PHASE BEHAVIOUR OF BINARY MIXTURES OF ETHANE + N-EICOSANE AND STATISTICAL MECHANICAL TREATMENT OF FLUID PHASES

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ter verkrijging van de graad van doctor in de technische wetenschappen aan de Technische Hogeschool Delft, op gezag van de Rector Magnificus prof. dr. J.M. Dirken, in het openbaar te verdedigen ten overstaan van het College van Dekanen op donderdag 16 januari 1986 te 14.00 uur

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"Goeie morgen" zei de nachtuil "Nu ga ik een uiltje knappen".

Truus Waaijers

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the vectoriging van de gread van doolor in de vectorische wetenstnagpen aan de Todmech higgeschool Datit, op gezeg van de Rectar Magniticus prot. dr. J.M. Dinten in bet openbaar te vandedigen ten overstean ven het Goltege van Dekanen op donderdog 15 januar 1988 te 14.00 op

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Aan Adri, Irene en Anneke

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1. INTRODUCTION

A first inspection of the content of this thesis may perhaps lead to the conclusion that it has a somewhat schizophrenic character with respect to its primary objectives. These objectives are:

- the experimental determination of the phase behaviour of the binary system ethane + n-eicosane as well as the thermodynamic description of the experimental results using empirical equations of state;
- the calculation of the thermodynamic properties of rather simple fluids and their mixtures using theories based on elementary statistical mechanical principles.

Between both objectives there seems to be no immediate correlation. However, a closer look makes clear that both primary objectives have at least an indirect relationship.

Since the introduction of the still rapidly growing abilities of modern computers banking, correlating, retrieving, etc. of phase equilibrium data have become tools of important value. This development sometimes leads to the impression that these activities reduce the need of new experimental data or the experimental approval of already existing data. In the practice of chemical engineering, however, there is even an increased need to have available new and more accurate data [1], which is confirmed by the following facts:

- application of inaccurate basic data can cause large errors in the prediction of the behaviour of a particular process and consequently dramatic losses of production and/or money may occur [2,3,4];
- the development of new products in general require also basic data of these products;
- improvement in the design of production methods or separation techniques usually require additional and/or more accurate basic data;
- 4. to predict the behaviour of strongly non-ideal mixtures the correlation and prediction methods used currently in chemical engineering are usually based on pure component information only and are in general not accurate enough, i.e. nearly always experimental data of mixtures are necessary.

In this thesis the binary system ethane + n-eicosane was investigated. For this choice there existed various reasons:

1. experimental data of binaries of a volatile n-alkane on the one hand

1

and a non-volatile higher n-alkane on the other hand are generally of particular importance for the petrochemical as well as for the natural gas industry;

- 2. in connection with data of similar ethane binaries the data of ethane + n-eicosane extend the possibility to understand and predict systematic changes in phase behaviour in such hydrocarbon systems due to changes of the carbonnumber of the higher n-alkane;
- to develop adequate equations of state to describe quantitatively the phase behaviour of such pure fluids and mixtures accurate experimental data are essential.

Because of their mathematical simplicity in chemical engineering cubic equations of state such as those of Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson have become extremely popular to describe multicomponent fluid phase properties. In this thesis these three cubic equations of state are compared in their behaviour to represent vapour + liquid equilibria in the system ethane + n-eicosane. Especially the influence of binary interaction parameters is investigated, as originally proposed by Deiters [5] and Deiters et al. [6].

The second major objective of this study was to make the non-analytical statistical mechanical virial equation of state accessible for practical purposes. In its original form this equation requires information on the intermolecular interaction between the molecules of the fluid as well as the radial distribution function for the chosen intermolecular interaction model as a function of density and temperature. These requirements make this equation of state unsuitable for practical purposes. In that respect several authors [7,8,9] proposed approximate equations using simple approximations for the intermolecular interaction and/or the radial distribution function. As a consequence of such approximations analytical expressions are obtained which have lost much of their original physical relevance. Moreover the problem arises that quite similar shortcomings may occur as with the currently used cubic equations of state. Consequently the objective of this study was to apply the non-analytical virial equation of state in such a way that a maximum of physical significance was to be retained. In order to achieve that the following boundary conditions were fulfilled:

 a realistic pair-potential model, the Lennard-Jones (12,6) pairpotential, was chosen to describe the intermolecular interactions;
using this pair-potential radial distribution functions were calculated in the whole fluid phase region;

 in addition a suitable and fast calculation method was developed to determine thermodynamic properties of pure substances and their mixtures.

The physical model chosen is essentially only valid for monoatomatic fluids, i.e. the application of the calculation technique proposed in first instance seems to be meaningless for the binary system investigated experimentally. In this study, however, it is obvious that, in principle, similar calculation techniques may be developed for physically more realistic models which allow to handle mixtures of chainlike molecules of moderate length. Until accurate, physically realistic models will become available it seems that much effort has to be made to understand on a molecular basis the behaviour of mixtures of chain molecules in dependence of temperature and pressure. In that respect computer methods such as molecular dynamics may be very helpful.

Finally it should be noticed that the development of physically relevant equations of state becomes more and more important in practical chemical engineering. This has already been emphasized by several authors [10,11,12]. Van de Kraats [4] pointed out that experimental data seldom are available at the conditions where they are needed, i.e. at extreme values of temperature and pressure. In order to be able to make accurate and reliable predictions in temperature and pressure ranges where no data are available physically relevant models have to be used. Application of the non-analytical virial equation of state as proposed in this study is a first step in that direction.

The first objective of this thesis is treated in chapters 2, 3, 4, 5 and 6. After a theoretical introduction to the phase behaviour possible (chapter 2) in chapters 3 and 4 the experimental method used and the results obtained are discussed respectively. Then in chapter 5 cubic equations of state are discussed briefly and in chapter 6 some of these equations are applied to describe phase equilibria in the binary ethane + n-eicosane.

In chapter 7, 8 and 9 the second objective of this thesis is developed. Chapter 7 presents the major statistical mechanical principles used. In chapter 8 the calculation of radial distribution functions from an integral equation is treated.

Finally in chapter 9 the applicability of the calculation technique proposed to fluid phases is investigated. Conclusive remarks are summarized in chapter 10.

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2.1. Introduction

A more or less general discussion of the phase behaviour of several different types of binary mixtures of hydrocarbons was first given by Davenport et al. [1]. These authors studied the solubility of hydrocarbons in liquid methane from their melting points to the critical temperature of methane. Van der Kooi [2] extended this discussion to the systematic change in phase behaviour due to increasing carbonnumber of binary mixtures of methane and higher n-alkanes. This latter study revealed that in those systems essentially four different types of phase behaviour must be expected with increasing carbonnumber of the higher n-alkanes. These four types of phase behaviour possible were already discussed by Diepen [3] and recently also by Luks [4]. The phase behaviour of several types of hydrocarbons in ethane near its critical point was studied by Rowlinson et al. [5]. From this study as well as the phase behaviour of binary mixtures of ethane and higher n-alkanes already known in literature (section 2.2) a similar systematic change in phase behaviour with increasing carbonnumber of the higher nalkanes, as observed in the methane systems, was to be expected in the ethane systems. Before special attention will be given to the phase behaviour of the binary system ethane + n-eicosane, the several types of phase behaviour possible in the ethane systems will be discussed from a general point of view in this chapter. The type of phase behaviour this system shows is in principle well-known. Kuenen et al. [6] and Kuenen [7] already have reported this type of phase behaviour in the vicinity of the critical point of ethane of binary mixtures of ethane and alcohols such as ethanol, 1-propanol, etc..

2.2. Mixtures of ethane and n-alkanes

In this work ethane - the more volatile component - will be indicated by component A and consecuently the higher n-alkane by component B respectively.

Templin [8] found that higher n-alkanes such as n-tetracosane, n-hexacosane, n-octacosane and n-dotriacontane show a solid first order transition a few degrees below the normal melting temperature. Further it is known [8] that nhexatriacontane has even two of such solid state transitions and that n-eicosane shows no solid state transition of this nature. In order to simplify the general discussion in this section it is supposed that only one solid modification of both pure components exists. The different types of phase behaviour which occur in the ethane + higher n-alkane mixtures can be most conveniently distinguished by considering the two three phase lines $S_B + L + V$ and $L_1 + L_2 + V$. In the first type no partial miscibility occurs in the liquid phase and consequently a three phase line $L_1 + L_2 + V$ does not exist. The three phase lines $S_B + L + V$ originating in the quadruple point $S_A + S_B + L + V$ and ending in the triple point of the higher n-alkane (component B) has a continuous course. Figure 2.1 shows schematically such a phase behaviour by means of a p,T,x-projection. From this figure it can be seen that the critical line L \equiv V also has a continuous course between both critical points of the pure components. Mixtures of ethane + higher n-alkanes up to n-heptadecane [9] satisfy to this p,T,x-projection. Recently De Goede et al. [10] found this type of phase behaviour in mixtures of ethane + n-hexadecane.

In the second type of phase behaviour of binary mixtures of ethane + higher n-alkanes the course of the three phase line $\boldsymbol{S}_{\boldsymbol{p}_i} + \boldsymbol{L} + \boldsymbol{V}$ is quite similar as just discussed. However, now partial miscibility in the liquid phase occurs in the vicinity of the critical point of ethane and consequently a three phase equilibrium $L_1 + L_2 + V$ is to be found. This type of phase behaviour is shown - also schematically - in the p,T,x-projection of figure 2.2. As it can be seen from this figure the critical line L Ξ V is now separated into two branches. One branch starts in the critical point of ethane and ends in the upper critical endpoint (UCST) ${\rm L}_1$ = V + ${\rm L}_2$ of the three phase line ${\rm L}_1$ + ${\rm L}_2$ +V. A second branch originates in the lower critical point (LCST) $\rm L_1$ Ξ $\rm L_2$ + V of the three phase line ${\rm L}_1$ + ${\rm L}_2$ + V and goes with a maximum in pressure to the critical point of the higher n-alkane. This type of phase behaviour has already been observed in the binary systems of ethane with n-octadecane, nnonadecane and n-eicosane [9]. Peters et al. [11] also found this type of phase behaviour in the binary system ethane + n-docosane. For these systems the temperature and pressure of both the lower and upper critical endpoints [9,12] are summarized in table 2.1. From this table it can be concluded that with increasing carbonnumber n the lower as well as the upper critical endpoints are shifted to lower temperatures. Moreover the temperature range ΔT = $T_{\underline{u}}$ - $T_{\underline{1}}$ of the $L_{\underline{1}}$ + $L_{\underline{2}}$ + V equilibrium increases with increasing carbonnumber.

A lower critical endpoint at a lower temperature means the three phase equilibrium starts at lower temperatures. On the other hand with increasing carbonnumber the triple point of the higher n-alkane shifts to higher





Figure 2.2.

Figure 2.1.

n	Т1/К	p ₁ /MPa	T _u /K	p _u /MPa
18	312.29	5.511	312.45	5.531
19	309.49	5.211	310.78	5.363
20	306.69	4.927	309.62	5.260
22	300.72	4.388	307.98	5.145

Table 2.1. Lower and upper critical endpoints in binary systems of ethane and n-octadecane, n-nonadecane, n-eicosane and n-docosane [9,12].

temperatures. Both effects will finally result in an interference of both three phase lines $L_1 + L_2 + V$ and $S_B + L + V$ and a quadruple point $S_{B} + L_{1} + L_{2} + V$ will exist. Figure 2.3 shows this type of phase behaviour schematically. The three phase locus S_{B} + L + V is separated into two branches. A lower temperature branch $S_{B}^{}$ + $L_{1}^{}$ + V originating in the quadruple point $S_A + S_B + L + V$ and ending in the quadruple point $S_B + L_1 + L_2 + V$. The high temperature branch S_{B} + L_{2} + V starts in the quadruple point $S_p + L_1 + L_2 + V$ and ends in the triple point of the higher n-alkane. As from a quadruple point four three phase lines must originate, two more three phase lines have to exist: the three phase lines $L_1 + L_2 + V$ and $S_B + L_1 + L_2$ respectively. From figure 2.3 it is also shown that no lower critical endpoint (LCST) is present but that the three phase line S_{B} + L_{1} + L_{2} ends in a critical point $S_{B} + L_{1} \equiv L_{2}$. In this point the critical behaviour $L_{1} \equiv L_{2}$ in the presence of $\rm S_{R}$ occurs. From this point the critical line $\rm L_{1}$ $\stackrel{_{\scriptstyle 2}}{=}$ $\rm L_{2}$ (L $_{2}$ $\stackrel{_{\scriptstyle 2}}{=}$ V) goes to the critical point of the pure higher n-alkane. The low temperature branch of the critical line L_1 Ξ V starts in the critical point of ethane and ends in the upper critical endpoint of the three phase equilibrium $L_1 + L_2 + V$. Peters et al. [13,14] measured this type of phase behaviour in binary systems of ethane with n-tetracosane and n-pentacosane respectively.

There are experimental indications that in the system ethane + n-hexacosame no quadruple point S_B + L₁ + L₂ + V is existing. Some preliminary measurements in the system ethane + n-heptacosane did prove that this system belongs to a type where no longer stable liquid + liquid demixing occurs and consequently a quadruple point S_B + L₁ + L₂ + V does not exist. This phenomenon can be well understood. As the carbonnumber further increases a shift of the triple point of the higher n-alkane up to higher temperature will take place and consequently also the quadruple point S_B + L₁ + L₂ + V is shifted to higher temperature [13,14]. At the same time with increasing carbonnumber the



Figure 2.3.

Figure 2.4.

three phase equilibrium $L_1 + L_2 + V$ shifts to lower temperatures (table 2.1). Finally both effects will result in a phase behaviour were stable liquid + liquid demixing will not occur anymore. This fourth type of phase behaviour is shown schematically in figure 2.4. The three phase locus $S_B + L + V$ as well as the critical locus $L \equiv V$ have separated branches in these types of binary mixtures. Both the low temperature branch of the three phase line $S_B + L + V$ and the critical locus $L \equiv V$ meet in a so-called first critical endpoint where the phase behaviour $S_B + L \equiv V$ exists. As the solubility of the higher n-alkane in liquid ethane decreases with increasing carbonnumber, the low temperature branch of the three phase equilibrium $S_B + L + V$ nearly coincides with the vapour pressure curve of ethane and consequently the first critical endpoint nearly coincides with the critical point of pure ethane.

Similarly the high temperature branch of the three phase line $S_B + L + V$ and the critical locus $L \equiv V$ also end in a point which they have in common: the so-called second critical endpoint. In the second critical endpoint $(S_B + L \equiv V)$ the solid phase S_B is in equilibrium with a critical fluid. It should be noted that in this type of binary mixtures of ethane + n-alkanes a temperature range exists where no stable critical phenomena are possible at all. This type of phase behaviour near the critical point of ethane was determined in the system ethane + n-octacosane [12,15]. From the previous discussion it can be concluded that in binary mixtures of ethane and higher n-alkanes essentially four different p,T,x-space models can be distinguished.

2.3. Literature data of binary ethane and n-alkane systems

In this section a collection of references containing experimental data of binary systems of ethane with n-alkanes is given. This information is divided up in the following groups:

- vapour + liquid equilibria;
- critical data;
- excess properties;
- three phase equilibria.

The data available are classified in these four groups and the literature references are summarized in table 2.2. It is obvious that the available data for ethane + n-alkane systems are rather scarce in literature.

Table 2.2. Available experimental data of binary ethane + n-alkane systems.

Carbonnumber	Vapour +	Critical data	Excess properties	Three phase	
n	liquid equilibria			equilibria	
1	[16,18,19,	[18,21,22,23]	[16,17]	1.10-22.3	
	20,21,22,				
	23,24,25]				
3	[22,26,27,	[22,26,27,28,	[17,26]		
	28,29]	29]			
4	[34,35]	[30,31,32,33,	[17]		
		34,35]			
5	[37]	[30,36,37]			
6	[38]	[38]			
7	[40,41]	[33,39,40]			
8	[42]				
10	[43,44]	[43,44]			
12	[45]		[45]		
18		[9]		[9]	
19		[9,46]		[9,46]	
20		[9,46,47]		[9,46,48]	
22		[12]		[11,12]	
23		[49]		[49]	
24		[13]		[13]	
25				[14]	
28				[12,15]	

2.4. Phase behaviour of binary mixtures of ethane and n-eicosane

In section 2.2 the four types of phase behaviour possible in binary mixtures of ethane and higher n-alkanes were discussed. It was pointed out that the system ethane + n-eicosane does belong to the second type. In this section this type will be discussed in more detail.

For that purpose figure 2.5 shows schematically a p,T,x-projection of the phase diagram of the system ethane + n-eicosane in about the temperature range of interest. In order to emphasize the schematical character of figure



Figure 2.5. Schematical p,T,x-projection of the system ethane + n-eicosane.

2.5 it should be noted that, for example, the critical points of ethane and n-eicosane are located much farther apart than shown in this figure. Moreover partial miscibility in the liquid phase will not occur at mole fractions of n-eicosane higher than about 0.10 [48].

From the p,T,x-projection a series of isothermal p,x-sections can be derived. In figure 2.5 the temperatures of the p,x-sections are marked by vertical dashed straight lines in the p,T,x-projection. Figure 2.6a shows the p,x-section at temperature T = T₁ of figure 2.5. The next p,x-section is taken at a temperature T = T₂ where the critical locus L₁ \equiv V is intersected (figure 2.6b). In figure 2.6c the p,x-section at T = T₃ - the temperature to T = T₄ gives a p,x-section (figure 2.6d) with an increased L₁ + L₂ - region on the one hand and a decreased L₁ + V - region on the other hand. In figure 2.6e the p,x-section is presented at a temperature T = T₅ where the upper critical endpoint just occurs. Finally in figure 2.6f (at T = T₆) the three phase equilibrium L₁ + L₂ + V is not present any longer.



Figure 2.6a

Figure 2.6b



Figure 2.6e



For some purposes it is useful to consider isobaric T,x-sections. In figure 2.5 the pressures, for which the T,x-sections are discussed, are marked by horizontal dashed straight lines. The series of subsequent T,xsections shown in figure 2.7 starts at a pressure $p = p_1$ at which the three phase equilibrium $S_{B}^{}$ + L + V is just intersected (figure 2.7a). Then at a pressure of $p = p_2$ this three phase equilibrium is intersected two times (figure 2.7b). Figure 2.7c shows the T,x-section at $p = p_3$. Now the three phase line $L_1 + L_2 + V$ is intersected. Both figures 2.7d and 2.7e are a straightforward extension of figure 2.7c up to higher pressures. The series of T,x-sections is completed with figure 2.7f at $p = p_6$. Now the critical locus $L_1 \equiv L_2$ ($L_2 \equiv V$) is intersected two times.

As the experimental determination of two phase boundaries is carried out at constant values of the composition $x_{\rm R}$, p,T-sections are of direct practical value in this research. They will be discussed briefly in this section. In the T,x-part of figure 2.5 the compositions of the p,T-sections are marked by dashed straight lines. The first p,T-section at $x_{p} = x_{1}$ is represented in figure 2.8a. It can be seen from figure 2.5 that the vapour branch of the three phase equilibrium S_{R} + L + V is intersected and up to higher temperatures intersection with the critical locus $L_1 \equiv V$ occurs. At a composition $x_{R} = x_{2}$ also the three phase equilibrium $L_{1} + L_{2} + V$ is intersected and a p,T-section results with the presence of the lower critical





Figure 2.7a

Figure 2.7b





Figure 2.7c

Figure 2.7d









Figure 2.8a







Figure 2.8c

Figure 2.8d



Figure 2.8e

Figure 2.8. p,T-Sections at various mole fractions.

endpoint (figure 2.8b). The p,T-section at $x_B = x_3$ as shown in figure 2.8c represents the case where the lower as well as the upper critical endpoint are to be seen. Increasing the composition to $x_B = x_4$ leads to a p,T-section (figure 2.8d) with no lower critical endpoint of the three phase equilibrium $L_1 + L_2 + V$. The upper critical endpoint however is still to be seen in the p,T-section. Figure 2.8e completes the series of p,T-sections with the one at $x_B = x_5$. Only the three phase equilibrium $S_B + L + V$ and the critical locus $L_2 \stackrel{<}{=} V$ are intersected. The practical use of the p,T-sections will be discussed in chapter 3.

2.5. Discussion

In addition the experimental data available in literature (section 2.3) the mutual relation of the several types of phase behaviour possible is now discussed briefly. Firstly figure 2.9 shows the three phase equilibrium $S_B + L + V$ (or $S_B + L_1 + V$ and $S_B + L_2 + V$) of the binaries ethane and higher n-alkanes known in literature so far. This figure clearly demonstrates how with increasing carbonnumber the low temperature branch of the $S_B + L + V$ -line coincides more and more with the saturated vapour pressure curve of pure ethane, i.e. the solubility of higher n-alkanes in liquid ethane decreases with increasing carbonnumber. From this figure it can also be seen that the first binary having a quadruple point $S_B + L_1 + L_2 + V$ is ethane + n-tetracosane [13]. As already discussed in section 2.2 there is experimental evidence that the binary system ethane + n-hexacosane has no quadruple point $S_B + L_1 + L_2 + V$; ethane + n-alkanes only two systems have a quadruple point $S_B + L_1 + L_2 + V$; ethane + n-tetracosane and ethane + n-pentacosane.

Dissimilar behaviour of the high temperature branches of the $S_B + L + V$ line of n-paraffins with odd and even carbonnumbers is to be seen also in figure 2.9. For example, the high temperature branches of the $S_B + L + V$ -line of n-tricosane and n-pentacosane lie rather close to the similar branches of the three phase lines of n-docosane and n-tetracosane respectively. If we, however, consider the normal melting temperatures of n-alkanes as a function of the carbonnumber (figure 2.10), this behaviour can be well understood. Obviously the normal melting temperatures are representative for the temperatures of the triple point of the higher n-alkanes. Figure 2.10 clearly shows relatively small temperature differences in the melting temperature of a



Figure 2.9. Three phase behaviour S_B + L + V of binaries of ethane and n-hexadecane, n-eicosane, n-docosane, n-tricosane, n-tetracosane, n-pentacosane, nhexacosane and n-octacosane. Open circles = experimental data; full curves = best fit; dashed curves = to be measured.



Figure 2.10. Normal melting temperatures of n-alkanes as a function of the carbonnumber n.

n-alkane with an even carbonnumber and the subsequent n-alkane with an odd carbonnumber. This means that both triple point temperatures of such two n-alkanes lie close together and consequently both corresponding high temperature branches of the ${\rm S}_{\rm B}$ + L + Vlines will do so too.

Figure 2.11 shows the three phase lines $L_1 + L_2 + V$ in the systems ethane + n-octadecane, ethane + n-nonadecane, ethane + n-eicosane and ethane + n-doco-

sane. Besides the saturated vapour pressure curve of pure ethane also both quadruple points $\mathrm{S}_{\mathrm{B}} + \mathrm{L}_1 + \mathrm{L}_2 + \mathrm{V}$ in the systems ethane + n-tetracosane and ethane + n-pentacosane are represented. This figure visualizes how with increasing carbonnumber the temperature range of the three phase lines $\mathrm{L}_1 + \mathrm{L}_2 + \mathrm{V}$ increases. Moreover it is seen how the lower critical endpoints shift faster to lower temperatures with increasing carbonnumber than the corresponding upper critical endpoints. This is also illustrated in figure 2.12.

It has been found, as shown in figure 2.13, that between the temperatures of the lower critical endpoints and the carbonnumber of the higher n-alkane an almost linear relationship exists. However, between the corresponding upper critical endpoints and the carbonnumber such a linear relationship does not exist.

Finally in figure 2.14 critical data available for ethane + higher nalkane binaries are compared. Only the critical line of ethane + n-eicosane is calculated using the Soave-Redlich-Kwong equation of state. This calculation will be discussed in chapter 6.



Figure 2.11. Three phase behaviour L_1 + L_2 + V, S_B + L_1 + L_2 and S_B + L_2 + V of some binaries of ethane and higher n-alkanes.



Figure 2.12. Relationship between T_{u} and T_{1} of higher n-alkanes.

Figure 2.13. UCST and LCST of higher n-alkanes as a function of the carbonnumber n.



Figure 2.14. Critical data of some binaries of ethane and other n-alkanes (open circles). The critical line of ethane + n-eicosane is calculated with the Soave-Redlich-Kwong equation of state.

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3. EXPERIMENTAL

3.1. Introduction

The experimental equipment as well as the applied experimental methods will be discussed in this chapter.

For all measurements a so-called Cailletet-apparatus was used. As this apparatus is part of the standard equipment of the laboratory since a long time it has already been described in literature [1,2]. This justifies that here only a concise description of this apparatus will be given. Details of the equipment can be found elsewhere [1,2].

3.2. Equipment

With respect to the pressures and temperatures which were expected to be necessary in the experimental work a so-called Cailletet-apparatus appeared to be most suitable to perform all measurements. On the one hand in this apparatus pressures up to at least 18 MPa can be applied and on the other hand the temperature range from about 260 K up to 450 K is attainable. Another advantage of this apparatus is that phase transitions can be observed visually. A schematical representation of this Cailletet-apparatus is given in figure 3.1. Essentially a Cailletet-tube consists of thick-walled Pyrex glass of a length of about 500 mm and with an inner and outer diameter of 3 and 10 mm respectively. One end is closed and the open end of the Cailletettube is provided with a conical thickening which allows to mount the tube into a stainless-steel autoclave. Using mercury as a sealing and pressure transmitting fluid a sample - pure component or mixture - can be confined inside the closed top of the Cailletet-tube. Within the autoclave the open end of the tube is always immersed in mercury separating the sample from the oil which is used to generate the pressure by hydraulic equipment outside the autoclave. A soft-iron rod coated with glass allows to stirr the sample in the top of the high pressure tube magnetically.

A pressure balance (Budenberg) was used to measure pressures and in order to maintain a constant pressure, the pressure balance was combined with a pneumatic hydraulic pump. In addition the high pressure circuit was provided with a high precision Heise gauge. The pressure balance has been designed for two ranges: a low pressure range from 0.2 MPa up to 5.61 MPa and a high



Figure 3.1. The Cailletet-apparatus: A = autoclave; B = magnets; C = Cailletettube; D = drain; E = stirring-motor; H = hydraulic pump; Hg = mercury; I =inlet thermostat liquid; L = connection with dead weight pressure gauge; M =sample or mercury; Ma = manometers; O = outlet thermostat liquid; Or = oilreservoir; P = closing plug; R = O-rings; S = silicone rubber stopper; T =mercury trap; Th = glass thermostat; V = valve. pressure range from 2.1 MPa to 110.3 MPa. In the low pressure range a maximum accuracy of \pm 0.001 MPa and in the high pressure range \pm 0.02 MPa could be achieved. With the Heise gauge pressures up to 16.0 MPa could be determined with an accuracy of 0.002 MPa. Temperatures were determined using a 100 Ω platinum resistance-thermometer according to IPTS 68. The thermometer was connected to a modified Wheatstone bridge (type Bleeker). Equilibrium of the bridge was achieved and detected respectively by applying a decade resistance box and a μ V-meter (type Bleeker). The thermometer was tested with a 25 Ω platinum resistance-thermometer (Leeds and Northrup), which had been calibrated with some primary and secondary transition points according to IPTS 68.

In order to be able to perform measurements in the whole temperature range of interest (260 K - 450 K) different thermostat liquids were required:

260 K - 273 K: ethanol/water mixture;

273 K - 360 K: water;

350 K - 450 K: silicone oil.

Application of silicone oil as thermostat liquid did require some modification of the equipment.

Depending on the temperature region an accuracy in the stability as well as the measurement of the temperature of \pm 0.02 K could be attained. Details of the Cailletet-apparatus can be found elsewhere [1,2].

3.3. Experimental results

3.3.1. Two phase boundaries

The greater part of the measurements in the Cailletet-apparatus did consist of the determination of two phase boundaries such as L + V + L, $S_{\rm B}$ + L + L, etc.

Using figure 3.2 - a slight modification of figure 2.8 e - the determination of the two phase boundary $L + V \rightarrow L$ will be demonstrated. First the temperature is adjusted at a fixed value and the pressure is brought at a value where both phases L and V can exist. Then pressure is gradually increased until the vapour phase just disappears. It is essential that after each change in pressure equilibrium between the coexisting phases is established. At the pressure where the vapour phase just disappears a homogeneous liquid phase results and consequently the composition of this liquid



is the same as the original overall composition. A point of the two phase boundary is obtained when a small increase or decrease of the pressure can respectively let disappear or appear small amounts of the vapour phase. In the case of the two phase boundaries $L + V \rightarrow L$ in general this small variation of the pressure is less than the accuracy of the pressure balance, i.e. in the low pressure range

Figure 3.2. p.T-Section.

 \pm 0.001 MPa and in the high pressure range \pm 0.02 MPa. The collection of experimental data, determined in this way, are also called bubble-point curves.

In principle the two phase boundary $L + V \rightarrow V$ can be determined in a similar way. Again the measurement starts at a fixed temperature in the L+V-region but now the pressure is gradually decreased until the liquid phase has just disappeared. However, as in practice the disappearance of a small amount of a liquid phase in the neighbourhood of the mercury meniscus is very difficult to observe visually, this type of measurement is less accurate. An additional problem in determining these so-called dew points is the extremely low volatility of n-eicosane at the experimental conditions. This low volatility requires an expansion of the sample to a very low pressure, i.e. to a large volume in the Cailletet-tube above the mercury meniscus and this causes that the mercury meniscus is no longer visible.

As in the system ethane + n-eicosane partial miscibility occurs in the liquid phase also two phase boundaries of the type $L_2 + V \rightarrow L_1$ were determined. The measurement of these boundaries were performed in a quite similar way as the L + V \rightarrow L-boundaries. In order to determine two phase boundaries of the type $S_B + L + L$ a somewhat different experimental strategy had to be applied. Now the pressure was adjusted at a fixed value using the pneumatic hydraulic pump of the equipment and the temperature was set at a value where both phases S_B and L were present. Increasing the temperature gradually the disappearance of the solid phase S_B was observed. It was found that in this way the two phase boundaries $S_B + L + L$ could be determined more accurate than

with the experimental procedure discussed before. Such a boundary has in general a steep slope in the p,T-diagram and consequently small deviations in temperature cause large errors in pressure. Errors of the order of magnitude of + 0.2 MPa were observed.

A source of serious error which can occur more or less in all determinations of two phase boundaries is the loss of material of the sample below the mercury meniscus causing an unknown change in the composition of the sample if a mixture is investigated. Heating the Cailletet-tube far above the normal melting temperature of n-eicosane however allows in most cases to recollect all material of the sample in the top of the Cailletet-tube.

3.3.2. Three phase equilibria

If we consider the p,T-section shown in figure 3.2 it is obvious that the intersection of the two-phase boundaries L + V + L and S_B + L + L results in a point of the three phase locus S_B + L + V. An advantage of this indirect method of determining this three phase equilibrium is that besides the p,T-values also the liquid composition x_R at the equilibrium is known.

The p,T-behaviour of three phase equilibria can in general also be measured directly using a Cailletet-equipment. As three phase equilibria in binary mixtures are univariant the only condition to measure the pressure of the equilibrium is that at an adjusted value of the temperature the three phases are present and that equilibrium between them is established. Depending on the overall composition of the sample, the presence of the three phases can mostly be attained in an acceptable temperature range by varying the volume in the top of the Cailletet tube. An important condition which must be fulfilled during the experimental determination is the stability of the temperature around the equipment involved. This was achieved by mounting the Cailletet-apparatus in a thermostated air bath. The measurement of the pressure of the three phase equilibria was performed using the high precision Heise gauge as discussed in section 3.2. Both the three phase equilibria $S_{\rm B}$ + L + V and L_1 + L_2 + V were measured according to this direct method.

3.3.3. Volume measurements

The Cailletet-apparatus also allows to perform volume-measurements. For that purpose the Cailletet-tube is provided with calibration marks, which are related to the internal volume of the tube. This relation was obtained by gauging with mercury. This gauging technique has been discussed in detail by Van Welie [3].

Van der Kooi [1] showed that the main sources of experimental error are caused by gauging the tube and the measurement of the distance between the mercury meniscus and the calibration mark on the tube. An error analysis showed that in the volume-measurements an experimental error of $\Delta V/V \ge 100\% =$ 0.2% has to be expected. Some of the experimental data reported in this investigation were compared with the rather scarce pVT-data known in literature [4]. A maximum deviation of 0.5\% between these data was found.

An excellent and detailed discussion of the experimental method to perform volume-measurements with the Cailletet-apparatus as well as the treatment of the experimental data was already given by Van der Kooi [1] and will not be repeated in this work.

3.4. Experimental procedure

In order to prepare a sample of the mixture n-eicosane was filled into the top of the Cailletet-tube and its amount was determined by weighing. Under high vacuum conditions this amount was melted and degassed several times. Then degassed mercury was used to add a known quantity of ethane into the top of the Cailletet-tube which was cooled simultaneously with liquid nitrogen. The next step is to remove the Cailletet-tube from the gas-dosing apparatus and then mounting it into the stainless-steel autoclave. Finally the autoclave is closed and by means of the hydraulic system pressure is applied. As the volume, pressure and temperature of the amount of ethane is known, the number of moles $n_{\rm A}$ could easily be calculated from the equation:

$n_{A} = \frac{pV}{RT (1 + \gamma t) + Bp}$

(3.1)

In eq. (3.1) B is the second virial coefficient of ethane, γ the cubic thermal expansion coefficient of mercury and t the temperature of ethane in °C. The remaining quantities (p,V,T and R) have their usual meaning. In eq. (3.1) the term (1 + γ t) was inserted to correct the temperature dependence of the specific gravity of mercury. The numerical values of R, B and γ are:

 $R = 82.057 \text{ cm}^3 \text{atm} \text{K}^{-1} \text{mol}^{-1}$ $B = -191.0 \text{ cm}^3 \text{mol}^{-1}$ [5] $\gamma = 1.8182.10^{-4} \text{ °C}^{-1}$

Main sources of an error in the mole fraction of the sample are due to measuring the pressure of the amount of ethane dosed and the weight of the neicosane. In samples with high mole fractions of n-eicosane the first source of error dominates and the second source of error is important in samples with low mole fractions of n-eicosane.

Applying a similar error analysis with respect to the mole fraction, as discussed in detail by Van der Kooi [1], it was found that in the samples with high and low mole fractions of n-eicosane the errors in this quantity are \pm 0.006 and \pm 0.001 respectively.

3.5. The pure components

The ethane with which this research was started, was a Matheson Research Grade product. In order to verify its purity the vapour pressure curve of liquid ethane was measured. It was found that this saturated vapour pressure curve was about 0.08 MPa higher in pressure than the accepted vapour pressure curve of ethane measured by Douslin et al. [6]. By means of a GC-analysis it appeared that this ethane was contaminated with air. Additionally the ethane supplied by AGA was checked. This product had a specified minimum purity level of 99.995 moles per cent. Again the saturated vapour pressure curve of liquid ethane was measured and with the experimental error (\pm 0.001 MPa) excellent agreement with the measurements of Douslin et al. [6] was found. All measurements were performed using the AGA-ethane.

The n-eicosane used in this research was obtained from Shell Research in Houston (U.S.A.). A minimum purity level of 98.0 moles per cent of this pure substance was ascertained by this company.

Both ethane and n-eicosane were used throughout the experimental work without further purification.

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4. EXPERIMENTAL RESULTS

4.1. Introduction

This chapter contains the experimental results determined. Several types of two phase boundaries are presented e.g. L + V and S_B + L. Also the three phase lines S_B + L + V and L_1 + L_2 + V were determined experimentally. Finally pVT-measurements of ethane and n-eicosane are reported as well as pVT-measurements of their mixtures. For reasons of clarity all tables of this chapter are given at the end of this chapter.

4.2. L + V- and S_{B} + L-boundaries

In section 3.3.1. it was discussed how the two phase boundaries L + V and $S_B + L$ were determined experimentally. As at lower mole fractions of n-eicosane partial miscibility in the liquid phase occurs [1] also $L_1 + V_-$, $L_1 + L_2^-$ and L_2 + V-boundaries have to be expected in that region. In an ample discussion this behaviour was considered in detail in section 2.4.

Two different series of fillings were used for the measurements in the whole mole fraction range: one series in the temperature range from about 260 K up to 360 K and a second series from about 350 K up to 450 K. From the low temperature series L + V- (or $L_1 + L_2$ and $L_2 + V$) as well as $S_B + L$ -boundaries were determined and for the high temperature series only L + V-boundaries were measured. Table 4.1 gives the primary experimental results of the low temperature measurements.

Figure 4.1 shows graphically a part of the obtained experimental data of table 4.1 (open circles). The black dots in figure 4.1 were obtained from intersecting the fitting curves (full lines) of the experimental data points of each type of boundary to low degree polynomials of the form:

$$p = a_0 + a_1 T + a_2 T^2 + \dots$$
(4.1)

In this equation a_0 , a_1 , ... are adjustable parameters calculated using a linear least-squares program. It appeared that for the L + V - boundaries at highest a third degree polynomial was sufficient to represent the experimental data within the experimental error. As the $S_B + L$ - boundaries are nearly straight lines, a polynomial of the first degree was sufficient. In table 4.2 the experimental L + V - boundaries of the high temperature measurements are summarized.





Similarly figure 4.2 shows graphically the data of table 4.2 (open circles). Again the full lines are low degree polynomial representations of the experimental data.

The polynomial fits of the L + V - boundaries were used to calculate p,x-sections at chosen values of the temperature.Table 4.3 contains the p,x-data derived from the low temperature measurements (table 4.1). From table 4.1 also a table with T,x-data was derived. These data are to be found in table 4.4. With an exception of the fillings with a mole fraction of n-eicosane of 0.0183 and 0.0355, table 4.5 contains the calculated p,x-data of the high temperature measurements (table 4.2).



Fig. 4.2. Experimentally determined L + V - boundaries (open circles) and low degree polynomial fits (full lines) according to eq. (4.1.).

4.3. Three phase equilibria

4.3.1. The S_R + L + V equilibrium

From the work of Puri et al. [2] and Kohn et al. [1] it is acceptable to regard the vapour phase of the three phase equilibrium $S_B + L + V$ to be pure ethane in the region of interest. Figure 4.1 shows how of this three phase equilibrium p,T-values as well as liquid compositions x_B can be obtained by intersection of corresponding L + V- and $S_B + L$ - two phase boundaries, i.e. corresponding boundaries with the same overall composition x_B . In figure 4.1 these points of intersection are shown by black dots. The p,T-values of these points of intersection were calculated from the low degree polynomials with which the two phase boundaries were fitted. Table 4.6 gives the obtained p,T,x-data of the three phase equilibrium. Puri et al. [2] also measured this three phase equilibrium. Figure 4.3 shows a comparison of the p,T,x-data obtained by these authors (black squares) and those reported in this work (open circles). The full curves are drawn as well as possible through the open circles.



Fig. 4.3. Comparison of p.T.x-data of the three phase equilibrium $S_B + L + V$ reported by Puri et al. [2] (black squares) with those obtained in this work (open circles).

In section 3.3.2 it was pointed out how the three phase equilibrium $S_{\rm B}$ + L + V can also be measured directly. The experimental technique used for these direct measurements did only allow to obtain p,T-data of this

equilibrium. In table 4.7 these p,T-data as well as the overall composition of the low temperature fillings from which the data were obtained are given. Figure 4.4 shows a comparison of the p,T-data taken from table 4.6 (black dots) and some p,T-data taken from table 4.7 (open squares).



Fig. 4.4. Comparison of the p.T-data taken from table 4.6 (black dots) and some p.T-data taken from table 4.7 (open squares).

4.3.2. The $L_1 + L_2 + V$ equilibrium

As discussed in section 2.4 at low mole fractions of n-eicosane partial miscibility in the liquid phase occurs. From the series of subsequent p,T-sections (figures 2.8a until 2.8e) it can be concluded that in principle a point of the three phase equilibrium $L_1 + L_2 + V$ can be obtained by intersection of corresponding $L_1 + V$ - and $L_1 + L_2$ - boundaries, i.e. boundaries at the same overall composition. In order to calculate these points of intersection again low degree polynomial fits of the two phase boundaries were used. This method results in the determination of the pressure, temperature and the composition of the liquid phase L_1 . The obtained data are summarized

in table 4.8.

The three phase equilibrium $L_1 + L_2 + V$ was also determined by means of direct p,T-measurements. In table 4.9 these p,T-data as well as the overall composition of the low temperature fillings from which the data were obtained are given.

In figure 4.5 the p,T-data of table 4.8 (open squares), some selected data of table 4.9 (open circles) and experimental data taken from Kohn et al. [1] (black dots) and Specovius et al. [3] (black squares) are compared. The full lines in this figure are drawn as well as possible through the p,T-data of Kohn et al. [1] and the p,T-data of this work respectively.



Fig. 4.5. Comparison of p,T-data of the three phase equilibrium $L_1 + L_2 + V$. Open squares are taken from table 4.8, open circles from table 4.9, black dots from Kohn et al. [1] and black squares from Specovius et al. [3].

4.4. Volume measurements

From ethane as well as n-eicosane pVT-data are reported in literature by Douslin et al. [4] and Vargaftik [5] respectively. As the pVT-data of liquid n-eicosane lie somewhat outside the temperature region of interest additional pVT-measurements of this pure component appeared to be necessary. No pVTmeasurements of mixtures of ethane + n-eicosane are known in literature. In table 4.10 the volume-measurements of mixtures of ethane + n-eicosane including those of both pure components - are given. Figures 4.6a and 4.6b show the obtained volume-measurements of pure liquid n-eicosane graphically (open circles). The full curves in those figures were obtained by fitting the experimental data to the original Redlich-Kwong (RK) equation of state. In figure 4.6a the parameters were chosen temperature-independent and in figure 4.6b they were not. However, this will be discussed in chapter 6.

4.5. Discussion

Low degree polynomial representations of the experimental data of the two phase boundaries were used to calculate the points of intersection of two corresponding boundaries. In practice this means that some extrapolation is required with both polynomials. To perform this extrapolation with the highest accuracy possible, only a limited number of data points in the vicinity of the point of intersection were used for that purpose. Then it is possible to fit these data on the one hand with sufficient accuracy by means of a second degree polynomial and on the other hand these second degree polynomials allow some extrapolation. In order to calculate the p,x-data of tables 4.3 and 4.5 respectively and the T,x-data of table 4.4 overall polynomial fits of the boundaries were used. However it never appeared to be necessary to use higher degrees of the polynomials than three.

Figure 4.3 shows that our data of the three phase equilibrium $S_B + L + V$ obtained by intersection of corresponding two phase boundaries (open circles) are in good agreement with similar data of Puri et al. [2] (black squares). From this figure 4.3 it can also be observed that to lower temperatures the p,T-data of Puri et al. [2] have a tendency to deviate more and more from the vapour pressure curve of liquid ethane.

Figure 4.4 shows that the p,T-data of the three phase equilibrium $S_B + L + V$ obtained by intersection (open squares) are in good agreement with the p,T-data obtained by direct measurement of this three phase equilibrium (black dots).

Table 4.8 shows that the p,T,x-data of the three phase equilibrium $L_1 + L_2 + V$ obtained by intersection are not consistent. The reason of this inconsistency lies in the fact that both intersecting boundaries $(L_1 + V \text{ and } L_1 + L_2)$ meet each other in the p,T-plane with a very small difference in slope and consequently large errors in the evaluation of the points of intersection have to be expected. Kohn et al. [1] as well as Specovius et al. [3] measured the lower critical endpoint (LCST) and the upper critical endpoint (UCST) of this three phase equilibrium. From figure 4.5 it can be concluded that these results do not agree. This figure also shows that the p,T-measure-



ments of the three phase equilibrium $L_1 + L_2 + V$ reported in this work lie at a pressure of about 0.02 MPa lower than the measurements of Kohn et al. [1]. However, the ethane used by these authors had a minimum purity level of 99 moles per cent while the ethane used in this work had a purity of 99.995 moles per cent. From the work of Rodriques et al. [6] it may also be concluded that the ethane used by Kohn et al. [1] did contain methane and nitrogen as major impurities. This fact was already discussed by Peters et al. [7].

In section 3.3.3 it was pointed out that our experimental method to measure pVT-data did not have a comparable accuracy as the method applied by Douslin et al. [4] for ethane. For that reason the data of ethane determined by Douslin et al. [4] must be preferred for practical purposes.

Table 4.1. Experimental results of L + V - (L_1 + V, L_1 + L_2 or L_2 + V) and $S_{\rm B}^{}$ + L - boundaries.

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
rugen az-	and double-interface	x _B = 0.0018, L	+ V - boundary	(Englishing)	and the second
264.89	1.941	304.10	4.714	308.84	5.170
268.31	2.116	305.08	4.806	308.87	5.172
270.56	2.237	306.06	4.902	308.89	5.174
274.11	2.440	307.05	4.996	308.97	5.178
274.65	2.469	307.08	4.997	308.95	5.180
277.07	2.616	308.03	5.092	309.01	5.185
279.56	2.770	308.52	5.137	309.00	5.185
281.98	2.930	308.54	5.141	309.00	5.186
284.46	3.100	308.52	5.142	309.06	5.189
287.39	3.308	308.59	5.146	309.06	5.190
289.36	3.455	308.62	5.147	309.10	5.193
292.29	3.683	308.64	5.150	309.15	5,200
294.27	3.842	308.70	5.157	309.21	5.204
297.19	4.089	308.72	5.158	309.26	5.208
299.19	4.260	308.74	5.160	309.35	5.217
301.14	4.434	308.80	5.166	309.40	5.222
302.10	4.524	308.82	5.168	309.44	5.226
303.12	4.619	308.82	5.168	309.49	5.229
304.05	4.702	308.85	5.170	309.54	5.234
		$x_{B} = 0.0018, S_{B}$	+ L - boundary		
263.43	4.050	262.06	8.050	261.39	10.050
262.75	6.050				

Table 4.1. (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
		x _B = 0.0099, L -	⊦V - boundary		
280.58	2.808	302.35	4.494	326.97	8.098
283.13	2.974	307.27	4.978	331.85	8.803
285.88	3.163	312.28	5.765	336.36	9.471
288.43	3.348	317.17	6.580	341.65	10.110
293.33	3.723	322.07	7.356	352.42	11.390
298.24	4.127	110.00		1. 1078 . C	
	1- 25. EAR	$x_{B} = 0.0099, S_{B}$	+ L - boundary	and the second	
278.80	2.749	277.41	5.550	276.39	8.550
278.20	3.548	277.05	6.551	276.15	9.550
277.98	4.551	276.67	7.551	275.90	10.550
100.51	10.200	x _B = 0.0183, L -	+ V - boundary	E-49.2 12	
283.10	2.957	307.40	5.030	327.38	8.492
284.49	3.051	308.60	5.259	331.82	9.180
286.74	3.209	310.56	5.616	336.71	9.867
289.68	3.423	311.94	5.867	341.78	10.622
292.72	3.658	312.35	5.933	346.68	11.325
296.43	3.963	314.89	6.391	351.39	11.875
299.87	4.258	317.54	6.850	354.27	12.211
302.15	4.465	319.82	7.239	358.96	12.761
305.09	4.751	322.13	7.632	362.03	13.101
307.05	4.965				
086,8-	10,500	$x_{B} = 0.0183, S_{B}$	+L-boundary	TIBLE	295.20
282.17	3.050	280.69	6.251	290.05	8.551
281.61	4.150	280.44	7.251	279.84	10.050
281.10	5.050				

Table 4.1. (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
		x _B = 0	.0355		
285.18	3.072	307.73	5.132	327.74	8.722
287.23	3.216	308.24	5.232	330.66	9.182
289.39	3.374	309.25	5.423	333.61	9.651
291.32	3.522	310.32	5.623	336.58	10.102
293.32	3.678	311.68	5.882	339.53	10.542
295.99	3.899	311.88	5.912	342.37	10.942
298.38	4.104	313.05	6.139	345.32	11.362
300.63	4.307	316.01	6.688	351.13	12.161
303.74	4.607	318.92	7.204	354.20	12.560
305.84	4.827	321.19	7.607	357.15	12.921
306.10	4.851	321.80	7.722	360.12	13.281
306.75	4.943	324.79	8.222	363.03	13.621
307.25	5.043				
	x	$_{\rm B} = 0.0355, S_{\rm B}$	+ L - boundary	10.5	1938
284.36	3.050	283.74	5.501	283.37	8.051
284.35	3.151	283.61	6.051	283.24	9.051
284.07	4.050	283.46	7.051	283.21	10.051
284.07	4.051				
18-CE		$x_{B} = 0.0527, L$	+ V - boundary	200.2	× - della
289.46	3.357	306.79	4.924	327.04	8.518
292.40	3.582	307.73	5.042	328.91	8.830
295.28	3.817	308.97	5.277	332.37	9.390
299.17	4.155	311.07	5.677	335.51	9.884
301.62	4.389	313.98	6.208	338.40	10.327
304.15	4.636	318.18	6.973	346.14	11.467
305.80	4.814	323.14	7.854	347.19	11.620
	>	$x_{\rm B} = 0.0527, S_{\rm B}$	+ L - boundary		
285.23	3.551	285.12	5.051	284.90	10.051
285.21	4.051	284.95	8.051		

Table 4.1. (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
		$x_{B} = 0.0967, L$	+ V - boundary		
293.12	3.566	322.25	6.991	341.09	10.009
296.95	3.882	322.25	6.994	351.12	11.444
303.61	4.466	331.33	8.485	351.13	11.452
311.87	5.395	331.30	8.489		Select.
15 Pb.	10-05-03	$x_{B} = 0.0967, S_{B}$	+ L - boundary	1999-12-10 ⁵	1.18-149
287.07	3.101	287.23	5.299	287.50	8.700
287.10	3.405	287.40	6.951	287.64	9.899
287.28	5.279				291.32
	1.6.6	$x_{B} = 0.1421, L$	+ V - boundary	100-2-00-2-	224,489
289.02	3.091	306.11	4.447	333.41	7.659
292.25	3.317	311.01	4.920	341.14	8.709
296.26	3.616	319.79	5.885	349.23	9.778
299.10	3.840	326.54	6.741	355.92	10.646
302.13	4.098				
19.02		$x_{B} = 0.1421, S_{B}$	+ L - boundary	- 21 -	40. 259
289.13	3.254	289.56	6.453	289.89	8.553
289.36	5.053	289.70	7.453	290.30	11.053

Table 4.1. (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
		$x_{B} = 0.1908, L$	+ V ~ boundary		
292.31	3.094	316.82	5.012	341.33	7.546
297.21	3.425	321.72	5.472	346.25	8.093
302.08	3.780	326.64	5.963	351.25	8.093
306.99	4.159	331.53	6.481	356.03	9.185
311.92	4.569	336.43	7.006	360.95	9.726
	ocular -	$x_{B} = 0.1908, S_{B}$	+ L - boundary	101.2	- TOUCHS
291.15	3.051	291.71	6.051	292.08	8.050
291.33	4.051	291.91	7.051	292.46	10.050
291.53	5.051				
24.20.5	in the left	$x_{B} = 0.2693, L$	+ V ~ boundary	1- 56/192-1-	14.381
298.15	3.008	317.78	4.261	337.37	5.749
303.06	3.295	322.68	4.608	342.28	6.144
307.96	3.602	327.59	4.976	349.12	6.712
312.86	3.923	332.49	5.355	356.07	7.294
134.39		$x_{B} = 0.2693, S_{B}$	+ L - boundary	229.35	1.075
294.23	2.847	294.86	5.548	295.42	8.550
294.38	3.547	295.02	6.550	295.63	9.550
294.64	4.547	295.23	7.550	295.72	10.049

Table 4.1 (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
	1. 3 (<u>5</u> .6)	$x_{B} = 0.3349, L$	+ V - boundary	12435	
298.63	2.602	317.77	3.589	341.25	4.982
302.74	2.801	325.28	4.023	349.10	5.505
309.89	3.164	333.11	4.494	356.95	6.023
		$x_{B} = 0.3349, S_{B}$	+ L - boundary		in the
296.75	3.052	297.40	6.051	298.20	9.051
296.97	4.052	297.63	7.052	298.43	10.051
297.20	5.052	297.97	8.052		
	ind.	$x_{B} = 0.4191, L$	+ V - boundary	020.4.7	31,200
300.20	2.171	316.09	2.801	344.77	4.107
302.37	2.251	325.88	3.227	354.51	4.588
307.27	2.440	334.97	3.643	AND 10 1	- 10 PM
		$x_{B} = 0.4191, S_{B}$	+ L - boundary		and the
299.41	2.253	300.09	5.5053	300.80	8.052
299.61	3.053	300.34	6.053	301.05	9.053
299.85	4.053	300.58	7.052	301.28	10.053
10,050	01.808	$x_{B} = 0.4959, L$	+ V - boundary	140,8 ····	06.308
303.16	1.844	319.33	2.353	335.99	2.930
310.02	2.053	323.74	2.502	345.78	3.287
316.90	2.273	329.11	2.688	355.56	3.655
070.1	129,23	$x_{B} = 0.4959, S_{B}$	+ L - boundary	1882.0 - 10	in altradio
301.47	2.050	302.22	5.050	302.95	8.050
301.73	3.050	302.46	6.050	303.18	9.050
301.97	4.050	302.71	7.050	303.45	10.049

Table 4.1. (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
		x _B = 0.5850, L	+ V - boundary		
305.94	1.466	333.59	2.135	350.87	2.595
314.00	1.650	343.20	2.384	358.70	2.808
323.80	1.886				
		$x_{B} = 0.5850, S_{B}$	+ L - boundary	375.27	1
303.15	1.650	304.02	5.050	304.76	8.050
303.26	2.050	304.26	6.050	305.01	9.050
303.51	3.050	304.51	7.050	305.25	10.050
303.75	4.050				
181.24	a reisigner	x _B = 0.7151, L ·	+ V - boundary	Traine .	95.025
307.17	0.919	324.67	1.166	344.43	1.462
309.18	0.946	334.58	1.310	354.09	1.616
315.06	1.026				
	a Guidel ji	$x_{B} = 0.7151, S_{B}$	+ L - boundary	125 MARCO	1.16
305.80	1.051	306.80	5.047	307.59	8.047
306.06	2.051	307.07	6.047	307.84	9.050
306.30	3.047	307.35	7.047	308.10	10.050
306.59	4.047	and the state			
est de	Brickt	$x_{B} = 0.8008$, L -	+ V - boundary	ERGES T	5 32.602
308.44	0.608	326.57	0.770	345.67	0.954
316.78	0.682	336.36	0.864	355.23	1.050
8.050	302+95	$x_{B} = 0.8008, S_{B}$	+ L - boundary	2.030	301.42
307.20	1.052	308.24	5.052	308.98	8.052
307.46	2.052	308.49	6.052	309.25	9.052
307.72	3.052	308.74	7.052	309.48	10.052
307.98	4.052				

Table 4.1. (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
Surl.4	1911	$x_{B} = 0.9174, L$	+ V ~ boundary	2. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.	211
310.06	0.234	325.97	0.286	345.55	0.353
316.24	0.252	335.76	0.319	355.99	0.391
Al Bearly and	91.282	$x_{B} = 0.9174, S_{B}$	+ L - boundary	4941.340	04-27122
308.75	0.550	309.65	4.052	310.70	8.052
308.87	1.051	309.91	5.052	310.95	9.052
309.14	2.052	310.17	6.052	311.20	10.052
309.39	3.052	310.45	7.052		

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
642.0	Care and	$x_{B} = 0.0519, L$	+ V - boundary	у	1.000.00
342.48	10.923	352.03	12.248	369.26	14.336
344.40	11.194	353.91	12.493	374.11	14.856
346.30	11.466	355.84	12.745	378.98	15.358
348.20	11.727	359.73	13.226	383.86	15.828
350.10	11.987	364.54	13.804	388.73	16.268
	1	x _B = 0.0953, L	+ V - boundary	y	2012 QC. VS
352.03	11.574	378.38	14.772	396.80	16.551
360.71	12.707	386.93	15.648	401.51	16.847
369.37	13.765	391.93	16.117		
	2.646	$x_{B} = 0.2055, L$	+ V - boundary	y	1.4
355.97	8.781	382.10	11.388	418.20	14.388
364.61	9.660	390.94	12.198	427.04	14.993
369.26	10.140	400.70	13.038	435.85	15.548
373.17	10.528	409.46	13.738	444.72	16.048
CHALTER -		$x_{B} = 0.3057, L$	+ V - boundary	V	
366.99	7.280	405.32	9.948	434.93	11.680
373.77	7.779	415.20	10.563	444.80	12.180
385.59	8.621	425.07	11.138	450.72	12.460
395.45	9.298				

Table 4.2. Experimental results of the L + V - boundaries in the high temperature range.

Table 4.2. (continued).

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
	18.3.8.	$x_{B} = 0.4200, L$	+ V - boundary		1
350.65	4.373	386.85	6.138	423.33	7.796
360.92	4.865	395.92	6.557	432.16	8.164
369.26	5.280	404.80	6.981	441.94	8.547
378.20	5.620	413.55	7.377	451.75	8.907
- Carlos		$x_{B} = 0.5033$, L	+ V - boundary		0,0127
353.94	3,505	388.85	4.794	423.93	6.015
362.67	3.827	397.64	5.113	432.71	6.307
371.03	4.136	406.37	5.421	441.59	6.576
379.84	4.464	415.12	5.724	450.37	6.836
R. 3- 1 (PT	ele stat	$x_{B} = 0.6020, L$	+ V - boundary		1. 1. 1. 1. 1.
355.48	2.540	390.73	3.443	425.01	4.283
364.17	2.799	399.52	3.663	433.77	4.481
372.73	2.981	408.10	3.877	442.84	4.680
381.34	3.202	417.07	4.094	451.54	4.862
		$x_{B} = 0.7412, L$, + V - boundary		
354.86	1.435	390.58	1.939	425.35	2.416
363.58	1.556	399.34	2.062	434.14	2.530
373.02	1.691	408.06	2.182	442.84	2.639
381.81	1.816	416.67	2.299	451.67	2.746

T/K =	270.0	280.0	290.0	300.0	310.0	320.0	330.0	340.0	350.0
х _в			- Olebo	р	/MPa		1		
0.0018	2.206	2.800	3.505	4.333	5.8% S				
0.0099		2.769	3.464	4.282		7.035	8.551	9.913	11.122
0.0183			3.451	4.266		7.270	8.894	0.376	11.707
0.0355			3.430	4.237		7.400	9.080	10.611	12.004
0.0527			3.397	4.231		7.304	9.005	10.573	
0.0967				4.086	5.197	6.542	8.252	9.861	11.302
0.1421			3.178	3.891	4.833	5.953	7.200	8.524	9.873
0.1908				3.614	4.403	5.315	6.322	7.394	8.506
0.2693				3.115	3.731	4.418	5.164	5.957	6.784
0.3349				2.667	3.171	3.717	4.299	4.914	5.559
0.4191					2.550	2.968	3.412	3.879	4.364
0.4959					2.052	2.376	2.718	3.076	3.445
0.5850					1.557	1.793	2.042	2.301	2.570
0.7151					0.958	1.097	1.243	1.394	1.550
0.8008					0.622	0.710	0.803	0.899	0.998
0.9174					0.233	0.266	0.299	0.334	0.369
			A STATE AND						

Table 4.3. p,x-Data derived from table 4.1.

Table 4.4. T,x-data derived from table 4.1.

p/MPa ≈	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
х _в					T/K		100	1.00		
0.0018		264.13	263.79	263.45	263.11	262.76	262.42	262.08	261.74	261.40
0.0099			278.62	278.12	277.66	277.25	276.88	276.55	276.27	276.02
0.0183			282.19	281.66	281.19	280.79	280.45	280.18	279.98	279.85
0.0355				284.08	283.82	283.61	283.45	283.33	283.25	283.22
0.0527				285.20	285.12	285.06	285.00	284.96	284.92	284.90
0.0967				287.15	287.23	287.31	287.39	287.47	287.55	287.63
0.1421				289.22	289.35	289.49	289.64	289.79	289.95	290.12
0.1908				291.33	291.51	291.70	291.89	292.08	292.26	292.45
0.2693			294.27	294.50	294.71	294.93	295.13	295.33	295.52	295.70
0.3349			296.74	296.95	297.18	297.41	297.65	297.91	298.17	298.44
0.4191			299.59	299.84	300.08	300.32	300.56	300.80	301.03	301.27
0.4959		301.47	301.71	301.96	302.20	302.45	302.69	302.94	303.18	303.43
0.5850		303.24	303.50	303.75	304.00	304.25	304.50	304.75	304.99	305.24
0.7151		306.04	306.30	306.55	306.81	307.07	307.32	307.58	307.83	308.09
0.8008	307.19	307.45	307.71	307.97	308.22	308.48	308.73	308.98	309.23	309.47
0.9174	308.86	309.12	309.38	309.64	309.90	310.16	310.42	310.68	310.94	311.20
1.0000	309.92	310.18	310.44	310.69	310.95	311.21	311.47	311.73	311.99	312.25

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ipn-v									0 01.
0	370.0	380.0	390.0	400.0	410.0	420.0	430.0	440.0	450.0
				p/MPa					
879	ST0.18	WALCINE .							
267									
260	14.419	15.456							
608	13.835	14.958	15.944	16.760					
196	10.216	11.188	12.109	12.974	13.779	14.519	15.190	15.789	16.310
755	7.502	8.228	8.929	9.601	10.241	10.847	11.415	11.943	12.426
813	5.292	5.777	6.263	6.742	7.210	7.659	8.085	8.480	8.840
729	4.100	4.470	4.836	5.195	5.547	5.888	6.217	6.530	6.825
667	2.920	3.174	3.426	3.677	3.922	4.163	4.395	4.395	4.831
507	1.648	1.790	1.931	2.071	2.209	2.344	2.476	2.604	2.726
				Sherris.	SHORE IT	tar galo m	01.1030		

<i>Table</i>	4.6.	р,Т,	x-Data	of	the	three	phase	equilibriu	SB	÷	L	+	V	calculated	
from i	5 + 1	- and	SR +	L -	bour	ndaries	s (tabi	e 4.1).							

T/K	p/MPa	×в
264.16	1.906	0.0018
278.62	2.683	0.0099
282.21	2.897	0.0183
284.39	3.018	0.0355
285.25	3.064	0.0527
287.07	3.103	0.0967
289.07	3.099	0.1421
291.15	3.039	0.1908
294.25	2.799	0.2693
296.58	2.504	0.3349
299.39	2.141	0.4191
301.42	1.793	0.4959
303.10	1.404	0.5850
305.76	0.900	0.7151
307.10	0.597	0.8008
308.66	0.229	0.9174

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
2.54	The Land	filling $x_B = 0$.0099	145	
264.01	1.883	270.85	2.232	274.77	2.449
265.96	1.979	271.83	2.289	275.94	2.523
267.91	2.075	272.91	2.346	277.11	2.583
268.91	2.126	273.98	2.408	278.07	2.651
	Ser en	filling $x_B = 0$.0183		10.585
273.68	2.402	N			of ges
		filling $x_B = 0$.0355		- يقد لية
275.67	2.510			inst to a	i ka Ma
1994	Alter Second	filling $x_B = 0$.0967		06. Ý75
264.43	1.923	279.42	2.732	286.06	3.080
270.20	2.219	281.95	2.882	286.67	3.099
273.33	2.381	283.85	2.989	287.07	3.111
276.30	2.550	285.10	3.046	287.12	3.116
277.97	2.653				
Section 2.		filling $x_B = 0$.1421	Evress - m	
287.59	3.108	288.05	3.110	288.86	3.101
287.60	3.111	288.58	3.108	289.18	3.092

Table 4.7. Direct measurements of the three phase equilibrium ${\rm S}_{\rm B}$ + L + V.

Table 4.7. (continued).

	(100	m ///	/\\D	TP /1/	- /MD-
Т/К	р/мРа	1/K	p/mPa	1/K	р/мРа
19 1		filling $x_B = 0$.1908	- 10 - 12 - 14	1/1
292.29	2.950	294.06	2.793	296.08	2.570
292.67	2.914	294.57	2.742	296.57	2.512
293.05	2.887	295.06	2.690	297.07	2.446
293.55	2.836	295.60	2.631		
		filling $x_B = 0$.2693		
295.22	2.668	298.12	2.291	299.89	1.808
296.18	2.551	298.61	2.222	300.47	1.908
297.04	2.442	299.31	2.110	301.05	1.808
A start	N. Pro. 30 282	filling $x_B = 0$.3349		Subury Sac as
298.25	2.289	301.87	1.672	303.85	1.290
298.94	2.185	302.36	1.573	304.35	1.188
360,11	1.990	302.86	1.471	304.83	1.056
300.89	1.849	303.36	1.379	305.22	0.971
301.39	1.761		Sec. Sec.	is mare	2 Packor
4.10	Epg	filling $x_B = 0$.4191	(20.2	Softee -
299.24	2.166	299.71	2.072		State and
1.1	Re File and	filling $x_B = 0$.5850	San anga ak	R 808
303.94	1.283	305.39	0.952	306.78	0.630
304.43	1.173	305.89	0.842	307.18	0.530
304.91	1.071	306.38	0.728		
	130	filling $x_B = 0$.7151	101.0	
306.18	0.781	307.17	0.550	308.15	0.281
306.66	0.670	307.64	0.427		

Table 4.8. p,T,x-Data of the three phase equilibrium $L_1 + L_2 + V$ calculated from $L_1 + V$ - and $L_1 + L_2$ - boundaries.

T/K	p/MPa	x _B (L ₁)
306.29	4.868	0.0183
306.79	4.911	0.0355
307.49	4.996	0.0527

Table 4.9. Direct measurements of the three phase equilibrium ${\rm L}_1$ + ${\rm L}_2$ + V.

T/K	p/MPa	filling	T/K	p/MPa	filling
306.75	4.921	$x_{\rm B} = 0.0355$	309.20	5.191	$x_{\rm R} = 0.0355$
306.85	4.931	D	309.35	5.211	D
306.89	4.935		309.50	5.227	
306.94	4.947		309.63	5.250	
307.12	4.966		309.68	5.250	
307.42	5.008		306.99	4.947	$x_{\rm R} = 0.0527$
307.68	5.031		307.13	4.963	D
307.89	5.053		307.32	4.983	
308.01	5.068		307.41	4.995	
308.15	5.080		307.50	5.003	
308.24	5.087		307.71	5.024	
308.34	5.096		307.91	5.046	
308.44	5.108		308.11	5,066	
308.62	5.129		308.40	5.105	
308.72	5.141		308.69	5.130	
308.82	5.154		309.08	5.180	
308.83	5.149		309.46	5.223	
308.92	5.169		309.56	5.234	
308.95	5.167				
309.07	5.173				

Table 4.10. Molar volumes in $\operatorname{cm}^3 \operatorname{nol}^{-1}$ of liquid mixtures of ethane + n-eicosane.

					$x_{B} = 0.00$	00				
o/MPa	274.02 K	283.01 K	292.71 K	303.44 K	313.19K	322.75K	332.81 K	342.54 K	352.30K	362.68K
4.049	72.32	76.79	85.42							
6.049	70.63	73.96	79.88	89.49	115.51	206.70	262.10	292.05	332.73	361.58
8.049	69.32	72.12	76.56	83,36	60°16	106.00	136.69	173.31	206.18	234.54
640.01	68.34	70.87	74.58	79.69	84.82	92.48	104.31	121.22	143.07	165.94
12.049	67.18	69.50	72.78	77.22	80.94	86.75	93.74	103.33	117.01	131.36
14.049	66.44	68.69	71.58	75.09	78.36	82.77	87.94	96.96	102.94	112.60
16.049	85.68	67.56	70.17	73.64	76.36	80.01	87.40	89.81	95.90	106.16
					$x_{B} = 0.05$	37				
p/MPa	287.96K	293.88K	302.70K	314.11 K	322.81 K	332.71 K	342.62 K			
4.050	82.18	83.47								
6.050	81.00	82.24	84.09							
7.050				88.35						
8.050	80.07	81.19	83.57	87.34	90.94					
9.050					89.52					
10.050	79.08	80.42	82.54	85.75	88.71	92.62				
11.050					87.77	91.22	95,35			
12.050	78.42	79.55	81.49	84.46	87.60	90.14	93.61			
13.050					86.23	89.15	92.50			
14.050	77.62	78.77	80.53	83.32	85.47	88.39	91.34			
15.050					85.08	87.75	90.45			
16.050	77.05	78.16	79.75	82.40	84.59	87.05	89.50			

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8 Table 4.10 (continued).

				0.7 4.0	$x_{B} = 0.10$	060			
p/MPa	292.48 K	302.52 K	312.63 K	322.76 K	331.95 K	342.19 K	352.01 K	362.51 K	
4.057	93.11				C. C. L. C.	S OF THE	in an inst		
6.057	92.54	94.23	96.92						
8.057	91.98	93.70	96.03	98.79					
10.057	91.40	93.00	95.23	97.70	100.39				
12.057	89.20	92.50	94.50	96.88	99.01	101.37	104.48		
14.057	88.74	92.03	93.89	96.06	98.02	100.33	103.04	106.04	
16.057	88.30	91.52	93.28	95.43	97.24	99.35	101.79	104.48	
PUGMA	3.581.381	5.69 1997	303,708	314 1 / K	$x_{B} = 0.21$	113	- PHANESK		
p/MPa	342.45 K	352.64 K	362.83 K						
8.062	129.95	1.125-20	10.11	1 43.64	36.36	ROTAT	1,03,145	186161" / 62 60	
10.062	129.19	131.29							
12.062	128.45	130.51	132.73						
14.062	127.79	129.66	131.81						
16.062	127.08	128.96	130.94						
18.062		128.23	130.12	and a	112.51	24 1962 - 1	1 305 10	100.05 332.73	191 3

Table 4.10 (continued).

			1011120	Sale Sale	$x_{B} = 0.22$	218	and a second		
p/MPa	297.99 K	303.32 K	313.20 K	322.44 K	332.69 K	342.93 K	352.58 K	362.51 K	
6.057	124.76	125.68	28270210	3293.30	5307.78	152.34	324,49		
8.057	124.15	125.28	127.08	129.08					
10.057	123.47	124.88	126.62	128.36	130.46	131.37			
12.057	123.17	124.49	126.16	127.86	129.80	130.74	132.15		
14.057	122.72	124.01	125.58	127.31	129.10	129.99	131.45	135.06	
16.057	122.48	123.56	125.05	126.72	128.19	129.38	130.89	134.35	
18.057		123.15	124.56	126.31	127.98	128.71	130.25	133.64	
					$x_{B} = 0.30$	065	in the		
p/MPa	297.96 K	303.49 K	308.03 K	313.29 K	323.00 K	332.55 K	342.25 K	352.27 K	362.55 K
4.061	150.19	151.57	152.30	153.40	and sea	600425	-500-13		
6.061	149.81	151.02	151.92	152.82	155.24	156.83	158.71		
8.061	149.33	150.62	151.41	152.36	154.78	156.22	158.23	160.34	162.10
10.061	148.89	150.15	150.82	151.99	154.30	155.60	157.74	159.57	161.28
12.061	148.43	149.72	150.46	151.41	153.73	155.05	156.96	158.92	160.49
14.061	148.02	149.31	150.01	150.97	153.30	154.45	156.37	158.21	159.73
16.061	147.63	148.81	149.66	150.57	152.78	154.09	155.78	157.55	159.07
18.061	alia kar	148.44	149.27	150.25	152.24	153.55	155.21	157.05	158.41

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				andra (Maria andra) Andra (Maria andra)	$x_{B} = 0.44$	73		
p/MPa	308.02 K	312.90 K	322.90 K	332.23 K	342.71 K	352.27 K	362.46 K	astro a state and and
4.063	197.06	198.39	200.80	TROTES	123138	154.09	12:19:40	nastales (1894.01
6.063	196.60	197.94	200.12	201.59	204.31	207.01	209.04	
8.063	196.07	197.44	199.60	201.03	203.73	205.99	208.26	
10.063	195.59	196.97	199.20	200.47	203.11	205.24	207.46	
12.063	195.15	196.47	198.60	199.90	202.45	204.76	206.72	
14.063	194.78	196.05	198.13	199.51	201.96	204.17	206.14	
16.063	194.32	195.57	197.60	198.96	201.43	203.57	205.42	
18.063	193.94	195.17	197.13	198.43	200.92	203.06	204.73	
		New gery	36 C. 63 L 50		$x_{B} = 0.51$	48		
p/MPa	308.43 K	312.90 K	322.78 K	332.43 K	342.95 K	353.11 K	362.02 K	BERTHER STREET
2.063	215.23		122,05	120.12	11291/11	126 261	3 8 68	and the second second
4.063	214.55	216.47	218.19	220.40	222.63			
6.063	214.01	215.93	217.49	219.81	222.00	224.22	226.54	
8.063	213.38	215.24	216.97	219.18	221,37	223.55	225.77	
10.063	212.98	214,74	216.48	218.74	220.81	222.88	225.09	
12.063	212.56	214.17	216.05	218.20	220.16	222.14	224.49	
14.063	212.06	213.71	215.59	217.69	219.60	221.62	223.80	
16.063	211.68	213.28	215.01	217.08	219.09	220.99	223.07	
18.063	211.12	212.83	214.52	216.59	218.61	220.36	222.52	

Table 4.10 (continued).

191090	- The set of	1357 815	100712-18		$x_{B} = 0.62$	129		
p/MPa	308.54 K	313.36 K	323.52 K	332.78 K	342.56 K	352.41 K	362.32K	367.59K
2.066	246.08	247.05	249,65	252.04				
4.066	245.50	246.60	249.06	251.23	253.74	256.32	258.61	259.87
6.066	245.02	246.01	248.42	250.71	253.10	255.53	257.87	258.96
8.066	244.49	245.49	247.89	250.10	252.30	254.90	257.10	258.04
10.066	243.92	244.96	247.34	249.58	251.78	254.20	256.51	257.49
12.066	243.57	244.43	246.79	249.02	251.28	253.51	255.85	256.84
14.066	243.07	244.03	246.34	248.40	250.76	252.87	255.15	256.18
16.066	242.69	243.46	245.94	247.83	250.08	252.30	254.55	255.61
18.066		243.08	245.32	247.41	249.58	251.71	254.02	254.92
328	alente		1004	2012	$x_{B} = 0.72$	188		
p/MPa	308.70 K	313.20 K	322.68 K	332.85 K	342.64 K	353.76 K	362.21 K	
2.066	276.39	277.09	279.71	282.29	284.95	288.13	290.69	
4.066	275.67	276.55	278.98	281.65	284.26	287,33	289.90	
6.066	275.14	276.07	278.11	280.94	283.55	286.59	289.14	
8.066	274.48	275.58	277.76	280.31	282.92	285.92	288.31	
10.066	274.01	275.07	277.27	279.73	282.33	285.20	287.63	
12.066	273.56	274.58	276.71	279.21	281.66	284.49	286,91	
14.066	273.09	274.05	276.14	278.63	280.99	283.82	286.30	
16.066	272.61	273.57	275.59	278.04	280.38	283.16	285.53	
18.066	272.17	273.08	275.11	277.47	279.83	282.49	284.78	

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16,004	2027-61	533724			$x_{B} = 0.83$	138	0.002123		
p/MPa	313.40K	323.28 K	332.79K	342.37K	352.28K	362.72K			
2.066	308.22	310.69	312.84	316.09	318.94	322.11			
4.066	307.39	310.15	312.04	315.30	318.18	320.71			
6.066	306.75	309.45	311.43	314.55	317.33	319.76			
8.066	306.12	308.93	310.76	313.87	316.58	318.93			
10.066	305.62	308.07	310.14	313.21	315.85	318.02			
12.066	305.01	307.60	309.44	312.38	315.10	317.33			
14.066	304.51	306.99	308.83	311.75	314.59	316.56			
16.066	303.97	306.56	308.33	311.18	313.99	315.81			
18.066	303.46	305.98	307.68	310.62	313.34	315.10			
Negaee -	275 P.	Starge .	N.S.S.S.	TRANK STR	x _B 0.891	10	5.8.24	1222.51	
p/MPa	322.99 K	342.58 K	351.79 K	362.36 K		2019-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-	- statistic	- 630-16	11100
2.060	332.80	338.07	338.09	343.15	Service A	100 100			the state
4.060	331.69	337.12	337.30	342.19					
6.060	331.05	336.53	336.50	341.40					
8.060	330.50	335.57	335.75	340.57					
10.060	329.82	334.94	335.00	339.81					
12.060	329.15	334.26	334.32	338.98					
14.060	328.17	333.63	333.73	338.30					
16.060	327.64	332.91	333.13	337.51					
18.060	327.33	332.20	332.34	336.75					

Table 4.10 (continued).

11111	a seriente	346.14			$x_{B} = 0.91$.69
p/MPa	313.57K	322.98K	332.75K	341.81K	352.08K	362.81 K
2.057	336.90	339.68	343.10	346.05	349.01	352.63
4.057	336.19	339.13	342.23	345.25	348.14	351.66
6.057	335.10	338.32	341.53	344.18	347.08	350.51
8.057	334.50	337.74	340.55	343.13	346.19	349.57
10.057	333.83	337.07	339.69	342.49	345.31	348.46
12.057	333.15	336.41	339.02	341.53	344.46	347.67
14.057	332.53	335.73	337.92	340.99	343.56	346.86
16.057	331.82	334.96	336.93	340.25	342.96	346.03
	. 189.89		the free	195 12	$x_{B} = 0.92$	285
p/MPa	313.63 K	323.40 K	333.07 K	343.13K	353.14K	363.31 K
2.067	341.52	344.44	347.29	350.30	353.32	356.31
4.067	340.70	343.76	346.52	349.49	352.41	355.38
6.067	340.14	343.01	345.89	348.81	351.68	354.49
8.067	339,48	342.35	345.12	347.97	350,89	353.61
10.067	338.85	341.77	344.48	347.20	350.12	352.76
12.067	338.28	341.11	343.73	346.54	349.35	351.93
14.067	337.78	340.43	343.07	345.93	348.60	351.13
16.067	337.19	339.84	342.44	345.25	347.92	350.34
18.067	336.60	339.21	341.83	344.57	347.19	349.68

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DI TORS.	1,220,00				$x_{B} = 0.95$	583	an a star in the second starting of the
p/MPa	313.71 K	323.50 K	333.57 K	343.36 K	352.63 K	362.44 K	
2.067	348.94	351.82	354.92	357.77	360.76	363.82	
4.067	348.07	350.99	354.21	357.06	359.89	362.84	
6.067	347.41	350.33	353.37	356.29	359.05	361.99	
8.067	346.91	349.69	352.66	355.60	358.27	361.19	
10.067	346.22	348.98	351.95	354.96	357.47	360.30	
12.067	345.68	348.39	351.33	354.25	356.71	359.52	
14.067	344.97	347.75	350.69	353.53	355.89	358.72	
16.067	344.17	347.13	350.01	352.83	355.23	357.90	
18.067	343.87	346.52	349.32	352.15	354.50	357.19	
16,033			1,208,93	1992-18 L	$x_{B} = 0.95$	739	
p/MPa	313.44 K	323.56K	333.06 K	342.35K	352,66K	362.32K	
2.063	346.90	350.87	353.77	357.50	360.80	363.92	
4.063	346.35	350.20	352.92	356.40	359.61	362.88	
6.063	345.56	349.53	352.28	355.61	358.85	361.79	
8.063	345.01	348.86	351.76	355.00	358.03	361.12	
10.063	344.25	348.10	350.94	354.18	357.24	360.17	
12.063	343.73	347.46	350.27	353.30	356.45	359.38	
14.063	343.16	346.79	349.66	352.60	355.56	358.62	
16.063	342.61	346.16	349.03	351.93	354.92	357.62	

Table 4.10 (continued).

					$x_{B} = 0.98$	344
p/MPa	313.59 K	323.16 K	332.57 K	342.96 K	352.99K	364.19К
2.069	355.36	358.36	361.59	365.03	368.22	372.01
4.069	354.55	357.59	360.84	364.17	367.29	371.04
6.069	353.91	356.84	360.08	363.41	366.51	369.83
8.069	353.35	356.11	359.35	362.66	365.75	368.95
10.069	352.73	355.42	358.52	361.78	364.82	368.19
12.069	352.00	354.81	357.79	361.05	364.14	367.36
14.069	351.45	354.12	357.10	360.79	363.34	366.51
16.069	350.79	353.48	356.55	359.63	362.58	365.78
18.069	350.25	352.92	355.91	358.94	361.82	364.95
				12.	$x_{B} = 1.00$	000
p/MPa	313.19K	322.95K	332.50K	342.40K	352.51K	362.62K
2.065	361.96	365.08	367.95	371.13	374.14	377.53
4.065	361.05	364.23	367.11	370.20	373.26	376.50
6.065	360.29	363.48	366.23	369.39	372.47	375.66
8.065	359.66	362.78	365.45	368.60	371.60	374.87
10.065	358.97	362.06	364.72	367.78	370.75	373.97
12.065	358.28	361.36	364.00	366.94	369.91	373.21
14.065	357.70	360.73	363.31	366.27	369.15	372.28
16.065	357.17	360.16	362.73	365.55	368.37	371.46
18.065		359.50	362.16	364.86	367.65	370.68

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5. CUBIC EQUATIONS OF STATE

5.1. Introduction

Since the introduction of the famous Van der Waals equation of state [1] in 1873 hundreds of alternative equations have been proposed. The development of further modifications and/or variations is still in progress.

With respect to the current use as well as the origin of equations of state Leland [2] classified the large number of equations into four general groups:

1. the Van der Waals type of equations;

2. the Benedict-Webb-Rubin (BWR) type of equations;

3. the reference fluid type of equations;

4. the augmented rigid body type of equations.

The Van der Waals type of equations is the most numerous and the attractiveness of this type of equations on the one hand lies in its mathematical simplicity. On the other hand it was already shown by Smits [3,4] and more recently in detail by Van Konynenburg [5] that the first member of this group - the original Van der Waals equation of state - has the ability to predict various types of two- and three-phase behaviour in binary fluid systems. Obviously much effort has been given to improve the basic ideas of Van der Waals. Nearly all equations of this group are cubic in volume, i.e. analytical solutions for the volume may readily be obtained. Moreover, also other thermodynamic properties such as vapour pressure, latent heat of vaporization, vapour + liquid equilibria, etc. are obtained with a minimum of computer effort.

In spite of the fact that precursors are known [6,7], the first member of the second group was proposed by Benedict et al. [8] and is now called the BWR equation of state. The original BWR equation of state has eight adjustable parameters and it is the first equation from which vapour + liquid equilibria in mixtures could be calculated accurately. Also the BWR equation of state belongs to a group with many members today. In this group equations are known with up to more than fifty constants. Because of the usually high number of adjustable parameters in the BWR type of equations, they have been utilized for high-precision calculations of pure component data. In chapter 9 a modification of the BWR equation of state will be used. Leland [2] pointed out that with increasing accessibility of large computers, a third type of equations has become extremely important and which are called the reference fluid type of equations. In these equations in general no attention is given to a simple mathematical and analytical structure suitable for representing many pure components or mixtures, i.e. this type of equations has been designed for special purposes. Rather than a traditional equation of state, it should be regarded as a compact representation of the pVT-data of single components suitable for accurate numerical operations to obtain thermodynamic properties [2]. This type of equations provides the very accurate description of the pure reference fluid properties as required for modern corresponding states theories of mixtures. Examples of this type of equations have been developed by Vennix et al. [9] and Bender [10].

In Lelands classification [2] the fourth general type of equations of state is called the augmented ridged body type of equations. Leland [2] pointed out that this type of equations starts with an equation of state for a rigid body and is then followed by terms which account for contributions of molecular attraction. The rigid bodies interact only with an infinite repulsion at their points of contact. Hansen et al. [11] discussed that the Van der Waals repulsive term cannot be correct. However, at present simple analytical expressions, derived from integral equation theory for hard spheres, are available and give a more accurate representation of the repulsive term in the equations of state. For hard spheres the equations proposed by Gibbons [13], Boublik [14,15] and Nezbeda et al. [16] are available.

Adding terms which account for the contribution of molecular attraction the fourth type of equations of state is defined. Obviously, this type of equations has the most physical relevant meaning and consequently is a promise for the near future.

As cubic equations of state are widely applied in chemical engineering, in this work equations belonging to the Van der Waals type will be used to calculate phase equilibria. For that reason they will be discussed in the following section from a more or less general point of view.

5.2. Cubic equations of state

Abbott [17], Martin [18] and Kumar et al. [19] have shown that all cubic equations of state known in literature are special cases of a general five-parameter polynomial expression. If it is required that this general equation is explicit in pressure and moreover that for $V_m \rightarrow \infty$ the compressibility factor Z = 1, this equation has to be of the following form:

$$\rho = \frac{\mathrm{RT} \left(\mathrm{V}_{\mathrm{m}}^{2} + \alpha \mathrm{V}_{\mathrm{m}} + \beta \right)}{\mathrm{V}_{\mathrm{m}}^{3} + \gamma \mathrm{V}_{\mathrm{m}}^{2} + \delta \mathrm{V}_{\mathrm{m}} + \varepsilon}$$
(5.1)

In eq. (5.1) the parameters α , β , γ , δ and ε may be functions of the temperature and in the case of mixtures also functions of the composition.

To make this equation more reliable for representing liquid volume behaviour, eq. (5.1) must have steep isotherms in a p,V-diagram for small values of V_m . In order to achieve this Abbott [17] introduced a zero in the denumerator at $V_m = b$ in eq. (5.1), where b is a small positive number. Finally eq. (5.1) can be rewritten as:

$$p = \frac{RT}{V_{m} - b} - \frac{\theta (V_{m} - \lambda)}{(V_{m} - b)(V_{m}^{2} + \mu V_{m} + \nu)}$$
(5.2)

with

θ

$$V_m^3 + \gamma V_m^2 + \delta V_m + \varepsilon = (V_m - b)(V_m^2 + \mu V_m + v)$$
(5.3)

$$= RT (\mu - \alpha)$$
(5.4)

 $\lambda = (\beta - \nu)/(\mu - \alpha) \tag{5.5}$

In eq. (5.2) the parameters b, $\lambda,~\mu,~\nu$ and θ depend generally on temperature and composition.

Eq. (5.2) can be considered as the general cubic equation of state. Substituting particular values of the parameters lead to well-known cubic equations of state. Some examples are summarized in table 5.1.

Substitution of other values and/or expressions for the parameters $\theta,\ \lambda,\ \mu$ and ν will give other cubic equations of state.

In the sections 5.2.1, 5.2.2 and 5.2.3 the cubic equations of state used in chapter 6 will be discussed. Table 5.1. Some cubic equations of state derived from eq. (5.2).

Equation	θ	λ	μ	ν
Van der Waals	а	b	0	0
Berthelot	a/T	b	0	0
Redlich-Kwong	$a/T^{\frac{1}{2}}$	b	b	0
Peng-Robinson	a(T)	b	2ъ	-b ²

5.2.1. The Redlich-Kwong equation of state

In the time between the introduction of the Van der Waals equation of state (1873) and the Redlich-Kwong equation (1949) nearly all attention was given to the development of equations with much more algebraic complexity and in addition also an increasing number of adjustable parameters, i.e. equations of state which belong to the second group discussed in section 5.1.

With the introduction of the Redlich-Kwong (RK) equation of state [20] the basic ideas of Van der Waals were reconsidered and in addition this was also the beginning of an extensive development of alternatives. The original RK equation of state mathematically reads:

$$p = \frac{RT}{V_m - b} - \frac{a}{T^2 V_m (V_m + b)}$$
(5.6)

In a similar way as in the Van der Waals equation of state eq. (5.6) accounts for separated contributions of repulsive effects due to the molecular size and of attractive effects caused by the intermolecular interaction. However, the RK equation of state - which is essentially still empirical - has some additional features.

First Redlich et al. [20] found that up to very high pressures the molar volume V_m of all gases approaches a limiting value of 0.26 $V_{m,c}$, with $V_{m,c}$ as the molar critical volume. For that reason the RK equation was constructed to satisfy the condition: $b = 0.26 V_{m,c}$. A second condition which had to be satisfied, was that at low gas densities a reasonable temperature dependence of second virial coefficients must be obtained. For that purpose Redlich et al. [20] introduced the factor $T^{\frac{1}{2}}$ in the denumerator of the second term in eq. (5.6). In order to meet these conditions as well as that of the critical point Redlich et al. [20] inserted the factor ($V_m + b$) in the denumerator of the second term of eq. (5.6).

With the conditions of the critical point expressions of a and b in terms of the critical temperature T_c and critical pressure p_c can be determined:

$$a = 0.42747 \frac{R^2 T_c^{5/2}}{P_c}$$
(5.7)

$$p = 0.08664 \frac{\text{RT}_{c}}{p_{c}}$$
 (5.8)

5.2.2. The Soave-Redlich-Kwong equation of state

One of the very best modifications of the original RK equation is the one proposed by Soave [21]. This investigator discussed that the poor results in calculating multicomponent vapour + liquid equilibria is not only caused by imperfections of the mixing rules used. In order to obtain more accurate multicomponent vapour + liquid equilibria calculations with an equation of state Wilson [22] pointed out that the equation used should also represent pure component vapour + liquid equilibrium data adequately. To achieve this, Soave [21] forced the RK equation to represent vapour pressures of pure non-polar components at a reduced temperature $T_{\rm R}$ = 0.7. As the vapour pressure of a pure component at $T_{\rm R}$ = 0.7 is related to its acentric factor ω , Soave [21] replaced eq. (5.7) for the parameter a by the following temperature dependent relation:

$$(T) = a(T_c) \alpha(T), \qquad (5.9)$$

with

$$a(T_c) = 0.42747 \frac{R^2 T_c^2}{P_c}$$
(5.10)

$$\alpha(T) = [1 + m \{1 - (\frac{T}{T})^{\frac{1}{2}}\}]$$
(5.11)

$$m = 0.480 + 1.574 \omega - 0.176 \omega^2$$
(5.12)

The relation of the parameter b with $\rm T_{c}$ and $\rm p_{c}$ was retained (eq. (5.8)) and the SRK equation of state reads:

$$p = \frac{RT}{V_{m} - b} - \frac{a(T)}{V_{m}(V_{m} + b)}$$
(5.13)

5.2.3. The Peng-Robinson equation of state

0 0

Although the SRK equation of state strongly improved the possibility to calculate accurate vapour + liquid equilibria of multicomponent systems this

equation of state still has some shortcomings. The most important one is the failure to predict accurately liquid phase densities. Peng et al. [23] discussed that this is caused by the too large value Z_c , i.e. $Z_c = 1/3$ for the SRK equation of state. In order to obtain smaller values of Z_c Peng et al. [23] proposed the following equation:

$$\rho = \frac{RT}{V_m - b} - \frac{a(T)}{V_m (V_m + b) + b (V_m - b)}$$
(5.14)

Similarly as for the SRK equation of state the parameter a was chosen to be temperature dependent and was related to the acentric factor ω too:

$$a(T) \approx a(T_c) \alpha(T)$$
(5.15)

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c}$$
(5.16)

$$\alpha(T) = [1 + m \{1 - (\frac{T}{T_c})^{\frac{1}{2}}\}]$$
(5.17)

$$m = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$$
(5.18)

$$b = 0.07780 \frac{RT_c}{P_c}$$
(5.19)

The critical compressibility factor obtained from eq. (5.14) is $Z_c = 0.30740$, which is in most cases still a too high value.

5.3. Discussion

In general the cubic equations of state discussed here allow to calculate vapour + liquid equilibria as well as other thermodynamic properties for a wide class of substances and their mixtures. Because of their mathematical simplicity on the one hand and the fact that - usually with an exception of derived properties such as the heat capacity at higher densities - seldom meaningless results of these equations are obtained on the other hand, they have become extremely popular in industrial applications. For that reason in the last decade much effort has been given to develop further improvements of the cubic equations of state. Substantially the improvements were focussed on the rather inaccurate molar volumes of the liquid phase which in general are calculated with the cubic equations of state [24]. With respect to this lack of ability to calculate accurate liquid molar volumes recently Prausnitz [25] pointed out that at present it is often forgotten that originally, for example, the RK equation of state was designed for the accurate representation of the vapour phase of pure substances and/or mixtures only. Today these equations are widely used for the calculation of vapour + liquid equilibria, i.e. they are applied for the calculation of molar volumes of the vapour as well as the liquid phase.

In order to obtain improved descriptions of the molar volume of the liquid phase numerous alternative cubic equations of state have been proposed. However, in nearly all these alternatives the improvement was achieved introducing one or more additional parameters. Examples of such improved cubics are discussed by Fuller [26], Usdin et al. [27], Martin [28] and Freze et al. [29].

The influence of the value of the critical compressibility factor Z_c on the ability to calculate accurate molar liquid volumes, as found for example for the PR equation of state, forced several investigators to reconsider a generalized Van der Waals cubic equation of state of the form:

$$p = \frac{RT}{V_{m} - b} - \frac{a(T)}{V_{m}^{2} + ubV_{m} + wb^{2}}$$
(5.20)

with u +

$$+ w = 1$$
 (5.21)

From eq. (5.20) the original PR equation of state is obtained for u = 2 and w = -1.

Cubic equations of state derived from the generalized Van der Waals theory, defined by eq. (5.20), are proposed by Harmens et al. [30], Schmidt et al. [31] and Patel et al. [32]. All of them show a better volumetric behaviour of the liquid phase. However, in some other respects less accurate results are obtained.

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6. CALCULATIONS WITH CUBIC EQUATIONS OF STATE

6.1. Introduction

A detailed discussion of the Redlich-Kwong (RK) [1], the Soave-Redlich-Kwong (SRK) [2] and the Peng-Robinson (PR) [3] equations of state was given in chapter 5. In this chapter these cubic equations of state will be tested in their applicability to represent the phase equilibria in the binary system ethane + n-eicosane determined experimentally. For reasons of convenience the equations of state are given here once more; the RK-family is defined as:

$$p = \frac{RT}{V_{m} - b} - \frac{a(T)}{V_{m} (V_{m} + b)}$$
(6.1)

In the original RK equation of state a(T) was chosen to be $a/T^{\frac{1}{2}}.$ The PR equation of state reads:

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m (V_m + b) + b (V_m - b)}$$
(6.2)

As pointed out in chapter 5 the parameters a and b of these equations of state can generally be determined in two different ways:

- application of correlations of a and b with the critical temperature T_c and critical pressure p_c as well as Pitzer's [4] acentric factor ω of the pure components;
- calculation of a and b from pVT-measurements and/or from experimental data of the saturated vapour pressure curve of each component.

With respect to the SRK and the PR equations of state the correlations to T_c , p_c and ω were applied. The values of a and b of the RK equation of state for ethane and n-eicosane were determined from experimental pVT-data. In order to calculate phase equilibria in binary mixtures, suitable mixing rules of the pure component parameters have to be used. This will be discussed in section 6.2.

In section 6.3 the temperature dependence of the pure component parameters a and b will be discussed. Its phase equilibria are most conveniently expressed in terms of the fugacity. The calculation of the fugacity in the vapour as well as the liquid phase of both components will be treated in section 6.4. Also the fugacity of solid n-eicosane will be subject of discussion in this section. Sections 6.5, 6.6 and 6.7 contain the results of the calculations of the several types of phase equilibria using cubic equations of state. Critical phenomena in the system ethane + n-eicosane will be discussed in section 6.8.

6.2. Mixing rules

In order to apply the RK, the SRK and the PR equations of state to mixtures, suitable mixing rules have to be chosen for calculating the parameters a and b of a mixture from those of the pure components. For this purpose the following generalized quadratic expressions were used:

$$a = \sum_{i=1}^{\infty} \sum_{j=1}^{a_i^2 a_j^2} x_i x_j$$
(6.3)

$$b = \frac{1}{2} \sum_{i=1}^{\Sigma} \sum_{j=1}^{\Sigma} (b_i + b_j) x_i x_j$$
(6.4)

In both equations (6.3) and (6.4) the summations have to be performed over the total number of components in the mixture. For binary mixtures both equations (6.3) and (6.4) respectively reduce to:

$$a = a_1 x_1^2 + 2 (a_1 a_2)^{\frac{1}{2}} x_1 x_2 + a_2 x_2^2$$
(6.5)

$$b = b_1 x_1^2 + (b_1 + b_2) x_1 x_2 + b_2 x_2^2$$
(6.6)

In general these mixing rules do not allow to represent quantitatively the behaviour of the binary mixture, i.e. from pure component information only [5]. This is especially the case if the molecules of the components differ strongly in size and shape. For that reason binary interaction parameters k_{12} and l_{12} have to be introduced in eqs. (6.5) and (6.6) respectively. The binary mixing rules applied in the RK, SRK as well as the PR equations of state are then given as:

$$a = a_1 x_1^2 + 2 (a_1 a_2)^{\frac{1}{2}} (1 - k_{12}) x_1 x_2 + a_2 x_2^2$$
(6.7)

$$b = b_1 x_1^2 + (b_1 + b_2) (1 - 1_{12}) x_1 x_2 + b_2 x_2^2$$
(6.8)

Using experimental binary equilibrium data both parameters \mathbf{k}_{12} and \mathbf{l}_{12} can be calculated. This calculation procedure will be discussed in detail in section 6.5.

6.3. Temperature dependence of the pure component parameters

6.3.1. The RK equation of state

Experimental pVT-data of ethane and n-eicosane were used to determine the pure component parameters a and b of the RK equation of state. For ethane experimental data were taken from Douslin et al. [6] and for n-eicosane the experimental data reported in section 4.4 were used.

In order to fit the experimental pVT-data to the RK equation several objective functions may be chosen to minimize a sum of squares. It was found that minimizing the sum of squares of the relative deviations in the molar volume did yield the best pure component parameters:

$$S = \sum_{i=1}^{n} \left\{ \frac{V_{m} (exp.) - V_{m} (calc.)}{V_{m} (exp.)} \right\}$$
(6.9)

Marquardt's [7] non-linear least-squares algorithm was used ot minimize this sum of squares S. For ethane as well as n-eicosane the minimization was performed for each isotherm separately. In tables 6.1 and 6.2 the calculated values of a and b for ethane and n-eicosane are summarized respectively.

Table 6.1. RK-parameters of ethane calculated from pVT-data of Douslin et al. [6].

T/K	a/MPa dm ⁶ K ¹ mol ⁻²	b/dm ³ mol ⁻¹
323.15	9.453	0.042048
348.15	9.510	0.042398
373.15	9.542	0.042836
398.15	9.541	0.043224
423.15	9.479	0.043378
448.15	9.443	0.043719
473.15	9.333	0.043766

For practical purposes it appeared to be useful to represent the calculated a and b values of table 6.1 and 6.2 by means of second degree polynomials:

$$A(T) = A_0 + A_1 T + A_2 T^2$$
(6.10)

$$b(T) = B_0 + B_1 T + B_2 T^2$$
(6.11)

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Table 6.2. RK-parameters of n-eicosane calculated from pVT-data (section 4.4).

T/K	a/Mpa $dm^6 K^{\frac{1}{2}}mol^{-2}$	b/dm ³ mol ⁻¹
313.19	370.626	0.331460
322.95	380.956	0.333579
332.50	387.689	0.335150
342.40	391.113	0.336703
352.51	400.963	0.338603
362.62	411.579	0.340762

In eqs. (6.10) and (6.11) T is in K and a(T) and b(T) have the units as given in the tables 6.1 and 6.2. The parameters of the polynomials were calculated using a linear least-squares program. In table 6.3 the obtained parameters are summarized.

Table 6.3. Parameters of the polynomials representing the RK-parameters a and b of ethane and n-eicosane as a function of the temperature.

	et	thane	n-eic	osane
i	A _i	B _i	Ai	B _i
0	5.933864	0.030976	362.00775	0.291674
1	$1.887669.10^{-2}$	4.93451.10 ⁻⁵	-0.610111	7.99356.10 ⁻⁵
2	-2.470476.10 ⁻⁵	-4.700952.10 ⁻⁸	$2.051339.10^{-3}$	1.519832.10 ⁻⁷

6.3.2. Temperature dependence of the pure component parameters of the SRK equation of state

As discussed in chapter 5 the parameter a_i in the SRK equation of state of the i-th component is related to its critical temperature $T_{c,i}$ and pressure $P_{c,i}$ as well as its acentric factor ω_i . For completeness these relations are given here again:

$$a_{i}(T) = a_{i}(T_{c,i}) \alpha_{i}(T)$$
(6.12)

$$a_i(T_{c,i}) = 0.42747 \frac{R^2 T_{c,i}^2}{P_{c,i}}$$
 (6.13)

$$\alpha_{i}(T) = [1 + m_{i} \{1 - (\frac{T}{T_{c,i}})^{\frac{1}{2}}]$$
(6.14)

$$m_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2$$
 (6.15)

The pure component parameter b, is defined as:

$$i = 0.08664 \frac{RT_{c,i}}{P_{c,i}}$$
 (6.16)

In table 6.4 the critical temperature and pressure as well as the acentric factor of both ethane and n-eicosane are given [8,9].

Table 6.4. Critical temperature and pressure and Pitzer's acentric factor of ethane and n-eicosane [8,9].

30	T_/K	p_/MPa	ω
Colle	305.33	4.8717	0.0908
C ₂₀ H ₄₂	767.00	1.1170	0.9065

6.3.3. Temperature dependence of the pure component parameters of the PR equation of state

The correlations of $a_i(T)$ and b_i to $T_{c,i}$, $p_{c,i}$ and ω_i for the PR equation of state are quite similar to those given in the previous section for the SRK equation of state. These relations are:

$$a_{i}(T) = a_{i}(T_{c,i}) \alpha_{i}(T)$$
(6.17)

$$a_{i}(T_{c,i}) = 0.45724 \frac{R^{2}T_{c,i}^{2}}{P_{c,i}}$$
(6.18)

$$\alpha_{i}(T) = [1 + m_{i} \{1 - (\frac{T}{T_{c,i}})^{\frac{1}{2}}\}]$$
(6.19)

$$m_i = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2$$
 (6.20)

The pure component parameter b, is defined as:

$$p_{i} = 0.07780 \frac{RT_{c,i}}{P_{c,i}}$$
 (6.21)

6.4. The fugacity

In order to use the cubic equation of state discussed before to calculate phase equilibria expressions for the fugacity have to be derived. The fugacity f_i of the i-th component can be obtained from the general equation [10]:

$$\operatorname{RT} \ln \left(\frac{f_{i}}{px_{i}}\right) = \int_{V}^{\infty} \left[\left(\frac{\partial p}{\partial n_{i}}\right)_{V,T,\hat{n}_{i}} - \frac{RT}{V}\right] \, dV - \operatorname{RT} \ln Z$$
(6.22)

Inserting the mixing rules given by eqs. (6.7) and (6.8) into the equation of state of interest and application of eq. (6.22) yields the required equation for the fugacity f_i .

6.4.1. The fugacity of the components in the vapour and the liquid phase.

As discussed before the equations of state will be used for the vapour as well as the liquid phase. This can easily be achieved by changing in all equations the liquid phase composition x_i into the vapour phase composition y_i . In this section the fugacity equations derived for the liquid phase will be given. Obviously these relations also hold for the vapour phase. The fugacity f_i for the RK equation of state reads:

$$\ln \left(\frac{f_{i}}{px_{i}}\right) = \ln \left(\frac{V_{m}}{V_{m} - b}\right) + \frac{\sum_{j=1}^{2} (b_{i} + b_{j}) x_{j} - b}{V_{m} - b} - \frac{2\sum_{j=1}^{2} (a_{i}a_{j})^{2}x_{j}}{bRT^{3/2}} \ln \left(\frac{V_{m} + b}{V_{m}}\right) - \frac{(\sum_{j=1}^{2} a_{j}^{\frac{1}{2}}x_{j})^{2} (\sum_{j=1}^{2} (b_{i} + b_{j}) x_{j} - b)}{\frac{j=1}{RT^{3/2}}} \left\{\frac{1}{b(V_{m} + b)} - \frac{1}{b^{2}} \ln \left(\frac{V_{m} + b}{V_{m}}\right)\right\} - \ln Z$$

$$(6.23)$$

In comparison with the RK equation of state the SRK equation of state differs only by a factor $1/T^{\frac{1}{2}}$ in the second term. This means its fugacity equation will be quite similar to eq. (6.23). The fugacity equation for the SRK equation of state is given by:

$$\ln \left(\frac{f_{i}}{px_{i}}\right) = \ln \left(\frac{V_{m}}{V_{m}-b}\right) + \frac{\sum_{j=1}^{2} (b_{i}+b_{j})x_{j}-b}{V_{m}-b} - \frac{\sum_{j=1}^{2} (a_{i}a_{j})^{2}x_{j}}{\sum_{j=1}^{2} (a_{j}a_{j})^{2}x_{j}} \ln \left(\frac{V_{m}+b}{V_{m}}\right) - \frac{V_{m}}{2} \ln \left(\frac{V_{m}+b}{V_{m}}\right) + \frac{V_{m}}{2} \ln \left(\frac{V_{m}+$$

$$-\frac{(\sum_{j=1}^{n}a_{j}^{\frac{1}{2}}a_{j})^{2}\{\sum_{j=1}^{n}(b_{i}+b_{j}) \times_{j}^{-b}\}}{RT} \left\{\frac{1}{b(V_{m}+b)} - \frac{1}{b^{2}}\ln(\frac{V_{m}+b}{V_{m}})\right\} - \ln Z \quad (6.24)$$

Finally the fugacity equation for the PR equation of state is:

$$(\frac{f_{i}}{px_{j}}) = \ln \left(\frac{V_{m}}{V_{m}-b}\right) + \frac{\sum_{j=1}^{2} (b_{i}+b_{j}) - b}{V_{m}-b} - \ln Z + + \left[2\sum_{j=1} (a_{i}a_{j})^{\frac{1}{2}} x_{j}(2b/2) - \left\{\sum_{j=1} (b_{i}+b_{j}) x_{j} - b\right\} (2a/2)\right] \cdot + \frac{1}{8b^{2}RT} \ln \left(\frac{V_{m}+b-b/2}{V_{m}+b+b/2}\right) + \frac{a}{2bRT/2} \left[\frac{2(1-\sqrt{2})(\sum_{j=1} (b_{i}+b_{j}) x_{j} - b)}{V_{m}+b+b/2} - - \frac{2(1+\sqrt{2})\{\sum_{j=1} (b_{j}+b_{j}) x_{j} - b\}}{V_{m}+b+b/2}\right]$$

$$(6.25)$$

In eqs. (6.23), (6.24) and (6.25) Z = pV_m/RT.

It should be noted that in eqs. (6.23), (6.24) and (6.25) that - if required - the binary parameters \mathbf{k}_{12} and \mathbf{l}_{12} have to be inserted.

6.4.2. The fugacity of solid n-eicosane

1n

In some equilibria discussed in this thesis solid n-eicosane is present. Consequently an expression for the fugacity of solid n-eicosane has to be available. Unfortunately the cubic equations of state applied here are not capable to represent the behaviour of a solid phase. For that reason a separate description of the fugacity of solid n-eicosane has to be introduced. This can be achieved starting from the following general relation for the fugacity of a pure substance [10]:

$$\operatorname{RT} \ln \left(\frac{f}{p}\right) = \int_{0}^{p} \left(V_{m} - \frac{RT}{p}\right) dp$$
(6.26)

To calculate the fugacity of a pure solid at given temperature T and pressure p, the integral in eq. (6.26) is separated into two parts. The first part gives the fugacity of the saturated vapour at temperature T and sublimation pressure p* and the second part gives the correction due to the compression

of the solid phase upon going from p* to the pressure p.

At sublimation pressure p* the fugacity of saturated vapour is equal to the fugacity of the solid because the vapour and solid phases are in equilibrium. Equation (6.26) can now be rewritten:

RT ln
$$(\frac{f^{S}}{p}) = \int_{0}^{p^{*}} (V_{m,V}^{*} - \frac{RT}{p}) dp + \int_{p^{*}}^{p} (V_{m,S}^{*} - \frac{RT}{p}) dp$$
 (6.27)

In this equation the first integral represents the fugacity coefficient of the pure component at its vapour pressure p* while the second integral accounts for the compression effect of the solid at the system pressure p. From eq. (6.27) one can readily derive:

RT
$$\ln \left\{\frac{f^{S}(p)}{p}\right\} = RT \ln \left\{\frac{f^{V}(p^{*})}{p}\right\} + \int_{p^{*}}^{p} V_{m,S}^{*} dp$$
 (6.28)

In eq. (6.28) $f^{\rm S}(p)$ is the fugacity of the solid phase at pressure p and $f^{\rm V}(p^*)$ is the fugacity of the pure substance at its sublimation pressure $p^*.$ The second term on the righ-hand side is the so-called Poynting correction term.

The description of the pVT-behaviour of a solid phase can in principle be based on the definitions of the isothermal compressibility κ and the isobaric cubic expansion coefficient γ . These definitions are given by the following equations respectively:

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_{\rm T} \tag{6.29}$$

$$\gamma = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{\rm p} \tag{6.30}$$

Considering V as a function of p and T, one gets:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p} dT + \left(\frac{\partial V}{\partial p}\right)_{T} dp$$
(6.31)

Insertion of both eqs. (6.29) and (6.30) into eq. (6.31) and assuming κ as well as γ to be constant the resulting equation can be integrated to:

$$\ln \left\{ \frac{V(p,T)}{V(p_0,T_0)} \right\} = \gamma(T - T_0) - \kappa(p - p_0)$$
(6.32)

This equation allows to calculate the volume of solid n-eicosane for arbitrary values of p and T if the volume of this component is known at a pressure ${\rm p}_0$ and a temperature ${\rm T}_0.$

Substitution of eq. (6.32) into the integral of eq. (6.28) results in an expression for the fugacity of solid n-eicosane:

$$RT \ln \left\{\frac{f^{S}(p)}{p}\right\} = RT \ln \left\{\frac{f^{V}(p^{*})}{p}\right\} - \frac{V_{m,S}^{*}(p_{0},T_{0})}{\kappa} e^{\gamma(T - T_{0})} \cdot \left\{e^{-\kappa(p - p_{0})} - e^{-\kappa(p^{*} - p_{0})}\right\}$$
(6.33)

In spite of the fact that experimental data of solid n-eicosane are rather scarce, Van der Kooi [11] succeeded to determine satisfactory values for $V(p_{\Omega},T_{\Omega})$, κ and γ .

From experimental data of the molar volume of n-eicosane of Templin [12] Van der Kooi [11] obtained at the normal melting point – i.e. $p_0 = 0.101325$ MPa and $T_0 = 309.68 \text{ K} - V(p_0, T_0) = 305.0 \text{ cm}^3 \text{mol}^{-1}$. At a tempeature of 294 K Weir et al. [13] performed measurements of the compressibility of n-eicosane in the pressure range from 100 MPa up to 1000 MPa. From these data Van der Kooi [11] calculated for solid n-eicosane $\kappa = 2.4.10^{-10}$ Pa⁻¹. The cubic expansion coefficient γ of solid n-eicosane could be calculated from experimental data of Templin [12]. At a pressure of 0.101325 MPa and in a temperature range from 303.15 K up to 309.55 K Van der Kooi [11] calculated $\gamma =$ $5.89.10^{-4}$ K⁻¹. In order to calculate the fugacity $f^{\rm S}(p)$ with eq. (6.33) the fugacity $f^{\rm V}(p^*)$ is required. As in the experimental region of interest in this work the vapour pressure of solid n-eicosane is extremely low it is allowed to consider the vapour phase as an ideal gas, i.e. $f^{\rm V}(p^*) = p^*$. From the scarce experimental information available Van der Kooi [11] derived an equation for the sublimation curve of n-eicosane:

$$\ln \left(\frac{p^*}{9.2.10^{-3}}\right) = 16.786 - 7.7095.10^{-2} T + + 2.39223.10^{-4} T^2 - 3.01357.10^{-7} T^3 - - \frac{2.13805.10^3}{T} - 2.06509 \ln \left(\frac{T}{309.65}\right) + + \frac{1.684.10^5}{8.31441} \left(\frac{1}{309.65} - \frac{1}{T}\right)$$
(6.34)

In this equation T is in K and p* in Pa.

6.5. Calculation of binary interaction parameters

As already pointed out mixtures of ethane + n-eicosane behave strongly non-ideal. Consequently the calculation of phase equilibria using an equation of state with pure component information only is generally not satisfying. For a more or less quantitative description of phase equilibria, parameters which are correlated with binary experimental data are required. Here these data are necessary to evaluate the binary interaction parameters k_{12} and l_{12} which were introduced in the mixing rules (eqs. 6.7 and 6.8). If one wants, for example, to determine these parameters from vapour + liquid equilibria in principle p,T,x,y-data are required. Unfortunately with the experimental equipment used in this work it was not possible to measure dew points and thus the vapour phase composition could not be determined. This lack of binary information forces to calculate both parameters k_{12} and l_{12} from p,T,x-data only. Let us consider the evaluating of k_{12} and l_{12} from vapour + liquid equilibria without using the vapour phase composition. Binary vapour + liquid equilibria are defined by the following equilibrium conditions for the fugacity:

$$f_1^{V}(p,T,y_1) = f_1^{L}(p,T,x_1)$$
 (6.35)

$$f_2^{\nu}(p,T,y_2) = f_2^{L}(p,T,x_2)$$
 (6.36)

Taking into account $y_1 + y_2 = 1$ and $x_1 + x_2 = 1$ in both eqs. (6.35) and (6.36) the vapour phase composition y_1 and y_2 can be eliminated. Because of the implicit character of the composition dependence of the fugacity equations this elimination has to be performed numerically. Evidently this elimination results in one equation which only requires experimental values of p,T and x. With one set of p,T,x-data this equation can be solved for one binary interaction parameter. To extend the calculation procedure to two binary interaction parameters a second set of experimental data - e.g. p',T',x' - has to be available in the calculation. Consequently by eliminating the vapour phase composition both binary interaction parameters k_{12} and l_{12} can be evaluated from the following set of equations, using only two sets of p,T,x-data:

$$f_{1}^{V}(p,T,y_{1}) = f_{1}^{L}(p,T,x_{1})$$
 (6.37)

$$f_2(p,T,y_2) = f_2(p,T,x_2)$$
 (6.38)

$$f_{1}^{\nu}(p',T',y_{1}') = f_{1}^{L}(p',T',x_{1}')$$
(6.39)

$$f_{2}^{V}(p',T',y_{2}') = f_{2}^{L}(p',T',x_{2}')$$
(6.40)

with additional conditions: y_1 + y_2 = 1, x_1 + x_2 = 1, y_1' + y_2' = 1 and x_1' + x_2' = 1.

The complete numerical process is summarized in the following scheme:

- starting values of k_{12} and l_{12} are estimated as good as possible;
- using two sets of experimental data p,T,x and p',T',x' from both eqs. (6.37) and (6.39) y, and y' are calculated respectively;
- after application of $y_2 = 1 y_1$ and $y'_2 = 1 y'_1$ respectively the sets of data T, x_2 , y_2 and T', x'_2 , y'_2 are substituted into eqs. (6.38) and (6.40) respectively;
- from eqs. (6.38) and (6.40) the pressures p and p' are calculated respectively;
- the obtained pressure values p (calc.) and p' (calc.) are compared with the available experimental values p (exp.) and p' (exp.);
- optimum values of \mathbf{k}_{12} and \mathbf{l}_{12} are obtained by minimizing the following sum of squares S:

$$S = \{1 - \frac{p(calc.)}{p(exp.)}\}^2 + \{1 - \frac{p'(calc.)}{p'(exp.)}\}^2$$
(6.41)

 this numerical scheme is repeated until a satisfactory low value of S is obtained.

In all cases Marquardt's [14] non-linear least-squares algorithm was used to solve the non-linear equations iteratively. From the foregoing discussion it is obvious that the minimization of eq. (6.41) can be extended to an arbitrary number of sets of p,T,x-data. Another conclusion is that if only one binary parameter has to be evaluated - i.e. $k_{12} = 0$ or $1_{12} = 0$ - in principle only one set of p,T,x-data is necessary. This calculation procedure allows to calculate the vapour phase composition.

In a similar way the vapour phase composition was eliminiated in the calculation of k_{12} and l_{12} from the three phase equilibrium solid n-eicosane + liquid + vapour (S $_{\rm R}$ + L + V) using a cubic equation of state.

6.6. Calculation of vapour + liquid equilibria

In this section the results are reported of the investigation to apply the RK (section (6.6.2), the SRK (section 6.6.3) and the PR (section 6.6.4) equations of state for the calculation of vapour + liquid equilibria in binary mixtures of ethane + n-eicosane. Particularly the calculation of p.x, y-sections at T = constant will be discussed. In order to be able to compare the behaviour of the three cubic equations of state the calculations were performed for the same sets of experimental data. Firstly in section 6.6.1 the calculation procedure in general applicable to calculate p.x,y-sections from cubic equations of state will be discussed.

6.6.1. Calculation of p,x,y-sections

The calculation of a p,x,y-section starts with the decision whether binary interaction parameters (k_{12} and/or 1_{12}) should be used or not. If necessary the calculation procedure for k_{12} and/or 1_{12} as described in section 6.5 has to be applied. To calculate a p,x,y-section at a temperature T and a selected value of liquid composition x the following fugacity equations have to be solved simultaneously for the pressure p and the vapour phase composition y:

$$f_1^V(p,T,y_1) = f_1^L(p,T,x_1)$$
 (6.42)

$$f_2^V(p,T,y_2) = f_2^L(p,T,x_2)$$
 (6.43)

Into eqs. (6.42) and (6.43) each of the fugacity equations given in section 6.3 can be substituted. Schematically the calculation procedure followed in this work is:

- calculate k12 and/or 112 or not;
- select the temperature T of the p,x,y-section to be calculated;
- select a liquid phase composition x;
- choose a starting value of the pressure p;
- eliminate numerically the vapour phase composition from both eqs. (6.42) and (6.43);
- continue the iterative calculation until an acceptable low value of the objective function to be minimized is obtained;
- this calculation scheme is repeated for other values of the liquid phase composition x.

At temperatures of 350.0, 400.0 and 450.0 K p,x,y-sections were calculated for the three cubic equations of state of interest. In order to calculate the binary interaction parameters ${\bf k}_{12}$ and/or ${\bf 1}_{12}$ experimental binary data were selected from tables 4.3 and 4.4. The data used for that purpose are summarized in table 6.5.

6.6.2. The RK equation of state

According to the method discussed in section 6.6.1 p,x,y-sections were calculated at 350.0, 400.0 and 450.0 K using the original RK-equation of state. The RK-parameters were interpolated from the data given in tables 6.1

and 6.2. In table 6.6 these parameters are summarized.

Table 6.5. Selected p,T,x-data from tables 4.3 and 4.4 to calculate the binary parameters k_{12} and/or 1_{12} .

×B	T/K
0.1908	350.0
0.7151	350.0
0.2055	400.0
0.7412	400.0
0.2055	450.0
0.7412	450.0
_	450.0

Table 6.6. RK-parameters interpolated from tables 6.1 and 6.2. (* = extrapolated values.)

-	T/K	$a/MPa dm^6 K^2 mol^{-2}$	b/dm ³ mol ⁻¹
C ₂ H ₆	350.0	9.5144	0.042488
2 0	400.0	9.5318	0.043192
	450.0	9.4257	0.043661
C ₂₀ H ₄₂	350.0	399.7578	0.338269
	400.0	446.1775*	0.347965*
	450.0	502.8538*	0.358421*

Using the p,T,x-data of table 6.5 k_{12} and/or l_{12} were evaluated. The results are given in table 6.7. From this table it follows that each p,x,y-section was calculated with four different sets of binary interaction parameters. In order to compare the results the standard deviations (RMS) with respect to pressure were calculated and are also given in table 6.7. In figures 6.1, 6.2 and 6.3 the calculated p,x,y-sections at 350.0, 400.0 and 450.0 K respectively are compared graphically with the experimental results. For the sake of clarity in each figure the p,x,y-section calculated with $k_{12} = 0$ and $l_{12} \neq 0$ is omitted.



calculated p,x,y-Section 6.3. Fig.

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Table 6.7. Calculated k_{12} and/or 1_{12} values as well as the standard deviations (RMS) with respect to the pressure for the RK equation of state.

T/K	k ₁₂	1 ₁₂	RMS
350.0	0.0000	0.0000	12.2125
350.0	-0.0068	0.0000	13.0258
350.0	0.0000	0.0149	12.0283
350.0	0.0525	0.0423	2.2417
400.0	0.0000	0.0000	10.2076
400.0	-0.0279	0.0000	15.6623
400.0	0.0000	0.0265	8.3207
400.0	0.0281	0.0396	1.6430
450.0	0.0000	0.0000	13.0384
450.0	~0.0682	0.0000	11.7776
450.0	0.0000	0.0419	5.9425
450.0	-0.0190	0.0338	0.5476

Table 6.8. Calculated k_{12} and/or \boldsymbol{I}_{12} values as well as the standard deviations (RMS) with respect to the pressure for the SRK equation of state.

T/K	k ₁₂	112	RMS
350.0	0.0000	0.0000	8.6930
350.0	-0.0054	0.0000	9.7213
350.0	0.0000	0.0118	8.4387
350.0	0.0320	0.0252	2.0992
400.0	0.0000	0.0000	11.8845
400.0	-0.0092	0.0000	14.0898
400.0	0.0000	0.0169	11.4878
400.0	0.0394	0.0324	2.5918
450.0	0.0000	0.0000	10.8249
450.0	-0.0077	0.0000	12.4410
450.0	0.0000	0.0200	11.3275
450.0	0.0453	0.0377	0.6493

54.0 21.0 16.0 15.0 12.0 0.0

DAMI



6.6. p.x.y-Section calculated SRK equation of state. experimental data the with rig.

0.0000 0.0000 0.0377 0.0453, 112 112 112 0.0077. 0.0000. k12 k 12 k12 :000 ----

0.0000



p, x, y-Section calculated 0.0324 0.0000 the SRK equation of state. 0.0394, 112 -0.0092, 1₁₂ $^{1}_{12}$ experimental data 0.0000. 6.5. k12 k 12 with rig. :000 -----



6.4. p.x.v-Section calculated state. SRK equation of 0.0320. 112 experimental data k12 the lith rig. :000

0.0000 0.0000 112 112 -0.0054. 0.0000. k12 k12 6.6.3. The SRK equation of state

In an almost similar way, as discussed in section 6.6.2, calculations of p.x.y-sections were performed using the SRK equation of state. Now the pure component parameters of ethane and n-eicosane given in table 6.4 were used. Again the calculations were performed for p.x.y-sections at 350.0, 400.0 and 450.0 K. Table 6.8 gives the calculated k_{12} and/or l_{12} values as well as the standard deviation in pressure. Omitting the calculated p,x,y-locus for $k_{12} =$ 0 and $1_{12} \neq 0$ the figures 6.4, 6.5 and 6.6 show the obtained results graphically.

6.6.4. The PR equation of state

Using the critical data as well as the acentric factors of both ethane and n-eicosane (table 6.4) p,x,y-sections at 350.0, 400.0 and 450.0 K were evaluated applying the PR equation of state. Table 6.9 presents the calculated \mathbf{k}_{12} and/or \mathbf{l}_{12} data as well as the standard deviations with respect to the pressure. A graphical representation of the results is shown in figures 6.7, 6.8 and 6.9. Again the results with $k_{12} = 0$ and $1_{12} \neq 0$ are omitted in these figures.

Table 6.9. Calculated k_{12} and/or 1_{12} values as well as the standard deviations (RMS) with respect to pressure for the PR equation of state.

T/K	k ₁₂	112	RMS
350.0	0.0000	0.0000	8.8509
350.0	-0.0073	0.0000	10.2392
350.0	0.0000	0.0127	8.6040
350.0	0.0297	0.0259	1.1110
400.0	0.0000	0.0000	12.0313
400.0	-0.0123	0.0000	15.1857
400.0	0.0000	0.0183	11.5987
400.0	0.0365	0.0337	1.7191
450.0	0.0000	0.0000	10.5992
450.0	-0.0125	0.0000	13.2456
450.0	0.0000	0.0226	11.0921
450.0	0.0432	0.0407	1.0503



The equilibrium conditions for the three phase equilibrium $S_B + L + V$ in the system ethane + n-eicosane are given by the following fugacity equations:

$${}^{L}_{1}(p,T,x_{1}) = f_{1}^{V}(p,T,y_{1})$$
 (6.44)

$$L_{2}^{L}(p,T,x_{2}) = f_{2}^{V}(p,T,y_{2})$$
 (6.45)

$$f_2^S(p,T) = f_2^L(p,T,x_2)$$
 (6.46)

In addition:

 $x_1 + x_2 = 1$ and $y_1 + y_2 = 1$ (6.47)

These 5 equations contain 6 variables. If, for example, a value of the temperature is chosen, these 5 equations can be solved iteratively.

The vapour and liquid phase will be described by the SRK equation of state and consequently in eqs. (6.44), (6.45) and (6.46) the fugacity according to eq. (6.24) has to be used.

Critical temperatures and pressures as well as Pitzer's acentric factor of both ethane and n-eicosane were taken from table 6.4. In order to calculate the fugacity of solid n-eicosane eq. (6.33) was applied and the sublimation pressure required in this equation was obtained from eq. (6.34). As the mixture behaves strongly non-ideal binary interaction parameters k_{12} and 1_{12} were used in the mixing rules given by eqs. (6.7) and (6.8). As only p,T,x-data of this three phase equilibrium could be determined experimentally (table 4.5) the vapour phase composition y was eliminated in eqs. (6.44) - (6.47) in a similar way as discussed in section 6.4.

The binary interaction parameters k_{12} and l_{12} were calculated using all p,T,x-data of table 4.5. These parameters were determined to be 0.0259 and 0.0290 respectively. In figures 6.10, 6.11 and 6.12 respectively the calculated p,x-, T,x- and p,T-projections (full curves) are compared with the experimental data (open circles) of table 4.5.

6.8. Critical phenomena

In figure 2.14 (section 2.5) the high temperature branch of critical locus L \equiv V of the binary system ethane + n-eicosane was compared with the critical loci of other binaries of ethane and higher n-alkanes. As neither experimental data of the critical locus were available in literature nor this





g. 6.9. p.x.y-Sect	th the PR equation	o: experimental da	$-: k_{12} = 0.0432,$	$-: k_{12} = 0.0000,$	$-: k_{13} = -0.0125$.
calculated Fi	state. wi	00	= 0.0337	= 0.0000	= 0.0000 =
p.x.y-Section	PR equation of	imental data	· 0.0365, 112	. 0.0000, 1 ₁₂	-0.0123, 1,2

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Fig. 6.10. p,x-Projection of the three phase equilibrium $S_B + L + V$. ooo: experimental data —: calculated with the SRK equation of state.



Fig. 6.12. p.T-projection of the three phase equilibrium $S_B + L + V$. ooo: experimental data. —: calculated with the SRK equation of state. locus was determined experimentally in this study it was decided to estimate this critical locus using the SRK equation of state.

Redlich et al. [14] derived general critical conditions for a binary mixture:

$$\bigvee_{\infty}^{V} \left(\frac{\partial^2 p}{\partial y_1^2}\right)^2 \, \mathrm{d}V - \frac{\left(\frac{\partial p}{\partial y_1}\right)^2}{\left(\frac{\partial p}{\partial V}\right)} = \frac{\mathrm{RT}}{y_1 y_2} \tag{6.48}$$

$$\begin{smallmatrix} J \\ (\frac{\partial^3 p}{\partial y_1^3}) \\ (\frac{\partial^3 p}{\partial y_1^3}) \\ dV \\ - \frac{3 (\frac{\partial p}{\partial y_1})(\frac{\partial^2 p}{\partial y_2^3})}{(\frac{\partial p}{\partial y})} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial^2 p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1 \partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})^2} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})} \\ + \frac{3 (\frac{\partial p}{\partial y_1})^2(\frac{\partial p}{\partial y_1})}{(\frac{\partial p}{\partial y_1})} \\ + \frac{3 (\frac{\partial p}{\partial$$

$$-\left(\frac{\partial^2 p}{\partial v^2}\right)\left(\frac{\partial p}{\partial y_1}\right)^3\left(\frac{\partial p}{\partial v}\right)^3 = \frac{\text{RT}\left(y_1 - y_2\right)}{y_1^2 y_2^2}$$
(6.49)

Joffe et al. [15] determined the partial derivatives in eqs. (6.48) and (6.49) for the RK equation of state which are also valid for the SRK equation of state.

Table 6.10. The high temperature branch of the critical locus L \equiv V in the system ethane + n-eicosane calculated with the SRK equation of state (k_{12} = 1_{12} = 0).

T _c /K	P _c /MPa	$V_{m,c}/cm^3mol^{-1}$	y _{2,c}
310.0	5.623	110.2	0,0109
350.0	11.115	120.2	0.0244
400.0	15.847	137.6	0.0390
450.0	18.468	159.6	0.0545
500.0	19.272	188.1	0.0727
550.0	18.502	227.3	0.0962
600.0	16.354	285.7	0.1295
650.0	12.992	383.1	0.1834
700.0	8.553	580.4	0.2906
750.0	3.153	1203.9	0.6255

Together with the SRK equation of state eqs. (6.48) and (6.49) form a set of three complicated non-linear equations with p_c , T_c , V_c and y_c as unknown

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quantities. These equations were solved simultaneously at a fixed critical temperature T_c for a series of temperatures between the critical temperatures of ethane and n-eicosane (table 6.4). The calculations were performed with binary parameters $k_{12} = l_{12} = 0$. In table 6.10 the results are given and figure 2.14 shows the critical locus graphically.

6.9. Discussion

In order to calculate vapour + liquid equilibria in the binary system ethane + n-eicosane the RK, SRK and PR equations of state were applied. Calculations of p,x,y-sections at 350.0, 400.0 and 450.0 K were performed. The standard deviations (RMS) summarized in tables 6.7, 6.8 and 6.9 obtained with the RK, SRK and PR equations respectively lead to some conclusive results with respect to the binary parameters:

- ~ comparison of the calculations with the three cubic equations of state with $k_{12} = l_{12} = 0$ and $k_{12} \neq 0$, $l_{12} = 0$ in general does not improve the result in terms of a decrease of RNS-values;
- ~ comparison of the calculations with k_{12} = 0, 1_{12} = 0 and k_{12} = 0, $1_{12} \neq 0$ shows an improved result, i.e. lower RMS-values for the latter case;
- ~ application of both binary parameters, i.e. $k_{12} \neq 0$, $l_{12} \neq 0$ results in a markedly improved representation of the p,x,y-data for each of the three cubic equations of state applied here.

Evidently, from these observations it may be concluded that the influence of the binary parameter l_{12} is more important than k_{12} . As this behaviour of the binary parameters was also observed in similar calculations of vapour + liquid equilibria in binaries of methane + n-hexadecane [16], ethane + n-hexadecane [17], ethane + n-docosane [18] and ethane + n-tetracosane [19], apparently this behaviour is characteristic for binaries of n-alkanes with a volatile component on the one hand and a non-volatile component on the other hand.

The fact that the binary parameter l_{12} is more important than k_{12} in mixtures of n-alkanes, as discussed above, is difficult to understand from a physical point of view. As the RK, SRK and PR equations of state are semi-empirical relations and the mixing rules applied in this work are also empirical expressions and moreover the binary parameters k_{12} and l_{12} are empirical corrections to the mixing rules, it will be obvious that a quantitative physical interpretation is practically impossible. However, relating the parameter a of the cubic equations of state used here

to an intermolecular pair-potential parameter ε , the negligible influence of the parameter k_{12} can be understood more or less qualitatively. Referring to the extension of the principle of corresponding states to chain molecules, originally proposed by Prigogine et al. [20], chain molecules are replaced by a set of quasi-spherical segments. The predicted properties of the fluid do not change if some of these segments are imagined to be moved from one molecule to another, since such a move changes neither the total number of segments nor that of the molecules. Donohue et al. [21] discussed that in mixtures of n-alkanes a particular segment only interacts with a limited number of other segments at one time. This number, called the coordination number, is generally believed to be between six and twelve for liquids. Obviously, the majority of interactions are between CH₂-segments, i.e. like interactions. Therefore nearly always unlike interactions are rather scarce in these types of fluids and consequently it may be expected that application of the binary parameter k_{12} is in general not necessary.

Also qualitatively the role of the binary parameter l_{12} has to be recognized to account for the size-ordering effects which will undoubtedly occur in mixtures of alkanes as discussed here. From X-ray studies of Brady [22] it was found that in solutions of mixtures of short and long alkanes the short molecules, when in large concentration, group into satellite appendages of the long chain aggregates. At present the knowledge of the molecular structure of fluids, as discussed here, is still very incomplete and additional informaton - X-ray and/or molecular dynamics, for example - is required to study these size-ordering effects.

The necessity to use two binary interaction parameters k_{12} and l_{12} to calculate accurately fluid phase equilibria for mixtures of molecules which differ largely in size and shape, was already recognized by Deiters [5] and Deiters et al. [23]. A similar conclusion was also drawn by De Loos et al. [24], who calculated vapour + liquid equilibria of binaries of ethylene and higher *n*-alkanes.

In literature some values of k_{12} (with $l_{12} = 0$) of the system ethane + neicosane are known. A value of $k_{12} = 0.0214$ was reported by Donohue [21] and a value of $k_{12} = 0.17$ was recommended by Teja [25]. From second virial cross coefficients Kaul et al. [26] derived that for n-alkane systems, as those discussed here, k_{12} -values of ± 0.20 have to be expected. Besides the fact that the literature values do not agree with each other, in this study even negative values of k_{12} (with $l_{12} = 0$) are to be found in all calculations (tables 6.7, 6.8 and 6.9). Differences between the k_{12} -values may be caused by the different sources of experimental data used to calculate the parameter k_{12} . Also the method of correlation as well as the equation used for the correlation may have some influence on the k_{12} -values.

In order to calculate the three phase equilibrium $S_B + L + V$ all p,T,xdata available (table 4.6) were used to evaluate k_{12} and l_{12} (section 6.7). These values, which were obtained in applying the SRK equation of state, are in good agreement with the k_{12} - and l_{12} - values as reported in table 6.7. From figures 6.10, 6.11 and 6.12 it may be observed that, according to the method discussed in section 6.7, the experimental data of this three phase equilibrium can be represented at least qualitatively by the model proposed.



Fig. 6.13. Comparison of molar liquid volumes of mixtures of ethane + n-eicosane calculated with the RK, SRK and PR equations of state.

With respect to the representation of p,x,y-data in the system ethane + n-eicosane the RK, SRK and PR equations of state were compared in this chapter. If, for example, the representation for $k_{12} = 0$ and $l_{12} = 0$ is considered, then from tables 6.7, 6.8 and 6.9 it can be concluded that at 350.0 K the PR equation gives the best result. However, at 400.0 K and 450.0 K the original RK equation gives a better representation of the experimental p,x,y-data. For practical purposes it is also important to consider the ability of the equations of state to calculate molar fluid volumes of the binary mixture accurately. This is shown in figure 6.13. In this figure the full curves were calculated with the three cubic equations of state. For the

SRK and PR equations of state the parameters from table 6.4 were used and for the RK equation the parameters at 350.0 K were adopted from table 6.5. In all cases two binary parameters k_{12} and 1_{12} were used. The open circles in figure 6.13 are experimental data taken from table 4.10 and from Van der Kooi [11] (n-eicosane).

Figure 6.13 shows clearly how at 350.0 K up to higher mole fractions of neicosane the volume behaviour of the SRK and PR equations of state deviates from the RK equation. Considering the experimental data of table 4.10 leads to the conclusion that the RK equation of state gives the best molar volumes of mixtures of ethane + n-eicosane. Peneloux et al. [27] discussed that only in case of small values of the acentric factor $\boldsymbol{\omega}$ correct predictions of the molar volumes have to be expected. With increasing acentric factors the calculated molar volumes become larger than those determined experimentally. Moreover, for higher n-alkanes also the critical parameters required in the SRK and PR equations become inaccurate and consequently an additional source of error is introduced. This means that for binaries, as discussed here, the temperature dependent correlations to the acentric factor of the SRK and PR equations are not valid. In order to apply the SRK and PR equations of state it is to be preferred to calculate the parameters from pure component information. For binaries of ethylene and higher n-alkanes this method was applied by De Loos et al. [24].

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First of all (section 7.2) the structure of fluids in terms of the radial distribution function will be introduced and then a general and quantitative treatment of distribution functions will be given (section 7.3). The relationship between the radial distribution function and bulk thermodynamic equilibrium properties of fluids is presented in section 7.4. In particular the equations for the internal energy, the pressure (virial equation of state) and the compressibility will be derived. In this work radial distribution functions are calculated from an integral equation based on the Percus-Yevick (PY) and hypernetted chain (HNC) theories and, therefore, these approximate relations will be derived using the method of functional differentiation

(section 7.5).

General statistical mechanical fundamentals used in this work are e.g. found in the following books: Hill [1,2], Evring et al. [3], Munster [4,5], McQuarrie [6] and Eyring et al. [7]. Excellent reviews on applied statistical mechanical theories of fluids are given by Frenkel [8], Born et al. [9], De Boer [10,11], Green [12,13], Hirschfelder et al. [14], Cole [15], Rowlinson [16,17,18], Barker [19], Levelt et al. [20], Henderson [21], Fisher [22], Frisch et al. [23] and Rice et al. [24].

In addition more recent reviews are available from Eyring et al. [25,26], Kohler [27], Barker et al. [28], Reed et al. [29], Singer [30], Barker et al. [31], Hansen et al. [32], Boublik et al. [33], Rowlinson [34] and Gray et al.

STATISTICAL MECHANICS OF FLUIDS 7

7.1. Introduction

In chapter 1 it was discussed in which ways structure of fluids has been investigated experimentally and that at the same time the development of statistical mechanical theories did lead to a better understanding of the observed experimental results. It was also pointed out qualitatively that the knowledge of the radial distribution function allows to calculate macroscopic thermodynamic properties. In this chapter the relationship between the radial distribution function and thermodynamic properties is to be discussed quantitatively.

7.2. Structure of fluids

In comparison with a solid a fluid does not have such a distinct structure which extends over a long range of intermolecular distances. The same holds for the stability of the structure with time. In general one observes always averages of the molecular arrangements possible.



Figure 7.1 shows schematically two volume elements $d\underline{r}_1$ and $d\underline{r}_2$ of a fluid at distances \underline{r}_1 and \underline{r}_2 respectively from an arbitrary origin in that fluid. The volumes $d\underline{r}_1$ and $d\underline{r}_2$ have been chosen to be small in comparison with the volume of a molecule of that fluid. Considering, for example $d\underline{r}_1$, sometimes a molecule will be found inside $d\underline{r}_1$ and sometimes $d\underline{r}_1$ will be empty. Obviously the probability that a molecule will be found inside $d\underline{r}_1$ depends on:

- the size of the molecule;

- the molecular density ρ of the fluid.

The same holds for volume element $d\underline{r}_2$. If $d\underline{r}_1$ and $d\underline{r}_2$ are a many of molecular diameters apart; i.e. $r_{12} = |\underline{r}_1 - \underline{r}_2|$, then the occupation of $d\underline{r}_1$ by a molecule is independent of the occupation of $d\underline{r}_2$.

Distribution functions are defined as the probability to have molecules in one or more volume elements. A rather similar definition is the period of time a volume element is occupied by a molecule.

The probability to have a molecule in \underline{dr}_1 is designated as $n^{(1)}(\underline{r}_1)\underline{dr}_1$ and - as any probability is a dimensionless number - $n^{(1)}(\underline{r}_1)$ must have the dimension of a reciprocal volume or a particle density. At equilibrium in an isotropic fluid $n^{(1)}(\underline{r}_1)$ is equal to the average particle density ρ i.e.:

$$n^{(1)}(\underline{r}_1) = \frac{N}{V} = \rho \tag{7.1}$$

The probability to have a molecule inside of each of the volumes ${\rm d}\underline{r}_1$ and ${\rm d}\underline{r}_2$ at the same time is designated as

$$d^{(2)}(\underline{r}_1, \underline{r}_2) d\underline{r}_1 d\underline{r}_2.$$

If the fluid is considered to be isotropic $n^{(2)}(\underline{r}_1,\underline{r}_2)$ only depends on $r_{12} = |\underline{r}_1 - \underline{r}_2|$ and not on the absolute locations \underline{r}_1 and \underline{r}_2 of $d\underline{r}_1$ and $d\underline{r}_2$. It has to be noted that in the case of non-spherical particles the mutual orientation is of particular interest. As in fluids regularity over many intermolecular distances does not exist the probability of simultaneous occupation of $d\underline{r}_1$ and $d\underline{r}_2$ is equal to the product of the two independent probabilities for each occupancy. Mathematically this can be summarized as follows:

$$\lim_{\substack{r_{12} \neq \infty}} n^{(2)}(\underline{r}_1, \underline{r}_2) d\underline{r}_1 d\underline{r}_2 = n^{(1)}(\underline{r}_1) d\underline{r}_1 n^{(1)}(\underline{r}_2) d\underline{r}_2 = \rho^2 d\underline{r}_1 d\underline{r}_2$$
(7.2)

In the case that the occupancy for each volume element is not independent from the other one eq. (7.2) can be rewritten:

$$n^{(2)}(\underline{r}_{1},\underline{r}_{2})d\underline{r}_{1}d\underline{r}_{2} = \rho^{2}g^{(2)}(r_{12})d\underline{r}_{1}d\underline{r}_{2}$$
(7.3)

where function $g^{(2)}(r_{12})$ is the radial distribution function and accounts for local density fluctuations in the fluid due to intermolecular interactions. The definition of g(r) is so that at the one hand

$$\lim_{r \to \infty} g(r) = 1 \tag{7.4a}$$

and at the other hand:

$$\lim_{r \to 0} g(r) = 0 \tag{7.4b}$$

Eq.(7.4b) represents the fact that two molecules cannot occupy the same volume element at the same time.

7.3. Distribution functions

In this section distribution functions will be defined in terms of the grand partition function. However, before doing this some general statistical mechanical fundamentals are recapitulated [1,2,3,4,5,6].

The grand partition function Ξ of a N-particle fluid with volume elements $d\underline{r}_1, \ldots, d\underline{r}_N$ located at $\underline{r}_1, \ldots, \underline{r}_N$, with moments in the elements $d\underline{p}_1, \ldots, d\underline{p}_N$ located at $\underline{p}_1, \ldots, \underline{p}_N$ and an energy E of the configuration is given by:

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{N\mu/kT}}{N! \ h^{3N}} \int_{V} \dots \int_{V} e^{-E/kT} d\underline{r}_1 \ \dots \ d\underline{r}_N \int \dots \int d\underline{p}_1 \ \dots \ d\underline{p}_N$$
(7.5)

In this equation $\Xi = \Xi$ (V,T, μ); i.e. it is depending on a volume V, temperature T and chemical potential μ .

If the particles only interact via pairwise additive forces and there are no external fields, then the energy of the N-particle configuration is given by: 2

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2\Sigma} u(r_{ij})$$
(7.6)

In eq. (7.6) m is the mass of the particle, $r_{ij} = |\underline{r}_i - \underline{r}_j|$ and $u(r_{ij})$ the intermolecular pair potential between the particles i and j. Substitution of eq. (7.6) into eq. (7.5) and integration over the momenta yields:

$$\Xi = \sum_{N=0}^{\infty} \frac{z^{N}}{N!} \int_{V} \dots \int_{V} e^{-\frac{1}{2} \sum_{i \neq j} u(r_{ij})/kT} d\underline{r}_{1} \dots d\underline{r}_{N}$$
(7.7)

with

$$z = \frac{(2\pi m kT)^{3/2}}{h^3} e^{\mu/kT}$$
(7.8)

If X is some quantity which is a function of the positions $\underline{r}_1,\ \ldots,\ \underline{r}_N$ and momenta $\underline{p}_1,\ \ldots,\ \underline{p}_N$ of the particles of a fluid, its average value \overline{X} can be expressed in terms of the grand partition function:

$$\overline{X} = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{e^{N\mu/kT}}{|\mathbf{1}| |\mathbf{h}|^{2N}} \int_{V} \dots \int_{V} X e^{-E/kT} d\underline{\mathbf{r}}_{1} \dots d\underline{\mathbf{r}}_{N} \int \dots \int d\underline{\mathbf{p}}_{1} \dots d\underline{\mathbf{p}}_{N}$$
(7.9)

Extension of the discussion given in the previous section the distribution function for L particles $n^{(L)}(\underline{r}_1, \ldots, \underline{r}_L)$ is defined so that $n^{(L)}(\underline{r}_1, \ldots, \underline{r}_L) \, d\underline{r}_1 \, \ldots \, d\underline{r}_L$ is the probability of finding a particle in each of the L volume elements $d\underline{r}_1, \ldots d\underline{r}_L$, which are located at positions $\underline{r}_1, \cdots \underline{r}_L$.

Application of straightforward statistical mechanical fundamentals [3]

lead to the following L-particle distribution function in a system of a total of N with N \geqq L:

$$n^{(L)}(\underline{\mathbf{r}}_{1},\ldots,\underline{\mathbf{r}}_{L}) = \frac{1}{\Xi} \sum_{N=L}^{\infty} \frac{z^{N}}{(N-L)!} \int_{V} \cdots \int_{V} e^{-\frac{1}{2}\sum_{i\neq j} u(\mathbf{r}_{i,j})/kT} d\underline{\mathbf{r}}_{L+1} \cdots d\underline{\mathbf{r}}_{N}$$
(7.10)

The one-particle distribution function $n^{(1)}(\underline{r}_1)$ is simply the number density of particles at \underline{r}_1 . For a homogeneous fluid this density has a uniform value ρ (section 7.2) and consequently:

$$n^{(1)}(\underline{r}_{1}) = \rho = \frac{\widetilde{N}}{\widetilde{V}} , \qquad (7.11)$$

where \overline{N} is the mean number of particles in the fluid.

The pair distribution function $n^{(2)}(\underline{r}_1,\underline{r}_2)$ is of particular interest since the thermodynamic properties of a fluid can be calculated from it. As pointed out in the previous section, for a homogeneous fluid of molecules interacting via central forces $n^{(2)}(\underline{r}_1,\underline{r}_2)$ depends only on the distance r_{12} between the particles, and not on the position of the pair of molecules, or its orientation; thus:

$$n^{(2)}(\underline{r}_{1},\underline{r}_{2}) = \rho^{2}g(r_{12})$$
(7.12)

7.4. The pair distribution function and thermodynamic properties

With the definition of distribution functions it is now possible to relate the pair distribution function to macroscopic thermodynamic properties. In this section this is done explicitly for the internal energy and also the virial as well as the compressibility equation of state will be expressed in terms of the pair distribution function. Straightforward thermodynamics allows to derive other important properties e.g. the entropy, the Helmholtz and Gibbs energy etc..

7.4.1. The internal energy

The internal energy U is simply the mean value \overline{E} of the energy E. Replacing X by E of eq. (7.9) and performing the integrations over the momenta yields:

$$U = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^{N}}{N!} \int \dots \int [\frac{3}{2} NkT + \frac{1}{2} \sum_{i \neq j} u(r_{ij}) e^{-\frac{1}{2} \sum_{i \neq j} u(r_{ij})} d\underline{r}_{1}, \dots d\underline{r}_{N}$$
(7.13)

The contribution of the first term within the brackets is $3\overline{N}kT/2$ while each of the N(N-1)/2 terms u(r_{i,i}) gives the same integral; thus:

$$U = \frac{3}{2} \overline{N}kT + \frac{1}{2\Xi} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int_V \dots \int_V u(r_{12}) e^{-\frac{1}{2}\sum_{i\neq j} u(r_{ij})} d\underline{r}_1 \dots d\underline{r}_N$$
(7.14)

Comparing the series on the right-hand side of eq. (7.10) with the definition of the pair distribution function $n^{(2)}(\underline{r}_1,\underline{r}_2)$, it follows that:

$$U = \frac{3}{2} \overline{N}kT + \frac{1}{2} \frac{ff}{V} u(r_{12}) n^{(2)} (\underline{r}_1, \underline{r}_2) d\underline{r}, d\underline{r}_2$$

$$(7.15)$$

Substitution of eq. (7.12), taking into account the limit of V large and using eq. (7.11), eq. (7.15) becomes:

$$U = \frac{3}{2} \overline{N}kT + \frac{1}{2}\overline{N}\rho \int u(r) g(r) d\underline{r}$$
(7.16)

Using spherical polar coordinates this equation can be rewritten as:

$$U = \frac{3}{2} \overline{N}kT + 2\pi \overline{N}\rho \int_{0}^{\infty} r^{2}u(r) g(r) dr$$
(7.17)

7.4.2. The virial equation of state

In order to derive the virial equation of state via the grand partition function conveniently a coordinate transformation is introduced:

$$\underline{s}_{i} = \frac{\underline{r}_{i}}{v^{1/3}}$$
 (7.18)

Inserting this into eq. (7.7) the grand partition function becomes:

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N v^N}{N!} \int \dots \int e^{-\frac{1}{2} \sum_{i \neq j} u(V^{1/3} s_{ij})/kT} d\underline{s}_1 \dots d\underline{s}_N$$
(7.19)

Differentiation of this equation with respect to V yields:

$$\begin{aligned} &(\frac{\partial\Xi}{\partial V})_{\mu,T} = \sum_{N=0}^{\infty} \frac{z^{N}v^{N}}{(N-1)!} \int \dots \int e^{-\frac{1}{2}\sum_{i\neq j} u(V^{1/3}s_{ij})/kT} d\underline{s}_{1} \dots d\underline{s}_{N} \\ &- \frac{1}{6} \sum_{N=0}^{\infty} \frac{z^{N}v^{N}}{(N-2)!} \int \dots \int e^{-\frac{1}{2}\sum_{i\neq j} u(V^{1/3}s_{ij})/kT} v^{1/3}s_{12} \\ &\cdot u'(V^{1/3}s_{12}) d\underline{s}_{1} \dots d\underline{s}_{N} \end{aligned}$$
(7.20)

In this equation u'(r) is the derivative of u(r) and it is taking into account that differentiating the exponential term gives N(N-1)/2 equal terms.

Transformation back to the original coordinates \underline{r}_1 , ..., \underline{r}_N and application of eq. (7.10) with L = 1 and L = 2 respectively eq. (7.20) becomes:

$$\frac{\underline{v}}{\underline{z}} \left(\frac{\partial \underline{z}}{\partial V} \right)_{\mu, T} = \int_{V} n^{(1)}(\underline{r}_{1}) \ d\underline{r}_{1} - \frac{1}{6} \int_{V}^{ff} r_{12} u'(r_{12}) n^{(2)}(\underline{r}_{1}, \underline{r}_{2}) \ d\underline{r}_{1} d\underline{r}_{2}$$
(7.21)

Application of eqs.(7.11) and (7.12) and taking into account the limit for V to be very large this results in:

$$\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\mu,T} = \rho - \frac{\rho^2}{6} \int ru'(r) g(r) d\underline{r}$$
(7.22)

With ln Ξ = pV/kT and using spherical polar coordinates for the integration yields:

$$\frac{p}{pkT} = 1 - \frac{2\pi\rho}{3} \int_{0}^{\infty} r^{3} \frac{d}{dr} \frac{u(r)}{dr} g(r) dr, \qquad (7.23)$$

which is the so-called virial equation of state.

7.4.3. The compressibility equation of state

In classical thermodynamics the isothermal compressibility is defined as:

$$\alpha_{\rm T} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{\rm V,T} \tag{7.24}$$

With $\ln \Xi \approx pV/kT$ and application of eq. (7.11) the following equation is obtained:

$$kT \left(\frac{\partial \rho}{\partial p}\right)_{V,T} = \left(\frac{\partial \overline{N}}{\partial \ln \Xi}\right)_{V,T}$$
(7.25)

For given values of V and T, both Ξ and \overline{N} can be considered as functions of z, which was already defined by eq. (7.8). Thus:

$$T \left(\frac{\partial \rho}{\partial p}\right)_{V,T} = \frac{z(\frac{\partial N}{\partial z})_{V,T}}{z(\frac{\partial \ln z}{\partial z})_{V,T}}$$
(7.26)

If in eq. (7.9) the variable X only depends on the number of particles in the fluid, and not on their coordinates or momenta eq. (7.9) becomes upon using eqs. (7.8) and (7.6) and integrating over the momenta:

$$\overline{X} = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^{N} x}{N!} \int_{V} \cdots \int_{V} e^{-\frac{1}{2} \sum_{i \neq j} u(r_{ij})} d\underline{r}_{i} \cdots d\underline{r}_{N}$$
(7.27)

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The contribution of the first term within the brackets is $3\overline{N}kT/2$ while each of the N(N-1)/2 terms u(r_{i,i}) gives the same integral; thus:

$$U = \frac{3}{2} \overline{N}kT + \frac{1}{2\Xi} \sum_{N=2}^{\infty} \frac{z^N}{(N-2)!} \int_{V} \dots \int_{V} u(r_{12}) e^{-\frac{1}{2}\sum_{i\neq j} u(r_{ij})} d\underline{r}_1 \dots d\underline{r}_N$$
(7.14)

Comparing the series on the right-hand side of eq. (7.10) with the definition of the pair distribution function $n^{(2)}(\underline{r}_1,\underline{r}_2)$, it follows that:

$$U = \frac{3}{2} \overline{N}kT + \frac{1}{2} \int_{V} u(r_{12}) n^{(2)} (\underline{r}_1, \underline{r}_2) d\underline{r}_1 d\underline{r}_2$$
(7.15)

Substitution of eq. (7.12), taking into account the limit of V large and using eq. (7.11), eq. (7.15) becomes:

$$U = \frac{3}{2} \overline{N}kT + \frac{1}{2}\overline{N}\rho \int u(r) g(r) dr$$
(7.16)

Using spherical polar coordinates this equation can be rewritten as:

$$U = \frac{3}{2} \overline{N}kT + 2\pi \overline{N}\rho \int_{0}^{\infty} r^{2}u(r) g(r) dr$$
(7.17)

7.4.2. The virial equation of state

In order to derive the virial equation of state via the grand partition function conveniently a coordinate transformation is introduced:

$$\underline{s}_{i} = \frac{\underline{r}_{i}}{\sqrt{1/3}}$$
(7.18)

Inserting this into eq. (7.7) the grand partition function becomes:

$$\Xi = \sum_{N=0}^{\infty} \frac{z^{N} v^{N}}{N!} \int \dots \int e^{-\frac{1}{2} \sum_{i \neq j} u(v^{1/3} s_{ij})/kT} d\underline{s}_{1} \dots d\underline{s}_{N}$$
(7.19)

Differentiation of this equation with respect to V yields:

$$\begin{split} & (\frac{\partial \Xi}{\partial V})_{\mu, \mathrm{T}} = \sum_{\mathrm{N=0}}^{\infty} \frac{z^{\mathrm{N}} \mathrm{v}^{\mathrm{N}}}{(\mathrm{N-1})!} \int \dots \int e^{-\frac{1}{2} \sum_{i \neq j} u(\mathrm{v}^{1/3} \mathrm{s}_{i \, j})/\mathrm{k} \mathrm{T}} \mathrm{d} \mathrm{s}_{1} \dots \mathrm{d} \mathrm{s}_{\mathrm{N}} \\ & - \frac{1}{6} \sum_{\mathrm{N=0}}^{\infty} \frac{z^{\mathrm{N}} \mathrm{v}^{\mathrm{N}}}{(\mathrm{N-2})!} \int \dots \int e^{-\frac{1}{2} \sum_{i \neq j} u(\mathrm{v}^{1/3} \mathrm{s}_{i \, j})/\mathrm{k} \mathrm{T}} \mathrm{v}^{1/3} \mathrm{s}_{12} \\ & \cdot u'(\mathrm{v}^{1/3} \mathrm{s}_{12}) \mathrm{d} \mathrm{s}_{1} \dots \mathrm{d} \mathrm{s}_{\mathrm{N}} \end{split}$$
(7.20)

In this equation u'(r) is the derivative of u(r) and it is taking into account that differentiating the exponential term gives N(N-1)/2 equal terms.

Transformation back to the original coordinates \underline{r}_1 , ..., \underline{r}_N and application of eq. (7.10) with L = 1 and L = 2 respectively eq. (7.20) becomes:

$$\frac{\underline{v}}{\underline{z}} \left(\frac{\partial \underline{z}}{\partial V} \right)_{\mu, T} = \int_{V} n^{(1)}(\underline{r}_{1}) \ d\underline{r}_{1} - \frac{1}{6} \int_{V}^{\int \int} r_{12} u'(r_{12}) n^{(2)}(\underline{r}_{1}, \underline{r}_{2}) \ d\underline{r}_{1} d\underline{r}_{2}$$
(7.21)

Application of eqs.(7.11) and (7.12) and taking into account the limit for V to be very large this results in:

$$\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\mu,T} = \rho - \frac{\rho^2}{6} \int r u'(r) g(r) d\underline{r}$$
(7.22)

With ln Ξ = pV/kT and using spherical polar coordinates for the integration yields:

$$\frac{p}{pkT} = 1 - \frac{2\pi\rho}{3} \int_{0}^{\infty} r^{3} \frac{d u(r)}{dr} g(r) dr, \qquad (7.23)$$

which is the so-called virial equation of state.

7.4.3. The compressibility equation of state

In classical thermodynamics the isothermal compressibility is defined as:

$$u_{\rm T} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \rho}\right)_{\rm V,T} \tag{7.24}$$

With $\ln \Xi = pV/kT$ and application of eq. (7.11) the following equation is obtained:

$$kT \left(\frac{\partial \rho}{\partial p}\right)_{V,T} = \left(\frac{\partial \overline{N}}{\partial \ln \overline{z}}\right)_{V,T}$$
(7.25)

For given values of V and T, both Ξ and \overline{N} can be considered as functions of z, which was already defined by eq. (7.8). Thus:

$$\langle T \left(\frac{\partial \rho}{\partial p}\right)_{V,T} = \frac{z \left(\frac{\partial T}{\partial z}\right)_{V,T}}{z \left(\frac{\partial \ln z}{\partial z}\right)_{V,T}}$$
(7.26)

If in eq. (7.9) the variable X only depends on the number of particles in the fluid, and not on their coordinates or momenta eq. (7.9) becomes upon using eqs. (7.8) and (7.6) and integrating over the momenta:

$$\overline{X} = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N x}{N!} \int_{V} \cdots \int_{V} e^{-\frac{1}{2} \sum_{i \neq j} u(r_{ij})} d\underline{r}_{1} \cdots d\underline{r}_{N}$$
(7.27)

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where z is defined by eq. (7.8).

Differentiation of eq. (7.7) with respect to z results in:

$$z \left(\frac{\partial \ln \Xi}{\partial z}\right)_{V,T} = \overline{N}$$
(7.28)

Inserting N for X in eq. (7.27) and then differentiating with respect to z and application of eq. (7.28) gives:

$$z \left(\frac{\partial \overline{N}}{\partial z}\right)_{V,T} = \overline{N^2} - \overline{N}^2$$
(7.29)

Now eq. (7.26) can be rewritten as:

$$kT \left(\frac{\partial \rho}{\partial p}\right)_{V,T} = \frac{\overline{N^2} - \overline{N}^2}{\overline{N}} , \qquad (7.30)$$

or:

$$kT \left(\frac{\partial \rho}{\partial p}\right)_{V,T} = \frac{\overline{(N-\bar{N})}^2}{\bar{N}}$$
(7.31)

This equation makes clear that the compressibility is a measure of the magnitude of the fluctuations of N about its mean value. The right-hand side of eq. (7.30) can now be expressed in terms of the pair distribution function $n^{(2)}(\underline{r}_1, \underline{r}_2)$. From eqs. (7.10) and (7.27) it follows:

$$\int_{V} \cdots \int_{V} n^{(L)} \left(\underline{r}_{1}, \dots, \underline{r}_{L} \right) = \frac{\overline{N!}}{(N-L)!}$$
(7.31)

With the relation

 $\overline{N^2} - \overline{N}^2 = \overline{N} + \overline{(N(N-1))} - \overline{N}^2$ (7.32)

the following equation results:

$$\overline{\mathbb{N}} + \int_{\mathbb{V}} \cdots \int_{\mathbb{V}} \{ \mathfrak{n}^{(2)}(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2) - \mathfrak{n}^{(1)}(\underline{\mathbf{r}}_1) \ \mathfrak{n}^{(2)}(\underline{\mathbf{r}}_2) \} \ d\underline{\mathbf{r}}_1 d\underline{\mathbf{r}}_2 = \overline{\mathbb{N}^2} - \overline{\mathbb{N}^2}$$
(7.33)

Application of eqs. (7.11) and (7.12) and taking into account the limit at very large V eq. (7.33) becomes:

$$\overline{N} \{1 + \rho \int [g(r) - 1] dr \} = N^2 - \overline{N}^2$$
(7.34)

Comparing this equation with eq. (7.30) and inserting spherical polar coordinates the final result reads:

$$kT \left(\frac{\partial \rho}{\partial p}\right)_{V,T} = 1 + 4\pi\rho \int_{0}^{\infty} r^{2} \left[g(r) - 1\right] dr, \qquad (7.35)$$

which is the compressibility equation of state.

7.5. Integral equations

In the previous section it was shown clearly that calculations of thermodynamic properties of a fluid require the knowledge of the radial distribution function (RDF) as a function of temperature and density. As it was an objective of this study to apply the macroscopic thermodynamic relations without introducing too many approximations it was essential to calculate the RDF for a wide range of temperature and density. In chapter 1 the several methods to obtain the RDF were reviewed briefly and it was decided to calculate the RDF using a parametric integral equation. Essentially the integral equation chosen for that purpose is a combination of the Percus-Yevick (PY) and hypernetted chain (HNC) equations.

In this section details of the theoretical background for calculating the RDF will be discussed.

7.5.1. The equation of Ornstein and Zernike

Nowadays the equation of Ornstein and Zernike [36] plays the central role in the integral equation method to calculate radial distribution functions. However, the original purpose of this equation was to understand the phenomena of critical opalescence.

In the theory of Ornstein and Zernike [36] two correlation functions were introduced:

- the total correlation function $h(r_{12})$;

- the direct correlation function $c(r_{12})$.

The total correlation function is simply related to the radial distribution function $g(r_{1\,2})$ by

$$h(r_{12}) = g(r_{12}) - 1 \tag{7.36}$$

In a similar way as the radial distribution function $h(r_{12})$ is a measure of the total effect that a molecule exerts to a second one. From the definition of $h(r_{12})$ it follows that in the limit $r_{12} \rightarrow \infty h(r_{12})$ goes to zero; i.e. there is no correlation. In comparison to the intermolecular pair-potential $u(r_{12})$ the functions $g(r_{12})$ and $h(r_{12})$ have a range with longer r_{12} .

On a heuristic basis Ornstein and Zernike [36] introduced the so-called direct correlation function $c(r_{12})$. They separated the total correlation function $h(r_{12})$ between molecules 1 and 2 into two contributions:

- a direct correlation between molecules 1 and 2 expressed by $c(r_{12})$;
- an indirect correlation whereby molecule 1 extends its influence on some other molecule 3, which in turn exerts its influence on molecule 2, directly or indirectly through other molecules. This effect is weighted

by the density and averaged over all locations possible for molecule 3. Mathematically this is expressed by the integral equation of Ornstein and Zernike [36]:

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{23}) c(r_{13}) d\underline{r}_3$$
(7.37)

In this equation the first term on the right-hand side gives the direct part and the second term the indirect part of $h(r_{12})$.

The indirect part in eq. (7.37) can easily be written in terms of direct correlations between molecules 1 and 2 and other ones. Using eq. (7.37) $h(r_{23})$ can be eliminated and the result is:

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})c(r_{23})d\underline{r}_3 + \rho^2 \iint c(r_{13})c(r_{34})c(r_{24})d\underline{r}_3d\underline{r}_4 + \dots$$
(7.38)

From eq. (7.37) it is obvious that for $r_{12} + \infty$ as well as for dilute gases $h(r_{12}) = c(r_{12})$ i.e. all indirect effects disappear.

Eq. (7.37) is nothing more than a definition of the direct correlation function. However, in comparison to the radial distribution function g(r) the physical meaning of the direct correlation function is not quite clear. In comparison to the functions g(r) and h(r) the function c(r) has a much simpler structure. The importance of the direct correlation function is that it has a much shorter range than the functions h(r) and g(r).

7.5.2. The method of functional differentiation

Essentially the Ornstein-Zernike equation gives a relation between the radial distribution function and the direct correlation function (section 7.5.1.). In order to be able to solve the Ornstein-Zernike equation a second relation between g(r) and c(r) is required.

Based on the OZ-equation a whole class of approximate relations between g(r) and c(r) have been derived [37,38,39,40,41,42]. The first approximate relation was proposed by Percus and Yevick [37] and originates from the study of Bohm et al. [43] about the behaviour of ionized gases.

The original derivation of the Percus-Yevick-approximation [37] is very

complicated and will not be given in this work. A concise review of the original theory of Percus and Yevick is given by Eyring et al. [44]. A particularly elegant alternative derivation was given later by Percus [38]. In this method Percus used a functional Taylor expansion as discussed by Volterra [45]. An important advantage of this functional method is that alternative approximations can readily be obtained. The general principles of this method are also discussed by Verlet [46] and Lux et al. [47,48].

In this work the derivation given by Eyring et al. [3] is shortly reported. The derivation starts with the consideration of a distribution function $n^{(1)}(\underline{r}_1,\ldots,\underline{r}_L)$ for L particles in the presence of an external potential $\Psi(\underline{r})$. Later this potential will be considered as a potential due to a particle which was added to the system. The L-particle distribution function in the presence of $\Psi(\underline{r})$ is then proportional to the L + l - particle distribution function function without $\Psi(\underline{r})$.

The L-particle distribution function in the presence of an external potential $\psi(\mathbf{r})$ is given by:

$$\mathbf{n}^{(\mathrm{L})}(\underline{\mathbf{r}}_{1},\ldots,\underline{\mathbf{r}}_{L}) = \frac{1}{\Xi} \sum_{\mathrm{N}=\mathrm{L}}^{\Sigma} \frac{z^{\mathrm{N}}}{(\mathrm{N}-\mathrm{L})!} \int_{\mathrm{V}} \cdots \int_{\mathrm{V}} e^{-\phi/k\mathrm{T}} \mathrm{d}\underline{\mathbf{r}}_{\mathrm{L}+1} \cdots \mathrm{d}\underline{\mathbf{r}}_{\mathrm{N}}$$
(7.39)

with

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \dots \int e^{-\phi/kT} d\underline{r}_1 \dots d\underline{r}_N$$
(7.40)

as the grand partition function.

Considering $n^{(L)}$ under the influence of an external potential $\psi(\underline{r})$ the potential energy function ϕ is now defined as:

$$\phi = \frac{1}{2}\sum_{i \neq j} u(\mathbf{r}_{ij}) + \sum_{i=1} \psi(\underline{\mathbf{r}}_i)$$
(7.41)

Taking β = 1/kT the quantity $-\beta \psi$ will be considered as a functional – i.e. a function of a function – and the functional derivative of ln Ξ will be determined. The variation (ln Ξ) due to a variation $\delta \Psi(\underline{r})$ will be:

$$\delta(\ln \Xi) = \frac{1}{\Xi} \sum_{N=1}^{\infty} \frac{z^N}{N!} \int_{V} \dots \int_{V} e^{-\frac{1}{2}\beta \sum_{i\neq j} u(r_{ij})} \delta\{e^{-\beta \sum_{i=1}^{\omega} \psi(\underline{r}_{i})}\} d\underline{r}_1 \dots d\underline{r}_N$$
(7.42)

This can be rewritten as:

- a direct correlation between molecules 1 and 2 expressed by c(r12);
- an indirect correlation whereby molecule 1 extends its influence on some other molecule 3, which in turn exerts its influence on molecule 2, directly or indirectly through other molecules. This effect is weighted

by the density and averaged over all locations possible for molecule 3. Mathematically this is expressed by the integral equation of Ornstein and Zernike [36]:

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{23}) c(r_{13}) d\underline{r}_3$$
(7.37)

In this equation the first term on the right-hand side gives the direct part and the second term the indirect part of $h(r_{12})$.

The indirect part in eq. (7.37) can easily be written in terms of direct correlations between molecules 1 and 2 and other ones. Using eq. (7.37) $h(r_{23})$ can be eliminated and the result is:

$$\begin{split} h(\mathbf{r}_{12}) &= c(\mathbf{r}_{12}) + \rho \int c(\mathbf{r}_{13}) c(\mathbf{r}_{23}) d\underline{\mathbf{r}}_3 + \rho^2 \int \int c(\mathbf{r}_{13}) c(\mathbf{r}_{34}) c(\mathbf{r}_{24}) d\underline{\mathbf{r}}_3 d\underline{\mathbf{r}}_4 + \dots \end{split} \eqno(7.38)$$

From eq. (7.37) it is obvious that for $r_{12} \rightarrow \infty$ as well as for dilute gases $h(r_{12}) = c(r_{12})$ i.e. all indirect effects disappear.

Eq. (7.37) is nothing more than a definition of the direct correlation function. However, in comparison to the radial distribution function g(r) the physical meaning of the direct correlation function is not quite clear. In comparison to the functions g(r) and h(r) the function c(r) has a much simpler structure. The importance of the direct correlation function is that it has a much shorter range than the functions h(r) and g(r).

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Based on the OZ-equation a whole class of approximate relations between g(r) and c(r) have been derived [37,38,39,40,41,42]. The first approximate relation was proposed by Percus and Yevick [37] and originates from the study of Bohm et al. [43] about the behaviour of ionized gases.

The original derivation of the Percus-Yevick-approximation [37] is very

complicated and will not be given in this work. A concise review of the original theory of Percus and Yevick is given by Eyring et al. [44]. A particularly elegant alternative derivation was given later by Percus [38]. In this method Percus used a functional Taylor expansion as discussed by Volterra [45]. An important advantage of this functional method is that alternative approximations can readily be obtained. The general principles of this method are also discussed by Verlet [46] and Lux et al. [47,48].

In this work the derivation given by Eyring et al. [3] is shortly reported. The derivation starts with the consideration of a distribution function $n^{(1)}(\underline{r_1},\ldots,\underline{r_L})$ for L particles in the presence of an external potential $\Psi(\underline{r})$. Later this potential will be considered as a potential due to a particle which was added to the system. The L-particle distribution function in the presence of $\Psi(\underline{r})$ is then proportional to the L + 1 - particle distribution function without $\Psi(\underline{r})$.

The L-particle distribution function in the presence of an external potential $\Psi(\underline{r})$ is given by:

$$n^{(L)}(\underline{r}_{1},\ldots,\underline{r}_{L}) = \frac{1}{\Xi} \sum_{N=L}^{\infty} \frac{z^{N}}{(N-L)!} \int_{V} \cdots \int_{V} e^{-\phi/kT} d\underline{r}_{L+1} \cdots d\underline{r}_{N}$$
(7.39)

with

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_{V} \dots \int_{V} e^{-\phi/kT} d\underline{r}_1 \dots d\underline{r}_N$$
(7.40)

as the grand partition function.

Considering $n^{(L)}$ under the influence of an external potential $\Psi(\underline{r})$ the potential energy function ϕ is now defined as:

$$P = \frac{1}{2\Sigma} u(\mathbf{r}_{ij}) + \sum_{i=1}^{\Sigma} \psi(\underline{\mathbf{r}}_i)$$
(7.41)

Taking $\beta = 1/kT$ the quantity $-\beta \Psi$ will be considered as a functional - i.e. a function of a function - and the functional derivative of ln Ξ will be determined. The variation (ln Ξ) due to a variation $\delta \Psi(\mathbf{r})$ will be:

$$\delta(\ln \Xi) = \frac{1}{\Xi} \sum_{N=1}^{\infty} \frac{z^N}{n!} \int \dots \int e^{-\frac{1}{2}\beta\Sigma} i \neq j \quad u(r_{ij}) \quad \delta\{e^{-\beta\Sigma} i = 1 \quad \psi(\underline{r_i})\} \quad d\underline{r_1} \dots d\underline{r_N}$$
(7.42)

This can be rewritten as:

$$\begin{split} \delta(\ln \Xi) &= \frac{1}{\Xi} \sum_{N=1}^{\infty} \frac{z^N}{N!} \int_{V} \dots \int_{V} e^{-\frac{1}{2}\beta \sum_{i\neq j} u(\mathbf{r}_{i,j})} e^{-\beta \sum_{i=1} \psi(\underline{\mathbf{r}}_{i})} \cdot \\ &\cdot \delta(-\beta \sum_{i=1} \psi(\underline{\mathbf{r}}_{i})) d\underline{\mathbf{r}}_{1} \dots d\underline{\mathbf{r}}_{N} \end{split}$$
(7.43a)

Taking into account eq. (7.41) this equation becomes:

$$\delta(\ln \Xi) = \sum_{N=1}^{\infty} \frac{\sum_{i=1}^{N} \sum_{i=1}^{N} \int \dots \int e^{-\beta \varphi} \delta(-\beta \Psi_{\underline{i}}) d\underline{r}_{\underline{i}} \dots d\underline{r}_{\underline{N}}$$
(7.43b)

As the integral is symmetric with respect to permutations of identical particles in eq. (7.43b) the summation over i can be replaced by a factor N. If in addition only the variation $\delta \Psi_1$ is taken into account, eq. (7.43b) becomes:

$$\delta(\ln \Xi) = \frac{1}{\Xi} \sum_{N=1}^{\infty} \frac{z^N}{N!} N \int \dots \int e^{-\beta \Phi} \delta(-\beta \psi_1) d\underline{r}_1 \dots d\underline{r}_N, \qquad (7.44)$$

or

$$\delta(\ln \Xi) = \int \left[\frac{1}{\Xi} \left\{ \sum_{N=1}^{\infty} \frac{z^N}{(N-1)!} \int_V \dots \int_V e^{-\beta \varphi} d\underline{\mathbf{r}}_2 \dots d\underline{\mathbf{r}}_N \right\} \right] \delta(-\beta \Psi_1) d\underline{\mathbf{r}}_1$$
(7.45)

A comparison of the part between the brackets of eq. (7.45) to eq. (7.39) yields:

$$\delta(\ln E) = \int n^{(1)}(\underline{r}_1 | \Psi) \quad \delta(-\beta \Psi_1) \, d\underline{r}_1 \tag{7.46}$$

and thus the derivative of the functional becomes:

$$\frac{\delta(\ln \Xi)}{\delta(-\beta\psi(\underline{r}_1))} = n^{(1)}(\underline{r}_1|\psi)$$
(7.47)

Differentiating once more:

$$\frac{\delta^{2}(\underline{1}n \underline{z})}{\delta(-\beta\psi(\underline{r}_{1})) \delta(-\beta\psi(\underline{r}_{2}))} = \frac{\delta\{n^{(1)}(\underline{r}_{1}|\psi)\}}{\delta(-\beta\psi(\underline{r}_{2}))} = n^{(2)}(\underline{r}_{1},\underline{r}_{2}|\psi) - n^{(1)}(\underline{r}_{1}|\psi) n^{(1)}(\underline{r}_{2}|\psi) + n^{(1)}(\underline{r}_{1}|\psi) \delta(\underline{r}_{1} - \underline{r}_{2})$$
(7.48)

In eq. (7.48) $\delta(\underline{r}_1 - \underline{r}_2)$ is the Dirac deltafunction. The function $c(\underline{r}_1, \underline{r}_2)$ will be defined as:

$$-\beta \frac{\delta \psi(\underline{r}_{2})}{\delta \{n^{(1)}(\underline{r}_{1}|\psi)\}} = \frac{\delta(\underline{r}_{1} - \underline{r}_{2})}{n^{(1)}(\underline{r}_{1}|\psi)} - c(\underline{r}_{1}, \underline{r}_{2})$$
(7.49)

From functional analysis it is known [45]:

$$\int \frac{\delta\{n^{(1)}(\underline{r}_{1}|\psi)\}}{\delta\psi(\underline{r}_{3})} - \frac{\delta\psi(\underline{r}_{3})}{\delta\{n^{(1)}(\underline{r}_{2}|\psi)\}} d\underline{r}_{3} = \delta(\underline{r}_{1} - \underline{r}_{2})$$
(7.50)

Substitution of eqs. (7.48) and (7.49) into eq. (7.50) and application of eqs. (7.11) and (7.12) the following expression is obtained:

$$g(\underline{r}_1, \underline{r}_2) - 1 = c(\underline{r}_1, \underline{r}_2) + \rho \int \{g(\underline{r}_1, \underline{r}_3) - 1\} c(\underline{r}_2, \underline{r}_3) d\underline{r}_3$$
(7.51)

Inserting the total correlation function defined by eq. (7.36) gives the equation of Ornstein and Zernike (eq. (7.37)).

In the same way as a normal analytical function can be expanded in a Taylor series this can also be done with a functional. A first order expansion of a functional $f(\underline{r}_1,\ldots,\underline{r}_L|\psi)$ around $\psi=0$ gives:

$$f(\underline{r}_{1},..,\underline{r}_{L}|\Psi) = f(\underline{r}_{1},..,\underline{r}_{L}) + \int \left[\frac{\delta(f(\underline{r}_{1},..,\underline{r}_{L}|\Psi))}{\delta(n^{(1)}(\underline{r}_{L+1}|\Psi))}\right]_{\Psi=0} \cdot [n^{(1)}(\underline{r}_{L+1}|\Psi) - n^{(1)}(\underline{r}_{L+1})] d\underline{r}_{L+1}$$
(7.52)

The quintessence of the functional method is now to choose a functional $f(\underline{r}_1,\ldots,\underline{r}_L|\psi)$ in such a way that all important properties will be preserved, in spite of the fact that the Taylor expansion is truncated after the linear term. Depending on the functional that will be chosen several different approximate relations can be derived. The method to derive approximate relations between the radial distribution function and the direct correlation function is known as the method of functional differentiation.

7.5.3. The Percus-Yevick approximation

Here the following functional will be chosen in the first instance:

$$f(\underline{\mathbf{r}}_{1}|\boldsymbol{\Psi}) = n^{(1)}(\underline{\mathbf{r}}_{1}|\boldsymbol{\Psi}) e^{\beta \boldsymbol{\Psi}(\underline{\mathbf{r}}_{1})}$$
(7.53)

Substitution of this equation into eq. (7.52) requires a functional differentiation with respect to $n^{(1)}(\underline{r}_{2}|\Psi)$:

$$\begin{bmatrix} \frac{\delta\{n^{(1)}(\underline{r}_{1}|\psi) \ e^{\beta\psi(\underline{r}_{1})}\}}{\delta\{n^{(1)}(\underline{r}_{2}|\psi)\}} \end{bmatrix}_{\psi=0} = \begin{bmatrix} e^{\beta\psi(\underline{r}_{1})} \ \frac{\delta\{n^{(1)}(\underline{r}_{1}|\psi)\}}{\delta\{n^{(1)}(\underline{r}_{2}|\psi)\}} + e^{\beta\psi(\underline{r}_{1})}n^{(1)}(\underline{r}_{1}|\psi) \\ \cdot \frac{\delta\{\beta\psi(\underline{r}_{1})\}}{\delta\{n^{(1)}(\underline{r}_{2}|\psi)\}} \end{bmatrix}_{\psi=0}$$
(7.54)

Further the following relation holds [45]:

$$\delta\{n^{(1)}(\underline{\mathbf{r}}_{1}|\psi)\} = \int \delta\{n^{(1)}(\underline{\mathbf{r}}_{2}|\psi)\}\delta(\underline{\mathbf{r}}_{1} - \underline{\mathbf{r}}_{2}) \, d\underline{\mathbf{r}}_{2}$$
(7.55)

Eq. (7.55) allows to replace the first terms of the right-hand side of eq. (7.54) by the Dirac deltafunction and substituting eq. (7.49) for the second term leads to:

$$\begin{bmatrix} \frac{\delta\{n^{(1)}(\underline{r}_{1}|\psi) e^{\beta\psi(\underline{r}_{1})}\}}{\delta\{n^{(1)}(\underline{r}_{2}|\psi)\}} & \downarrow = 0 \\ \downarrow = 1 e^{\beta\psi(\underline{r}_{1})} \delta(\underline{r}_{1} - \underline{r}_{2}) + e^{\beta\psi(\underline{r}_{1})} n^{(1)}(\underline{r}_{1}|\psi) \{c(\underline{r}_{1},\underline{r}_{2}) - \frac{\delta(\underline{r}_{1} - \underline{r}_{2})}{n^{(1)}(\underline{r}_{1}|\psi)}\} \\ \downarrow = 0 \\ = \delta(\underline{r}_{1} - \underline{r}_{2}) + n^{(1)}(\underline{r}_{1}) c(\underline{r}_{1},\underline{r}_{2}) - \delta(\underline{r}_{1} - \underline{r}_{2}) = n^{(1)}(\underline{r}_{1}) c(\underline{r}_{1},\underline{r}_{2}) \quad (7.56)$$

As already discussed the external potential was caused by the additon of an identicle particle to the system. Placing this particle at a distance \underline{r}_0 , it can be shown [24,49] that:

$$\psi(\underline{r}_{1}) = u(\underline{r}_{0}, \underline{r}_{1})$$
(7.57)
$$n^{(1)}(\underline{r}_{1}|\psi) = \frac{n^{(2)}(\underline{r}_{0}, \underline{r}_{1})}{n^{(1)}(\underline{r}_{0})}$$
(7.58)

Substitution of the eqs. (7.53), (7.56), (7.57) and (7.58) into the Taylor expansion leads to the following result:

$$\frac{n^{(2)}(\underline{r}_{0},\underline{r}_{1})}{n^{(1)}(\underline{r}_{0})} e^{\beta u(\underline{r}_{0},\underline{r}_{1})} = n^{(1)}(\underline{r}_{1}) + \int n^{(1)}(\underline{r}_{1}) c(\underline{r}_{1},\underline{r}_{2}) \cdot \\ \cdot \left[\frac{n^{(2)}(\underline{r}_{0},\underline{r}_{2})}{n^{(1)}(\underline{r}_{0})} - n^{(1)}(\underline{r}_{2})\right] d\underline{r}_{2}$$
(7.59)

Application of eqs. (7.11) and (7.12) gives:

$$g(\underline{r}_0,\underline{r}_1) e^{\beta u(\underline{r}_0,\underline{r}_1) = 1 + \rho \int c(\underline{r}_1,\underline{r}_2) \{g(\underline{r}_0,\underline{r}_2) - 1\} d\underline{r}_2}$$
(7.60)

A comparison of eq. (7.60) and eq. (7.37) (the Ornstein-Zernike equation) yields:

$$g(\underline{\mathbf{r}}_{0},\underline{\mathbf{r}}_{1}) e^{\beta u(\underline{\mathbf{r}}_{0},\underline{\mathbf{r}}_{1})} - 1 = g(\underline{\mathbf{r}}_{0},\underline{\mathbf{r}}_{1}) - 1 - c(\underline{\mathbf{r}}_{0},\underline{\mathbf{r}}_{1})$$
(7.61)

This equation can be written as:

$$c(r) = g(r) \{1 \sim e^{\beta u(r)}\},$$
 (7.62)

which is the PY-approximation. Besides the original derivation by Percus et al. [37], Stell [50] obtained this equation by diagrammatic techniques.

7.5.4. The hypernetted-chain approximation

A second choice of practical importance is the functional:

$$f(\underline{r}_{\underline{l}}|\Psi) = \ln \{n^{(1)}(\underline{r}_{\underline{l}}|\Psi) e^{\beta \Psi(r_{\underline{l}})}\}$$
(7.63)

In a similar way as discussed in the previous section the functional differentiation of the Taylor expansion of eq. (7.52) has to be performed:

$$\frac{\delta \ln (n^{(1)}(\underline{r}_{1}|\psi) e^{\beta \psi(\underline{r}_{1})})}{\delta (n^{(1)}(\underline{r}_{2}|\psi))} |_{\psi=0} \approx \frac{\delta (\underline{r}_{1} - \underline{r}_{2})}{n^{(1)}(\underline{r}_{1})} + \beta \left[\frac{\delta \psi (\underline{r}_{1})}{\delta (n^{(2)}(\underline{r}_{2}|\psi))} \right]_{\psi=0} = e c(\underline{r}_{1}, \underline{r}_{2})$$

$$(7.64)$$

Application of straightforward functional operations as discussed in section 7.5.3. leads finally to the following relation between c(r) and g(r):

$$c(r) = g(r) - 1 - \ln \{g(r)\} - \beta u(r)$$
(7.65)

Equation 7.65 is called the hyper-netted chain approximation. Originally this equation was derived by several investigators [39,40,41,51,52,53,54,55,56] who used diagrammatic techniques.

7.5.5. The PY and HNC integral equation

In section 7.5.1. it was discussed how the Ornstein-Zernike equation relates the direct correlation function c(r) to the total correlation function h(r) and thus to the radial distribution function g(r). As the OZ-equation contains two unknown functions a second relation between those functions is required to be able to solve the OZ-equation.

The PY as well as the HNC-equation are approximate relations which give the required second relationship.

Substitution of one of these approximations leads to an integral equation

with only one unknown function.

If the PY-approximation, defined by eq. (7.62), is substituted into the OZ-equation the Percus-Yevick integral equation results:

$$g(r_{12}) e^{\beta u(r_{12})} = 1 + \rho \int [1 - e^{\beta u(r_{12})}] g(r_{13}) [g(r_{23}) - 1] d\underline{r}_3$$
(7.66)

In a similar way the hypernetted chain integral equation can be obtained by substitution of eq. (7.65) into the OZ-equation. The result is:

$$\ln g(r_{12}) + \beta u(r_{12}) = \rho \int [g(r_{13}) - 1 - \ln g(r_{13}) - \beta u(r_{13})][g(r_{23}) - 1] d\underline{r}_3$$
(7.67)

7.6. Discussion

At present the PY and/or HNC integral equations are most commonly used to calculate radial distribution functions (RDF) for an arbitrary chosen intermolecular pair-potential.

However, already in the early nineteen-thirties the development of statistical mechanical theories to calculate the RDF was initiated. Originally Yvon [57] and independently about ten years later Born et al. [58] derived a hierarchy of integro-differential equations to calculate distribution functions. The general formulation of this hierarchy reads:

$$kT \frac{\frac{\partial n^{(L)}(\underline{r}_{1}, \dots, \underline{r}_{L})}{\partial \underline{r}_{1}} = -\sum_{j=2}^{L} n^{(L)}(\underline{r}_{1}, \dots, \underline{r}_{L}) \frac{\partial u(r_{i,j})}{\partial \underline{r}_{1}} - \int n^{(L+1)}(\underline{r}_{1}, \dots, r_{L+1}) \frac{\partial u(r_{1,L+1})}{\partial \underline{r}_{1}} d\underline{r}_{L+1}$$
(7.68)

Although eq. (7.68) is an exact relation in which the $n^{L+1}(\underline{r}_1, \ldots, r_{L+1})$ distribution function is coupled with the $n^{(L)}(\underline{r}_1, \ldots, r_L)$ distribution function it is necessary to know the $n^{(L+1)}(\underline{r}_1, \ldots, \underline{r}_{L+1})$ distribution function in order to be able to calculate $n^{(L)}(\underline{r}_1, \ldots, \underline{r}_L)$. For that purpose Kirkwood [59] suggested the so-called superposition principle. This principle allows for example to express $n^{(3)}(\underline{r}_1, \underline{r}_2, \underline{r}_3)$ in terms of distribution functions of lower order:

$$n^{(3)}(\underline{r}_{1}, \underline{r}_{2}, \underline{r}_{3}) = \frac{n^{(2)}(\underline{r}_{1}, \underline{r}_{2}) n^{(2)}(\underline{r}_{1}, \underline{r}_{3}) n^{(2)}(\underline{r}_{2}, \underline{r}_{3})}{(n^{(1)}(\underline{r}_{1}))^{3}}$$
(7.69)

with $n^{(1)}(\underline{r}_1) = \frac{N}{V} = \rho$.

Substitution of eq. (7.69) into eq. (7.68) and taking L = 2 yields:

$$kT \frac{\partial \ln n^{(2)}(\underline{r}_{12})}{\partial \underline{r}_{1}} = -\frac{\partial u(\underline{r}_{12})}{\partial \underline{r}_{1}} - \frac{1}{\rho} \int n^{(2)}(\underline{r}_{13}) n^{(2)}(\underline{r}_{23}) \frac{\partial u(\underline{r}_{13})}{\partial \underline{r}_{1}} d\underline{r}_{3}$$
(7.70)

Eq. (7.70) is known as the Born-Green-Yvon (BGY) integral equation and allows to calculate radial distribution functions. Kirkwood [59] obtained a similar hierarchy of equations, however, according to the studies of Garcia-Colin et al. [60] and Raveche et al. [61] it is now accepted that both hierarchies are equivalent.

In spite of the fact that Rowlinson [62] and Alder [63] found that the superposition principle is quite correct for a dense fluid, the combinaton of this approximation with one of the two exact hierarchies of integral equations exaggerates the errors in the calculation of thermodynamic properties. More recent results of Wang et al. [64] and Raveche et al. [65] showed that in general the superposition principle is not good for the high density Lennard-Jones (12,6) fluid.

Several suggestions are known to improve the superposition approximation [66,67,68,69, 70,71]; however, none of these proposed improvements appeared to be successful.

Münster [5] compared the three fundamental integral equation methods (BGY, PY and HNC) to results obtained from molecular dynamics (MD) and Monte Carlo (MC) calculations. From this comparison it could be concluded that for the hard sphere potential the PY-approximation gave the best results and the BGY-equation - with application of the superposition principle-did yield the poorest results.

A similar comparison of the three theories for a Lennard-Jones (12,6) pair-potential - also discussed by Münster [5] - showed that again the PYapproximation is superior to both the HNC- and BGY-approximation.

Münster [5] did also compare the virial and compressibility equation of state - eqs. (7.23) and (7.35) respectively - to Monte Carlo calculations of Wood et al. [72]. It was found that the virial equation of state did represent the Monte Carlo results somewhat better than the compressibility equation of state. As only Monte Carlo data were available in the supercritical region it is possible that this conclusion is not correct in the subcritical region. However, based on the incomplete comparison, in this work the virial equation of state was preferred for practical purposes.

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8. CALCULATION OF THERMODYNAMIC PROPERTIES FROM INTEGRAL EQUATIONS

8.1. Introduction

After introducing the fundamental statistical mechanical principles of fluids in the previous chapter now these principles can be applied to practice. In chapter 7 it was pointed out how the microscopic structure of a real monoatomic fluid in terms of the radial distribution function is related to macroscopic thermodynamic properties. In other words the radial distribution function g(r) in dependence of temperature and density in the whole fluid phase range is required in order to calculate thermodynamic properties.

In this study an integral equation method was preferred to calculate radial distribution functions. As the integral equation theories are usually based on approximations such as PY, HNC, etc. deviations from more reliable computer experiments (molecular dynamics and Monte Carlo) have to be expected. Reed et al. [1] compared the PY and HNC-theories with computer experiments and concluded:

- both theories work well at low and moderate densities, but fail to give quantitative agreement at high densities, particularly in the liquid state;
- in particular calculation of the pressure appeared to be sensitive for differences in $g(\mathbf{r})$;
- in most cases the PY-theory is superior to the HNC-theory; however, at low temperatures and moderate densities the HNC-theory is superior;
- in case g(r) is calculated with a pairwise additive intermolecular potential by an approximate theory - e.g. PY- or HNC- inconsistent results for the virial and compressibility equations of state are obtained.

In addition a more serious problem with respect to integral equation theories was pointed out by Watts [2]. This investigator found that for a pair-potential with an attractive term such as the Lennard-Jones (12,6) pair-potential the PY as well as the HNC integral equations have no convergent solutions in a region enclosed by the spinodal curve of a pure substance. In other words in a region important for the calculation of vapour + liquid equilibria in fluid phases there will be a gap in the possibility to calculate radial distribution functions and consequently no thermodynamic properties can be derived in that region too. The latter difficulty can be resolved by introducing the perturbation theory. In section 8.3 it will be discussed how integral equation theory was combined successfully with perturbation theory.

In order to overcome a problem such as the inconsistency between the virial and compressibility equations of state alternative approximate relations between the direct correlation function c(r) and the radial distribution function g(r) were proposed by Hurst [3] and Rowlinson [4]. A general procedure to derive such so-called self-consistent approximations was given by Stell [5] and Rowlinson [4]. Lado [6] discussed details of the calculation method. Reed et al. [1] concluded that in general the self-consistent approximations provide better results than either the PY or HNC approximations.

In this study a parametric approximate relation between the direct correlation function c(r) and the radial distribution function g(r), originally proposed by Carley [7], was adopted. Essentially this approximation is a combination of the PY and HNC approximation and will be introduced in section 8.2.

If the parametric approximation is substituted into the Ornstein-Zernike integral equation a parametric integral equation will result.

In combination with perturbation theory this parametric integral equation was applied to calculate radial distribution functions in a wide range of temperatures and densities including the in principle non-convergent region.

Once radial distribution functions are available in dependence of temperature and density all macroscopic thermodynamic properties can be evaluated in terms of dimensionless quantities.

8.2. The parametric integral equation

 $c(r) = g(r) \{1 - e^{\beta u(r)}\}$ (PY) (8.1) $c(r) = g(r) - 1 - \ln \{g(r)\} - \beta u(r)$ (HNC) (8.2)

In both equations u(r) is the intermolecular pair-potential and β is defined as: β = 1/kT.

Carley [7] suggested the following parametric relationship between the direct correlation function c(r) and the radial distribution function g(r):

$$c(r) = g(r) - 1 - \frac{1}{a} \ln \{ag(r) e^{\beta u(r)} - a + 1\}$$
(8.3)

This equation contains parameter a, which can generally be considered to be a function of the intermolecular distance r, the particle density ρ and the

temperature T. Note that eq. (8.3) for parameter a approaching zero reduces to eq. (8.1) - the PY approximation - and for a = 1 to eq. (8.2), i.e. the HNC approximation.

Substitution of the parametric approximation into the Ornstein-Zernike equation:

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{23}) c(r_{13}) d\underline{r}_3, \qquad (8.4)$$

with

$$h(r) = g(r) - 1,$$

gives finally the parametric integral equation:

$$\frac{1}{a} \ln \{ag(r_{12}) e^{\beta u(r_{12})} - a + 1\} = \rho f(g(r_{12}) - 1) \{g(r_{12}) - 1 - \frac{1}{2} \ln \{ag(r_{13}) e^{\beta u(r_{13})} - a + 1\}] d\underline{r}_{3}$$
(8.6)

Carley [7] tested this equation for constant values of the parameter a for a system of hard-spheres. The radial distribution function was calculated and then the pressure of the system was evaluated. Comparison of the PY and HNC calculations on the one hand with "exact" computer calculations (molecular dynamics and/or Monte Carlo) on the other hand showed that for the parameter a = 0.27 the best results were obtained from eq. (8.6) in the whole density range.

In a subsequent paper Carley [8] investigated eq. (8.6) for a Lennard-Jones (12,6) pure fluid at a supercritical temperature. Now the value $a \approx 0.12$ did yield excellent agreement with Monte Carlo calculations.

Carley [9] did also study the behaviour of parameter a for a Lennard-Jones (12,6) liquid and found that for a = 0.248 thermodynamic properties can be calculated with acceptable accuracy. From Carley's studies [8,9] it can be concluded that in order to obtain optimum agreement with exact computer calculations at least the parameter a must be taken temperature dependent.

As in this investigation the practical application (chapter 9) mainly refers to the two phase region liquid + vapour, radial distribution functions were calculated with a = 0.248.

8.3. Pair-potential and perturbation theory

In section 8.1 it was already mentioned that integral equations in general have a region where no convergent solutions can be obtained using a pairpotential with an attractive term.

(8.5)

As in this study it is a primary objective to calculate the behaviour of real fluids, application of a pair-potential with an attractive term is essential and therefore the Lennard-Jones (12,6) pair-potential is chosen:

$$\mathbf{u}(\mathbf{r}) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\}$$

$$(8.7)$$

In this equation ε is the depth of the potential well and σ the value of r which makes u(r) = 0. The parameters ε and σ are characteristic for a particular pure substance. A graphical representation of this pair-potential is shown in the upper part of figure 8.1.



In order to be able to calculate radial distribution functions in the whole density region of fluids, advantage of perturbation theory will be utilized. This theory was originally introduced by Zwanzig [10] and essentially in this theory a pair-potential u(r) is separated into a reference part $u_p(r)$ and a perturbation $u_n(r)$ in the following way:

 $u(r) = u_{R}(r) + \lambda u_{p}(r)$

In eq. (8.8) λ is a perturbation parameter which can vary from 0 to 1. For λ = 1 the pair-potential of the actual fluid results.

Further the Helmholtz energy A is described by a so-called λ -expansion:

$$A = A_{R} + \left(\frac{\partial A}{\partial \lambda}\right)_{\lambda=0} + \frac{\lambda^{2}}{2} \left(\frac{\partial^{2} A}{\partial \lambda^{2}}\right)_{\lambda=0} + \dots$$
(8.9)

which essentially is a Taylor series about $\lambda = 0$. Truncating this series after the first derivative and setting $\lambda = 1$ gives first order perturbation theory. Zwanzig [10], McQuarrie [11] and Boublik et al. [12] have presented excellent discussions on this subject and the following expression for the Helmholtz energy was derived:

$$A = A_{R} + A_{p} = A_{R} + 2\pi N\rho \int_{0}^{\beta} r^{2}g_{R}(r) u_{p}(r) dr \qquad (8.10)$$

Eq. (8.10) shows that the Helmholtz energy of a substance is also separated into a contribution of the reference part (A_R) of the pair-potential and a contribution of the perturbation (A_p). Moreover eq. (8.10) shows that the term A_p can be calculated from the reference part of the pair-potential only. In section 8.5 it will be discussed how eq. (8.10) can be utilized to calculate all thermodynamic properties of a system.

The first successful perturbation theory to describe the liquid state was introduced by Barker et al. [13]. In the Barker-Henderson theory (BH) the pairpotential was separated into a positive and a negative part. Later Chandler et al. [14] and Weeks et al. [15] suggested a separation of the pair-potential into a part containing all repulsive forces and a part containing all attractive forces. Singer [16] discussed that the Weeks, Chandler and Anderson (WCA) perturbation theory shows better convergence of the expansion in comparison with the BH-theory. In order to obtain comparable results the BHtheory must be taken second order whereas the WCA-theory is first order.

Carley [17,18] adopted the WCA-theory to separate the Lennard-Jones (12,6) pair-potential into a repulsive part $u_{\rm R}(r)$ and an attractive part $u_{\rm p}(r)$. This WCA perturbation method was also chosen in this investigation:

$u_{R}(r) = u(r) + \alpha \epsilon$	$r < 2^{1/6} \sigma$	(8.11)
$u_{R}(r) = (1 - \alpha) u(r)$	$r \ge 2^{1/6} \sigma$	(8,12)
$u_{p}(r) = -\alpha\varepsilon$	$r < 2^{1/6} \sigma$	(8,13)
$u_{p}(r) = \alpha u(r)$	$r \geq 2^{1/6} \sigma$	(8.14)

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(8.8)

In these equations u(r) is the Lennard-Jones (12,6) pair-potential. If in eqs. (8.11) - (8.14) α = 1 the separation is the same as in the original WCA perturbation [14,15], and if α = 0 there is no separation at all. The lower part of figure 8.1 shows the WCA perturbation: i.e. α = 1.

From integral equations in general reliable thermodynamic properties can be calculated for potentials with attractive wells at high temperatures, whereas below the critical temperature these results become less accurate [19]. On the other hand perturbation theory has been found to be quite successful in the high density liquid state [20,21]. In order to make use of the advantages of the integral equation method as well as the perturbation theory the separation parameter α was introduced in eqs. (8.11) - (8.14). Obviously this separation parameter in principle should be a function of temperature and density. However, similarly as proposed by Carley [9] this parameter is chosen to be a function of the dimensionless temperature $T^{*} = kT/\epsilon$ as follows:

 $\alpha = 1 - \frac{T^*}{T^*_{\rm H}} \tag{8.15}$

In eq. (8.15) $T_{\rm H}^{\rm s}$ has a fixed value and is chosen in such a way that in the whole temperature and density range of interest convergent solutions for eq. (8.6) can be obtained using the repulsive part $u_{\rm R}^{\rm (r)}$ of the Lennard-Jones (12,6) pair-potential only. This means that at high temperatures α must approach zero and at lower temperatures α must have such a value that divergence of the parametric integral equation does not occur.

8.4. Calculation of the radial distribution function

As eq. (8.6) cannot be solved analytically for a pair-potential with an attractive part, this has to be performed numerically by means of a suitable iterative cycle. Chosing values for the temperature T and the density ρ an initial guess for the radial distribution function (RDF) is to be substituted into the righthand side of eq. (8.6) and then performing the integrations an improved RDF can be obtained. Substitution of this improved RDF again into the righthand side of eq. (8.6) closes the iterative cycle. This numerical process is repeated until a satisfactorily accurate solution is obtained. Broyles [22,23] originally introduced this iterative method; Mandel et al. [24] and Van der Kooi [25] applied this method to calculate the RDF for the PY integral equation for a Lennard-Jones (12,6) pair-potential.

With respect to the applied iterative technique Broyles [22,23] found that

at higher densities this iterative cycle diverges. In other words: a too rapidly converging numerical process leads to divergence. To avoid this problem Broyles [22,23] proposed a damping technique. In this damping technique essentially the results of two previous iterations are mixed linearly using a mixing parameter γ . Indicating the results of two previous iterations by $g(r)_n$ and $g(r)_{n-1}$ respectively, a new initial guess $g(r)_{n+1}$ is obtained from the equation:

$$g(r)_{n+1} = \gamma g(r)_n + (1 - \gamma) g(r)_{n-1}$$
(8.16)

The mixing parameter γ varies between 0 and 1. Obviously for γ approaching 0 there is a maximum damping and for γ approaching 1 there is no damping at all.

An alternative iterative numerical technique to calculate the RDF from an integral equation was used by Van Leeuwen et al. [26], De Boer et al. [27], Levesque [28] and Carley [7]. This method makes advantage of the fact that the integral equations as discussed here are of a convolution type, i.e. it is convenient to use the Fourier transform of these equations. For that purpose Carley [7] defined a new function S(r):

$$S(r) = g(r) - 1 - c(r) = h(r) - c(r)$$
 (8.17)

Application of this equation together with eq. (8.3) allows to express g(r) as well as c(r) in terms of the new function S(r):

$$g(r) = e^{-\beta u(r)} \left\{ \frac{1}{a} e^{aS(r)} - \frac{1}{a} + 1 \right\}$$
(8.18)

$$c(r) = e^{-\beta u(r)} \left\{ \frac{1}{a} e^{aS(r)} - \frac{1}{a} + 1 \right\} - 1 - S(r)$$
(8.19)

Substitution of eq. (8.17) into the Ornstein-Zernike equation (eq. (8.4)) gives:

$$S(r_{12}) = \rho \int \{S(r_{23}) c(r_{23}) + c(r_{23}) c(r_{13})\} d\underline{r}_3$$
(8.20)

Taking the three dimensional Fourier transform of both sides of eq. (8.20) results in:

$$\hat{S}(k) = \frac{\rho \left(\hat{c}(k)\right)^2}{1 - \rho \hat{c}(k)}$$
(8.21)

In this equation $\hat{S}(k)$ and $\hat{c}(k)$ are the Fourier transforms of the functions S(r) and c(r) respectively and are related to one another by the equations:

$$\hat{S}(k) = \frac{4\pi}{k} \int_{0}^{\infty} rS(r) \sin(kr) dr$$
(8.22)

$$S(r) = \frac{1}{2\pi^2 r} \int_{\Gamma}^{\infty} k\hat{S}(k) \sin(kr) dk$$
(8.23)
$$\hat{c}(k) = \frac{4\pi}{k} \int_{0}^{k} rc (r) \sin (kr) dr \qquad (8.24)$$

$$c(r) = \frac{1}{2\pi^{2}r} \int_{0}^{r} k\hat{c} (k) \sin (kr) dk$$
 (8.25)

As the RDF is calculated at discrete values of the intermolecular distance r eqs. (8.22) - (8.25) have to be rewritten into their discrete analogs. Assuming that the functions c(r) and S(r) vanish for a particular upper bound b of r and similarly that also the Fourier transforms $\hat{c}(k)$ and $\hat{S}(k)$ vanish for an upper bound of $k = N\pi/b$, with N as the number of discrete intervals, the following numerical sums were obtained by Lado [29]:

$$\hat{S}(k_j) = \frac{4\pi}{k_j} \sum_{i=1}^{N-1} r_i S(r_i) \sin(k_j r_i) \Delta r$$
(8.26)

$$S(r_{i}) = \frac{1}{2\pi^{2}r_{i}} \sum_{j=1}^{N-1} k_{j} \hat{S}(k_{j}) \sin(k_{j}r_{i}) \Delta k$$
(8.27)

$$\hat{c}(k_j) = \frac{4\pi}{k_j} \sum_{i=1}^{N-1} r_i c(r_i) \sin(k_j r_i) \Delta r \qquad (8.28)$$

$$c(r_{i}) = \frac{1}{2\pi^{2}r_{i}}\sum_{j=1}^{N-1} k_{j} \hat{c}(k_{j}) \sin(k_{j}r_{i}) \Delta k$$
(8.29)

with

$$r = b/N; r_i = i\Delta r;$$
 (8.30a)

$$k = \pi/b; \quad k_j = j\Delta k.$$
 (8.30b)

It should be noted that the condition of vanishing functions c(r), S(r), $\hat{c}(k)$ and $\hat{S}(k)$ is fulfilled. Additional details with respect to the calculation of Fourier transforms are given by Filon [30], Cooley et al. [31], Starshak et al. [32] and Davis et al. [33].

The calculations were performed using dimensionless quantities for the intermolecular distance r, the temperature T and the density ρ . These quantities are defined as:

$$r^* = r/\sigma; \quad T^* = kT/\epsilon; \quad \rho^* = \rho\sigma^3$$
 (8.31)

In these relations ϵ and σ are the Lennard-Jones (12,6) pair-potential parameters.

Also in the Fourier transform method it appeared to be necessary to apply the damping technique as discussed above.

In order to calculate radial distribution functions the following conditions were applied in the numerical process:

-	temperature range	:	0.72	\leq T* \leq	5.00
-	density range	:	0.001	<u>≤</u> ρ* <u>≤</u>	1.000
-	$T_{\rm H}^*$ -value in eq. (8.15)	:	5.00	[9]	
-	a-value in eq. (8.3)	:	0.248	[9]	
-	range of r*	:	0.0	<pr *="" <="" p=""></pr>	6.0
_	∆r*		0.05		

To avoid divergence on the one hand and to have always available accurate starting functions on the other hand, some strategy in the calculations is required. The calculations are started at the highest temperature (T* = 5.00) and at the lowest density ($\rho^* = 0.001$). The results of a previous density are used as an initial guess for a next higher density. After all densities of a particular isotherm have been evaluated the next lower isotherm is evaluated in a similar way.

The algorithm can be summarized schematically as follows:

- 1. suitable starting functions of c(r*) and S(r*) are obtained at ρ^* = 0.001;
- the separation parameter α of the Lennard-Jones (12,6) pair-potential is calculated from eq. (8.15);
- 3. the Fourier transform $\hat{c}(k)$ is calculated from eq. (8.28);
- 4. the Fourier transform $\hat{S}(k)$ is calculated from eq. (8.21);
- 5. the function $\hat{S}(k)$ is transformed into the function $S(r^*)$ using eq. (8.27);
- 6. the cut-off criterion is tested for each discrete value of the function $S(r^*)$: $|S(r^*)_n S(r^*)_{n-1}| \le 10^{-4}$, with iterationnumber n;
- 7. if the cut-off criterion is fulfilled the functions g(r) and c(r) can be obtained from eq. (8.18) and (8.19) respectively; if not, a new starting function $S(r^*)_{n+1}$ is calculated applying the mixing parameter γ , with $0 < \gamma \le 1.0$, for the functions $S(r^*)_n$ and $S(r^*)_{n-1}$: $S(r^*)_{n+1} = \gamma S(r^*)_n + (1 - \gamma) S(r^*)_{n-1}$ (8.32)

8. the steps 3 until 7 are repeated.

In the temperature range of interest 43 isotherms were evaluated and each isotherm was calculated at 48 densities, i.e. in the ρ^* and T* range of interest 2064 radial distribution functions were determined. Figures 8.2





until 8.10 show some calculated radial distribution functions. From these figures it can be observed how the oscillating character of the RDF increases with the density ρ^* .

With respect to the number of iterations n required for the calculation of a RDF it was found that this quantity strongly depends on the particular ρ^* - and T*-value. The same holds for the mixing parameter γ . In table 8.8 some information about n and γ is summarized for the isotherm T* = 2.00.

Table 8.1. Number of iterations n and values of the mixing parameter γ for some $\rho^*-values$ and T^* = 2.00.

n	γ	ρ*	n	γ
1	1.00	0.600	72	0.70
4	1.00	0.800	280	0.40
13	1.00	0.900	552	0.30
	n 1 4 13	n Y 1 1.00 4 1.00 13 1.00	n Υ ρ* 1 1.00 0.600 4 1.00 0.800 13 1.00 0.900	n γ ρ* n 1 1.00 0.600 72 4 1.00 0.800 280 13 1.00 0.900 552

At T^{\ast} = 0.72 and ρ^{\ast} = 1.00 – the low temperature dense liquid state \sim it appeared to be necessary to take γ = 0.10 and over 2000 iterations were required before the cut-off criterion was fulfilled.

8.5. Calculation of thermodynamic properties

In section 8.3 it was already pointed out how - as a result of first order perturbation theory - the Helmholtz energy A is related to the RDF ${\rm g}_R(r)$ of the repulsive part of the pair-potential and the perturbation part ${\rm u}_p(r)$ of the pair-potential:

$$A = A_{R} + A_{p} = A_{R} + 2\pi N\rho \int_{0}^{\infty} e^{2}g_{R}(r) u_{p}(r) dr$$
(8.33)

From eq. (8.33) the Helmholtz energy Ap can be calculated.

Introduction of the dimensionless quantities A* = 2A/3NkT and U* = 2U/3NkT and remembering Z = pV/NkT, T* = kT/ ϵ and ρ * = $\rho\sigma^3$ = N σ^3 /V from straight-forward thermodynamics can be derived;

$$dA^* = \left(\frac{2Z}{3\rho^*}\right) d\rho^* - \left(\frac{U^*}{T^*}\right) dT^*$$
(8.34)

and consequently:

$$\mathcal{L} = \frac{3\rho^*}{2} \left(\frac{\partial A^*}{\partial \rho^*}\right)_{\mathrm{T}^*} \tag{8.35}$$

and thus:

$$Z = Z_{R} + Z_{P}$$
(8.36)

Using the collection of calculated RDF's as a function of ρ^* and T^* it is possible to obtain $Z_{V,R}$, i.e. the compressibility factor of the virial equation of state for the repulsive part $u_p(r)$ of the pair-potential:

$$Z_{V,R} = 1 - \frac{2\pi\rho}{3} \int_{0}^{\infty} r^{3} \frac{du_{R}(r)}{dr} g_{R}(r) dr$$
(8.37)

As the Helmholtz energy $A_{\rm p}$ of the attractive part of the pair-potential can be calculated from eq. (8.33), the compressibility factor $Z_{\rm V,P}$ of the virial equation of state for the perturbation part $u_{\rm p}(r)$ of the pair-potential can be obtained from eq. (8.35). Finally application of eq. (8.36) gives the compressibility factor $Z_{\rm v}$ of the virial equation of state:

$$Z_{V} = Z_{V,R} + Z_{V,P}$$

$$(8.38)$$

As $Z_V \approx Z_V$ (ρ^*, T^*) is now available, the Helmholtz energy A for the total pair-potential can be obtained. Integration of eq. (8.34) at T^* = constant gives:

$$A^{*} (\rho^{*}, T^{*}) = A^{*} (\rho^{*}_{0}, T^{*}) + \frac{2}{3} \int_{\rho^{*}_{0}}^{\rho^{*}} \frac{Z_{V} (\rho^{*}, T^{*})}{\rho^{*}} d\rho^{*}$$
(8.39)

In eq. (8.39) ρ_0^* = 0.001; the lowest value of ρ^* at which the RDF's were evaluated. To obtain A* (ρ^*,T^*) for each temperature T* the RDF was calculated at ρ^* = 0.001 for the total Lennard-Jones (12,6) pair-potential u(r).

Applying eq. (7.17) the internal energy U* = U* (ρ *,T*) of the total pairpotential is obtained. Setting A* (ρ *,T*) = 0 for ρ * = 0.001 and T* = 5.00 eq. (8.34) can be integrated at ρ * = ρ_{Λ}^* = constant:

$$A^{*} (\rho_{0}^{*}, T^{*}) = - \int_{5.0}^{T^{*}} \frac{U^{*} (\rho_{0}^{*}, T^{*})}{T^{*}} dT^{*}$$
(8.40)

At this point the Helmholtz energy $A^* = A^* (\rho^*, T^*)$ is known from eqs. (8.39) and (8.40). Differentiation of the Helmholtz energy A^* with respect to T^* gives the internal energy $U^* = U^* (\rho^*, T^*)$:

$$U^{*} (\rho^{*}, T^{*}) = -T^{*} \left(\frac{\partial A^{*}}{\partial T^{*}}\right)_{\rho^{*}}$$
(8.41)

With the availability of $Z_{\rm V}$, A* and U* as a function of ρ^{*} and T* all other macroscopic thermodynamic properties are readily be determined using straightforward thermodynamics. Introduction of dimensionless quantities for



Fig. 8.12. Compressibility factors ${\rm Z}_{C}$ of compressibility equation of state.

the

the



Fig. 8.13. Internal energy U*.





Fig. 8.15. Enthalpy H*.

Fig. 8.16. Gibbs energy G*.

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Fig. 8.17. Helmholtz energy A*.

the entropy, enthalpy and Gibbs energy, defined by $S^* = 2S/3Nk$, $H^* = 2H/NkT$ and $G^* = 2G/3NkT$ respectively, the following relationships can be derived:

$$S^* = U^* - A^*$$
 (8.42)

$$H^* = U^* + \frac{2}{2} Z_{..}$$
(8.43)

$$3^* = A^* + \frac{2}{3} Z_V$$
 (8.44)

In this work also the compressibility factor $Z_{\rm C}$ for the compressibility equation of state was calculated. For that purpose eq. (7.35) was used. Finally from this equation the compressibility factor $Z_{\rm C,R}$ of the repulsive part of the applied pair-potential can be calculated after eq. (7.35) is integrated over the density ρ^{*} .

Then the compressibility factor \boldsymbol{Z}_{C} of the total pair-potential was found from the equation:

$$Z_{\rm C} = Z_{\rm C,R} + (Z_{\rm V} - Z_{\rm V,R})$$
(8.45)

Sofar several equations - eqs. (8.33), (8.37), (7.17) and (7.35) - had to be integrated over r* in the range from zero to infinity. However, as the RDF was evaluated up to a maximum value of r* = 6.0 the integration of these equations could be performed only up to that upper boundary. Therefore a cut-off term should be taken into account. For all these integrations $g_R(r)$ was taken 1.0 for r* > 6.0 and the cut-off term was determined analytically. In nearly all cases the influence of the cut-off term was negligible.

The stepsizes in the numerical integrations over r*, T* and ρ^* were respectively: $\Delta r^* = 0.00625$, $\Delta T^* = 0.001$ and $\Delta \rho^* = 0.001$. In order to investigate the influence of these stepsizes the calculation of the thermodynamic properties was repeated with $\Delta r^* = 0.00125$, $\Delta T^* = 0.00001$ and $\Delta \rho^* = 0.00001$. The highest relative deviation resulting in the thermodynamic properties was 0.02%.

For selected values of ρ^{*} and T* the obtained thermodynamic properties Z_{V} , Z_{C} , U*, S*, H*, G* and A* are summarized in tables 8.2 - 8.8 respectively at the end of this chapter. Figures 8.11 - 8.17 show graphically some of the results.

8.6. Discussion

In this chapter it was discussed how the integral equation method can successfully be combined with perturbation theory.

However, Carley's [9] choice to separate the pair-potential in a repulsive

and an attractive part according to eq. (8.15) cannot be very realistic. At low temperatures and low densities the separation is too strong. In other words the separation parameter α should also be a function of the density ρ^* , as already discussed previously by Peters et al. [34].

Introducing the parameter a in eq. (8.3) - the parametric approximation aimed more consistent results for the virial and compressibility equation of state. Looking more carefully to figures 8.11 and 8.12 as well as tables 8.2 and 8.3 show that only up to moderate densities this objective is achieved. Parameter a should at least be taken temperature dependent. Some preliminary calculations did already prove that a should also be taken density dependent.

In a quite similar way as in this study Carley [17,18] performed calculations with the virial equation of state. In table 8.9 some of his results are compared with those obtained in this work.

Table 8.9. Comparison of the calculated virial equation of state with literature [17,18].

	T* = 0	.72	$T^{*} = 1$.30	T* = 2	.00
ρ*	Z _V (lit.)	ZV	Z _V (lit.)	ZV	Z _V (lit.)	ZV
0.10	0.36	0.36	0.74	0.74	0.89	0.90
0.20	-0.32	-0.32	0.49	0.49	0.88	0.83
0.30	-1.01	-1.01	0.28	0.28	0.83	0.81
0.40	-1.67	-1.67	0.15	0.15	0.91	0.89
0.50	-2.18	-2.18	0.17	0.18	1.13	1.09
0.60	-2.37	-2.36	0.44	0.45	1.55	1.51
0.70	-2.02	-2.00	1.09	1.11	2.25	2.22
0.80	-0.80	-0.74	2.30	2.34	3.33	3.34
0.90	1.75	1.79	4.31	4.36	4.91	5.02

This table shows that for low temperatures excellent agreement with Carley's [17,18] results is obtained. However, for $T^* = 2.00$ significant deviations exist already at low densities. This difference is caused by the influence of the parameter a in eq. (8.3). Up to $T^* = 1.30$ Carley [18] used a = 0.248 and up to higher T^* -values the parameter a was taken 0.12 [17]. In this work for all temperatures the value a = 0.248 was used and consequently differences in the high temperature region have to be expected.

Finally in table 8.10 some Z_V -values are compared with Z-values obtained from Monte-Carlo calculations of Hansen et al. [35], Levesque et al. [36] and

Hansen [37].

Table 8.10 shows that for $T^* = 1.35$ and $T^* = 2.74$ the agreement with the Monte-Carlo results is rather good in the whole density range. However, for $T^* = 0.75$ this agreement is rather poor; especially at moderate densities.

Table 8.10. Comparison of the calculated virial equation of state with Monte-Carlo (MC) calculations [35,36,37].

*	Z _V (MC)	ZV	Z _V (MC)	ZV	Z _V (MC)	ZV
0.10	0.27	0.39	0.74	0.75	0.99	0.98
0.20	-0.27	-0.25	0.48	0.53	0.99	0.99
0.30	-0.80	-0.90	0.35	0.34	1.03	1.06
0.40	-1.20	-1.50	0.28	0.23	1.20	1.22
0.50	-1.68	-1.96	0.30	0.28		1.50
0.60	-2.04	-2.10		0.57		1.96
0.70	-1.71	-1.70	1.17	1.24	2.59	2.66
0.80	-0.53	-0.44	2.42	2.46	3.61	3.69
0.90		2.12	4.58	4.45	5.15	5.15
1.00		6.38		7.43	7.39	7.12

Table 8.2. Compressibility factors $\boldsymbol{Z}_{\boldsymbol{V}}$ of the virial equation of state.

					Z	v	1.19	2 2 5		
0# 1#	= 0.720	0.800	1.000	1.200	1.300	1.500	2.000	2.740	4.000	5.000
0.001	0.994	0.995	0.996	0.997	0.997	0.998	0.999	1.000	1.000	1.001
0.005	0.969	0.973	0.980	0.985	0.987	0.990	0.994	0.998	1.001	1.003
0.010	0.937	0.945	0.960	0.969	0.973	0.979	0.989	0.996	1.003	1.005
0.050	0.683	0.724	0.799	0.848	0.867	0.897	0.946	0.984	1.016	1.029
0.100	0.358	0.443	0.597	0.698	0.737	0.799	0.898	0.977	1.040	1.066
0.150	0.023	0.156	0.394	0.551	0.611	0.707	0.859	0.978	1.075	1.113
0,200	-0.319	-0.135	0.193	0.409	0.491	0.622	0.830	0.992	1.120	1.172
0.250	-0.667	-0.429	-0.004	0.275	0.381	0.548	0.814	1.019	1.180	1.243
0.300	-1.014	-0.718	-0.192	0.152	0.283	0.489	0.814	1.063	1.256	1.331
0.350	-1.352	-0.996	-0.363	0.049	0.205	0.451	0.836	1.128	1.352	1.437
0.400	-1.669	-1.250	-0.509	-0.027	0.154	0.440	0.885	1.219	1.471	1.564
0.450	-1.950	-1.467	-0.616	-0.066	0.141	0.465	0:967	1.341	1.617	1.716
0.500	-2.175	-1.630	-0.672	-0.055	0.176	0.537	1.092	1.500	1.794	1.897
0.550	-2.322	-1.717	-0.658	0.020	0.274	0.667	1.269	1.703	2.008	2.110
0.600	-2.363	-1.704	-0.554	0.177	0.449	0.870	1.507	1.958	2.264	2.361
0.650	-2.268	-1.562	-0.338	0.436	0.722	1.162	1.819	2.274	2.568	2.653
0.700	-1.995	-1.256	0.019	0.818	1.111	1.559	2.219	2.660	2.927	2.992
0.750	-1.502	-0.747	0.548	1.349	1.641	2.084	2.721	3.128	3.348	3.384
0.800	-0.743	0.010	1.282	2.059	2.338	2.757	3.342	3.689	3.839	3.836
0.850	0.347	1.051	2.258	2.976	3.230	3.602	4.098	4.356	4.407	4.353
0.900	1.786	2.497	3.540	4.151	4.360	4,658	5.017	5.145	5.065	4.943
0.950	3.782	4.302	5.140	5.592	5.737	5.929	6.102	6.059	5.814	5.615
1.000	6.233	6.595	7.120	7.352	7.410	7.459	7.384	7.121	6.666	6.378

Table 8.3. Compressibility factors \mathbf{Z}_{C} of the compressibility equation of state.

					Z	5	1200			1.5
D# 1.4	= 0.720	0.800	1.000	1.200	1.300	1.500	2.000	2.740	4.000	5.000
0.001	0.994	0.995	0.996	0.997	0.997	0.998	0.999	1.000	1.000	1.001
0.005	0.969	0.973	0.980	0.985	0.987	0.990	0.994	0.998	1.001	1.003
0.010	0.937	0.945	0.960	0.969	0.973	0.979	0.989	0.996	1.003	1.005
0.050	0.683	0.724	0.799	0.848	0.867	0.897	0.946	0.984	1.016	1.029
0,100	0.357	0.443	0.596	0.698	0.736	0.798	0.898	0.976	1.040	1.066
0,150	0.021	0.154	0.392	0.549	0.609	0.705	0.857	0.977	1.073	1.112
0,200	-0.326	-0.142	0.187	0.403	0.486	0.617	0.825	0.987	1.117	1.168
0,250	-0.681	-0.442	-0.017	0.263	0.369	0.537	0.804	1.010	1.172	1.236
0,300	-1.040	-0.743	-0.215	0.131	0.262	0.469	0.796	1.047	1.242	1.318
0.350	-1.394	-1.036	-0.401	0.013	0.170	0.417	0.806	1.101	1.329	1.416
0.400	-1.734	-1.313	-0.568	-0.083	0.100	0.388	0.838	1.177	1.435	1.532
0.450	-2.047	-1.561	-0.704	-0.148	0.061	0.389	0.899	1.280	1.565	1.669
0.500	-2.313	-1,763	-0.796	-0.172	0.063	0.429	0.996	1.414	1.721	1.831
0.550	-2.511	-1,901	-0.828	-0.139	0.119	0,521	1.137	1.587	1.910	2.021
0.600	-2.616	-1.949	-0.781	-0.034	0.244	0.676	1.333	1.805	2.135	2.244
0.650	-2.598	-1,880	-0.631	0.162	0.457	0.911	1.596	2.079	2.403	2.504
0.700	-2.417	-1.661	-0.352	0.473	0.777	1.245	1.940	2.417	2.722	2.807
0.750	-2.031	-1.254	0.087	0.923	1.229	1.696	2.379	2.831	3.098	3.159
0.800	-1.393	-0.610	0.722	1.543	1.841	2.291	2.932	3.335	3.541	3.568
0.850	-0.430	0.306	1.591	2.365	2.641	3.053	3.619	3.942	4.061	4.041
0.900	0.879	1.617	2.762	3.443	3.681	4.025	4.468	4,673	4.671	4.588
0.950	2.705	3.300	4.258	4.796	4.975	5.223	5.494	5.539	5.379	5.219
1.000	5.020	5.475	6.151	6.488	6.587	6.700	6.735	6,568	6.204	5.947

					H*			1119766		
0# T#	= 0.720	0.800	1.000	1.200	1.300	1.500	2.000	2.740	4.000	5.000
0.001	1,652	1.654	1.658	1.660	1.661	1.662	1.664	1.665	1.666	1.666
0.005	1.602	1.619	1.632	1.639	1.642	1.646	1.653	1.658	1.663	1.676
0.010	1.555	1.577	1.599	1.613	1.618	1.626	1.640	1.650	1.659	1.675
0.050	1.173	1.234	1.335	1.402	1.427	1.468	1.535	1.588	1.633	1.663
0.100	0.683	0.795	0.999	1.135	1.187	1.271	1.406	1.514	1.604	1.653
0.150	0.177	0.344	0.657	0.866	0.946	1.074	1.280	1.445	1.583	1.649
0.200	-0.345	-0.120	0.309	0.595	0.704	0.879	1.160	1.384	1.569	1.654
0.250	-0.882	-0.595	-0.043	0.324	0.464	0.687	1.046	1.331	1.564	1.669
0.300	-1.429	-1.077	-0.397	0.055	0.228	0.502	0.942	1.288	1.571	1.694
0.350	-1.982	-1.561	-0.746	-0.206	0.000	0.327	0.850	1.260	1.592	1.733
0.400	-2.530	-2.038	-1.084	-0.453	-0.212	0.169	0.775	1.249	1.629	1.788
0.450	-3.063	-2.498	-1.401	-0.678	-0.403	0.032	0.723	1.259	1.686	1.860
0.500	-3.566	-2.928	-1.688	-0.872	-0.562	-0.074	0.699	1.295	1.765	1.954
0.550	-4.022	-3.311	-1.930	-1.024	-0.680	-0.140	0.712	1.364	1.872	2.072
0.600	-4.409	-3.628	-2.111	-1.119	-0.744	-0.155	0.769	1.470	2.010	2.218
0.650	-4.704	-3.856	-2.214	-1.143	-0.739	-0.106	0.880	1.622	2.184	2.396
0.700	-4.875	-3.969	-2.215	-1.077	-0.649	0.020	1.056	1.826	2.400	2.611
0.750	-4.884	-3.935	-2.092	-0.900	-0.455	0.240	1.309	2.093	2.664	2.867
0.800	-4.703	-3.716	-1.814	-0.591	-0.135	0.573	1.652	2.431	2.982	3.169
0.850	-4.256	-3.286	-1.354	-0.123	0.333	1.038	2.101	2.851	3,362	3.522
0.900	-3.590	-2.546	-0.661	0.541	0.983	1.663	2.674	3.367	3.810	3.935
0.950	-2.504	-1.524	0.279	1.413	1.828	2.459	3.379	3,982	4.333	4.408
1.000	-1.022	-0.125	1.519	2.538	2.905	3.458	4.240	4.715	4.937	4.948

Table 8.7. Gibbs energy G*.

	C. S. Stand	1 100	1. 1. 200 L	21000	G*	7.024	1 25.02	i linge	5.7 25 396	6. 200
0# T* =	0.720	0.800	1.000	1.200	1.300	1.500	2.000	2.740	4.000	5.000
0.001	2.594	2.490	2.270	2.089	2.009	1.867	1.581	1.267	0.890	0.667
0.005	3.634	3.534	3.322	3.146	3.069	2.930	2.648	2.339	1.965	1.743
0.010	4.054	3.960	3.757	3.588	3.513	3.378	3.103	2.798	2.429	2.209
0.050	4.789	4.739	4.615	4.498	4.444	4.341	4.118	3.854	3.518	3.313
0.100	4.822	4.829	4.808	4.760	4.731	4.670	4.513	4.302	4.009	3.820
0.150	4.654	4.722	4.809	4.832	4.831	4.812	4.725	4.567	4.317	4.145
0.200	4.399	4.531	4.732	4.830	4.857	4.884	4.867	4.765	4.557	4.403
0.250	4.094	4.294	4.615	4.791	4.848	4.921	4.978	4.932	4.768	4.630
0.300	3.761	4.032	4.478	4.736	4.823	4.945	5.077	5.088	4.966	4.845
0.350	3.415	3.759	4.335	4.677	4.796	4.967	5.176	5.243	5.164	5.057
0.400	3.069	3.489	4.200	4.627	4.778	5.000	5.285	5.408	5.368	5.275
0.450	2.740	3.238	4.083	4.597	4.781	5.052	5.413	5.590	5.587	5.505
0.500	2.445	3.020	4.001	4.600	4.815	5.135	5.568	5.795	5.824	5.752
0.550	2.204	2.855	3.967	4.649	4.894	5.259	5.760	6.032	6.087	6.022
0.600	2.040	2.764	4.001	4.759	5.031	5.439	5.999	6.308	6.382	6.318
0.650	1.979	2.771	4.121	4.947	5.243	5.687	6.296	6.631	6.713	6.646
0.700	2.055	2.905	4.350	5.232	5.548	6.018	6.661	7.010	7.088	7.011
0.750	2.302	3.197	4.715	5.635	5.964	6.451	7.109	7.454	7.512	7.419
0.800	2.758	3.684	5.243	6.181	6.513	7.003	7.653	7.975	7.994	7.875
0.850	3.475	4.399	5.964	6.893	7.219	7.695	8.307	8,581	8.539	8.385
0.900	4.474	5.429	6.928	7.811	8,116	8.555	9.093	9.287	9.157	8.955
0.950	5.903	6.753	8.149	8.946	9.215	9.592	10.015	10.099	9.852	9.593
1.000	7.707	8.467	9.678	10.340	10.555	10.840	11.100	11.031	10,633	10.307

A#.
energy
<i>Helmholtz</i>
8.8.
Table

					A*					
= *1: d	0.720	0.800	1.000	1.200	1.300	1.500	2.000	2.740	4.000	5.000
0.001	1.931	1.827	1.606	1.424	1,345	1.202	0.915	0.601	0.223	0.000
0.005	2.988	2.886	2.668	2.490	2.411	2.270	1.986	1.673	1.297	1.075
0.010	3.429	3.330	3.117	2.941	2.864	2.725	2.444	2.134	1.760	1.539
0.050	4.334	4.256	4.083	3.933	3.866	3.743	3.487	3.198	2.841	2.626
0.100	4.583	4.534	4.410	4.294	4.240	4.137	3.914	3.651	3.315	3.109
0.150	4.638	4.617	4.546	4.464	4.423	4.341	4.152	3.915	3.600	3.403
0.200	4.611	4.621	4.603	4.557	4.529	4.469	4.314	4.104	3.810	3.622
0.250	4.539	4.580	4.618	4.608	4.594	4.556	4.436	4.253	3.981	3.801
0.300	4.438	4.510	4.606	4.634	4.634	4.619	4.535	4.379	4.129	3.957
0.350	4.316	4.423	4.578	4.645	4.659	4.667	4.619	4.491	4.263	4.099
0.400	4.182	4.323	4.539	4.645	4.675	4.706	4.696	4.596	4.388	4.232
0.450	4.040	4.216	4.494	4.641	4.687	4.742	4.768	4.696	4.509	4.361
0.500	3.895	4.107	4.449	4.637	4.697	4.776	4.840	4.795	4.628	4.488
0.550	3.751	4.000	4.406	4.635	4.711	4.814	4.915	4.897	4.749	4.615
0.600	3.615	3.900	4.370	4.641	4.732	4.858	4.995	5.002	4.872	4.744
0.650	3.491	3.812	4.346	4.656	4.762	4.912	5.083	5.115	5.001	4.877
0.700	3.384	3.742	4.337	4.687	4.807	4.979	5.182	5.236	5.136	5.017
0.750	3.303	3.695	4.350	4.736	4.870	5.062	5.295	5.369	5.280	5.163
0.800	3.253	3.678	4.388	4.808	4.954	5.165	5.425	5.515	5.434	5.318
0.850	3.244	3.698	4.458	4.909	5.066	5.293	5.575	5.677	5.601	5.483
0.900	3.283	3.764	4.568	5.044	5.210	5.450	5.748	5.858	5.781	5.660
0.950	3.381	3.885	4.723	5.218	5.391	5.639	5.947	6:059	5.976	5.850
1.000	3.552	4.071	4.932	5.439	5.615	5.868	6.177	6.284	6.189	6.054

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9. APPLICABILITY OF THE STATISTICAL MECHANICAL VIRIAL EQUATION OF STATE TO FLUID PHASES

9.1. Introduction

In chapter 7 the statistical mechanical fundamentals of fluid phases were introduced and in chapter 8 these basic principles were applied to calculate the radial distribution function from a parametric integral equation.

From the microscopic behaviour of a Lennard-Jones (12,6)-fluid macroscopic thermodynamic properties were derived using straightforward thermodynamics. One of the main objectives of this study was to apply the statistical mechanical virial equation of state for practical purposes. In this chapter the applicability of this physically relevant equation of state will be tested.

9.2. Analytical representation of the statistical mechanical equations of state

In section 8.5 it was discussed how data-collections of $Z = Z(\rho^*, T^*)$ of 2064 discrete values were calculated to represent the non-analytical virial and compressibility equation of state respectively. However, for practical purposes it is very inconvenient to apply such data-collections and therefore a suitable analytical expression to represent these data-collections will be more convenient to practice.

In selecting a suitable equation for that purpose the following conditions must be fulfilled:

- the equation must be sufficiently flexible to represent the obtained data-collections Z = $Z(\rho^*, T^*)$ in a wide range of temperatures $(0.72 \le T^* \le 5.00)$ and of densities $(0.0 \le \rho^* \le 1.0)$;
- for practical thermodynamic calculations it is convenient to have an equation which is explicit in pressure;
- numerical convenience requires a minimum number of non-linear terms in the equation;
- the equation should possess the characteristic behaviour of an equation of state.

The expression chosen is a 33-constant modification of the well-known Benedict-Webb-Rubin (MBWR) equation of state. This equation was first proposed by Jacobsen [1] to represent the pVT-behaviour of nitrogen. Stewart et al. [2] used the equation for oxygen and McCarty [3] for methane. Nicolas et al. [4] discussed that because of the larger number of adjustable parameters the MBWR equation should give a more accurate representation of the high density region than either the 16-constant Strobridge [5] or 20-constant Bender [6] modifications of the Benedict-Webb-Rubin equation of state. Transforming the variables p,V and T of the original equation into the dimensionless quantities $P^* = \rho^*T^*Z$, with $\rho^* = \rho\sigma^3$ and $T^* = kT/\epsilon$ the MBWR equation is:

$$\begin{split} \mathbf{P}^{*} &= \rho^{*}\mathbf{T}^{*} + \rho^{*2}(\mathbf{a}_{1}\mathbf{T}^{*} + \mathbf{a}_{2}\mathbf{T}^{*\frac{1}{2}} + \mathbf{a}_{3} + \mathbf{a}_{4}\mathbf{T}^{*-1} + \mathbf{a}_{5}\mathbf{T}^{*-2}) \\ &+ \rho^{*3}(\mathbf{a}_{6}\mathbf{T}^{*} + \mathbf{a}_{7} + \mathbf{a}_{8}\mathbf{T}^{*-1} + \mathbf{a}_{9}\mathbf{T}^{*-2}) \\ &+ \rho^{*4}(\mathbf{a}_{10}\mathbf{T}^{*} + \mathbf{a}_{11} + \mathbf{a}_{12}\mathbf{T}^{*-1}) + \rho^{*5}(\mathbf{a}_{13}) \\ &+ \rho^{*6}(\mathbf{a}_{14}\mathbf{T}^{*-1} + \mathbf{a}_{15}\mathbf{T}^{*-2}) + \rho^{*7}(\mathbf{a}_{16}\mathbf{T}^{*-1}) \\ &+ \rho^{*8}(\mathbf{a}_{17}\mathbf{T}^{*-1} + \mathbf{a}_{18}\mathbf{T}^{*-2}) + \rho^{*9}(\mathbf{a}_{19}\mathbf{T}^{*-2}) \\ &+ \rho^{*3}(\mathbf{a}_{20}\mathbf{T}^{*-2} + \mathbf{a}_{21}\mathbf{T}^{*-3}) \exp\left[-\gamma\rho^{*2}\right] \\ &+ \rho^{*5}(\mathbf{a}_{22}\mathbf{T}^{*-2} + \mathbf{a}_{23}\mathbf{T}^{*-4}) \exp\left[-\gamma\rho^{*2}\right] \\ &+ \rho^{*7}(\mathbf{a}_{24}\mathbf{T}^{*-2} + \mathbf{a}_{25}\mathbf{T}^{*-3}) \exp\left[-\gamma\rho^{*2}\right] \\ &+ \rho^{*9}(\mathbf{a}_{26}\mathbf{T}^{*-2} + \mathbf{a}_{27}\mathbf{T}^{*-4}) \exp\left[-\gamma\rho^{*2}\right] \\ &+ \rho^{*11}(\mathbf{a}_{28}\mathbf{T}^{*-2} + \mathbf{a}_{31}\mathbf{T}^{*-3} + \mathbf{a}_{32}\mathbf{T}^{*-4}) \exp\left[-\gamma\rho^{*2}\right] \end{split}$$

In this equation a_1 , a_2 , ..., a_{32} and $\gamma = a_{33}$ are adjustable parameters. Nicolas et al. [4] found that eq. (9.1) was not very sensitive to the value of the parameter γ and it appeared that a fixed value of $\gamma = 3.0$ is acceptable. The remaining 32 parameters were calculated from both data-collections $Z_V = Z_V(\rho^*, T^*)$ and $Z_C = Z_C(\rho^*, T^*)$, i.e. data of the virial and compressibility equations of state respectively. As pointed out in chapter 8 the greater part of the data-collections were evaluated in the low density region. Each isotherm $Z = Z(\rho^*)$ was calculated at 48 values of ρ^* and 27 of these densities are below $\rho^* = 0.10$. To avoid an unreal influence of the low density region, from each isotherm 23 densities in the region below 0.10 were not taken into account in the calculation of the parameters a_1 . This means that the estimation of 32 parameters was performed using only 25 x 43 = 1075 values of $Z = Z(\rho^*, T^*)$ in the density range $0.0 \le \rho^* \le 1.0$ and the temperature range $0.72 \le T^* \le 5.00$. The parameters were calculated minimizing the sum of squares S:

 $Z_V(\rho^*,T^*)$ JO with calculat state. of MBWR-param 9.1. Table

(9.1)

				1	
i.	a,	i	aj	i	a.
1	-6.079724591064191'-01	12	+9.865065901739604'+00	23	-1.765677928282865'+01
2	+6.352010136523086'+00	13	-3.458587125883151'+00	24	+1.971179732307215'+00
3	-4.800569938389428'+00	14	+8.801610650940503'+00	25	-5.796471044795243'+04
4	+2.413861031623654'-01	15	+1.183080549056126'+01	26	-2.323211354072304'+01
5	+8.599641009219969'+00	16	-4.348207830850952'+01	27	+7.866548713566618'+03
9	+7.804120951209071'+01	17	-3.371300798323273'+01	28	+2.147269340180587'+04
~	-1.293276900331794'+04	18	+5.797700886736678'+04	29	+3.055055583392651'+00
8	+1.727340472126677'+05	19	+1.591975832773062'+00	30	+2.365172925490529'+05
6	-2.363944256862142'+01	20	+2.082648940200330'+05	31	-6.173608496270030'+00
10	+9.875433417236832'+04	21	+4.900540778795762'+01	32	+6.067061221516495'+04
11	-9.175581641263215'+01	22	+1.726843146442333'+01	33	+3.0000000000000000'+00

	CC				
·	ai	i	aj	i	ai
П	-8.523268977229862'-01	12	+1.093617085748907'+01	23	-2.005106075372679'+01
5	+9.938341072457532'+00	13	-4.7806623630884551+00	24	+2.173320083037234'+00
3	+8.139504063625351'-01	14	-1.981454043905310'+00	25	-3.470892203954638'+04
4	-1.448169507552052'-01	15	-3.983570133213836'+00	26	-4.603065035392373'+00
5	+1.8387232393874'+01	16	-1.393732620179330'+01	27	+4.836046393899813'+03
9	-4.172674037671390'+00	17	+1.012544859203445'+01	28	+1.270194575865516'+04
1	-7.677262536356069'+03	18	+3.471406872596435'+04	29	+6.442438076075879'+00
00	+1.034131655408602'+05	19	-4.736915486295207'+00	30	+1.413103157351593'+05
6	+2.938446940245026'+01	20	+1.246126568689451'+05	31	+2.543808111266903'+00
0	+5.893119644337628'+04	21	-8.548312832312666'+01	32	+3.628678953622687'+04

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9.2.

Table

= Y).

Z(p*, T*) (a,,

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 $S = \sum_{i=1}^{1075} \left\{ P_i^* \text{ (data)} - P_i^* \text{ (MBWR)} \right\}^2$

with $P^* = \rho^* T^* Z$.

+1.029501821347715'+01

+00

+8.983913043678164

11

In tables 9.1 and 9.2 respectively the obtained parameters for the virial (V) and compressibility (C) equations of state are summarized.

The fit of the data of the virial and the compressibility equations of state to eq. (9.2) did result in a standard deviation with respect to $P^* = \rho^*T^*Z^*$ of 0.0040 and 0.0026 respectively. As corner-stone in the application of the nonanalytical statistical mechanical virial and compressibility equations of state it is important that eq. (9.1) with the calculated parameters a_i is able to represent the behaviour of any substance in the gaseous as well as in the liquid state. Because of the dimensionless character of eq. (9.1) it is in principle a corresponding states relation and thus applicable to each pure substance. Clearly that holds only within the limitations of the original assumptions of the model.

9.3. Calculation of the equation of state of pure fluids

Because each collection of Z-values Z = $Z(\rho^*, T^*)$ of both the virial and compressibility equations of state was calculated directly the obtained coefficients of the MBWR equation must characterize these equations too. In other words a fit of pVT-data of a pure substance to eq. (9.1) with ε/k and σ as effective adjustable parameters, is also a fit to the non-analytical virial and compressibility equations of state. If an initial guess of ε/k and σ of the pure substance of interest is chosen, the experimental pVT-data can be transformed into corresponding dimensionless ρ^* - and T*-values using the relations:

$$r = \frac{N\sigma^3}{V}$$
; $T^* = \frac{kT}{\epsilon}$ (9.4)

Minimizing the relative sum of squares S7:

p

S7

$$= \sum_{i=1}^{n} \left\{ 1 - \frac{Z_{i}(exp)}{Z_{i}(calc.)} \right\}^{2}$$
(9.5)

with Z = pV/NkT, enables to find optimum effective values of ε/k and σ of the Lennard-Jones (12,6) pair-potential for the chosen set of pVT-data. In eq. (9.5) Z(calc.) is related to P* of eq. (9.1) by P* = ρ *T*Z. The minimum of the sum of squares S₇ of eq. (9.5) was calculated applying Marquardt's non-linear

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least-squares algorithm [7].

In section 8.3 it was pointed out that the Lennard-Jones (12,6) pairpotential is applicable specifically for spherical molecules. Therefore, it appears to be obvious to test the proposed calculation technique for a type of molecule such as argon. However, in this work we are interested in the behaviour of the virial as well as the compressibility equation of state for molecules of practical interest and therefore it was decided to use methane and ethane for this test. Experimental pVT-data of methane and ethane were taken from Angus et al. [8] and Douslin et al. [9] respectively. From the pVTdata of methane [8] 16 isotherms with a total number of 485 experimental datapoints in a temperature range from 130 up to 390 K and a pressure range from 0 up to 60 MPa were selected. The pVT-data of ethane [9] were chosen in a temperature range from 273 up to 473 K and a pressure range from 1 up to 40 MPa. The 193 experimental data-points of ethane were distributed over 16 isotherms.

In order to minimize the sum of squares $S_{\rm Z}$ of eq. (9.5) with ε/k and σ as effective adjustable parameters suitable starting values of these parameters must be available. For that purpose the values of ε/k and σ recommended by Rodrigues [10] were adopted. To get an impression of the ability to fit pVT-data to both statistical mechanical equations of state the same pVT-data of methane and ethane were also fitted to the Redlich-Kwong (RK) equation of state. This equation is:

$$p = \frac{RT}{V_m - b} - \frac{a}{T^{\frac{1}{2}}V_m (V_m + b)}$$
(9.6)

With parameters a and b which have to be adjusted to a similar sum of squares as of eq. (9.5). Table 9.3 gives the literature values of ϵ/k and σ [10] as well as the calculated values from the virial (V) and the compressibility (C) equation of state. Moreover this table also contains the values of S_Z of the three equations of state.

From table 9.3 it can be concluded that with respect to the pVT-behaviour of methane and ethane the virial equation of state gives somewhat better results. Moreover the $\epsilon/k-$ and σ -values of this equation of state are in better agreement with the corresponding literature values [10]. For that reason it was decided to use for the further investigations the virial equation of state only.

Table 9.3 presents the results of an overall calculation of the potential

parameters ε/k and σ . However, to obtain information about the temperature dependence of these parameters ε/k - and σ -values were calculated for each isotherm of methane and ethane separately. Figures 9.1 and 9.2 show the results for methane and ethane respectively. From the temperature dependence of ε/k and σ , as shown in figures 9.1 and 9.2, it may be observed that near their critical point both hydrocarbons show a change of sign in the slopes of this temperature dependence.

Table 9.3. Comparison of the virial (V), the compressibility (C) and the Redlich-Kwong (RK) equations of state. S_Z is sum of squares defined by eq. (9.5).

	ε/k (lit.)	σ (lit.)	ε/k (V) K	σ (V)	ε/k (C) K	σ (C) Å	S _Z (V)	S _Z (C)	S _Z (RK)
methane	149.0	3.759	144.5	3.702	139.3	3.744	2.13	2.41	3.13
ethane	231.0	4.339	231.7	4.199	224.5	4.260	0.68	0.83	0.73



Fig. 9.1. Temperature dependence of ϵ/k (open circles) and σ (black dots) of methane.

Fig. 9.2. Temperature dependence of ε/k (open circles) and σ (black dots) of ethane.

In figures 9.3 and 9.4 the experimental pVT-data of methane are compared graphically with the fit to the virial equation of state as discussed above. Figure 9.3 compares the experimental data with the virial equation of state using only one set of ε/k - and σ -values (table 9.3) for all isotherms. In figure 9.4 the experimental data are compared with the equation of state using temperature dependent potential parameters as shown in figure 9.1. A similar comparison for ethane is made in figures 9.5 and 9.6 respectively.

In addition, overall ε/k - and σ -values of some other pure fluids were calculated from their experimental pVT-data using the virial equation of state. This calculation allows to compare our results with those known in literature [10,11,12]. Nearly all these parameters available in literature are obtained from second virial coefficient or from viscosity data. The first method is discussed by Sherwood et al. [13] and the second method by Hirschfelder et al. [12]. However, Rodriguez [10] presented an elegant method to calculate the Lennard-Jones (12,6) pair-potential parameters of pure substances from compressibility data of their binary gas mixtures.

With respect to the field of interest discussed in this work the importance of knowledge of pair-potential parameters is that these parameters are related to expressions which allow to estimate binary interaction parameters k_{12} . In principle this is possible from pure substance information such as ε , σ and α (polarizability) only. A review of these relations is given by Pesuit [11]. In table 9.4 the literature values of ε/k and σ are compared with those calculated from the virial equation of state. Moreover table 9.4 gives the temperature and pressure range and the used pVT-data as well as the critical temperature of the pure substance. From this information it is concluded that in most cases the calculated ε/k and σ are valid in the gaseous as well as the liquid state.

9.4. Calculation of vapour + liquid equilibria of binary mixtures

In principle the calculation of vapour + liquid equilibria using the statistical mechanical virial equation of state is quite similar to the calculation techniques as discussed in chapter 6. Now suitable mixing rules for ε/k and σ have to be chosen and then an expression for the fugacity of each component in the binary mixture must be derived. As the virial equation of state is represented by eq. (9.1) the fugacity equation has to be derived from this MBWR equation of state.



Fig. 9.3. pVT-Behaviour of methane calculated with temperature independent ε/k and σ. Open circles experimental data of Angus et al. [8], full curves calculated with the virial equation of state. Dashed curve twophase boundary.



Fig. 9.4. pVT-Behaviour of methane calculated with temperature dependent ɛ/k and o. Open circles experimental data of Angus et al. [8], full curves calculated with the virial equation of state. Dashed curve twophase boundary.



Fig. 9.5. pVT-Behaviour of ethane calculated with temperature independent E/k and G. Open circles experimental data of Douslin et al. [9], full curves calculated with the virial equation of state. Dashed curve two-phase boundary.



Fig. 9.6. pVT-Behaviour of ethane calculated with temperature dependent c/k and 0. Open circles experimental data of Douslin et al. [9], full curves calculated with the virial equation of state. Dashed curve two-phase boundary.

Table 9.4. Comparison of literature values of ϵ/k and σ with those obtained from the virial equation of state.

Substance	Temperature range in K	Pressure range in	Lit. ref. of pVT-	T _c /K	Number of isotherms	Number of data	ε/k (lit.)	σ (lit.)	Lit. ref. of ε/k	ε/k (calc.)	o (calc.)
		MPa	data			points	in K	in A	and o	in K	in A
Neon	50- 140	1 - 20	[14]	44.4	11	220	35.6	2.749	[12]	34.1	2.785
Argon	86- 300	0 -101	[19]	150.86	16	887	118.0	3.410	[10]	117.9	3.402
Krypton	273- 573	2 - 42	[15]	209.4	13	175	164.9	3.631	[10]	166.4	3.635
Xenon	290- 573	2 - 38	[16]	289.7	13	178	227.2	3.988	[10]	219.6	4.031
Methane	130- 390	0 - 60	[8]	190.6	16	485	149.0	3.759	[10]	144.5	3.702
Ethane	273- 473	1 - 40	[9]	305.33	9	193	231.0	4.339	[10]	231.7	4.199
Propane	230- 600	1 - 60	[14]	369.85	16	433	282.0	4.748	[10]	285.1	4.637
n-Butane	311- 511	5 - 62	[14]	425.2	7	263	324.0	5.076	[10]	324.9	5.034
i-Butane	373- 548	1 - 16	[14]	408.1	8	155	308.0	5.117	[10]	300.7	5.310
Neopentane	434- 548	2.5- 30	[17]	433.8	6	62	336.8	5.621	[10]	327.6	5.469
Cyclohexane	313.15	0.24	[14]	553.4	1	1	324.0	6.093	[12]	329.8	4.576
Benzene	280- 600	1 - 50	[14]	562.1	14	201	439.6	5,261	[11]	429.6	5.000
Ethene	248- 448	1 - 40	[20]	282.4	13	330	210.0	4.366	[10]	213.8	4.056
Tetrafluoromethane	273- 623	1.5- 40	[18]	227.45	16	290	178.2	4.306	[11]	168.1	4.254
Carbonmonoxide	203- 673	0 -100	[14]	133.15	12	264	101.0	3.702	[10]	100.7	3.656
Carbondioxide	273- 600	1 ~ 60	[22]	304.2	34	1088	232.0	3,682	[10]	230.2	3.589
Nitrogen	80- 300	0.6- 50	[21]	126.25	15	269	95.0	3,702	[10]	96.7	3.586
Dinitrogenoxide	243- 423	0 ~ 32	[23]	309.6	13	336	189.0	4.590	[12]	233.1	3.630
Water	373-1073	0 ~ 60	[14]	647.3	15	390	506.6	3.181	[11]	561.1	2.994
Sulfurdioxide	348- 523	1 ~ 32	[14]	430.8	9	282	337.1	4.107	[11]	325.4	3.924
Fluorine	100- 300	0 ~ 50	[14]	144.0	16	288	112.0	3.653	[12]	108.4	3.227
Ammonia	380- 580	0 ~110	[[4]	405.55	11	394	317.3	3.453	[11]	231.7	4.199

9.4.1. Mixing rules

Leland et al. [24,25] and Reid et al. [26] proposed an alternative onefluid prescription as suggested in the original work of Van der Waals. In his original treatment Van der Waals assumed that the equation of state for mixtures has the same form as that of the pure components but involves constants which are quadratic sums of the pure component parameters. This was discussed already in section 6.2. In terms of intermolecular pair-potential parameters ε_{ii} and σ_{ii} of the i-th component the values ε_{M} and σ_{M} are related to the pure component values [24,25,26]:

$$\epsilon_{\rm M} = \frac{\sum_{i=j}^{\sum_{j=1}^{\infty} x_i x_j} \epsilon_{ij} \sigma_{ij}^3}{\sigma_{\rm M}^3}$$
(9.7)

$$\sigma_{M}^{3} = \sum_{i j} \sum_{j} x_{i} x_{j} \sigma_{ij}^{3}$$
(9.8)

In these euqations, with x_i as mole fractions, the parameter ε_{ij} for $i \neq j$ is obtained from the geometric mean of ε_{ii} and ε_{jj} and σ_{ij} for $i \neq j$ is obtained from the arithmetical mean of σ_{ii} and σ_{jj} . Similarly as discussed for the mixing rules of the cubic equations of state (section 6.2) also in eqs. (9.7) and (9.8) sometimes correction factors for ε_{ij} and σ_{ij} with $i \neq j$ are required. Especially in mixtures whose components differ largely in physical properties these correction factors are necessary.

For i \neq j the values of ε_{ij} and σ_{ij} are respectively: $\varepsilon_{ii} = (\varepsilon_{ii}\varepsilon_{ii})^{\frac{1}{2}} (1 - k_{ii})$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} (1 - l_{ij})$$
(9.10)

9.4.2. The fugacity

The fugacity f_i of the i-th component in a mixture can be evaluated using the general expression adopted from Prausnitz [27]:

$$RT \ln \left(\frac{f_i}{px_i}\right) = \int_{V}^{\infty} \left[\left(\frac{\partial p}{\partial n_k}\right)_{V,T,\hat{n}_i} - \frac{RT}{V}\right] dV - RT \ln Z$$
(9.11)

Transforming the variables P*, ρ^* and T* in eq. (9.1) into the variables p, V and T respectively of eq. (9.11) using P* = ρ^*T^*Z , $\rho^* = N\sigma^3/V$ and T* = kT/ε and inserting the mixing rules eqs. (9.6) - (9.10) allows to derive an analytical equation for the fugacity f_i . This rather complicated equation - again expressed in the dimensionless variables ρ^* and T* - is:

$$\ln \left(\frac{f_i}{px_i}\right) = \frac{S_A + S_B + S_C}{\varepsilon_M T_M^*} - \ln Z, \qquad (9.12)$$

with

(9.9)

$$T_{M}^{*} = kT/\varepsilon_{M};$$

$$\rho_{M}^{*} = n_{T}N\sigma_{M}^{3}/V;$$

$$Z = nV/NkT$$

 ${\bf n}_{\rm T}$ = total number of moles in the mixtures. ${\bf S}_{\rm A},\,{\bf S}_{\rm R}$ and ${\bf S}_{\rm C}$ are defined respectively:

$$\begin{split} S_{A} &= \sum_{i=2}^{9} = \{ (\sum_{j=1}^{n} x_{j} \varepsilon_{jk} \sigma_{jk}^{3} - 2\varepsilon_{M} \sum_{j=1}^{n} x_{j} \sigma_{jk}^{3} + \varepsilon_{M} \sigma_{M}^{3} \} \frac{2B_{i}}{\sigma_{M}^{3}} + \\ &+ \frac{\varepsilon_{M}}{\sigma_{M}^{3}} \{ iB_{i} \ (2\sum_{j=1}^{n} x_{j} \sigma_{jk}^{3} - \sigma_{M}^{3}) - \frac{2T_{M}^{*}B_{i}^{*}}{\varepsilon_{M}} \ (\sum_{j=1}^{n} x_{j} \varepsilon_{jk} \sigma_{jk}^{3} - \varepsilon_{M} \ \sum_{j=1}^{n} x_{j} \sigma_{jk}^{3}) \} \} \cdot \\ &\{ \frac{(\rho_{M}^{*})^{i-1}}{i-1} \} \end{split}$$
(9.13)
$$S_{B} &= -\frac{13}{2} \sum_{i=3}^{1} \{ \sum_{j=1}^{n} x_{j} \varepsilon_{jk} \sigma_{jk}^{3} - 2\varepsilon_{M} \ \sum_{j=1}^{n} x_{j} \sigma_{jk}^{3} + \varepsilon_{M} \sigma_{M}^{3} \} \frac{2C_{i}}{\sigma_{M}^{3}} + \\ &+ \frac{\varepsilon_{M}}{\sigma_{M}^{3}} \{ iC_{i} \ (2\sum_{j=1}^{n} x_{j} \sigma_{jk}^{3} - \sigma_{M}^{3}) - \frac{2T_{M}^{*}C_{i}^{*}}{\varepsilon_{M}} \ (\sum_{j=1}^{n} x_{j} \varepsilon_{jk} \sigma_{jk}^{3} - \varepsilon_{M} \ \sum_{j=1}^{n} x_{j} \sigma_{jk}^{3}) \} \} I_{i} \end{cases}$$
(9.14)

 Σ' means summation only over odd terms.

$$S_{C} \approx \sum_{i=3}^{13} \left[\frac{\gamma \epsilon_{M} C_{i}}{\sigma_{M}^{3}} \left(2\Sigma_{j=1}^{n} x_{j} \sigma_{jk}^{3} - \sigma_{M}^{3} \right) I_{i+2} \right]$$
(9.15)

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$$I_{i} = \gamma^{(i-3)/2} \left(\rho_{M}^{*i-3} e^{-\gamma(\rho_{M}^{*})^{2}} + \frac{i-3}{2} I_{i-2} \right)$$
(i = 5, 7, 9...)
with
$$I_{0} = e^{-\gamma(\rho_{M}^{*})^{2}} - 1.$$

The coefficients B_i , B_i^* , C_i and C_i^* are given by

$$\begin{split} & B_2 = a_1 T_{\rm H}^a + a_2 \ (T_{\rm H}^a)^{\frac{1}{2}} + a_3 + \frac{a_4}{T_{\rm H}^a} + \frac{a_5}{(T_{\rm H}^a)^2}; \\ & B_3 = a_6 T_{\rm H}^a + a_7 + \frac{a_8}{T_{\rm H}^a} + \frac{a_9}{T_{\rm H}^a})_2; \\ & B_4 = a_{10} T_{\rm H}^a + a_{11} + \frac{a_{12}}{T_{\rm H}^a}; \\ & B_6 = \frac{a_{14}}{1_{\rm H}^a} + \frac{a_{15}}{(T_{\rm H}^a)^2}; \\ & B_7 = \frac{a_{16}}{1_{\rm H}^a}; \\ & B_8 = \frac{a_{17}}{T_{\rm H}^a} + \frac{a_{18}}{(T_{\rm H}^a)^2}; \\ & B_8 = \frac{a_{17}}{(T_{\rm H}^a)^2} + \frac{a_{21}}{(T_{\rm H}^a)^3}; \\ & C_7 = \frac{a_{24}}{(T_{\rm H}^a)^2} + \frac{a_{29}}{(T_{\rm H}^a)^3}; \\ & C_{11} = \frac{a_{28}}{(T_{\rm H}^a)^2} + \frac{a_{29}}{(T_{\rm H}^a)^3}; \\ & B_{\rm H}^a = \frac{a_{10} - \frac{a_{27}}{(T_{\rm H}^a)^2} + \frac{a_{29}}{(T_{\rm H}^a)^3}; \\ & B_{\rm H}^a = a_{10} - \frac{a_{12}}{(T_{\rm H}^a)^2} + \frac{a_{29}}{(T_{\rm H}^a)^3}; \\ & B_{\rm H}^a = a_{10} - \frac{a_{12}}{(T_{\rm H}^a)^2}; \\ & B_{\rm H}^a = \frac{a_{12}}{(T_{\rm H}^a)^2}; \\ & B_{\rm H}^a$$

In the expressions for B_i , C_i , B_i^* and C_i^* a_1 , a_2 , a_3 , ..., a_{33} are the calculated parameters of eq. (9.1).

9.4.3. Calculation of p,x,y-sections of binary mixtures of simple molecules

In order to calculate fluid phase equilibria in binary mixtures, first ε/k and σ of both pure components have to be obtained. Depending on the experimental pure component data available as well as the temperature at which the p,x,y-section must be calculated, generally in this work two methods were applied to calculate these parameters:

- calculation of ϵ/k and σ from experimental pVT-data;
- calculation of ϵ/k and σ from the saturated vapour pressure curve of the pure components.

The first method was already discussed in detail in section 9.3. To calculate ϵ/k and σ from the saturated vapour pressure curve the following equations were solved simultaneously for ϵ/k and σ :

$$V_{m,L}(p^*,T)_{exp} = V_{m,L}(p^*,T)_{calc}.$$
 (9.16)

$$L(p^*,T) = f^V(p^*,T)$$
 (9.17)

in these equations $V_{m,L}(p^*,T)_{exp}$ is the experimental saturated liquid volume at temperature T and saturated vapour pressure p*. $V_{m,L}(p^*,T)_{calc.}$ is the molar liquid volume calculated from the MBWR-equation which represents the virial equation of state. From eq. (9.12) both fugacities $f^{-1}(p^*,T)$ and $f^{V}(p^*,T)$ of the liquid and gas phase were evaluated respectively. Using Marquardt's [7] non-linear least-squares algorithm the calculation of ϵ/k and σ was performed after suitable starting values of these parameters were chosen.

In nearly all cases the temperature at which ϵ/k and σ were determined did not correspond with that of the p,x,y-section to be calculated. Then ϵ/k and σ were calculated at some other temperatures from experimental data and the values of ϵ/k and σ at the temperature of the p,x,y-section were obtained by interpolation. After pure component parameters had been evaluated by the

methods mentioned, the mixing rules defined by eqs. (9.7) - (9.10) were being applied to obtain the pair-potential parameters of the mixture. To calculate a p,x,y-section using the virial equation of state equilibrium conditions expressed in the fugacities had to be solved:

$$f_1^V(p,T,y_1) = f_1^L(p,T,x_1)$$
 (9.18)

(9.19)

$${}_{2}^{V}(p,T,y_{2}) = f_{2}^{L}(p,T,x_{2})$$

with additional conditions:

 $x_1 + x_2 = 1$ and $y_1 + y_2 = 1$. (9.20)

From these equations the pressure and the vapour phase composition y were calculated after, at a fixed temperature, liquid compositions were chosen. Again Marquardt's [7] algorithm was applied to solve the non-linear equations iteratively.

To test the calculation procedure experimental vapour + liquid data of a number of suitable binary mixtures of simple molecules were selected from literature.

Data of the three binary mixtures nitrogen + argon, nitrogen + methane and argon + methane at 112.0 K were taken from Miller et al. [28]. Application of eqs. (9.16) and (9.17) to the experimental value of the saturated molar liquid volume and the corresponding vapour pressure at 112.0 K of each pure substance, allowed to calculate ε/k and σ of the three pure components. The experimental information of the saturation line of nitrogen, argon and methane was taken from Angus et al. [21],Angus et al. [19] and Angus et al. [8] respectively. In table 9.5 the calculated pure component parameters are collected and compared with literature values (table 9.4).

At 112.0 K the three p,x,y-sections can be calculated only chosing values of the liquid composition and then solving eqs. (9.18) - (9.20) simultaneously for the pressure and gas phase composition. In the systems nitrogen + argon, nitrogen + methane and argon + methane the binary interaction parameters ${\rm k}_{12}$ and ${\rm l}_{12}$ in eqs. (9.9) and (9.10) were set zero.

Figures 9.7, 9.8 and 9.9 show the results of the calculations for the systems nitrogen + argon, nitrogen + methane and argon + methane respectively. For these mixtures good agreement was obtained between the experimental data (open circles) and the calculated p,x,y-sections (full curves).

A quite similar calculation was carried out for the binary mixture methane + ethane at 158.15 K. The pure component parameters ϵ/k and σ were



Fig. 9.7. p.x,y-Section of nitrogen + argon. Open circles experimental data of Niller et al. [28], full curve calculated with the virial equation of state with $k_{12} = l_{12} = 0$.

Fig. 9.8. p.x,y-Section of nitrogen + methane. Open circles experimental data of Miller et al. [28], full curve calculated with the virial equation of state with $k_{12} = l_{12} = 0$.



Fig. 9.9. p.x.y-Section of argon + methane. Open circles experimental data of Miller et al. [28], full curve calculated with the virial equation of state with $k_{12} = l_{12} = 0$.

Fig. 9.10. p.x.y-Section of methane + ethane. Open circles experimental data of Wichterle et al. [29], full curve calculated with the virial equation of state with $k_{12} = 1_{12} = 0$. Table 9.5. Comparison of ϵ/k - and σ -values calculated from experimental data with literature values (table 9.4).

Substance	T/K	$\frac{\varepsilon}{k}/K$	σ/Å	$\frac{\varepsilon}{v}/K$	σ/Å
		calc.	calc.	lit.	lit.
Nitrogen	112.0	98.0	3.614	95.0	3.702
Argon	112.0	116.8	3.397	118.0	3.410
Methane	112.0	147.8	3.725	149.0	3.759
Methane	158.15	148.5	3.732	149.0	3.759
Ethane	158.15	249.0	4.232	231.0	4.339
Carbondioxide	273.15	243.4	3.678	232.0	3.682
Propane	273.15	302.6	4.694	282.0	4.748
Benzene	313.15	487.0	5.070	439.6	5.261
Cyclohexane	313.15	477.4	5.419	324.0	6.093
Nitrogen	200.0	96.9	3.708	95.0	3.702
Ethene	200.0	266.6	4.080	210.0	4.366

calculated from experimental data of the saturation line of both components [8,9] and summarized in table 9.5. Experimental data of the binary are given by Wichterle et al. [29]. With $k_{12} = 1_{12} = 0$ the result of this calculation is shown in figure 9.10. Excellent agreement between the experimental data and the calculated p,x,y-diagram was obtained.

Finally three binaries were tested for which it appeared to be necessary to apply binary interaction parameters k_{12} and l_{12} . In all cases only one p,x,y-measurement (black dots) was used at the temperature of the p,x,y-section to evaluate k_{12} and l_{12} . For the mixture carbondioxide + propane at 273.15 K pure component parameters ε/k and σ were calculated from experimental data of the saturation line of both components [22,14] (table 9.5). Experimental p,x,y-data at 273.15 K are reported by Nagahama [30]. The comparison between the experimental data and the calculated p,x,y-section is given in figure 9.11.

In the binary mixture benzene + cyclohexane a maximum pressure azeotrope occurs. Experimental p,x,y-data of this binary were taken from Inoue et al. [31]. In order to obtain ε/k and σ of both pure components again experimental data of the saturation lines of benzene and cyclohexane were used [14] and given in table 9.5. The azeotropic point in this binary was used to calculate k_{12} - and l_{12} -values. Figure 9.12 shows the comparison between the experimental



Fig. 9.11. p,x,y-Section of carbondioxide + propane. Open circles and black dots experimental data of Nagahama [30], full curve calculated with the virial equation of state with $k_{12} = 0.1552$, $1_{12} =$ -0.0866.

Fig. 9.12. p.x.y-Section of benzene + cyclohexane. Open circles and black dot experimental data of Inoue et al. [31], full curve calculated with the virial equation of state with $k_{12} = 0.0154$, $l_{12} = 0.0661$.

data and the calculated p,x,y,-section at 313.15 K. In the binary system nitrogen + ethene at 200.0 K nitrogen is supercritical. From Angus et al. [21] pV-measurements at 200.0 K were used to calculate ε/k and σ of nitrogen. The pure component parameters of ethene were obtained from measurements of the saturation line of ethene [20]. In table 9.5 the pure component parameters are collected and compared with literature values. The p,x,y-data of this binary were taken from Grausø et al. [32]. Figure 9.13 shows the result.



Fig. 9.13. p.x.y-Section of nitrogen + ethene. Open circles and black dots experimental data of Grausø et al. [32], full curve calculated with the virial equation of state with $k_{12} = 0.0608, 1_{12} = -0.0747$.

In the system nitrogen + ethene the quality of the representation of the experimental p,x,y-data is largely influenced by the choice of the p,x,y-data from which k_{12} and l_{12} were evaluated. The same observation holds for the system cyclohexane + benzene.

In all it may be concluded that application of binary interaction parameters allows to represent experimental vapour + liquid equilibrium data of mixtures with a more or less non-ideal behaviour.

9.5. Calculation of other thermodynamic properties

Besides the calculations using the virial equation of state for pure fluids (section 9.3) as well as for the phase behaviour of binary mixtures of simple



Fig. 9.14. $\Delta_{vap} H_m$ of methane. Open circles experimental data of Angus et al. [8], full curve calculated.



Fig. 9.15. $\Delta_{vap} S_m$ of methane. Open circles experimental data of Angus et al. [8], full curve calculated.



Fig. 9.16. ${}^{}_{\rm Vap}{}^{H}_{\rm m}$ of nitrogen. Open circles experimental data of Angus et al. [21], full curve calculated.



Fig. 9.17. $\Delta_{vap} {}^{S}_{m}$ of nitrogen. Open circles experimental data of Angus et al. [21], full curve calculated.

Table 9.6. Calculated enthalpy and entropy of vaporization of methane with $\varepsilon/k \approx 144.5 \text{ K}$ and $\sigma = 3.702 \text{ \AA}$ (table 9.4).

T/K	T*	ρ <u>*</u>	ρ *	∆ _{vap} H*	∆ _{vap} S*	∆ _{vap} H _m Jmol ⁻¹	∆ _{vap} S _m JK ⁻¹ mol ⁻¹
130.0	0.8997	0.7509	0.0114	4.4857	4.6142	7272.3	57.54
140.0	0.9689	0.7183	0.0194	3.9470	4.0580	6891.3	50.61
150.0	1.0381	0.6824	0.0311	3.4485	3.5285	6450.9	44.00
160.0	1.1073	0.6411	0.0484	2.9673	3.0050	5920.9	37.48
170.0	1.1765	0.5913	0.0744	2.4662	2.4544	5228.5	30.61
180.0	1.2457	0.5257	0.1171	1.8727	1.8136	4203.7	22.62
182.0	1.2595	0.5090	0.1295	1.7274	1.6608	3920.7	20.71
184.0	1.2734	0.4900	0.1442	1.5641	1.4918	3589.2	18.60
186.0	1.2872	0.4674	0.1626	1.3716	1.2955	3181.6	16.16
188.0	1.3010	0.4379	0.1879	1.1208	1.0452	2627.7	13.03
190.0	1.3149	0.3838	0.2370	0.6586	0.6010	1560.6	7.50

Table 9.7. Calculated enthalpy and entropy of vaporization of nitrogen with ε/k = 96.7 K and σ = 3.586 Å (table 9.4).

T/K	T*	ρ <u>*</u>	ρ [*]	∆ _{vap} H*	∆ _{vap} S*	∆ _{vap} H _m Jmol ⁻¹	∆ _{vap} S _m JK ⁻¹ mol ⁻¹
70.0	0.7239	0.8338	0.0019	6.0326	6.2968	5266.2	78.53
80.0	0.8273	0.7896	0.0060	5.0668	5.2776	5055.1	65.82
90.0	0.9307	0.7398	0.0150	4.2242	4.3566	4741.2	54.33
100.0	1.0341	0.6829	0.0317	3.4684	3.5197	4325.4	43.89
110.0	1.1375	0.6149	0.0619	2.7267	2.7014	3740.6	33.69
115.0	1.1892	0.5733	0.0862	2.3220	2.2626	3330.1	28.22
120.0	1.2410	0.5207	0.1234	1.8390	1.7506	2752.2	21.83
122.0	1.2616	0.4930	0.1457	1.5921	1.4963	2422.4	18.66
124.0	1.2823	0.4555	0.1782	1.2621	1.1652	1951.8	14.53
126.0	1.3030	0.3701	0.2590	0.5061	0.4512	795.3	5.63

molecules (section 9.4) the introduced calculation technique in this work also allows to derive in principle all other macroscopic thermodynamic properties. As an example, in this section the enthalpy and entropy of vaporization of methane and nitrogen will be calculated and compared with experimental values from literature.

In order to calculate the enthalpy of vaporization of a pure fluid, the following calculation scheme was applied:

- a temperature T of the vapour + liquid equilibrium was selected;
- at the chosen temperature T molar volumes $V_{m,\,L}$ and $V_{m,\,V}$ of both coexisting phases were taken from literature;
- from table 9.4 the calculated overall values of ε/k and σ were taken;
- then a transformation into the dimensionless variables T^{\ast} and ρ^{\ast} was performed:

$$T^* = kT/\epsilon; \qquad \rho_L^* = N\sigma^3/V_{m,L}; \qquad \rho_V^* = N\sigma^3/V_{m,V}$$

- using a spline interpolation technique the following dimensionless enthalpies were calculated from table 8.6: H_L^{τ} (ρ_L^{*}, T^*) and H_V^{*} (ρ_V^{*}, T^*);
- the dimensionless enthalpy of vaporization is obtained from;

$$\Delta_{vap}^{H*} = H_{V}^{*} (\rho_{V}^{*}, T^{*}) - H_{L}^{*} (\rho_{L}^{*}, T^{*})$$
(9.21)

- application of H* = 2H/3NkT results in the enthalpy of vaporization:

$$\Delta_{\text{vap}}^{\text{H}} = \frac{3NkT}{2} \Delta_{\text{vap}}^{\text{H}*}$$
(9.22)

A quite similar calculation scheme holds for the evaluation of the entropy of vaporization $\Delta_{\rm wan} S_{\rm m}$; however, then eq. (9.22) has to be replaced by:

$$v_{ap}S_{m}^{s} = \frac{3Nk}{2} \Delta_{vap}S^{*}$$
(9.23)

In table 9.6 the results for methane are summarized. Figures 9.14 and 9.15 compare the experimental values (open circles) of $\Delta_{va} P_{m}$ and $\Delta_{va} S_{m}$ of methane [8] with the calculated values of table 9.6 (full curves).

Similarly table 9.7 as well as figures 9.16 and 9.17 show the results for nitrogen.

9.6. Discussion

In this chapter it was shown how the non-analytical statistical mechanical virial equation of state could be represented by a modified Benedict-Webb-Rubin (MBWR) equation of state. As the variables of the MBWR equation of state are expressed in dimensionless variables ρ^* , T* and P*, which are

related to the Lennard-Jones (12,6) pair-potential parameters ϵ/k and σ , this equation is independent of the substance considered. In the subsequent sections of this chapter it also appeared that the two-parameter (ϵ/k and σ) character of the virial equation of state was retained.

It was found that the MBWR equation is flexible enough to represent the data collections $Z_v = Z_v (\rho^*, T^*)$ and $Z_c = Z_c (\rho^*, T^*)$ accurately in the whole temperature and density region. A comparison of both overall standard deviations (0.0040 and 0.0026 respectively) shows that the compressibility equation of state could be fitted somewhat better to the MBWR equation. However, both fits are significantly better than the fit of the $Z = Z (\rho^*, T^*)$ data obtained from molecular dynamics (MD) [4]. A reason for this difference in representation will undoubtedly be caused by the fact that Nicolas et al. [4] used MD-data from several different sources and moreover some scattering in the MD-data was observed. In section 9.3 it was pointed out that - in comparison with the compressibility equation of state - the virial equation gives somewhat better results in representing the pVT-behaviour of methane and ethane. This is in contradiction with the conclusions of Van der Kooi [33], who found in general better results for the compressibility equation of state. The contrary conclusion may be due to the fact that the accessible dimensionless temperature (T*) and density (ρ^*) regions in this investigation were much more larger than in the work of Van der Kooi [33]. Moreover in this work also pVT-data of the two phase region liquid + vapour have been used. For these two reasons different conclusions had to be expected.

From table 9.4 it can be concluded that in general the pair-potential parameters ε/k and σ calculated from experimental pVT-data directly are in good agreement with literature values. Strictly the chosen Lennard-Jones (12,6) pair-potential in this study only allows to calculate the equation of state of monoatomatic fluids. However, it was found that even molecules that differ largely from the chosen model can be represented very well with reasonable realistic values of the pair-potential parameters ε/k and σ . This means that the virial equation of state is flexible in its applicability.

The thermodynamic treatment of mixtures is more or less straightforward. In this study a Van der Waals one fluid model, defined by eqs. (9.7) and (9.8) was preferred. In spite of the fact that size-ordering effects are important in mixtures of molecules with different sizes, it is not quite clear how the applied mixing rules account for these effects.

In order to calculate equilibria of fluid phases in mixtures again

equilibrium conditions were defined in terms of the fugacity. For that purpose from the MBWR equation of state an analytical expression for the fugacity of the i-th component in a mixture was derived. With the available expression of the fugacity it was possible to calculate fluid phase equilibria using Lennard-Jones (12,6) pair-potential parameters of the pure components. However, for accurate representations it is obvious that binary parameters are still necessary. This was shown in section 9.4.3.

In section 9.4.4. it was shown that also other thermodynamic properties such as enthalpies, entropies, etc. can easily be derived applying a simple calculation technique.

A disadvantage of the proposed calculation technique in this study is that for all types of calculations more computer effort is required than with simple analytical equations of state. However, as this calculation technique was based on sound physical principles, it may be expected that this disadvantage will be compensated by the predictive ability of the proposed method. An example of the improved predictive ability of these types of equations of state was already given by Van der Kooi [33].

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10. CONCLUSIONS

From the experimental results as well as the thermodynamic description of the phase equilibria determined in the binary system ethane + n-eicosane (chapters 2, 3, 4, 5 and 6) the following major conclusions can be drawn:

- the experimental results obtained (chapter 4) are an useful supplement to the rather scarce basic data of binaries of ethane and higher nalkanes available (chapter 2);
- 2. in connection with similar experimental data of other binaries of ethane and higher n-alkanes [1,2,3,4,5] as well as those of binaries of methane and higher n-alkanes [6,7] the fundamental understanding of a systematic change in phase behaviour of binaries of n-alkanes has been extended and predictions are now possible at least qualitatively (chapter 2);
- a disadvantage of the Cailletet apparatus used (chapter 3) is that in the system ethane + n-eicosane no dew-points could be determined experimentally, i.e. no vapour phase compositions could be measured;
- 4. as accurate parameters for the SRK and PR equations of state (T_c , p_c and ω) are generally not available for higher n-alkanes, these equations should not be used in their original form (chapter 5 and 6) to calculate phase equilibria for mixtures containing these components;
- 5. to describe vapour + liquid equilibria in the binary system ethane + neicosane using simple cubic equations of state (chapter 5 and 6) with an acceptable accuracy two binary interaction parameters $(k_{12} \text{ and } 1_{12})$ are required;
- 6. in binary mixtures of a volatile and a non-volatile n-alkane the binary parameter l_{12} is more important than k_{12} to describe vapour + liquid equilibria of these binaries using a simple cubic equation of state (chapter 6).

With respect to the development and the applicability of simple equations of state - nearly always cubic - it is not understandable at all that at present the incorrect Van der Waals free-volume term $(V_m - b)^{-1}$ is still retained in all these equations. Already since many years several authors [8,9,10] advise to replace this incorrect free-volume term by an expression which describes

the hard-sphere fluid more adequately. Retaining of the Van der Waals freevolume term causes the second term in these equations of state not only to account for the effect of attractive forces but also to compensate for the incorrect behaviour of the free-volume term.

De Santis et al. [11] replaced the Van der Waals free-volume term in the RK equation of state by the expression for hard-spheres of Carnahan-Starling [12]. It was shown that in calculating vapour + liquid equilibria of nonpolar mixtures at least comparable results with the original RK equation of state were obtained. However, it should be noted that De Santis [11] probably did not use the most suitable attractive part in combination with the Carnahan-Starling repulsive part.

Finally the mixing rules applied for the current equations of state (chapters 5 and 6) are not correct, especially in dilute mixtures of molecules which differ largely in size. Prausnitz [13] pointed out that density dependent mixing rules are required. In that respect Mansoori [14] recently derived mixing rules for cubic equations of state from statistical mechanical principles. However, particular results are not known at this time.

With respect to chapters 7, 8 and 9 also some concluding remarks can be given:

- the combination of the integral equation method with perturbation theory (chapter 8) allows to calculate radial distribution functions in the whole fluid phase region;
- 2. in order to obtain thermodynamically consistent results with the virial and compressibility equations of state as well as with results from molecular dynamics and/or Monte Carlo calculations, the parameter a in the parametric approximation (eq. 8.3) should be taken temperature and density dependent;
- 3. the separation parameter α , defined by eq. (8.15), should also be taken density dependent [15];
- 4. the dimensionless MBWR equation of state, defined by eq. (9.1), is capable to represent the non-analytical statistical mechanical virial equation of state in the whole fluid phase region;
- 5. in spite of the fact that the physical model used is only valid for monoatomic fluids, the pair-potential parameters ε/k and σ show such a flexibility that also simple polyatomic fluids, e.g. such as methane and ethane (chapter 9), can be represented rather accurately;
- 6. the pair-potential parameters ϵ/k and σ calculated from experimental

pVT-data are in good agreement with those obtained from other sources (chapter 9);

- 7. the equation derived for the fugacity (eq. (9.12)) allowed to calculate the phase behaviour of mixtures with the pair-potential parameters ϵ/k and σ of the pure substances as input parameters;
- 8. using the pair-potential parameters ϵ/k and σ as input parameters other thermodynamic properties are readily obtained applying the introduced calculation method (chapter 9).

The results obtained in chapter 8 and 9 look promising with respect to the practical applicability in chemical engineering. In principle all required thermodynamic properties can readily be obtained by applying the proposed calculation technique. As shown in this work (chapter 8 and 9), the introduced method is quite suitable for pure substances or mixtures of simple molecules.

In order to describe the phase behaviour and/or other thermodynamic properties of systems in which the molecules of the components differ largely in size and/or in mutual interaction, theories of molecular fluids [16] have to be applied. In that case the basic statistical mechanical calculations will become more complex and will consequently require much more computer effort. However, these calculations have to be performed only once.

The main idea of this statement is that models with more physical background will always increase the ability to predict thermodynamic properties outside that region used to obtain system-specific parameters. With the availability of more and cheaper computer power the introduction of equations of state based on sound physical principles should be encouraged and then even the binaires investigated in this work can be treated.

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The primary objectives of this study were:

- the experimental determination of the phase behaviour of the binary system ethane + n-eicosane and the description of the results using empirical equations of state;
- the calculation of the thermodynamic properties of rather simple fluids and their mixtures using theories based on elementary statistical mechanical principles and its application in practice.

The first objective is described in chapters 2, 3, 4, 5 and 6. In chapter 2 the classification of the binary ethane + n-eicosane among other related ethane binaries is discussed and it is pointed out that in the system ethane + n-eicosane a three phase equilibrium liquid + liquid + vapour $(L_1 + L_2 + V)$ with a lower and upper critical endpoint - LCST and UCST respectively - is present.

Chapter 3 gives a brief description of the experimental equipment used and in chapter 4 the experimental results are reported. In the temperature range from 260 K up to 450 K and pressures up to 18 MPa two phase boundaries L + V and up to 310 K also $\rm S_B$ + L (index B = n-eicosane) were determined experimentally. In addition the three phase equilibria $\rm S_B$ + L + V and $\rm L_1$ + $\rm L_2$ + V were measured. In addition the volume-behaviour of liquid mixtures of ethane + n-eicosane was investigated experimentally.

After discussing cubic equations of state in chapter 5, three of them - the Redlich-Kwong, the Soave-Redlich-Kwong and the Peng-Robinson equations of state - were used in chapter 6 to represent the vapour + liquid equilibrium data determined in this work. In order to obtain an acceptable accuracy two binary parameters k_{12} and l_{12} were necessary. It was found that the binary parameter l_{12} is more important than k_{12} for mixtures such as ethane + n-eicosane. Using a suitable expression for the fugacity of solid n-eicosane and application of the SRK equation of state for both fluid phases allowed to describe the three phase equilibrium $S_p + L + V$.

The second objective is discussed in chapters 7, 8 and 9. In chapter 7 fundamental statistical mechanical principles are introduced. Then in chapter 8 the radial distribution function as a function of temperature and density is evaluated from a parametric integral equation. The Lennard-Jones (12,6) pair-potential was chosen to represent the intermolecular interaction. Solutions of this parametric integral equation in the non-convergent region were achieved using perturbation theory in combination with the integral equation method. The collection of radial distribution functions obtained allows to calculate several macroscopic thermodynamic properties of a fluid from the low density gas state up to the high density liquid state including the two phase region.

In chapter 9 a suitable calculation technique is developed which allows to apply the non-analytical statistical mechanical virial equation of state for practical purposes. The pVT-behaviour of simple fluids is described with the Lennard-Jones (12,6) pair-potential parameters as effective adjustable parameters. It is shown that the calculated parameters are in excellent agreement with those obtained in other ways such as from second virial coefficients. Using the virial equation of state vapour + liquid equilibria of mixtures of simple molecules could be calculated. The results obtained in chapter 8 and 9 look promising with respect to the practical applicability in chemical engineering. In principle all required thermodynamic properties can readily be obtained by applying the proposed calculation technique.

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SAMENVATTING

De primaire doelstellingen van deze studie kunnen als volgt worden samengevat:

- de experimentele bepaling van het fasegedrag van het systeem ethaan + neicosaan alsmede de beschrijving van de gemeten evenwichten met behulp van empirische toestandsvergelijkingen;
- de berekening van thermodynamische eigenschappen van fluida bestaande uit eenvoudige moleculen en hun mengsels met behulp van elementaire statistisch mechanische principes alsmede een onderzoek naar praktische toepasbaarheid ervan.

De eerste doelstelling wordt beschreven in de hoofdstukken 2, 3, 4, 5 en 6. In hoofdstuk 2 wordt de relatie van het binaire systeem ethaan + n-eicosaan bepaald tot andere overeenkomstige binaire ethaansystemen. Daarbij werd vastgesteld dat in het systeem ethaan + n-eicosaan een driefasenevenweiht vloeistof + vloeistof + damp ($L_1 + L_2 + V$) met een onder- en bovenkritisch eindpunt (respectievelijk aangeduid door LCST en UCST) aanwezig is.

Hoofdstuk 3 geeft een beknopte beschrijving van de gebruikte meetapparatuur en in hoofdstuk 4 zijn de meetresultaten ondergebracht. In een temperatuurgebied van 260 K tot 450 K en drukken tot 18 MPa zijn tweefasenbegrenzingen L + V en tot 310 K ook S_B + L (index B = n-eicosaan) gemeten. Ook de driefasenevenwichten S_B + L + V en L₁ + L₂ + V zijn experimenteel bepaald. Vervolgens is het volumegedrag van vloeibare mengsels van ethaan + n-eicosaan gemeten.

In hoofdstuk 5 worden kubische toestandsvergelijkingen besproken en in hoofdstuk 6 worden drie van dergelijke vergelijkingen - te weten de Redlich-Kwong (RK), de Soave-Redlich-Kwong (SRK) en de Peng-Robinson (PR) - toegepast ter beschrijving van vloeistof + damp evenwichten die in deze studie zijn gemeten. Om deze evenwichten met een aanvaardbare nauwkeurigheid te kunnen weergeven blijkt een tweetal binaire parameters k_{12} en l_{12} onontbeerlijk. Vast kwam te staan dat in mengsels als ethaan + n-eicosaan de invloed van de binaire parameter l_{12} belangrijker is dan die van k_{12} . Met behulp van een geschikte uitdrukking voor de fugaciteit van vast n-eicosaan en toepassing van de SRK toestandsvergelijking voor de beide fluide fasen kon het driefasenevenwicht S_p + L + V worden beschreven.

De tweede doelstelling wordt behandeld in de hoofdstukken 7, 8 en 9. In

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hoofdstuk 7 worden fundamentele statistisch mechanische principes besproken. Vervolgens wordt in hoofdstuk 8 uit een integraalvergelijking de radiale distributie functie als functie van temperatuur en dichtheid berekend. De intermoleculaire wisselwerking wordt daarbij beschreven door de Lennard-Jones (12,6) potentiaal. Met toepassing van storingsrekening in combinatie met de integraalvergelijking bleek het mogelijk de integraalvergelijking ook op te lossen in het niet-convergente gebied. De verzameling radiale distributie functies werd gebruikt om een aantal macroscopische thermodynamische eigenschappen van een fluidum, variërend van de ideale gastoestand tot de hoge dichtheid vloeistoftoestand met inbegrip van het tweefasengebied, te berekenen.

In hoofdstuk 9 wordt de ontwikkeling van een geschikte rekentechniek beschreven waardoor het mogelijk wordt de niet-analytische statistisch mechanische viriaal toestandsvergelijking in de praktijk toe te passen. Het pVTgedrag van eenvoudige fluida wordt beschreven waarbij de Lennard-Jones (12,6) potentiaal parameters fungeren als effectieve aanpasbare parameters. Daarbij blijken deze berekende parameters uitstekend overeen te stemmen met de overeenkomstige waarden die langs een andere weg zoals via tweede viriaal coëfficiënten zijn berekend. Verder is de viriaal toestandsvergelijking ook gebruikt om vloeistof + damp evenwichten van binaire mengsels bestaande uit eenvoudige moleculen te beschrijven. De resultaten zoals deze in de hoofdstukken 8 en 9 zijn beschreven lijken veelbelovend met betrekking tot de praktische toepasbaarheid. Met behulp van de voorgestelde rekentechniek laten alle thermodynamische eigenschappen zich eenvoudig berekenen.

STELLINGEN

 De constatering van Rowlinson dat in binaire systemen van ethaan en hogere n-alkanen voor het eerst met n-nonadecaan ontmenging in de vloeistoffase optreedt, is onjuist. Reeds in het binaire systeem ethaan + n-octadecaan treedt over een temperatuurtraject van 0.2 K ontmenging op. J.S. Rowlinson and F.L. Swinton, Liquids and Liquid Mixtures, third edition, 1982, London.

J. Specovius, N.A. Leiva, R.L. Scott and C.M. Knobler, J. Phys. Chem., 85 (1981) 2313.

2. De bewering van Rowlinson dat in binaire systemen van ethaan en hogere nalkanen geen ontmenging in de vloeistoffase zal optreden indien de tripelpuntstemperatuur van het hogere n-alkaan boven de kritische temperatuur van ethaan ligt, wordt door recente experimentele resultaten tegengesproken.

J.S. Rowlinson and F.L. Swinton, Liquids and Liquid Mixtures, third edition, 1982, London. Dit proefschrift, hoofdstuk 2.

- 3. In tegenstelling tot de meeste empirische en semi-empirische toestandsvergelijkingen geeft de statistisch mechanische viriaal toestandsvergelijking gaande naar hogere dichtheden een daling van de soortelijke warmte. Dit laatste is in overeenstemming met de fysische realiteit. Dit proefschrift, hoofdstuk 5 en 8.
- 4. De door Perram voorgestelde afleiding van een numerieke methode ter berekening van de radiale distributiefunctie voor een systeem van harde bollen is erg elegant, maar leidt wel tot een onjuist eindresultaat. J.W. Perram, Mol. Phys., 30 (1975) 1505.
- 5. De keuze van Gmehling en Onken om bij de berekening van parameters uit vergelijkingen voor activiteitscoëfficiënten de gemodificeerde simplexmethode van Nelder en Mead te gebruiken wijst op onzorgvuldigheid. J. Gmehling and U. Onken, Vapor-Liquid Equilibrium Data Collection, vol. 1, part 1, 1977, Frankfurt.

6. De bewering van Van de Kraats dat toestandsvergelijkingen gebaseerd op de vergelijking van Carnahan en Starling niet leiden tot verbeterde thermodynamische beschrijvingen vergeleken met kubische toestandsvergelijkingen is slecht onderbouwd.

E.J. van de Kraats, Proceedings of the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Industry, 1980, Berlin (West).

- Het is verwonderlijk dat bij de berekening van parameters uit lineaire regressiemodellen slechts zelden rekening wordt gehouden met het feit dat in beide coördinaten experimentele fouten aanwezig kunnen zijn.
 York, Can. J. Phys., 44 (1966) 1079.
- Het verdient aanbeveling om in publicaties DTA- en DSC-figuren op eenduiduige wijze weer te geven; d.w.z. zodanig dat de pieken van exotherme effecten omhoog en die van endotherme effecten omlaag wijzen.
 C. Lombardi. For Better Thermal Analysis, 1980. Rome. Thermochimica Acta, 95 (2) (1985).
- 9. De berekening van de vloeistofbegrenzing van het tweefasengebied vast + vloeistof in het systeem neon + xenon, zoals door Van den Bergh et al. wordt voorgesteld, is fysisch onjuist. L.C. van den Bergh, J.A. Schouten and N.J. Trappeniers, Physica, 132A, (1985) 549.
- De reactiesnelheidsconstanten, zoals bepaald door Röbschläger en Christoffel, voor een complex eerste orde reactiesysteem zijn thermodynamisch inconsistent.
 K.H. Röbschläger and Z.G. Christoffel, Can. J. Chem. Eng., 58 (1980) 517.
- De nog steeds toenemende overbevolking van honden in Nederland werkt kortzichtigheid van haar bewoners in de hand.

C.J. Peters