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# A Survey of Equations of State for Polymers

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Additional information is available at the end of the chapter

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## 1. Introduction

The thermodynamics of polymeric systems play an important role in the polymer industry and are often a key factor in polymer production, processing and material development, especially for the design of advanced polymeric materials. Many polymeric products are produced with a solvent or diluent (or a mixture of them) and often with other low molecular weight compounds (plasticizers, among others). A problem which often arises is how to remove the low molecular weight constituent(s) from the final product (polymer). The solution to this problem involves, among other tasks, solving the vapor-liquid equilibrium (VLE) and/or the vapor-liquid-liquid equilibrium (VLLE) problem. Other applications of polymer thermodynamics directly involve the polymerization processes. For example, several processes such as the production of PET (polyethylene terephthalate) are carried out in two-phase (vapor-liquid) reactors. Phase equilibrium compositions of the reacting components will determine their phase concentrations and thus the outcome of the polymerization reaction. Another example is the case of LDPE (Low Density PolyEthylene) made in autoclave reactors where it may be desirable to perform the polymerization reaction nearby but outside the two-liquid phase region, but close to it, which makes accurate liquid-liquid equilibrium (LLE) information at high pressure essential. During PE (polyethylene) or PP (polypropylene) industrial processing, for example, deposition of the polymer on the reactor surface, heat exchangers and flash drums frequently occurs and this can cause clogging in pipelines. Modeling solid-liquid equilibrium (SLE) is a useful basis from which to gain a better understanding of these industrial polymer problems and thus to avoid their occurrence.

Analogous to the modeling of conventional phase equilibrium, there are two basic approaches available to describe phase equilibrium of polymer-solvent mixtures: activity coefficient models and equations of state (EOS). There are several drawbacks to the activity coefficient approach, for example: it is hard to define standard states, especially for

supercritical components; the parameters of the activity coefficient models are very temperature dependent, and critical phenomena are not predicted because different models are used for the vapor and liquid phases. Furthermore, other thermodynamic properties such as densities, enthalpies, entropies, among others, cannot usually be obtained from the same model because the excess Gibbs free energy is rarely known as a function of temperature and pressure.

EOS are powerful tools for investigating thermodynamic properties and phase behavior of pure fluids and their mixtures. There are many well-tested EOS available for fluid mixtures of conventional substances. For mixtures of polymers with solvents, on the other hand, problems arise due to the different characteristics of the components. To address these many polymer-specific EOS have been proposed, which focus on the polymer component(s) of the mixture. Efforts to represent conventional systems with these EOS have not always been very successful; indeed some of these models perform less successfully than traditional cubic EOS in this regard. This may be a handicap when these models are used for the VLE of the polymer-solvent mixtures. In such cases, little or no polymer is present in the vapor phase and the solvent compressibility plays an important role in the phase behavior. Consequently, there is a strong incentive to extend the conventional EOS developed for small molecules to polymers.

There are two basic issues in extending cubic EOS to apply to polymers and their use. The first issue is the description of the pure component EOS parameters for polymers. To obtain these parameters, various techniques have been suggested. The second issue in extending cubic EOS to apply to polymers is the selection of mixing rules (MR) for the EOS parameters. The classical mixing rules of van der Waals (vdW) have already been tested for polymer solvent mixtures, however, it has been observed that, in order to fit the experimental data, some unrealistic values are necessary for the binary interaction parameters (BIP).

The use of equations of state in phase equilibrium modeling instead of activity coefficient models is mainly a result of the recent development of a class of mixing rules that enable the use of liquid activity coefficient models in the EOS formalism. The implication of this change is far-reaching as an EOS offers a unified approach in thermodynamic property modeling. With this approach, the applicability of simple cubic EOS has been extended to complex systems, such as polymeric systems, if coupled with the appropriate activity coefficient model. Therefore, there is much interest in mixture EOS models capable of describing higher degrees of nonideality than that possible with the van der Waals one-fluid model and its modifications.

Future development of EOS for polymer mixtures is unclear and some contradictory statements can be found in the literature. Some authors indicate that cubic equations can be extended to correlate and predict VLE in polymer mixtures accurately. On the other hand, others state that, considering the complexity of this type of mixture, simplicity is not a necessary requirement for an EOS, as the calculation of parameters for the mixture components is more important. There is agreement, however, on the fact that future

development of EOS for polymer mixtures must emphasize the study of mixing rules and that EOS input parameters should be related to the commonly measured properties of the polymers.

The most apparent progress toward EOS with the ability to describe phase behavior with polymers has been made by applying statistical mechanics. Some early models derived from statistical thermodynamics assumed molecules to be arranged in a lattice, whereas many of the more recent theories picture molecules to be moving freely in continuous space. In lattice models, the molecules are assumed to have one or more segments, and the partition function of the system can be obtained by counting the possible configuration when these segments are arranged in hypothetical cells which are like the lattices in solid materials. Then the thermodynamic quantities can be calculated from the partition function on the basis of statistical mechanics.

A huge amount of work has been done on the understanding of phase behavior in polymeric mixtures, either from an experimental or theoretical point of view. As well as supplying important data, experiments enable the evaluation of EOS models for the correlation and/or prediction of phase behavior. A model, on the other hand, takes much less experimental effort and can guide the researcher/analyst in the right direction.

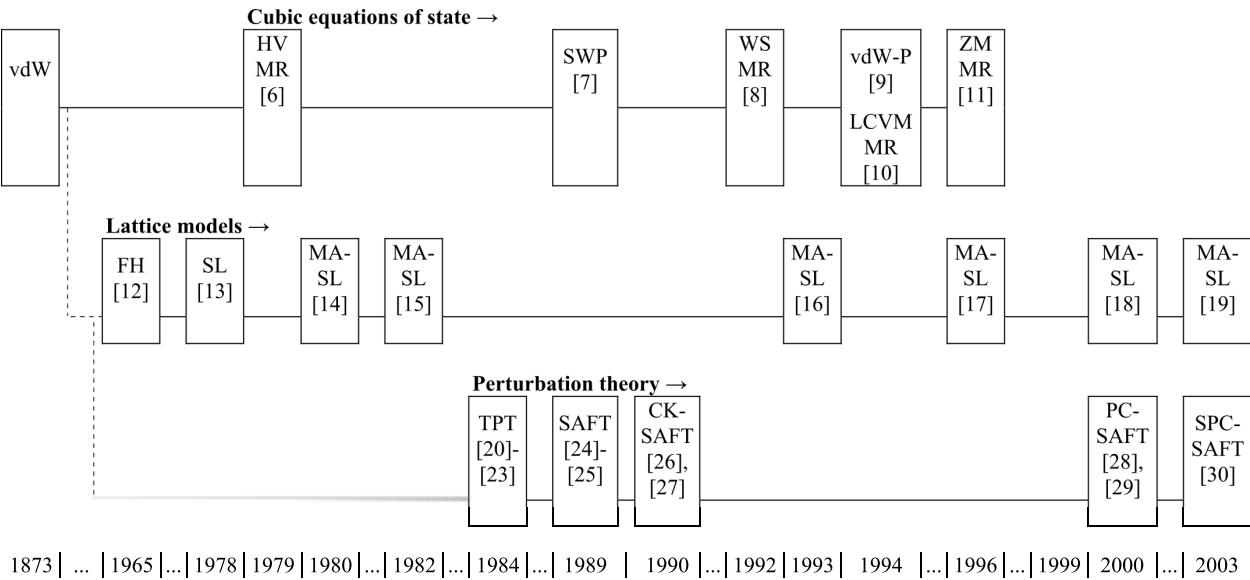
A detailed review of the different lines of developing equations of state for the calculation of fluid phase equilibria is given by [1]. Recently [2] presented and discussed in depth both classical and novel thermodynamic models, which have been developed and can potentially be used for industrial applications. A review of the use of some equations of state (EOS) for LDPE process simulation can be found in Orbey *et al.* [3] and Valderrama [4].

Although there have been some analyses on equations of state that can describe the phase equilibria involving polymers, additional assessments are necessary. In general, the available works concern a specific approach, not taking into account others. In addition, these reviews and surveys focus on detailed model theory or theoretical possibilities of model variations, with a few quotes from practical applications. This chapter therefore presents an overview of the progress on EOS models for polymer systems considering the following approaches:

- Cubic EOS (mixing rules incorporationg excess Gibbs free energy models)
- Lattice models [Sanchez-Lacombe (SL) equation of state]
- Perturbation theory (SAFT equation: the original version and its variants)

In EOS applications only works dealing with phase equilibrium are discussed, other types of applications, such as solvent absorption and/or polymer swelling, are not addressed. The timeline diagram in Figure 1 shows some of the key developments and outstanding papers related to the development of equations of state for polymer systems, which are discussed in this chapter. The following notation is used:

- Cubic Equations of State [Huron and Vidal (HV) Mixing Rule (MR); Sako-Wu-Prausnitz (SWP) Equation; Wong and Sandler (WS) MR; vdW Applied to Polymer Solutions (vdW-P) by Kontogeorgis, Harismiadis, Fredeslund and Tassios; Linear Combination of Vidal and Michelsen (LCVM) Mixing Rules by Boukouvalas, Spiliotis, Coutisikos, Tzouvaras and Tassios; Zhong and Masuoka (ZM) MR]
- Lattice Models [Flory-Huggins (FH); Sanchez and Lacombe (SL) equation; key Modifications and Applications (MA) of SL by Kleintjens and Koningmehl, Panayiotou and Vera, Kiran and Xiong and Zhuang, Koak and Heidemann, Gauter and Heidemann, Krenz and Heidemann and de Loos]
- Perturbation theory [Wertheim Thermodynamic Perturbation Theory (TPT); Statistical Associating Fluid Theory (SAFT) by Chapman, Gubbins, Jackson, Radosz; Chen and Kreglewski [5] SAFT (CK-SAFT) by Huang and Radosz; Perturbed-Chain SAFT (PC-SAFT) by Gross and Sadowski; Simplified PC-SAFT (sPC-SAFT) by von Solms, Michelsen and Kontogeorgis]



**Figure 1.** Timeline of some Key Model Developments Addressed in this Chapter from van der Waals (vdW) Equation in 1873.

## 2. Cubic equations of state and mixing rules

The first group of models to describe the phase behavior (by calculating the equilibrium constant) corresponds to the van der Waals equations of state, known as cubic equations, in either the original version or variants thereof. They are extremely simple and efficient for experimental data correlation. In this group, modifications of the Redlich-Kwong equation stand out, especially the Soave-Redlich-Kwong (SRK) [31] and the Peng-Robinson (PR) [32], which can calculate, often successfully, the vapor-liquid equilibrium for normal fluid and mixtures. However, application of the cubic equations of state for polymeric blends is not immediately obvious as this application does not follow standard procedures. The conventional method for calculating the pure parameters in

cubic equations of state requires components' critical properties and vapor pressure, which do not exist for polymers. Therefore, two basic issues should be addressed when extending cubic equations of state for polymers and their mixtures. The first, presented in the following paragraphs is the description of the parameters of pure components, and the second is the choice of the mixing rule, which will be discussed later in sections 2.1-2.3.

There are four conditions to be satisfied when selecting the pure component parameters of a cubic equation of state. First, a polymer is non-volatile and therefore should not exhibit any vapor pressure. If there are oligomers in the mixture though, low vapor pressures might be considered. Therefore, critical properties may be assigned for the oligomers, treating them as conventional components. The second condition is that the equation of state should predict densities of molten polymers. The third condition requires that the parameters reflect the polymers' basic characteristics such as the degree of polymerization. This is important because experimental data demonstrate that these polymer characteristics directly affect the vapor-liquid equilibrium in polymer-solvent mixtures. The fourth point, somewhat connected to the third, requires easily accessible and physical meaning characteristics as input parameters for calculating the parameters of the equation of state. As stated before, the SRK equation of state is expressed by:

$$P = \frac{R \cdot T}{V - b} - \frac{a(T)}{V \cdot (V + b)} \quad (1)$$

and the PR equation is given by:

$$P = \frac{R \cdot T}{V - b} - \frac{a(T)}{V \cdot (V + b) + b \cdot (V - b)} \quad (2)$$

where  $T$  is temperature,  $V$  is molar volume,  $P$  is pressure and  $R$  is the universal gas constant. The parameter  $a$  is a measure of the attractive forces between molecules, and the parameter  $b$  is the co-volume occupied by these molecules.

The first attempt to apply a cubic equation to polymers was made by Sako *et al.* [7] in order to calculate the high pressure vapor-liquid equilibrium for a polyethylene-ethylene system. To overcome the problem of calculating the pure parameters for the polymer, Sako *et al.* [7] calculated the attractive parameter in the SRK equation using the London dispersion formula, and extrapolated the co-volume ( $b$ ) values from n-alkane data. To take into account external degrees of freedom, they also added a third parameter  $c$ , whose values were fitted from density data. The SWP (Sako-Wu-Prausnitz) equation is a member of the cubic family:

$$P = \frac{R \cdot T \cdot (V - b + b \cdot c)}{V \cdot (V - b)} - \frac{a(T)}{V \cdot (V + b)} \quad (3)$$



The SWP equation was used with relative success by Tork *et al.* [33] when calculating the phase equilibria in binary and ternary systems of polyolefins. The calculations focused on the high pressure phase equilibrium for ethylene-polyethylene systems and for liquid-liquid equilibrium in systems containing either high density polyethylene or polyethylene-polypropylene copolymer. The results for the copolymer-solvent system were compared with those provided by the SAFT (Statistical Associating Fluid Theory) equation. The two equations of state can describe the UCST (Upper Critical Solution Temperature) and LCST (Lower Critical Solution Temperature) behavior as well as U-LCST, with similar precision. When using the SAFT equation, the binary interaction parameter is maintained constant, while in the SWP equation this parameter is expressed as a function of temperature. In addition, Sako *et al.* [7] investigated the influence of an inert gas on the LCST for the polyethylene-hexane system. The polydispersity of different polyethylene resins is considered when computing the phase equilibrium using pseudocomponents, chosen using the moments of experimental molecular weight distributions.

Kontogeorgis *et al.* [9] used the van der Waals equation of state to correlate vapor-liquid equilibrium data of polymer solutions. They proposed a method to calculate the interaction parameter  $a$  and co-volume  $b$  in the equation of state for polymers from two volumetric datasets at low pressure. Both parameters  $a$  and  $b$  (assumed to be independent of temperature) can be analytically expressed from two experimental molar volumes, each one at a different temperature. The pressure in the van der Waals equation is then considered equal to zero. The parameters  $a$  and  $b$  are linear functions of molecular weight. When dealing with polymer solutions, these parameters are obtained from van der Waals mixing rules as well as from the classic combination rules. Fitting only one binary parameter, the van der Waals equation of state is able to correlate the equilibrium pressure for various solutions of polyethylene and polyisobutylene accurately. However, large negative values for the binary interaction parameters, very different from typical values, are frequently required, indicating that this procedure, although empirically successful, does not have a significant physical basis. For almost athermal solutions, the Berthelot combining rule [34] is considered, and the binary interaction parameter is predicted by a simple function of the molecular weight of the solvent. Thus, satisfactory results are obtained.

The performance of cubic equations of state is directly related to the efficiency of mixing rules to represent the phase equilibria at high pressures. Basically, the mixing rules can be divided into two classes: van der Waals-type and those that incorporate excess Gibbs energy ( $G^E$ ).

## 2.1. van der Waals mixing rules

In order to extend the application of PR and SRK cubic equations of state for polymer-solvent systems, the conventional mixing rules employed are those from van der Waals (vdW) [34], which are expressed as:

$$a = \sum_i \sum_j x_i \cdot x_j \cdot a_{ij} \quad (4)$$

$$b = \sum_i \sum_j x_i \cdot x_j \cdot b_{ij} \quad (5)$$

where  $x_i$  and  $x_j$  are the mol fractions,  $a_{ij}$  is the cross-energy parameter and  $b_{ij}$  is the cross co-volume parameter.

It should be stressed that these rules are limited to non-polar fluids and therefore are unable to represent the highly non-ideal behavior of polar or associative fluids.

An empirical approach to overcome the shortcomings of the vdW mixing rule has been to simply add new parameters and composition dependence to the combination rule for parameter  $a$ , usually keeping the combination rule for parameter  $b$ . Some examples may be cited: Adachi and Sugie [35]; Panagiotopoulos and Reid [36] and Schwartzentruber *et al.* [37]. These modified rules usually aim to solve specific problems, and the number of binary interaction parameters is quite variable. There are many problems associated with these multiparametric combination rules which limit their use in process design for mixtures containing many components (such as mixtures of isomers). Among them, the dilution effect may be cited: as the number of components in a mixture increases, the molar fraction of any component becomes smaller. This leads to small contributions of the new added parameters and terms that are strongly composition dependent. Consequently, as the number of components increases, the mixing rule is effectively reduced to a quadratic dependence, as in the one-fluid van der Waals fluid theory [38].

## 2.2. Mixing rules for excess free energy ( $G^E$ ) models

Like conventional phase equilibrium modeling, there are two basic modeling tools for dealing with polymer-solvent mixtures: excess Gibbs free energy ( $G^E$ ) models (or activity coefficient models) and equation of state models. There are plenty of models in each category and selecting the best model for a specific project can often be quite difficult. Furthermore, equation of state and activity coefficient models have varying abilities in extrapolating data beyond given ranges of temperature and pressure, which further hampers the choice of the best model. These models also behave differently when predicting vapor-liquid equilibrium from other measured properties, such as the infinite dilution activity coefficient for a polymer in solvent.

Over the last two decades several methods combining activity coefficient models with equations of state have emerged. These methods are useful for correlating/predicting the phase equilibria of conventional mixtures, and are promising for mixtures containing polymers. Moreover, they allow us to investigate an activity coefficient model in two ways: first as a conventional model (i.e. in the approach  $\gamma$ - $\phi$ ); secondly as part of an equation of state. In general, activity coefficient models are considered more flexible to accommodate a highly complex phase behavior. Equation of state models, on the other hand, may take into



account the effects of compressibility in a thermodynamically more consistent way, and are most useful at higher pressures.

Huron and Vidal [6], pioneers in this field, incorporated an excess Gibbs free energy model into a mixing rule. Their method is based on three assumptions: (i) the excess Gibbs free energy, calculated from an equation of state at infinite pressure equals the excess Gibbs free energy calculated from an activity coefficient model for the liquid phase (ii) the co-volume parameter  $b$  is set to the volume at infinite pressure (iii) the excess volume equals zero. Thus the mixing rule is written as:

$$\alpha_V = \frac{1}{q_2} \cdot \frac{G^E}{R \cdot T} + \sum_i x_i \cdot \alpha_i \quad (6)$$

where  $\alpha_V = a/(b \cdot R \cdot T)$  and  $q_2 = -\ln 2$  for SRK equation. Huron and Vidal [6] showed that their mixing rule gives good results for non-ideal mixtures. Soave [39] showed that the Huron and Vidal rule represents an improvement over the classical quadratic mixing rules and can accurately correlate the vapor-liquid equilibrium for highly nonideal systems. The Huron and Vidal mixing rule has also been applied to several polar and asymmetric systems [40]–[42].

The Huron and Vidal mixing rule has some undesirable characteristics, such as: it does not reproduce the quadratic dependence of the second virial coefficient (QDSVC) with the composition at low pressure; it has no predictive value because the parameters of the activity coefficient model, estimated at low pressure, have to be re-estimated at high pressure; furthermore, these parameters are temperature dependent. Various proposals [43]–[44] have tried to cope with these constraints, however, they fail to succeed as discussed below.

Mollerup [45] suggested an alternative method to that of Huron and Vidal, assuming that the excess volume is zero at low pressure and that the excess Gibbs free energies calculated from an equation of state and from an activity coefficient model can be matched in this condition. Therefore, the activity coefficient parameters do not need be re-estimated if pressure and temperature conditions correspond to those at which they are fitted. However, since this theory cannot be applied to supercritical fluids, as well as the difficulty of computing roots (of the equation of state) for the liquid phase at zero pressure, its application is restricted.

Heidemann and Kokal [46], in accordance with Mollerup [45], also take the reference state at null pressure, attempting, however, to overcome the problem of calculating the root for the liquid phase at zero pressure. The major contribution of this method is to propose an extrapolation procedure from the system pressure, enabling calculation at temperatures near and above the critical point. Important to mention is that this method requires the solution of a transcendental equation when calculating the mixing rule. Comparative studies demonstrate a better performance of the Heidemann and Kokal rule when compared to the Huron and Vidal rule [6].

A method very similar to Heidemann and Kokal's [46] was proposed by Michelsen [47]. The main difference between them lies in the extrapolation method used for supercritical components. The mixing rule in the Michelsen approach also requires the solution of a transcendental equation. The SRK-Wilson model (using SRK equation of state and Wilson activity coefficient model), obtained using this method, was tested to obtain the phase envelope, including the critical points, and to calculate the phase diagrams at high pressure, without re-estimating the parameters of the Wilson model. Good results were achieved.

Michelsen [48] modified his own method, considering an explicit mixing rule, i.e. avoiding the solution of the transcendental equation. The only drawback of this modification lies in the impossibility of ensuring the accurate reproduction of the  $G^E$  model at low temperatures. Thus, imposing a linear mixing rule to the parameter  $a$ , an expression similar to the Huron and Vidal rule [6] was obtained, and therefore it is called the first-order Modified Huron and Vidal (MHV1) mixing rule.

Dahl and Michelsen [49] found out that replacing the linear approach (MHV1) by a quadratic approximation considerably improves the reproductibility of the  $G^E$  model. The resulting mixture rule, a second-order modification of the Huron and Vidal rule, became known as the MHV2 (second-order Modified Huron and Vidal mixing rule), where the linear rule for the co-volume  $b$  was maintained. Like the Huron and Vidal mixing rule, the MHV2 does not satisfactorily describe the excess molar volume. Additionally, it is theoretically incorrect at the lower bound pressure (when the pressure goes to zero), where it does not show the QDSVC with the mole fraction.

Attempting to straighten out the theoretical inconsistency of the aforementioned mixing rules, Wong and Sandler [8] proposed a new method in which the rules fulfill the QDSVC with the composition at low pressure condition. The basic idea was to consider the excess Helmholtz free energy as much less dependent on pressure than the excess Gibbs free energy. In this way, the excess Helmholtz free energy at high pressure might be equal to the excess Gibbs free energy at low pressure. Therefore, this mixing rule is given by:

$$a = b \cdot \left( \sum_i \frac{x_i \cdot a_i}{b_i} + \frac{G^E}{c} \right) \quad (7)$$

where:

$$b = \frac{\sum_i \sum_j x_i \cdot x_j \cdot (b - a/R \cdot T)_{ij}}{1 - \sum_i x_i \cdot (a_i/b_i \cdot R \cdot T) - (G^E/c \cdot R \cdot T)} \quad (8)$$

$$(b - a/R \cdot T)_{ij} = \frac{1}{2} \cdot \left[ (b - a/R \cdot T)_i + (b - a/R \cdot T)_j \right] \cdot (1 - K_{ij}) \quad (9)$$

and  $c$  is a constant, equals  $-\ln(2)$  for the SRK equation. The mixing rule gives the correct low density limit (the mixture second virial coefficient has a quadratic dependence on mole fraction). The high density limit, in turn, is consistent with experimental data: the equation of state provides the same molar excess Helmholtz free energy at infinite pressure as a function of composition, as well as that obtained from the selected activity coefficient model. The Wong and Sandler [8] mixing rule is not density dependent. It should be highlighted that, unlike the methods proposed above, the Wong-Sandler mixing rule introduced an additional binary interaction parameter besides those predicted by the activity coefficient model, which is the second virial coefficient binary interaction parameter itself. According to the authors, this parameter as well as those from the activity coefficient model, estimated at low pressure, may be interchangeably used (i.e. without restriction) at high pressure.

Boukouvalas *et al.* [10] proposed a new mixing rule for the parameter  $a$  in the attractive term of cubic equations of state. The idea was to make a linear combination between the Huron and Vidal and the MHV1 mixing rules, producing the name LCVm (Linear Combination of Vidal and Michelsen mixing rules), which may be expressed as:

$$\alpha = \lambda \cdot \alpha_V + (1 - \lambda) \cdot \alpha_M \quad (10)$$

where  $\alpha_V$  and  $\alpha_M$  are given by Vidal and Michelsen rules, respectively. The contributions related to  $\alpha$  are weighted by a factor  $\lambda$ , which is proposed by Boulouvalas *et al.* [10] to be 0.36. For the parameter  $b$ , a classical linear rule was considered. The performance of this model was compared to MHV2 and MHV1 models, using the Soave equation and the UNIFAC [UNIQUE (UNiversal QUAsiChemical) Functional-group Activity Coefficient] for nonpolar and polar systems, symmetrical and asymmetrical, low and high pressures. The results indicate an equivalent performance of LCVm compared to the other two models when investigating systems containing molecules of similar sizes. In mixtures composed of molecules with quite different sizes, in particular gas systems with alkanes, the LCVm rule showed superior results.

Zhong and Masuoka [50], based on experimental data, evaluated the MHV1 mixing rule with SRK equation of state and the original UNIFAC model for  $G^E$ . They found out that: 1) SRK equation with MHV1 can not reproduce the  $G^E$  of the  $G^E$  model used in the mixing rule for asymmetric systems, even at low pressure; 2) the original UNIFAC is not accurate for asymmetric systems with large alkanes. The first point reflects the deficiency of MHV1 for asymmetric systems, while the second is caused by the low predictive ability of UNIFAC for systems containing large alkanes. Moreover, it is evident that, although MHV1 is able to reproduce the  $G^E$  model exactly, it may not be as accurate for gas-large alkane systems as UNIFAC can not describe these systems properly. As a result, it is pointless to pursue exact reproduction of the  $G^E$  model when attempting to improve the predictive capability for these systems. However, it is interesting to observe that the SRK equation with MHV1 can satisfactorily reproduce  $G^E$  experimental data if a correction factor is added to  $G^E$  in the original UNIFAC model used in MHV1. With this observation, a new mixing rule was proposed: the MR1 (mixing rule 1), obtained by Zhong and

Masuoka [50]. The MR1 rule is very accurate for systems composed of gas and large alkanes, when the correction parameter is obtained as a simple correlation function of the carbon number for a given gas.

A new mixing rule for cubic equations of state, particularly suitable for highly symmetric systems, was proposed by Zhong and Masuoka [51]. It was validated by two cubic equations of state: a modification of Peng-Robinson equation proposed by Stryjek and Vera (PRSV) [52] and the SRK equation. As there is no critical point for polymers, parameters  $a$  and  $b$  in the equation of state cannot be calculated from critical properties and because polymers are almost non-volatile, their vapor pressures are very low. Therefore, it is possible to use zero-pressure experimental densities to determine them. Alternatively, the approach adopted by Orbey and Sandler [38] may be employed, i.e. to use densities at low pressure with a hypothetical and very low vapor pressure, for example  $10^{-7}$  MPa. Zhong and Masuoka [51], in the proposal of this new mixing rule, considered a null Helmholtz free energy in the limit when pressure tends to infinity. This is the only difference between this mixing rule and the one proposed by Wong and Sandler [8]. As a result, only one parameter is necessary in the new mixing rule, which is much simpler than the method of Wong and Sandler [8], and is as simple as Kontogeorgis *et al.* method [9]. When using the new mixing rule for ten polymer solutions in a wide temperature range, the results show that it allows cubic equations of state to correlate the vapor-liquid equilibrium of polymer solutions precisely even if just one temperature independent parameter is used. These results verify that the assumption, namely the excess Helmholtz free energy is null at infinite pressure, is feasible, or at least acceptable, for polymer solutions. The authors demonstrate that accurate correlations for polymer solutions are insensitive to parameters  $a$  and  $b$  in the equation of state.

In recent years, many studies have focused on improving hybrid models, i.e. equations of state which embody  $G^E$  models into mixing rules. They attempt to expand their applicability to more complex systems, such as those containing highly polar components or molecules with significantly different sizes (e.g., polymer-solvent), without losing versatility and simplicity. Recently, Ahlers and Gmehling [53] proposed the VTPR model (Volume Translated Peng-Robinson) which brings together the UNIFAC and Peng-Robinson equation with translated volume. In the VTPR model, the two Flory-Huggins (FH) type combinatorial terms [12], which come from the equation of state and from the UNIFAC model, as well as the Staverman-Guggenheim [54] contribution of the UNIFAC combinatorial term, were eliminated. Moreover, an empirical approach in VTPR incorporates different exponents in the combination rule for the crossed co-volume of the equation of state, depending on the system studied: for those without polymer, it was set to 0.75, whereas for solvent-polymer systems, it was set to 0.5. This empirical approach, however, introduces some uncertainties. For example, it is not possible to set a single parameter for mixtures containing two solvents and a polymer. Furthermore, it is difficult to choose two exponents for some systems containing a molecule similar to a polymer, for example, propane/hexacontane.

Voutsas *et al.* [55] proposed a new mixing rule, UMR (Universal Mixing Rule), for cubic equations of state applicable to symmetric and asymmetric systems. For the cohesion parameter of the cubic equation, this mixing rule includes the Stavermann-Guggenheim combinatorial term and the residual term of the original UNIFAC model. For the co-volume parameter in the cubic equation, a quadratic mixing rule in the composition is used. This rule has been applied to the *t*-PR (Translated Peng-Robinson) [56] equation [also known as the *t*-mPR (Translated and Modified Peng-Robinson) equation], which is a modification of the PR equation. Very satisfactory results were obtained using the original interaction parameters from the UNIFAC model in predicting vapor-liquid and liquid-liquid equilibria at low and high pressures for several asymmetric systems including polymer mixtures.

### 2.3. Modeling polymeric systems with equations of state embodying Gibbs free energy ( $G^E$ ) models

Orbey and Sandler [57] applied the PRSV cubic EOS, along with the mixing rules proposed by Wong and Sandler [8], to correlate vapor-liquid equilibrium data for some polymer solutions. For pure solvents, they used the conventional method to determine the parameters of the equation of state from the critical properties and the acentric factor. For polymers, however, in order to determine these parameters, they chose an arbitrary value for the vapor pressure,  $10^{-7}$  MPa, and used experimental data of molten polymer densities. As expected, the parameters  $a$  and  $b$  are at least slightly dependent on the molecular weight. Orbey and Sandler [57] used the Flory-Huggins [12] expression to calculate the activity coefficient.

Orbey *et al.* [57] used the SRK cubic equation [31], combined with the Flory-Huggins  $G^E$  model in the Huron and Vidal [6] mixing rule, to correlate the vapor-liquid equilibrium of polymer-solvent mixtures. To extend the SRK equation for pure polymers, suitable critical constants were selected based on available information about long-chain hydrocarbons. For applications in mixtures, the single binary interaction parameter from the Flory-Huggins [12] model was obtained from activity coefficient data at infinite dilution, without using any experimental data for vapor-liquid equilibrium. The results showed that this approach, i.e. an equation of state coupled with mixing rules which incorporate  $G^E$ , may represent the vapor-liquid equilibrium of the polymer-solvent with good accuracy. It was also observed that the binary interaction parameter from Flory-Huggins [12] is much less dependent on temperature and composition when the Flory-Huggins model is coupled with the SRK than when it is used directly in the activity coefficient model.

An equation of state based on ASOG (Analytical Solution Of Groups), called PRASOG (Peng-Robinson-ASOG), was developed by Tochigi [58] to predict the vapor-liquid equilibrium of non-polymeric and polymeric solutions. It makes use of the zero-pressure  $G^E$  mixing rule, hence is consistent with the second virial coefficient dependence, in order to compute the mixture parameters of the Peng-Robinson equation of state and it predicts  $G^E$  by the ASOG method. To apply PRASOG to polymer solutions, the PRASOG-FV (PRASOG Free Volume) has been proposed calculating  $G^E$  from ASOG-FV, and then the vapor-liquid equilibrium in polyisobutylene solutions is predicted.



Tochigi *et al.* [59] extended the application of PRASOG, presented by Tochigi [58] for other polymer solutions. Nine binary systems were investigated in a temperature range from 298.15 K to 361.25 K, with six solvents (benzene, toluene, acetone, methyl ethyl ketone, ethyl acetate, propyl acetate) and four polymers (polystyrene, polyethylene oxide, polypropylene oxide, polyvinyl acetate). When using PRASOG-FV, the accuracy achieved was comparable to those of ASOG-PV and UNIFAC-FV.

Kang *et al.* [60] performed a comparative study for polymers and associating systems using the Peng-Robinson equation with the Wong-Sandler mixing rule (PR-WS), SAFT equation and NLF-HB (Non-Random Lattice Fluid Theory with Hydrogen Bonding) equation. The comparison was based on the prediction accuracy of the bubble point pressure, the molar fraction in vapor phase and the activity of the component in the liquid phase. Several factors were considered for comparison: model evaluation through their modeling errors, characteristics of the estimated parameters and computational issues. In general, when using appropriate parameters, all models provided good results when far away from critical regions, except in the case of non-polar polymers dissolved in non-associating polar solvents.

An evaluation of vapor-liquid equilibrium in polymer-solvent systems with cubic equation of state was performed by Louli and Tassios [61]. In this study the parameters  $a$  and  $b$  of PR equation were fitted from PVT (Pressure-Temperature-Volume) data of pure polymers, assuming that the ratio parameters/(molecular weight) are independent from the molecular weight. Several polymer-solvent systems were evaluated using three different mixing rules, all requiring only one adjustable parameter: vdW [34], ZM (Zhong and Masuoka) [11] and MHV1 [48]. The ZM rule gave the best results and the same performance was achieved when extrapolating predictions regarding temperature and molecular weight.

Using the PRSV cubic equation of state, Haghtalab and Espanani [62] studied the vapor-liquid equilibrium in polymer binary solutions with different molecular weights and temperatures. The parameters of the cubic equation of state were calculated using the Wong-Sandler mixing rule [8] incorporating the FH-NRTL-NRF (Flory-Huggins Non-Random Two Liquid Non-Random-Factor) excess Gibbs free energy model. The total vapor pressure of the polymer solutions was correlated using two adjustable energy parameters as functions of temperature with six constants for the entire temperature range. The modeling results showed very good agreement with the experimental data of several binary polymer solutions.

Voutsas *et al.* [63] showed that the UMR rule with the binary interaction parameters of the original UNIFAC model, independent of temperature, leads to poor predictions of vapor-liquid equilibrium at high temperatures and poor predictions for the heat of mixing. For this reason, Voutsas *et al.* [63] used the model proposed by Hansen *et al.* [64], which consider the binary interaction parameters temperature dependent, overcoming the drawbacks mentioned before. The performance of the new model was evaluated for the prediction of heat of mixing and also vapor-liquid, liquid-liquid and solid-gas equilibria in binary and multicomponent systems with different degrees of non-ideality and asymmetry, including polymer-solvent systems, showing good results.



The SRK and the Sanchez and Lacombe (SL) equations of state were applied by Costa *et al.* [65]-[66] to the flash simulation in a low-pressure separator (LPS) and also in a high-pressure separator (HPS) in an industrial polyethylene facility (specifically, 8 low-density polyethylene resins and 25 linear low-density polyethylene resins were investigated). Three mixing rules were used in the SRK equation: van der Waals (vdW) one-fluid, Wong-Sandler and LCVm. The latter two mixing rules incorporate the Bogdanic and Vidal activity coefficient model [67]. All these models involve two adjustable parameters. The results for the LPS separator indicate that SL and SRK-vdW are the best models. The results for the HPS indicate that the SL is the best model. The SRK-LCVm and SRK-WS are unable to describe the HPS overhead composition.

Costa *et al.* [68] modeled the SLE in polyethylene and polypropylene solutions using SRK and PC-SAFT (Perturbed-Chain SAFT) equations of state. Two mixing rules were coupled with SRK: the Wong-Sandler rule and the LCVm rule, both considering the activity coefficient model from Bogdanic and Vidal [67]. The models were evaluated using SLE data at atmospheric and high pressure, obtained from literature. The binary interaction parameters of SRK and PC-SAFT equations of state were estimated to describe the experimental behavior of 20 different polymer-solvent systems at atmospheric pressure and 31 other polymer-solvent systems at high pressure better. The SRK-LCVm model showed the best performance with the SLE atmospheric data, although when evaluating equations predictive ability, PC-SAFT showed advantages as it is not easy to generate a good correlation of the  $G^E$  (SRK-LCVm) parameter with temperature, whereas the PC-SAFT parameter correlated very well with temperature for all the systems analyzed. In high pressure conditions, interaction parameter correlations as a function of molecular weight and polymer concentration were developed for PC-SAFT and SRK-LCVm (SRK-WS model was not appropriate for the high pressure calculations carried out). PC-SAFT provided the best performance with excellent results, showing suitable interpolating and extrapolating (predictive ability) features.

### 3. Lattice models

In the second group of models for calculating the equilibrium constant, it is assumed that the molecules have one or more segments, and that the partition function of the system can be obtained by counting the number of possible configurations when these segments are arranged in hypothetical cells that resemble the crystal lattice of a solid. The thermodynamic functions can be calculated using the formalism of statistical mechanics. These crystal lattices can be considered compressible or incompressible. Incompressible lattices are generally used to model liquids at low pressures, a condition in which the concept of activity coefficient is used. The most widely used activity coefficient models are based on this formalism, e.g. [12], [69]-[71]. For compressible lattices, equations of state based on lattice models result. An example of such models is the lattice fluid theory [13], [72].

The lattice model, originally developed to describe the liquid phase, considers the liquid in a quasi-crystalline state, in which the molecules do not translate fully chaotically as in a gas, but each one tends to stay in a small region, a more or less fixed position in space, around which it vibrates back and forth. The quasi-crystalline picture of the liquid state supposes that the molecules are regularly arranged in space as in a lattice, and therefore models for liquid and liquid mixtures are called lattice models. Molecular considerations suggest that deviations from ideal behavior in liquid solutions are mainly due to the following effects: first, the attraction forces between unlike molecules are quantitatively different from those between alike molecules, giving rise to a nonzero enthalpy of mixing; second, if the molecules differ significantly in size or shape, the molecular arrangement in the mixture can be appreciably different from that for pure liquids, resulting in a non-ideal entropy of mixing; finally, in binary mixtures, if the attraction forces in one among the three possible interaction pairs are much stronger (or much weaker) than the other two pairs, there will be some preferred orientation of the molecules in the mixture what, in extreme cases, can lead to instability or incomplete miscibility [34].

The most simple lattice model considers a mixture of two liquids whose molecules are small, symmetrically spherical and similar in size (the ratio of their sizes is close to one). This model assumes that the molecules of each pure liquid are regularly arranged and equidistant from each other in the lattice. The molecular movement is limited to vibrations around equilibrium positions and is not affected by the mixing process. This model also assumes that for a fixed temperature the lattice spacing in both pure liquids and in the mixture are the same, regardless of composition (excess volume is null). The first step is to obtain an expression for the potential energy of a pure liquid or a mixture, assuming that the potential energy is pair-to-pair additive for every pair of molecules and that only the nearest neighbors are considered in this sum. This means that the potential energy of a large number of molecules in the lattice is given by the sum of the potential energy of all pairs of molecules situated immediately next to each other. Therefore, considering the excess volume and the excess entropy as null, the excess Gibbs free energy for the two-suffix Margules model can be obtained from the total potential energy in the lattice [34].

This lattice model is particularly useful for describing polymeric solutions in liquid solvents. Flory and Huggins [34] independently developed a theory for polymeric solutions which have formed the foundation of most subsequent developments in the last fifty years. In the Flory-Huggins [12] model the system polymer-solvent is modeled as a lattice structure, where each site is occupied by a molecule of solvent or a polymer segment. The combinatorial contributions to the thermodynamic mixing functions are calculated from the number of possible arrangements of the polymer molecules and solvent in the lattice. These combinatorial contributions correspond to the entropy of mixing. The combinatorial contributions of Flory-Huggins [12] model implicitly state that the mixing volume and the enthalpy of mixing are zero. The number of possible molecular arrangements leads to the well-known Flory-Huggins expression for the entropy of mixing [34]. The Flory-Huggins theory and its variations have been successful in correlating and/or predicting the UCST behaviour and loop phase behavior. Variations of this theory include making the interaction

parameter of the enthalpy of mixing dependent on composition and/or temperature. In this context, the works of Cheluget *et al.* [73] and Bae *et al.* [74] may be cited. The UCST behavior, i.e. transition from two-phase to one phase, takes place as a result of energetic effects. The loop behavior normally occurs when specific interactions such as hydrogen bonds take place. Compressibility of a polymeric solution is not the key issue therefore it can be modeled by an incompressible lattice theory. As mentioned above, however, polymeric solutions also exhibit LCST behavior which occurs when polymer and solvent molecules experience different volumetric expansions. For these systems a theory that takes into account the effects of compressibility is required. Significant work has been done to extend the Flory-Huggins theory for such systems by the inclusion of vacant sites (holes) in the lattice, which may vary to enable compressible lattice representation. Within this approach the models of Kleintjens and Koningveld [14] and Panayiotou and Vera [15] may be cited but the Sanchez and Lacombe model [13] should be highlighted given its wide application in polymeric systems.

### 3.1. Sanchez and Lacombe (SL) equation

The lattice fluid theory for liquid and gaseous mixtures developed by Sanchez and Lacombe [13], [75] is formally similar to the Flory-Huggins theory. However, the essential and important difference is that the Sanchez and Lacombe theory introduces holes to account for variations in compressibility and density, i.e. the mixture density may vary by increasing the fraction of holes in the lattice. The Sanchez and Lacombe equation uses a random mixing expression for the attractive energy term. Random mixture means that the composition everywhere in the solution equals the total composition, i.e. there are no effects of local composition. The energy of the lattice depends only on nearest neighbors interactions. For a pure component the only non-zero interaction energy corresponds to mer-mer pair interaction. The interaction energies of types mer-hole and hole-hole are zero. The Sanchez and Lacombe equation assumes a random mixture of holes and mers. Therefore, the number of mer-mer nearest neighbors is proportional to the probability of finding two neighboring mers in the system. The Sanchez and Lacombe EOS [13] is given by:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \cdot \left[ \ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \cdot \tilde{\rho} \right] = 0 \quad (11)$$

where:

$$\tilde{T} = \frac{T}{T^*} \quad \tilde{P} = \frac{P}{P^*} \quad \tilde{\rho} = \frac{\rho}{\rho^*} \quad (12)$$

$$T^* = \frac{\varepsilon^*}{k} \quad P^* = \frac{\varepsilon^*}{v^*} \quad \rho^* = \frac{MW}{r \cdot v^*} \quad (13)$$

and  $T$  is the absolute temperature,  $P$  is the pressure,  $\rho$  is the density,  $MW$  is the molecular weight,  $k$  is the Boltzmann constant, and  $r$ ,  $\varepsilon^*$ , and  $v^*$  are pure component parameters

related to the corresponding scale factors  $T^*$ ,  $P^*$  and  $\rho^*$ , respectively. These scale factors are independent of the molecular size of the polymer. For mixtures, the model parameters become composition dependent through the following mixing rules:

$$v_{mix}^* = \sum_i \sum_j \phi_i \cdot \phi_j \cdot v_{ij}^* \quad (14)$$

$$\varepsilon_{mix}^* = \frac{1}{v_{mix}^*} \cdot \sum_i \sum_j \phi_i \cdot \phi_j \cdot \varepsilon_{ij}^* \cdot v_{ij}^* \quad (15)$$

$$\frac{1}{r_{mix}} = \sum_j \frac{\phi_j}{r_j} \quad (16)$$

where the segment fraction of component  $i$ ,  $\phi_i$ , is calculated as a function of the weight fraction  $w_i$ , given by:

$$\phi_i = \frac{\frac{w_i}{\rho_i^* \cdot v_i^*}}{\sum_j \left( \frac{w_j}{\rho_j^* \cdot v_j^*} \right)} \quad (17)$$

The cross parameters are:

$$v_{ij}^* = \frac{1}{2} \cdot [v_{ii}^* + v_{jj}^*] \cdot (1 - l_{ij}) \quad (18)$$

$$\varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^* \cdot \varepsilon_{jj}^*} \cdot (1 - k_{ij}) \quad (19)$$

where  $l_{ij}$  and  $k_{ij}$  are binary interaction parameters.

Thus, the Sanchez and Lacombe equation obtains the PVT properties of pure component assuming that it is broken into parts or mers which are placed on a lattice and can interact with intermolecular potential. In order to calculate the density of the system correctly, an appropriate number of holes are also placed at specific sites in the lattice. In principle, this equation of state is appropriate to describe the thermodynamic properties of fluids in a wide range of conditions, from normal liquid or gaseous state to supercritical fluid at high temperatures and pressures. A real fluid is characterized by three molecular parameters or by three equation of state parameters, which must be known if the equation of state is to be used. In fact these parameters can be determined through any configurational thermodynamic property obtained experimentally. Vapor pressure data though, are particularly useful for solvents because they are readily available for a wide variety of fluids. For polymers, these characteristic parameters can be estimated by experimental data of the liquid density over a wide range of pressures and temperatures, using for example a

numerical procedure based on non-linear least squares. When few PVT data are available, the parameters can be estimated from experimental values of density, thermal expansion coefficient and compressibility factor at ambient temperature and pressure.

Gauter and Heidemann [18] proposed a procedure to obtain parameters of the pure solvent from the critical temperature, critical pressure and acentric factor, as usually done with cubic equations of state. The polymer parameters were determined through PVT data regression.

Gauter and Heidemann [76] suggested that the polymer's parameters can be adjusted to simultaneously reproduce cloud-point data of polymer-solvent equilibrium and PVT data. They managed to obtain parameters for the Sanchez and Lacombe equation for polyethylene that could be applied for different samples, regardless of molecular weight and molecular weight distribution. The degree of branching and/or the presence of comonomers may also influence the parameters of the polymer.

### 3.2. Modeling polymeric systems using the Sanchez and Lacombe equation

Although there are few references in the literature for vapor-liquid equilibrium (e.g. [3], [77]) and one using industrial plant data [65], a large number of SL EOS evaluations have been reported in the literature regarding liquid-liquid equilibrium.

Kiran *et al.* [16] evaluated the efficiency of the Sanchez and Lacombe equation in predicting the high pressure phase behavior of varying molecular weight (16400, 108000 and 420000) polyethylene solutions in n-pentane and in binary solvents [(n-pentane)-(carbon dioxide)]. It was shown that concentration and pressure variations are correctly predicted if the characteristic temperature of the polymer is suitable adjusted using data from a sample with a specific molecular weight. The model also correctly predicts the behavior shift (solvent dependent) from LCST to UCST as the amount of carbon dioxide in solvent [(n-pentane)-(carbon dioxide)] increases.

Xiong and Kiran [78] modeled ternary systems of [polyethylene-(n-pentane)-(carbon dioxide)] using the Sanchez and Lacombe equation. Phase diagrams were generated for pressures up to 300 MPa and temperatures up to 460 K. The results show that the system can exhibit two or three phases depending on the pressure. At a given temperature, the three phase region disappears with increasing pressure. Depending on the pressure, the calculations also predict the displacements observed experimentally from LSCT to UCST, which are illustrated in ternary diagrams as displacements of the phase boundaries with temperature. It was shown that for polymer samples with high molecular weight, ternary calculations can be simplified by assuming that the polymer-poor phase is essentially free of polymer. Xiong and Kiran [79]-[80] investigated polyethylene binary systems with n-butane, n-pentane and CO<sub>2</sub>.

Koak and Heidemann [17] studied the phase behavior of polymer-solvent systems under conditions close to the vapor pressure curve of the solvent where the vapor-liquid-liquid



equilibrium can occur. Experimental data of High Density Polyethylene (HDPE) in n-hexane were modeled using the following equations: Sanchez and Lacombe, Kleintjens and Koningsfeld [14] and the Perturbed Hard-Sphere-Chain (PHSC) [81]. The phenomena of interest include the LCST behavior and the liquid solvent, vapor solvent and polymer three-phase equilibrium. All the three models examined provided a reasonable representation of the cloud-point for the system HDPE and n-hexane along the three-phase line in the conditions investigated. Phoenix and Heidemann [82] used the SL EOS to develop an algorithm to determine the cloud and shadow point curves of polydisperse polymer/solvent systems using continuous thermodynamics to represent the polymer.

Wang *et al.* [83] compared the performance of the Group Contribution Lattice Fluid equation of state (GCLF) with the Sanchez and Lacombe equation for liquid-liquid equilibrium data in polymer-solvent systems. The authors showed that both equations of state are able to predict the UCST and LCST behaviors, simultaneous or otherwise, as well as the hourglass shape behavior in which there is no LCST or UCST. The systems studied were: (acetic acid)-dodecane, polyisobutylene-(n-pentane), polyethylene-(n-hexane), polystyrene-(n-hexane), polyisobutylene-(n-pentane) and polystyrene-acetone. In all cases the GCLF equation performed better than the SL equation. The GCLF equation showed good sensitivity for the polymer molecular weight, but failed to correctly describe the sensitivity regarding the pressure. The best performance of the GCLF equation was attributed to the simultaneous use of the saturated steam and liquid properties in the regression of group parameters for the equation.

The applicability of equations of state for the modeling and simulation of phase equilibria in polymer production processes is investigated by Orbey *et al.* [57]. A two-stage flash separation of unreacted ethylene from polyethylene, which mimics the separation process in the production of LDPE, is used as a prototype for the simulation, where three equations of state (SAFT, SL and SRK-MHV1-FH) are compared when correlating volumetric, calorimetric and vapor-liquid phase equilibrium properties for ethylene and LDPE. Each equation of state has some unique characteristics that influence the modeling results of the pure components as well as the mixtures. When extended to binary mixtures of ethylene with polyethylene, the results show that the three equations can satisfactorily fit the data, although the best results are obtained with the SRK equation. As expected, all models exhibit less satisfactory results when no binary parameter is fitted to the data. For SRK and SAFT equations, only one binary parameter significantly affected the model performance. On the other hand, the authors observed that in the SL equation the second binary interaction parameter can also make a significant difference.

Koak *et al.* [84] studied the high pressure phase behavior of some industrially important polymer systems: polyethylene-ethylene and polybutene-(1-butene). New experimental data were presented for the system polybutene-(1-butene) in the pressure range from (9 to 17) MPa and in the temperature range from (405 to 447) K. The range of polymer concentration, expressed as polymer weight percent, ranged from 0.31 to 16.65. The system showed LCST behavior. Data from polybutene-(1-butene) and polyethylene-ethylene mixtures, presented



by de Loos *et al.* [85], were modeled using the SAFT and the SL equations. The phase equilibrium calculations were carried out for two scenarios: i) the polymer is considered monodisperse ii) the polymer polydispersity is taken into account, characterizing the polymer through pseudo-components. The polymer polydispersity has a significant effect on the phase behavior of the system under investigation. The results show that, although the model is suitable for polyethylene-ethylene, interaction parameters are required, which depend on the system and on the temperature. Additionally, polymer polydispersity has a significant effect on the phase behavior of the mixture, even for reasonably monodisperse samples. The modeling effort for the system polybutene-(1-butene) showed that, if the models are used in their standard forms, alternative strategies are needed to estimate the polymer parameters so that correlation and/or reasonable prediction of the phase behavior of the polymer solution can be obtained.

In order to verify if a single set of parameters can be used to obtain useful correlations for different polyethylene resins with different solvents, Gauter and Heidemann [76] used the Sanchez and Lacombe equation to model the cloud point isotherms for two systems of ethylene and polyethylene and a system of polyethylene in n-hexane. The three polyethylene samples examined differ considerably in average molecular weight and polydispersity. The polymer parameters were obtained by adjusting volumetric data of pure polyethylene, using an additional volume displacement coefficient. The results showed that the cloud point behavior of the polymer-solvent equilibrium for a variety of polymers and solvents can be correlated with the same set of polymer parameters. The required interaction parameters are relatively small in magnitude. Unfortunately, the calculated results are extremely sensitive to these numbers, even to the third decimal place. In addition, the temperature dependence, although slight, is essential to obtain a reasonable data fit.

Trumpi *et al.* [86] measured cloud point data for a binary system of monodisperse LDPE and ethylene. The cloud points were measured between (395 and 440) K and pressures up to 175 MPa. The experimental data were modeled with the SL equation. The LDPE parameters were obtained from a sequence of non-linear regression analysis based on experimental data for both cloud point and PVT data for polyethylene melt. The results show that the SL equation fits the experimental data well for a wide range of temperatures, pressures and compositions. For diluted mass fractions, on the other hand, the data fit is less accurate. The experimental uncertainty in this region is higher than for polymer-rich mixtures, however, it is smaller than the deviations between model prediction and experimental data. The difference in cloud point pressures between calculated and experimental data increases at the lowest polymer mass fractions.

Krenz *et al.* [19] used the technique described by Trumpi *et al.* [86] to adjust the SL parameters to fit both polyethylene-solvent cloud points and polyethylene density data. The molar mass distribution of the various polyethylene samples were represented by a number of pseudocomponents ranging from 7 to 16. When correlating the cloud points of polyethylene in a variety of solvents, it seemed that there was a unique set of polyethylene

parameters that would work for all mixtures. The polyethylene energy parameters,  $\varepsilon_i$ , could also be adjusted to fit the critical point of a polyethylene-solvent mixture and still provide an accurate representation of the cloud points. The polyethylene parameters, derived from fitting the critical point of the mixture, were more consistent than those found from the cloud points alone [87].

The effect of using different molar mass distributions to represent the same polymer on the HDPE-ethylene cloud points, was examined by Krenz *et al.* [88]. The HDPE parameters were taken from Krenz *et al.* [19]. Log-normal and gamma distributions approximated by nine pseudocomponents were used to match the reported average molar masses. The amount of branching was not known for these HDPE samples but it was believed to be reflected in the different HDPE-ethylene binary interaction parameters [87].

Cloud points for three hydrogenated PolyButaDiene (hPBD)-(n-hexane) mixtures were calculated using the SL equation by Schnell *et al.* [89] and compared to experimental measurements. The SL parameters were directly regressed from pure component PVT data and the hPBD samples were assumed to be monodisperse. The cloud point calculations are predictive because no BIP was used.

Correlation and prediction of miscibility involving binary blends of a variety of homopolymers [polypropylene, polybutadiene, polyisoprene, poly(methyl methacrylate), polystyrene, among others] were investigated by Voutsas *et al.* [90] considering three models: EFV-UNIFAC [91], PR and SL. The performances were evaluated in terms of i) liquid-liquid equilibrium correlation in polymer blends ii) prediction of the effect of polymer molecular weight by using interaction parameters obtained from a pair of molecular weights iii) prediction of the effect of the system pressure on miscibility using interaction parameters obtained from miscibility data at low pressures. All the experimental data used correspond to those of monodisperse polymers. Satisfactory correlation results were obtained with all models but their quality depended on whether the interaction parameters were temperature dependent or not. A satisfactory prediction of the effect of polymer molecular weight on the blend was obtained only with the EFV-UNIFAC model and the SL equation. The SL model showed the best performance and also successfully predicted the effect of pressure on the solution critical temperature, albeit with a poorer prediction of the composition at this temperature.

Chen *et al.* [92] set out to measure important phase equilibria for the industrial production of LLDPE (Linear LDPE) using metallocene catalyst technology. The phase equilibria for (n-hexane)-polyethylene and ethylene-(n-hexane)-polyethylene mixtures were measured from (373.2 to 473.2) K at pressures up to 20 MPa. Approximate monodisperse polymers and their mixtures were used to investigate the effect of polymer molecular weight on phase behavior. All the systems exhibit liquid-liquid equilibrium with UCST. The SL equation was used to correlate the phase behavior of these systems, and the effect of adding supercritical ethylene provided quantitative agreement with experimental equilibrium data. The Hosemann-Schramek function [33] provided a suitable characterization of the molecular weight distribution used in some calculations.

Nagy *et al.* [93] measured cloud point, bubble point and liquid-liquid-vapor bubble point data for binary LLDPE-(n-hexane) and ternary LLDPE-(n-hexane)-ethylene systems. Experimental data were collected in the temperature range of (400 to 500) K at pressures up to 14 MPa. Experimental data of LLDPE-ethylene and LLDPE-hexane were modeled with a modified SL equation [94]. The LLDPE parameters were obtained by performing a sequence of non-linear regression analyses from PVT data of molten polyethylene and experimental cloud point data of the LLDPE-(n-hexane) and LLDPE-(ethylene) systems. From this information and from the adjustment of the SL equation for (n-hexane)-ethylene data, the phase behavior of the ternary system LLDPE-(n-hexane)-ethylene could be predicted. Using this procedure, the effect of the ethylene concentration on the cloud point pressure is slightly overestimated. Therefore, the BIP of the pair LLDPE-ethylene was fitted to the cloud point data of the LLDPE-hexane-ethylene triplet. The SL equation provided a good description of the cloud point curve and an almost quantitative prediction of the ternary bubble point and phase-boundary curves of the vapor-liquid-liquid equilibrium.

One or more polyethylene samples with varying molecular configurations can be mixed to produce a blend with different physical characteristics. Krenz and Heidemann [95] used the MSL (Modified Sanchez Lacombe) equation [96] to calculate the cloud points of a blend of two polydisperse LLDPE resins in a hydrocarbon solvent. The MSL equation is a lattice equation that can be used to calculate polydisperse polymer solutions. The considered polyethylene resins were hPBD type. The cloud points were compared with experimental data available for the systems (hPBD-1)-(hPBD-2)-(n-hexane) and (hPBD-3)-(hPBD-4)-(n-pentane). The four hPBD samples have different molecular weight distributions, although the other properties of the mixture are unknown (degree, type and frequency of branching in the polyethylene molecule). The temperature dependent BIP for LLDPE-hydrocarbon were previously fitted to binary mixture cloud points.

Kanellopoulos *et al.* [97] used the SL equation to calculate the solubility of  $\alpha$ -olefins in polyolefins over a wide range of temperatures and pressures. The characteristic parameters of the pure components ( $T^*$ ,  $P^*$ ,  $\rho^*$ ) were estimated using a dynamic molecular procedure: using commercial software, each selected species (i.e. penetrating molecules and the polymer chain) had its molecular architecture firstly built and its geometry optimized by minimizing the system energy. For all the binary systems investigated, just a single BIP between the penetrating molecules and the polymer chains was estimated. The binary parameter value depends on the penetrating molecule, the comonomer, the polymer crystallinity, as well as the selected experimental conditions (temperature and pressure). The calculated theoretical solubility showed excellent agreement with the experimental measurements and demonstrated the ability of the SL equation to predict the solubility of olefins in semicrystalline  $\alpha$ -polyolefins.

Nagy *et al.* [98] measured equilibrium data at high pressure for the LLDPE-isohexane system which exhibits LCST behavior. The following measurements were performed with weight fractions of polymers ranging from 0 to 0.25, at temperatures of (380-500) K and a pressure

of 12 MPa: cloud point data, bubble points and three-phase liquid-liquid-vapor bubble points. The data were modeled using the Sanchez and Lacombe equation.

#### 4. Perturbation theory

Equations of state based on molecular structures not only provide a useful thermodynamic basis for deriving chemical potentials or fugacities (necessary for phase equilibrium simulation) but they can also help separate and quantify the effects of molecular structure and interactions on global properties and phase behavior. Examples of these effects are the molecular size and shape (e.g. chain length and chain branch), energy of association (e.g. hydrogen bonding), average field energy (e.g. dispersion and induction). Ideally, a single equation of state should incorporate all these effects [26].

Much progress has been made in the development of molecular theories of associative solutions and those containing macromolecules. The essence of this progress is the use of statistical mechanics methods, such as perturbation theory, to correlate the molecular properties with the macroscopic properties of the system under study. In perturbation models, a simple system is initially used as reference, which should characterize the essential aspects of the system and it is usually obtained using a theory with well-defined assumptions. The difference between the actual and ideal system (i.e. the reference system) is then computed using some correction terms, called perturbation terms, which are often based on semi-empirical models. The complexity and magnitude of these perturbations depend on the degree of accuracy with which the reference term, representing the ideal system, can be specified.

With this method, Beret and Prausnitz [99] used the results of Carnahan and Starling [100] for hard spheres, which can be characterized by square well potential to describe the reference state, and proposed the so-called Perturbed Hard-Chain Theory (PHCT). A further refinement, the Perturbed Anisotropic Chain Theory (PACT), was made by Vimalchand and Donohue [101] and Vimalchand et al. [102]. The PACT equation of state takes into account the effects of different molecular sizes, shape and intermolecular forces, including anisotropic dipole and quadrupole forces. The calculations from Vimalchand et al. [102] show that the explicit inclusion of multipolar forces can predict the properties of highly non-ideal mixtures with reasonable accuracy, without the use of binary interaction parameters. However, for pure fluids, the prediction behavior of the PACT equation of state is similar to other comparable equations of state. Kim et al. [103] developed a Simplified version of the PHCT equation (SPHCT), replacing the attractive term of the PHCT equation with a simpler theoretical expression. This simpler equation has been used in a large number of applications, including mixtures of molecules which greatly differ in size. Ikonomou and Donohue [104] derived the Associated PACT equation (APACT). This equation takes into account isotropic repulsive and attractive interactions, anisotropic interactions due to the dipole and quadrupole moments of molecules and hydrogen bonding, and it can predict the thermodynamic properties of associative pure components as well as associative multicomponent mixtures.

#### 4.1. SAFT equation

More recently, a new model in the family of perturbation models was developed by Chapman *et al.* [24]-[25] and by Huang and Radoz [26]. This model is known as SAFT (Statistical Associating Fluid Theory) and is based on the TPT (Thermodynamic Perturbation Theory) work from Wertheim who presented a series of papers [20]-[23] in which a coherent statistical mechanical theory of associating fluids was proposed, expanding the Helmholtz free energy in a series of integrals of molecular distribution function and potential association. Here molecules are treated as different species according to the number of bonded associating sites, and separate singlet densities are defined for each possible bonding state of a molecule. Chapman *et al.* [24]-[25] derived the expression for the Helmholtz free energy of this new reference fluid and compared the results to Monte-Carlo based simulations, obtaining satisfactory results. Huang and Radoz applied the SAFT theory to a number of real pure compounds in 1990 (also known as CK-SAFT, because they applied a different dispersion term proposed by Chen and Kreglewski [5]) [26] and proposed an extension to mixtures in 1991 [27], concluding that the equation is suitable for most of the components/systems investigated.

The essence of the SAFT equation is to use a reference system which incorporates the chain length (molecular size and shape) and the molecular association, rather than the reference fluid with hard (rigid) spheres, which is much simpler. It is expected that the effects due to other types of intermolecular forces (dispersion, induction, among others) are weaker, and therefore, considered through a perturbation term. Thus, it is expected that this theory is able to describe most real fluids, including polymers and polar fluids. In the SAFT model, the molecules are interpreted as a mixture of spherical segments of equal size, interacting according to a square-well potential. In addition, two types of bonds between these spheres can occur: covalent bonds to form chains and association bonds for specific interactions [26], [25].

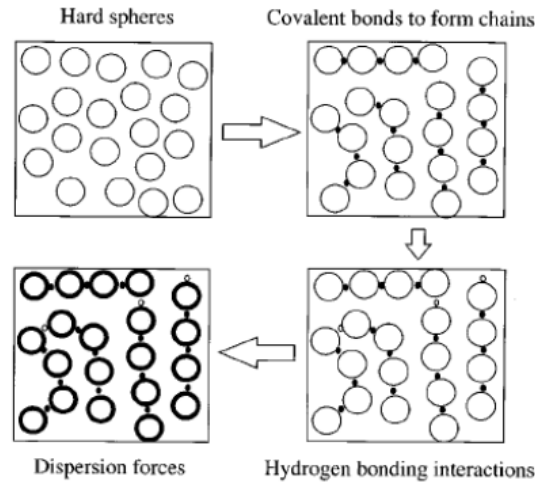
When developing the equation of state, it is assumed that the molecules are formed from segments of rigid spheres, according to the diagram in Figure 2. Initially, the fluid is composed only of rigid spheres of equal size, and only the effect of rigid spheres are considered. The reference fluid consists of rigid spheres forming chains (tetramers) via covalent bonds. Hydrogen bonds between terminal sites of different chains result in oligomer chains. The last step takes into account weak dispersion forces.

The equation is derived in terms of the residual Helmholtz free energy  $a^{res}$  :

$$\frac{a^{res}(T, \rho)}{R \cdot T} = \frac{a^{total}(T, \rho)}{R \cdot T} - \frac{a^{ideal}(T, \rho)}{R \cdot T} \quad (20)$$

where  $T$  is the temperature and  $\rho$  is the density of the system. The residual Helmholtz free energy  $a^{res}$  is expressed with regard to the Helmholtz free energy of an ideal gas  $a^{ideal}$  at the same  $T$  and  $\rho$ . If the Helmholtz free energy of a fluid is known, all other properties such as pressure, chemical potential, among others, can be calculated using basic thermodynamic equations.





**Figure 2.** Illustrative Picture of Molecule Formation in the Theory Underlying the SAFT Model [105].

Formation of rigid spheres ( $a^{hs}$ ) and chains ( $a^{chain}$ ), as well as association ( $a^{assoc}$ ) and dispersion (attraction,  $a^{disp}$ ) interactions, all contribute to the residual Helmholtz free energy:

$$\frac{a^{res}(T, \rho)}{R \cdot T} = \frac{a^{hs}(T, \rho)}{R \cdot T} + \frac{a^{chain}(T, \rho)}{R \cdot T} + \frac{a^{assoc}(T, \rho)}{R \cdot T} + \frac{a^{disp}(T, \rho)}{R \cdot T} \quad (21)$$

For a pure fluid, the formation of one mol of each chain, consisting of  $m$  segments, requires  $m$  moles of hard sphere. For the hard-sphere term  $a^{hs}$ , the Carnahan-Starling [100] expression is used. The parameters of the pure components used to calculate  $a^{chain}$  are identical to those used to calculate  $a^{hs}$ . No additional parameter is required to take into account connectivity. For the dispersion term  $a^{disp}$ , Chapman *et al.* [24]–[25] used the expression originally proposed by Cotterman *et al.* [106] while Huang and Radosz [26] used a polynomial expression based on molecular dynamic simulation with square-well fluid. The contribution due to chain formation  $a^{chain}$  is given by Wertheim's association theory [20]–[23] where the association bonds are replaced by chain formation covalent bonds, as well as the association term  $a^{assoc}$ . The number of association sites in a single molecule is unlimited, however, it must be specified. Wertheim's contribution terms (chain and association) are essentially unchanged in the several versions of SAFT.

#### 4.2. PC-SAFT equation

Gross and Sadowski [28]–[29] developed a modification to the SAFT equation referred to as PC-SAFT (Perturbed-Chain SAFT). In the structure of the PC-SAFT equation, molecules are assumed to be chains of spherical segments, freely linked and exhibiting attraction forces among them. The repulsive interactions are described by an expression of rigid chain (hard sphere + chain) developed by Chapman *et al.* [107], which is the same as used in the SAFT equation of state. The attraction interactions are in turn divided into dispersion interactions and a contribution due to association. Figure 2 illustrates the formation of a molecule according to the PC-SAFT theory. Earlier versions of SAFT assume that the dispersive interactions of molecule chains are the same as those of spherical molecules. Further



investigation, however, demonstrates that equations of state may be improved when the dependence on chain length is considered in the dispersive interactions. A new version, which explicitly takes into account this dependence, has been developed, leading to the PC-SAFT equation. The dispersion term was obtained by extending Barker and Henderson's [108] theory for chain molecules. This theory considers that a chain segment is connected to neighboring segments. It also considers the effect of the nearest neighbor segments in segment interactions.

When the systems under investigation do not contain associative fluids, the term that takes into account such interactions can be ignored.

In the literature, pure component parameters for various substances can be found, either small molecules or macromolecules. The model is already available in commercial software.

### 4.3. Other modifications of the SAFT equation

Although the PC-SAFT equation provides excellent results when simulating polymeric systems, a brief survey of other modifications involving the original form of the SAFT equation is given in this section. Four comprehensive reviews of the development and application of the various types of SAFT have appeared recently [1], [2], [105], [109].

Instead of using the hard sphere fluid as reference, Blas and Veja [110] used the Lennard-Jones fluid, leading to the soft-SAFT equation. The chain and association terms remained similar to those in the original SAFT formulation. The soft-SAFT equation was successfully applied to pure n-alkanes, 1-alkenes, 1-alcohols and binary and ternary mixtures of n-alkanes including the critical region. In the case of mixtures, two binary parameters should be used even for mixtures of n-alkanes.

Another version of the SAFT equation is the SAFT-VR (SAFT Variable Range) equation [111]–[114]. The differences between SAFT-VR and PC-SAFT arise from the specific treatment of the attractive interactions between segments and the choice of the reference fluid. The SAFT-VR takes as reference the hard-sphere fluid, while PC-SAFT takes the hard-sphere-chain fluid. The SAFT-VR equation describes a fluid of associating molecules with the chain segments interacting through attractive forces of variable range (VR). In SAFT-VR a reference system with interacting monomers is used to build the molecule.

The Simplified PC-SAFT (sPC-SAFT) equation [30], [114], [115] is not in fact a new equation of state, rather it is a simplified version of the original PC-SAFT regarding mixing rules. Therefore, the parameters of the pure components of the original and simplified PC-SAFT are the same. The sPC-SAFT equation assumes that all segments in the mixture have the same average diameter which provides a volume fraction of the mixture which is identical to the actual mixture. This simplified version is simpler to implement and improves computational performance compared to the original PC-SAFT with negligible differences in accuracy.

#### 4.4. Polymeric systems modeling using the SAFT equation and its modifications

This section presents a brief review of studies that used the SAFT equations of state and its modifications for the modeling of polymeric systems. A crucial aspect for the success of modeling with SAFT and PC-SAFT equations is the correct selection of the parameters of the pure components. In general, the estimation of these parameters may not be easy for macromolecular compounds [116]. Moreover, the fit to experimental data through the estimation of binary interaction parameter  $k_{ij}$  is another important point for successful modeling. In this sense some works in which the SAFT and PC-SAFT equations are used for polymer solutions will be discussed, highlighting the results achieved.

From the work of Chapman *et al.* [24]-[25] and Huang and Radosz [26] several applications of the SAFT model can be found in the literature. Table 1 presents a summary of some applications of the SAFT model for systems consisting of homopolymers and copolymers. A more detailed review of the application of SAFT model to polymeric systems can be found in [116] and [2].

Chen *et al.* [117]-[118] studied different phase transitions, from liquid to liquid-vapor (L to LV) and liquid to liquid-liquid (L to LL) in binary, ternary and quaternary systems containing the solvents ethylene, propylene, 1-butene, 1-hexene, n-hexane and methylcyclopentane, and Poly(Ethylene-co-Propylene) (PEP). SAFT modeling was used for PEP of varying molecular weights at low and moderate pressures [(0-500) bar]. The BIP set was defined as an exponential function of the polymer molecular weight and adjusted by three parameters.

Xiong and Kiran [80] compared the performance of SAFT with SL to model cloud point curves in polyethylene systems with n-butane and n-pentane. The pure component parameters were taken from literature [26] and the BIP were assumed to be equal to zero. For all temperature-pressure-composition ranges, the SAFT model was superior to SL.

The approach used by Han *et al.* [119] was to measure the cloud point and the coexistence pressures in propylene and ethylene solutions of alternating PEP of well-controlled polydispersity directly, from monodisperse to broadly polydisperse. These experimental data were modeled using the SAFT equation. More specifically they fitted the cloud point pressure for monodisperse PEP and used the model for predicting the cloud point and coexistence pressure of bimodal polydisperse PEP, without any refitting.

Pan and Radosz [120] used the SAFT equation for copolymers to describe the fluid-liquid and solid-liquid transitions in solutions of polyethylene and poly(ethylene-co-olefin-1) in propane as well as the fluid-liquid transition in solutions of polystyrene in n-hexane. The parameters of the pure solutes were estimated based solely on the molecular weight and on the structure. Copolymer SAFT EOS has been also used to model SLE in systems containing polyethylene, m-xylene and amyl acetate [121].

Polymer	Solvent	Reference
Poly(ethylene-glycol) (PEG)	Propane, nitrogen, CO <sub>2</sub>	[125]
PolyEthylene (PE)	Ethylene	[33], [84], [126], [127], [128]
	Propane (also SLE)	[120], [129]
	n-butane, n-pentane	[80], [130]
	Toluene	[126]
	Isobutane	[129]
	CO <sub>2</sub>	[126], [129]
	1-hexene	[127]
	Cyclohexane	[122]
	Hexane, heptane, octane	[123]
	SLE in amyl acetate and m-xylene	[121]
PolyPropylene (PP)	1-butene, n-butane, propane, propylene	[116]
PolyButylene (PB)	1-butene	[84]
PolyStyrene (PS)	Cyclohexane, methylcyclohexane, ethylbenzene, chlorobenzene, CO <sub>2</sub>	[126]
	Propane	[131]
	Cyclohexane	[122]
	Cyclohexane, CO <sub>2</sub>	[132], [133]
Polyisobutylene (PIB)	Ethane, ethylene, propane, propylene, dimethyl ether	[134]-[136]
PolyCarbonate (PC)	n-alkane (C <sub>8</sub> -C <sub>12</sub> ), alcohol (C <sub>3</sub> -C <sub>10</sub> ), benzene, toluene, o, m, p-xylene, ethylbenzene	[137]
Poly(ethylene-co-vinyl-acetate) (EVA)	vinyl acetate, ethylene, alkanes	[127], [138], [139]
Poly(vinyl-acetate) (PVA)	Benzene, Vinyl acetate	[132]
Poly(ethylene-co-olefin)	Ethylene, propylene, propane (also SLE), 1-butene, 1-hexene, n-alkane (C <sub>6</sub> -C <sub>8</sub> )	[120], [127], [140]
Poly-methyl methacrylate (PMMA)	CO <sub>2</sub> -methyl methacrylate	[141]
Poly(Ethylene-co-Propylene) (PEP)	Ethylene, ethane, propylene, 1-butene, and 1-hexene, methylcyclopentane	[33], [117], [118], [119], [142]
Poly(1,1-dihydroperfluorooctylacrylate) (poly(FOA))	CO <sub>2</sub>	[143]

**Table 1.** Polymeric Systems Modeled with SAFT Equation

Dariva [116] applied the SAFT equation of state to model PolyPropylene (PP)-solvent systems at low and moderate pressures. Two non-metallocene polypropylenes (molecular weights: 476745 and 244625 g/mol; and polydispersities: 4.4 and 5.0) and a metallocene polypropylene (molecular weight: 197150 g/mol; and polydispersity: 2.9) were used. As solvents, propylene, n-propane, 1-butene and n-butane were used. The author modeled transitions L to LV, L to LL and LL to LLV using the SAFT model with and without fitting the BIP. A large amount of experimental data for these systems can be found in this work.

Horst *et al.* [122] studied the influence of supercritical gases in the phase behavior of the systems polystyrene-cyclohexane-gas and polyethylene-cyclohexane-gas, modeling the experimental data with the SAFT equation of state. As supercritical gases, the authors used ethane, propane and nitrogen. The experimental data were collected at moderate pressures, and the binary interaction parameters used for the adjustment were defined as quadratic functions of temperature. Good results were obtained in the modeling, although a larger model mismatch in regions of higher polymer concentration can be observed.

Jog *et al.* [123] used the SAFT equation to model the liquid-liquid equilibrium of LLDPE with hexane, octane and heptanes [124]. The effects of temperature, pressure, polymer concentration and molecular weight on the phase separation were successfully evaluated. The effect of polydispersity on cloud point was also considered. Although the SAFT predictions are sensitive to the binary interaction parameters, a constant value for the binary parameters was considered to model the cloud point in varying conditions (temperature, pressure and polymer concentration) and varying solvents. The SAFT equation showed a good predictive capacity for this system.

Besides the works already mentioned, the SAFT equation of state has also been applied in more recent works as a “reference” model, its performance being compared to PC-SAFT model, as will be shown below. After the work of Gross and Sadowski [28]-[29], some applications of the PC-SAFT model may be found in literature. Table 2 presents a summary of some of the applications of the PC-SAFT model for systems consisting of homopolymers and copolymers. A more detailed review of the application of PC-SAFT model to polymeric systems can be found in [2].

Tumakaka *et al.* [144] used the PC-SAFT equation to model cloud point curves for polymeric systems consisting of polyolefins, using ethane, ethene, propane, propylene, n-butane, 1-butene and CO<sub>2</sub> as solvent. Here, the good results obtained for modeling the systems LDPE-solvents and HDPE-ethylene at high pressures should be highlighted. As well as modeling systems consisting of polyolefins, polyethylene copolymers and PVA (polyvinyl acetate vinyl) systems were also modeled. Good results were obtained when representing a system consisting of polypropylene with moderate polydispersity ( $MW/MN = 2.2$ ), assuming that the polypropylene was monodisperse. The monodisperse assumption was also considered for the LDPE-solvent system, whereas for the HDPE-ethylene system the polyethylene was modeled using pseudocomponents.

Polymer	Solvent	Reference
Polyethylene (PE)	Ethylene, ethane, propylene, propane, butane, 1-butene, hexane	[73], [152], [153], [154], [155], [159], [161]
	n-heptane	[162]
	Toluene	[126]
	CO <sub>2</sub>	[126]
	Cyclohexane, 1-octene	[155]
	SLE in n-alkanes and in m-xylene	[158]
	SLE with a variety of solvents	[68]
Polypropylene (PP)	Propane, n-pentane, CO <sub>2</sub>	[126], [151], [163]
	SLE with a variety of solvents	[68]
	Diisopropyl ketone	[147]
Polystyrene (PS)	Cyclohexane, CO <sub>2</sub> , methylcyclohexane, ethylbenzene, chlorobenzene	[126], [162]
	Ethylbenzene, butyl acetate	[147]
Polyamide (PA)	Caprolactam, water	[150]
Poly(methyl acrylate) (PMA)	2-octanone	[146], [164]
Poly(ethylene-co-methacrylic acid) (EMA or PE-co-MA)	Ethylene, propylene, butane, 1-butene	[146], [160]
	Propylene, butane	[148]
Poly(ethylene-co-acrylic acid) (EAA or PE-co-AA)	Ethylene	[160]
Poly(ethylene-co-vinyl-acetate) (EVA)	Cyclopentane	[146]
	Ethylene	[148]
Poly(ethylene)-co-olefine	Ethylene, propylene, propane, 1-butene, 1-hexene, n-alkane (C <sub>6</sub> -C <sub>8</sub> )	[144], [146], [163]
Poly(vinyl-acetate) (PVA)	Methyl ethyl ketone, propyl acetate, 1-propylamine, 2-propylamine, 2-methyl-1-propanol, 2-propanol	[147]
Polyolefins and PVA	Ethane, ethene, propane, propylene, n-butane, 1-butene, CO <sub>2</sub>	[144]
PE, PP, PB, PIB, PS	Ethylene, n-butane, 1-butene, n-pentane, cyclohexane	[145]
Biopolymers: poly(d,l-lactide) (PLA), poly(butylene succinate) (PBS) and poly(butylenes succinate-co-adipate) (PBSA)	Cloro difluorometane, CO <sub>2</sub> , dimetil ether, difluorometane, trifluorometane, tetrafluorometane	[165]
Polycarbonate (PC)	CO <sub>2</sub> , cyclohexene oxide	[166]
Poly(dimethylsiloxane) (PDMS)	Pentane	[167]
PMMA, poly(butyl methacrylate) (PBMA), PVA, PS, PP, Polybutadiene (BR), PIB, PMA, poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), Polyphthalamide (PPA)	CCl <sub>4</sub> , CH <sub>2</sub> Cl <sub>2</sub> , methyl acetate, methyl ethyl ketone, 1-propanol, 4-heptanone, chlorobutane, octane, cyclohexane, benzene, toluene, ethylbenzene, xylene, acetone, diethylketone	[156]
PDMS, PE, PS, PBMA, PIB, PB, poly(alpha-methylstyrene) (P-αMS), PMMA, PVA	Benzene, toluene, alkane (C <sub>5</sub> -C <sub>8</sub> ), cyclohexane, methylcyclohexane, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, methyl acetate, prothyl acetate, methyl ethyl ether, acetone, propylamine, isopropylamine	[157]

**Table 2.** Polymeric Systems Modeled with PC-SAFT Equation



Gross and Sadowski [145] used the fractionation of LDPE in three pseudocomponents to represent the cloud point curves for the ethylene-LDPE system ( $MW/MN = 8.56$ ). The pure component parameters for ethylene and polyethylene and one binary interaction parameter  $k_{ij}$  (interaction ethylene-LDPE) were estimated from the simultaneous regression of polymer density data and a single cloud point curve, requiring the optimization of four parameters ( $m, \sigma, \varepsilon/k, k_{ij}$ ). Additionally, the modeling of other polymeric systems in varying equilibrium conditions was carried out for a wide range of temperatures [(75-197) °C], pressures [(0-2000) bar] and weight compositions [(0-100)%]. Polymeric systems consisting of LDPE, HDPE, PP, polybutene, polyisobutene and polystyrene were evaluated. As solvents, ethylene, n-butane, 1-butene, n-pentane and cyclohexane were used. Comparisons of results obtained from SAFT and PC-SAFT models corroborate that PC-SAFT shows the best performance.

Gross and Sadowski [145] proposed changes to the PC-SAFT equation, adding two more parameters concerning the association term. Simulations of liquid-liquid and vapor-liquid equilibrium of systems consisting of simple molecules were compared with the SAFT model. Slightly better results were observed for the PC-SAFT equation. The pure component parameters were obtained from the simultaneous regression of vapor pressure and liquid phase density data. Thus, a total of five parameters were optimized for each component  $i$ : segment diameter ( $\sigma_i$ ), segment number ( $m_i$ ), segment energy ( $\varepsilon_i/k$ ), association energy ( $\varepsilon^{AiBi}/k$ ) and effective association volume ( $k^{AiBi}$ ). The BIP  $k_{ij}$  parameter for each system was optimized later.

Cheluget *et al.* [73] applied the PC-SAFT equation of state to model a flash separation system of an industrial LLDPE plant. The system under study consisted of ethylene, 1-butene, cyclohexane and polymer at 267 °C and 33 bar. The PC-SAFT parameters used in this study were estimated from binary system liquid-liquid and vapor-liquid equilibrium data obtained from literature. The authors did not re-estimate the binary interaction parameters to fit the model to the industrial data, to compare the predicted (using interaction parameters from literature) and industrial data. The lack of parameter re-estimation is the most likely cause of the significant deviations between experimental and predicted values.

Gross *et al.* [146] extended the PC-SAFT model [28]-[29] for copolymers. The authors modeled phase equilibrium for ethylene copolymer systems with random alternating chains in a wide range of compositions (including homopolymer) and with molecular weights ranging between 709 and 242000 g/mol. The studied polymers were composed of repeating apolar [poly([ethylene oxide]-co-propylene) and poly([ethylene oxide]-co-[butene-1])] and polar [poly([ethylene oxide]-co-[vinyl acetate]) and poly(ethylene-co-[methyl acrylate])] units. Additionally, the authors reported binary interaction parameters of phase equilibrium for systems consisting of homopolymers, whose repeating units are present in the copolymers, and varying solvents, and some of these interaction parameters also considered the composition of the copolymer. The BIP were estimated from equilibrium data of binary polymer-solvent systems.



Kouskoumvekaki *et al.* [147] implemented a simplified version of the PC-SAFT equation of state, developed by von Solms *et al.* [30] with little repercussion for polymeric systems made up of a variety of solvents, including polar, apolar and associative compounds. Pure component parameters were estimated from vapor pressure and liquid phase density data. The simplified model showed similar results to those obtained by the original PC-SAFT equation, thus presenting some advantages due to its simplicity and lower computational cost.

In the work of Tumakaka and Sadowski [148], the PC-SAFT equation was applied to pure polar compounds as well as to the vapor-liquid and liquid-liquid equilibrium of binary mixtures containing polar compounds, with low molecular weight, and polar copolymers. As the original PC-SAFT is unable to describe polar systems, the authors used an extended version of the equation for polar systems. The dipolar interactions, which contribute significantly to the total intermolecular forces, are explicitly explained in molecular theory [149]. Due to the inclusion of a term of polar interactions in the molecular theory, it was also necessary to include a pure component parameter in the term. When dealing with mixture modeling, the authors defined the binary interaction parameter either as an independent term or as a function of the comonomer molar fraction.

The sPC-SAFT equation (Simplified PC-SAFT equation) was applied by Kouskoumvekaki *et al.* [150] to the vapor-liquid equilibrium of binary and ternary systems of polyamide-6 with several solvents (water, caprolactam, ethyl benzene and toluene). Binary interaction parameters between polyamide-6, caprolactam and water were estimated using experimental data of the binary mixtures. The estimated parameters were used to predict and correlate the ternary mixture of polyamide-6, caprolactam and water. When optimizing the pure parameters of polyamide-6, the corresponding values of caprolactam were considered as initial estimates, and just the segment diameter needed to be adjusted using experimental data of liquid volume. The results showed that the sPC-SAFT equation is a versatile tool for modeling multi-component systems containing polyamide.

Arce and Aznar [151] modeled the systems PP-(n-pentane) and PP-(n-pentano)-CO<sub>2</sub> using the PC-SAFT equation of state. In this work resins of low molecular weight (MW = 50400 and 95400) at moderate pressure (below 350 bar) were considered. The PC-SAFT, Sanchez-Lacombe and Peng-Robinson models were used to predict the cloud point pressures from experimental data on each system. Although all the models were able to describe the system, the PC-SAFT equation showed superior performance. For all the models, the authors used the temperature dependent BIP.

Spyriouni and Economou [152] evaluated the performance of SAFT and PC-SAFT equations of state to describe the phase behavior of mixtures containing polydisperse polymers and copolymers at high pressure. Although there are several studies showing the application of both equations in modeling the phase behavior of polymer systems, the major contribution of this work was to compare the performance of both models for a wide variety of homopolymers and copolymers. The authors concluded that both models show a similar performance in modeling the equilibrium, however, from the data presented, the PC-SAFT model shows superior results for most systems.

Pedrosa *et al.* [153] presented phase equilibrium calculations for polyethylene solutions with varying solvents using two different versions of the SAFT equation: PC-SAFT and the soft-SAFT. The soft-SAFT equation uses the spherical fluid of Lennard-Jones as a reference, including attractive and repulsive interactions, while the reference term in the PC-SAFT equation is the rigid sphere chain. The studies carried out by Pedrosa *et al.* [153], which also dealt with vapor-liquid equilibrium, showed that results with soft-SAFT equation are slightly more accurate than those obtained with PC-SAFT in some cases.

Buchelli *et al.* [154] investigated the performance of the PC-SAFT equation of state for modeling the HPS and LPS units downstream from a low-density polyethylene tubular reactor. Plant data were used to validate the equilibrium stage model prediction for the two gas-liquid flash separators, however, the pure component parameters and BIP of this model were obtained exclusively from experimental data published in the literature. The authors achieved good agreement between the model and LPS plant data, although the predicted solubility was not in agreement with plant-measured values for the HPS.

Guerrieri [155] investigated the behavior of polymeric systems in two industrial polyethylene plants, a LDPE plant and a HDPE/LLDPE plant, using the PC-SAFT equation. The liquid-liquid equilibrium at high pressure, observed in the reactor, and the vapor-liquid equilibrium, observed in the low-pressure separator, were investigated in the LDPE plant. For this study, 8 commercial resins were considered. In the HDPE/LLDPE plant, the vapor-liquid equilibrium in the intermediate pressure separator was investigated. Here, 25 commercial resins were investigated. The experimental data were taken from measurements and mass/energy balances available in both plants, and the modeling of binary and multicomponent systems consisting of ethylene, ethane, propylene, propane, 1-butene, cyclohexane, 1-octene and polymer was carried out.

Tihic *et al.* [156]-[157] developed a group contribution method to be used in PC-SAFT equation to predict their pure parameters. If pure polymer parameters in SAFT-type equations are obtained only from density data, poor predictions of phase equilibrium may result. Therefore, the group contribution method for parameter estimation was developed through the adjustment of vapor pressure and density data based on a database of 400 components of low molecular weight. The data required to calculate the phase equilibrium for polymers using this contribution method are the polymer molecular structure in terms of functional groups and a single interaction parameter for accurate mixture calculations.

Understanding the phase behavior of polymer solutions is of great theoretical and practical importance. Some work has also been done on the development of algorithms for real-time prediction of SLE in solution polymerization of polyethylene based on PC-SAFT EOS and to study the effects of monomer and polymer polydispersity in solution polymerization processes [158]. Costa *et al.* [68] also modeled the SLE in polyolefins (polyethylene and polypropylene) solutions using PC-SAFT EOS for a variety of different polymer-solvent systems at atmospheric and high pressure with very good results. Pressure *versus* temperature ( $P$ - $T$ ) isopleths can be used to determine the number of phases present at a given  $T$ ,  $P$ , and overall mixture composition. The PC-SAFT EOS was applied by Costa *et al.*

[159] to simulate the curves that describe the borderlines between several distinct regions depicted in  $P$ - $T$  isopleths for polyethylene solutions. A new strategy was used and the simulation results show good agreement with experimental cloud point isopleths data from the literature. In order to track the operational performance of industrial reaction systems safely, a strategy to calculate the distance between a given operational point (specified through a given pressure and a given temperature) and the corresponding point in the interface, for a fixed molecular weight and a fixed polymer fraction weight, has been developed which could also be extended for real-time prediction applications.

Kleiner *et al.* [160] extended the association term of the PC-SAFT EOS to account for the polydispersity of the copolymer samples. This EOS was used to model cloud-point curves of the systems poly(ethene-co-acrylic acid)-ethene and poly(ethene-co-methacrylic acid)-ethene. Both copolymer composition and molecular weight distribution were varied. To account for polydispersity the concept of pseudocomponents has been applied and they were generated such as to match the molecular weight distribution. An algorithm has been developed for calculating phase equilibria of polydisperse associating copolymer-solvent systems. The PC-SAFT approach turns out to be capable of adequately modeling and even predicting the phase behavior of the polydisperse polymeric systems by using two pseudocomponents for each copolymer, but no additional adjustable parameters.

Phase-dependent BIP were computed by Costa *et al.* [161] with PC-SAFT EOS by correlating the flash results for both high and low pressure separators (HPS and LPS) for the industrially significant mixture ethylene-ethane-propane-propylene-LDPE. HPS and LPS data were correlated for five of eight LDPE resins. A pressure, composition and molar mass dependent binary interaction parameter model was proposed for both the vapour and liquid phase. The resulting model was able to provide a good representation of the experimental data. The polydispersity and branching of the LDPE resins, as well as the temperature, were lumped into the BIP. Clearly, the proposed phase-dependent BIP model provides a good representation of the phase behaviour in two industrial separators for very complex polydisperse mixtures.

## 5. Conclusions

This chapter has presented a review of equation of state models for polymers, demonstrating their increasing evolution in performance for describing phase equilibria in polymer systems. The development of EOS for polymers remains a very active area of research and it is difficult to recommend a specific EOS [2].

In general the equations of state using  $G^E$  models are unable to describe high-pressure phase equilibria with the desired quality [65], thus have a more restricted application. On the other hand, their equations and mixing rules are simple, which facilitates their convergence and the obtaining of terms required for the calculation of other thermodynamic properties, e.g. mixture specific heat.

Regardless of the model used, the calculation of the parameters of the pure components for polymers is a major challenge. When using an equation of state, the need for other applications besides the description of phase equilibria and PVT data, such as the calculation of Joule-Thompson coefficient and general energy balances should be borne in mind. Despite its importance, little research has been done in this respect with polymer systems. Note that the simpler the equation and its mixing rule, the easier it will be to obtain these properties and other important thermodynamic properties.

Although the PC-SAFT equation seems to show certain superiority in performance when compared to other models, no agreement was observed in the reviewed literature on which concept and/or thermodynamic model structure is better. Thus the choice of the model remains dependent on the system and its conditions. Although many studies address polymeric systems with a high concentration of polymers in a wide range of molecular weights, very few studies can be found that model oligomers (low molecular weight polymers), despite being a relevant problem as in many cases the quality of its measurement/prediction is critical for the proper functioning of important process equipment.

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