

CHAPTER 8

SAFT Associating Fluids and Fluid Mixtures

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8.1 Introduction

While we could argue that the goals of modelling fluid phase equilibria have not changed greatly since the time of van der Waals, there is little doubt that the systems of interest have gradually increased in complexity; surfactants, polymers, hydrogen-bonding molecules such as water, and polyfunctional molecules such as amino acids and peptides are now routinely considered. The demand for effective, accurate theoretical tools grows constantly as more complex systems are considered and modelling is expected to play a more prominent role in the design of new products and processes. Thus, the need to develop a thermodynamic modelling framework that considers anisotropic association interactions (such as occur in hydrogen bonding fluids), molecular shape, and electrostatic interactions (Coulombic, dipolar, quadrupolar *etc.*) becomes increasingly acute. Wertheim's work in the 1980's on associating and polymeric fluids¹⁻⁴ and its implementation as an equation of state in the statistical associating fluid theory (SAFT) have constituted a major advancement towards a theoretical framework for modelling these complex fluids.

Associating systems present unique challenges to the determination of their thermodynamic properties. Short-ranged attractive directional interactions lead to aggregate and network formation and as a result the behaviour of associating fluids deviates from that seen in so-called simple fluids. To give but one example, if water molecules did not form hydrogen bonds, water would most likely be a gas at room temperature and pressure, much like methane, which has a very similar molecular mass (16 g mol^{-1} compared to 18 g mol^{-1} for water) but does not have a permanent dipole. If water did not hydrogen bond strongly, it would not exhibit the unusual density maximum seen in the liquid phase.⁵ The first attempts to model associating systems appeared as early as the 1900's and were carried out in the framework of chemical bonding by Dolezalek.⁶ Association between molecules was described as a chemical reaction and so the main drawback of the approach was that the aggregate species need to be specified a priori; while this is feasible in dimerizing fluids, and in models leading to infinite, linear-chain aggregates, branched and three-dimensional networks such as those formed in aqueous systems cannot be easily described. In contrast, in the theory of Wertheim an anisotropic intermolecular potential that incorporates short-ranged attractive interactions to form associated aggregates and networks is proposed; the different aggregate species are obtained as a result of this potential (*i.e.* they are a product of, rather than an input to, the theory), and in the limit of complete association the theory provides an accurate description of the thermodynamic properties of chain fluids.^{7,8}

In this chapter we provide some background on the development of Wertheim's theory of association and then review the main versions of the SAFT equation of state used in the current literature. Rather than focus on the systems that have been studied using the different versions, which was recently reviewed by Tan and co-authors,⁹ we have striven to provide a survey of the latest theoretical developments directed at enhancing the capability of the SAFT framework for the study of increasingly complex fluids.

8.2 Statistical Mechanical Theories of Association and Wertheim's Theory

Approaches to developing a statistical mechanical theory of associating fluids (specifically, hydrogen bonding) and fluids undergoing reaction date back at least to the seminal text of Hill.¹⁰ The modern theory of associating and reacting fluids begins with the work of Andersen,^{11,12} who developed a statistical mechanics approach for associating fluids using a graph-theoretical approach. Andersen's approach was quite general: he assumed that the potential between two molecules, $u(1,2)$, which can depend on both the position and orientation of molecules 1 and 2, has the form

$$u(1,2) = u_0(1,2) + u_{\text{HB}}(1,2), \quad (8.1)$$

where u_0 is the reference potential and u_{HB} is the hydrogen-bonding part of the potential. The hydrogen bonding part is non-zero only for a small range of relative positions (and orientations, if it is not spherically symmetric), and has a deep negative potential well consistent with hydrogen bonding. The key assumed property of the potential in Andersen's theory is *saturation at the dimer level*. That is, the reference potential u_0 contains an infinitely repulsive short-ranged part (*i.e.* a hard-sphere core) that prevents two molecules from both bonding simultaneously to a third molecule. If

$$u_{\text{HB}}(1, 3) \neq 0 \text{ and } u_{\text{HB}}(2, 3) \neq 0, \quad (8.2)$$

then the distance between molecules 1 and 2, r_{12} , is less than the hard-core radius for the molecules and $u_0(1,2) = \infty$. The Mayer f -function, given by

$$f(1, 2) = \exp[-u(1, 2)/k_{\text{B}}T] - 1, \quad (8.3)$$

where T is temperature and k_{B} is Boltzmann's constant, can then be written as

$$f(1, 2) = f_0(1, 2) + f_{\text{HB}}(1, 2), \quad (8.4)$$

where

$$\begin{aligned} f_0(1, 2) &= \exp[-u_0(1, 2)/k_{\text{B}}T] - 1, \\ f_{\text{HB}}(1, 2) &= \exp[-u(1, 2)/k_{\text{B}}T] - \exp[-u_0(1, 2)/k_{\text{B}}T]. \end{aligned} \quad (8.5)$$

When eq 8.3 is substituted into the cluster expansion for the distribution functions in the fluid, and simplified through cancellations in graphs by taking into account eq 8.2, the result is a formal graphical expansion for the pair distribution function in terms of renormalized hydrogen-bond f -functions. This concept of saturation at the dimer level is a key element in Wertheim's theory, discussed below.

Chandler and Pratt¹³ developed a similar approach based on graph theory to study systems undergoing chemical reaction. The formal theory is quite complex, but the application to a simple bimolecular reaction, *e.g.* the chemical equilibrium between nitrogen dioxide and di-nitrogen tetroxide ($\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$), illustrates the results obtained. For this reaction, Chandler and Pratt illustrated their results by calculating the solvent effect on the chemical equilibrium constant,

$$K = \rho_{\text{NO}_2}^2 / \rho_{\text{N}_2\text{O}_4}, \quad (8.6)$$

where ρ_{NO_2} and $\rho_{\text{N}_2\text{O}_4}$ are the number densities of the product and reactant, respectively. Under simplifying assumptions, the value of K in a

liquid solvent versus its value in the ideal gas state at the same temperature K_0 is given by

$$K_0/K = \int y_{\text{N}_2\text{O}_4}(r) b_{\text{N}_2\text{O}_4}(r) d\mathbf{r} / \int b_{\text{N}_2\text{O}_4}(r) d\mathbf{r}, \quad (8.7)$$

where $y_{\text{N}_2\text{O}_4}(r)$ is the cavity distribution function for N_2O_4 and $b_{\text{N}_2\text{O}_4}(r)$ is a bonding Boltzmann factor. For the case that the bond is highly localized, so that $b_{\text{N}_2\text{O}_4}(r)$ can be modelled as a Dirac delta function that is non-zero only at the bond length L , eq 8.7 simplifies to

$$K_0/K = y_{\text{N}_2\text{O}_4}(r = L). \quad (8.8)$$

We note that the characterization of the degree of reaction in terms of the cavity distribution function is also one of the results of Wertheim's theory of association.

Returning to the concept of steric saturation, Høye and Olaussen¹⁴ implemented Andersen's idea^{11,12} for a specific model. They considered a fluid consisting of a binary mixture of hard spheres, all of the same diameter σ , so that the like intermolecular potentials are given by

$$u_{11}(r) = u_{22}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}. \quad (8.9)$$

while the unlike or cross intermolecular interaction has a deep attractive region located inside $\sigma/2$. That is,

$$u_{12}(r) = \begin{cases} \ll 0 & r < \sigma/2 \\ 0 & r > \sigma/2 \end{cases}. \quad (8.10)$$

The functional form inside $\sigma/2$ was not specified; however, it is assumed to be many $k_B T$, as would be expected for a chemical bond or strong association. The Høye-Olaussen model is a realization of the conditions given by eqs 8.1 and 8.2, so that Andersen's analysis can be applied. Because of the choice of spherically symmetric potentials, the analysis is considerably simplified, and Høye and Olaussen¹⁴ explicitly derived formulae for the equilibrium constant.

In the spirit of the Høye and Olaussen model, Cummings and Stell¹⁵ later considered an equimolar mixture of hard spheres of type A (species 1) and B (species 2), with potentials

$$u_{11}(r) = u_{22}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}, \quad (8.11)$$

and a cross-interaction that has a deep attractive region located inside $\sigma/2$ of the form,

$$u_{12}(r) = \begin{cases} \varepsilon_1 & r < L - w/2 \\ -\varepsilon_2 & L - w/2 < r < L + w/2 \\ \varepsilon_1 & L + w/2 < r < \sigma \\ 0 & r < \sigma \end{cases} \quad (8.12)$$

centred at the distance L and of width w . Such a model system is capable of forming dimers (*i.e.* the reaction $A + B \rightleftharpoons AB$ is possible, and similar to the Høye and Olaussen model, the reaction/association saturates at the level of dimers due to excluded volume of A and B). By considering the limits $\varepsilon_1 \rightarrow \infty$, $\varepsilon_2 \rightarrow \infty$ and $w \rightarrow 0$, while holding the integral of the corresponding Mayer f -function constant, Cummings and Stell defined a model in which the AB interaction becomes a sticky shell inside the hard core located at position $r = L$. In addition to steric saturation at the level of dimers, the model can be solved analytically in the Percus-Yevick¹⁶ (PY) approximation, making it possible to calculate the impact of temperature and density on the degree of association/reaction. Cummings and Stell went on to extend the model to homogeneous association ($2A \rightleftharpoons A_2$),¹⁷ to reactions within a solvent,¹⁸ as well as a near-critical solvent.¹⁹ A number of interesting results come from this analysis – in particular, the solution of the PY approximation for homogeneous association, in the limit of complete association, recovers the analytic solution of the reference interaction site model (RISM)^{20,21} for homonuclear diatomics.

Following these works, in a series of seminal papers, Wertheim¹⁻⁴ performed a general analysis of the statistical mechanics of fluids that could associate into dimers, as well as (in the general case) higher-order multimers. By using a graphical expansion, Wertheim's approach is similar in spirit to that of Andersen^{11,12} and Chandler and Pratt,¹³ in that cluster expansions are manipulated in view of simplifications arising from steric considerations. Wertheim's theory is developed within the context of a specific model for association, specifically

$$u(1,2) = u_0(1,2) + \sum_{\alpha} \sum_{\beta} \phi_{\alpha\beta}(|\mathbf{r}_2 + \mathbf{d}_{\beta}(\Omega_2) - \mathbf{r}_1 - \mathbf{d}_{\alpha}(\Omega_1)|), \quad (8.13)$$

where $\mathbf{r}_1, \mathbf{r}_2$ are the centres of mass and Ω_1, Ω_2 are the orientations of particles 1 and 2, $\mathbf{d}_{\alpha}, \mathbf{d}_{\beta}$ are vectors from the molecular centres of particles 1,2 to the centres of the association sites α, β respectively, u_0 is a reference potential (typically, a hard-sphere potential with hard-sphere diameter σ) and $\phi_{\alpha\beta}$ is the association potential between site α on molecule 1 and site β on molecule 2. The simplest model for association, assuming sites α and β to be identical, is of the form

$$\phi(x) = \begin{cases} \ll 0 & x < a \\ = 0 & x > a \end{cases}, \quad x = |\mathbf{r}_2 + \mathbf{d}(\Omega_2) - \mathbf{r}_1 - \mathbf{d}(\Omega_1)|, \quad (8.14)$$

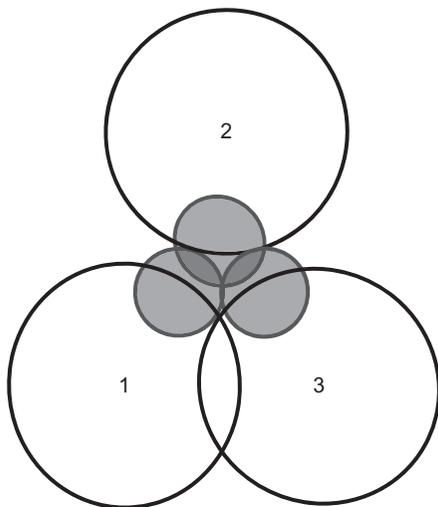


Figure 8.1 Illustration of steric inhibition of bonding beyond the dimer level. The black lines represent the boundary of the hard-core potential $u_0(i,j)$ while the small grey spheres represent the association sites. If molecules 1 and 2 are in a bonded state (overlap of the association sites), the site of molecule 3 cannot overlap that of either molecule 1 or molecule 2 without experiencing a hard sphere overlap with molecule 1 or molecule 2. Thus, three-molecule bonding is forbidden.

where, to ensure steric saturation, $(\sigma - a)/2 < d = |\mathbf{d}| < \sigma/2$, which is illustrated in Figure 8.1. The case of a short-ranged attractive associating interaction located at the edge of the hard core follows when $a = \sigma$. In the first paper in the series,¹ for the case of a single association site, Wertheim derived the Mayer cluster expansions for thermodynamic properties in terms of a singlet density ρ and monomer density ρ_0 . This includes the Helmholtz energy A , and specifically the association contribution, $A^{\text{Assoc.}}$. In the second paper in the series,² Wertheim derived both perturbation theory and integral equation approximations to the full expressions obtained using the formalism developed in the first paper. In particular, a simple first-order perturbation theory approach yields

$$\frac{A^{\text{Assoc.}}}{k_B T} = \frac{A - A_0}{k_B T} = N \left(\ln X - \frac{X}{2} + \frac{1}{2} \right), \quad \mathbf{X} = \frac{\rho_0}{\rho}, \quad (8.15)$$

where N is the total number of monomeric units, whether bonded or not, and X is the fraction of segments that are non-bonded, determined from

$$\rho(1) = \rho_0(1) + \rho_0(1) \int g_0(12) f_A(12) \rho_0(2) d2, \quad (8.16)$$

where $g_0(12)$ is the pair distribution of the reference fluid, $f_A(12)$ is the Mayer f -function of the association interaction $\phi(x)$, the integral is over all possible positions and orientations of molecule 2 and the dependence of ρ and ρ_0 on position and orientation corresponds to the general case of a spatially inhomogeneous fluid. For the spatially uniform case, eq 8.16 becomes

$$\rho = \rho_0 + \rho_0^2 \int g_0(12)f_A(12) d2 \cong \rho_0 + \rho_0^2 g_0(\sigma) \exp(\varepsilon_{\text{HB}}/k_{\text{B}}T)K. \quad (8.17)$$

The second approximate expression follows when the association potential $\phi(x)$ is a square well of depth ε_{HB} and when, assuming that the bonding region is limited to a small range of distances near the hard-sphere diameter (*i.e.* $a = \sigma$), we invoke

$$\int g_0(12) d2 \cong g_0(\sigma) \int_{f_A \neq 0} d2 = g_0(\sigma)K, K = \int_{f_A \neq 0} d2, \quad (8.18)$$

so that K is the volume available for bonding. From the definition of X in eq 8.15, eq 8.17 becomes

$$\begin{aligned} \frac{\rho_0}{X} &= \rho_0 + \rho_0^2 g_0(\sigma) \exp(\varepsilon_{\text{HB}}/k_{\text{B}}T)K \Rightarrow X \\ &= \frac{1}{1 + \rho_0 g_0(\sigma) \exp(\varepsilon_{\text{HB}}/k_{\text{B}}T)K}. \end{aligned} \quad (8.19)$$

In the subsequent papers in the series, Wertheim extended his analysis to multiple association sites³ and to systems undergoing polymerization.⁴ His key contribution was to show that it is possible to obtain the properties of an associating or chain fluid based on knowledge of the thermodynamic properties (the Helmholtz energy and structure) of the monomer fluid. This is the basis of the now well-known Wertheim thermodynamic perturbation theory, and in turn, the basis of all SAFT equations of state. Interestingly, in this series of four papers, Wertheim did not present a single calculated result or any numerical tests of his proposed theories.

In the following years Gubbins and co-workers extended Wertheim's theory to mixtures of spheres and chain molecules of given length, by considering the limit of complete association and replacing the association bonds with covalent, chain-forming bonds. These studies culminated in a paper presented in Fluid Phase Equilibria titled "SAFT: equation of state solution model for associating fluids".²² In this and subsequent works, Gubbins and his co-workers presented Wertheim's key result in an equation of state form that could be used to model fluid-phase behaviour.²²⁻²⁴ The SAFT approach has proven to be extremely successful for modelling associating and chain-like fluids, including polymers. Today, it is arguably considered the state-of-the-art method for modelling the thermodynamic properties and phase behaviour of complex fluids and has found application from small molecules such as xenon, carbon dioxide and

water, through to complex copolymers, and more recently, room temperature ionic liquids and amino acids.

8.3 SAFT Equations of State

In the SAFT approach, molecules are modelled as associating chains formed of bonded spherical segments (referred to also as monomers), with short ranged attractive sites, of the form described in the previous section, used as appropriate to mediate association interactions (*cf.* Figure 8.2). The Helmholtz energy is written as the sum of four separate contributions:^{22,23}

$$\frac{A}{Nk_B T} = \frac{A^{\text{Ideal}}}{Nk_B T} + \frac{A^{\text{Mono.}}}{Nk_B T} + \frac{A^{\text{Chain}}}{Nk_B T} + \frac{A^{\text{Assoc.}}}{Nk_B T}, \quad (8.20)$$

where A^{Ideal} is the ideal free energy, $A^{\text{Mono.}}$ the contribution to the free energy due to the monomer-monomer repulsion and dispersion interactions, A^{Chain} the

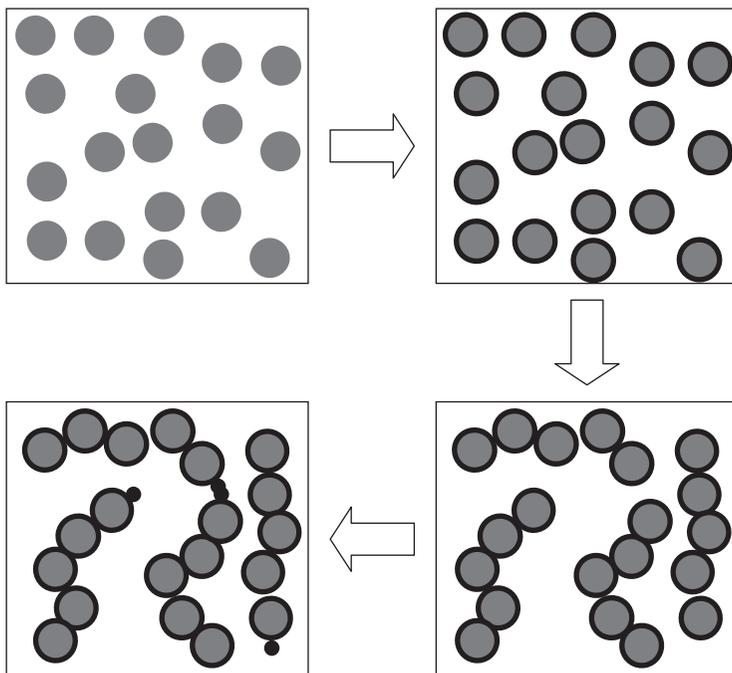


Figure 8.2 Schematic illustration of the perturbation scheme for a fluid within the SAFT framework. The reference fluid consists of spherical hard segments to which dispersion forces are added and chains can be formed through covalent bonds. Finally association sites allow for hydrogen bonding-like interactions. Adapted from Fu and Sandler and reprinted with permission of *Ind. Eng. Chem. Res.*²⁵

contribution due to the formation of bonds between monomeric segments, and $A^{\text{Assoc.}}$ the contribution due to association.

We consider each of the terms in eq 8.20 in turn beginning with the free energy of an ideal gas, which is given by

$$\frac{A^{\text{Ideal}}}{Nk_{\text{B}}T} = \ln(\rho\Lambda^3) - 1, \quad (8.21)$$

where $\rho = N/V$ is the number density of chain molecules, V the volume of the system, and Λ the thermal de Broglie wavelength incorporating the kinetic (translational, rotational, and vibrational) contributions to the partition function of the molecule. Since the ideal term is separated out, the remaining terms are noted as residual free energies. The contribution to the Helmholtz energy due to the monomer-monomer interactions can be written as,²⁵

$$\frac{A^{\text{Mono.}}}{Nk_{\text{B}}T} = m \frac{A^{\text{Mono.}}}{N_s k_{\text{B}}T} = ma^{\text{Mono.}}, \quad (8.22)$$

where N_s is the total number of monomer segments, m is the number of segments per molecule and $a^{\text{Mono.}}$ the Helmholtz energy per monomer segment. The chain contribution is given by

$$\frac{A^{\text{Chain}}}{Nk_{\text{B}}T} = -(m-1) \ln y^{\text{Mono.}}(\sigma), \quad (8.23)$$

where $y^{\text{Mono.}}(\sigma)$ is the cavity distribution function of the monomer fluid and is related to the radial distribution function $g^{\text{Mono.}}(\sigma)$ by $y^{\text{Mono.}}(\sigma) = g^{\text{Mono.}}(\sigma) \exp[u^{\text{Mono.}}(r)/k_{\text{B}}T]$, where $u^{\text{Mono.}}(r)$ is the pair potential between tangentially bonded monomers with σ the monomer segment diameter.

If appropriate, association interactions are included in the model and described via short-range (square-well) bonding sites. The contribution due to association for s sites on a molecule is then given by:²⁶

$$\frac{A^{\text{Assoc.}}}{Nk_{\text{B}}T} = \sum_{a=1}^s \left(\ln X_a - \frac{X_a}{2} \right) + \frac{s}{2}, \quad (8.24)$$

where the sum is over all s sites of type a on a molecule, and X_a is the fraction of molecules not bonded at site a , which can be obtained from the mass-action equation:

$$X_a = \frac{1}{1 + \sum_{b=1}^s \rho X_b \Delta_{a,b}}. \quad (8.25)$$

The function $\Delta_{a,b}$, which characterizes the association between site a and site b on different molecules, can be written as

$$\Delta_{a,b} = K_{a,b} f_{a,b} g^{\text{Mono.}}(\sigma), \quad (8.26)$$

where $f_{a,b} = \exp\left(\frac{\epsilon_{a,b}^{\text{HB}}}{k_{\text{B}}T}\right) - 1$ is the Mayer f -function of the $a-b$ site-site bonding interaction of potential depth $\epsilon_{a,b}^{\text{HB}}$ and bonding volume $K_{a,b}$.²⁷

In the original SAFT approach^{22,23} chains of Lennard-Jones (LJ) monomer segments were modelled using the equation of state for argon developed by Twu and co-workers,²⁸ and later the expression proposed by Cotterman *et al.*²⁹ In these approaches, the radial distribution function in the chain and association terms is evaluated at the hard-sphere contact instead of at contact for the true monomer LJ fluid. An interesting comment on the impact of this approximation can be found in reference 30.

Since the SAFT equation of state has a firm basis in statistical mechanical perturbation theory for well-defined molecular models, systematic improvement (*e.g.* by improving expressions for monomer free energy and structure) and extension of the theory (*e.g.* by considering new monomer fluids, bonding schemes and polar interactions) is possible by direct comparison of the theoretical predictions with computer simulation results for the same molecular model. At each stage in the development of the SAFT theory by Gubbins and co-workers, the model was carefully verified against molecular simulation data for associating spheres, mixtures of associating spheres and non-associating chains.^{24,27,31,32} Due to its role in improving and validating the theory, the importance of having an underlying molecular model (in contrast to traditional engineering equations of state) cannot be overemphasized. In those cases where SAFT does not compare well with simulation, the theory can be improved through the use of better reference systems or higher-order perturbation theory. In comparing with experimental data, it is important to be aware of the errors inherent in the theory, as revealed by comparison with computer simulation results, before attempting to estimate intermolecular model parameters. This invaluable advantage over empirical equations of state is one of the keys to the success of the SAFT equation and has led to many extensions and variations of the original SAFT expressions. These essentially correspond to different choices for the monomer fluid, and different theoretical approaches to the calculation of its the free energy and structure. In what follows we describe the main SAFT based-approaches found in the literature.

8.3.1 SAFT-HS and SAFT-HR

The simplest SAFT approach, usually referred to as SAFT-HS, describes associating chains of hard-sphere segments with the long-range attractive interactions described at the van der Waals mean-field level.^{26,27} The Helmholtz

energy per monomer in this case is described by,

$$a^{\text{Mono.}} = a^{\text{HS}} - \frac{\alpha_{\text{vdw}}\rho_s}{k_{\text{B}}T}, \quad (8.27)$$

where a^{HS} is the Helmholtz energy of the hard-sphere fluid, ρ_s is the number density of monomer segments and α_{vdw} the attractive van der Waals constant characterising the dispersion interactions. For pure fluids a^{HS} is determined from the expression due to Carnahan and Starling,³³ with the corresponding hard-sphere radial distribution function evaluated at contact used in the chain and association terms. This simple approach is particularly suited to the study of strongly associating fluids, such as water^{34,35} and hydrogen fluoride,³⁶ where hydrogen-bonding interactions mask the simplified description of the weaker dispersion forces.^{34–38}

The most extensively applied version of SAFT, due to Huang and Radosz^{39,40} and commonly denoted SAFT-HR, corresponds to a similar level of theory. In SAFT-HR the dispersion interactions are described through the expression of Chen and Kreglewski,⁴¹ which was fitted to argon physical-property data, with the hard-sphere radial distribution function used in the chain and association terms. SAFT-HR has been applied to study the phase behaviour in a wide range of fluid systems and polymers.^{42–60} Comparisons with SAFT-HR are often provided when a new version of SAFT is developed to demonstrate the improved ability of a new equation; however, it should be noted that when comparisons are made, it is probably more relevant to refer to one of the more recent “second-generation” SAFT equations described below.

8.3.2 Soft-SAFT

Johnson *et al.*'s⁶¹ proposed equation of state to treat LJ chains in which the free energy of the chain fluid was obtained using the free energy and radial distribution function of a monomer LJ fluid, the expressions for which were fitted to simulation data.^{61,62} This approach was extended to mixtures by Ghonasgi *et al.*⁶³ and Blas and Vega,⁶⁴ who referred to the approach as the soft-SAFT equation of state.

The equation of Johnson *et al.*⁶¹ is one of most accurate available for LJ chains, since it is heavily based on computer simulation data. Equally the soft-SAFT equation is very accurate for modelling mixtures of associating LJ fluids. In their extension to mixtures Blas and Vega performed extensive simulations on model homo- and heteronuclear fluids and their mixtures to test the soft-SAFT approach, before application of the theory to real fluids in a subsequent paper was undertaken by the authors.⁶⁵ Soft-SAFT has been applied to the study of alkanes and their binary and ternary mixtures,^{65–75} perfluoroalkanes,^{76–82} alcohols,^{71,83} carbon dioxide,^{70,71,83–87} polymers,^{88,89} and more recently room temperature ionic liquids.^{90,91}

8.3.3 SAFT-VR

SAFT was extended to describe associating chain molecules formed from hard-core monomers with attractive potentials of variable range in the SAFT-VR equation.^{92,93} Although, in the original publication, several potentials of variable range were studied (square-well, LJ, Mie and Yukawa), typically a square-well potential is implemented in the modelling of real fluids. In the SAFT-VR approach the monomer fluid is therefore usually a square-well (SW) fluid, with the monomer Helmholtz energy given by,

$$a^M = a^{\text{HS}} + \frac{a_1}{k_B T} + \frac{a_2}{(k_B T)^2}, \quad (8.28)$$

where a_1 and a_2 are the first two perturbative terms associated with the attractive energy. The radial distribution function of the square-well monomer fluid, which is obtained analytically using a self-consistent method for the pressure from the Clausius virial theorem and the density derivative of the Helmholtz energy, is used in the chain and association terms. The SAFT-VR equation has been extensively tested against simulation data^{93–98} and successfully used to describe the phase equilibria of a wide range of industrially important systems; for example, alkanes of low molar mass through to simple polymers,^{92,99–103} and their binary mixtures,^{103–116} perfluoroalkanes,^{117–121} alcohols,^{83,122,123} water,^{35,124,125} refrigerant systems,^{126–129} and carbon dioxide,^{111,114,130–135} have all been studied.

While the application of the SAFT-VR equation has primarily focused on a square-well potential, recent work has looked at the family of $m-n$ potentials.¹³⁶ The SAFT-VR Mie approach of Lafitte *et al.*¹³⁶ when compared to the original SW-based SAFT-VR equation, PC-SAFT (discussed below) and a LJ-based SAFT-VR, was found to provide a more accurate description of both the phase behaviour and derivative properties, such as condensed phase isothermal compressibility and speed-of-sound, of alkanes, alcohols and their mixtures, suggesting that the variable ranged repulsive term is needed to describe derivative properties.^{136–138}

In related work, a modified SAFT-VR equation for square well potentials termed SAFT1 has been proposed in which a truncation term is added to the monomer free energy expansion (eq 8.28) to account for higher-order terms.¹³⁹ SAFT1 has been successfully used to study both simple fluids such as alkanes,^{140,141} alcohols,¹⁴² polymers,^{143–145} and more recently room temperature as well as ionic liquids.¹⁴⁶

8.3.4 PC-SAFT

In contrast to the other popular versions of the SAFT equation, the PC-SAFT^{147,148} approach considers a hard-chain, rather than a hard-sphere, as the reference system for the application of standard high-temperature perturbation theory to obtain the dispersion contribution. Thus the Helmholtz

energy is written,

$$\frac{A}{Nk_B T} = \frac{A^{\text{Ideal}}}{Nk_B T} + \frac{A^{\text{HC}}}{Nk_B T} + \frac{A^{\text{PC}}}{Nk_B T} + \frac{A^{\text{Assoc.}}}{Nk_B T}, \quad (8.29)$$

where A^{HC} corresponds to the free energy of a reference hard-sphere-chain fluid, given by equation 8.23, *i.e.* in the usual form of Wertheim's theory where the monomer fluid at this point is a fluid of hard-spheres, and A^{PC} describes the chain perturbation contribution, which is usually taken to second-order. A^{PC} is based on an earlier theory for square-well chain molecules¹⁴⁹ and is determined from a Taylor series expansion fitted to the vapour-liquid phase envelopes of pure alkanes.¹⁴⁷ This fitting greatly enhances the accuracy of the approach in comparison with experimental systems, but unfortunately means that it is no longer straight forward to define the underlying intermolecular potential of the model and so comparison against computer simulations cannot be used in the assessment of further theoretical developments. The association contribution used in PC-SAFT follows directly from Wertheim's theory as given by eqs 8.24 to 8.26.

In the original presentation of PC-SAFT parameters were correlated against vapour pressure and saturated liquid density data for 78 non-associating pure fluids and shown to work well in the description of mixture systems. Subsequently the equation has been successfully applied to the study of a wide range of industrially important fluids from simple binary mixtures involving hydrocarbons^{150–173} to associating fluids,^{149,162,171,174–181} pharmaceuticals,¹⁸² and asphaltenes,^{183–187} and, in particular, polymer systems.^{88,188–215}

In related work a simplified version of the PC-SAFT equation of state, denoted sPC-SAFT has been developed by von Solms and co-workers²¹⁶ in an effort to reduce the complexity of the original equation when studying mixture systems. While the ideal and dispersion contributions to the free energy remain unchanged from those of the original PC-SAFT equation, the hard chain is simplified through the use of an average segment diameter and the use of the Carnahan-Starling expressions for the free energy and radial distribution function of a pure component hard-sphere system. The assumption that all of the segments in the mixture have the same diameter in turn simplifies the calculation of the association contribution. The sPC-SAFT equation has been successfully used to study both simple fluids^{217–221} and a wide range of polymer systems.^{191,192,196,199,207,222–225}

8.3.5 Summary

Comparisons between the different versions of SAFT are difficult in that many factors contribute to the observed agreement or disagreement with experimental data. For example, the type of thermodynamic data and the range of thermodynamic conditions used in the parameter optimization procedure must be consistent for a direct comparison and unfortunately such information is not always clearly described in the literature. A true comparison between the different versions of SAFT is therefore only meaningful if a

direct comparison between the different versions of SAFT is carried out within a given study. While there have been such comparisons with SAFT-HR, a limited number of studies have compared the *second-generation* versions of SAFT,^{83,88,122,175,181,207,226} from which it is clear that any one version is not superior over the others in general terms. The choice of one version of SAFT over another is often more “philosophical” (versions like SAFT-VR keep a more formal link with the molecular model, while PC-SAFT provides higher accuracy in systems where dispersion dominates), than objective in terms of overall performance and capability. A more interesting point to note here, is the versatility of the SAFT method as highlighted by the examples in the previous sections, both in terms of the accuracy of prediction of the phase behaviour of fluids and fluid mixtures ranging from very simple systems to highly complex ones, and in terms of its firm molecular basis, which allows for a systematic improvement of the theoretical approximations (the subject of the following sections). In this respect, the method constitutes a major advance over traditional cubic engineering equations.

8.4 Extensions of the SAFT Approach

8.4.1 Modelling the Critical Region

As with all equations of state that are analytical in the free energy, the SAFT equation does not accurately capture the behaviour of fluids in the critical region. In the vicinity of the critical point the behaviour of a fluid is strongly influenced by long-range fluctuations in the density that act to lower the critical point and flatten the vapour-liquid coexistence curve. Near the critical point, the thermodynamic behaviour is described by non-analytic scaling laws, with universal scaling functions and universal critical exponents,²²⁷ while the SAFT equation as a mean-field theory exhibits classical critical exponents, leading to a parabolic coexistence curve in the critical region. For a review of the thermodynamic behaviour of fluids in the critical region the reader is referred to Chapter 10.

In order to study critical lines and global fluid phase diagrams, one method to overcome the theoretical over prediction of the critical point in mean-field approaches is to re-scale the model parameters to the experimental critical temperature and pressure; however, agreement at the critical point comes at the cost of poorer agreement at low temperatures and pressures, as this approach has the effect of *shifting* the coexistence curves to lower temperatures and pressures, without changing the shape of the vapour pressure curve, and results in poor descriptions of the coexisting densities. An accurate thermodynamic description of the whole fluid phase diagram is possible through the use of so-called crossover treatments that correct the classical equation of state to satisfy the asymptotic power laws near the critical point and incorporate a *crossover* to regular thermodynamic behaviour far from the critical point, where the effects of critical fluctuations become negligible.

The modern theory of critical phenomena is based on renormalization-group techniques that yield asymptotic scaling laws with critical exponents and critical-amplitude ratios, which for systems with short-range interactions depend on the dimensionality of the system and the number of components of the order parameter.²²⁹ Fluids are believed to belong to the universality class of three-dimensional Ising-like systems, *i.e.* systems with a scalar order parameter; however, the validity of the asymptotic scaling laws for fluids near the critical point is restricted to a rather small range of temperatures and densities.²³⁰ Therefore several attempts to develop a theory that accurately treats the crossover from critical behaviour asymptotically close to the critical point to classical behaviour sufficiently far from the critical point have been made by a number of investigators; here we naturally focus on those applied to the SAFT family of equations. In particular, the approach of White,^{231–235} as implemented by Prausnitz and co-workers,^{236–239} and that of Kiselev,^{240–242} have been the most widely used and applied to many of the SAFT equations described in section 8.3. Although most crossover-SAFT studies to date have focused on pure fluids, both approaches have been extended to mixtures using the so called iso-morphism assumption, which assumes that the thermodynamic potential for a mixture has the same universal form as that for a pure fluid when an appropriate isomorphic variable is chosen. While the density of the system would be a natural choice to replace the density of the pure fluid as the order parameter, the isomorphism approximation requires the evaluation of the chemical potentials of each component as independent variables, rather than the mole fraction typically used in equations of state. A general procedure for incorporating the scaling laws into any classical equation of state for mixtures with the mole fractions as independent variables was proposed by Kiselev and Friend²⁴² and adopted by Cai and Prausnitz in the application of the method of White to mixtures.²⁴³

White's approach, based on the work of Wilson,²⁴⁴ incorporates density fluctuations in the critical region using the phase-space cell approximation and uses a recursive procedure to modify the free energy for non-uniform fluids, thereby accounting for the fluctuations in density. The interaction potential is divided into a reference contribution u^{ref} , due mainly to the repulsive interactions, and a perturbative contribution u^{p} , due mainly to the attractive interactions. Given the short-range nature of the repulsive term, the renormalization is only applied to the attractive part of the potential, which is then divided into short-wavelength and long-wavelength contributions. The effect of the short-wavelength contributions less than a given cut off length L is calculated using mean-field theory, while the contributions due to the long-wavelength fluctuations are taken into account through the phase-space cell approximation in a set of recursive relations that successively take into account the contribution of longer and longer wavelength density fluctuations. The Helmholtz energy density $a_n(\rho)$ for a system at a density ρ can be described in a recursive manner as:

$$a_n(\rho) = a_{n-1}(\rho) + da_n(\rho) \quad (8.30)$$

and accounts for the long-wavelength fluctuations through the following relations:

$$da_n(\rho) = -K_n \ln \frac{\Omega_n^s(\rho)}{\Omega_n^l(\rho)}, \quad 0 \leq \rho \leq \frac{\rho_{\max}}{2}, \quad (8.31)$$

$$da_n(\rho) = -0, \quad \frac{\rho_{\max}}{2} \leq \rho \leq \rho_{\max}. \quad (8.32)$$

Here Ω^s and Ω^l are the density fluctuations for the short-range and long-range attraction, respectively, ρ_{\max} the maximum possible molecular density, and K_n is defined by

$$K_n = k_B T / 2^{3n} L^3. \quad (8.33)$$

The density fluctuations are calculated through evaluation of the following integral,

$$\Omega_n^s(\rho) = \int_0^\rho \exp \left[\frac{-G_n^\beta(\rho, x)}{K_n} \right] dx, \quad (8.34)$$

where

$$G_n^\beta(\rho, x) = \frac{\bar{f}_n^\beta(\rho + x) + 2\bar{f}_n^\beta(\rho) - \bar{f}_n^\beta(\rho - x)}{2} \quad (8.35)$$

and β refers to both the short (*s*) and long (*l*) range attraction and G^β depends on the function \bar{f} as

$$\bar{f}_n^l(\rho) = f_{n-1}(\rho) + \alpha(m\rho)^2, \quad (8.36)$$

$$\bar{f}_n^s(\rho) = f_{n-1}(\rho) + \alpha(m\rho)^2 \frac{\phi w^2}{2^{2n+1} L^2}, \quad (8.37)$$

where ϕ is an adjustable parameter, α is the interaction volume, and w represents the range of the attractive potential, defined as

$$w^2 = -\frac{1}{3\alpha} \int r^2 u^p(r) dr. \quad (8.38)$$

Vega and co-workers have applied the method of White to the soft-SAFT equation^{68,71,74,245} to study the vapour-liquid equilibrium and derivative properties of the *n*-alkanes, carbon dioxide and 1-alkanols and their mixtures. The approach has also been combined with the PC-SAFT equation by Fu

*et al.*¹⁵⁸ and by Bymaster and co-workers²⁴⁶ to study the vapour-liquid equilibria of the alkanes, and by Mi *et al.*^{247–252} who have considered several SAFT-like equations.^{247–252}

The advantages of this method are that only a small number of additional parameters are needed (between 2 and 3) and in principle the crossover treatment can be applied without altering the original SAFT molecular parameters; however, in practice such an approach is rarely taken, and the SAFT and crossover parameters are more commonly simultaneously fitted to experimental data in order to obtain accurate agreement with experiment both near to and far from the critical region. As discussed by Bymaster and co-workers,²⁴⁶ one or both of the additional crossover parameters ϕ and L can be fitted or fixed depending upon the implementation of White's method. Llovell and co-workers⁶⁸ were the first to use both ϕ and L as adjustable parameters in their application of White's method to the soft-SAFT equation and a new set of parameters were proposed. Subsequently, Bymaster and co-workers²⁴⁶ found that good results could be obtained using the soft-SAFT equation without altering the original SAFT parameters, while in the case of the PC-SAFT equation of state a soft additional fitted parameter (beyond ϕ and L) is needed in order to describe the critical region of longer chain molecules precisely; an effect most likely due to the fitted nature of the dispersion potential in the PC-SAFT equation. Bymaster *et al.*²⁴⁶ also noted that while Fu and co-workers¹⁵⁸ fixed both ϕ and L they made several changes to the implementation of White's method. A drawback of White's method is that it can only be solved numerically and so does not lead to a closed-form expression for the equation of state.

The approach of Kiselev, based on the work of Sengers and co-workers^{253–255} and Kiselev and co-workers,^{240–242} utilizes a renormalized Landau expansion that smoothly transforms the classical Helmholtz energy density into an equation that incorporates the fluctuation-induced singular scaling laws near the critical point, and reduces to the classical expression far from the critical point. The Helmholtz energy density is separated into ideal and residual terms, and the crossover function applied to the critical part of the Helmholtz energy $\Delta a(\Delta T, \Delta v)$, where $\Delta a(\Delta T, \Delta v) = a(T, v) - a_{\text{bg}}(T, v)$ and the background contribution $a_{\text{bg}}(T, v)$ is expressed as,

$$a_{\text{bg}}(T, v) = -\Delta v \bar{P}_0(T) + a_0^{\text{res}}(T, v) + a_0(T). \quad (8.39)$$

More explicitly,^{240–242}

$$\Delta a(\Delta T, \Delta v) = a^{\text{res}}(\Delta T, \Delta v) - a_0^{\text{res}}(\Delta T) - \ln(\Delta v + 1) + \Delta v \bar{P}_0(\Delta T). \quad (8.40)$$

In eqs 8.39 and 8.40 $\Delta T = T/T_{0c} - 1$ and $\Delta v = v/v_{0c} - 1$ are dimensionless distances from the calculated classical critical temperature (T_{0c}) and classical critical molar volume (v_{0c}), $a_0(T)$ is the dimensionless temperature-dependent ideal-gas term, and $\bar{P}_0(T) = P(T, v_{0c})v_{0c}/RT$ and $a_0^{\text{res}}(T, v)$ are the dimensionless pressure and residual Helmholtz energy along the critical isochore, respectively. The ΔT and Δv are then replaced with the renormalized values in

the critical part of the free energy, using

$$\bar{\tau} = \tau Y^{-\alpha/2\Delta_1} + (1 + \tau)\Delta\tau_c Y^{2(2-\alpha)/3\Delta_1} \quad (8.41)$$

and

$$\Delta\bar{\varphi} = \Delta\varphi Y^{(\gamma-2\beta)/4\Delta_1} + (1 + \Delta\varphi)\Delta v_c Y^{(2-\alpha)/2\Delta_1}, \quad (8.42)$$

so that $\Delta T \rightarrow \bar{\tau}$ and $\Delta v \rightarrow \Delta\bar{\varphi}$ in eq 8.40, where the superscripts correspond to the critical exponents (see Table 8.1), $\tau = T/T_c - 1$ is the dimensionless deviation of the temperature from the real critical temperature T_c , $\Delta\varphi = V_m/V_{m,c} - 1$ is the dimensionless deviation of the molar volume from the real critical molar volume $V_{m,c}$, and $\Delta\tau_c = \Delta T_c/T_{0c} = (T_c - T_{0c})/T_{0c}$ and $\Delta V_{m,c} = \Delta V_{m,c}/V_{m,0c} = (V_{m,c} - V_{m,0c})/V_{m,0c}$ are the dimensionless shifts of the critical parameters. The crossover function $Y(q)$ is given by,

$$Y(q) = \left(\frac{q}{1+q} \right)^{2\Delta_1}, \quad (8.43)$$

where q is a renormalized distance to the critical point and is obtained from the solution of the crossover sine model,

$$\begin{aligned} & \left(q^2 - \frac{\tau}{Gi} \right) \left[1 - \frac{p^2}{4b^2} \left(1 - \frac{\tau}{q^2 Gi} \right) \right] \\ & = b^2 \left(\frac{\Delta\varphi [1 + v_1 \Delta\varphi^2 \exp(-10\Delta\varphi) + d_1 \tau]}{Gi^\beta} \right) Y^{\frac{1-2\beta}{\Delta_1}}, \end{aligned} \quad (8.44)$$

where v_1 , d_1 , and Gi are system-dependent parameters and p^2 and b^2 universal parameters.^{256–258} The term proportional to $d_1\tau$ in equation (8.44) corresponds

Table 8.1 Definitions and values of the major critical exponents.^{227,228} The quantities K_T and c_V are the isothermal compressibility and constant volume specific heat capacity respectively. ρ_{liq} and ρ_{vap} are the densities of the coexisting liquid (liq) and vapour (vap) phases, T the temperature, and T_c and P_c the critical temperature and pressure respectively.

Exponent	Definition	Classical	Non-classical
α	$c_V \approx (T - T_c)^{-\alpha}$, $\rho = \rho_c$, $T \rightarrow T_c^+$	0	0.110 ± 0.003
β	$\rho_{\text{liq}} - \rho_{\text{vap}} \sim (T_c - T)^\beta$, $T \rightarrow T_c^-$	0.5	0.326 ± 0.002
γ	$K_T \equiv -\frac{1}{V} \frac{\partial V}{\partial P} \sim (T - T_c)^{-\gamma}$, $T \rightarrow T_c^+$	1	1.239 ± 0.002
δ	$P - P_c \sim \rho_{\text{liq}} - \rho_{\text{vap}} ^\delta$, $T = T_c$	3	4.8 ± 0.02

to the rectilinear diameter of the coexistence curve, while the term proportional to $v_1 \Delta \phi^2 \exp(-10\Delta\phi)$ ensures that $Y=1$ at the triple point, hence, ensuring the crossover is complete.

While the approach of Kiselev requires more system-dependent parameters (3-5) than the method of White, it does yield a closed-form analytical expression. We also note that Kiselev recently proposed an analytical formulation for the crossover sine model, which simplifies the calculation of the crossover function and its first and second order derivatives.²⁵⁹ Crossover equations of state based on the approach of Kiselev have been developed for non-associating^{241,256,257} and associating fluids²⁵⁸ based on the SAFT expressions of Huang and Radosz^{39,40} (SAFT-HR) and applied to study the phase behaviour of alkanes,^{241,259} refrigerants,²⁵⁶ water and ammonia.²⁶⁰ However, while the crossover formulation improved the theoretical description in the vicinity of the critical point compared to the classical equation of state alone, deviations from experimental data were in general observed at lower temperatures, which can be attributed to the use of the SAFT-HR equation. The need for an accurate underlying classical equation of state was demonstrated by McCabe and Kiselev¹⁰² with the development of the SAFT-VRX equation based on the combination of Kiselev's crossover technique and the SAFT-VR equation of state (see Figure 8.3). The SAFT-VRX approach has been shown to provide an excellent description of the PVT and phase behaviour of both low and high

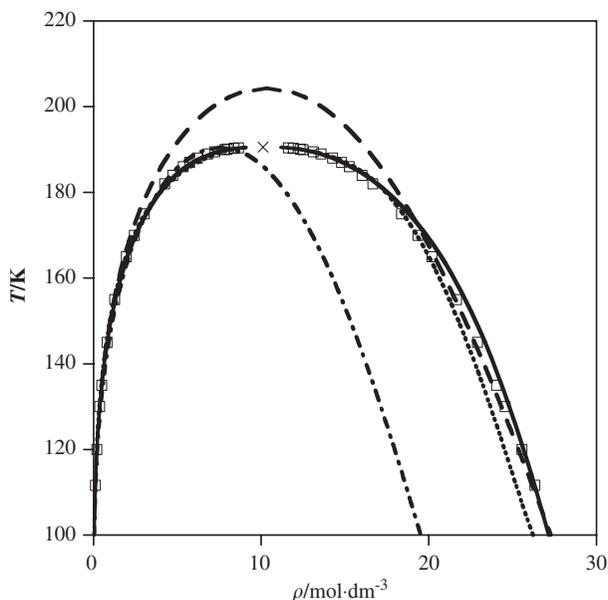


Figure 8.3 Temperature T as a function of coexisting liquid and gas densities ρ for methane. — SAFT-VRX; - - -, SAFT-VR; - · -, SAFT-VR with rescaled parameters; · · · · ·, crossover SAFT-HR; □, experimental data. Reprinted with permission of *Ind. Eng. Chem. Res.*¹⁰²

molar mass alkanes, carbon dioxide, water and their mixtures close to and far from the critical point.^{101,102,111,112}

We conclude by noting that while it has been shown that crossover versions of classical equations of state, including SAFT-like equations, typically provide accurate predictions for vapour-liquid equilibria, PVT ,^{112,261} and derivative properties^{74,245} of both pure fluids and their mixtures close to and far from the critical region, such methods have yet to be applied to the study of liquid-liquid equilibria with the SAFT approach.

8.4.2 Polar Fluids

As described in section 8.3, the original form of the SAFT equation of state does not explicitly account for polar (permanent and induced) interactions. In applications of the SAFT equation of state to fluids with dipolar and quadrupolar interactions, their effect is often taken into account implicitly through fitted model parameters for the dispersion interaction, and sometimes through the use of association sites.²⁶² For example, for a polar (1) and non-polar (2) mixture the presence of a 1-1 dipole interaction and absence of a 1-2 dipole interaction can be modelled by a 1-2 *dispersion* term that is much less than the geometric mean average of the 1-1 and 2-2 values. A possible justification for the latter approach is that at high temperature a Boltzmann averaging of the dipole-dipole interaction energy over all orientations leads to an angle-averaged (*i.e.* angle-independent) interaction varying as the sixth inverse power of intermolecular distance, called the Keesom potential,²⁶³ which can be treated as contributing to the overall van der Waals (dispersion) intermolecular interaction, while directional effects such as the formation of chains seen at low temperature in dipolar fluids are treated via association sites. Of course, direct incorporation of dipolar interactions treats both of these regimes automatically. The absence of explicit polar terms in the model typically leads to large deviations from the usual geometric mean for the cross dispersion interaction and the need for binary-interaction parameters in order to study mixtures of polar fluids, and so makes the approaches more dependent on experimental data and hence less predictive. Though we should note that the SAFT-VR approach⁹² (see section 8.3.3), which accounts for the dispersion interactions through a variable-ranged potential, provides added flexibility over versions of SAFT based on fixed range potentials in terms of describing polar interactions; however, binary-interaction parameters fitted to experimental data are still typically needed in order to study polar fluids with the SAFT-VR equation. In recent work Haslam *et al.*¹³³ propose a predictive method to obtain unlike intermolecular interaction parameters in these systems with some degree of success (see section 8.5.3).

Since polar interactions can have a significant effect on the phase behaviour of both simple fluids and polymers, various approaches to *explicitly* incorporate polar interactions have been proposed; in principle, these should provide a more precise description of the interactions in polar fluids and greater predictive capabilities.

Methods to describe polarity can be broadly classified into two groups: so-called molecule-based and segment-based approaches. Within the latter a distinction can also be made between expressions in which the polar contribution is applied only at the level of the thermodynamics (the Helmholtz energy) of the monomer fluid and those in which the effect of polar interactions is also considered at the level of the structure of the fluid.

The first attempts to account for polar interactions within a SAFT-based equation used perturbation theory to include the dipolar interaction approximated as a third-order expansion in which the two- and three-body terms are calculated explicitly, while the higher terms are approximated by the Padé approximant following the work of Stell.^{264–266} Examples include the work of Walsh *et al.*²⁶⁷, who incorporated the expressions of Gubbins *et al.*²⁶⁸ for the polar expansion together with a LJ version of SAFT, Kraska and Gubbins^{269,270} who used the dipole-dipole interaction term of Gubbins and Twu^{271,272} to extend the Lennard-Jones-based SAFT equation (LJ-SAFT) of Müller and Gubbins²⁷³ to study the phase behaviour of alkanes, alcohols, water and their mixtures, and Li *et al.*²⁷⁴ who studied the critical micellar concentrations of aqueous non-ionic surfactant solutions, again using the expressions of Gubbins and Twu to describe the dipole-dipole interactions in a Lennard-Jones-based SAFT equation. We note that Kraska and Gubbins also attempted to account for the effects of polarizability through a state-dependent effective dipole moment, since dipole-dipole induction leads to an increase in the effective dipole moment in the liquid phase, following the work of Wertheim.^{275,276}

A drawback of these molecule-level approaches is that the polar term is introduced by assuming a single spherical segment, which is then used as the reference for the polar expansion, that effectively maps onto the chain; this is somewhat inconsistent with the description of dispersion interactions on a segment basis. As noted by Jog and Chapman,²⁷⁷ although this approach preserves the idea that the contribution to the fluid properties of a single dipole on a molecule becomes weaker as the size of the molecule increases, it is in poor agreement with molecular simulation results and underestimates the effect of dipolar interactions for chain molecules. Additionally, application of the dipolar contribution at the molecular level only allows for the description of a single polar group per molecule, which makes the extension of the approach to polymers with multiple polar groups in the repeat unit difficult. To overcome these issues Jog and Chapman proposed a SAFT-HR-based approach for dipolar fluids in which the Padé approximant dipolar term of Rushbrook²⁷⁸ was applied at the segment, rather than molecular, level,²⁷⁹ with an additional model parameter x_p introduced to determine the fraction of dipolar segments in the molecule. For chains with a single dipolar site, x_p should be equal to $1/m$; however, for real fluids it is treated as an adjustable parameter. The authors also showed that the contact value of dipolar hard-spheres can be approximated by that of hard spheres in specific orientations²⁷⁷ and use the radial distribution function of a hard-sphere fluid in the chain term instead of that for a mixture of hard and dipolar segments (*i.e.* the monomer fluid). The association and chain

terms remain unchanged from those in the original SAFT-HR equation and so the effects of the dipole are not considered at the chain level of the theory. This polar-SAFT-HR approach was then applied to study the phase behaviour of (acetone + alkanes), with significant improvement over the original SAFT-HR equation seen, and to the study of cloud points in poly(methylpropenoate; ethene) + butane, which further illustrated dipolar effects play an important role in the phase behaviour.²⁷⁹ Note poly(methylpropenoate; ethene) is also known as poly(ethylene-co-methyl acrylate).

The Jog and Chapman term (referred to from hereon by JC) has been applied by a number of authors to model polar fluids in combination with several SAFT equations of state.^{280–283} In particular, Chapman and co-workers^{281,282} applied this approach to the PC-SAFT equation of state and evaluated the performance of the JC dipolar term compared to a segment-level version of a term proposed by Saager and Fischer.^{284,285} In the approach of Saager and Fischer (SF) the polar contribution to the Helmholtz energy is based on empirical expressions fitted to simulation results of the vapour-liquid equilibria for two-centre LJ plus point dipole (2CDLJ) molecules. These were then modified in the spirit of the JC approach in order to apply the expressions at the segment level and take into account the non-spherical shape, and multiple-polar groups, of molecules; as in the original JC approach a model parameter x_p was introduced. The addition of the dipolar contribution in both cases does not modify the remaining contributions to the free energy as given in the original PC-SAFT equation. The two approaches (PC-SAFT-JC and PC-SAFT-SF) were used to study the phase equilibrium of ethers and esters and found to yield very similar results; however, the parameters obtained from the PC-SAFT-JC equation were thought more physically meaningful and therefore expected by the authors to be superior to those obtained from the PC-SAFT-SF equation.²⁸¹

Following the approach of Saager and Fischer of using molecular simulation data to develop empirical expressions for the polar contributions to the Helmholtz energy, Gross and Vrabec (GV) have proposed a contribution for dipolar interactions in non-spherical molecules, again based on a fit to vapour-liquid equilibrium data for 2CDLJ molecules.²⁸⁶ The contribution, based on third-order perturbation theory written in the Padé approximation, overcomes the problems encountered when applying the SF term to strongly asymmetric systems due to the empirical nature of the polar expressions. The proposed GV term, has been implemented in the PC-SAFT equation of state, resulting in the PCP-SAFT equation, which has been used to study the phase behaviour of (dimethylsulfoxide + methylbenzene) and (propanone + alkane) binary mixtures.²⁸⁶ We note that the inclusion of the GV dipolar contribution does not introduce an additional fitted model parameter (*i.e.* beyond x_p), if experimental values are used to determine the dipole moment as done in the original work of Gross and Vrabec.²⁸⁶ The PCP-SAFT and PC-SAFT-JC methods have been compared in a number of ways: when the experimental value of the dipole moment is used and x_p is assumed equal to $1/m$, and not treated as an adjustable model parameter, the PC-SAFT-JC equation incorrectly predicts

liquid-liquid demixing at conditions where the corresponding experimental systems are fully miscible; when either x_p or the dipole moment are fitted to pure-component experimental data, the best results are obtained when these parameters are zero (*i.e.* when the dipole term goes to zero); and finally, if binary mixture data are also used in the determination of the pure-component parameters, as in the work of Dominik *et al.*,²⁸¹ the PC-SAFT-GV model is shown to be in better overall agreement with experimental data for the systems studied than the PC-SAFT-JC model. The PC-SAFT equation with the SF dipolar contribution has also been studied, though minimal improvement over the original PC-SAFT equation was seen for the systems studied.²⁸⁶

Kleiner and Gross subsequently considered the effect of molecular polarizability and induced dipole interactions through the combination of PCP-SAFT and the renormalized perturbation theory of Wertheim,^{275,276} however, for the 36 polar fluids and their mixtures with hydrocarbons studied only slight improvements in the agreement with experimental data was observed compared to the results obtained from the PCP-SAFT equation alone.²⁸⁷

Using the perturbation theory proposed by Larsen *et al.*,²⁸⁸ Karakatsani and Economou^{289,290} have extended the PC-SAFT equation to account for dipole-dipole, dipole-quadrupole, quadrupole-quadrupole and dipole-induced dipole interactions. The exact second- and third-order perturbation terms in the work of Larsen are however rather complex and so a simplified version of the two terms was also proposed based on the work of Nezbeda and co-workers.^{291,292} While simplifying the equation, in an effort to generate a more usable, engineering-type, approach, the simplification of the dipolar term in the model introduces an additional pure-component model parameter. We refer to these as the PC-SAFT-KE and truncated PC-SAFT-KE (denoted PC-PSAFT and tPC-PSAFT by the authors respectively) approaches. In both KE approaches, the multipoles are assumed to be uniformly distributed over all segments in the molecule. The truncated and full PC-SAFT-KE approaches have been applied to study a wide range of polar fluids and their mixtures,^{289,290,293,294} with the truncated equation found to be as accurate as the full PC-SAFT-KE model,²⁹⁰ and the inclusion of polar interactions found to improve the theoretical predictions in most cases.²⁹³

Recently, Al-Saifi and co-workers²⁹⁵ published an excellent comparison of the ability of the PC-SAFT equation of state with the JC, GV and KE dipolar terms to describe the phase behaviour of 53 binary mixtures containing water, alcohol, or hydrocarbons. As an example, Figure 8.4 shows the results reported in ref 295 for (methanol + hexane). In general the PC-SAFT-JC equation was found to exhibit the best overall agreement with experimental data; although both PC-SAFT-JC and PC-SAFT-GV predict erroneous liquid-liquid behaviour for the methanol-hydrocarbon system at low temperatures. The agreement in the case of the JC method was in part attributed to the magnitude of the dipolar contribution, which is larger than in the GV and KE terms; this results, for example, in better predictions for systems with two polar functional groups.

As is clear from the discussion above, the majority of SAFT-based equations for polar fluids focus on the dipole-dipole term, though some studies have also

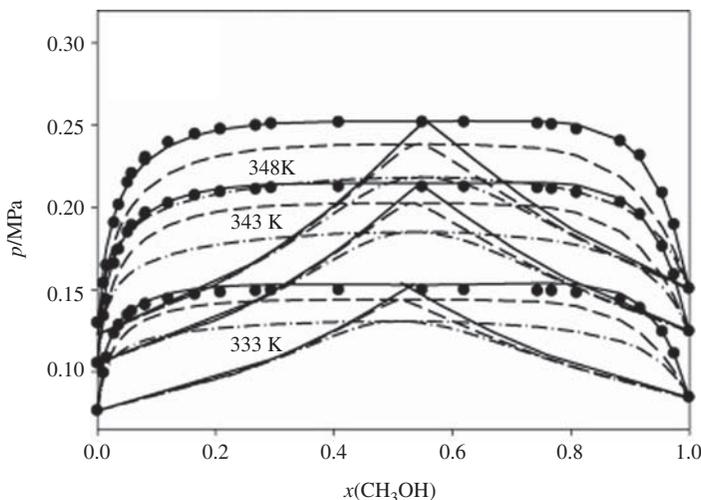


Figure 8.4 Pressure p as a function of methanol mole fraction $x(\text{CH}_3\text{OH})$ for the methanol + hexane vapour–liquid equilibrium at temperatures of (333, 343 and 348) K. ●, measurements; —, results predicted from the PC-SAFT equation with the JC polar term; ---, results predicted from the PC-SAFT equation with the GV polar term; and - · - · -, results predicted from the PC-SAFT equation with the KE polar term. Reprinted with permission of Fluid Phase Equilibria.²⁹⁵

considered dipole-quadrupole and quadrupole-quadrupole interactions. The effect of the inclusion of a quadrupolar term on the phase behaviour of (nitrogen + hydrocarbon) was studied by Zhao *et al.*¹¹³ using the SAFT-VR equation and a quadrupolar term due to Benevides,²⁹⁶ which in turn is based in the work of Larsen.²⁸⁸ Although the improvement in the prediction of the phase behaviour was small, the inclusion of a quadrupolar term reduced the number of binary-interaction parameters needed to study the nitrogen with alkane homologous series from two to one. Additionally, a quadrupolar term was proposed by Gross²⁹⁷ in work similar to the development of the GV dipolar term; namely an expression for quadrupole-quadrupole interactions was derived on the basis of third-order perturbation theory with model constants fitted to molecular simulation data for the two-centre LJ plus quadrupole fluid. The approach was tested through implementation in the PC-SAFT equation of state for mixtures of carbon dioxide and hydrocarbons, with improvement over the original equation of state being observed. Recently, Vrabc and Gross have also proposed a term to describe the dipole-quadrupole cross interactions,²⁹⁸ however it has not yet been implemented and tested within the SAFT framework.

Lucas and co-workers²⁹⁹ recently performed an extensive study to probe the applicability and predictability of the PC-SAFT equation of state with both the GV dipolar term²⁸⁶ and a quadrupolar term due to Gross.²⁹⁷ We note this equation is also termed the PCP-SAFT equation by Lucas and co-workers.

Gross and Vrabec developed the polar terms used for systems consisting of one multipolar molecule with either a dipole or a quadrupole and one non-polar molecule. Perhaps not surprisingly, therefore the theory was found to fail for systems in which one molecule has a significant dipole and the other a significant quadrupole.²⁹⁹ Lucas and co-workers use multiple moments determined from quantum mechanical calculations and so the experimental dipole and quadrupole moments are not needed (see Section 8.5.2). In a subsequent paper³⁰⁰ they compared their PCP-SAFT equation with a new approach in which the PC-SAFT equation is combined with polar terms derived from perturbation theory with a spherical reference (based on a Padé approximation for multipolar species with constants from one-centre LJ MC simulations)³⁰¹ and an equation that combines the PC-SAFT equation with the GV term for the dipolar interactions and spherical-reference perturbation theory for all other multipolar terms (dipole-quadrupole and quadrupole-quadrupole). The equation based on the latter approach was found to out-perform both their original PCP-SAFT model and the new polar contribution.

An alternative to perturbation expansions for inclusion of polar terms into SAFT-based equations of state is via integral-equation theory. Whilst perhaps more complex, integral-equation approaches do have the advantage of yielding analytic expressions for both the structure and the thermodynamics of the fluid, that are applicable (although not necessarily accurate) over wide ranges of temperature, density, and interaction strength. In this spirit, Liu *et al.*³⁰² have proposed a Yukawa-based SAFT equation in which dipole-dipole interactions are treated in a molecule-based (as opposed to segment-based) approach and explicitly calculated with the analytical solution of the mean-spherical approximation (MSA) for the hard and dipolar Yukawa fluids due to Duh and Mier-y-teran³⁰³ and Henderson *et al.*³⁰⁴ respectively; the corresponding terms for the structure of the fluid are not considered in the chain term. Although the new SAFT-based approach was found to provide a better representation of both polar and non-polar fluids than SAFT-HR, for non-polar and associating fluids SAFT-LJ²⁶⁹ was in general in better overall agreement with experimental data.

Zhao and McCabe have also used integral equation theory to propose a SAFT-VR-based equation for polar fluids (SAFT-VR + D) in which dipolar interactions are described through the solution of the generalized mean-spherical approximation (GMSA) of Stell and co-workers.³⁰⁵ In the SAFT-VR + D equation the dipolar contribution is given at the segment level, with the dipolar square-well fluid (or a mixture of square-well and dipolar square-well fluids) describing the monomer fluid from which chains are formed. The effect of the dipolar interactions on the structure of the fluid is taken into account in the chain term through the use of a dipolar square-well radial distribution function. This explicit account of the effects of the dipolar interactions on both the thermodynamics and structure of the fluid is unique to the SAFT-VR + D equation. Following testing of the theory through comparison with molecular simulation data,^{306,307} the SAFT-VR + D equation has been applied to study the phase behaviour of hydrogen sulphide, water, and their binary mixtures,³⁰⁸

as well as (hydrogensulphide + alkanes).³⁰⁹ Since experimental values for the dipole moment are used, no additional parameters are introduced into the theory compared to the original SAFT-VR equation. In general, the SAFT-VR + D equation is found to improve the agreement with experimental data over the original SAFT-VR approach; however, the improvement in some cases is slight, which could be due to the incorporation of a variable range potential in SAFT-VR (see section 8.3.3).

We conclude this section by noting that the general consensus from SAFT studies involving polar contributions is that the explicit inclusion of a dipolar term in general helps the predictive ability, as was shown most clearly in the work of Sauer and Chapman who compared polar versions of the PC-SAFT and original SAFT approach.²⁸³ However, the effect on the predictive capability of including polarizability and induced dipoles appears to be minimal and the added complexity not justified.²⁸⁷ One problem to note is the use of fixed dipole moments, be they experimental values or obtained from *ab initio* calculations, they will always limit the predictive capability of the approach since the effect of changes in temperature and state conditions on changes in the multipole moments is not captured. This is clearly seen when one considers the bare dipole moment of water, which has a value of 1.8 D ($1 \text{ D} \approx 3.33564 \cdot 10^{-30} \text{ C} \cdot \text{m}$), compared to condensed-phase estimates of between (2 and 3) D and the effect on the solvation properties.³¹⁰ While this is not an issue in the study of single-phase systems or systems over narrow ranges of temperature and pressure, this will have an effect when studying phase-equilibria properties and will hamper the development of a truly predictive approach.

8.4.3 Ion-Containing Fluids

The presence, or addition, of charged species, yielding an electrolyte solution, significantly affects the thermodynamic properties of fluids. Electrolyte solutions are ubiquitous and of fundamental importance in both naturally occurring and industrial processes (such as natural biological and batch biochemical processes, geochemistry, energy conversion, electrochemistry, corrosion and pollution).^{311–314} The development of a successful theory for charged fluids relies on the solution of two problems: firstly, an accurate intermolecular potential model must be proposed and secondly, the statistical mechanics relevant to the system must be solved with some precision. The long-range Coulombic interactions, including permanent and possibly induced multiple moments, make the solution of the statistical mechanics of systems containing ions particularly difficult.

Many models for electrolyte solutions have evolved from the Debye-Hückel (DH) limiting law,³¹⁵ which regards the ions as point charges immersed in a dielectric continuum. In solution each ion of charge q_i is surrounded by a co-sphere of oppositely charged ions, in a way that the ions interact not through their bare Coulomb potential but through a screened potential, which is found to take the form of a Yukawa-type potential ($\approx A \exp(-\kappa r)/r$ where κ is the inverse of the Debye screening length) and is obtained by solving the Poisson equation assuming a Boltzmann distribution for the charge distribution. The

DH model yields a simple analytical expression for the Helmholtz energy, in the form

$$\frac{A^{\text{Elect.}}}{Nk_{\text{B}}T} = -\frac{\kappa^3}{12\pi\rho}, \quad (8.45)$$

where $1/\kappa$, the Debye screening length, is a measure of the diameter of the co-sphere, and is calculated from

$$\kappa^2 = \frac{4\pi}{\epsilon k_{\text{B}}T} \sum_i q_i^2 \rho_i. \quad (8.46)$$

In this equation, ρ_i is the number density of ionic species i , ϵ is the dielectric constant of the solvent, and the sum is over all ionic species.

The DH theory has served as the basis for many semi-empirical models for electrolyte solutions, including the extended DH model,³¹⁶ the models of Reilly and Wood^{317,318} and Scatchard *et al.*³¹⁹ Perhaps the most widely accepted such theory is the ion-interaction model of Pitzer,^{320–323} which consists of an extended Debye-Hückel theory with virial-like coefficients to give a concentration expansion of the excess Gibbs energy. The model is capable of correlating electrolyte data very well over wide ranges of temperature and salt composition up to several molal. Variations of the model have been developed which take into account ion pairing^{324,325} and asymmetry in salt mixtures,³²⁶ and have been applied to near-critical and supercritical aqueous salt solutions.^{327–330} Reviews by Pitzer^{325,329} attest to the success of these models in interpolating and facilitating the interpretation of experimental data. Another successful approach in this region is the extended corresponding-states description of Gallagher and Levelt Sengers.^{331–333} A large class of models for activity coefficients in electrolyte solutions^{334–347} can be classified as consisting of the Debye-Hückel model (usually in the extended form or Pitzer-modified form) to which a model for the non-electrostatic short-range contribution (such as the non-random two liquid (NRTL) model of Renon and Prausnitz³⁴⁸ or the UNIQUAC model³⁴⁹) is added.

A more fundamental approach is to attempt to model electrolyte solutions using statistical mechanical methods, of which there are two kinds of models (reviewed extensively elsewhere^{350–355}): Born-Oppenheimer (BO) level models in which the solvent species as well as the ionic species appear explicitly in the model for the solution and McMillan-Mayer (MM) level models in which the solvent species degrees of freedom are integrated out yielding a continuum solvent approximation. Thus, for a BO level model, in addition to the interionic pair potentials one must specify the ion-solvent and solvent-solvent interactions for all of the ionic and solvent species. In this case, the interionic potentials do not contain the solvent dielectric constant in contrast to the MM-level models. Kusalik and Patey^{356,357} carefully discuss the distinction between these two approaches.

The DH model (eqs 8.45 and 8.46), can also be derived from statistical mechanics as the solution of the mean spherical approximation (MSA) for an electro-neutral mixture of point ions in a continuum solvent (*i.e.* it is an example of a MM-level model). It represents a limiting behaviour of electrolyte solutions and breaks down quickly for concentrations higher than $\approx 0.01 \text{ mol} \cdot \text{dm}^{-3}$; the extended DH model is accurate to $\approx 0.1 \text{ mol} \cdot \text{dm}^{-3}$. For more concentrated solutions, it is natural to consider replacing the point ions with finite-size ions; this leads to the consideration of so-called primitive models (PMs), which are MM models consisting of an electro-neutral mixture of charged hard spheres in a continuum solvent. The simplest PM is the restricted primitive model (RPM) consisting of an equimolar mixture of equal-diameter charged hard spheres in a dielectric continuum (*i.e.* $\rho_+ = \rho_- = \rho/2$, $\sigma_+ = \sigma_- = \sigma$).

To calculate the properties of the RPM, one approach is to solve the relation between the direct correlation function and the pair correlation function given by the Ornstein-Zernike (OZ) integral equation.^{358,359} The solution of the RPM in the MSA yields a simple analytical expression for the Helmholtz energy, given by,³⁶⁰

$$\frac{A^{\text{Elect.}}}{Nk_{\text{B}}T} = -\frac{3x^2 + 6x + 2 - 2(1 + 2x)^{3/2}}{12\pi\rho\sigma^3}, \quad (8.47)$$

where $x = \kappa\sigma$. The OZ equation has also been solved within the MSA for the unrestricted PM, consisting of an electro-neutral mixture of hard-sphere ions of arbitrary size and diameter.^{361,362} The solution is again analytical, although an iterative method is required to solve for the scaling parameter, which is a generalization of the parameter x in eq 8.47. Using the analytic solution of the unrestricted PM, Triolo *et al.*^{363–366} showed that by choosing an ionic-strength-dependent dielectric constant and taking into account hydration in the ion diameter, the unrestricted PM could fit the osmotic pressure and activity coefficients of alkali halide electrolyte solutions up to $2 \text{ mol} \cdot \text{dm}^{-3}$.

Primitive models have been very useful to resolve many of the fundamental questions related to ionic systems. The MSA in particular leads to relatively simple analytical expressions for the Helmholtz energy and pair distribution functions; however, compared to experiment, a PM is limited in its ability to model electrolyte solutions at experimentally relevant conditions. Consider, for example, that an aqueous solution of NaCl of concentration $6 \text{ mol} \cdot \text{dm}^{-3}$ (a high concentration, close to the precipitation boundary for this solution) corresponds to a mole fraction of salt of just 0.1; *i.e.* such a solution is mostly water. Thus, we see that to estimate the density of such solutions accurately the solvent must be treated explicitly, and the same applies for many other thermodynamic properties, particularly those that are not excess properties. The success of the Triolo *et al.*^{363–366} approach can be attributed to the incorporation of some of the solvent effect through state-dependent parameters, as well as their focus on excess properties. Treating the solvent explicitly at some level is crucial to modelling real solutions; thus, we turn to BO-level models.

The properties of BO-level models can be obtained from perturbation theory or integral equations, and both have been used to develop versions of SAFT suitable for modelling electrolyte solutions.

We consider first obtaining the properties of BO models using perturbation theories, where solvent-solvent, solvent-ion and ion-ion interactions can be easily identified with different terms in the expansion. Chan³⁶⁷ combined the perturbation expansion of Stell and Lebowitz³⁶⁸ for the RPM with the Carnahan-Starling³³ equation of state for hard-spheres and noted that substituting the six-term expansion of Stell and Lebowitz by the much simpler DH expression (eq 8.45) leads to little difference in comparison to experimental mean activity coefficients, hence highlighting the key contribution of the repulsive term. In a second paper³⁶⁹ he tested the expansion of Henderson *et al.*³⁷⁰ for the ion-dipole BO model but poor results were again obtained.

Following the success of Chan's simple proposition, and given the accuracy of SAFT in modelling the properties of non-ionic fluids, it is a natural extension to combine a treatment of the solvent and other non-Coulombic terms using SAFT with a contribution to treat charge-charge interactions from a primitive model theory. The Helmholtz energy of the electrolyte solution is usually therefore written as

$$\frac{A}{Nk_B T} = \frac{A^{\text{Ideal}}}{Nk_B T} + \frac{A^{\text{Mono.}}}{Nk_B T} + \frac{A^{\text{Chain}}}{Nk_B T} + \frac{A^{\text{Assoc.}}}{Nk_B T} + \frac{A^{\text{Elect}}}{Nk_B T}, \quad (8.48)$$

where the first four terms in the right hand side correspond to those described in section 8.3 and A^{Elect} refers to the term or terms taking into account the electrostatic interactions. Most of the versions of SAFT described earlier have been tested in combination with Coulombic terms in the PM to treat a variety of experimental electrolyte systems. For the most part, research to date has concentrated on strong (fully dissociated) electrolytes and single solvent systems (usually an aqueous solution). In the first attempt to model electrolyte fluids with SAFT Liu *et al.*³⁷¹ combined the original SAFT approach (with the expression of Cotterman for the dispersion term)²³ with the MSA in the PM approximation and ion-dipole and dipole-dipole terms from the expansion of Henderson *et al.*³⁷⁰ to regress the mean ionic activity coefficients (γ_{\pm}) of single-salt and mixed salt aqueous electrolyte solutions at $T = 298$ K. Using the diameter of the cation as an adjustable parameter for each electrolyte average errors for density and γ_{\pm} of the order of $< 3\%$ for concentrations up to 6 molal were obtained. In later work the approach was used to correlate the critical micellar concentrations of charged surfactant solutions.³⁷²

Liu *et al.*³⁷³ have also considered the low density expansion of the non-primitive MSA to treat the electrostatic interactions and discuss how the first three leading terms can be identified with the solvent-solvent, solvent-ion and ion-ion electrostatic contributions to the Helmholtz energy. Although expressions can be obtained for each of these terms, for example, as provided in ref 373, it was found to be more accurate to use an expansion as presented in section 8.4.2 for solvent-solvent interactions that include dipole-dipole terms and the usual

expressions of the MSA in the PM for the ion-ion interactions. It is interesting that a term related to solvent-ion interactions is also identified which can be related to the Born term for the contribution to the free energy due to ion solvation at infinite dilution. In their work³⁷³ this term takes the form,

$$\frac{A^{\text{Solvent-ion}}}{Nk_{\text{B}}T} = -\frac{z_{\text{ion}}^2 e^2}{k_{\text{B}}T \epsilon \sigma_{\text{ion}}} \frac{\epsilon - 1}{(1 + \sigma_{\text{dipole}}/(\sigma_{\text{ion}} \lambda))}, \quad (8.49)$$

where λ is a function related to the dielectric of the solvent and σ_{ion} and σ_{dipole} are the diameters of the ions and dipole, respectively. The expression above reduces to the Born-term expression in the PM, when the diameter of the solvent is neglected; *i.e.*

$$\frac{A^{\text{Born}}}{Nk_{\text{B}}T} = -\frac{z_{\text{ion}}^2 e^2}{k_{\text{B}}T \epsilon \sigma_{\text{ion}}} (\epsilon - 1). \quad (8.50)$$

The dielectric constant in this model is concentration dependent and as such contributes to the chemical potential (activity coefficient) of the ions. It is common, however, not to take the derivative of the Born term with composition as it is seen to introduce large discrepancies between the calculated values and the experimental ones. As shown by O'Connell,³⁷⁴ these problems typically arise through the inconsistent mixed use of MM and BO-level quantities without paying due attention to the ensembles in which each property is derived.

The SAFT-VR approach has been extended to treat electrolyte solutions using both the primitive and non-primitive models within the DH model and MSA.^{375–378} In the first approach, SAFT-VRE,³⁷⁵ a MM level of theory is used to describe the Coulombic interactions using either the solution of the DH or MSA in the RPM, and the vapour pressure of solutions in temperature ranges between (273 and 373) K (higher temperatures would require consideration of ion pairing) were modelled and the solution densities predicted. In contrast with other approaches the ion diameters were not correlated, but instead taken from experimental Pauling radii. In the SAFT-VRE approach the solvent is treated implicitly; it is described as a non-polar solvent and so no dipole-dipole or ion-dipole terms are included. The attractive interactions that lead to the formation of hydration shells are treated effectively through square-well potentials of variable range. An advantage of the SAFT-VRE approach is that only one adjustable parameter per ion is used; *i.e.* this is an ion-based salt-independent approach and so a parameter table per ion can be presented and then used in a predictive fashion for salts not previously investigated, similar to a group contribution method. This idea has been tested in mixed salt solutions and also applied successfully to predict the salting out of methane from aqueous solutions with added NaCl.³⁷⁹ Behzadi *et al.*^{377,380} later showed that the Yukawa potential can also be used to model the ion-water and water-water

interactions combined with the mean spherical approximation as extended by Blum³⁶¹ for the non-restricted primitive model.

In a second approach, the SAFT-VR + DE equation,³⁷⁸ a BO level model with electrostatic properties obtained from integral equation solutions, rather than perturbation theory, is proposed. This approach draws heavily on the solution of the OZ equation with the MSA closure for ionic and dipolar hard spheres due to Blum³⁸¹ and on its extension to the generalized MSA (GMSA) and related approximations.^{305,382} In this modification of the SAFT-VR equation, a dipolar solvent is described explicitly and dipole-dipole and ion-dipole terms included. The importance of describing the size of the ions (*i.e.* using the PM over the DH approach) and an accurate description of the dielectric constant was clearly shown through comparison of the SAFT-VR + DE approach and other models with computer simulation data.³⁷⁸ The approach has been used to study simple electrolyte solutions and the effect of the solvent dipole moment on the system dielectric constant investigated as shown in Figure 8.5.³⁸³ The importance of using an explicit solvent over a

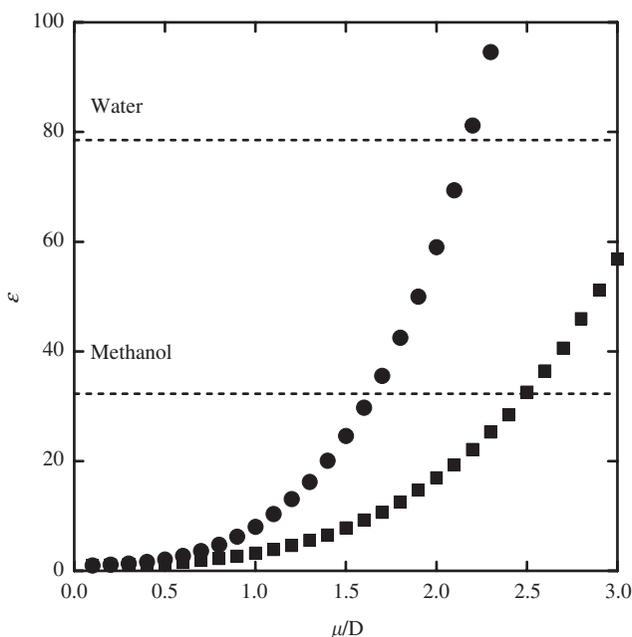


Figure 8.5 Prediction of the water and methanol dielectric constant ϵ as a function of dipole moment μ ($1\text{ D} \approx 3.33564 \cdot 10^{-30}\text{ C}\cdot\text{m}$) from the SAFT-VR + DE equation of state at room temperature and pressure. ● and ■, the theoretical predictions; - - - -, the experimental value of the dielectric constant for each solvent at room temperature and pressure. As would be expected when the experimental bare dipole moment of water or methanol is used in the calculations the theory under predicts the dielectric constant, while values of the dipole moment for condensed phases yield predictions in good agreement with experimental data. Taken from ref. 383.

dielectric continuum to describe the hydration of the ions was also demonstrated through a study of the Gibbs energy of hydration which was found to be in good quantitative agreement with experimental data using the SAFT-VR + DE approach, but not even in qualitative agreement when an implicit solvent model is used.³⁸³

The ePC-SAFT³⁸⁴ (electrolyte PC-SAFT) equation follows similar ideas to those used in the development of the SAFT-VRE equation, in that the DH approach in the primitive model is used to account for the electrostatic interactions. The electrostatic term in references 384 and 385 is given in the general form

$$\frac{A^{\text{Elect.}}}{Nk_{\text{B}}T} = -\frac{\kappa^3}{12\pi\rho} \sum_i \chi_i, \quad (8.51)$$

where

$$\chi_i = \frac{3}{(\kappa\sigma_i)^3} \left[\ln(1 + \kappa\sigma_i) - \kappa\sigma_i + \frac{\kappa^2\sigma_i^2}{2} \right], \quad (8.52)$$

which leads to $\chi_i \approx 1$ by expanding the logarithm, so eq 8.45 is recovered. The ePC-SAFT has been successfully used to describe the vapour pressure, density of solution and mean-ionic coefficient of 115 salts.³⁸⁵

Another strategy to fit ion-water solvation parameters is to develop salt-specific (or salt-dependent) models. The advantage here is that accuracy is usually higher,^{373,377} although also more reliant on experimental data. Tan *et al.*^{386,387} have proposed a hybrid method based on the SAFT1 equation where a hydrated diameter for the combined salt is used in addition to the usual ionic volumes and ion-water dispersion (hydration) energies. Vapour pressures, activity coefficients and densities of the solutions are very well reproduced, which is difficult with ion-specific approaches. A key limitation, however, is that the study of properties of solutions with mixed salts in this model requires added combining rules for the salt-specific parameters, and usually added adjustable parameters that limit the predictive ability of the method.^{388,389} However, versions of the SAFT1 and SAFT2 (for divalent ions) approaches formulated as ion-specific are also available.^{146,390–392}

In this area a key challenge remains the study of mixed-solvent systems. The preliminary works of Wu and Prausnitz³⁹³ and Patel *et al.*³⁷⁹ on salting out in aqueous solutions are promising, but are also simple cases in which the extreme phase separation and difference in dielectric constant allows the electrolyte to be considered only in one of the two phases; this greatly simplifies the treatment of mixture dielectrics. The SAFT-VR + DE approach provides another promising route for mixed solvent electrolyte systems, since the dielectric constant is a product of, and not a required input to, the calculations (see for example Figure 8.5). Non-aqueous solvents will also mean that ion pairing will need to

be treated at some level. Initial work on combining a SAFT-like treatment with a chemical approach to treat ion-pairing has already been considered with encouraging results.³⁹⁴

8.4.4 Modelling Inhomogeneous Fluids

The use of SAFT within theories for inhomogeneous fluids^{395–397} such as the square-gradient theory^{398–400} (usually called density-gradient theory, DGT) and density-functional theory^{401,402} (DFT), provides a route towards the quantitative prediction of interfacial properties (interfacial thickness, interfacial tension, adsorption, wetting and confinement effects) of complex fluids. Interfacial systems are of interest throughout industrial, technological and living processes and involve increasingly complex molecules. Through the combination of an underlying SAFT treatment of the fluid and DGT or DFT treatments, non-spherical and associating or hydrogen bonding fluids can be considered in these frameworks.

In DGT the thermodynamics of the system with an interface between two fluid phases is described assuming that the density gradient between the two phases is small compared to the reciprocal of the intermolecular distance, so that the density and its derivatives can be treated as independent variables. The Helmholtz energy of the inhomogeneous system is then obtained as a Taylor series around the equilibrium state. One of the first attempts to examine interfacial properties of real fluids with a SAFT approach and the DGT method was carried out by Kahl and Enders.⁴⁰³ The combination of the accuracy provided by SAFT in terms of the bulk properties (liquid + liquid coexistence densities) of the fluids and the DGT method, where one temperature-independent influence parameter is used, leads to very accurate correlations of the surface tension of real fluids. In the first paper of a series they investigated non-polar, and aromatic compounds, alcohols and water and go on to treat mixtures using both the original version of SAFT^{22,23} and PC-SAFT.^{404–406} The group of Fu and co-workers^{158,407–412} have also combined the PC-SAFT approach with the DGT method to correlate the surface tension of a number of pure compounds and mixtures, and have studied in detail the critical regions using the renormalization group approach (see section 8.4.1). The SAFT-VR¹⁰² and LJ^{413–415} versions of SAFT have also been implemented in DGT formalisms to study interfacial properties of real fluids.

While the DGT-based SAFT approach is easy to implement and can provide a good representation of the surface tension of pure fluids and mixtures, it typically requires the use of empirical adjustable parameters, the so-called “influence” parameters, which limit the predictive ability of the method. In contrast, DFT treatments, although more complex and numerically more demanding, do not rely on adjustable parameters to provide information on the interfacial properties. Chapman³⁹⁵ was the first to suggest the possibility of incorporating a SAFT-like description of associating fluids within a DFT

approach, where the thermodynamic properties of the inhomogeneous fluid are expressed as a function of a spatially varying density.⁴⁰¹ Different levels of approximation are possible in DFT, such as the local-density approximation (LDA) in which the short-range correlations are neglected, weighted-density approximations (WDA) in which the short-range correlations are included, and the fundamental measure theory (FMT) due to Rosenfeld⁴¹⁶ in which a set of geometric “measures” define the weighted densities. Numerous works have concentrated on the behaviour of model associating systems in the presence of walls^{417–425} and in confinement,^{426,427} and have provided useful comparisons with computer simulation data.

Recently the DFT method combined with SAFT equations of state has been used to predict the interfacial properties of real fluids. LDA methods are accurate enough to treat liquid-liquid and liquid-liquid interfaces where the density profiles are usually smooth functions, and have been used in combination with the SAFT-VR approach to predict the surface-tension of real fluids successfully.^{428,429} The intermolecular model parameters required to treat real substances are determined by fitting to experimental vapour-pressure and saturated liquid density data in the usual way (see section 8.5.1) and the resulting model is found to provide accurate predictions of the surface tension. A local DFT treatment has also been combined with the simpler SAFT-HS approach,^{430,431} but in this case only qualitative agreement with experimental surface tension data is found due to the less accurate description of the bulk properties provided by the SAFT-HS equation. Kahl and Winkelmann⁴³² have followed a perturbation approach similar to the one proposed with the SAFT-VR⁴³³ equation and have coupled a local DFT treatment with a Lennard-Jones based SAFT equation of state. They predict the surface tension of alkanes from methane to decane and of cyclic and aromatic compounds in excellent agreement with experimental data.

The most sophisticated DFT approaches incorporate weighted densities, which depend on several weighting factors,⁴⁰¹ often based on the FMT.⁴¹⁶ The implementation of WDA in DFT provides accurate oscillatory profiles, such as those found in solid-fluid interfaces (near walls, in confined fluids) or in solid and other structured phases. The DFT for associating fluids of Segura *et al.*⁴¹⁸ combines Tarazona’s WDA DFT for hard-spheres with Wertheim’s thermodynamic perturbation theory and has been used in a number of studies of associating fluids in pores^{418,419,434} and with functionalized walls;⁴³⁵ in the limit of complete association a DFT for polymeric fluids is obtained in this method.^{435–440} Based on these works, Chapman and co-workers have presented the interfacial-SAFT (iSAFT) equation,⁴⁴¹ which is a DFT for polyatomic fluids formulated by considering the polyatomic system as a mixture of associating atomic fluids in the limit of complete association; this approach allows the study of the microstructure of chain fluids. Interfacial phenomena in complex mixtures with structured phases, including lipids near surfaces, model lipid bilayers, copolymer thin films and di-block copolymers,^{421,441,442} have all been studied with the iSAFT approach.

8.4.5 Dense Phases: Liquid Crystals and Solids

Although not strictly the main interest of this chapter, it is useful for completeness to include briefly recent efforts that are considering applications of Wertheim's perturbation theory to study structured phases. For example, Thies and co-workers^{444,445} have combined the SAFT-HR equation with the classic theory of nematic formation of Maier and Saupe and study carbonaceous pitches (large polyaromatic compounds that can present liquid crystalline phase behaviour in toluene solution) with some success. A note of caution is however necessary here, as a correct treatment of mesogens (liquid crystal molecules) requires the integration of the attractive energy as a function of contact distance, which is a function of orientation; failure to carry out this integration accurately can lead to predictions of the wrong type of phase behaviour. In a more formal approach the association theory of Wertheim has been used to study dimerizing liquid-crystal molecules combined with Onsager's theory for the isotropic-nematic phase transition.⁴⁴⁶ In a series of works Vega and co-workers⁴⁴⁷⁻⁴⁵² have shown that the fundamental proposition of Wertheim's theory, in which the Helmholtz energy of a chain molecule is obtained through the use of the free energy and structure of a reference monomer system can also be applied to solid phases. In this way global (solid + liquid + vapour) phase diagrams for pure model chain systems have been studied. This idea has been followed and used to correlate the solid-liquid equilibria of (argon + krypton) and (argon + methane).⁴⁵³

8.5 Parameter Estimation: Towards more Predictive Approaches

The molecular model on which SAFT is based has the advantage of incorporating important molecular details that allow the description of large chain-like molecules as well as treating molecular interactions such as hydrogen bonding. A price to pay is, however, the larger number of intermolecular parameters that need to be determined to characterize any given substance or mixture, compared to traditional cubic equations of state. The study of mixtures adds additional complexity to the problem in terms of parameter estimation. In this section we discuss approaches concerned with minimizing the need to fit parameters to experimental data.

8.5.1 Pure-component Parameter Estimation

SAFT intermolecular-potential model parameters are traditionally determined by fitting to experimental data, as other equations of state; for pure compound parameters vapour pressure and saturated liquid densities are typically used. These properties are chosen as the vapour pressure is of key interest in practical applications and depends strongly on the energy parameters, while the use of liquid density data is important in determining size related parameters.

A least-squares objective function with the chosen residuals, given by

$$\begin{aligned} \min_{\theta} F_{Obj} = & \frac{1}{N_P} \sum_{i=1}^{N_p} \left[\frac{P_{sat,i}^{exp.} - P_{sat,i}^{calc.}(\theta)}{P_{v,i}^{exp.}} \right]^2 \\ & + \frac{1}{N_{\rho}} \sum_{j=1}^{N_{\rho}} \left[\frac{\rho_{sat,j}^{exp.} - \rho_{sat,j}^{calc.}(\theta)}{\rho_{sat,i}^{exp.}} \right]^2, \end{aligned} \quad (8.53)$$

where θ is the vector of intermolecular model parameters, N_P is the number of experimental vapour pressure points, N_{ρ} the number of experimental saturated liquid density points, P_{sat} corresponds to the vapour pressure and ρ_{sat} to the saturated liquid density, is minimized. Gas-phase density data are rarely included since they naturally yield parameters not well suited to modelling dense-phase properties. In addition, the fit is usually restricted to subcritical conditions, since they are more accessible experimentally (and hence a lot more data are available) and since the critical point is typically over predicted by the theories (see section 8.4.1).

It has been shown however that the traditional use of vapour-pressure and saturated-liquid density data in SAFT approaches can lead to sub-optimal parameters^{125,136} due to a large degeneracy of models (*i.e.* different intermolecular parameter sets that lead to essentially the same error in comparison to the experimental data considered). A technique that proposes to make the parameter space discrete in order to carry out a global investigation of the parameter space illustrates the large degeneracy of models that result from the use of only two properties in determining parameters for associating compounds,¹²⁵ and even in non-associating, relatively simple systems.⁴⁵⁴ In the case of water, for example, using the SAFT-VR approach it has been shown that four-site models with association energies between (1000 and 1400)K can lead to combined absolute average deviations in vapour pressure and saturated liquid density of less than 1 %. When the enthalpy of vaporization and the interfacial tension are included in the fitting process, they are found not to facilitate the discrimination between models; however, the use of spectroscopic data, which provides information on the fraction of associated (or free) molecules, was found to allow the differentiation between possible sets of parameters.²⁶⁷ Unfortunately, such data are rarely available over large temperature ranges. In section 8.5.2 the use of quantum mechanical calculations to obtain hydrogen bond information is also discussed.

Using the SAFT-Mie approach, Lafitte *et al.*¹³⁶ have shown that if the equation of state is precise enough at the level of the second-order derivative properties, a combination of vapour pressure, saturated-liquid density and single-phase density, together with speed of sound data leads to parameters that follow physical trends within a homologous series. This result suggests that the existence of many local minima that can lead to sub-optimal models when using local-optimization methods⁴⁵⁴ is resolved to a great extent when derivative properties are incorporated.

A different approach is to reduce the number of parameters that need to be determined by proposing transferable models. Towards this end, the use of

parameter information transferable within a homologous series, usually from smaller members of the series where more experimental data are available to higher-molar mass ones has been explored^{34,35,113,114,117,131,379,455–457} and typically works well due to the physical basis of the SAFT model. While this method has not generally been very successful in the study of polymer systems beyond simple polymers such as polyethylene,^{100,457} due to the difficulty in obtaining parameters for an appropriate homologous series, it has been successfully applied to study poly(ethane-1,2-diol) (commonly known as polyethylene glycol) with the SAFT-VR approach.¹²⁵

8.5.2 Use of Quantum Mechanics in SAFT Equations of State

The combination of *a priori* quantum mechanics (QM) calculations with equations of state is a very interesting proposition⁴⁵⁸ that is gathering interest with more readily available computer power and equations of state that implement more physical models, which can lead to better, and even fully predictive approaches. Specifically with the SAFT equation of state, Wolbach and Sandler were the first to propose the use of quantum mechanical calculations to determine SAFT parameters.^{459–463} Starting with small pure-component hydrogen-bonding molecules, they relate an equilibrium constant of association K obtained from molecular orbital calculations to the $\Delta_{a,b}$ parameter that characterizes the strength of association in SAFT. A relation between the SAFT size parameters (m and σ) and the molecular volume calculated from QM was also derived in their original work.⁴⁵⁹ Calculations were performed with the Hartree-Fock method and density functional theory (DFT) using the B3LYP functional and 6-31 + g(2d,p) basis set to determine if a rigorous level of theory was needed; the Hartree-Fock calculations were found to be sufficiently accurate to model pure hydrogen-bonding fluids,⁴⁵⁹ such as water and methanol, and binary mixtures of an associating fluid with a non-associating dilutant.⁴⁶⁰ In subsequent work the phase behaviour of binary mixtures in which cross association can occur were considered and a combining rule for cross-association parameters in mixtures based on self-associating ones proposed.⁴⁶¹ In general the combined SAFT-QM approach proposed by Wolbach and Sandler was found to enable the description of mixture vapour-liquid equilibrium data for water, methanol and three acids with fewer adjustable parameters and no loss of accuracy compared to the original SAFT equation. More recently, Yarrison and Chapman¹⁵⁵ have used the original SAFT equation²³ and the association parameters developed by Wolbach and Sandler to study the phase behaviour of (methanol + alkanes) with good results, especially when the Hartree-Fock calculations were used.

Similar to the work of Wolbach and Sandler for the molecular size parameters, Sheldon and co-workers⁴⁶⁴ derived values for m and σ by mapping the molecular dimensions calculated from Hartree-Fock calculations onto a spherocylinder; the remaining parameters were then determined by comparison to the usual vapour pressure and saturated liquid density data. Promising

results using this approach were obtained for the *n*-alkane series, nitrogen, carbon monoxide, carbon dioxide, benzene, cyclohexane, water and two refrigerants.

Although QM calculations can be expected to be more useful to determine single-molecule, or dimer, properties (since they usually involve one or two molecules, treated in vacuum), Lucas and co-workers^{465,299,300} have been able to develop a successful framework to determine multipole moments and dispersion interactions from QM. Using a fairly rigorous level of theory (MP2/aug-cc-Pvdz/B3LYP/TZVP) dipole and quadrupole moments, dipole polarizability and dispersion coefficients were determined and subsequently used with the PCP-SAFT approach to study a number of pure fluids and their binary mixtures (see section 8.4.2).⁴⁶⁴

8.5.3 Unlike Binary Intermolecular Parameters

In the case of calculations of mixture properties and phase equilibria in mixtures, mixture-specific parameters have to be calculated based on the pure-component (like, *ii*) and binary-interaction (unlike, *ij*) parameters with the use of mixing and combining rules. The simplest mixing rules for use in an equation of state are those presented by van der Waals,⁴⁶⁶ which use quadratic functions of composition involving like and unlike parameters; *e.g.* in the one-fluid approximation $\sigma_x = \sum \sum x_i x_j \sigma_{ij}$, where the subscript *x* indicates a mixture parameter⁴⁶⁶. Usually arithmetic and geometric (Lorentz-Berthelot) combining rules are then used to determine the unlike size and energy parameters, respectively,

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad (8.54)$$

and

$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\varepsilon_{ii} \varepsilon_{jj}}. \quad (8.55)$$

The quadratic form of the mixing rule has a theoretical basis in the composition dependence of the second virial coefficient, but the Lorentz-Berthelot combining rules are well-known to fail in the case of highly non-ideal mixtures.^{133,466–468} A correcting adjustable parameter k_{ij} that is mixture specific and typically determined by fitting to relevant experimental data for the mixture of interest is commonly introduced to improve agreement with experimental data.

Given the failure of the Lorentz-Berthelot rules, in order to increase the predictability of mixture models (be it equations of state or computer simulations) different combining rules have been proposed and investigated. Schnabel *et al.*⁴⁶⁹ have recently provided a quantitative assessment of eleven combining rules in terms of their performance in describing binary mixtures classified by the molecular shape and polarity of the components. Of particular interest is a

new combining rule based on the original work of Hudson and McCoubrey for LJ mixtures,⁴⁷⁰ which can be used with potentials of general form and can be implemented in SAFT-like models.¹³³ The idea of the theory is to relate the model potential to a more realistic compound potential (*e.g.* the London potential for the case of dispersion interactions) so that an equation is obtained for one of the mixture parameters as a function of the others. For example, for the case of molecules modelled as spherical segments interacting via SW potentials, the unlike SW potential depth is obtained as

$$\varepsilon_{ij} = \frac{2\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6} \left(\frac{(\lambda_{ii}^3 - 1)^{1/2} (\lambda_{jj}^3 - 1)^{1/2}}{(\lambda_{ij}^3 - 1)^{1/2}} \right) \left(\frac{(I_i I_j)^{1/2}}{I_i + I_j} \right) \sqrt{\varepsilon_{ii}\varepsilon_{jj}}, \quad (8.56)$$

where, σ , ε , and λ correspond to the usual SW parameters and I_i is the ionization potential of pure compound i (in the case of chain molecules a correlation between the molecular ionization potentials and the model chain length m is proposed so that the approach can also be used in non-spherical models). It can be seen from this expression that the usual geometric (Berthelot) mean is recovered in the special case of mixtures involving components of identical ionization potential, molecular size and potential range. In mixtures where these parameters are different for the two components values of $k_{ij} \neq 0$ should be expected. The combining rule given in eq 8.56 has been shown to yield better agreement with experimental data than the traditional geometric mean. For example, in the case of mixtures of alkanes and perfluoroalkanes use of the traditional Lorentz-Berthelot rules leads to the wrong type of phase behaviour while the use of eq 8.56 to obtain k_{ij} leads to the correct behaviour (see for example Figure 8.6). The treatment has also been extended to deal with mixtures involving polar and hydrogen-bonded molecules, although the results in this case were found to be more varied. Huynh *et al.*^{471,472} have followed the work of Haslam *et al.*¹³³ using the Hudson-McCoubrey method to develop an approach to predict binary parameters based on the pseudo-ionization energy of functional groups in a group-contribution based method (see section 8.6).

It is also worth noting that in the case of SAFT equations of state, the molecular basis of the theory means that it is possible to transfer binary-interaction parameters when studying mixtures within a homologous series very successfully. This idea has been used in numerous works to predict the phase behaviour of (alkanes + water),^{34,75,379} (alkanes + perfluoroalkanes),¹¹⁷ (alkanes + carbon dioxide),^{114,130} (alkanes + hydrogen chloride)¹⁰⁶, and (alkanes + nitrogen)¹¹³, and aqueous solutions of surfactants,^{123,455,473} to name but a few.

8.6 SAFT Group-Contribution Approaches

In group-contribution (GC) methods the properties of the system of interest (a pure compound or a mixture) are described in terms of the functional groups

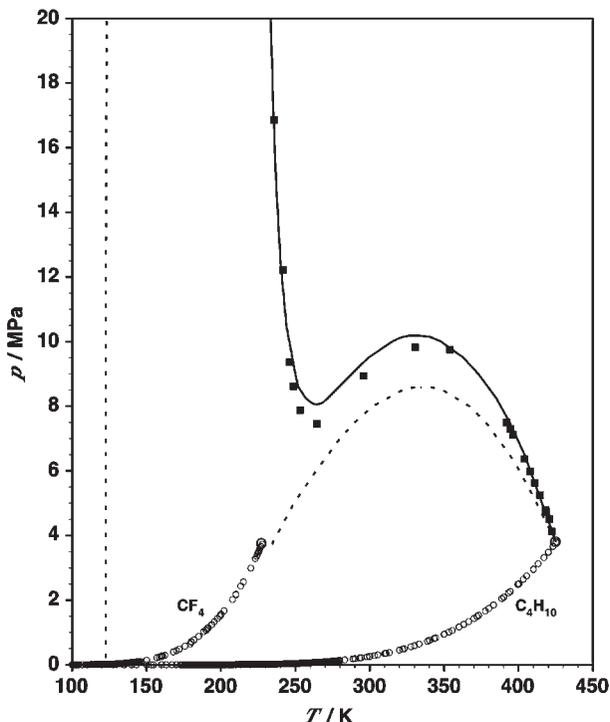


Figure 8.6 Pressure p as a function of temperature T for the phase diagram of ($\text{C}_4\text{H}_{10} + \text{CF}_4$). \square , pure component critical point; \circ , pure component critical part; \circ , vapour pressure of the pure substances; \blacksquare , critical points of the mixture; —, predictions obtained from SAFT-VR equation with the predicted value of $k_{ij} = 0.063$ determined from the use of eq 8.56 correctly indicating $1^p \text{Aln}Q$ phase behaviour; - - - - , estimates obtained from SAFT-VR with $k_{ij} = 0$ predicted an erroneous type of phase behaviour. Reprinted with permission of Fluid Phase Equilibria.¹³³

making up the molecules; for example, a simple molecule like monoethanolamine (MEA) would be described in terms of one OH, one NH_2 , and two CH_2 groups. The groups, or the contributions of the groups, are characterized by sets of inter- and intra-molecular group parameters, and the assumption is that combinations of these lead to the thermodynamic properties of the molecules or mixtures of interest. As such GC methods can turn into very useful predictive tools, since from the description of a few groups the thermodynamic properties and phase equilibria of a large number of pure compounds and mixtures can be accessed without additional fitting to experimental data.

The GC concept is not new; it has been widely implemented for example in the calculation of pure component properties (an overview is provided in ref 474), for the estimation of activity coefficients of liquids in the successful UNIFAC approach,⁴⁷⁵ and more recently, in equations of state.⁴⁷⁶ The

advantage of equation of state GC methods is that equations of state are not limited, in principle, in their range of application, and more importantly, can treat liquid and vapour phases continuously, and through thermodynamic relations, can be used to calculate any thermodynamic property, which is important in process design applications.

8.6.1 Homonuclear Group-Contribution Models in SAFT

Based on the original homonuclear molecular SAFT model for chain molecules (see Figure 8.2), one of the first attempts to combine a group-contribution method with the SAFT methodology was presented by Lora *et al.*⁵⁹ who use the parameters of low-molecular-weight propanoates³⁹ (homomorphs of the acrylate repeat groups) to calculate the size and energy parameters of polyenoates.⁶⁰ Following these ideas, Tobaly and co-workers have presented a series of papers proposing a predictive implementation of the SAFT equation of state.^{477,478,479} The authors present two approaches for the predictive use of the equation of state within substances of the same chemical family. In approach 1, the parameters describing the members of a chemical family are obtained by fitting to experimental data in the usual way (*i.e.* by using experimental vapour-pressure and saturated-liquid density data for each compound) and then deriving relations between the molecular parameters and molecular properties (*e.g.* molar mass); note that this approach amounts to using different parameters for each molecule. In approach 2, all molecules of a series (*e.g.* the alkane family) are assumed to be formed from identical segments, and so only one set of segment parameter values is used. In the case of alkanes, this means that the CH₃, and CH₂ chemical segments are described by the same size and energy group parameters, and differences between members of the same chemical family are treated simply by assigning different values of the chain length, *m*. Approach 2 was found to predict heavier *n*-alkane phase behaviour more accurately than approach 1 and was therefore used to study the phase behaviour of other hydrocarbons, including alkenes, cyclic compounds and mixtures of these,^{477,479} and alcohols,⁴⁷⁸ yielding good results. Unfortunately, the predictive ability of this technique is rather limited, since it is not fully formulated within the scope of contributions of functional groups, but more an effort to model the behaviour of parameters within a certain homologous series by transferring parameters.

A more sophisticated group-contribution approach, termed GC-SAFT, was later introduced by the same authors.⁴⁷⁹ In this case, the molecules are decomposed into functional groups and distinct group contributions are estimated. The authors implement the group-contribution method within the original SAFT²³ and the SAFT-VR^{92,93} approaches. The concept of groups building up to molecules is introduced explicitly in this approach, but the underlying molecular model is still a homonuclear one in which group parameters need to be averaged to predict pure and mixture properties. This method has been used to study alkanes, α -olefins, 1-alkanols, alkyl-benzenes and alkyl-cyclohexanes and their

mixtures,^{479,480} and later alkyl-esters and formates,^{481,482} and their mixtures, using the segment-based polar contribution of Jog and Chapman.²⁷⁷ The phase equilibria of mixtures of esters with alkanes, cyclohexanes, alkyl-benzenes and 1,4-dimethylbenzene have also been studied in detail and the performance of the method was found to lie within an uncertainty of a few percent in a fully predictive manner (*i.e.* no binary interaction parameters were used).

Group-contribution based approaches have also been studied within the PC-SAFT framework. As discussed in section 8.3.4, the basis of the perturbed-chain SAFT approach (PC-SAFT)¹⁴⁷ is slightly different to other versions of SAFT in that the Helmholtz energy of a homonuclear hard chain fluid (as opposed to that of the monomer fluid) is first considered and the dispersion interactions are described by a perturbation expansion with the hard-chain fluid as reference. As such, it is, in principle, not the best suited to be recast as a GC approach, though relations between molecular model parameters and molecular properties (*e.g.* molar mass) can be derived so as to identify the contribution of different chemical groups to the properties of molecules. For example, the intermolecular model parameters for a series of hydrofluoroethers where experimental data (saturated liquid densities and pressures) are available have been determined and used to calculate the contribution of each functional group (CH₃, CH₂, CF₃, CF₂ and O groups are identified).⁴⁸³ In a later study the ester series was considered⁴⁸⁴ and the phase-behaviour predictions of esters not included in the regression database were found to compare well using the GC-SAFT approach, including dipole-dipole interactions using the perturbation expansion of Twu and Gubbins,²⁷¹ and the original SAFT, SAFT-VR and PC-SAFT equations; however for large esters the deviation from experimental data is rather significant (*e.g.* 50 % standard deviation was found for methyl tetracosanoate). The same method, with a term also describing a quadrupolar-quadrupolar contribution,²⁷² has also been used for the prediction of equilibrium properties of polycyclic aromatic hydrocarbons and their mixtures.⁴⁸⁵ The vapour pressures of 19 chemical families including hydrocarbons, cyclic and aromatic hydrocarbons, alcohols, amines, nitriles, esters, ketones, ethers, and others have also been considered.⁴⁸⁶ The recent work of Tihic *et al.*,⁴⁸⁷ in which the PC-SAFT equation is combined with the group contribution of Constantinou *et al.*⁴⁸⁸ to incorporate first and second-order groups so that isomers and proximity effects can be considered, is interesting and has been used to study a wide range of polymer systems.^{218,487,489} Unfortunately, as in previous approaches, the underlying homonuclear model does not enable the differentiation of groups at the molecular level.

8.6.2 Heteronuclear Group Contribution Models in SAFT

Following the original first-order thermodynamic perturbation theory of Wertheim heteronuclear models can be proposed where the segments in a given model molecule are arbitrarily different. The earliest works in this direction

considered molecules formed from heteronuclear hard-spherical segments with attractive interactions treated at the van der Waals mean-field level;^{490–493} expressions for heteronuclear SW chains^{139,494–496} and LJ chains^{64,497,498} have also been presented.

A heteronuclear model, which allows the free energy of the fluid to be written explicitly in terms of group parameters that are different, is ideally suited to developing a detailed molecular-level group-contribution model and if the heteronuclear nature of the model is retained in both the monomer and chain fluid, the detailed connectivity of the segments can be preserved and hence some isomers differentiated. Although Wertheim's theory is based on tangentially bonded segments, a tangential model with integer values of m to represent each functional group is not capable of describing multifunctional molecules accurately.⁴⁹⁹ This is also seen in homonuclear versions of SAFT when modelling chain fluids; for example the commonly used relationship for the number of segments in the model chain to describe alkanes as a function of the number of carbon atoms C , $m = 1/3(C + 1) - 1$, prescribes m values of 1.33 for ethane, 1.67 for propane and 2 for butane. Therefore, butane is modelled by two tangentially bonded segments, while ethane and propane are essentially modelled by fused segments. The implementation of a heteronuclear-based GC SAFT approach has recently been proposed in the SAFT- γ ^{499,500} and GC-SAFT-VR⁵⁰¹ approaches, where the difficulties associated with the underlying tangential models in SAFT using generalizations of the SAFT-VR equation of state to model heteronuclear chain molecules are addressed.

In SAFT- γ ^{499,500} a model of fused segments is proposed; each group is described by an integer number of segments ν_k^* and a parameter reflecting the contribution of each group k , the so-called shape factor S_k , to the overall molecular properties is introduced to describe molecules as fused segments. The shape factor S_k ,⁵⁰⁰ describes the contribution that a given segment k of diameter σ_{kk} makes to the overall molecular geometry and contributes to the mean radius of curvature, the surface area and the volume of the molecule. A given group k is then fully described by the number of segments in the group ν_k^* , the shape factor S_k , a diameter σ_{kk} , a dispersive energy ϵ_{kk} and range λ_{kk} . In cases of associating groups, two additional parameters are introduced for each site-site a - b interaction, namely the energy $\epsilon_{kk,ab}^{\text{HB}}$ and range $r_{kk,ab}^c$, and for unlike group interactions, ϵ_{kl} , $\epsilon_{kl,ab}^{\text{HB}}$ and $r_{kl,ab}^c$ also need to be determined. In the GC-SAFT-VR⁵⁰¹ approach non-integer values of m are considered for each functional group and therefore, although still based on the tangentially bonded approach of Wertheim, the model can also be considered as describing fused chains. In this approach a given group k is described by its chain length m_k , diameter σ_{kk} , dispersive energy ϵ_{kk} and range λ_{kk} , as well as the same additional parameters as in the SAFT- γ approach when considering associating groups. In comparing the two approaches, using

$$\nu_k^* S_k = m_k, \quad (8.57)$$

where ν_k^* is the number of segments in a group of type k following the notation in,⁵⁰⁰ m_k is the chain length as defined in ref 501 and

$$x_{s,k} = \sum_{i=1}^{\text{NC}} x_{s,ki}, \quad (8.58)$$

where NC is the number of components in the mixture, to change between the definition of the fraction of segments of type k in the mixture used in ref 500 and the fraction of segments of type k in a molecule of type i used in ref 501. It can be seen that the two theories are fundamentally the same with respect to the ideal and monomer terms. In SAFT- γ the original mapping for the effective density⁹² is used to obtain the mean attractive Helmholtz energy a_1 (see section 8.3.3), while in GC-SAFT-VR a mapping suitable for longer square-well ranges⁵⁰³ is used, but the two lead to essentially identical results for the shorter ranges. A second small difference is in the use of a different mixing rule for the effective diameter of the mixture σ_x in the A_1 term; the original (m \times 1b) mixing rule⁹³ does not lead to the correct limit when the diameter of one segment goes to zero, however this limit is not encountered in applications to model real fluids, and so is not an issue, in the group-contribution approaches.

The key difference between the two approaches lies in the treatment of the chain term, A^{Chain} . In SAFT- γ the SAFT-VR chain term is used; through the use of effective parameters, the contribution to the Helmholtz energy due to chain formation is a function of the number of segment-segment contacts in the chain and the contact radial distribution function of an effective fluid. In the case of the GC-SAFT-VR the heterogeneity of the segments is explicit in A^{Chain} , through a generalization of the Wertheim expression that reduces to the original Wertheim term (as used in SAFT-VR) in the limit of homonuclear chains and/or an integer number of chain segments.

In both the GC-SAFT-VR and SAFT- γ approaches, compared in Figure 8.7, the group parameters are determined by fitting to the experimental vapour pressures and saturated-liquid densities of the smaller members of chosen chemical families (*i.e.* alkanes, branched alkanes, 1-alkenes, alkylbenzenes, ketones, alkyl acetates and methyl esters, among others). The predictive capability of the methods is then tested by assessing the description of the fluid phase behaviour of larger molar mass compounds that were not included in the determination of the group parameters.

A key additional advantage of both SAFT- γ and GC-SAFT-VR is that mixtures can be treated in a fully predictive manner without the need to propose combining rules and adjustable parameters. In this context both methods have been shown to provide a good description of the pressure and composition of mixtures including binary mixtures of alkanes, alkenes, alkanols, namely (alkanes + alkylbenzenes), (alkane + ketones), (alkane + esters), (alkane + acids), (alkanes + amines) and even cases with highly non-ideal behaviour; including liquid-liquid equilibrium (LLE) and polymer systems.⁵⁰⁰⁻⁵⁰²

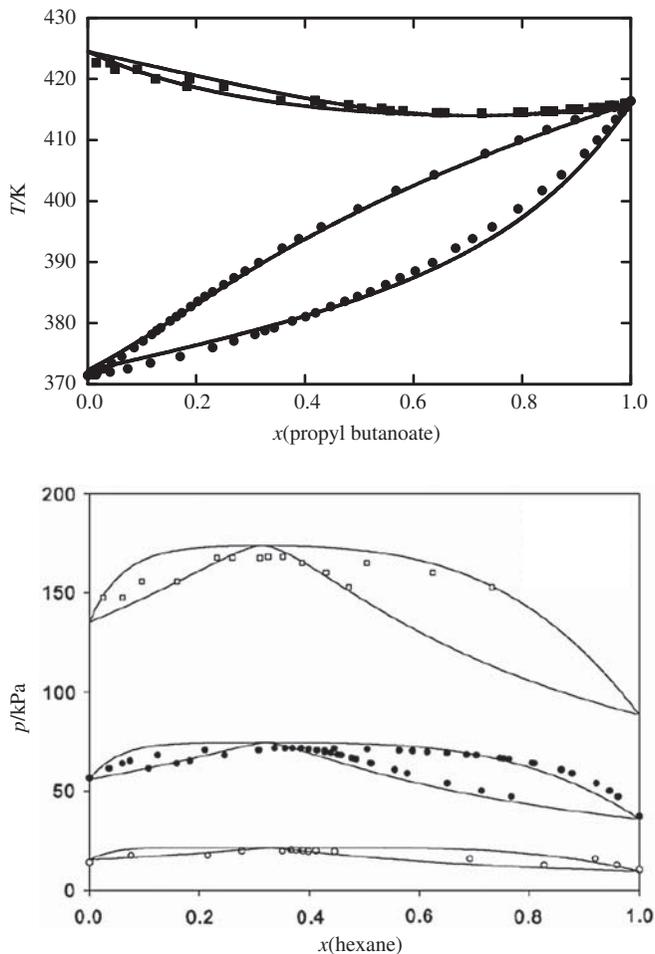


Figure 8.7 TOP: Temperature T as a function of propyl butanoate mole fraction $x(\text{propyl butanoate})$ for the mixtures (heptane + propyl butanoate) and (nonane + propyl butanoate). ●, measurements of (heptane + propyl butanoate);⁵⁰⁶ ■, measurement of (nonane + propyl butanoate);⁵⁰⁶ —, predictions from the GC-SAFT-VR equation using CH_3 , CH_2 , CO and OCH_2 groups without recourse to a fit against any measurements that further demonstrates the versatility of the GC approach. Simply the addition of two CH_2 segments as the alkane chain is increased in length is sufficient to capture the dramatic change in phase behaviour. Reprinted with permission of Fluid Phase Equilib.⁵⁰¹ BOTTOM: Pressure p as a function of hexane mole fraction $x(\text{hexane})$ for the mixtures (hexane heptane + propan-2-one). ○, measurements at $T = 283.15 \text{ K}$;⁵⁰⁶ ●; measurements at $T = 313.15 \text{ K}$;⁵⁰⁶ □, measurements at $T = 338.15 \text{ K}$;⁵⁰⁶ —, predictions obtained from the SAFT- γ equation with CH_3 , CH_2 , and CO groups without recourse to a fit against any measurements that further demonstrates the versatility of the approach. Reprinted with permission of Fluid Phase Equilibria.⁵⁰²

These are promising approaches, which incorporate a detailed molecular model in which groups can be differentiated. In this way, they benefit from advantages of the successful UNIFAC approach, and overcome the difficulties associated with its underlying lattice model. They are accurate over large pressure ranges and can be used consistently for liquid and vapour phases. In addition, as mentioned above, their formulation as continuum fluid theories means that the binary interaction parameters can be determined from pure component data.

8.7 Concluding Remarks

SAFT approaches in any of their many variants provide a means towards modelling complex fluids from detailed molecular models. They all share a common basis stemming from the thermodynamic perturbation theory of Wertheim, which provides the key expressions to obtain the free energy of associating chain fluids from knowledge of the thermodynamics and structure of a monomer reference fluid; the choice and level of detail incorporated in treating this reference fluid lead to the differentiation of the many versions. A fundamental strength of the method is its close link to the proposed molecular model; this often allows direct comparison with simulation data, and helps the continuous improvement of the approach. We have presented an overview of the most popular SAFT-based approaches and their application to modelling the thermodynamics and phase behaviour of fluids, and provided a survey of recent efforts to extend the applicability of SAFT-based equations to more complex systems (such as polar fluids, electrolyte solutions, and critical and inhomogeneous fluids). We have specifically tried to focus on methodological advances since the comprehensive reviews of Economou⁵⁰⁴ and Müller and Gubbins,⁵⁰⁵ rather than aim at a comprehensive review of all systems studied.

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