

Effect of Dispersive Long-Range Corrections to the Pressure Tensor: Vapor-Liquid Interfacial Properties of Pure and Mixtures of Lennard-Jones Systems

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We propose an extension of the improved version of the inhomogeneous long-range corrections of Janecek [J. Phys. Chem. B 129, 6264 (2006)], presented recently by MacDowell and Blas [J. Chem. Phys. 131 074705 (2009)] to account for the intermolecular potential energy of spherical, rigid, and flexible molecular systems, to deal with the contributions to the microscopic components of the pressure tensor due to the dispersive long-range corrections. We have performed Monte Carlo simulations in the canonical ensemble to obtain the interfacial properties of spherical Lennard-Jones molecules with different cutoff distances, $r_c=2.5, 3, 4$, and 5σ . In addition, we have also considered cutoff distances $r_c=2.5$ and 3σ in combination with the inhomogeneous long-range corrections proposed in this work. The normal and tangential microscopic components of the pressure tensor are obtained using the mechanical or virial route in combination with the recipe of Irving and Kirkwood, while the macroscopic components are calculated using the Volume Perturbation thermodynamic route proposed by de Miguel and Jackson [J. Chem. Phys. 125 164109 (2006)]. The vapor-liquid interfacial tension is evaluated using three different procedures, the Irving-Kirkwood method, the difference between the macroscopic components of the pressure tensor, and the Test-Area methodology. In addition to the pressure tensor and the surface tension, we also obtain density profiles, coexistence densities, vapor pressure, critical temperature and density, and interfacial thickness as functions of temperature, paying particular attention to the effect of the cutoff distance and the long-range corrections on these properties. According to our results, the main effect of increasing the cutoff distance (at fixed temperature) is to sharpen the vapor-liquid interface, to decrease the vapor pressure, and to increase the width of the biphasic coexistence region. As a result, the interfacial thickness decreases, the width of the tangential microscopic component of the pressure tensor profile increases, and the surface tension increases as the cutoff distance is larger. We have extended the procedure to deal with different mixtures of Lennard-Jones molecules, including asymmetric and symmetric binary mixtures. We have also checked the effect of the impulsive contribution to the pressure due to the discontinuity of the intermolecular interaction potential when it is cut. If this contribution is not accounted for in the calculation of the microscopic components of the pressure tensor, incorrect values of both components as well as a wrong structure along the vapor-liquid interface are obtained.