THE CRITICAL BEHAVIOUR OF ETHYLENE AND HYDROGEN by
JOHN ROY de BRUYN
B.Sc. Physics and Astronomy, University of British Columbia, 1979 M.Sc. Physics, Queen's University, 1982

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

THE FACULTY OF GRADUATE STUDIES (DEPARTMENT of PHYSICS)
We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
October 1987
(C) John Roy de Bruyn, 1987

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

Department of Physics

The University of British Columbia 1956 Main Mall
Vancouver, Canada
V6T 1Y3
Date 29 Oct. 1987


#### Abstract

Optical techniques have been used to study the behaviour of ethylene and hydrogen near their liquid-vapour critical points. From measurements of the coexistence curve of ethylene over the reduced temperature range $1.5 \times 10^{-6}<t<$ $4.5 \times 10^{-2}$, where $t=\left(T_{c}-T\right) / T_{c}$ and $T_{c}$ is the critical temperature, we find the critical exponent $\beta=0.327 \pm .002$ and the corrections-to-scaling exponent $\Delta=0.46 \pm .02$. Similar measurements for hydrogen over the range $3.2 \times 10^{-5}<t<7.0 \times 10^{-2}$ give $\beta=0.326 \pm .002$ and $\Delta=0.46 \pm .02$. Measurements of the compressibility of hydrogen give the critical exponent $\gamma=1.19 \pm .05$ and the critical amplitude ratio $\Gamma_{0}^{+} / \Gamma_{0}^{-}=5.2 \pm .4$. With the exception of $\Delta$, which is slightly lower than its predicted value of 0.5 , the results for these universal quantities are in agreement with theoretical predictions.

The leading coexistence curve amplitude for hydrogen, $B_{0}=1.19 \pm .03$, is lower than the corresponding values for ethylene, $B_{0}=1.56 \pm .03$, and for other roomtemperature fluids. This decrease is in qualitative agreement with the predictions of a theory of quantum effects on critical behaviour. Measurements of the coexistence curve diameter for both fluids show an anomaly near the critical point having a form consistent with the predicted $t^{1-\alpha}$ temperature dependence. These results are in agreement with a recent theory of the effects of many-body forces on the diameter; the hydrogen data indicate that these forces are attractive in that fluid. This suggests that quantum mechanical exchange interactions are important near the critical point of hydrogen.


## Table of Contents

Abstract ..... ii
List of Tables ..... vi
List of Figures ..... vii
Acknowledgments ..... x
Chapter I Introduction ..... 1
I-1 An Introduction to Critical Phenomena in Fluids .....  1
I-2 Summary of Past Work ..... 4
I-3 Summary of This Work ..... 9
Chapter II Theory ..... 11
II-1 The van der Waals Equation in the Critical Region ..... 11
II-2 Homogeneity and Scaling ..... 15
II-3 Renormalization Group ..... 22
II-4 Corrections to Scaling ..... 26
II-5 Universal Amplitude Ratios ..... 28
II-6 Quantum Mechanical Effects on Critical Behaviour ..... 29
Chapter III The Experiments ..... 32
III-1 The Focal Plane and Image Plane Experiments ..... 32
III-2 The Ethylene Experiment ..... 40
III-3 The Hydrogen Experiment ..... 46
III-4 The Prism Cell Experiment ..... 56
III-5 Experimental Limitations ..... 61
Gravitational Rounding ..... 61
Temperature Gradients ..... 63
III-6 Data Reduction and Experimental Error ..... 64
Chapter IV Results, Part 1: Ethylene ..... 67
IV-1 The Prism Experiment ..... 67
The Lorenz-Lorentz Function ..... 67
The Coexistence Curve ..... 70
The Coexistence Curve Diameter ..... 77
IV-2 The Fringe Experiment ..... 82
IV-3 Combined Results ..... 84
Chapter V Results, Part 2: Hydrogen ..... 91
V-1 The Coexistence Curve ..... 91
V-2 The Coexistence Curve Diameter ..... 99
V-3 The Compressibility ..... 103
Chapter VI Discussion ..... 109
VI-1 Comparison with Previous Work ..... 109
VI-2 Universal Critical Parameters ..... 111
VI-3 Non-Universal Properties and Quantum Effects ..... 112
The Coexistence Curve and the Compressibility ..... 112
The Coexistence Curve Diameter ..... 118
VI-4 Crossover Effects ..... 119
Chapter VII Conclusions ..... 124
References ..... 126
Appendix A Conversion of Refractive Indices to Densities ..... 132
Appendix B Data Listings ..... 136
B-1 Lorenz-Lorentz Coefficient for Ethylene ..... 137
$\mathcal{L}(\rho)$ at 298.4 K ..... 137
$\mathcal{L}(\rho)$ on the Coexistence Curve ..... 138
B-2 Ethylene Coexistence Curve Data ..... 139
Prism Data ..... 139
Fringe Data ..... 141
B-3 Hydrogen Coexistence Curve Data ..... 150
Order Parameter Data ..... 150
Coexistence Curve Diameter Data ..... 155
B-4 Hydrogen Compressibility Data ..... 159
Appendix C Computer Programs ..... 160
C-1 BIGFIT - Coexistence Curve Data Analysis Program ..... 160
Listing of BIGFIT ..... 162
C-2 LLNEWER and COEX86 - Prism Cell Data Analysis Programs ..... 179
Listing of LLNEWER ..... 180
Listing of COEX86 ..... 185
C-3 Temperature Sweeping Program ..... 189
Listing of the Temperature Sweeping Program ..... 190

## List of Tables

I-1: Critical Exponents. ..... 5
I-2: Universal Amplitude Ratios. ..... 5
II-1: Scaling Laws. ..... 18
II-2: Corrections-to-Scaling Series. ..... 27
IV-1: Refractometric Virial Coefficients and Electronic Polarizability for Ethylene.68
IV-2: Fits of the ethylene order parameter data to eq. (1-6) with $\Delta=0.5$. ..... 76
IV-3: Fits of the ethylene order parameter data to eq. (1-6) with $\Delta$ a free parameter.78
IV-4: Fits to the Coexistence Curve Diameter of Ethylene. ..... 81
IV-5: Fits to the Coexistence Curve Diameter of Ethane. ..... 82
$\mathrm{V}-1$ : Fits of the hydrogen order parameter data to eq. (1-6) with $\Delta=0.5$. ..... 96
$\mathrm{V}-2$ : Fits of the hydrogen order parameter data to eq. (1-6) with $\Delta$ a free param- eter. ..... 98
V-3: Fits to the Coexistence Curve Diameter of Hydrogen. ..... 101
V-4: Fits to the Compressibility of Hydrogen. ..... 107
VI-1: Summary of Results. ..... 112

## List of Figures

1-1: The pressure-temperature phase diagram of a typical fluid. ..... 2
$2-1$ : The phase diagram of a van der Waals fluid. ..... 13
2-2: A schematic representation of the Kadanoff scale transformation. ..... 19
3-1: Gravity-induced density gradients in a fluid near the critical point. ..... 34
3-2: The optical setup for the fringe experiments. ..... 36
3-3: Formation of the Fraunhofer diffraction pattern. ..... 39
3-4: A block diagram of the ethylene apparatus. ..... 41
3-5: The temperature control circuit used in the ethylene experiment. ..... 43
3-6: The computer interface electronics. ..... 45
3-7: The cryostat used in the hydrogen experiment. ..... 47
3-8: The hydrogen cell assembly. ..... 48
3-9: The low temperature valve. ..... 50
3-10: The temperature controller for the hydrogen experiment. ..... 52
3-11: The gas handling system used in the hydrogen experiment. ..... 55
3-12: The optical setup for the hydrogen experiment. ..... 57
3-13: The optical arrangement for the prism experiment. ..... 59
3-14: A phase diagram showing the path followed in taking a data point in the prism experiment. ..... 60
3-15: Gravitational rounding. ..... 62
3-16: The Lorenz-Lorentz coefficient for $\mathrm{H}_{2}$, adapted from ref. 63. ..... 65
4-1: The Lorenz-Lorentz coefficient as a function of density for ethylene. ..... 69
4-2: The coexistence curve of ethylene and its diameter as measured in the prism experiment. ..... 71
4-3: A log-log plot of the order parameter vs. reduced temperature for the ethylene prism data. ..... 72
4-4: A $\log -\log$ plot of $\Delta \rho / t^{\beta}$ vs. reduced temperature for the ethylene prism data.74
4-5: Residuals of fits to the order parameter data of fig. (4-4). ..... 75
4-6: A schematic diagram of the coexistence curve diameter. ..... 79
4-7: The coexistence curve diameter of ethylene. ..... 80
4-8: The coexistence curve diameter of ethane. ..... 83
4-9: A $\log -\log$ plot of the order parameter vs. reduced temperature for the ethylene fringe data. ..... 85
4-10: A $\log -\log$ plot of $\Delta \rho / t^{\beta}$ vs. reduced temperature for the ethylene fringe data.86
4-11: Residuals for the fit shown in fig. (4-10). ..... 87
4-12: A log-log plot of the order parameter vs. reduced temperature for both sets of ethylene data. ..... 88
4-13: A $\log -\log$ plot of $\Delta \rho^{*} / t^{\beta}$ vs. reduced temperature for both sets of ethylene data. ..... 90
5-1: A log-log plot of the order parameter vs. reduced temperature for hydrogen. ..... 93
5-2: A log-log plot of $\Delta \rho^{*} / t^{\beta} v s$. reduced temperature for hydrogen. ..... 94
5-3: A $\log -\log$ plot of $\Delta \rho^{*} / t^{\beta}$ vs. reduced temperature for set 250287.4 of the hydrogen data. ..... 97
5-4: Residuals for the fit shown in fig. (5-3). ..... 98
5-5: The coexistence curve diameter of hydrogen as a function of reduced temper- ature. ..... 100
5-6: The coexistence curve diameter of hydrogen from data set 250287.2. ..... 102
5-7: The effective compressibility of hydrogen vs. reduced temperature. ..... 106
6-1: The coexistence curve amplitude, $B_{0}$, for a number of fluids as a function ofthe quantum parameter $\lambda_{T} / \xi_{0}$.114
6-2: The first correction amplitude, $B_{1}$, for a number of fluids as a function of$\lambda_{T} / \xi_{0}$.115
6-3: The leading compressibility amplitude, $\Gamma_{0}^{+}$, for a number of fluids vs. $\lambda_{T} / \xi_{0}$.117
6-4: The coexistence curve diameter slope, $A_{2}$, for several fluids vs. $\bar{\alpha} \rho_{c}$. ..... 120
6-5: The coexistence curve diameter slope, $A_{2}$, vs. the coexistence curve amplitude, $B_{0}$, for a number of fluids. ..... 121

## Acknowledgments

It is a pleasure to thank my supervisor, David Balzarini, for his advice and assistance at all stages of this work. I am also grateful to J. Carolan, M. Crooks, H. Gush and W. Hardy, whose loans of equipment, supplies and expertise were very much appreciated, and to J. Berlinsky for stimulating my interest in the field of critical phenomena. I have enjoyed and benefitted from numerous discussions with P. Palffy-Muhoray, S. Morris, E. Wishnow, M. Halpern and many others. I thank U. Narger for doing some shifts of data taking as well as for helpful discussions. I also thank the Natural Sciences and Engineering Research Council for several years' worth of scholarship support. Finally, I am grateful to my wife Sally for many discussions, for assistance in the preparation of this thesis, and for her unfailing support and patience throughout my involvement in this work. This thesis is dedicated to her.

## CHAPTER I

## Introduction

## I-1 An Introduction to Critical Phenomena in Fluids

Under certain conditions of temperature and pressure, a pure substance can exist in coexisting liquid, $\ell$, and vapour, $v$, phases. This situation is illustrated with a phase diagram in fig. (1-1). The liquid-vapour coexistence curve traces out a path in the pressure-temperature plane from the triple point, where the two fluid phases coexist with a solid phase, to the critical point at the critical pressure, temperature and density $P_{c}, T_{c}$ and $\rho_{c}$.

At a point on the coexistence curve the two phases are distinguished by their different densities $\rho_{\ell}$ and $\rho_{v}$; beyond the critical point this distinction vanishes and only a single fluid phase exists. Near the critical point, the density difference behaves like a power law ${ }^{1}$ :

$$
\begin{equation*}
\Delta \rho^{*} \equiv \frac{\rho_{\ell}-\rho_{v}}{2 \rho_{c}}=B_{0} t^{\beta} \tag{1-1}
\end{equation*}
$$

where $t=\left|T_{c}-T\right| / T_{c}$ is the reduced temperature and $\beta$ is a critical exponent. Experimental ${ }^{2-4}$ and theoretical ${ }^{5-9}$ determinations give $\beta \sim 0.327$; the amplitude $B_{0}$ is system dependent. $\Delta \rho^{*}$ is called the order parameter for the liquid-vapour


Figure 1-1 The pressure-temperature phase diagram of a typical fluid. The heavy line is the liquid-vapour coexistence curve. The triple point is labeled $T$; the critical point, C .
system, since it characterizes the ordering that occurs at the liquid-vapour phase transition.

The behaviour of many thermodynamic properties in the critical region is qualitatively different from their behaviour elsewhere. For example, the dimensionless isothermal compressibility $\kappa_{T}^{*}=\left(P_{c} / \rho_{c}^{2}\right)(\partial \rho / \partial \mu)_{T}$, where $\mu$ is the chemical potential, diverges at the critical point as

$$
\begin{equation*}
\kappa_{T}^{*+}=\Gamma_{0}^{+} t^{-\tau} \tag{1-2a}
\end{equation*}
$$

as the critical point is approached along the critical isochore $\rho=\rho_{c}$ from above $T_{c}$, and as

$$
\begin{equation*}
\kappa_{T \ell, v}^{*-}=\Gamma_{0 \ell, v}^{-} t^{-\gamma} \tag{1-2b}
\end{equation*}
$$

as the critical point is approached along the liquid and vapour branches of the coexistence curve. The critical exponent $\gamma$ is ${ }^{2,4-10}$ approximately 1.24 , and the amplitudes $\Gamma_{0}^{ \pm}$are again system dependent. Similarly, the specific heat at constant volume $C_{v}$ diverges at the critical point as

$$
\begin{equation*}
C_{v}^{ \pm}=F^{ \pm} t^{-\alpha} \tag{1-3}
\end{equation*}
$$

with $\alpha \sim 0.11$ and $F^{ \pm}$system dependent.
Near the critical point, the critical isotherm can be described in terms of the reduced chemical potential $\Delta \mu^{*}=\left(\rho_{c} / P_{c}\right)\left(\mu(\rho, T)-\mu\left(\rho_{c}, T\right)\right)$ and the reduced density by

$$
\begin{equation*}
\left|\Delta \mu^{*}\right|=D_{0}\left|\left(\rho-\rho_{c}\right) / \rho_{c}\right|^{\delta} ; \tag{1-4}
\end{equation*}
$$

$\delta$ is predicted ${ }^{5-9}$ to be 4.82 while $D_{0}$ is another system dependent amplitude.
Finally, consider a system on the critical isochore with $T>T_{c}$. Far from the critical point, it is energetically unfavourable for regions of the fluid to be at densities larger or smaller than $\rho_{c}$; local fluctuations in the density will therefore be very small. Closer to the critical point, density fluctuations become less unfavourable and their size accordingly increases. Finally, below $T_{c}$, these regions of high and low density become stable and the system phase separates.

If we denote the typical dimension of the fluctuations by a correlation length $\xi$, then close to $T_{c} \xi$ diverges as

$$
\begin{equation*}
\xi=\xi_{0} t^{-\nu} \tag{1-5}
\end{equation*}
$$

where $\xi_{0}$ is the bare correlation length and ${ }^{5-9} \nu \sim 0.65$. This divergence of the correlation length gives some insight into the unusual behaviour of a fluid near its critical point. Far from critical the fluid is well described by an equation of state involving some microscopic length scale $\sigma$ which characterizes the intermolecular
interactions - for example the van der Waals equation. Close to the critical point, however, $\sigma$ is no longer the important length scale. Regions of size of order $\boldsymbol{\xi}$ become correlated, and when $\xi \gg \sigma$ it is the behaviour of these fluctuations that determines the behaviour of the bulk fluid; thus $\xi$ becomes the dominant length scale. The details of the short-range ( $<\xi$ ) intermolecular interactions become unimportant.

It follows from this picture that all fluids should in some sense display the same critical behaviour, since for all fluids it is the divergence of $\xi$ that determines that behaviour. This is the principle of universality. It turns out that the critical exponents and certain combinations of the critical amplitudes are common to all members of a given universality class ${ }^{11}$. A system's universality class is determined by its dimensionality, $d$, the number of components in its order parameter, and the general nature of the microscopic interactions in the system. Pure fluids belong to the universality class characterized by $d=3$, a scalar order parameter, and short range interactions. Other systems in this class include the 3 -D Ising model, isotropic ferromagnets, and binary fluids.

Calculated values of the critical exponents and universal amplitude ratios for this universality class are given in Tables $\mathbf{I}-\mathbf{1}$ and $\mathbf{I}-2$. The exponent values given in Table I-1 are "best" values based on the results of a number of theoretical studies using renormalization group (RG) and high temperature series (HTS) techniques. Also given in this table are the classical exponent values applicable to the van der Waals equation, to be discussed below.

## I-2 Summary of Past Work

The study of critical phenomena began in the second half of the nineteenth century when experiments on $\mathrm{CO}_{2}$ showed that above a certain temperature, liquidvapour coexistence could not be observed ${ }^{12}$. This phenomenon was explained qualitatively by van der Waals' (VDW) equation of state ${ }^{13,14}$, which predicted a region

Table I-1 Critical Exponents

| Exponent | Associated <br> Quantity | Classical <br> Value | Calculated Values |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{RG}^{\mathrm{a}}$ | $\mathrm{HTS}^{\mathrm{b}}$ |
| $\alpha$ | $C_{v}$ | 0 | 0.11 | 0.11 |
| $\beta$ | $\Delta \rho^{*}$ | $1 / 2$ | 0.325 | 0.327 |
| $\gamma$ | $\kappa_{T}^{*}$ | 1 | 1.241 | 1.238 |
| $\delta$ | $\left.\Delta \mu^{*}(\rho)\right\|_{T_{c}}$ | 3 | 4.82 | 4.79 |
| $\nu$ | $\xi$ | $1 / 2$ | 0.630 | 0.630 |
| $\Delta$ | Corrections <br>  <br>  <br>  <br>  to scaling | - | 0.50 | 0.52 |

a) References 5,6
b) References 8,9

Table I-2 Universal Amplitude Ratios

| Ratio | Calculated Values $^{2}$ |  |
| :---: | :---: | :---: |
|  | RG | HTS |
| $\Gamma_{0}^{+} / \Gamma_{0}^{-}$ | 4.80 | 5.07 |
| $\Gamma_{0}^{+} D_{0} B_{0}^{\delta-1}$ | 1.6 | 1.75 |
| $F_{0}^{+} \Gamma_{0}^{+} / B_{0}^{2}$ | 0.066 | 0.059 |
| $F_{0}^{+} / F_{0}^{-}$ | 0.55 | 0.51 |
| $B_{1} / \Gamma_{1}^{+}$ | 0.5 | - |

a) References 1,44
of liquid vapour coexistence and a critical point. The quantitative predictions of VDW theory, however, did not agree with measurements in the critical region specifically, the critical exponents were wrong.

A clue as to the reasons for this discrepancy came from Onsager's exact solution of the 2-D Ising model ${ }^{15}$. While VDW-type theories involved thermodynamic functions that were everywhere analytic, Onsager's solution was nonanalytic at the critical point. Widom's formulation of a nonanalytic equation of state for fluids ${ }^{16}$ in 1965 and the subsequent development of the ideas of scaling ${ }^{17,18}$, discussed in Chapter II, led in the early 1970s to Wilson's ${ }^{19,20}$ development of the renormalization group approach to the theory of critical phenomena ${ }^{21,22}$. This approach provides a systematic way of dealing mathematically with the long range correlations that arise in a system as its correlation length diverges, and has been very successful both in helping our understanding of critical phenomena and in producing numerical results.

At the same time as Wilson's theory was being developed, experimental techniques began to probe more closely the critical region in fluids. Prior to this time, most measurements of the coexistence curve gave $\beta \sim 0.35$, somewhat higher than the calculated values of approximately $0.325^{14}$. In 1972 , Balzarini and $\mathrm{Ohrn}^{23}$ reported measurements on $\mathrm{SF}_{6}$ indicating that $\beta$ was temperature dependent, tending towards 0.33 for $t \sim 10^{-4}$. Other work around the same time led to similar results ${ }^{24,25}$. In 1976, Hocken and Moldover ${ }^{4}$ performed measurements on several fluids at $t \sim 1 \times 10^{-5}$; they found limiting values of $\beta$ and $\gamma$ in the ranges $0.321-$ 0.329 and 1.23-1.28 respectively, in good agreement with calculations for the 3-D Ising model.

In 1972 Wegner ${ }^{26}$ introduced the idea of corrections-to-scaling. The critical power laws in eqs. (1-1)-(1-5) are valid only asymptotically close to the critical point. At nonzero $t$, correction terms must be added. The observed temperature dependence of the effective order parameter exponent mentioned above is an indication that these corrections are significant in pure fluids even for $t \sim 10^{-4}$.

Wegner's theory ${ }^{26}$ was applied to fluids by Ley-Koo and Green ${ }^{27}$ in 1981. They obtained series expressions for various thermodynamic quantities of interest.

For example, eq. (1-1) for the order parameter becomes

$$
\begin{equation*}
\Delta \rho^{*}=B_{0} t^{\beta}\left(1+B_{1} t^{\Delta}+B_{2} t^{2 \Delta}+\cdots\right) \tag{1-6}
\end{equation*}
$$

while the isothermal compressibility of eq. (1-2) becomes

$$
\begin{equation*}
\kappa_{T}^{* \pm}=\Gamma_{0}^{ \pm} t^{-\gamma}\left(1+\Gamma_{1}^{ \pm} t^{\Delta}+\Gamma_{2}^{ \pm} t^{2 \Delta}+\cdots\right) \tag{1-7}
\end{equation*}
$$

and the critical isotherm, eq. (1-3) is

$$
\begin{equation*}
\left|\Delta \mu^{*}\right|=D_{0}\left|\left(\rho-\rho_{c}\right) / \rho_{c}\right|^{\delta}\left(1+D_{1}\left|\left(\rho-\rho_{c}\right) / \rho_{c}\right|^{\Delta / \beta}+\cdots\right) \tag{1-8}
\end{equation*}
$$

The diameter of the coexistence curve, which is the average of the liquid and vapour densities, is given by

$$
\begin{equation*}
\rho_{d} \equiv \frac{\rho_{\ell}+\rho_{v}}{2 \rho_{c}}=1+A_{1} t^{1-\alpha}+A_{2} t+A_{3} t^{1-\alpha+\Delta}+\cdots \tag{1-9}
\end{equation*}
$$

The correction amplitudes $B_{1}, \Gamma_{1}$, etc. are system dependent, and the universal exponent $\Delta$ has a calculated ${ }^{5,7,28,29}$ and measured ${ }^{2}$ value of approximately $0.5 \pm .02$.

Recently, many fluids have been studied in order to measure both the asymptotic critical exponents and corrections-to-scaling effects ${ }^{2,3,10,30,31}$. The former goal requires precise measurements close to $T_{c}$; the latter, data covering a wide range of reduced temperature to permit meaningful fits to the corrections-to-scaling expressions given above. The best experimental determinations of the exponents $\beta$ and $\gamma$ are in good agreement with the theoretical results summarized in Table $\mathbf{I}-\mathbf{1}$. Results for other exponents are less precise but generally agree with the calculated values.

Many previous determinations of amplitude ratios ${ }^{30}$ have relied on combining the results of different experiments. Since the values of the individual amplitudes tend to be sensitive to the choice of $T_{c}$ and to the exponent values used in analysing
the data, the reliability of ratios determined in this way is limited. The measurements of Pestak and Chan ${ }^{2}$ do not have this problem; their results for three ratios are in agreement with the theoretical predictions.

Two techniques have proven very useful for measuring thermodynamic quantities near the liquid-vapour critical point. Both are based on the fact that, close to the critical point, the compressibility of the fluid becomes large enough that the weight of the fluid on itself is enough to cause a measurable density gradient in the sample.

A capacitive method used by Pittman et al. ${ }^{3}$ for studies of ${ }^{3} \mathrm{He}$ and by Pestak and Chan ${ }^{2}$ on $\mathrm{N}_{2}, \mathrm{Ne}$ and HD uses a stack of small capacitors to measure the dielectric constant as a function of height in the sample. The dielectric constant $\epsilon$ is related to the density by the Clausius-Mossotti equation,

$$
\begin{equation*}
\frac{4 \pi N_{\mathrm{A}} \bar{\alpha}}{3}=\frac{1}{\rho} \frac{\epsilon-1}{\epsilon+2} \tag{1-10}
\end{equation*}
$$

where $\bar{\alpha}$ is the molecular polarizability and $N_{A}$ is Avogadro's number. This method has the advantage that capacitance can be measured very precisely using bridge techniques, but the disadvantage that the finite thickness of the capacitors limits reliable measurements to a region far enough from $T_{c}$ that the density within a single capacitor is uniform ${ }^{32}$.

The second method is the one used in this work. It is an optical technique developed by Balzarini ${ }^{24,33,34}$ and since used to study a number of fluids ${ }^{4,23,30,31,35,36}$. In one version of the method, a laser beam is passed through a fluid sample and focussed by a lens; the Fraunhofer diffraction pattern due to the sample is observed in the focal plane of the lens. In a second version, the beam passing through the sample is mixed with a reference beam and the resulting interferogram viewed in the image plane of a lens. In each case changes in the observed fringe pattern with temperature give information related to the liquid-vapour refractive index difference
below $T_{c}$. In the case of the image plane experiment, the spacing between interference fringes can be related to the compressibility. The Lorenz-Lorentz coefficient

$$
\begin{equation*}
\mathcal{L}=\frac{1}{\rho} \frac{n^{2}-1}{n^{2}+2} \tag{1-11}
\end{equation*}
$$

is used to convert refractive indices $n$ to densities. This technique can be used at smaller reduced temperatures than the capacitive technique, since a smaller height in the fluid is sampled by a ray of the laser beam ${ }^{32}$, but it loses precision close to $T_{c}$ because of the "digitization error" inherent in counting small numbers of interference fringes.

## 1-3 Summary of This Work

The experiments described in this thesis use the above optical techniques to study the critical behaviour of two fluids. Ethylene, $\mathrm{C}_{2} \mathrm{H}_{4}$, has its liquid-vapour critical point at 282.4 K , slightly below room temperature. Hydrogen, $\mathrm{H}_{2}$, has its critical point at about 33 K . Ethylene was also studied using another optical technique in which the refraction of a laser beam by a prism-shaped sample was measured to determine $\mathcal{L}(\rho)$ and the densities of the coexisting phases ${ }^{37-39}$.

These experiments were undertaken for two major reasons. First, it was hoped that measurements of several properties on the same sample would provide better values for some of the universal amplitude ratios given in Table 1-2. Second, we wished to investigate the effects of quantum mechanics on the critical behaviour of fluids. Because of the low mass and critical temperature of $\mathrm{H}_{2}$, quantum corrections to its critical behaviour may be significant. A theory, discussed in Chapter II, predicts that the critical exponents should not be affected, but that the critical amplitudes should change ${ }^{40}$.

Our results in general show very good agreement with both theory and previous experimental work on fluids near the critical point. From measurements of the
coexistence curves of both ethylene and hydrogen, we find values of the exponents $\beta$ and $\Delta$ which agree within our experimental error with the theoretical predictions. The coexistence curve amplitude $B_{0}$ shows at least qualitative agreement with the predicted effects of quantum mechanics, but our results for the correction amplitude $B_{1}$ are not conclusive in this regard.

Our measurements of the coexistence curve diameters of the two fluids show the presence of the predicted $t^{1-\alpha}$ critical anomaly, and the hydrogen diameter data show strong evidence for quantum mechanical effects in this fluid.

Finally, our results for the compressibility of hydrogen are less trustworthy because of experimental problems to be discussed below. Nevertheless we find values of the exponent $\gamma$ and the amplitude ratio $\Gamma_{0}^{+} / \Gamma_{0}^{-}$in agreement with theoretical predictions.

The remainder of this thesis is organized as follows: Chapter II contains a more detailed discussion of the theory of critical phenomena. The experiments and important related considerations are described in Chapter III and the results presented in Chapters IV and V. Chapter VI is a discussion of our findings, which are summarized along with some concluding remarks in Chapter VII.

## CHAPTER II

## Theory

In this chapter the ideas behind the modern theory of critical phenomena are discussed. The development of the theory from the van der Waals equation to the renormalization group is outlined, with emphasis on the important concepts of universality, homogeneity of thermodynamic functions, and scaling. A complete exposition of the methods of calculating numerical results is beyond the scope of this thesis, but results relevant to this work will be presented. The chapter ends with a discussion of the possible effects of quantum mechanics on critical phenomena.

## II-1 The van der Waals Equation in the Critical Region

Van der Waals' equation ${ }^{13}$ is the most successful of what are now called classical equations of state. While the VDW description of the critical point is incorrect, it is discussed here as a means of introducing several important ideas. The equation relates the pressure $P$, temperature $T$, and molar volume $v$ of a fluid by

$$
\begin{equation*}
\left(P+\frac{a}{v^{2}}\right)(v-b)=R T \tag{2-1}
\end{equation*}
$$

where $R$ is the universal gas constant. Here $a$ is a measure of the attractive interaction between molecules and $b$ represents the finite molecular size by a repulsive hard-core interaction. With $a$ and $b$ chosen to fit experimental data, this equation
of state describes the behaviour of real gases away from the critical point reasonably well.

Eq. (2-1) predicts a liquid-vapour phase transition. The equation is cubic in $v$, and so in general has three solutions for a given $T$ and $P$. At high temperatures, only one of these solutions is real, but below some critical temperature $T_{c}$ all three are. In this region the compressibility, which is proportional to $\partial v /\left.\partial P\right|_{T}$, is negative near the middle root, and the system is thermodynamically unstable; it separates into a high density (low $v$ ) liquid phase and a low density (high $v$ ) vapour phase. Maxwell's construction removes the region of instability and determines the coexistence curve by imposing the condition

$$
\begin{equation*}
\int_{v_{1}}^{v_{2}} P d v=P\left(v_{2}-v_{1}\right) \tag{2-2}
\end{equation*}
$$

on the coexisting phases 1 and 2. This forces equality of pressure, temperature and chemical potential on the two phases. The phase diagram of a VDW fluid is shown in Fig. (2-1).

The parameters $a$ and $b$ depend on the microscopic properties of a given system. They can be eliminated from eq. (2-1) in favour of quantities related to the critical point, at which the three roots of eq. (2-1) coalesce to one. At this point,

$$
\begin{equation*}
\left.\frac{\partial P}{\partial v}\right|_{c}=0 \quad \text { and }\left.\quad \frac{\partial^{2} P}{\partial v^{2}}\right|_{c}=0 \tag{2-3}
\end{equation*}
$$

where the subscript $c$ refers to the critical point. Using eqs. (2-3) and (2-1), the temperature, pressure and molar volume at the critical point are found to be

$$
\begin{equation*}
v_{c}=3 b, \quad R T_{c}=\frac{8 a}{27 b}, \quad P_{c}=\frac{a}{27 b^{2}} \tag{2-4}
\end{equation*}
$$



Figure 2-1 The phase diagram of a van der Waals fluid. The fine solid lines are isotherms. The dashed portion indicates a region of negative compressibility, which is eliminated by Maxwell's construction (dotted line). The coexistence curve is shown as a heavy line and the critical point is labelled C.

Using these relations to eliminate $a$ and $b$ from eq. (2-1) gives

$$
\begin{equation*}
\left(\frac{P}{P_{c}}+3\left(\frac{v_{c}}{v}\right)^{2}\right)\left(\frac{v}{v_{c}}-\frac{1}{3}\right)=\frac{8 T}{3 T_{c}} \tag{2-5}
\end{equation*}
$$

which depends only on the ratios of the thermodynamic variables to their critical values. This is known as the law of corresponding states. While of limited validity experimentally, it embodies the important idea of universality - different systems exhibit similar behaviour independent of their microscopic details. In particular, aspects of the critical behaviour of VDW fluids, including the critical exponents, should be universal.

The critical exponents of the VDW equation can be calculated from eq. (2-5). For example, the dimensionless isothermal compressibility at the critical density is

$$
\begin{equation*}
\kappa_{T}^{*}=-\left.\frac{P_{c}}{v_{c}} \frac{\partial v}{\partial P}\right|_{T, v_{c}}=\frac{1}{6\left(\frac{T}{T_{c}}-1\right)}=\frac{1}{6 t} \sim t^{-1} \tag{2-6}
\end{equation*}
$$

where $t=\left|T_{c}-T\right| / T_{c}$, so the exponent $\gamma=1$. On the critical isotherm, eq. (2-5) can be expanded in powers of $p=\left(P-P_{c}\right) / P_{c}$ and $\Delta \rho=\left(\rho-\rho_{c}\right) / \rho_{c}$ with $\rho=v^{-1}$ to give $p \sim \Delta \rho^{3}$ near the critical point, so $\delta=3$. These and other exponents for the VDW equation are listed in Table $\mathbf{I}-\mathbf{1}$. These values are common to generalizations of the VDW equation and to mean field theories of the liquid-vapour critical point; they are referred to as the classical critical exponents.

To make contact with results to be discussed later, it is useful to write eq. (2-5) in a different form. We use the chemical potential $\mu$ rather than the pressure; from basic thermodynamics ${ }^{41}$, changes in $\mu(T, P)$ are related to changes in the intensive variables by

$$
\begin{equation*}
d \mu=-\frac{S}{N} d T+\frac{V}{N} d P \tag{2-7}
\end{equation*}
$$

where $S$ is the entropy, $V$ the total volume, and $N$ the number of molecules. At constant $T$ then,

$$
\begin{equation*}
\rho d \mu=d P \tag{2-8}
\end{equation*}
$$

where $\rho=N / V$ is the number density. Near the critical point we can write

$$
\begin{equation*}
\Delta \mu^{*}=\frac{\rho_{c}}{P_{c}}\left(\mu(\rho, T)-\mu\left(\rho_{c}, T\right)\right)=\frac{P(\rho, T)-P\left(\rho_{c}, T\right)}{P_{c}} \tag{2-9}
\end{equation*}
$$

and using eq. (2-5) we calculate the right hand side of (2-9) to find

$$
\Delta \mu^{*}=\rho_{c}\left(6 t \Delta \rho+\frac{3}{2} \Delta \rho^{3}\right)
$$

$$
\begin{equation*}
=a_{1} \Delta \rho^{3}\left(1+\frac{a_{2} t}{\Delta \rho^{2}}\right) \tag{2-10}
\end{equation*}
$$

where $a_{1}=3 \rho_{c} / 2$ and $a_{2}=4$. The critical isotherm, $t=0$, is therefore given by

$$
\begin{equation*}
\Delta \mu^{*}=a_{1} \Delta \rho^{3} \tag{2-11}
\end{equation*}
$$

while on the coexistence curve, $\Delta \mu^{*}=0$ and so

$$
\begin{equation*}
\Delta \rho= \pm a_{2}^{1 / 2}|t|^{1 / 2} \tag{2-12}
\end{equation*}
$$

A more general equation of state permitting non-classical critical exponents, which will be discussed below, is often written in a form similar to that of eq. (2-10).

It was clear as early as the end of the nineteenth century that the VDW equation was quantitatively incorrect near the critical point ${ }^{14}$. The strongest evidence for this came from measurements of the coexistence curves of various fluids, which seemed to be well described by a critical exponent $\beta=\frac{1}{3}$ rather than the classical exponent $\frac{1}{2}$.

The cause of this discrepancy was not understood for several decades. In fact it is related to the importance of fluctuations and the change of length scale near the critical point, as discussed in Chapter I, and to the nonanalytic nature of the equation of state.

## II-2 Homogeneity and Scaling

In 1965 Widom proposed a form for the equation of state near the critical point which was nonanalytic at the critical point and consistent with known nonclassical critical behaviour ${ }^{16}$. His suggestion has since been given a firm theoretical basis as a result of the ideas of scaling and the development of the renormalization group, to be discussed below.

The distance from the critical point in temperature is just $T-T_{c}$. The distance in density is $\rho-\rho_{c}$, which can be expressed in temperature units by writing

$$
\begin{equation*}
T_{c}-T(\rho) \sim\left|\rho-\rho_{c}\right|^{1 / \beta} \tag{2-13}
\end{equation*}
$$

where $T(\rho)$ is the temperature on the coexistence curve corresponding to the density $\rho$. Widom suggested ${ }^{16,18}$ that comparable values of $T-T_{c}$ and $T_{c}-T(\rho)$ should have comparable effects on the thermodynamic properties of the system. Mathematically, he proposed that certain thermodynamic functions become homogeneous functions of $T-T_{c}$ and $T_{c}-T(\rho)$ near the critical point. (A homogeneous function $\phi(x, y)$ of degree $n$ has the property that

$$
\begin{equation*}
\phi(x, y)=x^{n} \phi\left(1, \frac{y}{x}\right)=y^{n} \phi\left(\frac{x}{y}, 1\right)=y^{n} \psi\left(\frac{x}{y}\right), \tag{2-14}
\end{equation*}
$$

i.e., $\phi$ can be written as a power of one of its arguments times a function of the ratio of its arguments.)

Widom's homogeneous equation of state can be written as

$$
\begin{equation*}
\Delta \mu^{*}=\Delta \rho|\Delta \rho|^{\delta-1} h\left(\frac{t}{|\Delta \rho|^{1 / \beta}}\right) \tag{2-15}
\end{equation*}
$$

The VDW equation as written in eq. (2-10) has the form (2-15) with classical exponent values and

$$
\begin{equation*}
h_{c l}(u)=a_{1}\left(1+a_{2} u\right) \tag{2-16}
\end{equation*}
$$

where $u=t /|\Delta \rho|^{1 / \beta}$. Widom's form, however, allows non-classical exponents and does not restrict $h(u)$ to its classical form.

The above suggests a rigorous expression of the universality hypothesis ${ }^{14}$ : the critical exponents for all systems in a given universality class should be the same, and $h(u)$ should be a universal function, except for two non-universal scale factors.

These set the scales of $u$ and $h$; in the classical case, they are $a_{2}$ and $a_{1}$ respectively. The critical behaviour of various quantities, as well as scaling laws relating the critical exponents, follow from eq. (2-15). For example, on the critical isotherm, $t=0$, and so

$$
\begin{equation*}
\Delta \mu^{*}=\Delta \rho|\Delta \rho|^{\delta-1} h(0) \sim \Delta \rho^{\delta} \tag{2-17}
\end{equation*}
$$

as expected. As another example, consider the isothermal compressibility at $\rho=\rho_{c}$. This quantity is expected to behave like $t^{-\gamma}$. Using (2-15),

$$
\begin{equation*}
\left.\kappa_{T}^{*-1} \sim \frac{\partial \mu}{\partial \rho}\right|_{T} \sim \Delta \rho^{\delta-1} h(u)+\cdots \tag{2-18}
\end{equation*}
$$

Now, if $\kappa_{T}^{*-1}$ is to be finite for all nonzero $t$ at $\Delta \rho=0$, the powers of $\Delta \rho$ in (2-18) must cancel. Therefore we must have, for $u \rightarrow \infty$,

$$
\begin{equation*}
\lim _{u \rightarrow \infty} h(u) \sim u^{\beta(\delta-1)} \tag{2-19}
\end{equation*}
$$

so that

$$
\begin{align*}
\kappa_{T}^{*-1} \sim \Delta \rho^{\delta-1} u^{\beta(\delta-1)} & \sim \Delta \rho^{\delta-1} \frac{t^{\beta(\delta-1)}}{\Delta \rho^{\delta-1}} \\
& \sim t^{\beta(\delta-1)} \tag{2-20}
\end{align*}
$$

from which follows the scaling law

$$
\begin{equation*}
\gamma=\beta(\delta-1) \tag{2-21}
\end{equation*}
$$

This and other scaling laws are tabulated in Table II-1.

Table II-1 Scaling Laws

$$
\begin{aligned}
\gamma & =\beta(\delta-1) \\
2-\alpha & =2 \beta+\gamma \\
& =\beta(\delta+1) \\
& =d \nu
\end{aligned}
$$

Homogeneity of thermodynamic functions near the critical point follows naturally from the scaling ideas of Kadanoff ${ }^{17,18}$. Here it is convenient to consider an Ising model and to use the language of magnetism rather than of fluids. Instead of $\Delta \mu^{*}$, we use the applied field $h$; instead of $\Delta \rho$, the magnetization $M$.

Consider a lattice in $d$ dimensions, with lattice spacing $a$, and with an Ising spin on each lattice site. The free energy per spin can be written as the sum of a regular and a singular part,

$$
\begin{equation*}
f(t, h)=f_{r}(t, h)+f_{s}(t, h) \tag{2-22}
\end{equation*}
$$

where $f_{s}$ contains all of the nonanalytic critical behaviour. We now divide the lattice up into blocks of side $L a$, each containing $L^{d}$ spins. We restrict $L$ to values such that $a<L a \ll \xi$, where $\xi$ is the correlation length; the spins on a block should thus be well correlated. Each block will contribute $L^{d} f_{s}(t, h)$ to the singular part of the free energy.

We now rescale the system by replacing the $L^{d}$ spins in each block by an average "block spin," and by measuring lengths in units of the block size La rather than $a$. This scale transformation is illustrated schematically in fig. (2-2). $\xi$ as measured in the units of the rescaled system is smaller than in the original system by a factor of $L$. Since $\xi$ grows like $t^{-\nu}$ as the critical point is approached (eq. (15)), the rescaled system appears to be further from its critical point than was the
original system, and, since $t=h=0$ at the critical point, the rescaled system must also appear to be at larger values of $t$ and $h$. We assume that $t$ and $h$ scale like

$$
t \rightarrow L^{y} t, \quad h \rightarrow L^{x} h,
$$

with $x$ and $y$ positive, when the system is scaled by a factor of $L$ as above. The singular part of the free energy per block spin in the rescaled system is then $f_{8}\left(L^{y} t, L^{x} h\right)$.


Figure 2-2 A schematic representation of the Kadanoff scale transformation. a) The original lattice showing a block of size $L a$; here $L=2$. b) The lattice of block spins. c) The lattice of (b) rescaled by a factor $L$.

These two contributions to the free energy are the same quantity expressed in terms of the system before and after scaling. Thus

$$
\begin{equation*}
L^{d} f_{s}(t, h)=f_{s}\left(L^{y} t, L^{x} h\right) . \tag{2-23}
\end{equation*}
$$

Since the length $L$ is arbitrary, eq. (2-23) must hold for all $L$. For this to be the case, $f_{s}$ must be a homogeneous function of the form

$$
f_{s}(t, h)=t^{d / y} \phi\left(t^{-x / y} h\right),
$$

or, returning to the language of fluids,

$$
\begin{equation*}
f_{s}\left(t, \Delta \mu^{*}\right)=t^{d / y} \phi\left(t^{-x / y} \Delta \mu^{*}\right) . \tag{2-24}
\end{equation*}
$$

This formulation in terms of the free energy is equivalent to that discussed above based on the equation of state. One can again derive the asymptotic critical power laws and various scaling laws from eq. (2-24), and express $x$ and $y$ in terms of the conventional critical exponents.

Consider first the specific heat on the coexistence curve, where $\Delta \mu^{*}=0$ :

$$
C_{v}=-\frac{\partial^{2} f_{s}}{\partial T^{2}} \sim \phi(0) t^{\frac{d}{y}-2} \sim t^{-\alpha}
$$

so

$$
\begin{equation*}
\frac{d}{y}=2-\alpha . \tag{2-25}
\end{equation*}
$$

Also, on the critical isotherm, we know that

$$
\begin{equation*}
\Delta \rho \sim \frac{\partial f_{s}}{\partial \mu} \sim\left(\Delta \mu^{*}\right)^{1 / \delta} \tag{2-26}
\end{equation*}
$$

so $f_{s}\left(0, \Delta \mu^{*}\right)$ must behave like $\left(\Delta \mu^{*}\right)^{\frac{1}{8}+1}$. For a finite $t=0$ limit to exist we need

$$
\begin{equation*}
\lim _{t \rightarrow 0} \phi(u) \sim u^{d / x} \tag{2-27}
\end{equation*}
$$

so that the powers of $t$ cancel:

$$
\begin{equation*}
f_{s}\left(0, \Delta \mu^{*}\right) \sim t^{d / y}\left(t^{-x / y} \Delta \mu^{*}\right)^{d / x} \sim\left(\Delta \mu^{*}\right)^{d / x} \tag{2-28}
\end{equation*}
$$

From this we get

$$
\begin{equation*}
\frac{d}{x}=\frac{1}{\delta}+1 \tag{2-29}
\end{equation*}
$$

Finally, on the coexistence curve,

$$
\begin{equation*}
\Delta \rho \sim \frac{\partial f_{s}}{\partial \Delta \mu^{*}} \sim t^{d / y} t^{-x / y} \phi^{\prime}(0) \sim t^{\beta} \tag{2-30}
\end{equation*}
$$

Combining eqs. (2-25),(2-29), and (2-30), we get

$$
\frac{d-x}{y}=2-\alpha-\frac{\delta(2-\alpha)}{1+\delta}=\frac{2-\alpha}{1+\delta}=\beta
$$

giving the scaling law

$$
\begin{equation*}
2-\alpha=\beta(\delta+1) \tag{2-31}
\end{equation*}
$$

This result and the second scaling law given in Table II-1 can be derived as inequalities from thermodynamic or statistical mechanical arguments. The equalities in these two cases, as well as the other scaling laws, result from the scaling or homogeneity hypotheses.

The above results allow us to rewrite $f_{s}$ using the conventional critical exponents:

$$
\begin{equation*}
f_{s}\left(t, \Delta \mu^{*}\right)=t^{2-\alpha} \phi\left(\frac{h}{t^{\beta \delta}}\right) \tag{2-32}
\end{equation*}
$$

Relations involving the correlation length exponent $\nu$ can be obtained by applying similar arguments to the correlation function $G(t, r)^{18}$.

## II-3 Renormalization Group

The ideas discussed in the preceding pages provide some understanding of the nature of the liquid-vapour critical point. They allow prediction of the behaviour of thermodynamic quantities in the critical region and give scaling laws that relate the critical exponents. They do not, however, provide a means of calculating the exponents or other quantities. In 1971 Wilson ${ }^{19,20}$ developed the technique of the renormalization group (RG), which does provide that means, as well as lending a sounder basis to the ideas of homogeneity and universality. RG embodies scaling ideas in an essential way, but, unlike Kadanoff scaling, is formulated in a way that makes explicit calculations possible, at least in principle ${ }^{21,22}$.

The RG is a set of transformations applied to the Hamiltonian of a system which are conceptually very similar to Kadanoff's scaling transformation discussed above. The properties of these transformations under certain special conditions are related to the critical behaviour of the system. The discussion here will be brief and very general, treating the concepts behind the RG and relating them to those introduced above. For more details, the reader is referred to textbooks on the subject by $\mathrm{Ma}^{42}$ and by Pfeuty and Toulouse ${ }^{43}$.

While the discussion below applies equally to continuous systems, for simplicity we consider again a spin system on a lattice with lattice constant $a$. We can write down a very general Hamiltonian,

$$
\begin{equation*}
\mathcal{H}\left(\mathbf{K},\left\{\sigma_{\mathbf{x}}\right\}\right)=K_{0}+K_{1} \sum_{\mathbf{x}} \sigma_{\mathbf{x}}+K_{2} \sum_{\mathbf{x}, \delta} \sigma_{\mathbf{x}} \sigma_{\mathbf{x}+\delta}+\cdots \tag{2-33}
\end{equation*}
$$

where $K$ is a vector containing the coupling constants $K_{i}$ and $\left\{\sigma_{\mathbf{x}}\right\}$ is the set of values of the spin variables. We label the Hamiltonian by the vector $\mathbf{K}$; this vector represents a point in a many-dimensional parameter space. The RG transformation
$R_{s}$ transforms the Hamiltonian represented by $\mathbf{K}$ to one represented by $\mathbf{K}^{\prime}$ :

$$
\begin{equation*}
\mathbf{K}^{\prime}=R_{s} \mathbf{K} \tag{2-34}
\end{equation*}
$$

$R_{s}$ involves a number of steps. First, the system is coarse-grained by averaging out all spin fluctuations of wavelength shorter than sa. This is analogous to the formation of block spins carried out above, and effectively increases the length scale by a factor $s$. Next, the spin variables and the length scale are rescaled such that

$$
\begin{equation*}
\sigma_{\mathbf{x}} \rightarrow \zeta_{s} \sigma_{\mathbf{x}^{\prime}}^{\prime}, \quad \mathbf{x} \rightarrow s \mathbf{x}^{\prime} \tag{2-35}
\end{equation*}
$$

This shrinks the system by a factor $s$, so the lattice constant is again $a$. Finally, the transformed Hamiltonian is rewritten in the form (2-33) and the new set of parameters $\mathbf{K}^{\prime}$ determined.

The operator $R_{s} R_{s^{\prime}}=R_{s s^{\prime}}$ is well defined if $\zeta_{s}=s^{b}$ with $b$ independent of $s$, but the inverse transformation $R_{s}^{-1}$ is not.

In general, the mathematics of the RG transformation will be complicated and a large number of new parameters $K_{i}$ will be generated with each application of $R_{s}$. It is, however, possible, but by no means guaranteed, that there exist fixed points in the parameter space such that

$$
\begin{equation*}
R_{s} \mathbf{K}^{*}=\mathbf{K}^{*} \tag{2-36}
\end{equation*}
$$

that is, points that are invariant under the transformation. The critical surface of $\mathbb{K}^{*}$ is defined as the set of points $\mathbf{K}$ for which

$$
\begin{equation*}
\lim _{s \rightarrow \infty} R_{s} \mathbf{K}=\mathbf{K}^{*} \tag{2-37}
\end{equation*}
$$

points on the critical surface of a fixed point are eventually driven to that fixed point by repeated application of the RG transformation.

To the extent that the Hamiltonian under consideration represents that of a real system, the mathematics of the RG is connected to the physics of critical phenomena by the hypothesis that a point in the parameter space representing a system at its critical point is on the critical surface of a fixed point. The behaviour of $R_{s}$ near the fixed point determines the critical behaviour of the system. The concept of universality is a simple consequence of this hypothesis: critical points represented by different points on the same critical surface will display the same critical phenomena, since for each of these points the behaviour of $R_{s}$ is governed by the same fixed point.

Let us assume that a fixed point $\mathbf{K}^{*}$ does exist and study the behaviour of $R_{s}$ near that point. We can formally write

$$
\begin{equation*}
\mathbf{K}=\mathbf{K}^{*}+\delta \mathbf{K} \tag{2-38}
\end{equation*}
$$

so

$$
\begin{align*}
\mathbf{K}^{\prime}=R_{s} \mathbf{K}=R_{s}\left(\mathbf{K}^{*}+\delta \mathbf{K}\right) & =\mathbf{K}^{*}+R_{s} \delta \mathbf{K}+O(\delta \mathbf{K})^{2} \\
& =\mathbf{K}^{*}+\delta \mathbf{K}^{\prime} \tag{2-39}
\end{align*}
$$

If terms of order higher than linear in $\delta \mathbf{K}$ are ignored, then $R_{s}$ can be approximated by a linear operator $R_{s}^{L}$, and

$$
\begin{equation*}
\delta \mathbf{K}^{\prime}=R_{s}^{L} \delta \mathbf{K} \tag{2-40}
\end{equation*}
$$

This linear operator can be represented by a matrix

$$
\begin{equation*}
\left(R_{s}^{L}\right)_{\alpha \beta}=\left(\frac{\partial \mathbf{K}_{\alpha}^{\prime}}{\partial \mathbf{K}_{\beta}}\right)_{\mathbf{K}=\mathbf{K}^{*}} \tag{2-41}
\end{equation*}
$$

with eigenvalues $\lambda_{j}(s)$ and eigenvectors $\mathbf{e}_{j}$, for which

$$
\begin{equation*}
R_{s} \mathbf{e}_{j}=\lambda_{j} \mathbf{e}_{j} \tag{2-42}
\end{equation*}
$$

Since $R_{s} R_{s^{\prime}} \mathbf{e}_{j}=R_{s s^{\prime}} \mathbf{e}_{j}=\lambda_{j}(s) \lambda_{j}\left(s^{\prime}\right) \mathbf{e}_{j}=\lambda_{j}\left(s s^{\prime}\right) \mathbf{e}_{j}$, we must have

$$
\begin{equation*}
\lambda_{j}(s)=s^{y_{j}} \tag{2-43}
\end{equation*}
$$

Using the eigenvectors as basis vectors near the fixed point, we can write

$$
\begin{equation*}
\delta \mathbf{K}=\sum_{j} t_{j} \mathbf{e}_{j}, \quad \delta \mathbf{K}^{\prime}=\sum_{j} t_{j}^{\prime} \mathbf{e}_{j} \tag{2-44}
\end{equation*}
$$

where

$$
\begin{equation*}
t_{j}^{\prime}=\lambda_{j}(s) t_{j}=s^{y_{j}} t_{j} \tag{2-45}
\end{equation*}
$$

Clearly if $y_{j}>0$, repeated application of $R_{s}$ will cause $t_{j}$ to grow, while if $y_{j}<0, t_{j}$ will decrease. We refer to the $t_{j}$ as scaling fields. On the critical surface, repeated application of $R_{s}$ drives the system towards the fixed point at $\delta \mathbf{K}=0$, therefore the scaling fields associated with positive $y_{j}$ must be zero on the critical surface. These scaling fields are called relevant, since only they are relevant to the asymptotic critical behaviour. The eigenvectors associated with negative $y_{j} \mathrm{~s}$ span the critical surface near the fixed point; the corresponding scaling fields are called irrelevant.

For Hamiltonians in the universality class of the 3-D Ising model fixed points do exist; the fixed point associated with the liquid-vapour critical point has two relevant scaling fields. Since for a fluid the critical point is defined by $t=0$, $\Delta \mu^{*}=0$, it seems reasonable from the above discussion to associate $t$ and $\Delta \mu^{*}$ with these two fields. Now consider the free energy as a function of $t$ and $\Delta \mu^{*}$ before and after application of $R_{s}$. Using arguments similar to those used in the discussion of Kadanoff scaling above, and noting that $t$ and $\Delta \mu^{*}$ will scale as in eq. (2-45), we get

$$
\begin{equation*}
s^{d} f_{s}\left(t, \Delta \mu^{*}\right)=f_{s}\left(s^{y_{1}} t, s^{y_{2}} \Delta \mu^{*}\right), \tag{2-46}
\end{equation*}
$$

which is of the same form as eq. (2-23); $f_{s}$ is again a homogeneous function of its variables.

The critical exponents are related to the exponents $y_{1}$ and $y_{2}$ and to the dimensionality $d$. The RG can be used to calculate numerical values of these exponents, although in general this is a difficult task. It turns out for this fixed point, however, that the calculations are easy for $d \geq 4$; the exponents then assume their classical values. For $d=4-\epsilon$, a perturbation expansion in $\epsilon=4-d$ is possible. This $\epsilon$-expansion technique has led to good results for the critical exponents when extrapolated to $\epsilon=1$, although the power series obtained appear to be poorly convergent.

Other methods of calculating exponents apply field theoretical techniques to the RG equations ${ }^{5,6}$ or use high temperature series expansions ${ }^{7-9}$. The results of these different calculations have begun to agree reasonably well with each other ${ }^{9}$, and the exponent values obtained can be regarded as quite reliable. Table $\mathbf{I}-1$ gives some of these calculated exponents.

## II-4 Corrections to Scaling

It was pointed out in Chapter I that the simple critical power laws resulting from, for example, eq. (2-32) do not adequately describe experimentally observed behaviour except extremely close to the critical point. Corrections to these power laws are required; these arise from inclusion of the irrelevant scaling fields as variables in the free energy ${ }^{26}$. Physically, these fields correspond to operators involving high order products of the spin variables in the Hamiltonian of eq. (2-33). The theory of corrections-to-scaling was developed by Wegner ${ }^{26}$ and applied to fluids by Ley-Koo and Green ${ }^{27}$ in 1981.

Consider the thermodynamic potential of a fluid to be a function not only of the two relevant scaling fields related to $t$ and $\Delta \mu^{*}$, which we write as $g_{E}$ and $g_{h}$, but also of the two most important irrelevant scaling fields, $g_{A}$ and $g_{s}$. As discussed
above, $g_{E}$ and $g_{h}$ will be zero on the critical surface, but $g_{A}$ and $g_{s}$ will not. Ley-Koo and Green ${ }^{27}$ write this potential as

$$
\begin{equation*}
\tilde{p}=p_{r}+p_{s}\left(g_{h}, g_{E}, g_{A}, g_{S}\right) \tag{2-47}
\end{equation*}
$$

and require that the singular part, $\boldsymbol{p}_{s}$, be a homogeneous function of all of its variables. They then use homogeneity properties and symmetry arguments to determine the form of $p_{s}$ in each region of the phase diagram. Substituting physical variables for the scaling fields in these expressions; they get equations for various quantities along thermodynamic paths of experimental interest. Equations (1-6)-(1-9) are examples. These corrections-to-scaling series are listed in Table II-2.

Table II-2 Corrections-to-Scaling Series

On the coexistence curve, $T<T_{c}$,

$$
\begin{aligned}
\Delta \rho^{*} & =B_{0} t^{\beta}\left(1+B_{1} t^{\Delta}+B_{2} t^{2 \Delta}+B_{3} t+\cdots\right) \\
\rho_{d} & =1+A_{1} t^{1-\alpha}+A_{2} t+A_{3} t^{1-\alpha+\Delta}+A_{4} t^{2-\alpha-\beta \delta+\Delta_{A}}+\cdots \\
\kappa_{T}^{*-} & =\Gamma_{0}^{-} t^{-\gamma}\left(1+\Gamma_{1}^{-} t^{\Delta}+\Gamma_{2}^{-} t^{2 \Delta}+\Gamma_{3}^{-} t^{\beta \delta-1}+\cdots\right)
\end{aligned}
$$

On the critical isochore, $T>T_{c}$,

$$
\kappa_{T}^{*+}=\Gamma_{0}^{+} t^{-\gamma}\left(1+\Gamma_{1}^{+} t^{\Delta}+\Gamma_{2}^{+} t^{2 \Delta}+\Gamma_{3}^{+} t^{2(\beta \delta-1)}+\cdots\right)
$$

On the critical isotherm, $T=T_{c}$,

$$
\Delta \mu^{*}=D_{0}\left|\frac{\rho-\rho_{c}}{\rho_{c}}\right|^{\delta}\left( \pm 1+D_{1}\left|\frac{\rho-\rho_{c}}{\rho_{c}}\right| \mp D_{2}\left|\frac{\rho-\rho_{c}}{\rho_{c}}\right|^{\Delta / \beta}+\cdots\right)
$$

The universal exponent $\Delta$ in these expressions is associated with the scaling field $g_{S}$. The exponent $\Delta_{A}$ associated with $g_{A}$ enters to higher order in the tabulated series and in expressions for other quantities. Values of $\Delta$ have been calculated using the methods mentioned above ${ }^{28,29}$ and are given in Table I-1.

## II-5 Universal Amplitude Ratios

The amplitudes in the expressions given in Table II-2 are system dependent. However, just as scaling laws exist which relate the critical exponents, certain combinations of these amplitudes are universal. There are only two independent exponents; similarly, there are only two independent leading amplitudes ${ }^{44}$. In addition, the ratio of any two of the first correction amplitudes is universal ${ }^{45,46}$.

In the discussion following eq. (2-15) it was noted that the equation of state involves a function $h(u)$ which is universal except for two factors which determine the scales of $h$ and $u$. We can write ${ }^{44}$

$$
\begin{equation*}
h(u)=h_{0} \tilde{h}\left(u_{0} \tilde{u}\right) \tag{2-48}
\end{equation*}
$$

to show these scale factors, $h_{0}$ and $u_{0}$, explicitly. It is possible through manipulation of eq. (2-15) to write all of the leading amplitudes $B_{0}, \Gamma_{0}$, etc. in terms of $h_{0}, u_{0}$, and universal quantities. Combinations of these amplitudes that are independent of the two non-universal scale factors will thus be universal. The four universal combinations of the six amplitudes $F_{0}^{ \pm}, B_{0}, \Gamma_{0}^{ \pm}$and $D_{0}$ so determined are given in Table I-2 along with their values as calculated by $\epsilon$-expansion and series techniques.

Aharony and Ahlers ${ }^{45}$ showed that, to zeroth order in $\epsilon$, the ratio of the first correction amplitudes $X_{1} / Y_{1}$ for any two thermodynamic quantities $X$ and $Y$ was given by

$$
\begin{equation*}
\frac{X_{1}}{Y_{1}}=\frac{\lambda_{X}-\lambda_{0 X}}{\lambda_{Y}-\lambda_{0 Y}} \tag{2-49}
\end{equation*}
$$

where $\lambda_{X}$ is the asymptotic critical exponent corresponding to quantity $X$ and $\lambda_{0 X}$ is the associated classical exponent. Chang and Houghton ${ }^{46}$ used renormalized perturbation theory to calculate the first correction amplitudes to second order in $\epsilon$ and confirmed that the ratio of any two of them was universal. Results for the ratios of interest in this work are given in Table I-2.

## II-6 Quantum Mechanical Effects on Critical Behaviour

Early measurements of the coexistence curves and compressibilities of the low temperature fluids ${ }^{3} \mathrm{He}$ and ${ }^{4} \mathrm{He}$ appeared to give exponent values that differed from those for room temperature fluids ${ }^{14}$. It is now clear that this was due to neglect of corrections-to-scaling effects. At the time, however, the question was raised as to whether quantum mechanics should have any effect on the critical behaviour of these fluids ${ }^{47}$.

It is easy to see why quantum mechanics could modify the critical behaviour to some degree ${ }^{48}$. As discussed in Chapter I, for a classical fluid far from its critical point, the length scale that determines the physics of the system is the intermolecular interaction distance, $\sigma$. Closer to the critical point the correlation length $\xi=\xi_{0} t^{-\nu}$ increases and in the critical region, where $\xi \gg \sigma$, it is $\xi$ that dominates the physics; the details of the short-range interactions are unimportant.

For a quantum system, there is another fundamental length scale: the thermal De Broglie wavelength $\lambda_{T}=\frac{\hbar}{2 \sqrt{m k_{B} T}}$, where $\hbar$ is Planck's constant divided by $2 \pi$, $k_{B}$ is Boltzmann's constant and $m$ is the molecular mass. For a system in a state for which $\lambda_{T} \gtrsim \sigma$ and $\lambda_{T} \gtrsim \xi$, quantum modifications to the thermodynamic properties might be expected. Of course, since $\xi$ diverges, it will eventually become much greater than $\lambda_{T}$ no matter how quantum mechanical the system is, and so the universality class of a quantum fluid must be the same as that of a classical fluid. The critical exponents and universal amplitude ratios should therefore not change. It would be reasonable, however, to expect the individual amplitudes to change systematically as the fluid becomes more quantum mechanical.

A complete theory of the effect of quantum corrections to the equation of state near the critical point does not exist. A semi-quantitative theory has been developed by Young ${ }^{40}$; while not very rigorous, with some numerical adjustment it does predict reasonably accurately the location of the critical points of the helium isotopes, their second virial coefficients, and other properties. Young ${ }^{40}$ starts with
a Lennard-Jones 6-12 potential that describes well the behaviour of a classical fluid away from the critical point:

$$
\begin{equation*}
V(r)=4 \varepsilon\left(\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right) \tag{2-50}
\end{equation*}
$$

where $\varepsilon$ is the potential well depth and $\sigma$ determines the length scale. He modifies this potential by averaging it over a gaussian "wavepacket" given by $\left(\alpha^{\prime} / \pi\right)^{\frac{3}{2}} \mathrm{e}^{-\left|r-r^{\prime}\right|^{2}}$, where $\sqrt{\alpha^{\prime}}=\left(3 m k_{B} T / \hbar^{2}\right)^{1 / 2} \sim \lambda_{T}^{-1}$ to obtain an effective potential

$$
\begin{equation*}
\tilde{V}(r)=\left(\frac{\alpha^{\prime}}{\pi}\right)^{3 / 2} \int d^{3} r^{\prime} V\left(r^{\prime}\right) \mathrm{e}^{-\alpha^{\prime}\left|r-r^{\prime}\right|^{2}} \tag{2-51}
\end{equation*}
$$

He evaluates $\tilde{V}(r)$ near its minimum and defines parameters $\tilde{\varepsilon}$ and $\tilde{\sigma}$, which are analogous to $\varepsilon$ and $\sigma$ above but describe the quantum mechanically modified potential $\tilde{V}(r)$. These parameters are functions of $\alpha^{\prime}$ and so of $T$, as well as of $\varepsilon$ and $\sigma$, and contain all of the quantum corrections to $V(r)$.

Young's procedure then amounts to the following. He writes down an equation satisfied by the classical system. He rescales the energies and distances of the critical point properties by factors of $\tilde{\varepsilon} / \varepsilon$ and $\tilde{\sigma} / \sigma$ respectively so that $T_{c} \rightarrow T_{c} \tilde{\varepsilon} / \varepsilon$ and $V_{c} \rightarrow V_{c}(\tilde{\sigma} / \sigma)^{3}$, and then replaces $T_{c}, V_{c}$ and $P_{c}$ by their classical values in terms of $\varepsilon$ and $\sigma$. For example, for the leading term in the expression for the density difference on the coexistence curve,

$$
\begin{align*}
\Delta \rho^{*} & =B_{0}\left(1-\frac{T}{T_{c}}\right)^{\beta} \\
& \rightarrow B_{0}\left(1-\frac{T}{T_{c} \tilde{\varepsilon} / \varepsilon}\right)^{\beta} \rightarrow B_{0}\left(1-\frac{T}{1.26 \tilde{\varepsilon}}\right)^{\beta} \tag{2-52}
\end{align*}
$$

since classically $T_{c}=1.26 \varepsilon$. By using expansions for $\tilde{\varepsilon}$ and $\tilde{\sigma}$ about their values at the critical point, he finds for the coexistence curve and compressibility respectively

$$
\begin{align*}
\Delta \rho & =\tilde{B}_{0} t^{\beta}=B_{0}(1-y)^{\beta} t^{\beta}  \tag{2-53}\\
\kappa_{T}^{*} & =\tilde{\Gamma}_{0} t^{-\gamma}=\Gamma_{0}(1-y)^{-\gamma} t^{-\gamma} \tag{2-54}
\end{align*}
$$

where $y$ is a positive parameter depending on $\varepsilon, \sigma$ and $T_{c}$ which vanishes in the classical limit. Thus the theory predicts that the leading coexistence curve amplitude should decrease and the leading compressibility amplitude increase as quantum corrections become more important. It also predicts no change in the asymptotic exponents, as expected. Similarly, Young finds that quantum corrections should reduce the first correction amplitudes:

$$
\begin{align*}
& \tilde{B}_{1}=B_{1}(1-y)^{\Delta}  \tag{2-55}\\
& \tilde{\Gamma}_{1}=\Gamma_{1}(1-y)^{\Delta} \tag{2-56}
\end{align*}
$$

These predictions will be compared with the results of this and other work in Chapter VI.

## CHAPTER III

## The Experiments

In this chapter, the optical experiments undertaken to study the critical behaviour of ethylene and of hydrogen are described. These experiments measure various thermodynamic quantities via measurements of the refractive index $n$. Three experimental techniques were used, as described briefly in Chapter I. These will be referred to as the image plane, the focal plane and the prism experiments. We begin with a discussion of the general principles and the optics of the first two of these. Detailed descriptions of the experiments performed on ethylene and hydrogen using these techniques are given in sections III-2 and III-3. The prism experiment is described in section III-4. Section III-5 is a discussion of the major experimental limitations with which we were faced, and section III-6 contains an outline of the data reduction procedures and a discussion of the accuracy of the raw data obtained.

## III-1 The Focal Plane and Image Plane Experiments

The ethylene and hydrogen experiments differed in detail because of the very different critical temperatures of the two fluids. The basic principles of the two experiments were the same, however. A sample container is filled with the experimental fluid to the critical density $\rho_{c}$. The sample temperature is precisely
controlled to allow measurements very close to $T_{c}$. A laser beam is used to probe the sample using one of the two optical arrangements described below, and data are recorded on film as the temperature is changed. The data take the form of interference fringes; the recorded information is converted to thermodynamic quantities as outlined below.

The experiments described here exploit the fact that in the critical region the compressibility of the fluid becomes large. This leads to a significant density gradient - and hence a refractive index gradient - in the sample container due to the weight of the sample on itself. This is illustrated in fig. (3-1) for a cell filled to an average density $\rho_{c}$. Above the critical point, the density changes continuously over the height of the cell (fig. (3-1a)). Closer to $T_{c}$, the increased compressibility near $\rho=\rho_{c}$ leads to a larger density gradient near the middle of the cell (fig. (3-1b)), and below $T_{c}$ a discontinuity in the density appears as the system phase separates. This discontinuity grows as the temperature is further lowered (fig. (3-1c)).

Two slightly different optical arrangements - the image plane and focal plane experiments - provide complementary measurements of this behaviour. The focal plane technique was first applied to the study of critical phenomena by Balzarini and Wilcox ${ }^{24,33}$ and the image plane technique by Balzarini ${ }^{34}$; both have since been used to study a number of pure fluids ${ }^{4,23,30,31,35,36}$ and binary fluid systems ${ }^{49,50}$.

In the image plane experiment, the sample is placed in one arm of a MachZender interferometer ${ }^{51}$ as shown in fig. (3-2). A spatially filtered, expanded and collimated HeNe laser beam is split by a beam cube. One beam passes through the sample while the second is directed around it. The two beams are then recombined and the exit plane of the cell imaged with a magnification $m$ on the film plane of a modified 35 mm camera using a large aperture ( 306 mm focal length, $f / 2.5$ ) lens. The fringe pattern observed in the image plane is an interferogram of the sample; a difference of $N$ fringes over a distance $x$ in the interferogram corresponds to a


Figure 3-1 Gravity-induced density gradients in a fluid near the critical point. a) $T>T_{c}$, b) $T \gtrsim T_{c}$, c) $T<T_{c}$.
change in the refractive index equal to $\delta n=N \lambda / L$ over a height $z=x / m$ in the sample. Here $L$ is the sample thickness and $\lambda=6328 \AA$ is the laser wavelength.

In the one-phase region, where $n(z)$ is continuous, the recorded interferograms can be interpreted as $\mu(\rho)$ isotherms. The chemical potential $\mu$ is related to pressure by eq. (2-9), and the change in pressure with height in the cell is

$$
\begin{equation*}
P(\rho, T)-P\left(\rho_{c}, T\right)=\rho_{c} g\left(z-z_{0}\right) \tag{3-2}
\end{equation*}
$$

where $z_{0}$ is the height at which $\rho=\rho_{c}$ and $g$ is the acceleration due to gravity. This gives

$$
\begin{equation*}
\Delta \mu^{*}(z)=\frac{\rho_{c} g\left(z-z_{0}\right)}{P_{c}} \tag{3-3}
\end{equation*}
$$

$\delta N\left(z-z_{0}\right)$ obtained as above can be related to $\Delta \rho\left(z-z_{0}\right)$ using eq. (3-6) below. The slope of these isotherms gives the isothermal compressibility $\kappa_{T}^{*+}$.

Below $T_{c}$, as the temperature is lowered, fringes "disappear" into the image of the meniscus due to the growing difference in index between liquid and vapour. The number of fringes missing from each phase, $N_{\ell, v}$ is related to the corresponding refractive index by

$$
\begin{aligned}
& N_{\ell}=\frac{L}{\lambda}\left(n_{\ell}-n_{c}\right) \\
& N_{v}=\frac{L}{\lambda}\left(n_{c}-n_{v}\right)
\end{aligned}
$$

where $n_{c}$ is the refractive index at the critical point. Thus

$$
\begin{equation*}
n_{\ell}-n_{v}=\left(N_{\ell}+N_{v}\right) \frac{\lambda}{L} \tag{3-4}
\end{equation*}
$$

and

$$
\begin{equation*}
n_{\ell}+n_{v}-2 n_{c}=\left(N_{\ell}-N_{v}\right) \frac{\lambda}{L} \tag{3-5}
\end{equation*}
$$



Figure 3-2 The optical setup for the fringe experiments. The focal plane is at F ; the image plane at $I$.
these quantities are related to $\Delta \rho^{*}$ and $\rho_{d}$ respectively by

$$
\begin{equation*}
\Delta \rho^{*}=\frac{n_{\ell}-n_{v}}{2 \rho_{c}\left(d n / d \rho+\rho_{c} \rho_{d}^{*} d^{2} n / d \rho^{2}\right)} \tag{3-6}
\end{equation*}
$$

and

$$
\begin{align*}
\rho_{d}^{*} & =\frac{\rho_{\ell}+\rho_{v}-2 \rho_{c}}{2 \rho_{c}}=\rho_{d}-1 \\
& =\frac{\left(n_{\ell}+n_{v}-2 n_{c}\right)-\frac{1}{2} d^{2} n / d \rho^{2}(d \rho / d n)^{2}\left[\left(n_{\ell}-n_{c}\right)^{2}+\left(n_{v}-n_{c}\right)^{2}\right]}{2 \rho_{c} d n / d \rho} \tag{3-7}
\end{align*}
$$

Eqs. (3-6) and (3-7) and expressions for $d n / d \rho$ and $d^{2} n / d \rho^{2}$ are derived in Appendix A. $\kappa_{T}^{*-}$ can be determined from the fringe spacing below $T_{c}$ in the same way that $\kappa_{T}^{*+}$ is above $T_{c}$. The image plane interference pattern can thus in principle yield data on $\Delta \rho(T), \rho_{d}(T),\left.\mu\left(\rho_{\ell, v}\right)\right|_{T}$ and $\kappa_{T \ell, v}^{*-}$ below $T_{c}$, and $\left.\mu(\rho)\right|_{T}$ and $\kappa_{T}^{*+}$ above $T_{c}$.

The optical layout for the focal plane experiment is similar to that for the image plane experiment (fig. (3-2)) except that the reference beam is blocked. The filtered and collimated laser beam passes through the sample and is focussed by the lens, and the Fraunhofer diffraction pattern due to the cell contents is recorded in the focal plane of the lens. The electric field of the laser in the focal plane is the Fourier transform of that at the cell exit:

$$
\begin{equation*}
E_{f}\left(k_{z}\right)=\int_{-h / 2}^{h / 2} E_{s}(z) \mathrm{e}^{i k_{z} z} d z \tag{3-8}
\end{equation*}
$$

where $E_{f}$ and $E_{s}$ are the fields at the focal plane and cell exit respectively, and $k_{z}$ is the spatial frequency. If absorption and scattering by the sample are negligible, only the phase $\phi$ of the laser beam changes on passing through the sample, and so

$$
\begin{equation*}
E_{s}(z)=E_{0} \mathrm{e}^{i(\phi(z)+\omega t)}=E_{0} \mathrm{e}^{i\left(\frac{2 \pi L n(z)}{\lambda}+\omega t\right)} \tag{3-9}
\end{equation*}
$$

where $E_{0} \mathrm{e}^{i \omega t}$ is the spatially uniform field of the laser entering the cell and $\phi(z)=$ $2 \pi \operatorname{Ln}(z) / \lambda$ is the phase shift caused by the sample. The intensity recorded in the focal plane is then given by

$$
\begin{equation*}
I\left(k_{z}\right)=E_{f}^{*} E_{f}=E_{0}^{2}\left|\int_{-h / 2}^{h / 2} \mathrm{e}^{i\left(\frac{2 \pi L n(z)}{\lambda}+k_{z} z\right)} d z\right|^{2} \tag{3-10}
\end{equation*}
$$

which has a series of maxima at spatial frequencies for which the exponent in the integrand is zero.

This pattern can also be understood by considering individual rays traversing the sample as illustrated in fig. (3-3). A ray entering the cell horizontally will be deflected by the refractive index gradient and emerge from the cell at an angle $\theta$ from the horizontal given by

$$
\begin{equation*}
\theta=\frac{L}{n_{a}} \frac{d n}{d z} \tag{3-11}
\end{equation*}
$$

where $n_{a}$ is the refractive index of air and $\theta$ is assumed to be small. This ray is focussed to a point in the focal plane a distance $y$ from the optical axis, where

$$
\begin{equation*}
y=f \tan \theta \approx f \theta \tag{3-12}
\end{equation*}
$$

$f$ being the focal length of the lens. A ray passing through a given gradient in the top half of the cell will therefore be focussed to the same point as a ray passing through the same gradient in the bottom half of the cell. Their phases at this point will, however, be different because each ray encounters a different value of $n$. A fringe pattern will result, with each fringe corresponding to an additional $2 \pi$ phase difference between interfering rays.

In the one-phase region, fringes corresponding to phase differences of $\Delta \phi=$ $\phi_{t o p}-\phi_{\text {bottom }}=0,2 \pi, 4 \pi, \ldots$ exist in the diffraction pattern. As the density discontinuity appears at $T_{c}$, fringes disappear from the pattern as no pairs of rays leave


Figure 3-3 Formation of the Fraunhofer diffraction pattern. Rays passing through the same refractive index gradient are refracted through the same angle $\theta$ and focussed to the same point in the focal plane $F$. A fringe pattern results because of their different phases at that point.
the cell with $\Delta \phi=0,2 \pi, \ldots$ and so on. The number of missing fringes $N$ gives the minimum value of $\Delta \phi$ in the pattern, corresponding to rays which pass through the sample just above and just below the liquid-vapour interface. This therefore gives the index difference between the phases:

$$
\begin{equation*}
n_{\ell}-n_{v}=\frac{N \lambda}{L} \tag{3-13}
\end{equation*}
$$

which is related to the order parameter by eq. (3-6).

## III-2 The Ethylene Experiment

A diagram of the apparatus used in the ethylene experiment is given in fig. (3-4). Much of this apparatus has been used in previous studies of the critical properties of room temperature fluids done in this laboratory ${ }^{30,31,36}$. Modifications to the existing equipment for this work included computer control of the temperature changes and an improved temperature controller on the outer stage of the thermostatic housing. These additions and the rest of the experiment are discussed in this section.

The ethylene sample cell body was made of Kovar and had sapphire windows 0.64 cm thick by 1.91 cm in diameter brazed into it. The thickness of the fluid sample was 0.503 cm . The cell was evacuated, then filled to a density $\rho>\rho_{c}$ with research grade ( 99.94 mole $\%$ ) $\mathrm{C}_{2} \mathrm{H}_{4}{ }^{52}$ while attached to a gas handling system. The sample density was adjusted to $\rho_{c}$ by observing the meniscus as the cell was warmed through the critical temperature. When the cell was overfilled, the meniscus rose to the top of the cell as the temperature increased. Fluid was bled out in steps until this no longer happened, but rather the meniscus vanished in the middle of the cell. When the cell was critically filled, a valve mounted on its top was closed and the cell disconnected from the gas handling system.

The cell was placed in an aluminum jacket which fit snugly in a 5.1 cm diameter by 17.5 cm tall copper cylinder which was the innermost stage of the thermostat.


Figure 3-4 A block diagram of the ethylene apparatus.

The next stage was a passive metal shield, and the next an outer cylinder wrapped with a coil of copper tubing. Each stage was isolated from the next by a layer of styrofoam. A final layer of styrofoam and a wooden box completed the housing. Small openings to allow passage of the laser beam were made in each layer; some of these were covered with microscope slides to eliminate air currents within the thermostat.

The temperature of the outer copper jacket was controlled by circulating a mixture of water and ethylene glycol antifreeze through the coil of copper tubing, using a commercial refrigerated circulating bath ${ }^{53}$. The original temperature controller on the bath was replaced with an electronic controller which monitored the jacket temperature with a thermistor whose resistance was compared to that of an adjustable set resistance in a bridge. The error signal from the bridge controlled the duty cycle of a monostable multivibrator which switched on a heater in the bath. This controller held the jacket temperature stable to $\pm 0.005 \mathrm{~K}$.

The innermost copper cylinder was further temperature controlled using the proportional-integral controller shown in fig. (3-5). A thermistor embedded in a copper bolt and screwed into the cylinder monitored its temperature. The thermistor was one arm of a Wheatstone bridge, another arm of which was a decade resistance box. The bridge error signal was amplified by a Hewlett-Packard 419A DC null voltmeter whose output was fed to a Kepco OPS 7-2 operational power supply with the feedback network shown in the figure. The output of the OPS drove a heater wound non-inductively around the cylinder. This system controlled the cell temperature to better than $\pm 0.1 \mathrm{mK}$ over periods of several hours.

Temperature was measured by means of calibrated thermistors embedded in the copper cylinder. The thermistor resistance was determined to $0.01 \Omega$ by nulling the error signal of a Wheatstone bridge, one arm of which was a General Radio decade resistor. This corresponds to a precision of $\pm 20 \mu \mathrm{~K}$ in temperature for this experiment. Thermistors at the top and bottom of the cylinder allowed detection

Figure 3-5 The temperature control circuit used in the ethylene experiment.

of temperature gradients; these were determined to be less than 0.001 K over the height of the fluid sample. The thermistors were calibrated in a separate apparatus against a HP 2804A quartz thermometer, which was itself calibrated at the triple point of water using a Jarrett type $B$ triple point cell. The quartz thermometer was also used to monitor the cell temperature, but since it was known to exhibit long-term drifts, the thermistors were used for the most accurate thermometry.

Temperature changes were controlled by a Commodore Pet microcomputer which turned on a motor to drive a ten-turn potentiometer in the control bridge arms (fig. (3-5)), thus unbalancing the bridge and causing the cell to warm or cool. The computer also recorded the quartz thermometer temperature output at the end of each step and turned on LEDs to mark the data film at the beginning of each temperature step.

Fig. (3-4) shows the computer connected to the rest of the experiment, and fig. (3-6) is a diagram of the interface electronics. The Pet has a parallel output port, to which a four bit binary number was sent by the control program. This number was input to a one-of-ten decoder, from which several relays were controlled. These switched on and off the motor, changed its direction, and controlled the LEDs. The computer program used is listed in Appendix C.

The interference fringe data were recorded on photographic film. An old 35 mm camera was modified so that a synchronous motor drove the film continuously at a rate of roughly $10 \mathrm{~cm} / \mathrm{h}$. The camera's lens was removed and replaced with a vertical slit. The film thus recorded the fringe pattern as a function of time. The output of the temperature monitor bridge and the quartz thermometer were recorded continuously on a chart recorder.

The procedure for a run was straightforward. The sample was cooled to a starting temperature below $T_{c}$. The camera was loaded with 24 h worth of film and its motor started. The computer was programmed to execute a sequence of timed temperature sweeps followed by waiting periods sufficiently long that the fluid


Figure 3-6 The computer interface electronics. The relays control a motor which changes the temperature and LEDs which mark the data film. The 7442 chip is a one-of-ten decoder; the 7473 is a J-K flip-flop.
reached hydrostatic equilibrium. After 24 h , the film was removed and replaced and the process repeated until the fluid had warmed through its critical point.

Only the focal plane experiment was performed for ethylene; our results are presented in Chapter IV.

## III-3 The Hydrogen Experiment

While the hydrogen experiment was similar in principle to the ethylene experiment, the low critical temperature of $\mathrm{H}_{2}$ made the details of the experiments very different.

The experiment was done in a commercial optical access cryostat ${ }^{54}$. The sample cell assembly was mounted on a removeable insert that fit into the central column of the cryostat as shown in fig. (3-7). The cell assembly is shown in detail in fig. (3-8). It consists of the cell itself and an outer jacket, both mounted below a copper platform. A valve and catalyst chamber are mounted on a second, smaller platform above the main one.

The cell body was machined from OFHC copper. Sapphire windows 0.63 cm thick by 2.54 cm in diameter were mounted on the cell with copper flanges and indium O-ring seals. The enclosed sample space is 1.91 cm in diameter and 0.525 cm thick.

The cell is suspended from the main platform by three thermally insulating nylon posts 0.48 cm in diameter; crushed thin-walled stainless steel (TWSS) tubing and a short length of copper wire connect the bottom of the cell to the outer jacket. This arrangement provides similar thermal links to the jacket at the two ends of the cell to help minimize thermal gradients.

The copper outer jacket is 9.1 cm high and 5.4 cm in diameter. Together with the main platform, it forms a thermal shield surrounding the cell. Openings in the jacket to allow passage of the laser beam were covered with microscope slide windows to limit circulation of the exchange gas in the central column between the


Figure 3-7 The cryostat used in the hydrogen experiment.


Figure 3-8 The hydrogen cell assembly.
outside and inside of the jacket. Three small nylon triangles positioned around the bottom of the jacket centred the assembly in the central column of the cryostat.

The upper platform is mounted above the main platform on four 0.64 cm nylon posts. These serve to thermally isolate the upper platform from the rest of the assembly. The valve and catalyst chamber on the upper platform are part of the fill line connecting the hydrogen supply cylinder at room temperature with the cell. A 0.32 cm diameter TWSS tube enters the top of the cryostat through a vacuum seal and passes down the central column to the catalyst chamber. For most of its length a jacket of 0.64 cm tubing surrounds the smaller tube to prevent hydrogen from freezing in it. When the apparatus is cooled, the air in the 0.64 cm tube freezes, and the resulting vacuum insulates the inner fill line.

The catalyst chamber is a cylindrical copper container of volume about $6 \mathrm{~cm}^{3}$, loosely filled with a commercial hydrogen catalyst ${ }^{55}$. Molecular hydrogen has a rotational state with total angular momentum $J=1$ lying 172 K above the $J=0$ ground state ${ }^{56}$. Hydrogen in the $J=1$ state is called orthohydrogen $\left(0-\mathrm{H}_{2}\right)$; in the $J=0$ state, parahydrogen $\left(\mathrm{p}-\mathrm{H}_{2}\right)$. At room temperature the states are populated with an $o: p$ ratio of $3: 1$ due to the three-fold degeneracy of the ground state. At the critical point near 33 K the equilibrium $\mathrm{p}-\mathrm{H}_{2}$ concentration is $95 \%^{57}$. The critical temperature and density are functions of the o:p ratio; catalysis is needed to convert the hydrogen from its room temperature concentration to its equilibrium concentration at 33 K because the very slow uncatalyzed conversion would cause $T_{c}$ to vary with time.

A length of 1 mm stainless steel (SS) capillary runs from an outlet at the bottom of the catalyst chamber to the low temperature valve, shown in fig. (3-9). This valve is similar in design to one described by Oversluizen ${ }^{58}$, with the difference that it is more easily disassembled, making replacement of the valve tip a simple procedure. The SS valve stem is soft soldered to the top of a SS bellows, the bottom of which is soft soldered to a copper collar piece. The valve tip is attached to the
stem with a drop of 5 -minute epoxy, and can be easily removed for replacement if necessary. A SS tip was used for this work. The complete bellows assembly fits over a copper seat and is sealed to it with an indium O-ring at the shoulder of the seat. A copper jacket fits over the bellows and screws onto the base of the seat to put pressure on the indium and ensure a leak-tight seal. Assembled, the valve is 5.0 cm tall and 1.6 cm in diameter.


Figure 3-9 The low temperature valve.

The valve is actuated from room temperature by means of a 0.32 cm diameter rod that runs from the top of the cryostat down to the valve. The threaded end of this rod screws into the top of the valve jacket and pushes the stem down, causing the tip to seal the central hole in the seat.

A 12 cm length of 0.5 mm SS capillary, stuffed with SS wire to reduce its volume, connects the valve outlet to the cell. It is important that the volume between the valve seal and the cell entrance be small, since near the critical point the fluid in this volume will become compressible and flow into the cell, changing the sample's average density and the level of the meniscus. In our case, this unwanted volume was $0.32 \%$ of the cell volume.

The cell was cooled by means of a weak thermal link between the cell assembly and a liquid helium bath at 4.2 K , provided by a small amount ( $\sim 1 \mathrm{mtorr}$ ) of helium exchange gas in the central column of the cryostat.

Two independent temperature controllers were used to maintain the cell temperature stable to $\pm 30 \mu \mathrm{~K}$ for periods of a few hours. A DC controller, similar to that used in the ethylene experiment, was used to control the outer jacket to about $\pm 0.005 \mathrm{~K}$. A carbon resistor with a room temperature resistance of $1 \mathrm{k} \Omega$ was used as the temperature sensor; it was mounted on the underside of the main platform (see fig. (3-7)). At 30 K , it had a temperature coefficient of $100 \Omega / \mathrm{K}$. This sensor was one arm of a Wheatstone bridge, another arm of which was a decade resistance box. The error signal of the bridge was amplified by a home-made DC nullmeter based on the ICL 7605 instrumentation amplifier. The output of the nullmeter was fed to a Kepco PAT 7-2 operational power supply with a feedback network similar to that on the power supply in fig. (3-6), which powered a $50 \Omega$ heater wound around the outer jacket.

The inner cell was temperature controlled with an AC controller similar to that described by Ihas and Pobell ${ }^{59}$; it is shown in fig. (3-10). The sensor, a Scientific Instruments type 6 germanium resistor with a temperature coefficient of


Figure 3-10 The temperature controller for the hydrogen experiment. The thermometer is one arm of an AC bridge. The bridge error signal is detected by the lock-in amplifier and shaped by the proportional-integral-differential controller, then fed back to a heater on the sample cell.
$20 \Omega / \mathrm{K}$ at 30 K , was mounted in a hole drilled in the side of the cell body. A $100 \Omega$ coil of Evanohm wire, with a negligible temperature coefficient, was wound around the main platform and used as a standard resistance. These two resistors formed two arms of an AC bridge. The other two arms were provided by a Dekatran DT-72 seven decade ratio transformer. The bridge was excited at 430 Hz by the internal oscillator of an Ithaco 393 lock-in amplifier. The bridge error signal was detected by the lock-in and shaped by the proportional-integral-differential controller shown in fig. (3-10). The output of this went to a Kepco OPS 21-1 power supply which drove $50 \Omega$ heaters wound around the top and bottom of the cell. This arrangement allowed for the elimination of thermal gradients across the cell; the relative amounts of heat input to the two ends of the cell could be varied by adjusting a resistor at room temperature. The temperature was changed in small steps by changing the ratio transformer setting and thus the bridge balance.

A number of resistance thermometers were mounted on the cell assembly to allow monitoring of the temperature in various places. The main thermometer that used to measure the sample temperature - was a second SI type 6 germanium resistor mounted in a hole in the side of the cell body. Its resistance could be measured in a 4-wire configuration using a home-made constant current supply and a Keithley 177 digital voltmeter, or in a 3-wire configuration using a DC bridge with a decade resistor in one arm. By monitoring the error signal from this bridge with a HP 419A voltmeter and a chart recorder, the thermometer resistance could be determined to $\pm 0.0003 \Omega$, corresponding to a temperature resolution of $\pm 20 \mu \mathrm{~K}$.

This germanium thermometer had been calibrated by the supplier. While the calibration was occasionally roughly checked in this apparatus against the vapour pressure of $\mathrm{H}_{2}$, absolute temperatures were not of primary importance in this study. Temperatures measured with this thermometer are estimated to be accurate on an absolute scale to $\pm 0.020 \mathrm{~K}$.

Four carbon resitors on the cell assembly were monitored occasionally with a 2-wire ohmmeter to check the temperature at various locations. These were located at the top and bottom of the cell, on the bottom of the main platform, and on the valve platform (see fig. (3-9)).

Manually controlled $50 \Omega$ heaters powered by 12 V batteries were wound on the catalyst chamber (see below) and on the fill line, in case of blockage by frozen hydrogen. All automatically controlled heaters could also be manually controlled if necessary.

The hydrogen used for the experimental samples was commercial ${ }^{60}$ ultra-high purity $(99.999 \%) \mathrm{H}_{2}$, contained in a pressurized gas cylinder at room temperature. It was passed through a cold trap at 77 K to remove any condensible impurities before entering the cryogenic system. The gas handling system is shown in fig. (311).

A typical run of the experiment proceeded as follows. The vacuum spaces in the cryostat were evacuated and the helium dewar flushed with helium gas. The liquid nitrogen space was filled and the system pre-cooled for several hours. An automatic liquid nitrogen filler similar to that described by Reid and Hyde ${ }^{61}$ was used to top up the nitrogen periodically throughout the run.

A few millitorr of He exchange gas in the central column of the cryostat facilitated pre-cooling of the cell assembly. This gas was pumped out prior to transferring liquid helium. After the transfer, a small, measured amount of exchange gas was let into the column and the system allowed to cool to below 30 K .

With the system cold, the low temperature valve was closed and sufficient $\mathrm{H}_{2}$ slowly let into the catalyst chamber, where it was allowed to sit for at least an hour. Occasional warming of the chamber ensured thorough mixing of the $\mathrm{H}_{2}$ in the catalyst. The valve was then opened and the fluid let into the sample cell. The amount of fluid in the cell was adjusted by manually heating the catalyst chamber to force fluid into the cell, and by either cooling the chamber or releasing $\mathrm{H}_{2}$ from


the system at room temperature to draw fluid out of the cell. When the cell was filled so that the liquid-vapour interface disappeared in the middle of the cell when it was warmed up through the critical temperature, the valve was closed and data collection began.

The optical setup for the $\mathrm{H}_{2}$ experiment, shown in fig. (3-12), allowed simultaneous recording of both the focal plane and image plane patterns, using two continuously motor-driven cameras.

The cell was cooled below $T_{c}$, then warmed in steps by adjusting the ratio transformer setting. The time required for the system to equilibrate after a change in temperature varied from less than one minute far from $T_{c}$ to of order an hour very close to the critical point. Since the liquid helium had to be refilled roughly every 10 hours, and since helium transfers tended to disrupt the equilibrium of the sample, this limited the number of data points that could be obtained very close to the critical point. The more frequent nitrogen transfers had no effect on the sample.

Relaxation times above the critical point were considerably longer than those below, being of order an hour even quite far from $T_{c}$. This rather seriously limited the amount of supercritical data obtained from a given run.

The results of the hydrogen measurements are presented in Chapter $\mathbf{V}$.

## III-4 The Prism Cell Experiment

The refractive index of a fluid is related to its density by eq. (1-10). While the Lorenz-Lorentz coefficient $\mathcal{L}$ is approximately constant for dilute gases, at higher densities $\mathcal{L}$ becomes a function of density due to the density dependence of the molecular polarizability ${ }^{62}$. $\mathcal{L}$ can then be written as a power series in the density,

$$
\begin{equation*}
\mathcal{L}(\rho)=A_{R}(T)+B_{R}(T) \rho+C_{R}(T) \rho^{2}+\cdots \tag{3-14}
\end{equation*}
$$

where $A_{R}, B_{R}$, etc. are called the refractometric virial coefficients and are in general temperature dependent. In this section an experiment to measure $\mathcal{L}(\rho)$ and the


Figure 3-12 The optical setup for the hydrogen experiment. Data can be recorded in the focal plane ( F ) and image plane (I) simultaneously.
coexisting fluid densities in the two-phase region is described; the results of measurements on ethylene are presented in section IV-2. The experiment was developed in this laboratory and has been used for similar studies of other fluids ${ }^{37-39}$.

The sample cell, made of aluminum, consists of a wedge shaped head and a cylindrical body. Two sapphire windows in the head allow the cell to be used as a prism. The wedge angle of the prism was measured to be $20.733 \pm .017^{\circ}$ for these experiments. The sample density was determined from the mass of the cell, the empty mass and volume of which were accurately known.

Fig. (3-13) shows the experimental setup. A spatially filtered, collimated laser beam was passed through the cell while a beam splitter and two pentagonal prisms directed a reference beam around the thermostatic housing. Both beams were directed by a micrometer-driven adjustable mirror (Lansing model 10-253) into a Davidson model D 275 autocollimating telescope. The cell was filled with ethylene, weighed on a Sauter monopan balance accurate to $\pm 0.0002 \mathrm{~g}$ and placed inside a temperature controlled housing similar to that described in section III-2. The refraction angle of the sample beam was determined by adjusting the micrometerdriven mirror to direct the beam into the telescope, where it was focussed to a spot. The micrometer was calibrated by measuring the positions of the diffraction spots from a 50 lines/inch Ronchi grating placed in the thermostat in place of the sample cell.
$\mathcal{L}(\rho)$ was measured on the supercritical isotherm at 298.2 K and on the coexistence curve. The measurements at 298.2 K were straightforward. The cell mass and beam refraction angle were measured, ethylene was bled out of the cell, and the process repeated until the cell was empty. The temperature was held constant using a controller similar to that described in section III-2.

The coexistence curve measurements were only slightly more involved. The cell was filled and cooled until both phases were present in it. It was then warmed in small steps and the sample beam angle monitored. Since the fluid density and

thermostat



Figure 3-14 A phase diagram showing the path followed in taking a data point in the prism experiment. The sample, with density $\rho_{1}$, is cooled to a temperature $T_{1}$ in the two-phase region (solid circles), then warmed until it re-enters the one-phase region at a temperature $T_{2}$ (open circle). The refractive index is measured when the system has just moved off the coexistence curve.
thus the refractive index changed as the cell was warmed, the refraction angle also changed. At some temperature the sample left the coexistence curve and entered the one-phase region of the phase diagram, as illustrated in fig. (3-14). The density of the single phase remained constant and so the refractive index changed very little as the cell was warmed further. At this point the micrometer reading was recorded and the cell weighed. Fluid was bled out and the process repeated. When the sample density was close to $\rho_{c}$, refracted beams from both the liquid and vapour phases were observed. One of these eventually vanished as the system left the coexistence curve, which one depending on whether the average density was above or below $\rho_{c}$. At $\rho=\rho_{c}$ the two refraction angles became equal at the critical temperature. At
this density, the coexistence curve was measured by recording the refraction angles of each of the two beams as a function of temperature below $T_{c}$.

In both cases, when the cell was finally emptied of fluid it was evacuated and its empty mass determined. It was then filled with air at atmospheric pressure, placed in the thermostat, and the refraction angle measured; this provided a reference angle for use in the data reduction. The cell volume was measured by filling it with distilled water and reweighing it.

## III-5 Experimental Limitations

There are two major experimental problems that can affect the results of the above experiments close to the critical point. One is so-called gravitational rounding, which is unavoidable; the second is thermal gradients, which can in principle be eliminated.

## Gravitational Rounding

As discussed above, the contribution of the earth's gravitational field to the chemical potential causes the fluid density to vary with height in the cell. In the region close to the critical point where $\kappa_{T}^{*}$ diverges, this variation becomes large.

Any experimental measurement of the fluid density involves some sort of averaging over a finite height in the sample. In the case of the image and focal plane experiments, the averaging comes about because the laser beam is deflected by the refractive index gradient and so traverses a small vertical distance on passing horizontally through the sample, as shown in fig. (3-15). Close enough to the critical point, the gravitationally induced change in density with height becomes so large that the density varies significantly over the distance sampled by the beam. Under these conditions, the fringe patterns observed no longer provide information about the local density. This is known as gravitational rounding, or, for these optical experiments, the thick cell effect.


Figure 3-15 Gravitational rounding. A light ray is bent by the refractive index gradient in the fluid and so traverses a height $h$ as it passes through the cell. If the sample density changes significantly over this height, the observed fringe pattern is affected.

This problem has been analyzed in detail by Moldover et al ${ }^{32}$. Using a parametric representation of the equation of state in the critical region, they calculate how close to $T_{c}$ data can be gathered that is accurate to a given precision. Following their procedure for the image and focal plane experiments and specifying a precision of $1 \%$, we find for ethylene that gravitational rounding should limit our measurements to $t>t_{\min }=2.3 \times 10^{-5}$ above $T_{c}$, with a lower $t_{\min }$ below $T_{c}$ where the compressibility is smaller. In fact our $\mathrm{C}_{2} \mathrm{H}_{4}$ data show no noticeable gravitational rounding down to the lowest reduced temperature of $t=1.5 \times 10^{-6}$. For hydrogen, a similar calculation gives $t_{\min }=1.2 \times 10^{-4}$ in the one-phase region, smaller in the two-phase region.

In the prism experiment the effect is much more serious, since the laser samples the entire sample height of approximately 1 cm . A calculation for ethylene gives $t_{\min }=1.9 \times 10^{-4}$ above $T_{c}$ and $5.2 \times 10^{-5}$ below. Experimentally, a smearing of the laser spot observed in the telescope was present for $t \lesssim 10^{-4}$ and meaningful data could not be obtained for $t \lesssim 3 \times 10^{-5}$.

## Temperature Gradients

A temperature gradient across the sample will cause a variation in chemical potential with height in addition to that due to gravity, given by

$$
\begin{equation*}
\left(\frac{\partial \mu}{\partial z}\right)_{g r a v}=\frac{\partial \mu}{\partial T} \frac{d T}{d z}=\frac{1}{\rho_{c}} \frac{\partial P}{\partial T} \frac{d T}{d z} \tag{3-15}
\end{equation*}
$$

Such a gradient would make determination of $\kappa_{T}^{*}$ difficult since the cell would not be isothermal; there would be contributions to $\partial \rho / \partial \mu$ from both gravitationally and thermally induced density gradients. In $\mathrm{H}_{2}$ a thermal gradient of on the order of $0.1 \mathrm{mK} / \mathrm{cm}$ will contribute to the chemical potential an amount similar to that due to gravity. The effects of thermal gradients on the coexistence curve measurements are not as serious, since these measurements are done at a single height in the cell, i.e., the height of the liquid-vapour interface.

The hydrogen cell was designed with the minimization of temperature gradients in mind. However, while the gradient could be varied by adjusting the the heat inputs to the two ends of the cell, we had no way of actually measuring it; in particular we had no way of knowing when it was zero. Our compressibility measurements, to be discussed below, were strongly affected by the small gradients present, and this made it impossible to determine the amplitudes $\Gamma_{0}^{+}, \Gamma_{0}^{-}$, etc. As shown in Chapter $\mathbf{V}$, however, we were still able to obtain estimates of the exponent $\gamma$ and the amplitude ratio $\Gamma_{0}^{+} / \Gamma_{0}^{-}$.

## III-6 Data Reduction and Experimental Error

Interference fringe data for the image plane and focal plane experiments were recorded on photographic film. Coexistence curve data were extracted by counting these fringes to determine the number of missing fringes after each temperature step. This was done manually with the aid of a travelling microscope or a magnifying eyepiece. A typical run might involve on the order of 500 fringes. The uncertainty in the count at low fringe numbers is about $\pm 0.5$ fringes in the focal plane and $\pm 0.2$ fringes in the image plane; at large fringe numbers it is about $0.5 \%$ due to the difficulty in determining exactly when a fringe disappears. This translates into an uncertainty in $\rho_{\ell}-\rho_{v}$ of from $0.5 \%$ far from critical to $2 \%$ at the lowest values of $t$. The fringe counts were converted to order parameter and coexistence curve diameter data using eqs. (3-4)-(3-7).

For ethylene, $\mathcal{L}(\rho)$ and $\rho_{c}$ were measured using the prism cell apparatus described in section III-4. For hydrogen, $\mathcal{L}(\rho)$ was obtained from the measurements of Diller ${ }^{63}$. His results for $\mathcal{L}(\rho)$ on the coexistence curve are not accurate close to the critical point or on the vapour branch of the curve, therefore only his high density data were used in this analysis. Since his measurements were done at a wavelength of $\lambda=5462 \AA$ while our work was at $6328 \AA$, we scaled his $\mathcal{L}$ data down by a factor of 0.994 . This factor was calculated from a linear interpolation of available refractive index data ${ }^{57}$ at $6939 \AA$ and $5462 \AA$.

The scaled data was fitted to a quadratic in the density that was constrained to peak at the critical density, for which we used ${ }^{57} \rho_{c}=0.03143 \mathrm{~g} / \mathrm{cm}^{3}$. Diller's scaled data and our fit to it are shown in fig. (3-16). The fit gives

$$
\begin{equation*}
\mathcal{L}(\rho)=1.02565+0.05373 \rho-0.85469 \rho^{2} \tag{3-16}
\end{equation*}
$$

Index data from the prism experiment were obtained in the form of micrometer readings, which were converted to angles using the Ronchi grating calibration and


Figure 3-16 The Lorenz-Lorentz coefficient for $\mathrm{H}_{2}$, adapted from ref. 63. The line is a fit to the high density data. Points used in the fit are marked $\times$, other points are marked + . The large variations in $\mathcal{L}$ near the critical density are due to gravitational rounding.
then to refractive indices using the equation

$$
\begin{equation*}
n=n_{a}\left(1+\cos \theta-\cos \theta_{a}+\frac{\sin \theta-\sin \theta_{a}}{\tan \alpha}\right) \tag{3-17}
\end{equation*}
$$

obtained from a straightforward analysis of the prism cell optics. Here $\alpha$ is the prism angle and $\theta_{a}$ the refraction angle measured with the cell filled with air. In the experiment to measure $\mathcal{L}(\rho)$, densities were obtained from the full and empty masses of the cell, measured to $\pm 0.0002 \mathrm{~g}$, and its volume, measured to $\pm 0.06 \%$. $\mathcal{L}(\rho)$ was calculated using eq. (1-10); the results have an estimated uncertainty of $0.1 \%$ at higher densities and $0.3 \%$ at low densities. For the coexistence curve measurements, $\mathcal{L}$ was fitted to a quadratic in $n$ and the density determined from the equation

$$
\begin{equation*}
\rho=\frac{1}{\mathcal{L}(n)} \frac{n^{2}-1}{n^{2}+2} \tag{3-18}
\end{equation*}
$$

These densities are accurate to $\pm 0.2 \%$ at high $t$, but become less accurate at very low $t$ due to gravitational rounding.

The precision of the compressibility data was limited by how accurately the spacing between fringes on the data films could be measured. Far from $T_{c}$, when the fringes were widely spaced, it was impossible to obtain any reliable data. Closer to the critical point, when several fringes appeared across the film, the compressibility could be determined to roughly $5 \%$ at best.

Temperature data were obtained from a continuous chart record of the temperature monitor bridge error signal. For both the room temperature and low temperature measurements, temperatures could be determined to a (relative) accuracy of $\pm 20 \mu \mathrm{~K}$.

## CHAPTER IV

## Results, Part 1: Ethylene

Two experiments were performed on $\mathrm{C}_{2} \mathrm{H}_{4}$ : the prism experiment of section III-4 and the focal plane fringe experiment described in sections III-1 and III2. The results of these experiments are presented in this chapter. The data are tabulated in Appendix B.

## IV-1 The Prism Experiment

The prism experiment produced two distinct sets of results. These are the Lorenz-Lorentz function $\mathcal{L}(\rho)$ and the liquid and vapour densities on the coexistence curve. The computer programs used to extract these results from the raw data are given in Appendix C.

## The Lorenz-Lorentz Function

$\mathcal{L}(\rho)$ was measured on the coexistence curve and on the supercritical isotherm at 298.2 K . The primary purpose of these measurements was to make possible the conversion of measured refractive indices to densities for analysis of the critical behaviour. The measurements of $\mathcal{L}$ are, however, of some interest in themselves, since a knowledge of the refractometric virial coefficients of eq. (3-4) can lead to information on intermolecular forces ${ }^{62,64-66}$.

Our results are plotted in fig. (4-1) along with fits to the expansion (3-14) carried to second order in the density,

$$
\begin{equation*}
\mathcal{L}(\rho)=A_{R}+B_{R} \rho+C_{R} \rho^{2} \tag{4-1}
\end{equation*}
$$

The fit parameters are given in Table IV-1. Since the measurements on the coexistence curve are limited to a small region around the critical density, the uncertainties in the fit parameters for these data are large. We find $A_{R}=10.55 \pm .10 \mathrm{~cm}^{3} / \mathrm{mole}$, $B_{R}=32.8 \pm 30.3 \mathrm{~cm}^{6} / \mathrm{mole}^{2}$ and $C_{R}=-2300 \pm 2100 \mathrm{~cm}^{9} / \mathrm{mole}^{3}$. Simply averaging the coexistence curve data gives $\overline{\mathcal{L}}_{\text {coex }}=10.665 \pm .021 \mathrm{~cm}^{3} / \mathrm{mole}$.

## Table IV-1

Refractometric Virial Coefficients and Electronic Polarizability for Ethylene

| Data Set | $A_{R}\left(\mathrm{~cm}^{3} / \mathrm{mole}\right)$ | $B_{R}\left(\mathrm{~cm}^{6} / \mathrm{mole}^{2}\right)$ | $C_{R}\left(\mathrm{~cm}^{9} / \mathrm{mole}^{3}\right)$ | $\alpha_{e}\left(\AA^{3}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| Coex. curve | $10.55 \pm .10$ | $32.8 \pm 30.3$ | $-2300 \pm 2100$ | $4.14 \pm .04$ |
|  | $10.665 \pm .021$ | $(0)$ | $(0)$ | $4.23 \pm .01$ |
| 298.2 K | $10.50 \pm .02$ | $40.2 \pm 8.7$ | $(0)$ | $4.162 \pm .008$ |
| Both sets | $10.48 \pm .02$ | $64.3 \pm 9.1$ | $-5100 \pm 830$ | $4.154 \pm .008$ |

It is, of course, not quite legitimate to use eq. (3-14) to describe $\mathcal{L}(\rho)$ on the coexistence curve. Since the temperature is not constant, the refractometric virial coefficients will in principle vary along the curve. It is, however, useful to parametrize the behaviour of $\mathcal{L}(\rho)$ in this way so that these results can be applied to the analysis of our critical phenomena data.

The 298.2 K data agree in magnitude with the coexistence curve data although the density ranges covered by the two data sets do not overlap much. The results of fits to this data and to both sets of data combined are given in Table IV-1.


St. Arnaud and Bose ${ }^{65}$ find $A_{R}=10.610 \pm .009 \mathrm{~cm}^{3} / \mathrm{mole}$ and $B_{R}=40.8 \pm$ $2.0 \mathrm{~cm}^{6} /$ mole $^{2}$ for ethylene at 303 K ; they see no evidence for a quadratic term in $\mathcal{L}(\rho)$ up to densities of about 0.008 mole $/ \mathrm{cm}^{3}$. This density is higher than the critical density of ethylene, 0.0076 mole $/ \mathrm{cm}^{3}$. The $1 \%$ difference in $A_{R}$ between our results and those of ref. (65) may be due to sample impurities or to a systematic error in density determination. The value of $\rho_{c}$ obtained with our apparatus and sample (see below) is $0.3 \%$ higher than previously published values; this is not enough to account for the above difference.

The zero density limit of $\mathcal{L}(\rho)$ is related to the molecular electronic polarizability $\alpha_{e}$ by

$$
\begin{equation*}
\mathcal{L}(0)=A_{R}=\frac{4 \pi \alpha_{e} N_{\mathrm{A}}}{3} \tag{4-2}
\end{equation*}
$$

From our values of $A_{R}$ we find $\alpha_{e}=4.16 \pm .04 \AA^{3}$ on the coexistence curve and $\alpha_{e}=4.162 \pm .008 \AA^{3}$ at 298.2 K .

## The Coexistence Curve

The refractive index measurements on the coexistence curve are converted to density data as described in section III-6 using the $\mathcal{L}(\rho)$ data presented above. The resulting coexistence curve and its diameter are plotted in fig. (4-2).

A log-log plot of the reduced density difference $\Delta \rho^{*}$ against the reduced temperature $t$ is given in fig. (4-3). The critical density and temperature used for this plot were determined from fits to the data as described below. In fig. (4-4) the same data is plotted as $\Delta \rho^{*} / t^{\beta}$ vs. $t$ on a log-log plot. Here the leading temperature dependence in eq. (1-6) has been divided out; the value of the exponent $\beta$ used in this and other similar figures is that from the fit plotted in the figure. This type of plot $^{23}$ is very sensitive to deviations of the data from pure power law behaviour. A straight horizontal line would imply $\Delta \rho^{*} \propto t^{\beta}$. Curvature of the plot as $t$ increases indicates deviations from a power law due to corrections-to-scaling


Figure 4-3 A $\log -\log$ plot of the order parameter $v s$. reduced temperature for the ethylene prism data.
effects. An upturn in the data at low $t$ could signal the presence of the gravitational rounding effects discussed in section $\mathbf{I I I}-5$, although an incorrect choice of $T_{c}$ would also cause an upturn or a downturn in the low $t$ data. As the figure shows, this set of data deviates from a simple power law at high $t$. It was therefore analysed using the corrections-to-scaling series for the order parameter, eq. (1-6).

It is well known that, with an incorrect choice of $T_{c}$, fits to eq. (1-6) or to its asymptotic power law form can be misleading. For example, a fit of the data in fig. (4-4) to a simple power law, $\Delta \rho^{*}=B t^{\beta}$, with $B, T_{c}$ and $\beta$ all free parameters gives $\beta=0.355$ and $T_{c}=282.3823 \mathrm{~K}$. Fitting only the data with $t \leq 7.2 \times 10^{-4}$ gives $\beta=0.328$ and $T_{c}=282.3750 \mathrm{~K}$. The difference is due to neglect of corrections-toscaling terms in the first fit, which includes data well out of the asymptotic critical region. Fig. (4-5a) is a plot of the residuals for the first of these fits; systematic deviations from the fit are visible. The critical temperatures used in the analysis of this and other data sets were determined from simple power law fits like the second one, using only data close to the critical point. These determinations of $T_{c}$ were checked by fitting the data over the full range of $t$ with the corrections-to-scaling expression. For the prism data under consideration here, a fit to eq. (1-6) with two correction terms and $\beta$ fixed gives $T_{c}=282.3754 \pm .0004 \mathrm{~K}$ for $\beta=0.327 \pm .002$, consistent with the result obtained above. The value $T_{c}=282.3750 \pm .0010 \mathrm{~K}$ was therefore adopted for this data set.

Table IV-2 gives the results of several fits to this data which cover the range $8.7 \times 10^{-5}<t<4.5 \times 10^{-2}$. The fits in this table were performed with the correction exponent fixed at the value 0.5 , roughly its calculated value ${ }^{7,9}$ and the value conventionally used in analyses of this type ${ }^{2,3}$. Fits were done using one or two correction terms and with $\beta$ either fixed at values near its predicted value ${ }^{5-9}$ or free. Parameter values enclosed in parentheses were fixed for that fit.


Figure 4-4 $\mathrm{A} \log -\log$ plot of $\Delta \rho / t^{\beta}$ vs. reduced temperature for the ethylene prism data. The line is fit 1 from Table IV-2.



Figure 4-5 Residuals of fits to the order parameter data of fig. (4-4). a) Residuals for a fit to a simple power law (fit 6 of Table IV-2). Note the systematic behaviour of the residuals. b) Residuals for fit 1 of table IV-2, which includes two corrections-to-scaling terms.

Table IV-2
Fits of the ethylene order parameter data to eq. (1-6) with $\Delta=0.5$

| data set | fit \# | $\beta$ | $B_{0}$ | $B_{1}$ | $B_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| prism data | 1 | 0.3286 | 1.586 | 0.89 | -1.58 |
|  | 2 | (0.325) | 1.538 | 1.09 | -2.01 |
| $t_{\text {max }}=4.5 \times 10^{-2}$ | 3 | (0.327) | 1.564 | 0.98 | -1.77 |
| $t_{\min }=8.7 \times 10^{-5}$ | 4 | 0.3399 | 1.749 | 0.25 | (0) |
|  | 5 | (0.327) | 1.598 | 0.535 | (0) |
|  | 6 | 0.3549 | 1.924 | (0) | (0) |
| fringe data set \#2 | 7 | (0.327) | 1.490 | 1.65 | -19.7 |
|  | 8 | 0.3278 | 1.511 | 0.85 | (0) |
| $t_{\max }=7.5 \times 10^{-4}$ | 9 | (0.325) | 1.467 | 1.22 | (0) |
| $t_{\text {min }}=2.5 \times 10^{-6}$ | 10 | (0.327) | 1.498 | 0.95 | (0) |
| set \#3 | 11 | (0.327) | 1.493 | 1.16 | $-1.30$ |
|  | 12 | 0.3272 | 1.498 | 1.05 | (0) |
| $\begin{aligned} t_{\max } & =4.4 \times 10^{-3} \\ t_{\min } & =2.1 \times 10^{-5} \end{aligned}$ | 13 | (0.325) | 1.468 | 1.19 | (0) |
|  | 14 | (0.327) | 1.495 | 1.06 | (0) |
| set \#4 | 15 | (0.327) | 1.513 | -0.10 | (0) |
|  | 16 | 0.3268 | 1.509 | (0) | (0) |
| $\begin{aligned} t_{\max } & =1.4 \times 10^{-4} \\ t_{\min } & =2.8 \times 10^{-6} \end{aligned}$ | 17 | (0.325) | 1.482 | (0) | (0) |
|  | 18 | (0.327) | 1.512 | (0) | (0) |
| set \#5 | 19 | (0.327) | 1.496 | 1.09 | -1.34 |
|  | 20 | 0.3269 | 1.499 | 0.97 | (0) |
| $t_{\text {max }}=7.1 \times 10^{-3}$$t_{\text {min }}=1.5 \times 10^{-6}$ | 21 | (0.325) | 1.473 | 1.09 | (0) |
|  | 22 | (0.327) | 1.500 | 0.97 | (0) |
| all sets | 23 | (0.327) | 1.496 | 1.12 | -1.49 |
|  | 24 | 0.3269 | 1.497 | 0.99 | (0) |
| $\begin{aligned} t_{\max } & =7.1 \times 10^{-3} \\ t_{\min } & =1.5 \times 10^{-6} \end{aligned}$ | 25 | (0.325) | 1.471 | 1.12 | (0) |
|  | 26 | (0.327) | 1.499 | 0.99 | (0) |
| all data | 27 | 0.3288 | 1.585 | 0.96 | $-1.89$ |
|  | 28 | (0.325) | 1.530 | 1.23 | -2.64 |
| $\begin{aligned} t_{\max } & =4.5 \times 10^{-2} \\ t_{\min } & =1.5 \times 10^{-6} \end{aligned}$ | 29 | (0.327) | 1.559 | 1.09 | -2.24 |
|  | 30 | 0.3359 | 1.699 | 0.35 | (0) |
|  | 31 | (0.327) | 1.585 | 0.61 | (0) |

The computer program used for curve fitting is listed and described in Appendix $\mathbf{C}$. It is based on a standard non-linear least squares fitting routine called NL2SNO ${ }^{67}$.

Fits to this data set give $\beta=0.328 \pm .004, B_{0}=1.59 \pm .05, B_{1}=0.90 \pm .15$ and $B_{2}=-1.6 \pm .3$. Fits with $B_{2}=0$ had significantly larger $\chi^{2}$ values than did fits with $B_{2}$ free, indicating the need for at least two correction terms in the analysis. The quoted uncertainties are several times larger than the statistical uncertainties from the fits and are intended to include uncertainties due to correlations between the parameters and to the uncertainty in $T_{c}$. Correlations between parameters are strong, as can be seen from inspection of Table IV-2. Fit 1 from the table is shown in fig. (4-4); residuals for this fit are plotted in fig. (4-5b).

Fits were also performed with $\Delta$ a free parameter. The data were not precise enough to permit meaningful fits with both $\beta$ and $\Delta$ free, but with $\beta$ fixed at values close to its predicted value, $\Delta$ could be determined. The results of these fits are given in Table IV-3. We find for this data that $\Delta=0.44 \pm .02$ for $\beta=0.327 \pm .002$. The amplitudes obtained from these fits are significantly lower than when $\Delta=0.5$; $B_{1}$ decreases by about $20 \%$ and $B_{2}$ by about $50 \%$. The leading amplitude $B_{0}$ decreases by about $1 \%$.

## The Coexistence Curve Diameter

The corrections-to-scaling expression for the coexistence curve diameter was given in eq. (1-9):

$$
\begin{equation*}
\rho_{d} \equiv \frac{\rho_{\ell}+\rho_{v}}{2 \rho_{c}}=1+A_{1} t^{1-\alpha}+A_{2} t+A_{3} t^{1-\alpha+\Delta}+\cdots \tag{1-9}
\end{equation*}
$$

Classically, the diameter is rectilinear, i.e., only the amplitude $A_{2}$ is non-zero. In the case of a VDW fluid, $A_{2}=2 / 5$. The term $\sim t^{1-\alpha+\Delta}$ is a corrections-to-scaling term, and the $t^{1-\alpha}$ term arises due to thermodynamic field-mixing. Although predicted by various theoretical treatments ${ }^{68-70}$, this $t^{1-\alpha}$ anomaly has proven very difficult to

## Table IV-3

Fits of the ethylene order parameter data to eq. (1-6) with $\Delta$ a free parameter

| data set | fit \# | $\beta$ | $B_{0}$ | $B_{1}$ | $B_{2}$ | $\Delta$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| prism data | 32 | $(0.325)$ | 1.520 | 0.84 | -1.02 | 0.42 |
|  | 33 | $(0.327)$ | 1.553 | 0.81 | -1.07 | 0.44 |
| fringe data | 34 | $(0.325)$ | 1.461 | 0.80 | $(0)$ | 0.42 |
|  | 35 | $(0.327)$ | 1.496 | 0.88 | $(0)$ | 0.47 |
| all data | 36 | 0.299 | 1.034 | 1.52 | -0.76 | 0.23 |
|  | 37 | $(0.325)$ | 1.512 | 0.85 | -1.02 | 0.40 |
|  | 38 | $(0.327)$ | 1.548 | 0.83 | -1.14 | 0.43 |

observe experimentally ${ }^{72-74}$, mainly because it is quite weak; its exponent, $1-\alpha$, is only slightly smaller than unity. Separation of the anomaly from the analytic background thus requires precise data in the vicinity of the critical point. The predicted shape of the coexistence curve diameter is illustrated in fig. (4-6).

In Section III-3 the physical variables $t$ and $\Delta \mu^{*}$ were associated with the two relevant scaling fields of the liquid-vapour critical point. For real fluids the scaling fields are not simply equal to $t$ and $\Delta \mu^{*}$, but are analytic functions of them that vanish at the critical point ${ }^{71}$. In the simplest expression of this "revised" scaling ${ }^{76}$, the scaling fields are $t+c \Delta \mu^{*}$ and $\Delta \mu^{*}$, where $c$ is a universal constant. This fieldmixing is a manifestation of the lack of particle-hole symmetry in real fluids. It has been argued that its microscopic origin is many-body interactions in the fluid; a theory based on three-body, primarily repulsive Axilrod-Teller interactions has been found to agree well with experimental results ${ }^{73,74}$.

The diameter data from fig. (4-2) for ethylene are replotted in fig. (4-7) on an expanded scale. While there is some scatter in the data, a small ( $0.1 \%$ ) systematic deviation from the classical rectilinear behaviour is seen for $t \lesssim 3 \times 10^{-3}$.


Figure 4-6 A schematic diagram of the coexistence curve diameter. The dashed line is the classical rectilinear diameter; the dotted line shows the expected $1-\alpha$ anomaly.

The critical density for ethylene was determined by fitting these data to eq. (43) below and adjusting $\rho_{c}$ to give $\rho_{d}=1$ at $t=0$. This procedure gives $\rho_{c}=$ $0.007659 \pm .000008 \mathrm{~mole} / \mathrm{cm}^{3}$.

The diameter data were analyzed by fitting to the form

$$
\begin{equation*}
\rho_{d}=A_{0}+A_{1} t^{1-\alpha}+A_{2} t \tag{4-3}
\end{equation*}
$$



Figure 4-7 The coexistence curve diameter of ethylene. The line is a fit of the data in the range $0.02>t>0.008$ to a straight line. The inset shows the deviations from this fit at low $t$. These are systematically negative for $t \lesssim 0.002$.
with $A_{0}, A_{1}$ and $A_{2}$ parameters. The exponent $\alpha$ was fixed at its theoretical value of 0.11. The corrections-to-scaling term was not included in the analysis because the precision of the data did not justify the introduction of additional free parameters.

Fits were performed over an "inner" temperature range, $0.0003<t<0.002$, an "outer" range, $0.008<t<0.02$, and an "entire" range, $0.0003<t<0.02$. The data shown in fig. (4-7) include points outside these ranges; the fits were done as described for consistency with the analysis of data for other fluids in refs. (73) and (74).

Results of these fits are given in Table IV-4. Data in the outer region were fit to the form

$$
\begin{equation*}
\rho_{d}=A_{0}+A_{2} t \tag{4-4}
\end{equation*}
$$

to determine the slope of the diameter away from the critical point; we find $A_{2}=$ $0.878 \pm .037$. Fits over the inner and entire ranges show that the observed deviation from rectilinear is consistent with the predicted $t^{1-\alpha}$ anomaly with $A_{1}$ positive, although a determination of the exponent was not possible because of the scatter in the data and the weakness of the critical anomaly.

Table IV-4 Fits to the Coexistence Curve Diameter of Ethylene

| range of t | $A_{0}$ | $A_{1}$ | $A_{2}$ | $\chi^{2}$ |
| :---: | :---: | ---: | ---: | :---: |
| outer | $1.00058(52)$ | $(0)$ | $0.878(37)$ | 1.20 |
| inner | $1.00017(26)$ | $0.517(121)$ | $(0)$ | 1.02 |
| inner | $1.00027(23)$ | $(0)$ | $0.988(226)$ | 0.99 |
| entire | $1.00008(11)$ | $0.576(7)$ | $(0)$ | 1.14 |
| entire | $1.00057(11)$ | $(0)$ | $0.885(11)$ | 1.27 |
| entire | $1.00058(19)$ | $0.401(182)$ | $0.269(280)$ | 1.14 |

In fig. (4-8) the coexistence curve diameter of ethane, $\mathrm{C}_{2} \mathrm{H}_{6}$ is shown. This set of data was obtained by Burton in $1973^{38,75}$ in the same way as the ethylene data, but the coexistence curve diameter was not carefully analysed until now. These data also show an anomaly for $t \lesssim 3 \times 10^{-3}$. Results of fits of eq. (4-3) to this data over the same temperature ranges as for ethylene are given in Table IV-5. Here the slope of the diameter away from $T_{c}$ is $A_{2}=0.795 \pm .038$; again the anomaly is consistent with the predicted form.

Table IV-5 Fits to the Coexistence Curve Diameter of Ethane

| range of t | $A_{0}$ | $A_{1}$ | $A_{2}$ | $\chi^{2}$ |
| :---: | :---: | ---: | ---: | :---: |
| outer | $1.00159(55)$ | $(0)$ | $0.795(38)$ | 1.58 |
| inner | $1.00013(20)$ | $0.567(82)$ | $(0)$ | 1.00 |
| inner | $1.00027(19)$ | $(0)$ | $1.053(155)$ | 1.03 |
| entire | $1.00017(10)$ | $0.564(8)$ | $(0)$ | 1.14 |
| entire | $1.00062(11)$ | $(0)$ | $0.865(14)$ | 1.44 |
| entire | $1.00010(17)$ | $0.661(180)$ | $-0.150(276)$ | 1.08 |

## IV-2 The Fringe Experiment

The focal plane fringe experiment yields the difference in refractive index between the coexisting phases, $n_{\ell}-n_{v}$. This quantity is converted to the reduced density difference $\Delta \rho^{*}$ using the results for $\mathcal{L}(\rho)$ presented in the previous section, and eq. (3-6); the algebraic details of the conversion are given in Appendix $\mathbf{A}$ and the relevant computer programs listed in Appendix C.

Four sets of fringe data were obtained for ethylene. For each set the critical temperature was determined as above to $\pm .0001 \mathrm{~K}$; the four values obtained were in the range $282.4882 \pm .0024 \mathrm{~K}$. These data are shown on a $\log -\log$ plot in fig. (4-9)


Figure 4-8 The coexistence curve diameter of ethane. The line is a fit of the data in the range $0.02>t>0.008$ to a straight line. The inset shows the deviations from this fit at low $t$. These are systematically negative for $t \lesssim 0.004$.
and on a sensitive plot in fig. (4-10). The different symbols in the figures identify data from the different runs.

Fits to these data sets individually, as well as inspection of fig. (4-10), indicate that the four sets are consistent with each other. All four sets were therefore analysed together. We found that one correction term in eq. (1-6) was sufficient to describe the data, which extended to a maximum reduced temperature of $t_{\max }=$ $8 \times 10^{-3}$. If a second correction term was included, its value was not well determined and varied greatly with the temperature range of the fit. The results of fits to these data are given in Table IV-2. Since the data extend very close to $T_{c}, \beta$ could be determined quite precisely. The fits give $\beta=0.3269 \pm .0010, B_{0}=1.50 \pm .03$, and $B_{1}=1.0 \pm .1$ with $\Delta=0.5$. Fit 24 from the table is shown in fig. (4-10), and a plot of the residuals for this fit is given in fig. (4-11).

Gravitational rounding effects can lead to and be masked by an incorrect value of $T_{c}$, as discussed above. For this reason, fits were also performed excluding those points at the lowest values of $t$, where rounding was expected to be most important. The results of these fits were consistent with fits to the entire data set, implying that such effects are small in this case.

These data were also fitted with $\Delta$ a free parameter; we find $\Delta=0.47 \pm .05$ for $\beta=0.327 \pm .002$. As before, the correction amplitudes decrease significantly from their values when $\Delta=0.5$. Results of these fits are given in Table IV-3.

## IV-3 Combined Results

The order parameter data from the two ethylene experiments differ by 0.11 K in critical temperature. In addition, the fringe data are systematically $4 \%$ lower than the prism data in the region where the two sets overlap, as shown in fig. (4-12). The cause of these differences is not known.

One possibility is a difference in impurity content between the two samples. The sample used in the fringe experiment was from a bottle purchased in 1968 which


Figure 4-9 A log-log plot of the order parameter vs. reduced temperature for the ethylene fringe data.


Figure 4-10 A $\log -\log$ plot of $\Delta \rho / t^{\beta}$ vs. reduced temperature for the ethylene fringe data. The line is fit 24 from Table IV-2.


Figure 4-11 Residuals for the fit shown in fig. (4-10).
had been unused until this work began. The sample used in the prism experiment was purchased in 1985. A possible impurity in ethylene is ethane. Following the procedure of Hastings et al. ${ }^{76}$, the amount of ethane impurity required to cause the observed difference in $T_{c}$ is estimated to be $0.48 \%$, which is large. Even this amount of impurity, however, would only cause a shift in $\rho_{c}$ of $0.06 \%$ and in $n_{c}$ of about $0.02 \%$, nowhere near the $4 \%$ required to reconcile the two sets of data. Mass spectra of ethylene samples from both the old and new bottles were virtualy identical, apparently ruling out impurities as the source of the discrepancy.

Possible systematic errors stemming from the calibration of the prism apparatus are expected to be at worst $0.2 \%$. Other possible errors, for example in the determination of $\rho_{c}$, would affect both sets of data in the same way and so cannot explain the differences between them.


Figure 4-12 A $\log -\log$ plot of the order parameter vs. reduced temperature for both sets of ethylene data.

Since the sample used in the prism experiment was nominally more pure and also much newer, the order parameter data from the fringe experiment were scaled up by $4.0 \%$. When this was done, the fringe and prism data agreed within the scatter. A sensitive plot of the combined data is given in fig. (4-13). Results of fits to these combined data are given in Table IV-2. From these fits we get $\beta=0.3288 \pm 0.0012, B_{0}=1.58 \pm .03, B_{1}=0.96 \pm .15$ and $B_{2}=-1.9 \pm .3$ with $\Delta=0.5$. Fit 27 from the table is shown in fig. (4-13) as a dashed line; the solid line is fit 24 to the fringe data only. With $\Delta$ free we find $\Delta=0.43 \pm .03$ for $\beta=0.327 \pm .002$, and again the correction amplitudes decrease.

It can be seen from fig. (4-13) that there are some difficulties with the fits obtained using eq. (1-6). Specifically, the unphysical "turnover" of the fitted curve at $t \sim 7 \times 10^{-2}$ seems to indicate the need for an additional, positive correction term at reduced temperatures in this vicinity. Small systematic deviations of the fit from the "best fit" as determined by eye are also evident. We believe these problems to be indications of crossover effects, caused by the fact that the corrections to scaling series does not converge to any classical limit away from the critical region. This point will be discussed further in Chapter VI.

Figure 4-13 A log-log plot of $\Delta \rho^{*} / t^{\beta}$ vs. reduced temperature for both sets of
ethylene data.

reduced temperature

## CHAPTER V

## Results, Part 2: Hydrogen

The coexistence curve of hydrogen and its diameter were measured using the focal plane and image plane techniques, as described in sections III-1 and III-3. These results are presented below in sections $V-1$ and $V-2$; the data are tabulated in Appendix B. Our attempts to measure the isothermal compressibility from the image plane data were not completely successful due to the presence of temperature gradients. We found the compressibility to vary substantially for runs with different temperature gradients. Despite this, the compressibility measurements provide useful information; they are presented in section $\mathbf{V}-\mathbf{3}$.

## V-1 The Coexistence Curve

The focal plane and image plane fringe counts were converted to densities as described in Chapter III. The values of $\Delta \rho^{*}$ obtained from the two techniques for a given run should be identical, within fringe counting errors, since the data were recorded simultaneously. Although the image plane fringes could be counted with slightly better precision, adding the liquid and vapour fringe counts to obtain $n_{\ell}-n_{v}$ made the overall counting uncertainties about the same for the two techniques; they are as discussed in section III-6. The $\Delta \rho^{*}$ data analysed in this chapter are from the focal plane counts; the image plane data were used as a check.

Several experimental runs were done for hydrogen. The critical temperature, determined as for the ethylene data, covered a range of $32.85 \mathrm{~K}<T_{c}<33.30 \mathrm{~K}$ as
measured with the calibrated Ge resistance thermometer. Five of the seven runs analysed had $T_{c}$ in the range $32.9735 \mathrm{~K}<T_{c}<33.0030 \mathrm{~K}$ with a mean and standard deviation of $32.984 \pm .013 \mathrm{~K}$. $T_{c}$ for each run could be determined to a precision of from $\pm 0.0002 \mathrm{~K}$ to $\pm 0.0005 \mathrm{~K}$, depending on how many near-critical data points there were in each data set.

The observed variations in $T_{c}$ are probably due to changes in the thermometer calibration on thermal cycling, and possibly also to slightly different ortho-para concentrations in the samples used for different runs. The accepted value ${ }^{57}$ of $T_{c}$ for pure $\mathrm{p}-\mathrm{H}_{2}$ is 32.976 K , and for normal (i.e., room temperature composition) $\mathrm{H}_{2}$ it is 33.19 K . Assuming that $T_{c}$ varies linearly with $\mathrm{p}-\mathrm{H}_{2}$ concentration, the critical point of equilibrium ( $95 \%$ para) $\mathrm{H}_{2}$ should be at 32.990 K . The observed critical temperatures are consistent with this value.
$\Delta \rho^{*}$ obtained from the focal plane data is plotted against reduced temperature on a $\log -\log$ plot in fig. (5-1). Fig. (5-2) is a sensitive plot of the same data. Data from seven runs are shown; the different symbols distinguish data from the different runs. There are slight ( $\lesssim 0.5 \%$ ) systematic differences between the various runs which may be due to variations in o-p concentration (although no systematic variation of $B_{0}$ with $T_{c}$ was observed) or, more likely, to systematic errors in fringe counting. Basically, however, the different runs overlap within the expected experimental error. The systematic differences do not have a very significant effect on the analysis of the data, as discussed below. No systematic variation of $B_{0}$ with the temperature gradient was observed, indicating as expected that the coexistence curve measurements are relatively insensitive to that problem.

The hydrogen data plotted in figs. (5-1) and (5-2) have a larger $t_{\max }(7.0 \times$ $\left.10^{-2}\right)$ and $t_{\min }\left(3.2 \times 10^{-5}\right)$ than do the corresponding ethylene data, for two reasons. First, since the critical temperature of hydrogen is roughly a factor of 10 lower than $T_{c}$ for ethylene, the reduced temperature scale for hydrogen is stretched by a factor of 10 compared to ethylene's. Second, the lower refractive index of hydrogen ${ }^{57}$


Figure 5-1 A log-log plot of the order parameter vs. reduced temperature for hydrogen.


Figure 5-2 A log-log plot of $\Delta \rho^{*} / t^{\beta}$ vs. reduced temperature for hydrogen. The different symbols distinguish data from different runs. The line is fit 27 from Table V-1.
( $n_{c}=1.049$ ) means that fewer interference fringes per unit reduced temperature are observed; this limits how close to $T_{c}$ accurate data can be obtained.

These data were fitted to eq. (1-6) in the same way as were the ethylene data. Table V-1 shows the results of several fits to the individual data sets and to all seven sets combined. For two sets with $t_{\max }=1.4 \times 10^{-3}$ and $1.3 \times 10^{-3}$ respectively, a simple power law described the data adequately. The other sets required two correction terms; setting $B_{2}=0$ resulted in a significant increase in the $\chi^{2}$ value for the fit. Since the individual data sets have relatively few data points, especially at low $t$, the uncertainties in the fit parameters due to the uncertainty in $T_{c}$ are large. Typically, $\beta$ varied by $\pm 0.008$ and $B_{0}$ by $\pm 0.07$ when $T_{c}$ was varied by $\pm 0.0002 \mathrm{~K}$. Simply averaging the values of the parameters obtained from these fits with the best values of $T_{c}$ gives $\beta=0.324 \pm .002, B_{0}=1.17 \pm .03, B_{1}=1.4 \pm .3$ and $B_{2}=-2.4 \pm 1.3$. One data set gives $B_{2}=-4.5$, which is quite different from the other results; excluding this value from the average gives $B_{2}=-1.9 \pm .6$. The uncertainties here are standard deviations. The most extensive data set (250287.4) and a fit to it (no. 16 from the table) are shown in fig. (5-3); residuals for this fit are plotted in fig. (5-4).

The results of fits to the seven data sets combined are also given in Table $\mathbf{V}-\mathbf{1}$. We find from these fits that $\beta=0.327 \pm .004, B_{0}=1.20 \pm .04, B_{1}=0.98 \pm 0.18$ and $B_{2}=-1.1 \pm .4$. Here the errors are twice the statistical uncertainties from the fits. These values all agree within error with the results given above for the individual data sets. Fit 27 from the table is shown in fig. (5-2).

In an effort to determine the effect of the small systematic differences between the various runs, the individual data sets were scaled slightly so that they overlapped more exactly. A fit to this scaled data is shown in the table; the parameters are slightly but not significantly different from those for the unscaled data.

The combined data were also fitted to the corrections-to-scaling series with $\Delta$ a free parameter. Results of these fits are given in Table $\mathbf{V}-2$. The unscaled

Table V-1
Fits of the hydrogen order parameter data to eq. (1-6) with $\Delta=0.5$

| data set | fit \# | $\beta$ | $B_{0}$ | $B_{1}$ | $B_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 211186.1 | 1 | 0.3255 | 1.229 | (0) | (0) |
| $t_{\text {max }}=1.3 \times 10^{-3}$ | 2 | (0.325) | 1.225 | (0) | (0) |
| $t_{\text {min }}=4.9 \times 10^{-5}$ | 3 | (0.327) | 1.243 | (0) | (0) |
| 171286.1 | 4 | 0.3265 | 1.168 | 1.67 | -4.51 |
|  | 5 | (0.325) | 1.153 | 1.78 | -4.85 |
| $t_{\max }=1.6 \times 10^{-2}$ | 6 | (0.327) | 1.173 | 1.64 | -4.40 |
| $t_{\text {min }}=2.6 \times 10^{-4}$ | 7 | (0.327) | 1.204 | 0.88 | (0) |
| 250287.1 | 8 | 0.3216 | 1.129 | 1.48 | -2.73 |
|  | 9 | (0.325) | 1.161 | 1.30 | -2.28 |
| $t_{\text {max }}=3.2 \times 10^{-2}$ | 10 | (0.327) | 1.181 | 1.19 | -2.02 |
| $t_{\text {min }}=9.0 \times 10^{-5}$ | 11 | (0.327) | 1.203 | 0.74 | (0) |
| 250287.2 | 12 | 0.3262 | 1.175 | 1.09 | -1.21 |
|  | 13 | (0.325) | 1.164 | 1.14 | -1.29 |
| $t_{\text {max }}=7.0 \times 10^{-2}$ | 14 | (0.327) | 1.182 | 1.06 | -1.16 |
| $t_{\min }=7.9 \times 10^{-5}$ | 15 | (0.327) | 1.210 | 0.68 | (0) |
| 250287.4 | 16 | 0.3248 | 1.177 | 1.13 | -1.68 |
|  | 17 | (0.325) | 1.178 | 1.12 | -1.67 |
| $t_{\text {max }}=6.1 \times 10^{-2}$ | 18 | (0.327) | 1.198 | 1.03 | -1.49 |
| $t_{\min }=3.2 \times 10^{-5}$ | 19 | (0.327) | 1.225 | 0.60 | (0) |
| 070487.1 | 20 | 0.3208 | 1.135 | 1.35 | -2.06 |
|  | 21 | (0.325) | 1.177 | 1.12 | -1.57 |
| $t_{\text {max }}=4.2 \times 10^{-2}$ | 22 | (0.327) | 1.197 | 1.01 | -1.34 |
| $t_{\min }=9.2 \times 10^{-5}$ | 23 | (0.327) | 1.218 | 0.66 | (0) |
| 070487.2 | 24 | 0.3210 | 1.183 | (0) | (0) |
| $t_{\text {max }}=1.4 \times 10^{-3}$ | 25 | (0.325) | 1.218 | (0) | (0) |
| $t_{\text {min }}=4.0 \times 10^{-5}$ | 26 | (0.327) | 1.237 | (0) | (0) |
| all sets | 27 | 0.3270 | 1.197 | 0.98 | -1.11 |
|  | 28 | (0.325) | 1.177 | 1.07 | $-1.27$ |
| $t_{\text {max }}=7.0 \times 10^{-2}$ | 29 | (0.327) | 1.196 | 0.98 | -1.11 |
| $t_{\text {min }}=3.2 \times 10^{-5}$ | 30 | (0.327) | 1.218 | 0.65 | (0) |
| all sets, scaled | 31 | 0.3283 | 1.214 | 0.91 | -0.89 |



Figure 5-3 A $\log -\log$ plot of $\Delta \rho^{*} / t^{\beta}$ vs. reduced temperature for set 250287.4 of the hydrogen data. The line is fit 16 from Table V-1.


Figure 5-4 Residuals for the fit shown in fig. (5-3).
data give $\Delta=0.46 \pm .02$ for $\beta=0.327 \pm .002$ and, as with ethylene, the critical amplitudes decrease significantly from their values with $\Delta=0.5$. The scaled data give $\Delta=0.44 \pm .02$, not significantly different from the unscaled result.

> Table V-2

Fits of the hydrogen order parameter data to eq. (1-6) with $\Delta$ a free parameter

| data set | fit \# | $\beta$ | $B_{0}$ | $B_{1}$ | $B_{2}$ | $\Delta$ |
| :---: | ---: | :---: | :---: | :---: | :---: | :---: |
| all data | 32 | 0.248 | 0.370 | 3.63 | -0.16 | 0.20 |
|  | 33 | $(0.325)$ | 1.166 | 0.88 | -0.70 | 0.44 |
|  | 34 | $(0.327)$ | 1.190 | 0.86 | -0.76 | 0.46 |
| all data, scaled | 35 | $(0.325)$ | 1.169 | 0.81 | -0.48 | 0.42 |
|  | 36 | $(0.327)$ | 1.193 | 0.80 | -0.53 | 0.44 |

## V-2 The Coexistence Curve Diameter

Fig. (5-5) is a plot of the coexistence curve diameter of hydrogen obtained from the image plane data. Data from six runs are shown. There are some systematic differences between the various data sets but despite this, the data sets agree within acceptable scatter. Shifts in the recorded interference pattern due to, for example, changes in room temperature, have a large effect on the diameter data and probably cause the observed systematic differences.

These data are strikingly different from the diameter data for ethylene and ethane presented in the previous chapter, and for other fluids ${ }^{73,74}$. A critical anomaly is again present for $t \lesssim 2 \times 10^{-3}$, but in this case it is larger ( $\sim 0.5 \%$ compared to $0.1-0.2 \%$ for other fluids) and in the opposite direction, i.e., the diameter bends towards higher densities as the critical point is approached.

It is shown in ref. (74) that, for fluids having a diameter anomaly in this direction, the liquid and vapour compressibilities should obey the inequality

$$
\begin{equation*}
\kappa_{T, \ell}^{*-}-\kappa_{T, v}^{*-}<0 \tag{5-1}
\end{equation*}
$$

Our compressibility data (see below) clearly show this to be the case for hydrogen. These results are consistent with the presence of attractive many-body interactions in fluid hydrogen, possibly quantum mechanical exchange interactions. This idea is discussed further in Chapter VI.

The hydrogen diameter data were analysed in the same way as the data for the other fluids. For consistency, fits to the form

$$
\begin{equation*}
\rho_{d}^{*}=\frac{\rho_{\ell}+\rho_{v}-2 \rho_{c}}{2 \rho_{c}}=A_{0}+A_{1} t^{1-\alpha}+A_{2} t \tag{5-2}
\end{equation*}
$$

were done over the inner, outer, and entire $t$ ranges as defined in section $\mathbf{I V}-1$, but because of the distribution of the data points and the nature of the anomaly in this case, fits were also done over broader ranges to include the several data points


Figure 5-5 The coexistence curve diameter of hydrogen as a function of reduced temperature. The different symbols distinguish data from different runs. The inset shows the deviations of the near-critical data from a straight line fit to the data away from critical.
close to $T_{c}$, and to get a better value of the diameter slope away from the critical point. The results of fits to the data set 250287.2 , which covers the largest range of $t$, are given in Table $\mathbf{V}-3$. Fits to the other data sets and to all of the data together were qualitatively the same but were slightly affected by the systematic effects mentioned above.

Table V-3 Fits to the Coexistence Curve Diameter of Hydrogen

| range of t | $A_{0}$ | $A_{1}$ | $A_{2}$ | $\chi^{2}$ |
| :---: | ---: | ---: | ---: | :---: |
| outer | $-0.00492(35)$ | $(0)$ | $0.315(25)$ | 0.73 |
| inner | $-0.00377(34)$ | $-0.136(149)$ | $(0)$ | 1.81 |
| inner | $-0.00381(31)$ | $(0)$ | $-0.255(284)$ | 1.82 |
| entire | $-0.00466(10)$ | $0.183(8)$ | $(0)$ | 1.68 |
| entire | $-0.00451(9)$ | $(0)$ | $0.283(12)$ | 1.36 |
| entire | $-0.00406(16)$ | $-0.519(157)$ | $1.080(242)$ | 1.02 |
| $0.008-0.04$ | $-0.00537(17)$ | $(0)$ | $0.344(7)$ | 0.88 |
| $0-0.002$ | $-0.00203(40)$ | $-0.859(215)$ | $(0)$ | 9.58 |
| $0-0.002$ | $-0.00217(39)$ | $(0)$ | $-1.642(443)$ | 10.30 |
| $0-0.002$ | $-0.00009(40)$ | $-17.1(2.8)$ | $32.2(17.4)$ | 2.97 |
| $0-0.04$ | $-0.00428(22)$ | $0.200(10)$ | $(0)$ | 14.22 |
| $0-0.04$ | $-0.00410(20)$ | $(0)$ | $0.292(13)$ | 11.67 |
| $0-0.04$ | $-0.00310(23)$ | $-0.914(157)$ | $1.612(718)$ | 6.81 |

From a fit to the data in the range $0.008<t<0.04$ we find the slope away from critical to be $0.344 \pm .007$. The intercept of this straight line fit is $A_{0}=-0.0054 \pm .0002$, indicating that the critical density obtained by extrapolation of the rectilinear diameter is $0.54 \%$ too low; the critical density of hydrogen implied by this result is $\rho_{c}=0.03160 \mathrm{~g} / \mathrm{cm}^{3}$.

Data in the temperature range $0<t<0.002$ are reasonably well described by the functional forms $A_{0}+A_{2} t$ and $A_{0}+A_{1} t^{1-\alpha}$, with the latter slightly preferred on the basis of the $\chi^{2}$ value, but much better described by an expression including


Figure 5-6 The coexistence curve diameter of hydrogen from data set 250287.2. The solid line is a straight line fit to the data away from the critical point, the dashed line is a three-parameter fit to the data close to critical and the dotted line is a three-parameter fit to all of the data. The inset shows the near-critical data in more detail.
both $t$ and $t^{1-\alpha}$ terms. A fit to this expression does not extrapolate well to higher $t$, though, and fits to the entire data set show strong systematic deviations from the data in the near-critical region. Inclusion of a corrections-to-scaling term proportional to $t^{1-\alpha+\Delta}$ does not improve the situation. Fig. (5-6) shows the data from set 250287.2 along with three fits - the straight line fit away from the critical point mentioned above, and fits with both $t$ and $t^{1-\alpha}$ terms over the ranges $0<t<0.002$ and $0<t<0.04$. It is clear that the fit over the large temperature range does not describe the observed anomaly adequately. This may be another example of crossover effects.

## V-3 The Compressibility

As mentioned above, our compressibility measurements were strongly affected by the presence of thermal gradients in the hydrogen sample. For example, values of the amplitude $\Gamma_{0}^{+}$determined from two different runs differed by a factor of three and were $3-10$ times larger than values of $\Gamma_{0}^{+}$for other fluids. This implies that the gravitationally induced density gradient was enhanced by a thermally induced gradient, and so that the cell bottom was colder than the top. Despite this, a fair amount of information can be extracted from our data.

The total density gradient in the sample is the sum of density gradients due to gravity and to thermal gradients. Thus

$$
\begin{align*}
\frac{d \rho}{d z} & =\left.\frac{\partial \rho}{\partial \mu}\right|_{T}\left(\frac{\partial \mu}{\partial z}\right)_{\text {grav }}+\left.\frac{\partial \rho}{\partial \mu}\right|_{T}\left(\frac{\partial \mu}{\partial z}\right)_{\nabla T} \\
& =\kappa_{T}^{*} \frac{\rho_{c}^{2} g}{P_{c}}\left(1+\left.\frac{1}{\rho_{c} g} \frac{\partial P}{\partial T}\right|_{\rho=\rho_{c}} \frac{d T}{d z}\right), \tag{5-3}
\end{align*}
$$

where we have used eq. (3-15). Rearranging, we get

$$
\begin{equation*}
\frac{P_{c}}{\rho_{c}^{2} g} \frac{d \rho}{d z}=\kappa_{e f f}^{*}=\kappa_{T}^{*}\left(1+\left.\frac{1}{\rho_{c} g} \frac{\partial P}{\partial T}\right|_{\rho=\rho_{c}} \frac{d T}{d z}\right) \tag{5-4}
\end{equation*}
$$

which shows that analysis of the image plane fringe spacing yields an effective compressibility $\kappa_{\text {eff, }}^{*}$ which depends on $d T / d z$. Assuming that the quantity in parentheses in eq. $(5-4)$ is constant, or at least slowly varying, in the critical region, $\kappa_{\text {eff }}^{*}$ will have the same $t$ dependence as $\kappa_{T}^{*}$, i.e.,

$$
\begin{equation*}
\kappa_{e f f}^{*}=\Gamma_{0, e f f}^{ \pm} t^{-\gamma}+\cdots . \tag{5-5}
\end{equation*}
$$

This implies that the amplitude ratio

$$
\begin{equation*}
\frac{\Gamma_{0, e f f}^{+}}{\Gamma_{0, e f f}^{-}}=\frac{\Gamma_{0}^{+}}{\Gamma_{0}^{-}} \tag{5-6}
\end{equation*}
$$

which is universal. This shows that our data can provide the exponent $\gamma$ and the amplitude ratio $\Gamma_{0}^{+} / \Gamma_{0}^{-}$despite the presence of temperature gradients. In addition, if the true compressibility is known, eq. (5-4) can be used to obtain an estimate of the size of the gradient.

We begin by calculating $d T / d z$, assuming it to be uniform over the sample. Our best compressibility data set (see below) was obtained below $T_{c}$; it gives $\Gamma_{0, e f f}^{-} \simeq$ 0.10. Tables of the thermophysical properties of $\mathrm{H}_{2}{ }^{77}$ give $\partial P /\left.\partial T\right|_{\rho=\rho_{c}}=1.89 \times$ $10^{5} \mathrm{~J} / \mathrm{m}^{3} \mathrm{~K}$ at the critical point. Assuming that $\Gamma_{0}^{-}$for $\mathrm{H}_{2}$ is equal to 0.014 , the value obtained by Pestak ${ }^{2}$ for HD, we find from eq. (5-4) that

$$
\frac{d T}{d z}=\left(\frac{\kappa_{e f f}^{*}}{\kappa_{T}^{*}}-1\right) /\left.\frac{1}{\rho_{c} g} \frac{\partial P}{\partial T}\right|_{\rho=\rho_{c}}
$$

$$
\begin{align*}
& =\left(\frac{\Gamma_{0, e f f}^{-}}{\Gamma_{0}^{-}}-1\right) /\left.\frac{1}{\rho_{c} g} \frac{\partial P}{\partial T}\right|_{\rho=\rho_{c}} \\
& =0.010 \mathrm{~K} / \mathrm{m} \tag{5-7}
\end{align*}
$$

which corresponds to a temperature difference of 0.0002 K between the top and bottom of the cell. This is by most standards a small gradient.

We turn now to the compressibility data itself. Unfortunately not much supercritical data was obtained due to the long times required (typically several hours) for the fluid to achieve hydrostatic equilibrium following a change in temperature. Good data was, however, obtained in the two-phase region. The best data was recorded with the interferometer reference beam (see fig. (3-12)) slightly misaligned. This caused a number of fringes to be present in the interferogram even with a uniform sample, and so the fringe spacing could be accurately measured over a reasonable range of $t$. Without this misalignment, the fringes became too widely spaced to measure for $t \gtrsim 1 \times 10^{-4}$.

Fig. (5-7) shows compressibility data from several runs for which the temperature gradients, characterized by the outer jacket temperature and the heat input to the cell, were approximately the same. The critical temperatures used in analysing these data were obtained from the coexistence curve analyses presented in section V-1 above.

It is clear from the figure that $\kappa_{\text {eff }}^{*-}$ is larger in the vapour phase than in the liquid phase, as mentioned above in connection with the diameter results. A critical divergence of the difference $\kappa_{T, v}^{-}-\kappa_{T, \ell}^{-}$, depending on temperature like $t^{\beta-1}$ is predicted as a consequence of thermodynamic field-mixing ${ }^{71}$; our data are not precise enough to show this clearly.

The two-phase compressibility data were fitted to the critical power law (5-5) both with $\gamma$ free and fixed at its theoretical value of 1.24 . The results of these fits are given in Table $V-4$. From fits to the liquid and vapour data together,


Figure 5-7 The effective compressibility of hydrogen vs. reduced temperature. The solid and dashed lines are fits 6 and 8 from Table $V-4$ to the sub- and supercritical compressibilities respectively.

## Table V-4

Fits of the hydrogen compressibility data to eq. (5-5)

| data set | fit \# | $\gamma$ | $\Gamma_{0, e f f}^{-}$ | $\Gamma_{0, e f f}^{+}$ |
| :---: | :---: | :---: | :---: | :---: |
| vapour | 1 | 1.231 | 0.133 | - |
|  | 2 | $(1.24)$ | 0.122 | - |
| liquid | 3 | 1.135 | 0.223 | - |
|  | 4 | $(1.24)$ | 0.082 | - |
| both phases | 5 | 1.192 | 0.161 | - |
| $<T_{c}$ | 6 | $(1.24)$ | 0.102 | - |
| 260387.1 | 7 | 1.192 | - | 0.894 |
| $>T_{c}$ | 8 | $(1.24)$ | - | 0.532 |
| 250287.6 | 9 | 1.125 | - | 0.456 |
| $>T_{c}$ | 10 | $(1.24)$ | - | 0.113 |

we find with $\gamma$ free that $\Gamma_{0, e f f}^{-}=0.16 \pm .02$ and $\gamma=1.19 \pm .10$; with $\gamma=1.24$, $\Gamma_{0, e f f}^{-}=0.102 \pm .006$. The uncertainties here are approximate and take no account of uncertainties in $T_{c}$. Fit 6 from the table is shown in fig. (5-7). Results of fits to the liquid and vapour data separately are also given in the Table V-4.

Fig. (5-7) also shows some data for the supercritical compressibility, taken during one of the runs from which the plotted subcritical compressibility was obtained. Fits to this data are also given in the table and fit 8 is shown in the figure. We find $\Gamma_{0, e f f}^{-}=0.89 \pm .02$ and $\gamma=1.19 \pm .10$; with $\gamma=1.24, \Gamma_{0, e f f}^{-}=0.532 \pm .023$. Taking the values of $\Gamma_{0, e f f}^{ \pm}$obtained with $\gamma$ fixed at its theoretical value, we find the amplitude ratio

$$
\begin{equation*}
\frac{\Gamma_{0, e f f}^{+}}{\Gamma_{0, e f f}^{-}}=5.2 \pm .4 . \tag{5-8}
\end{equation*}
$$

Also given in the table are the results of fits to a set of supercritical data from a different run. In this case $\Gamma_{0, e f f}^{+}=0.113 \pm .002$ when $\gamma=1.24$. The amplitude
here is much lower than that for the first data set, demonstrating the effects of changing the temperature gradient.

## CHAPTER VI

## Discussion

In this chapter the results presented above are discussed both in relation to previous results for the particular fluids and in terms of the general picture of critical phenomena in fluids. Evidence for quantum mechanical effects from our hydrogen data is considered, and, finally, some limitations of the corrections-toscaling approach to the analysis of critical behaviour are discussed.

## VI-1 Comparison with Previous Work

The thermophysical properties of both ethylene and hydrogen have been extensively studied because of the important industrial applications of these fluids. Most previous work, however, has been done relatively far from the critical point and so is not directly comparable with the present results.

Some PVT studies of ethylene have extended into the critical region ${ }^{76,78,79}$. The measurements of Hastings et al. ${ }^{76}$ reach a minimum reduced temperature of $7 \times 10^{-4}$; their coexistence curve results over the range $7 \times 10^{-4}<t<10^{-2}$ give an effective critical exponent $\beta_{e f f}=0.338$ when fitted to a simple power law. This is higher than the expected asymptotic value of $\beta$ due to neglect of corrections-toscaling effects. When their data are fitted to a scaled equation of state that includes one corrections-to-scaling term ${ }^{1}$, they find $B_{0}=1.56 \pm .03$ and $B_{1}=1.06 \pm .02$, assuming $\beta=0.325$ and $\Delta=0.5$. This value of $B_{0}$ agrees well with the prism results in Table IV-2, and the value of $B_{1}$ is in agreement with both sets of ethylene results.

Douslin and Harrison ${ }^{78}$ find $\beta=0.35$ from a simple power law fit to coexistence curve data in the range $1.4 \times 10^{-3}<t<1.4 \times 10^{-1}$.

Levelt Sengers et al. ${ }^{80}$ have analysed a number of experimental results for ethylene. Fitting these to a scaled equation of state as above they find $B_{0}=1.54$ and $B_{1}=1.22$ for the same exponent values; again these results agree within error with the present results. Both of the above analyses rely on fitting the data to a given form for the equation of state and assuming specific values for the critical exponents. In the present work no assumptions were made concerning the exponent values; they were obtained as parameters from our fits.

From the data tabulated in ref. (80), the slope of the coexistence curve diameter away from the critical point can be calculated to be 0.79 . This is somewhat lower than our value of $0.88 \pm .04$. The difference may be due to the different temperature ranges and analysis procedures used in the two cases.

The critical temperature of ethylene determined in ref. (76) is $282.3452 \pm$ .0017 K , obtained as a parameter in a fit to the above equation of state. Moldover ${ }^{81}$ obtained a value of $282.344 \pm .004 \mathrm{~K}$ by visual observation of the disappearance of the meniscus. Our value of $282.3750 \pm .0010 \mathrm{~K}$ obtained from the prism experiment is slightly higher than these results, but agrees with that of Thomas and Zander ${ }^{79}$, who find $T_{c}=282.37 \pm .02 \mathrm{~K}$. The difference may be due to differences in sample purity, in data analysis procedures, or, possibly, to an unknown systematic difference in temperature scales.

Measurements of the thermophysical properties of hydrogen, while extensive away from the critical region ${ }^{57,77,82}$, have apparently not been thouroughly analysed using a scaled equation of state that includes corrections-to-scaling terms. Estimates of critical amplitudes tabulated in the literature ${ }^{32,84}$ give $B_{0}=1.28$ and 1.35 for pure p- $\mathrm{H}_{2}$. Fig. (6) of ref. (69) gives $B_{0}=1.65$; this value comes from an unpublished pure power law analysis of the data of Goodwin et al ${ }^{83}$. This estimate is higher than the present result, $B_{0}=1.19 \pm .03$, no doubt due to the different analysis
procedures and to neglect of corrections-to-scaling. An estimate of $\Gamma^{+}=0.093$ is given in ref. (84).

The diameter of the coexistence curve away from critical can be calculated from the tabulated data of Roder et al. ${ }^{77}$, giving $A_{2}=0.347$. Fig. (6) of ref. (69) gives a value of 0.37 . Our value of $0.344 \pm .007$ is in good agreement with both of these results.

As discussed in Chapter $\mathbf{V}$, our values of $T_{c}$ for hydrogen are in agreement within error with the expected value for equilibrium $\mathrm{H}_{2}$.

## VI-2 Universal Critical Parameters

Table VI-1 summarizes our results for the various critical exponents, amplitudes and the amplitude ratio $\Gamma_{0}^{+} / \Gamma_{0}^{-}$, along with the appropriate theroetical values, if any. We find $\beta=0.327 \pm .002$ for ethylene and $0.326 \pm .003$ for hydrogen. These agree within experimental error with each other, with results for other fluids ${ }^{2-4}$, and with the theoretical value of ${ }^{5-9} 0.327$. This supports the widely-held belief in critical point universality in fluids, and the belief that the liquid-vapour critical point belongs to the universality class of the 3-D lsing model. The hydrogen result demonstrates that a fluid for which quantum effects may be significant in fact belongs to the same universality class as do other fluids.

For the correction exponent $\Delta$ we find $\Delta=0.46 \pm .04$ for ethylene and $0.46 \pm .02$ for hydrogen. These two results agree within error. They are slightly but probably not significantly lower than previously measured values ${ }^{2}$ and the theoretical value ${ }^{5,7,28,29}$ of close to 0.5 . These results confirm the universality of this exponent within our experimental error.

Our value of $\gamma$ from the hydrogen compressibility data is less precise and also less reliable due to the problems with thermal gradients. We find $\gamma=1.19 \pm$ .05 , which agrees within error both with previous results ${ }^{2,4,10}$ and theory ${ }^{5-9}$, again confirming the predictions of critical point universality within our experimental

Table VI-1 Summary of Results

|  | $\mathrm{C}_{2} \mathrm{H}_{4}$ | $\mathrm{H}_{2}$ | Theory |
| :---: | :---: | :---: | :---: |
| $T_{c}$ | $282.3750 \pm .0010$ | $32.984 \pm .013$ |  |
| $\beta$ | $0.327 \pm .002$ | $0.326 \pm .002$ | 0.327 |
| $\gamma$ | - | $1.19 \pm .05$ | 1.238 |
| $\Delta$ | $0.46 \pm .04$ | $0.46 \pm .02$ | 0.50 |
| $\Gamma_{0}^{+} / \Gamma_{0}^{-}$ | - | $5.2 \pm .4$ | $4.80,5.07$ |
| $\mathrm{~B}_{0}$ | $1.56 \pm .03$ | $1.19 \pm .03$ |  |
| $\mathrm{~B}_{1}$ | $0.98 \pm .10$ | $0.98 \pm .09$ |  |
| $\mathrm{~B}_{2}$ | $-1.9 \pm .3$ | $-1.1 \pm .2$ |  |
| $\mathrm{~A}_{2}$ | $0.88 \pm .04$ | $0.344 \pm .007$ |  |

error. The universal ratio $\Gamma_{0}^{+} / \Gamma_{0}^{-}$was found to be $5.2 \pm .4$. This result is also somewhat unreliable due to the effects of thermal gradients, but nonetheless agrees within error with theoretical predictions ${ }^{44}$ and previous determinations ${ }^{2}$. The fact that these two quantities are in agreement with their predicted values suggests that the assumptions made in using eq. (5-4) are justified.

## VI-3 Non-Universal Properties and Quantum Effects

## The Coexistence Curve and the Compressibility

The critical coexistence curve amplitudes determined from our data are summarized in Table VI-1. Young's theory of quantum effects near the critical point ${ }^{40}$ predicts systematic variations of these amplitudes as quantum mechanics becomes more important. To investigate this, the amplitudes $B_{0}$ and $B_{1}$ from this work and for other fluids are plotted as a function of the dimensionless quantum parameter
$\lambda_{T} / \xi_{0}$, where $\lambda_{T}$ is the thermal De Broglie wavelength and $\xi_{0}$ is the bare correlation length, in figs. (6-1) and (6-2). Values of $B_{0}$ for the fluids ${ }^{3} \mathrm{He}, \mathrm{Ar}, \mathrm{Kr}, \mathrm{H}_{2} \mathrm{O}, \mathrm{D}_{2} \mathrm{O}$, $\mathrm{CO}_{2}, \mathrm{SF}_{6}$ and iso- $\mathrm{C}_{4} \mathrm{H}_{10}$ were taken from Table 1 of ref. (1), as were values of $\xi_{0}$. Values of $B_{0}$ for $\mathrm{Ne}, \mathrm{N}_{2}$ and HD were taken from ref. 2, and for $\mathrm{Xe}, \mathrm{GeH}_{4}$ and $\mathrm{C}_{2} \mathrm{H}_{6}$ from refs. (30), (31) and (85) respectively. The $B_{1}$ values plotted in fig. (6-2) for the fluids $\mathrm{H}_{2} \mathrm{O}, \mathrm{D}_{2} \mathrm{O}$, iso- $\mathrm{C}_{4} \mathrm{H}_{10}, \mathrm{C}_{2} \mathrm{H}_{4}, \mathrm{HD}, \mathrm{Ne}, \mathrm{N}_{2},{ }^{3} \mathrm{He}, \mathrm{Xe}, \mathrm{GeH}_{4}$ and $\mathrm{C}_{2} \mathrm{H}_{6}$ are from refs. ( $1,2,3,30,31$ and 85 ). Some of these data come from corrections-to-scaling fits, others from fits to an equation of state, but all come from analyses involving at least one correction-to-scaling term in some form.

There is a considerable amount of scatter in the $B_{0}$ data for the various "classical" fluids, clustered at low values of $\lambda_{T} / \xi_{0}$ in fig. (6-1). This may be due in part to the different analysis procedures used in the different cases, but may also reflect the predicted non-universality of $B_{0}$ and its dependence on factors affecting the intermolecular interactions. It is interesting that the points for water and heavy water are significantly higher than those for the other classical fluids, which are clustered in the range $B_{0}=1.4-1.65$. These other fluids have roughly spherical molecular symmetry, whereas intermolecular interactions in the waters will presumably be influenced by hydrogen bonding; this may account for their higher $B_{0} \mathrm{~s}$.

The low temperature fluids $\mathrm{Ne}, \mathrm{HD}, \mathrm{H}_{2}$ and ${ }^{3} \mathrm{He}$ show a clear decrease in $B_{0}$ with an increase in the quantum parameter, in at least qualitative agreement with the predictions of ref. (40). The heavy line plotted in fig. (6-1) shows the predicted trend,

$$
\begin{equation*}
B_{0}=B_{0}^{c l}(1-y)^{\beta} \tag{6-1}
\end{equation*}
$$

where the "classical" amplitude $B_{0}^{c l}$ has (arbitrarily) been set equal to 1.437 so that the theoretical curve passes through the data point for neon. The fine line is a straight line,

$$
\begin{equation*}
B_{0}=1.514\left(1-0.134 \frac{\lambda_{T}}{\xi_{0}}\right) \tag{6-2}
\end{equation*}
$$



Figure 6-1 The coexistence curve amplitude, $B_{0}$, for a number of fluids as a function of the quantum parameter $\lambda_{T} / \xi_{0}$. Results from the present work are shown as open circles. The heavy line shows the behaviour predicted in ref. (40); the fine line is a straight line fit to the four data points with $\lambda_{T} / \xi_{0} \geq 0.75$.


Figure 6-2 The first correction amplitude, $B_{1}$, for a number of fluids as a function of $\lambda_{T} / \xi_{0}$. Results from the present work are shown as open circles. The line shows the behaviour predicted in ref. (40).
where the numerical factors were obtained from a least-squares fit to the data for the four low-temperature fluids. It is amusing that the straight line describes the data better than the predicted form does, but the physical content of this fact is not clear.

The $B_{1}$ data plotted in fig. (6-2) are less precise than the corresponding data for the leading amplitude. The predicted trend,

$$
\begin{equation*}
B_{1}=B_{1}^{c l}(1-y)^{\Delta} \tag{6-3}
\end{equation*}
$$

is shown by the solid line. $B_{1}^{c l}$ has been set equal to 1.033 , again to fit the neon data. While the predicted trend seems to describe the data within the error bars, the agreement is not very impressive, and the large error bars make it difficult to make any quantitative statements. Indeed, it is almost fair to say that $B_{1}=1$ describes the data within experimental error.

Fig. (6-3) is a plot of values of $\Gamma_{0}^{+} v s . \lambda_{T} / \xi_{0}$ for the thirteen fluids tabulated in ref. (1). The data are clustered around $\Gamma_{0}^{+}=0.055$ with the exception of the point for ${ }^{3} \mathrm{He}$, which is a factor of three higher. The trend predicted by Young's theory,

$$
\begin{equation*}
\Gamma_{0}^{+}=\Gamma_{0}^{+c l}(1-y)^{-\gamma} \tag{6-4}
\end{equation*}
$$

is also shown; $\Gamma_{0}^{+}$has been set equal to 0.053 . The data appear to follow this trend at least qualitatively, but this appearance is based entirely on the high value of $\Gamma_{0}^{+}$for ${ }^{3} \mathrm{He}$; the other data are essentially constant. A good value for $\mathrm{H}_{2}$ would obviously have been helpful in assessing the effects of quantum mechanics on the compressibility. The values of $\Gamma_{0, e f f}^{+}$obtained from this work are not shown in the figure; they lie well above the theoretical curve.


Figure 6-3 The leading compressibility amplitude, $\Gamma_{0}^{+}$, for a number of fluids vs. $\lambda_{T} / \xi_{0}$. The line shows the behaviour predicted in ref. (40).

## The Coexistence Curve Diameter

The behaviour of the coexistence curve diameters of several fluids (including ethane and ethylene) has been analysed recently by Goldstein, Pestak et al ${ }^{73,74}$. They explain the origin of the thermodynamic field-mixing that leads to the presence of the $t^{1-\alpha}$ anomaly in terms of many-body interactions in the fluid. By modifying the free energy of a VDW gas to include a term due to three-body interactions, they predict an anomaly of the correct form. This process introduces a new energy scale into the system, characterized by a dimensionless parameter $x=q / a b$ where $q$ is the integrated strength of the three-body potential and $a$ and $b$ are the usual VDW parameters. $x$ is thus the ratio of three-body to two-body interaction strengths. For the special case of the primarily repulsive Axilrod-Teller triple-dipole interaction ${ }^{86}$, $x$ is proportional to the product, $\bar{\alpha} \rho_{c}$, of the polarizability and the critical density.

Pestak et al. ${ }^{74}$ derive expressions for various thermodynamic quantities from this model. In particular, they find that the diameter slope is

$$
\begin{equation*}
A_{2}=\frac{2}{5}+\frac{22}{15} x+\cdots \tag{6-5}
\end{equation*}
$$

and that the order parameter amplitude and the slope of the diameter are related by

$$
\begin{equation*}
B_{0}=\frac{20}{11}+\frac{5}{11} A_{2} \tag{6-6}
\end{equation*}
$$

Fig. (6-4) is a plot of the diameter slope as a function of $\bar{\alpha} \rho_{c}$ for the six fluids analysed in ref. (74) $\left(\mathrm{SF}_{6}, \mathrm{C}_{2} \mathrm{H}_{4}, \mathrm{C}_{2} \mathrm{H}_{6}, \mathrm{~N}_{2}, \mathrm{Ne}\right.$ and HD$)$ as well as for hydrogen. The first six fluids show the predicted linear relationship. A least-squares fit to these data gives

$$
\begin{equation*}
A_{2}=0.41+25.2 \bar{\alpha} \rho_{c} \tag{6-7}
\end{equation*}
$$

This fit is plotted in the figure; the intercept is in surprisingly good agreement with the VDW value of 0.4. The point for $\mathrm{H}_{2}$ is clearly significantly below the line defined
by the other fluids. A fit to all seven points still lies well above the hydrogen point and describes the rest of the data less well. In fig. (6-5), $B_{0}$ is plotted against $A_{2}$ for the same fluids. Here the predicted linear relationship is followed by all of the data. A least-squares fit gives

$$
\begin{equation*}
B_{0}=(0.892 \pm .011)+(0.826 \pm .005) A_{2} \tag{6-8}
\end{equation*}
$$

As mentioned in Chapter $V$, the critical anomaly in the hydrogen diameter is in the opposite direction to those for other fluids, and the compressibility in the vapour phase is larger than that in the liquid. The fact that the hydrogen data fit the linear relation between $B_{0}$ and $A_{2}$ suggests that the three-body interaction model remains valid for hydrogen, but fig. (6-4) implies that the relevant interactions in this case are not of the Axilrod-Teller type. In addition, the diameter slope for $\mathrm{H}_{2}$ is slightly lower than the VDW value of 0.4 . Eq. (6-5) thus says that the parameter $x$ is negative for hydrogen; i.e., that the three-body interactions in hydrogen are attractive. While no critical anomalies in the diameters of the helium isotopes have been observed, their diameter slopes are substantially lower than the VDW value, indicating even stronger attractive interactions in these fluids ${ }^{69,74}$. It is known that three-body exchange interactions, which are primarily attractive, are important in helium. Our data provide evidence that such an attractive interaction is also significant in hydrogen.

## VI-4 Crossover Effects

There are some minor problems with the corrections-to-scaling fits to the coexistence curve of ethylene and to the coexistence curve diameter of hydrogen. For example, the fitted functions in figs. (4-4) and (4-13) turn over and start to decrease above a certain temperature because the highest order term in the fit is negative. The beginnings of similar behaviour are seen in the plots for hydrogen. This behaviour is clearly unphysical. In addition, there are small but systematic


Figure 6-4 The coexistence curve diameter slope, $A_{2}$, for several fluids vs. $\bar{\alpha} \rho_{c}$. The line is a fit to the data excluding the point for $\mathrm{H}_{2}$.


Figure 6-5 The coexistence curve diameter slope, $A_{2}$, vs. the coexistence curve amplitude, $B_{0}$, for a number of fluids. The line is a fit to the data.
differences between the fitted function and the best fit as determined by eye in the ethylene fits. Inclusion of additional terms, of order $t^{3 \Delta}$ and higher, to the series could improve the quality of the fits over a given temperature range. The physical meaning of these terms soon becomes lost, however, since the full corrections-toscaling series contains several terms of order $t^{1.5}\left(t^{3 \Delta}, t^{1+\Delta}\right.$, etc.), $t^{2}$, and so on. In fact, even the meaning of our $t^{2 \Delta}$ term is obscure.

A similar, but more obvious, problem arose in fitting the hydrogen diameter data. While the theoretical form described the data well over a restricted temperature range, it could not simultaneously describe the anomaly close to the critical point and the diameter away from critical.

The problem in both cases is that the corrections-to-scaling series do not converge to any classical limit away from the critical region. In fact, it is not clear that the series converge at all. Since a classical description of fluid behaviour is correct far from the critical point, there is clearly a missing ingredient in the theoretical description.

Recently, much effort has been directed towards the developement of physically reasonable "crossover" theories - descriptions of fluid behaviour that cross over from scaling behaviour in the critical-region to classical behaviour away from critical ${ }^{1}$. Early efforts in this direction predicted unphysical behaviour in the crossover region ${ }^{87}$. More recently, however, a formalism based on RG ideas has been developed by Albright and co-workers ${ }^{88}$. It includes a crossover function that depends on two parameters - one related to the wavelength cut-off of the RG transformation, i.e., the size of the smallest important fluctuations, and one related to the rate of convergence of the appropriate corrections-to-scaling series. This formalism has been used successfully to describe measurements of the specific heat of carbon dioxide ${ }^{89}$.

It is probable that our data, which extend from very close to the critical point to several degrees away from it, cover a large enough range that the corrections-to-scaling approach is being stretched close to the limits of its applicability in our analysis. It would be of interest to reanalyse our data in terms of such a crossover theory.

## CHAPTER VII

## Conclusions

In this work we have presented measurements of the coexistence curve and its diameter near the critical points of hydrogen and ethylene, and measurements of the compressibility of hydrogen in the critical region. Our results are in good quantitative agreement with the predictions of the theory of critical phenomena and support the idea of critical point universality in fluids. Our values of the critical exponents $\beta=0.327 \pm .002$ and $\gamma=1.19 \pm .05$ agree with the theoretical values. Our result for the corrections-to-scaling exponent $\Delta=0.46 \pm .02$ is slightly lower than the predicted value of 0.5 , but was the same within error for both fluids.

The hydrogen results show evidence for the presence of quantum mechanical effects. The coexistence curve amplitudes $B_{0}$ for $\mathrm{H}_{2}$ and other fluids decrease as quantum effects become more important, as predicted. On the other hand, no systematic trend in the correction amplitudes $B_{1}$ was observed within experimental error.

The data for the coexistence curve diameters of ethylene, hydrogen and ethane show the importance of many-body effects near the critical point. The hydrogen results, in particular, are consistent with the presence of attractive many-body interactions, possibly quantum mechanical exchange.

It would be useful to obtain better compressibility data for hydrogen using a sample cell which allowed more complete elimination of thermal gradients. This
would permit a better assessment of the effects of quantum mechanics on the compressibility amplitudes. It would also be interesting to extend this work to lower critical temperatures and presumably larger quantum effects by studying ${ }^{4} \mathrm{He}$. The data quality for such a study using these techniques would be limited, however, by the low refractive index of helium.

The ultimate precision of these experiments is limited by uncertainties in the critical temperatures. A much more precise determination of $\beta$, for example, would require a redurtion of the uncertainty in $T_{c}$ to a few tens of microkelvins. This would be a difficult task.

## References

1. J.V. Sengers and J.M.H. Levelt Sengers, Ann. Rev. Phys. Chem. 37, 189 (1986).
2. M.W. Pestak and M.H.W. Chan, Phys. Rev. B 30, 274 (1984); M.W. Pestak, Ph.D. Thesis, The Pennsylvania State University, 1984.
3. C. Pittman, T. Doiron and H. Meyer, Phys. Rev. B 20, 3678 (1979).
4. R.J. Hocken and M.R. Moldover, Phys. Rev. Lett. 37, 29 (1976).
5. J.C. LeGuillou and J. Zinn-Justin, Phys. Rev. Lett. 39, 95 (1977); Phys. Rev. B 21, 3976 (1980).
6. B. Nickel and M. Dixon, Phys. Rev. B 26, 3965 (1982).
7. K.E. Newman and E.K. Reidel, Phys. Rev. B 30, 6615 (1984).
8. R.Z. Roskies, Phys. Rev. B 24, 5305 (1981).
9. M.J. George and J.J. Rehr, Phys. Rev. Lett. 53, 2063 (1984).
10. H. Guttinger and D.S. Cannell, Phys. Rev. A 24, 3188 (1981).
11. J.V. Sengers in Phase Transitions: Cargèse 1980, ed. M. Lévy, J.C. Le Guillou and J. Zinn-Justin (Plenum, New York, 1982).
12. T. Andrews, Phil. Mag. 4, (39) 150 (1870).
13. J.D. van der Waals, Doctoral Dissertation, Leiden, 1873.
14. J.M.H. Levelt Sengers, Physica 73, 73 (1974).
15. L. Onsager, Phys. Rev. 65, 117 (1944).
16. B. Widom, J. Chem. Phys. 43, 3898 (1965).
17. L.P. Kadanoff, Physics 2, 263 (1966).
18. B. Widom, Physica 73, 107 (1974).
19. K.G. Wilson, Phys. Rev. B 4, 3174 (1971).
20. K.G. Wilson, Phys. Rev. B 4, 3184 (1971).
21. K.G. Wilson and J. Kogut, Phys. Rep. 12, 75 (1974).
22. M.E. Fisher, Rev. Mod. Phys. 46, 597 (1974).
23. D.A. Balzarini and K. Ohrn, Phys. Rev. Lett. 29, 840 (1972).
24. D. Balzarini, Ph.D. Thesis, Columbia University, 1968.
25. L.M. Stacey, B. Pass and H.Y. Carr, Phys. Rev. Lett. 23, 1424 (1969).
26. F.J. Wegner, Phys. Rev. B5, 4529 (1972).
27. M. Ley-Koo and M.S. Green, Phys. Rev. A 23, 2650 (1981).
28. G.A. Baker, B.G. Nickel and D.J. Meiron, Phys. Rev. B 17, 1365 (1978).
29. J.H. Chen, M.E. Fisher and B.G. Nickel, Phys. Rev. Lett. 48, 630 (1982).
30. D. Balzarini and O.G. Mouritsen, Phys. Rev. A 28, 3515 (1983).
31. D. Balzarini, O.G. Mouritsen and P. Palffy-Muhoray, Can. J. Phys. 61, 1301 (1983).
32. M.R. Moldover, J.V. Sengers, R.W. Gammon and R.J. Hocken, Rev. Mod. Phys. 51, 79 (1979).
33. L.R. Wilcox and D. Balzarini, J. Chem. Phys. 48, 753 (1968).
34. D. Balzarini, Can. J. Phys. 50, 2194 (1972).
35. W.T. Estler, R. Hocken, T Charlton and L.R. Wilcox, Phys. Rev. A 12, 2118 (1975).
36. D. Balzarini and M. Burton, Can. J. Phys. 57, 1516 (1979).
37. D. Balzarini and P. Palffy, Can. J. Phys. 52, 2007 (1974).
38. M. Burton and D. Balzarini, Can. J. Phys. 52, 2001 (1974).
39. P. Palffy-Muhoray and D. Balzarini, Can. J. Phys. 56, 1140 (1978).
40. R.A. Young, Phys. Rev. Lett. 45, 638 (1980) Phys. Rev. A 23, 1498 (1981).
41. L.D. Landau and E.M. Lifshitz, Statistical Physics, 2nd edition, p. 69 (Pergammon, Oxford, 1969).
42. S.K. Ma, Modern Theory of Critical Phenomena, (Benjamin, Reading, 1976).
43. P. Pfeuty and G. Toulouse, Introduction to the Renormalization Group and Critical Phenomena, (Wiley, Chichester, 1977).
44. A. Aharony and P.C. Hohenberg, Phys. Rev. B 13, 3081 (1976).
45. A. Aharony and G. Ahlers, Phys. Rev. Lett. 44, 782 (1980).
46. M.-C. Chang and A. Houghton, Phys. Rev. Lett. 44, 785 (1980).
47. M.E. Fisher, Phys. Rev. Lett. 16, 11 (1966).
48. M. Suzuki, Prog. Theor. Phys. 56, 1007 (1976).
49. 

D. Balzarini, Can. J. Phys. 52, 499 (1974).
50. J. Shelton and D. Balzarini, Can. J. Phys. 59, 934 (1981).
51. E. Hecht and A. Zajac, Optics, (Addison-Wesley, Reading, 1974).
52. Matheson Gas Products Canada Ltd., Edmonton, Canada.
53. Forma Scientific, Inc., Marietta, U.S.A.
54. Janis Research Company, Inc., Wilmington, U.S.A.
55. Houdry HSC 197, Air Products, Inc., Allentown, U.S.A.
56. A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen, (Cambridge U. Press, Cambridge, 1935).
57. R.D. McCarty, ed., Hydrogen, Its Technology and Implcations, (CRC Press, Cleveland, 1976).
58. T. Oversluizen, Rev. Sci. Inst. 46, 788 (1975).
59. G.G. Ihas and F. Pobell, Phys. Rev. A 9, 1278 (1974) .
60. Medigas Pacific, Burnaby, Canada.
61. I.D. Ried and M.R. Hyde, J. Phys. E 17, 555 (1984).
62. C.J.F. Bottcher and P. Bordewijk, Theory of Eletronic Polarization, (Elsevier, New York, 1978) Vol. II, chap. 12. .
63. D.E. Diller, J. Chem. Phys. 49, 3096 (1968).
64. J.F. Ely, H.J.M. Hanley and G.C. Straty, J. Chem. Phys. 59, 842 (1973).
65. J.M. St. Arnaud and T.K. Bose, J. Chem. Phys. 68, 2129 (1978).
66. J.F. Ely and G.C. Straty, J. Chem. Phys. 61, 1480 (1974).
67. C. Moore, UBC CURVE - Curve Fitting Routines, University of British Columbia Computing Centre, 1981.
68. N.D. Mermin, Phys. Rev. Lett. 26, 169 (1971); Phys. Rev. Lett. 26, 957 (1971).
69. G.W. Mulholland, J.A. Zollweg and J.M.H. Levelt Sengers, J. Chem. Phys. 62, 2535 (1975).
70. B. Widom and J.S. Rowlinson, J. Chem. Phys. 52, 1670 (1970).
71. J.J. Rehr and N.D. Mermin Phys. Rev. A 8, 472 (1973).
72. J. Weiner, K.H. Langley and N.C. Ford, Jr., Phys. Rev. Lett. 32, 879 (1974).
73. 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).
74. M.W. Pestak, R.E. Goldstein, M.H.W. Chan, J.R. de Bruyn, D.A. Balzarini and N.W. Ashcroft, Phys. Rev. B 36, 599 (1987).
75. M. Burton, M.Sc. Thesis, University of British Columbia, 1973.
76. J.R. Hastings, J.M.H. Levelt Sengers and F.W. Balfour, J. Chem Thermodynamics 12, 1009 (1980).
77. H.M. Roder, L.A. Weber and R.D. Goodwin, NBS Monograph 94, (U.S. National Bureau of Standards, Washington, 1965).
78. D.R.Douslin and R.H. Harrison, J. Chem. Thermodynamics 8, 301 (1976).
79. W. Thomas and M. Zander, Int. J. Thermophysics 1, 383 (1980).
80. J.M.H. Levelt Sengers, G.A. Olchowy, B. Kamgar-Parsi and J.V. Sengers, NBS Tech. Note 1189, (U.S. National Bureau of Standards, Washington, 1984).
81. M.R. Moldover, J. Chem. Phys. 61, 1766 (1974).
82. R.D. McCarty and L.A. Weber, NBS Tech. Note 617, (U.S. National Bureau of Standards, Washington, 1972).
83. R.D. Goodwin, D.E. Diller, H.M. Roder and L.A. Weber J. Res. NBS 67A, 173 (1963).
84. J.V. Sengers and J.M.H. van Leeuwen, Physica 116A, 345 (1982).
85. J.R. de Bruyn and D.A. Balzarini, unpublished analysis of data from refs. (36) and (75).
86. B.M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943).
87. G.A. Chapela and J.S. Rowlinson, J. Chem. Soc. Faraday Trans. I 70, 594 (1974).
88. P.C. Albright, J.V. Sengers, J.F. Nicoll and M. Ley-Koo, Int. J. Thermophysics 7, 75 (1986).
89. P.C. Albright, Z.Y. Chen and J.V. Sengers, Phys. Rev. B 36, 877 (1987).

## APPENDIX A

## Conversion of Refractive Indices to Densities

In this Appendix, eqs. (3-6) and (3-7), used to convert refractive index-related quantities to density-related quantities in the analysis of the fringe data, are derived. We deal first with the calculation for the order parameter $\Delta \rho^{*}$.

We start by expanding $n-n_{c}$ in a Taylor's series about $\rho-\rho_{c}$ for both liquid and vapour phases:

$$
\begin{align*}
& n_{\ell}-n_{c}=\frac{d n}{d \rho}\left(\rho_{\ell}-\rho_{c}\right)+\frac{1}{2} \frac{d^{2} n}{d \rho^{2}}\left(\rho_{\ell}-\rho_{c}\right)^{2}+\cdots  \tag{A-1}\\
& n_{v}-n_{c}=\frac{d n}{d \rho}\left(\rho_{v}-\rho_{c}\right)+\frac{1}{2} \frac{d^{2} n}{d \rho^{2}}\left(\rho_{v}-\rho_{c}\right)^{2}+\cdots \tag{A-2}
\end{align*}
$$

where the derivatives are evaluated at the critical point. Taking the difference between these two equations gives an expression for $n_{\ell}-n_{v}$, which is the quantity determined from the experimental fringe counts:

$$
\begin{align*}
n_{\ell}-n_{v} & =\frac{d n}{d \rho}\left(\rho_{\ell}-\rho_{v}\right)+\frac{1}{2} \frac{d^{2} n}{d \rho^{2}}\left[\left(\rho_{\ell}-\rho_{c}\right)^{2}+\left(\rho_{v}-\rho_{c}\right)^{2}\right] \\
& =\frac{d n}{d \rho}\left(\rho_{\ell}-\rho_{v}\right)+\frac{1}{2} \frac{d^{2} n}{d \rho^{2}}\left[\left(\rho_{\ell}-\rho_{v}+2 \rho_{c}\right)\left(\rho_{\ell}-\rho_{v}\right)\right] \\
& =2 \rho_{c}\left(\frac{d n}{d \rho}+\rho_{c} \rho_{d}^{*} \frac{d^{2} n}{d \rho^{2}}\right) \Delta \rho^{*} \tag{A-3}
\end{align*}
$$

where

$$
\Delta \rho^{*}=\frac{\rho_{\ell}-\rho_{v}}{2 \rho_{c}} \quad \text { and } \quad \rho_{d}^{*}=\frac{\rho_{\ell}+\rho_{v}-2 \rho_{c}}{2 \rho_{c}}
$$

Solving eq. $(\mathrm{A}-3)$ for $\Delta \rho^{*}$ gives

$$
\begin{equation*}
\Delta \rho^{*}=\frac{n_{\ell}-n_{v}}{2 \rho_{c}\left(d n / d r+\rho_{c} \rho_{d}^{*} d^{2} n / d \rho^{2}\right)} \tag{3-6}
\end{equation*}
$$

The evaluation of the derivatives of $n$ will be treated below.
In the case of the coexistence curve diameter $\rho_{d}^{*}$, we add eqs. (A-1) and (A-2) to get

$$
\begin{equation*}
\left(n_{\ell}-n_{c}\right)+\left(n_{v}-n_{c}\right)=\frac{d n}{d \rho}\left(\rho_{\ell}+\rho_{v}-2 \rho_{c}\right)+\frac{1}{2} \frac{d^{2} n}{d \rho^{2}}\left[\left(\rho_{\ell}-\rho_{c}\right)^{2}+\left(\rho_{v}-\rho_{c}\right)^{2}\right] . \tag{A-5}
\end{equation*}
$$

But to first order in $\rho-\rho_{c}$,

$$
\begin{equation*}
n_{\ell}-n_{c}=\frac{d n}{d \rho}\left(\rho_{\ell}-\rho_{c}\right) \quad \text { and } \quad n_{v}-n_{c}=\frac{d n}{d \rho}\left(\rho_{v}-\rho_{c}\right) \tag{A-6}
\end{equation*}
$$

Substituting the expressions (A-6) into the second term of eq. (A-5) gives

$$
\begin{equation*}
\left(n_{\ell}+n_{v}-2 n_{c}\right)=\frac{d n}{d \rho}\left(\rho_{\ell}+\rho_{v}-2 \rho_{c}\right)+\frac{1}{2} \frac{d^{2} n}{d \rho^{2}}\left(\frac{d n}{d \rho}\right)^{-2}\left[\left(n_{\ell}-n_{c}\right)^{2}+\left(n_{v}-n_{c}\right)^{2}\right] \tag{A-7}
\end{equation*}
$$

so

$$
\begin{equation*}
\rho_{d}^{*}=\frac{\left(n_{\ell}+n_{v}-2 n_{c}\right)-\frac{1}{2} d^{2} n / d \rho^{2}(d \rho / d n)^{2}\left[\left(n_{\ell}-n_{c}\right)^{2}+\left(n_{v}-n_{c}\right)^{2}\right]}{2 \rho_{c} d n / d \rho} \tag{3-7}
\end{equation*}
$$

The quantities $n_{\ell}-n_{c}$ and $n_{v}-n_{c}$ are determined from the image plane fringe counts.

To determine $d n / d \rho$ and $d^{2} n / d \rho^{2}$, we write $n$ as a function of $\rho$ and $\mathcal{L}$ using eq. (1-11):

$$
\begin{equation*}
n(\mathcal{L}, \rho)=\left(\frac{1+2 \rho \mathcal{L}}{1-\rho \mathcal{L}}\right)^{1 / 2} \tag{A-9}
\end{equation*}
$$

Then

$$
\begin{equation*}
\left.\frac{d n}{d \rho}\right|_{c}=\frac{\partial n}{\partial \rho}+\frac{\partial n}{\partial \mathcal{L}} \mathcal{L}^{\prime} \tag{A-10}
\end{equation*}
$$

and

$$
\begin{equation*}
\left.\frac{d^{2} n}{d \rho^{2}}\right|_{c}=\frac{\partial^{2} n}{\partial \rho^{2}}+2 \mathcal{L}^{\prime} \frac{\partial^{2} n}{\partial \rho \partial \mathcal{L}}+\mathcal{L}^{\prime \prime} \frac{\partial n}{\partial \mathcal{L}}+\left(\mathcal{L}^{\prime}\right)^{2} \frac{\partial^{2} n}{\partial \mathcal{L}^{2}} \tag{A-11}
\end{equation*}
$$

where $\mathcal{L}^{\prime}=d \mathcal{L} /\left.d \rho\right|_{c}$ and $\mathcal{L}^{\prime \prime}=d^{2} \mathcal{L} /\left.d \rho^{2}\right|_{c}$ are obtained from a fit to $\mathcal{L}(\rho)$ on the coexistence curve.

The various partial derivatives required are calculated in a straightforward manner. In the experessions below, the relation

$$
\mathcal{L}_{c}=\frac{1}{\rho_{c}} \frac{\left(n_{c}^{2}-1\right)}{\left(n_{c}^{2}+2\right)}
$$

has been used to write these expressions in terms of $n_{c}$ and $\rho_{c}$. The results are

$$
\begin{align*}
\left.\frac{\partial n}{\partial \rho}\right|_{c} & =\frac{\left(n_{c}^{2}-1\right)\left(n_{c}^{2}+2\right)}{6 n_{c} \rho_{c}}  \tag{A-12}\\
\left.\frac{\partial n}{\partial \mathcal{L}}\right|_{c} & =\frac{\rho_{c}\left(n_{c}^{2}+2\right)^{2}}{6 n_{c}}  \tag{A-13}\\
\left.\frac{\partial^{2} n}{\partial \rho^{2}}\right|_{c} & =\frac{\left(n_{c}^{2}-1\right)^{2}\left(n_{c}^{2}+2\right)\left(3 n_{c}^{2}-2\right)}{36 n_{c}^{3} \rho_{c}^{2}}  \tag{A-14}\\
\left.\frac{\partial^{2} n}{\partial \rho \partial \mathcal{L}}\right|_{c} & =\frac{\left(n_{c}^{2}+2\right)^{2}\left(3 n_{c}^{4}+n_{c}^{2}+2\right)}{36 n_{c}^{3}} \tag{A-15}
\end{align*}
$$

and

$$
\begin{equation*}
\left.\frac{\partial^{2} n}{\partial \mathcal{L}^{2}}\right|_{c}=\frac{\rho_{c}^{2}\left(n_{c}^{2}+2\right)^{3}\left(3 n_{c}^{2}-2\right)}{36 n_{c}^{3}} \tag{A-16}
\end{equation*}
$$

## APPENDIX B

## Data Listings

## B-1 Lorenz-Lorentz Coefficient for Ethylene

$\mathcal{L}(\rho)$ at 298.2 K

| 1 | $\underset{\text { CELL MASS }}{\text { COLECULAR }} \mathbf{W T}=$188.7700 <br> 28.0540$\quad$ CELL VOL. $=12.0050$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3 l |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |
| 4 | ALPHA $=20.4170$ |  |  |  |  |  |
| 5 | MICROMETER FIT | PARAMETERS: -0. | -0.3773316100E-04 | -0.654399800 | 20.0 |  |
| 6 | No. OF PTS. - | 21 |  |  |  |  |
| 7 | Cell 11085 | Mic. Rog |  |  | n | LL coeff |
| 8 | (g) | Wic. Raw. | (deg) | (mole/cm3) |  | (cm3/mole) |
| 10 (00.4564 0.030022 |  |  |  |  |  |  |
| 11 | 190.4664 | 5. 4235 | 0.030022 | 0.005037 | 1.081801 | 10.664215 |
| 12 | 180.4031 | 5.6023 | 0.028851 | 0.004849 | 1.078692 | 10.663115 |
| 13 | 190.3410 | 5.7743 | 0.027725 | 0.004665 | 1.075699 | 10.669435 |
| 14 | 190.2880 | 5.9220 | 0.026759 | 0.004507 | 1.073128 | 10.672388 |
| 15 | 190.2258 | 6.0968 | 0.025614 | 0.004323 | 1.070084 | 10.671582 |
| 16 | 190.1640 | 6.2725 | 0.024464 | 0.004139 | 1.067023 | 10.654354 |
| 17 | 190. 1009 | 6.4495 | 0.023306 | 0.003952 | 1.063938 | 10.662263 |
| 18 | 190.0331 | 6.6380 | 0.022072 | 0.003750 | 1.060651 | 10.663856 |
| 19 | 189.9668 | 6.8213 | 0.020872 | 0.003554 | 1.057453 | 10.667821 |
| 20 | 189.8992 | 7.0113 | 0.019628 | 0.003353 | 1.054137 | 10.660647 |
| 21 | 189.8213 | 7.2278 | 0.018211 | 0.003122 | 1.050357 | 10.658643 |
| 22 | 189.7591 | 7.3980 | 0.017097 | 0.002937 | 1.047384 | 10.665971 |
| 23 | 189.7023 | 7.3613 | 0.016028 | 0.002768 | 1.044530 | 10.639908 |
| 24 | 189.6413 | 7.7285 | 0.014934 | 0.002587 | 1.041606 | 10.643195 |
| 25 | 189.5844 | 7.8823 | 0.013928 | 0.002418 | 1.038916 | 10.655876 |
| 26 | 189.5214 | 0.0650 | 0.012732 | 0.002231 | 1.035719 | 10.606764 |
| 27 | 189.4618 | 8.2245 | 0.011688 | 0.002054 | 1.032927 | 10.625418 |
| 28 | 189.4047 | 8.3838 | 0.010646 | 0.001885 | 1.030137 | 10.605461 |
| 29 | 189.3408 | 8.5540 | 0.009464 | 0.001695 | 1.026975 | 10.561324 |
| 30 | 189.2144 | 8.8968 | 0.007193 | 0.001320 | 1.020892 | 10.517488 |
| 31 | 189.1307 | 9.1308 | 0.005662 | 0.001071 | 1.016787 | 10.419365 |

## $\mathcal{L}(\rho)$ on the Coexistence Curve

Listing of -OUT2(67) at 14:45:50 on JUL 12. 1987 for CCid=DBRU


## B-2 Ethylene Coexistence Curve Data

## Prism Data

Listing of -M at 14:41:27 on AUG 16. 1987 for CCid=DBRU

## Ethylene prism cell data.

Number of data points
77
Critical Temperature $=282.3750$

| Temp (K) | $t$ | $\begin{gathered} \text { rho } v \\ (\mathrm{~mol} / \mathrm{cm} 3) \end{gathered}$ |
| :---: | :---: | :---: |
| 269.83740 | 0.4646E-01 | 0.0030741 |
| 270.25635 | 0.4484E-01 | 0.0031176 |
| 271.49194 | 0.4009E-01 | 0.0032741 |
| 272.80786 | 0.3507E-01 | 0.0034454 |
| 272.81299 | 0.3505E-01 | 0.0034519 |
| 273.74341 | $0.3153 \mathrm{E}-01$ | 0.0035819 |
| 273.74878 | 0.3151E-01 | 0.0035884 |
| 274.72900 | 0.2783E-01 | 0.0037527 |
| 275.26099 | 0.2584E-01 | 0.0038325 |
| 275.50342 | O.2494E-O1 | 0.0038843 |
| 275.76074 | 0.2399E-01 | 0.0039382 |
| 276.01587 | 0.2304E-01 | 0.0039813 |
| 276.53809 | 0.2111E-01 | 0.0040804 |
| 276.85352 | 0.1994E-01 | 0.0041536 |
| 277.07397 | 0.1913E-01 | 0.0042009 |
| 277.44165 | 0.1778E-01 | 0.0042718 |
| 277.62842 | $0.1710 \mathrm{E}-01$ | 0.0043190 |
| 277.97632 | 0.1582E-01 | 0.0044027 |
| 278.19702 | 0.1502E-O1 | 0.0044585 |
| 278.36646 | 0.1440E-01 | 0.0045121 |
| 278.73633 | 0.1305E-01 | 0.0046085 |
| 278.78296 | 0.1288E-01 | 0.0046192 |
| 279.10742 | 0.1171E-01 | 0.0047112 |
| 279.23047 | 0.1126E-01 | 0.0047693 |
| 279.33545 | 0.1088E-01 | 0.0047881 |
| 279.48584 | 0.1034E-01 | 0.0048546 |
| 279.49048 | 0.1032E-01 | 0.0048394 |
| 279.74365 | 0.9406E-02 | 0.0049367 |
| 279.87671 | 0.8926E-02 | 0.0049845 |
| 279.90332 | 0.8830E-02 | 0.0049781 |
| 280.00562 | 0.8462E-02 | 0.0050336 |
| 280.27002 | $0.7511 \mathrm{E}-02$ | 0.0051295 |
| 280.27026 | 0.7510E-02 | 0.0051400 |
| 280.43384 | 0.6922E-02 | 0.0051955 |
| 280.53809 | 0.6548E-02 | 0.0052494 |
| 280.54443 | 0.6525E-02 | 0.0052465 |
| 280.81152 | 0.5568E-02 | 0.0053905 |
| 280.81592 | 0.5552E-02 | 0.0053805 |
| 281.08740 | 0.4581E-02 | 0.0055293 |
| 281.09204 | 0.4564E-02 | 0.0055291 |
| 281.25342 | 0.3988E-02 | 0.0056330 |
| 281.37085 | 0.3569E-02 | 0.0056881 |
| 281.42188 | 0.3387E-02 | 0.0057398 |
| 281.48145 | 0.3174E-02 | 0.0057665 |
| 281.59204 | 0.2780E-02 | 0.0058666 |
| 281.64893 | 0.2578E-02 | 0.0059019 |
| 281.65210 | 0.2567E-02 | 0.0059040 |
| 281.70605 | 0.2375E-02 | 0.0059625 |
| 281.76636 | 0.2160E-02 | 0.0060012 |
| 281.82080 | 0.1966E-02 | 0.0060648 |


| rho 1 | rho d |
| :---: | :---: |
| (mol/cm3) | (mol/cm3) |
| 0.0128468 | 0.0079604 |
| 0.0127714 | 0.0079445 |
| 0.0125655 | 0.0079198 |
| 0.0123207 | 0.0078831 |
| 0.0123167 | 0.0078843 |
| 0.0121371 | 0.0078595 |
| 0.0121310 | 0.0078597 |
| 0.0119309 | 0.0078418 |
| 0.0118227 | 0.0078276 |
| 0.0117573 | 0.0078208 |
| 0.0117042 | 0.0078212 |
| 0.0116552 | 0.0078183 |
| 0.0115244 | 0.0078024 |
| 0.0114426 | 0.0077981 |
| 0.0113915 | 0.0077962 |
| 0.0112728 | 0.0077723 |
| 0.0112278 | 0.0077734 |
| 0.0111317 | 0.0077672 |
| 0.0110682 | 0.0077633 |
| 0.0110047 | 0.0077584 |
| 0.0108941 | 0.0077513 |
| 0.0108778 | 0.0077485 |
| 0.0107651 | 0.0077381 |
| 0.0107413 | 0.0077553 |
| 0.0106851 | 0.0077366 |
| 0.0106473 | 0.0077510 |
| 0.0106236 | 0.0077315 |
| 0.0105442 | 0.0077404 |
| 0.0104657 | 0.0077251 |
| 0.0104677 | 0.0077229 |
| 0.0104390 | 0.0077363 |
| 0.0103035 | 0.0077165 |
| 0.0103255 | 0.0077327 |
| 0.0102317 | 0.0077136 |
| 0.0101907 | 0.0077200 |
| 0.0101721 | 0.0077093 |
| 0.0100588 | 0.0077246 |
| 0.0100262 | 0.0077033 |
| 0.0098951 | 0.0077122 |
| 0.0098637 | 0.0076964 |
| 0.0097873 | 0.0077102 |
| 0.0096908 | 0.0076895 |
| 0.0096682 | 0.0077040 |
| 0.0096043 | 0.0076854 |
| 0.0095367 | 0.0077016 |
| 0.0094621 | 0.0076820 |
| 0.0094662 | 0.0076851 |
| 0.0094315 | 0.0076970 |
| 0.0093549 | 0.0076781 |
| 0.0093192 | 0.0076920 |
|  |  |


| 59 | 281.82642 |
| :--- | :--- |
| 60 | 281.93604 |
| 61 | 281.95898 |
| 62 | 281.99878 |
| 63 | 282.05176 |
| 64 | 282.05688 |
| 65 | 282.10986 |
| 66 | 282.14548 |
| 67 | 282.16821 |
| 68 | 282.17358 |
| 69 | 282.20337 |
| 70 | 282.22632 |
| 71 | 282.23096 |
| 72 | 282.23315 |
| 73 | 282.25879 |
| 74 | 282.27051 |
| 75 | 282.27661 |
| 76 | 282.29785 |
| 77 | 282.31494 |
| 78 | 282.31592 |
| 79 | 282.32544 |
| 80 | 282.33301 |
| 81 | 282.33618 |
| 82 | 282.33765 |
| 83 | 282.34253 |
| 84 | 282.34448 |
| 85 | 282.35059 |
| 86 | 282.36963 |

[^0]0.0060646
0.0061890
0.0062587
0.0062482
0.0063361
0.0063304
0.0064254
0.0064251
0.0065313
0.0065156
0.0065850
0.0066466
0.0066628
0.0066460
0.0067111
0.0067586
0.0067636
0.0068307
0.0069154
0.0069020
0.0069251
0.0069754
0.0070089
0.0070219
0.0070299
0.0070689
0.0070927
0.0072789
0.0092909
0.0091873
0.0090886
0.0090844
0.0090429
0.0090039
0.0089507
0.0089129
0.0088502
0.0088095
0.0087494
0.0087270
0.0086749
0.0086832
0.0086169
0.0086078
0.0085610
0.0084988
0.0084462
0.0084221
0.0083806
0.0083474
0.0083266
0.0083390
0.0082893
0.0083040
0.0082249
0.0080462
0.0076778
0.0076881
0.0076736
0.0076663 0.0076895 0.0076671 0.0076880 0.0076690 0.0076908 0.0076625 0.0076672 0.0076868 0.0076688 0.0076646 0.0076640 0.0076832
0.0076623 0.0076648 0.0076808 0.0076621 0.0076528 0.0076614 0.0076678 0.0076805 0.0076596 0.0076864 0.0076588 0.0076626

## Fringe Data

Listing of -OUT3 at 15:08:27 on JUL 12, 1987 for CCid=DBRU
Ethylene fringe data, set $\# 2$.
Number of data points $=42$
Critical Temperature $=282.48940 \mathrm{~K}$

| Temp (k) | $t$ | Fringe | Delta rho |
| :---: | :---: | :---: | :---: |
| 282.48870 | 0.2478E-05 | 46.0 | 0.022198 |
| 282.48660 | 0.9912E-05 | 72.0 | 0.034883 |
| 282.48440 | 0.1770E-04 | 87.0 | 0.042201 |
| 282.48260 | 0.2407E-04 | 96.0 | 0.046592 |
| 282.48040 | 0.3186E-04 | 105.0 | 0.050983 |
| 282.47830 | 0.3929E-04 | 113.0 | 0.054886 |
| 282.47610 | 0.4708E-04 | 119.0 | 0.057813 |
| 282.47390 | 0.5487E-04 | 125.0 | 0.060741 |
| 282.47160 | 0.6301E-04 | 131.0 | 0.063668 |
| 282.46940 | 0.7080E-04 | 136.0 | 0.066107 |
| 282.46720 | 0.7859E-04 | 141.0 | 0.068546 |
| 282.46510 | 0.8602E-04 | 145.0 | 0.070498 |
| 282.46210 | 0.9664E-04 | 151.0 | 0.073425 |
| 282.46060 | 0.1020E-03 | 154.0 | 0.074889 |
| 282.45720 | 0. $1140 \mathrm{E}-03$ | 160.0 | 0.077816 |
| 282.45410 | O. 1250E-03 | 165.0 | 0.080255 |
| 282.45140 | O. 1345E-03 | 169.0 | 0.082207 |
| 282.44800 | 0.1466E-03 | 173.0 | 0.084158 |
| 282.44470 | 0.1582E-03 | 178.0 | 0.086598 |
| 282.44120 | 0.1706E-03 | 182.0 | 0.088549 |
| 282.43840 | 0.1805E-03 | 186.0 | 0.090500 |
| 282.43510 | 0.1922E-03 | 190.0 | 0.092452 |
| 282.43190 | 0.2035E-03 | 194.0 | 0.094403 |
| 282.42850 | 0.2156E-03 | 197.0 | 0.095867 |
| 282.42530 | 0.2269E-03 | 201.0 | 0.097818 |
| 282.42200 | 0.2386E-03 | 204.0 | 0.099282 |
| 282.41840 | 0.2513E-03 | 207.0 | 0.100746 |
| 282.41450 | 0.2651E-03 | 212.0 | 0.103185 |
| 282.41020 | 0.2804E-03 | 216.0 | 0.105136 |
| 282.40580 | 0.2959E-03 | 220.0 | 0. 107088 |
| 282.40130 | 0.3119E-03 | 224.0 | 0.109039 |
| 282.39710 | 0.3267E-03 | 227.0 | 0.110503 |
| 282.39300 | $0.3413 \mathrm{E}-03$ | 230.0 | 0.111966 |
| 282.38010 | 0.3869E-03 | 240.0 | 0.116845 |
| 282.36720 | 0.4326E-03 | 250.0 | 0.121723 |
| 282.35400 | 0.4793E-03 | 259.0 | 0.126114 |
| 282.34180 | 0.5225E-03 | 266.0 | 0. 129529 |
| 282.32860 | 0.5692E-03 | 274.0 | 0.133431 |
| 282.31580 | 0.6145E-03 | 281.0 | 0.136846 |
| 282.30270 | 0.6609E-03 | 287.0 | 0.139773 |
| 282.28940 | $0.7080 \mathrm{E}-03$ | 293.0 | 0.142700 |
| 282.27620 | 0.7547E-03 | 300.0 | 0.146115 |

Listing of -OUT3(50) at 15:11:15 on JUL 12, 1987 for CCid=DRRU

| $\begin{aligned} & 50 \\ & 51 \end{aligned}$ | Ethylene fringe data, set $/ 3$. |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| 52 | Number of data points = 91 |  |  |  |
| 53 |  |  |  |  |
| 54 |  |  |  |  |
| 55 | Temp (K) | $t$ | Fringe * | Delta rho |
| 56 |  |  |  |  |
| 57 | 282.48000 | 0.2053E-04 | 88.0 | 0.044153 |
| 58 | 282.47885 | 0.2460E-04 | 93.0 | 0.046592 |
| 59 | 282.47800 | 0.2761E-04 | 97.0 | 0.048544 |
| 60 | 282.47679 | 0.3190E-04 | 102.0 | 0.050983 |
| 61 | 282.47640 | 0.3328E-04 | 104.0 | 0.051959 |
| 62 | 282.47520 | 0.3752E-04 | 108.0 | 0.053910 |
| 63 | 282.47430 | $0.4071 \mathrm{E}-04$ | 111.0 | 0.055374 |
| 64 | 282.47350 | 0.4354E-04 | 114.0 | 0.056838 |
| 65 | 282.47250 | 0.4708E-04 | 117.0 | 0.058301 |
| 66 | 282.47130 | 0.5133E-04 | 120.0 | 0.059765 |
| 67 | 282.47010 | 0.5558E-04 | 123.0 | 0.061228 |
| 68 | 282.46900 | 0.5947E-04 | 126.0 | 0.062692 |
| 69 | 282.46800 | 0.6301E-04 | 128.0 | 0.063668 |
| 70 | 282.46690 | 0.6691E-04 | 131.0 | 0.065131 |
| 71 | 282.46590 | 0.7045E-04 | 133.0 | 0.066107 |
| 72 | 282.46486 | 0.7413E-04 | 135.0 | 0.067083 |
| 73 | 282.46390 | 0.7753E-04 | 138.0 | 0.068546 |
| 74 | 282.46290 | 0.8107E-04 | 140.0 | 0.069522 |
| 75 | 282.45790 | 0.9877E-04 | 149.0 | 0.073913 |
| 76 | 282.45360 | 0.1140E-03 | 157.0 | 0.077816 |
| 77 | 282.44920 | 0.1296E-03 | 164.0 | 0.081231 |
| 78 | 282.44460 | 0.1458E-03 | 171.0 | 0.084646 |
| 79 | 282.44180 | 0.1558E-03 | 174.0 | 0.086110 |
| 80 | 282.43980 | 0.1628E-03 | 176.0 | 0.087085 |
| 81 | 282.43780 | 0.1699E-03 | 179.0 | 0.088549 |
| 82 | 282.43630 | 0.1752E-03 | 181.0 | 0.089525 |
| 83 | 282.43430 | 0.1823E-03 | 183.0 | 0.090500 |
| 84 | 282.42990 | 0.1979E-03 | 189.0 | 0.093428 |
| 85 | 282.42570 | $0.2128 \mathrm{E}-03$ | 194.0 | 0.095867 |
| 86 | 282.42130 | 0.2283E-03 | 198.0 | 0.097818 |
| 87 | 282.41820 | 0.2393E-03 | 201.0 | 0.099282 |
| 88 | 282.40780 | 0.2761E-03 | 212.0 | 0. 104648 |
| 89 | 282.40100 | 0.3002E-03 | 217.0 | 0. 107088 |
| 90 | 282.38800 | 0.3462E-03 | 228.0 | 0. 112454 |
| 91 | 282.38460 | 0.3582E-03 | 231.0 | 0.113918 |
| 92 | 282.37710 | $0.3848 \mathrm{E}-03$ | 237.0 | 0.116845 |
| 93 | 282.36560 | 0.4255E-03 | 245.0 | 0. 120747 |
| 94 | 282.36120 | 0.4411E-03 | 248.0 | O. 122211 |
| 95 | 282.34843 | $0.4863 \mathrm{E}-03$ | 257.0 | 0. 126602 |
| 96 | 282.33850 | 0.5214E-03 | 263.0 | 0. 129529 |
| 97 | 282.33460 | 0.5352E-03 | 264.0 | O. 130016 |
| 98 | 282.36520 | 0.4269E-03 | 245.0 | 0. 120747 |
| 99 | 282.36080 | 0.4425E-03 | 247.0 | 0.121723 |
| 100 | 282.35260 | 0.4715E-03 | 253.0 | 0. 124650 |
| 101 | 282.34830 | $0.4868 E-03$ | 256.0 | O. 126114 |
| 102 | 282.33630 | 0.5292E-03 | 263.0 | 0. 129529 |
| 103 | 282.33460 | 0.5352E-03 | 264.0 | 0. 130016 |
| 104 | 282.32900 | 0.5551E-03 | 268.0 | 0.131968 |
| 105 | 282.31860 | 0.5919E-03 | 274.0 | 0. 134895 |
| 106 | 282.30510 | 0.6397E-03 | 281.0 | 0.138310 |
| 107 | 282.29160 | $0.6875 \mathrm{E}-03$ | 288.0 | 0.141724 |


|  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| 108 | 282.27860 | $0.7335 \mathrm{E}-03$ | 295.0 | 0.145139 |
| 109 | 282.27010 | $0.7636 \mathrm{E}-03$ | 298.0 | 0.146603 |
| 110 | 282.26830 | $0.7700 \mathrm{E}-03$ | 300.0 | 0.147578 |
| 111 | 282.25240 | $0.8262 \mathrm{E}-03$ | 308.0 | 0.151481 |
| 112 | 282.25520 | $0.8163 \mathrm{E}-03$ | 306.0 | 0.150505 |
| 113 | 282.23930 | $0.8726 \mathrm{E}-03$ | 314.0 | 0.154408 |
| 114 | 282.22910 | $0.9087 \mathrm{E}-03$ | 318.0 | 0.156359 |
| 115 | 282.21590 | $0.9554 \mathrm{E}-03$ | 324.0 | 0.159286 |
| 116 | 282.20290 | $0.1001 \mathrm{E}-02$ | 329.0 | 0.161725 |
| 117 | 282.18710 | $0.1057 \mathrm{E}-02$ | 335.0 | 0.164652 |
| 118 | 282.17960 | $0.1084 \mathrm{E}-02$ | 338.0 | 0.166115 |
| 119 | 282.14020 | $0.1223 \mathrm{E}-02$ | 353.0 | 0.173432 |
| 120 | 282.10080 | $0.1363 \mathrm{E}-02$ | 367.0 | 0.1802611 |
| 121 | 282.06230 | $0.1499 \mathrm{E}-02$ | 379.0 | 0.186115 |
| 122 | 282.03570 | $0.1593 \mathrm{E}-02$ | 387.0 | 0.190017 |
| 123 | 281.98801 | $0.1762 \mathrm{E}-02$ | 400.0 | 0.196358 |
| 124 | 281.94900 | $0.1900 \mathrm{E}-02$ | 411.0 | 0.201723 |
| 125 | 281.91080 | $0.2036 \mathrm{E}-02$ | 421.0 | 0.206601 |
| 126 | 281.86820 | $0.2186 \mathrm{E}-02$ | 432.0 | 0.211966 |
| 127 | 281.82990 | $0.2322 \mathrm{E}-02$ | 441.0 | 0.216356 |
| 128 | 281.81370 | $0.2379 \mathrm{E}-02$ | 445.0 | 0.218306 |
| 129 | 281.79400 | $0.2449 \mathrm{E}-02$ | 449.0 | 0.220257 |
| 130 | 281.75560 | $0.2585 \mathrm{E}-02$ | 458.0 | 0.224647 |
| 131 | 281.72460 | $0.2695 \mathrm{E}-02$ | 465.0 | 0.228061 |
| 132 | 281.68610 | $0.2831 \mathrm{E}-02$ | 473.0 | 0.231962 |
| 133 | 281.64730 | $0.2968 \mathrm{E}-02$ | 481.0 | 0.235864 |
| 134 | 281.62120 | $0.3061 \mathrm{E}-02$ | 487.0 | 0.238790 |
| 135 | 281.59010 | $0.3171 \mathrm{E}-02$ | 493.0 | 0.241716 |
| 136 | 281.54750 | $0.3322 \mathrm{E}-02$ | 500.0 | 0.245130 |
| 137 | 281.50950 | $0.3456 \mathrm{E}-02$ | 508.0 | 0.249032 |
| 138 | 281.46979 | $0.3597 \mathrm{E}-02$ | 514.0 | 0.251957 |
| 139 | 281.44180 | $0.3696 \mathrm{E}-02$ | 521.0 | 0.255371 |
| 140 | 281.42410 | $0.3758 \mathrm{E}-02$ | 524.0 | 0.256834 |
| 141 | 281.40530 | $0.3825 \mathrm{E}-02$ | 527.0 | 0.258297 |
| 142 | 281.38900 | $0.3883 \mathrm{E}-02$ | 528.0 | 0.258784 |
| 143 | 281.37000 | $0.3950 \mathrm{E}-02$ | 533.0 | 0.261223 |
| 144 | 281.34410 | $0.4042 \mathrm{E}-02$ | 537.0 | 0.263173 |
| 145 | 281.30620 | $0.4176 \mathrm{E}-02$ | 544.0 | 0.266587 |
| 146 | 281.28330 | $0.4257 \mathrm{E}-02$ | 547.0 | 0.268050 |
| 147 | 281.22880 | $0.4450 \mathrm{E}-02$ | 555.0 | 0.271950 |
|  |  |  |  |  |



| 199 | 282.46416 | $0.8121 \mathrm{E}-04$ | 143.0 | 0.069522 |
| :--- | :--- | :--- | :--- | :--- |
| 200 | 282.46300 | $0.8531 \mathrm{E}-04$ | 146.0 | 0.070986 |
| 201 | 282.46203 | $0.8875 \mathrm{E}-04$ | 147.0 | 0.071474 |
| 202 | 282.46088 | $0.9282 \mathrm{E}-04$ | 149.0 | 0.072449 |
| 203 | 282.46061 | $0.9377 \mathrm{E}-04$ | 150.0 | 0.072937 |
| 204 | 282.45946 | $0.9785 \mathrm{E}-04$ | 152.0 | 0.073913 |
| 205 | 282.45824 | $0.1022 \mathrm{E}-03$ | 154.0 | 0.074889 |
| 206 | 282.45738 | $0.1052 \mathrm{E}-03$ | 155.0 | 0.075377 |
| 207 | 282.45635 | $0.1089 \mathrm{E}-03$ | 157.0 | 0.076352 |
| 208 | 282.45511 | $0.1132 \mathrm{E}-03$ | 159.0 | 0.077328 |
| 209 | 282.45413 | $0.1167 \mathrm{E}-03$ | 161.0 | 0.078304 |
| 210 | 282.45210 | $0.1239 \mathrm{E}-03$ | 164.0 | 0.079767 |
| 211 | 282.45077 | $0.1286 \mathrm{E}-03$ | 166.0 | 0.080743 |
| 212 | 282.44872 | $0.1359 \mathrm{E}-03$ | 169.0 | 0.082207 |
| 213 | 282.44789 | $0.1388 \mathrm{E}-03$ | 170.0 | 0.082695 |

Listing of -OUT3(418) at 15:16:58 on JUL 12, 1987 for CCId=DBRU

| 418 | Ethylene fringe data, set $\mathbf{W}$. |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| 419 ( 418 |  |  |  |  |
| 420 | Number of data points = 199 |  |  |  |
| 421 Critical Temperature $=282$ |  |  |  |  |
| 422 |  |  |  |  |
| 423 | Temp (K) | $t$ | Fringe * | Delta rho |
|  |  |  |  |  |
| 425 | 282.49017 | 0.1522E-05 | 39.0 | 0.018783 |
| 426 | 282.48986 | 0. 2620E-05 | 47.0 | 0.022686 |
| 427 | 282.48957 | 0.3646E-05 | 52.0 | 0.025126 |
| 428 | 282.48922 | $0.4885 \mathrm{E}-05$ | 57.0 | 0.027565 |
| 429 | 282.48898 | 0.5735E-05 | 60.0 | 0.029029 |
| 430 | 282.48857 | 0.7186E-05 | 64.0 | 0.030980 |
| 431 | 282.48824 | 0.8354E-05 | 68.0 | 0.032932 |
| 432 | 282.48793 | 0.9452E-05 | 70.0 | 0.033907 |
| 433 | 282.48776 | 0.1005E-04 | 72.0 | 0.034883 |
| 434 | 282.48748 | 0.1104E-04 | 75.0 | 0.036347 |
| 435 | 282.48717 | 0. $1214 \mathrm{E}-04$ | 77.0 | 0.037323 |
| 436 | 282.48686 | O. 1324E-04 | 79.0 | 0.038298 |
| 437 | 282.48661 | 0.1412E-04 | 81.0 | 0.039274 |
| 438 | 282.48636 | 0.1501E-04 | 83.0 | 0.040250 |
| 439 | 282.48602 | 0.1621E-04 | 85.0 | 0.041226 |
| 440 | 282.48571 | 0.1731E-04 | 87.0 | 0.042201 |
| 441 | 282.48539 | O. 1844E-04 | 89.0 | 0.043177 |
| 442 | 282.48497 | 0.1993E-04 | 90.0 | 0.043665 |
| 443 | 282.48466 | 0.2103E-04 | 92.0 | 0.044641 |
| 444 | 282.48430 | 0.2230E-O4 | 94.0 | 0.045616 |
| 445 | 282.48403 | 0.2326E-04 | 95.0 | 0.046104 |
| 446 | 282.48371 | O. 2439E-04 | 96.0 | 0.046592 |
| 447 | 282.48346 | O.2528E-04 | 97.0 | 0.047080 |
| 448 | 282.48314 | 0.2641E-04 | 99.0 | 0.048056 |
| 449 | 282.48291 | O.2722E-04 | 100.0 | 0.048544 |
| 450 | 282.48258 | 0.2839E-04 | 102.0 | 0.049519 |
| 451 | 282.48234 | 0.2924E-04 | 102.0 | 0.049519 |
| 452 | 282.48217 | 0.2984E-04 | 103.0 | 0.050007 |
| 453 | 282.48175 | O.3133E-04 | 104.0 | 0.050495 |
| 454 | 282.48140 | 0.3257E-04 | 106.0 | 0.051471 |
| 455 | 282.48110 | 0.3363E-04 | 107.0 | 0.051959 |
| 456 | 282.48083 | 0.3459E-04 | 108.0 | 0.052447 |
| 457 | 282.48064 | 0.3526E-04 | 109.0 | 0.052935 |
| 458 | 282.48038 | 0.3618E-04 | 110.0 | 0.053422 |
| 459 | 282.48015 | 0.3699E-04 | 111.0 | 0.053910 |
| 460 | 282.47983 | 0. $3813 \mathrm{E}-04$ | 112.0 | 0.054398 |
| 461 | 282.47953 | 0.3919E-04 | 113.0 | 0.054886 |
| 462 | 282.47928 | 0.4007E-04 | 114.0 | 0.055374 |
| 463 | 282.47895 | 0.4124E-04 | 115.0 | 0.055862 |
| 464 | 282.47839 | 0.4322E-04 | 116.0 | 0.056350 |
| 465 | 282.47809 | 0.4428E-04 | 117.0 | 0.056838 |
| 466 | 282.47781 | 0.4528E-04 | 118.0 | 0.057325 |
| 467 | 282.47754 | 0.4623E-04 | 119.0 | 0.057813 |
| 468 | 282.47695 | 0.4832E-04 | 121.0 | 0.058789 |
| 469 | 282.47670 | 0.4921E-04 | 122.0 | 0.059277 |
| 470 | 282.47641 | 0.5023E-04 | 123.0 | 0.059765 |
| 471 | 282.47613 | 0.5122E-04 | 123.0 | 0.059765 |
| 472 | 282.47575 | O.5257E-04 | 124.0 | 0.060253 |
| 473 | 282.47529 | 0.5420E-04 | 125.0 | 0.060741 |
| 474 | 282.47501 | 0.5519E-04 | 126.0 | 0.061228 |
| 475 | 282.47473 | O.5618E-04 | 127.0 | 0.061716 |


| 476 | 282.47412 | 0.5834E-04 | 128.0 | 0.062204 |
| :---: | :---: | :---: | :---: | :---: |
| 477 | 282.47385 | 0.5929E-04 | 129.0 | 0.062692 |
| 478 | 282.47352 | 0.6046E-04 | 130.0 | 0.063180 |
| 479 | 282.47299 | 0.6234E-04 | 131.0 | 0.063668 |
| 480 | 282.47271 | 0.6333E-04 | 132.0 | 0.064156 |
| 481 | 282.47217 | 0.6524E-04 | 133.0 | 0.064644 |
| 482 | 282.47171 | 0.6687E-04 | 134.0 | 0.065131 |
| 483 | 282.47141 | 0.6793E-04 | 135.0 | 0.065619 |
| 484 | 282.47101 | 0.6935E-04 | 136.0 | 0.066107 |
| 485 | 282.47053 | 0.7105E-04 | 137.0 | 0.066595 |
| 486 | 282.46993 | 0.7317E-04 | 138.0 | 0.067083 |
| 487 | 282.46930 | $0.7540 \mathrm{E}-04$ | 140.0 | 0.068059 |
| 488 | 282.46857 | 0.7798E-04 | 141.0 | 0.068546 |
| 489 | 282.46810 | 0.7965E-04 | 142.0 | 0.069034 |
| 490 | 282.46746 | 0.8191E-04 | 143.0 | 0.069522 |
| 491 | 282.46679 | 0.8429E-04 | 145.0 | 0.070498 |
| 492 | 282.46614 | 0.8659E-04 | 146.0 | 0.070986 |
| 493 | 282.46547 | 0.8896E-04 | 147.0 | 0.071474 |
| 494 | 282.46449 | 0.9243E-04 | 149.0 | 0.072449 |
| 495 | 282.46385 | 0.9469E-04 | 150.0 | 0.072937 |
| 496 | 282.46261 | 0.9908E-04 | 153.0 | 0.074401 |
| 497 | 282.46150 | 0.1030E-O3 | 155.0 | 0.075377 |
| 498 | 282.46082 | 0. 1054E-03 | 156.0 | 0.075865 |
| 499 | 282.45971 | 0.1093E-03 | 158.0 | 0.076840 |
| 500 | 282.45886 | 0.1124E-03 | 159.0 | 0.077328 |
| 501 | 282.45852 | 0.1136E-03 | 159.0 | 0.077328 |
| 502 | 282.45813 | 0.1149E-03 | 160.0 | 0.077816 |
| 503 | 282.45755 | 0.1170E-O3 | 162.0 | 0.078792 |
| 504 | 282.45677 | 0.1198E-03 | 163.0 | 0.079280 |
| 505 | 282.45570 | O. 1235E-03 | 164.0 | 0.079767 |
| 506 | 282.45491 | 0.1263E-03 | 166.0 | 0.080743 |
| 507 | 282.45382 | 0.1302E-03 | 167.0 | 0.081231 |
| 508 | 282.45283 | 0.1337E-03 | 169.0 | 0.082207 |
| 509 | 282.45194 | 0. 1369E-03 | 170.0 | 0.082695 |
| 510 | 282.45075 | 0.1411E-03 | 172.0 | 0.083670 |
| 511 | 282.44976 | 0.1446E-03 | 173.0 | 0.084158 |
| 512 | 282.44877 | 0.1481E-03 | 175.0 | 0.085134 |
| 513 | 282.44779 | O.1515E-03 | 176.0 | 0.085622 |
| 514 | 282.44590 | O. 1582E-03 | 179.0 | 0.087085 |
| 515 | 282.44241 | 0.1706E-03 | 183.0 | 0.089037 |
| 516 | 282.44102 | 0.1755E-03 | 185.0 | 0.090013 |
| 517 | 282.43773 | 0.1872E-03 | 189.0 | 0.091964 |
| 518 | 282.43604 | 0.1931E-03 | 190.0 | 0.092452 |
| 519 | 282.43344 | 0.2023E-03 | 194.0 | 0.094403 |
| 520 | 282.43035 | 0.2133E-03 | 197.0 | 0.095867 |
| 521 | 282.42746 | 0.2235E-03 | 200.0 | 0.097331 |
| 522 | 282.42467 | 0.2334E-03 | 203.0 | 0.098794 |
| 523 | 282.42128 | 0.2454E-03 | 206.0 | O. 100258 |
| 524 | 282.42160 | 0.2443E-03 | 207.0 | 0. 100746 |
| 525 | 282.41480 | 0.2683E-03 | 213.0 | 0. 103673 |
| 526 | 282.40920 | 0.2882E-03 | 218.0 | 0. 106112 |
| 527 | 282.39980 | 0.3214E-03 | 226.0 | 0.110015 |
| 528 | 282.39520 | 0.3377E-03 | 229.0 | 0.111478 |
| 529 | 282.39040 | 0.3547E-03 | 233.0 | 0. 113430 |
| 530 | 282.38390 | 0.3777E-03 | 238.0 | 0.115869 |
| 531 | 282.37800 | 0.3986E-03 | 242.0 | 0. 117820 |
| 532 | 282.37060 | $0.4248 \mathrm{E}-03$ | 248.0 | 0. 120747 |
| 533 | 282.36020 | 0.4616E-03 | 255.0 | 0.124162 |


| 534. | 282.35130 | 0.4931E-03 | 261.0 | 0. 127089 |
| :---: | :---: | :---: | :---: | :---: |
| 535 | 282.34340 | 0.521.1E-03 | 265.0 | 0. 129041 |
| 536 | 282.33330 | O.5568E-03 | 271.0 | 0.131968 |
| 537 | 282.32330 | 0.5922E-03 | 276.0 | 0. 134407 |
| 538 | 282.31580 | 0.6188E-03 | 281.0 | 0.136846 |
| 539 | 282.31460 | 0.6230E-03 | 283.0 | 0.137822 |
| 540 | 282.30530 | 0.6560E-O3 | 287.0 | 0.139773 |
| 541 | 282.29680 | 0.6860E-03 | 291.0 | 0.141724 |
| 542 | 282.28640 | 0.7229E-03 | 296.0 | 0.144164 |
| 543 | 282.27830 | 0.7515E-03 | 300.0 | 0.146115 |
| 544 | 282.27280 | $0.7710 \mathrm{E}-03$ | 302.0 | 0.147091 |
| 545 | 282.26270 | 0.8068E-03 | 307.0 | 0.149530 |
| 546 | 282.25600 | 0.8305E-03 | 310.0 | 0.150993 |
| 547 | 282.24570 | 0.8669E-03 | 315.0 | 0.153432 |
| 548 | 282.23870 | 0.8917E-03 | 318.0 | 0.154896 |
| 549 | 282.22820 | 0.9289E-03 | 322.0 | 0. 156847 |
| 550 | 282.21820 | 0.9643E-03 | 326.0 | 0. 158798 |
| 551 | 282.21560 | $0.9735 \mathrm{E}-03$ | 327.0 | 0. 159286 |
| 552 | 282.20850 | 0.9986E-03 | 330.0 | 0. 160749 |
| 553. | 282.19980 | 0.1029E-02 | 334.0 | 0. 162701 |
| 554 | 282. 18990 | 0.1064E-02 | 338.0 | 0. 164652 |
| 555 | 282. 18970 | 0.1065E-02 | 339.0 | 0.165140 |
| 556 | 282.17559 | 0.1115E-02 | 344.0 | 0. 167579 |
| 557 | 282. 16258 | 0.1161E-02 | 349.0 | 0.170018 |
| 558 | 282.14957 | 0.1207E-O2 | 353.0 | 0.171969 |
| 559 | 282.14047 | O. 1239E-02 | 356.0 | 0. 173432 |
| 560 | 282.12506 | 0.1294E-02 | 361.0 | 0.175871 |
| 561 | 282.11745 | 0.1321E-02 | 364.0 | 0. 177335 |
| 562 | 282.10434 | 0.1367E-02 | 368.0 | 0. 179286 |
| 563 | 282.09123 | 0.1414E-02 | 373.0 | 0.181725 |
| 564 | 282.08102 | 0.1450E-O2 | 376.0 | O. 183188 |
| 565 | 282.06601 | 0.1503E-02 | 381.0 | 0. 185627 |
| 566 | 282.05250 | O.1551E-02 | 385.0 | 0.187578 |
| 567 | 282.04210 | O. 1588E-O2 | 388.0 | 0. 189041 |
| 568 | 282.02779 | 0.1638E-02 | 392.0 | O. 190992 |
| 569 | 282.02088 | 0.1663E-O2 | 394.0 | 0.191968 |
| 570 | 282.00747 | 0. $1710 \mathrm{E}-\mathrm{O2}$ | 398.0 | 0. 193919 |
| 571 | 281.99376 | 0.1759E-02 | 402.0 | 0. 195870 |
| 572 | 281.98265 | 0.1798E-02 | 406.0 | 0.197821 |
| 573 | 281.97084 | 0.1840E-02 | 409.0 | 0. 199284 |
| 574 | 281.95753 | 0.1887E-02 | 412.0 | 0.200748 |
| 575 | 281.94433 | 0.1934E-02 | 416.0 | 0.202699 |
| 576 | 281.93582 | 0.1964E-02 | 418.0 | 0.203674 |
| 577 | 281.92201 | 0.2013E-02 | 422.0 | 0.205625 |
| 578 | 281.90960 | 0.2057E-02 | 425.0 | 0.207088 |
| 579 | 281.89729 | 0.2100E-02 | 427.0 | 0.208064 |
| 580 | 281.89750 | 0.2100E-02 | 428.0 | 0.208552 |
| 581 | 281.89328 | 0.2114E-02 | 429.0 | 0.209039 |
| 582 | 281.87305 | 0.2186E-02 | 434.0 | 0.211478 |
| 583 | 281.85293 | 0.2257E-02 | 439.0 | 0.213917 |
| 584 | 281.83291 | 0.2328E-02 | 444.0 | 0.216356 |
| 585 | 281.81289 | 0.2399E-02 | 449.0 | 0.218794 |
| 586 | 281.79356 | 0.2467E-02 | 453.0 | 0.220745 |
| 587 | 281.77344 | 0.2539E-02 | 458.0 | 0.223184 |
| 588 | 281.75370 | 0.2609E-02 | 462.0 | 0.225135 |
| 589 | 281.73375 | 0.2679E-02 | 467.0 | 0.227573 |
| 590 | 281.71353 | 0.2751E-02 | 471.0 | 0.229524 |
| 591 | 281.69301 | 0.2823E-02 | 476.0 | 0.231963 |


| 592 | 281.67298 | $0.2894 \mathrm{E}-02$ | 480.0 | 0.233313 |
| :--- | :--- | :--- | :--- | :--- |
| 593 | 281.65256 | $0.2967 \mathrm{E}-02$ | 484.0 | 0.235864 |
| 594 | 281.65256 | $0.2967 \mathrm{E}-02$ | 485.0 | 0.236352 |
| 595 | 281.63484 | $0.3029 \mathrm{E}-02$ | 489.0 | 0.238303 |
| 596 | 281.62522 | $0.3063 \mathrm{E}-02$ | 490.0 | 0.238790 |
| 597 | 281.59430 | $0.3173 \mathrm{E}-02$ | 496.0 | 0.241716 |
| 598 | 281.57958 | $0.3225 \mathrm{E}-02$ | 499.0 | 0.243179 |
| 599 | 281.54896 | $0.3333 \mathrm{E}-02$ | 505.0 | 0.246106 |
| 600 | 281.52605 | $0.3414 \mathrm{E}-02$ | 509.0 | 0.248056 |
| 601 | 281.49533 | $0.3523 \mathrm{E}-02$ | 515.0 | 0.250982 |
| 602 | 281.46851 | $0.3618 \mathrm{E}-02$ | 519.0 | 0.252933 |
| 603 | 281.43759 | $0.3728 \mathrm{E}-02$ | 524.0 | 0.255371 |
| 604 | 281.40545 | $0.3841 \mathrm{E}-02$ | 529.0 | 0.257809 |
| 605 | 281.37513 | $0.3949 \mathrm{E}-02$ | 535.0 | 0.260735 |
| 606 | 281.31474 | $0.4162 \mathrm{E}-02$ | 545.0 | 0.265611 |
| 607 | 281.28457 | $0.4269 \mathrm{E}-02$ | 551.0 | 0.2685377 |
| 608 | 281.25420 | $0.4377 \mathrm{E}-02$ | 555.0 | 0.270488 |
| 609 | 281.22395 | $0.4484 \mathrm{E}-02$ | 559.0 | 0.272438 |
| 610 | 281.19698 | $0.4579 \mathrm{E}-02$ | 563.0 | 0.274388 |
| 611 | 281.17871 | $0.4644 \mathrm{E}-02$ | 566.0 | 0.275851 |
| 612 | 281.15974 | $0.4711 \mathrm{E}-02$ | 569.0 | 0.277314 |
| 613 | 281.12916 | $0.4819 \mathrm{E}-02$ | 574.0 | 0.279752 |
| 614 | 281.09862 | $0.4928 \mathrm{E}-02$ | 578.0 | 0.281702 |
| 615 | 281.03225 | $0.5162 \mathrm{E}-02$ | 588.0 | 0.286578 |
| 616 | 280.96514 | $0.5400 \mathrm{E}-02$ | 599.0 | 0.291942 |
| 617 | 280.89772 | $0.5639 \mathrm{E}-02$ | 607.0 | 0.295842 |
| 618 | 280.82990 | $0.5879 \mathrm{E}-02$ | 616.0 | 0.300230 |
| 619 | 280.76229 | $0.6118 \mathrm{E}-02$ | 625.0 | 0.304618 |
| 620 | 280.69477 | $0.6357 \mathrm{E}-02$ | 632.0 | 0.308030 |
| 621 | 280.62695 | $0.6597 \mathrm{E}-02$ | 641.0 | 0.312418 |
| 622 | 280.55963 | $0.6836 \mathrm{E}-02$ | 648.0 | 0.315830 |
| 623 | 280.49142 | $0.7077 \mathrm{E}-02$ | 656.0 | 0.319730 |

## B-3 Hydrogen Coexistence Curve Data

## Order Parameter Data

Listing of -OUT1 at 13:37:26 on AUG 14. 1987 for CCid=DBRU
Hydrogen focal plane fringe data, set 211486.1

Number of data points : 12
Critical Temperature $=33.3004 \times$

| Temp (K) | Fringe | Oelta rho |  |
| :--- | ---: | ---: | ---: |
| 33.29876 | $0.4925 E-04$ | 41.0 | 0.049536 |
| 33.29656 | $0.1153 E-03$ | 53.5 | 0.064824 |
| 33.29346 | $0.2084 E-03$ | 63.5 | 0.077055 |
| 33.29052 | $0.2967 E-03$ | 71.5 | 0.086840 |
| 33.28682 | $0.4078 \mathrm{E}-03$ | 79.5 | 0.096625 |
| 33.28369 | $0.5018 \mathrm{E}-03$ | 85.0 | 0.103352 |
| 33.27992 | $0.6150 \mathrm{E}-03$ | 91.0 | 0.110690 |
| 33.27648 | $0.7183 \mathrm{E}-03$ | 96.0 | 0.116806 |
| 33.27266 | $0.8330 \mathrm{E}-03$ | 100.5 | 0.122310 |
| 33.26794 | $0.9748 \mathrm{E}-03$ | 106.0 | 0.129036 |
| 33.26317 | $0.1118 \mathrm{E}-02$ | 110.5 | 0.134540 |
| 33.25846 | $0.1259 \mathrm{E}-02$ | 115.0 | 0.140044 |

Listing of -OUT1 at 13:39:10 on AUG 14. 1987 for CCid=DBRU Hydrogen focal plane fringe data, set 171286.1

Number of data points $=22$ Critical Temperature 32.9918 K

| Temp (K) | t | Fringe | Delta rho |
| :--- | ---: | ---: | ---: |
| 32.98314 | $0.2625 E-03$ | 66.5 | 0.080725 |
| 32.97495 | $0.5107 E-03$ | 84.0 | 0.102129 |
| 32.96713 | $0.7478 E-03$ | 96.0 | 0.116806 |
| 32.95459 | $0.1128 E-02$ | 110.0 | 0.133929 |
| 32.94177 | $0.1516 E-02$ | 121.5 | 0.147994 |
| 32.92977 | $0.1880 E-02$ | 131.5 | 0.160224 |
| 32.91730 | $0.2258 E-02$ | 140.0 | 0.170620 |
| 32.90115 | $0.2748 E-02$ | 150.0 | 0.182851 |
| 32.88499 | $0.3237 E-02$ | 159.0 | 0.193858 |
| 32.86896 | $0.3723 E-02$ | 167.5 | 0.204253 |
| 32.85259 | $0.4220 E-02$ | 175.0 | 0.213425 |
| 32.82884 | $0.4939 E-02$ | 185.5 | 0.226267 |
| 32.80528 | $0.5654 E-02$ | 194.5 | 0.237273 |
| 32.76533 | $0.6864 E-02$ | 208.5 | 0.254394 |
| 32.72507 | $0.8085 E-02$ | 221.5 | 0.270291 |
| 32.68462 | $0.9311 E-02$ | 233.0 | 0.284354 |
| 32.64546 | $0.1050 E-01$ | 243.0 | 0.296582 |
| 32.60632 | $0.1168 E-01$ | 252.0 | 0.307587 |
| 32.56789 | $0.1285 E-01$ | 261.0 | 0.318591 |
| 32.52912 | $0.1402 E-01$ | 269.5 | 0.328984 |
| 32.49065 | $0.1519 E-01$ | 277.5 | 0.338766 |
| 32.45204 | $0.1636 E-01$ | 285.0 | 0.347935 |

Listing of -OUT1 at 13:40:57 on AUG 14, 1987 for CCid=DBRU
Hydrogen focal plane fringe data, set 250287.1

```
Number of data points = 45
Critical Temperature = 32.9769 K
```

| Temp (K) | $t$ | Fringe | Delta rho |
| :---: | :---: | :---: | :---: |
| 32.97372 | 0.9643E-04 | 49.0 | 0.059320 |
| 32.97113 | 0.1750E-03 | 58.5 | 0.070940 |
| 32.96719 | 0.2944E-03 | 70.0 | 0.085005 |
| 32.96325 | 0.4139E-03 | 78.5 | 0.095402 |
| 32.95902 | 0.5422E-03 | 85.5 | 0.103963 |
| 32.95036 | 0.8048E-03 | 97.0 | 0.118029 |
| 32.94186 | 0. 1063E-02 | 107.0 | 0. 130260 |
| 32.93366 | O.1311E-02 | 115.0 | 0.140044 |
| 32.92550 | 0.1559E-02 | 121.5 | 0.147994 |
| 32.91713 | O. $1812 \mathrm{E}-02$ | 128.5 | 0. 156555 |
| 32.91279 | O.1944E-02 | 132.0 | 0. 160836 |
| 32.90847 | 0.2075E-02 | 135.0 | 0. 164505 |
| 32.90431 | 0.2201E-02 | 138.0 | 0.168174 |
| 32.90183 | 0.2276E-02 | 139.0 | 0. 169397 |
| 32.89935 | 0.2352E-02 | 141.0 | 0.171843 |
| 32.89681 | 0.2429E-02 | 142.0 | 0.173066 |
| 32.89450 | 0.2499E-02 | 144.0 | 0. 175512 |
| 32.89199 | 0.2575E-02 | 145.0 | 0. 176735 |
| 32.88870 | 0.2675E-02 | 147.0 | 0.179181 |
| 32.88543 | 0.2774E-02 | 149.0 | 0.181627 |
| 32.88128 | 0.2900E-02 | 152.0 | 0.185296 |
| 32.87704 | 0.3028E-02 | 154.0 | 0.187742 |
| 32.86883 | 0.3277E-02 | 158.0 | O. 192634 |
| 32.86074 | 0.3522E-02 | 162.0 | 0. 197526 |
| 32.84476 | 0.4007E-02 | 170.0 | 0.207310 |
| 32.82876 | 0.4492E-02 | 177.0 | 0.215871 |
| 32.81286 | 0.4974E-O2 | 184.0 | 0.224432 |
| 32.78082 | 0.5946E-02 | 195.5 | 0.238496 |
| 32.74888 | 0.6915E-02 | 206.5 | 0.251948 |
| 32.71696 | 0.7882E-02 | 216.5 | 0.264176 |
| 32.68638 | $0.8810 \mathrm{E}-02$ | 225.5 | 0.275182 |
| 32.64617 | 0. 1003E-01 | 236.5 | 0.288633 |
| 32.60690 | 0.1122E-O1 | 246.5 | 0.300861 |
| 32.56674 | 0.1244E-01 | 256.0 | 0.312477 |
| 32.52769 | O.1362E-01 | 264.0 | 0.322259 |
| 32.49637 | O.1457E-O1 | 270.5 | 0.330206 |
| 32.45045 | O.1596E-01 | 280.0 | 0.341821 |
| 32.40434 | 0.1736E-01 | 287.5 | 0.350990 |
| 32.34283 | 0.1923E-01 | 298.0 | 0.363827 |
| 32.28167 | 0.2108E-01 | 309.0 | 0.377275 |
| 32.22252 | 0.2288E-O1 | 318.5 | 0.388888 |
| 32.14699 | 0.2517E-01 | 329.0 | 0.401723 |
| 32.07264 | 0.2742E-01 | 340.0 | 0.415169 |
| 32.00015 | 0.2962E-O1 | 351.0 | 0.428614 |
| 31.92745 | 0.3482E-01 | 360.0 | 0.439614 |

Listing of -OUT1 at 13:42:OB on AUG 14, 1987 for CCtd=DBRU
Hydrogen focal plane fringe data. set 250287.2

```
Number of data polnts =
58
Critical Temperature = 32.9766 K
```

| Temp (K) | $t$ | Fringe | Delta rho |
| :---: | :---: | :---: | :---: |
| 32.97399 | 0.7915E-04 | 45.5 | 0.055040 |
| 32.97235 | 0.1289E-03 | 53.0 | 0.064213 |
| 32.97058 | 0.1826E-03 | 59.5 | 0.072163 |
| 32.96797 | 0.2617E-03 | 67.0 | 0.081336 |
| 32.96523 | $0.3448 \mathrm{E}-03$ | 73.5 | 0.089286 |
| 32.96261 | 0.4242E-03 | 78.5 | 0.095402 |
| 32.96014 | 0.4991E-03 | 83.0 | 0. 100906 |
| 32.95776 | 0.5713E-03 | 87.0 | 0. 105798 |
| 32.95404 | 0.6841E-03 | 92.0 | 0.111913 |
| 32.95017 | 0.8015E-03 | 97.0 | 0.118029 |
| 32.94578 | 0.9346E-03 | 101.5 | 0. 123533 |
| 32.94182 | 0.1055E-02 | 106.0 | 0. 129036 |
| 32.93683 | 0.1206E-02 | 111.0 | 0. 135152 |
| 32.93175 | 0.1360E-02 | 116.0 | 0. 141267 |
| 32.92495 | 0.1566E-02 | 121.5 | 0.147994 |
| 32.91748 | 0.1793E-02 | 128.0 | 0. 155944 |
| 32.90925 | 0.2042E-02 | 134.0 | 0. 163282 |
| 32.90091 | 0.2295E-02 | 139.0 | 0.169397 |
| 32.89208 | 0.2563E-02 | 145.0 | 0. 176735 |
| 32.88238 | 0.2857E-02 | 150.5 | 0.183462 |
| 32.87193 | 0.3174E-02 | 156.0 | 0. 190188 |
| 32.86146 | 0.3492E-02 | 161.5 | 0. 196915 |
| 32.85096 | $0.3810 \mathrm{E}-\mathrm{O2}$ | 166.0 | 0.202418 |
| 32.83893 | 0.4175E-02 | 172.0 | 0.209756 |
| 32.81528 | 0.4892E-02 | 182.0 | 0.221986 |
| 32.79129 | 0.5619E-02 | 194.5 | 0.233604 |
| 32.76724 | 0.6349E-02 | 200.0 | 0.243999 |
| 32.73519 | 0.7321E-02 | 210.5 | 0.256839 |
| 32.69671 | 0.8488E-02 | 222.5 | 0.271514 |
| 32.65702 | 0.9691E-02 | 233.0 | 0.284353 |
| 32.61784 | -. 1088E-01 | 243.0 | 0.296581 |
| 32.56972 | O.1234E-01 | 254.5 | 0.310643 |
| 32.51512 | O.1399E-01 | 266.0 | 0.324704 |
| 32.45301 | 0.1588E-01 | 279.0 | 0.340599 |
| 32.39117 | O. 1775E-01 | 290.0 | 0.354047 |
| 32.33009 | O.1961E-01 | 301.0 | 0.367495 |
| 32.26881 | 0.2146E-01 | 311.0 | 0.379720 |
| 32.21045 | 0.2323E-01 | 320.0 | 0.390722 |
| 32.14992 | 0.2507E-01 | 329.5 | 0.402335 |
| 32.09132 | 0.2685E-01 | 338.0 | 0.412724 |
| 32.03215 | 0.2864E-01 | 346.5 | 0.423114 |
| 31.97410 | 0.3040E-01 | 354.0 | 0.432281 |
| 31.91345 | 0.3224E-01 | 362.0 | 0.442058 |
| 31.85501 | 0.3401E-01 | 369.0 | 0.450613 |
| 31.78175 | 0.3623E-01 | 379.0 | 0.462834 |
| 31.71472 | 0.3827E-01 | 386.5 | 0.471999 |
| 31.64357 | 0.4042E-01 | 395.5 | 0.482997 |
| 31.56788 | 0.4272E-01 | 404.5 | 0.493995 |
| 31.50149 | 0.4473E-01 | 411.5 | 0.502548 |
| 31.42623 | 0.4701E-01 | 420.0 | 0.512933 |
| 31.35672 | 0.4912E-01 | 426.5 | 0.520874 |
| 31.28788 | 0.5121E-01 | 433.5 | 0.529426 |
| 31.18943 | 0.5420E-01 | 443.5 | 0.541642 |
| 31.08377 | 0.5740E-01 | 451.0 | 0.550800 |
| 30.95415 | 0.6133E-01 | 462.0 | 0.564235 |
| 30.81670 | 0.6550E-01 | 473.0 | 0.577668 |
| 30.75567 | 0.6735E-01 | 479.5 | 0.585607 |
| 30.68196 | 0.6958E-01 | 484.0 | 0.591100 |



Listing of -OUT1 at 13:35:13 on AUG 14, 1987 for CCId=DBRU

```
Hydrogen focal plane fringe data, set 070487.1
```

Number of data points = 19
Critical Temperature = 32.8522

| Temp (K) | $t$ | Fringe | Delta rho |
| :---: | :---: | :---: | :---: |
| 32.84919 | 0.9162E-04 | 48.0 | 0.058097 |
| 32.84696 | 0.1595E-03 | 57.5 | 0.069717 |
| 32.84483 | 0.2243E-03 | 64.5 | 0.078278 |
| 32.84202 | 0.3099E-03 | 71.0 | 0.086229 |
| 32.83840 | 0.4201E-03 | 79.5 | 0.096625 |
| 32.81124 | 0.1247E-02 | 114.5 | 0.139433 |
| 32.77912 | 0.2225E-02 | 139.0 | 0. 169397 |
| 32.74175 | 0.3362E-02 | 161.0 | 0.196304 |
| 32.65921 | 0.5B74E-02 | 195.0 | 0. 237884 |
| 32.53859 | 0.9546E-02 | 232.5 | 0.283742 |
| 32.42560 | 0.1299E-01 | 259.5 | 0.316757 |
| 32.31286 | 0.1642E-01 | 283.0 | 0.345489 |
| 32.20823 | 0.1960E-O1 | 303.0 | 0.369941 |
| 32.13804 | $0.2174 E-01$ | 314.5 | 0.383999 |
| 32.06094 | 0.2409E-01 | 326.0 | 0.398057 |
| 31.91109 | 0.2865E-01 | 348.0 | 0.424948 |
| 31.76504 | 0.3309E-01 | 366.5 | 0.447558 |
| 31.62350 | 0.3740E-01 | 384.0 | 0.468945 |
| 31.48555 | 0.4160E-01 | 398.0 | 0.486051 |



Listing of -OUT at 16:45:03 on AUG 14. 1987 for CCid=DBRU

| Number of data points - 29 Critical Temperature $=32.9769 \mathrm{~K}$ |  |  |  |
| :---: | :---: | :---: | :---: |
| Temp (K) | $t$ | N1-Nv | rho d |
| 32.97614 | 0.2305E-04 | 1.9 | 0.002309 |
| 32.97372 | 0.9643E-04 | 1.3 | 0.001557 |
| 32.97113 | 0.1750E-03 | 0.9 | 0.001053 |
| 32.96719 | 0.2944E-03 | 0.8 | 0.000911 |
| 32.96325 | 0.4139E-03 | 0.6 | 0.000648 |
| 32.95902 | 0.5422E-03 | 0.7 | 0.000754 |
| 32.95036 | 0.8048E-03 | -0.2 | -0.000374 |
| 32.94186 | 0.1063E-02 | -0.8 | -0.001138 |
| 32.93366 | 0.1311E-02 | -1.1 | -0.001531 |
| 32.92550 | 0.1559E-02 | -0.9 | -0.001310 |
| 32.91713 | 0.1812E-02 | -0.6 | -0.000965 |
| 32.91279 | 0.1944E-02 | -0.6 | -0.000976 |
| 32.90847 | 0.2075E-02 | -1.0 | -0.001478 |
| 32.90431 | 0.2201E-02 | -1.5 | -0.002100 |
| 32.90183 | 0.2276E-02 | -2.0 | -0.002718 |
| 32.89935 | 0.2352E-02 | -2.0 | -0.002725 |
| 32.89681 | 0.2429E-02 | -2.0 | -0.002732 |
| 32.89450 | 0.2499E-02 | -2.3 | -0.003104 |
| 32.89199 | 0.2575E-02 | -2.4 | -0.003232 |
| 32.88870 | 0.2675E-02 | -2.4 | -0.003241 |
| 32.88543 | 0.2774E-02 | -2.7 | -0.003616 |
| 32.88128 | 0.2900E-02 | -2.6 | -0.003504 |
| 32.87704 | 0.3028E-02 | -2.6 | -0.003513 |
| 32.86883 | 0.3277E-02 | -2.5 | -0.003409 |
| 32.86074 | 0.3522E-02 | -2.2 | -0.003062 |
| 32.84476 | 0.4007E-02 | -2.0 | -0.002852 |
| 32.82876 | 0.4492E-02 | -2.1 | -0.003011 |
| 32.81286 | 0.4974E-02 | -2.0 | -0.002923 |
| 32.78082 | 0.5946E-02 | -1.5 | -0.002376 |

Listing of -OUT at 16:43:38 on AUG 14. 1987 for CCid=DBRU

```
Hydrogen Image plane fringe data, set 250287.2
Number of data points = 49
Critical Temperature = 32.9766 K
```

| Temp (K) | $t$ | $\mathrm{Ni}-\mathrm{NV}$ | rho d |
| :---: | :---: | :---: | :---: |
| 32.97613 | 0.1425E-04 | 0.3 | 0.000356 |
| 32.97399 | 0.7915E-04 | -1.1 | -0.001373 |
| 32.97235 | 0.1289E-03 | -1.9 | -0.002362 |
| 32.97058 | 0.1826E-03 | -2.5 | -0.003 106 |
| 32.96797 | 0.2617E-03 | -2.1 | -0.002630 |
| 32.96523 | 0.3448E-03 | -2.2 | -0.002766 |
| 32.96261 | 0.4242E-03 | -3.1 | -0.003875 |
| 32.96014 | 0.4991E-03 | -2.9 | -0.003641 |
| 32.95776 | 0.5713E-03 | -3.2 | -0.004017 |
| 32.95404 | 0.6841E-03 | -3.2 | -0.004028 |
| 32.95017 | 0.8015E-03 | -3.0 | -0.003797 |
| 32.94578 | 0.9346E-03 | -3.5 | -0.004423 |
| 32.94182 | 0.1055E-02 | -3.6 | -0.004559 |
| 32.93683 | 0.1206E-02 | -3.5 | -0.004452 |
| 32.93175 | D. 1360E-02 | -2.5 | -0.003248 |
| 32.92495 | 0.1566E-02 | -3.4 | -0.004364 |
| 32.91748 | 0.1793E-02 | -3.3 | -0.004262 |
| 32.90925 | 0.2042E-02 | -3.0 | -0.0039 16 |
| 32.90091 | 0.2295E-02 | -3.0 | -0.003938 |
| 32.89208 | 0.2563E-02 | -3.2 | -0.004205 |
| 32.88238 | 0.2857E-02 | -3.0 | -0.003984 |
| 32.87193 | 0.3174E-02 | -2.9 | -0.003887 |
| 32.86146 | 0.3492E-02 | -3.0 | -0.004032 |
| 32.85096 | $0.3810 \mathrm{E}-02$ | -2.6 | -0.003567 |
| 32.83893 | 0.4175E-02 | -2.5 | -0.003470 |
| 32.81528 | 0.4892E-02 | -2.2 | -0.003156 |
| 32.79129 | $0.5619 \mathrm{E}-02$ | -2.0 | -0.002959 |
| 32.76724 | 0.6349E-02 | - 1.8 | -0.002763 |
| 32.73519 | 0.7321E-02 | -1.6 | -0.002580 |
| 32.69671 | 0.8488E-02 | -1.1 | -0.002038 |
| 32.65702 | 0.9691E-02 | -0.8 | -0.001743 |
| 32.61784 | 0.1088E-01 | -0.9 | -0.001924 |
| 32.56972 | 0.1234E-01 | 0.1 | -0.000777 |
| 32.51512 | 0.1399E-01 | 0.2 | -0.000743 |
| 32.45301 | 0.1588E-01 | 0.9 | 0.000016 |
| 32.39117 | 0.1775E-01 | 1.5 | 0.000658 |
| 32.33009 | 0.1961E-01 | 2.2 | 0.001423 |
| 32.26881 | 0.2146E-01 | 2.4 | 0.001580 |
| 32.21045 | 0.2323E-01 | 3.1 | 0.002354 |
| 32.14992 | 0.2507E-04 | 3.8 | 0.003126 |
| 32.09132 | 0.2685E-01 | 4.5 | 0.003901 |
| 32.03215 | 0.2864E-01 | 5.0 | 0.004434 |
| 31.97410 | 0.3040E-01 | 5.5 | 0.004968 |
| 31.91345 | 0.3224E-01 | 5.9 | 0.005383 |
| 31.85501 | 0.3401E-01 | 6.7 | 0.006289 |
| 31.78175 | 0.3623E-01 | 7.8 | 0.007530 |
| 31.71472 | 0.3827E-01 | 8.4 | 0.008178 |
| 31.64357 | 0.4042E-01 | 10.4 | 0.010527 |
| 31.56788 | 0.4272E-01 | 11.2 | 0.011395 |

L18ting of -OUT at 16:41:14 on AUG 14. 9987 for CCideDBRU
Hydrogen image plane fringe data. set 250287.6
Number of data points $=6$
Critical Temperature = 32.9720 K

| Temp (K) | t | Ni-Nv | rho d |
| :--- | :---: | :---: | :---: |
|  |  |  |  |
| 32.97167 | $0.1004 E-04$ | 0.0 | -0.000006 |
| 32.97093 | $0.3245 E-04$ | -0.5 | -0.000628 |
| 32.96943 | $0.7794 E-04$ | -1.6 | -0.001986 |
| 32.96783 | $0.1265 E-03$ | -1.5 | -0.001875 |
| 32.95941 | $0.3818 E-03$ | -1.7 | -0.002163 |
| 32.95113 | $0.6330 E-03$ | -2.2 | -0.002806 |

Listing of -OUT at 16:39:59 on AUG 44. 1987 for CCid=DBRU

| 1 | Hydrogen image plane fringe data, set 260387.1 |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| 3 | Number of data points = 9 |  |  |  |
| 3 |  |  |  |  |
| 4 | Critical Ten | ture = 32 | K |  |
| 5 (k) |  |  |  |  |
| 6 | Temp (K) | $t$ | N1-Nv | rho d |
| 7 ( 7 ( 7 NV |  |  |  |  |
| 8 | 32.92961 | 0.7561E-04 | -1.7 | -0.002114 |
| 9 | 32.92155 | 0.3204E-03 | -1.9 | -0.002399 |
| 10 | 32.91328 | 0.5715E-03 | -1.9 | -0.002432 |
| 11 | 32.90503 | 0.8220E-03 | -1.9 | -0.002460 |
| 12 | 32.87263 | 0.1806E-02 | -3.5 | -0.004482 |
| 13 | 32.82498 | 0.3253E-02 | -2.6 | -0.003492 |
| 14 | 32.76949 | 0.4938E-02 | -1.9 | -0.002751 |
| 15 | 32.71372 | 0.6631E-02 | -1.5 | -0.002367 |
| 16 | 32.65207 | 0.8503E-02 | -0.9 | -0.001757 |

Listing of -OUT at $16: 38: 07$ on AUG 14. 1987 for CCidxDBRU


Listing of -DUT at 16:42:29 on AUG 14, 1987 for CCid=DBRU


B-4 Hydrogen Compressibility Data
Listing of -OUT at 14:52:54 on AUG 14, 1987 for CCid=DBRU

| 1 | Hydrogen compressibility data. |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| 2 3 | Data set | $t$ | $k$ (fringes/mm) | k* |
| 4 |  |  |  |  |
| 5 | 260387.1 | 8.584E-4 | 0.006 | 146. |
| 6 | vapour | 3.568E-4 | 0.009 | 219. |
| 7 |  | 1.120E-4 | 0.424 | 10308. |
| 8 |  |  |  |  |
| 9 | 070487.1 | 1.247E-3 | 0.010 | 243. |
| 10 | vapour | 4.201E-4 | 0.066 | 1605. |
| 11 |  | 3.099E-4 | 0.113 | 2747. |
| 12 |  | 2.243E-4 | 0.201 | 4887. |
| 13 |  | 1.595E-4 | 0.273 | 6637. |
| 14 |  | 9.162E-5 | 0.412 | 10017. |
| 15 |  | 5.814E-5 | 0.453 | 11015. |
| 16 |  |  |  |  |
| 17 | 070487.2 | 3.557E-4 | 0.119 | 2893. |
| 18 | vapour | 2. 197E-4 | 0.178 | 4328. |
| 19 |  | 1.742E-4 | 0.197 | 4790. |
| 20 |  | 1.321E-4 | 0.304 | 7391. |
| 21 |  | 6.272E-5 | 0.799 | 19425. |
| 22 |  | 6.848E-5 | 0.899 | 21857. |
| 23 - 24 ( ${ }^{\text {a }}$ |  |  |  |  |
| 24 | 070487.3 | 4.215E-4 | 0.066 | 1605. |
| 25 | vapour | 2.245E-4 | 0. 158 | 3841. |
| 26 |  | 1.300E-4 | 0.322 | 7829. |
| 27 |  | 6.181E-5 | 1.230 | 29903. |
| 28 |  |  |  |  |
| 29 | 260387.1 | 3.477E-4 | 0.026 | 632. |
| 30 | 1 iquid | 1.029E-4 | 0.288 | 7002. |
| 31 |  |  |  |  |
| 32 | 070487.1 | 1.247E-3 | 0.010 | 243. |
| 33 | 1 iquid | 4.201E-4 | 0.080 | 1945. |
| 34 |  | 3.099E-4 | 0.096 | 2334. |
| 35 |  | 2.243E-4 | 0. 184 | 4473. |
| 36 |  | 1.595E-4 | 0.277 | 6734. |
| 37 |  | 9.162E-5 | 0.427 | 10381. |
| 38 |  | 5.814E-5 | 0.652 | 15851. |
| 39 |  |  |  |  |
| 40 | 070487.2 | 3.557E-4 | 0.056 | 1362. |
| 41 | 1 iquid | 2. 197E-4 | 0. 123 | 2990. |
| 42 |  | 1.742E-4 | 0.149 | 3623. |
| 43 |  | 1.321E-4 | 0.197 | 4790. |
| 44 |  | 6.272E-5 | 0.490 | 11913. |
| 45 |  | 6.848E-5 | 0.587 | 14271. |
| 46 |  |  |  |  |
| 47 | 070487.3 | 4.215E-4 | 0.048 | 1167. |
| 48 | 1 1quid | 2.245E-4 | 0.096 | 2334. |
| 49 |  | 1.300E-4 | 0.168 | 4084. |
| 50 |  | 6.181E-5 | 0.417 | 10438. |
| 51 ( 51 |  |  |  |  |
| 52 | 260386.1 | 1.913E-5 | 15.49 | 376593. |
| 53 | $>\mathrm{TC}$ | 6.859E-5 | 2.53 | 61509. |
| 54 |  | 9.170E-5 | 2.76 | 67101. |
| 55 |  | 9.838E-5 | 2. 12 | 51541. |
| 56 |  | 1.691E-4 | 2. 13 | 51785. |
|  |  |  |  |  |
| 58 | 250287.6 | 4.850E-6 | 17.92 | 435456. |
| 59 | > TC | 2.090E-5 | 3.57 | 86751. |
| 60 |  | 3.400E-5 | 1.976 | 48017. |
| 61 |  | 5. 190E-5 | 1.142 | 27751. |
| 62 |  | 8. 160E-5 | 0.711 | 17277 . |
| 63 |  | 1. 460E-4 | 0.352 | 8554 |

## APPENDIX C

## Computer Programs

## C-1 BIGFIT - Coexistence Curve Data Analysis Program

BIGFIT performs nonlinear least-squares fits to data consisting of temperatures and fringe numbers or temperatures and densities. It will fit up to six parameters to the order parameter or up to five parameters to the diameter. The number of parameters and their initial values are chosen interactively by the user. BIGFIT can plot the data and the fit to assist the user in the selection of starting parameter values or to allow visual evaluation of the fit.

Data is read in from Unit 10. Unit 11 is an additional input file containing constants such as $\rho_{c}, n_{\boldsymbol{c}}$, etc. Fit results and additional information are output to Unit 4. While BIGFIT is intended to be an interactive program, it can be run in batch if an additional input file assigned to Unit 5 is provided. This file would contain the commmands that would normally be entered from the terminal.

With simple modifications, BIGFIT can be used to fit compressibility data. By altering the fitting function provided in the subroutine CALCR and the plotting routines in GRAF2 and GRAF3, fits to other types of data could be done.

BIGFIT contains a number of subroutines whose functions are as follows:
START gets the type of input data and the type of fit required.
GETDAT reads in the data and converts it to Kelvin temperatures and densities.

LL reads in supplementary data from Unit 11.
RHOD calculates values of the coexistence curve diameter to be used in calculating densities.

SETLIN sets up for and calls a routine to do a linear fit to $\Delta \rho^{4} v s . T$, and plots the results.

NONLIN gets parameters and constants for nonlinear fits, calls fitting and plotting routines and outputs the fit results.

CALCR is called by the nonlinear fitting routine. It calculates the fitting function and resuiduals.

GRAF2 plots the order parameter data and the nonlinear fit to it on a sensitive $\log -\log$ plot, and plots the residuals.

GRAF3 plots the diameter data and fit.
DUMP writes the data, fit, and residuals to the output file.
INTGET reads an integer from the keyboard.
AID is a rudimentary HELP routine; it contains information about data input formats.

## Listing of BIGFIT

```
listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
C BIGFIT ---- PURE FLUID COEXISTENCE CURVE ANALYSIS PROGRAM
                JOHN DEBRUYN
                WRITTEN MARCH }8
        IMPLICIT REAL*B (A-H,O-Z)
        DIMENSION A(6),Q(6),DATL(500),DATV(500),DATAR(500),DATAT(500)
        DIMENSION SIGMAY(500)
        LOGICAL*4 IFLAG,JFLAG
        COMMON/Q/ A,Q,DATL,DATV,DATAR,DATAT
        COMMON /INFO/ COR,NS,NE,NN,NPTS
        COMMON /LLUUNK/ A1B1,ABCD2,ACELL
        COMMON /DIAM/ TC,DX1.DX2.DX3
    C
    c
        TC=0.000
        IFLAG=.FALSE.
        JFLAG=.FALSE.
    CALL START(IDAT,ITEMP,IFIT,JFLAG)
    CALL GETDAT(IDAT.ITEMP.IFIT.IFLAG)
        JFIT=IFIT+1
        GOTO(20,30,10).JFIT
    LINEAR FIT TD N**1/B VS T
        CALL SETLIN(NN)
        GOTO 40
    C
    ORDER PARAMETER FIT
    2O CALL NONLIN(NN,IFIT,IDAT)
    GOTO 4O
    C OIAMETER FI
    30
    c
    40 WRITE (6,600)
    NOYES=1NTGET(1)
    IF(NOYES.EQ.1) GOTO 5
    WRITE(6.601)
    C
    600 FORMAT(1X,'Again? (1,0)')
    601 FORMAT(/,/,1X.'End of run')
    C
        CALL PLOTND
        STOP
        END
    C
    c
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
    59 SUBROUTINE START(IDAT,ITEMP,IFIT,JFLAG)
60 C C THIS SUBROUTINE GETS THE FORMAT OF THE INPUT DATA
    C FROM THE DATA FILE AND FIT INSTRUCTIONS FROM THE KEYBOARD
    C
        LOGICAL*4 JFLAG
    C
        IF(JFLAG) GOTO 10
        IFIT=O
        JFLAG=.TRUE.
        WRITE(6,600)
    C
        READ(10.100) IDAT.ITEMP
        IF((IDAT.GT.2).OR.(ITEMP.GT.2)) GOTO 998
    C
        JDAT = IDAT+ 1
        JTEMP = ITEMP+1
        GOTO (1,2,3),JDAT
    C WRITE(6,610)
        WRITE(4.610)
        GOTO 4
        WRITE(6,611)
        WRITE(4,611)
        gOTO 4
        WRITE(6,612)
        WRITE(4.612)
    C GOTO (5,6,7).JTEMP
    5 WRITE(6.620)
        WRITE(4,620)
        GOTO 10
        WRITE(6,621)
        WRITE(4.621)
        GOTO 10
    7 WRITE (6.622)
        WRITE(4.622)
    C
    10 IF(IDAT.EQ.O) GOTO 11
        WRITE(6.601)
        GOTO }1
    11 WRITE(6,602)
    12 IFIT=INTGET(3)
        IF(IFIT.EQ.3) GOTO 999
        IF((IDAT.EQ.O).AND.((IFIT.NE.O).AND.(IFIT.NE.2))) GOTO I1
    C RETURN
    C
    998 CALL AID(O)
        STOP
    999 CALL AID(1)
        STOP
    C FORMAT STATEMENTS
    c
    600 FORMAT(/,1X,'GENERAL COEXISTENCE CURVE ANALYSIS PROGRAM'./.
        :10X,'WRITTEN 03/87')
    601 FORMAT(/.1X.'TyPE O to fit ORDER PARAMETER'./,
```

```
Listing of BIGFIT at 12:33:41 on AUG 14. 1987 for CCid=DBRU
l17 :6X,'1 ...... DIAMETER',/' 
119 :6X,'3 ...... to get HELP.')
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
    602 FORMAT(1X,'Type 0 to fit ORDER PARAMETER'./.
        :6X.'2 ...... LINEAR FIT to N**1/beta'./.
        :6X,'3 ...... to get HELP.')
    610 FORMAT(/.1X.'Input file contains FOCAL PLANE data.')
    611 FORMAT(/,1X,'Input file contains IMAGE PLANE data.')
    612 FORMAT(/,1X.'Input file contains DENSITY data.')
    620 FORMAT(1X.'Input temperatures are in KELVIN.')
    621 FORMAT(4X.'Input temperatures are in CELSIUS.')
    622 FORMAT(1X,'Input temperatures are REDUCED.')
    100 FORMAT(2I\)
    c
        END
    C
    C
    C
    C
        SUBROUTINE GETDAT(IDAT,ITEMP.IFIT.IFLAG)
        IMPLICIT REAL*8(A-H.O-Z)
        DIMENSION A(6),Q(6),DATL(500),DATV(500),DATT(500),DATR(500),DATAR(500)
        DIMENSION DATD(500), DATAT(500)
        LOGICAL*4 IFLAG
        COMMON/Q/ A,Q,DATL,DATV,DATAR,DATAT
        COMMON /INFO/ COR,NS,NE,NN,NPTS
        COMMON /LLJUNK/ A1B1,ABCD2,ACELL
        COMMON /DIAM/ TC,DX1,DX2.DX3
    C
    C...GETDAT READS IN DATA FROM FILE }1
    C. . .DATT =TEMPERATURES
    C...DATR=FRINGE COUNT
    C
        IF (IFLAG) GOTO 43
        IFLAG=.TRUE.
    C IFLAG=.TRUE
    READ(10,100) NPTS,COR1,COR2
    C
        JDAT = IDAT+1
        GOTO (10,20,30), JDAT
    C
    C...fOCAL PLANE DATA
    C
    10 IF(ITEMP.EQ.2) GOTO 11
    C
        DO 12 I=1,NPTS
            READ(10,101) DATT(I),DATR(1)
            CONTINUE
        GOTO 4!
    C
    C T IS REDUCED IN DATA FILE
    11 DO 13 I=1,NPTS
        READ(10.102) DATT(I).DATR(I)
        CONTINUE
        goto 44
    C
    C...IMAGE PLANE DATA
```

```
Listing of BIGFIT at 12:33:41 On AUG 14, 1987 for CCid=DBRU
    175
177 C
178
179
180
181
182
183
184
185
186
187
188
1 8 9
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
        DO 22 I=1,NPTS
            READ(10,103) DATT(I),DATR(I),DATL(I),DATV(I)
            DATD(I)=DATL(I)-DATV(I)
            IF (DATR(I).EQ.O.) DATR(I)=DATL(I)+DATV(I)
    22 CONTINUE
        GOTO 41
    C
    C T IS REDUCED IN DATA FILE
    21 DO 23 I= 1,NPTS
        READ(10,104) DATT(I),DATR(I),DATL(I),DATV(I)
        DATD(I)=DATL(I)-DATV(I)
        IF (DATR(I).EQ.O.) DATR(I)=DATL(I)+DATV(I)
        CONTINUE
        GOTO 41
    C...DENSITY DATA
    30 IF(ITEMP.EQ.2) GOTO 31
    C DO 32 I=1,NPTS
        READ(10,105) DATT(I),DATV(I),DATL(I),DATD(I)
        DATR(I)=DATL(I)-DATV(I)
        IF(DATD(I).EQ.O.) DATD(I)=DATL(I)+DATV(I)
        CONTINUE
        GOTO 41
    C T IS REDUCED IN DATA FILE
    31 DO 33 I=1,NPTS
        READ(10.106) DATT(I),DATV(I),DATL(I),DATD(I)
        DATR(I)=DATL(I)-DATV(I)
        IF(DATD(I).EQ.O.) DATD(I)=DATL(I)+DATV(I)
    33 CONTINUE
    C
    C...fORMAT STATEMENTS FDR DATA INPUT
    C
    101 FORMAT(1X,F13.5,3X,F7.1)
    102 FORMAT(1X,E16.8,2X,F5.1)
    103 FORMAT(4X,F13.5,3X,F8.2,3X,F8.2,3X,F8.2)
    104 FORMAT(1X,E16.8,2X,F6.2,4X,F8.2,3X,FB.2)
    105 FORMAT(1X,F9.5,3X,F10.7,3X,F10.7,3X,F10.7)
    106 FORMAT(1X,E16.8,3X,F10.7,3X,F10.7,3X,F10.7)
    C
    C READ LORENTZ-LORENZ STUFF FROM II IF IT HAS BEEN SPECIFIED
    CI ILL=O
        IF(IDAT.EQ.2) GOTO }4
    C
        WRITE(6.600)
        ILL=INTGET(1)
        IF(ILL.NE.1) GOTO 42
        WRITE(6.601)
        READ(5.501) TC
        CALL LL
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
```

233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 254 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266
267 268
269 270 271 272 273 274

```
                            GOTO }4
C
C
C
C
C
WRITE(6,602) NPTS
    WRITE(4,602) NPTS
    C
        WRITE (6,603)
        WRITE(6.604)
        READ(5.500) ANS, ANE
    C
        IF (ANE .EQ.O.)ANE = DFLOAT (NPTS)
        IF(ANS.EQ.O.) ANS=1.ODO
        NS=ANS
        NE = ANE
        WRITE(6,605)NS,NE
        WRITE(4,400)
        WRITE(4,401)NS,NE
    C
    C CORRECTION TO FRINGE NUMBER
    C
        IF(IDAT.EQ.O) COR=COR2-0.5DO
        IF(IDAT.EQ.1) GOTO 45
        IF(IDAT.EQ.2) COR=0.ODO
        GOTO }4
    C
    45 IF(IFIT.NE. 1) GOTO 46
        COR=COR2
        COR3=(COR1-1.ODO)/2.ODO
        GOTO 47
    C
    46 COR=COR1-1.ODO
    C
    C TEMP CORRECTION
    C7 TCOR=273.15DO
        IF(ITEMP.NE.1) TCOR=O.ODO
    C
    C
        NN=NE-NS+1
        FACTLL=1.ODO
        DO 50 I=1,NN
            J=I+NS-1
            DATAT(I)=DATT(U)+TCOR
            IF(IFIT.EQ.1) GOTO 52
    C
    C...ORDER PARAM FIT
    C
        IF((ILL.NE.1).OR.(IDAT.EQ.2)) GOTO 54
        FACTLL=ACELL/(2*(A1B1+ABCD2*RHOD(DATAT(I))))
    51 DATAR(I)=(DATR(U)+COR)*FACTLL
        GOTO 50
    C
    C...DIAM FIT
    C
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
```

```
291 52 IF((ILL.NE.1).OR.(IDAT.EO.2)) GOTO 53
```

291 52 IF((ILL.NE.1).OR.(IDAT.EO.2)) GOTO 53

```
        W1=0.5DO*ABCD2/(A1B1**2)
```

        W1=0.5DO*ABCD2/(A1B1**2)
        W2=(DATL(J)+COR3+COR2/2.ODO)**2 + (DATV(J)+COR3-COR2/2.ODO)**2
        W2=(DATL(J)+COR3+COR2/2.ODO)**2 + (DATV(J)+COR3-COR2/2.ODO)**2
        DATAR(I)=((DATD(U)+COR)*ACELL - W1*W2*ACELL**2)/(2*A1B1)
        DATAR(I)=((DATD(U)+COR)*ACELL - W1*W2*ACELL**2)/(2*A1B1)
        GOTO 5O
        GOTO 5O
        53 DATAR(I)=(DATD(J)+COR)*FACTLL
        53 DATAR(I)=(DATD(J)+COR)*FACTLL
    C
    C
    5O CONTINUE
    5O CONTINUE
    C...FORMAT STATEMENTS
    C...FORMAT STATEMENTS
    600 FORMAT(1X./.'Did you specify FILE 11 containing LL data? (1.0)')
    600 FORMAT(1X./.'Did you specify FILE 11 containing LL data? (1.0)')
    601 FORMAT(1X.'Input TC to use for diameter correction.')
    601 FORMAT(1X.'Input TC to use for diameter correction.')
    FORMAT(ix,'Number of data points in file =',I6)
    FORMAT(ix,'Number of data points in file =',I6)
    FDRMAT(iX,'Start and end data points for fit')
    FDRMAT(iX,'Start and end data points for fit')
    FORMAT(1X,9x,':',9X,':')
    FORMAT(1X,9x,':',9X,':')
    605 FORMAT(2I1O)
    605 FORMAT(2I1O)
    500 FORMAT(F10.4,F10.4)
    500 FORMAT(F10.4,F10.4)
    501 FORMAT(F12.6)
    501 FORMAT(F12.6)
    400 FORMAT(/, 1X,'****************************************************',
    400 FORMAT(/, 1X,'****************************************************',
    401 FORMAT(IX,/,'Fit starts at pt #', 2X,I4,2X,'and ends at pt #', 2X,I4,/)
    401 FORMAT(IX,/,'Fit starts at pt #', 2X,I4,2X,'and ends at pt #', 2X,I4,/)
    100 FORMAT(I6,F4.1,F4.1)
    100 FORMAT(I6,F4.1,F4.1)
    C
    C
    C
    C
        RETURN
        RETURN
        END
        END
    C
    C
    C
    C
    C
    C
    C
    C
        SUBROUTINE LL
        SUBROUTINE LL
    C
    C
    C...READS LORENZ-LORENTZ DATA FROM FILE 11
    C...READS LORENZ-LORENTZ DATA FROM FILE 11
    C
    C
        IMPLICIT REAL*8(A-H,O-Z)
        IMPLICIT REAL*8(A-H,O-Z)
        COMMON /LLUUNK/ A1B1.ABCD2.ACELL
        COMMON /LLUUNK/ A1B1.ABCD2.ACELL
        COMMON /DIAM/ TC,DX1,0\times2.DX3
        COMMON /DIAM/ TC,DX1,0\times2.DX3
    C
    C
    C ALC=LCRIT...DLDR=SLOPE AT CRIT...D2LDR2=2ND DERIV AT CRIT
    C ALC=LCRIT...DLDR=SLOPE AT CRIT...D2LDR2=2ND DERIV AT CRIT
    C RHOC=CRIT DENS...ANC=CRIT REFR INDEX
    C RHOC=CRIT DENS...ANC=CRIT REFR INDEX
    C DXi=COEFFS OF DIAMETER FIT
    C DXi=COEFFS OF DIAMETER FIT
    C
    C
        READ(11,110) ALC,DLDR,D2LDR2,RHDC, ANC
        READ(11,110) ALC,DLDR,D2LDR2,RHDC, ANC
        READ(11,111) DX1,DX2,DX3
        READ(11,111) DX1,DX2,DX3
    111 FORMAT(F2O.10./,F20.10./,F20.10)
    111 FORMAT(F2O.10./,F20.10./,F20.10)
    110 FORMAT(F20.10./.F20.10,/.F20.10./.F20.10./.F20.10)
    110 FORMAT(F20.10./.F20.10,/.F20.10./.F20.10./.F20.10)
    C
    C
        ANSQ = ANC * ANC
        ANSQ = ANC * ANC
        AN1=ANSQ-1.ODO
        AN1=ANSQ-1.ODO
        AN2 =ANSO+2.ODO
        AN2 =ANSO+2.ODO
        AN3 =3.ODO*ANSQ-2.ODO
        AN3 =3.ODO*ANSQ-2.ODO
    C
    C
        BB1=RHOC*DLDR/ALC
        BB1=RHOC*DLDR/ALC
    C
    C
        A1=AN1*AN2/(6.ODO*ANC)
        A1=AN1*AN2/(6.ODO*ANC)
        A2=A1*AN1*AN3/(6.00O*ANSO)
        A2=A1*AN1*AN3/(6.00O*ANSO)
    C
    ```
    C
```

```
Listing of BIGFIT at 12:33:41 on AUG 14. 1987 for CCid=DBRU
```



350 351 352 353 354 355
356
357
358
359
360
361
362
363
364
365
366
367 368
369 370
371
372
373
374
375
376
377
378
379
380
381
382
383
384 385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406

```
BB2 \(=\) BB 1*2.ODO* (3.ODO*ANSQ*ANSQ+ANSQ+2.ODO)/(AN1*AN3) CC2=6.ODO*ANSQ*D2LDR2*RHOC*RHOC/(AN1*AN3*ALC) DD2 \(=\) BR 1*BB 1
C
A1B1=A1* (1.000+BB1)
\(A B C D 2=A 2 *(1.0 D 0+B B 2+C C 2+D D 2)\)
C
c
ALAMDA \(=6.328 \mathrm{D}-5\)
CELL=0.525DO
ACELLEALAMDA/CELL
C
C
RETURN
END
C
C
DOUBLE PRECISIDN FUNCTIDN RHOD(T)
IMPLICIT REAL*B(A-H,O-Z)
COMMON /DIAM/ TC.DX1,DX2,DX3
C
c. . CALC diameter of coex curve using fit from prism data
C . . . RHOD \(=(\) RHOL + RHOV- \(2 *\) RHOC \() /(2 *\) RHOC \()\)
C
IF (TC.NE.O.O) GOTO 10
RHOD \(=0.000\)
RETURN
C
c
\(10 \quad\) SMALLT=(TC-T)/TC
IF (SMALLT.LT.O.O)SMALLT \(=0.000\)
D \(1=\mathrm{DX} 1\)
D2=DX2*SMALLT**0. 89
D3=DX3*SMALLT
C
C
C
RETURN
END
C
C
C
C
C
C
c
SUBROUTINE SETLIN(NN)
IMPLICIT REAL* 8 (A-H,O-Z)
LOGICAL* 4 LK
DIMENSION A (6), Q(6), DATL(500), DATV(500), DATAR(500). DATAT (500)
OIMENSION Y(500), YF(500),YD(500),WT(500)
DIMENSION S(10), SIGMA (10), AA (10), B( 10), P(10)
REAL*4 TP(500),YP(500),FX(10),FY(10)
C
COMMON/Q/ A,Q,DATL,DATV,DATAR,DATAT
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCId=DBRU
    4 0 7
    4 0 8
    4 0 9
    410
    411
    4 1 2
    4 1 3
    414
    415
    4 1 6
    417
    4 1 8
    419
    4 2 0
    4 2 1
    4 2 2
    4 2 3
    4 2 4
    4 2 5
    4 2 6
    4 2 7
    4 2 8
    4 2 9
    4 3 0
    4 3 1
    4 3 2
    4 3 3
    4 3 4
    435
    4 3 6
    4 3 7
    4 3 8
    4 3 9
    440
    4 4 1
    4 4 2
    4 4 3
    444
    4 4 5
    446
    4 4 7
    448
    4 4 9
    450
    451
    4 5 2
    4 5 3
    4 5 4
    4 5 5
    456
    457
    4 5 8
    4 5 9
    4 6 0
    4 6 1
    4 6 2
    4 6 3
    4 6 4
    C
    c SETLIN SETS UP FOR AND CALLS LINEAR LSF ROUTINE
    C FITS TO DRHO**1/BETA VS T
    C
        WRITE (6,600)
        READ(5.500) BETA1
        IF(BETA1.EQ.O) BETA1=0.327DO
        ABETA=1.ODO/BETA1
        DO 2OI=1,NN
            Y(I)=DATAR(I)**ABETA
            YP(I)=Y(I)
            TP(I)=DATAT(I)
    2O CONTINUE
    C
        LK=.TRUE.
        K=1
        NWT=O
    C...CALL FITTING ROUTINE
    C C
        CALL DOLSF(K,NN,DATAT,Y,YF,YD,WT,NWT,S,SIGMA,AA,B,SS,LK,P)
    C O
    C...OUTPUT RESULTS
        TC=-1.ODO*(P(1)/P(2))
        WRITE(6,601)BETA1.TC
        WRITE(4,601)BETA1,TC
    C
    C
        WRITE(6,602)
        IF (INTGET(1).NE.1) GOTO 30
    C...plot results
        CALL ALAXIS('Temperature (K)'. 15,'N**(1/b)'.8)
        CALL ALSCAL(O..O..O..O.)
            CALL ALGRAF(TP,YP,NN,-4)
        C
        C
    C FX(1)=TC
        FX(1)=TC
        FX(2)=DATAT(1)
        FY(2)=YF(1)
        FX(3)=DATAT(NN)
        FY(3)=YF(NN)
    C
        CALL ALGRAF(FX,FY,-3,0)
        CALL ALDONE
    c
    500 FORMAT(F16.8)
    600 FORMAT(1X.'Input value, to use for beta (CR for 0.327)')
    601 FORMAT(1X,'STRAIGHT LINE FIT OF COEX CURVE DATA USING BETA= '
        :,F6.4,2X,'GIVES'./.'TC= ',F11.5)
    602 FORMAT(1X,'PLOT? (1=YES, O=NO)')
    C
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
    465 30 RETURN
    4 6 6 ~ E N D
    467
    4 6 8
    4 6 9
    4 7 0
    4 7 1
    4 7 2
    4 7 3
    474
    4 7 5
    4 7 6
    4 7 7
    478
    4 7 9
    4 8 0
    481
    4 8 2
    4 8 3
    4 8 4
    4 8 5
    4 8 6
    487
    4 8 8
    4 8 9
    4 9 0
    4 9 1
    4 9 2
    4 9 3
    4 9 4
    4 9 5
    4 9 6
    4 9 7
    4 9 8
    4 9 9
    5 0 0
    501
    502
    5 0 3
    504
    504
5 0 5
506
5 0 7
    508
5 0 9
    510
    511
512
513
514
515
516
517
518
519
5 2 0
5 2 1
522
C
        SUBROUTINE NONLIN(NN,IFIT,IDAT)
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION A(6),Q(6),DATL(500),DATV(500),DATAR(500),DATAT(500)
        DIMENSION P(6),V(5000),IV(70)
        COMMON/Q/ A,Q,DATL,DATV,DATAR,DATAT
        COMMON /DIAM/ TC.DX1.DX2.DX3
        EXTERNAL CALCR
    C
    C...NONLIN CONTROLS NONLINEAR FITTING I/O
    C...SET INITIAL PARAMETERS AND CONSTANTS
    C M=0
            M=0
            NP=6
            WRITE(6,600)
            GOTO }1
10 NP=5
            WRITE(6,601)
    c
    1f IF (IFIT.NE.O) GOTO 12
            WRITE(6,606)
            GOTO }1
    12 WRITE (6.607)
    C C...NUMBER OF PARAMETERS
13 WRITE (6.602)
    M1=INTGET(NP)
            IF (M1.EQ.O.AND.M.NE.O) M1=M
            IF(M1.EQ.O) GOTO 92
            M=M1
    c
    c...input initial values
    c
            WRITE(6.603)
            WRITE(6,604)
            WRITE(6.605)
            WRITE(6,608)
    C
            J=1
            DO 20 I=1.NP
            WRITE(6,609) I
            READ(5,500)K,X
            IF (K.EQ.1) GOTO 21
            IF (K.EQ.2) GOTO 23
            Q(I)=X
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
```

523
524
525
526
527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543
544
545
546
547
548 549
550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575
576
577
578
579 580

```
GOTO 20
21 P(J)=x
                O(I)=9999.
                J= J+1
                GOTO 2O
23 IF (Q(I).EQ.9999.) J=J+1
C
2O CONTINUE
C }\quadJ=J-
        IF (J.NE.M) GOTO 92
    C PLOT FIT AND RESIDUALS
    c ROUTINE GRAF2 DOES THE WORK
    WRITE(6,610)
        IF(INTGET(1).NE.1) GOTO 31
    30 WRITE(6,611)
        IRES=INTGET(1)
    C
        IF (IFIT.EQ.O) CALL GRAF2(NN,P,IRES)
        IF (IFIT.EQ.1) CALL GRAF3(NN,P,IRES)
    C
    C...FIND OUT WHAT TO DO NEXT
    31 WRITE(6,612)
        NOYES=INTGET(2)
        IF (NOYES.EQ.1)GOTO 11
        IF (NOYES.EQ.O)GOTO 5O
    C
    c SET UP NL2SNO
        CALL DFALT(IV,V)
        IV(14)=1
        IV(21)=4
        IV(15)=-2
        V(42)=0.
        V(29)=1.00-13
        V(40)=1.00-13
        IV (17)=400
        IV (18)=400
        IPARM=IFIT
    C
    35 CALL NL2SNO(NN,M,P,CALCR,IV,V,IPARM,RPARM,FPARM)
    C OUTPUT RESULTS TO SCREEN AND FILE 4
        DO 40 I=1.NP
            IF (Q(I).EQ.9999.O) GOTO 41
            WRITE(4,400)I,A(I)
            WRITE(6,400)I,A(I)
            GOTO 40
            WRITE(4,401)I,A(1)
            WT WRITE(6,401)I,A(I)
            40 CONTINUE
            C
            THIS VALUE OF TC IS SENT BACK TO RHOD
            AND USED TO CALC DIAMETER CORRECTION
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
```



```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCId=DBRU
    639 DIMENSION A(6),Q(6),DATL(500).DATV(500),DATAR(500),DATAT(500),SMALLT(500)
    640 COMMON/Q/ A.Q,DATL,DATV,DATAR,DATAT
641
642
643
644
645
646
647
648
6 4 9
650
6 5 1
652
653
654
655
656
657
658
659
660
6 6 1
662
663
664
665
666
667
668
669
6 7 0
6 7 1
672
6 7 3
674
675
676
677
678
679
680
6 8 1
682
683
684
685
686
687
688
689
690
691
692
6 9 3
694
695
696
C
C...CALCR CALCULATES NONLINEAR FUNCTION AND RESIDUALS
C...FOR NONLINEAR FITTING PROGRAM
c
    NP=6
    IF (IPARM.EQ.1) NP=5
    C
        J=1
        DO 10 I= I,NP
            IF (Q(I).EQ.9999.0) GOTO 11
            A(I)=Q(I)
            GOTO 10
            1 A(I)=P(U)
                J=J+1
    10 CONTINUE
    C
    C CONSTRAINTS GO HERE IF WANTED
    IF (IPARM.NE.O) GOTD 30
    C C. . . COEX CURVE
    DO 20 I=1,N
                SMALLT(I)=DABS((A (2)-DATAT(I))/A(2))
                R(I)=A(1)*SMALLT(I)**A(3)
                RZ=A(4)*SMALLT(I)**A(6) + A(5)*SMALLT(I)**(2*A(6))
                R(I)=R(I)*(1.ODO+RZ)
        R(I)=R(I)-DATAR(I)
    20 CONTINUE
    C
        RETURN
    C
    C. . DIAMETER
    C
    30 DO 31 I=1,N
        SMALLT(I)=DABS((A(1)-DATAT(I))/A(1))
        R(I)=A(2)+A(3)*SMALLT(I)**0.89 + A(4)*SMALLT(I)
        R(I)=R(I)+A(5)*SMALLT(I)**1.39
        R(I)=R(I)-DATAR(I)
    31 CONTINUE
    C
        RETURN
        ENO
    C
    C
    C
        SUBROUTINE GRAF2(NN,P,IRES)
        REAL*B A(6),Q(6),DATL(500),DATV(500),DATAR(500).DATAT(500)
            REAL*B P(6)
            REAL*4 RESID(500), XT(500), YR(500), YRT(500), ZX(10), ZY(10)
            REAL*4 RD(500), XD(500),YD(500), YD 1(500)
            COMMON/Q/ A,Q,DATL,DATV,DATAR,DATAT
    C
    C GRAF2 PLOTS DATA AND NONLINEAR FIT
    C ON SENSITIVE LOG-LOG PLOT
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
\begin{tabular}{llcl}
697 & \(C\) & ARRAYS:DUMP...PLOT & \\
698 & \(C\) & RD RESID & \(\ldots\) RESIDUALS \\
699 & \(C\) & XD XT & \(\ldots\) REDUCED TEMP \\
700 & \(C\) & \(Y D\) & YR \\
701 & \(C\) & YD & \(\ldots\) FIT TO DENSITY/T**BETA \\
702 & \(C\) & &
\end{tabular}
        J=1
        DO 10 I= 1,6
            IF (Q(I).EQ.9999.O) GOTO 11
            A(I)=0(I)
            GOTO 10
            A(I) =P(U)
            J= J+1
        CONTINUE
        DO 2O I=1,NN
            AXT=ABS(SNGL((A(2)-DATAT(1))/A(2)))
            XD(I)=AXT
            XT(I) =ALOG1O(AXT)
            X3=AXT**A(3)
            YR1(I)=DATAR(I)/X3
            R=A(1)*AXT**A(3)
            RZ=A(4)*AXT**A(6) + A(5)*AXT**(2,*A(6))
            YR(I)=R*(1.O+RZ)/X3
            RESID(I)=(YRI(I)-YR(I))/YR(I) *100.
            RD(I)=RESID(I)
            YR1(I)=ALOG1O(YR1(I))
            YD1(I)=YR1(I)
            YR(I)=ALOG 10(YR(I))
            YD(I)=YR(I)
            CONTINUE
            CALL PLCTRL('METRIC',1)
            SCALE ARRAYS AND DRAW GRAPH
            SCAL=5.O
            DO 35 I=1.NN
            XT(I)=(XT(I)+6.0)*SCAL
            CONTINUE
        CALL AXCTRL('LDGS',1)
            CALL AXPLOT('SMALL'T; ',0.0,20.,-6.0,-2.0)
            CALL AXCTRL('LOGS'.O)
            CALL SCALE(YR1,NN.20.,XMIN1,DX1.1)
            DO 55 I=1.NN
                    YR(I)=(YR(I)-XMIN1)/DX1
                    CONTINUE
            CALL AXPLOT('LOG (DELTA RHO/(T**BETA)): ',90.,20.,XMIN1,DX1)
            DO 45 I=1.NN
            CALL SYMBOL(XT(1),YR1(I),0.2,4,0.0,-1)
            CONTINUE
            CALL LINE(XT,YR,NN,1)
            c
            C DO RESIDUALS PLOT IF REQUIRED
```

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
```



```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
```

813 814 815 816 817 818

820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
$\operatorname{XT}(1)=\operatorname{ABS}(\operatorname{SNGL}((\mathrm{A}(1)-\operatorname{DATAT}(1)) / \mathrm{A}(1)))$
YR1(I)=DATAR(I)
$Y R(1)=A(2)+A(3) * X T(I) * * 0.89+A(4) * X T(I)+A(5) * X T(I) * * 1.39$ $\operatorname{RESID}(\mathrm{I})=(\mathrm{YR}(\mathrm{I})-\mathrm{YR}(\mathrm{I}))$ CONTINUE
20
c. . DRAW GRAPH

CALL ALAXIS('(T-TC)/TC',9,'DIAMETER'. 8 )
CALL ALSCAL(O.,O.,O.,0.)
CALL ALGRAF (XT,YR1,NN,-4)
CALL ALGRAF (XT, YR,-NN.O)
CALL ALDONE
C
C... RESIDUALS PLOT

If(IRES.NE. 1) GOTO 30
C
$2 T(1)=0$.
$2 T(2)=0.1$
ZR(1)=0.
$2 R(2)=0$.
CALL ALAXIS('(T-TC)/TC'.9.'RESIDUAL',8)
C CALL ALSCAL(0.0.1,0.0.)
CALL ALGRAF (XT,RESID,NN,-4)
CALL ALGRAF (ZT, ZR,-2.0)
call aldone
C
c... DUMP DATA

C
30
CALL DUMP(RESID,XT,YR,YR1,NN)
c
RETURN
END
C
c
SUBROUTINE DUMP (RD,XD,YD,YD1,NN)
REAL*4 RD(500), XD(500), YD(500), YD1(500)
C
C DUMPS DATA TO FILE 4
WRITE 6,600 )
IF(INTGET(1).NE.1) GOTO 20
C
WRITE(4.400)
DO $10 \mathrm{I}=1$. NN
WRITE(4,401) 1,XD(I),YDI(I),YD(I),RD(I)
CONTINUE
${ }^{10}$
400 FORMAT(13X,'SMALL T',9X,'DATA',9X,'FIT'.7X,'\% RESID'/)
401 FORMAT(1X,16,E16.6,2X,F10.5,2X,F10.5,2X,F10.5)
600 FORMAT( $1 \times .{ }^{\prime}$ Dump data to unit 4? (1.0)')
c
c
20 RETURN
END
C

```
Listing of BIGFIT at 12:33:41 on AUG 14, 1987 for CCid=DBRU
    871 C
    872
    873
    874
    875
    876
    877
    8 7 8
    879
    880
    881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
899
C
INTEGER FUNCTION INTGET(MAX)
    C READS AN INTEGER BETWEEN O AND MAX FROM KEYBOARD
C
    IF(MAX.GT.9) GOTO 3
1 IF(MAX.GT.9)L
        IF(L.GT.MAX) GOTO 2
        INTGET=L
        RETURN
C
    2 WRITE(6,600) MAX
        GOTO 1
C
    C MAX TOO BIG
892 
    C
    3 WRITE(6.601)
        MAX=9
        gOTO 1
    c
    600 FORMAT(1X.'INPUT A NUMBER BETWEEN O AND'.1X,I1)
    500 FORMAT(II)
        601 FORMAT(1X,'...WARNING... VALUE OF MAX SENT TO INTGET TOD BIG, SET = 9')
    C
        END
    C
    C
C
```

SURROUTINE AIO(I)
IF(I.EQ.1) GOTO 10
WRITE(4.400)
WRITE (6.400) GOTO 11 WRITE (4.410) WRITE $(6,410)$ WRITE (4,411) WRITE (4.412) WRITE (4, 413) WRITE (6,411) WRITE(6,412) WRITE(6.413)
C
C
C
400
FORMAT( $/ \mathrm{iX}^{\text {' Your }}$ input file appears to be in the wrong format
'./. 'for this program. A description of the proper input'./."
format follows. ')
410 FORMAT(/.20X,'Fitting program HELP routine')
411 FORMAT(/.'A copy of these instructions is being written onto your output file wi. ././.'The firgt ifne of your inpu t file must coritain a two digit number in the'./. ifirst two colums. This mumber identifies the type of input data as fol lows:'
$: / f / f$ tox, 'first digit: 0. . Focal plane data'./.

```

```

10x.'Second digit: O...T in Keivin'./,24X.'1...T in Ceisius'..
:24X,'2...t in reduced temperature'./)
412 FORMAT''The second line must be in the form NNNNNNAA.ABB.B, starting in column i.'./.'Here NNNNNN is the number of data points in the file in 16 format: AA.A'./.'is O. for i-plane data which is to have 1. subtracted from the total'
./. "fringe number, and is i. otherwise: BB.B is a correction
$\because$ to be added to the'./.'total fringe number for f-plane'
.' data or to NI-Nv for i-plane data.'./)
413 FORMAT('The data follows. starting on the third ifne of the file. The format statements'. $/$. below ere used to read in the data. They are labelled by the appropriate'./.'two-digit number as described above, and followed by the quantities to be'
: .' read.'././

```


```

: 4X.'T.Ntot .NI,Nv'./
:.5X,'12 FORMAT(1X,E16.8.2X,F6.2,4X,FB.2.3X,F8.2)'.
:4X.'t.Ntot.NI.Nv'./
: 5X,'20.21 FORMAT(1X,F9.5,3X,F10.7,3X,F10.7.3X,F10.7)'.
2X.'T,Rhov,Rhol.Rhod'.'
$.5 \mathrm{X}, \mathrm{C}^{22}$ FORMAT(1X,E16.8,3X,F10.7,3X,F10.7.3X,F10.7)'
1x. 't.Rhov, Rho I, Rhod'./)
RETURN
END

```

C-2 LLNEWER and COEX86 - Prism Cell Data Analysis Programs
The two programs listed in this section were used to analyze the data for \(\mathcal{L}(\rho)\) and the coexisting densities obtained from the prism experiment.

LLNEWER reads in data in the from of micrometer readings and cell masses, calculates the Lorenz-Lorentz coefficient, fits the results to a polynomial in the density, then plots and outputs the results. A variant of this program called LLFITTON (not listed here) fits \(\mathcal{L}\) to a polynomial in the refractive index.

COEX86 reads in micrometer and thermistor readings and calculates the densities of the coexisting phases as a function of temperature, using the fit to \(\mathcal{L}(n)\) determined by LLFITTON. The coexistence curve as output by COEX86 can be analyzed by BIGFIT, described above.

\section*{Listing of LLNEWER}
```

Listing of LLNEWER at 12:43:06 on AUG 14, 1987 for CCid=DBRU
c
c
C NEW VERSION JULY 1986 INCLUDES POLYNOMIAL FIT TO LL(RHO)
C
C
C
C GET DATA FROM FILE \#4
C GET DATA FROM FILE \#4
READ(4,401) M
C
C GET CELL DATA

```

```

403 FORMAT(F10.5,1X,F8.4,1X,F8.4)
C
WRITE(8,606) CELLM,CELLV,WTMOL
WRITE(6,606) CELLM,CELLV,WTMOL
FORMAT(1X,'CELL MASS = ,F10.4.8X.'CELL VOL. = ,F10.4./.1X.'MOLECULAR
606
C
C PARAMETERS FOR 3RD ORDER POLY FIT TO CALIB DATA
C AND CELL ANGLES
READ(4,404) ALPHA,THFIT(1),THFIT(2),THFIT(3)
WRITE(8.808) ALPHA.(THFIT(I),I=1.3)
808 FORMAT(iX'ALPHA =',F8.4,/, 1X,'MICROMETER FIT PARAMETERS:'.,3E20.10)
404 FORMAT(F8.4,2X,E2O.10.E20.10.E2O.10)
PI=3.14159265DO
ALPHA=ALPHA*PI/180.
C
C
WRITE(8,601) M
601 FORMAT(ix,'NO. DF PTS. = .3X,14,1)
401 FORMAT(1X.14)
C
c
DATA FOR AIR
READ(4,402) AIRM,AIRMIC.ZEROAR
AIRMIC=AIRMIC-ZEROAR
SINAIR=FUNC(AIRMIC,THFIT,3)
THAIR=DARSIN(SINAIR)
COSAIR=DCOS(THAIR)
C
TANALF=DTAN(ALPHA)
C
C
DIMENSION AMASS(200),THFIT(10), ANGAS(200), BMIC(200),AMIC(200),THETA (200)
DIMENSION WT(200),WT2(200),XX(50),YY(50),YYN(50),YYM(50),XXM(50)
DIMENSION ZERO(200),FUNX(200),FUNY(200)
DIMENSION INC(2OO)
LOGICAL*4 LK
CONSTANTS
DATA ANAIR,ANSAFF/1.00029.1.66/
PIETC=12.00O*3.1415927DO
READ(4,403) CELLM,CELLV,WTMOL
C
READ dATA

```
```

Listing of LLNEWER at 12:43:06 on AUG 14. 1987 for CCId=DBRU
59 DO 10 I=1.M
61 IF(ZERO(I).EO.O.) GOTO 2
6 2
63
65
67
402
C
6 9
70
71
72
73
7 4
7 5
76
77 C
78
79
80
81
82
83 C
84
85
86 C
87
88
8 9
90
91
92
93
94
94
95
96
97
98
98
100
101
102
103
104
105
106
107
108
109
109
110
111
112
113
114
115 30
116 605
READ(4,402) AMASS(I), AMIC(I), ZERO(I), INC(I)
BMIC(I)=AMIC(I)-ZERO(I)
GOTO 10
M=M-1
GOTO 1
CONTINUE
FORMAT(1X,F8.4,1X,F7.4.1X,F7.4,2X,I1)
C
CALC SIN THETA
J=M
C
DO 20 I=1.M
SINTH=FUNC(BMIC(I),THFIT,3)
THETA(I)=DARSIN(SINTH)
COSTH=DCOS(THETA(I))
C
C
CALC INDEX OF REFR.
ANGAS(I)=ANAIR*(1.ODO+COSTH-COSAIR+ (SINTH-SINAIR)/TANALF)
C
C
C
RHO(I)=RHO(I )/WTMOL
IF (INC(I).EO.1) GOTO 21
AN2=ANGAS(I)*ANGAS (I)
AN2 1 = AN2-1. ODO
AN22 = 2.ODO*AN2+1.ODO
FUNY(I)=PIETC*AN2*RHD(I)/(AN21*AN22)
FUNX(I)=2.ODO*AN2 1/AN22
C
C
C
CALC LL
ALL(I)=(AN2-1.ODO)/((AN2+2.ODO)*RHO(I))
SUM=SUM+ALL(I)
GOTO 2O
C
21 J=J-1
ALL(I)=0.0
C
2O CONTINUE
AVGLL=SUM/DFLOAT(U)
c
C
OUTPUT RESULTS
WRITE(8,604)
DO 30 I = 1,M
WRITE(B,605) RHO(I),ANGAS(I),ALL(I)
30 CONTINUE
605 FORMAT(3(3X,F12.6))

```
```

Listing of LLNEWER at 12:43:06 on AUG 14, 1987 for CCid=DBRU
117 604 FORMAT(7X,'MASS(G)'.7X.'MIC. RDG.',5X.'DENSITY(G/CC)',3X,'THETA(RAD)',
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174

```
```

    C
    ```
    C
    CALL FIT(FUNX,FUNY,WT2,YYM,XXM,NWT2,J,1)
    CALL FIT(FUNX,FUNY,WT2,YYM,XXM,NWT2,J,1)
    140 C CALL GRAF(RHD,ALL,ANGAS,FUNX,FUNY,XX,YY,YYN,YYM,XXM,M,J)
    140 C CALL GRAF(RHD,ALL,ANGAS,FUNX,FUNY,XX,YY,YYN,YYM,XXM,M,J)
```

    C
    ```
    C
    C
    C
    C FIT TO INDEX DATA
    C FIT TO INDEX DATA
    NWT 2 =0
    NWT 2 =0
    NWT =0
    NWT =0
    C
    C
    ANGAS(I)=
    ANGAS(I)=
        (1)-1.000)/RHO(I)
        (1)-1.000)/RHO(I)
        CONTINUE
        CONTINUE
        CALL FIT(RHO,ANGAS,WT2,YYN,XX,NWT2,M,2)
        CALL FIT(RHO,ANGAS,WT2,YYN,XX,NWT2,M,2)
    C
    C
    C
    C
    C
    C
        FIT TO LL DATA
        FIT TO LL DATA
        CALL FIT(RHO,ALL,WT,YY,XX,NWT,U,2)
        CALL FIT(RHO,ALL,WT,YY,XX,NWT,U,2)
        C FIT TO FUNNY FUNC
        C FIT TO FUNNY FUNC
    C
    C
        c
        c
        STOP
        STOP
        END
        END
        C
        C
        C
        C
        c
        c
        C
        C
        C
        C
        C
        C
        c
        c
        SUBROUTINE GRAF(RHO,ALL,ANGAS,FUNX,FUNY,XX,YY,YYN,YYM,XXM,M,J)
        SUBROUTINE GRAF(RHO,ALL,ANGAS,FUNX,FUNY,XX,YY,YYN,YYM,XXM,M,J)
        REAL*8 RHO(1),ALL(1), ANGAS(1),XX(1),YY(1),YYN(1)
        REAL*8 RHO(1),ALL(1), ANGAS(1),XX(1),YY(1),YYN(1)
        REAL*B FUNX(1),FUNY(1),XXM(1),YYM(1)
        REAL*B FUNX(1),FUNY(1),XXM(1),YYM(1)
        DIMENSION X(200),Y1(200),Y2(200),XX1(50),YY1(50),YY2(50)
        DIMENSION X(200),Y1(200),Y2(200),XX1(50),YY1(50),YY2(50)
        DIMENSION Y3(200),X3(200),XX3(50),YY3(50)
        DIMENSION Y3(200),X3(200),XX3(50),YY3(50)
    C
    C
        OO 40 I=1,M
        OO 40 I=1,M
        X(I)=SNGL(RHO(I))
        X(I)=SNGL(RHO(I))
        Y1(I)=SNGL(ALL(I))
        Y1(I)=SNGL(ALL(I))
        Y2(I)=SNGL(ANGAS(I))
        Y2(I)=SNGL(ANGAS(I))
        Y3(I)=FUNY(I)
        Y3(I)=FUNY(I)
        X3(I)=FUNX(I)
        X3(I)=FUNX(I)
        4O CONTINUE
        4O CONTINUE
        C
        C
            MM=40
            MM=40
    c
    c
        DO 50 I=1,MM
        DO 50 I=1,MM
            XX1(I)=SNGL(XX(I))
            XX1(I)=SNGL(XX(I))
            YY1(I)=SNGL(YY(I))
            YY1(I)=SNGL(YY(I))
            YY2(I)=SNGL(YYN(I))
```

            YY2(I)=SNGL(YYN(I))
    ```
```

Lfsting of LLNEWER at 12:43:06 on AUG 14, 1987 for CCId=DBRU
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232

```
```

        XX3(I)=XXM(I)
    ```
        XX3(I)=XXM(I)
        YY3(I)=YYM(I)
        YY3(I)=YYM(I)
    50 CONTINUE
    50 CONTINUE
C
C
C PLOT LL
C PLOT LL
C
C
        CALL ALAXIS('DENSITY (MOLE/CC)',17.'LL (CC/MOLE)'.12)
        CALL ALAXIS('DENSITY (MOLE/CC)',17.'LL (CC/MOLE)'.12)
        CALL ALSCAL(0.0.0.015,0.000,0.0)
        CALL ALSCAL(0.0.0.015,0.000,0.0)
        CALL ALGRAF(X,Y1,U,-4)
        CALL ALGRAF(X,Y1,U,-4)
        CALL ALGRAF(XX1,YY1,-MM.O)
        CALL ALGRAF(XX1,YY1,-MM.O)
c.
c.
C PLOT INDEX
C PLOT INDEX
C
C
        CALL ALAXIS('DENSITY (MOLE/CC)'.17.'INDEX'.5)
        CALL ALAXIS('DENSITY (MOLE/CC)'.17.'INDEX'.5)
        CALL ALSCAL(0.0,0.015,0.0.0.0)
        CALL ALSCAL(0.0,0.015,0.0.0.0)
        CALL ALGRAF(X,Y2,M,-4)
        CALL ALGRAF(X,Y2,M,-4)
        CALL ALGRAF(XX1,YY2,-MM,0)
        CALL ALGRAF(XX1,YY2,-MM,0)
C
C
c PLOT FUNNY
c PLOT FUNNY
        CALL ALAXIS('FUNX',4,'FUNY',4)
        CALL ALAXIS('FUNX',4,'FUNY',4)
        CALL ALSCAL(0.,O.,O..0.)
        CALL ALSCAL(0.,O.,O..0.)
        CALL ALGRAF(X3,Y3,U,-4)
        CALL ALGRAF(X3,Y3,U,-4)
        CALL ALGRAF(XX3,YY3,-MM,O)
        CALL ALGRAF(XX3,YY3,-MM,O)
        CALL ALDONE
        CALL ALDONE
    C
    C
    c
    c
        RETURN
        RETURN
        END
        END
C
C
c
c
        SUBROUTINE FIT(X,Y,WT,YY,XX,NWT,M,K)
        SUBROUTINE FIT(X,Y,WT,YY,XX,NWT,M,K)
        IMPLICIT REAL*8 (A-H,O-Z)
        IMPLICIT REAL*8 (A-H,O-Z)
        DIMENSION YF(200), YD(200),YYD(200),S(20),SIGMA(20),A(20),B(20),P(20)
        DIMENSION YF(200), YD(200),YYD(200),S(20),SIGMA(20),A(20),B(20),P(20)
        DIMENSION X(1),Y(1),WT(1),YY(1),XX(1)
        DIMENSION X(1),Y(1),WT(1),YY(1),XX(1)
        LOGICAL*4 LK
        LOGICAL*4 LK
    C
    C
C
C
        MM=40
        MM=40
        LK=.TRUE.
        LK=.TRUE.
        C
        C
        CALL DOLSF(K,M,X,Y,YF,YD,WT,NWT,S,SIGMA,A,B,SS,LK,P)
        CALL DOLSF(K,M,X,Y,YF,YD,WT,NWT,S,SIGMA,A,B,SS,LK,P)
C
C
    KK=K+1
    KK=K+1
    C
    C
    C USE FIT PARAMETERS TO CALC FIT FUNCTION
    C USE FIT PARAMETERS TO CALC FIT FUNCTION
C
C
    AINC=X(1)/40.
    AINC=X(1)/40.
    DO 8O I=1,MM
    DO 8O I=1,MM
        XX(I)=(DFLOAT(I))*AINC
        XX(I)=(DFLOAT(I))*AINC
            YY(I)=FUNC(XX(I),P.KK)
            YY(I)=FUNC(XX(I),P.KK)
    8O CONTINUE
    8O CONTINUE
    C
    C
C
C
    WRITE(8,801) KK
```

    WRITE(8,801) KK
    ```
```

List1ng of LLNEWER at 12:43:06 on AUG 14. 1987 for CCid=DBRU
233 DO 10 I =1,M
234 WRITE(8,802) X(I).Y(I),YF(I),YD(I)
235 10 CONTINUE
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
C
C
IF(K.NE. 1) GOTO 5
C CALC POLARIZABILITY,MOL VOL
C
POL=1.ODO/P(1)
POL=POL/6.023D23*1.0024
C
AA=1.ODO/P(2)
AA = -AA/6.023E23
AA=AA**O.3333333333*1.OD8
C
WRITE(6.611)POL,AA
WRITE(8,611)POL,AA
611 FORMAT(/,1X,'POLARIZABILITY =',2X,F8.4,' A**3'./.1X,
|'MOLECULAR RADIUS =,,2X,FB.4.,'2',')
C
801 FORMAT('IRESULTS OF FIT:'././,I3,2X,'PARAMETERS FIT TO DATA'.
|/,/,8X,'DENSITY'.24X.'FIT',1OX.'DEVIATIONS',/)
802 FORMAT(4(3X,F12.6))
C
5 WRITE(8.805) SS
805 FORMAT(1X,'SUM OF SQUARES ='.E12.6)
C
C
WRITE(8.804)
WRITE(6,804)
DD 20 I=1.KK
WRITE(8,803) P(I)
WRITE(6,803) P(I)
20 CONTINUE
C
804 FORMAT(/,1X,'FIT PARAMETERS:')
803 FORMAT(3X,E16.B)
C
RETURN
END
C
C
c
c
C
C
C
FUNCTION FUNC(X,COEF,NOTERM)
REAL*B FUNC,X,COEF(1)
C
FUNC=0.000
C
DO 10 1=1,NOTERM
IF (X.EQ.O.O) GOTO 20
FUNC=FUNC+COEF(1)*X**(1-1)
10 CONTINUE
C RETURN
END

```

\section*{Listing of COEX86}
```

Listing of COEX86 at 12:34:07 on AUG 14, 1987 for CCid=DBRU
1 2
3 3
COMMON ANAIR,ANSAFF,ALPHA,COSAIR,SINAIR
CONSTANTS
ANAIR=1.00029
ANSAFF=1.66
PARAMETERS FOR 3RD ORDER POLY FIT TO CALIB OATA
READ(3,301) THFIT(1),THFIT(2),THFIT(3),THFIT(4)
READ(3,302) THAIR
READ(3,304) ALPHA
READ(3,303) AL(1), AL(2), AL(3)
FORMAT(1X,E2O.8,/.1X,E2O.8,/,1X,E2O.8,/, 4X,E2O.8)
FORMAT(1X,E2O.10)
FORMAT(1X,F12,6, iX,F12.6,1X,F12,6)
FORMAT(1X,F12.6)
WRITE(6,301) THFIT(1),THFIT(2),THFIT(3),THFIT(4)
WRITE(8,301) THFIT(1),THFIT(2),THFIT(3),THFIT(4)
WRITE(6,302) THAIR
WRITE(8,302) THAIR
WRITE(6.304) ALPHA
WRITE(8,304) ALPHA
WRITE(6,303) AL(1),AL(2),AL(3)
WRITE(8,303) AL(1),AL(2),AL(3)
C
C
C
C
TEMP 1=0.1349639945E-2
TEMP2 =0.235466 1076E-3
TEMP3=0.3282390265E-5
C
C
C
C
C
CELL ANGLES
PI=3.141592650O
ALPHA =ALPHA*PI/180.DO
COSAIR=DCOS(THAIR)
SINAIR=DSIN(THAIR)
C
GET DATA FROM FILE \# 4
READ(4,401) M
WRITE(6.601) M
WRITE(8.601) M
FORMAT(1X,'NO. OF PTS. = ,.3X,I4./)
FORMAT(1X,I4)

```
```

Listing of COEX86 at 12:34:07 on AUG 14, 1987 for CCid=DBRU
DO 10 I=1.M
READ(4,402) RES(I),AMICV(I),AMICL(I),AMICO
WRITE(6.402) RES(I),AMICV(I),AMICL(I),AMICO
AMICL(I)=AMICL(I)-AMICO
AMICV(I)=AMICV(I)-AMICO
CONTINUE
FORMAT(2X,F7.2,1X,F7.3,3X,F7.3,3X,F7.3)
4
DO 22 I=1,M
C CALC INDEX OF REFR
ANV(I)=DEX(AMICV(I),THFIT)
ANL(I)=DEX(AMICL(I).THFIT)
CALCULATE TEMPERATURES
FOR RES=GY USE FIT TO 1/T=A+BLNR+CLNR**2
T2(I)=TEMP 1+TEMP2*DLOG(RES(I))+TEMP3*DLOG(RES(I))**2
T2(I) =1.000/T2(I)
T(I)=T2(I)-273.15DO
C
C
ALLV(I)=CALCLL(ANV(I),AL)
C
ALLL(I)=CALCLL(ANL(I),AL)
C
C CALC DENSITIES
RHOV(I)=DENS(ANV(I),ALLV(I))
C
RHOL(I)=DENS(ANL(I),ALLL(I))
C CALC DIAMETER
DIAM(I)=(RHOV(I)+RHDL(I))/2.00O
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116

```
```

Listing of COEX86 at 12:34:07 on AUG 14. 1987 for CCid=DBRU
117 C
118 C
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
\$57
158
159
160
161
162
163
164
165
166
167
468
169
170
171
472
173
174
NNCTION CALCLL(AN,AL)
IMPLICIT REAL*B (A-H,O-Z)
DIMENSIDN AL(1)
C
AN1=AN-1.ODO
C
C FIT OF LL TO N ....
NUMBERS FROM LLFITTION ....
READ IN ABOVE FROM 3
CALCLL=AL(1)+AL(2)*AN1+AL(3)*AN1*AN1
C

```
```

Listing of COEX86 at 12:34:07 on AUG 14, 1987 for CCid=DBRU
175 RETURN
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
2O2
203
204
205
206
207
208
C
C
C
SUBROUTINE GRAF (T,RHOV,RHOL,DIAM,M)
REAL*8 T(1),RHOV(1),RHOL(1),DIAM(1)
REAL*4 TT(100),VV(100),EL(100),DD(100)
REAL*4 T2(100)
C
C
C
DO 10 I=1,M
TT(I)=T(I)
T2(I)=TMAX-TT(I)
VV(I)=RHOV(I)
EL(I)=RHOL (I)
DD(I)=DIAM(I)
10 CONTINUE
C
CALL ALAXIS('TEMP'.4,'DENS'.4)
CALL ALSCAL(O.,0.015,270..285.)
CALL ALGRAF(VV,TT,M,-1)
CALL ALGRAF(EL,TT,-M,-4)
CALL ALGRAF(DD,TT,-M,-3)
C
C
CALL ALSCAL(0.0,0.0,0.0.0.0)
CALL ALAXIS('TEMP',4,'DIAM'.4)
CALL ALGRAF(T2,DD,M,-3)
CALL ALDONE
RETURN
END

```

\section*{C-3 Temperature Sweeping Program}

This program was used with a Commodore PET microcomputer to sweep the temperature of the ethylene experiment, as described in section III-2. Lines 1-150 are a machine language program that reads the temperature from the HP 2804A quartz thermometer. This program is loaded into memory by lines 155-240. The rest of the program gets a sequence of sweep and wait times from the keyboard and executes them, turning on and off the motorized potentiometer in the temperature control circuit and marking the data film before each sweep by turning on and off the LEDs.

The address. 59457 is the output port to which the interface shown in fig. (3-6) is connected. Numbers sent to this address have the following effects:

0 - everything off
1 -LED \#1 on
2 - LED \#2 on
5 - motor on
6 - motor reverse
7 - reset.

\section*{Listing of the Temperature Sweeping Program}

```

260 D=0 : I2=0
262 GOSUB 4000
264 PRINT"MINITIAL TEMP=",TQ(0,0)
270 :
272 FOR 12=1 TO 11-1
275 FOR D=1TONS(I2)
280 GOSUR 3000:REM SWEEP
290 IF OFO22 THEN390
300 PRINT\#4,D;I2;TI%,TQ(D,I2)
390 NEXT D
3 9 5 ~ N E X T ~ 1 2 ~
415 PRINT".END OF RUN..."
418 FRINT"INITIAL TEMP=',TQ(0,0)
4 2 2 ~ F O R C C = 1 ~ T O ~ I I - 1 ~
4 2 5 ~ F O R C D = 1 T O ~ N S ( C C ) ~
4 2 8 ~ F R I N T C D , C C , T Q ( C D , C C ) ~
43@ IF OP<\2 THEN }43
432 PRINT\#4,CD,CC,TQ(CD,CC)
435 HEXTCD
4 4 0 ~ N E X T C C ~
4 4 5 ~ I F ~ O F O \ 2 T H E N ~ 4 5 2 ~
450 CLOSE4
451 :
452 GET A$: IFA$="" THEN 452
454 TF=1
456 GOSUR 4000
462 PRINT"TEMP =",TU
4EE GOGUP 2000: X1=CLOCK
468 GOSUE 2000 : X2=CLOCK
472 IF X2-X1=5 OR X2-X1=55 THEN }45
476 GET AS : IF As="nTHEN 468
480 GOTO 255
4 9 0 ENII
4 9 8
4 9 9
500 E=ASC\E%)
510 IF B`64 THEN B=B-55 : RETURN
520 R=B-48
5 3 0 ~ R E T U P N
540
1000 REM SETUP
1010:
1015 Q=59457
1020 POKE Q+2,255
1030 POKE Q.0
1040 POKE Q.?
1050 POKE Q,O
1655 PRINT"3"
1060 PRINT"HMHELLO, WELCOME TO THE TEMPERRTUREMHHEPMPHPMHMPBI SUEEPING PROGRAM"
1061 PRINT:PRINT
1065 INPUT"IS THE QURRTZ THERMOMETER THERE"; Y%
1066 IF LEFT$(Y'$,1)="Y"THEN1070
1067 TT=0
1068 GOTO 1080
1070 TT=1
1071 IHPLT"XIT RAHGE (1,2,3)";RT\$
1072 TR\&="T":GOSLIB 50@0
1073 INPUT"XR RANGE (1,2,3)";RT\$
1074 TRक="R": GOSUB 5000
1075 REM
1080 INPUT "MOUTPUT TO SCREEN,TAPE,OR PRINTER";O\$
1090 IF LEFT\&(OS,1)="S"THEN OP=0
1100 IF LEFT*(O%,1)="T"THEN OP=1
1110 IF LEFT年(O\&,1)="P"THEH OP=2
1119 I1=1
1120 THPUT"\&NUMEER OF T STEPSHiHE<I1)

```
```

1125 IF MS(I1)=0 GOTO 1155
1130 INFUT"MUUMBER OF MINUTES SINEEFING";TS(I1)
1135 IF TS(I1)>6@ OR TS(II)(a THEN FRINT"MMFNIMLM E0":GOTO 1130

```

```

1143 HR(I1)=INT(TW'60)
1145 MIN(II)=IHT((TW/60-HR(II))*60+.01)
1150 I = I 1+1
1152 FRINT"MFOLLOWED BY .7";
1154 GOTO1120
1155 INFUT "XINITIRL WRIT";IW
1160 GOSUP 200@:W1=CLOCK
1162 GOSUE 2000:W2=CLOCK
1164 IF W2-W1=IW OR W1-W2=60-IW THEN1170
1166 GOTO 1160
1170
1175 POKE 59457,1
1180 FOR F=1TO 10000:NEXT
1190 POKE 59457,0
1200 FOR F=1TO 10000:NEXT
1205 POKE 59457.1
1207 FOR F=1TO 10000: NEXT
1210 RETURN
1990
1995
2000 CLOCK=VAL(MID$(TI$,3,2))
2010 FETLIRN
2099
2100
2110
2120
2125
2130
3006 REM SNEEP
3010 GOSUE 2000
30%0 S1=CLOCK
3440 FOKE Q.E:FOR Y=1TO100:NEXT't
3060 FFIHT"SNEEF'\# ";D;"...ON"
3070 GOSUF 2900
3080 S2=CLOCK
3090
3100
3200
3210
3220
32L
3230
3246
3245
3248
3250
3255
3260
3265
3270
3275
3280
3290
3300
3308 POKE Q,1:FOR Y=1TC5GOQ:HEXT:FOKE Q,0
3312 IF I//3=INT (D'S')THENS350
3320 GOTO 3360
3350
3360
3370 PFIIHT"TIME= ";TI\$;TAB(6);"TEMF= ";TQ(D,I2)
3 4 0 0 ~ R E T U R N
3498 :
3499 :

```
```

4 9 0 0 ~ R E M ~ R E R I I ~ T ~
4 0 1 0
4915 IF TT=0 THEN TQ=0 : RETURH
4020 S4'S(772)
4030 C=906:D\&=""
4040 R=PEEK(C)
4050 C=C+1
406(1) IF RO)13 THEN D$=DF+CHR$(A):GOT04040
40EE IF TF=0 THEN 4090
4070 TLI=VRL(D\&)
4 0 8 0 ~ R E T U R N
4 0 8 5
4090 TQ(D,CC)=VAL(D$)
    4 1 0 0 ~ R E T U R H .
    4 9 9 8
    4999 :
    5900 FOKE 871,ASC(TRS):FOKE 878,RSC(RT$):SYS(847):SYS(847)
5010 RETURN
RERI'%.

```
```


[^0]:    0.1947E-02 0. 1557E-02 0. 1475E-02 0. 1334E-02 0.1146E-02 0. $112 \mathrm{BE}-02$ 0.9398E-03 0.9199E-03 0.7329E-03 0.7138E-03 0.6082E-03 0.5268E-03 0.5104E-03 0.5026E-03 0.4117E-03 0.3702E-03 0.3486E-03 0.2733E-03 0.2127E-03 0.2093E-03 0.1755E-03 0.1487E-03 0. 1375E-03 0.1323E-03 0.1150E-03 0. $1081 \mathrm{E}-03$ $0.8647 E-04$ 0.1902E-04

