OPTICAL STUDY OF THE CRITICAL BEHAVIOUR OF PURE FLUIDS AND BINARY MIXTURES

By

Ulrike Närger

Diplom, Technische Universität München, 1983

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES

PHYSICS

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

March 1990

© Ulrike Närger, 1990

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

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

Date:

May 30 / 1990

Abstract

Optical techniques were used to study the critical behaviour of the pure fluids CHF₃, CClF₃ and Xe, and binary mixtures He-Xe and nicotine + water. We find that for all these substances, the order parameter is described by a power law in the reduced temperature $t = (T_c - T)/T_c$ with a leading exponent $\beta = 0.327 \pm 0.002$. Also, we determine the first correction to scaling exponent to be $\Delta = 0.43 \pm 0.02$ for the pure fluids and $\Delta = 0.50 \pm 0.02$ for the He-Xe system.

The coexistence curve diameter in CHF_3 and $CClF_3$ exhibits a deviation from rectilinear diameter, in agreement with a modern theory which interprets this behaviour as resulting from three-body effects. In contrast, no such deviation is observed in Xe where, according to that theory, it should be more pronounced than in other substances.

In the polar fluid CHF₃, the order parameter, isothermal compressibility and the chemical potential along the critical isotherm were simultaneously measured in the same experiment in an effort to ensure self-consistency of the results. From the data, two amplitude ratios which are predicted to be universal are determined: $\Gamma_0^+/\Gamma_0^- = 4.8 \pm 0.6$ and $D_0\Gamma_0^+B_0^{\delta-1} = 1.66 \pm 0.14$.

In the binary liquid system nicotine + water, the diffusivity was measured both by light scattering and by interferometry. The results agree qualitatively, but differ by a factor of ≈ 2 . From the light scattering data, the critical exponent of the viscosity is found to be $z_{\eta} = 0.044 \pm 0.008$.

The interferometric experiments on Xe and He-Xe furnish a direct way to maesure the effects of wetting: From the data, the exponent of the surface tension is found to be $n = 1.24 \pm 0.06$. The similarity of the order parameter and compressibility in Xe and a He-Xe mixture containing 5% He indicate that the phase transition in this He-Xe mixture is of the liquid-gas type rather than the binary liquid type.

Table of Contents

Al	Abstract						
Li	List of Tables viii						
Li	st of	Figure	28	x			
A	cknov	wledgn	nents	xiii			
1	Intr	oducti	on	1			
	1.1	Critica	al Points	1			
	1.2	Order	Parameter, Susceptibility and Critical Isotherm	4			
	1.3	Univer	rsality of Amplitude Ratios	6			
	1.4	The C	oexistence Curve Diameter and Dipolar Interactions	7			
	1.5	Diffusi	vities	9			
	1.6	"Gas-(Gas Equilibrium"	11			
	1.7	Outlin	e of the Thesis	14			
2	The	eory		15			
	2.1	Critica	al Phenomena in Pure Fluids	15			
		2.1.1	Critical Exponents	15			
		2.1.2	Van der Waals Equation of State	16			
		2.1.3	Scaling	19			
		2.1.4	Lattice Gas, Ising Model and Series Expansions	22			
		2.1.5	Renormalization Group	23			

	· · ·	
	2.1.6 Implementation of the Renormalization Group	27
	2.1.7 Monte Carlo "Experiments"	28
2.2	Subtleties and Applications	29
	2.2.1 Corrections to Scaling	29
	2.2.2 Universal Amplitude Ratios	30
	2.2.3 Long Range Forces	31
	2.2.4 Asymmetric Lattice Gas and Deviation from Rectilinear Diameter	31
2.3	Dynamic Critical Phenomena: Diffusivities	33
8 C.	eral Experimental Considerations. Temperature Control and Op-	
tice	ierai Experimental Considerations. Temperature Control and Op-	37
31	Temperature Control	37
3.2	Optics	40
0.2	3.2.1 Prism Cell Experiments	41
	3.2.2 Focal Plane Interference Technique	43
	3.2.3 Image Plane Interference Technique	48
	3.2.4 Gravitational Rounding	5 5
	3.2.5 Light Scattering Experiments	56
	3.2.6 The Correlator	58
4 Exp	periments	61
4.1	Freon Experiments	61
4.2	Nicotine + Water Experiment	62
4.3	High-pressure experiment	63
	4.3.1 Cell Design	64
	4.3.2 Pressure Handling System	68.
	4.3.3 Dimensioning of the Gas Handling System	72
	v	

		4.3.4	Filling the Cell	73
		4.3.5	Thermal Control of the Cell	76
5	Free	on Exp	eriments: Results and Discussion	78
	5.1	Lorent	z-Lorenz Data	78
	5.2	Order	Parameter Measurements	82
		5.2.1	Order Parameter of $CClF_3$	82
		5.2.2	Order Parameter of CHF_3	83
	5,3	Coexis	stence Curve Diameter for CHF_3 and $CClF_3$	89
	5.4	Comp	ressibility of CHF_3	93
	5.5	Critica	al Isotherm of CHF_3	95
	5.6	Critica	al Temperature of $CClF_3$ and CHF_3	97
	5.7	Discus	sion	99
6	Nic	otine -	+ Water Experiment: Results and Discussion	105
6	Nic 6.1	otine - Order	+ Water Experiment: Results and Discussion Parameter	105 105
6	Nic 6.1 6.2	otine - Order Diffus	+ Water Experiment: Results and Discussion Parameter	105 105 109
6	Nic 6.1 6.2	otine - Order Diffus 6.2.1	+ Water Experiment: Results and Discussion Parameter	105 105 109 109
6	Nic 6.1 6.2	otine - Order Diffus 6.2.1 6.2.2	+ Water Experiment: Results and Discussion Parameter ivites Fringe Data Light Scattering Data	105 105 109 109 111
6	Nic 6.1 6.2 6.3	otine - Order Diffus 6.2.1 6.2.2 Poten	+ Water Experiment: Results and Discussion Parameter ivites ivites Fringe Data Light Scattering Data tial Sources of Error	105 105 109 109 111 117
6	Nic 6.1 6.2 6.3	otine - Order Diffus 6.2.1 6.2.2 Poten 6.3.1	+ Water Experiment: Results and Discussion Parameter ivites ivites Fringe Data Light Scattering Data tial Sources of Error Gravitational Concentration Gradients	 105 109 109 111 117 117
6	Nic 6.1 6.2 6.3	otine - Order Diffus: 6.2.1 6.2.2 Poten 6.3.1 6.3.2	+ Water Experiment: Results and Discussion Parameter ivites ivites Fringe Data Light Scattering Data tial Sources of Error Gravitational Concentration Gradients Equilibration Times	105 109 109 111 117 117 118
6	Nic 6.1 6.2 6.3	otine - Order Diffus 6.2.1 6.2.2 Poten 6.3.1 6.3.2 Discus	+ Water Experiment: Results and Discussion Parameter ivites ivites Fringe Data Light Scattering Data tial Sources of Error Gravitational Concentration Gradients Equilibration Times ssion	 105 109 109 111 117 117 118 123
6	Nic 6.1 6.2 6.3 6.4 He-	otine - Order Diffus: 6.2.1 6.2.2 Poten 6.3.1 6.3.2 Discus	+ Water Experiment: Results and Discussion Parameter ivites fringe Data Light Scattering Data tial Sources of Error Gravitational Concentration Gradients Equilibration Times ssion periments: Results and Discussion	 105 109 109 111 117 118 123 128
6	Nic. 6.1 6.2 6.3 6.4 He- 7.1	otine - Order Diffus: 6.2.1 6.2.2 Poten 6.3.1 6.3.2 Discus -Xe Exper	Water Experiment: Results and Discussion Parameter ivites ivites Fringe Data Light Scattering Data tial Sources of Error Gravitational Concentration Gradients Equilibration Times ssion periments: Results and Discussion iments on Pure Xe	 105 109 109 111 117 117 118 123 128 128

		7.1.2	Coexistence Curve Diameter and Critical Density	131	
		7.1.3	Coexistence Curve	134	
	7.2	He-Xe	Mixtures	139	
		7.2.1	Coexistence Curve	139	
		7.2.2	Compressibilities	141	
		7.2.3	Wetting	144	
	7.3	Discus	sion	147	
8	Con	clusio	ns	150	
Appendices 150					
A	Erre	or Ana	lysis for Prism Cell Measurements	156	
	A.1	Calcul	ation of refractive index from refraction angle	156	
		A.1.1	Error Estimates	158	
в	Crit	tical R	efractive Index and Critical Density of Nicotine + Water	160	
	B.1	Critica	al Refractive Index Measurement	160	
	B.2	Densit	ies of Nicotine + Water Mixtures	161	
С	The	ermal (Gradients in the Sample Cell	166	
Bi	Bibliography				

List of Tables

•

~

2.1	Values of some critical exponents, as obtained from the van der Waals		
	equation of state, experiments on pure fluids and renormalization group		
	theoretical calculations.	18	
4.1	Critical parameters of He-Xe mixtures	72	
5.1	Results of a quadratic fit to the Lorentz-Lorenz data of CHF_3 and CClF_3 .	79	
5.2	Results of coexistence curve fits for $CClF_3$	83	
5.3	Results of coexistence curve fits for CHF_3	85	
5.4	Results of fits of the coexistence curve diameter for CHF_3 and CClF_3	92	
5.5	Compressibility fits of CHF_3 data $\ldots \ldots \ldots$	95	
5.6	Critical amplitudes of CHF_3	100	
5.7	Critical amplitude ratios	100	
6.1	Results of fits of the order parameter of nicotine + water	107	
6.2	Equilibration times for quenches into the spinodal and the nucleation re-		
	gions of the phase diagram, for a binary liquid	121	
7.1	Results of fits to the Lorentz-Lorenz function in Xe	129	
7.2	Results of fits to the coexistence curve diameter of Xe	131	
7.3	Critical density of Xe	134	
7.4	Results of fits to the coexistence curve of Xe	135	
7.5	Results of coexistence curve fits of a He-Xe mixture	141	
7.6	Compressibility fits of a He-Xe mixture	143	

8.1	1 Comparison of critical polarizability product, order parameter amplitude			
	and diameter slope for substances with different strength of dipolar inter-			
	actions.	150		
8.2	Comparison of the order parameter exponent β and the correction to scal-			

ix

List of Figures

1.1	Projection of the equation of state of a pure fluid onto the $P-T$ plane .	2
1.2	Phase diagram of a pure fluid in the $T - \rho$ plane (a) and the $P - \rho$ plane (b)	2
1.3	Phase diagram of gas-gas equilibrium of the first kind	12
2.1	Schematic illustration of the motion of the Hamiltonian of a real physical	
	system under the influence of the RG transformation, in parameter space.	25
3.1	Thermal control system for conducting optical experiments on fluids close	
	to the critical point.	3 8
3.2	Refractive index profile as a function of temperature in a cell of critical	
	overall density	40
3.3	Optical setup of the prism cell experiment	42
3.4	Optics of the focal plane interference technique.	44
3.5	Formation of the Fraunhofer diffraction pattern in the focal plane	45
3.6	Schematic of the nicotine + water phase diagram	46
3.7	Schematic of the optical setup for image plane interference experiments	49
3.8	Effect of a tilted reference beam on the interference pattern	51
3.9	Optical setup for light scattering experiments.	57
3.10	Schematic diagram of the autocorrelator	59
4.1	Technical drawing of the high-pressure cell	65
4.2	Photograph of the high-pressure cell	66
4.3	Components of the windows for the high-pressure cell	68

4.4	High pressure gas handling system	70
4.5	Schematic phase diagram of the He-Xe system at 14.5°C $\ldots \ldots \ldots$	75
5.1	Lorentz-Lorenz function of CHF_3	80
5.2	Lorentz-Lorenz function of CClF_3	81
5.3	Coexistence curve of $CClF_3$	84
5.4	Coexistence curve of CHF_3	87
5.5	Coexistence curve diameter of CHF_3	89
5.6	Coexistence curve diameter of $CClF_3$	91
5.7	Compressibility of CHF_3	94
5.8	Graphical method used to extract the amplitude of the critical isotherm .	96
5.9	Drift of the critical temperature of CHF_3 as a function of time	9 8
6.1	Order parameter of the binary liquid system nicotine + water	107
6.2	Plot of the reduced order parameter of nicotine + water	108
6.3	Evaluation of the diffusivity from interferometric data in the nicotine +	
	water system	110
6.4	Concentration dependence of the diffusivity	110
6.5	Diffusivities of nicotine + water as a function of reduced temperature, as	
	measured in the interferometric experiment	112
6.6	Diffusivities of nicotine + water as a function of temperature, as measured	
	in the light scattering experiment	114
6.7	Evaluation of the effective exponent z_{eff}	116
6.8	Schematic phase diagram of nicotine + water	119
6.9	Concentration profile in a binary liquid cell after a quench into the nucle-	
	ation region of the phase diagram	122 -

6.10	Comparison of the diffusivities obtained by two different methods in the			
	nicotine + water system	4		
7.1	Lorentz-Lorenz data of Xe	0		
7.2	Coexistence curve diameter of Xe	2		
7.3	Coexistence curve of Xe, prism cell experiment	6		
7.4	Coexistence curve of Xe, interference experiment	8		
7.5	Coexistence curve of a He-Xe mixture	0		
7.6	Compressibility of a He-Xe mixture	2		
7.7	Meniscus width of a He-Xe mixture and of pure Xe as a function of reduced			
	temperature	5		
8.1	Order parameter amplitude B_0 vs. diameter slope A_1 for a variety of fluids 15	1		
8.2	Diameter slope A_1 as a function of critical polarizability product for a			
	variety of fluids	2		
A.1	Refraction geometry of the prism cell experiment	7		
B.1	Determination of the critical refractive index of nicotine + water: Plot of			
	the number of interference fringes as a function of the cell's rotation angle 16	2		
B .2	Temperature dependence of the density of nicotine + water mixtures for			
	a variety of compositions	4		

xii

Acknowledgments

I would like to thank Dr. David Balzarini for his advice and assistance during this work. I am very grateful to Dr. John de Bruyn for many discussions, instruction and assistance on the experiments, and for a critical reading of this thesis.

Many thanks also to the technical staff of the Physics Department, for their excellent work and helpful advice in many instances.

I am very grateful to UBC and the Killam Foundation for several years of scholarship support.

Finally I would like to thank my friends in the Physics Department for many interesting discussions, help and encouragement. And of course, I am grateful to Dan for his unfailing support, encouragement and interest.

Chapter 1

Introduction

1.1 Critical Points

The thermodynamic state of a pure fluid at pressure P and temperature T can be described by an equation of state [1, 2]

$$f(P,T,\rho) = 0,$$
 (1.1)

where ρ is the density. This equation defines a two-dimensional surface in the threedimensional space (P, T, ρ) . In some regions on this surface, the system is not thermodynamically stable. These regions are bordered by lines called the coexistence curves. The projection of these lines onto the P-T plane is shown in figure 1.1: There is a region of solid phase at low temperatures and high pressures, a region of gas phase at high temperatures and low pressures, and in between a region of liquid phase. At the triple point all three phases coexist. The liquid-vapour coexistence curve ends at a critical point (T_c, P_c) . Therefore it is possible to take the system from any point in the liquid region to any point in the vapour region without crossing a phase boundary. Figures 1.2a and 1.2b show projections of the coexistence curve sonto the $T - \rho$ and $P - \rho$ planes. In the $T - \rho$ plane, the coexistence curve divides the plane into a single-phase region (above the curve) and a two-phase region (below the curve) in which liquid and vapour coexist.

In general, the critical point of a system is characterized as a point in the parameter space at which a continuous transition between two phases occurs [3, 4]. In pure fluids the critical point is the end point of the liquid-vapour coexistence curve, at which point





Figure 1.1: Projection of the equation of state of a pure fluid onto the P-T plane



Figure 1.2: Phase diagram of a pure fluid in the $T - \rho$ plane (a) and the $P - \rho$ plane (b)

2

Chapter 1. Introduction

the liquid and vapour densities become the same, and in binary liquids it is the point at which the concentration difference between the two coexisting phases goes to zero. Close to the critical point, phenomena occur which are universal in two respects:

- They are present in a wide range of very different physical systems: Pure and binary fluids, magnets, superconductors, etc.
- Certain thermodynamic quantities diverge or go to zero close to the critical point as powers of the temperature difference or density difference from the critical values, with exponents which are quantitatively the same in very different systems; their values depend only on a few very general characteristics of the system.

In the last two decades, great progress has been made both experimentally and theoretically towards an understanding of critical behaviour and a determination of the critical exponents to very high accuracy. As theories make more and more precise predictions and as large computer power allows for more and more sophisticated numerical calculations, there is a need for very accurate experiments to test the theoretical predictions. Thus, experiments are carried out to approach the critical point as closely as possible so as to measure the true asymptotic behaviour.

The advantage of performing experiments on systems in their fluid state (i.e., on gas-liquid systems or on binary fluids) over experiments on solids is that the constituent particles are free to move within the system, and complications due to the underlying crystal structure, lattice defects etc. do not have to be taken into account. Also, transparent fluids can be probed using optical methods. However, in binary liquids and pure fluids the effects of gravity can hinder the observation of true critical behaviour as discussed below. In order to approach the critical point as closely as possible, systems and experimental methods have to be chosen carefully so as to reduce gravitational effects.

3

This can be attained by matching the densities of multi-component systems, or by choosing experimental techniques which are inherently less susceptible to gravitational effects. Optical interferometry is an example of such a technique which minimizes the effects of gravity. Whenever this method was not applicable, as for measuring diffusivities using light scattering, we chose a binary liquid system which is closely density matched.

As we will demonstrate in this thesis, these methods are precise and furnish results that are easy to interpret.

1.2 Order Parameter, Susceptibility and Critical Isotherm

In order to characterize the different thermodynamic phases, one defines an "order parameter" Ψ which has the property that, upon approach to the critical point in the two-phase region, it goes to zero continuously, and it is identical to zero in the one-phase region. For pure fluids, the order parameter is proportional to the density difference between the coexisting liquid and gas phases ($\Psi \propto \rho_l - \rho_v$), whereas for binary liquids (of molecular species A and B) it is proportional to the concentration difference of one species (say A) in the two coexisting phases I and $II: \Psi \propto x_A^I - x_A^{II}$. Close to the critical temperature T_c , Ψ obeys a power law with an exponent β in the reduced temperature $t = (T_c - T)/T_c$:

$$\Psi = B_0 t^{\beta}. \tag{1.2}$$

Experimentally, the exponent β was found to be a have the same value for a variety of systems [1]. These systems are said to belong to the same "universality class". The universality class of a given system is determined by its dimensionality d, the number of components n of the order parameter, and whether the interparticle forces are shortor long-range. Both binary liquids and pure fluids have d = 3, n = 1 (scalar order parameter) and short-range, van der Waals-like interactions and thus belong to the same

4

universality class. This is also the universality class of the three-dimensional Ising model, in which each site in a three-dimensional square lattice is occupied by a spin which can point either up or down and interacts with the other spins in the lattice. As the Ising model is easier to handle theoretically than microscopic theories of gases, most theoretical results have been obtained for this model. There is a one-to-one correspondence between the variables of an Ising model with those of the so-called "lattice gas" model [5]. In the lattice gas model, each site of the lattice can either be occupied by a molecule or it can be empty, with interactions between occupied neighbouring sites. The lattice gas is thus a model of a real fluid.

Besides the order parameter, there are also other quantities that exhibit power laws with universal exponents close to the critical point. One of them is the generalized isothermal susceptibility χ_T above (+) and below (-) the critical point:

$$\chi_T^{\pm} = \Gamma_0^{\pm} (\mp t)^{-\gamma^{\pm}} \tag{1.3}$$

For pure fluids, $\chi_T \propto (\partial \rho / \partial P)_T$ is the compressibility, whereas for binary liquids, $\chi_T \propto (\partial x / \partial \mu)_T$ is the "osmotic compressibility" (with μ the chemical potential and x the concentration of one of the species).

Also, along the critical isotherm, the chemical potential $\mu - \mu_c$ is expected to obey a power law in the reduced density:

$$\frac{\mu - \mu_c}{\mu_c} = D_0 \left| \frac{\rho - \rho_c}{\rho_c} \right|^{\delta}$$
(1.4)

Here, ρ_c is the critical density, $\mu_c = \mu(T_c, \rho_c)$ the critical chemical potential, and δ is another universal exponent.

The exponents β , γ and δ have been calculated for the three-dimensional Ising model both by high-temperature series expansions [6, 7] and ϵ -expansions [8, 9]. Recent results obtained by these methods agree well and yield values of β in the range from 0.325 to 0.327 and $\gamma^+ = \gamma^-$ between 1.237 and 1.241. The quantities B_0 , Γ_0^{\pm} and D_0 defined in the above equations are called the critical amplitudes. They are nonuniversal, i.e., their values depend on the particular system under consideration.

1.3 Universality of Amplitude Ratios

Scaling theory [4, 10] states that the three exponents β , γ^{\pm} and δ are connected by the two scaling relations, $\gamma^{+} = \gamma^{-}$ and $\gamma^{\pm} = \beta(\delta - 1)$. Given β and γ^{\pm} , δ thus can be calculated. One obtains δ between 4.79 and 4.82 [11]. Scaling also predicts that, even though the individual critical amplitudes are system dependent, certain combinations of them are universal. For example, the ratios $\Gamma_{0}^{+}/\Gamma_{0}^{-}$ and $D_{0}\Gamma_{0}^{+}B_{0}^{\delta-1}$ are expected to be the same for all systems in the same universality class [12]. Measurements of these amplitude ratios have been reported earlier [13, 14]. In these publications, results obtained from different experiments were combined to determine the amplitude ratios. This method, however, is subject to errors due to the different data evaluation methods and different samples used in the different experiments and, in particular, susceptible to effects caused by different determinations of the critical temperatures, which affect the critical amplitude ratios considerably. For a consistent determination of the amplitude ratios, all the amplitudes should therefore be extracted from a single experiment. In this way, the critical temperature can be determined independently in the evaluation of the various quantities, and agreement is an important check on the consistency of the results.

This approach was followed by Weber [15] and later improved by Pestak and Chan [16, 17] who used a stack of capacitors to measure the density as a function of chemical potential in Ne, N₂ and HD. Their results are very self-consistent and show good agreement with theory. However, close to the critical point, their data are affected by gravitational rounding, which they correct for by analyzing it using the restricted cubic model [18, 19].

Chapter 1. Introduction

We have measured these amplitude ratios in the pure fluid system CHF₃, a strongly polar fluid. By using an optical interference technique [20, 21] which is less susceptible to gravitational rounding, we minimized gravitational effects [22]. Like the capacitor method, our method allows measurements of the coexistence curve, compressibility and critical isotherm in a single experiment. By confining the sample to a thin cell, gravity effects are negligible even close to the critical point, so that no corrections due to gravitational rounding have to be made. We used a cell only 1.86 mm thick, which enabled us to approach the critical point as closely as $|t| \approx 10^{-6}$ without encountering appreciable errors due to gravitational rounding. For measurements on the critical isotherm, only reduced densities $\Delta \rho^* = |\rho - \rho_c|/\rho_c > 4 \times 10^{-4}$ were used for the evaluation, for which beam bending errors are less than 0.1% [23]. We have thus obtained values of the amplitude ratios Γ_0^+/Γ_0^- and $D_0\Gamma_0^+B_0^{\delta-1}$ which are probably the most accurate to date. Our data are in excellent agreement with theoretical predictions. They also agree well with measurements performed on nonpolar fluids [17], and are thus in accordance with the universality principle.

1.4 The Coexistence Curve Diameter and Dipolar Interactions

Another quantity of interest is the coexistence curve diameter ρ_d^* , defined as the average of liquid and vapour densities:

$$\rho_d^* = \frac{\rho_l + \rho_v}{2\rho_c} \tag{1.5}$$

In early experiments, the diameter was found to vary linearly with t, a property known as the "law of rectilinear diameter" [24]. In the framework of scaling theory, however, due to the lack of particle-hole symmetry in real fluids, there is a deviation from linear behaviour close to the critical point, and the diameter takes the form [25]

$$\rho_d^* = A_0 + A_{1-\alpha} t^{1-\alpha} + A_1 t. \tag{1.6}$$

Chapter 1. Introduction

Recently, this expression has been interpreted by Goldstein *et al.* in terms of the microscopic interactions of the system [26]. Within this model, the term $A_{1-\alpha}t^{1-\alpha}$ results from three-body interactions, and the amplitudes $A_{1-\alpha}$ and A_1 are related to the relative strengths of three-body and two-body interactions. If the dominant three-body interactions are of the Axilrod-Teller type [27], then the order parameter amplitude B_0 , the diameter slope A_1 and the strength of the deviation from rectilinear diameter are expected to be proportional to the dimensionless quantity $\alpha_p \rho_c$, the so-called "critical polarizability product" [28]. (Here α_p is the molecular polarizability and ρ_c is the critical density).

Recent precise measurements on a number of nonpolar fluids [26, 28, 29] indeed show a small deviation from a straight line close to the critical point, consistent with the predicted behaviour. Also, in agreement with the theory of Goldstein *et al.* [26], the diameter slope A_1 was found to vary linearly with $\alpha_p \rho_c$ in these nonpolar substances.

For polar fluids, the situation is somewhat more complex [28, 30]. Even though dipolar couplings between the molecules do not change the universality class of the system, they do influence the values of the critical amplitudes. In particular, the theory of Goldstein *et al.* predicts that the coexistence curve diameter amplitude A_1 is expected to be proportional to the quantity $\tilde{\alpha}_p \rho_c$ rather than $\alpha_p \rho_c$, where the "effective" polarizability $\tilde{\alpha}_p$ of the polar fluid includes the effects of dipole-dipole interactions and is given by

$$\tilde{\alpha_p} = \left[\alpha_p^2 + \frac{8}{3} \frac{\mu_0^2 \alpha_p}{I} + \frac{4}{9} \frac{\mu_0^4}{I k_B T_c} \right]^{1/2}.$$
(1.7)

Here, μ_0 is the molecular electric dipole moment of the molecule, I is its dissociation energy and T_c is the critical temperature.

In order to compare the behaviour of a strongly polar fluid close to its critical point to that of weakly polar and nonpolar fluids, we have carried out experiments to measure the order parameter and coexistence curve diameter of the pure fluids CHF_3 , $CClF_3$ and Xe. CHF₃ and CClF₃ have fairly similar critical temperatures, pressures and densities, but very different dipole moments: CHF₃ is strongly polar ($\mu_0 = 1.65$ D [31]), whereas CClF₃ is only weakly polar ($\mu_0 = 0.50$ D [32]). Also, CHF₃ molecules, which contain electronegative atoms together with hydrogen atoms, will form hydrogen bonds, which are absent in CClF₃. In contrast, the interactions between the nonpolar Xe atoms are purely via van der Waals interactions. Thus, by examining the critical behaviour of these three fluids, one can obtain important information about the relevance of dipolar interactions and hydrogen bonds close to the critical point. We find that in all three fluids, the relation between A_1 and B_0 is linear, in accordance with the data taken on nonpolar fluids [28]. This indicates that three-body interactions indeed play a role, as proposed by the theory of Goldstein *et al.* The expected proportionality between A_1 and $\tilde{\alpha}_p \rho_c$ is well fulfilled for CClF₃; however, Xe and CHF₃ exhibit deviations, suggesting that three-body interactions other than the Axilrod-Teller forces play a dominant role.

1.5 Diffusivities

Up to now we have only considered static critical phenomena. Their universality class was determined by the dimensionality of the system, the number of components of the order parameter and the range of the interactions. When discussing dynamic critical phenomena, the universality class is also determined by the number of relevant hydrodynamic modes [33]. In fluids and fluid mixtures, there are two relevant (and coupled) modes: the diffusive decay of the order parameter fluctuations and that of the transverse momentum fluctuations. Thus we expect pure fluids and binary fluids to belong to the same dynamic universality class and to exhibit the same critical exponents and scaling functions for dynamic as well as static properties [33].

We have performed experiments on the binary liquid system nicotine + water and

measured the generalized diffusivity D, which is proportional to the decay rate of order parameter fluctuations in the fluid mixture. According to the fluctuation-dissipation theorem [34], D can be written as the ratio of a transport coefficient ℓ and a generalized static susceptibility χ_T : $D = \ell/\chi_T$ [33]. In the case of a binary mixture, D is the concentration diffusivity, ℓ the mass conductivity and $\chi_T = (\partial x/\partial \mu)_T$ the osmotic compressibility [35]. χ_T diverges strongly at the critical point; ℓ also diverges, but more weakly than χ_T , and therefore the diffusivity D goes to zero as the critical point is approached. This phenomenon, known as "critical slowing down", reduces the speed of equilibration in the critical region and leads to long time constants close to T_c .

The conventional method for measuring diffusivities is by the method of light scattering [36, 37, 35, 38]. The light is scattered by fluctuations of the refractive index of the medium, which are related to order parameter fluctuations. The range of these fluctuations is the correlation length ξ which diverges at the critical point as $\xi \propto t^{-\nu}$. The exponent ν has a value of approximately 0.63 in pure fluids and binary mixtures. In the light scattering experiments, one keeps the fluid at a given fixed temperature in the one-phase region and probes the **equilibrium** density fluctuations; their characteristic decay time gives information about the **equilibrium** diffusivity D and is obtained by measuring the density-density autocorrelation function in the fluid.

A second method of obtaining information about the diffusivity consists of putting the system into a **nonequilibrium** situation and observing its decay to equilibrium. This corresponds to quenching the fluid under investigation from the two-phase region into the one-phase region and watching the subsequent relaxation of the density profile of the fluid in the cell under the influence of gravity. From the relaxation one can again obtain a diffusivity, which now, however, is a **nonequilibrium** diffusivity.

We performed experiments on the binary liquid mixture nicotine-water using both methods. This system is well suited for the study of critical phenomena, because the densities of the two constituents are very closely matched and thus gravity effects, which otherwise limit the accuracy of light scattering data, play a minor role. In binary liquids, the order parameter is proportional to the difference in concentration $\Delta x^* = x_A^I - x_A^{II}$ of one of the constituents (say A) in the two phases I and II.

We show that due to the density-matching of the constituents, gravitational rounding effects due to the divergence of the osmotic compressibility χ_T are negligible on the time scale of this experiment. From the light-scattering experiment, we measure the critical exponent of the viscosity and find good agreement with results of other experiments and with theory. The diffusivity measured by the interferometric method is found to be a function of the order parameter Δx^* in the two-phase region before the quench. The diffusivity is thus concentration-dependent. In the limit $\Delta x^* \rightarrow 0$, corresponding to a quench from the critical point into the one-phase region, the diffusivity data from the interferometric method are found to be consistently larger than the data from the light scattering experiment. This is the first time a comparison like this has been performed.

1.6 "Gas-Gas Equilibrium"

Finally, a set of experiments were carried out on a system that exhibits features of both a binary liquid and a gas-liquid system. Whereas in pure fluids only gas-liquid equilibria exist, three different types of two-phase equilibria have to be considered in fluid mixtures: liquid-gas, liquid-liquid, and the so-called "gas-gas" equilibria [39, 40]. They all consist of two coexisting fluid phases of different densities separated by a meniscus. At a critical point of the mixture the intensive properties of the two phases in equilibrium become identical. Whereas pure substances are characterized by a critical point for the liquidgas equilibrium, binary systems exhibit a **critical line** in three-dimensional T - p - xspace (where x is the concentration). The various phase behaviours of binary fluids can



Figure 1.3: Phase diagram of gas-gas equilibrium of the first kind: line AB corresponds to the liquid-gas coexistence curve of the less volatile conponent and ends at the critical point B. From there, the critical line of second order phase transition points starts (dashed line).

be classified by looking at the p(T) projections of these critical curves. An example of a system with liquid-liquid equilibrium was encountered above, in the binary liquid nicotine-water, under its equilibrium vapour pressure.

"Gas-gas" equilibria can occur in systems of binary fluids at pressures and temperatures **above** the critical temperature of the less volatile substance. The critical curve is interrupted and consists of two branches. The branch starting form the critical point of the more volatile component (I) ends at the so-called critical end point. The other branch begins at the critical point of the less volatile component (II) and either immediately tends to higher temperatures and pressures ("gas-gas equilibrium of the first kind", see figure 1.3) or goes through a temperature minimum first and then runs to increasing pressures and temperatures ("gas-gas equilibrium of the second kind"). The

Chapter 1. Introduction

term "gas-gas equilibrium" is somewhat confusing for these systems, because in fact both substances are, at these temperatures and pressures, beyond the critical point, and so the distinction between "gas" and "liquid" does not exist any more. Rather, the coexistence is between two supercritical fluids of differing compositions.

These phase separation effects were predicted by Van der Waals [41] and have been found in a wide range of systems (for a review see [42]). More and more sophisticated calculations of equations of state have enabled theorists to predict with reasonable accuracy which type of "gas-gas" equilibrium will be found in a given system [43], and to calculate the phase diagram. However, no investigations have been made up to now on the critical behaviour of the system along the second-order phase transition line. As the universality class of the system is the same as for binary liquids and pure fluids, we expect to observe the same critical exponents as for the three-dimensional Ising model. However, whereas the nonequilibrium density profiles in cells with pure fluids are known to relax quite fast, this process is much slower in binary liquids. We thus expect to observe a crossover from gas-liquid equilibrium at the end point of the second order critical line (pure component II) to the behaviour of a binary fluid as the concentration of component I is increased. In the vicinity of the critical line, we expect both the compressibility and the osmotic compressibility to diverge.

We have investigated the system Helium-Xenon which exhibits a "gas-gas equilibrium curve of the first kind". The phase diagram of this system has been studied by de Swaan-Arons and Diepen [44] for pressures up to 2000 atm and temperatures up to 60° C. We performed experiments on a sample of critical density and concentration of this system, containing $\approx 5\%$ He, and measured the coexistence curve, compressibility and diffusivities close to the critical point. We found no appreciable difference between the behaviour of this binary fluid sample and a pure Xenon sample, suggesting that the phase transition in this binary fluid is more of the gas-liquid type, rather than the binary liquid type. The

Chapter 1. Introduction

only effect of the presence of He in the mixture seems to be an increase in the critical temperature and the pressure of the system. This is in agreement with a recent neutron scattering experiment on a noncritical He-Xe mixture [45] which finds that the structure factor of the Xe-Xe pairs is unchanged by the presence of He-atoms.

In the two-phase region, our optical technique provided a novel way of measuring the surface tension: It enabled us to directly measure the width of the meniscus between the two coexisting phases in the cell, which is a measure of the rise height of a wetting layer on the cell windows. We used this method to extract the critical exponent of the surface tension and find it to be in good general agreement with other experiments.

1.7 Outline of the Thesis

The remainder of this thesis is organized as follows: Chapter 2 gives an overview of the theory of critical phenomena and defines the quantities which we have measured. Chapter 3 describes the optics and the data extraction from the measurement. In Chapter 4 the experimental setups of the various experiments are described. Chapter 5, 6 and 7 present the results of the freon, nicotine + water and He-Xe experiments respectively, and Chapter 8 contains the conclusions.

Chapter 2

Theory

2.1 Critical Phenomena in Pure Fluids

2.1.1 Critical Exponents

As was discussed in the Introduction, the phase diagram of a pure fluid contains a region in which the liquid and vapour phases coexist (see figure 1.2). In the P-T plane, this region is represented by the liquid-vapour coexistence curve, which ends in the critical point as shown in figure 1.1. For many fluids it is found experimentally that the variation of the liquid and the vapour densities $\rho_l(T)$ and $\rho_v(T)$ with temperature is identical for different fluids when density and temperature are rescaled by their critical values ρ_c and T_c . Since the difference in density between the phases goes to zero as the critical point is approached, the width of the coexistence curve

$$\Delta \rho^* = \frac{\rho_l - \rho_v}{2\rho_c} \tag{2.1}$$

is called the order parameter of the gas-liquid phase transition. Setting $t = (T - T_c)/T_c$, the width of the coexistence curve in many fluids is measured to behave approximately as [1] $\Delta \rho^* \propto |t|^{1/3}$. More generally, one can write

$$\Delta \rho^* = B_0 |t|^\beta \tag{2.2}$$

The exponent β is found experimentally to be the same for all fluids close to the critical point. It is thus a universal quantity.

Similarly, other thermodynamic quantities in fluids near their critical points are observed to obey universal power laws, for example:

• the specific heat above (+) and below (-) the critical point

$$C_V(T) = A_0^{\pm} |t|^{-\alpha_{\pm}}$$
(2.3)

• the compressibility above (+) and below (-) the critical point

$$\kappa_T^{\pm}(T) = \Gamma_0^{\pm} |t|^{-\gamma_{\pm}} \tag{2.4}$$

• the chemical potential along the critical isotherm

$$\frac{|\mu(\rho, T_c) - \mu_c)|}{\mu_c} = D_0 \left| \frac{\rho - \rho_c}{\rho_c} \right|^{\delta}.$$
 (2.5)

• the correlation length

$$\xi = \xi_0 t^{-\nu} \tag{2.6}$$

A satisfactory theory of critical phenomena is expected to explain why the exponents $\alpha, \beta, \gamma, \delta$ and ν are universal, and to produce numerical values for them which agree with experiment.

2.1.2 Van der Waals Equation of State

Many attempts have been made in the past to find an analytical formula describing the equation of state of a pure fluid. The earliest attempt at a quantitative description is due to van der Waals; his equation of state is

$$(P + a\rho^2)(\frac{1}{\rho} - b) = RT$$
 (2.7)

Chapter 2. Theory

where R is the gas constant and a and b are system-dependent parameters. The critical point is determined by the simultaneous conditions

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0$$
 and $\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0.$ (2.8)

The solution is $\rho_c = 1/3b$, $T_c = 8a/27bR$ and $P_c = a/27b^2$. Introducing the reduced variables $t = (T - T_c)/T_c$, $\Delta \rho = (\rho - \rho_c)/\rho_c$ and $p = (P - P_c)/P_c$, the van der Waals equation can be written:

$$p(2 - \Delta \rho) = 8t(\Delta \rho + 1) + 3\Delta \rho^3$$
(2.9)

This equation is independent of the system-dependent parameters a and b and thus has the same functional form for all gases, in agreement with the principle of corresponding states [1] which postulates that for a group of similar fluids the equation of state can be written in the form

$$p = \Phi(t, \Delta \rho) \tag{2.10}$$

where Φ is the same function for all substances in the group.

For t < 0, there is a segment along the isotherms with $(\partial p/\partial \Delta \rho)_T < 0$ (drawn as a dotted line in figure 1.2b) which corresponds to a region of mechanically unstable thermodynamic states. This is clearly not a physical solution. Instead, in this region the system demixes spontaneously into two coexisting phases, the equilibrium densities of which can be found from the van der Waals equation using the Maxwell equal-area construction. This is based on the condition that in equilibrium the chemical potential, pressure and temperature of the two phases have to be the same, and corresponds to replacing the van der Waals equation in the two-phase region by a line of constant pressure such that the areas A^+ and A^- (see figure 1.2b) are the same [34].

Eq. (2.9) can be used to extract values for the critical exponents and amplitudes in

exponent	van der Waals	Experimental	RG value
α	0	0.08 - 0.13	0.110
β	1/2	0.3 - 0.4	0.325 - 0.327
γ^{\pm}	1	1.2 - 1.3	1.237 - 1.241
δ	3	4 - 5	4.82

Table 2.1: Values of some critical exponents, as obtained from the van der Waals equation of state, experiments on pure fluids and renormalization group theoretical calculations.

the van der Waals model: Along the critical isotherm (t = 0) one obtains

$$p = 3\Delta\rho^3 (2 - \Delta\rho)^{-1} = (3/2)\Delta\rho^3 (1 + \Delta\rho/2 \pm ...)$$
(2.11)

from which one deduces, by comparison with definition (2.5), that in the van der Waals model, $\delta = 3$ and $D_0 = 3/2$. Similarly, one can calculate the isothermal compressibility

$$\kappa_T = \frac{P_c}{\rho_c} \left(\frac{\partial\rho}{\partial p}\right)_T = \left(\frac{\partial\Delta\rho}{\partial P}\right)_t = \frac{(2+\Delta\rho)^2}{24t+6\Delta\rho^2(3+\Delta\rho)}.$$
(2.12)

Along the critical isochore $(\Delta \rho = 0)$ in the one-phase region, we thus obtain $\kappa_T^+ = 1/6t$, from which we deduce, by comparison with eq. (2.4), that in the van der Waals equation $\gamma^+ = 1$ and $\Gamma_0^+ = 1/6$.

The extraction of the exponent β is much more difficult, since in the two-phase region, for any given temperature and pressure, there exist three solutions for the density, from which only two are physical. It can be shown however [34, 2] that $\beta = 1/2$ and $B_0 = 2$.

Experimentally, one finds very different values of the critical exponents in real fluids. Table 2.1 gives an overview of some experimental results in comparison with values obtained from the van der Waals equation of state. The discrepancy between the values is due to the fact that the van der Waals theory is a mean field theory, which means that it can be derived by assuming that each particle moves in the mean field of all the other particles. Mean field theories do not give the correct values for the critical exponents, because they ignore fluctuations and thus do not correctly take into account correlations which are important near the critical point. Thus, even though the van der Waals equation gives a qualitatively correct picture of the behaviour in the critical region, correlations have to be considered explicitly to obtain quantitatively correct results.

2.1.3 Scaling

Mean field theories assume that the free energy at the critical point can be expanded as a power series in integral powers of the order parameter $\Delta \rho^*$. The fact that the exponents which are found experimentally deviate strongly from the mean-field values indicates that this is not a good assumption. Rather, the free energy in the critical region will contain a singular part $f_s(T,\mu)$ which contains the leading critical behaviour. The scaling assumption postulates that f_s is a generalized homogeneous function [2], i.e., that

$$\lambda f_s(t,\mu) = f_s(\lambda^{a_t}t,\lambda^{a_\mu}\mu) \tag{2.13}$$

for any value of the number λ . By differentiating the free energy f_s with respect to its variables one obtains the various thermodynamic quantities, and one can thus express the critical exponents in terms of the exponents a_t and a_{μ} . One obtains

$$\beta = \frac{1 - a_{\mu}}{a_t}, \quad \delta = \frac{a_{\mu}}{a - a_{\mu}}, \quad \gamma^{\pm} = \frac{2a_{\mu} - 1}{a_t}, \quad \alpha^{+} = 2 - \frac{1}{a_t}.$$
 (2.14)

Since in this scaling form the free energy contains only two exponents, a_{μ} and a_t , it follows that the critical exponents are not independent, but related by so-called scaling relations:

$$\gamma^{+} = \gamma^{-} = \beta(\delta - 1) \text{ and } \alpha^{+} = \alpha^{-} = 2 - \beta(\delta + 1)$$
 (2.15)

Choosing $\lambda = t^{-1/a_t}$, one can then write singular part of the free energy as

$$f_s = t^{2-\alpha} f_s(1, \mu/|\Delta\rho|^{\delta}) \tag{2.16}$$

More scaling relations can be obtained from the conjecture that the long range correlations of density fluctuations near T_c are responsible for all singular behaviour [3]. The correlation length ξ is a measure of the range of the density fluctuations. The singularities in various physical quantities at T_c can thus be understood as a result of the divergence of ξ at T_c . Empirical data show that ξ obeys a power law close to T_c with an exponent ν (see eq. (2.6)). As ξ diverges at the critical point, close to T_c it becomes much larger than any other length scale in the system and therefore is the only relevant length scale as far as the singular behaviour of the free energy is concerned.

The density-density correlation function is a quantity that is experimentally accessible and gives information about the fluctuations in the system. The static correlation function $G(\mathbf{r})$ between the densities in infinitesimal volume elements spaced a distance \mathbf{r} apart can be written as [2]

$$G(\mathbf{r}) = \langle \rho(\mathbf{r})\rho(0) \rangle - \langle \rho \rangle^2 \tag{2.17}$$

where $< \rho >$ is the average density of the sample and is assumed to be independent of position. Away from the critical point, the correlation function is found to fall off exponentially with r for large distances. The general behaviour is therefore given by $G(r) \propto \exp(-r/\xi)$. At the critical point, the correlation length ξ becomes infinite; as the correlation function experimentally is still measured to decay to zero as $r \to \infty$, one expects an inverse power law in r for the correlation function close to the critical point:

$$G_c(r) \propto r^{-(d-2+\eta)} \quad \text{for} \quad r \to \infty$$
 (2.18)

where d is the dimensionality of the system and η is another critical exponent.

This correlation function can be measured by quasielastic light scattering. The intensity I(q) scattered at wave number q is, from the Wiener-Khinchin theorem, proportional to the Fourier transform of the correlation function:

$$I(q) \propto \int d^3 \mathbf{r} \exp(-i\mathbf{q} \cdot \mathbf{r}) G(\mathbf{r})$$
 (2.19)

On the other hand, from the fluctuation-dissipation theorem [34] it follows that the scattering intensity in the forward direction (q = 0) is proportional to the compressibility:

$$I(0) \propto \int d^3 \mathbf{r} G(\mathbf{r}) = \kappa_T^+ \tag{2.20}$$

This indicates that the phenomena observed close to the critical point,

- the increase in the size of the density fluctuations
- the increase in the range of the density correlation function
- the increase in the compressibility

are all interrelated phenomena. As a consequence one expects the exponents η and ν to be related to the thermodynamic exponents α, β, γ and δ . Indeed from the fluctuationdissipation theorem it follows that

$$\gamma = (2 - \eta)\nu \tag{2.21}$$

Furthermore, a dimensional analysis of the free energy yields the "hyperscaling relation"

$$d\nu = 2 - \alpha. \tag{2.22}$$

We thus have a scaling theory which determines all exponents from a knowledge of two of them. While the scaling relations hold for all dimensions d, the hyperscaling relation fails for dimensions $d \ge 4$, where the classical, mean field exponents are valid.

2.1.4 Lattice Gas, Ising Model and Series Expansions

In order to calculate the critical exponents, one needs a microscopic model which contains the important features of the physical system under consideration while at the same time being simple enough to be treated theoretically. For pure fluids, such a model is the socalled lattice gas model [5], which consists of a system of "occupied" and "unoccupied" sites on a lattice. In order to model the repulsive cores of the fluid molecules, we assume that each site can be occupied by at most one molecule. If two adjacent lattice sites are occupied, their interaction energy is $-\epsilon_0$. The potential between two molecules i, j is thus:

$$u_{ij} = \begin{cases} \infty & \text{if } i = j \\ -\epsilon_0 & \text{if } i, j \text{ are nearest neighbours} \\ 0 & \text{otherwise} \end{cases}$$
(2.23)

It can be shown [5] that the lattice gas is mathematically equivalent to the Ising model, which is the simplest model for treating magnetic phase transitions and has been widely analysed in the literature. Again, the space is divided up into a lattice, and each lattice point *i* is occupied by a spin s_i which can point "up" ($s_i = +1$) or "down" ($s_i = -1$). The Ising spin is thus a scalar. The simplest Hamiltonian for the interaction between Ising spins on a lattice with N sites in an external magnetic field H can be written as

$$\tilde{\mathcal{H}}_{N}(\{s_{i}\}) = -H \sum_{i=1}^{N} s_{i} - J \sum_{\langle i,j \rangle} s_{i} \cdot s_{j}.$$
(2.24)

When the strength of the interaction J > 0, this describes a ferromagnet. $\langle i, j \rangle$ indicates summation between nearest neighbours. In order to extract thermodynamic quantities from this microscopic model, one has to calculate the partition function

$$\mathcal{Z}_N = \operatorname{Tr}_{s_i = \pm 1} \exp(-\mathcal{H}_N/k_B T)$$
(2.25)
from which the total free energy (i.e., the sum of the singular part and the background term) can be obtained in the thermodynamic limit:

$$F = -k_B T \lim_{N \to \infty} \ln \mathcal{Z}_N \tag{2.26}$$

Analytic solutions exist for the one-dimensional Ising model and for the two-dimensional Ising model in zero field, but the three-dimensional model can only be solved approximately.

One approximate method, called high-temperature expansion, consists in expanding the partition function in powers of the reduced coupling strength J/k_BT [46]. In the limit of high temperatures, J/k_BT is small, and the exponential in eq. (2.25) can be approximated by a power series in J/k_BT . The various thermodynamic quantities correspond to the derivatives of the free energy and are thus also represented by a power series in J/k_BT . From the ratios of successive coefficients in these power series expansions the critical exponents can be obtained. Through tedious and time-consuming calculations, the values of the exponents are found to be [7, 47]:

$$\alpha = 0.105(10), \quad \beta = 0.328(8), \quad \gamma = 1.239(2), \quad \nu = 0.632(2)$$

2.1.5 Renormalization Group

The idea giving the deepest insight into the physics of critical phenomena is the application of the renormalization group (RG) transformation to systems close to the critical point [48, 49]. The RG is capable of explaining scaling, universality and where the critical power laws come from.

The effective Hamiltonian $\mathcal{H} = \tilde{\mathcal{H}}/k_B T$ is a function of a set of parameters $\{K, h, ...\}$, with $K = J/k_B T$, $h = H/k_B T$, etc. The set of all Hamiltonians $\mathcal{H}(K, h, ...)$ forms a space of Hamiltonians in which every Hamiltonian $\mathcal{H}(K, h, ...)$ is represented by a point.

The dimensionality of this space is, in general, infinite. The renormalization group is a set of transformations on the set of parameters $\{K, h, ...\}$ of the system's Hamiltonian.

In practical terms, the RG transformation consists in partially carrying out the trace in the partition function, thus summing over selected spins while leaving others unaffected. By carrying out this partial sum, one decimates the number of spins in the trace, while replacing the parameters $\{K, h, ...\}$ in the Hamiltonian by new, effective, "renormalized" parameters $\{K', h', ...\}$. Thus the RG procedure can be written formally as

$$\mathcal{H}'(K',h',\ldots) = \mathcal{R}(\mathcal{H}(K,h,\ldots)) \tag{2.27}$$

A fixed point $\{K^*, h^*, ...\}$ of the renormalization group satisfies the equation

$$\{K^*, h^*, \ldots\} = \mathcal{R}\{K^*, h^*, \ldots\}$$
(2.28)

This fixed point can be shown to coincide with a critical point: if we rescale the whole lattice by a factor b, i.e., substitute each "block" of b^d lattice sites (b > 1) by a single new renormalized spin, then in the new lattice the correlation length ξ' has the length $\xi' = \xi/b$. The RG transformation thus has the effect of reducing the correlation length, which is equivalent to driving the system away from criticality. As ξ is a function of the parameters $\{K, h, ...\}$, the flow of the correlation length under the RG transformation can be written as $\xi(K, h, ...) \rightarrow \xi(K', h', ...) = \xi(K, h, ...)/b$. At the fixed point of the transformation this implies that $\xi(K^*, h^*, ...) = \xi(K^*, h^*, ...)/b$, which, since b > 1, has the solutions $\xi^* = \infty$ (critical point) or $\xi^* = 0$ (trivial fixed point). The divergence of the correlation length was recognized earlier as the crucial feature of a critical point, and we conclude that the fixed point of the RG transformation is a critical point.

How is all of this related to "real" systems? Figure 2.1 illustrates the consequences of an RG transformation on the Hamiltonian of a real system. In the space spanned by the parameters of the system, the Hamiltonian corresponding to the neighbourhood of the



Figure 2.1: Schematic illustration of the motion of the Hamiltonian of a real physical system under the influence of the RG transformation, in parameter space.

25

"physical critical point" of, say, Xenon, is expressable as a function of the parameters t and μ as $\mathcal{H}^0(t,\mu)$. At the critical point $(t = 0, \mu = 0)$, we have $\xi = \infty$; however, $\mathcal{H}_c^0 = \mathcal{H}^0(0,0)$ is in general not a fixed point. After an RG transformation, we obtain a renormalized set of Hamiltonians $\mathcal{H}'(t',\mu')$ into which is embedded the renormalized critical Hamiltonian $\mathcal{H}'_c = \mathcal{R}(\mathcal{H}^0_c)$. Thus, under repeated RG transformations, a line of critical points is generated. The Hamiltonian wandering along this line may eventually end up at a fixed point \mathcal{H}^* , at which the RG does not cause any further motion. That means that the initial Hamiltonian \mathcal{H}^0 lies on the stable critical manifold of the fixed point \mathcal{H}^* . All systems lying on the critical manifold of the same fixed point will display identical critical behaviour because they flow to the same point under RG transformations. This explains the concept of universality classes. If the initial Hamiltonian is perturbed in such a way that it lies in a manifold flowing into a different fixed point, then this perturbation is relevant. For our example of the critical point of a fluid, this is true for the parameters t and μ . They are called relevant scaling fields (i.e., in order for the system to be at the critical point, they have to be zero), whereas other parameters of the system (like the shape of the molecules or short-range interactions between them) are irrelevant.

Close to the critical point, the RG transformation, which in general is nonlinear, can be linearized. As a consequence of the semi-group property of the RG, the eigenvalues of the linearized transformation can be expressed as $\Lambda_1 = b^{\lambda_1}, \Lambda_2 = b^{\lambda_2}, \dots$ Small deviations from the critical point can then be written as linear combinations of the eigenvectors belonging to these eigenvalues. If $\lambda_i > 0$, then $\Lambda_i > 1$ for b > 1, and successive RG transformations carry the system away from criticality; the conjugate scaling fields are then called **relevant**. If $\lambda_i < 0$, then $\Lambda_i < 1$, and successive RG transformations eventually make these terms imperceptibly small; the conjugate scaling fields are **irrelevant**. The fixed point is thus insensitive to irrelevant variables, but depends strongly on the

relevant variables. In the vicinity of the fixed point, where the RG transformation can be linearized, the linear scaling fields g_i behave like

$$g_i' = g_i \Lambda_i = b^{\lambda_i} g_i \tag{2.29}$$

under the RG transformation. Since each RG iteration changes the length scale of the system by a factor of b, the free energy per unit volume transforms as

$$f[\mathcal{H}'] = b^d f[\mathcal{H}]. \tag{2.30}$$

Expressed in the set of scaling fields $t, \mu, g_i, ...,$ the flow equation for the free energy then takes the asymptotic form

$$f(t,\mu,g_i,...) = \frac{1}{b^d} f(b^{\lambda_1}t,b^{\lambda_2}\mu,...,b^{\lambda_i}g_i,...) = t^{2-\alpha} f(1,\mu/t^{\delta\beta},...,g_i/t^{\phi_i},...)$$
(2.31)

choosing $b^{\lambda_1} = 1/t$ and setting $\lambda_1 = d/(2 - \alpha)$, $\lambda_2 = \delta\beta d/(2 - \alpha)$ and $\lambda_i = \phi_i d/(2 - \alpha)$, where ϕ_i is a so-called correction to scaling exponent. Bearing in mind that $\Delta \rho \propto t^{\beta}$, this equation is seen to be identical to eq. (2.16). The scaling form of the free energy thus follows in a natural way from the RG transformation.

2.1.6 Implementation of the Renormalization Group

In order to calculate numerical values for the exponents, the RG has to be implemented explicitly, starting from a microscopic model of the system under consideration. This can be accomplished either in real space [50] or in momentum space [48, 49]. Once the RG transformation has been constructed, fixed points can be found and tested for stability. For Ising models of dimensionality d < 4, the classical (mean field) fixed point is found to be unstable, and the system flows instead into the so-called Ising fixed point under RG transformations. The critical exponents are obtained from the eigenvalues

of the linearized RG transformation around that fixed point (see eq. (2.31)). For the three-dimensional Ising model one obtains [51, 52]:

$$\alpha = 0.116, \quad \beta = 0.325, \quad \gamma = 1.238, \quad \nu = 0.628.$$

2.1.7 Monte Carlo "Experiments"

One way to check the theoretical results and to develop a quantitative understanding of the local microscopic correlations in a system (which are not accessible to experiment) is to carry out computer simulations on a lattice, producing various microstates of the system and summing over them with their respective thermodynamic weights. These "Monte Carlo Experiments" give some insight into the thermodynamic states that a system goes through under thermodynamic equilibrium conditions. In particular, the evolution of fluctuations can be followed explicitly. Monte Carlo simulations also give values of the critical exponents and critical amplitudes. However, due to limited computer power and time, the "thermodynamic limit" $N \to \infty$ is not directly accessible but has to be obtained by extrapolation of data obtained for finite (and actually quite small) N. Since the correlation length $\xi \to \infty$ as the critical point is approached, the size of the lattice used in the simulation limits the degree to which the critical point can be approached.

This problem can be avoided by combining Monte Carlo (MC) simulations with RG analysis of the critical properties [53, 10]. The MC simulation on a system at its critical point produces a sequence of microscopic configurations, and the RG is applied directly to these individual configurations, yielding a sequence of configurations for the "blocks". As the original Hamilitonian is critical, the renormalized Hamiltonian flows towards the fixed point. This model yields accurate values for the exponents [54]:

$$\alpha = 0.113, \quad \beta = 0.324, \quad \gamma = 1.238, \quad \nu = 0.629.$$

2.2 Subtleties and Applications

In this section we look at some consequences of the theory developed above, and their applications to real fluid systems.

2.2.1 Corrections to Scaling

The terms in the free energy (see eq. (2.31)) containing the scaling fields g_i deserve some consideration, because they are of importance in experimental situations where data are taken not only in the critical region, but also further away from the critical point. If the exponent $\phi_i < 0$, then g_i is an irrelevant variable, and the free energy close to T_c can be expanded in powers of $g_i t^{-\phi_i}$; this leads to the so-called **corrections to scaling** [55]. The exponents ϕ_i can be calculated from the RG equations. In Ising-like systems, the most important correction exponent Δ is due to the scaling field u in the Landau-Ginzburg-Wilson expansion [4] and is irrelevant for dimensions d < 4. It has been calculated to be $\Delta \approx 0.5$ [6, 7, 8, 56]. In addition to these singular corrections to the asymptotic scaling form, there are also analytic corrections due to the fact that at appreciable distances from the critical point, the linearization of the RG transformation is no longer valid and terms nonlinear in the scaling fields have to be included. This leads to added terms of the form t, t^2, \ldots . Since Δ is found to be so close to 0.5 for the three-dimensional Ising model, these terms can be assumed to have exponents of $2\Delta, 4\Delta$ etc. [11].

Taking these corrections to scaling into account, the order parameter then can be written

$$\Delta \rho^* = B_0 t^\beta (1 + B_1 t^\Delta + B_2 t^{2\Delta} + ...) \tag{2.32}$$

Other thermodynamic quantities can be expanded in a similar way into power series in t^{Δ} .

For large reduced temperatures, the correction to scaling expansion requires too many

correction terms and therefore too many parameters to be useful. Here, an equation of state incorporating the crossover to classical mean field behaviour can be introduced [57].

In the experiments of this thesis, corrections to scaling play a role in all the pure fluids considered and the exponent Δ can be determined with considerable accuracy.

2.2.2 Universal Amplitude Ratios

From the free energy in eq. (2.16) follows an equation of state [58, 59]

$$\Delta \mu^* = (\mu - \mu_c)/\mu_c = \Delta \rho |\Delta \rho|^{\delta - 1} h(x), \quad \text{with} \quad x = t/|\Delta \rho|^{1/\beta}$$
(2.33)

where h is a nonuniversal function. By rescaling the function h and the variable x by two (nonuniversal) constants h_0 and x_0 , this equation of state can be made universal; i.e., the rescaled function $\tilde{h}(\tilde{x}) = h(x/x_0)/h_0$ is the same for all systems in a given universality class. Thus, from the knowledge of the two system-dependent scale factors h_0 and x_0 all critical amplitudes can be calculated. This leads to universal relations between the critical amplitudes [12], analogous to the scaling laws for the exponents. For example [12], $B_0 = x_0^{-\beta}$, $D_0 = h_0$ and $\Gamma_0^+ = x_0^{\gamma} h_0^{-1} \lim_{\tilde{x}\to\infty} [\tilde{x}^{\gamma}/\tilde{h}(\tilde{x})]$. Using the scaling relation $\gamma = \beta(\delta - 1)$, it follows that

$$R_{\chi} = \Gamma_0^+ D_0 B_0^{\delta-1} = \lim_{\tilde{x} \to \infty} [\tilde{x}^{\gamma} / \tilde{h}(\tilde{x})]$$

$$(2.34)$$

is independent of h_0 and x_0 and is thus universal. Similarly,

$$R_{\Gamma} = \Gamma_0^+ / \Gamma_0^- \tag{2.35}$$

can be shown to be universal [12]. R_{χ} and R_{Γ} have been calculated by high-temperature series expansion and by implementation of the renormalization group (ϵ -expansion [4]) and have been found to have values $R_{\Gamma} \approx 4.8 - 5.07$ and $R_{\chi} \approx 1.6 - 1.75$ [12]. Similarly, certain ratios of the correction to scaling amplitudes are expected to be universal [60, 61]. We have measured the quantities R_{χ} and R_{Γ} in the polar fluid CHF₃. Our experiments give the most accurate experimental values to date for these amplitude ratios. The results are discussed in Chapter 5.

2.2.3 Long Range Forces

If there are long-range forces present between the molecules of the fluid, for example dipolar forces varying as $1/r^3$ between molecules with permanent electric dipole moments, will they affect the universality class? In ferromagnets, dipolar interactions can be shown to be relevant and thus change the universality class of the system [62]. In fluids, however, the dipolar interaction does not couple to the order parameter, and therefore, when calculating the partition function in eq. (2.25), the trace over the orientations of the dipoles can be performed independently of the configurational trace [63]. As the angle integral over dipolar interactions is zero, the lowest contribution is proportional to $1/r^6$ and is irrelevant to the Ising fixed point [64]. The dipolar coupling therefore does not change the universality class of the fluid, and we expect polar fluids to exhibit the same critical exponents and amplitude ratios as nonpolar ones. This hypothesis is tested in this thesis by comparing results of experiments on CHF₃, a strongly polar fluid, with those on CClF₃, a weakly polar fluid, and Xe, a nonpolar fluid. These experiments are described in Chapters 5 and 7.

2.2.4 Asymmetric Lattice Gas and Deviation from Rectilinear Diameter

In section 2.1.4 we found that the lattice gas model is useful because it maps onto the Ising model, and because it correctly describes many features of real fluid systems. The lattice gas has the property that the sum of the liquid and vapour densities is constant [5], which closely resembles the "law of rectilinear diameter" [24], found experimentally to

be quite well obeyed for fluids. The lattice gas model is artificial, however, in assuming symmetrical behaviour of occupied lattice sites (particles) and empty ones (holes).

Some models have been invented that circumvent this shortcoming [65, 66] by treating the fluid particles as interpenetrable spheres rather than point particles on a lattice. In these models, the law of rectilinear diameter is no longer obeyed. Rather, close to the critical point, the diameter acquires the leading temperature dependence

$$\rho_d = \frac{\rho_l + \rho_v}{2\rho_c} = 1 + A_{1-\alpha} t^{1-\alpha} + \dots$$
 (2.36)

The exponent α is identical to the specific-heat exponent. An alternate way of obtaining the same result [67] is by extending the scaled equation of state, valid in the close proximity of the critical point, by a parametric representation, thereby introducing corrections to scaling. Even though the law of rectilinear diameter is violated, the scaling relations between the exponents can be shown to be still valid in these models [68], and the universality class of the system is still the same as that of the Ising model [69].

Recently, a microscopic theory [26] has interpreted this deviation of the diameter from a straight line as resulting from many-body interactions between the fluid molecules. The strength and direction of the deviation from rectilinear diameter thus give information about the importance of many-body interactions.

We have carried out experiments to measure the critical behaviour of the coexistence curve diameter in CHF_3 , $CClF_3$ and Xe. Both CHF_3 and $CClF_3$ exhibit a diameter singularity close to the critical point, in accordance with the microscopic theory. This singularity is absent in Xe, indicating that interactions not included in the microscopic theory play a role in this system.

2.3 Dynamic Critical Phenomena: Diffusivities

By measuring the spectrum of light scattered from a fluid sample close to the critical point, one can obtain information about the order parameter fluctuations and their decay times. The two relevant hydrodynamic modes in a fluid correspond to two types of decay processes and give rise to two types of lines in the spectrum of the scattered radiation: The line due to the thermal fluctuations is centered at the incident frequency, and its width is proportional to the the diffusivity D; mechanical fluctuations, or equivalently phonons, produce lines shifted from the incident frequency by an amount $\pm \Delta \omega$, proportional to the sound velocity in the medium [70].

To obtain information about the dynamics of the system, one wants to measure time-dependent correlation functions. The quantity of interest is the order-parameter correlation function, obtained from measurement of the autocorrelation function $< \delta n^*(\mathbf{r}, \tau) \delta n(\mathbf{r}, 0) >$ of refractive index fluctuations at times τ and 0 in an infinitesimal volume of fluid centered at position \mathbf{r} . Equivalently, one can investigate its Fourier transform $< \delta n^*(\mathbf{q}, \tau) \delta n(\mathbf{q}, 0) >$. By assuming a linear relation between $\delta n(\mathbf{q}, \tau)$ and the scattered electric field $E_s(\mathbf{q}, \tau)$, one can relate the order parameter correlation function to the electric field correlation function

$$g^{(1)} = \langle E^*(\mathbf{q}, \tau) E(\mathbf{q}, 0) \rangle / \langle E^* E \rangle.$$
(2.37)

In practice, the electric field itself cannot be detected, but only its intensity. Thus, the simplest correlation function that can be determined experimentally is the intensity correlation function

$$g^{(2)} = \langle I(\mathbf{q}, \tau) I(\mathbf{q}, 0) \rangle / \langle I \rangle^{2}, \qquad (2.38)$$

where $\langle I \rangle = \langle E^*E \rangle$. If the scattered field is Gaussian distributed (which is normally the case when the number of scattering centers is high, i.e., when the correlation length is much smaller than the linear dimension of the scattering volume), it can be shown that [71]

$$g^{(2)}(\mathbf{q},\tau) = 1 + \Upsilon |g^{(1)}(\mathbf{q},\tau)|^2, \qquad (2.39)$$

where Υ is a factor of order unity depending on the scattering geometry.

The order parameter correlation function, to a good approximation, decays exponentially [35]:

$$\frac{| < \delta n^{*}(\mathbf{q},\tau) \delta n(\mathbf{q},0) > |}{|\delta n(\mathbf{q})|^{2}} = \frac{| < E^{*}(\mathbf{q},\tau) E(\mathbf{q},0) > |}{< I(\mathbf{q}) >} = \exp(-\Gamma(\mathbf{q})\tau), \quad (2.40)$$

with $\Gamma(\mathbf{q}) = D(\mathbf{q})q^2$. Here, $D(\mathbf{q})$ is the wavenumber dependent diffusivity. The halfwidth $\Gamma(\mathbf{q})$ measured in the autocorrelation measurements is identical to the linewidth of the Rayleigh line, which is the central line in the spectrum of the scattered radiation [70].

In the hydrodynamic limit $q\xi \ll 1$, when the characteristic length of the order parameter fluctuations is much smaller than the wavelength of light, the diffusivity can be written as the ratio of a generalized conductivity ℓ and a generalized susceptibility χ as

$$\lim_{q \notin \to 0} D(\mathbf{q}) = \ell/\chi. \tag{2.41}$$

 χ diverges strongly at the critical point, with an exponent $\gamma \approx 1.24$, and ℓ is also expected to exhibit a singular behaviour close to T_c . The main contribution to the anomaly in ℓ comes from couplings between the hydrodynamic modes [72, 73]. In the framework of the mode-coupling theories, the conductivity can be expressed in terms of the generalized susceptibility χ and the shear viscosity $\bar{\eta}$ as [33]

$$\ell\bar{\eta} = Rk_B T \chi \xi^{2-d}.\tag{2.42}$$

Similar results have been obtained by renormalization group calculations [74]. Using this the singular part of the diffusivity can be written as [75]:

$$D^{s}(\mathbf{q}) = D(\mathbf{q}) - \bar{D} = \left(\frac{Rk_{B}T}{\bar{\eta}\xi}\right)\Omega(q\xi), \qquad (2.43)$$

where \overline{D} is the nonsingular background contribution to the diffusivity. Experimentally, \overline{D} can be obtained by extrapolating diffusivity data taken far from critical into the critical region [76]. It can be written as $\overline{D} = \ell_0/\chi(q)$, where ℓ_0 is the background contribution to the conductivity. R is a universal constant and is expected to have a value of $R = 1/6\pi$ (from mode coupling calculations), or $R = 1/5\pi$ (from renormalization group calculations). The shear viscosity $\overline{\eta}$ consists of a background term η^0 and a singular term η^s : $\overline{\eta} = \eta^0 + \eta^s$. Close to T_c , the dynamic renormalization group predicts η^s to diverge as $\xi^{z_{\eta}}$ [33, 75], whereas in mode-coupling theory the viscosity, to a first approximation, can be written as $\overline{\eta} = \eta^0 [1 + (8/15\pi^2) \ln(Q\xi)]$, with Q a system-dependent amplitude [33]. The two predictions agree if one considers $\overline{\eta}$ to obey a power law

$$\bar{\eta} = \eta^0 (Q\xi)^{z_\eta}. \tag{2.44}$$

The viscosity exponent $z_{\eta} = 8/15\pi^2 = 0.054$ [77] is related to the static exponent η introduced in eq. (2.18) by a scaling law [33].

The universal dynamic scaling function Ω has the form [78]

$$\Omega(x) = \Omega_K(x) [1 + (x/2)^2]^{z_\eta/2}$$
(2.45)

with the Kawasaki function [73]

$$\Omega_K(x) = (3/4x^2)[1 + x^2 + (x^3 - 1/x)\arctan x]$$
(2.46)

According to eq. (2.43), the linewidth of the decay curve can be written as a power law in the scattering vector q:

$$\Gamma(q) = q^{z} \Omega(q\xi). \tag{2.47}$$

The dynamic scaling function satisfies the boundary conditions:

$$\lim_{x \to \infty} \Omega(x) = C_{\infty} x^{-(1+z_{\eta})} \quad \text{and} \quad \lim_{x \to 0} \Omega(x) = C_0$$
(2.48)

where C_0 and C_{∞} are constants. The dynamic scaling exponent z and the viscosity exponent z_{η} should obey the scaling relation

$$z = 3 + z_{\eta}.$$
 (2.49)

This can be used to obtain an estimate of the viscosity exponent from autocorrelation measurements, even if the viscosity itself is not being measured.

In Chapter 6 of this thesis, experiments to measure the diffusivity in the binary liquid system nicotine + water are described. Two different experimental techniques were used, and their results are compared. From the light-scattering data, the exponent z_{η} can be determined.

Chapter 3

General Experimental Considerations: Temperature Control and Optics

This chapter describes the general experimental techniques used. In section 3.1 the temperature control system is discussed. In section 3.2 the optical methods are introduced and the physical quantities of interest are derived.

3.1 Temperature Control

In order to obtain data on the asymptotic power laws close to the critical point, measurements have to be extended into the scaling region which, for pure fluids, is limited to reduced temperatures $t \leq 10^{-4}$. Approaching the critical point so closely requires very precise temperature control: For the fluids investigated in this thesis, which have $T_c \approx 300$ K, reduced temperatures of the order of $t \approx 10^{-5}$ corresponds to stabilizing the system at 3mK from the critical point. Thus we needed a temperature control system that controlled the cell temperature to within at least 1mK over several hours.

This was accomplished by placing the sample cell in the center of a two-stage thermostat (see Figure 3.1). The inner heating stage consisted of a copper or aluminium block wrapped with heating wire or heating foil. A thermistor embedded in this block sensed its temperature and formed one arm of a Wheatstone bridge. The remaining arms were formed by a decade resistance box and, in series with standard resistors, a potentiometer which could be turned by switching on a toy motor. The error signal of the Wheatstone bridge was fed into an HP nullmeter (model #419A DC) which amplified it; the output of the HP served as the input of a Kepco operational power supply (model OPS 7-2). Chapter 3. General Experimental Considerations: Temperature Control and Optics 38



Figure 3.1: Thermal control system for conducting optical experiments on fluids close to the critical point.

The output of the OPS drives a heater on the metal block encasing the sample cell. The OPS was supplemented by an "amplification box" which enabled us to vary the time response and the amplification of the heater circuit.

The switching of the toy motor driving the Wheatstone bridge was controlled by a Commodore PET computer: A "Sweeping Program" written in BASIC contained information on the number of sweeps, the sweep times (i.e., the "on" times of the motor) and the waiting times between individual sweeps. It also contained commands to light LEDs which could be used as time markers on the film used to record the data. The output of the PET was fed into an interface box, which contained a solid-state switch for turning the motor on and off. Details of the computer-motor interface are found in Ref. [79].

The innermost heating stage was surrounded by a layer of styrofoam 2.5 cm thick, followed by an outer heating stage which consisted of a cylindrical shell of copper to which 3/8" copper tubing was soldered. For the CHF₃, CClF₃ and He-Xe-experiments water from a temperature regulated bath (FORMA model # 2095) was circulated through the copper tubing and kept the cylinder at a chosen temperature, always between 0.5° and 1.0° below the cell temperature. In the nicotine + water experiment the critical temperature was about 61°C, where water evaporates at a fairly high rate, so the outermost heating stage was heated electrically.

In the nicotine + water and the He-Xe setups, a passive heat shield, consisting of a cylindrical shell of 1/16" thickness copper sheet, was inserted into the insulation between the inner and outer shells. Windows in the metal thermal stages and the styrofoam allowed an expanded laser beam to be fed through the cell.

Chapter 3. General Experimental Considerations: Temperature Control and Optics 40



Figure 3.2: Refractive index n as a function of height z in a cell of critical overall density. (a) Two-phase region, (b) one-phase region close to T_c and (c) one-phase region far from T_c .

3.2 Optics

In this section we discuss the optical setups for the experiments and derive formulas for the quantities that can be obtained from the experiments.

Figure 3.2 shows the refractive index profiles in a cell of critical overall density as the temperature is changed. Far below the critical point $(T << T_c)$, two phases of different refractive index coexist in the cell, separated by a sharp transition line called meniscus (see figure 3.2a). Far inside the one-phase region, the refractive index is homogeneous over the whole cell, as shown in figure 3.2c. Close to the critical point, in a pure fluid the compressibility $(\partial \rho / \partial P)_T$ diverges, leading to a strongly curved refractive index profile inside the cell (figure 3.2b). In binary liquids, the corresponding osmotic susceptibility $(\partial x / \partial \mu)_T$ diverges, but in a much smaller temperature region close to the critical point. Due to the very similar densities of the constituents, the divergence of the osmotic susceptibility is not observable in the nicotine + water experiment.

The refractive index profile contains a wealth of information about various thermodynamic properties of the system. In order to utilize it, though, in pure fluids the refractive index has to be related to the fluid's density, and in binary liquids to the composition. An experimental method which provides the link between the refractive index and the density in pure fluids, is described in section 3.2.1. An estimate of the concentration dependence of the refractive index in nicotine + water is presented in chapter 6.

The interference methods used in this thesis are geared to mapping out the refractive index profile as a function of temperature. Sections 3.2.2 and 3.2.3 describe these methods and outline the data analysis procedures. Limitations of the methods due to gravity effects are discussed briefly in section 3.2.4. Finally, Section 3.2.5 describes how diffusivities can be measured by light scattering.

3.2.1 Prism Cell Experiments

The prism cell experiment can be used to measure the density and the refractive index of the fluid simultaneously. Thus it gives information on the Lorentz-Lorenz function $\mathcal{L}(\rho)$ which characterizes the density dependence of the refractive index n:

$$\rho \mathcal{L}(\rho) = \frac{n^2 - 1}{n^2 + 2}$$
(3.1)

The sample cell used for these experiments [80] had an aluminium body with a prismshaped head. Two sapphire windows mounted on the prism faces allowed a laser beam to be shone through the cell's head. By measuring the deflection angle of this laser beam from the incident direction one can deduce the refractive index of the medium inside the cell. This calculation is carried out in Appendix A.

Figure 3.3 shows a schematic of the optical setup: The expanded beam from a He-Ne laser passes through the prism and hits a micrometer driven mirror (Lansing Research Corp. model 10.253) which reflects it into an autocollimating telescope (Davison model



Figure 3.3: Optical setup of the prism cell experiment.

D275). By adjusting the angle of the mirror, the deflection angle due to refraction by the prism and thus the refractive index can be measured. A reference beam passing outside the cell is used to monitor the stability of the alignment.

In order to obtain precise measurements, a series of calibrations had to be carried out. Appendix A describes these calibrations and shows the effects of the various errors on the results.

The measurements of the Lorentz-Lorenz function proceeded as follows: The cell, containing a measured mass of fluid, was cooled into the two-phase region where the fluid phase separates into liquid and vapour phases, in each of which the refractive index is temperature-dependent. The temperature of the cell was then raised until the system passed from the two-phase region into the one-phase region where the refractive index becomes essentially independent of temperature. The refractive index was measured just above the coexistence curve in the one-phase region. The mass of the fluid in the cell and thus its density was determined by weighing the cell on a chemical balance. By repeating this procedure for different overall densities, the Lorentz-Lorenz coefficient \mathcal{L} was measured and thus the relationship between density and refractive index on the coexistence curve obtained. Details of the calibrations are given in Appendix A.

For the measurement of the coexistence curve and its diameter, the prism cell was filled with the fluid at its critical density. In the two-phase region, the refractivities of both liquid and vapour phases were measured as a function of temperature and converted to densities using the Lorentz-Lorenz relation. After changing the cell temperature, the system was allowed to equilibrate for at least two hours. This experiment thus yielded $\rho_l(T)$ and $\rho_v(T)$ along the coexistence curve, from which the order parameter and the diameter could be calculated.

3.2.2 Focal Plane Interference Technique

Figure 3.4 shows the optical setup of the focal plane experiments. The sample was contained in a flat cell of length L with parallel windows, which was placed in a thermostatic block. A laser beam from a He-Ne laser, expanded by a pinhole filter and then collimated into a parallel beam, traversed the sample cell. The light was then collected by a focussing lens which was positioned as closely behind the cell as physically feasable to collect as much of the refracted radiation as possible. In the focal plane of this lens, a Fraunhofer interference pattern was formed which contains information on the refractive index profile in the cell. A slit camera with continuous film transport was used to record the interference pattern as a function of time on film.

We now derive the formulae necessary for the interpretation of the data. The Fraunhofer diffraction pattern from a flat cell far from the critical point (see Fig. 3.2a and 3.2c) is just a point. As the cell temperature is changed from a temperature T_i in the two-phase region to a temperature T_f in the one-phase region, the refractive index profile inside the Chapter 3. General Experimental Considerations: Temperature Control and Optics 44



Figure 3.4: Optics of the focal plane interference technique.

cell evolves from the profile given in figure 3.2a to the one in 3.2c.

The construction of the interference pattern due to an intermediate density profile is shown in figure 3.5. A ray travelling in the y-direction through a medium with varying refractive index n(z) is being bent by an angle θ given by

$$\frac{d\theta}{dy} = -\frac{1}{n}\frac{dn}{dz} \tag{3.2}$$

For a thin cell, where the total bending is small, eq. 3.2 can be integrated to give the total deflection angle θ_i inside the cell

$$\theta_i = -L \, \frac{1}{n} \, \frac{dn}{dz} \tag{3.3}$$

where L is the cell thickness. Upon emerging from the cell, the ray is refracted according to Snell's law: $n \sin \theta_i = n_{air} \sin \theta$, where θ is the angle at which the ray leaves the cell. One thus obtains

$$\theta = -\frac{L}{n_{air}} \frac{dn}{dz} \tag{3.4}$$





Figure 3.5: Formation of the Fraunhofer diffraction pattern in the focal plane.

for the total bending angle of a ray passing through a cell of length L at a height z where the refractive index profile exhibits a slope (dn/dz).

Two rays entering the cell at heights z_1 and z_2 where the gradient of the refractive index profile at z_1 and z_2 is the same are bent by the same angle θ and thus are mapped onto the same spot in the focal plane. They will interfere constructively if the total optical path difference between them is an integral multiple of the laser wavelength. The multitude of rays passing through the cell in the height interval $[z_{min}, z_{max}]$ around the meniscus thus gives rise to a pattern of light and dark interference spots in the focal plane. This pattern, which changes with time after a change of the cell temperature, is recorded on film. This experimental method was used to measure the order parameter and the diffusivity of a binary liquid mixture. In a binary liquid of two constituents A and B, the order parameter Δx^* is proportional to the difference in concentration of one species, say A, in the two coexisting phases I and II. Thus $\Delta x^* \propto x_I^A - x_{II}^A$. The relation between the

Chapter 3. General Experimental Considerations: Temperature Control and Optics 46



Figure 3.6: Schematic of the nicotine + water phase diagram. Temperature is plotted as a function of refractive index which is proportional to the concentration of nicotine [81]. The order parameter is proportional to the refractive index discontinuity in the two-phase region.

refractive index Δn and the order parameter Δx^* for the binary liquid nicotine + water can be approximated by assuming a linear relationship between Δn and Δx^* [81]. The interferometric data can then be used to measure the order parameter and the diffusivity.

Order Parameter

The refractive index discontinuity $n_1 - n_2$, of the initial refractivity profile at a temperature $T = T_i$ in the one-phase region can be measured by quenching the system into the one-phase region and counting the total number of interference minima $N_m(T_i)$. Figure 3.6 illustrates the various quantities in an inverted phase diagram of the type encountered in the nicotine + water system. The difference $n_1 - n_2$ is related to the Chapter 3. General Experimental Considerations: Temperature Control and Optics 47

number of minima $N_m(T_i)$ by

$$n_1 - n_2 = \Delta n(T_i) = (N_m(T_i) - 1/2)\lambda/L$$
(3.5)

where λ is the laser wavelength and L the thickness of the cell. The temperature dependence of the order parameter was obtained by repeated quenches from the two-phase region into the one-phase region for different initial temperature T_i . A set of experiments then proceeded in the following way [82]: The sample cell was removed from the thermostat, mixed by shaking, and then replaced and heated to a temperature $T_i^{(1)}$ in the two-phase region, where demixing into two liquid phases occurs. After an equilibration period of several hours, the cell was quenched into the one-phase region in one temperature step which was quick on the time scale of the diffusivity, but slow enough to avoid convection in the cell. The interference pattern due to the relaxation of the concentration profile was recorded on film in the focal plane. The number of interference minima was used to calculate $\Delta n(T_i^{(1)})$. Subsequently, the cell was heated to a temperature $T_i^{(2)} > T_i^{(1)}$ deeper inside the two-phase region, equilibrated, and the interference pattern was recorded as the cell was cooled into the one-phase region again. The number of interference minima gives $\Delta n(T_i^{(2)})$. The purpose of this experimental procedure is to obtain an equilibrium profile in the cell by increasing the composition discontinuity in each successive step. This question will be discussed in detail below (see section 6.3.2).

Diffusivity

After a temperature step taking the system from the two-phase to the one-phase region, an initial refractive index profile

$$n(z) = \begin{cases} n_c - \Delta n/2 & \text{for } z < 0\\ n_c + \Delta n/2 & \text{for } z > 0 \end{cases}$$
(3.6)

Chapter 3. General Experimental Considerations: Temperature Control and Optics 48

will "relax" according to the diffusion equation

$$\frac{\partial}{\partial \tau} n(z,\tau) = D \frac{\partial^2}{\partial z^2} n(z,\tau)$$
(3.7)

Here, τ is the time and z is the height in the cell, as measured from the meniscus, and D is assumed to be concentration independent. n_c is the critical refractive index and, for a critically filled cell, equal to the refractive index in the one-phase region. The solution to eq. (3.7) is [83]

$$n(z,\tau) = n_c - \frac{\Delta n}{2} \Phi(\frac{z}{2\sqrt{D\tau}}), \qquad (3.8)$$

where

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\rho^2) d\rho \tag{3.9}$$

is the error function. Close to the meniscus, i.e., for small z, the error function can be approximated by $\Phi(r) \approx 2r/\sqrt{\pi}$, so that

$$n(z,\tau) - n_c = -\frac{z\Delta n}{2\sqrt{\pi D\tau}}.$$
(3.10)

The maximum refraction angle θ_{max} in the Fraunhofer pattern is due to rays refracted in the center of the cell where the slope of the density profile is highest. The time evolution of θ_{max} after a quench from T_i in the two-phase region to T_f in the one-phase region is related to the diffusivity $D(T_f)$ by

$$\theta_{max}(\tau) = \frac{L[n_c - n(z + \delta z, \tau)]}{n_{air}\delta z} = (L/2)\Delta n/\sqrt{\pi D(T_f)\tau}$$
(3.11)

Thus, the diffusion constant $D(T_f)$ can be determined from a measurement of the maximal refraction angle as a function of time.

3.2.3 Image Plane Interference Technique

The image plane technique uses a Mach-Zehnder interferometer which forms an interference pattern between an expanded laser beam passing through the sample confined



Figure 3.7: Schematic of the optical setup for image plane interference experiments.

in a flat cell and a reference beam. Figure 3.7 shows a schematic of the experimental setup. A laser beam from a He-Ne laser enters a spatial filter which expands it into a collimated beam of about 1" diameter. It is subsequently split by a beam splitter into a "cell beam" which passes through the sample, and a reference beam. A second beam splitter recombines the two beams, thus producing an interference pattern between them. A lens focusses this interference pattern onto the image plane, where it is recorded on film by a slit camera with continuous film transport. Each part of the cell maps directly onto a unique point in the image plane. Thus, by measuring the interference pattern, one obtains direct information about the refractive index as a function of height in the cell. The distance s_0 between the sample cell and the focussing lens determines the magnification M is given by $M = f/(s_0 - f)$,

where f is the focal length of the lens. In order to resolve the interference pattern around the meniscus as well as possible, a rather large magnification was chosen. The length of the optical table and the power of the laser place a limit on M; in our experiments, we had $M \approx 3-5$. M is determined by measuring the height of the image of the cell in the image plane h_i and dividing it by the original height of the cell h_o : $M = h_i/h_o$.

By mixing a plane wave (corresponding to the reference beam) with the wave which has interacted with and has thus been distorted by the refractive index profile in the cell, one obtains an interference pattern consisting of horizontal fringes. The change in refractive index Δn between two neighbouring fringes is $\Delta n = \lambda/L$, where λ is the wavelength of the laser light (in our case, 6328Å), and L is the cell thickness.

Far away from the critical point, the compressibility is small and thus the densities of each phase are almost height-independent. In the one-phase region, the whole cell is filled by the sample at (almost) uniform density (see Figure 3.2c), leading to a field of uniform intensity in the image plane. In the two-phase region, far from T_c , the density at any given temperature is uniform in both liquid and vapour phases (Figure 3.2a). Thus, the cell's image contains no interference fringes, but is only a field of uniform intensity.

As the temperature is changed, the change in densities of the coexisting phases leads to a phase change between the cell beam and the reference beam. This appears as a periodic change in intensity in the image plane. Since the whole field corresponding to one phase is of uniform intensity, however, it is difficult to see whether the refractive index difference between the two phases is actually decreasing or increasing. The interpretation of the data can be greatly facilitated by slightly tilting the reference beam wave fronts with respect to the cell beam, thereby "misaligning" the beams with respect to each other (see Figure 3.8). Then even far from the critical point, one obtains interference fringes in the image plane, the spacing of these fringes depending on the tilt angle of the mirror. For our experiments, the tilt angle was between 0.01° and 0.02°, corresponding

Chapter 3. General Experimental Considerations: Temperature Control and Optics 51



Figure 3.8: Effect of a tilted reference beam on the interference pattern.

to 2 - 4 fringes per cm of cell height.

On passing through the cell, the plane wavefront of the incident beam is distorted into a shape which mirrors the density profile in the cell. The propagation speed v of a light ray through a medium of refractive index n is v = c/n, so that the rays passing through the bottom of the cell (where n is larger) are retarded relative to the rays passing higher in the cell (where n is smaller). An interference maximum between the reference and the cell beams occurs whenever there is a path difference of $2\pi N\lambda$ between them (where Nis an integer).

In order to obtain the refractive index profile from the interference pattern, one has to deconvolve the interference pattern by subtracting the effect of the tilted reference beam, which distorts the image of the cell as indicated in Figure 3.8. The total path around the interferometer, L_{tot} , can be written as $L_{tot} = L_0 + Ln(z = 0)$ where L_0 is the path through air, L is the length of the cell and n(z = 0) is the refractive index at height z = 0, in the middle of the cell. A ray passing through the cell at height z interferes with the tilted reference beam with a phase $\phi(z)$ given by

$$Ln(z) + L_0 + z \tan \alpha = \lambda \phi(z)/2\pi$$
(3.12)

Here, α is the tilt angle of the mirror, and λ is the laser wavelength. Two rays passing at heights z and z' will therefore interfere with a phase $\delta \phi = \phi(z) - \phi(z')$, when

$$L(n(z) - n(z')) + (z - z') \tan \alpha = \lambda \,\delta\phi/2\pi \tag{3.13}$$

These rays will form adjacent interference fringes in the image plane if $\delta \phi = 2\pi$, i.e.,

$$L\Delta n + \Delta z \tan \alpha = \lambda \tag{3.14}$$

Thus, if a ray passing through the cell at height z_1 interferes with the reference beam to give an interference maximum, then a ray passing at height z_2 will also interfere to produce a maximum if the refractive index difference at the two heights z_1 and z_2 is $n(z_1)-n(z_2) = [\lambda - (z_1 - z_2) \tan \alpha]/L$. The height difference $z_1 - z_2 = \Delta z$ is related to the height difference $\Delta \tilde{z}$ as measured on film by $\Delta z = \Delta \tilde{z}/M$, where M is the magnification factor of the lens. The refractive index profile in the cell can thus be directly inferred from a measurement of the interference pattern as a function of height, provided the tilt angle α and the magnification factor M are known. α can be obtained from the interference pattern of the cell far from T_c , where any curvature of the refractive index profile is negligible.

Order Parameter and Coexistence Curve Diameter

The image plane interference technique can be used to measure the order parameter and the coexistence curve diameter of the fluid. As the temperature of the cell is lowered below T_c , the fluid phase separates. As T is lowered further, the liquid density increases, whereas the vapour density decreases. The density discontinuity at the meniscus in the middle of the cell (i.e., the order parameter) becomes larger, which causes interference fringes to "disappear" into the image of the meniscus. The number of missing fringes is related through the Lorentz-Lorenz function to the density differences $\rho_l - \rho_c$ and $\rho_c - \rho_v$ of the liquid and vapour phases from their critical value. At each temperature, the order parameter is obtained from the sum of the number of fringes missing from each phase, while the diameter is obtained from the difference.

Before each experimental run, the cell was cooled deep into the two-phase region. Then it was warmed up in small steps ($\approx 0.1^{\circ}$ far from T_c , and as small as 0.001° close to T_c) and the evolution of the interference pattern was recorded on film in the image plane. Between steps, the system's temperature was held constant for 1-2 hours to allow the cell to reach equilibrium. After the waiting period, the fringe pattern near the meniscus was found to be stationary, which lead us to believe that thermal equilibrium had been reached (at least locally).

Compressibility

To evaluate the isothermal compressibility κ_T , the slope of the density profile in the middle of the cell had to be measured. Due to critical slowing down, even for pure fluids the equilibrium slope takes hours to establish itself in the critical region. Therefore, when taking compressibility data, the sample was allowed to equilibrate for $\approx 12 - 24$ hours before a data point was taken.

A difference in chemical potential $\Delta \mu$ is related to the corresponding pressure difference ΔP and the corresponding height difference Δz by the equation

$$\Delta \mu = \Delta P / \rho = -g \mathcal{M} \Delta z \tag{3.15}$$

where ρ is the density in moles/cm³, \mathcal{M} is the molar mass of the fluid, and g = 9.81 m/s². For $T > T_c$, one can approximate $\rho \approx \rho_c$. For $T < T_c$, in the two-phase region, corrections have to be taken into account. However, these corrections are small (of the order of < 8% for our experiments, see section 5.4), and are much smaller than the experimental scatter of the compressibility data in the two-phase region.

The compressibility can thus be expressed as:

$$\kappa_T = \frac{P_c}{\rho_c^2} \left(\frac{\partial \rho}{\partial \mu}\right)_T = \frac{P_c}{\rho_c^2 g \mathcal{M}} \left(\frac{\Delta \rho}{\Delta z}\right)_T$$
(3.16)

We approximate the slope of the density profile by the density difference corresponding to one interference fringe, divided by the vertical distance in the cell over which this difference occurs. Using the Lorentz-Lorenz relation (see eq. (3.1)), $\Delta \rho$ can be expressed approximately as

$$\frac{\Delta\rho}{\rho_c} = \frac{6n_c\Delta n_0}{(n_c^2 - 1)(n_c^2 + 2)}$$
(3.17)

where $\Delta n_0 = \lambda/L$ is the refractive index difference corresponding to one fringe. From this relation, κ_T can be evaluated, because Δz can be directly inferred from the measurements of the fringe spacing on film (after correcting for the magnification factor of the lens and the tilt of the reference beam).

Chemical Potential Profile along the Critical Isotherm

The reduced chemical potential

$$\Delta \mu^* = \left| \frac{\mu(\rho) - \mu_c}{\mu_c} \right|_{T_c} = D_0 \left| \frac{\rho - \rho_c}{\rho_c} \right|_{T_c}^{\delta}$$
(3.18)

is evaluated using eq. (3.15). Over the height of the image, the difference $\Delta \mu = \mu - \mu_c$ is very small, so that we can approximate:

$$\left|\frac{\mu - \mu_c}{\mu_c}\right| \approx \frac{\rho_c g \mathcal{M}}{P_c} |\delta z| \tag{3.19}$$

Chapter 3. General Experimental Considerations: Temperature Control and Optics 55

where δz is the height in the cell as measured from the meniscus, and \mathcal{M} is the molar mass of the fluid. The critical amplitude D_0 is thus determined by

$$D_0 = \frac{\rho_c g \mathcal{M}}{P_c} |\Delta z| \cdot \left| \frac{\rho - \rho_c}{\rho_c} \right|^{-\delta}$$
(3.20)

Diffusivity

The diffusivity D is obtained from the image plane interferometric data in a similar fashion as from the focal plane experiment. After a quench from the two-phase region into the one-phase region of the phase diagram, the initial refractive index discontinuity decays as described in eq. (3.8). Near the meniscus the decay can be approximated by eq. (3.10). Thus the time evolution of the fringe spacing close to the middle of the cell can be used to estimate the diffusivity:

$$\frac{\Delta n \Delta z}{2\sqrt{\pi D\tau}} = n(z,\tau) - n(z + \Delta z,\tau) = \lambda/L$$
(3.21)

Here, Δn is the initial refractive index discontinuity, Δz is the fringe spacing in the middle of the cell, and τ is the time. Calling N the number of interference fringes (corresponding to the initial discontinuity), one gets:

$$D\tau = (N\Delta z)^2 / 4\pi. \tag{3.22}$$

3.2.4 Gravitational Rounding

A possible source of error in all optical experiments is the effect of gravitational rounding [84, 22]. It limits the accuracy of data in the critical region and determines the minimum distance in temperature to which the critical point can be approached.

To see how this effect comes about and how it influences the data, recall eq. (3.4) which describes the amount by which a ray traversing the cell is bent. According to this equation, a ray entering the cell at height z = H will emerge from the cell at the height

z = H - h, where $h \approx L\theta$. This ray will therefore probe a slab of fluid of height h; it will not only contain information on the refractive index at height H, but will average over the refractive indices between heights H - h and H. Gravitational effects are important when the change in refractive index over the height h becomes significant. The height averaging becomes larger as the density profile in the cell becomes more strongly curved. It is most noticeable close to the critical point, where the compressibility diverges and thus $dn/dz \rightarrow \infty$ at the meniscus.

The gravitational rounding effect can be made small by choosing a very thin cell, so that L is small. This was the case in our interference measurements: The cell lengths in all experiments were ≤ 2 mm, leading to negligible rounding effects even as close to the critical point as $t \approx 5 \times 10^{-6}$. Gravitational rounding thus does not play an appreciable role in the interference experiments described in this thesis. The situation is different in the case of the prism experiment, however [80]. Here, the optical path through the cell is of the order of ≈ 0.5 cm, so that gravitational rounding comes into play for the fluids considered here at reduced temperatures of the order $t < 10^{-4}$. Data taken closer to the critical point are strongly smeared and difficult to correct for gravitational rounding effects.

3.2.5 Light Scattering Experiments

Light scattering experiments were performed on the nicotine-water system in order to compare diffusivities obtained by the interference method to ones obtained in a more conventional way. For these experiments, the same optical cell was used as for the fringe method.

Figure 3.9 shows a schematic of the optical setup. The light source was a 10 mW He-Ne laser whose intensity was for the most part further reduced to minimize optical heating. The beam was expanded and rendered uniphase by a spatial filter. Lens L1

Chapter 3. General Experimental Considerations: Temperature Control and Optics 57



Figure 3.9: Optical setup for light scattering experiments.

collimated the emerging beam, and L2 (with a long focal length ≈ 400 mm) focussed the beam to a diameter of ≈ 0.1 mm inside the scattering volume. Polarizers P1 and P2 in front and behind the cell defined the polarization of the incident and scattered radiation. In our experiment, the polarization direction was chosen perpendicular to the plane of scattering.

The photomultiplier tube was mounted on a turntable which could be rotated around the scattering cell. The scattered light entered the photomultiplier through an iris the diameter of which was variable from 0.5 mm to 6 mm. Far from T_c , where the scattered intensity is low for large scattering angles, the iris was opened up to 2 mm. Close to T_c , it was reduced to 0.5 mm. The photomultiplier tube contained a built-in adjustable lens which forms an image of the scattering volume on the pinhole filter inside the tube. To align the photomultiplier optics, and to assure that the fluid cell was properly positioned at the centre of the turntable, the cell was replaced by a hollow pipette (diameter ≈ 1

Chapter 3. General Experimental Considerations: Temperature Control and Optics 58

mm) containing a strongly scattering substance (latex spheres). The spot illuminated by the laser beam in the pipette provided a bright target for alignment of the photomultiplier lens. Further checks on the correct alignment of the optics were carried out as in Ref. [85].

3.2.6 The Correlator

Our correlator was a Malvern K7023 digital correlator. Its operation and the method of photocount autocorrelation have been discussed in detail in the literature [37, 71, 86]. Here, only the features of relevance for the experiments in this thesis are presented.

Prior to processing by the correlator, the photon signal was digitized: in each time interval T_s , the number of photons detected by the photomultipier was counted. At any instant, the probability (per unit time) of detecting a photon was proportional to the intensity.

The photomultiplier, discriminator and amplifier assembly used was an EMI D307K, which produced pulses of height -1.2V and width 30ns, with a uniform rise and fall time, each pulse corresponding to a single photon. The method of integrating the total signal arriving between two sample time clock pulses had the advantage that no photocounts were lost due to dead time between sample times.

The number of photons detected in the sample time T_s was processed by the autocorrelator, which operated in the time domain and used a set of M parallel channels. The operation of the autocorrelator is shown schematically in Figure 3.10. The principle of operation of the correlator is, by taking N samples, to construct the sum

$$C_m = \sum_{i=1}^{N} n(\tau_i) n(\tau_{i-m}), \qquad (3.23)$$

where $\tau_{i+1} - \tau_i = T_s$ and m lies in the interval $1 \le m \le M$. This is achieved in the following way:

The signal accumulated during the time T_s is fed into the first channel, while the




Autocorrelator

Figure 3.10: Schematic diagram of the autocorrelator.

contents of the remaining M-1 channels are shifted down by one position each, the last one being discarded. The signal in the first channel is multiplied with the contents of the other channels and stored, thus building up the autocorrelation function C_m . The frequency attained by the instrument is determined by the total sample length $T = MT_s$, chosen to be 2-3 times the correlation time $\tilde{\tau}$, which is of the order of microseconds or less. In order to make the multiplications of the correlation function as fast as possible, the signal, before being stored in the shift register, is "clipped", i.e., it is compared to a preset threshold k; if n(0) > k, $n_k(0)$ is set to 1, otherwise $n_k(0)$ is set to zero. The shift register then contains a set of 0s and 1s, and the multiplication operations can be replaced by simple "AND" gates, controlled by the bit in the appropriate shift register: If $n_k(mT_s) = 1$ (with $1 \le m \le M$), then n(0) is added to the storage position m, and if $n_k(mT_s) = 0$, nothing is added. It can be shown [71] that the "single-clipping" operation here described does not distort the time dependence of the intensity autocorrelation function.

The Malvern K7023 autocorrelator has a store of M = 24, and the sample time T_s can be varied from 50 ns to 1 s. Three additional channels collect the total number of photon counts, the total number of clipped counts and the number of sample times N.

The autocorrelator was interfaced to the UBC Amdahl 5850 mainframe via a Z-80 microcomputer (built by the UBC electronics shop). Details of this interface are described in reference [87].

Chapter 4

Experiments

This chapter describes the experimental details of the apparatus and materials used in this thesis. The experimental setups and sample cells of the Freon experiments and the nicotine + water experiments are similar to those used in previous experiments [80, 82, 87, 88, 89] and are therefore not discussed in detail here. Only information specific to the individual experiments is given (sections 4.1 and 4.2). The high-pressure cell for the He-Xe experiment was designed and built especially for this thesis and is therefore described in detail (see section 4.3).

4.1 Freon Experiments

The CHF₃ ("Freon 23") and the CClF₃ ("Freon 13") used in these experiments were obtained from Matheson Gas Products. The CHF₃ was rated to be 98% pure, and the CClF₃ was rated to be 99% pure. Prism cell experiments were performed on both CHF₃ and CClF₃, using the technique and the equipment described in section 3.2.1.

In order to get very accurate data close to the critical point, an image plane interference experiment was carried out on CHF₃. The sample cell consisted of an aluminium body with two sapphire windows (diameter 1", thickness 1/4") spaced 1.86 ± 0.01 mm apart [88]. Before filling, the cell was evacuated to minimize contamination of the sample. Subsequently the cell was filled with CHF₃ at the critical density. The deviation from critical filling can be estimated by observing the rise or fall of the meniscus between the liquid and vapour phases as the critical point is approached. Our cell was slightly

overfilled, the deviation from critical density being less than 0.1%. The cell was placed into a two-stage thermostat which controlled the temperature to an accuracy of ± 0.2 mK. Its temperature was measured by an HP 2804A quartz thermometer, the probe of which was embedded in the innermost heating stage of the thermostat.

The interference pattern is extremely sensitive to changes in ambient room temperature, which change the optical path length of the reference arm of the interferometer, but not that of the temperature-controlled sample arm. In order to minimize this source of error, the whole interferometer was contained in a temperature-stabilized box which controlled temperature to better than 10 mK over a day and largely eliminated air temperature fluctuations. Still, changes in humidity and barometric pressure lead to a scatter in the diameter data which is somewhat larger than that for the prism cell data.

4.2 Nicotine + Water Experiment

For this experiment, a flat spectrophotometer cell (Hellma QS 282) of inside thickness 2 mm was filled with a critical mixture of nicotine and water, corresponding to about 40 wt% nicotine [81], and fire-sealed.

Nicotine is a clear liquid of similar appearance to water, but with a higher viscosity. It is very hygroscopic and reacts with air, thereby acquiring a brownish tinge. In an effort to have as clean a sample as possible, the nicotine, purchased from Kodak, was purified by distillation under a nitrogen atmosphere at a pressure of ≈ 5 mm Hg, where the boiling point occurs at $\approx 95^{\circ}$ C. Immediately after distillation, the nicotine was sealed into the cell together with the appropriate amount of deionized water. From observing the meniscus close to the critical point, we deduce that the cell was critically filled to about $\pm 0.2\%$ of the critical composition.

The phase diagram of nicotine + water in the T - x plane is a "closed loop" [81].

Phase separation occurs only in the temperature interval from $\approx 60^{\circ}$ C to $\approx 210^{\circ}$ C. Our experiments were carried out at the lower critical point, where the phase diagram is "inverted", i.e., cooling rather than heating takes the system from the two-phase into the one-phase region (see figure 3.6).

Prior to the measurement of order parameter and diffusivity, the critical refractive index had to be determined. Due to the high refractive index of the mixture, our prism cell setup could not be used for this measurement. Instead, the Hellma cell containing the mixture was slowly rotated around its vertical axis in one arm of a Mach-Zehnder interferometer, and the resulting interference pattern was used to calculate the critical refractive index. The experimental method and the results are discussed in Appendix B.

In an effort to determine the critical density and the densities of the two coexisting phases close to the critical point, precision densitometry was carried out. The densitometer consisted of a bulb-shaped glass bubble of volume ≈ 63 ml connected to a pipette. Nicotine-water mixtures in the composition range 30 wt% $\leq x_{nico} \leq 49$ wt% were investigated, at temperatures ranging from 55°C to 67°C. The results of this measurement are also presented in Appendix B.

Having measured the density and refractive index of the mixture, focal plane interference experiments and light scattering experiments were carried out. The same sample cell was used for all these experiments. The cell temperature was measured by thermistors embedded in the innermost heating stage of the thermostat.

4.3 High-pressure experiment

The He-Xe system was studied through two experiments: in one of them we measured the order parameter and diameter as a function of density in Xe to as high an accuracy as possible, using the prism cell setup. Our objective was to obtain an estimate of the

critical density and of the variation of ρ_c for samples from different sources. Two different samples were studied: One of them had been purchased from Matheson Gas Products just prior to the experiments and was rated to be 99.995% pure. The other one was obtained from Professor R. Gammon at the University of Maryland. It is currently being analysed for impurities, but the result is not available at the time of this writing.

The other experiment used the image plane interference technique, and was carried out in a high-pressure cell designed for pressures up to ≈ 400 atm. The cell design is described in detail in the following section. Two samples were investigated: One of them consisting of pure Xe, the other one of a He-Xe mixture containing $\approx 5\%$ He. Both gases for these experiments were purchased from Matheson Gas products (rated 99.995% pure for both Xe and He).

Because of the high pressures involved in the He-Xe experiment, special care had to be taken in designing and dimensioning the equipment that was to come in contact with the gas under high pressure. The gas-handling system was made up of two connected parts: One of them was designed for low pressures only and consisted of the containers of the uncompressed gases and the overflow volumes. The other one was designed for pressures up to 500 atm and contained the gases after compression.

4.3.1 Cell Design

The cell was designed for pressures up to ≈ 400 atm, allowing for a safety factor of 5×. The body was made out of 316 Stainless Steel, and the cell valve was directly worked into the cell body, in an effort to minimize the cell's "dead volume". Several tapped holes (1/2" deep, 1/4-20 thread) in the outside wall of the cell allowed thermistors to be implanted for temperature measurements. Figure 4.1 shows a technical drawing of the cell and Figure 4.2 a photograph. The window construction was based on the design by Poulter [90] and uses the principle of "unsupported area" which employs the high



Figure 4.1: Technical drawing of the high-pressure cell.



Figure 4.2: High-pressure stainless steel cell. In the actual experiments, the fill line points vertically, with the valve being in the horizontal. The windows are shown with retaining rings and sealing O-rings in position.

pressure to force the window against its support (see also [91, 92, 93]). For windows we used sapphire single crystal cylinders (1" in diameter and 1/2" thick), flat to 2λ and c-cut in order minimize effects due to the polarization of the laser beam. Their surfaces were coated with a thin film (1/4 λ thickness of MgF₂) to reduce stray reflections at the windows.

The windows were then mounted onto SS support plugs. Two types of plug-window assemblies were made: One set, using a higher plug stem, made the optical path length in the cell 0.195 ± 0.002 cm long, whereas the other, with a shorter stem, made the cell length 1.167 ± 0.002 cm.

In order to provide a good seal between the sapphire window and the steel support plug, the plug surface had to be perfectly flat. The plug was lapped on a polishing machine with diamond paste down to $1/4 \ \mu m$ grain size. During the polishing process, the plug was fastened to a 4" diameter SS lapping block in order to prevent curvature of the surface. The smoothness and flatness of the surface were checked optically by observing Newton's rings between the plug surface and a high-quality glass plate, using a sodium lamp. All the plugs were lapped until the surfaces were very shiny, no scratches were apparent, and at most 2 Newton's rings were visible over the whole 1" diameter surface.

The windows were then glued to the support plugs using low-vapour-pressure epoxy as a sealant. Care was taken to squeeze out any air trapped in the epoxy. After setting of the glue, the assembly was cured under ≈ 10 atm for about 24 hours. A retaining ring held the window and the plug together in good alignment during the glueing and curing process. No leaks were encountered at the windows when this procedure was carefully implemented.

The seal between the window support and the body of the cell was made with a rubber O-ring. The support plug was forced into position by a SS sealing bolt. In order



Figure 4.3: Components of the windows for the high-pressure cell

to ensure good slippage between the bolt and the plug, a thin disk of softer steel was interleaved between the two. This thin disk also contained weepholes for pressure relief. The various components of the windows are shown in Figure 4.3. The force exerted on the bolts during the tightening process deformed the O-rings, so that, even when the tension of the sealing bolts was released, the window plugs could not be easily removed. To facilitate the extraction of the the windows, the inside of the SS support plugs was threaded, so that an extraction bolt could be inserted to pull the windows out.

4.3.2 Pressure Handling System

Aside from safety, the main consideration in designing the high-pressure gas handling system was the cost of Xe. As 1 mole of Xe costs about \$700, we tried to minimize the

amount of Xe needed, and built the gas handling system in such a way that all the Xe used for the experiments could be recovered in storage cylinders.

To reach pressures of the He-Xe mixture up to 500 atm, two procedures could be used:

- 1. Mix He and Xe in the correct stoichiometric ratios at a lower pressure and then use a compressor to compress them up to the desired pressure.
- 2. Compress the two components separately without use of a compressor and then mix them at high pressure.

The first procedure has the disadvantage that it is not certain that He and Xe are compressed equally efficiently by the compressor, i.e., that the mixture at the discharge end has the same stoichiometry as at the inlet. Moreover, the compressor cannot be operated efficiently for suction pressures below 500 psi; however, due to the high cost of Xe, only a small gas bottle would be available in which the pressure would quickly drop below the required suction pressure. Thus, an initial precompression stage would be necessary. As the gas out of the precompression stage is compressed into the highpressure part, the amount of gas in the precompression volume decreases, leading to a pressure drop which will make the compressor more and more inefficient, thus preventing a continuous operation.

Our decision was therefore made in favour of the second procedure, which seemed more straightforward and easier to realize. The strategy was to freeze out a well-defined quantity of Xe in a cylinder submerged into liquid air (at which temperature Xe is solid), then add an appropriate quantity of He such that the desired concentration ratio would be reached. Upon warming up of the Xe, the mixture has the correct ratio and (hopefully) the correct pressure to make it critical.



Figure 4.4: High pressure gas handling system. Components shown in red, yellow and blue are dimensioned for pressures up to 500 atm or more, components in black and green are for low pressures.

For sample pressures up to about 300 atm, the (unregulated) pressure of our He bottle (1800 psi) was enough to produce a sufficiently high partial He pressure. For mixtures of higher He concentration, the He would have to be precompressed. This compression could be effected by cooling the He down to liquid nitrogen temperatures, where its density is 3 times as high as at room temperature; in this manner a threefold compression could be obtained.

Our gas-handling system consisted of several separate sections, as indicated by the different colours in Figure 4.4. The heart of the system was the "high-pressure part" shown in red (from now on called V_{red}) containing the cell and two pressure gauges, one

which went up to 200 atm, the other to 1000 atm. Connected to it were the compression stages for the gases: the Xe freeze-out cylinder C_{Xe} (shown in yellow) and the He compression stage C_{He} (shown in blue). Both freeze-out cylinders were mounted in such a way that they could be immersed into dewars with LN_2 for cooldown. The cylinders were equipped with relief values (from supplier HIP), set at 7000 psi (≈ 500 atm). Whereas the outlet of the relief value on the He cylinder went straight into the room (He being cheap), the outlet of the valve on the Xe cylinder was connected to the storage volume C_S , so that in case of the bursting of the value the Xe would be instantly recovered. All the components described so far were designed for pressures up to 500 atm. All tubing, valves and containers were made out of 316 SS, and the connections were made with high-pressure connectors. The valves were rotating-stem valves (Autoclave), and the tubing had 1/4" o.d. and 0.083" i.d. We picked the heavy wall tubing in order to keep the gas volume inside the tubing as small as possible. The physical dimensions of the apparatus were, among other things, determined by the large minimum bend radius of the heavy wall tubing (1.25" [94]). The connectors were purchased from Autoclave, and the tubing was prepared in our lab: the joints were coned and threaded, and the connections were tightened at 40 ft lbs [94] in order to make a good seal. The connections to Autoclave components (valves and tees) seemed to cause less trouble than the ones to HIP components (safety valves).

Also connected to the high-pressure volume V_{red} were the Xe supply and the Xe storage cylinder C_s . Moreover, there was a low-pressure "measurement circuit" (shown in green) which permitted precision measurements of the He-Xe concentrations: It contained a small cylinder (volume $\approx 16 \text{ cm}^3$) for freezing out Xe and a large cylinder of $\approx 1000 \text{ cm}^3$. This part of the system contained the gases only at low pressures (below 5 atm), and therefore the ideal gas law could be used to estimate densities from pressures. A precision gauge (Heise, for pressures < 35 atm) was used for measuring the partial pressures of He

\overline{P}	ċ	T _c	x_{xe}^c	ρ_c^{tot}	ρ_{xe}	ρ_{he}
(atı	m)	[°C]	[%]	$[moles/cm^3]$	$[moles/cm^3]$	$[moles/cm^3]$
75.	.7	16.25	95.1	0.00876	$0.00833 ~(\sim 0.98 \rho_c)$	$0.0004 \ (\sim 10 atm)$
102	2.8	16.9	89.5	0.00941	$0.00842 ~(\sim 0.99 \rho_c)$	$0.0010 \ (\sim 20 \mathrm{atm})$
132	2.0	18.4	84.65	0.01016	$0.00860 ~(\sim 1.01 \rho_c)$	$0.0016 \ (\sim 35 atm)$
184	.9	19.3	76.15	0.01138	$0.00866 ~(\sim 1.02 \rho_c)$	$0.0027 \ (\sim 60 \mathrm{atm})$
198	8.0	19.65	74.56	0.01166	$0.00869 ~(\sim 1.02 \rho_c)$	$0.0030 ~(\sim 65 { m atm})$
239).3	20.35	69.64	0.01226	$0.00853 ~(\sim 1.00 \rho_c)$	0.0037 (~ 84atm)
298	3.3	22.55	64.67	0.01372	$0.00887 ~(\sim 1.04 \rho_c)$	$0.0049 ~(\sim 114 atm)$
375	5.7	23.75	59.47	0.01520	$0.00904 \ (\sim 1.06 \rho_c)$	$0.0062 \ (\sim 144 \mathrm{atm})$

Table 4.1: Critical parameters of He-Xe mixtures [44]. Here, P_c is the critical pressure, T_c the critical temperature, ρ_c^{tot} the total critical density and x_{xe}^c the critical Xe-fraction of the mixture. ρ_{he} and ρ_{xe} are the partial He and Xe densities.

and Xe.

4.3.3 Dimensioning of the Gas Handling System

In order to calculate the sizes of the freeze-out volumes, we needed an estimate of the pressures, densities and critical temperatures involved. Table 4.1 gives an overview of approximate values of the critical parameters [44] and the He and Xe densities that are needed to reach them. The Xe densities for all mixtures up to 400 atm are only slightly larger than the critical density (and thus the partial pressures of Xe are < 70 atm at room temperature). The required partial pressures of He rise quickly with increasing He concentration.

As we owned about 2 moles of Xe, we chose C_{Xe} large enough so that our total amount of Xe could be frozen out and thus compressed. Since the solid density of Xe is $\rho_{xe}^s = 3.52 \text{ g/cm}^3$, this meant that $C_{Xe} \approx 74 \text{ cm}^3$. The total volume of V_{red} , including the 200atm pressure gauge and the cell (with window spacing = 2mm) was about 33 cm³. The vessel used to compress He had a volume of $V_{He} = 115 \text{ cm}^3$, the tubing in that part of the system being negligible compared to the freeze-out cylinder. The volumes were chosen in such a way as to minimize C_{Xe} while still enabling us to reach mixture pressures of ≈ 400 atm and compositions of $\approx 50\%$ Xe in the cell.

4.3.4 Filling the Cell

In order to reach the appropriate composition of the gases corresponding to the desired pressure, the necessary densities of He and Xe were estimated using Table 4.1. By referring to the literature values for isotherms of the pure gases at room temperature [95, 96], the pressures corresponding to these densities could be determined. Before the first filling of the cell, the gas handling system was evacuated for about 2 weeks with a diffusion pump. The required amount of Xe was then taken out of the storage cylinder by freezing it out into C_{Xe} . The partial pressure of Xe corresponding to the amount of Xe frozen out could be checked by warming up C_{Xe} and letting the fluid fill V_{red} . If the pressure was too high, the gas could be bled back into the storage vessel. As the pressure around P_c is a very weak function of density, it is difficult to estimate the actual Xe density by measuring its pressure. So, in order to be on the safe side, we retained more Xe than necessary. This Xe was then frozen back into C_{Xe} , filling up about 35cm³ of its volume. Subsequently, V_{red} and the empty portion of C_{Xe} were filled with He at the desired pressure. If the He bottle pressure was not high enough (as is the case for the larger He concentrations), the He could be precompressed by cooling it to 77K in C_{He} .

When the Xe frozen out in C_{Xe} was allowed to warm up, it mixed with the He, giving the desired mixture. As long as the room temperature was kept well above T_c , the gas mixture was homogeneous. In the cell, which was kept at a temperature below T_c , demixing into two phases (one He-rich and the other Xe-rich) occurred.

Whereas there exists a well-tested procedure for critically filling a pure fluid cell (see section 4.1 and Ref. [88]), filling the He-Xe cell is more complicated. Here, at a given

temperature, one has to adjust two variables, e.g. density ρ and Xe concentration x_{xe} to their appropriate values (the value of the third one, pressure, then being determined by the equation of state). As it is extremely unlikely that the correct values of these two variables would be reached at a first attempt, the following procedure was applied to fill the cell iteratively: The cell was filled, at a certain temperature $T^* < T_c$, with fluid at a total density and Xe concentration slightly higher than the desired one. As the cell was overfilled, the Xe-rich phase occupied a larger fraction of the volume. Since the cell valve was located horizontally exactly in the middle of the cell, any bleed swept out fluid from the Xe-rich (heavier) phase, and reduced both the overall density and the overall Xe concentration. So, by iteratively bleeding the cell, the fluid mixture in the cell travelled along the dotted line in the phase diagram indicated in Figure 4.5. Eventually, one reached the line onto which the manifold of critical points maps for the given temperature T^* . At this intersection the cell was critically filled, the meniscus was exactly in the middle of the cell, and both density and concentration were adjusted to their critical value. In order to check that the cell was really critically filled, it was warmed up to a temperature $T \approx T_c$, and the position of the meniscus was observed.

For example (see the schematic in Figure 4.5), if we start at an overall Xe concentration of 91.6% and total density 0.0117 moles/cm³, this fluid mixture decomposes, at 14.5°C, into one phase with $x_{xe}^{I} = 76\%$ and density $\rho^{I} = 0.0067$ moles/cm³ and another phase with $x_{xe}^{II} = 93\%$ and density $\rho^{II} = 0.0128$ moles/cm³. The bleed then takes the system along the dotted line to an overall density $\rho_{c}^{tot} = 0.0093$ moles/cm³, overall composition $x_{xe}^{c} = 90\%$, and pressure $P_{c} = 102$ atm. On warming, the system thus prepared passes through a second order phase transition point into the one-phase region.



Figure 4.5: Phase diagram of the He-Xe system at 14.5°C (semiquantitative schematic): The dashed lines correspond to lines of constant composition. The set of critical points maps onto the bold line.

4.3.5 Thermal Control of the Cell

The cell itself was used as the innermost stage of the thermal regulating system. Because the thermal conductivity of steel is so small, the cell was wrapped with a layer of copper, to which the heater was attached. The cylindrical copper shells were bent out of 1/2" thick copper sheet and then machined to the correct diameter on a lathe. Copper end plates were screwed to it, so that the whole cell was covered with copper sheet (at least 1/4" thick), except for holes for the windows, valve and thermistor screws. The copper cylinder was wrapped with heating foil (MINCO, four sheets, each 2"×9", with 10.6 Ω each).

The cell was heated using a feedback circuit as described in section 3.1. A thermistor embedded directly inside the copper sheet served as a "control" thermistor. As the thermistor measured the temperature of the copper sheet, its feedback was fast and temperature oscillations did not pose a problem. The thermal response of the cell as a whole was slow: After a change of temperature, the cell took about 1 hour to reach thermal equilibrium.

The cell, consisting of such a large mass of stainless steel, was very slow to respond to heating. The 4 heating foils were connected in parallel. As the total current supplied by the OPS was $\approx 2A$, the total heating power available was $\approx 5W$. In normal operation, the cell was heated to about half a degree above the temperature of the outer temperature stage. In this case, the heating power was about 0.5 - 1 W.

Three thermistors used for temperature monitoring were embedded in different places in the stainless steel body of the cell and measured using Wheatstone bridges. The imbalance of the Wheatstone bridges were amplified by HP nullmeters and monitored on an x-t chart recorder.

The inner heating stage of the cell was surrounded by a layer of styrofoam as thermal

insulator, then by a thin copper cylinder as a heat shield, followed by another layer of styrofoam and the outer temperature control cylinder. The outer cylinder had 3/8" o.d. copper tubing soldered to its outside in a spiral, and water flowing through it from a temperature regulated water bath (FORMA) kept it at a chosen temperature (always between 0.5° and 1°C below the cell temperature).

The cell was tested for temperature gradients by attaching one calibrated thermistor to the inside top and another one to the inside bottom of the cell, and feeding the leads out through a styrofoam plug replacing one of the windows. In one experiment, heating the cell to a temperature of about 1°C above the surroundings, we measured the bottom of the cell to be warmer than the top by 2-3 mK. In another experiment, heating the cell to higher temperatures in small steps (imitating the actual experimental conditions), we discovered no systematic temperature difference between top and bottom. The consequences of thermal gradients on the experiment are discussed in Appendix C.

Chapter 5

Freon Experiments: Results and Discussion

This chapter presents the results of experiments on CHF_3 , a strongly polar fluid, and $CClF_3$, a weakly polar fluid. We measured the Lorentz-Lorenz function (section 5.1), the order parameter (section 5.2) and the coexistence curve diameter (section 5.3) of these two substances. We found them to exhibit considerable differences, suggesting that dipolar interactions play a major role in determining the values of the critical amplitudes and the Lorentz-Lorenz function. On the other hand, the critical exponents were observed to be the same, in accordance with the principle of universality. Sections 5.2.2, 5.4 and 5.5 present measurements on the order parameter, compressibility and critical isotherm of CHF_3 , from which universal critical amplitude ratios were obtained with very high accuracy. They were found to be in excellent agreement with values obtained from nonpolar fluids and with theoretical results. Finally, section 5.6 describes the determination of the critical temperature from the experiments, and section 5.7 contains a discussion of the results.

All experiments on $CClF_3$ were carried out using the prism cell method; on CHF_3 , data were taken both by prism cell and image plane interference method [23, 97].

5.1 Lorentz-Lorenz Data

Information on the density dependence of the refractive index was obtained from the prism cell experiment, in which the refractive index and density are measured simultaneously in the one-phase region. The Lorentz-Lorenz function \mathcal{L} , as defined by eq. (3.1),

Substance	$\mathcal{L}_0(\mathrm{cm}^3/\mathrm{mole})$	$\mathcal{L}_1(\mathrm{cm}^6/\mathrm{mole}^2)$	$\mathcal{L}_2(\mathrm{cm}^9/\mathrm{mole}^3)$	$\mathcal{L}_c(\mathrm{cm}^3/\mathrm{mole})$
CHF ₃	6.905	37.6	$-2.8 imes10^3$	7.03 ± 0.02
CClF ₃	11.735	41.3	$-3.7 imes 10^3$	11.85 ± 0.02

Table 5.1: Results of a quadratic fit to the Lorentz-Lorenz data of CHF₃ and CClF₃. exhibits a weak density dependence along the coexistence curve, and can be expanded as a power series in ρ :

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_1 \rho + \mathcal{L}_2 \rho^2 + \dots \tag{5.1}$$

Figures 5.1 and 5.2 show the Lorentz-Lorenz data for CHF₃ and CClF₃ respectively, and the lines are a quadratic fit to them. The fit parameters are given in Table 5.1, together with the critical value $\mathcal{L}_c = \mathcal{L}(\rho_c)$. The Lorentz-Lorenz results for CHF₃ can be compared to the results of the experiment of Buckingham and Graham [98] who measured the Lorentz-Lorenz function of CHF₃ as a function of density for pressures up to 5 atm. They fit \mathcal{L} to a straight line and found $\mathcal{L}_0 = 7.05$ cm³/mole and $\mathcal{L}_1 = 3.4$ cm⁶/mole². By extrapolation they found for the critical value $\mathcal{L}_c = \mathcal{L}(\rho_c) = 7.08$ cm³/mole. Our measurements, which extend up to 50 atm, yield $\mathcal{L}_c = 7.03 \pm 0.02$ cm³/mole, in reasonable agreement with their result.

From the Lorentz-Lorenz data, the electronic (optical) polarizability α_p can be determined using [99]

$$\lim_{\rho \to 0} \mathcal{L}(\rho) = \frac{4\pi\alpha_p}{3} N_A, \tag{5.2}$$

where N_A is Avogadro's number. For CHF₃, we obtained α_p to be 2.74±0.02Å³, which agrees with the value $\alpha_p = 2.8Å^3$ cited in the literature [98, 100]. The polarizability of CClF₃, as measured in our experiment, is $\alpha_p = 4.65 \pm 0.02Å^3$, and thus considerably larger than the value for CHF₃.

For a polar fluid, the molecular polarizability α_p calculated from eq. (5.2) differs



Figure 5.1: Lorentz-Lorenz function of CHF_3 as a function of density. The line is a quadratic fit to the data.



Figure 5.2: Lorentz-Lorenz function of $CClF_3$ as a function of density. The line is a quadratic fit to the data.

from the effective polarizability $\tilde{\alpha}_p$ due to dipole-dipole and dipole-induced-dipole interactions [28, 30] according to eq. (1.7). For the case of CHF₃, with dipole moment $\mu_0 = 1.65 \times 10^{-18}$ esu [31], polarizability $\alpha_p = 2.74 \text{Å}^3$ and dissociation energy $I \approx 12.5 \text{eV}$ [101], these effects enhance the polarizability α_p , resulting in the so-called effective polarizability [28, 30] (corresponding to a low-frequency polarizability) which then has the value $\tilde{\alpha}_p \approx 3.5 \text{Å}^3$. For CClF₃, with $\mu_0 \approx 0.50 \times 10^{-18}$ esu [32], $\alpha_p = 4.65 \text{Å}^3$ and $I \approx 12.5 \text{eV}$ [101], the effective polarizability becomes $\alpha_p \to \tilde{\alpha}_p \approx 4.67 \text{Å}^3$.

The prism cell experiment also yields the critical density: A fit to the coexistence curve diameter gives the refractive index at the critical temperature, which can be converted into the critical density using the Lorentz-Lorenz relation. For CHF₃, we measured $n_c = 1.0806(2)$, from which we obtained $\rho_c = 0.5272 \pm 0.0015$ g/cm³, in close agreement with other experiments [102, 103], which find ρ_c in the range 0.525 - 0.526 g/cm³. For CClF₃, we measured the refractive index to be $n_c = 1.1009(3)$, slightly higher than cited in the literature ($n_c = 1.0996$, see Ref [104]). Our measurement thus gives a critical density of $\rho_c = 0.582 \pm 0.002$ g/cm³ and agrees well with the values $\rho_c = 0.578$ g/cm³ [102] and $\rho_c = 0.581$ g/cm³ [105] reported in the literature.

5.2 Order Parameter Measurements

5.2.1 Order Parameter of CClF₃

The coexistence curve data obtained in the prism cell experiment on CClF_3 were fitted to the expression

$$\Delta \rho^* = B_0 t^\beta (1 + B_1 t^\Delta + B_2 t^{2\Delta} + B_3 t^{3\Delta}).$$
(5.3)

Some results are shown in Table 5.2. Data were taken in the temperature interval $10^{-4} < t < 6.5 \times 10^{-2}$, and all the fits were performed over the whole temperature interval. For some of the fits the critical exponent β and the correction exponent Δ were held fixed

β	Δ	Bo	B ₁	B ₂	B ₃
(0.327)	(0.5)	1.645	0.654	-1.00	(0.0)
(0.325)	(0.5)	1.619	0.733	-1.14	(0.0)
0.3298	(0.5)	1.681	0.554	-0.80	(0.0)
(0.327)	0.43	1.632	0.555	-0.63	(0.0)
(0.327)	(0.5)	1.639	0.754	-1.74	1.65
0.3257	(0.5)	1.621	0.838	-2.08	2.20

Table 5.2: Results of the coexistence curve fit of $CClF_3$. Parameters shown in parentheses were kept fixed for the fit.

at the theoretically expected values, $0.325 \le \beta \le 0.327$ and $\Delta = 0.5$. When β is treated as a free parameter, and two correction terms are taken into account, the value of β is slightly larger than theoretically expected. However, when one more correction term is taken into account, the value of β obtained by the fit agrees very well with theory.

The correction to scaling exponent Δ , when fitted as a free parameter, favours a value of 0.43 ± 0.01 , which is somewhat smaller than the theoretically predicted value. Similar values have been reported for ethylene and hydrogen [89, 106].

A plot of the data from two independent runs (total of 204 data points) is shown in Figure 5.3, where $\log_{10}(\Delta \rho^*/t^{\beta})$ is plotted versus the reduced temperature t. The line corresponds to a fit which treats β as a free parameter with a fitted value of 0.3257, Δ fixed at 0.5, and includes three correction to scaling terms. The fit is seen to describe the data quite well.

5.2.2 Order Parameter of CHF₃

The order parameter data obtained from both the fringe and the prism cell experiment were fitted to the expression (5.3). Table 5.3 shows several fits to this equation, with various combinations of the amplitudes and exponents as free parameters. Fits were performed for both experiments separately, and then for all the data taken together. For



Figure 5.3: log-log plot of coexistence curve data of CClF₃. The curve corresponds to a fit with three correction to scaling terms and with $\Delta = 0.5$ held fixed and $\beta = 0.3257$ a free parameter.

β	Δ	B ₀	B_1	B_2	<i>B</i> ₃	
Image plane interference data						
0.326	_	1.75	-	_	-	
(0.325)	(0.50)	1.717	0.96	-1.85		
(0.327)	(0.50)	1.747	0.85	-1.59	-	
0.331	(0.50)	1.806	0.64	-1.08	. –	
(0.327)	0.42	1.748	0.65	-0.77	-	
(0.327)	(0.50)	1.739	1.03	-3.39	5.3	
0.3287	(0.50)	1.770	0.85	-2.34	2.9	
(0.327)	0.42	1.731	0.68	-1.00	0.5	
		Prism cell data				
(0.325)	(0.50)	1.723	0.87	-1.41	_	
(0.327)	(0.50)	1.748	0.80	-1.31		
0.332	(0.50)	1.813	0.60	-0.70	_	
(0.327)	0.43	1.742	0.60	-0.60		
All data						
(0.327)	(0.50)	1.747	0.85	-1.55	_	
0.331	(0.50)	1.810	0.62	-1.01	-	
(0.327)	0.40	1.727	0.60	-0.60	-	
0.326	0.37	1.703	0.60	-0.55	-	
(0.327)	(0.50)	1.739	1.03	-3.44	5.5	
0.3287	(0.50)	1.768	0.86	-2.45	3.3	

Table 5.3: Coexistence curve fits for CHF₃. The first fit was done in the temperature range $10^{-6} < t < 10^{-4}$. All other fits were done over the temperature range $10^{-6} < t < 4 \times 10^{-2}$. Parameters in parentheses were held fixed for the fit. the fringe data, a fit to a pure power law was performed over an "inner" temperature range $10^{-6} < t < 10^{-4}$, where the corrections to scaling in eq. (5.3) are expected to contribute on the order of 1% and are therefore smaller than the statistical scatter of the data. (At t=10⁻⁴, the number of missing fringes is about 50, and the resolution is of the order of half a fringe). The value of $\beta = 0.326 \pm 0.001$ found in this temperature interval is in excellent agreement with the theoretical value $0.325 \leq \beta \leq 0.327$ (Ref. [11]) and with other experimental data [89, 17]. The prism cell data do not extend close enough to T_c to allow a similar fit to that data.

Fits over the whole temperature interval $10^{-6} < t < 4 \times 10^{-2}$ consistently yield a higher value for β . When two correction to scaling terms are included in the fit, we obtain $\beta = 0.331 \pm 0.001$ for the fringe and $\beta = 0.332 \pm 0.003$ for the prism data; both of these values are slightly larger than the theoretical value. Adding a third correction term results in $\beta = 0.329 \pm 0.001$ for the combined data, which is close to the theoretically predicted value.

Figure 5.4 shows the coexistence curve data from both experiments. The fringe data consist of 604 points from four individual runs, and the prism data consist of 70 points from two runs. As in figure 5.3, the leading t^{β} temperature dependence has been divided out, and $\log_{10}(\Delta \rho^*/t^{\beta})$ is plotted versus t. For reduced temperatures $t > 10^{-4}$, the data exhibit a clear deviation from a horizontal straight line, indicating that a pure power law is insufficient to describe the data and demonstrating the importance of the correction to scaling terms. The curves in the figure correspond to fits with the exponents fixed at $\beta = 0.327$ and $\Delta = 0.5$, and with the amplitudes as free parameters. The dashed curve is a fit with two, and the solid curve with three correction terms. These fits are seen to describe the data very well; however, the tendency of the data to favour values of β larger than the theoretical value, even when more correction to scaling terms are included, suggest that the correction to scaling series for $\Delta \rho^*$ is not adequate over the



Figure 5.4: Coexistence curve data of CHF₃, from interference experiment (·) and prism cell experiment (o). The curves correpond to fits with $\beta = 0.327$ and $\Delta = 0.5$. The dashed curve is a fit with two, the solid curve with three correction to scaling terms.

large temperature range covered in this work. In order to obtain a more satisfactory description of the coexistence curve in the whole temperature interval, the crossover from the asymptotic scaling behaviour near the critical point to the regular behaviour away from the critical point should be taken into account [57, 107].

As was the case for CClF₃, the correction to scaling exponent Δ for CHF₃ also exhibits a trend to values smaller than theoretically expected. We find $\Delta = 0.42 \pm 0.02$ for CHF₃. This may be another indication that the correction to scaling series is not a good approximation for the large temperature intervals covered in our experiments. It may also mean that Δ is indeed smaller than 0.5, as suggested by other experiments [106].

In addition to the statistical error in B_0 due to the scatter in the data, there is an additional systematic uncertainty in the fringe data due to the uncertainty in the cell thickness. To make the data of the prism and the interference experiments coincide, L_{cell} was fixed at 1.865 mm, which is equal to the measured thickness within our experimental error.

The resulting values of the critical amplitude B_0 depend on the value of β and to a lesser extent on how many correction to scaling terms are taken into account. The interference data, extending further into the critical region, furnish a more reliable estimate of the critical amplitude B_0 . Averaging over the results of various fits of the CHF₃ fringe data, we obtain $B_0 = 1.743 \pm 0.003$ when keeping $\beta = 0.327$ fixed, and $B_0 = 1.722 \pm 0.003$ when keeping $\beta = 0.325$ fixed. The error on B_0 is thus very small for fixed β . These values are in good agreement with previous measurements [102], which were fitted using $\beta = 0.324$ and found $B_0 = 1.74$ [108].





Figure 5.5: Coexistence curve diameter ρ_d as a function of t for CHF₃. Data from interference experiment (•) and prism cell experiment (•). The dashed line corresponds to a straight-line fit to data with $t > 8 \times 10^{-3}$.

5.3 Coexistence Curve Diameter for CHF₃ and CClF₃

The coexistence curve diameter of CHF₃ from the prism and fringe experiment are shown in Figure 5.5. Each point of the fringe data in the figure is the average of from 5 to 30 individual data points. In this way, the scatter of the original data, due to fringe counting uncertainties and variations in room pressure and humidity, was averaged out. (The fits, however, were performed on the raw, unaveraged, data.) The dashed line is a straight-line fit to data with reduced temperatures $t > 8 \times 10^{-3}$.

Both data sets agree very well for reduced temperatures $t > 10^{-3}$. For small reduced

temperatures, they do not quite coincide, but show the same general behaviour: Close to T_c both data sets bend downward from a straight-line fit to the data far from T_c . This behaviour is consistent with the expected $t^{1-\alpha}$ anomaly [68]; according to the model of Goldstein *et al.*, the downward bend is indicative of repulsive three-body forces between the molecules [26, 28].

Figure 5.6 shows a plot of the coexistence curve diameter of CClF₃. The dashed line in the figure corresponds to a straight-line fit to the data for reduced temperatures $t > 8 \times 10^{-3}$. The straight line seems to describe the data very well. However, as is obvious from the more detailed graph of data with $t < 2 \times 10^{-2}$, the CClF₃ data bend away from the straight line close to T_c . Even though this effect is not as pronounced in CClF₃ as it was in CHF₃, there is still evidence for the critical diameter anomaly, and, as in CHF₃, the downward bend of the data from the straight line can be interpreted, in the framework of the Goldstein model [26], as due to repulsive three-body interactions between the fluid molecules.

Table 5.4 shows fit results of the diameter data of CHF₃ and CClF₃ to expression (2.36). To get a value of the amplitude A_1 , the data were fitted to a straight line in the outer temperature interval $t > 8 \times 10^{-3}$. The fits give $A_1 = 1.31 \pm 0.01$ and 1.33 ± 0.06 for the CHF₃ fringe and prism cell experiments respectively, and $A_1 = 0.860 \pm 0.002$ for the CClF₃ prism experiment. The remainder of the table contains fits over the total temperature range of the experiments. When both A_1 and $A_{1-\alpha}$ are fitted as free parameters to the CHF₃ data, the prism data give a much smaller error in the amplitudes than the fringe data. Due to the scatter in the CHF₃ data, fits with additional terms in eq. (2.36), corresponding to corrections to scaling, do not yield any further useful information.



Figure 5.6: Coexistence curve diameter ρ_d of CClF₃. (a) whole temperature range, (b) temperature range $t < 2 \times 10^{-2}$. The dashed line corresponds to a straight-line fit to the data with $t > 8 \times 10^{-3}$.

	A ₁	A _{1-α}	A ₀
CHF ₃ data		<u></u>	
outer temperature range			
$(t > 8 \times 10^{-3})$			
Interference data:	1.31 ± 0.01	(0.0)	1.0022 ± 0.0002
Prism cell data :	1.31 ± 0.06 (0.0) 1.002		1.002 ± 0.01
total temperature range			
$(10^{-6} < t < 1.8 \times 10^{-2})$			
Interference data:	1.40	(0.0)	1.001
	(0.0)	0.94	1.001
	-1.4 ± 1.0	1.8 ± 1.0	1.001 ± 0.001
Prism cell data:	1.46	(0.0)	1.006
	(0.0)	0.95	1.0002
	0.32 ± 0.04	0.69 ± 0.02	1.00014 ± 0.00002
CClF ₃ data			
outer temperature range			
$(t > 8 \times 10^{-3})$			
. ,	0.860 ± 0.002	(0.0)	1.0010 ± 0.0002
total temperature range			
$10^{-4} < t < 6.5 \times 10^{-2}$			
	0.869	(0.0)	1.0005
	(0.0)	0.631	0.9992
,	0.482	0.261	1.00005

Table 5.4: Fit results of the coexistence curve diameter of CHF_3 and $CClF_3$. Parameters shown in parentheses were kept fixed for the fit.

5.4 Compressibility of CHF₃

The isothermal compressibility κ_T^{\pm} , as given by eq. (2.4), is measured from our data by measuring the fringe spacing in the middle of the cell (i.e., close to the meniscus in the two-phase region), where the gradient of the density is largest and where the average density equals the critical density (see eq. (3.16)). Figure 5.7 shows a plot of the compressibilities of CHF₃ in both the one and the two phase regions. In the one phase region, a least squares fit of the logarithm of κ_T^+ as a function of the logarithm of t (shown as a solid line in the figure) yields an exponent $\gamma^+ = 1.230(8)$ and a critical amplitude $\Gamma_0^+ = 0.058(3)$. The critical temperature was determined as a free parameter from the compressibility data and was found to agree with the value determined in the coexistence curve fit to within 0.2 mK. The figure shows that the straight line is sufficient to describe the data. Correction to scaling terms in this temperature range are expected to be of the order of 1% and cannot be distinguished from the statistical scatter of the data.

In the two-phase region, data extraction is much more difficult, due to a lower curvature of the interference pattern (i.e., a smaller compressibility), and thus the data in this region are somewhat more scattered. A two parameter fit for $T < T_c$, for which the critical temperature was kept fixed at the value found in the one-phase region, yields $\gamma^- = 1.18(3)$, which is substantially lower than the theoretical value ($\gamma^- = \gamma^+ = 1.24$). In order to determine the critical amplitudes Γ_0^{\pm} consistently, data in both regions were fitted by power laws with $\gamma = 1.23$ (corresponding to the exponent in the one-phase region) and $\gamma = 1.24$ (the theoretical value). For these fits, the critical temperature was held fixed at the value found in the coexistence curve fit. The results are summarized in Table 5.5.





Figure 5.7: Compressibility of CHF₃. The data for $T < T_c$ (two-phase region) are represented by open circles (vapour phase) and open triangles (liquid phase). Data in the one-phase region $(T > T_c)$ are represented by solid circles, and the curve is a power-law fit to them, with exponent $\gamma = 1.230$.
	γ^+	Γ+
$T > T_c$	1.230 ± 0.008	0.058 ± 0.005
(one-phase region)	(1.23)	0.058 ± 0.003
	(1.24)	0.052 ± 0.002
	· · ·	
· · · · · · · · · · · · · · · · · · ·	γ^{-}	Γ-
$T < T_{c}$	1.18 ± 0.03	0.019 ± 0.008
(two-phase region)	(1.23)	0.012 ± 0.002
·	(1.24)	0.011 ± 0.001

Table 5.5: Compressibility fits of CHF_3 data. Parameters in parentheses were held fixed for the fit.

5.5 Critical Isotherm of CHF₃

In order to extract the critical amplitude D_0 of the critical isotherm for CHF₃ (see eq. (3.20)), we follow the approach suggested by Pestak and Chan [17]: At temperatures close to T_c the distance Δz of each of several interference fringes from the meniscus was measured. Then, for each temperature, the quantity

$$D_t = \frac{P - P_c}{P_c (\Delta \rho)^{\delta}} = \frac{\rho_c g}{P_c} \frac{\Delta z}{(\Delta \rho)^{\delta}}$$
(5.4)

was calculated for the reduced density

$$\Delta \rho = |\rho(\Delta z) - \rho_c|/\rho_c \tag{5.5}$$

corresponding to this fringe. The value of δ was determined using the scaling relation $\gamma = \beta(\delta - 1)$ and the values of γ and β obtained earlier in the same experiment. On the critical isotherm, all the values of D_t thus calculated should coincide (this will give the value of the critical amplitude D_0). However, for data taken at temperatures away from T_c , the functional relation $\Delta \mu = D_0 |(\rho - \rho_c)/\rho_c|^{\delta}$ is not correct: below T_c , the density profile is "steeper" than on the critical isotherm and thus the values of D_t , as calculated



Figure 5.8: Example of the graphical method used for extracting D_0 . The lines correspond to interference fringes with a fixed density difference $\Delta \rho$ from the critical density. The lines intersect at the critical temperature, determining the critical amplitude D_0 .

from formula (5.4), are smaller than the critical value D_0 . At any given temperature $T < T_c$, the values of D_t decrease with increasing distance Δz from the meniscus. Above T_c , the density profile is "less steep", and therefore the D_t values are larger than D_0 .

In order to assure that gravitational rounding does not play an appreciable role, only data with $\Delta \rho > 4 \times 10^{-2}$ were taken into account, for which beam-bending errors are less than 0.1% [22]. An antisymmetric density profile was assumed, and the Δz used for the evaluation was the mean of the vapour and liquid values. The data of one run (with $\delta = 4.80$) are shown in Figure 5.8. As can be seen, lines corresponding to various values of $\Delta \rho$ indeed do intersect at the critical temperature, and this furnishes the amplitude D_0 . Using $\delta = 4.76$ (corresponding to $\beta = 0.327, \gamma = 1.23$), one obtains $D_0 = 3.5 \pm 0.2$, whereas for $\delta = 4.80$ (corresponding to $\beta = 0.327, \gamma = 1.24$), one obtains $D_0 = 3.85 \pm 0.3$.

5.6 Critical Temperature of CClF₃ and CHF₃

In the data evaluation of the prism cell experiments of CClF₃ and CHF₃, the critical temperature was determined as a free parameter of the coexistence curve fits. In the CClF₃ experiment, in which two coexistence curve runs were performed, T_c was found to be 28.104 ± 0.001°C, considerably lower than the values cited by other researchers $(T_c \approx 28.400^{\circ}C \ [102], T_c \approx 28.715^{\circ}C \ [104])$. The reason for this difference might be attributed to the presence of different impurities in the system [109].

In the CHF₃ prism cell experiment, in which three runs were performed, we found $T_c = 26.008 \pm 0.007^{\circ}$ C, higher than the value cited in the literature ($T_c \approx 25.81^{\circ}$ C [102]). For the evaluation of the diameter data, the critical temperature was held fixed at the value obtained from the coexistence curve fit for each particular run.

In the interference experiment on CHF_3 , the critical temperature in each run was determined in three different ways: from a least-squares fit to the coexistence curve data, from a power-law fit to the one-phase compressibility, and from the intersection of D_t -lines belonging to different densities near the critical isotherm. The three values of T_c thus obtained agree to within 0.2 mK, which indicates that the results for the critical amplitudes and exponents are quite consistent. This suggests also that the system was in thermal equilibrium.

Interference data on CHF₃ were taken over a period of about 8 months in 11 consecutive runs. During this time, we observerd a steady drift of the critical temperature at a rate of approximately 4mK/month, from 26.01°C initially to 26.04°C. A run performed one year before this set of experiments, using the same sample, found $T_c \approx 25.80$ °C.



Figure 5.9: Drift of the critical temperature of CHF_3 as a function of time, as measured in the interference experiment.

Figure 5.9 shows a graph of the critical temperature as a function of time in the CHF_3 interference experiment. The temperature stability was regularly checked by a triple point cell and was found to be better than 2 mK/year. This temperature drift seems to have no observable effect on the critical amplitudes. Whenever several data sets were evaluated together, their difference in critical temperature was corrected for.

We suspect that chemical reactions of the CHF_3 or impurities coming out of the cell walls or the windows may be responsible for the drift in critical temperature, and also for the difference between our values of T_c and literature values for $CClF_3$ and CHF_3 .

5.7 Discussion

The prism cell experiment and the interference experiment are two equivalent methods of measuring the order parameter and the coexistence curve diameter of a fluid. The prism

5.7 Discussion

The prism cell experiment and the interference experiment are two equivalent methods of measuring the order parameter and the coexistence curve diameter of a fluid. The prism cell method has the advantage of measuring directly the densities of liquid and vapour phase as a function of temperature. Close to the critical point, however, there is some uncertainty in the data due to gravitational rounding [22]: As the laser samples regions of strongly varying density in the cell, one observes a continuous distribution of deflection angles. This makes the determination of the liquid and vapour densities at the meniscus difficult and limits the temperature range accessible to this experiment to $t > 3 \times 10^{-5}$. In contrast, the interference method is much less affected by gravitational rounding [22]. Due to the short path length of the CHF_3 sample cell, the error introduced by beam bending is negligible in comparison to the statistical scatter: At reduced temperatures as small as $t = 2 \times 10^{-6}$, gravitational rounding introduces an error of only about 1/5fringe close to the meniscus, which is smaller than the accuracy with which fringes can be measured close to the critical point. For the CHF_3 experiment, in which order parameter and coexistence curve diameter were measured both by the fringe and the prism cell method, the two experiments give consistent results.

From the results of the interference experiment of CHF_3 , some amplitude ratios can be calculated. Table 5.6 presents a collection of the various critical amplitudes obtained in fits with different critical exponents, and Table 5.7 shows the corresponding values of the critical amplitude ratios. The experimental values are in good agreement with theoretical predictions [12], independent of the precise values of exponents one chooses for the fits. There is excellent agreement between the amplitude ratios obtained by different choices of the critical exponents. Our results are not accurate enough, however, to decide whether high-temperature series expansions or explicit implementations of the

β	γ	δ	B_0	Γ,+	Γ_0^-	D_0
(0.327)	(1.23)	(4.76)	1.743 ± 0.003	0.058 ± 0.003	0.012 ± 0.002	3.5 ± 0.2
(0.327)	(1.24)	(4.80)	1.743 ± 0.003	0.052 ± 0.002	0.011 ± 0.001	3.85 ± 0.30
(0.325)	(1.23)	(4.79)	1.722 ± 0.003	0.058 ± 0.003	0.012 ± 0.002	3.75 ± 0.30
(0.325)	(1.24)	(4.82)	1.722 ± 0.003	0.052 ± 0.002	0.011 ± 0.001	4.1 ± 0.3

Table 5.6: Critical amplitudes of CHF_3 . Exponent values in parentheses were kept fixed for the fit.

	Γ_0^+/Γ_0^-	$D_0\Gamma_0^+B_0^{\delta-1}$
Our data		
$(\beta = 0.327, \gamma = 1.23)$	4.8 ± 0.6	1.64 ± 0.12
$(eta=0.327,\gamma=1.24)$	4.8 ± 0.6	1.61 ± 0.14
$(\beta = 0.325, \gamma = 1.23)$	4.8 ± 0.6	1.70 ± 0.14
$(eta=0.325,\gamma=1.24)$	4.8 ± 0.6	1.69 ± 0.14
Pestak et al.		
N_2	4.8 ± 0.6	1.71 ± 0.5
Ne	4.8 ± 0.8	2.05 ± 0.8
Theory		
high-temperature series	5.07	1.75
ϵ -expansion	4.80	1.6

Table 5.7: Critical amplitude ratios

renormalization group (ϵ -expansions [12]) yield the better values of the ratios.

We also find good agreement with the results of Pestak and Chan [17] from measurements on N₂ and Ne. For the product $D_0 \Gamma_0^+ B_0^{\delta-1}$ the uncertainty in our results is lower than theirs due to the fact that close to the critical point, their data are strongly influenced by gravitational rounding which causes a large error in the amplitude D_0 . Our experiment, being less affected by gravitational rounding errors, determines D_0 to much higher accuracy, resulting in a more precise value of the amplitude ratio.

In order to check the self-consistency of our CHF_3 interference data, the critical temperature was determined separately from fits to the coexistence curve and compressibility data and from the intersection of the lines of constant density as used for the evaluation of the critical isotherm. The values of T_c obtained by these three different methods agree to within 0.2 mK. A discrepancy of the T_c values can be an indication of gravitational rounding or insufficient equilibration time between temperature steps. We thus conclude that our data are to a large extent free of these errors.

Also, capillary effects do not play an appreciable role in CHF_3 ; they would manifest themselves as a smearing out of the meniscus separating the liquid and the vapour phase. On our films, the meniscus is always very narrow, which indicates that there is negligible wetting of the sapphire windows, even far from the critical point.

The compressibility data of CHF₃ do not extend far enough away from T_c to detect any deviation from pure power-law behaviour, but the evaluation of the coexistence curve clearly shows the importance of correction to scaling terms. Even though three correction terms are sufficient to describe the data in the temperature interval $10^{-6} < t < 2 \times 10^{-2}$, the large variations in the amplitudes B_2 and B_3 from fit to fit indicate that using a power law series for the evaluation is not satisfactory any more, and that the data should instead be evaluated using crossover theories [107, 57]. However, when both β and Δ are kept fixed at their theoretically expected value, the amplitude B_0 changes very little (by less than 0.5%) when more correction to scaling terms are included. Thus the leading critical amplitude can be reliably extracted independent of the exact behaviour of the coexistence curve far from critical.

The absolute value of the critical amplitude B_0 in CHF₃ is considerably higher than the ones measured for nonpolar gases [17, 89, 110, 111], whereas D_0 is appreciably lower [17]. This is probably due to the fact that in the polar gas fluoroform the intermolecular interactions are of a different nature than in nonpolar fluids, and thus fluoroform is not expected to obey the "principle of corresponding states" as well as nonpolar fluids do [1]. The same trend has also been observed for H₂O and D₂O [107]. However, even though the absolute values of the critical amplitudes deviate from the ones found in nonpolar fluids, polar fluids still furnish the same amplitude ratios as nonpolar ones, in accord with the universality principle.

The evaluation of the coexistence curve clearly shows the importance of corrections to scaling, for both CHF₃ and CClF₃. Even though three correction terms are sufficient to describe the data over the whole temperature interval, the correction amplitudes B_2 and B_3 vary greatly with β and Δ . Also, the value of β depends on the temperature interval considered and on the number of correction terms. This suggests that the correction to scaling series is not sufficient over the large range of reduced temperatures studied in these experiments.

For both fluids, the diameter data close to T_c exhibit a deviation from the law of rectilinear diameter towards smaller densities, in agreement with the model of Goldstein *et al* [28, 26] for systems with repulsive many-body interactions. The diameter slope of CClF₃, as obtained from a straight-line fit to the data with $t > 8 \times 10^{-3}$, gives $A_1 = 0.86$ and has thus a value very similar to those observed in nonpolar fluids, which typically have A_1 values between 0.5 and 1.0 [28]. In contrast, CHF₃ has a diameter slope of $A_1 = 1.32 \pm 0.01$, considerably larger than those for nonpolar gases. According to the

theory of Goldstein *et al.*, A_1 should increase linearly with the molecular polarizability α_p . Whereas this prediction holds well in the case of CClF₃, the polarizability of CHF₃ is in fact smaller than that of most nonpolar fluids [99]. Due to its larger dipole moment, the polarizability of CHF₃ becomes considerably enhanced by dipole-dipole and dipole-induced-dipole interactions. (In contrast, taking the dipole-dipole and dipole-induced-dipole interactions into account has a negligible effect on the polarizability of CClF₃.) Even when the enhancement of the polarizability due to dipole-dipole and dipole-induced-dipole interactions is taken into consideration, CHF₃ still does not exhibit the same relationship between $\tilde{\alpha}_p \rho_c$ and A_1 as one would expect from Goldstein's theory. A similar discrepancy is observed for H₂O which also has a high value of A_1 [112] accompanied by a small polarizability. This deviation may be due to hydrogen bonding, which is known to play an important role in systems containing electronegative atoms (like O, N, F, Cl) together with hydrogen atoms [30]. These hydrogen bonds strongly influence the intermolecular potentials.

A more subtle point is the behaviour of the Lorentz-Lorenz function close to the critical point. Both diameter and refractive index have been predicted to have a critical anomaly [113, 114], both with the same exponent $1 - \alpha$, which makes it difficult experimentally to distinguish between the two phenomena. We observe a weak critical anomaly in the diameter close to T_c for both CHF₃ and CClF₃, of the same order of magnitude as observed in other experiments on nonpolar substances [28]. This effect, which seems to be more pronounced in CHF₃ than in CClF₃, may result from the fact that CHF₃ is more polar than CClF₃. No definite experimental evidence exists for the anomaly of the refractive index at optical frequencies [115]. Our method of determining the Lorentz-Lorenz function does not allow us to perform the precise measurements close to T_c which would detect such an anomaly. The Lorentz-Lorenz data of neither CHF₃ nor CClF₃ show such an anomaly with our experimental accuracy. Even though the Lorentz-Lorenz data of

CHF₃ show a slight increase close to the critical point (see figure 5.5), it is doubtful whether this is a real effect or just a statistical scatter in the data. We therefore assume \mathcal{L} to have the form of eq. (5.1) and not to exhibit any singularity in the critical region.

Chapter 6

Nicotine + Water Experiment: Results and Discussion

On the binary liquid system nicotine + water, focal plane interference measurements and light scattering experiments were carried out. In this way, the order parameter and the diffusivity were measured. Section 6.1 presents the order parameter measurements. The data suggest that corrections to scaling are of relatively minor importance in this system. Section 6.2 compares the results of the diffusivity experiments using the interference method and the light scattering method. In the interference method, a systematic dependence of the diffusivity on concentration was observed. The light scattering data were used to extract the critical exponent of the viscosity. In section 6.3 potential errors due to gravitational effects and nonequilibrium effects are discussed. Finally, section 6.4 presents a discussion of the results.

6.1 Order Parameter

For binary liquids, the order parameter Δx^* is defined as the difference in concentration x of one of species (say nicotine) between the two coexisting phases I and II:

$$\Delta x^* = x_{nico}^I - x_{nico}^{II} = B_0 t^\beta (1 + B_1 t^\Delta + ...)$$
(6.1)

There is no definite agreement in the literature on whether x should be picked as the mole fraction, mass fraction or volume fraction [116]. Usually, one chooses the one that produces the most symmetric phase diagram. Since our experiments did not measure x_{nico}^{I} and x_{nico}^{II} separately, but only their difference, we could not make a decision based

on our data; but since the nicotine + water phase diagram looks very symmetric when expressed in terms of mass fraction [81], we decided to define our order parameter in wt%. This choice has no influence on the exponent β [116], but affects the values of the amplitudes.

The order parameter Δx^* is related to the refractive index difference between the coexisting phases, which is the quantity measured in our experiments. According to the data of Campbell *et al.* [81], the refractive index *n* varies linearly with composition x_{nico} in a region $x_{nico}^c - 0.3 < x_{nico} < x_{nico}^c + 0.3$ around the critical composition, so that we can write

$$\Delta x^* = \left(\frac{dx}{dn}\right)_c \Delta n \quad \text{with} \quad \left(\frac{dx}{dn}\right)_c = 4.72.$$
 (6.2)

 Δn is related to the number of recorded interference minima N_m by $\Delta n = (N_m - 1/2)\lambda/L$ (see section 3.2.2), where $\lambda = 6328$ Åis the laser wavelength and L = 0.2 cm the cell thickness.

On the nicotine + water system, data were collected during a period of over two years. The order parameter data could be grouped into six data sets. Within each set the temperature was measured using the same thermistor, but because different thermistors (or different Wheatstone bridges or batteries) were used in different sets, the critical temperatures varied somewhat, between 61.37°C and 61.43°C. Within each data set, the critical temperature was determined by a power law fit to the order parameter data, and when fitting several data sets together, corrections were made for their differences in (apparent) critical temperature.

Figure 6.1 shows a log-log plot of Δx^* as a function of reduced temperature, in the reduced temperature interval $10^{-6} < t < 2 \times 10^{-2}$. Δx^* was fitted to the expression 6.1 with various amplitudes and exponents as free parameters. The results are shown in Table 6.1. In the first two fits to a pure power law (i.e., $B_1 = 0$ in eq. (6.1)) the



Figure 6.1: log-log plot of the order parameter Δx^* of nicotine + water as a function of reduced temperature (six data sets).

β	B_0	Δ	B_1
(0.325)	1.644	-	-
(0.330)	1.691	-	-
0.3153	1.557	-	-
(0.325)	1.692	(0.5)	-0.403
0.3292	1.750	(0.5)	-0.535

Table 6.1: Results of fits of the order parameter of the nicotine + water system. Parameters shown in parentheses were held fixed for the fit.





Figure 6.2: log-log plot of $\Delta x^*/t^{\beta}$ with $\beta = 0.3153$, as a function of reduced temperature. exponent β was held fixed at values obtained in other experiments [82, 117] or expected theoretically. In the third fit β was treated as a free parameter and was found to be $\beta = 0.3153$, considerably lower than values obtained in other experiments on binary liquids [116]. Figure 6.2 shows a plot of $\Delta x^*/t^{\beta}$ as a function of reduced temperature, with $\beta = 0.3153$. The lines drawn into the graph indicate slopes that the data would exhibit for exponent values $\beta = 0.325$ and $\beta = 0.330$. Clearly, when fitting the data by a pure power law, $\beta = 0.315$ gives the most satisfactory result. Introducing one correction term $B_1 t^{\beta+\Delta}$ leads to a value of $\beta = 0.329$ in much better agreement with the results of

other researchers. The amplitude B_1 is then found to be negative. Including one more correction term may make B_1 positive, but the statistics of our data do not justify fitting so many free parameters.

6.2 Diffusivites

6.2.1 Fringe Data

As discussed in section 3.2.2, the diffusivity can be obtained from a measurement of the maximum deflection angle θ_{max} as the system is quenched from a temperature T_i in the two-phase region to a temperature T_f in the one-phase region (see also figure 3.6). If one plots $K\theta_{max}^{-2}$ (where $K = (L\Delta n)^2/4\pi$, and Δn is the initial refractive index discontinuity) as a function of time, the data points in a given run are expected to follow a straight line. The slope of this line determines the diffusivity $D(T_f)$. Figure 6.3 shows examples for three different runs, all with $t_f = (T_c - T_f)/T_f \approx 1.5 \times 10^{-4}$, but with different initial temperatures T_i and consequently with different initial refractive index discontinuities Δn and order parameters Δx^* . The data are seen to be well described by straight lines in the time interval considered (≤ 15 hours after the quench), indicating that the approximations made in section 3.2.2 are indeed valid. Thus, the slopes are well defined and $D(t_f)$ can be extracted quite accurately. However, as is seen from figure 6.3, the slopes of the runs with different initial temperature T_i (or equivalently, different Δn ,) do not agree, indicating that $D(t_f)$ depends also on the the initial composition discontinuity Δx^* across the meniscus in the two-phase region. Thus D is in fact concentration dependent (in contrast to the assumption in eq. (3.7), and this manifests itself in our experiment as a dependence of D on the order parameter, so that $D = D(\Delta x^*, t_f)$. Figure 6.4 illustrates the dependence of D on the order parameter Δx^* for the data taken at $t_f = 1.5 \times 10^{-4}$: D is seen to increase with decreasing composition discontinuity Δx^* across the meniscus.



Figure 6.3: Examples for the evaluation of the diffusivity D. Plot of $K\theta_{max}^{-2}$ as a function of time for three runs with the same value of the final quench temperature T_f , but different initial refractive index discontinuities Δn , corresponding to different initial order parameters Δx^* : $\Box - \Delta n = 0.020$ ($\Delta x^* = 0.094$), $\Delta - \Delta n = 0.025$ ($\Delta x^* = 0.118$), $\diamond - \Delta n = 0.032$ ($\Delta x^* = 0.151$).

Figure 6.4: Plot of the diffusivity $D(t_f, \Delta x^*)$ as a function of composition discontinuity Δx^* .

This dependence of D on Δx^* is strongest for small t_f , and less pronounced further from the critical point. In order to compare the diffusivities measured by the interferometric method with the results of the light scattering experiment (which measures D in the one-phase region where $\Delta x^* \equiv 0$), $D(\Delta x^*, t_f)$ has to be extrapolated to $\Delta x^* \rightarrow 0$, and we get

$$D(t_f) = \lim_{\Delta x^* \to 0} D(\Delta x^*, t_f)$$
(6.3)

For lack of a better estimate, the logarithm of D as a function of Δx^* was fitted by a straight line, and the zero intercept was taken as the value for $D(t_f)$. Figure 6.5 shows a log-log plot of all diffusivity data $D(\Delta x^*, t_f)$ as a function of reduced temperature t_f . The limiting values $D(t_f)$ are marked by full circles. A power law fit of the form $D(t_f) = D_0(t_f)^{\kappa}$ (see eq. (2.43)) yields $\kappa = 0.61 \pm 0.05$.

6.2.2 Light Scattering Data

The autocorrelation data accumulated in the storage of the Malvern autocorrelator were transferred into the UBC Amdahl 5850 and fitted to a relation of the form

$$G_k^{(2)}(\tau) = A[1 + C\exp(-2\Gamma\tau + \mu_2\tau^2)]$$
(6.4)

where τ stands for time. $A = \langle n \rangle \langle n_k \rangle$, where $\langle n \rangle$ is the total number of unclipped counts and $\langle n_k \rangle$ is the number of clipped counts. C is a parameter depending on the experimental geometry, $\langle n \rangle$, and the sampling time, and is a constant for a given experimental run. The diffusivity D is given by the equation

$$\Gamma = 1/\tilde{\tau} = Dq^2 \tag{6.5}$$

where $\tilde{\tau}$ is the correlation time and **q** is the scattering vector. q can be expressed in terms of the refractive index n of the medium, the wavelength λ of the laser light and



Figure 6.5: log-log plot of diffusivity data as a function of reduced final quench temperature t_f . Data of $D(\Delta x^*, t_f)$ are indicated by crosses (+), and the limiting values $D(t_f)$, with their corresponding error bars, by the symbol \bullet .

Chapter 6. Nicotine + Water Experiment: Results and Discussion

the scattering angle θ as

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2) \tag{6.6}$$

Since the refractive index n enters the diffusivity D quadratically, a precise measurement of D requires a precise knowledge of n. Our experiments were carried out on a critically filled cell in the one-phase region, and thus we had $n = n(T) = n_c$. The critical refractive index was determined in a separate experiment (see Appendix B) and found to be $n_c =$ 1.3811 ± 0.0004 .

The parameter μ_2 in eq. (6.4) is a measure of the variance of the distribution of diffusivities given by [118]:

$$\mu_2 = <(\Gamma - <\Gamma >)^2 > = Q < \Gamma >^2 \quad \text{where} \quad Q = \frac{<(\Gamma - <\Gamma >)^2 >}{<\Gamma >^2} \tag{6.7}$$

Thus, Q is a measure of the polydispersivity of the sample. For our experiments, only data with Q < 0.02 were taken into account for the evaluation. Whereas Q is usually quite small far from the critical point, it increases as T_c is approached. This is due to the fact that in the critical region the fluctuations become so important that the approximation of single scattering of the incident light is not valid any more. Rather, multiple scattering comes into play, distorting the spectrum of scattered radiation. A large Q can also be an indication of insufficient equilibration time. Therefore, in our experiments data were only taken after waiting long enough so that Q had reached a constant value.

We have taken data of D in the one-phase region at four different scattering angles $(\theta = 30^{\circ}, 60^{\circ}, 80^{\circ} \text{ and } 90^{\circ})$, the uncertainty in angle being about 0.5°. At angles 30° and 80°, the diffusivities were measured out to a reduced temperature of $\approx 10^{-2}$, and at angles 60° and 90° in a somewhat smaller temperature interval. Measurements further from T_c are difficult, because the intensity of the scattered radiation is very low. A transition into the two-phase region is accompanied by the appearance of a meniscus. We defined the

113



Figure 6.6: Diffusivities of nicotine + water, as obtained from light scattering experiments at different angles θ : $\circ = 30^{\circ}$, $\Box = 60^{\circ}$, $\triangle = 80^{\circ}$ and $\diamond = 90^{\circ}$. Error bars are indicated for each data point.

critical temperature as the temperature beyond which a meniscus was observed. This allowed us to determine T_c with an accuracy of 2-3 mK.

Figure 6.6 shows a log-log plot of the diffusivity data as a function of reduced temperature. Equation (2.43) describes the behaviour of the diffusivity $D(q) = \Gamma(q)/q^2$ as a function of reduced temperature and wavevector. In the hydrodynamic limit $q\xi \ll 1$ the dynamic scaling function $\Omega(q\xi)$ becomes a constant (see eq. (2.48)), so in this limit the diffusivity

$$\lim_{q\xi\to 0} D(q) = \frac{Rk_B T C_0}{\bar{\eta}\xi}$$
(6.8)

is expected to be independent of the scattering vector q. Indeed, our data show that for large reduced temperatures, where ξ is much smaller than the wavelength of the laser light, the data obtained at different scattering angles agree. The variation of Dwith temperature in the hydrodynamic limit can be used to obtain an estimate of the viscosity exponent z_{η} : Since $\bar{\eta} \propto \xi^{z_{\eta}}$, the diffusivity in the hydrodynamic limit behaves as $D \propto \xi^{-(1+z_{\eta})} \propto t^{\kappa}$ with $\kappa = \nu(1 + z_{\eta})$. Fitting the diffusivity data for $t > 10^{-4}$ and $\theta = 30^{\circ}$ by a power law in reduced temperature, we obtain $D_0 = 4.4 \times 10^{-6}$ and $\kappa = 0.658 \pm 0.005$. Assuming $\nu = 0.630$, this implies $z_{\eta} = 0.044 \pm 0.008$, slightly lower but in good general agreement with other experiments and theory.

Diffusivity data in the critical region can be used to obtain an estimate of z, the exponent characterizing the wavevector dependence of the Rayleigh linewidth in the critical limit $q\xi \gg 1$ (see eq. (2.47)). Since we have not measured the bare correlation length ξ_0 and thus cannot calculate how far the critical region ($q\xi \gg 1$) extends, we use the method suggested by Chu and Lin [119] to evaluate z: We calculate an "effective" exponent $z_{eff}(t)$ as a function of reduced temperature t by fitting our data to the expression

$$\Gamma(q,t) = C_{\infty} q^{z_{eff}(t)} \tag{6.9}$$

(see eq. (2.47 and eq. (2.48)). For large t (hydrodynamic limit $q\xi \ll 1$), z_{eff} should approach the value 2, whereas for $t \to 0$, z_{eff} tends to the critical value z. Figure 6.7 shows a plot of the z_{eff} data. A straight line fit of z_{eff} as a function of t, for $z_{eff} > 2.6$, $t < 5 \times 10^{-5}$, gives $z \equiv z_{eff}(t=0) = 3.104 \pm 0.026$, slightly higher than the value z = 3.063 ± 0.024 found by Burstyn and Sengers [76]. From the relation between the dynamic scaling exponent z and the viscosity exponent z_{η} (see eq. (2.49)) we calculate that $z_{\eta} =$



Figure 6.7: Plot of the effective exponent $z_{eff}(t)$ as a function of reduced temperature. The exponent z is obtained as the limit of $z_{eff}(t \to 0)$.

 0.104 ± 0.026 , somewhat higher than the value calculated above from considering data in the hydrodynamic limit.

6.3 Potential Sources of Error

Two potential sources of error in these experiments will be discussed in some detail: The question of gravity effects and the problem of equilibration times.

6.3.1 Gravitational Concentration Gradients

Concentration gradients are known to develop in binary liquid systems due to the divergence of the osmotic susceptibility close to the critical point. However, because of the small diffusivities in the critical region, they take a long time ($\gg 10$ days) to develop and reach their equilibrium value [120, 121]. The effects of gravity close to the liquid-liquid critical point in nicotine + water can be calculated following Ref. [122]. The variation of equilibrium concentration x with height z in thermal equilibrium can be written as

$$\frac{dx}{dz} \approx \frac{g}{\rho_c} \left(\frac{\partial \rho}{\partial x}\right)_{P,T} \left(\frac{\partial x}{\partial \mu}\right)_{P,T}.$$
(6.10)

Here, $(\partial x/\partial \mu)_{P,T}$ is the osmotic susceptibility and expected to diverge close to the critical point with an exponent γ . Since the exact values for the nicotine + water system are not known, we use the result of Ref. [122] as an estimate: $(\partial x/\partial \mu)_{P,T} \approx 5.75 \times 10^{-7} (T - T_c)^{-1.2}$. In the nicotine + water system, around the critical composition, $(\partial \rho/\partial x)_{P,T} \approx$ 0.064 g/cc [81], and $\rho_c \approx 0.995 \text{ g/cm}^3$. Thus we obtain $dx_{nico}/dz \approx 10^{-5} (T_c - T)^{-1.2}/\text{cm}$. Hence, the equilibrium composition profile in the one-phase region is not uniform, as assumed in section 3.2.2, but has a finite slope at the site of the meniscus of order of magnitude (dx_{nico}/dz) . This leads to a finite equilibrium refraction angle θ_{max} , so that for times $\tau \to \infty$ one expects that

$$\theta_{max}(\tau \to \infty) = \frac{L}{(dx/dn)_c} \frac{dx_{nico}}{dz} \approx 5 \times 10^{-7} (T_c - T)^{-1.2}$$
(6.11)

with $(dx/dn)_c = 4.72$ (see eq. (6.2)) and L = 0.2 cm = cell length. This effect is thus just barely detectable close to the critical point: at $T_c - T = 0.001$ K, $\theta_{max}(\tau \to \infty) \approx 0.1^{\circ}$. However, for temperatures so close to T_c , the diffusivities are so small that this state would only be observed after a very long time ($\gg 10$ days [123]), much longer than any of our experiments. Thus we conclude that, due to the close density matching, in the nicotine + water system gravity effects play a negligible role.

6.3.2 Equilibration Times

The long equilibration times, due to the critical slowing down in the critical region, raise the question of the validity of experiments performed close to the critical point. We present here an estimate of equilibration times in the two-phase region of the nicotine + water system.

If the critically filled cell, before it is heated from the one-phase into the two-phase region, is thoroughly mixed (by removing it from the thermostat block and shaking it), we can assume that it is at a homogeneous composition x_c . After heating to a reduced temperature $t_i = (T_i - T_c)/T_c$ in the two-phase region (see Fig. 6.8), phase separation occurs via spinodal decomposition [124]. This means that one phase will form a network of interconnected domains on all length scales in the other phase. The dominant length scale of the domains, r, increases with time τ as a power law, $r \propto \tau^{-\phi}$, where ϕ depends on the reduced temperature t_i and on the time regime. In the time interval of interest to us, corresponding to the "late stages of spinodal decomposition", ϕ lies between -0.6 and -0.8 [124, 125]. To simplify calculations, we assume that we are dealing with droplets of radius $r(\tau)$ of the "wrong" composition x_1 (and thus the "wrong" density ρ_1) embedded



Figure 6.8: Phase diagram of a binary liquid of the type of nicotine + water (with an inverted phase diagram). We assume that the system, after a temperature step from T_i^0 to T_f , has not reached thermal equilibrium, so that concentrations in the range $x_1^0 < x < x_2^0$ are present in the cell. A subsequent temperature step to temperature T'_i in the two-phase region then takes only part of the liquid mixture in the cell into the spinodal region: fluid in the composition range $x_1^e < x < x_2^e$ will demix via spinodal decomposition, whereas fluid in the ranges $x_1^0 < x < x_1^e$ and $x_2^e < x < x_2^0$ will demix via nucleation.

into a fluid of the "right" density ρ_2 , which will thus sink down or float up under the influence of gravity. The time it takes these droplets to reach the meniscus can be used to determine the relaxation time $\tilde{\tau}$. The droplets' velocity is given by Stokes' law,

$$v_s = \frac{2gr^2(\rho_1 - \rho_2)}{9\eta},$$
 (6.12)

where η is the viscosity of the medium and will be approximated as $\eta \approx 0.8$ cP (using the weighted mean with $\eta_{water} = 0.45$ cP and $\eta_{nico} = 1.7$ cP [126]).

In the case of nicotine + water, the density difference $\rho_1 - \rho_2$ in the region around the critical composition is proportional to the composition difference [81], i.e., $\Delta \rho = \tilde{c} \Delta x^*$, with $\tilde{c} \approx 0.06$ g/cc. In order to approximate r, we use results of a light-scattering experiment on isobutyric acid + water [124] which give

$$r = \frac{\pi}{q} = \frac{\pi\xi}{q_0} \left(\frac{D\sigma}{\xi^2}\right)^{-\phi}$$
(6.13)

Here, q_0 is a dimensionless scattering vector which can be estimated to be roughly equal to 4 [124]. For an estimate of r in the nicotine + water system, we use the same value. We also assume that the bare correlation length $\xi_0 \approx 3\text{\AA}$ [123]. In section 6.2.2 we found that $D = D_0 t_i^{\kappa}$ with $D_0 \approx 4.4 \times 10^{-6} \text{cm}^2/\text{s}$ and $\kappa \approx 0.66$; also, from our order parameter measurements in section 6.1 we obtained $\Delta x^* = B_0 t_i^{\beta}$ with $B_0 = 1.6$ and $\beta = 0.315$. Finally, using $\xi = \xi_0 t_i^{-\nu}$ with $\nu \approx 0.63$ we can write

$$v_s(\sigma) = v_0 t_i^{\epsilon_{eff}} \sigma^{-2\phi} \tag{6.14}$$

with $v_0 = (2g\pi^2 \tilde{c} B_0 \xi_0^{2(2\phi+1)})/(9\eta q_0^2 D_0^{2\phi})$ and $\epsilon_{eff} = \beta - 2\nu - 2\phi(2\nu + \kappa) \approx -0.95 - 3.85\phi$. From this equation the distance $d(\tilde{\tau})$ travelled in time $\tilde{\tau}$ can be calculated as

$$d(\tilde{\tau}) = \int_0^{\tilde{\tau}} v_s(\tau) d\tau = \frac{v_0 t_i^{\epsilon_{eff}}}{1 - 2\phi} \tilde{\tau}^{(1-2\phi)}$$
(6.15)

The time $\tilde{\tau}$ taken by a droplet to travel from the top (or bottom) of the cell to the meniscus can then be calculated using $d(\tilde{\tau}) = 1.6$ cm, corresponding to half of the fill

t_i	φ	$ ilde{ au}$	
10-4	-0.6	$\approx 6000 \text{ s}$	spinodal quench
10-4	-0.8	$\approx 1000 \text{ s}$	
10^{-3}	-0.8	$\approx 150 \text{ s}$	
10^{-2}	-0.8	$pprox 20 \mathrm{s}$	
10-4	-0.2	$\approx 10^7 \text{ s}$	quench into
10 ⁻³	-0.2	$pprox 10^7 \ s$	nucleation region
10-2	-0.2	$\approx 10^7 s$	·

Table 6.2: Estimated equilibration times $\tilde{\tau}$ for quenches to reduced temperature t_i in the two-phase region, into the spinodal and the nucleation region of the nicotine + water system

height of the liquid in the cell. Table 6.2 gives an estimate of the equilibration time $\tilde{\tau}$ as a function of reduced temperature t_i . For most reduced temperatures t_i , the equilibration times are on the order of a few hours or less for a spinodal quench.

A more complicated situation arises when the cell is not shaken between individual runs (see figures 6.8 and 6.9). After a quench from the two-phase region at temperature T_i^0 , where two compositions x_1^0 and x_2^0 coexist, into the one-phase region, the composition profile relaxes as described by the diffusion equation. Since the diffusivity is so small, the system has not reached equilibrium after a time ≈ 24 h after the quench, and exhibits a composition profile as shown in figure 6.9b. Thus, the top and the bottom of the cell contain liquid of different compositions x_1^0 and x_2^0 before the heatup into the two-phase region. When heating to a temperature T_i' in the nucleation region of the phase diagram, ϕ is much smaller ($\phi \approx -0.2$) [125] than for quenches into the spinodal region ($\phi \approx -0.8$), leading to much longer equilibration times (see Table 6.2). Thus we face the following situation for a cell heated into the nucleation region of the phase diagram: the liquid close to the meniscus, in the composition regime $x_1^s < x < x_2^s$, demixes rapidly via spinodal decomposition, whereas the rest of the cell demixes much more slowly via nucleation. This



Figure 6.9: Composition profile as a function of height in the cell (compare to figure 6.8). (a): in equilibrium at $T = T_i^0$, (b): after a quench into the one-phase region, (c): after a heat-up into the two-phase region to a temperature $T'_i > T_i^0$. In the density regime $x_1^s < x < x_2^s$, phase separation occurs via spinodal decomposition

may lead to a "warped" composition profile in the cell, as shown in figure 6.9c, where the composition and thus the refractive index are no longer monotonic functions of height. Since only the volume very close to the meniscus is important for the order parameter measurements, this effect is not expected to affect the order parameter data. However, as the relaxation of the composition profile close to the meniscus depends crucially on the composition profile in other parts of the cell, it may have severe consequences for the diffusivity measurements.

6.4 Discussion

The fits of the nicotine + water order parameter indicate that over the temperature interval $t < 2 \times 10^{-2}$ there are deviations from a pure power law. They cause the exponent β to differ from the theoretically expected value, but are less noticeable than in pure fluids, where corrections to scaling start playing a role at reduced temperatures $t > 10^{-4}$ (see figures 5.3 and 5.4). Similar results have been obtained in many other binary liquids [116] which leads to the conclusion that in binary liquids the scaling region extends to larger reduced temperatures $t \approx 5 \times 10^{-3}$.

The inclusion of one correction to scaling term results in a negative value of the amplitude B_1 , which at first sight is suspicious. However, the values of amplitudes depend strongly on the temperature range of the data: A similar result was obtained in experiments on n-heptane + acetic anhydride [127] and on carbon disulfide + nitromethane [128] where B_1 was also found to be negative when data in a reduced temperature interval $t < 2 \times 10^{-2}$ were fitted with one correction to scaling term.

For a comparison of the results of the diffusivity measurements obtained by light scattering and by the interference method, the diffusivities from both experiments are shown in the same log-log plot in figure 6.10. From the interference experiment, only



Figure 6.10: Comparison of the diffusivities obtained from light scattering experiments (open symbols) and interference measurements (with $\Delta x^* \rightarrow 0$, solid circles), as a function of temperature in the nicotine + water system.

the data $D(t_f)$ (i.e., with $\Delta x^* \to 0$) are included. Both data sets show the same qualitative trend: the diffusivity decreases as the critical point is approached, with the same exponent within error. However, there are some quantitative discrepancies: The diffusivities measured by the interference method are consistently larger than the diffusivities measured by light scattering.

This discrepancy is not due to nonequilibrium effects in the cell during the interference measurements: In the evaluation only those diffusivity data were considered for which the waiting time before the quench into the one-phase region was more than five equilibration times $\tilde{\tau}$ (as calculated in section 6.3.2 for quenches into the spinodal region). This was especially true for runs with small Δx^* , i.e., runs in which the cell was shaken before heating it into the two-phase region. The diffusivities $D(\Delta x^*, t_f)$ found for these runs lie close to the limiting values $D(t_f)$ and are thus consistently larger than the lightscattering data. Even if for some runs with large initial concentration discontinuities Δx^* the demixing occurred via nucleation, this has only very small influence on the limiting values $D(t_f)$ as $\Delta x^* \rightarrow 0$. We thus conclude that the larger values of the diffusivity in the interference experiment are to high probability not due to nonequilibrium concentration profiles at the outset of a run.

The reason of the discrepancy may lie in the fact that the interference method is inherently a nonequilibrium method, whereas in the light scattering experiment equilibrium concentration fluctuations are being probed. The diffusion process can be looked upon as a diffusion of little "droplets" of the size of the correlation length in a viscous medium (see eq. (2.43)). At a given temperature, the correlation length in a system of critical composition is larger than in a system whose composition is off-critical. Thus it is plausible that in the interference experiment, where diffusion occurs in two phases of off-critical composition, the size of the diffusing droplets is smaller than in the light scattering experiment, where the system is kept at critical composition. To our knowledge, the experiment presented here is the first measurement in which microscopic and macroscopic diffusivities are directly compared. Further studies on different systems are necessary to illuminate the discrepancy in more detail.

The light scattering diffusivity data, being less affected by statistical variations than the interference data, were used to calculate the viscosity exponent z_{η} . From our measurements we obtain that $z_{eff} = 3 + z_{\eta} = 3.104 \pm 0.026$. This value is slightly higher than theoretically expected, in contrast to some other experiments [129] which find $z = 2.992 \pm 0.014$, but they agree within error with the result obtained by Burstyn and Sengers [76] who found $z = 3.063 \pm 0.024$. We thus measure a viscosity exponent of $z_{\eta} = 0.104 \pm 0.026$, higher than the theoretical value which is $z_{\eta} = 0.054$ [77] from mode-coupling calculations and $z_{\eta} = 0.065$ [130] from RG. The reason for the deviation may be found in our evaluation method: The quality of the result in applying the method of Ref. [119] hinges on having as many precise data close to T_c as possible. We may not have approached T_c closely enough to observe the limiting behaviour of z_{η} . Moreover, a small change in the value used for the critical temperature will influence the value of z_{η} drastically. A change of 1mK in T_c changes the value of z_{η} by ≈ 0.05 . If our critical temperature was not correct, this may account for the discrepancy.

Another way of determining z_{η} is a fit of the diffusivity to a power law in the hydrodynamic limit. The exponent κ is then related to the viscosity exponent by $\kappa = \nu(1 + z_{\eta})$. From the light scattering data at scattering angle $\theta = 30^{\circ}$ at reduced temperatures $t > 10^{-4}$, we deduce that $z_{\eta} = 0.044 \pm 0.008$, in close agreement with other experiments and with theory. According to eq. (2.43), the diffusivity has a nonsingular contribution which we have not yet substracted from the total measured diffusivity as plotted in Figure 6.6. For some systems, the correction due to the background terms has been found to be as large as 1% at $q\xi = 1$ and several percent for smaller $q\xi$ [76]. Background terms in D lead to higher values of the exponent κ and thus z_{η} than expected theoretically [82, 131, 132]. Since the exponents found for nicotine + water in our experiment are of the same order of magnitude as the theoretical values, we conclude that background terms play a relatively small role in nicotine + water in the temperature regime covered in our experiment, so that their neglect has a minor impact on the diffusivity measurements.

Because the densities of the two constituents are so closely matched in the nicotine + water system, gravitational rounding of the composition profile plays a negligible role. Depending on the temperature, it is either too small an effect to be observed, or it takes too long to develop on the scale of the experiments to be noticeable. An interesting aspect is the possible observation of nonequilibrium density profiles. As we have shown, spinodal quenches lead to equilibrium after a relatively short time (a few hours or less), so that a wait of ≈ 12 h between runs is sufficient to assure equilibrium in most runs. If the cell is not thoroughly mixed between runs, however, there is a chance of quenching part of the cell into the nucleation region, even if in a series of runs the distance from the critical point, $T_i - T_c$, is increased with each run. One piece of evidence for this would be observed in the process of heating the cell from the one-phase to the two-phase region: Areas of the cell undergoing spinodal decomposition would exhibit critical opalescence, whereas regions of nucleation would remain clear. Indeed, we have observed in some of our runs that only the region of the cell close to the meniscus becomes milky close to the critical point.

The hypothesis of a "warped" concentration profile in the cell could explain the occurence of so-called "ghost fringes" which have have frequently been observed in our lab (and not just in the nicotine + water experiment): If the refractive index profile is not a monotonic function of height, but exhibits "bumps", these will lead to interference fringes at angles $\theta < 0$ and appear as ghost fringes on the films.

Chapter 7

He-Xe Experiments: Results and Discussion

This chapter discusses the results of the experiments on pure xenon and on a heliumxenon mixture containing 5% He. Section 7.1 presents the results of measurements of the Lorentz-Lorenz function, coexistence curve and diameter. The critical density of Xe is determined to very high accuracy and found to be insensitive to impurities in the sample. The coexistence curve diameter for Xe does not deviate appreciably from a rectilinear diameter, in apparent contradiction of the theory of Goldstein *et al* [26].

Section 7.2 gives the results of the experiments on the He-Xe mixture. The order parameter and compressibility of a He-Xe mixture are measured to be very similar to those of pure Xe, indicating that the addition of He does not change the liquid-gas character of the phase transition appreciably. We present a novel way of estimating the effect of wetting, by measuring indirectly the rise height of the wetting phase on the sapphire windows of the cell.

Finally, section 7.3 contains a discussion of the results.

7.1 Experiments on Pure Xe

In an effort to measure the critical density of xenon with as high precision as possible, experiments were performed using the prism cell setup. In order to test the consistency of the results for different samples, we performed prism cell experiments on two Xe samples (Sample #1 and Sample #2, described in Section 4.3) obtained from different suppliers. Subsequently, data were taken using the image plane interferomentric technique, as a

	\mathcal{L}_0	\mathcal{L}_1	\mathcal{L}_2	$\mathcal{L}_c(ext{fit})$	$< \mathcal{L}_c >$
	[cm ³ /mole]	$[\rm cm^6/mole^2]$	$[\rm cm^9/mole^3]$	[cm ³ /mole]	[cm ³ /mole]
Sample #1	10.413	25.28	-1569.	10.515 ± 0.001	10.510 ± 0.008
Sample $#2$	10.382	26.19	-1377.	10.505 ± 0.003	10.504 ± 0.006

Table 7.1: Results of a quadratic fit to the Lorentz-Lorenz data of two Xe samples. $\mathcal{L}_c(\text{fit})$ is the critical value of \mathcal{L} , obtained from quadratic fits. $\langle \mathcal{L}_c \rangle$ is the average of \mathcal{L} measurements in the density interval $0.88\rho_c < \rho < 1.12\rho_c$.

test of the high-pressure setup and in order to compare coexistence curve measurements in the high-pressure cell with those performed in the prism cell.

7.1.1 Lorentz-Lorenz Function

The Lorentz-Lorenz function, as defined in eq. (3.1), provides a link between the refractive index and the density of a fluid. It is measured by the prism cell method. The Lorentz-Lorenz function was fitted to a second order polynomial in the density ρ (see eq. (5.1)). Table 7.1 shows results of fits obtained in the density interval $0.3\rho_c < \rho < 1.4\rho_c$, and results of the critical value $\mathcal{L}_c = \mathcal{L}(\rho_c)$. Due to the scatter of the data points, the error in \mathcal{L}_c obtained from various fits, \mathcal{L}_c (fit) is considerably smaller than $< \mathcal{L}_c >$, calculated from averaging the Lorentz-Lorenz values over the interval $0.88\rho_c < \rho < 1.12\rho_c$. Figure 7.1 shows the Lorentz-Lorenz data of both samples, together with curves corresponding to the fit parameters given in Table 7.1. Note that the discrepancy between the \mathcal{L}_c -values of the two data sets is less than 0.1%. Our results for \mathcal{L} are in good agreement with other experiments which find the Lorentz-Lorenz function to have the value $\mathcal{L} = 10.52 \pm 0.02$ cm³/mole [133] and $\mathcal{L} = 10.53 \pm 0.07$ cm³/mole [134] on average in the density region $0.6\rho_c < \rho < 1.7\rho_c$.

Within the accuracy of our measurements, we observe no anomaly in \mathcal{L} close to the critical point, in agreement with the results of other researchers [133, 134]. Using eq. (5.2)



Figure 7.1: Lorentz-Lorenz data of Sample #1 (o) and Sample #2 (\bullet). The curves correspond to quadratic fits.
	A_1	$A_{1-\alpha}$	ρ_c [mole/cm ³]
outer temperature range			
$(t > 8 \times 10^{-3})$			
Sample $#1$	0.73 ± 0.04	(0.0)	0.008495(4)
Sample #2	0.65 ± 0.04	(0.0)	0.008481(8)
total temperature range $(10^{-5} < t < 2 \times 10^{-2})$			
Sample #1	0.73 ± 0.02	(0.0)	0.008497(2)
	(0.0)	0.47 ± 0.02	0.008492(1)
	1.3 ± 1.0	-0.5 ± 0.3	0.008502(2)
Sample #2	0.65 ± 0.01	(0.0)	0.008484(7)
	(0.0)	0.43 ± 0.02	0.008481(6)
	1.4 ± 1.0	-0.5 ± 0.3	0.008488(8)

Table 7.2: Fit results of the coexistence curve diameter of Xe. Parameters in parentheses were kept fixed for the fit.

we can calculate the electronic polarizability α_p from the limiting value of $\mathcal{L}(\rho)$ as $\rho \to 0$. We find $\alpha_p = 4.12 \pm 0.01$ Å.

7.1.2 Coexistence Curve Diameter and Critical Density

The prism cell data can be used to evaluate the coexistence curve diameter, $\rho_d = (\rho_l + \rho_v)/2\rho_c$, of Xe. For all fits of ρ_d the critical temperature was held fixed at the value obtained in the coexistence curve fits (see section 7.1.3).

Figure 7.2 shows a plot of the diameter data of Sample #1 and Sample #2 as a function of reduced temperature. In all cases, the data exhibit no significant deviations from straight lines. We thus do not observe any singularity of the coexistence curve diameter. Table 7.2 gives the diameter fit results. The first part of the table shows the parameters obtained from a straight line fit to the data with reduced temperatures



Figure 7.2: Coexistence curve diameter of the four experimental runs in the prism cell experiment. Open symbols correspond to the data of Sample #1, filled ones to the data of Sample #2.

 $t > 8 \times 10^{-3}$. For each sample, the data of the two runs were fitted together. The error is a measure of the difference between the two runs. The second part of the table gives results of fits treating A_1 and $A_{1-\alpha}$ as free parameters. The exponent α was kept constant at $\alpha = 0.11$. When only a linear term is fitted $(A_{1-\alpha} = 0)$, the values found for A_1 agree very well with the slopes of the straight-line fits in the outer temperature range $t > 8 \times 10^{-3}$. This indicates that there are indeed no systematic deviations from rectilinear diameter close to the critical point. Fitting both A_1 and $A_{1-\alpha}$ as free parameters does not give useful results, as indicated by the large errors.

The limiting value of the diameter ρ_d as $t \to 0$ determines the critical density ρ_c . We calculated the value of ρ_c for our samples by averaging the ρ_c -values obtained in the various diameter fits. The results are:

Sample #1:
$$\rho_c = 0.008496(4) \text{mole/cm}^3 = 1.1156(5) \text{g/cm}^3$$

Sample #2: $\rho_c = 0.008489(4) \text{mole/cm}^3 = 1.1139(5) \text{g/cm}^3$

For an evaluation of the uncertainty in the value of ρ_c due to systematic errors, it turns out to be easier to extract the limiting value n_c as $t \to 0$ of the refractive index diameter $(n_l + n_v)/2$ which is directly accessible experimentally and to calculate ρ_c using the Lorentz-Lorenz relation. The error calculation is presented in Appendix A. The results are:

Sample #1:
$$n_c = 1.1377 \pm 0.0001$$
 $\rho_c = 1.1160 \pm 0.0017 \text{g/cm}^3$
Sample #2: $n_c = 1.1374 \pm 0.0001$ $\rho_c = 1.1147 \pm 0.0017 \text{g/cm}^3$

The small differences of the critical densities found in the two evaluations are well within error.

Table 7.3 compares our values of the critical density with literature values. Our values are in good agreement with the literature values, but their error is considerably smaller.

Experimentor	ρ _c
Habgood et al. [135]	$1.099\pm? \text{ g/cm}^3$
Levelt [136]	$1.091 \pm ? \text{ g/cm}^3$
Chapman et al. [134]	$1.106 \pm 0.004 \text{ g/cm}^3$
Garside et al. [137]	$1.119 \pm 0.011 \text{ g/cm}^3$
Baidakov et al. [138]	$1.1128 \pm ? \text{ g/cm}^3$
Cornfeld and Carr [139]	$1.1113 \pm 0.0017 \text{ g/cm}^3$
_ " _	$1.1128 \pm 0.0003 \text{ g/cm}^3$
this work:	
Sample $#1$	$1.1160 \pm 0.0017 \text{ g/cm}^3$
Sample #2	$1.1147 \pm 0.0017 \text{ g/cm}^3$

Table 7.3: Critical density of Xe

Also, the values of Sample #1 and Sample #2 agree very well, indicating that whatever impurities they may have contained, these impurities have a minor impact on the critical density.

7.1.3 Coexistence Curve

Coexistence curve data were obtained both by the prism cell method (samples #1 and #2) and by the interferometric technique. The data were fitted to a power law in the reduced temperature t, with corrections to scaling as given in eq. (5.3).

In the prism cell experiment, two runs were performed on each of the two samples. Each data set was fitted separately. In order to be able to compare the results of the different samples and the different techniques, each data set was evaluated keeping the exponents fixed at their theoretically expected values ($\beta = 0.327$, $\Delta = 0.5$) and fitting the critical temperature and two amplitudes as free parameters. The fit results are given in Table 7.4. The values cited for each prism cell sample is the average of the results of the two runs. The fit results of the amplitudes of the two samples are seen to agree within error. Figure 7.3 shows a plot of $\Delta \rho^*/t^\beta$ as a function of reduced temperature t for

Sample	B ₀	B_1	B_2	T_{c} (K)
Prism cell data				
$(t < 3 \times 10^{-2})$,	
Sample $#1$	1.479 ± 0.011	1.15 ± 0.19	-2.6 ± 1.0	289.752 ± 0.001
Sample $#2$	1.470 ± 0.010	1.20 ± 0.17	-2.8 ± 1.1	289.789 ± 0.002
Image plane interference data				
$(5 \times 10^{-5} < t < 2 \times 10^{-2})$				
Sample #3 (long cell)	1.400	2.00	-5.5	289.920 ± 0.002
Sample $#4$ (short cell)	1.412	1.71	-4.1	289.882
Focal plane interference data				
$(5 \times 10^{-5} < t < 4 \times 10^{-2})$	1.444	1.41	-2.4	289.807

Table 7.4: Results of fits to the coexistence curve of Xe. For these fits, the exponents $\beta = 0.327$ and $\Delta = 0.5$ were held fixed.

the prism cell data of Samples #1 and #2. As is obvious from the figure, individual runs on the same sample show excellent agreement. There is a slight systematic difference between Sample #1 and Sample #2. In order to avoid overcrowding of the figure, the curves corresponding to the individual fits were omitted. The curves correspond to fits of all data collected on each sample with $\beta = 0.327$ and $\Delta = 0.5$ held fixed.

Interference experiments were carried out on Xe samples in cells of different thickness. By changing the window support plugs in our high-pressure cell, the cell length could be changed from L = 0.195(2) cm to L = 1.176(2) cm. As the high pressure cell and its temperature control system were so bulky, the second beam splitter in the optical setup could not be moved very close to the cell. Therefore light refracted from the neighbourhood of the meniscus, which is strongly bent close to the critical point, was lost from the image. This limited the reduced temperature regime accessible in this experiment to $t > 2 \times 10^{-5}$.

In order to compare the amplitudes obtained in the different experiments, the data .

Chapter 7. He-Xe Experiments: Results and Discussion



Figure 7.3: log-log plot of coexistence curve data of Xe, as measured in the prism cell. o - Sample #1, • - Sample #2. The dashed curves correspond to fits to data of Sample #1 and Sample #2 separately, with two correction to scaling terms and keeping $\beta = 0.327$ and $\Delta = 0.5$ fixed.

were fitted over the same reduced temperature range. Therefore, for the interference experiments only runs in the temperature interval $5 \times 10^{-5} < t < 2 \times 10^{-2}$ were taken into account. This leaves one set for each long cell (Sample #3) and short cell (Sample #4). The fit results on these data sets (again, with $\beta = 0.327$ and $\Delta = 0.5$ held fixed) are included in Table 7.4. The critical temperatures of the samples in the interference experiments are substantially higher than the ones measured in the prism cell experiments. Also, the critical amplitudes exhibit a marked deviation from the results obtained on Sample #1 and Sample #2.

As a comparison, Table 7.4 also contains results of a focal plane interference experiment [111], reevaluated using our measurements of the Lorentz-Lorenz function. Here, data were taken in the reduced temperature interval $8 \times 10^{-5} < t < 4 \times 10^{-2}$. The values of T_c and B_0 are between the values found in the prism cell experiment and those found in the image plane interference experiment.

Figure 7.4 shows a log-log plot of $\Delta \rho^*/t^\beta$ as a function of t for the interferometric data. The image plane data are seen to agree very well. There is some disagreement, however, with the focal plane experiment [111], both as far as the amplitudes and the critical temperature is concerned.

The interferometric data contain a curious feature which is absent in the prism cell data: Around a reduced temperature of $t < 3 \times 10^{-4}$, the data exhibit a "bump" which is the more pronounced the thinner the cell. As careful reevaluation of the data shows, this is **not** due to a miscount in interference fringes. Since the size of the effect decreases with increasing sample thickness, we assume that it has to do with an interaction of the fluid with the cell windows. We will come back to this feature later (see section 7.3).



Figure 7.4: log-log plot of the coexistence curve data of Xe from the interference experiments. \otimes – image plane interference, short cell, × – image plane interference, long cell, \diamond – focal plane interference [111].

7.2 He-Xe Mixtures

After the interferometric experiments on pure Xe, the cell was filled with a He-Xe mixture containing ≈ 5 mole% He. For this mixture, order parameter and compressibilities were measured. Since our prism cell was designed for pressures up to 60 atm, the Lorentz-Lorenz function in the critical region of this mixture (with a critical pressure $P_c \approx 90$ atm) could not be measured. We used the Lorentz-Lorenz data of pure Xe to convert refractivity data to densities in the He-Xe mixture.

7.2.1 Coexistence Curve

Two coexistence curve runs were performed on the He-Xe mixture. The data were fitted to a power law equation with corrections to scaling, as given in eq. (5.3). The critical temperature was found to be $T_c = 291.252(2)$ K for the first run and $T_c = 291.228(2)$ K for the second run. For the coexistence curve fits, in which both data sets were taken together, this difference in critical temperature was corrected for.

Data were taken in taken in the reduced temperature interval $3 \times 10^{-5} < t < 2 \times 10^{-2}$. Table 7.5 shows the fit results. When the data were fitted with two correction to scaling terms, a fit treating the exponent β as a free parameter gave $\beta = 0.3249$, in excellent agreement with theory. Also, keeping $\beta = 0.325$ fixed and fitting Δ as a free parameter yielded $\Delta = 0.498$, again very close to what is expected theoretically. Fitting the data with one more correction to scaling term has a negligible influence on B_0 and B_1 , and changes the value of B_2 only slightly. We thus conclude two corrections to scaling are sufficient for describing our data. Figure 7.5 shows a plot of $\Delta \rho^*/t^{\beta}$ as a function of reduced temperature for two experimental runs. The curve corresponds to a fit keeping $\Delta = 0.5$ fixed and treating β as a free parameter, with two correction to scaling terms.

Both data sets taken on the mixture exhibit a "bump" of the coexistence curve in the





Figure 7.5: log-log plot of $\Delta \rho^*/t^{\beta}$ as a function of reduced temperature t for a He-Xe mixture containing ≈ 5 mole% He. The curve corresponds to a fit with two correction to scaling terms, holding $\Delta = 0.5$ fixed and fitting $\beta = 0.3249$ as a free parameter.

	β	Δ	B_0	B_1	B_2	B_3
total temperature interval						
$2 imes 10^{-5} < t < 2 imes 10^{-2}$		•				
	(0.327)	(0.5)	1.370	1.96	-4.3	(0.0)
	(0.325)	(0.5)	1.344	2.12	-4.7	(0.0)
	0.3249	(0.5)	1.343	2.13	-4.8	(0.0)
	(0.325)	0.498	1.344	2.11	-4.7	(0.0)
	(0.327)	(0.5)	1.370	1.93	-3.8	-1.8
	(0.325)	(0.5)	1.343	2.17	-5.4	2.7
outer temperature range						
$5 \times 10^{-4} < t < 2 \times 10^{-2}$						
	(0.327)	(0.5)	1.373	1.93	-4.2	(0.0)
	(0.325)	(0.5)	1.349	2.06	-4.5	(0.0)

Table 7.5: Results of coexistence curve fits of a He-Xe mixture containing ≈ 5 mole% He. Parameters in parentheses were held fixed for the fit.

vicinity of $t < 3 \times 10^{-4}$ as observed in pure Xe. This feature causes deviations of the data from the assumed power law close to T_c . In order to make sure that this feature does not bias the fit results, fits were performed on the reduced temperature interval $t > 5 \times 10^{-4}$, where the effects of the bump are not noticeable. The results of these fits are also given in Table 7.5. Clearly, the bump has only a small effect on the amplitudes.

7.2.2 Compressibilities

The compressibilities can be obtained from the fringe spacing near the meniscus, in the manner described in reference to eq. (3.16). For the He-Xe mixture containing ≈ 5 mole% He, the critical pressure P_c was measured to be $P_c = 90 \pm 1$ atm and $\rho_c \approx 1.11$ g/cm³. The compressibilities were measured in the one-phase and the two-phase region. Figure 7.6 shows a log-log plot of the compressibility as a function of reduced temperature. The data were fitted to a power law $\kappa_T^{\pm} = \Gamma_0^{\pm} |t|^{-\gamma}$. Table 7.6 presents the results of this fit.

In the one-phase region, a power law fit to the data leaving γ a free parameter



Figure 7.6: Compressibilities of a He-Xe mixture containing 5 mole% He. \bullet - data in the one-phase region, \circ - data in the two-phase region, + - data point of pure Xe in the one-phase region.

· · · · · · · · · · · · · · · · · · ·	γ	Γ_0^{\pm}
One-phase region	1.07 ± 0.03	1.07 ± 1.0
	(1.241)	0.21 ± 0.04
Two-phase region	0.94 ± 0.02	1.05 ± 1.0
	(1.241)	0.07 ± 0.03

Table 7.6: Compressibility fits of a He-Xe mixture. Parameters in parentheses were held fixed for the fit.

yields $\gamma^+ = 1.07 \pm 0.03$, considerably lower than the theoretically expected value. In the two-phase region, a power law fit gives $\gamma = 0.942 \pm 0.018$, also substantially lower than the theoretical value. Fitting the compressibility data in the one-phase region with $\gamma^+ = 1.241$, we obtain $\Gamma_0^+ = 0.212 \pm 0.041$. This value is substantially higher than the one measured by Güttinger and Cannell [13], who found that for pure Xe $\Gamma_0^+ \approx 0.0575$.

One reason for the discrepancy might be that in our experiments the system was not in thermal equilibrium. Close to the critical point, the equilibration times become very long, due to the small diffusivities in the critical region. We found, however, that data taken after an equilibration period of 3-4 days do not exhibit significantly lower values of Γ_0^+ than data taken after ≈ 12 hours, and therefore we conclude that the discrepancy is not due to insufficient equilibration time.

Another possible explanation is the presence of temperature gradients in the cell [79]. The consequences of a thermal gradient on the compressibility are discussed in Appendix C. We find that the discrepancy in the compressibility can indeed be ascribed to a nonuniform temperature in the cell, with a gradient of $\approx 2 \text{ mK/cm}$.

The deviation of our measured value of γ from the theoretically expected value therefore could be attributed to a thermal gradient which depends on the temperature difference between cell and surroundings. Since the room temperature varied by several degrees, this also may explain the comparatively large scatter in the data. Figure 7.6 contains one data point of the compressibility of pure Xe in the one-phase region, which is seen to agree very well with the He-Xe data. Thus, there is no substantial difference in the compressibility of the mixture and the compressibility of pure Xe, and the large value of the compressibility of the mixture close to the critical point indicates that the phase transition in the binary fluid has very similar features to the liquid-gas phase transition.

7.2.3 Wetting

In the Xe and the He-Xe experiments, the image of the meniscus far from T_c is not seen as a narrow line (as in the CHF₃ experiment), but as a broad streak the width of which decreases as T_c is approached. This behaviour of the meniscus can be related to wetting of the walls by the fluid and suggests a novel experimental method for measuring the rise of a wetting fluid on the wall of the container. Figure 7.7 shows a log-log plot of the meniscus width as a function of reduced temperature for the two He-Xe runs and the Xe run using the thin cell. Far from T_c the the meniscus width is seen to approximately obey a power law in the reduced temperature, as indicated by the dotted lines which represent power-law fits to the Xe and He-Xe data in the temperature regime $4 \times 10^{-3} < t$. Around $t \approx 4 \times 10^{-3}$ deviations from this power law occur towards larger meniscus values. The data for pure Xe exhibit a similar exponent to the data for the He-Xe mixture, but with a slightly different amplitude. The deviation between the two data sets may be due to a small difference in magnification factor from the cell to the image which was not properly taken into account.

The results for the meniscus width can be understood in the framework of wetting: Classically, a liquid in equilibrium with its vapour partially wets a confining wall. The rise height adjusts itself in such a way that the pressure drop across the meniscus due to



Figure 7.7: log-log plot of the meniscus width as a function of reduced temperature. o, \Box -He-Xe experiment (two data sets), and \bullet - Xe experiment (one data set). The dashed (dotted) line corresponds to a power law fit to the He-Xe (Xe) data in the temperature range $t > 4 \times 10^{-3}$.

surface tension is balanced by the buoyancy force. The equilibrium rise height is [140]

$$h = \sqrt{\frac{2\Sigma}{g\Delta\rho}}\sqrt{1-\sin\theta} \tag{7.1}$$

where Σ is the surface tension, $\Delta \rho = \rho_l - \rho_v$ is the density difference between liquid and vapour and θ is the contact angle at the wall, determined by $\cos \theta = (\sigma_{sv} - \sigma_{sl})/\sigma$, where σ_{sv} (σ_{sl}) are the surface free energy between the vapour (liquid) and the solid wall and σ is the surface free energy of the liquid-vapour interface. As the contact angle is small [141, 142], we obtain that $h \approx \sqrt{2\Sigma/g\Delta\rho}$ [143]. The density difference varies with reduced temperature as $\Delta \rho \propto t^{\beta}$. The surface tension Σ obeys a power law $\Sigma \propto ((T_0 - T)/T_0)^n$ with n > 0, where T_0 is a temperature close to T_c [144]. Thus the rise height h decreases as the critical point is approached following a power law $h \propto t^{(n-\beta)/2}$. Wetting therefore leads to a curved meniscus, with fluid near the windows creeping up to wet them. Incident rays hitting the cell in the region of this meniscus are bent or scattered and lost in forming the image of that region of the cell. Identifying the meniscus width measured in the experiment with the rise height h, one can thus extract the exponent n. From a power law fit to our meniscus data, $M(t) \propto t^{\zeta}$, for reduced temperatures $t > 10^{-3}$, we get $\zeta = 0.441 \pm 0.020$ for the He-Xe runs and $\zeta = 0.473 \pm 0.018$ for pure Xe. From this, the surface tension exponent can be calculated. We obtain $n = 1.21 \pm 0.04$ for He-Xe and $n = 1.27 \pm 0.04$ for Xe. These values are in good general agreement with the one cited by Cahn [142] who finds n = 1.3.

The deviation of the meniscus widths from a power law for small reduced temperatures may be interpreted as an indication of total wetting close to the critical point [143, 142, 145]. This effect distorts the meniscus close to T_c from its classically expected shape, causing the denser phase to creep up very high ("infinitely high") along the walls. Thus a broader region around the meniscus, in which light rays are scattered and thus lost in the formation of the image, can be understood in terms of a critically expanded wetting height in the proximity of the critical point. The determination of the exact meniscus width is made difficult by the presence of interference fringes inside the image of the meniscus. Very close to T_c , the meniscus looks totally sharp, indicating that the meniscus height vanishes as the critical point is approached.

7.3 Discussion

Within the accuracy of our experiment, we observe no critical anomaly in the Lorentz-Lorenz function of Xe. The Lorentz-Lorenz data measured in two different samples of Xe agree to within 0.1% and agree with results obtained by other researchers. They can be adequately described by a second order polynomial in the density.

In our prism cell data on pure Xe, we observe no critical deviation from a rectilinear diameter. This is in contradiction with the theory of Goldstein *et al.* [26] according to which we would expect an anomaly whose magnitude should be proportional to $\alpha_p \rho_c$. For Xe, $\alpha_a \rho_c = 0.021$, larger than in any of the nonpolar gases studied in Ref. [28] which all display critical singularities in the diameter. Thus, we would expect the anomaly in Xe to be larger than observed in other fluids. However, there are indications [146] that in the Xe system the Axilrod-Teller interactions are not the most important three-body forces. Rather, exchange interactions play a dominant role. These, however, are not taken into account in the theory of Goldstein *et al.* This is a possible explanation of why the theory does not correctly predict the diameter anomaly of Xe.

From the diameter data, critical densities can be calculated. The values of ρ_c obtained from Sample #1 and Sample #2 agree to within 0.1%, demonstrating the reproducibility of the method and the insensitivity of the result to impurities.

The coexistence curve amplitudes, as obtained from fits on Sample #1 and Sample #2

agree very well. The critical amplitude B_0 is slightly lower in Sample #2 than in Sample #1. Also, the critical temperatures of the two samples differ by about 40 mK. Since the same experimental method and the same cell was used in the two measurements, this discrepancy must be due to differing impurities in the two samples. It is well known that the presence of impurities can strongly influence the critical temperature of a pure fluid sample [109]. As T_c in Sample #1 is so close to the literature value ($T_c = 289.74$ K), we assume that it is cleaner than Sample #2.

In contrast to this good agreement, the amplitudes obtained from fits to the interferometric data are markedly different: Even though the values of B_0 obtained from the image plane experiments on Xe agree well, they are substantially lower than the values obtained in the prism cell experiments. Also, the critical temperatures measured in the image plane experiment are considerably higher than in the prism cell experiments. This is probably due to He impurities in the high pressure sample cell: Since the setup was pressure-tested using He, and since the high-pressure tubing has such a small inner diameter, it is quite possible that not all the He was removed from the cell before filling it with Xe. A He contamination has the effect of increasing the critical temperature [44], as indeed observed in our experiment. The focal plane interference data exhibit values of B_0 and T_c between the image plane interferometric experiment and the prism cell experiment, indicating that the sample was probably also contaminated.

A He-Xe mixture containing 5 mole% He has a lower critical amplitude B_0 than pure Xe. Simultaneously, the critical temperature is substantially higher. The compressibility measurements were complicated by the presence of thermal gradients in the cell. This caused some scatter in the data, and led to distorted values of the critical amplitudes and exponents.

In the image plane interference experiments on Xe and the He-Xe mixture, and area in the vicinity of the meniscus appears as smeared; the streak is the broader, the further the system is from T_c . Identifying the width of this streak with the rise height of a wetting fluid, we measure an exponent of the surface tension which is in good general agreement with the value cited in the literature. This agreement indicates that it is indeed reasonable to assume that the finite meniscus width as seen in the image plane is due to wetting. The meniscus width data deviate from the power law at reduced temperatures $t \approx 4 \times 10^{-3}$. In the interference measurements on the order parameter of Xe and He-Xe, we observed a wiggle on the data in the reduced temperature regime of $t \approx 4 \times 10^{-4}$. Since this feature is the more pronounced for the thinner cell, we assume that it is also somehow related to wetting. The exact relation, however, is not clear at the moment.

Comparison of the coexistence curve data and compressibilities of Xe with those of the He-Xe mixture shows that there is no substantial difference between the two systems. This fact may be explained by the conjecture that the interference experiments cannot "see" the He, since He has a refractive index so close to unity. Moreover, the He atoms are small compared to the Xe atoms and could therefore easily slip through voids between the Xe atoms. In this case, they would not displace any Xe atoms, and would not have any effect on the density and refractive index of the xenon. An investigation of a He-Xe mixture using neutron scattering [45] found that the presence of He had a negligible effect on the Xe-Xe correlation function, so that the main effect of the presence of He is a shift of the critical temperature and pressure. This indicates that the phase transition has characteristics of the gas-liquid type rather than the binary liquid type.

Chapter 8

Conclusions

In this chapter, the results of the experiments performed in this thesis will be briefly reviewed and compared.

In order to test the influence of dipolar interactions on the order parameter and the coexistence curve diameter in pure fluids, experiments were carried out on CHF₃ (a strongly dipolar fluid), CClF₃ (a weakly dipolar fluid) and Xe (a nonpolar fluid). Table 8.1 gives an overview of the results. Here, $\tilde{\alpha_p}$ is the effective polarizability (as defined by eqn. (1.7)), A_1 is the linear term in the coexistence curve diameter (fitted for reduced temperatures $t > 8 \times 10^{-3}$), and B_0 is the critical amplitude of the order parameter. Our results for B_0 and A_1 can be compared to the theory of Goldstein *et al.* [26, 28], which, starting from a microscopic model of three-body interactions between the particles in a fluid, calculates the impact of these three-body forces on the critical amplitudes B_0 and A_1 . It is found that the amplitudes depend on a parameter x = q/ab, where q is the integrated strength of the three-body potential and a and b are the van der Waals parameters. In the limit of small x one obtains that $A_1 = 2/5 + 22x/15 + ...$

Substance	$\rho_c [\mathrm{g/cc}]$	$ ilde{lpha_p}[extsf{A}^3]$	$ ilde{lpha_p} ho_c$	A_1	B ₀
CHF ₃	0.527	3.5	0.016	1.31 ± 0.04	1.75 ± 0.02
CClF_3	0.582	4.67	0.016	0.86 ± 0.02	1.64 ± 0.02
Xe	1.115	4.12	0.021	0.69 ± 0.04	1.45 ± 0.03

Table 8.1: Comparison of critical polarizability product, order parameter amplitude and diameter slope for substances with different strength of dipolar interactions.



Figure 8.1: Plot of the order parameter amplitude B_0 as a function of the diameter slope A_1 for a variety of pure fluids. The line corresponds to a straight-line fit to the data.

and $B_0 = 2 + 2x/3 + \dots$ This implies that the order parameter amplitude B_0 increases linearly with the diameter slope A_1 like

$$B_0 = \frac{20}{11} + \frac{5}{11}A_1 \tag{8.1}$$

Figure 8.1 shows a plot of A_1 as a function of B_0 . The data of all substances investigated fall on a straight line, which supports the hypothesis of three-body interactions as postulated in the theory of Goldstein *et al.* Even though CHF₃, being a polar fluid, exhibits a value of A_1 which is markedly larger than for nonpolar fluids, its value of B_0 is also larger, so that the proportionality of A_1 and B_0 is still approximately satisfied for CHF₃.

If the dominant three-body forces are triple-dipole forces of the Axilrod-Teller type [27],



Figure 8.2: Plot of the diameter slope A_1 as a function of the critical polarizability product for a number of fluids. The line corresponds to a straight line fit to the data (without Xe and CHF₃).

then x is found to be proportional to the dimensionless quantity $\tilde{\alpha}_p \rho_c$, called the "critical polarizability product" [28]. Figure 8.2 shows a plot of A_1 as a function of $\tilde{\alpha}_p \rho_c$ for a number of nonpolar fluids investigated before [28], and the three fluids of this thesis. The agreement with the theoretically expected curve is good for CClF₃, but the values for Xe and CHF₃ deviate strongly from this curve. This suggests that in the case of CHF₃ and Xe the three-body interactions are not Axilrod-Teller dipole-induced-dipole forces. In the case of CHF₃, the reason may be due to the strong molecular dipole moment of the molecules. For Xe, there are indications [146] that the modification of the two-body

Chapter 8. Conclusions

potential due to three-atom exchange interactions is more important than the one due to Axilrod-Teller interactions. This may explain why Xe exhibits a different relationship of A_1 to $\tilde{\alpha_p}\rho_c$ than other nonpolar fluids [28].

Since hydrogen bonds between the molecules play an important role in CHF_3 , it is not easy a priori to decide whether the difference in the critical amplitudes of CHF_3 and nonpolar fluids are due to the dipolar coupling between the molecules or due to hydrogen bonds. This question must be addressed in a separate investigation.

A deviation from rectilinear diameter is observed in CHF₃ and CClF₃, but not in Xe. This is in contradiction to the theory of Goldstein *et al.*, according to which the strength of the diameter singularity is expected to be proportional to the critical polarizability product $\tilde{\alpha}_p \rho_c$. Xe, having a large value of $\tilde{\alpha}_p \rho_c$, should therefore exhibit an especially strong critical singularity. The reason for this discrepancy may again be the fact that the Axilrod-Teller forces, in the case of Xe, are less significant than the three-body exchange forces [146].

Precision measurements of the critical density of Xe give values that are in close agreement with other data, but are more accurate. Impurities are found to have a negligible influence on the value of the critical density.

The universality conjecture states that the critical exponents and certain amplitude ratios should be the same for all systems in a given universality class. Table 8.2 gives a comparison of the values of the order parameter exponent β and the correction to scaling exponent Δ found in the various systems studied in this thesis. The values of β found in these vastly different fluids and liquid mixtures agree within error, in agreement with the principle of universality. They are also in close agreement with values found in other experiments and expected theoretically. For CHF₃, CClF₃ and nicotine + water, the value of Δ is smaller than expected theoretically ($\Delta \approx 0.5$ [11]). This same trend has been previously observed in other experiments [89]. For He-Xe, Δ is significantly larger

Substance	β	Δ
CClF ₃	0.328 ± 0.002	0.43 ± 0.02
CHF_3	0.328 ± 0.002	0.41 ± 0.02
nicotine + water	0.329 ± 0.003	
Xe	0.328 ± 0.003	0.44 ± 0.02
He-Xe	0.325 ± 0.002	0.50 ± 0.02

Table 8.2: Comparison of the order parameter exponent β and the correction to scaling exponent Δ for the substances studied in this thesis.

than in the other substances investigated in this thesis and very close to theoretically calculated value.

From experiments on CHF₃, the universal amplitude ratios Γ_0^+/Γ_0^- and $D_0\Gamma_0^+B_0^{\delta-1}$ have been determined (see table 5.7). They are in excellent agreement with theoretical predictions and with values found for nonpolar fluids, indicating that, as expected, the dipolar interaction between the molecules does not influence the universality class.

In the experiments on the binary liquid system nicotine + water, diffusivities were measured both by light scattering, an equilibrium method, and by focal plane interference, a nonequilibrium method. In the nonequilibrium method, the diffusivity data depend on the initial concentration difference between the phases, and the values of the diffusivity to be compared with the light scattering data are obtained in the limit as the initial concentration discontinuity goes to zero. In each experimental run, lasting up to 15 hours, the diffusivity was found to be constant in time for the duration of the experiment, which indicates that boundary effects did not play a role. The data from light scattering and interference experiments follow the same trend, but exhibit quantitative differences. From the light scattering diffusivity data the critical exponent of the viscosity was extracted to yield $z_{\eta} = 0.05 \pm 0.01$, in good agreement with other experiments [76] and theory [77, 130].

Chapter 8. Conclusions

In the binary fluid system He-Xe, an example of "gas-gas equilibrium", the critical amplitude of the order parameter, B_0 , and the compressibility are close to those of pure Xe. The fact that the isothermal compressibility of the mixture is as high as that of the pure substance leads to the conclusion that the He-Xe mixture behaves more like a fluid than a binary liquid. Thus, it seems as if the presence of He has mostly the effect of increasing the critical temperature and the critical pressure [109]. Even though this effect may be explained by our experimental method being unable to "see" the He, there is strong evidence [45] that in fact the He-Xe phase transition is of the liquid-gas type. In order to obtain a conclusive answer, binary fluid systems like Xe-Ar, in which both constituents have refractive indices markedly different from 1, and in which the sizes of the atoms are less dissimilar, should be investigated.

Appendix A

Error Analysis for Prism Cell Measurements

This appendix describes how the refractive index of a fluid inside the prism cell can be obtained from the refraction angle, and presents an error evaluation for the critical density obtained from a prism cell measurement.

A.1 Calculation of refractive index from refraction angle

We assume that the incident beam hits the first (straight) window of the prism at right angles. The refracted beam leaves the prism at an angle κ with respect to the incident beam. Figure A.1 shows the geometry and defines the angles. All dotted lines (\cdots) correspond to directions parallel to the incident beam. All dashed lines $(-\cdots)$ indicate normals to the window faces. n_s , n_a and n_{xe} are the refractive indices of sapphire, air and xenon respectively. $\theta_s(\theta_t)$ is the wedge angle of the straight (tilted) window, and θ is the prism angle. Angles α_i are between the beam direction and a surface normal, κ_i are angles between the beam and the direction of the incident beam, and κ is the total (measured) refraction angle. For obtaining an expression of the refractive index n_{xe} of the substance in the cell as a function of the deflection angle κ , we use the following equations:

• Snell's law

 $n_s \sin \alpha_1 = n_{xe} \sin \alpha_2$ $n_{xe} \sin \alpha_3 = n_s \sin \alpha_4$ $n_s \sin \alpha_5 = n_a \sin \alpha_6$



Figure A.1: Refraction geometry of the prism cell experiment. For an explanation of the symbols, see text.

• Window wedges

$$\alpha_1 = \theta_s$$
 and $\alpha_5 - \alpha_4 = \theta_t$

• Direction of beam with respect to incident direction:

$$\kappa_1 + \alpha_1 = \alpha_2$$
 $\kappa_1 + \theta = \alpha_3$
 $\kappa_2 + \theta = \alpha_4$ $\alpha_6 - \kappa + \alpha_5 - \kappa_2$

As θ_s and θ_t are small, we can Taylor-expand to obtain:

 $\sin \theta_s \approx \theta_s$ $\sin \theta_t \approx \theta_t$ $\cos \theta_t \approx \cos \theta_s \approx 1$

One thus obtains, to first order in θ_s and θ_t :

$$n_{xe} = (n_a/\sin\theta) \left[\sin(\kappa+\theta) + \theta_t \left(\cos(\kappa+\theta) - \sqrt{n_s^2/n_a^2 - \sin^2(\kappa+\theta)} \right) + \theta_s \left(\sin(\kappa+\theta)\cot\theta - n_s\cos\theta \right) \right].$$
(A.1)

This relates the refractive index of the medium n_{xe} to the refraction angle κ .

A.1.1 Error Estimates

Careful calibrations and an estimate of errors was essential for judging the accuracy of the critical densities determined in the prism-cell experiments. The following quantities were measured with the given accuracy:

- Systematic errors:
 - 1. Prism angle $\theta = 20.525^{\circ}$, with $\delta \theta = 0.010^{\circ}$.
 - 2. Sapphire window wedges:

Straight window: $\theta_s = -0.00018$, $\delta \theta_s = 0.00002$

Tilted window: $\theta_t = -0.00041$, $\delta \theta_t = 0.00003$

3. Volume of prism cell V = 12.066 cm³, $\delta V = 0.003$ cm³.

4. Mass of empty prism cell: $M_0 = 179.3995$ g, $\delta M_0 = 0.0030$ g.

Items 1 and 2 limit the accuracy of refractive index measurements. They lead to errors δn_{pr} , δn_s and δn_t due to the error in the prism angle θ and the tilt angles θ_s and θ_t respectively. Items 3 and 4 limit the accuracy of the density $\rho = M/V$.

• Random errors

1. Mass readings

2. Micrometer reading

3. Temperature reading

These errors produce a random error $\delta \mathcal{L}_c$ in the value of the Lorentz-Lorenz function at the critical point and a statistical error δn_c in the critical refractive index. In our experiments we found that

$$\left(\frac{\delta n_c}{n_c}\right)_{stat} \approx 1.8 \times 10^{-4} \qquad \left(\frac{\delta \mathcal{L}_c}{\mathcal{L}_c}\right)_{stat} \approx 2.9 \times 10^{-4}$$

The total error in the critical density can then be evaluated to be

$$\frac{\delta\rho_c}{\rho_c} = \sqrt{\left(\frac{\delta\mathcal{L}_c}{\mathcal{L}_c}\right)^2_{stat} + C^2 \left(\frac{\delta n_c}{n_c}\right)^2_{tot} + \left(\frac{\delta\rho_c}{\rho_c}\right)^2_{sys}}$$
(A.2)

where

$$\begin{pmatrix} \frac{\delta n_c}{n_c} \end{pmatrix}_{tot}^2 = \left(\frac{\delta n_c}{n_c} \right)_{stat}^2 + \left(\frac{\delta n_{pr}}{n_c} \right)^2 + \left(\frac{\delta n_s}{n_c} \right)^2 + \left(\frac{\delta n_t}{n_c} \right)^2$$
and
$$\left(\frac{\delta \rho_c}{\rho_c} \right)_{sys}^2 = \left(\frac{\delta M}{M} \right)_c^2 + \left(\frac{\delta V}{V} \right)_c^2 \approx 3.4 \times 10^{-4}.$$

The parameter C is obtained from a Taylor expansion of the Lorentz-Lorenz relation around the critical point, and is given by

$$C = \frac{6n_c^2}{(n_c^2 + 2)(n_c^2 - 1)}.$$

Appendix B

Critical Refractive Index and Critical Density of Nicotine + Water

This appendix describes the experimental methods used for measuring the critical refractive index and the density of the nicotine + water mixture, and gives the results of the experiments.

B.1 Critical Refractive Index Measurement

As is clear from equations (6.5) and (6.6), the scattering vector \mathbf{q} and therefore the diffusivity D depend on the exact knowledge of the refractive index of the liquid mixture. In order to determine the refractive index n_c of the critical mixture of nicotine + water as accurately as possible, we used an interferometric method. The mixture of critical composition was contained in a Hellma cell with parallel windows which in turn was held in a cylindrical cell holder to whose end a gear was attached. A geared-down toy motor turned the cell slowly about its vertical axis at a rate of about 1/24 rph. The cell-motor assembly was placed inside the thermostat in one arm of a Mach-Zehnder interferometer (see figure 3.7). As the cell was rotated, the optical path through it changed, leading to a change in the interference pattern between the cell beam and the reference beam. This interference pattern was detected in one spot in the image plane by a light sensitive diode (Hamamatsu). The diode output was monitored on an x - t recorder. The number of interference fringes is simply related to the optical path through the cell which depends on the refractive index of the medium inside. Thus, a measurement of the interference minima and maxima as a function of time (and thus of the rotation angle of the cell)

could be used to extract the refractive index of the liquid.

As the cell is rotated around its vertical axis, the angle ϕ between the cell normal and the incident beam changes as a function of time τ . The number of interference fringes $N(\tau)$, as measured from normal incidence ($\phi = 0$) is

$$N(\tau) = \frac{2d}{\lambda_0} \left(\sqrt{n_0^2 - \sin^2 \phi} - \cos \phi - n_0 + 1 \right) + \frac{D}{\lambda_0} \left(\sqrt{n^2 - \sin^2 \phi} - \cos \phi - n + 1 \right)$$
(B.1)

where d is the thickness of the quartz windows of the cell, $n_0 = 1.45709$ is their refractive index, D is the sample thickness in the cell, n is the refractive index of the sample, and λ_0 is the laser wavelength. As the rotation frequency of the cell is known, one can relate the rotation angle $\phi(\tau)$ at any time τ to the number of interference maxima recorded on the chart, and thus $N(\tau)$. In order to determine the time τ_0 at which $\phi(\tau_0) = 0$, the run was started at $\phi \approx -10^\circ$ and τ_0 was taken such that the interference pattern was symmetric around τ_0 , i.e., that $N(\tau + \tau_0) = N(\tau - \tau_0)$.

A calibration run with an empty cell (n = 1) gave $2d = 0.246 \pm 0.001$ cm, and measurement of the total cell thickness yields $(D + 2d) = 0.445 \pm 0.001$ cm. Thus the window spacing was measured to be $D = 0.199 \pm 0.001$ cm.

For the run with a filled cell, the interference pattern was recorded from $\phi \approx -10^{\circ}$ to $\phi \approx 50^{\circ}$, where the number of fringes is 940. A least squares fit to expression (B.1) yielded

$$n_c = 1.3811 \pm 0.0004 \tag{B.2}$$

Figure B.1 shows a plot of the number of interference fringes as a function of angle ϕ .

B.2 Densities of Nicotine + Water Mixtures

The densitometer used for the measuring the densities of nicotine + water mixtures - consisted of a pyrex bulb with a 0.1 ml pipet of resolution 1/1000 ml attached to it. The



Appendix B. Critical Refractive Index and Critical Density of Nicotine + Water 162

Figure B.1: Plot of the number of interference fringes as a function of rotation angle ϕ . The line corresponds to a fit giving a refractive index of $n_c = 1.3811$.

volume of the bulb was calibrated by filling the bulb with deionized water at 20°C and weighing it on a chemical balance. We found $V_0(20^{\circ}\text{C}) = 63.274 \pm 0.002 \text{cm}^3$. Due to the thermal expansion of pyrex [147], the bulb's volume changes in the temperature range $20^{\circ}\text{C} < T < 80^{\circ}\text{C}$ approximately as

$$V(T) = V_0(20^{\circ}\text{C}) \left[1 + (T - 20) * 12 \times 10^{-6} \right],$$
(B.3)

with T given in °C. The pipet was also calibrated with dionized water. The empty densitometer weighed 22.664 ± 0.001 g.

For a measurement of the temperature dependence of the density ρ in a nicotine + water mixture of a given composition, the densitometer was filled with the mixture and weighed. The bulb was subsequently immersed into a carefully temperature regulated (to 0.1°C) stirred water bath, and the rise height of the liquid in the pipet and equivalently the volume occupied by the liquid, was determined. Since the density was measured over a large temperature interval, it was necessary to "bleed" liquid from the densitometer at regular intervals as the temperature was increased, in order to keep the liquid from overflowing, and to reweigh the densitometer.

Figure B.2 shows a plot of the mixture densities as a function of temperature for pure nicotine, pure water, and a variety of mixtures around the critical composition. Note that for $T > T_c$, a near-critical mixture is in the two-phase region, which means that the densitometer contains two phases in equilibrium. This may account for the fact that in the mixtures, the ρ vs. T curves exhibit a slight change in slope in the neighbourhood of the critical temperature, $\approx 61.4^{\circ}$ C.

The concentration dependence of the density around the critical temperature is measured from our experiments to be $0.273 \pm 0.044 \text{ mg/\%cm}^3$. This information can be used to "density-match" the liquid mixture close to the critical point, where the nicotine concentration is $\approx 40\%$ [81]: An increase in the water density by about 0.66% will make the



Figure B.2: Temperature dependence of the density ρ of nicotine + water mixtures of a variety of compositions. The numbers indicate nicotine concentration in weight %. The uncertainty in the compositions is $\approx 0.2\%$.

coexisting phases in the vicinity of the critical point have the same density. To accomplish this, 0.7 wt% heavy water D₂O have to be admixed to the "normal" dionized water. Under these circumstances all gravity effects, which are already small in the nicotine + water system (see section 6.3.1), can be made even smaller.

Appendix C

Thermal Gradients in the Sample Cell

In this appendix we study the influence of a thermal gradient in the sample cell on compressibility measurements. A thermal gradient has the effect that the measured variation of density with height z has two contributions, one isothermal and the other due to the temperature variation [79]:

$$\left(\frac{\partial\rho}{\partial z}\right)_{tot} = \left(\frac{\partial\rho}{\partial z}\right)_T + \left(\frac{\partial\rho}{\partial T}\right)_z \left(\frac{dT}{dz}\right)$$
(C.1)

For the extraction of compressibility data, we measure the spacing of the interference fringes in the vicinity of the meniscus (z = 0) where the pressure and density are at their critical value. There, one can write [2]

$$\left(\frac{\partial\rho}{\partial T}\right)_{z=0} = \left(\frac{\partial\rho}{\partial T}\right)_{P_c} = -\left(\frac{\partial\rho}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\rho_c} = \frac{1}{g\rho_c} \left(\frac{\partial\rho}{\partial z}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\rho_c}.$$
 (C.2)

Using the law of corresponding states [1], $(\partial P/\partial T)_{\rho_c}$ can be estimated to yield

$$\left(\frac{\partial P}{\partial T}\right)_{\rho_c} = \frac{R\rho_c}{1 - b\rho_c} \quad \text{with} \quad \frac{1}{b\rho_c} = 1.98$$
 (C.3)

where R is the gas constant and b is one of the parameters in the van der Waals equation. The compressibility as measured in the experiment can then be written as

$$\kappa_T^{eff} = \kappa_T \left[1 + \frac{1}{0.495} \frac{R}{g\mathcal{M}} \left(\frac{dT}{dz} \right) \right] \tag{C.4}$$

with \mathcal{M} denoting the molar mass of the fluid. If the temperature dependence of the second term is weak, then κ_T^{eff} has the same temperature dependence as κ_T , and we can write:

$$\kappa_T^{eff} = \Gamma_{eff}^{\pm} |t|^{-\gamma} \tag{C.5}$$

166
A comparison of the compressibility amplitude in the one-phase region of pure Xe, $\Gamma_{eff}^+ = 0.21$, (corresponding to the data point marked by "+" in figure 7.6) with the literature value $\Gamma_0^+ = 0.0575$ [13] permits a calculation of the temperature gradient in our experiment. We obtain:

$$\left(\frac{dT}{dz}\right) \approx 2\mathrm{mK/cm}.$$
 (C.6)

This corresponds to an overall temperature difference of 7.5 mK over the total height of the cell. This seems like a very large gradient. It must be due to some heat leak from the cell's environment, which for the actual running conditions was 2 - 4 degrees warmer than the cell. This result is in general agreement with the test for thermal gradients performed prior to the experiments (see section 4.3), in which we found the cell bottom to be < 3 mK warmer than the top when the cell was 0.1 - 1 degrees warmer than the environment. In order to test for possible influences of the temperature of the outer bath on the compressibility, the bath temperature was varied while keeping the cell temperature constant. This variation had little effect on the compressibility, well within statistical scatter, so that we conclude that a thermal gradient like this does not stem from a heat leak from the cell to the bath. Rather, it is probably due to the stainless steel gas fill line.

Bibliography

- [1] E. A. Guggenheim, Thermodynamics. North Holland, Amsterdam (1967).
- H. E. Stanley, Introduction to Phase Transition and Critical Phenomena. Oxford University Press, New York (1971).
- [3] S.-K. Ma, Modern Theory of Critical Phenomena. Benjamin/Cummings Publishing Co., Reading, Massachussetts (1976).
- [4] M. E. Fisher in Critical Phenomena: Proceedings of the Summer School held in Stellenbosch, South Africa. ed. F. J. W. Hahne, Springer Verlag, New York (1983).
- [5] F. D. Lee and C. N. Yang, *Phys. Rev.* 87, 410 (1952).
- [6] M. J. George and J. J. Rehr, Phys. Rev. 53, 2061 (1977).
- [7] J. H. Chen, M. E. Fisher, and B. G. Nickel, Phys. Rev. Lett. 48, 630 (1982).
- [8] J. C. LeGuillou and J. Zinn-Justin, Phys. Rev. Lett. 39, 95 (1977).
- [9] B. Nickel and M. Dixon, *Phys. Rev.* B26, 3965 (1982).
- [10] S. Ma, Phys. Rev. Lett. 37, 461 (1976).
- [11] K. E. Newman and E. K. Riedel, Phys. Rev. B30, 6615 (1984).
- [12] A. Aharony and P. C. Hohenberg, Phys. Rev. B13, 3081 (1976).
- [13] H. Güttinger and D. S. Cannell, Phys. Rev. A24, 3188 (1981).
- [14] M. Barmatz, P. C. Hohenberg, and A. Kornblit, Phys. Rev. B12, 1947 (1975).

Bibliography

- [15] L. A. Weber, *Phys. Rev.* A2, 2379 (1970).
- [16] M. W. Pestak, Ph.D. thesis. Pennsylvania State University (1983).
- [17] M. W. Pestak and M. H. W. Chan, Phys. Rev. B30, 274 (1984).
- [18] P. Schofield, Phys. Rev. Lett. 22, 606 (1969).
- [19] J. T. Ho and J. D. Litster, Phys. Rev. B2, 4523 (1970).
- [20] D. A. Balzarini, Can. J. Phys. 50, 2194 (1972).
- [21] L. R. Wilcox and D. Balzarini, J. Chem. Phys. 48, 753 (1968).
- [22] M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, Rev. Mod. Phys. 51, 79 (1979).
- [23] U. Närger and D. A. Balzarini, Phys. Rev. B39, 9330 (1989).
- [24] L. Cailletet and E. C. Matthias, R. Hebd. Seanc. Acad. Sci. (Paris) 102, 1202 (1886).
- [25] M. Ley-Koo and M. S. Green, Phys. Rev. A16, 2483 (1977).
- [26] R. E. Goldstein, A. Parola, N. W. Ashcroft, M. W. Pestak, M. H. W. Chan, J. R. de Bruyn, and D. A. Balzarini, *Phys. Rev. Lett.* 58, 41 (1987).
- [27] B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943).
- [28] M. W. Pestak, R. E. Goldstein, M. H. W. Chan, J. R. de Bruyn, D. A. Balzarini, and N. W. Ashcroft, Phys. Rev. B36, 599 (1987).
- [29] D. Balzarini, J. R. de Bruyn, U. Närger, and K. T. Pang, Int. J. Thermophysics 9, 739 (1989).

- [30] J. N. Israelachvili, Intermolecular and Surface Forces. Academic, New York (1985).
- [31] W. L. Meerts and I. Ozier, J. Chem. Phys. 75, 596 (1981).
- [32] P. C. Johnson, T. L. Weatherby, and Q. Williams, J. Chem. Phys. 35, 2261 (1961).
- [33] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. 49, 435 (1977).
- [34] L. E. Reichl, A Modern Course in Statistical Physics. University of Texas Press, Austin (1980).
- [35] W. I. Goldburg in Light Scattering near Phase Transitions. eds. H. Z. Cummins and A. P. Levanyuk, North-Holland, Amsterdam (1983).
- [36] B. J. Berne and R. Pecora, Dynamic Light Scattering. J. Wiley & Sons Inc., New York (1976).
- [37] H. Z. Cummins and H. L. Swinney in Progress in Optics VIII, p. 133, ed. E. Wolf, North Holland, Amsterdam (1970).
- [38] H. L. Swinney in Photon Correlation and Light Beating Spectroscopy. eds. H. Z. Cummins and F. R. Pike, Plenum, New York (1974).
- [39] M. L. McGlashan, J. Chem. Thermodynamics 17, 301 (1985).
- [40] W. B. Streett, Can. J. Chem. Eng. 52, 92 (1974).
- [41] J. D. van der Waals, Zittingsv. K. Akad. Wet., p. 133. Amsterdam (1894).
- [42] G. M. Schneider, Adv. Chem. Phys. XVII. Wiley, New York (1970).
- [43] R. L. Hurle, F. Jones, and C. L. Young, J. Faraday Trans. II 73, 613 (1977).
- [44] J. de Swaan Arons and G. A. M. Diepen, J. Chem. Phys. 44, 2322 (1966).

- [45] M. C. Bellissent-Funel, U. Buontempo, C. Petrillo, and F. P. Ricci, Phys. Rev. A40, 7346 (1989).
- [46] C. Domb, Adv. Phys. 9, 149 (1960).
- [47] J. Zinn-Justin, J. Physique 42, 783 (1981).
- [48] K. G. Wilson, Phys. Rev. B4, 3174 and 3184 (1971).
- [49] K. G. Wilson and J. Kogut, Phys. Rep. 12, 75 (1974).
- [50] L. P. Kadanoff, *Physics* 2, 263 (1966).
- [51] E. Brezin, J. C. LeGuillou, J. Zinn-Justin, and B. G. Nickel, *Phys. Lett.* 44A, 227 (1973).
- [52] A. A. Vladimirov, D. I. Kazakov, and O. Tarasov, JETP 50, 521 (1979).
- [53] R. H. Swendsen, Phys. Rev. Lett. 42, 859 (1979).
- [54] G. S. Pawley, R. H. Swendsen, D. J. Wallace, and K. G. Wilson, *Phys. Rev.* B29, 4030 (1984).
- [55] F. J. Wegner, *Phys. Rev.* B5, 4529 (1972).
- [56] J. Adler, M. Moshe, and V. Privman, Phys. Rev. B26, 3958 (1982).
- [57] P. C. Albright, J. V. Sengers, J. F. Nicoll, and M. Ley-Koo, Int. J. Thermophys.
 7, 75 (1986).
- [58] R. B. Griffiths, Phys. Rev. 158, 176 (1967).
- [59] J. Rudnick and D. R. Nelson, Phys. Rev. B13, 2208 (1976).
- [60] A. Aharony and G. Ahlers, Phys. Rev. Lett. 44, 782 (1980).

- [61] M.-C. Chang and A. Houghton, Phys. Rev. Lett. 44, 785 (1980).
- [62] M. E. Fisher and A. Aharony, Phys. Rev. Lett. 30, 559 (1973).
- [63] J. S. Rowlinson, Liquids and Liquid Mixtures. Butterworth, London (1969).
- [64] A. Aharony in Phase Transitions and Critical Phenomena, Vol. 6. Eds. C. Domb and M. S. Green, Academic Press, London (1977).
- [65] B. Widom and J. S. Rowlinson, J. Chem. Phys. 52, 1670 (1970).
- [66] B. Widom and F. H. Stillinger, J. Chem. Phys. 58, 616 (1973).
- [67] M. S. Green, M. J. Cooper, and J. M. H. Levelt Sengers, *Phys. Rev. Lett.* 26, 492 (1971).
- [68] J. J. Rehr and N. D Mermin, Phys. Rev. A8, 472 (1973).
- [69] J. F. Nicoll and R. K. P. Zia, *Phys. Rev.* B23, 6157 (1981).
- [70] R. D. Mountain, Rev. Mod. Phys. 38, 205 (1966).
- [71] E. Jakeman in Photon Correlation and Light Beating Spectroscopy. eds. H. Z. Cummins and F. R. Pike, Plenum, New York (1974).
- [72] L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968).
- [73] K. Kawasaki, Ann. Phys. (New York) 61, 1 (1970).
- [74] E. D. Siggia, *Phys. Rev.* B13, 3218 (1976).
- [75] J. V. Sengers, Int. J. Thermophysics 6, 203 (1985).
- [76] H. C. Burstyn and J. V. Sengers, Phys. Rev. A25, 448 (1982).

- [77] T. Ohta and K. Kawasaki, Progr. Theor. Phys. 55, 1384 (1976).
- [78] H. C. Burstyn, J. V. Sengers, J. K. Bhattacharjee, and R. A. Ferrell, *Phys. Rev.* A28, 1567 (1983).
- [79] J. R. de Bruyn, Ph.D. thesis. University of British Columbia, Vancouver (1987).
- [80] D. Balzarini and P. Palffy, Can. J. Phys. 52, 2007 (1974).
- [81] A. N. Campbell, E. M. Kartzmark, and W. E. Falconer, Can. J. Chem. 36, 1475 (1958).
- [82] D. A. Balzarini, Can. J. Phys. 52, 499 (1974).
- [83] W. Jost, Diffusion. D. Steinkopff, Darmstadt (1957).
- [84] P. C. Hohenberg and M. Barmatz, Phys. Rev. A6, 289 (1972).
- [85] Operating and Installation Manual, Type K7023. Malvern Digital Correlator.
- [86] R. Foord, E. Jakeman, C. J. Oliver, E. R. Pike, and R. J. Blagrave, Nature 227, 242 (1970).
- [87] L. Williams, M.Sc. thesis. University of British Columbia, Vancouver (1986).
- [88] M. P. Stein, M.Sc. thesis. University of British Columbia, Vancouver (1986).
- [89] J. R. de Bruyn and D. A. Balzarini, Phys. Rev. A36, 5677 (1987).
- [90] T. C. Poulter, Phys. Rev. 35, 297 (1930).
- [91] E. W. Comings, High Pressure Technology. McGraw Hill (1956).
- [92] I. L. Spain and J. Paauwe, High Pressure Technology. Marcel Dekker Inc., New York (1977).

- [93] p. 37, Aminco Superpressure Catalogue, #466D. American Instrument Co. Silver Spring, MD (1974).
- [94] Autoclave Engineers, Catalog 6000. Autoclave Engineers Inc., Pennsylvania, 16512.
- [95] A. Michels, T. Wassenaar and P. Louwerse, Physica 20, 99 (1954).
- [96] US Bureau of Mines Report Invest. 7639 (1972).
- [97] U. Närger, J. R. de Bruyn, M. Stein, and D. A. Balzarini, Phys. Rev. B39, 11914 (1989).
- [98] A. D. Buckingham and C. Graham, Proc. R. Soc. London A336, 275 (1974).
- [99] H. H. Landolt and R. Börnstein, Zahlenwerte und Tabellen 1/3, pages 509ff.
 Springer Verlag, Berlin, (1951).
- [100] F. Baas and K. D. Van Den Hout, Physica A95, 597 (1979).
- [101] Estimated from comparison with ionization potentials of similar molecules in Landolt & Börnstein, Zahlenwerte und Tabellen, Springer Verlag, Berlin (1951).
- [102] S. M. Khodeeva and I. V. Gubochkina, Zh. Fiz. Khim. 51, 1708 (1977).
- [103] T. E. Morsy, Kältetechnik 18, 203 (1966).
- [104] J. M. H. Levelt Sengers, J. Straub, and M. Vincentini-Missoni, J. Chem. Phys. 54, 5034 (1971).
- [105] H. H. Landolt and R. Börnstein, Zahlenwerte und Tabellen II/1, page 346. Springer Verlag, Berlin (1951).

- [106] J. R. de Bruyn and D. A. Balzarini, Phys. Rev. B39, 9243 (1989).
- [107] J. V. Sengers and J. M. H. Levelt Sengers, Ann. Rev. Phys. Chem. 37, 189 (1986).
- [108] Yu. E. Sheludyak and V. A. Rabinovich, High Temp. Sci. 21, 48 (1983).
- [109] J. R. Hastings, J. M. H. Levelt Sengers, and F. W. Balfour, J. Chem. Thermodynamics 12, 1009 (1980).
- [110] O. G. Mouritsen, D. Balzarini, and P. Palffy, Can. J. Phys. 61, 1301 (1983).
- [111] D. Balzarini and O. G. Mouritsen, Phys. Rev. A28, 3515 (1983).
- [112] J. M. H. Levelt Sengers and S. C. Greer, Int. J. Heat Mass Transfer 15, 1865 (1972).
- [113] S. Y. Larson, R. D. Mountain, and R. Zwanzig, J. Chem. Phys. 42, 2187 (1965).
- [114] R. Hocken and G. Stell, Phys. Rev. A8, 887 (1973).
- [115] J. V. Sengers, D. Bedeeaux, P. Mazur, and S. C. Greer, *Physica* 104A, 573 (1980).
- [116] A. Kumar, H. R. Krishnamurti, and E. S. R. Gopal, Phys. Reports 98, 58 (1983).
- [117] J. Shelton and D. Balzarini, Can. J. Phys. 59, 934 (1981).
- [118] D. E. Koppel, J. Chem. Phys. 57, 4814 (1972).
- [119] B. Chu and F. J. Lin, J. Chem. Phys. 61, 5132 (1974).
- [120] S. C. Greer, T. E. Block, and C. M. Knobler, Phys. Rev. Lett. 34, 250 (1975).
- [121] E. Dickinson, C. M. Knobler, V. N. Schumaker, and R. L. Scott, *Phys. Rev. Lett.*33, 180 (1975).

- [122] M. Giglio and A. Vendramini, Phys. Rev. Lett. 35, 168 (1975).
- [123] D. Beysens, J. Chem. Phys. 71, 2557 (1979).
- [124] W. I. Goldburg in NATO Advanced Study Series B73, Scattering Techniques Applied to Supramolecular and Nonequilibrium Systems, eds. S.H. Chen, B. Chu and R. Nossal. Plenum Press, New York (1981).
- [125] M. Takahashi, H. Horiuchi, S. Kinoshita, Y. Ohyama, and T. Nose, J. Phys. Soc. Japan 55, 2687 (1986).
- [126] H. H. Landolt and R. Börnstein, Zahlenwerte und Tabellen II/5. Springer Verlag, Berlin (1951).
- [127] N. Nagarajan, A. Kumar, E. S. R. Gopal, and S. C. Greer, J. Phys. Chem. 84, 2883 (1980).
- [128] S. C. Greer, *Phys. Rev.* A14, 1770 (1976).
- [129] C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 40, 777 (1978).
- [130] E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, Phys. Rev. B13, 2110 (1976).
- [131] D. L. Henry, H. L. Swinney, and H. Z. Cummins, Phys. Rev. Lett. 25, 1170 (1970).
- [132] H. L. Swinney and H. Z. Cummins, Phys. Rev. 171, 152 (1968).
- [133] D. Y. Parpia and B. L. Smith, J. Phys. C4, 2254 (1971).
- [134] J. A. Chapman, P. C. Finnimore, and B. L. Smith, Phys. Rev. Lett. 21, 1306 (1968).

- [135] H. W. Habgood and W. G. Schneider, Can. J. Chem. 32, 98 (1954).
- [136] J. M. H. Levelt, *Physica* 26, 361 (1960).
- [137] D. H. Garside, H. V. Molgaard, and B. L. Smith, J. Phys. B1, 449 (1968).
- [138] V. G. Baidakov, A. M. Rubshtein, V. R. Pomortsev, and I. J. Sulla, *Phys. Lett.* A131, 119 (1988).
- [139] A. B. Cornfeld and H. Y. Carr, Phys. Rev. Lett. 29, 28 (1972).
- [140] L. D. Landau and E. M. Lifshitz, Fluid Mechanics. Addison-Wesley, Reading (1959).
- [141] L. V. Mikheev, Phys. Lett. A129, 245 (1988).
- [142] J. W. Cahn, J. Chem. Phys., 66, 3667 (1977).
- [143] R. F. Kayser, J. W. Schmidt, and M. R. Moldover, Phys. Rev. Lett. 54, 707 (1985).
- [144] M. W. Zemansky and R. H. Dittman, Heat and Thermodynamics. McGraw Hill, New York (1981).
- [145] M. R. Moldover and R. W. Gammon, J. Chem. Phys. 80, 528 (1984).
- [146] E. E. Polymeropoulos, J. Brickmann, L. Jansen, and R. Block, Phys. Rev. A30, 1593 (1984).
- [147] R. J. Corrucini and J. J. Gniewek, Thermal Expansion Coefficients of Technical Materials. NBS Monograph 29, US Department of Commerce, Washington (1961).