

## Chapter 2 Critical Phenomena and Fluid Theories

The critical state provides a valuable insight into the general phase behaviour of a fluid and is closely linked with the nature and strength of intermolecular interactions. In this chapter, we discuss the pure component critical point, critical lines of binary mixtures, and the criteria for the critical state for multicomponent mixtures. We also briefly address both classical and non-classical concepts of critical behaviour. Calculation procedures and theory of fluids will be given.

### 2.1 Critical Point of Pure Components

The theory of critical phenomena was developed from the nineteenth century, and it gradually was understood clearly in the middle of the twentieth century. Within the

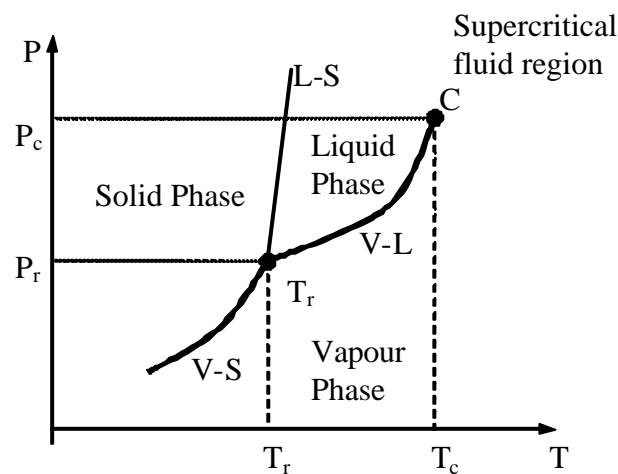


Figure 2.1 Pure component phase diagram

thermodynamic approach, a phase transition is considered as an abrupt change of one phase into another by changing parameters of the state such as temperature, volume and pressure. Usually a phase can have three thermodynamic states—stable, metastable and unstable. In phase equilibrium, for a given set of fixed parameters there always exists a thermodynamic potential having a minimum in the states. There

is an important point which is called critical point, at which the coexisting phases become indistinguishable. Figure 2.1 illustrates the phase diagram of a pure component in the p-T projection. Vapour-solid, vapour-liquid and liquid-solid two phase lines separate the diagram into three fields—vapour, liquid and solid phases. The point that is met by three lines is the triple point. The point  $c$  is the critical point,  $T_c$ ,  $V_c$  and  $p_c$  respectively present critical temperature, volume and pressure, and the area of  $T > T_c$  is the supercritical fluid region. At the critical point of a pure fluid,

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \quad (2.1)$$

This conclusion is very useful in that it allows the evaluation of two parameters of an equation of state in term of critical properties. In contrast, the critical conditions for binary and multicomponent mixtures are much more complicated.

## 2.2 Critical Phenomena of Binary Mixtures

For binary and other multicomponent fluids like in the case of pure substances, the critical states are identified as the condition at which the properties of different coexisting phases become indistinguishable. The existence of a second component can generate equilibria between different liquid phases in addition to vapour-liquid equilibria. The addition of a second component also generates a variety of critical phenomena. Figure 2.2, illustrates the simplest phase diagram of binary mixtures. The line 1 ending at  $c_1$  is the vapour-liquid coexistence curve of pure component 1, and the line 2 ending at  $c_2$  is vapour-liquid coexistence curve of pure component 2. The lines with  $V_{x1x2}$  and  $L_{x1x2}$  are the bubble point and dew point of a mixture with mole

fraction of component 2,  $x_2$ .  $x_1$  is the mole fraction of component 1,  $x_1 = 1 - x_2$ . The points  $c_1$ ,  $c_2$  and  $c_{x_1x_2}$  indicate critical points of pure component 1, pure component 2 and a mixture with mole fraction  $x_1$  and  $x_2$ .  $x_1 + x_2 = 1$ , and  $x_1, x_2 \in [0,1]$ , respectively. If  $x_2$  is equal to 0,  $c_{x_1x_2}$  is  $c_1$  that is critical point of component 1. If  $x_2$  equal to 1,  $c_{x_1x_2}$  is  $c_2$  that is critical point of component 2. While  $x_2$  changes in the range  $\in [0,1]$ , the critical points  $c_{x_1x_2}$  form a binary critical line.

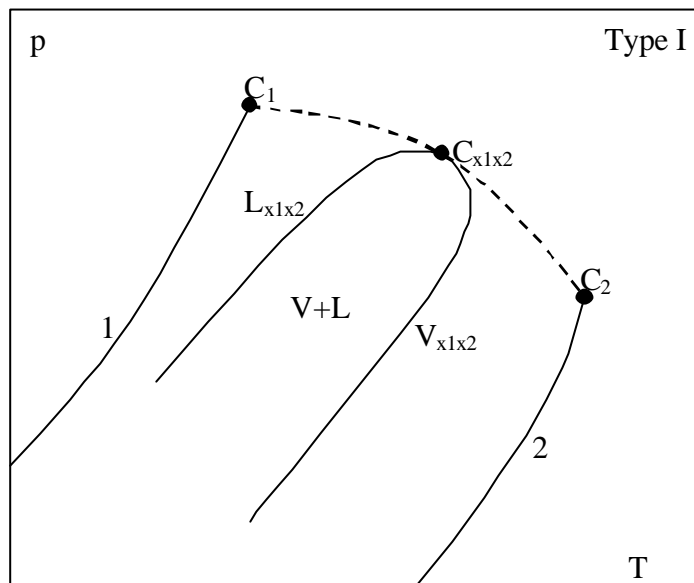


Figure 2.2. Pressure-temperature projection showing vapour-liquid critical line of a simple binary mixture binary mixture (type I).

The most important illustration of the role of the critical state is the phase behaviour classification proposed by van Konynenburg and Scott (1980). There are six main types of critical curves in the pressure-temperature projection (Figure 2.3). These six main types of critical diagrams are listed as following:

Type I. A vapour-liquid critical line connects the critical points of the two pure components.

Type II. Critical curve of type I with an additional liquid-liquid critical line, which start from upper critical end point (UCEP) and extends rapidly to high pressures.

Type III. There is a vapour-liquid critical line starting from one pure component critical point which extends to an UCEP at the end of a three phase liquid-liquid-vapour line. Another vapour-liquid critical line starts from the critical point of the other pure component connecting with a liquid-liquid critical line to very high pressures.

Type IV. There are two distinct vapour-liquid critical lines starting from either pure component critical point. A three-phase vapour-liquid-liquid line connects the other end of the lines, the two end points respectively represent an UCEP and a lower critical end point (LCEP). There is also a liquid-liquid critical line at low temperatures, which ends at another UCEP.

Type V. The critical curve is similar to type IV but without the low temperature liquid-liquid critical line.

Type VI. Critical curve of type I with a liquid-liquid critical line that is observed to rise and fall between a LCEP and an UCEP located at either end of a three-phase line.

Recently, some new type of critical curves - closed loop phase behaviour (van Pelt et al., 1991; Yelash and Kraska, 1998; Wang et al., 2000) have enriched the classification of phase behaviour (Figure 2.3),

Type VII. This phase behaviour has the same liquid-liquid immiscibility critical line as type VI phase behaviour, but the liquid-vapour critical line is composed of two sections, ending at UCEP and LCEP at either end of a three-phase liquid-liquid-vapour line.

Type VIII. Critical curve of type III with an additional liquid-liquid critical line, which starts from lower critical end point (LCEP) to high pressures (van Pelt et al., 1991).

Type Vm. The critical line is interrupted by a three-phase line, and exhibits a pressure maximum and a pressure minimum.

In some cases (eg., type I and type II), sub-classes critical curves depicted in figure 2.3 can be identified. These sub-classes depend on the positions of the critical locus. The characteristics of the phase behaviour classification are discussed in greater detail in Chapter 4.

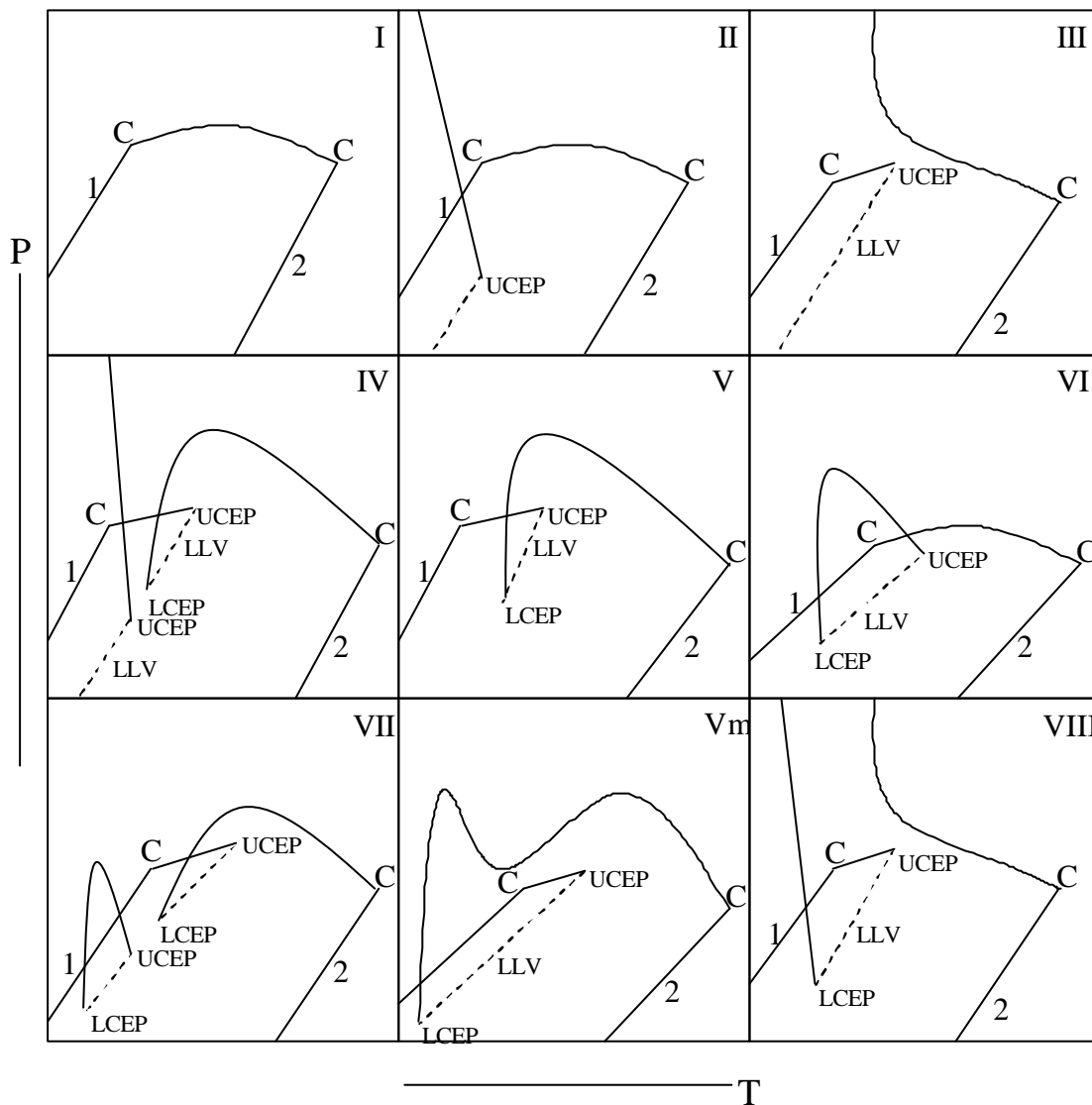


Figure 2.3 Phase behaviour classification scheme for binary mixtures. Type I, II, III, IV, V, VI and VIII behaviour is observed experimentally whereas behaviour of Type Vm and VII has only been reported in the literature from calculations. Critical equilibria of the binary mixtures (—), the critical points of the pure components (C), the vapour pressure curves (1, 2) and the three-phase liquid-liquid-vapour (- - -) equilibria are illustrated.

### 2.3 Criteria for the Critical State

The classical critical conditions of an  $m$ -component fluid mixture are due to Gibbs (Gibbs, 1928; Bumstead and van Name, 1906; Donnan and Hass, 1936). A critical transition is observed when the boundary between stable/metastable states (spinodal

curve) and the coexistence boundary between different stable phases (binodal curve) meet (Sadus, 1994). The critical transition can be geometrically interpreted as a point of inflection of the chemical potential with respect to composition. Therefore, in critical curves, the first and second derivatives of chemical potential with respect to composition equal zero, and a higher derivative respect to composition must be positive to obtain a stable critical transition. Gibbs (1928) showed (Donnan and Hass, 1936) that any thermodynamic function could be transformed from these critical criteria. Other workers (Beegle et al., 1974; Heidemann, 1975; Reid and Beegle, 1977; Modell, 1977; Sadus, 1992) have extensively described the nature of this transformation.

The critical properties of a m-component fluid can be obtained by determining the temperature, volume and composition which satisfy the following conditions,

$$W = \begin{vmatrix} -\left(\frac{\partial^2 A}{\partial V^2}\right)_T & -\left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \cdots & -\left(\frac{\partial^2 A}{\partial x_{m-1} \partial V}\right)_T \\ \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,V} & \cdots & \left(\frac{\partial^2 A}{\partial x_1 \partial x_{m-1}}\right)_{T,V} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \left(\frac{\partial^2 A}{\partial x_{m-1} \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_{m-1} \partial x_1}\right)_{T,V} & \cdots & \left(\frac{\partial^2 A}{\partial x_{m-1}^2}\right)_{T,V} \end{vmatrix} = 0 \quad (2.2)$$

$$X = \begin{vmatrix} \left(\frac{\partial W}{\partial V}\right)_T & \left(\frac{\partial W}{\partial x_1}\right)_{T,V} & \cdots & \left(\frac{\partial W}{\partial x_{m-1}}\right)_{T,V} \\ \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,V} & \cdots & \left(\frac{\partial^2 A}{\partial x_1 \partial x_{m-1}}\right)_{T,V} \\ \cdot & \cdot & \cdot & \cdot \\ \left(\frac{\partial^2 A}{\partial x_{m-1} \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1 \partial x_{m-1}}\right)_{T,V} & \cdots & \left(\frac{\partial^2 A}{\partial x_{m-1}^2}\right)_{T,V} \end{vmatrix} = 0 \quad (2.3)$$

and

$$Y = \begin{vmatrix} \left(\frac{\partial X}{\partial V}\right)_T & \left(\frac{\partial X}{\partial x_1}\right)_{T,V} & \cdots & \left(\frac{\partial^2 X}{\partial x_{m-1}}\right)_{T,V} \\ \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,V} & \cdots & \left(\frac{\partial^2 A}{\partial x_1 \partial x_{m-1}}\right)_{T,V} \\ \cdot & \cdot & \cdot & \cdot \\ \left(\frac{\partial^2 A}{\partial x_{m-1} \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1 \partial x_2}\right)_{T,V} & \cdots & \left(\frac{\partial^2 A}{\partial x_{m-1}^2}\right)_{T,V} \end{vmatrix} > 0 \quad (2.4)$$

where  $A$ ,  $T$ ,  $V$  and  $x$  denote the molar Helmholtz function, temperature, molar volume and mole fraction, respectively. Equations 2.2 to 2.4 represent the simplest form of the classical critical criteria in terms of the Helmholtz function, but they are not unique, Sadus (1992a) and Modell (1977) discuss this aspect in greater detail.

When  $m = 1$ , equations 2.2 to 2.4 are well known as conditions for a critical point of a one component fluid, and can be simplified to equation 2.1. If  $m$  equals 2, the equations 2.2 to 2.4 can be simplified to:

$$W = \begin{vmatrix} -\left(\frac{\partial^2 A}{\partial V^2}\right)_T & -\left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T \\ \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,V} \end{vmatrix} = 0 \quad (2.5)$$

$$X = \begin{vmatrix} \left(\frac{\partial W}{\partial V}\right)_T & \left(\frac{\partial W}{\partial x_1}\right)_{T,V} \\ \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,V} \end{vmatrix} = 0 \quad (2.6)$$

and

$$Y = \begin{vmatrix} \left(\frac{\partial X}{\partial V}\right)_T & \left(\frac{\partial X}{\partial x_1}\right)_{T,V} \\ \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,V} \end{vmatrix} > 0 \quad (2.7)$$

Spear et al. (1969), Peng and Robinson (1977), Hicks and Young (1977), Sadus et al. (1988) and Wang et al. (2000) calculated critical curves of binary mixtures using equations 2.5 to 2.7. There are relatively few examples of ternary and other multicomponent critical point calculations (Peng and Robinson, 1977; Spear et al., 1971; Sadus and Young, 1987, 1988; Wisniak, 1983, 1984a, b; Sadus, 1992a, b and Wei, 1998).

Calculations for binary mixtures are commonly reported to satisfy equations 2.5 and 2.6, but condition 2.7 is less frequently applied (Sadus 1994). The condition 2.7 is important to guarantee the material stability of the calculated critical point, because the solutions are yielded by equations 2.5 and 2.6 may represent unstable situations which cannot be observed experimentally. Omitting condition 2.7 is not usually a serious oversight for vapour-liquid critical properties because physically unrealistic

results can usually be detected by “inspection”, for example, by observing an anomalous trend in the predicted critical volume. Similarly, there are ample experimental precedents for binary mixtures to confidently identify physically erroneous solutions of equations 2.5 and 2.6. In addition, a critical point must satisfy the conditions for mechanical stability (Sadus, 1992a):

$$\left(\frac{\partial p}{\partial V}\right)_T < 0$$

$$\left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,v} \left(\frac{\partial^2 A}{\partial V^2}\right)_T - \left(\frac{\partial^2 A}{\partial x_1 \partial V}\right)_{T,v}^2 > 0 \quad (2.8)$$

$$\left(\frac{\partial^2 A}{\partial x_1^2}\right)_{T,v} > 0$$

## 2.4 Nonclassical Critical Phenomena

Critical behaviour is called ‘classical’ if the Helmholtz function can be expanded at the critical point in terms of  $dV = V - V_c$  and  $dT = T - T_c$ . Where  $V$  is the volume, and  $T$  is the temperature of the fluid. The subscript  $c$  denotes the critical values. However, it is well known (Levelt Sengers et al., 1986) that the critical state cannot be treated analytically. It is increasingly apparent that the nonclassical nature of the critical state must be taken into account to genuinely improve the prediction of critical or near critical equilibria. It can be argued that the use of optimising parameters is at least, partly due to an inadequate description of the critical state. On the other hand, the predictive capabilities of current nonclassical models of the critical state are very restricted.

The variation of the physical properties of fluids such as specific heat and isothermal compressibility approaching the critical point has been extensively investigated by Stanley (1971), Levelt Sengers (1983) and Levelt Sengers et al. (1983). These studies can be used to define critical exponents, which provide an insight into the nature of the critical transition. Consider a function  $f(e)$ , where  $e \sim 1 - T/T_c$  is a dimensionless variable that reflects the difference in temperature from the critical temperature. It is assumed that  $f(e)$  is both positive and continuous for sufficiently small positive values of  $e$  and that the following limit exists:

$$I \approx \lim_{e \rightarrow 0} [ \ln f(e) / \ln e ] \quad (2.9)$$

The limit  $I$  is the critical point exponent associated with the  $f(e)$  function. Four of the most common critical exponents of a pure substance are defined in Table 2.1. In Table 2.1, we also give values of these critical exponents which are typically obtained using the van der Waals equation of state or other mean field theories, and compare them to experimental values. The discrepancy between theory and experiment indicates that the critical state cannot be treated analytically. Analogous critical exponents of binary mixtures can also be defined (Scott, 1972; Rowlinson and Swinton, 1982; Kiselev and Rainwater, 1997; Jiang and Prausnitz, 1999; Agayan et al. 2001).

Extrapolations of careful experimental measurements in the region of the critical point of binary fluid mixtures (Scott, 1972) indicate that similar non-classical exponents are required for binary critical phenomena as for pure component near critical behaviour. The most common critical exponents of binary mixtures are also defined in Table 2.1. For classical behaviour of fluid mixtures, the Helmholtz function with  $x$  as the mole

fraction also can be expanded at the critical line in terms of its independent variables. The implications of classical behaviour can be visualized by assuming with van der Waals, that the mixture at constant composition  $x$  is in corresponding states with its components.

Table 2.1 Definition and values of Critical exponents for one-component and binary mixtures fluid.

Property	Definition		Classical Value	Experimental Value
	Pure Component	Binary mixtures		
Isochoric heat capacity	$C_v \sim  T - T_c ^a$	$C_{px} \sim  T - T_c ^a$	$a = 0$	$a = 0.08-0.15$
Saturation	$(\rho' - \rho'') \sim (T_c - T)^\beta$	$(x' - x'') \sim (T_c - T)^\beta$	$\beta = 0.5$	$\beta = 0.32-0.36$
Isothermal compressibility	$K_T \sim  T - T_c ^{-\gamma}$	$K_T \sim  T - T_c ^{-\gamma}$	$\gamma = 1$	$\gamma = 0.96-1.28$
Pressure	$ p - p_c  \sim  T - T_c ^d$	$ p - p_c  \sim  x - x_c ^d$	$d = 3$	$d = 4.3-5.1$

The scaling laws (Sengers and Levelt Sengers, 1978) that describe the thermodynamics of near-critical fluids can be viewed as a compact “packaging” of the table 2.1. They imply the exponent equalities

$$2 - a = b(d + 1); \quad g = b(d - 1) \quad (2.10)$$

So that only two exponents are independent. Scaling laws will be given in Chapter 3.

Griffiths and Wheeler (1970) developed an alternative to the conventional description of fluid properties based on a division of variables into fields and densities. This formalism has been applied to the detection of tricritical points in quasi-binary mixtures (Pegg et al., 1983). A scaling approach is frequently employed to

incorporate the effects of nonclassical behaviour. Leung and Griffiths (1973) constructed a scaled thermodynamic potential for vapour-liquid equilibria in binary mixtures by spitting the potential into a regular and scaled part. Rainwater and Moldover (1983) proposed a modified version of the Leung-Griffiths equation. For appropriately chosen isomorphic variables, the thermodynamic potential of binary mixtures has the same form as the thermodynamic potential of a one component fluid (Fisher, 1982), and scaling law calculations for vapour-liquid equilibrium of a wide variety of binary mixtures have been developed (Rainwater, 1992). The asymptotic singular critical behaviour of the thermodynamic properties can be described in terms of scaling laws with common critical exponents and common scaling function (Anisimov and Kiselev, 1992).

## **2.5 Fluid Models**

To calculate critical phenomena we need an expression for the Helmholtz function. In this work we have used conformal solution theory but often approaches based on perturbation theory or using the equation of state directly are also possible. We will introduce conformal solution and perturbation theories in this section. Equations of state will be discussed in Chapter 3.

### **2.5.1 Conformal Solution Theory**

Conformal solution theory was first proposed by Longuet-Higgins (1950), for mixtures in which the intermolecular forces between molecules are similar. It was developed by Brown (1957), Hicks and Young, (1975) and Shukla et al. (1986), and it

has been used for the prediction of critical phenomena of binary mixtures. It predicts mixture properties from the experimentally measured properties of one or more pure reference substances. This theory assumes that the molecules are conformal, and was originally devised for nonpolar, spherical molecules of similar size, but it has been successfully applied to a much more diverse range of mixtures (Toczytkin and Young, 1980; Sadus and Young, 1985; Christou et al., 1986). The van der Waals one-fluid (Scott, 1956), two-fluid (Leland et al., 1969), and three-fluid (Scott, 1956) models are examples of fluid models used with conformal solution theory. The predictions of conformal solution theory compare very favourably with the results of computer simulation of phase equilibria of mixtures of molecules that differ vastly in volume (Harismiadis et al., 1991). The works of Sadus and Young (1987, 1988) and Sadus (1992a, b) demonstrate that conformal solution theory is also useful for the prediction of critical phenomena of ternary mixtures. Wei (1998) extensively reviewed conformal solution and perturbation theories.

### 2.5.1.1 The Helmholtz Function

The principle of corresponding states (Brown, 1957, Rowlinson, 1969, Shukla et al. 1986) is fundamental to conformal solution theory. It enables us to relate the intermolecular potential of one pure substance to that of another. The Helmholtz function of a pure substance (1) to the Helmholtz function of a reference substance (0) can be related by

$$A_1^*(V, T) = f_{11} A_0^*(V / h_{11}, T / f_{11}) - RT \ln h_{11} \quad (2.11)$$

where  $A_I^*$  and  $A_0^*$  denote the configurational Helmholtz function of the pure fluid and the reference fluid respectively, and  $f_{11}$  and  $h_{11}$  are the conformal parameters,

$$h_{11} = g_{11}^3 \tag{2.12}$$

$$f_{11} = \mathbf{e}_{11} / \mathbf{e}_{00}$$

where  $g_{11} = \mathbf{s}_{11} / \mathbf{s}_{00}$ ,  $\mathbf{e}$  and  $\mathbf{s}$  terms are the characteristic energy and distance of an interaction between two molecules.

#### 2.5.1.2 One-Fluid Model

The simplest form of conformal solution theory is the van der Waals one-fluid model (Scott, 1956; Leland et al., 1968; Henderson and Leonard, 1971). In the model, a real mixture is considered to be a single hypothetical pure fluid. Mixture properties are expressed in the terms of the equation of state of a pure fluid with composition dependent size and energy parameters. In the van der Waals one-fluid model, the Helmholtz function  $A_m$  of the mixture can be approximated by that of a hypothetical pure substance, the equivalent substance (subscript  $es$ ).

The Helmholtz function for the binary mixtures  $A_m$  is obtained (Hicks and Young, 1975, Sadus, 1992a) from:

$$A_m = A_{es}^* + A_{cb} \tag{2.13}$$

The residual Helmholtz function  $A_{es}^*$  is represented:

$$A_{es}^* = f_{es} A_0^*(V/h_{es}, T/f_{es}) - RT \ln h_{es} \quad (2.14)$$

and the combinatorial Helmholtz energy of the mixture  $A_{cb}$  has the value:

$$A_{cb} = RT \sum_i x_i \ln x_i \quad (2.15)$$

where  $R$  is the universal gas constant,  $A_0^*$  is the configurational Helmholtz function of the reference substance. The configurational contribution can be obtained from an equation of state. The  $f$  and  $h$  terms are conformal parameters which can be deduced from the critical temperatures and volume, respectively. Normally, one of the components of the mixture is chosen as the reference (denoted by the subscript 0) and the conformal properties of the other pure substances are obtained relative to it, for example,  $f_{11} = T_{11}^c / T_{00}^c$ ;  $h_{11} = V_{11}^c / V_{00}^c$  etc.

The conformal parameters for the equivalent substance of binary mixtures are evaluated from the van der Waals prescriptions

$$f_{es} h_{es} = \sum_{i=1,2} \sum_{j=1,2} x_i x_j f_{ij} h_{ij} \quad (2.16)$$

$$h_{es} = \sum_{i=1,2} \sum_{j=1,2} x_i x_j h_{ij} \quad (2.17)$$

The contribution of unlike interactions  $f_{ij}$ ,  $h_{ij}$  ( $i \neq j$ ) are typically obtained from combining rules. Combining rules are discussed in Chapter 3.

### 2.1.5.3 Two or More Fluid Model

We have used the one-fluid model in our work, but we will briefly discuss multi-fluid models here.

The averaging for the two-fluid model (Leland et al., 1969) is made partly on the intermolecular interactions, and partly on the configurational Helmholtz energy. The average intermolecular interaction for both molecular species is calculated and used to generate the Helmholtz function  $A_m$  of the mixture.

$$A_m = (1-x)[f_1 A_0(V/h_1, T/f_1) - RT \ln h_1] + x[f_2 A_0(V/h_2, T/f_2) - RT \ln h_2] \quad (2.18)$$

Where the average reducing ratios for species  $i$ ,  $f_i$  and  $h_i$  are usually functions of composition.

In the van der Waals three-fluid model (Scott, 1956), there is no preliminary averaging of the conformal parameters to produce equivalent substances and the Helmholtz  $A_m$  of the mixtures is obtained directly from the set of  $f_{ij}$  and  $h_{ij}$ ,

$$A_m = (1-x)^2 A_{11} + 2x(1-x)A_{12} + x^2 A_{22} \quad (2.19)$$

and

$$A_{ij}(V, T) = f_{ij} A_0(V / h_{ij}, T / f_{ij}) - RT \ln h_{ij} \quad (2.20)$$

The  $n$ -fluid models were tested against computer simulation result by McDonald (1972, 1973), Henderson (1974a), and Shing and Gubbins (1982, 1983). The results showed that the van der Waals one-fluid model was superior to the two-fluid and three-fluid model (Wei, 1998). Hicks (1976) used the two-fluid model to calculate high pressure phase equilibria and critical properties of binary mixtures and found that the two-fluid model suffers from internal inconsistencies in the critical region and concluded that the three-fluid model suffers from the same defect as the two-fluid model. Rowlinson and Swinton (1982) also concluded that the two-fluid model is more difficult to use in practice and the three-fluid model imputes an unrealistically high degree of ordering to a dense fluid system. Therefore, the two-fluid and three-fluid models have not been widely used. Recently, Moore et al. (1995) applied the van der Waals one-fluid to model the temperature dependency of infinite dilution activity coefficients. Wei and Sadus (1999) used conformal solution theory in conjunction with the one-fluid model and the Guggenheim equation of state to calculate the critical properties of binary and ternary mixtures characterised by molecules of identical size but different energy parameters. Brandt et al. (2000) also applied the conformal solution theory in conjunction with the one-fluid model and the Guggenheim equation of state to supplement the experimental measurements.

#### 2.5.1.4 Hard-Sphere Expansion

Another conformal solution model is represented by the Hard-Sphere Expansion (HSE) conformal solution theory (Mansoori and Leland, 1972). This model uses the explicitly known properties of a hard sphere mixture for modelling the repulsive

interactions, and the attractive contributions were taken into account by a one-fluid model.

$$f^2 h \propto \mathbf{e}^2 \mathbf{s}^3 = \sum_i \sum_j x_i x_j \mathbf{e}_{ij}^2 \mathbf{s}_{ij}^3 \quad (2.21)$$

$$fh \propto \mathbf{e} \mathbf{s}^3 = \sum_i \sum_j x_i x_j \mathbf{e}_{ij} \mathbf{s}_{ij}^3 \quad (2.22)$$

Where  $x_i$  and  $x_j$  are the mole fraction of the component  $i$  and  $j$ , the  $s$  is the molecular diameter, and the double summation is over all the components of the mixture.

Mansoori and Leland (1972) tested the HSE model by doing a series of comparisons between the predicted excess properties on mixing and these properties from experimental and Monte Carlo data. Chang et al. (1979) developed a general method of prediction the effective molecular diameters and the thermodynamic properties for fluid mixtures based on the HSE model. Shukla et al. (1986) compared various forms of conformal solution theories, including HSE model, with computer simulation results for Lennard-Jones mixtures under different conditions. Dahmani and Wichterle (1999) presented a modification of the HSE mode with the polarity of molecules for prediction of vapour-liquid equilibrium at constant temperature in binary, ternary and quaternary mixtures consisting of chlorobutanes and C-7 hydrocarbons.

## 2.5.2 Perturbation Theories

Perturbation theories are a commonly used alternative to conformal solution theory (Wei, 1998). In perturbation theory, the Helmholtz function is determined from a reference system plus perturbation terms, which are obtained from the radial distribution function of the reference system. Different reference terms can be used to account for different fluid properties such as molecular size, shape or polarity. The perturbation theory approach is based on the assumption that the structure of a fluid is primarily determined by strong, short range repulsive forces and that the structure of a fluid is only slightly modified by weak, long range attractive forces. Therefore, in the perturbation theories for spherical molecules, the hard sphere fluid is taken as the reference and the weak attractive forces are taken as the perturbation. For example, Barker and Henderson (1967) considered the long-ranged attractive contributions can be perturbations, they determined the Helmholtz function form:

$$A = A_0 + \frac{1}{kT} A_1 + \left( \frac{1}{kT} \right)^2 A_2 + \dots \quad (2.23)$$

where  $k$  is Boltzmann's constant,  $T$  is temperature,  $A_0$  is the Helmholtz function of the reference system,  $A_1$  and  $A_2$  are the first and second order perturbation terms, respectively.

This approach has been exploited in different forms of perturbation theories of pure fluids (Barker and Henderson, 1967; Weeks et al., 1971; Verlet and Weis, 1972) and fluid mixtures (Mansoori and Leland, 1970; Grundke et al., 1973; Shukla, 1987; Lotfi and Fischer, 1989; Fotouh and Shukla, 1996a). Furthermore, Boublik (1976, 1987,

1988) proposed a convex molecule perturbation theory based on the Barker-Henderson (1967) perturbation theory. For associating fluids, Wertheim (1984a, b, 1986a, b) developed his thermodynamic perturbation theory.

Perturbation theories offer a possible improvement (Gubbins, 1983) over van der Waals *n*-fluid theories when the molecules differ in size. Fotouh and Shukla (1996a, b, 1997) compared van der Waals one-fluid theory and perturbation theory, and obtained results, which showed that perturbation theory is better than van der Waals one-fluid model for predicting thermodynamic properties when the size of molecules are different. Detailed discussion of perturbation theories were given in several reviews (McDonald, 1973; Henderson, 1974a; Barker and Henderson, 1976; Gray and Gubbins, 1984; Fotouh and Shukla, 1997).

Rogers and Prausnitz (1971) applied Eq. (2.23) with good success in the study of high pressure vapour-liquid equilibria in mixtures. Henderson (1974b) applied the Barker-Henderson theory to mixtures of square-well molecules simulated and obtained good results. By extending the perturbation expansion of Barker and Henderson (1967), Vimalchand and Donohue (1985) and Vimalchand et al. (1986) developed the Perturbed Anisotropic Chain Theory (PACT). Boublik (1976) proposed a simple perturbation method for systems of interacting convex molecules to have an extension of the Barker and Henderson theory via the Kihara pair potential (Kihara, 1963). Boublik (1990) applied the convex molecule perturbation theory to describe the two-phase behaviour of 21 pure nonpolar compounds with fair accuracy. Pavlicek and Boublik (1992) reported parameters of the Kihara generalised pair potential for *n*-alkanes, branched alkanes, and 1-chloroalkanes, all modelled as rod-like molecules. Pavlicek et al. (1995) found that the convex molecule perturbation theory represents a

suitable tool for calculating the equilibrium thermodynamic properties of real pure nonpolar nonspherical fluids along their vapour-liquid coexistence region. Boublik (1997) also extended the perturbation theory to ternary mixtures of polar nonspherical molecules.

The Weeks-Chandler-Andersen model (Weeks et al., 1971) is another widely cited perturbation theory. The model also divides the intermolecular (pair) potential into a reference system pair potential part and a perturbation potential part. However, in the Weeks-Chandler-Andersen model the reference system pair potential part includes all the repulsive forces in the Lennard-Jones potential, and the perturbation potential part includes all the attractions. The Weeks-Chandler-Andersen theory has been extended to fluids with linear molecules (Kohler et al., 1979), triangular, tetrahedra and octahedral molecules (Lustig, 1986, 1987) and to mixtures (Fischer and Lago, 1983). Shukla et al. (1986) combined the Lee and Levesque (1973) theory with the Grundke and Henderson (1973) theory of pair correlation function and presented an improved form of the Lee and Levesque theory, called WCA-LL-GH theory. Shukla (1987) presented an improved form of the first-order perturbation theory using some modifications in WCA-LL-GH. Based on these modifications, Fotouh and Shukla (1996b) presented another improved first-order hard sphere perturbation theory, which consists of the first-order perturbation theory of high temperature approximation (Shukla, 1987) and the random phase approximation (Andersen et al., 1972).

The work of Scalise et al. (1987) is an example of the application of a perturbation theory to critical phenomena. Typically, perturbation models determine the Helmholtz function from:

$$A = A_{iso} + A_2 + A_3 + \dots \quad (2.24)$$

where  $A_{iso}$  is the angle-independent isotropic contribution, and the  $A_2$ ,  $A_3$  terms are the pair and triplet correlation functions, respectively. The above series was obtained by applying the Padé approximation:

$$A = A_{iso} + A_2 / (1 - A_3 / A_2) \quad (2.25)$$

Scalise et al. (1987) specifically calculated critical phenomena of fluids with permanent quadrupole moments.

Wertheim (1984a, b) developed a thermodynamic perturbation theory (TPT) theory to explain the behaviour of fluids, which have short-range directional attractive interactions like those in associating or hydrogen-bonding fluids. Wertheim (1987) also extended his theory to chain fluids and developed the first-order and second-order thermodynamic perturbation theories (TPT1 and TPT2) for a polydisperse mixture of chains of varying lengths. Chapman et al. (1988) and Jackson et al. (1988) also extended Wertheim's theory to mixtures of spheres and of chain molecules and tested the theory against Monte Carlo simulation. This will be discussed in greater detail in Chapter 3, in the context of equations of state for hard chains.

## 2.6 Calculation Procedures for Binary Mixtures

To calculate phase equilibria, an effective numerical technique is required. There are many techniques (Henrici, 1964; Traub, 1964; Acton, 1970; Hicks and Young, 1977;

Press et al, 1988) available for equations of two or three variables. We will introduce two calculation methods.

### 2.6.1 Newton-Raphson Method

A common method involving successive refinement of an initial approximate solution until convergence is obtained. For isolated n-dimensional root geometries combined with starting values that are noticeably nearer to one root than any of the others, almost any reasonable method will converge to the root. If explicit first derivatives are calculable, the Newton-Raphson method (Henrici, 1964; Acton, 1970; Walas, 1985; Press et al, 1988) is the method of first choice. It is straightforward and converges quadratically. The application of the Newton-Raphson method to the critical conditions, allows us to determinate the critical temperature and volume from:

$$V^{i+1} = V^i - \{X^i (\partial W / \partial T)^i - W^i (\partial X / \partial T)^i\} / J \quad (2.26)$$

$$T^{i+1} = T^i - \{W^i (\partial X / \partial V)^i - X^i (\partial W / \partial V)^i\} / J \quad (2.27)$$

$$J = (\partial W / \partial T)^i (\partial X / \partial V)^i - (\partial W / \partial V)^i (\partial X / \partial T)^i \quad (2.28)$$

Although the Newton-Raphson method has been widely used for critical calculations, it is largely restricted to the calculation of vapour-liquid critical properties, but reliable estimates for liquid-liquid critical points cannot generally be obtained a priori. Consequently, the use of the Newton-Raphson method is restricted

to type I and II phenomena. To predict critical points of other types of binary mixtures, a more general solution is required (Sadus, 1994).

### 2.6.2 Hicks-Young Algorithm

In this work, the Hicks and Young algorithm (Hicks and Young, 1977, Sadus and Young, 1987) is used to locate all types of critical points. The algorithm works by tracking either Eq. (2.3) and (2.4) at a fixed composition and simultaneously by monitoring the sign of the other function in a temperature and volume search area. It is computationally easier to trace  $W = 0$  rather than  $X = 0$ , because the second derivatives of chemical potential is of increasing complexity in the latter condition. The search procedure is illustrated in Figure 2.4. Two points 1 and 6 are designated at a small interval on either side of the entry point, which lies on one side of a square defined by the points 2 to 5. The sign of  $W$  is compared between the adjacent pairs of points: 1-2; 2-3; 3-4; 4-5; and 5-6. A change of sign indicates that the condition  $W = 0$  was passed between the pair of points, and the times is odd number. The sign of  $X$  is checked at these points. If the sign of  $X$  also has changed, then an intersection of  $W = 0$  and  $X = 0$  has been passed. The search procedure is scaled down until the critical point is accurately found. If the sign of  $X$  is unchanged, then the new point is used to establish the direction of the  $W = 0$  curve and the next search square is arranged.

The major advantages of the Hicks-Young algorithm are:

1. In principle, all solutions of the critical conditions are located.
2. It does not require initial approximations.
3. No additional derivatives are required.

The first and second aspects are very important for the a priori prediction of critical equilibria. Van Pelt (1992) and Castier and Sandler (1997a, b) employed the Hicks and Young algorithm to perform critical point calculations in binary systems. Recently, Wang et al. (2000) applied the algorithm to calculate closed-loop liquid-liquid equilibria. A disadvantage of the algorithm is that it is much more computational expensive than simple iterative approaches. However, the ability to confidently locate all possible solutions to the critical conditions out weighs this disadvantage. This is particularly important for the calculation of global phase diagrams (Chapter 5 & 6).

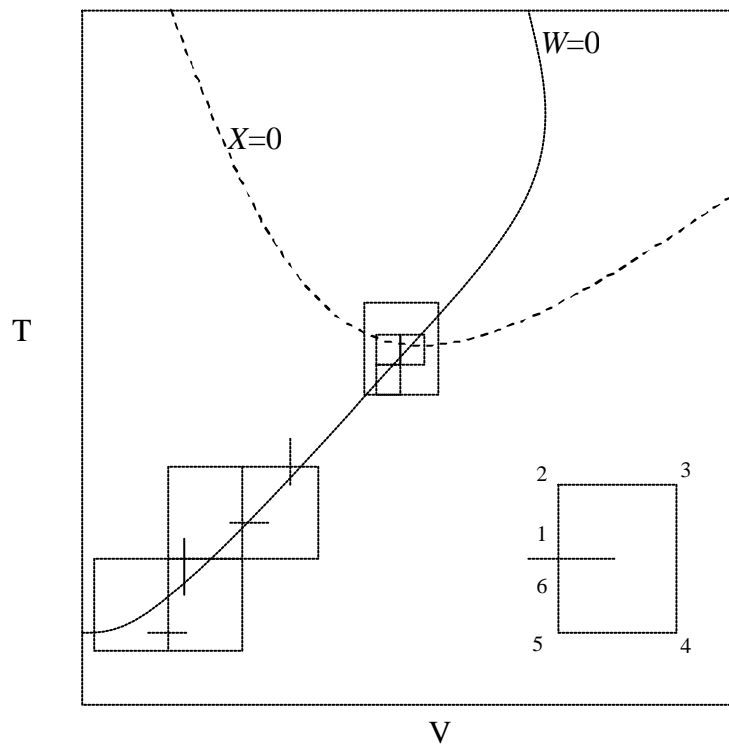


Figure 2.4. Hicks-Young algorithm for locating the critical point.

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