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Prediction of the Thermodynamic Properties of Complex Polyatomic Hydrogen Bonding Fluids[1]

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A new theory for intramolecular hydrogen bonding of flexible hard chain molecules in the absence of intermolecular association is presented. The theory predicts the change in thermodynamic properties due to intramolecular association and the fraction of nonbonded chains. Comparisons with molecular simulation results are presented to demonstrate the accuracy of the theory. By considering the limit of complete association, an accurate equation of state of cyclic molecules is obtained.

KEY WORDS: associating polymers; equations of state; intramolecular hydrogen bonding; molecular simulations; statistical mechanics.

1. INTRODUCTION

The accurate prediction and correlation of the thermodynamic properties and phase behavior of complex fluid mixtures containing polyatomic, cyclic, and hydrogen-bonding components remains one of the most difficult problems faced by scientists and engineers. These properties are necessary for the production, transmission, and processing of oil, gas, chemical, and biochemical streams. Specific applications include the prevention of asphaltene precipitation in the petroleum industry, separation of raw materials for spinning carbon fibers, modeling the phase behavior of associating polymer solutions, and understanding the phenomenon of protein unfolding and folding. All of these examples have in common the necessity to model systems containing highly nonspherical molecules with specific interactions. We have previously developed a theory for fluids containing

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linear and branched-chain molecules that can associate intermolecularly; however, neither this theory nor any other published theory is adequate to describe the intramolecular association and ring type structures of the systems mentioned above. In this paper we develop a new theory that describes intramolecular hydrogen bonding in polyatomic fluids. We also develop a theory for cyclic molecules which can be considered to be models for aromatics and polynuclear aromatics.

Several recent advances have led to accurate theories for systems containing linear and branched-chain polyatomic fluids. These include the reference interaction site model (RISM) [1–4], polymer RISM [5, 6], the perturbed-hard-chain theories (PHCT) [7, 8], lattice theories [9], generalized Flory dimer theory (GFD) [10], Wertheim's thermodynamic perturbation theory (TPT1 and TPT2) for a polydisperse mixture of polymers [11], the statistical associating-fluid theory (SAFT) [12, 13], Chiew's Percus–Yevick chain (PYC) equation of state for chain and star molecules [14], SAFT dimer (SAFT-D) [15], square-well-chain equation of state [16], and SAFT extended to chains of Lennard–Jones segments [17–19]. Except for RISM, which is an integral-equation theory, each of these theories is in the form of an equation of state. These theories have shown great promise and have built upon the successes of each other. However, since these equations of state were developed for systems composed of linear chains without intramolecular hydrogen bonding, they cannot model those systems in which molecules possess cyclic or ring type structures.

Recent results from some clever experiments have illustrated the principal deficiencies in the models mentioned above. Clarson [20] has performed experiments on poly dimethyl siloxanes that were synthesized into linear molecules and cyclic molecules. Clarson measured the mass density and found that the mass density of the linear chains is approximately linear in the reciprocal of molecular weight; however, the mass density of cyclic polysiloxanes is nearly independent of molecular weight except for small molecular weight (see Fig. 1). This indicates that an equation of state for linear chains, including SAFT-D, SAFT, TPT1 and TPT2, GFD, and PYC, will not be valid for cyclics.

In another set of interesting but seemingly unrelated experiments, Gregg et al. [21] demonstrated the effect of intramolecular hydrogen bonding on the cloud point of a polymer solution. In these experiments Gregg et al. considered three cases: a nonpolar polymer, the same polymer with a hydroxyl group added to one end, and the same polymer with hydroxyl groups added to both ends. They used SAFT to predict their experimental results. SAFT correctly predicted the results for the nonpolar polymer and the polymer with one hydroxyl group, while it predicted

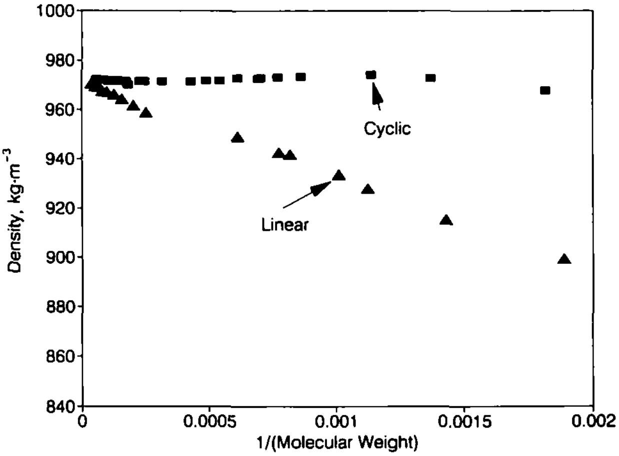

Fig. 1. The mass density of linear and cyclic poly dimethyl siloxanes versus reciprocal of molecular weight at 1 atm and 25°C [20]

results different from experiments for the polymer with two hydroxyl groups. Since the perturbation theory on which SAFT is based neglects all terms involving the formation of polyatomic rings, SAFT does not include intramolecular hydrogen bonding. Therefore, one possible explanation for the discrepancies between the experimental result and the SAFT result is the effect of intramolecular bonding; the polymer is flexible enough that the two hydroxyl groups on opposite ends of the polymer can hydrogen-bond. None of the equations of state mentioned above include the effect of intramolecular hydrogen bonding.

The results from Clarson's experiments and those of Gregg et al. are linked since ring formation is just the total bonding limit of an intramolecularly bonding fluid. Consider a linear polymer with hydrogen bonding groups on each end as in the experiments of Gregg et al. If no intermolecular hydrogen bonding occurs, we could consider the limit of "covalent"-strength intramolecular association in which a cyclic molecule is formed. SAFT and SAFT-D were developed in a similar way, by taking the limit of "covalent"-strength association for chains of associated molecules [12].

2. THEORY OF FLUIDS WITH INTRAMOLECULAR HYDROGEN BONDING

Based on statistical thermodynamic arguments, and assuming that a molecule bonds once intramolecularly, we have shown that the change in Helmholtz free energy due to intramolecular bonding can be written as [22]

$$\frac{\Delta A}{VkT} = \rho \ln\left(\frac{\rho_0}{\rho}\right) \tag{1}$$

where V is the volume, k is Boltzmann's constant, T is the temperature, ρ is the number density of molecules, and ρ_0 is the density of molecules that are not hydrogen-bonded intramolecularly. We have also shown that the density of molecules that are not hydrogen-bonded intramolecularly can be approximated by [22]

$$\rho_0 = \rho - \rho_0 \Delta_{\text{intra}} \tag{2}$$

where ρ_0 is the density of nonbonded molecules, ρ is the total number density, and $\rho_0 \Delta_{\text{intra}}$ is the density of molecules that are intramolecularly hydrogen bonded. Δ_{intra} is defined by

$$\Delta_{\text{intra}} = C \int g_{\text{R,intra}}(12) f_{\text{intra}}(12)\, d(12) \tag{3}$$

where C is a constant and $g_{\text{R,intra}}(12)$ is the intramolecular distribution function for the reference fluid between the two segments of the molecule that form an intramolecular hydrogen bond. $f_{\text{intra}} = \exp(-\phi_{\text{intra}}(12)/kT) - 1$ is a Mayer f-function, $\phi_{\text{intra}}(12)$ is the intramolecular hydrogen-bonding potential, and $d(12)$ denotes an unweighted average over all orientations and an integration over all separations of segments 1 and 2. The $\rho_0 \Delta_{\text{intra}}$ term is the density of molecules that are not yet hydrogen bonded intramolecularly multiplied by the probability that two segments will be in the correct orientation and that the bonding energy will be large enough to form a bond. In the calculations presented below, we have approximated the intramolecular distribution function for the reference fluid by the hard-sphere pair correlation function [22].

3. MOLECULAR SIMULATION OF FLUIDS WITH INTRAMOLECULAR HYDROGEN BONDING

To test our new theory, we have performed molecular simulations (Metropolis Monte Carlo [23]) of model fluids in which we can turn off all intermolecular hydrogen bonding and focus on intramolecular hydrogen bonding. Molecular simulation is a "brute force" method to determine the thermodynamic properties of a fluid. The only approximation in the molecular simulation is the force of interaction between the molecules. By comparing results of a theory with molecular simulation results obtained

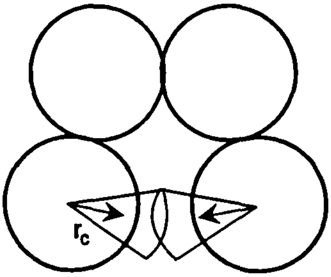

Fig. 2. Sketch of a tetramer in an intramolecular hydrogen-bonding configuration.

for the same force model, there are no adjustable parameters and the approximations that have been made in developing the theory can be rigorously tested.

The model that we chose was a fluid of freely flexible chains; each chain contains four hard-sphere segments with bond lengths equal to the hard-sphere diameter. The intermolecular potential is a sum of hard-sphere segment–segment interactions. The intramolecular potential includes hard-sphere segment–segment repulsions and a short range, orientation-specific attraction between the terminal segments. This hydrogen bonding interaction is zero unless certain orientation requirements are met as given by

$$\phi_{\text{intra}}(r, \Omega_1, \Omega_2) = -\varepsilon_{\text{intra}} \qquad \text{if} \quad r < r_c, \qquad \theta_l < \theta_c, \text{ and } \theta_2 < \theta_c \tag{4}$$

where Ω_l is the orientation of one of the terminal segments in a molecule, and θ_l is the angle between the vector connecting the center of terminal segment 1 to the hydrogen-bonding site on molecule 1 and the vector connecting the centers of the terminal segments on a molecule. These radial and angular restrictions on intramolecular hydrogen bonding are illustrated in Fig. 2, in which a bond will form if the conical sections, extending from the terminal segments, overlap. Simply stated, an intramolecular hydrogen bond between the end segments can form if the segments are at the correct distance and orientation to each other. This hydrogen-bonding potential model was used in previous studies of intermolecular hydrogen bonding [17, 18, 24] and is designed to be physically reasonable and fast to calculate.

4. RESULTS AND DISCUSSION

In Fig. 3, we compare the fraction of monomers (not intramolecularly bonded) from Eq. (2) (curves) with molecular simulation results (points) at two liquid densities for a range of hydrogen-bonding energies. As the temperature is lowered, the amount of intramolecular hydrogen bonding increases. The agreement between theory and simulation is very good. The change in Helmholtz free energy due to intramolecular hydrogen bonding was determined from molecular simulation by thermodynamic integration of the internal energy at constant density, and also of the pressure along an isotherm. In Fig. 4 we compare the Helmholtz free energy predicted from Eq. (1) with molecular simulation results. As the temperature of the system is lowered, the entropic cost of hydrogen bonding becomes less important compared to the reduction in internal energy; this is reflected in the Helmholtz free energy. Again, the agreement between predictions of theory and molecular simulation results is very good. We have found that Eqs. (1) and (2) are in very good agreement with molecular simulation results over a range of gas and liquid densities and for temperatures low enough to cause nearly complete bonding.

By taking the limit of complete intramolecular bonding, we have developed an analytic equation of state for cyclic molecules. In Fig. 5 we

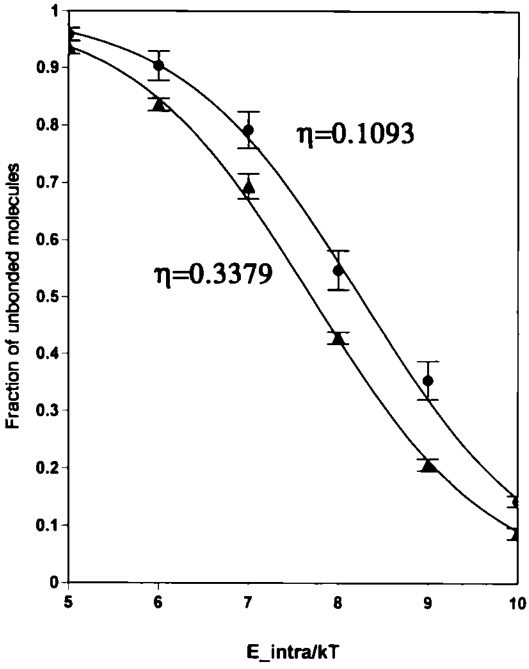

Fig. 3. The fraction of monomers from molecular simulation (points) and theory (lines) is plotted versus the intramolecular hydrogen-bonding energy for two liquid densities given by the packing fraction, $\eta = (\pi/6)\rho\sigma^3$, where ρ is the density and σ is the hard-sphere diameter.

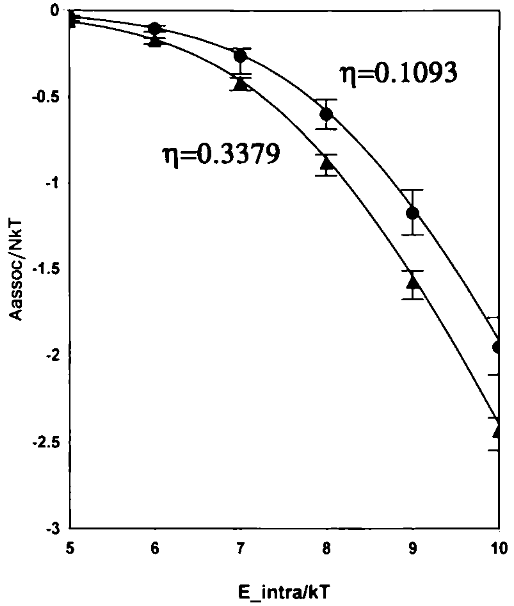

Fig. 4. The change in Helmholtz free energy due to intramolecular hydrogen bonding from molecular simulation (points) and theory (lines) is plotted versus the hydrogen-bonding energy for two liquid densities.

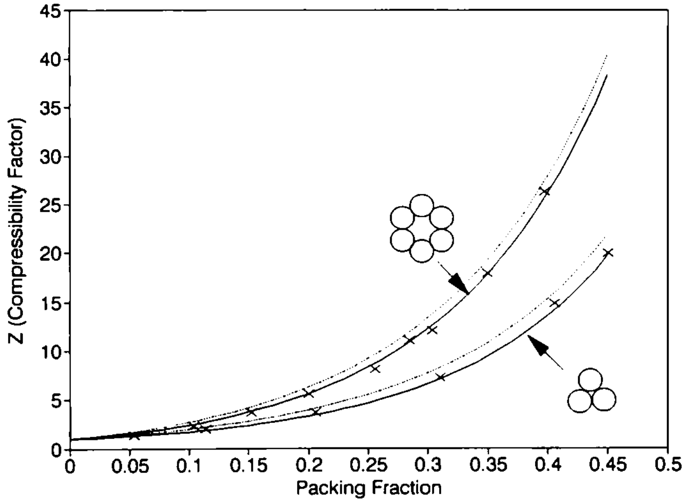

Fig. 5. The compressibility factor for rings of hard spheres from simulation (crosses) and theory (lines) is plotted versus the packing fraction as defined in Fig. 3 up to high-density liquid states. The solid lines are predictions for rings and the dotted lines are predictions for chains [11, 12].

show the compressibility factor for trimer and hexamer rings as a function of packing fraction from our theory and molecular simulation. We modeled the hexamer ring as a rigid, planar molecule of tangent hard spheres placed at the vertices of a hexagon. Over the range of liquid densities studied, we show in Fig. 5 that, at the same density and segment number, the compressibility factor for rings is lower than that of linear flexible chains. This is due to the reduced surface area available for collisions of the rings. The agreement between simulation and theory is very good.

5. CONCLUSIONS

We have presented a new theory for intramolecular association in the absence of intermolecular association. Agreement between the theory and molecular simulation results for the Helmholtz free energy and the fraction of monomers is excellent. By allowing the chain molecules to form strong intramolecular bonds, we developed an accurate equation of state for ring molecules. In future research we will study the competition between intramolecular and intermolecular association [25].

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