

Multibody Effects in Self-Assembly of Patchy Colloids and Associating Molecules

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Predicting the thermodynamic properties and self-assembly of patchy colloids and of hydrogen bonding molecules (e.g., hydrogen fluoride and water) continues to be a challenge of statistical mechanics based theories. The most commonly applied approach is Wertheim's theory and its extensions for associating particles. Most applications of the theory have considered the first order that includes only linear and branched structures, while ring formation is dominant at some conditions. The effect of bond angles on thermodynamics and structure of associated clusters is lacking in the first order theory. In addition, while most of the developments on the theory are performed with a hard sphere reference fluid, using a Lennard Jones reference makes the theory more realistic. In the work presented here, a higher order theory is developed. The effect of steric hindrance and also ring formation is included, and the equations of state derived for these systems are bond angle dependent. In our work, the bond angle refers to the angle separating the vectors connecting the centers of the two associating sites. The theory is capable of predicting the competition between ring and chain formation at various conditions. To verify the theory predictions, new Monte Carlo (MC) simulations have been performed. The theory predictions for internal energy and distribution of associated chain and ring structures as a function of bond angle are in an excellent agreement with MC simulation.