

Interfacial Properties of Fully Flexible Square-Well Chains from Monte Carlo and Density Functional Theory

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The square-well fluid, and particularly the fully flexible square-well chainlike system, has attracted from decades the interest of the theoretical community of Statistical Mechanics of liquids. Despite its apparent simplicity, molecular systems interacting through discontinuous potentials, such as the square-well model, exhibit a complex thermodynamic and structural behavior. From the computer simulation perspective, even the determination of simple properties, such as bulk pressure, or other more complex magnitudes, such as interfacial properties (particularly the surface tension or the components of the pressure tensor), has been a challenge problem not completely solved until very recently. During last decade there has been an intensive and increasingly development of the Monte Carlo methods for determining interfacial properties of complex liquids, including chainlike systems and associating fluids, with particular emphasis on the calculation of the fluid-fluid surface tension. New computer simulation methodologies proposed in last years, such as the Wandering Interface Method or Expanded Ensemble, among others, allow to determine the interfacial tension easily and in an elegant way, even for the most complex systems, even those interacting through discontinuous intermolecular potentials, such as the square-well model. From a theoretical point of view, the calculation of the interest interfacial properties has been less complicated, especially with the establishment of the Wertheim's thermodynamic perturbation theory and the development of new, more powerful and precise density functional theory approaches. In this work we use the Wandering Interface Method and the SAFT-VR DFT approach to analyze the behavior of the interfacial properties of molecular chains interacting through the discontinuous square-well intermolecular potential. Particularly, we focus on the behavior of the surface tension, density profile, vapour pressure, and interfacial thickness, as functions of temperature and molecular size. Special care has been taken in the determination of the vapor pressure (especially in the case of very-long molecules), and the statistical treatment of the errors associated to the thermodynamic integration calculations.