The RPA correction to the Helmholtz free energy of simple liquid metals within variational calculations

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The thermodynamic perturbation theory (TPT) is widely used for investigating the structure and thermodynamics of liquid and amorphous substances including metals [1]. The TPT is based on Zwanzigs approach [2] which treats a liquid that obeys the laws of classical statistical mechanics as the sum of two subsystems. One of them, called reference system, mainly includes the forces of repulsion between molecules, whereas the other, called perturbation, mainly includes the forces of intermolecular attraction.

When calculating the structure functions and macroscopic properties of a liquid with a given pair interaction potential, the TPT helps to avoid computational problems connected with solution of the Ornstein-Zernike (OZ) integral equation. This is of particular importance for calculations of the thermodynamic properties of metals. Indeed, on the one hand, metallic state is usually described using complex pair potentials. On the other hand, calculations of thermodynamic properties require additional numerical operations. Taken altogether, these features make direct calculations of the thermodynamic properties of metals using the OZ integral equation difficult.

Studies of liquid metals within the framework of the TPT began in the early 1970s and since then became an integral part of the physics of condensed matter. It is of importance that the TPT without any additional relatively to the theory of simple liquids restrictions can be applied to metals. In fact, to use the TPT instead of integral-equation theories of liquids means to search for some integral-equation approximation for the reference system rather than the entire system under study. There are two groups of the TPT methods: methods of the high temperature approximation (HTA) proposed by Zwanzig [2] and methods of the field theory (FT). In the HTA the entropy and structure functions of the entire system are respectively equal to those of the reference system. The FT approximations allow avoiding these equivalences and giving the correction to the HTA Helmholtz free energy. In the present work, the HTA+FT formalism [3] is developed for liquid metals described by the nearly-free-electron (NFE) approximation for the case when the HTA method is the variational one, the FT method is the random phase approximation (RPA) and the reference system is the hard-spheres (HS) model.

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