>-9 ± 1</td>
<td>9.6</td>
<td></td>
</tr>
</tbody>
</table>

the theoretical value of \( \beta \) and adding two correction terms in the scaling law (relation (4.3)). It has been suggested that different exponents for the second correction term can be tried when analyzing coexistence data [70, 27, 66]. Further fits to our coexistence data were then tried with the second correction terms being: \( \cdots + B_2 t^{2\Delta} \), with \( \Delta = 0.54 \) as already mentioned, \( \cdots + B_2' t^{1-\alpha} \), where \( \alpha = 0.11 \) is the specific heat critical exponent, and \( \cdots + B_2'' t^{2\beta} \) with (supposedly) \( \beta = 0.326 \). The rationale behind keeping the choice of the second term open is based on the experimental difficulty of distinguishing between a correction exponent that is slightly larger (2\( \Delta \)) or smaller (1 - \( \alpha \) or 2\( \beta \)) than one. The results of these fits are reported in table 4.3.

A different binary liquid

Although the ability of this method to measure the coexistence curve of a binary liquid mixture has been accepted [7], it was necessary to re-verify that this unexpected result for the value of \( \beta \) was not caused by an inherent, but so-far undiscovered flaw of the method. To this end the coexistence curve of another mixture was measured to get an estimate of \( \beta \) from another system. Using exactly the same apparatus (thermostat and thermometers), the same experimental method (focal plane method–Chapter 3) and the same data analysis approach as described above, the coexistence curve of the binary mixture cyclohexane+aniline (later C+A) was measured. The results are shown in Fig. 4.14 and Fig. 4.15, the (half) coexistence curve and the correction sensitive plot, respectively. The measured value of order parameter critical exponent is \( \beta = 0.330 \pm 0.010 \). The available data for C+A are much
Figure 4.14: The coexistence curve for the binary mixture cyclohexane+aniline plotted as the volume fraction $\Delta n$ as a function of the absolute temperature.

Figure 4.15: Sensitive log–log plot, $\Delta n/t^\beta$ versus $t$, of the coexistence data on cyclohexane+aniline. The data is plotted using a critical exponent $\beta = 0.330$. The sensitivity scale drawn in the graph indicates the slope of the data with $\beta = 0.350$ would definitely show up in this type of graph. The size of the error bars is comparable to the data scatter.
less than those for H+N, hence the larger error estimate on $\beta_{C+A}$. In spite of this drawback, the data in the sensitive plot (Fig. 4.15) show quite clearly that the method can distinguish between $\beta = 0.330$ and $\beta = 0.350$.

To summarize this section of the data analysis, it is observed that the measured critical exponent for the order parameter of the binary liquid mixture $n$-heptane+nitrobenzene is $\beta = 0.367 \pm 0.006$. This value is higher than the theoretically predicted value of $\beta = 0.326 \pm 0.002$. The coexistence curve is well described by the scaling law of equation (4.3) with one correction terms, while adding extra correction term does not improve on the fits nor does it seem statistically justifiable.

Because of the unexpected result, despite the trust in the experimental method that has produced notable results in the past (see, for example, the papers in [7, 9, 71, 60, 72, 59, 73] to name a few), it is of paramount importance to consider carefully all the potential sources of systematic errors that lurk behind experiments at the critical point of fluids. This is the subject of the next section.

### 4.5.2 Sources of systematic errors

The potentially harmful effects of temperature gradients and bad thermal stability in experiment on critical phenomena have been described in earlier sections. However, there are other known sources of systematic errors that constitute dangerous pitfalls for these experiments. Serious attention must be paid to the effect of gravitationally induced concentration gradients, the equilibration time of a binary mixture, the possible presence of wetting of the sample cell walls by one of the phases, and the definition of the order parameter.

#### The effect of gravity

Under the influence of Earth's gravitational field the refractive index vertical profile of a mixture below its consolute critical temperature is in principle distorted from a simple to a 'crooked' step–function as shown in Fig. 4.16 [31, 42, 74]. It is conceivable that a profile as in Fig. 4.16b would cause the appearance of diffraction fringes even when the system is at a temperature $T < T_c$, if the distortion from a step–like profile as in Fig. 4.16a is appreciable. However, no 'unwanted' fringes were ever detected in any of the experimental data sets. This can also be observed from Fig. 4.10 (top), where it can be
Figure 4.16: Qualitative picture of the refractive index profile of a binary mixture as a function of cell height at $T < T_c$: (a) ideal case; (b) distorted by Earth's gravitational field.
Figure 4.17: Measurement of the refractive index profile at a temperature $T > T_c$ after the sample was shaken to homogenize the phase.

seen that the film has not recorded any fringes before the temperature was raised above $T_c$.

To study this point in more depth, the image plane method (Chapter 3, section 3.3.3) was employed because of its ability to map directly the profile of the index of refraction. By counting the fringes as a function of their position on the film (the latter being related to the height in the sample cell), the profile can be plotted, as Figs. 4.17 and 4.18 illustrate. Profile measurements were taken at a temperature above $T_c$, after the sample was shaken and therefore in a situation where a homogeneous index of refraction is expected (Fig. 4.17) and below $T_c$, both shortly after and many hours after the temperature was lowered, shown in Fig. 4.18a and 4.18b, respectively.

To ensure that this method is sensitive enough to reproduce a sigmoidal profile if one is present, a measurement was made of the profile after the temperature was raised from below to above $T_c$, but without shaking the sample to homogenize the phase. In this situation a profile like Fig. 3.7b is expected, and is quite clearly measured by this method as is apparent from Fig. 4.19.

From the measured profiles above and below the critical point, there seems to be no evidence of a dramatic deviation of the index of refraction from a homogeneous behaviour, both in the one-phase and the two-phase regions.

This optical method has not been employed before to probe the refractive
index profile and, although its performance needs refinement, it has proven
very suitable for these measurements.

Gravitational effects are supposed to be more evident the larger the den­
sity difference between the two species of the mixture [75]. The densities of
n-heptane and nitrobenzene (see Appendix B), with a ratio of $\rho_N/\rho_H = 1.76$,
are not as closely matched as those of other compounds [29], however a study
on an even more density-mismatched mixture has revealed no influence of
gravitational effect on the measurements [53].

Given the results of our observations and of those reported in the lit­
erature, the influence of the gravitational field on the measurements of the
coeexistence curve of H+N can be neglected.

Equilibration

A very important issue to address, as several authors have pointed out in
the past [31], is that of the time a binary mixture takes to achieve equilib­
rium. As a consequence of the physical properties of the critical point, the
equilibration time gets longer the closer to $T_c$ the temperature is set. This is
understandable, for example, by recalling that the specific heat of the system
diverges at the critical point. However, more important in the determination
Chapter 4. Binary liquid experiment

Figure 4.19: Measurement of the refractive index profile at a temperature $T > T_c$ after the sample was heated from below to above critical. The sample was not shaken to speed up phase homogeneity as in Fig. 4.18.

of the equilibration time is the slowing down of the mutual diffusion between the species as the critical temperature is approached. The equilibration time issue is one of the reasons one needs a very stable thermal control system, as was mentioned earlier in this chapter. It is very important, therefore, to wait a long enough time for equilibrium to have occurred after a particular temperature has been set in the thermostat. An estimate of the diffusion coefficient for the n-heptane–nitrobenzene mixture from the experimental data has yielded a value of about $7 \times 10^{-12} \text{m}^2\text{s}^{-1}$ at less than $10^{-3}$ K from the critical temperature. This estimate is comparable to the coefficient found in diffusion studies on the nicotine+water system [56], where the cells were identical to the cells used in this experiment.

The image plane method used to measure the index of refraction profiles can also be used to estimate the equilibration time of the system, after a temperature change. This is done by monitoring the interference fringes at the image plane of the focusing lens (Fig. 3.10 of Chapter 3) with time as the film moves in the camera. For our purposes, equilibrium has been reached when the fringes appear horizontal on the film. The film is usually marked at regular intervals to keep track of time on it.

In the most significative measurement performed, the temperature was set at a value $T_i$ slightly above $T_c$ and held there for about two hours, it was
then decreased to a temperature $T_f$ below $T_c$, such that $T_i - T_f \leq 5 \times 10^{-4}$ K. The system was kept at this temperature and the fringes recorded on film for several days. While the chart recorder track of the thermistor outputs showed that $T_f$ was reached about 20 minutes after it was set, the fringes on the film do not appear to flatten to a horizontal slope until about 50 hours later.

The coexistence curve data close to $T_c$ were all taken after an equilibration time of about 50 hours, while for the rest of the data the equilibrium time allowance was between 10 and 20 hours. With this measurement and the diffusion constant estimate mentioned above, it is fairly safe to say that the issue of equilibration was well looked after. To my knowledge the image plane measurements have not been used in this fashion before in binary mixtures and constitute an interesting investigation tool wherever optical measurements can be applied.

**Wetting**

There is evidence that in binary mixtures one of the phases wets the walls of the cell containing the sample, sometimes surrounding the other phase completely, approximately as Fig. 4.20 shows [76, 77]. The effect of this phenomenon in the experimental conditions of this work is that the effective thickness of the light path the laser traverses inside the cell is different.

![Diagram](image)

**Figure 4.20:** Lower phase of a binary liquid mixture wetting the sample cell walls and surrounding the upper phase completely.
from the nominal thickness given by the manufacturer. Since the index of
refraction, and hence the order parameter, is measured by the number of
fringes detected at each temperature divided by the light path length, if the
latter is altered by the presence of a wetting film, the consequent refractive
index measurements will be affected and rendered wrong, unless the precise
thickness of the wetting film is known.

By comparing refractive index measurements taken with cells of different
thicknesses, the effect of a possible wetting layer can be monitored. Assuming
the wetting layer that forms has the same thickness independent of the nomi­
nal light path of the cell, if the data taken with different cells overlap, within
experimental error, the influence of the wetting film is negligible. The coex­
istence curve measurements were performed with different cell thicknesses to
be able to map the whole range of $t$ available for $n$-heptane+nitrobenzene
with equal ease and accuracy. Those measurements are reported in Figs. 4.11
and 4.13 and it can be observed that the data indeed all seem to follow the
same pattern. To emphasize this, I have selected two sets of data taken with
a 5 mm and a 10 mm cell and reported in Fig. 4.21. Within the accuracy
of the measurements the data overlap, indicating that if a wetting film is
present, it is, however, unmeasurable in these experiments.

In any case, there are indications from other observations [53, 4, 5] and
theoretical predictions [78] that wetting behaviour, although present at all
temperatures, usually becomes measurable at temperatures several degrees
below the critical temperature, a region of the coexistence curve that one is
less concerned with when determining the critical exponent $\beta$.

**Correct order parameter**

As described above, the index of refraction is used to extract the volume
fraction information to determine the coexistence curve of a mixture. In do­
ing this three assumptions are made. The first is that the index of refraction
does not present any anomaly at the critical point. There are theoretical
predictions [79] and experimental observations [80] dealing with this issue,
both showing that any anomaly in the refractive index is below 100 ppm,
less than the resolution of these experiments.

The second assumption made is that of zero mixing volume. In other
words, when the two individual species, A and B, are joined together to form
the mixture it is assumed that their volumes, $V_A$ and $V_B$, simply add, while in
general it is to be expected that $V_{\text{mixture}} = V_A + V_B \pm |V_E|$, where $V_E$ is called
Figure 4.21: Sensitive log–log plot, $\Delta \phi_H / t^\beta$ versus $t$, of the coexistence data on $n$–heptane+nitrobenzene taken with a 5–mm cell (black diamonds) and a 10–mm cell (white diamonds) to study the effect of a wetting film on the data. (The value used for the critical exponent is $\beta = 0.326$ and, as in analogous graphs, the data scatter and the size of the error bars are comparable.)
the excess volume and can be positive or negative. Experimental studies on two systems [62, 81] where \( V_E \neq 0 \) have shown that this had no consequences on the measured critical exponent \( \beta \). The first study has found that the critical amplitude \( B_0 \) remained the same within 3 to 4\%, while the second recorded an increase of up to 45\% in \( B_0 \) when the nonzero mixing volume is taken into account.

Thirdly, it is assumed that the Lorentz–Lorenz relation remains valid for binary mixtures to the same extent as it valid for pure fluids, for which it holds within about 1\%. According to an experiment aimed at determining the validity of this assumption [62], the Lorentz–Lorenz relation is verified within 0.5\%, when the volume loss upon mixing is considered.

Although no measurements were carried out on \( n \)-heptane+nitrobenzene to verify the above assumptions, I have assumed that they are valid for the results obtained with this system.
Chapter 5

Pure fluid experiment

5.1 Introduction

The experimental study of the critical region of the polar pure fluid 1,1-difluoroethylene \( (C_2H_2F_2) \) is presented in this chapter. The measurements were carried out using two different apparatus: the prism cell, already described in Chapter 3 and the combined cell, described in this chapter.

The data on the Lorentz–Lorenz function of \( C_2H_2F_2 \) are reported in the first section. Section 5.3 gives an overview of where these measurements fit in. Section 5.4 has experimental details on the combined cell experiment and the procedures followed in collecting the data. The results are reported in section 5.5.

5.2 Order parameter and Lorentz–Lorenz relation

It was explained in Chapter 3 how the coexistence curve of pure fluids can be studied with optical techniques, with very similar procedures to those described in the previous chapter for the case of binary liquid mixtures. It is actually with the study of pure fluids (in particular xenon) that the focal plane technique was introduced in critical phenomena experimentation [8, 9].

Recalling a few ideas from Chapter 3, the choice of order parameter to study pure fluids is usually more restricted than it is for binary fluids. Both the difference in molar volume and in either mass or number density between
the liquid and vapour phases could be used as pure-fluid order parameter. Once again, however, the quantity that yields a more symmetric coexistence curve is to be preferred, which biases the choice toward the density difference, usually normalized to the critical density of the system, \( \rho_c \) [48, 82]:

\[
\Delta \rho^* = \frac{\rho_L - \rho_V}{\rho_c}
\]

The relation between the index of refraction and the order parameter in the pure fluid case is given by the Lorentz-Lorenz (LL) relation:

\[
\frac{n^2 - 1}{n^2 + 2} = \rho \mathcal{L}(\rho)
\]

where \( \rho \) is the mass density of the fluid and the quantity \( \mathcal{L} \) is the LL coefficient or LL function, weakly dependent on \( \rho \) [10]. There is no evidence of any dependence of \( \mathcal{L} \) on \( T \). The Lorentz–Lorenz relation is employed to obtain the value of the density of the fluid from measurements of the index of refraction performed with the focal plane or the image plane techniques.

The coefficient \( \mathcal{L} \) needs to be determined accurately before it can be used in equation (5.1). This is done by measuring the density, \( \rho \), and the index of refraction, \( n \), independently with the prism cell technique.

**5.3 Motivation**

Focal plane and prism cell coexistence curve measurements on 1,1-difluoroethylene were carried out to test a new type of experimental apparatus developed in our laboratory. This substance was chosen both for its easily accessible critical temperature and because no accurate data on its critical region and LL coefficient seem to be available.

A new piece of apparatus was conceived and constructed a few years ago with the purpose of mapping the whole PVT space of a fluid [83]. One of the eventual goals of this apparatus is the measurement of the critical exponent \( \delta \), governing the critical isotherm, and the relative critical amplitude \( D_0 \) (see Chapter 1). Combined with coexistence curve and compressibility measurements, which yield values of the critical exponent \( \gamma \) and the amplitude \( \Gamma_0 \), these data can then be used to test universal critical amplitude ratios, and scaling laws [56, 84, 85, 86]. The idea is to have an experiment that combines
the three techniques used (the prism cell, the focal plane and image plane) together, so that different types of measurement can be performed on the same sample. Due to the effect of gravitational rounding of the index of refraction profile—this effect is more marked in pure fluids than in binary mixtures—the prism cell technique allows the coexistence curve to be measured only to about 3 mK of $T_c$ ($t \approx 10^{-5}$), while with the focal plane technique one can extend the range by almost another decade in terms of $t$, to $t \approx 10^{-6}$. On the other hand, prism cell measurements can be used for measurements performed far from $T_c$. However, when the measurements are performed on samples contained in different cells for different experiments, the critical temperatures of the data sets may differ enough to make it impossible to compare them meaningfully without adjustment of the data. Although this apparatus has already produced some data [83], however, a direct comparison of prism cell and focal plane data had yet to be performed.

With the combined cell the influence of potential wetting effects on the focal plane (and image plane) cell walls can be studied, as the data is taken "in parallel" with prism cell data, which should not suffer from wetting effects since it is based on the detection of the horizontal deviation of the light by the fluid.

5.4 Experimental apparatus

5.4.1 Combined cell

A drawing of the combined cell, used for some of the pure fluid measurements, is shown in Fig. 5.1. It is built from an aluminum, square cross section parallelepiped of dimensions $(101.1 \times 44.45 \times 44.45)$ mm$^3$. Two chambers were created by milling different recesses for the cell windows and flanges. On one chamber—which I will refer to as the flat chamber—the windows are mounted parallel to each other, the gap between the windows measures 2.16 mm and it is built with a tolerance of better than 0.10 mm. The windows of the other chamber—the prism chamber—form an angle $\theta = (20.775 \pm 0.017)^\circ$ with one another, with one window parallel to the flat chamber ones. The two chambers are in communication via a small bore between them. Needle valves are fitted at each end of the cell for fluid filling and bleeding purposes during the experiments [83].
5.4.2 Prism cell

One of the pieces of apparatus used for the pure fluid measurements is the prism cell described in some detail in Chapter 3, section 3.3.1. The whole apparatus is described in an earlier paper by Balzarini et al. [49].

Essentially, to complete the description of the pure fluid experiment apparatus, the cell (prism or combined) is placed in the centre of a thermostat operating on the same general principles described in Chapter 3, section 3.2.1. Unlike the binary liquid experiment, the pure fluid experiment thermostats are laid on their side to respond to different experimental operating needs, such as having to take the cells out for bleeding fluid and weighing very often during the experiments. The temperature is measured with both a quartz thermometer and two thermistors, one on either side of the thermostat. The calibration of the thermometers is carried out as described earlier.

5.4.3 Optics

The optical setup for experiments with the combined cell must enable us to use the three techniques described in Chapter 3 on the same experiment. This entails quite a bit of juggling of equipment on the optical table to find the
best experimental geometry for all types of measurements that are intended to be carried out. The setup is illustrated in Fig. 5.2. The two simultaneous measurements are carried out on opposite sides of the thermostat to avoid possible interference of the prism cell data collection operations with the focal (or image) plane measurements.

Aside from a few logistic problems which had to be overcome (e.g. aligning a larger number of optical components on a crowded optical bench), the measurement procedure resembles those made with a single prism cell or a single interferometer. More difficulties are encountered when this apparatus is used for the measurement of the critical isotherm [83], which however is beyond the purpose of this thesis.

Figure 5.2: The combined cell experiment setup.
5.4.4 Samples

The sample of 1,1-difluoroethylene used was purchased from Scott Specialty Gases in a lecture bottle of purity 99.4% (see appendix C for further properties of this fluid). Preparing the sample for the pure fluid experiments is a relatively easier process than for the binary liquid experiments. The cell—either the prism or the combined cell—is first leak-tested, since it will have to sustain pressures of up to about 150 atm (~15 MPa). Then, it is evacuated and pumped on for days. Then, it is repeatedly flushed with the sample gas and evacuated, in an effort to reduce the amount of impurities as much as possible.

Particular care must be put into the operation of filling the prism cell for the measurements of the LL coefficient at high densities. In that situation, the cell is usually kept immersed in an ice, or colder, bath, while the fluid is transferred from the lecture bottle to the cell.

Under these conditions, the cell is filled until its volume is occupied, almost entirely, by the liquid phase of the fluid. Referring to Fig. 5.3, the system is at a density $\rho_L$, on the coexistence curve, near the liquid phase region of the phase diagram. Clearly, then, if the cell is allowed to heat the fluid will all transform to liquid and the pressure in the cell will increase dramatically if the temperature is raised.

5.4.5 Experimental procedure

As anticipated in the previous section, to take LL data the sample cell is initially filled to a density, $\rho'$ in Fig. 5.3, such that at the temperature of the ice bath the sample is nearly all liquid with only a small amount of vapour present. The sample is then introduced into the thermostat set at a temperature $T_1 < T'$. In these conditions, the liquid phase refractive index, $n_L(\rho', T_1)$, can be measured. The temperature is then increased to $T_2$ and $n_L(\rho', T_2)$ is measured and found to be different from $n_L(\rho', T_1)$ as long as $T_2 < T'$. The procedure is repeated until, for temperatures above $T'$, the measurement of $n_L(\rho', T)$ is found to be practically independent of temperature. The system is then in the one phase region outside the coexistence curve and measurements of the refractive index in this situation yield $n_L(\rho', T')$ needed for the determination of $\mathcal{L}$ at density $\rho'$. The density of the fluid is determined using the known (previously measured) volume of the evacuated cell and its mass, as described in Chapter 3. The cell is
then taken out of the thermostat, the sample brought to another density \( \rho'' \) by bleeding out some fluid and the procedure repeated to obtain \( n_L(\rho'', T'') \) and so on. On the vapour side of the curve measurements are carried out similarly, by decreasing the temperature after each datum until room temperature is reached, at which point the temperature is left unchanged while fluid is bled at each point. The data used to calculate \( L \) are collected in the shaded area around the coexistence curve as indicated in Fig. 5.4. The high compressibility of the fluid around the critical point \((\rho_c, T_c)\) makes it difficult to obtain accurate measurements of \( n(\rho, T) \). The region is therefore "avoided", as shown near the top of the curve in Fig. 5.4, by heating the sample to about one degree above \( T_c \).

In the combined cell experiment, the sample is prepared at the critical density, \( \rho_c \), of the fluid, and inserted in the thermostatic housing for that experiment. The prism chamber data are read via a micrometer that is calibrated in the same manner described in section 3.3.1 of Chapter 3. Data are taken starting from the farthest temperature from \( T_c \) that one would like to be covered by the experimental run. At each set temperature, the quartz
Figure 5.4: Temperature and density region where the data for the LL measurements are collected. Due to its large density gradients the critical region must be "circumnavigated" to take accurate data.
thermometer as well as the thermistor values are recorded and micrometer readings are taken as the camera and film in the focal plane of the lens run continuously. After each reading the temperature is raised slightly and after equilibrium has been reached again another measurement is taken. The procedure is repeated until the system has been brought above the critical temperature. Data collection on the prism chamber usually must stop at more than a millidegree from $T_c$, due to the distortion in the beam produced by the gravitationally-induced density gradient in the fluid.

5.5 Results

Experimental data on pure fluids using the techniques described can normally be taken relatively more quickly than on binary liquid mixtures. The data presented here are the product of several prism–cell and combined–cell runs. Some of the data constitute the first available direct comparison of coexistence data produced by the focal plane technique and the prism cell technique on the same sample of fluid.

The measurements of the LL function, $\mathcal{L}$, are discussed first since it is a quantity needed for all the subsequent experiments. In the prism cell experiment, the importance of a careful analysis of the cell weighing operation is emphasized as it is suspected it can lead to a systematic error in the measurement of $\mathcal{L}$.

5.5.1 Prism cell experiment: measurements of the Lorentz–Lorenz function

The collected Lorentz–Lorenz data for 1,1-difluoroethylene are presented in the graph in Fig. 5.5. The LL function defined by relation (3.1) is often found to exhibit a weak dependence on density around the coexistence curve [56, 83, 87] with a maximum located approximately around the critical density. The present experiment confirms this trend and shows that, although $\mathcal{L}$ follows a roughly parabolic shape, its value is “constant” within about 1.2%. Around the critical density $\rho_c$, where an accurate determination of $\mathcal{L}$ is more crucial, the measured value does not vary by more than 1%. To obtain the temperature dependence of the order parameter of 1,1-difluoroethylene on temperature from refractive index measurements, the critical value $\mathcal{L}_c = 0.1668 \pm 0.0017 \text{ cc/g}$ was used.
Figure 5.5: Measured density dependence of the Lorentz–Lorenz function of 1,1-difluoroethylene. The line shown is a quadratic fit to the data. The fit parameters are in table 5.1. The size of the error bars is comparable to the scatter in the data.

Generally, the data suggest that the LL function can be expanded in a power series as a function of $\rho$:

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_1 \rho + \mathcal{L}_2 \rho^2 + \cdots$$ \hspace{1cm} (5.2)

The data in Fig. 5.5 are shown with a quadratic fit through them, with the fit parameters given in table 5.1.

The data at both ends of the density range investigated are affected by larger errors than the data around the critical density region. At the low density end, the accuracy in the determination of $\mathcal{L}$ is mainly limited by how

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\mathcal{L}_0$ (cc/g)</th>
<th>$\mathcal{L}_1$ (cc/g)$^2$</th>
<th>$\mathcal{L}_2$ (cc/g)$^3$</th>
<th>$\mathcal{L}_c$ (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_2F_2$</td>
<td>0.1639</td>
<td>0.0142</td>
<td>-0.0166</td>
<td>0.1668</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0002$</td>
<td>$\pm 0.0007$</td>
<td>$\pm 0.0007$</td>
<td>$\pm 0.0017$</td>
</tr>
</tbody>
</table>
accurately the mass of the empty prism cell can be measured at the end of the run. As the quantity one needs is the difference $m - m_{cell}$ (see equation 3.8), where $m$ is the mass of the cell+fluid system and $m_{cell}$ is the mass of the empty cell, the same degree of uncertainty on the empty cell mass yields a larger inaccuracy in the low density than in the high density measurements. Lorentz–Lorenz data were collected at lower densities than those reported in Fig. 5.5, but were not included in that graph. Due to the large errors in them, they were not very meaningful in the reported measurement of $\mathcal{L}$.

At the high density side of the data, one must watch for another experimental pitfall. At those densities the coexistence curve of 1,1-difluoroethylene is at temperatures much lower than the typical room temperature. The reported data were taken starting at the high density end, which meant maintaining the cell at temperatures down to about +3°C. Clearly, then, when the cell is taken out of the thermostatic housing to be weighed—an operation that must only last a few minutes for the reasons mentioned above—, condensation, and then evaporation, of air moisture on the cell body occurs quite rapidly thereby hindering one from taking a precise reading of the cell weight. I performed a rough, but still significant, study of this effect at the end of the experiment, when, with the empty cell, I could bring it to any given temperature and then monitor its weight on the precision balance as a function of time. This was done at several temperatures, with each measurement being carried out for about 24 hours. Not surprisingly, it was found that the difference $\Delta m = m_i - m_f$, between the measured cell weight as soon as the cell was taken out of the thermostat, $m_i$, and about one day later, $m_f$, depends on the difference between the cell's initial temperature in the thermostat and the room temperature $\Delta T = T_{\text{set}} - T_{\text{room}}$. The latter was measured quite often during the experiment and it averaged at about 23.3°. Fig. 5.6 shows the effect at the highest $\Delta T$ measured of about -5.8°. At $\Delta T = -5.8°$, it appears that the cell actual weight is overestimated by about 0.05 g. This would lead to an underestimation of the value of $\mathcal{L}$ of about 0.5%. At lower $\Delta T$s, the effect was less marked. From the measurements taken, a rough quantitative correction factor, decreasing with decreasing $\Delta T$ was extrapolated and used to "correct" the high density LL data. I report in Fig. 5.7 a comparison between the corrected and uncorrected data.
Figure 5.6: Variation of the weight of the prism cell with time, when the cell was initially at a temperature about 5.8° below room temperature.

Figure 5.7: Measured LL data with (white diamonds) and without (black diamonds) correction on the cell mass. The size of the error bars is comparable to the scatter in the data.
Chapter 5. Pure fluid experiment

Figure 5.8: Coexistence curve of 1,1-difluoroethylene as measured in the prism cell experiment.

The corrected data do yield a higher value of $L_{C_2H_2F_2}$ at high densities, suggesting that it has a weaker density dependence than previously observed in Fig. 5.5. However, from the increased scatter in the measurements, the data also show that a better study of this effect would be required before drawing sound quantitative conclusions.

5.5.2 Prism cell experiment: coexistence curve

The coexistence curve of $C_2H_2F_2$ was measured over the reduced temperature interval $4 \times 10^{-5} < t < 10^{-1}$. The pronounced density gradients in the fluid nearing its critical region render it arduous to take accurate data at values of $t \lesssim 10^{-4}$. The coexistence curve is presented in Fig. 5.8.

Using the value of $L$ mentioned in the previous section, the data were fitted to the expression:

$$\Delta \rho^* = B_0 t^\Delta (1 + B_1 t^\Delta + B_2 t^{2\Delta})$$

(5.3)

where the correction exponent $\Delta$ was held fixed at its theoretical values of 0.54 and 0.50 and the critical amplitudes were treated as free parameters in the nonlinear least square fit to the data. The critical density $\rho_c$ was measured at $0.418 \pm 0.2\%$ g/cc and it was found by extrapolation of the
Table 5.2: Parameter values of the fit of equation (5.3) to the prism cell data on \( C_2H_2F_2 \). Quantities in parentheses were held fixed during the fit.

<table>
<thead>
<tr>
<th>( \beta )</th>
<th>( \Delta )</th>
<th>( B_0 )</th>
<th>( B_1 )</th>
<th>( B_2 )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.326)</td>
<td>(0.54)</td>
<td>3.351 ± 0.005</td>
<td>0.62 ± 0.02</td>
<td>-1.01 ± 0.05</td>
<td>1.5</td>
</tr>
<tr>
<td>0.322 ± 0.004</td>
<td>(0.54)</td>
<td>3.25 ± 0.03</td>
<td>0.77 ± 0.05</td>
<td>-1.28 ± 0.09</td>
<td>1.2</td>
</tr>
<tr>
<td>(0.326)</td>
<td>(0.50)</td>
<td>3.339 ± 0.005</td>
<td>0.57 ± 0.02</td>
<td>-0.81 ± 0.05</td>
<td>1.7</td>
</tr>
<tr>
<td>0.320 ± 0.004</td>
<td>(0.50)</td>
<td>3.19 ± 0.03</td>
<td>0.79 ± 0.05</td>
<td>-1.15 ± 0.08</td>
<td>1.1</td>
</tr>
</tbody>
</table>

coexistence curve diameter, \( \rho_d = (\rho_L + \rho_V)/2 \), as a function of temperature, to the critical temperature. The fit values are given in table 5.2. It can be observed from the correction-sensitive plot in Fig. 5.9 that correction-to-scaling terms are certainly needed to interpret order parameter data on \( C_2H_2F_2 \). The fit values show that the theoretical values of the exponents fit the data well and that a two-term fit would seem more appropriate to interpret these data. A three-term fit showed no improvement on the two-term fit in the interpolation of the data. The best estimate of the critical temperature of 1,1-difluoroethylene from the prism cell experiment is \( T_c = 302.95 ± 0.006\% \) K.

### 5.5.3 Combined cell experiment

The data of the combined cell experiment cover a reduced temperature range of a little over three decades from \( 4.3 \times 10^{-6} \) to \( 1.6 \times 10^{-3} \). It is possible to carry out measurements over a much larger temperature span with this experiment, too. Once again, however, the aim of the combined cell measurements reported here is to compare focal plane and prism cell-type data near the critical region of 1,1-difluoroethylene taken with the same sample in order to study more closely the differences between the results obtained through the two techniques. The coexistence curve data of both kinds is presented in Fig. 5.10. The curves through the data correspond to a nonlinear least square fit, whose parameter best values are in table 5.3. The density difference \( \Delta \rho \) is obtained directly from \( \Delta n \) for the focal plane data, through the Lorentz–Lorenz relation, yielding:

\[
\Delta \rho = \frac{k}{\bar{c}} \Delta n \tag{5.4}
\]
Figure 5.9: Correction sensitive log–log plot of $\Delta \rho^*/t^\beta$ vs $t$ of the coexistence data of 1,1-difluoroethylene measured in the prism cell experiment. The value of $\beta$ was held fixed at 0.326. The size of the error bars is comparable to the scatter in the data.

Figure 5.10: Simultaneous prism cell–type (circles) and focal plane (x) data on 1,1-difluoroethylene measured with the combined cell experiment.
Table 5.3: Parameter values of the fit of equation (5.3) to the focal plane data on \( C_2H_2F_2 \) taken with the combined cell. Quantities in parentheses were held fixed during the fit.

<table>
<thead>
<tr>
<th>range</th>
<th>( \beta )</th>
<th>( \Delta )</th>
<th>( B_0 )</th>
<th>( B_1 )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t \lesssim 10^{-4} )</td>
<td>(0.326)</td>
<td>(0.54)</td>
<td>3.17 ± 0.004</td>
<td>(0)</td>
<td>3.1</td>
</tr>
<tr>
<td>( t \lesssim 10^{-4} )</td>
<td>0.329 ± 0.008</td>
<td>(0.54)</td>
<td>3.3 ± 0.03</td>
<td>(0)</td>
<td>3.2</td>
</tr>
<tr>
<td>( t \lesssim 1.6 \times 10^{-3} )</td>
<td>(0.326)</td>
<td>(0.54)</td>
<td>3.190 ± 0.009</td>
<td>1.36 ± 0.13</td>
<td>6.0</td>
</tr>
</tbody>
</table>

where \( k = 3(n_L + n_V)/[(n_L^2 + 2)(n_V^2 + 2)] \) and \( C = 0.1668 \) cc/g is the Lorentz–Lorenz coefficient found earlier with the prism cell experiment. The quantity \( k \) can be measured with the prism cell data from either the prism cell experiment or the present one. It is found to be equal to \( k = 0.6396 \) and constant within 0.02%. The data obey the theoretical order parameter law (equation (5.3)) with the critical exponent \( \beta = 0.326 \) and one correction term with the correction exponent fixed \( \Delta = 0.54 \). The critical amplitudes were left free. The best parameter values of the nonlinear least square fit to the prism and the focal plane data are reported in table 5.3.

Among the advantages of this experiment is that the prism–type data can be analyzed more precisely because the critical temperature can be determined via the focal plane data, which can be taken closer to critical. When this is done the order parameter data can be plotted on a log–log plot as usual.

The good agreement between the prism–type data and the focal plane data is evident in the log–log plot of the data versus the reduced temperature, as shown in Fig. 5.11.
Figure 5.11: Log–log plot of prism (circles) and focal plane (xs) data on 1,1-difluoroethylene measured with the combined cell experiment.
Chapter 6

Conclusion

6.1 Binary liquid

The critical region and the coexistence curve of the binary liquid mixture \(n\)-heptane+nitrobenzene was studied to a high degree of accuracy by optical methods. One of the goals was to measure the critical exponent \(\beta\), governing the power law followed by the order parameter as the temperature approaches the critical temperature \(T_c\).

The measured value of \(\beta\) is \(0.367 \pm 0.006\), which is consistently higher than the theoretical value of \(\beta_{th} = 0.326 \pm 0.002\). The critical consolute temperature for this system is measured at \(T_c = 291.78 \text{ K} \pm 0.03\% (= 18.63\text{°C})\).

In an effort to discover if an experimental flaw could account for the difference between the theoretical and experimental values of \(\beta\), the known potential sources of systematic error were carefully analyzed. In this process one of the optical techniques—the image plane technique—was employed to measure the profile of the index of refraction of the binary liquid sample in a way that had not been tried before. The results are interesting in that the shape of the refractive index vertical gradient can be mapped directly by this technique. The relatively new use of this optical tool has helped rule out the possibility that surface wetting by one of the phases could be responsible for the discrepancy between the measured and the theoretically predicted exponent \(\beta\). The influence of other effects such as impurities in the samples, the gravitational field of Earth and the exact definition of the order parameter also appear to be too small to account for the high measured value of \(\beta\).
Figure 6.1: A collection of experimental (black diamonds) and theoretical (white) values of the critical exponent $\beta$ in the past 35 years. The experimental data are from measurements on binary liquids only. The results obtained by the UBC laboratory of critical phenomena are the dotted circles.

A brief search of the past results has produce the data in Fig. 6.1. Indeed, it seems that experimentalists and theorists have slowly arrived at a good agreement in the last couple of decades. While it may look somewhat awkward that the present results stand out of the pack, the result is at least as accurate as many other measurement issued by this laboratory, and which have helped build the credibility of the modern understanding of critical phenomena.

It is concluded that the measurement of $\beta$ reported is accurate and precise and provides food for thought for both experimentalists, to look for other possible causes for the deviation from norm, and theorists to helps us in that quest.

6.2 Pure fluid

The critical region of the polar pure fluid 1,1-difluoroethylene ($C_2H_2F_2$) has been studied via two optical investigation methods, called the prism cell and the focal plane techniques.
In the prism cell experiment the Lorentz–Lorenz function of the fluid, relating the fluid density and its index of refraction, was determined as a function of density, in the density range below about 0.82 g/cc. It would not appear that this quantity has been measured before, at least, not to the accuracy that these experiments produce.

The coexistence curve of C$_2$H$_2$F$_2$ was also measured over a temperature range extending to about 28 degrees from the critical temperature. The critical temperature measured with this experiment is $T_c = 302.95$ K=29.80°C. The data obeys the order parameter scaling relation with two correction terms, and the theoretical values of the exponents $\beta$ and $\Delta$.

A novel experiment combining the three main optical techniques, focal and image plane and prism cell, in order to perform measurements of different kinds on the same sample has been tested. With the LL function measured in the prism cell experiment, the coexistence curve of C$_2$H$_2$F$_2$ was measured simultaneously with the prism cell and the focal plane methods.

The first data from both methods overlap quite well over the whole temperature range investigated, namely between $t = 4.3\times10^{-6}$ and $t = 1.6\times10^{-3}$.

The coexistence curve data on C$_2$H$_2$F$_2$ taken with the combined experiment are interpolated well by the theoretical scaling relation with the exponent values set at their theoretical values.
Bibliography


[12] Reference [10], page 312.


Bibliography


[33] Styrofoam SM of Dow Canada (The Dow Chemical Company), with the following physical properties: density \( \rho = 25 \text{ kg/m}^3 \), specific heat \( c_v = 1130.36 \text{ J/kg/K} \), and thermal conductivity \( \kappa = 0.0028 \text{ J/m/K/s} \) (\( \rho \) was measured in the lab, \( \kappa \) from CRC book [50], \( c_v \) from Dow Canada).


[35] HP Quartz Thermometer Model 2804A.


[37] The product is Thermopox 85CT (thermally conductive epoxy with thermal conductivity of 6.4 to 6.8 W/m/K), by Amepon Microelectronics, LTD., 90–268 Lódź ul. Jaracza 6, Poland—www.amepox.com

[38] The manual of the HP Quartz Thermometer in [35] has a good description of the equipment and procedure needed for a calibration at triple point of pure water.


[40] A tripe–point–of–water cell was used for this calibration. The cell was made by Jarrett Instrument Co., Inc., Wheaton, Md., U. S. A.


Bibliography


[102] see [101], page 962–963, no. 8451 5) and 6).


Appendix A

Heat flow problem on the binary liquid thermostat

In the thermostat, a layer of Styrofoam [33] of thickness $L$ attenuates external temperature fluctuations so that the internal temperature can be kept constant within $10^{-4} \text{K}$ (Fig. A.1). A time-periodic variation in the external temperature propagates towards the interior of the thermostat in the form of a wave with an amplitude that decreases exponentially with propagation distance, $z$. At the inner surface of the layer, the heat flux flows into the copper layer of thickness, $\Delta$.

An estimate of the amplitude of the temperature fluctuations at the inner edge of the styrofoam layer can be obtained by solving the one-dimensional heat conduction equation subject to the following boundary conditions:

1. at $z = 0$ and time $t$, the temperature, $T(0, t)$, is given by the expression,
   \[ T = T_0 + T_f e^{i\omega t} \]  \hspace{1cm} (A.1)
   where $\omega$ is the frequency of the temperature fluctuation of amplitude $T_f$ and $T_0$ (constant) is the ambient room temperature;

2. at the interior copper surface, the heat flux is very rapidly distributed throughout the copper layer so that its temperature can be calculated from the expression (Fourier’s law):
   \[ \kappa \frac{\partial T(z, t)}{\partial z} \bigg|_{z=L} = (\rho S)_{\text{Cu}} \Delta \frac{\partial T(z, t)}{\partial t} \bigg|_{z=L} \]  \hspace{1cm} (A.2)
Appendix A. Heat flow problem...

Figure A.1: Geometry of configuration used to assess the attenuation of external temperature fluctuation by a styrofoam layer.

where $\kappa$ is the thermal conductivity of the styrofoam, $\Delta$ is the thickness of the copper layer and $(\rho S)_{Cu}$ is the specific heat of the copper per unit volume. The above expression assumes that the copper layer is thin enough for the heat flowing into it from the styrofoam to raise its temperature to the same value throughout its entire volume.

The heat flux in the styrofoam is governed by the heat conduction equation,

$$\kappa \frac{\partial^2 T(z, t)}{\partial z^2} = (\rho S)_S \frac{\partial T(z, t)}{\partial t} \quad (A.3)$$

where $(\rho S)_S$ is the specific heat per unit volume of the styrofoam. The solution may be written in the form,

$$T = T_0 + (A e^{-\alpha L} e^{\alpha z} + B e^{\alpha L} e^{-\alpha z}) e^{i\omega t} \quad (A.4)$$

with $\alpha^2 = i\omega (\rho S)_S / \kappa \simeq i\omega \times 10^{-6}$, a result obtained by noting that, for Styrofoam SM, $(\rho S)_S / \kappa \simeq 10^{-6}$ m$^{-2}$s.

It follows from the boundary conditions in equations (A.1) and (A.2) and the above equations that,

$$T(L, t) = T_0 + 2A e^{i\omega t} / (1 + U) \quad (A.5)$$
Appendix A. Heat flow problem...

where

\[ U = \frac{\alpha \Delta (\rho S)_{Cu}}{(\rho S)_S} \]  

(A.6)

and

\[ A = \frac{T_f (1 + U)}{(1 + U)e^{-\alpha L} + (1 - U)e^{\alpha L}} \]  

(A.7)

To enhance the attenuation of the temperature fluctuation at \( z = L \), it transpires that \( L \) is chosen such that \( e^{-\alpha L} \lesssim 10^{-4} \). In this case, equations (A.5) and (A.7) take the form

\[ T(L, t) = t_0 + \frac{2T_f e^{-\alpha L}}{(1 - U)} e^{-i\omega t} \]  

(A.8)

Taking account of the specific heats per unit volume of copper and styrofoam, and that \( T_f \) has an observed fluctuation frequency, \( \omega \), of approximately \( 0.2 \text{ s}^{-1} \), it follows from equation (A.6) that \( |U| \gg 1 \), if \( \Delta > 10^{-3} \text{ m} \). To estimate a “safe” thickness for the styrofoam, such that the fluctuations in \( T(L, t) \) are less than \( 10^{-4} \) is suffices to choose \( L \) such that \( e^{-\alpha L} < 10^{-4} \). A styrofoam thickness of the order of 33 mm satisfies the requirement of keeping the internal temperature fluctuations below the required level, if \( T_f < 0.2 \text{ K} \). The 42 mm thick styrofoam layer used in the experiment is therefore more than adequate to screen the interior from the influence of external fluctuations at the level of 0.2 K or so.
Appendix B

Physical properties of the substances studied

The following data have been taken from references [50] and [57].

Table B.1: Critical temperature, melting point and boiling point temperatures of the substances studied.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_c$ (K)</th>
<th>$T_M$ (C)</th>
<th>$T_B$ (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-heptane ($C_7H_{16}$)</td>
<td>540.2</td>
<td>-90.6</td>
<td>98.5</td>
</tr>
<tr>
<td>nitrobenzene ($C_6H_5NO_2$)</td>
<td></td>
<td>5.7</td>
<td>210.8</td>
</tr>
<tr>
<td>aniline ($C_6H_7N$)</td>
<td>699</td>
<td>-6</td>
<td>184.1</td>
</tr>
<tr>
<td>cyclohexane ($C_6H_{12}$)</td>
<td>553.5</td>
<td>6.6</td>
<td>80.7</td>
</tr>
<tr>
<td>1,1-difluoroethylene ($C_2H_2F_2$)</td>
<td>302.75</td>
<td>-144</td>
<td>-85.7</td>
</tr>
</tbody>
</table>

Table B.2: Refractive index (at the D line of the spectrum of sodium and at 20°C), density (at 20°C, referred to the density of water at 4°C) and molecular weight of the substances studied.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$n_D^{20}$</th>
<th>$\rho^{20}$</th>
<th>mol. wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-heptane</td>
<td>1.3878</td>
<td>0.6837</td>
<td>100.20</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>1.5562</td>
<td>1.2037</td>
<td>123.11</td>
</tr>
<tr>
<td>aniline</td>
<td>1.5863</td>
<td>1.0217</td>
<td>93.13</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>1.4266</td>
<td>0.7785</td>
<td>84.16</td>
</tr>
<tr>
<td>1,1-difluoroethylene</td>
<td></td>
<td></td>
<td>64.03</td>
</tr>
</tbody>
</table>
Appendix C

Relation between $\Delta \phi$ and $
\Delta n$

In Chapter 4 the relation of direct proportionality between the index of refraction difference between the two liquid phases of a binary mixture and the difference in volume fraction of one of the species was stated without justification. It is derived in this appendix by means of the Lorentz–Lorenz relation applied to the case of a binary mixture.

Under the assumption of the additivity of the volumes of the two liquids upon mixing, in the one-phase region one has

$$\frac{n^2 - 1}{n^2 + 2} = \mathcal{L}_H \phi_H + \mathcal{L}_N (1 - \phi_H) \tag{C.1}$$

where $\mathcal{L}_{H,N}$ is the Lorentz–Lorenz coefficient of the two separate liquids H and N, (equation (3.1) of Chapter 3), and the $\phi_{H,N} = V_{H,N}/(V_H + V_N)$ are their respective volume fractions. In the two-phase region, relation (C.1) can be applied to the upper (U) and lower (L) phases, to obtain

$$\frac{n_U^2 - 1}{n_U^2 + 2} = \mathcal{L}_H \phi_{H,U} + \mathcal{L}_N (1 - \phi_{H,U}) \tag{C.2}$$

and

$$\frac{n_L^2 - 1}{n_L^2 + 2} = \mathcal{L}_H \phi_{H,L} + \mathcal{L}_N (1 - \phi_{H,L}) \tag{C.3}$$
Subtracting equation (C.2) from (C.3) and after some simple algebraic steps one finds the following relation:

\[ \phi_{H,L} - \phi_{H,U} = \left[ \frac{n_U + n_L}{(n_U^2 + 2)(n_L^2 + 2)} \frac{(n_U^2 + 2)(n_L^2 + 2)}{n_U^2 - n_L^2} \right] (n_L - n_U) \]

(C.4)

Through the introduction of the quantities \( \Delta \phi = \phi_{H,L} - \phi_{H,U} \) and \( \Delta n = (n_L - n_U) \), equation (C.4) can be rewritten as \( \Delta \phi = k \Delta n \), with \( k \) corresponding to the quantity in square brackets in equation (C.4). In other studies [89, 90], the quantity \( k \) was found to be constant within about 0.1% in the temperature range of the two-phase region of the n-heptane+nitrobenzene mixture, while the uncertainty in \( \Delta n \) is between 1% and 10% in the same range. In the conditions the experiment was carried out, it was therefore safe to consider the volume fraction \( \Delta \phi \) simply proportional to \( \Delta n \). In this case, the 'constant' \( k \) can be calculated in the particular case that \( n_L = n_U = n_c \), \( n_c \) being the critical index of refraction, which can be calculated from the Lorentz–Lorenz relation once the critical composition of the mixture is known.

From the physical properties of the two species used, listed in the previous appendix, the proportionality constant \( k \) is found to be: \( k = 6.045 \).
Appendix D

Bending of light by a refractive index gradient

In the focal plane technique described in Chapter 3, one exploits the fact that a gradient of index of refraction can bend a light ray passing through the medium exhibiting such gradient. It was stated that light encountering a medium with an index of refraction gradient (in the vertical direction, \( z \), in our particular case) \( \frac{dn}{dz} \) gets bent following the relation:

\[
\frac{d\theta}{dy} = -\frac{1}{n} \frac{dn}{dz}
\]  \hspace{1cm} (D.1)

Equation (D.1) derives from an application of Snell’s law to a medium with varying index of refraction, if the medium is thought of as stratified in layers each with different refractive indices, each differing from its neighbours by an amount \( dn \), such as \( dn \ll n \), as shown in Fig. D.1. Applying Snell’s law to the layer shown yields

\[
n \sin \theta = (n + dn) \sin (\theta + d\theta)
\]  \hspace{1cm} (D.2)

Since \( dn \) and \( d\theta \) are supposed infinitesimal, equation (D.2) can be approximated retaining only terms of order \( O(dn, d\theta) \), like this

\[
0 \approx dn \sin \theta + nd\theta \cos \theta
\]  \hspace{1cm} (D.3)
With simple rearranging of the terms in the last equation, one obtains

$$\frac{1}{n} dn \approx \cot \theta d\theta$$  \hspace{1cm} (D.4)

From the diagram in Fig. D.1, the term $\cot \theta$ can be written as: $\cot \theta = \frac{dz}{dy}$. Using this in equation (D.3), equation (D.1) is found [91].
Appendix E

Technical drawings of apparatus
Appendix E. Technical drawings of apparatus

Figure E.1: The cell holder.
Figure E.2: The inner cylinder.
Figure E.3: The outer cylinder.
Appendix F

Photographs of apparatus
Figure F.1: Some of the \(n\)-heptane+nitrobenzene samples. From left to right: 1-mm, 2-mm, and 10-mm samples.
Figure F.2: The cell holder with a 1-mm sample.
Figure F.3: The inner cylinder and cap with heating foils.
Figure F.4: From left to right: the cell holder, and the inner and outer cylinders.