

# Development and Evaluation of a New Equation of State for Polar Fluids: Pure Components and Mixtures

PhD thesis by Eirini Karakatsani  
National Center for Scientific Research "Demokritos",  
Aghia Paraskevi Attikis, Greece

*The PhD degree was granted by  
the National Technical University of Athens, Greece in May 2007*

## Extended Abstract

### Summary

In the framework of my PhD thesis on the thermodynamic modeling of polar fluids and mixtures, four molecular-based equations of state (EoS) have been developed aiming at the prediction and correlation of thermodynamic properties of polar fluids and their mixtures. Despite the existence of a significant number of thermodynamic models in the literature, there is still a need to improve our knowledge on the molecular mechanisms that drive polar interactions and to use such knowledge in the development of robust and accurate theories. In this respect, the Statistical Associating Fluid Theory (SAFT) is a suitable basis for such developments.

In this work, the original SAFT proposed by Huang and Radosz [1] and the Perturbed Chain-SAFT of Gross and Sadowski [2] were combined with the perturbation theory for polar fluids of Stell and coworkers [3]. The resulting theories known as Polar SAFT (PSAFT) and PC-Polar SAFT (PC-PSAFT) were subsequently simplified through a truncation of the perturbation expansion for the polar interactions, resulting in truncated PSAFT (tPSAFT) and truncated tPC-PSAFT (tPC-PSAFT). The new EoS maintain relatively low computational time requirements (especially the truncated versions) while they contain explicit terms for polar interactions that exist between similar and dissimilar molecules, contrary to most previous thermodynamic models.

At first, a comparison of molecular simulation calculations with PC-PSAFT predictions was very promising, thus ensuring the validity of our approach. Subsequently, the models were applied to a variety of pure polar fluids, including several aliphatic and aromatic hydrocarbons, alcohols, ketones, water, ammonia, chloromethane, chloroform, fluoroform, hydrogen sulfide, acetic acid, nitrogen, carbon dioxide, oxygen, ethylene, ethane, propylene, acetonitrile, as well as several ionic liquids (ILs).

Pure component parameters were regressed using experimental data for vapor pressure and saturated liquid density. Parameter values were shown to vary smoothly with the molecular weight for components of the same homologous series. For a number of commonly used components that include nitrogen, carbon dioxide, methanol and water, different thermodynamic properties were estimated, such as critical and supercritical properties, virial coefficients, Joule-Thomson coefficients, specific heat and monomer fractions. In all cases, the agreement with experimental data was excellent.

The simpler EoS tPSAFT and tPC-PSAFT were extended to mixtures using simple, standard combining and mixing rules. A temperature-independent binary interaction parameter

was fitted to experimental data. Binary mixtures of dipolar / non-polar, quadrupolar / non-polar, quadrupolar / quadrupolar, dipolar / quadrupolar and hydrogen-bonding polar / hydrogen-bonding polar substances were examined. Extensive calculations for multi-component (ternary and quaternary) mixtures exhibiting vapor – liquid, liquid – liquid and vapor – liquid – liquid equilibria (VLE, LLE and VLLE) were performed using interaction parameters fitted to corresponding binary mixtures. In most cases, predictions from the new models were superior than the models with no explicit account for polar interactions.

tPC-PSAFT, considered as the most suitable EoS for high molecular weight substances, was used for the description of phase behavior of binary and ternary mixtures of ionic liquids (ILs) with other substances, by taking explicitly into account the dipolar interactions between these components. Estimation of pure IL parameters was based on literature data and simple combining rules. The values obtained are highly accurate when it comes to liquid density data, and agree qualitatively (order-of-magnitude) with recent data / predictions for vapor pressure. The IL mixtures examined contained supercritical carbon dioxide, supercritical fluoroform, water, benzaldehyde and benzene as their second and / or third component.

In the final part of this thesis, three promising hydrogen bonding theories that are considered more accurate than the first order Thermodynamic Perturbation Theory (TPT1) of Wertheim, such as the microscopic theory for water of Debenedetti and co-workers [4], the mean-field theory of Dormidontova for aqueous solutions of PEO [5] and the analytical three-body theory of Jackson and Saar [6] which takes into account the cooperativity of hydrogen bonds, were combined with SAFT theory and their performance was examined. The limited applicability and the high complexity of the resulting equations did not seem to result in improved description of complex systems such as pure water and hydrogen bonding solutions.

## **Problem addressed**

Accurate models for thermodynamic property and phase equilibrium predictions of pure polar components over a wide range of temperature and pressure are of extreme importance for the optimization of existing and the design of new processes and / or materials in the chemical process industry

On the other hand, prediction and correlation of thermodynamic properties and phase equilibria of multi-component fluid mixtures with equations of state (EoS) remains an important goal in chemical and oil industries. Both academia and industry have concluded that one way to deal with such mixtures is using advanced thermodynamic models that are capable to account explicitly for the different molecular interactions and their influence on the thermodynamic properties.

The motivation of this work was exactly the development of thermodynamic models for polar fluids and polar mixtures with a strong molecular basis. The specific purposes of this work were to incorporate the higher order dipole – dipole, quadrupole – quadrupole, cross dipole – quadrupole as well as dipole – induced dipole interactions in a simple manner in already existing, successful EoS and to find whether these interactions have a detectable effect on the thermodynamics of pure fluids and more importantly on the thermodynamics of multicomponent mixtures.

The effect of a molecule's permanent electrostatic moments on the macroscopic physical behavior of the system has been in the forefront of research for several decades. It is well accepted today that EoS attain a more predictive character when strong dipolar and quadrupolar interactions are individually considered. Despite the early progress in modeling

polar molecules, modeling of interactions resulting from permanent charges remains a challenge for fluid theories because of the long-range nature of the involved forces.

In parallel, over the last decade ILs have emerged as potential candidates for the replacement of common volatile organic solvents to result in more environmentally friendly industrial processes. Their negligible vapor pressure of ILs associated with tunable physico-chemical properties as a result of the combination of a wide variety of cations and anions made ILs very attractive solvents for, among other applications, the performance of reactions and separations. As a result, a need for the development of thermodynamic models that allow effective prediction of the phase behaviour of IL mixtures has been created.

Most efforts have been restricted to low and medium pressure and applications to high pressures are limited. In most cases, cubic EoS including Redlich-Kwong and Peng-Robinson EoS have been used with multiple adjustable parameters. Furthermore, ILs mixtures have been modeled using the NRTL EoS, excess Gibbs energy methods and the UNIQUAC EoS. All these approaches invoke a large empiricism with very limited predictive capability.

A suitable predictive model should account explicitly for the various molecular features that characterize IL mixtures. For example, there is experimental and molecular simulation evidence that there is strong association between CO<sub>2</sub> acting as a Lewis acid and the anion of an IL acting as a Lewis base. Huang *et al.* [7] claimed that this association is due to the strong charge-quadrupole moment interaction between CO<sub>2</sub> and the anions. On the other hand, fully dissociated IL molecules in water are expected to be solvated. Such phenomena can be modeled accurately using models with strong theoretical background, such as the tPC-PSAFT EoS developed in this thesis.

Finally, in spite of past systematic work, many of the thermodynamic properties of water and aqueous mixtures remain puzzling and not properly modeled. It has been proven that the use of the TPT1 for the description of molecular systems with strongly orientation-dependent attractive interactions has its limits and that simplified models for the water molecule are not robust and predictions are often very sensitive to the precise model parameters. Models are still being developed and are generally more complex than earlier ones but they still generally have poor predictive value outside the conditions and physical parameters for which they are developed. Therefore, SAFT was combined with three molecular theories in order to investigate whether a significant improvement of the EoS capability to describe water and its mixtures could be obtained.

## State of the art

The development of new accurate EoS for polar fluids and mixtures is still a very active research area despite the great number of models proposed in recent years. A very successful class of EoS is based on perturbation theory. Gubbins and Twu [8] developed a set of readily applicable expressions to account for dipolar and quadrupolar intermolecular forces based on the perturbation theory of Stell *et al.* [9] and molecular dynamics results of Verlet [10]. These equations were developed assuming point-electrostatic multipoles on non-spherical molecules interacting with a Lennard-Jones intermolecular potential. The suggested polar expressions were subsequently used in engineering-like equations of state, based on the perturbed hard-chain theory (PHCT) EoS of Donohue and Prausnitz [11]. Later on, Donohue and co-workers suggested the Associated Perturbed Anisotropic Chain Theory (APACT) for real complex associating and / or polar fluids [12]. APACT is a very accurate model for polar fluids, but it never gained broad acceptance by the thermodynamic community because of its relatively high complexity.

Valderrama and Sandler developed the first perturbation theory parameterized for varying molecular elongations based on molecular simulation results for the radial distribution function of fused-sphere molecules [13]. Boublik suggested a perturbation theory for elongated molecules by approximating the radial distribution function of a convex molecule by that of the corresponding Gaussian overlap fluid [14-15]. A renormalized perturbation theory to account for the polarizability of dipolar fluids was already developed in 1977 by Wertheim, by applying a graph-theory approach [16-18]. Gray et al. extended the theory to mixtures and to quadrupolar fluids [19].

An alternative approach was adopted by Saager *et al.* [20] and Saager and Fischer [21], who performed extensive molecular simulations and obtained a dipole – dipole term and a quadrupole – quadrupole term by fitting empirical expressions to the simulation data. The two-center Lennard–Jones (2CLJ) plus point dipole fluid and 2CLJ plus point quadrupole fluid with fixed molecular elongation ( $L^* = 0.505$ ) were considered in their simulations (after studying the effect of molecular elongation on the polar contribution). Although the work of Saager and Fischer has clearly facilitated the fruitful interplay between molecular simulation and EoS development, a restriction of the model is the fixed elongation that, in combination with the empirical nature of the expression, makes it non-trivial to apply to strongly asymmetric mixtures.

The molecular model of tangent spheres is somewhat less elaborate than the 2CLJ model but it has shown to be well suited for strongly asymmetric mixtures. Chapman *et al.* developed a successful theoretical framework for tangent sphere molecules and proposed the statistical associating fluid theory (SAFT) EoS based on Wertheim’s TPT1 [22]. In order to overpass Saager and Fischer models deficiency, Gross et al. readjusted the model constants to comprehensive molecular simulation data of the two-center Lennard-Jones (2CLJ) plus point dipole / point quadrupole fluid from the literature [23-24].

Today, the most widely used perturbation model is based on Wertheim’s first order thermodynamic perturbation theory as developed into an engineering model, known as statistical associating fluid theory (SAFT).

## Key innovations

The work performed during this PhD thesis intended to advance the state of the art in EoS for polar fluids and mixtures moving towards SAFT-type models with simple expressions for dipolar, quadrupolar and induced dipolar interactions. For this reason, the recently proposed model by Nezbeda and Pavlíček for water was used [25, 26]. Other models of higher accuracy but considerably increased complexity (as for example the aforementioned model of Saager and Fischer [21]) would result in a complex model that would not be suitable for engineering calculations involving multiple components.

The major objective here was to develop a simple meaningful basis for describing polar substances and mixtures, as most engineering models ignore polar terms and especially the cross dipole – quadrupole terms, and so these models become less accurate when applied to mixtures with both dipolar and quadrupolar components.

For this reason, a simpler model for polar fluids was further developed, suitable for engineering calculations. The basic idea behind this simpler perturbation model is based on the following arguments: at short separations, all molecules are subject to strong repulsive interactions (excluded volume effects). If they hydrogen bond, they are subject to strong attractive interactions, restricted also to a narrow range of angles formed between the atoms involved. As far as long-range interactions are concerned, with the exception of some isotropic

interactions of the Lennard-Jones type that are present at any distance preventing collapse of the system, electrostatic interactions are gradually “turned on” outside the range of the hydrogen bonding interaction for associating fluids and, in any case, beyond the first coordination shell. This has been confirmed by several Monte Carlo (MC) and MD simulation results.

In contrast to most other SAFT-type models, tPC-PSAFT accounts explicitly for polar forces. Three pure-component parameters are required for non-polar and non-associating compounds, two additional parameters characterize the association contribution and one parameter is needed to account for polar interactions. The experimental dipole and / or quadrupole moment and / or polarizability of the component are used to calculate pure component parameters without any further adjustment, as is the case usually.

Within the mean-spherical approximation used, a short-range cutoff is introduced for the polar interactions, and its value is an adjustable parameter of constrained range to ensure that the range of polar interactions is extended beyond the first coordination shell of the polar molecule (where hydrogen bonding is dominant), a key innovative aspect of the PSAFT / tPSAFT and PC-PSAFT / tPC-PSAFT models.

Using a temperature-independent interaction parameter  $k_{ij}$  for each binary system, tPC-PSAFT provides accurate prediction of multi-component phase behavior over a wide range of conditions.

Concerning application of the model to pure ILs and IL mixtures, the tPC-PSAFT model is able to describe accurately the phase behavior of several imidazolium-based IL systems containing supercritical CO<sub>2</sub>, accounting explicitly for the dipolar interactions between IL molecules, the quadrupolar interactions between CO<sub>2</sub> molecules, and the Lewis acid-base cross association between the IL and the CO<sub>2</sub> molecules. Physically meaningful model pure-component parameters for ILs were estimated based on literature data. All experimental VLE data were correlated with a single linearly temperature-dependent binary interaction parameter. The ability of the model to describe accurately carbon dioxide solubility in various 1-alkyl-3-methylimidazolium-based ionic liquids with different alkyl chain length and different anion at pressures from 0 to 100 MPa and carbon dioxide fractions from 0 to 75 mol % is one more advantage of the proposed EoS.

The replacement of TPT1 hydrogen bonding term by other tested and accurate theories that take into account cooperatively and / or cyclic chain-like topology of hydrogen bonds and / or hydrophobic effect and / or steric hindrances, and so on, in order to override some of the inherent limitation of TPT1, is also an innovative aspect of the work performed.

## Applications, implementations and results

Following the pioneering work of Larsen, Rasaiah and Stell (LRS) [3], a mixed multipole term and a term accounting for the polarizability are added to treat polarizable polar substances and their mixtures.

Consequently, adding these two terms in the framework of SAFT-type EoS, the residual Helmholtz free energy per mole reads:

$$\begin{aligned} \frac{\alpha^{\text{res}}(T, \rho)}{RT} &= \frac{a(T, \rho)}{RT} - \frac{a^{\text{ideal}}(T, \rho)}{RT} = \frac{a^{\text{ref}}(T, \rho)}{RT} + \frac{a^{\text{disp}}(T, \rho)}{RT} + \frac{a^{\text{P}}(T, \rho)}{RT} + \frac{a^{\text{ind}}(T, \rho)}{RT} \\ &= \frac{a^{\text{hs}}(T, \rho)}{RT} + \frac{a^{\text{chain}}(T, \rho)}{RT} + \frac{a^{\text{assoc}}(T, \rho)}{RT} + \frac{a^{\text{disp}}(T, \rho)}{RT} + \frac{a^{\text{P}}(T, \rho)}{RT} + \frac{a^{\text{ind}}(T, \rho)}{RT} \end{aligned} \quad (1)$$

More specifically, dipole – dipole, quadrupole – quadrupole and dipole – quadrupole interactions are included in the same Padé approximant for the Helmholtz free energy:

$$\frac{a^p}{RT} = m \frac{a_2^p}{1 - a_3^p / a_2^p} \quad (2)$$

where  $a_2^p$  and  $a_3^p$  correspond to the polar terms of second and third level of approximation respectively. The effects of polarizability can be described by a similar Padé approximant for permanent dipoles and multipoles:

$$\frac{a^{ind}}{RT} = m \frac{a_2^{ind}}{1 - a_3^{ind} / a_2^{ind}} \quad (3)$$

with  $a_2^{ind}$  and  $a_3^{ind}$  being the induced second and third order terms, respectively.

Concerning pure component parameters, it was found that parameter values vary in a systematic way with molecular weight (MW) for a homologous series of components, as is expected for models with a strong theoretical basis whose parameters have a clear physical meaning.

tPC-PSAFT EoS was used for mixtures calculations because it is simpler than the new polar PC-SAFT model, as it uses only the leading term in the polynomial expansion for polar interactions.

tPC-PSAFT was parametrized for imidazolium-based ILs by fitting IL density data over a wide temperature range and restricting the model to predict very low vapor pressure values, in agreement with recent experimental evidence. Furthermore, the solubilities of carbon monoxide, oxygen, and trifluoromethane in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]) were correlated. In all cases, the agreement between tPC-PSAFT correlation and experimental data for mixtures was found to be very good.

The tPC-PSAFT EoS was used to describe the phase behavior of ternary mixtures with quadrupolar and non polar components (VLE of mixtures containing CO<sub>2</sub>), nitrogen (N<sub>2</sub>) and cyclohexane or *n*-butane), ternary and quaternary mixtures with dipolar, quadrupolar and non polar component (VLE of mixtures containing methanol, ethanol, acetone, benzene, chloroform and *n*-hexane), multicomponent aqueous and ionic liquid mixtures (VLLE of water / ethanol / cyclohexane mixture, VLE of [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] / acetone / CO<sub>2</sub> mixture). In all cases, calculations were based on pure component and binary interaction parameters ( $k_{ij}$ ). When applied to VLE of mixtures of non-associating compounds, tPC-PSAFT shows good predictive capabilities.

The phase equilibria of more complex multicomponent systems like aqueous and IL containing systems were also modeled successfully with tPC-PSAFT. In the case of water, its dipolar, quadrupolar and dipole – induced dipole interactions were taken into account, while for IL its polar character was taken into account by using a dipole moment value equal to that of methanol (1.70 D).

Overall, tPC-PSAFT is shown to model accurately different types of phase behavior and therefore can be safely extrapolated for the prediction of the phase behavior of complex systems over a wide range of conditions. In the Tables below, the various systems where the new models were applied are shown.

Table 1: Pure components for which parameters were estimated (other than ILs)

**Dipolar fluids**

- Alcohols: methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-ennanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol, methyl-ethyl-glycol
- Ketones: 2-butanone, 2-pentanone, 3-pentanone, 2-hexanone
- Ammonia, Chloroform, hydrogen sulfide, acetic acid
- ✓ tPSAFT: Overall % AAD for  $P^{sat} = 2.11$ , Overall % AAD for  $\rho^{liq} = 2.89$
- ✓ tPC-PSAFT: Overall % AAD for  $P^{sat} = 3.00$ , Overall % AAD for  $\rho^{liq} = 1.92$

**Quadrupolar fluids**

- Gases: nitrogen, carbon dioxide, oxygen
- Unsaturated hydrocarbons : ethylene, ethene, propylene
- Benzene derivatives : benzene, toluene, ethyl-benzene, propyl-benzene,  $\pi$ -xylene
- Naphthalene derivatives: naphthalene, methyl-naphthalene, ethyl-naphthalene
- Acetonitrile, water
- ✓ PC-PSAFT: Overall % AAD for  $P^{sat} = 1.07$ , Overall % AAD for  $\rho^{liq} = 1.50$
- ✓ tPC-PSAFT: Overall % AAD for  $P^{sat} = 1.05$ , Overall % AAD for  $\rho^{liq} = 1.45$

Table 2: Pure ILs for which parameters were estimated

- ✓ [emim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [hmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [omim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [emim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], [hmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], [omim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], [bmim<sup>+</sup>][NO<sub>3</sub><sup>-</sup>], [HOPmim<sup>+</sup>][NO<sub>3</sub><sup>-</sup>].
- ✓ tPC-PSAFT: Overall % AAD for  $\rho^{liq} = 1.26$

Table 3: Binary mixtures modeled by tPC-PSAFT (non-containing ILs)

- ✓ VLE of binary mixtures of methanol with: methane, ethane, propane, n-butane, n-pentane, n-hexane, n-heptane (tPC-PSAFT)
- ✓ VLE and LLE of methanol / cyclohexane
- ✓ VLE of ethanol / benzene and ethanol /  $\pi$ -toluene
- ✓ LLE of water with: n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, 1-hexene, 1-octene, 1-decene, cyclohexane, cycloheptane
- ✓ VLE of acetone with: n-hexane, n-decane, n-dodecane
- ✓ VLE and LLE of nitrogen / ethane
- ✓ VLE of carbon dioxide / nitrogen
- ✓ VLE of acetone / p-xylene
- ✓ VLE of carbon dioxide / acetone
- ✓ VLE and LLE of water with: methanol, ethanol, 1-propanol, 1-butanol

Table 4: IL binary and ternary mixtures modeled by tPC-PSAFT

- ✓ VLE of binary mixtures of CO<sub>2</sub> with [emim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [hmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], [hmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], [omim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>]
- ✓ VLE of CHF<sub>3</sub> / [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]
- ✓ VLE of benzene / [omim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>]
- ✓ VLE of benzaldehyde / [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]
- ✓ VLE of 1-hexene / trans-3-hexene / [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]
- ✓ VLE of [bmim<sup>+</sup>][NO<sub>3</sub><sup>-</sup>] / H<sub>2</sub>O / CO<sub>2</sub>
- ✓ VLE of [HOPmim<sup>+</sup>][NO<sub>3</sub><sup>-</sup>] / H<sub>2</sub>O / CO<sub>2</sub>

Table 5: VLE of multicomponent mixtures modeled by tPC-PSAFT (non containing ILs)

- ✓ Water / methanol / ethanol
- ✓ Methanol / water / n-hexane
- ✓ Ethanol / acetone / benzene
- ✓ Ethanol / acetone / benzene / n-hexane
- ✓ Carbon dioxide / nitrogen / cyclohexane
- ✓ Carbon dioxide / nitrogen / n-butane
- ✓ Acetone / methanol / benzene
- ✓ Acetone / methanol / chloroform
- ✓ Benzene / methanol / chloroform
- ✓ Acetone / chloroform / methanol / benzene
- ✓ Water / ethanol / cyclohexane



## References

- [1] Chapman WG, Gubbins KE, Jackson G, Radosz M. New reference equation of state for associating liquids. *Ind Eng Chem Res.* **1990**, *29*, 1709.
- [2] Gross, J.; Sadowski, G.; Perturbed-Chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.*, **2001**, *40*, 1244.
- [3] Larsen, B.; Rasaiah, J. C.; Stell, G. Thermodynamic perturbation theory for multipolar and ionic liquids. *Mol. Phys.* **1977**, *33*, 987.
- [4] Truskett, T.M.; Debenedetti, P.G.; Sastry, S.; Torquato, S. A single-bond approach to orientation-dependent interactions and its implications for liquid water. *J. Chem. Phys.* **1999**, *111*, 2647.
- [5] Dormidontova, E.E. Role of competitive PEO – water and water – water hydrogen bonding in aqueous solution. *Macromol.* **2002**, *35*, 987.
- [6] Sear, R.P.; Jackson, G. Thermodynamic perturbation theory for association with bond cooperativity. *J. Chem. Phys.* **1996**, *105*, 1113.
- [7] Huang, X.; Margulis, C.J.; Li, Y.; Berne, B.J. Why is the partial molar volume of CO<sub>2</sub> so small when dissolved in a room temperature ionic liquid? Structure and dynamics of CO<sub>2</sub> dissolved in [Bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]. *J. Amer. Chem. Soc.*, **2005**, *127*, 17842.
- [8] Gubbins KE, Twu CH. Thermodynamics of polyatomic fluid mixtures—I. Theory. *Chem Eng Sci.* **1978**, *33*, 863.
- [9] Stell G, Rasaiah JC, Narang H. Thermodynamic perturbation theory for simple polar fluids, I. *Mol Phys.* **1972**, *23*, 393. Some details of the developed theory were published only in subsequent articles: Rushbrooke GS, Stell G, Hψye JS. Theory of polar liquids. I. Dipolar hard spheres. *Mol Phys.* **1973**, *26*, 1199; Stell G, Rasaiah JC, Narang H. Thermodynamic perturbation theory for simple polar fluids, II. *Mol Phys.* **1974**, *27*, 1393.
- [10] Verlet L. Computer “experiments” on classical fluids. II. Equilibrium correlation functions. *Phys Rev.* **1968**, *165*, 201.
- [11] Donohue, M. D.; Prausnitz, J. M. Perturbed hard chain theory for fluid mixtures: Thermodynamic properties for mixtures in natural gas and petroleum technology. *AIChE J.* **1978**, *24*, 849.
- [12] Ikononou, G. D.; Donohue, M. D. Thermodynamics of hydrogen-bonded molecules: The Associated Perturbed Anisotropic Chain Theory. *AIChE J.* **1986**, *32*, 1716.
- [13] Valderrama JO, Sandler SI. The use of a non-spherical reference potential in statistical mechanical perturbation theory. III. The Helmholtz free energy and equation of state for pure, quadrupolar fluids. *Mol Phys.* **1983**, *49*, 925.
- [14] Boublik T. Perturbation theory for pure quadrupolar hard Gaussian overlap fluids. *Mol Phys.* **1990**, *69*, 497.
- [15] Boublik T. Equilibrium behaviour of quadrupolar Kihara molecule fluids. *Mol Phys.* **1991**, *71*, 417.
- [16] Wertheim MS. Theory of polar fluids. III. *Mol Phys.* **1977**, *35*, 1109.
- [17] Wertheim MS. Theory of polar fluids. V. Thermodynamics and thermodynamic perturbation theory. *Mol Phys.* **1979**, *37*, 83.
- [18] Wertheim MS. Equilibrium statistical mechanics of polar fluids. *Annu. Rev Phys Chem.* **1979**, *30*, 471.
- [19] Gray CG, Joslin CG, Venkatasubramanian V, Gubbins KE. Induction effects in fluid mixtures of dipolar– quadrupolar polarizable molecules. *Mol Phys.* **1985**, *54*, 1129.
- [20] Saager B, Fischer J, Neumann M. Reaction field simulations of monatomic and diatomic dipolar fluids. *Mol Simul.* **1991**, *6*, 27.

- [21] Saager B, Fischer J. Construction and application of physically based equations of state. Part II. The dipolar and quadrupolar contributions to the Helmholtz energy. *Fluid Phase Equilib.* **1992**, 72, 67.
- [22] Chapman WG, Jackson G, Gubbins KE. Phase equilibria of associating fluids. Chain molecules with multiple bonding sites. *Mol Phys.* **1988**;65:1057-1079.
- [23] Gross, J. An equation-of-state contribution for polar components: Quadrupolar molecules. *AIChE J.* **2005**, 51, 2556.
- [24] Gross, J.; Vrabec, J. An equation of state contribution for polar components: Dipolar molecules. *AIChE J.* **2006**, 52, 1194.
- [25] Nezbeda I, Pavlíček J. Application of primitive models of association: A simple theoretical equation of state of water. *Fluid Phase Equilib.* **1996**, 116, 530.
- [26] Nezbeda I, Weingerl U. A molecular-based theory for the thermodynamic properties of water. *Mol Phys.* **2001**, 99, 1595.