Equation of state of dense fluids in the high pressure – high temperature region

In our study we consider the problem of the statistical-mechanic foundation of the equation of state (EoS) of fluids within the framework of the generalized approach [1]. A variant of the thermodynamic perturbation theory based on scaling transformation of the partition function has been applied to the functional expansion of the free energy. We develop a new variant of the thermodynamic perturbation theory in which a reference thermodynamic state (P_0, V_0, T) is given instead of a reference system. Our approach involves an assumption that a functional form of the perturbed potential is identical to the potential of a reference system, thus we consider the deviation of the potential of the more compressed system from the potential of the less compressed system as the perturbation, and the scale transformation of the dynamical variable is equivalent to variation of a molecular size. The various modifications of EoS have been obtained for a number of simple model potentials on the basis of the free energy functional series at a certain choice of small expansion parameters. An analysis of the experimental data on isothermal compression has shown that the application of the proposed EoS to many molecular fluids gives good results upon extrapolation in the high pressure region or in the range of thermodynamic variables where the isothermal compressibility is low. The experimental data processing carried out for some substances has revealed the necessity of modification of some potential models in the high pressure region [2, 3]. The functional form of a repulsive potential is discussed on the base of results obtained by the processing of the high frequency asymptotics of the depolarised light scattering and temperature dependences for one-particle contributions to the selfdiffusion coefficient. The results yielded on the basis of these approaches correlate well. An analysis of the theoretical results is in a close agreement with the experimental data on selfdiffusion in liquid argon and molecular dynamics simulation.

The special attention is paid to the high pressure EoS for water. Here we started from an improved version of the Stillinger-David polarization potential [4]. The effective potential, taking into account the influence of H-bonds has been constructed. The processing of PVT-data by the proposed EoS gives fairly good agreement at comparison with experimental data.

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