Generalized approach to the equation of state of dense fluids and dilute gases

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1. Introduction

Despite an essential progress achieved during the last decades in the theoretical description of the equations of state for dense fluids [1-4], an equation describing the thermodynamics in a wide interval of pressure and temperature, including the stability boundaries, still remains to be developed. Interest to this problem is motivated by the fact that the liquid and gaseous phases have the same type of symmetry. It would, therefore, be reasonable to look for a unified description of their properties. In this sense it is important to carry out the development within a generalised framework as far as possible only specifying the type of phase when it is necessary. This approach can be extended to all kinds of low-weight molecular fluids which can be described by rotationally averaged intermolecular potentials similar to the potential of atomic fluids such as Ne, Ar, Kr, Xe. This was illustrated in [5] where the thermodynamic properties of water are defined by such an averaged potential.

In this 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 [6]. A form of the thermodynamic perturbation theory based on the scaling transformation of the partition function has been applied to the functional expansion of the free energy. We develop a new version of the perturbation theory in which a reference thermodynamic state (P_0, V_0, T) is specified rather than a reference system. Our approach involves an assumption that the functional form of the perturbed potential is identical to the potential of the 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 equivalent to the variation of the molecular size.

2. Equation of state

Various modifications of the EoS have been derived for a number of simple model potentials on the basis of the free energy functional series at a certain choice of small expansion parameters. We considered the derivation of the EoS in the high densities limit for realistic potential models, like the Lennard-Jones potential, and in the framework of short range potentials such as the Sutherland and Katz models.

It was shown that in the low densities limit (dilute gas) the functional expansion transforms to the usual viral series in the powers of density.

A special attention is paid to the high pressure EoS for water. Here we started from an improved version of the Stillinger-David polarisation potential [7]. An effective potential that takes into account the influence of the H-bonds has been constructed.

3. Conclusion

The functional expansion of the free energy allows to obtain, at various choices of the parameter expansion, the equations of state for dense fluids and dilute gases. The analysis of the experimental data on isothermal compression has shown that the application of the proposed EoS to many molecular fluids produces good results upon extrapolation to the high pressure region or in the range of the thermodynamic variables where the isothermal compressibility is low. This approach provides a connection between the parameters of the intermolecular potential and the thermodynamic properties of the system.

The experimental data for some substances required modifications of potential models in the high pressure region [8, 9]. The functional form of a repulsive potential is discussed on the basis of the data for the high frequency asymptotics of the depolarised light scattering and temperature dependences for the one particle contributions to the self-diffusion coefficient. The results yielded a good agreement of the experimental and theoretical data on self-diffusion in liquid argon and molecular dynamics simulation.

References

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