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Helmholtz free energy of liquid Na in the variational method with the square-well reference system

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Abstract

The possibility of using the square-well model (considered within the suggested by us recently semi-analytical modification of the mean spherical approximation) as a new reference system in the framework of the variational method of the thermodynamic perturbation theory is investigated.

A way to minimize the free energy, when uses only one free parameter of the square-well (diameter of the hard core) is used and the other two are determined from two additional conditions, is suggested. To define one of them (depth square well), it is proposed the use the condition that the structure-dependent part of the potential energy calculated from the pair potential found by the pseudopotential method is equal to the potential energy of the square-well model. Determination of the second parameter (the width of the square well) is achieved by locking the right boundary at the second intersection of the effective pair potential with the x-axis. Additionally the free energy minimization is fulfilled with respect to the mean atomic volume.

To describe the effective pair interaction we use the model Animalu-Heine in the local approximation and the Vashishta-Singwi exchange-correlation function proven earlier in the calculations of thermodynamic properties of metal melts by variational method with a reference system of hard spheres.

Calculating procedure is the following: at first for a given mean atomic volume using the above two additional conditions the free energy dependence on the diameter of the hard core is calculated and then the value of the diameter of the hard core giving the minimum value of the free energy is determined. Then, this operation is performed for the other atomic volumes and as a result the global minimum on the free energy as a function of two variables (the diameter of the solid core and the mean atomic volume) is determined.

The approach is applied to the liquid sodium near the melting temperature. The dependence of the free energy of liquid sodium on the hard-core diameter and the mean atomic volume is investigated and one global minimum is found. Obtained in the global minimum values of the free energy, mean atomic volume, internal energy and entropy very good agree with the experimental data. Thus, the prospect of the square-well model as a reference system in the variational method for studying the properties of liquid metals is shown.