Interfacial Properties of Lennard-Jones Fluids on the Fundamentals of van der Waals Gradient Theory

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The interfacial properties of Lennard-Jones (LJ) fluids were studied using the van der Waals gradient theory. The Ornstein-Zernike (OZ) equation using the Choudhury-Ghosh (CG) closure model was solved to determine the molecular distribution function over large density and temperature ranges. The vapor-liquid equilibrium of the LJ fluids was studied using the pressure equation and the compressibility equation. The interfacial tension calculated from the molecular distribution and the gradient theory cannot represent the experimental data well. There may be several reasons: (1) The influence parameter of the gradient theory only includes the second-order inhomogeneous structure information and cannot represent the inhomogeneous characteristics in the wide temperature range; (2) The truncated Helmholtz free energy densities are not sufficient in the low temperature range which requires higher-order terms; (3) The molecular distribution functions were calculated from the OZ equation and the CG closure. Although the equilibrium conditions calculated from the CG closure is better than using the HNC closure, it is still far from the experimental data in the low temperature range; (4) The OZ equation is based on the two-body potential, while there must be three-body or higher effects in the real fluid; (5) That the density gradient changes slowly at the interface is the basic assumption of the gradient theory. The interfacial tension calculated by the gradient theory is better near the critical region than near the triple point region. The Helmholtz free energy density is also expanded to higher order terms to calculate the interfacial tension of the LJ fluid.