

1 Introduction

Critical phenomena may be studied in various different ways. The principle of critical point universality indicates an analogy between critical points in a wide variety of physical systems. For example, many features of the magnetic, superfluid, superconducting and ferroelectric transitions are quite similar to those found in pure fluids or mixtures [1,2]. In the case of fluids, the study of critical phenomena is associated closely to the field of hydrodynamics. Many investigations have been troubled by the dynamics of pure fluids near their critical point and the interest was arisen in the effect of the anomalous behaviour of several fluid properties on the dynamics of equilibration. In earthbound experiments, the strong coupling between gravity and compressibility severely complicates the study of this behaviour. For this reason, many experiments dealing with critical point phenomena are performed in a low gravity (or microgravity) environment. Means to achieve such an environment are provided by drop tubes, towers and shafts, parabolic flights with an aircraft and sounding rockets [3], all with a limited duration of the low gravity period of the order of seconds or minutes. However, for the study of equilibration in critical fluids it is essential to retain longer periods of low gravity which are found only in a satellite, examples of which are a space-shuttle or a spacestation. This thesis mostly deals with an experiment, performed in the microgravity environment of a spaceshuttle in orbit, on heat transfer in a pure fluid near to its critical point.

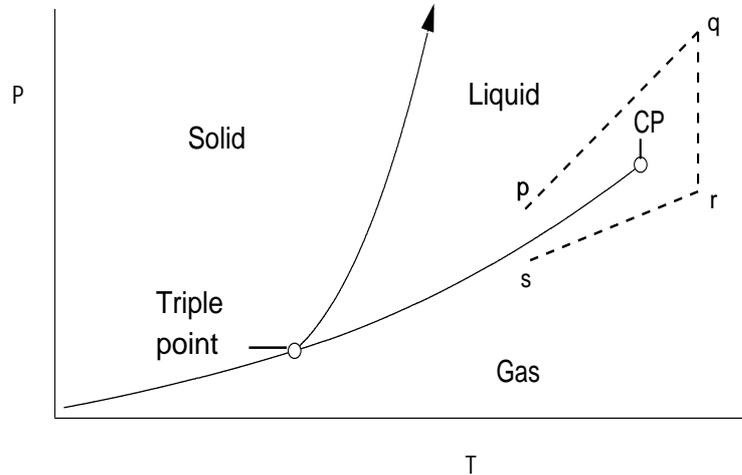
1.1 A Fluid

Everyone can recognize a liquid. It is popularly defined as a fluid which, if placed in a closed vessel, at once conforms to the shape of the vessel without necessarily filling the whole of its volume. The first property distinguishes it from a solid and the second from a gas. This simple definition is worth a closer examination for, although it is quite adequate for most purposes, it does not go very deeply into the relationship between solids, liquids and gases.

For most simple substances a clear distinction can be drawn between the solid state on the one hand and the fluid states, liquid and gas, on the other. If a fluid is cooled then it changes to a solid

state at a temperature which is a function of the applied pressure. At this melting temperature the solid and one of the fluid states can exist in mutual equilibrium. Only at the triple point can a solid phase be in equilibrium with both liquid and gas phases.

Figure 1.1 The (P,T) Phase Diagram.



The change from solid to fluid or from one fluid phase to the other is a sharp one at which the characteristic equilibrium properties of the substance change discontinuously. Such properties as the density, energy, heat capacities, coefficients of thermal expansion and of compressibility, and dielectric constant all have different values in the two phases. At the triple point the change from solid to liquid is less drastic than that from liquid to gas. However, at high pressures the situation is very different, for whereas the solid-fluid discontinuities are but little affected by the pressure, the size of the liquid-gas discontinuities decreases, slowly at first, but then with increasing rapidity as the two states finally become indistinguishable at the *liquid-vapour critical point* (CP in Figure 1.1). The existence of such an endpoint to the liquid-vapour coexistence curve implies an interesting characteristic; a fluid at point p, which might be said to be 'obviously' a liquid, can be changed to point s, 'obviously' a gas, first by heating at constant volume to q, expanding at constant temperature to r, and cooling at constant volume to s. At no point in this three-stage transformation has a change of phase occurred, and no dividing meniscus would have been observed in the vessel.

1.2 The Critical Point

The classical view of the critical point is that it is the state at which the densities of the coexisting phases are equal, and is also the highest temperature and pressure at which $(\partial P / \partial V)_T$ is zero. It has not been easy to study experimentally the behaviour of a fluid in the neighbourhood of its critical point. The difficulties arise from the unusual mechanical, thermal and optical properties of the fluid in this region. As one approaches the critical point, the heat capacities at constant pressure and at constant volume diverge which makes it hard to reach thermal equilibrium. Even slow changes of pressure are more nearly adiabatic than isothermal, and cyclic changes lead to hysteresis. Also, as the densities of the two phases approach each other the dividing meniscus becomes

first faint and then very hazy, and the measurement of the exact temperature of its disappearance needs great care.

But perhaps the most prominent feature is the divergence of the isothermal compressibility at the critical point; many of the exciting phenomena which can be observed in critical fluids are directly related to this. The density of a critical fluid, both on a local level as from a macroscopic point of view, becomes drastically sensitive to small disturbances. Microscopically, large density fluctuations occur spontaneously. The spatial extent of such density fluctuations may be described by a correlation length, which diverges also at the critical point. The occurrence of these large density fluctuations causes the phenomenon of *critical opalescence*, i.e. the strong scattering of light traversing a critical fluid. The observation of the system is made harder by this strong scattering of light which can lead to complete opacity at the critical point.

Macroscopically, the large compressibility induces the most severe restraint in the experimental obtention of the critical state [4]. In the earth's gravitational field, a critical fluid is being compressed under its own weight and large gradients of density arise in a vessel of a few centimetres high; critical conditions can only be reached in a very limited way and local properties may no longer be identified with those of the fluid as a bulk. In addition to this, the high value of the isobaric thermal expansion coefficient results in a diverging Rayleigh number and this leads inevitably to convective motion when temperature disturbances are imposed on the critical system.

All these effects make precise equilibrium measurements unusually difficult, and good agreement between critical constants measured in different ways is hard to achieve.

1.3 History

Many of the basic facts of critical phenomena were observed more than a century ago, while other aspects have been discovered only in recent years. It was already in 1869 that Andrews [5] discovered in the course of his measurements of the critical behaviour of carbon dioxide the, above mentioned, phenomena of critical opalescence. Since then, critical fluids have been studied extensively. Not much later, in 1873, Van der Waals succeeded in describing, at least qualitatively, the liquid and the gas phase with one single equation – the Van der Waals equation of state [6]. This equation, however, did not predict the occurrence of scattering and it was not until the beginning of this century that a qualitative explanation of this phenomenon was given due to the work of Einstein [7], and Ornstein and Zernike [8].

In the 1940's, Guggenheim [9] realized that the coexistence curve of a fluid system is not parabolic as the Van der Waals theory predicts, thereby inspiring the subject of critical-point exponents. The generally accepted conjecture is to describe near to the critical point the asymptotic behaviour of physical quantities, along selected paths in the phase diagram, in terms of simple power laws. With these power laws, critical exponents and power-law amplitudes are defined. In the early 1960's Heller and Benedek [10] came to recognize that the critical exponents were significant entities worthy of special attention in their own right and the study of critical phenomena came to focus more on the values of these exponents. Among these exponents, certain relations exist which are led by an assumption which has come to be called the scaling hypothesis. Widom [11] was largely responsible for the first clear and coherent mathematical exposition of the scaling hypothesis. In 1971 Wilson [12] developed the renormalization group theory for critical phenom-

ena in connection with phase transitions. This mathematical theory explains in detail and with accuracy how these phase transitions occur.

Until the end of the 1980's, both theoretical and experimental efforts have concentrated mostly on the derivation and measurements of the exponents and constants, and the relationships between them [2,13-16]. The study of fluids, however, belongs, in a general sense, to the field of hydrodynamics. In studying the anomalous behaviour of critical fluids and measuring the usual universal exponents, it was this hydrodynamic part which was little appreciated and it is precisely the anomalous behaviour of several thermodynamic functions which complicates the study of the dynamics of pure fluids near their critical point. Many troubling results have been reported which were related to these phenomena. On a workshop in 1989 on thermal equilibration near the critical point [17], it was Onuki who pointed out the importance of what has come to be known as *the piston effect* on the thermal response of a critical fluid to heating.

The mechanisms of heat transport governing the thermal response of a fluid sample to heating are well known. Under conditions where convective and radiant heat transport are suppressed, the only true heat-transport mechanism is thermal conduction and this leads to the usual assumption that the thermal diffusivity governs the transient thermal response of a fluid sample to heating. In the approach to the critical point of a pure fluid, where the thermal diffusivity is predicted to vanish, one would then expect heat transfer in the sample to slow down dramatically. Interestingly, pioneering microgravity experiments conducted over the last decade [18,19] demonstrated that, far from the slowing down presumption, heat seems to be transferred very rapidly in near-critical fluids. Indeed, equilibration time constants of a few seconds have been observed under conditions where hours or days would be expected on the basis of thermal conduction alone. On earth, such fast equilibration could arise from strong convective flows [20] but this mechanism could not be the agent in a space experiment.

Following these early observations in space experiments, theoretical work [21-24] showed that the "critical speeding up" phenomenon may be attributed to the increased importance of the isentropic temperature change in the bulk of the fluid. Fundamentally, this piston effect is not a mechanism of true heat transport; rather, it is a temperature change associated with isentropic compression of the fluid. Heating at the boundary causes thermal expansion of the adjacent fluid and, in a constant volume system, a pressure increase everywhere in the fluid. This pressure increase results in an essentially isentropic increase in temperature and density throughout the fluid. Thus there is a homogeneous temperature rise in the fluid which, although caused by application of heat at the boundary, is entirely independent of heat transport mechanisms except in a thin boundary layer. Experimental results soon followed, confirming the expected rapid and uniform thermal response in a near-critical fluid, ground-based [25] and from experiments in space [26-29].

The present conjecture is that thermal equilibration has an early, rapid stage based on the piston effect, as well as a later, slow stage. The early stage lasts only a few seconds, and leaves the near-critical fluid with an inhomogeneous temperature distribution that is close to the boundary temperature. The later, slow stage of thermal equilibration is governed by the thermal diffusivity.

1.4 Motivation

In a simple fluid the thermal conductivity is one of the thermodynamic quantities that has been shown, both theoretically and experimentally, to diverge when the critical point is approached. Some others are the isothermal compressibility, the isobaric thermal expansion coefficient and the specific heats, at constant pressure and at constant volume. These effects are related to the increase, both in spatial extent and amplitude, of the density fluctuations in the fluid on a microscopic scale [30-32]; hence the associated rates of divergence are interrelated. This interrelationship has been the subject of quite a number of theoretical and experimental studies.

The above-mentioned quantities all play a role in the flow of energy through a sample, and hence in the relaxation of the system to equilibrium after local heating or compression. As a consequence, the determination of the value of the thermal conductivity by experiment is always complicated by the requirement to know, or to determine simultaneously some other quantities.

Quantitative experimental corroboration of the theories that have been developed to account for the anomalous behaviour is, especially close to the critical point, incomplete [33-35]. For the reasons outlined in paragraph 1.2, it has not been possible to probe reliably either the thermal conductivity or the thermal diffusivity of a sample at the critical density much closer to the critical point than about 100 mK [36]. Thus experimental verification of the true singular behaviour has been indirect and has relied upon extensions of the theory into a region farther from the critical point, where it is necessarily less exact, but where comparisons with experiment have been possible.

This thesis sets out to study the processes of heat transfer in a locally heated fluid as close as possible to the critical point.

1.5 Outline of the Thesis

The processes of heat transfer are studied in a controlled way. A measuring technique is used, similar to that introduced by Becker and Grigull [37-40], in which the propagation of a plane thermal stepwise disturbance into an otherwise homogeneous sample is observed by interferometry and by temperature measurements. The fluid under investigation is sulphurhexafluoride (SF_6).

Chapter 2 starts with a brief overview of the properties, dynamic and static, of a fluid near its liquid-vapour critical point that are encountered in this thesis. Then, the evolution is considered analytically of the temperature-density field in a compressible fluid, following a plane thermal disturbance into an otherwise homogeneous sample. Apart from showing the profound influence of the piston effect on the thermal behaviour, the analytic exercise in this chapter suggests a new method to determine the isochoric specific heat near to the critical point.

Experiments have been performed in a microgravity environment ($g \approx 0$) in space and in the earth's gravity field ($g = 1$) on the ground. The experiments in space were carried out in ESA's Critical Point Facility (CPF) [41], which was flown in the cargo bay of the spaceship Columbia during the SpaceLab IML-2 mission. The experiments in our laboratory at the 'Van der Waals-Zeeman Instituut' were executed utilizing a set up which resembles CPF. The experimental equipment is discussed in **Chapter 3**.

Because of its essentially non-invasive nature, interferometry is used as a technique to monitor the behaviour of the density of critical fluids. In **Chapter 4** we discuss the conversion of an interferogram to a density distribution and we suggest a procedure for the determination of the thermal diffusivity by analysis of interferograms.

Interferometry hinges on the relation between the density and the refractive index of the fluid. It is generally assumed that this relation is most accurately described by the Lorentz–Lorenz relation [42]. However, this relation is only approximate and it was far from evident that this approximation is sufficiently accurate for our purpose. In **Chapter 5** we describe precision measurements of the refractive index and the density of SF₆ in a region around the critical density. Our results show that the Lorentz–Lorenz relation is not suited to describe this relation around the critical density with the accuracy we desire.

Finally, in **Chapter 6**, we will present the results from the space experiment concerning heat transfer in critical systems. We will start by giving a general impression of the space experiment before attention is given to some specific analysis features. The subsequent detailed presentation of the results is divided into three main subjects: the quantitative understanding of the piston effect, the measurement of the thermal diffusivity and the determination of the isochoric specific heat by the newly developed method.