Macromolecules **2005,** *38,* 1025−1027

Perturbed Dipolar Chains: A Thermodynamic Model for Polar Copolymers

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Received June 8, 2004

Revised Manuscript Received October 22, 2004

Introduction

Simultaneously modeling the effect of shape and dipolar interactions in chain molecules with multiple dipolar sites has been a challenge for conventional equation of states as well as statistical mechanical perturbation theories. Recently a theory was developed for dipolar hard chains by Jog and Chapman[1] which successfully accounts for the effect of shape as well as multiple dipolar sites on the thermophysical properties of dipolar hard chain molecules. To apply the theory to real chainlike molecules, it is important to consider the effect of attractive dispersion interactions along with repulsion, the dipolar interaction, and the chain formation perturbation. In this work we use new molecular simulation results to test the accuracy of modeling thermophysical properties of chains molecules with multiple dipolar sites by incorporating the dispersion interaction as a perturbation to the dipolar hard chain. This provides a theoretical basis for incorporating multiple dipolar interactions in chain equations of state such as the perturbed chain SAFT equation of state (PC-SAFT EOS).[2] The SAFT[3,4] formalism in general and PC-SAFT in particular have been successful[2,5,6] in modeling phase behavior in polymer solutions while accounting for comonomers, polydispersity, and chain branching. The development presented in this work will allow chain equations of state to explicitly account for multiple dipolar sites in modeling polar copolymers.

Previously Jog et al.[7] using the Chen Kreglewski dispersion term and Tumakaka and Sadowski[8] using the perturbed chain dispersion term, along with the dipolar hard chain theory,[1] had successfully modeled real polar fluids. The perturbed chain dispersion term is an improvement over the Chen Kreglewski dispersion term since the former unlike the latter accounts for the effect of chain connectivity on dispersion interactions. This paper improves over those works in two ways. First, we provide comparison of theory with simulation which provides greater confidence in the theory before it is applied to real fluids. Second, we use an improved chain term based on bonding dimers (SAFT-D) and use new molecular simulation results to show the validity of our approach.

The (perturbed chain) square-well (SW) dispersion term was fit to nonpolar chains by Gross and Sadowski.[9] This leads to the question, can this SW dispersion term be used for dipolar chains? We know that the dipolar chain EOS is accurate[1] without a dispersion term. Adding the SW dispersion as a perturbation to the dipolar chain and comparing theory results with simulation will allow us to address this question. In developing this theory, we perform three perturbations: (1) about a mixture of nonpolar hard spheres for a mixture of polar and nonpolar hard spheres using u-expansion;[10] (2) forming dipolar hard chains from a mixture of polar and nonpolar hard spheres using first-order thermodynamic perturbation theory (TPT1);[11−14] and (3) about a dipolar hard chain for a SW dipolar chain. The last perturbation expansion has previously only been compared to simulation for nonpolar hard chains.[9] Here we demonstrate the validity of this perturbation for dipolar chains through comparison with new molecular simulation results.

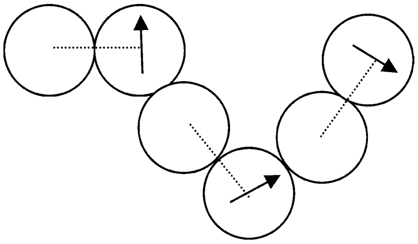

Figure 1. Model of the dipolar chain. The dipole is oriented so that it is perpendicular to the line joining the center of the spheres.

Model

In the present work, we consider a simple model of molecules with multiple polar sites. The molecular model we use is a flexible chain of tangent square well spheres in which every other sphere has a point dipole.[10] The dipole on a particular segment is perpendicular to the line joining the center of that segment with that of the immediately preceding segment as shown in Figure 1. This can be considered to be a generic model of an alternating dipolar copolymer chain.

The SW potential of interaction is given by

$$u_{\mathrm{SW}}(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \le r < \lambda\sigma \\ 0 & r \ge \lambda\sigma \end{cases} \tag{1}$$

where λ is the reduced well width, σ the segment diameter, and μ the dipole moment. The reduced dipole moment is given by

$$\mu^* = \frac{\mu}{\sqrt{\sigma^3 kT}} \tag{2}$$

The contribution of the dipole moment to the thermodynamic properties is determined by this combined parameter. For a SW dipolar fluid, the thermodynamic properties depend on the reduced dipole moment defined in eq 2, the reduced well width, density, and the reduced temperature

$$T^* = \frac{kT}{\epsilon} \tag{3}$$

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10.1021/ma048869f CCC: $30.25

where k is the Boltzmann constant and T is the absolute temperature.

Computer Simulation

Metropolis Monte Carlo simulations[15,16] were performed to study the structure and thermodynamics of SW dipolar chain molecules. Chains of length 2, 4, and 8 with dipoles on alternate segments were studied. The pressure calculations were done in the isothermal–isobaric (NPT) ensemble using 108 molecules for the dimer simulations and 54 molecules for the tetramer and octamer simulations to save computation time since the CPU time varies roughly as the square of the chain length at constant total number of molecules. Monte Carlo simulations involve displacement, reorientation of molecules, and volume changes in the system to generate new configurations in order to sample the phase space. Because the simulations were performed with flexible chains, a translational-jiggling algorithm developed by Dickman and Hall[17] was also used. In the simulations, around 10 million steps are required for equilibration on starting from a lattice. The production runs involve another 5–10 million steps to get the ensemble averages. The displacement, reorientation, and volume change parameters are adjusted so that the acceptance ratio of the moves is around 40–50%.

The dipole–dipole interaction is long-ranged. Truncating the potential at half the box length may introduce some errors.[16] Hence, we used the Ewald sum technique[16] to include the long-ranged dipole–dipole interactions.

The simulations for dimer, tetramer, and octamer SW dipolar chains with the dipole perpendicular to the molecular axis were performed in the NPT ensemble at a temperature of $T^* = 2$, a reduced dipole moment of $\mu^* = 0.8839$, and a well width of $\lambda = 1.5$.

Development of the Equation of State

To model SW dipolar chains the reference fluid is a chain composed of polar and nonpolar hard spheres bonded using TPT1.[11–14] The SW interaction, which is a model for dispersion interaction in real molecules, is treated as a perturbation to this dipolar hard chain.

The thermodynamic properties of the segments forming the chain are calculated by computer simulation and the u-expansion perturbation theory. The integrals in the u-expansion are calculated using the radial distribution function of the equimolar mixture of polar and nonpolar hard spheres as presented by Jog and Chapman.[1] Thus, the dipolar interactions are accounted for at the segment level. These segments are bonded based on Wertheim's theory. This gives the EOS for dipolar hard chains developed by Jog and Chapman.[1] Subsequently, the dispersion contribution due to SW interaction is added as a perturbation to the dipolar hard chain.

The perturbation expansion of the residual Helmholtz energy for the fluid under consideration is written as

$$A^{\text{res}} = A^{\text{segments}} + A^{\text{chain}} + A^{\text{dispersion}} \tag{4}$$

The derivation of the Helmholtz energy for the segment and chain term is as outlined earlier.[1] The segment contribution is that due to an equimolar mixture of polar and nonpolar hard spheres. For this mixture the Padé approximant to the perturbation expansion proposed by Rushbrooke et al.[18] is

$$A^{\text{segments}} = A_0 + A_2\left(\frac{1}{1 - A_3/A_2}\right) \tag{5}$$

where A_0 is the Helmholtz energy for a mixture of hard spheres.

To calculate the Helmholtz energy, we define the following integrals

$$I_2(\rho^*) = \frac{3\sigma^3}{4\pi}\int g_{\text{HS}}(r,\rho^*)\frac{1}{r^6}\,\mathrm{d}r \tag{6a}$$

$$I_3(\rho^*) = \frac{3\sigma^3}{5\pi^2}\int g_{\text{HS}}(123,\rho^*)\,u(123)\,\mathrm{d}r_2\,\mathrm{d}r_3 \tag{6b}$$

where $u(123)$ is the Axilrod–Teller three-body interaction[18] and the expression for the integrals as a function of the reduced density ($\rho^* = \rho\sigma^3$) is given by

$$I_2(\rho^*) = \frac{1 - 0.3618\rho^* - 0.3205\rho^{*2} + 0.1078\rho^{*3}}{(1 - 0.5236\rho^*)^2} \tag{7}$$

$$I_3(\rho^*) = \frac{1 + 0.62378\rho^* - 0.11658\rho^{*2}}{1 - 0.59056\rho^* + 0.20059\rho^{*2}} \tag{8}$$

The Helmholtz energy of the mixture of nonpolar and dipolar hard spheres is given by

$$\frac{A^{\text{segments}} - A_0}{NkT} = \frac{-\dfrac{2\pi}{9}\left(\dfrac{1}{T^*}\right)^2\rho^* {x_{\text{p}}}^2 I_2(\rho^*)}{1 + \dfrac{5\pi}{36}\dfrac{1}{T^*}\rho^* x_{\text{p}}\dfrac{I_3(\rho^*)}{I_2(\rho^*)}} \tag{9}$$

x_{p} is the mole fraction of polar hard spheres in the mixture. For chains longer than dimers, the bonding term obtained by using a dimer reference (the SAFT-D approach) gives better agreement with simulation data. To avoid any error due to the chain term, we apply the dimer reference chain term due to Ghonasgi and Chapman.[19]

$$\frac{A^{\text{chain}}}{NkT} = -\frac{m}{2}(\ln(g_{\text{HS}}) + \ln(g_{\text{HD}})) + \ln(g_{\text{HD}}) \tag{10}$$

where m is the chain length and g is the pair correlation function between hard spheres (g_{hs}) and hard dimers (g_{hd}).

The dispersion contribution due to square well interactions by Gross and Sadowski[2] incorporates the effect of chain length on the dispersion energy. This is given by

$$\frac{A^{\text{dispersion}}}{NkT} = \frac{{A_1}^{\text{dispersion}}}{NkT} + \frac{{A_2}^{\text{dispersion}}}{NkT} \tag{11}$$

The expressions for A_1 and A_2 can be found in the original publication.[2] This provides the Helmholtz energy for a SW chain with multiple dipolar sites. Other thermodynamic properties of the mixture of dipolar SW chains can be calculated by differentiating the Helmholtz energy.

Results and Conclusions

An equation of state for SW chains with multiple dipolar sites is presented. The compressibility factor for SW dimers, tetramers, and octamers with multiple

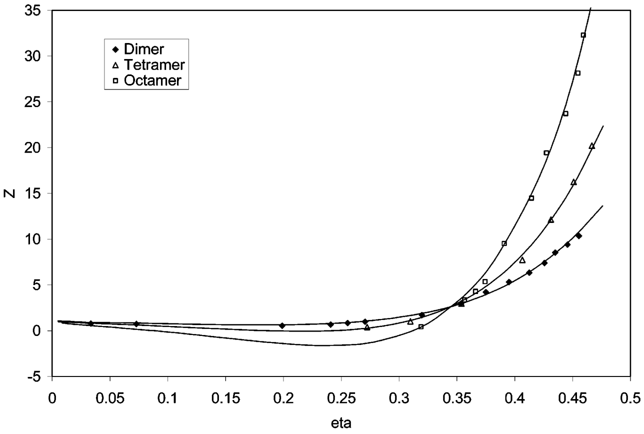

Figure 2. Compressibility factor for dipolar square-well dimers, tetramers, and octamers with dipoles on alternating segments. Comparison of theory (—) with simulation (symbols).

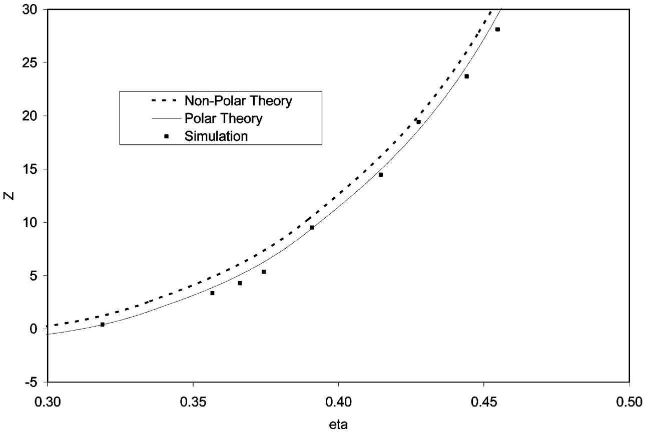

Figure 3. Compressibility factor for dipolar octamers with dipoles on alternating segments. Comparison of nonpolar theory (- - -) results with dipolar theory (—) results and simulation results (symbols).

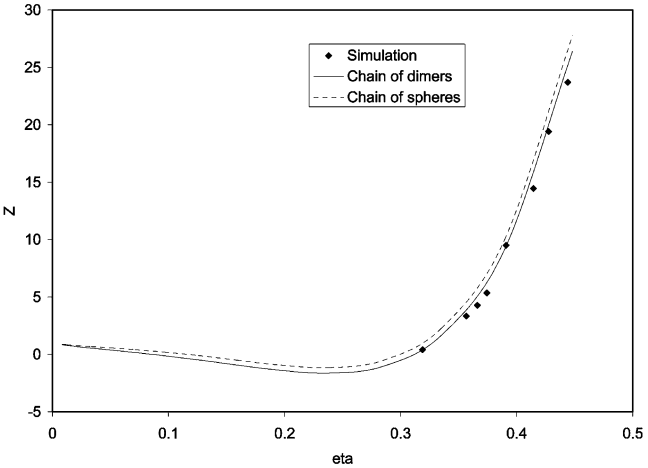

Figure 4. Compressibility factor for dipolar octamers with dipoles on alternating segments. Comparison of monomer bonding term (SAFT) (- - -) and dimer bonding term (SAFT-D) (—) with simulation results (symbols).

dipolar sites is calculated from theory and compared with simulation results in Figure 2. It is seen that there is excellent agreement between theory and simulation. Figure 3 shows the effect of the dipolar term by comparing results from the proposed dipolar SW chain theory with results from the SW chain theory. Figure 4 compares the monomer bonding term (SAFT) with the dimer bonding term (SAFT-D) and demonstrates the improved performance of the dimer bonding term. Comparison between the proposed theory and simulation demonstrates that incorporating the dipolar contribution at the segment level and the dispersion contribution as a perturbation to a hard chain with multiple dipolar sites accurately represents the thermophysical properties of the system of SW dipolar chains. Though we have considered the case of dipoles alternating in the chain, the theory is equally valid for chains with different dipolar segment fractions. The generality of the approach developed for dipolar hard chains[1] has been demonstrated by showing its applicability to SW dipolar chains. This provides the basis for explicitly incorporating dipolar interactions within chain equations of state.

Acknowledgment. We thank the Robert A. Welch foundation for financial support for this work. We also thank Wolfgang Arlt for making Jorg's Studienarbeit possible and Gabi Sadowski and Joachim Gross for helpful discussions.

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MA048869F