The Development of Soft-SAFT as a Versatile Molecular-Based Equation of State: Phase, Interface, and Derivative Properties Extensions

L.F. Vega$^{C, S}$
Molecular Simulation Group, Institut de Ciencia de Materials de Barcelona, Consejo Superior de Investigaciones Cientificas, Barcelona, Bellaterra, Spain
lvega@icmab.es

The soft-SAFT equation belongs to a family of molecular-based equations of state derived from the original SAFT equation (from the Statistical Associating Fluid Theory [1]). The advantage of using these types of equations versus classical equations of state is that it is possible to separate and quantify the different microscopic contributions governing the macroscopic behavior of the mixture; hence, the equation can be systematically improved by improving the underlying molecular model. Taking advantage of the molecular basis of the equation, we will discuss in this presentation several extensions of soft-SAFT [2] done in a systematic manner: the equation is first modified, taking into account different contributions (long density fluctuations in the near critical region, inhomogeneities in density in the case of interfacial properties, etc). The accuracy of the equation is then compared to molecular simulations for the same underlying model, with no fitted parameters. Once the equation has proved to be accurate it is then used to predict the behavior of experimental systems. We will concentrate on two recent extensions of the equation: the combination of soft-SAFT with the renormalization group theory [3] (done in the spirit of White and co-authors [4], and Prausnitz and collaborators [5]), and the combination of soft-SAFT with the Density Gradient Theory [6]. The first extension allows the equation to make quantitative predictions of the behavior of fluids in the near critical region, while the second extension enables the equation to obtain phase and interface properties simultaneously. Results from the extended equation will be compared to simulation and experimental systems in both cases. Emphasis will be made on the relevance of choosing the appropriate transferable molecular parameters, and the physical meaning of them, for reliable predictions at different thermodynamic conditions, for predicting the behavior of other members of the family, and of related binary mixtures. We will also discuss predictions of derivative properties such as heat capacities, the speed of sound and the Joule-Thomson coefficient, and their behavior in the near critical region. These properties are obtained with the same equation and parameters fitted from the vapour-liquid equilibrium data.

[1] W. G. Chapman, K. E. Gubbins, G. Jackson and M. Radosz, Ind. Eng. Chem. Res., **29**, 1709 (1989)
[2] F. J. Blas and L. F. Vega, Ind. Eng. Chem. Res., **37**, 660 (1998); J.C. Pàmies and L.F. Vega, Ind. Eng. Chem. Res., **40**, 2532 (2001)
[3] F. Llovell, J. C. Pàmies and L. F. Vega, J. Chem. Phys., 121(21) 10715 (2004); F. Llovell and L. F. Vega, J. Phys. Chem. B., **110**, 1350 (2006)
[4] J. A. White, Fluid Phase Equil., **75**, 53 (1992); J. A. White and S. Zhang, J. Chem. Phys., **99**, 2012 (1993)
[5] L. Lue and J. M. Prausnitz, J. Chem. Phys, **108**, 5529 (1998); L. Lue and J. M. Prausnitz, AIChE J., **44**, 1455 (1998)
[6] D. Duque, J. C. Pàmies and L. F. Vega, J. Chem. Phys., **121**, 11395 (2004); A. Mejía, J. C. Pàmies, D. Duque, H. Segura and L. F. Vega, J. Chem. Phys., **123**, 34505 (2005)