Improved vapor–liquid equilibria predictions for Lennard-Jones chains from the statistical associating fluid dimer theory: Comparison with Monte Carlo simulations

Felipe J. Blas[a)] and Lourdes F. Vega[b)]
Department d'Enginyeria Química, ETSEQ, Universitat Rovira i Virgili, Carretera de Salou s/n, 43006 Tarragona, Spain

The statistical associating fluid theory (SAFT), with monomer and dimer Lennard-Jones (LJ) reference fluids, is used to predict the phase equilibria of pure chains with different lengths. Predictions from the two versions of the theory are compared with Monte Carlo simulation results taken from the literature. We find that the additional structural information from the dimer version of the theory gives predictions in better agreement with simulation values. It is also found that the dimer version provides a much better description of the vapor pressure than the monomer one for long chains for which simulation data are available. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1390506]

I. INTRODUCTION

The statistical associating fluid theory (SAFT),[1,2] based on Wertheim's first-order perturbation theory for associating fluids,[3,4] has been used to predict the phase behavior of a wide variety of pure components and their mixtures,[5] and nowadays is considered one of the most powerful predictive tools for the study of fluid phase equilibria.

The original SAFT, proposed by Chapman *et al.*,[1,2] treats the chain molecules as hard sphere segments with attractive interactions described through a perturbation theory and has been successfully compared with Monte Carlo simulations.[6,7] Several modifications have appeared in the literature. In particular, the *soft*-SAFT equation of state (EOS), applied and extended by Blas and Vega[8] to deal with mixtures of homonuclear and heteronuclear LJ chains, accounts for the attractive and repulsive forces in a unique term. One of the weakest points of *soft*-SAFT is that it does not correctly account for the intramolecular interactions of chains; hence, it predicts an unphysical behavior in some properties at the low density limit, such as the internal configurational energy.[8] This is not a defect of the theory, but a consequence of the first-order perturbation approach. At this approximation level, the structure of the chain is given in terms of the pair radial distribution function of LJ spheres; in other words, at low densities only consecutive segments are correlated. This problem does not arise at high densities, since the chain–chain interpenetrations become more important and the structure of the fluid is dominated by the repulsive forces.[8,9] To avoid this problem, Ghonasgi and Chapman,[10] and Chang and Sandler[11] have independently proposed a dimer version of the SAFT equation (SAFT-D), which includes more struc-

tural information in the Helmholtz free energy of the system due to the chain formation through a dimer reference fluid (instead of a monomer one). Johnson[12] has extended this approach to LJ systems and predicted the thermodynamic behavior of pure chains at supercritical conditions. In particular, this author has clearly proved that the dimer theory provides a much better description of the pressure and internal configurational energy of Lennard-Jones chains, especially for long molecules. However, no systematic comparison has been made between simulation data and the SAFT-dimer theory for the phase equilibria of LJ chains. This comparison is necessary in order to evaluate the accuracy of the equation at subcritical conditions, since this region is very sensitive to any approximation made in the theory.

The aim of this work is to apply the soft-SAFT-dimer theory to predict the phase equilibria of pure LJ chains and to extend the theoretical approach for binary mixtures. The accuracy of including structural information in the reference fluid is checked by comparing the monomer and dimer versions of the theory versus Monte Carlo simulation data.

II. THE SAFT EQUATION OF STATE

Homonuclear chain molecules of component i are modeled as m LJ segments of equal diameter σ_{ii}, and the same dispersive energy ϵ_{ii}, bonded tangentially to form the chains. Intermolecular and intramolecular interactions between segments are taken into account through the LJ potential model. For binary mixtures, the unlike interaction parameters are calculated using the Lorentz–Berthelot mixing rules.[13]

The SAFT equation is written in terms of the Helmholtz free energy, and can be expressed as a sum of different microscopic effects. In particular, the *soft*-SAFT equation[8,14] is written as

$$\frac{A}{N_c k_B T} - \frac{A^{\text{ideal}}}{N_c k_B T} = \frac{A^{\text{LJ}}}{N_c k_B T} + \frac{A^{\text{chain}}}{N_c k_B T}, \quad (1)$$

a)Permanent address: Departamento de Física Aplicada e Ingeniería Eléctrica, Escuela Politécnica Superior, Universidad de Huelva, 21819 La Rábida, Huelva, Spain.
b)Author to whom correspondence should be addressed. Electronic-mail: lvega@etseq.urv.es

4355

where N_c is the number of chain molecules in the system, k_B is the Boltzmann's constant, T is the temperature, and A^{ideal} is the ideal contribution to the Helmholtz free energy. A^{LJ} is the Helmholtz free energy of a mixture of spherical LJ sites, proposed by Johnson et al.[15] The contribution due to the chain formation is accounted for in A^{chain}. This term takes different forms in the monomer and dimer versions.

A. Monomer version

The monomer contribution, independently introduced by Wertheim,[4] and Chapman et al.,[6,7] for mixtures of LJ chains with bond lengths equal to σ_{ii}, is written as

$$A^{\text{chain}} = N_c k_B T \sum_{i=1}^{n} x_i (1 - m_i) \ln g_{\text{LJ}}^{(M)}(\sigma_{ii}), \qquad (2)$$

where $g_{\text{LJ}}^{(M)}(\sigma_{ii})$ is the pair radial distribution function for spherical segments (monomers) of species i in the LJ mixture at the contact length.[16]

B. Dimer version

The chain contribution to the Helmholtz free energy in the dimer approach, introduced by Johnson,[12] is written as

$$\frac{A^{\text{chain}}}{N_c k_B T} = \left[-\frac{m}{2} \ln g_{\text{LJ}}^{(M)}(\sigma) + \left(1 - \frac{m}{2} \right) \ln g_{\text{LJ}}^{(D)}(\sigma) \right], \qquad (3)$$

where $g_{\text{LJ}}^{(D)}(\sigma)$ is the end–end pair radial distribution function of the dimer LJ fluid at the contact length. Although Eq. (3) is only valid for pure fluids, its extension for mixtures can be readily available using the same procedure as that for the monomer version. In this case, the chain contribution is written as

$$A^{\text{chain}} = \sum_{i=1}^{n} A_i^{\text{chain}}, \qquad (4)$$

where the summation index runs for all the different components of the mixture, and A_i^{chain} is the residual Helmholtz free energy due to the formation of the component i of the mixture. The form of the different terms, A_i^{chain}, depends on the chain length of each component

$$A_i^{\text{chain}} = \begin{cases} N_c k_B T x_i (1 - m_i) \ln g_{\text{LJ}}^{(M)}(\sigma_{ii}) & \text{if } m_i < 2 \\[2mm] N_c k_B T x_i \left[-\frac{m_i}{2} \ln g_{\text{LJ}}^{(M)}(\sigma_{ii}) + \left(1 - \frac{m_i}{2} \right) \ln g_{\text{LJ}}^{(D)}(\sigma_{ii}) \right] & \text{if } m_i \geqslant 2 \end{cases}, \qquad (5)$$

where $g_{\text{LJ}}^{(M)}(\sigma_{ii})$ and $g_{\text{LJ}}^{(D)}(\sigma_{ii})$ are the pair radial distribution functions for monomers and dimers of type i at the contact length in the LJ mixtures, respectively.[12]

To obtain the pair distribution functions of mixtures of LJ spheres and dimers, as well as the Helmholtz free energy of binary mixtures of LJ spheres, we use the usual van der Waals one-fluid theory (vdW-1f).[13] For more details see Blas and Vega.[8,14]

III. RESULTS AND DISCUSSION

In order to check the accuracy of the monomer and dimer versions of soft-SAFT for phase equilibria predictions, we compare the theory with Monte Carlo simulation data of pure LJ chains taken from the literature.[17–20] Temperature, pressure, and monomeric density are expressed in reduced units with respect to the molecular parameters. Symbols represent the simulation data and lines correspond to the theoretical predictions. The critical temperatures shown in figures are calculated by fitting the simulation data to the universal scaling laws corresponding to the Ising universality class, with the critical exponent given by $\beta = 0.326$ (Refs. 18 and 21).

First, we consider molecules with short and intermediate chain lengths, from a dimer fluid up to chains formed by 16 segments. As can be observed in Fig. 1, both versions of SAFT give similar results for short chains ($m = 2$, 3 segments), and agreement with simulation data is excellent in

the whole range of coexistence conditions. However, for trimer molecules, the simulation results ($T_c^* = 2.063$ and $\rho_c^* = 0.264$) are in better agreement with soft-SAFT-dimer ($T_c^* = 2.09$ and $\rho_c^* = 0.265$) than with the original soft-SAFT ($T_c^* = 2.16$ and $\rho_c^* = 0.2491$). At longer chain lengths ($m = 4$, 8, 16), the monomer version overestimates the phase diagram obtained from simulation, whereas the dimer version substantially improves predictions of the phase envelope, especially in the vapor phase and the region close to the critical point, where differences between results from both theories are larger.

Of particular interest is the liquid side of the coexistence curves. For chains formed up to 8 segments, and more clearly for those with 16 segments, a change in the slope of the liquid branch predicted by the dimer version is observed, resulting in a better agreement with simulation data. These results clearly indicate that the introduction of more structural information, through the reference fluid, greatly enhances the accuracy of the theoretical predictions of the phase diagram.

We have also applied the equation to obtain the coexistence diagrams of longer LJ molecules. In particular, we have considered chains of 20, 50, and 100 segments; results are shown in Figs. 2 and 3. It is important to note that the simulation results used to check the accuracy of the theory correspond to a slightly different chain model, namely, a bead-
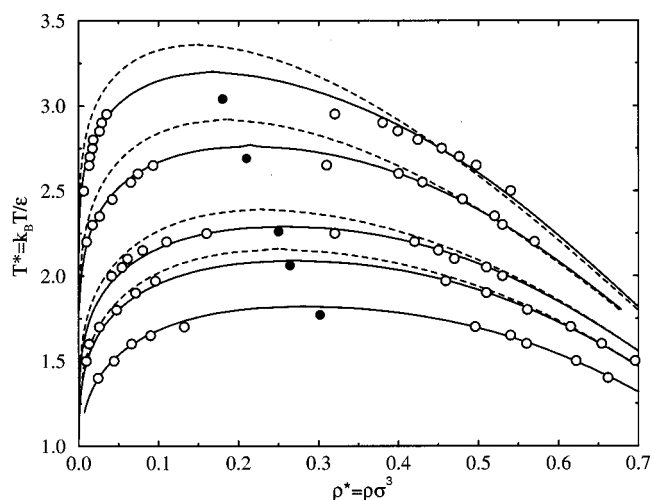
FIG. 1. Vapor–liquid equilibria of pure LJ chains with different chain lengths. Symbols represent simulation data and lines are the theoretical predictions from the monomer (dashed lines) and dimer (solid lines) versions of *soft*-SAFT. From bottom to top: $m = 2$, (Ref. 17) 3, (Ref. 18) 4, 8, and 16 (Ref. 19) sites.

FIG. 3. Enlargement for the vapor side of the coexistence diagrams shown in Fig. 2. Legends represent the same as in the previous figure.

spring polymeric model,[20] and are included here to check the sensitivity of the theory to the details of the model, and to longer chain lengths. Figure 2 shows the complete vapor–liquid phase diagram for the LJ chains considered here. The region corresponding to the vapor phase has been enlarged and presented in Fig. 3 to highlight the comparison between simulation data and predictions from both versions of the theory. It is observed that the *soft*-SAFT-D, as for the case of shorter chains, substantially improves predictions of the vapor phase and the region close to the critical point. Also, it is seen that, although both versions of the equation give similar results for the liquid envelope, the shape of the liquid branch predicted by the dimer theory seems to be in better agreement with simulation data than that corresponding to the
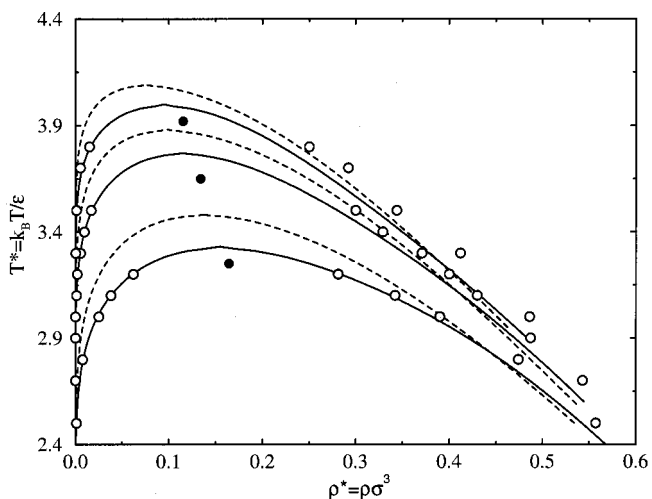
monomer version. We emphasize here that simulation results correspond to a slightly different model, which explicitly includes intramolecular interactions between consecutive segments. Deviations between simulation data and theoretical predictions corresponding to the denser coexisting phase can be attributed to this fact, since the liquid phase is especially sensitive to finer molecular details (such as the spring connecting the beads in the simulation model, versus simply freely jointed segments in the SAFT approach).

Finally, we have calculated the vapor pressure curves corresponding to the longest chains considered here. Figure 4 shows the comparison between simulation data taken from the literature[20] and predictions corresponding to both versions of the theory. As can be seen, the monomer version underestimates the vapor pressure of the three LJ chains considered, whereas the agreement between simulation results and predictions from the dimer version is excellent in all

FIG. 2. Vapor–liquid equilibria of pure LJ chains with different molecular sizes. Symbols correspond to simulation data taken from the literature (Ref. 20) and lines represent the theoretical predictions from the monomer (dashed lines) and dimer (solid lines) versions of the theory. From bottom to top: $m = 20$, 50, and 100 sites.
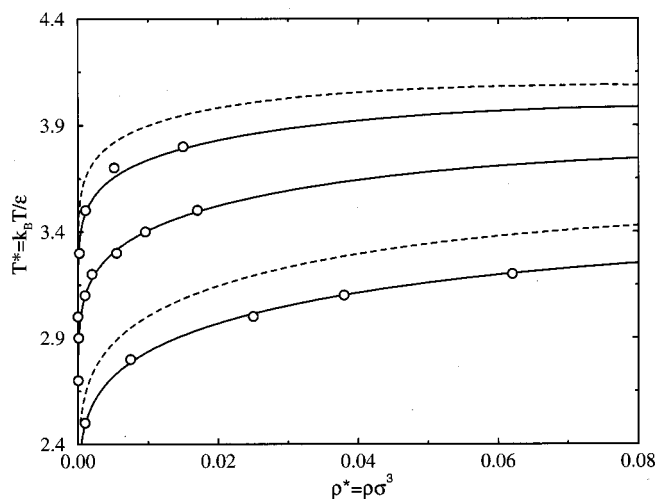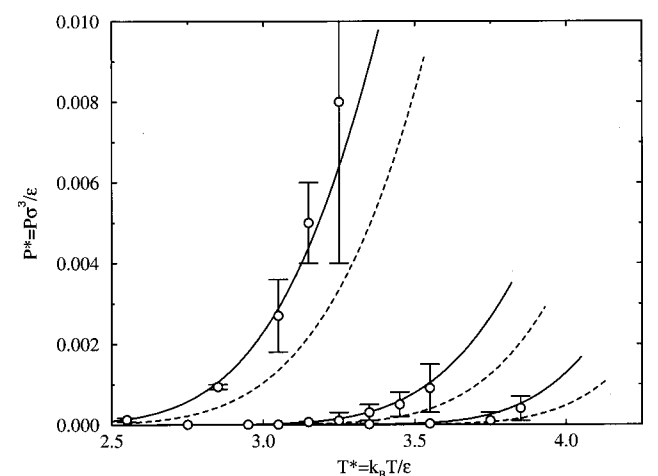

FIG. 4. Vapor pressure curves for LJ chains with different chain lengths. Symbols represent simulation data taken from the literature (Ref. 20) and lines correspond to the theoretical predictions from monomer (dashed lines) and dimer (solid lines) versions of the *soft*-SAFT. The curve at the lowest temperature corresponds to chains with 20 segments and that at the highest temperature to molecules formed by 100 LJ sites.
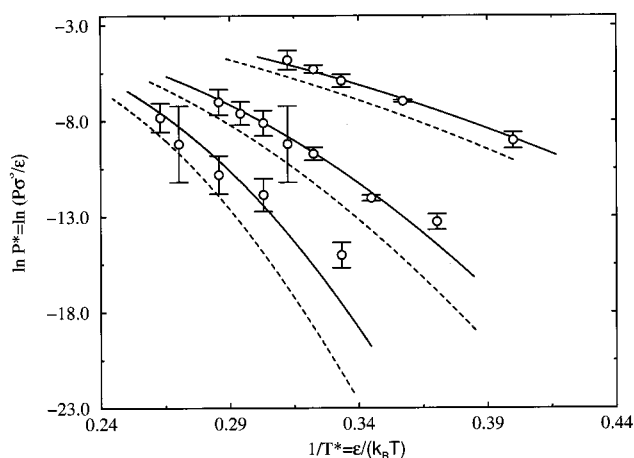
FIG. 5. Clausius–Clapeyron plot for the vapor pressure corresponding to the systems shown in Fig. 4. Legends represent the same as in the previous figure.

long chains, to decide which version of the theory is more accurate. It is expected that the use of the dimer equation should improve the *soft*-SAFT predictions for the case of long chains, as happens for pure fluids.

cases and in the whole range of coexisting temperatures. Figure 5 provides an additional Clausius–Clapeyron plot, showing a remarkable agreement between simulation data and predictions at low and intermeditate temperatures for the three chain lengths studied.

In summary, we have applied the *soft*-SAFT-dimer theory to describe the phase behavior of pure LJ chains, and extended the theoretical approach to deal with binary mixtures. The predictions from the theory have been compared with Monte Carlo simulation data, and show that the dimer version of *soft*-SAFT is more accurate than the monomer equation for all the chain lengths considered. Agreement between simulation and theory is excellent not only for the coexistence curves, but also for the vapor pressures in the whole range of temperatures studied. The overall improvement for the description of the vapor–liquid behavior is essentially due to the use of additional structural information included in the reference fluid. For the case of binary mixtures extensive simulation data is required, especially for

[1] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, Fluid Phase Equilibria **52**, 31 (1989).
[2] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, Ind. Eng. Chem. Res. **29**, 1709 (1990).
[3] M. S. Wertheim, J. Stat. Phys. **35**, 19 (1984); **35**, 35 (1984); **42**, 459 (1986); **42**, 477 (1986).
[4] M. S. Wertheim, J. Chem. Phys. **85**, 2929 (1986); **87**, 7323 (1987).
[5] S. H. Huang and M. Radosz, Ind. Eng. Chem. Res. **29**, 2284 (1990); *ibid.* **30**, 1994 (1991).
[6] G. Jackson, W. G. Chapman, and K. E. Gubbins, Mol. Phys. **65**, 1 (1988).
[7] W. G. Chapman, G. Jackson, and K. E. Gubbins, Mol. Phys. **65**, 1057 (1988).
[8] F. J. Blas and L. F. Vega, Mol. Phys. **92**, 135 (1997).
[9] F. J. Blas, Ph.D. thesis, Universitat Rovira i Virgili, Tarragona, Spain, 2000.
[10] D. Ghonasgi and W. G. Chapman, J. Chem. Phys. **100**, 6633 (1994).
[11] J. Chang and S. I. Sandler, Chem. Eng. Sci. **49**, 2777 (1994).
[12] J. K. Johnson, J. Chem. Phys. **104**, 1729 (1996).
[13] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1990).
[14] F. J. Blas and L. F. Vega, Ind. Eng. Chem. Res. **37**, 660 (1998).
[15] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).
[16] J. K. Johnson, E. A. Müller, and K. E. Gubbins, J. Phys. Chem. **98**, 6413 (1994).
[17] G. S. Dubey, S. F. O'Shea, and P. A. Monson, Mol. Phys. **80**, 997 (1993).
[18] O. R. Contreras and A. D. Mackie (private communication).
[19] F. A. Escobedo and J. J. de Pablo, Mol. Phys. **87**, 347 (1996).
[20] Y.-J. Sheng, A. Z. Panagiotopoulos, S. K. Kumar, and I. Szleifer, Macromolecules **27**, 400 (1997).
[21] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford Science, Oxford, 1982).