Effect of Molecular Size and Flexibility of Chainlike Molecules on the Vapour-Liquid Interfacial Properties

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The nature of the molecular interactions that occur at interfaces is key from a theoretical point of view: knowledge of how the molecular size, dispersive and other kind of intermolecular interactions, intramolecular and specific interactions, such as hydrogen bonding, or the molecular architecture and flexibility affect interfacial magnitudes, including thermodynamic and structural properties, is essential to understand the delicate interplay between surface and bulk contributions to the free energy. Particularly, chainlike molecular systems have attracted the attention of the soft matter community, not only due to the intrinsic theoretical interest in predicting their thermodynamic and structural properties, but also for the industrial importance of these systems in the molecular modeling field. 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. Traditionally, the virial method (or mechanical route) has been mainly used and is still considered as the standard method for calculating the surface tension of fluid phases in Monte Carlo and Molecular Dynamics simulation. New methodologies proposed in last years, such as the Test-Area, Wandering Interface Method, or Expanded Ensemble, among others, allow the determination of the interfacial tension easily and in an elegant way, even for the most complex systems. In this work we use some of these methods to analyze the behavior of the interfacial properties of molecular chains interacting through the Lennard-Jones intermolecular potential with different degree of flexibility. We focus on the behavior of the surface tension, density profile, critical temperature and density, vapour pressure, and interfacial thickness, as functions of temperature and molecular characteristics of the substances, including size and flexibility. Special care has been taken in the use of inhomogeneous long-range corrections, 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.