

Chapter 2 Theory of Fluids

Fluid theories are of fundamental importance to the prediction of phase equilibrium thermodynamics. There are many concepts and principles. In this chapter, we will review conformal solution and perturbation theories. Equations of state will be discussed in Chapter 3.

2.1 Conformal solution theory

Conformal solution theory (Brown, 1957; Hicks and Young, 1975; Massih and Mansoori, 1983; Naumann and Leland, 1984) is a successful theory for the prediction of equilibrium excess thermodynamic properties. It predicts mixture properties from the experimentally measured properties of one or more pure reference substances. Conformal solution theory assumes that the molecules are conformal; i.e., they obey the same intermolecular force law, differing only in the values of the energy and size parameters. It was originally devised for non-polar, spherical molecules of similar size but it has been successfully applied to a much more diverse range of mixtures (Toczyk and Young, 1980; Sadus and Young, 1985; Christou et al., 1986).

The van der Waals one-fluid (Scott, 1956; Leland et al., 1968), two-fluid (Leland et al., 1969), and three-fluid (Scott, 1956) models (also called n -fluid models) are examples of fluid models used with conformal solution theory. These theories have been tested against computer simulation results (McDonald, 1972, 1973; Henderson, 1974a; Shing and Gubbins, 1982, 1983a). The results showed that the van der Waals one-fluid model was superior to two-fluid and three-fluid model, giving good agreement with simulation results over a wide range of the energy parameter ratio when the molecules are of about the same size. Harismiadis et al. (1991) also concluded that the predictions of conformal solution theory, especially the van der Waals one-fluid model, compared favourably with the results obtained from computer simulation of the phase equilibria of mixtures of molecules which differ vastly in volume.

2.1.1 The principle of Corresponding States

The principle of corresponding states (Brown, 1957, Rowlinson, 1969, Rowlinson and Watson, 1969, Mollerup, 1980; Wong et al., 1983; Shukla, 1986) is fundamental to conformal solution theory. It enables us to relate the intermolecular potential of one pure substance to that of another. For example, the intermolecular potential of a pure substance (I) can be related to that of a reference substance (O) by

$$U_{11}(r) = f_{11}U_{00}(r/g_{11}) \quad (2.1)$$

where $U_{11}(r)$ is the interaction energy between a molecule of species (I) and a molecule of species (O) at a intermolecular distance r , $f_{11} = \mathbf{e}_{11}/\mathbf{e}_{00}$ and $g_{11} = \mathbf{s}_{11}/\mathbf{s}_{00}$, and \mathbf{e} and \mathbf{s} are the characteristic energy and distance of an interaction between two molecules. Potentials which satisfy Eq.(2.1) are said to be conformal.

Similarly, the Helmholtz functions of two substances (1) and (0) also can be related to each other by

$$A_1^*(V, T) = f_{11}A_0^*(V/h_{11}, T/f_{11}) - RT \ln h_{11} \quad (2.2)$$

where A_1^* and A_0^* denote the Helmholtz function of two different substances respectively and $h_{11} = g_{11}^3$.

When extended to mixtures, the pair interactions can be related to a common reference potential. By including interactions between unlike molecules, Eq.(2.1) can be rewritten as

$$U_{ij}(r) = f_{ij}U_{00}(r/g_{ij}) \quad (2.3)$$

where $U_{ij}(r)$ is the interaction energy between a molecule of species i and a molecule of species j at a intermolecular distance r , $f_{ij} = \mathbf{e}_{ij}/\mathbf{e}_{00}$ and $g_{ij} = \mathbf{s}_{ij}/\mathbf{s}_{00}$, while \mathbf{e}_{ij} and \mathbf{s}_{ij} are the characteristic energies and distances of the interaction of a molecule of species i with a molecule of species j , \mathbf{e}_{00} and \mathbf{s}_{00} are common reference potential parameters. The principle of corresponding states applies rigorously to any group of

substances that satisfy Eq.(2.3). The total Helmholtz function of a mixture A_m can be decomposed into a contribution from the configuration energy plus a contribution from the mixing process.

$$A_m = A^* + A_{cb} \quad (2.4)$$

where A^* is the contribution from the configuration energy and A_{cb} is the contribution from the mixing process and can often be determined by

$$A_{cb} = RT \sum x_i \ln x_i \quad (2.5)$$

2.1.2 One-Fluid Model

The van der Waals one-fluid model produces the simplest form of conformal solution theory. In the one-fluid model, a real mixture is considered to be a single hypothetical pure fluid. Mixture properties are expressed in terms of the equation of state of pure fluid with composition dependent size (σ) and energy (ϵ) parameters. The van der Waals one-fluid model (Scott, 1956; Leland et al., 1968; Henderson and Leonard, 1971) can be written as

$$h = \sum_i \sum_j x_i x_j h_{ij} \quad (2.6)$$

$$fh = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \quad (2.7)$$

where x_i and x_j are the mole fraction of the component i and j , fh and h are proportional to $\epsilon \mathbf{s}^3$ and \mathbf{s}^3 respectively, and the double summation is performed over all the components of the mixture.

In the van der Waals one-fluid model, the Helmholtz function A_m of the mixture can be approximated by those of a hypothetical pure substance, the equivalent substance (subscript es).

$$A_m = A_{es}^* + A_{cb} = f_{es} A_0^*(V/h_{es}, T/f_{es}) - RT \ln h_{es} + A_{cb} \quad (2.8)$$

where A_0^* is the configurational contribution to the Helmholtz function and the equivalent substance reducing ratios f_{es} and h_{es} are normally dependent on mixture composition and are given by Eq.(2.6) and Eq.(2.7) and the contribution of the energy of mixing A_{cb} can often be determined by Eq.(2.5). Smith (1972) showed that van der Waals one-fluid model can be derived from perturbation theory so he concluded that the van der Waals one-fluid model has the firmest theoretical foundation. The van der Waals one-fluid theory has been extended to second-order (Mo et al., 1974; Smith, 1971). The extended theory gives better results for molecules that differ in size, but some numerical calculations are more involved.

The Eq. (2.6) and Eq. (2.7) represent the van der Waals one-fluid model. It is simple and easy to apply. Leland et al. (1968) applied the van der Waals one-fluid model to mixtures with good results. McDonald (1972, 1973) reported that van der Waals one-fluid model compared well with molecular simulation results for the excess properties of systems with size parameter ratios from 1 to 1.134 and energy parameter ratios from 0.56 to 2.275. Shing and Gubbins (1982, 1983a) showed that van der Waals one-fluid model gave reasonable results for Henry's constant over a range of energy parameter ratios, but also indicated that the van der Waals model was poor in predicting its variation with size parameter ratio. Shukla et al. (1986) stated that the van der Waals one-fluid model can be used for the prediction of excess properties, total thermodynamic functions, the equation of state and chemical potentials when the energy parameter ratio is up to 1.5 and the size parameter ratio is up to 1.1.

Harismiadis et al. (1991) performed a study of the phase equilibria for binary Lennard-Jones mixtures with size and energy parameter ratios up to 2. They focused on pressure, concentration and density at coexistence of mixtures and used computer simulation to test the van der Waals one-fluid model. The results showed that the van der Waals one-fluid model and molecular simulation results agreed well in their predictions of phase coexistence envelopes for all the mixtures studied. Georgoulaki et al. (1994) examined the behaviour of binary mixtures and extended the range of asymmetries to 4:1 for both energy and size parameter ratios. Their results showed that the van der Waals one-fluid model agreed well with the simulations and concluded that

the ratio of the energy parameters influenced the performance of the van der Waals one-fluid theory more than the ratio of the size parameters.

Tsang et al. (1995) tested the applicability of the van der Waals one-fluid model in predicting the phase behaviour of ternary Lennard-Jones mixtures and found good agreement between theoretical predictions and simulation results for the systems studied. They concluded that the van der Waals one-fluid model was capable of predicting phase equilibria accurately in slightly asymmetric systems, for which the largest component size and energy parameter ratios were up to 2. For phase equilibria of highly asymmetric systems, with energy parameters ratios up to 6.7, the van der Waals one-fluid model was reasonably capable of predicting phase equilibria.

Other evaluations have been reported by Fotouh and Shukla (1996a & b, 1997a & b). For binary mixtures, Fotouh and Shukla (1997a) compared van der Waals one-fluid predictions with simulation results for pressure, residual chemical potentials at finite concentration and in infinite dilution, total and excess thermodynamic properties under highly nonideal conditions. The results showed that when size parameter ratios were less than 1.1 and energy parameter ratios were less than 1.5, the van der Waals one-fluid model was successful in predicting equation of state, residual chemical potentials at finite concentration and in infinite dilution in moderately nonideal mixtures. However, in highly nonideal mixtures, the van der Waals one-fluid model became less reliable in describing residual chemical potentials at infinite dilution. Their results also showed that van der Waals one-fluid theory was adequate in the parameter ranges $s_{22}/s_{11} < 1.25$ and $e_{22}/e_{11} < 1.8$ for the excess Gibbs free energy, $s_{22}/s_{11} < 1.1$ and $e_{22}/e_{11} < 1.4$ for the excess enthalpy and $s_{22}/s_{11} < 1.25$ and $e_{22}/e_{11} < 1.3$ for the excess volume. For moderately nonideal mixtures, they concluded that the van der Waals one-fluid model became unreliable in predicting excess properties.

For ternary mixtures, Fotouh and Shukla (1996a & b) examined the accuracy of van der Waals one-fluid model based on equation of state for pure Lennard-Jones fluids (Kolafa and Nezbeda, 1994). They tested three nonideal ternary model mixtures and a real ternary fluid mixture. For three ternary model mixtures, Fotouh and Shukla (1996a) compared van der Waals one-fluid predictions with simulation results for mixture density, internal energy, excess Gibbs free energy, excess volume and excess enthalpy. The van der Waals one-fluid theory was found to reproduce simulation results for total

properties of all the mixtures well and it can also describe excess properties of nearly ideal to moderately nonideal mixtures. However, as the nonideality in mixtures increases, van der Waals one-fluid theory became less accurate. For highly nonideal ternary model mixtures, van der Waals one-fluid theory became inadequate in describing excess properties. For the real ternary fluid mixtures ($N_2 / Ar / CH_4$), Fotouh and Shukla (1996b) compared the van der Waals one-fluid theoretical results with experimental data for mixture total volume, excess Gibbs energy and excess volume. The van der Waals one-fluid model was reliable in describing excess properties of such a moderately nonideal mixture. Fotouh and Shukla (1997b) also reported that for ternary fluid mixtures, the van der Waals one-fluid theory was successful in describing total properties in the range $1 \leq s_{33} / s_{11} \leq 1.18$ and excess properties in the range $1 \leq s_{33} / s_{11} \leq 1.25$ for all the energy parameter ratios from 1.0 to 2.0.

2.1.3 Multi-Fluid Models

The van der Waals two- and three-fluid models have been reported (Leland et al., 1969, Scott, 1956). In the van der Waals two-fluid theory (Leland et al., 1969), the properties of the mixture are those of an ideal mixture of the equivalent substance. It is assumed that each component has a mean energy of interaction with all other molecules, the mixing rules are:

$$h_i = \sum_j x_j h_{ij} \quad (2.9)$$

$$f_i h_i = \sum_j x_j f_{ij} h_{ij} \quad (2.10)$$

The average intermolecular interaction for both molecular species is calculated and used to generate the Helmholtz function A_m of the mixture.

$$A_m = (1-x)[f_1 A_0(V/h_1, T/f_1) - RT \ln h_1] + x[f_2 A_0(V/h_2, T/f_2) - RT \ln h_2] \quad (2.11)$$

where the average reducing ratios for species i , f_i and h_i are normally functions of composition and given by Eq.(2.9) and Eq.(2.10).

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 function A_m of the mixture is obtained directly from the set of f_{ij} and h_{ij} ,

$$A_m = (1-x)^2 A_{11} + 2x(1-x)A_{12} + x^2 A_{22} \quad (2.12)$$

where

$$A_{ij}(V,T) = f_{ij}A_0(V/h_{ij}, T/f_{ij}) - RT \ln h_{ij} \quad (2.13)$$

Scott (1956) pointed out that the van der Waals three-fluid model is a model more appropriate to gaseous densities than those of a liquid.

As we mentioned in the beginning of this chapter, the n -fluid models were tested against computer simulation results (McDonald, 1972, 1973; Henderson, 1974a; Shing and Gubbins, 1982, 1983a) and the results showed that the van der Waals one-fluid model was superior to two-fluid and three-fluid model. Hicks (1976) used the two-fluid model to calculate the 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; it is exact in the limit of the slightly imperfect gas but inappropriate for liquids. For the above reasons, the two- and three-fluid models have not been widely used.

2.1.4 Hard Sphere Expansion Conformal Solution Theory

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

repulsive interactions, while the attractive contributions were taken into account by a one-fluid model. The HSE model can be written as

$$f^2h \propto \mathbf{e}^2 \mathbf{s}^3 = \sum_i \sum_j x_i x_j \mathbf{e}_{ij}^2 \mathbf{s}_{ij}^3 \quad (2.14)$$

$$fh \propto \mathbf{e} \mathbf{s}^3 = \sum_i \sum_j x_i x_j \mathbf{e}_{ij} \mathbf{s}_{ij}^3 \quad (2.15)$$

where x_i and x_j are the mole fraction of the components i and j , f^2h and fh are proportional to $\mathbf{e}^2 \mathbf{s}^3$ and $\mathbf{e} \mathbf{s}^3$, the σ 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 those properties from experimental and Monte Carlo data. Their results showed that the excess enthalpy and especially the excess volume were generally predicted better by the HSE procedure despite the advantage of using an empirically fitted reference equation in the van der Waals one-fluid procedure. When the van der Waals one-fluid and the HSE models were both based on the same reference, the results showed that the HSE method was superior. An important factor in HSE model is to determine the molecular diameter. 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. The results showed the possibility to extend the HSE model to mixtures containing polar molecules. However, they also recognised that with their methods, the determination of diameter for fluids with unknown potential functions was not possible at all densities. Shukla et al. (1986) compared various forms of conformal solution theories, including HSE model, with computer simulations results for Lennard-Jones mixtures under different conditions. They concluded that the HSE model is not complete unless a consistent method is found to calculate the hard sphere diameter.

2.2 Perturbation theories

Perturbation theories are a commonly-used alternative to conformal solution theory. 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 perturbation theories for spherical molecules, the hard sphere fluid is taken as the reference and the weak attractive forces are taken as the perturbation. This approach has been exploited in different forms of perturbation theories of pure fluids (Barker and Henderson, 1967, 1976; Weeks et al., 1971; Verlet and Weis, 1972) and fluid mixtures (Mansoori and Leland, 1970; Grundke et al., 1973; Lee and Levesque, 1973; Fischer and Lago, 1983; Shukla et al., 1986; Shukla, 1987, Lotfi and Fischer, 1989, Fotouh and Shukla, 1996a). Furthermore, Boublik (1976, 1987, 1988) proposed a convex molecule perturbation theory based on 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, because the size difference is incorporated into the reference system of hard spheres. Fotouh and Shukla (1996a & b, 1997a & b) compared van der Waals one-fluid theory and perturbation theory. The results showed that perturbation theory is better than van der Waals one-fluid model for predicting thermodynamic properties when the size of molecules are different. In this section, we concentrate on some widely cited perturbation theories and some improved forms. The detailed discussion of perturbation theories were given in several reviews (McDonald, 1973; Henderson, 1974a; Barker and Henderson, 1976; Shing and Gubbins, 1983b; Gray and Gubbins, 1984).

2.2.1 Barker-Henderson Perturbation Theory

The properties of a fluid are determined largely by short-range repulsive forces. The long-range attractive forces can be considered to be perturbations. By using these concepts, Barker and Henderson (1967) assumed the pair potential to be of the form

$$u(r) = u_0(r) + u_1(r) \tag{2.16}$$

where $u_0(r)$ is the reference potential, given by

$$\left. \begin{aligned} u_0(r) &= u(r), & r < \mathbf{s} \\ &= 0, & r > \mathbf{s} \end{aligned} \right\} \quad (2.17)$$

and $u_1(r)$ is the perturbation part, given by

$$\left. \begin{aligned} u_1(r) &= 0, & r < \mathbf{s} \\ &= u(r), & r > \mathbf{s} \end{aligned} \right\} \quad (2.18)$$

where σ is the value of r for which $u(r)$ is equal to zero.

Using the perturbation approach, the Helmholtz function of a system can be expressed as an expansion in the inverse temperature around the Helmholtz function of a reference system whose structure and thermodynamic properties are known. The second order perturbation theory expansion of the Helmholtz function is of the form

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \left(\frac{1}{kT}\right) \frac{A_1}{NkT} + \left(\frac{1}{kT}\right)^2 \frac{A_2}{NkT} \quad (2.19)$$

where N is the number of molecules, 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.

According to Barker and Henderson (1967), the first-order and second-order perturbation contribution are given by

$$\frac{A_1}{NkT} = 2\mathbf{pr} \int_{\mathbf{s}}^{\infty} g_0(r) u(r) r^2 dr \quad (2.20)$$

$$\frac{A_2}{NkT} = -\mathbf{pr} \frac{\partial}{\partial p} \left(\mathbf{r} \int_{\mathbf{s}}^{\infty} g_0(r) u^2(r) r^2 dr \right) \quad (2.21)$$

where V is volume, p is pressure, $\mathbf{r} = \frac{N}{V}$, and $g_0(r)$ is the radial distribution function (RDF). Barker and Henderson (1967) showed that A_0 and $g_0(r)$ may be approximated by

$$A_0 = A_{HS} \quad (2.22)$$

$$g_0(r) = g_{HS}(r) \quad (2.23)$$

where A_{HS} and $g_{HS}(r)$ are the Helmholtz function and radial distribution function of a system of hard spheres of diameter σ , defined by

$$\mathbf{s} = \int_0^{\infty} [\exp\{-\mathbf{b}u(r)\} - 1] dr \quad (2.24)$$

A_{HS} can be calculated from the Carnahan-Starling (1969) equation (see Chapter 3). Eq.(2.22) has been tested by direct computer simulation (Levesque and Verlet, 1969) and found to be accurate.

Leonard et al. (1970) extended the Barker-Henderson perturbation theory to mixtures of Lennard-Jones 6-12 fluids and reported that the predictions of perturbation theory for the excess thermodynamic properties were in generally good agreement with experimental results and with the results of computer simulations over a wide range of potential parameters. Rogers and Prausnitz (1971) applied the Barker-Henderson perturbation theory 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 by Alder et al. (1973, 1974) 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 (see Chapter 3 for details).

2.2.2 Extension of Barker and Henderson theory

----- Boublik's Perturbation Theory of Convex Molecules

Boublik (1976, 1987, 1988) proposed a simple perturbation method for systems of convex molecules interacting via the Kihara pair potential (Kihara, 1963)

$$u(s) = 4\epsilon \left[\left(\frac{s}{\sigma} \right)^{12} - \left(\frac{s}{\sigma} \right)^6 \right] \quad (2.25)$$

where s is the shortest surface-to-surface distance between the convex cores of two interacting molecules, ϵ and σ are the energy and size parameters.

In the convex molecule perturbation theory, Boublik employed the Barker-Henderson-like (Barker and Henderson, 1967) division of the pair potential into repulsive ($s < \sigma$) and attractive ($s > \sigma$) parts,

$$u_0(s) = u(s) \quad s \leq \sigma \quad (2.26)$$

$$u_p(s) = u(s) \quad s > \sigma \quad (2.27)$$

where 0 and p denote the reference and perturbation functions. By considering the second-order perturbation expansion, the residual Helmholtz function A is expressed as

$$\frac{A - A^*}{NkT} = \frac{A^0 - A^*}{NkT} + \frac{A_1^p}{NkT} + \frac{A_2^p}{NkT} \quad (2.28)$$

where, an asterisk denotes the perfect gas contribution to the Helmholtz function. Boublik (1981) determined the reference term $A^0 - A^*$ from the hard body equation of state.

$$\frac{A^0 - A^*}{NkT} = (6\mathbf{a}^2 - 5\mathbf{a} - 1) \ln(1 - y) + \frac{(15\mathbf{a}^2 - 9\mathbf{a})y}{2(1 - y)} + \frac{(-3\mathbf{a}^2 + 5\mathbf{a})y^2}{2(1 - y)^2} \quad (2.29)$$

where $\mathbf{a} = RS/3V$, $y = \mathbf{r}V$, R is the mean curvature integrals divided by $4\mathbf{p}$, S is the surface area, V is the volume and $\mathbf{r} = N/V$ is the number density.

In the first-order and second-order perturbation terms

$$\frac{A_1^p}{NkT} = \frac{\mathbf{r}}{2kT} \int_0^\infty u(s) g^{hcb}(s) S_{i+s+j} ds \quad (2.30)$$

$$\frac{A_2^p}{NkT} = -\frac{\mathbf{r}}{4kT} \left(\frac{\partial \mathbf{r}}{\partial p} \right)^{hcb} \int_0^\infty [u(s)]^2 g^{hcb}(s) S_{i+s+j} ds \quad (2.31)$$

where the superscript hcb denotes the properties of the representative hard convex bodies (Boublik, 1981), $g^{hcb}(s)$ is the surface-to-surface correlation function of hard convex bodies and can be expressed in terms of the total correlation function h^{hcb} as

$$g^{hcb}(s) = 1 + h^{hcb}(s) \quad (2.32)$$

The mean surface area, S_{i+s+j} , of a pair of molecules i and j can be expressed in terms of the geometric characteristics of the respective cores as follows:

$$S_{i+s+j} = (S_i + S_j + 8\mathbf{p}R_i R_j) + 8\mathbf{p}(R_i + R_j)s + 4\mathbf{p}s^2 \quad (2.33)$$

where S_i is a surface area and R_i is a $(1/4\mathbf{p})$ multiple of the mean curvature integral.

Boublik (1990) applied the convex molecule perturbation theory to describe the two-phase behaviour of 21 pure nonpolar compounds with fair accuracy. Boublik and coworkers (Pavlicek and Boublik, 1992; Boublik, 1993; Pavlicek et al., 1995) reported parameters of the Kihara generalised pair potential for n-alkanes, branched alkanes, and 1-chloroalkanes, all modeled as rod-like molecules. Pavlicek and Boublik (1992) examined the variant of the perturbation theory of convex molecule fluids to evaluate the equilibrium pressures and densities of a series of n-alkanes, from ethane to n-hexadecane, and found that the perturbation approach made it possible to fit the experimental data with high accuracy. Pavlicek et al. (1995) also 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 and coworkers (Boublik, 1992; Pavlicek et al., 1993, 1995; Aim et al., 1996) also concluded that the convex molecule perturbation theory is able to describe the excess Gibbs function, excess enthalpy, and excess volume of n-alkane and the chloroalkane + n-alkane binary mixtures with varying difference in size of the constituents.

Based on their perturbation theory, Boublik and coworkers (Boublik, 1992a & b & c, Mueller et al. 1993) developed a method to predict the behaviour of pure fluids with permanent dipoles, quadrupoles and other electrostatic interactions and mixtures of polar-non-polar components. Recently, Boublik (1997) extended the perturbation theory to ternary mixtures of polar non-spherical molecules.

2.2.3 Weeks-Chandler-Andersen Theory

The Weeks-Chandler-Andersen model is another widely cited perturbation theory. In common with the Barker and Henderson (1967) approach, Weeks et al. (1971) also divided the intermolecular (pair) potential into a reference system pair potential part $u_0(r)$ and a perturbation potential part $u_1(r)$. The differences between Barker-Henderson model and Weeks-Chandler-Andersen approach are in the definition of the reference potential and the density dependence of the size of representative hard spheres. Weeks et al. (1971) assumed that $u_0(r)$ includes all the repulsive forces in the Lennard-Jones potential and $u_1(r)$ includes all the attractions and proposed the choice

$$\left. \begin{aligned} u_0(r) &= u(r) + \mathbf{e}, & r < R_m \\ &= 0, & r \geq R_m \end{aligned} \right\} \quad (2.34)$$

$$\left. \begin{aligned} u_1(r) &= -\mathbf{e}, & r < R_m \\ &= u(r), & r \geq R_m \end{aligned} \right\} \quad (2.35)$$

where $R_m = 2^{1/6} \mathbf{s}$ is the distance to the minimum in the Lennard-Jones pair potential.

According to the first-order perturbation theory, the Helmholtz function is written as

$$A = A_0 + \frac{Nr}{2} \int u_1(r) g_0(r) dr \quad (2.36)$$

where N is the number of molecules, $r = \frac{N}{V}$ is mixture number density, V is total volume, A_0 and $g_0(r)$ are the Helmholtz function and radial distribution function of the reference fluid and may be systematically approximated by

$$A_0 = A_{HS} \quad (2.37)$$

and

$$g_0(r) = y_0(r) \exp\{-\mathbf{b}u_0(r)\} \quad (2.38)$$

where $\mathbf{b} = \frac{1}{kT}$, k is Boltzmann's constant and T is temperature, A_{HS} and y_0 are the Helmholtz function and distribution function for hard spheres of diameter, defined by

$$\int_0^{R_H} r^2 y_0(r) dr = \int_0^{R_H} r^2 y_0(r) \exp\{-\mathbf{b}u_0(r)\} dr \quad (2.39)$$

Eq.(2.34) to Eq.(2.36) are called the high temperature approximation (HTA).

Lee and Levesque (1973) extended the Weeks-Chandler-Andersen theory to mixtures and presented first-order perturbation theory. In their theory, the Lennard-Jones pair potential was divided into a reference part and a perturbation part using Weeks-Chandler-Andersen criteria (1971). The reference part of the Helmholtz function was represented by the hard sphere fluid plus a first-order contribution to the Helmholtz function of the reference fluid. The perturbation part of the Helmholtz function was represented by the first-order term using the high temperature approximation (Weeks et al., 1971). Lee and Levesque (1973) neglected the first-order contribution to the reference mixture and introduced several approximations in evaluating the first-order perturbation term of the full Helmholtz function. Therefore, their theory could be

applied to predict simulation results of thermodynamic properties of slightly nonideal mixtures only.

The WCA theory has been extended to fluids with linear molecules (Kohler et al., 1979; Fischer, 1980), triangular, tetrahedral and octahedral molecules (Lustig, 1986; 1987) and to mixtures (Fischer and Lago, 1983). Furthermore, the WCA theory has been applied to several real pure substances (Fischer et al., 1984; 1987; Bohn et al., 1986a) and to predict excess properties of real mixtures (Bohn et al., 1985; 1986b; 1988, Almeida et al., 1989).

Shukla et al. (1986) combined the Lee and Levesque (1973) theory with the Grundke and Henderson (1972) theory of pair correlation function and presented an improved form of the Lee and Levesque theory, called WCA-LL-GH theory. The WCA-LL-GH theory was tested by comparing its predictions with computer simulation results for several mixtures under a variety of nonideal conditions, and was found to provide good predictions of thermodynamic properties for a size parameter ratio ≤ 1.3 and an energy parameter ratio up to 4, at sufficiently high densities. However, it was still inadequate for particular size and energy parameter ratios, and was unable to represent composition dependence of the excess functions accurately.

2.2.4 Extension to Weeks-Chandler-Andersen Perturbation Theory

--- Shukla's First-Order Hard Sphere Perturbation Theory

Following the Weeks-Chandler-Andersen criteria (Weeks et al., 1971), 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 (1996a) 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). This theory does not involve any mixing rules. In their perturbation theory, the pair potential $u_{ij}^{LJ}(r)$ is divided into a reference part $u_{ij}^0(r)$ and a perturbation part $u_{ij}^p(r)$

$$\left. \begin{aligned} u_{ij}^0(r) &= u_{ij}^{LJ}(r) + \mathbf{e}_{ij}, & r \leq R_{ij}^m \\ &= 0, & r > R_{ij}^m \end{aligned} \right\} \quad (2.40)$$

$$\left. \begin{aligned} u_{ij}^p(r) &= -\mathbf{e}_{ij}, & r \leq R_{ij}^m \\ &= u_{ij}^{LJ}(r), & r > R_{ij}^m \end{aligned} \right\} \quad (2.41)$$

where $R_{ij}^m = 2^{1/6} \mathbf{s}_{ij}$ is the distance to the minimum in the Lennard-Jones pair potential.

The residual Helmholtz function A^{res} of a mixture is written as

$$\frac{A^{res}}{NkT} = \frac{A^{HS,res}}{NkT} + \frac{A_{HTA}^1}{NkT} + \frac{A_{RPA}^1}{NkT} \quad (2.42)$$

where $A^{HS,res}$ is the Helmholtz function of hard sphere mixture and given by

$$\begin{aligned} \frac{A^{HS,res}}{NkT} &= -\ln(1-\mathbf{h}) + \frac{3\mathbf{h}_1\mathbf{h}_2}{\mathbf{h}_0(1-\mathbf{h})} + \frac{\mathbf{h}_2^3}{6\mathbf{h}_0\mathbf{h}^2(1-\mathbf{h})^2} \\ &\quad \times [16\mathbf{h} - 15\mathbf{h}^2 + 4\mathbf{h}^3 + 16(1-\mathbf{h})^2 \ln(1-\mathbf{h})] \end{aligned} \quad (2.43)$$

where

$$\mathbf{h}_l = (\mathbf{p}r/6) \sum_i x_i \mathbf{s}_i^l, \quad l = 0, 1, 2, 3 \quad (2.44)$$

σ is the hard sphere diameter, and $\mathbf{h}_3 = \mathbf{h}$ is the total packing fraction.

A_{HTA}^1 is the first order term of the Helmholtz function in terms of the high temperature approximation (HTA) and given by Shukla (1987)

$$\begin{aligned} \frac{A_{HTA}^1}{NkT} &= \left(\frac{2\mathbf{p}r}{kT} \right) \sum_{ij} x_i x_j \left\{ -\mathbf{e}_{ij} \int_0^{d_{ij}} \exp\left(\frac{-u_{ij}^0(r)}{kT} \right) y_{ij}^{HS}(r) r^2 dr \right. \\ &\quad \left. - \int_{d_{ij}}^{R_{ij}^m} \left[\mathbf{e}_{ij} \exp\left(\frac{-u_{ij}^0(r)}{kT} \right) + u_{ij}^{LJ}(r) \right] g_{ij}^{HS}(r) r^2 dr + \int_{d_{ij}}^{\infty} u_{ij}^{LJ}(r) g_{ij}^{HS}(r) r^2 dr \right\} \end{aligned} \quad (2.45)$$

A_{RPA}^1 is the first order term of the Helmholtz function in terms of the random phase approximation (RPA) and given by Andersen et al. (1972).

$$\frac{A_{RPA}^1}{NkT} = -[2(2\mathbf{p})^3 \mathbf{r}]^{-1} \sum_{ij} x_i x_j \int \left[\frac{u_{ij}^p(q) S_{ij}^{HS}(q)}{kT} - \ln \left(1 + \frac{u_{ij}^p(q) S_{ij}^{HS}(q)}{kT} \right) \right] d\bar{q} \quad (2.46)$$

In the above equations, $\mathbf{r} = N/V$ is the mixture number density, x_i and x_j are the compositions of the species i and j , respectively. g_{ij}^{HS} and Y_{ij}^{HS} are radial distribution function and background correlation function of the hard sphere mixture, respectively. In Eq.(2.46), $u_{ij}^p(q)$ is the Fourier transform of $u_{ij}^p(r)$

$$u_{ij}^p(q) = \mathbf{r} \int u_{ij}^p(r) \exp(-i\bar{q} \cdot \bar{r}) d\bar{r} \quad (2.47)$$

and $S_{ij}^{HS}(q)$ is the Fourier transform of $g_{ij}^{HS}(r)$

$$S_{ij}^{HS}(q) = 1 + \mathbf{r} \int [g_{ij}^{HS}(r) - 1] \exp(-i\bar{q} \cdot \bar{r}) d\bar{r} \quad (2.48)$$

Fotouh and Shukla (1996a & b, 1997a) examined the accuracy of the modified first order perturbation theory, Eq. (2.42), for binary and ternary mixtures. For binary mixtures, Fotouh and Shukla (1997a) compared theoretical prediction results with simulation data for pressure, residual chemical potentials at finite concentration and in infinite dilution, total and excess thermodynamic properties with good agreement. More specifically, Eq.(2.42) can predict accurately the density dependence of pressure in strongly nonideal mixtures having parameter ratios $\mathbf{s}_{22}/\mathbf{s}_{11} \leq 2$ and $\mathbf{e}_{22}/\mathbf{e}_{11} \leq 4.5$. However, its predictions are less accurate for the extreme nonideal conditions, $\mathbf{s}_{22}/\mathbf{s}_{11} = 2$ and $\mathbf{e}_{22}/\mathbf{e}_{11} = 4.5$, at very high density $\mathbf{r}\mathbf{s}^3 = 0.9$ and the very low density $\mathbf{r}\mathbf{s}^3 = 0.4$. Their results showed Eq. (2.42) is reliable in describing the residual chemical potentials at finite concentrations of nonideal mixtures. For the residual chemical potentials at infinite dilution, Eq.(2.42) is successful for highly nonideal mixtures, with parameter ratios up to $(\mathbf{s}_{22}/\mathbf{s}_{11})^3 = 5$, $\mathbf{e}_{22}/\mathbf{e}_{11} = 4$, for all the fluid densities, considered at different temperatures. Eq.(2.42) also represented well the excess free energy of several binary mixtures, differing in energy parameter of the components $2 \leq \mathbf{e}_{22}/\mathbf{e}_{11} \leq 4$ for $\mathbf{s}_{22}/\mathbf{s}_{11} = 1$. For the excess Gibbs energy, excess

enthalpy and excess volume over a range of parameter ratios, ($1 \leq \mathbf{s}_{22} / \mathbf{s}_{11} \leq 2$, $1 \leq \mathbf{e}_{22} / \mathbf{e}_{11} \leq 2$) the results showed that Eq.(2.42) is accurate in describing the excess properties.

For ternary mixtures, Fotouh and Shukla (1996a & b) tested the accuracy of Eq.(2.42) for three nonideal ternary model mixtures and a real ternary fluid mixture. For three nonideal model ternary mixtures, Fotouh and Shukla (1996a) used the same size parameters but difference energy parameters of the mixture components. The theoretical predictions compared well with simulation results for mixture density, internal energy, excess Gibbs free energy, excess volume and excess enthalpy. For the real ternary fluid mixtures ($N_2 / Ar / CH_4$), Fotouh and Shukla (1996b) compared the theoretical results with experimental data for mixture total volume, excess Gibbs energy and excess volume. The results showed that the modified first order perturbation theory, Eq.(2.42) is reliable and performed well for different pressures and compositions of the mixture. Fotouh and Shukla (1997b) also reported that for ternary fluid mixtures, comparisons of theoretical and simulation results for total and excess properties showed the good performance of Eq.(2.42) for all the energy and size parameter ratios of mixture components.

2.2.5 Perturbation Theory for Associating Fluids

--- Thermodynamic Perturbation Theory (TPT)

Wertheim (1984a & b; 1986a & 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 (1984a) proposed that the pair potential model between molecules 1 and 2 is:

$$\mathbf{f}(r, \mathbf{w}_1, \mathbf{w}_2) = \mathbf{f}_R(r, \mathbf{w}_1, \mathbf{w}_2) + \sum_A \sum_B \mathbf{f}_{AB}(r, \mathbf{w}_1, \mathbf{w}_2) \quad (2.49)$$

where r denotes the magnitude of the vector r connecting the centres of molecules 1 and 2, and $\mathbf{w}_1, \mathbf{w}_2$ denote the orientations of molecules 1 and 2 relative to vector r . The repulsive part of the potential, $\mathbf{f}_R(r, \mathbf{w}_1, \mathbf{w}_2)$, represents the interactions between two

hard cores. The hydrogen-bonding potential, $f_{AB}(r, \mathbf{w}_1, \mathbf{w}_2)$, is purely attractive, i.e., $f_{AB}(r, \mathbf{w}_1, \mathbf{w}_2) < 0$.

Using this model potential and using the system interacting with only the repulsive potential as a reference system, Wertheim developed a thermodynamic perturbation theory (TPT) for compounds with one or multiple association sites per molecule. The reference system was the hard-sphere system. The expression for the Helmholtz function A of N particles was obtained from (Wertheim, 1984b).

$$\frac{A - A_0}{NkT} = \ln X_a - \frac{X_a}{2} + \frac{1}{2} \quad (2.50)$$

where the subscript 0 denotes the reference system, $X_a = \frac{\mathbf{r}_0}{\mathbf{r}}$ is the mole fraction of molecules which are not bonded at site α , \mathbf{r} is the number density, \mathbf{r}_0 is the number density of monomers and must be determined in a self-consistent manner. The method to obtain \mathbf{r}_0 was given by Wertheim (1984b).

Wertheim (1987) 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 it against Monte Carlo simulation. Using Wertheim's theory, Chapman et al. (1990) and Huang and Radosz (1990) developed the Statistical-Associating-Fluid-Theory (SAFT) equation of state. Chang and Sandler (1994) proposed TPT-D1 and TPT-D2 theories. Sadus (1995) proposed the simplified Thermodynamic Perturbation Theory-Dimer (STPT-D) equation of state and extended (Sadus, 1996) STPT-D to hard-sphere chain mixtures with good results. More details about these equations of state will be discussed in Chapter 3.

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