Coarse-grained models for fluids and their mixtures: Comparison of Monte Carlo studies of their phase behavior with perturbation theory and experiment

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The prediction of the equation of state and the phase behavior of simple fluids (noble gases, carbon dioxide, benzene, methane, and short alkane chains) and their mixtures by Monte Carlo computer simulation and analytic approximations based on thermodynamic perturbation theory is discussed. Molecules are described by coarse grained models, where either the whole molecule (carbon dioxide, benzene, and methane) or a group of a few successive CH₂ groups (in the case of alkanes) are lumped into an effective point particle. Interactions among these point particles are fitted by Lennard–Jones (LJ) potentials such that the vapor-liquid critical point of the fluid is reproduced in agreement with experiment; in the case of quadrupolar molecules a quadrupole-quadrupole interaction is included. These models are shown to provide a satisfactory description of the liquid-vapor phase diagram of these pure fluids. Investigations of mixtures, using the Lorentz–Berthelot (LB) combining rule, also produce satisfactory results if compared with experiment, while in some previous attempts (in which polar solvents were modeled without explicitly taking into account quadrupolar interaction), strong violations of the LB rules were required. For this reason, the present investigation is a step towards predictive modeling of polar mixtures at low computational cost. In many cases Monte Carlo simulations of such models (employing the grand-canonical ensemble together with reweighting techniques, successive umbrella sampling, and finite size scaling) yield accurate results in very good agreement with experimental data. Simulation results are quantitatively compared to an analytical approximation for the equation of state of the same model, which is computationally much more efficient, and some systematic discrepancies are discussed. These very simple coarse-grained models of small molecules developed here should be useful, e.g., for simulations of polymer solutions with such molecules as solvent. © 2009 American Institute of Physics. [DOI: 10.1063/1.3050353]

I. INTRODUCTION

It has been a longstanding challenge to predict accurately the equation of state and in particular the phase diagrams of fluids and fluid mixtures from atomistic models via computer simulation.1–5 Such applications have required a widespread development of computer simulation methodology: significant advances were possible through the invention of Gibbs ensemble6–8 and configurational bias9–11 methodologies, grand canonical Monte Carlo simulations combined with histogram reweighting methods12–14 and finite size scaling15–18 including field mixing,19–22 umbrella sampling,23,24 and other expanded ensemble methods.25–27 A lot of effort has also been spent towards developing more and more accurate effective potentials from quantum chemistry methods (e.g., Refs. 28–32). However, for simple and industrially relevant fluids such as carbon dioxide33,34 it is still difficult to predict the equation of state with high accuracy, such that experimental data in the critical region and for temperatures ±30% around it are reproduced to an accuracy of a few percent.35,36 Extending such calculations to mixtures (in particular, solutions of polymers with supercritical carbon dioxide as a solvent) is even more of a problem, due to the less complete knowledge of effective potentials, and due to the extensive numerical effort required. A three-dimensional parameter space involving the variables temperature T, pressure p, and mole fraction x needs to be scanned for a binary system, and the phase diagrams are typically very complicated, because vapor-liquid and fluid-fluid phase equilibria need to be scanned for a binary system,
be interesting for applications to experiment and in the context of industrial processing. Such validated coarse-grained models that accurately reproduce thermodynamic bulk properties are also a starting point for investigating the kinetics of phase separation or spatially inhomogeneous systems (e.g., wetting and catalysis).

In the present work, we wish to make a step towards this goal, extending our previous study of a selected sample of simple pure fluids, in particular carbon dioxide35,36 to various binary mixtures. We want to stress that our aim is not to reach the most accurate prediction of the phase diagram of a specific system. Indeed, motivated by the excellent results obtained for the pure carbon dioxide and for simple quadrupolar molecules in general,35 we want to investigate how this model performs for mixtures, especially solutions of various alkanes. In particular we will show that the new coarse grained (CG) model avoids the need for a big violation of the Lorentz-Berthelot (LB) combining rules (that was required in previous work44). This violation destroys the predictivity of the model because extensive experimental data for the mixture would be required to determine a parameter describing the violation of the LB combining rule. Due to the generality of the approach and the level of accuracy for the pure components,42 the present investigation is relevant both for practical purposes and for a general understanding of coarse graining procedures.43–45 We will also present results of an analytical equation of state (EOS) which (apart from some region of the phase diagram near critical points) is able to yield rather satisfactory predictions in agreement with Monte Carlo results. It is very important to note that this EOS uses the same model parameters as the Monte Carlo simulation. This implies that in principle we are in a position to attempt to predict the phase diagram of a binary mixture (which is very complex37–40) with comparatively small computational effort. In this view the reader should also interpret our choice to use LB combining rules: of course there are no reasons to believe that such approximations should be exact, and certainly there will be cases where more complicated combining rules are preferable. However, the simple LB combining rules used here suffice for a wide class of systems with quite acceptable errors.

Due to the generality of the scheme presented in this work we expect discrepancies, and some regions of the phase diagram might not be predicted properly. This is related to several limitations of the present procedure such as (i) the large T expansion involved in the building of the CG model for quadrupolar solvents35,36 and (ii) limitations related to our simple modeling approach such as the simple potentials involved (LJ), the neglect of atomistic details, and the use of the LB combining rules for which discrepancies are46 known to arise (see, e.g., Ref. 47 for some systems also investigated in this work). In order to disentangle point (i) from point (ii) we also present investigations of similar apolar mixtures for which the new CG model35,48 does not result in any improvement. The results show similar discrepancies from experiment as the polar phase diagrams, confirming the quality of the choice done in Refs. 35 and 48. We want to stress that in order to test the goodness of our CG model, the only reliable method is a Monte Carlo investigation. Indeed, without MC simulation it is impossible to distinguish the bias related to the approximations involved in the EOS from the bias involved in the CG model [point (ii) above]. For instance, we will present results for the mixture of methane and carbon dioxide for which EOS results will be in better agreement with experiments than MC results: this is clearly a fortuitous cancellation!

It is important to report that other interesting and significant attempts to build a systematic description of mixture phase diagrams are present in the literature. For instance in Refs. 49 and 50 mixtures are treated with models previously investigated in Ref. 51. For some of the molecules studied, these models allow for an additional parameter that can be adjusted and consequently a more accurate fit of experimental data is possible. On the other hand, there is a loss in predictivity because the full phase diagrams of the pure substances are required in order to determine the simulation parameters (computed in a χ square fit which minimizes discrepancies with experiment44) plus mixture data50 to determine the mixing parameters.52 So the strategy of the present work is to deal with relatively simple models, where (in the framework of Monte Carlo simulations) the statistical mechanics can be dealt with at a very good level of accuracy (e.g., long runs employing advanced Monte Carlo techniques are possible to minimize statistical and systematic errors due to finite size effects which are avoided by finite size scaling analysis). These models are suitable for analytic EOS models as well, and can serve as a starting point for the CG modeling of polymer solutions. Of course, we do not imply that a complementary simulation strategy (making models as detailed as possible, to account for the packing of molecules in the liquid as accurately as possible, including polarizability, etc.) is not worth pursuing in its own right, but it is outside of the scope of the present work.

II. COMPUTATIONAL DETAILS AND OUTLINE

It is well established5,19–22,41,54–58 that the most reliable approach to study the phase behavior of fluids is based on grand canonical Monte Carlo simulations together with histogram reweighting and finite size scaling techniques, especially if one wishes to include the critical region. In this study, we follow this approach and amend it by successive umbrella sampling54 to obtain coexistence curves far from criticality. This method has the additional advantage that the interfacial free energy between the coexisting phases can be extracted as well.59–62 As we are interested in a very fast simulation code, we omit any potential including effective charges, and restrict our attention to short range effective potentials. Three-body (nonbonded) forces are avoided as well. Electrostatic quadrupole-quadrupole interactions are treated as a perturbation (which is practically justifiable36), such that an effective angular-independent (but temperature-dependent) quadrupole-quadrupole interaction decaying proportionally to the power r−10 of the interparticle distance r results. The dispersion forces are modeled by Lennard–Jones (LJ) potentials. For the sake of computational efficiency, all potentials are cut at the distance r = r_c = 2(1.06)σ and shifted to zero at r_c (σ is the range parameter of the LJ potential).
When we deal with alkane chains, we disregard any torsional forces and bond-angle potentials and integrate a few successive chemical monomers into one effective monomeric unit (cf. Fig. 1). This is done in the way that one such unit contains three carbon-carbon bonds between successive carbon atoms, and we do not distinguish between interior CH\(_2\) monomers and the CH\(_3\) groups at the chain ends. Thus, for example, hexadecane (C\(_{16}\)H\(_{34}\)) is represented by a chain molecule containing five effective monomers (see Fig. 1).\(^{41,63}\) The procedure of coarsening three carbon atoms in a bead has been proven to be optimal in several theoretical investigations\(^{65}\) (see Sec. IV C). We stress that the particular choice of coarsening three carbon units into one bead has nothing to do with some physical lengths of the chain (like for instance the Kuhn length), but is a choice that depends more on the potentials used. Indeed as neighboring beads along a chain interact with a bonding potential (see Sec. III C for definitions) in addition to the LJ potential, the coarse grained model of the chain exhibits a degree of local stiffness, although neither bond angle nor torsional potentials are included explicitly. This implies that the Kuhn length is longer than the diameter of our beads.

Of course, the suitable choice of parameters is crucial for such CG models: we choose the strength of the quadrupole moment \(Q\) (if there is one) such that it is compatible with experimental data, and adjust the range \(\sigma\) and strength \(\epsilon\) of the LJ potential such that the experimental critical density \(\rho_c\) and critical temperature \(T_c\) are reproduced precisely in the simulation. In Sec. III, we will briefly discuss the accuracy of this procedure for a variety of pure systems (noble gases, CO\(_2\), CH\(_4\), C\(_6\)H\(_6\), and short alkanes) while Sec. IV contains the central part of our work, in which we present a variety of results for binary mixtures. The additional interactions needed for the mixtures are chosen by the simple LB combining rules.\(^{64}\)

Technical aspects of our simulations are similar to previous studies.\(^{35,36,41}\) Far from the critical point coexistence densities are computed using the successive umbrella sampling algorithm of Virnau and Müller\(^{24}\) in which high free energy barriers are overcome constraining the algorithm—at a certain time of the simulation—to sample configurations of a system where the number of particles is \(n\) or \(n+1\). Varying \(n\) from \(n=0\) to \(n=N_{\text{MAX}}\) one is able to reconstruct (after proper reweighting) the free energy profile \(F(n)\) at coexistence in the range of densities of interest. At phase coexistence, we expect a distribution \(F(n)\) with two peaks (corresponding to the two coexisting phases that differ in particle number) which have equal weight. In few very fast runs (using a small cubic box \(L=7\sigma_M\), where \(\sigma_M\) is the biggest LJ length parameter of the model), invoking the equal weight rule for \(F(n)\), we are able to tune the chemical potential(s) to their coexistence values, with a reasonable error \((\approx 1\%–5\%)\) which in some cases should be enough. Then, we start a second long simulation for a larger elongated box (to enhance the formation of the liquid-gas interface) \(V=2L^3\) with \(L=9\sigma_M\) in which every window is sampled with \(2\times10^4\) MC steps. Every MC step includes: 100 grand canonical moves in which we try to insert/delete solvent (and chain) particles, 1 local move in which a number of monomers equal to the total number of monomers are rearranged, and \(10N_{\text{chain}}\) reptation moves, where \(N_{\text{chain}}\) is the number of the chains in the box. Such a run requires on average 10 h of CPU time on 32 nodes of an IBM Power4 cluster. The precision of the measured coexistence densities (for instance) is roughly 1%. Using a spherical averaged potential allows us to speed up computations by a factor \(\approx 5\)\(^{36}\) in comparison with the full quadrupolar model. A number of chains \(N_{\text{MAX}}=1100\) usually allows a complete sampling of the liquid peak, while the number of solvent particles is typically of the same order of magnitude. We emphasize that—unlike simulations in the Gibbs ensemble—in addition to the densities and compositions of the coexisting phases and their compressibilities, the simulation technique also provides information about the interface tension. At the critical point, we use the same kind of simulation described above, but unconstrained. (At every time the number of particles is free to fluctuate in all the region \([0,N_{\text{MAX}}]\)). For more detail on the finite size analysis used we refer the reader to Sec. IV C.

Even with all these simplifying approximations, establishing the phase behavior and thermodynamic properties of binary mixtures comprehensively still requires a lot of work with Monte Carlo simulations. Far away from critical points, such an effort is not needed, and one can try to use an analytical EOS. We use a previously developed theory based on Wertheim thermodynamic perturbation theory\(^{66}\) (TPT). We strictly follow Refs. \(^{67}\) and \(^{68}\). In particular the free energy of the system \(A\) is decomposed in a contribution due to a mixture of unbonded monomers (the reference system) plus a contribution due to chain associativity \(A_{\text{chain}}\): \(A=A_{\text{ref}}+A_{\text{chain}}\). Wertheim’s theory allows us to compute \(A_{\text{chain}}\) perturbatively using quantities of the reference system (like pair correlation functions) and the known bonding potential. We use a first order perturbation theory (TPT1) which (at this point) reduces the problem to the computation of pair correlation functions and the free energy \((A_{\text{corr}})\) of a binary mixture of nonbonded monomers interacting with LJ potentials (chain-chain monomers and solvent-chain monomer pairs).
and the LJ+quadrupolar interaction (see Sec. III B) for solvent-solvent monomer pairs. $A_{ref}$ is computed using standard perturbation theory: the Ornstein–Zernike equation is solved using a mean spherical (MSA) closure.66 In particular, one chooses as reference system a mixture of hard spheres with diameters computed using the repulsive part of the monomer-monomer potential in a Barker Henderson approximation,70 while the attractive part of the potential is treated as a perturbation. A MSA solution is then obtained using the analytical implementation of Lu and co-workers71,72 in which the repulsive part of the LJ potential is fitted by a couple of Yukawa tails which allow to obtain an analytical result.58 In our present modeling approach we need to consider LJ potentials plus quadrupolar interactions. This problem has been solved in Ref. 35 (see Appendix A of Ref. 35) by applying a second pair of Yukawa tails to fit the quadrupolar interaction. In our MSA scheme we also use a “one fluid approximation.”69 Our results will show how this simple theory is able to reproduce results in rather good agreement with MC data away from the critical point. On the other hand, big discrepancies occur near the critical points, due to the mean field nature of the MSA while experimental results exhibit critical behavior characteristic of the Ising universality class. We are aware of significant efforts to design proper EOS which include Ising fluctuation near the critical point.73,74 However, such investigations are beyond the scope of the present paper. Another popular method based on TPT1 is known as “statistical associating fluid theory.”75

We want to stress that Monte Carlo simulations remain an indispensable tool in investigations of the phase behavior of polymer solutions and mixtures. Indeed, in the present study the model parameters ($\epsilon$, $\sigma$, and $q_i$) have been determined35 using the simulation critical points which were obtained by Monte Carlo simulation in Ref. 35. (Any mean field approximation has difficulties in reproducing the critical line with sufficient accuracy.) Note that supercritical fluids are interesting and useful for practical applications, mainly due to their high compressibility and the concomitant large variations of density upon small changes of pressure, which are the origin of the breakdown of a mean field approximation like TPT. This means that in some very interesting regions of the phase diagram Monte Carlo simulations are indeed a very valuable tool.

III. PHASE BEHAVIOR OF SELECTED PURE SYSTEMS

When we discuss the extent to which the LB combining rule can account for the phase behavior of mixtures, we need to distinguish between inaccuracies arising from an imperfect description of the pure components and those arising from the LB rule. Therefore it is necessary to give an overview of our modeling of the pure components at the outset. Note that a possible additional source of errors are entropic packing effects of nonspherical molecules that may show up differently in a mixture of two molecules having different shapes rather than for a pure system, where all molecules have the same shape. Such effects are lost in our CG models. However, this latter criticism cannot be applied when we consider mixtures of noble gases, since in the framework of classical statistical mechanics the description of noble gas atoms as point particles, where two such atoms interact with a potential depending on the absolute value of their distance only, is certainly appropriate. (Disregarding the case of He, quantum effects are negligible indeed at temperatures of interest76). For that reason, noble gases are also included in our discussion, because they will bring out the possible limitations of our modeling in terms of pairwise effective potentials between pointlike particles most clearly. Thereafter, we shall deal with $\text{CO}_2$, $\text{C}_6\text{H}_6$, $\text{CH}_4$, and selected short alkanes.

A. Noble gases

The interaction between neutral pointlike particles in our work is always described by the LJ potential,

$$U_{ij}^{\text{LJ}} = 4\epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right).$$

(1)

Rather than working with the full LJ potential as written in Eq. (1), we find it computationally more convenient and efficient to cut off this potential at $r=r_c=2^{7/6}\sigma$ and shift it to zero there, such that

$$U_{ij}(r) = U_{ij}^{\text{LJ}}(r) + 4\epsilon S, \quad U_{ij}(r \geq r_c) = 0.$$

(2)

where $S=127/16384$ for our choice of $r_c$, so that the potential is continuous everywhere. When we require that Eqs. (1) and (2) yield a vapor-liquid phase diagram such that the critical temperature $T_c$ coincides with the experimental critical temperature $T_c^{\text{exp}}$ of a particular system, the strength ($\epsilon$) of the LJ potential is fixed once $T_c^{\text{exp}}=k_BT_c/\epsilon$ has been determined for the model. Likewise, requiring that the critical density $\rho_c$ of the model coincides with the experimental critical density $\rho_c^{\text{exp}}$ of that system the range ($\sigma$) of the LJ potential is fixed once $\rho_c^{\text{exp}}=\rho_c\sigma^3$ is known for the model. Here, $T_c^{\text{exp}}=k_BT_c/\epsilon$ and $\rho_c^{\text{exp}}=\rho_c\sigma^3$ are dimensionless temperature and density, respectively. Actually, the phase diagrams of both the full (untruncated) LJ potential and of its truncated version [Eqs. (1) and (2)] have been estimated with high precision.41,61 Figure 11 of Ref. 35 compares these phase diagrams with each other and with experimental data for the noble gases Ne, Ar, Kr, and Xe.77 It was found that in this scaled representation the differences between the phase diagrams based on full and truncated LJ models are quite minor. Although noble gases are thought to be the best possible experimental realization of LJ fluids, the agreement is not perfect either: while Ne and Ar are very close to the LJ prediction, the data for the fluid branch of Kr and Xe are somewhat off. This implies that even noble gases do not strictly satisfy the “law of corresponding states,” and hence a description in terms of classical point particles interacting with purely pairwise potentials of the same functional form, $U_{ij}(r) = \epsilon f(r/\sigma)$, with one parameter for the strength ($\epsilon$) and another for the range ($\sigma$) of the potential cannot be strictly true, irrespective of the form of the function $f(r/\sigma)$; either a more complicated form of the pairwise interaction, involving a third system-specific parameter is needed, or (what is usually assumed) some effect of three-body interactions78–80 is present.
An even more pronounced deviation from the simple LJ model shows up, however, when additional quantities are analyzed, such as the vapor pressure \( p_{\text{coex}}(T) \) at liquid-vapor coexistence and the interfacial tension \( \gamma(T) \) between the coexisting vapor and liquid phases of the fluid (see Figs. 2 and 3). It is clear that adjusting \( \sigma \) from \( \rho_{\exp}^{\text{exp}} \) implies that the whole curve for the coexistence pressure \( p_{\text{coex}}(T) \) in the \((p,T)\) plane is underestimated for both Kr and Xe. This is a serious drawback for the description of binary mixtures, of course, where one wishes to work in the liquid phase of the fluid existing vapor and liquid phases of the fluid. Therefore, we have tried an alternative, namely, adjusting \( \sigma \) such that the experimental critical pressure \( \rho_{c}^{\exp} = p_{\text{coex}}(T_{c}) \) is correctly reproduced. For Kr the critical temperature \( T_{c}^{\exp} = 209.46 \text{K} \) (Ref. 77) implies \( \epsilon = 2.8971 \times 10^{-21} \text{J} \). If one uses \( \rho_{c} = 11.0 \text{ mol/l} \) (Ref. 77) to fit \( \sigma \) one obtains \( \sigma = 3.6524 \text{ Å} \), while using \( \rho_{c}^{\exp} = 55.20 \text{ bar} \) (Ref. 77) instead would yield \( \sigma = 3.5878 \text{ Å} \). (For a discussion of the accuracy of our estimation of \( \epsilon \) and \( \sigma \), we refer to Table I. In order to guarantee the reproducibility of our results we always present \( \epsilon \) and \( \sigma \) with all the digits that have been used in our programs.) Figure 3 shows that a somewhat better description of the vapor pressure \( p_{\text{coex}}(T) \) is obtained over the full temperature regime from \( 140 \text{K} < T < T_{c}^{\exp} \). The deviation from the data for the surface tension \( \sigma \) has also become smaller [Fig. 2(b)], but now there is a strong deviation between the data for the liquid branch of the coexistence curve and the model [Fig. 2(a)]. Similar problems are observed for Xe, where \( T_{c}^{\exp} = 289.74 \text{K} \) yields \( \epsilon = 4.00747 \times 10^{-21} \text{J} \), while the use of \( \rho_{c}^{\exp} = 8.371 \text{mol/l} \) yields \( \sigma = 4.00053 \text{ Å} \) and the use of \( \rho_{c}^{\exp} = 58.41 \text{bar} \) yields \( \sigma = 3.923 \text{Å} \). Figures 2 and 3 show that for these noble gases the description of the coexistence curve, vapor pressure at coexistence, and surface tension is clearly not as good as for the model of CO\(_2\) and C\(_6\)H\(_6\) proposed in Ref. 35. These problems carry over to our modeling of binary noble gas mixtures (see Sec. III A), as the comparison with experimental data shows. At this point we recall that as outlined in the Introduction, the investigation of such a system has been undertaken in order to get an order of magnitude estimate of the errors inherent to our very simple models: the goal is not the derivation of a very elaborate description of noble gas mixtures. Figure 3 clearly shows that this model allows for a fairly good description of the mixture phase diagram (if compared to other mixtures presented in this work). In the present context it was not necessary to include more complex potentials available in the literature since long times (e.g., Refs. 82–84).

### 2. Small molecules: Methane, carbon dioxide, and benzene

Methane (CH\(_4\)) is also described as a point particle, and again we take Eqs. (1) and (2) as a CG description of the interaction between methane molecules. Using \( T_{c}^{\exp} = 130.6 \text{ K} \) (Ref. 77) and \( \rho_{c}^{\exp} = 10.1 \text{ mol/l} \) (Ref. 77) as experimental input to determine \( \epsilon \) and \( \sigma \), we obtain \( \epsilon = 2.63624 \times 10^{-21} \text{J} \) and \( \sigma = 3.75792 \text{ Å} \). Figure 4 compares the resulting model prediction for the coexistence curve in the temperature-density plane, the vapor pressure at coexistence and the surface tension with the corresponding experimental data. It is remarkable that in this case the simple potential model [Eqs. (1) and (2)] works better than in the case of the noble gas.

For molecules such as carbon dioxide (CO\(_2\)) and benzene (C\(_6\)H\(_6\)) the situation is more complicated: while CH\(_4\) is a molecule of approximately spherical shape and does not have a quadrupole moment, both CO\(_2\) and C\(_6\)H\(_6\) have quadrupole moments. Note that (at least to a very good approximation) CO\(_2\) is a linear molecule while C\(_6\)H\(_6\) is disklike. In Ref. 35 we have shown that a very good description for both molecules is obtained when Eq. (1) and Eq. (2) are augmented by a quadrupole-quadrupole interaction term. As the latter is only a relatively small perturbation of the LJ-type interaction, it suffices to treat the (angular-
TABLE I. We report all the simulation parameters used in the present work and the critical parameters of the pure components that have been used. In brackets we also report the errors (if > digits are reported, the error applies to the last digits). The errors for \( \varepsilon \) and \( \sigma \) have been estimated using the experimental errors for the critical points (Ref. 77) and an error of 0.5% in the simulation critical points as estimated previously (Ref. 35).

As a consequence we note for instance that in the three models used for \( \text{C}_5\text{H}_8 \) the three values for \( \sigma \) are almost compatible within our error bar. It is important to observe that in this discussion we have disregarded the huge error in the quadrupolar moment \( \mathcal{Q} \) (and as a consequence in \( \varrho \)). We refer to the text for a discussion of this point.

<table>
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<th>( \varepsilon \left( 10^{-21} \text{ J} \right) )</th>
<th>( \sigma \left( \text{Å} \right) )</th>
<th>( T_c ) (K)</th>
<th>( \rho_c ) (mol/L)</th>
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</table>

(3)

Here, \( \mathcal{Q} \) is the strength of the quadrupole moment of the considered molecule. Note that the interaction is isotropic and inversely proportional to temperature. We also cut off this part of the interaction at the same radius \( r_c \), as the LJ interaction, and shift it to zero at \( r_c \) as well, which yields the following total pairwise interaction for these molecules:

\[
U(r_{ij}) = \begin{cases} 
4\varepsilon \left[ (\sigma/r_{ij})^6 - (\sigma/r_c)^6 - \frac{27}{20} q (\sigma/r_{ij})^4 + S \right], & r \leq r_c \\
0, & r > r_c,
\end{cases}
\]

(4)

where

\[
S = \frac{127}{16384} + \frac{7}{5} \frac{q}{256}
\]

(5)

and \( q \) is the reduced quadrupolar interaction parameter,

\[
q = \frac{\mathcal{Q}^3}{(e\sigma^{10}k_B T)^2} = q_c T_c / T, \quad q_c = q(T_c).
\]

(6)

Note that Eq. (6) is given in CGS units; in SI units, there would be an additional factor \( (4\pi\varepsilon_0)^2 \).

Using Eqs. (4)–(6), one can fix \( \varepsilon \) and \( \sigma \) such that critical temperature \( T_c^{\text{exp}} \) and density \( \rho_c^{\text{exp}} \) are reproduced. (For \( \mathcal{Q} \), the experimental value is taken as a first guess). As discussed in Ref. 35, this leads to a self-consistency problem, since Eq. (6) must hold together with

FIG. 4. (Color online) Coexistence curve for \( \text{CH}_4 \) in the temperature-density plane (a), vapor pressure at coexistence (b), and surface tension plotted vs temperature (c). Broken curves show experimental data (Ref. 77), dots the Monte Carlo simulation results, while the full lines show the MSA predictions.
\[ e(q_c) = k_BT_c^{\text{exp}}/T_c^a(q_c), \quad \sigma^3(q_c) = \left[ \frac{\rho_c^*(q_c)M_{\text{Mol}}}{\rho_c^{\text{exp}}N_A} \right], \]  

(7)

where \( M_{\text{Mol}} \) is the molar mass of the molecule and \( N_A \) is Avogadro’s number. This problem was solved in Ref. 35 by determining the functions \( T_c^a(q_c)/T_c^a(0) \), and \( \rho_c^*(q_c)/\rho_c(0) \) by extensive Monte Carlo simulations for a broad range of values for \( q_c \). It turns out that for CO\(_2\) the experimental value \( Q = 4.3 \pm 0.2D \ \text{Å} \) yields

\[ q_c = 0.387, \quad \epsilon = 3.491 \times 10^{-21} \text{ J}, \quad \sigma = 3.785 \text{ Å}, \]  

(8)

while for the case of benzene the value \( Q = 12D \ \text{Å} \) would imply

\[ q_c = 0.247, \quad \epsilon = 6.910 \times 10^{-21} \text{ J}, \quad \sigma = 5.241 \text{ Å}. \]  

(9)

The corresponding results for the vapor-liquid coexistence curves in the \( (T, \rho) \) and \( (\rho, T) \) planes as well as the temperature dependence of the interfacial tension for both CO\(_2\) and C\(_6\)H\(_6\) were already presented in Ref. 35 and shown to give a rather good agreement with experiments.\(^77\)

Of course, the disregard of the angular dependence of the quadrupolar part of the interactions is a matter of concern. This point was investigated by us in Ref. 36, where detailed comparisons of Monte Carlo results for the full angular-dependent quadrupole-quadrupole interaction and the isotropic approximation [Eqs. (3)–(6)] were performed for the case of CO\(_2\). It was shown\(^36\) that the model with LJ + full quadrupolar interactions (which is still a crude CG model, in comparison with all-atom models including partial charges etc.) does not provide a better account of the experimental data than the spherically averaged one.

Another point of concern is the possible sensitivity of the results of such models to the precise value of \( q_c \). Note that \( q \) is proportional to \( Q^4 \) [Eq. (6)]. Consequently, a small experimental error in \( Q \) is magnified considerably. There may also be systematic effects since \( Q \) is often determined in the dilute gas phase. Here, we are interested in using densities around the critical density, and \( Q \) could be slightly renormalized there. Packing effects should also be taken into account. Indeed, CO\(_2\) is not a spherical molecule, and at high density a local orientational order could arise. This packing could enhance some favorable angular correlations that give rise to a higher effective quadrupolar moment. One can argue that high temperature perturbative theory [see Eq. (3)] may not be very accurate and higher order terms could be important: in fact our previous investigation in which a full (angular dependent) quadrupolar interaction was considered,\(^36\) proves that this is not the case. In addition, one may argue that the model of Eqs. (3)–(6) is an effective model, intended for a good representation of EOS data, particular for vapor-liquid equilibria (VLE). Therefore, \( q_c \) should be treated as an effective parameter which can be used to optimize the description of such VLE data. In this spirit, we have also tried different choices of \( q_c \) and found that a slightly better description of CO\(_2\) is obtained for

\[ q_c = 0.47, \quad \epsilon = 3.349 \times 10^{-21} \text{ J}, \quad \sigma = 3.803 \text{ Å}. \]  

(10)

This choice was already included in our previous work.\(^35,36\) For benzene, a very good agreement with experiments can be achieved for

\[ q_c = 0.38, \quad \epsilon = 6.472 \times 10^{-21} \text{ J}, \quad \sigma = 5.284 \text{ Å}. \]  

(11)

Figure 5 presents the coexistence curve describing vapor-liquid equilibrium for benzene (C\(_6\)H\(_6\)) in the temperature-density plane (a), temperature dependence of the vapor pressure (b), and the interfacial tensions (c) at phase coexistence. The full curve is the result of fitting \( T_c^{\text{exp}}, \rho_c^{\text{exp}} \) (Ref. 77) to a simple CG model without taking into account any contribution from quadrupolar interactions, while triangles are Monte Carlo results using Eq. (9) and asterisks using Eq. (11), respectively. Broken curves are the experimental data (Ref. 77).

**FIG. 5.** (Color online) Coexistence curve describing vapor-liquid equilibrium for benzene (C\(_6\)H\(_6\)) in the temperature-density plane (a), temperature dependence of the vapor pressure (b), and the interfacial tensions (c) at phase coexistence. The full curve is the result of fitting \( T_c^{\text{exp}}, \rho_c^{\text{exp}} \) (Ref. 77) to a simple CG model without taking into account any contribution from quadrupolar interactions, while triangles are Monte Carlo results using Eq. (9) and asterisks using Eq. (11), respectively. Broken curves are the experimental data (Ref. 77).
We note that in Eq. (12) \( \epsilon \) and \( \sigma \) are the same parameters as in the LJ potential between the monomers. The parameters of the FENE potential have been chosen to prevent the crossing of macromolecules in the course of their motion. We note that this choice does not reproduce the characteristic ratio of alkanes accurately. This means that the FENE potential is fully constrained, and the model remains a two parameter model with parameters chosen to match the critical temperatures and densities.

On this CG level both torsional and bond-angle potentials between effective beads are ignored. Hence, it is worthwhile to test whether such crude models are still able to reproduce the phase diagram and other thermodynamic properties of the real system correctly. Thus, Figs. 6–8 show results for the phase diagrams of several members of the alkane series (including \( \text{C}_3\text{H}_8 \), \( \text{C}_5\text{H}_{12} \), and \( \text{C}_{16}\text{H}_{34} \)) in the \( T-\rho \) plane, as well as the corresponding coexistence pressures and interfacial tensions between the coexisting vapor and liquid phases. The agreement between the model results and the corresponding experimental data\(^{77}\) is remarkable, again, although it is not as convincing as for methane (which we have included for comparison). In particular, for \( \text{C}_5\text{H}_{12} \) deviations clearly occur. Table I collects the experimental critical temperatures, densities, and pressures,\(^{77}\) as well as our choices for \( \epsilon \) and \( \sigma \) for the materials studied, and the prediction for the critical pressure that results from our model.

In all cases the critical pressure is predicted with an accuracy of a few percent, and a glance on Fig. 7 shows that the slope of the vapor pressure versus temperature curve is close to the slope derived from experiments, too. For temperatures away from the critical region (say, 20% below \( T_c \)), deviations between experiment and the model predictions become visible, both in the coexistence curve, coexistence pressure, and interface tension (Fig. 8), in particular for propane and pentane. Of course, the accuracy of the modeling could be enhanced by allowing for additional adjustable parameters like in many models in the literature, e.g., by introducing a bond-angle potential, or more interaction sites (see, e.g., Ref. 45). Then, quantities such as the acentric factor [referring to the shape of the coexistence curve 30% below \( T_c \) (Ref. 91)] can presumably be fitted nicely. However, the simplicity of the CG model is lost. Experience with such
somewhat more complicated models show that these models still require correction parameters $\xi$ to the LB combining rules that deviate from unity by about 10% (see, e.g., Ref. 50). Without these additional parameters (note that it is not at all straightforward to find optimal values for these parameters) the gain in accuracy that such models yield for the description of mixtures is rather modest. Note that an important motivation for the present work is to develop simple models suitable for the simulation of polymer solutions (the case of hexadecane in CO$_2$ being just a prototype case). We are not focusing on pushing the accuracy of modeling of pure short alkanes to its limit.

IV. PHASE BEHAVIOR OF SELECTED BINARY MIXTURES

Extending our treatment to binary systems $(A,B)$ one wishes to describe the interactions between unlike particles by a potential of the same functional form as it is used for the interactions between particles of the same type, i.e., the LJ potential in our case. The simplest choice, most often used in the literature, is the LB combining rule

$$\sigma_{AB} = \left(\sigma_{AA} + \sigma_{BB}\right)/2, \quad \epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}}. \quad (13)$$

As is well known, there is really no convincing derivation of Eq. (13), so there is no reason to believe that Eq. (13) is exact. At best it is a practically useful approximation. As a matter of fact, several alternatives to Eq. (13) have been proposed in the literature.\cite{64,92-95} Although it has been demonstrated that there are some cases where some of these alternative combining rules work better, in general none of these alternative combining rules has a really clear advantage.\cite{54} Since we wish to explore a very simple and general approach, we do not implement any alternatives to the simple LB rule in our paper, even when one has to pay the price of sacrificing a small improvement in the accuracy of our modeling. We also note that the LB rule works very well for the prediction of virial coefficients for the mixture of argon plus CO$_2$, a mixture of an apolar and a quadrupolar fluid.\cite{96} We want to stress that proceeding in such a way no experimental input from the mixture phase diagram is required for testing a full predictive model for the mixture. This also holds for the TPT1 computations which require only $\epsilon$ and $\sigma$ that can be obtained using Monte Carlo results of the pure component critical line.\cite{35} Coexistence densities and pressure have been computed as in pure component systems.\cite{24} On the other hand, the computation of the critical points is more complicated. Indeed, in binary mixtures close to criticality the proper identification of the order parameter is a subtle problem.\cite{97} In principle, complete scaling\cite{98-100} in the case of binary mixtures implies that three scaling fields occur, which are linear combinations of four independent intensive variables: the deviations of two chemical potentials, temperature, and pressure from their values at the critical point. Consequently, the order parameter density becomes a function of the appropriate conjugate variable, and the relevant physical densities (particle number densities, entropy density) become nonlinear functions of the proper scaling fields.\cite{97} Since this formalism is somewhat cumbersome for the case of compressible binary fluid mixtures, we simplify the problem by applying “field-mixing”-procedures analogous to the method of Wilding and co-worker\cite{10-21} which is rather successful for most one-component fluids. Details on this procedure are reported in the Appendix, presenting the analysis done for a critical point of the krypton xenon mixture. In order to estimate systematic errors of this procedure, in the Appendix we also present results with a full finite size analysis with cumulants crossing\cite{16} for a highly asymmetric mixture like carbon dioxide in hexadecane.

A. Mixtures of small apolar molecules

As a first example of apolar mixture we present results for krypton plus xenon. As it has been discussed in Sec. III, the noble gases already exhibit rather large deviations between the experimental data and the model calculations based on the LJ potential. Thus, it is interesting to see whether these problems get even worse when mixtures are considered. The resulting critical line in the $(\rho, T)$ plane is shown in Fig. 3 for both choices of $\epsilon$ and $\sigma$ as discussed in Sec. III A. If we fit $\rho_c$ and $T_c$ for the pure systems, the predicted critical points for the mixture deviate from the experimental curve about as much as for the pure systems. If we adjust $\epsilon$, $\sigma$ such that $\rho_c$, $T_c$ is reproduced, the data\cite{81} for the two mixed systems are almost perfectly reproduced. The variation of the critical concentration with temperature is also rather well reproduced (Fig. 9) by both models where $\rho_c$ and $T_c$ are fitted to experimental values.

As a second case we now consider methane in butane. In Secs. III B and III C we showed that the simple LJ model gives a fairly accurate account of the EOS of both CH$_4$ and C$_4$H$_8$. Therefore, it is natural to consider a mixture of those two molecules as a next step. Of course, a comprehensive study of the phase behavior of such mixtures in the space of all three variables ($T, p, x$) is a nontrivial effort. Therefore we limit ourselves to consider only isothermal slices through the phase diagram, following a standard practice in the literature.\cite{54,56} As an example, Fig. 10 shows two such slices at $T=327$ K (a) and $T=277$ K (b), and compares experimental data\cite{101} with selected Monte Carlo data and results from our implementation of the TPT1-MSA (which is described in Appendix B of Ref. 35). We emphasize that the various parameters characterizing the interactions among the various molecules are those obtained from Monte Carlo simulations.
of the pure materials (Sec. II), together with the LB rule. These parameters also serve as input for TPT1-MSA: there are no additional parameters that enter the latter approach. Thus we present comparisons between experiments, simulations and theory in which no adjustable parameters for the mixture have been used.

It should be noted that both chosen temperatures in Fig. 10 fall below the critical temperature of C3H8 but exceed the critical temperature of CH4. Therefore, the characteristic bubble-shaped liquid-vapor coexistence curve results, starting out at the ordinate axis at the vapor-liquid coexistence point of pure C3H8, but not extending to CH4 concentrations close to \( x = 1 \). The critical point occurs at the maximum of this closed loop. (The liquid phase is located on the upper part of the loop to the left of the critical point, the remaining part of the curve describes the vapor). For \( T = 327 \) K and \( x \ll 0.35 \) both experiment, TPT1 and Monte Carlo agree nicely. For larger \( x \), however, a systematic discrepancy between Monte Carlo data and experiment shows up. The TPT1-MSA approximation overestimates the critical pressure substantially. This problem already occurs in the pure systems, as is well known, and is an inevitable consequence of simple mean-field-like approximations.\(^{35,65,67}\) Figure 4 shows that the critical temperature and pressure of pure CH4 are both overestimated. The same holds for pure C3H8, and the whole line of critical points \( T_c(x) \) that connects \( T_c(0) \) and \( T_c(1) \) when we would project them into the \((p,T)\) plane as we did for the Kr–Xe mixture (Fig. 3). As in the latter case, the mixture of CH4 and C3H8 has a simple “type I” phase diagram in the classification scheme of fluid binary mixtures\(^{37-39}\) (type I\(^p\) in the modern classification\(^{40}\)). As a consequence, we expect that TPT1-MSA predicts too large vapor-liquid coexistence loops in the \((p,x)\) plane at all temperatures that are supercritical for CH4 but subcritical for C3H8.

A more disturbing discrepancy seems to occur between the data\(^ {101}\) and the theoretical results at the lower temperature \((T = 277 \) K\), where at small \( x \) the vapor pressure at coexistence falls slightly but systematically below the experimental data. For molar concentrations well below criticality, Monte Carlo results and TPT1-MSA agree very well, and our numerical procedures are accurate for our model. Hence, assuming that the experimental data are accurate enough so that the discrepancy is meaningful, this result indicates that some limitations of our model become apparent. This is not really a surprise, of course, because in the data for pure propane at this temperature discrepancies of the order of a few percent do occur as well (Figs. 6–8).

As a third case we now consider the mixture of CH4, and C5H12, because for pentane slightly larger deviations between the predicted and observed coexistence vapor pressure do occur over a much broader temperature range (Fig. 7). Indeed, the corresponding isothermal slices through the phase diagram of that mixture (Fig. 11), which still is a type-I phase diagram, show that slight but systematic discrepancies are now seen at the higher temperature as well. At the lower temperature, the phase diagram can only be reproduced in a rather qualitative manner. Note, however, that \( T = 237 \) K is less than 50% of the critical temperature of pentane, where the effective interactions of pentane were adjusted; of course, the CG modeling used in our work should not be pushed to too low temperatures. Keeping this limitation in mind, we conclude that a rather satisfactory descrip-
tion of mixing behavior of these systems is in fact reached by our models. Hoping for perfect agreement would have been premature, in view of the simplicity of our models. But the phase diagram predictions should allow a useful first orientation at temperatures not too far below of the higher critical temperature of the components in such a binary mixture.

B. Mixtures of small molecules, one of which has a quadrupole moment

We begin with a mixture of CH$_4$ and CO$_2$, because for both pure molecules a particularly accurate description of the equation of state was obtained (see Sec. II). Again we note that the CH$_4$+CO$_2$ system belongs to the category of type I phase diagram in the classification scheme of Scott and van Konynenburg (1$^P$ in the modern classification) and the temperature regime of interest for our modeling is the regime in between the critical temperatures of the two constituents of this mixture. Note that Eq. (13) only applies to the LJ part of the interactions of CO$_2$, since CH$_4$ has no quadrupole moment.

In Fig. 12 we present isothermal slices through the phase diagram in the space of variables ($T$, $p$, $x$). If one uses TPT1-MSA the model for CO$_2$ based on Eq. (10) can describe the mixing behavior with CH$_4$ very accurately at molar concentrations $x$ of CH$_4$ and pressures that are not close to criticality. As emphasized above, mean-field theories such as TPT1-MSA are not expected to be accurate near critical points. Hence, the discrepancy that TPT1-MSA predicts a too large loop inside of which two-phase coexistence occurs, is inevitable and expected. But for the model [Eq. (10)] the part of the loop at not too large $x$ is significantly more accurate (full curves) than a simple LJ model for CO$_2$ would be (broken curves). As expected, at low temperatures (such as $T = 230$ K) the quadrupolar model for CO$_2$ [Eq. (8)] also starts to show slight but systematic deviations from the experiment at the vapor branch of the vapor-liquid coexistence curve. This is similar to our finding for the apolar mixtures (Sec. III B).

In order to verify that the good agreement between experiment and theory for the quadrupolar model of CO$_2$ in the CH$_4$+CO$_2$ mixture is not just fortuitous, we show in Fig. 13 corresponding results for the mixture of benzene (C$_6$H$_6$) and methane (CH$_4$). This is a more stringent test, since the critical temperatures of the two constituents are rather far apart from each other (cf. Figs. 4 and 5). Nevertheless, the conclusions are the same as in the case of CH$_4$+CO$_2$: using interaction parameters that were optimized for the pure systems, namely, those of Eq. (11) in the case of C$_6$H$_6$, and adjusting them to Monte Carlo results as described in Sec. II, we can proceed to the description of the mixture data and estimate the missing mixed interaction parameters from the LB rule, Eq. (13). The use of these interaction parameters in a simple and fast analytical theory for the EOS such as TPT1-MSA then provides a satisfactory description of the phase behavior of the mixture, apart from the vicinity of critical points (this drawback can be rectified by carrying out MC work for the mixture as well, of course) and for not too low temperatures. (For temperatures of the order of 50% of the critical temperature $T_c$ of the constituent with the higher $T_c$ systematic deviations start to appear rather generally.)

The last example of this section deals with a slightly more complicated case, namely, the CO$_2$+C$_6$H$_6$ system (Fig. 14): while CO$_2$ is still represented as a point particle with a quadrupole moment, as in the previous examples, the other partner of this mixture (C$_6$H$_6$) should not be CG into a point particle any more, but rather needs to be represented as a dimer (i.e., a dumbbell-like effective molecule). In this case the TPT1-MSA theory predicts unmixing over a far too large range of molar CO$_2$ concentrations, and the improvement provided by the inclusion of the quadrupolar moment at small $x$ is only qualitative, but not quantitative. On the other hand, the Monte Carlo results for this model are in rather good agreement with the corresponding experimental data.

Since MC and TPT1-MSA are using precisely the same interaction parameters, we conclude that for this particular case TPT1-MSA is somewhat inaccurate for the vapor branch of
improve the description by using an empirical factor moment. They found that using the LB rule revisited enough to capture the statistical mechanics of flexible dimers well.

C. Polymer solutions: The CO2+C6H12 system revisited

Virnau et al.\textsuperscript{41,57,58} already attempted to model this system, describing CO2 as a point particle with no quadrupole moment. They found that using the LB rule [Eq. (13)] the phase diagram predicted by the model belongs to type I, while experiments suggest\textsuperscript{106,107} that this system belongs to the type III class (1C\textsuperscript{2}), according to Ref. 40, where 1C means that the critical line emanating from the pure component critical point of the hexadecane goes to high pressure regions without joining the solvent critical point like in diagrams starting with 1D. Virnau et al.\textsuperscript{41} proposed that one can improve the description by using an empirical factor \( \xi \) to modify Eq. (13), assuming that \( \epsilon_{AB} = \xi \epsilon_{AA} \epsilon_{BB} \) instead of \( \epsilon_{AB} = \epsilon_{AA} \epsilon_{BB} \). In the literature, the value of \( \xi \) depends on the specific mixture and typically is written in the form \( \xi = 1 - k_{AB} \), with \( k_{AB} \geq 0 \). Of course, there is not really a theoretical justification for doing so, and \( \xi \) simply plays the role of a fitting parameter. By trial and error it was found that \( \xi = 0.886 \) provides a description compatible with the experimental data.

In the present subsection of our paper, we show that the main source of the problems encountered in Ref. 41 was the neglect of the quadrupole moment. Thus, we have repeated the study of the CO2+C16H34 system, insisting on the LB model (open circles) and comparing them to the results of the previous simulations (Ref. 41), with \( q_c = 0, \xi = 1 \) (full dots), and \( q_c = 0, \xi = 0.886 \) (asterisks). Squares show two sets of experimental data (Ref. 108) at two temperatures that bracket the temperature used in the simulation. Triangles are MC results for the critical point.
rule [Eq. (13)] but using Eq. (10) as an improved model for CO2, as in the previous subsection. Again, the LB rule is only applied to the LJ part of the interactions, since C16H34 does not have a quadrupole moment.

Following the strategy of the previous subsection, we have computed an isothermal slice through the phase diagram at $T=486$ K, where data from the previous simulation were available both for $\xi=1$ and for $\xi=0.886$ (Fig. 15). Indeed it is found that the data of the present model ($\xi=1$, but optimized quadrupolar interaction $q_c=0.47$ for pure CO2) are well compatible with the experimental data and almost fall on top of the results of the previous calculation with $q_c=0$ and $\xi=0.886$.

Of course, we have already seen in the previous subsections that often a very good agreement between our descriptions based on a very simplified model occurs at high enough temperatures. In order to test, to what extent this problem arises for the present system, we have followed the strategy of Ref. 41 to compute the full critical line $T_c(x)$, $p_c(x)$ for the full range of molar concentrations $x$ of CO2. Figure 16 shows the resulting projection into the $p^*$, $T^*$ plane. (Here $p$, $T$ are given in LJ units, with the LJ parameters of the effective monomers used to rescale the variables). One sees that the simulations with nonzero quadrupole moment included in the figure are close to those for $\xi=0.9$, $q_c=0$, for $T^* \approx 1.3$. As a consequence, the model that we have developed for CO2, Eq. (10), is still not able to yield the correct phase diagram topology. (For $\xi=0.9$, transition type IV was observed in Ref. 41, as opposed to type III which was observed experimentally.) For $T^* < 0.8$ the model does not yet describe the properties of hexadecane + carbon dioxide mixtures accurately, although for $T^* \geq 1.3$ ($T \geq 545$ K) the properties of the system are predicted rather satisfactorily. Of course, this result is not unexpected. For $T \leq 0.57T^*_{\text{hex}} \approx 360$ K the model based on fitting the critical parameters of hexadecane to fix its interaction parameters starts to become inaccurate. On the other hand, the proper prediction of the phase diagram type is a very stringent test. Indeed, variation of the interaction parameters by a few percent could drastically change the type of the phase diagram.

V. CONCLUSIONS

In this paper, we have studied the phase diagrams of a variety of fluid binary mixtures, with particular emphasis on mixtures of alkanes in supercritical carbon dioxide and benzene. In order to better understand the performance of our modeling for these systems, we have also investigated mixtures with apolar solvents including noble gases and methane. We have investigated the accuracy of the use of the LB rules for describing the mixing behavior, based on interaction parameters for the pure systems that are tuned such that the critical point (critical temperature, critical density, or pressure) of the pure systems are well reproduced. Using a simple LJ model for interaction parameters of pure apolar fluids, Monte Carlo calculations in the grand-canonical ensemble, analyzed by appropriate finite size scaling methods, readily yield the desired accuracy for this procedure. For the polar molecules we use a spherically averaged pointlike quadrupolar interaction, which was shown to produce very good phase diagrams, also if compared to more realistic atomistic models. Our model takes as experimental input the critical temperatures and densities of the pure components (like in previous coarse grained schemes) plus the experimental quadrupolar moments. For pure CO2 and C6H6 this choice leads to a significant improvement in comparison with a simple LJ model without explicitly accounting for the polar interactions. In Ref. 35 and Fig. 5, as a second option, we have treated the quadrupole moment as an effective parameter in an attempt to optimize agreement with experiments. We tune this parameter such that the liquid branch of the vapor-liquid coexistence curve of pure CO2 or pure C6H6 is optimally represented. In the case of benzene, for which the optimization procedure seems to work very well, the agreement with the coexistence pressure is also improved. (This is not the case of CO2 which is, however, better described than benzene if the experimental values for the quadrupole moments are used.) The physical reason for this requirement to work with an effective quadrupole moment is presumably that actual molecules are not pointlike particles, of course: CO2 is a rather elongated molecule, while C6H6 is disklike. So packing effects should occur, i.e., local orientational correlations, which are underestimated by the quadrupolar interaction. Thus, it is gratifying to note that a remarkable improvement of accuracy in the prediction of the phase behavior of mixtures is achieved if this effective quadrupole moment is used.

These energy parameters, which we fixed from the description of the pure systems, together with the LB rules, allow us to predict phase diagrams of mixtures, with no ambiguity whatsoever, since no further adjustable parameters occur. Two methods of prediction are used: (i) Monte Carlo simulations and (ii) TPT1-MSA calculations. The Monte Carlo approach has the substantial advantage that it is also accurate near critical points of the mixture. In principle, we obtain the exact statistical mechanics of the model system. Any discrepancy between experiment and prediction is entirely due to a shortcoming of the (simplified) model. The TPT1-MSA approach has the merit that relatively little computational effort is necessary to implement it. However, it
clearly involves various approximations and hence the interpretation of discrepancies between TPT1-MSA and experiment is not so clear—part of them being due to inadequacies of the model, part of them stem from inaccurate approximations. For instance, TPT1-MSA, like all mean-field theories, overestimates the critical temperature and pressure, so the isothermal slices through the phase diagram of the mixture always involve two-phase regions which are too large.

We note that fluids such as CO2 have an important application as supercritical solvents. If one aims at describing the behavior in the critical region of the pure solvent and of the mixtures correctly, Monte Carlo methods have a clear advantage. Now, one could try to readjust parameters in the TPT1-MSA approach to improve agreement with experiment (like done for instance in Ref. 68, where $e$ and $\sigma$ for the EOS have been rescaled in comparison to the model used in MC simulations in order to properly reproduce the critical points of the pure compounds), but this would be just an attempt to provide a partial cancellation of errors, and in other regions of the phase diagram the description would necessarily get worse.68 Since we feel that relatively little physical insight is gained by such fitting procedures, they have not been implemented in our paper. Our overall conclusion is that in the framework of the modeling as defined above the LB rules work very well, in the sense that an $ad$ hoc change of mixed binary interactions by at most a few percent (typically one or two percent) would lead to almost perfect agreement with experiment. As a piece of evidence for this claim, we note that in the study of the CO2+C16H34 system by Virnau et al.,41 where the CO2 molecule was modeled as a point particle with LJ interactions with no account of the quadrupole moment, a correction factor $\xi = 0.886$ to the LB rule was required to produce good agreement with experiment. However, the present model (with a quadrupolar interaction and no correction factor) yields results that are almost identical to those of Virnau et al.41 when $\xi = 0.900$ is chosen. As a consequence, we conclude that in the present model a correction factor $\xi = 0.985$ would suffice to reproduce the results. Noting that the LB rule assumes that the mixed correlation functions in the fluid described atomistically behave in the same way as in the CG descriptions, deviations of such a fitting parameter $\xi$ from unity in the range from 1% to 2% are no surprise at all.

Thus we feel that the present level of accuracy cannot easily be improved in the framework of our model. As it has been emphasized already in the Introduction, many more complicated models for fluids are discussed in the literature (see Refs. 28–32 and 109). Optimizing parameters in those models such that the critical properties of the pure systems and their vapor-liquid coexistence curves are very well reproduced might be an alternative starting point to test the validity of combining rules.39–41 However, even for our very simple model the Monte Carlo runs require substantial computer resources, and hence we have not attempted to generalize our approach to other models. The strength of our method, if compared to more detailed models with a lot of parameters whose optimization would require massive computation, is its generality. It is possible to have the potentials for a given mixture, without any extra computational efforts from the results of the pure components.35 It is also important to mention that the present work validates the use of the spherically averaged quadrupolar potential.35,48,87

Finally, it is important to observe that our way to coarse grain solvent molecules into single beads has the advantage, with respect to atomistic models like multicenter Lennard-Jones, to be accessible to advanced EOS machineries. In this paper we have shown how, with rather small efforts, significant results can be obtained. We are also aware of the fact that several improvements could be done (e.g., using some integral equation scheme which should improve the MSA solution near the critical point). However, most of the advanced methods in EOS modeling, apply only for reference systems that are mixture of monomers (i.e., beads with point-like interactions), the associating part being taken into account by TPT1. On the other hand TPT1 gives a reasonable description only if in the “associated molecule” diameters of the beads do not overlap. This is of course the case in our CG model for alkanes in which the experimental distance between three carbon units ($d = 4.59 \text{ Å}$) is bigger than the typical $\sigma$ used ($\sigma = 4 \text{ Å}$). (This is another reason the FENE potential uses the same simulation parameters of the LJ interaction.) The condition $d > \sigma$ guarantees that the reference system (a mixture of monomers) is a good starting point for a perturbation theory. On the other hand if $d < \sigma$ association is too strong and cannot be properly taken into account by TPT1 (i.e., the monomer reference system is not the adequate starting point for a perturbation expansion). In models which describe simple solvent molecules with several interacting points (see, e.g., Table 1 of Ref. 51 for typical parameters of two-center LJ) we have $d < \sigma$: this implies that these models cannot be investigated with associating theories. In conclusion, our modeling approach might enable the application of modern EOS which is another important motivation of our work.

We do feel that the approach based on the present models is able to make nontrivial and practically useful predictions for a large class of systems. Hopefully more experimental data on mixtures will become available to allow for more stringent tests.

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APPENDIX: DETERMINATION OF THE CRITICAL POINT

In this Appendix we describe how the critical points for the mixtures (e.g. Figs. 3 and 16) have been obtained. As mentioned in the Sec. IV in asymmetric binary mixtures the determination of the order parameter is difficult97 and a com-
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FIG. 17. (Color online) Final normalized order parameter histogram \( P(M) \) of xenon-krypton mixtures (curve) at \( T_i=228.78 \). The simulated (s) and reweighted (r) parameters (in units of \( \epsilon_i \) and \( \sigma_i \)) are \( \mu_{x}^s = -2.254 \), \( \mu_{x}^r = -2.512 \), \( \mu_{x}^s = -3.972 \), \( \mu_{x}^r = -3.9792 \), \( x_1 = 0.4 \), and \( x_2 = 0.03 \). The dots show the universal 3d Ising model distribution.

due to the lacking of the particle—hole symmetry, the two peaks will not be symmetric such as the two peaks of the universal Ising model distribution at criticality. Thus, as a second step the other chemical potential is also tuned (and step 1 is repeated), so that one gets somewhat closer to the critical point of the system. Still, the universal shape of the distribution is not yet obtained. The third step consists in a variation of \( x_1 \) (and repeating steps 1 and 2) such that the two peaks of the distribution become as similar to each other as possible. The fourth step amounts to a variation of \( x_2 \) (again repeating steps 1 and 2). In this way (for the investigated cases) it is possible to obtain a final histogram of the order parameter \( M \) that reproduces the universal Ising shape at criticality almost exactly (Fig. 17).

On the other hand the previous approach is not totally correct because it neglects finite size corrections for the critical parameters but simply “supposes” that the simulation box is large enough. In order to elucidate this point in this Appendix we also report the full finite size analysis\(^{16} \) with crossing cumulants for several simulation boxes. We do this investigation for the polymer solution studied in this paper (\( \text{CO}_2 + \text{C}_{16}\text{H}_{34} \)) which should be more sensitive to mixing effects being a highly asymmetric mixture in which the coupling between two order parameters (total density and relative concentration, respectively) may be more of a problem rather than for some noble gas or small molecule mixtures. In Fig. 18 we report our finite size analysis for the critical point at \( T=486 \text{ K} \). From extensive \( \mu_s, \mu_p, V_T \) simulations (\( \mu_s \) being the chemical potential of the solvent, \( \text{CO}_2 \) in this case, and \( \mu_p \) the chemical potential of the polymer \( \text{C}_{16}\text{H}_{34} \)) histo-

FIG. 18. (Color) (a) Plot of \( B_1 \) and \( B_2 \) as a function of \( \mu_s \) for the \( \text{CO}_2 + \text{C}_{16}\text{H}_{34} \) mixture (\( T=1.16 \)). The chemical potential \( \mu_s \) was always chosen such that the equal weight rule was obeyed. Three different box linear dimensions are included, as indicated. The broken horizontal lines indicate the universal values \( B_1^* \) and \( B_2^* \) of the Ising model at criticality, where the intersections of the curves for \( B_1 \) and \( B_2 \) in the finite size scaling limit (\( L \rightarrow \infty \)) should occur. These data have been generated for the mixing parameter \( x_1 = 0.09 \). The inset shows a plot of \( B_1 \) vs \( x_1 \) for \( L=13.5 \sigma_p \) for three different values of \( \mu_s \). (b) Probability distribution \( P(n_p, n_i) \) of the numbers of polymers \( (n_p) \) and solvent molecules \( (n_i) \) for \( L=13.5 \sigma_p \) at criticality.

complete scaling\(^ {98-100} \) requires a lot of work which has to be repeated for every critical point. For this reason in the present work the method of Wilding and co-worker\(^{19-21} \) has been used. Taking as an example the krypton xenon mixture (but the same procedure has been done for all the other mixtures), we take the order parameter \( M \) as a linear combination of the particle numbers of Kr atoms \( (N_k) \) and of Xe atoms \( (N_k) \) and of the total potential energy \( E_{\text{tot}} \)

\[
M = N_k x_1 + N_x x_2 E_{\text{tot}},
\]

where the parameters \( x_1, x_2 \) are determined by the following iterative procedure. First, the chemical potential \( \mu_{x}^s \) (in LJ units) is tuned to get vapor-liquid phase coexistence (i.e., the distribution \( P(M) \) satisfies the equal area rule). Normally,
grams have been generated for the total energy $E_{\text{tot}}$, the number of solvent particles $N_s$, and the number of polymers $N_p$. The probability distribution for the order parameter $M = N_p + x_1 N_s + x_2 E_{\text{tot}}$ is computed, using $x_1 = 0.08$ as an initial guess (it turns out that the final results depend on the parameter $x_2$ so weakly, that one may choose $x_2 = 0$ here; on the other hand the choice $x_1 = 0.08$ was suggested comparing $P(M)$ with the universal Ising curve, similarly to what has been done above for the krypton-xenon mixture). The simulation box linear dimensions were $L = 9 \sigma_p$, $L = 11.3 \sigma_p$, and $L = 13.5 \sigma_p$. For a fixed $x_1$ and $\mu_a$, $\mu_p$ is always fixed so that $P(M)$ satisfies the equal area rule. Then, we compute second and fourth order cumulants $B_2 = \langle O^2 \rangle / \langle \langle O \rangle \rangle^2$, $B_4 = \langle O^4 \rangle / \langle \langle O \rangle \rangle^2$ (where $O = M - \langle M \rangle$) as a function of $\mu_a$, for different $L$ [Fig. 18(a)]. It is seen that rather well-defined intersection points of the curves $B_2$ and $B_4$ versus $\mu_a$ for different $L$ do in fact occur at $\mu_a = -2.058 \pm 0.001$. Using a simple comparison with the universal critical curve (which is the method we have used for all the critical lines of Fig. 16) we previously obtained a value $\mu_a = -2.06$, which is very close to the value determined above (in particular within the 0.5% which is our general estimate of error bars). The intersection for $B_2$ occurs close to the theoretical value $^{21}B_2^{\text{th}} = 1.223 \times 82$, while the intersection point for the curves $B_4$ is somewhat too low. This may indicate that the choice of the mixing parameter $x_1$ is not optimal. However, varying $B_2$ as a function of $x_1$, at fixed choices of $\mu_a$ we observe that $B_4$ has a shallow minimum near the chosen value $x_1 = 0.08$ [see inset of Fig. 18(a)]. This could justify in some sense the a priori chosen value for $x_1$ and gives an estimate of the systematic error related to the choice of $x_1$, which is very small. [We notice that variation of $B_4$ with $x_1$ is not strong enough that one could tune the parameters such that the intersection occurs strictly at the theoretical value, and with a distribution function $P(M)$ which is far from looking like the Ising curve]. We conclude that all the sizes from $L = 9 \sigma_p$ up to $L = 13.5 \sigma_p$ are not yet in the asymptotic regime of finite size scaling, and so various corrections to finite size scaling occur which could only be disregarded if a much wider range of $L$ were at our disposal. In view of such possible systematic errors, we have allowed an error bar for the critical values of $\mu_a$ and $\mu_p$ of three parts in a thousand, three times as large as one would conclude from a naive analysis of Fig. 18(a). In any case, the uncertainties resulting from these finite size analysis are much less than the deviation between our model predictions and the experimental data.

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37. Indeed using results of Ref. 35 the CG parameters for given substances (with a reasonable quadrupolar moment) can be computed in a straightforward way without additional simulations.
41. However, sometimes it is far from being clear if deviations from LB combining rules are in fact compensation of some bias of the model used. For instance in the case of polar substances the present work shows very clearly how strong violations of the rules in Ref. 41 were more properly due to a bad modeling for the solvents.
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52 It is interesting to observe how atomicistic models that are not improved to describe all the pure substances phase diagram but take as experimental input only the critical temperature and density (like in our case) are less accurate than our simpler model (see for instance the discussion of EPM2 model (Ref. 53) in Ref. 35).
77 http://webbook.nist.gov/chemistry/.