

Molecular Simulation and Theory of Associating Chain Molecules¹

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A closed-form statistical mechanical based equation of state for associating chain fluids is presented. A Lennard-Jones chain is used as a reference to account for the repulsive, dispersive and anisotropic (size) contributions, while the short-range directional attraction is treated as a perturbation expansion based on Wertheim's first-order theory of associating fluids. A model fluid composed of a chain of tangently bonded Lennard-Jones spheres with an associating square-well site at one of the end spheres is studied. Isobaric-isothermal Monte Carlo simulations were performed for this model at subcritical and supercritical temperatures at a association strength typical of hydrogen-bonding systems. The theory is seen accurately to predict the simulation results subject to the limitations of the equation of state of the reference fluid. The system studied has some of the main complexities found in associating chain molecules such as organic acids, alkanols, and primary amines.

KEY WORDS: associating fluids; chain fluids; computer simulations; equation of state; hydrogen bonding; Lennard-Jones; Monte Carlo.

1. INTRODUCTION

In recent years there has been considerable interest in molecular-based theories for the thermodynamic properties of fluids which associate strongly. In spite of the inherent complexities present in these systems, the prediction of the thermophysical properties of associating chain systems is usually

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based on equations of state for simple fluids with force-fitted parameters. The result is usually an equation of state which extrapolates poorly and does not give reliable mixture predictions. The strong, anisotropic molecular interactions found in associating systems provide a challenging test for any equation of state. Associating chain systems present the additional problem of dealing with the effect of chain length, further complicating the description of these systems. Reliable equations of state can be formulated for these complex systems only through the early incorporation of chain effects and strong directional short-range attraction forces into a suitable theory firmly based in statistical mechanics.

In our approach we have used Wertheim's first-order perturbation theory [1] for associating fluids and extended its application to a reference system composed of nonbonding chains which interact by a segment-segment Lennard-Jones (LJ) potential. By incorporating the main effects of repulsion, dispersion, and covalent bonding into the reference terms, we have simplified the perturbation approach and effectively separated the contributions of chain length from those of the association. The theory is tested against computer simulations which calculate in an exact manner the thermodynamic properties of a fluid with the same potential function specified in the theory.

2. THEORY

Wertheim's theory of associating fluids [1] has been applied successfully to study a series of model associating fluids. For brevity we present here just the most pertinent results. The details of the theory can be found elsewhere [1-5].

The residual Helmholtz free energy A^r can be expressed a sum of a reference term, A_R^r , and a perturbation term, A_{HB} , which explicitly takes into account contribution due to the association,

$$A^r = A_R^r + A_{HB} \quad (1)$$

Equation (1) is a closed-form equation of state, whose appropriate derivatives give explicitly the pressure and configurational energy of the system.

We have tested Wertheim's first- and second-order theory using both a hard sphere [2-9] and a Lennard-Jones [10-12] spherical reference and using different potentials to model the association. The latter reference potential has the advantage that it allows the incorporation of dispersion forces directly in the reference term. Ghonasgi and Chapman [13] have shown, using a similar model for associating LJ dimers, that it is possible

to obtain good agreement between the theory and simulations even in the case that the reference potential is an anisotropic LJ chain, but care must be taken to use an accurate reference term. We wish to explore this result further using a recently proposed [14] equation of state for LJ chains and to examine the limits to which the associating fluid theory may be used. For that purpose we use as a reference fluid a chain of m tangentially bonded LJ spheres. The potential for the chain LJ molecules is given by the sum of the sphere-sphere interactions

$$\phi_{\text{LJ}} = 4 \sum_i \sum_j \epsilon_{\text{LJ}} \left[\left(\frac{r_{ij}}{\sigma_{\text{LJ}}} \right)^{-12} - \left(\frac{r_{ij}}{\sigma_{\text{LJ}}} \right)^6 \right] \quad (2)$$

where ϵ_{LJ} and σ_{LJ} are the characteristic energy and size parameters of the LJ potential and r_{ij} is the center-to-center distance between any two beads i and j in the fluid. Note that this potential includes the intramolecular interactions due to the intrinsic flexibility of the chain but does not include a covalent bonding contribution, since the bead-bead distance between two neighbors in the same chain, i.e., the bond distance, is fixed and equal to σ_{LJ} . We have previously [14] developed a closed-form equation of state for these fluids based on the polymerization limit of Wertheim's theory. The reference equation of state is a function of the three characteristic parameters (ϵ_{LJ} , σ_{LJ} , m) and has been shown accurately to predict the thermodynamic properties of rigid and flexible chains. Therefore, this model fluid lends itself to be an appropriate reference since it incorporates the repulsive and dispersive forces and allows fixing a significant degree of anisotropy to the system.

For the case of a unique associating site per molecule, A_{HB} is given by [1-5]

$$\frac{A_{\text{HB}}}{NkT} = \ln X + \frac{1}{2}(1 - X) \quad (3)$$

where N is the number of molecules in the system, X is the fraction of these molecules not involved in an associating bond, i.e., fraction of monomers, k is Boltzmann's constant, and T is the temperature. The fraction of monomers is obtained from

$$X = \frac{1}{1 + \rho X \Delta} \quad (4)$$

with Δ defined as

$$\Delta = \int g_{\text{R}}(12) f_{\text{HB}}(12) d(12) \quad (5)$$

where ρ is the number density, $g_R(12)$ is the reference fluid correlation function, $f_{\text{HB}} = \exp(-\phi_{\text{HB}}(12)/kT) - 1$ is the Mayer f function of the association potential, and $d(12)$ denotes an unweighted average over all orientations and an integration over all separation of molecules 1 and 2. For this application we have chosen to mimic the association by means of a spherical square-well site potential,

$$\phi_{\text{HB}} = \begin{cases} -\varepsilon_{\text{HB}} & \text{if } r_{\alpha\beta} < \sigma_{\text{HB}} \\ 0 & \text{otherwise} \end{cases} \quad (6)$$

where ε_{HB} is the depth of the square well, σ_{HB} is the diameter of the site, and $r_{\alpha\beta}$ is the site-site distance. This potential is more realistic than other types that have been employed [12] while still retaining computational simplicity and mimicking the correct experimental behavior of hydrogen bonding fluids in both the subcritical and the supercritical range.

The integration implied in Eq. (5) is not straightforward since the reference fluid correlation function is not available. For this reason we have chosen to approximate the reference fluid correlation function with the radial distribution function of LJ spheres evaluated at the temperature and density of the spheres, $m\rho$. This function has been obtained previously [15] in a tabular fashion from molecular simulations of the LJ fluid. With this input, Eq. (5) has been evaluated numerically for the square-well geometry used and the results fit to an *ad hoc* polynomial in density and temperature. The final expression for Δ and details of the fitting procedure are presented elsewhere [16].

3. SIMULATIONS

We have performed Monte Carlo (MC) simulations of LJ chain fluids composed of four freely jointed tangent spheres with an associating spherical site at one of the end spheres in accord with the potential described in

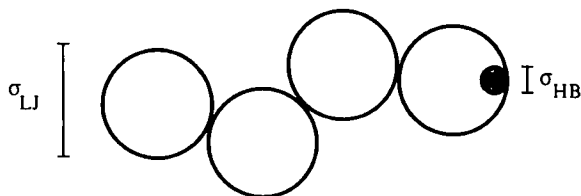


Fig. 1. Two-dimensional view of the molecules studied. The system consists of four freely jointed tangent Lennard-Jones spheres with a single-square well site (shaded) in one of the end spheres. The Lennard-Jones core and the square-well core are mutually tangent.

the preceding section. A square-well site of diameter $\sigma_{\text{HB}} = 0.2\sigma_{\text{LJ}}$ is placed tangent to the LJ core as shown in Fig. 1. The depth of the square-well site, ϵ_{HB} , was set equal to 20 times the characteristic LJ energy, ϵ_{LJ} . This value represents the typical order of magnitude of the interactions in hydrogen bonding systems [16, 17].

The simulations were performed in the isobaric–isothermal (MC-NPT) ensemble, which allows the *a priori* specification of the pressure of the system. Due to the discontinuous nature of the interaction potential, the calculation of the pressure in another ensemble, e.g., a canonical ensemble, would be extremely difficult. A total of $N = 100$ molecules were initially placed randomly in a cubic simulation box. The usual [18] periodic boundary conditions and minimum image conventions were applied. The molecules were moved according to a reptation algorithm [19] and the appropriate acceptance criteria [18] was applied. After every N attempts to displace molecules, a volume change was attempted and a cycle was completed. The potential cutoff distance was set to half the box size and the usual [18] long range corrections were applied.

The system was left to equilibrate a minimum of 10^4 cycles. Averages of the density, configurational energy, and fraction of nonbonded molecules were taken for at least 10^5 cycles.

4. RESULTS AND DISCUSSION

For the given association strength, a subcritical ($T^* = kT/\epsilon_{\text{LJ}} = 2.0$) and a supercritical ($T^* = 3.0$) isotherm were studied. The reduced pressure $P^* = P\sigma_{\text{LJ}}^3/\epsilon_{\text{LJ}}$ was fixed in the simulation and the reduced density, $\rho^* = \rho\sigma_{\text{LJ}}^3$, the configurational internal energy, $U^* = U/N\epsilon_{\text{LJ}}$, and the fraction of nonbonded molecules X were obtained from ensemble averages.

In Fig. 2 we plot the reduced pressure as a function of density for the supercritical isotherm. For chain systems, the pressure is a very weak function of the degree of association, and therefore, for a given temperature, the theoretical curves for all association energies studied will present only a very slight deviation from that of the reference fluid, indistinguishable in graphical form. This behavior is expected, since even in the limit of complete association, (the formation of a fluid of 8-mers) the pressure is not very different from that of the 4-mers [14]. The theory predicts the pressures with an accuracy apparently limited only by that of the original reference equation.

On the other hand, the configurational energy of the system varies significantly with the degree of association of the system, since the energy of association is noticeably larger than that of the LJ interactions. For the other association strengths studied, the system undergoes significant

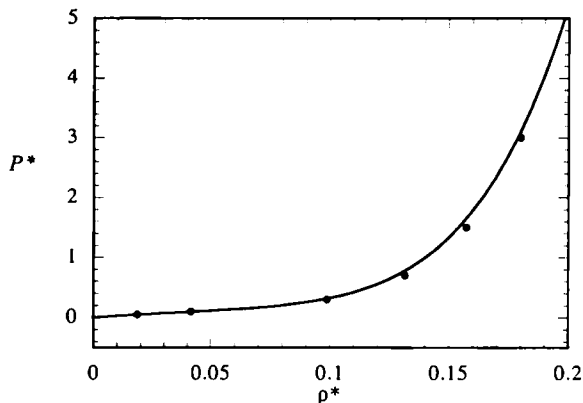


Fig. 2. Reduced pressure P^* as a function of the molecular number density ρ^* at a reduced temperature $T^* = 3.0$ and an association strength $\epsilon_{HB}/\epsilon_{LJ} = 20$. Symbols are the simulation results; the solid line is the theory.

association. In Fig. 3 we show the configurational energy corresponding to the systems with $\epsilon_{HB}/\epsilon_{LJ} = 20$. The bottom curve corresponds to a subcritical isotherm (therefore the lack of data points at low densities), $T^* = 2.0$, while the top isotherm, $T^* = 3.0$, is a supercritical one. The agreement between the theory is good in all cases except at low densities. This disagreement is not a failure of the associating theory but a defect of the

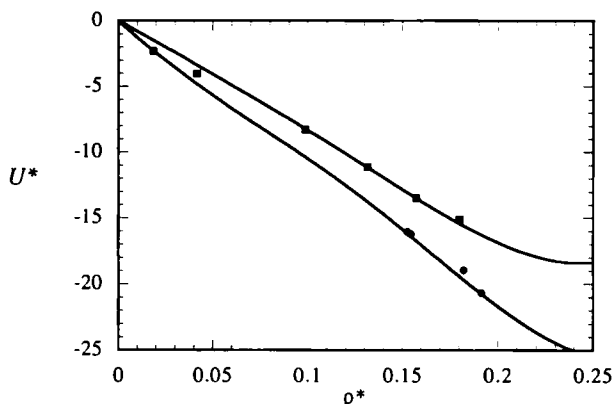


Fig. 3. Reduced configurational energy U^* as a function of the molecular number density ρ^* for an association strength $\epsilon_{HB}/\epsilon_{LJ} = 20$. Circles and squares are the simulation results for reduced temperatures of $T^* = 2.0$ and 3.0 , respectively; the solid line is the theory.

reference equation which does not take into account the intramolecular interactions due to the total flexibility of the molecule, e.g., the possibility of the chain "coiling up" at low densities. This problem has been documented elsewhere [14] and its importance decreases for constrained chains, e.g., alkanes.

The fraction of nonbonded molecules, X , is a quantity which can be obtained from both the simulations and the theory. For high associating strengths, this quantity becomes small, indicating that the system is reaching the limit of complete association ($X=0$). In Fig. 4 we show the comparison between the simulation results and the theory. The upper curve corresponds to the supercritical isotherm, while the lower curve corresponds to the subcritical one. It is seen that in the subcritical liquid region there is appreciable association while in the supercritical region, even at high densities, there is very little association.

While our test molecule is far from being a model of a real fluid, some of the most important features of real associating chains, e.g., organic acids, are present. The extended length-to-diameter ratio of the tetramers studied is 4, which is roughly similar to that of decanoic acid. In a similar way, the ratios of the association strength vs the characteristic dispersion energy studied are of the same order of magnitude [16, 17] as those found in alkanols. The behavior of the hydrogen bonding, e.g., the diminished presence of bonds at dense supercritical conditions vs the appreciable amount available at subcritical liquid-like conditions is typical of that observed by spectroscopy [20] and by neutron scattering [21]. The theory

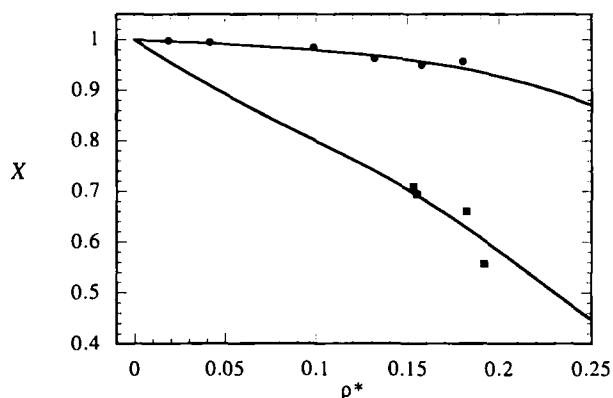


Fig. 4. Fraction of nonbonded molecules X as a function of the molecular number density ρ^* for an association strength $\epsilon_{\text{HB}}/\epsilon_{\text{LJ}} = 20$. Circles and squares are the simulation results for reduced temperatures of $T^* = 2.0$ and 3.0 , respectively; the solid line is the theory.

is presented for only one associating site, nevertheless, the extension to multiple associating sites is straightforward.

The excellent agreement found between the simulations and the theory leads us to believe that the present implementation of the theory can be used to correlate the volumetric properties of associating chain molecules with relative confidence. The extrapolation to polymer systems must take into account the limits of validity of the reference equation, mainly the neglect of intramolecular interactions and the as-of-yet untested behavior of the theory when multiple sites are placed regularly along the backbone of the chain.

5. CONCLUSIONS

We have developed an equation of state which can take into account explicitly the effects of both molecular shape and association along with the usual repulsive and dispersive terms. The comparison of the theoretical predictions with the computer simulations show an excellent agreement for all properties studied. Small deviations observed in the internal energy at low densities arise from an inaccuracy in the reference chain equation of state. The equation of state presented may be used to correlate the volumetric properties of associating chain fluids, e.g., organic acids, alkanols and primary amines.

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