

Interfacial properties of square-well chains using molecular dynamics

A. Morales, C. Romero, J. Algaba, P. Gómez-Álvarez, and Felipe J. Blas

Laboratorio de Simulación Molecular y Química Computacional,
CIQSO-Centro de Investigación en Química Sostenible and Departamento de Ciencias Integradas,
Universidad de Huelva, 21006 Huelva

Fully-flexible chains formed from tangentially-bonded monomeric units that interact through effective-type potentials represent perhaps the simplest option retaining the basic microscopic characteristics of molecular chains: segment connectivity, molecular flexibility, and attractive and repulsive interactions. Square-well (SW) potential is possibly the simplest interaction accounting for both attractive and repulsive interactions. However, its discontinuous functional form makes it extremely difficult to be used in molecular simulation, either Monte Carlo (MC) or Molecular Dynamics (MD) methods. Chapela and Alejandre [1] used special techniques in MD simulations to explicitly account the impulsive forces generated in a system of SW chains with a potential range of $\lambda = 1.5\sigma$. The discontinuity in the interaction forces makes unfeasible to simulate this interaction potential with commercial MD programs such as GROMACS [2] or LAMMPS [3]. Very recently, Zerón *et al.* [4] have presented a parameterization of the SW potential that allows its use for simulation packages since the intermolecular potential and force are described by continuous mathematical functions. They determined the interfacial properties and the phase equilibrium of SW potentials of ranges $\lambda = 1.25, 1.5$ and 2.0σ using GROMACS. The excellent agreement of the obtained results with available experimental data pointed to the reliability of the reported continuous form. Since the phase equilibrium and interfacial properties of SW molecular chains with different range of interaction provide valuable information to discern whether different microscopic theories, such as those based on the density

functional theory or equations of state, are capable of predicting this type of system, we extend here the study carried out by Zerón *et al.* [4] to other ranges of attractive interaction, in particular $\lambda = 1.5$ and 1.75σ . Simulations for $\lambda = 1.5\sigma$ were conducted for chains of 4 monomers and the results compared with the previously reported computational predictions¹ using distinct methodology. For the potential range of $\lambda = 1.75\sigma$, which had not yet been studied, we considered systems comprising 4, 8 and 16 monomers per molecule. Thus, the effect of the chain length is additionally assessed on the calculated properties, namely density profiles, coexistence densities, vapor pressures, temperature and critical density and surface tension. Overall, liquid-vapor interface sharpens with the increase in the chain length due to an increase in the width of the envelope of the coexistence phase, and the resulting increase in surface tension.

-
- [1] G. A. Chapela and J. Alejandre, *Liquid-vapor interfacial properties of vibrating square well chains*, J. Chem. Fis. x **1**, 1-11 (2011).
- [2] D. Van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H.J.C. Berendsen, *GROMACS: Fast, flexible, and free*, J. Comput. Chem. **26**, 1701 (2005).
- [3] S. Plimpton, *Fast parallel algorithms for short-range Molecular Dynamics*, J. Comput. Phys. **117**, 1-19 (1995).
- [4] I. M. Zerón, C. Vega, and A. L. Benavides, *Continuous version of a square-well potential of variable range and its application in molecular dynamics simulations*, Mol. Phys. **116**, 3355 (2018).