ELSEVIER

CrossMark

A general treatment of polar-polarizable systems for an equation of state

Nayef M. Alsaifi [a,*], *G.N. Patey* [b], *Peter Englezos* [c]

[a] *Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia*
[b] *Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1*
[c] *Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC, Canada V6T 1Z3*

A B S T R A C T

In this work, a general theory to account for any kind of polarization arising from polar as well as ions induced interactions in fluid mixtures is proposed. The general treatment is based on the self-consistent mean field theory (SCMF) that was originally proposed and applied for pure components using integral equation theories and molecular simulation studies. The extended SCMF is consistent with theory-based equations of state applied to hard chain mixtures. The theory is extended to mixtures and compared to molecular simulation data. The comparison to molecular simulation data shows good to excellent results for phase co-existence properties, energy and effective dipole moment. The validity of the theory is demonstrated by studying VLE of highly non-ideal mixtures of aldehyde and ketones using statistical association fluid theory.

1. Introduction

Significant progress has been made in developing theories for polar molecules characterized by permanent multipole moments. The developments have mainly been attributed to statistical mechanical perturbation theories. Various models are now available for dipolar, quadrupolar and octupolar molecules with fairly good accuracy (e.g. Twu and Gubbins, 1978b). These non-polarizable models are derived based on pairwise additive approximation. Polar molecules, however, exhibit many-body induced polarization interactions and their energies are impossible to express as a sum of pairs. The effect of polarization interactions is not by any means negligible. For example, the average dipole moment of water increases up to 40% as a result of the large polarization (Gregory et al., 1997). The non-additivity of induced interactions undoubtedly complicates the theoretical treatment of the induction effect since knowledge of fourth and higher order correlation functions is required (Joslin et al., 1985). Unfortunately, taking into account the many-body interactions is crucial if accurate results are desired. Thus, it is not surprising that the theoretical techniques of Mcdonald (1974), Larsen et al. (1977) and Winkelmann (1983, 1985) for the treatment of the induction effect were inaccurate since the many-body interactions were ignored. Therefore, inclusion of the many-body interactions is inevitable in any theoretical route to the treatment of the polarizability effect.

A convenient approach to the problem of the many-body interactions is to replace these interactions with an effective potential that incorporates the average many-body interaction into the interaction between pairs. The approach has been adopted by Wertheim (1973, 1977a,b,c), Høye and Stell (1980), Carnie and Patey (1982) and Høye and Lomba (1994) as a basis for theoretical treatment of the polarizability effect. The studies just mentioned were successful in faithfully reproducing the microscopic structure and thermodynamic properties of

polarizable particles. Unlike other approaches, the Wertheim approach, which is called the renormalization perturbation theory (RPT), has been utilized with theory-based equations of state. The RPT was formulated based on a cumbersome graphical theory for dipolar-dipolar polarizable particles. Extension to mixtures and dipolar–quadrupolar polarizable particles was presented by Venkatasubramanian et al. (1984) and Gray et al. (1985). The RPT has been incorporated into equations of state to take into account the polarizable dipolar–dipolar systems (Kraska and Gubbins, 1996; Kleiner and Gross, 2006). Although the RPT showed good results, it is not an easy task to make it applicable to higher polarizable multipolar molecules. Even the extension to polarizable dipolar–quadrupolar molecules that has been carried out by Gray et al. (1985) was not trivial; it was derived with a different approach from that of the original complex graphical theory approach used by Wertheim.

An alternative theory to the renormalized perturbation theory is the self-consistent mean field (SCMF) theory proposed by Carnie and Patey (1982). The SCMF is equivalent to the RPT in terms of accuracy (Carnie and Patey, 1982). It is however based upon physical arguments rather than a mathematical approach. Further, the SCMF can be extended to take account of any polarizable multipolar interaction in a straightforward manner. The theory has been tested for various types of molecules such as water and ammonia using integral equation theories (Carnie and Patey, 1982; Perkyns et al., 1986; Caillol et al., 1987). It has also been tested with molecular simulation for a fluid of polarizable Lennard–Jones particles with dipoles and quadrupoles (Caillol et al., 1985; Patey et al., 1986). The results of SCMF/molecular simulation were in very good agreement with the exact molecular simulation data obtained by taking account of the many-body forces. Because the SCMF was originally derived to be used with integral equation theories and molecular simulation, only the energy term was derived. In this article, the free energy term is derived and the SCMF is incorporated into the equation of state. A comparison with molecular simulation data is also given to phase coexistence, energy and effective dipole moment. Moreover, the SCMF is extended to mixtures and applied to simplified statistical association fluid theory (Fu and Sandler, 1995) to study real mixtures.

2. Self-consistent mean field theory

As previously indicated, the SCMF theory approximates the many body polarization interactions with an effective pairwise-additive interaction. In particular, the theory replaces all the instantaneous dipole moments with an effective permanent dipole moment (μ_e) by ignoring the fluctuations in the local electric field. The polarizable medium is characterized by the average total molecular dipole moment ($\bar{\mu}$) and renormalized polarizability ($\bar{\alpha}$) in the same way that permanent dipole moment (μ) and polarizability (α) characterize a non-polarizable system. The values describing the effective system (μ_e, $\bar{\alpha}$ and $\bar{\mu}$) are determined to be self-consistent with a given dipole moment and polarizability by solving the following system of equations (Carnie and Patey, 1982):

$$\bar{\mu} = \mu + C(\bar{\mu})\mu \cdot \bar{\alpha} \tag{2.1}$$

$$\bar{\alpha} = \alpha + C(\bar{\mu})\alpha \cdot \bar{\alpha} \tag{2.2}$$

$$\mu_e^2 = \bar{\mu}^2 + 3\bar{\alpha}kT \tag{2.3}$$

where k, N and T are Boltzmann constant, number of particles and temperature. $C(\bar{\mu})$ is a scalar dependent function related to the energy of the effective system:

$$C(\bar{\mu}) = \frac{2\langle U^{DD}\rangle_e}{\mu_e^2 N} - \frac{\langle U^{DQ}\rangle_e}{\mu_e \bar{\mu} N} - \frac{\langle U^{DO}\rangle_e}{\mu_e \bar{\mu} N} = \frac{\langle U^{ID}\rangle_e}{\mu_e \bar{\mu} N} \tag{2.4}$$

where the energy superscripts D, Q, O and I denote the dipolar, quadrupolar, octopolar and ionic contributions, respectively.

The total average energy of the polarizable system is given by (Carnie and Patey, 1982; Caillol et al., 1985):

$$\langle U \rangle = \langle U^{LJ}\rangle_e + \langle U^{QQ}\rangle_e + \frac{\mu\bar{\mu}}{\mu_e^2}\langle U^{DD}\rangle_e + \frac{(\mu+\bar{\mu})}{2\mu_e}\langle U^{DQ}\rangle_e$$

$$+ + \frac{(\mu+\bar{\mu})}{2\mu_e}\langle U^{DO}\rangle_e + \frac{(\mu+\bar{\mu})}{2\mu_e}\langle U^{ID}\rangle_e \tag{2.5}$$

Hence, the total average energy of a polarizable system is determined by obtaining μ_e, $\bar{\mu}$ and the effective energies by solving simultaneously Eqs. (2.1)–(2.5). The effective energies are determined from any suitable non-polarizable multipole model. However, the solution procedure requires a replacement of the permanent dipole moment in the non-polarizable multipole model by the obtained effective dipole moment without any modification in the non-polarizable model. It should be noted that each term of the 3rd–6th terms on the right hand side of Eq. (2.5) consists of two energy contributions; namely, the effective energy and the self-consistent energy. The self-consistent energy describes the energy required to charge up the molecule having a permanent dipole moment and polarizability up to the polarizable state characterized by the average total molecular dipole moment and renormalized polarizability.

3. The free energy of the SCMF

To facilitate the application of the SCMF theory to an equation of state, it is essential to derive a general Helmholtz free energy term for the polarizable system in the NVT ensemble. Consider a polarizable system where the particles could have dipole, quadrupole, octupole and/or ions. The Helmholtz free energy of the polarizable system (*polz*) could be decomposed into an effective Helmholtz free energy term (A_e) and a self-consistent Helmholtz free energy term (A_{self}) as follows:

$$\frac{A_{polz}}{NkT} = \frac{A_e}{NkT} + \frac{A_{self}}{NkT} \tag{3.1}$$

The effective Helmholtz free energy is obtained from the non-polarizable model but with the replacement of the permanent dipole moment by the effective one. The self-consistent Helmholtz free energy, on the other hand, could be derived by starting from Eq. (2.5). As indicated previously, the energy of the polarizable system in Eq. (2.5) contains both the effective and the self-consistent contributions. Therefore, it is possible to obtain the self-consistent energy by deducting the effective term from Eq. (2.5). For instance, the self-consistent energy of the dipolar contribution is given by:

$$\langle U^{DD}\rangle_{self} = \frac{\mu\bar{\mu}}{\mu_e^2}\langle U^{DD}\rangle_e - \langle U^{DD}\rangle_e \tag{3.2}$$

It should be noted that the first term on the right hand side is a contribution of both the self-consistent and effective energies of the polarizable dipole–dipole term. The effective energy is