Evaluation of thermodynamic properties of metals by a perturbation theory by example of aluminum

Yu A Bogdanova, S A Gubin, I V Maklashova and A V Kudinov
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe Shosse 31, Moscow 115409, Russia
E-mail: bogdanova.youlia@bk.ru

Abstract. For the first time we demonstrate the application of the equation of state based on a perturbation theory to calculate the properties of condensed aluminum on isothermal and shock compression. For a description of the interatomic interaction in metals the Morse pair potential is used. The calculation results are in good agreement with an experimental data and calculations based on empirical equations described in the literature. Thus, developed on the basis of perturbation theory equation of state with the corresponding intermolecular interaction potential is a reliable universal tool for the calculation of the thermodynamic properties of a gas (fluid) systems and condensed matter. This model of equation of state allows to analyze the dynamics of changes in the atomic structure and phase transformations of matter during heating and compression.

1. Introduction
The development of theoretically equation of state (EOS) of the dense fluid systems based on modern methods of statistical physics and realistic intermolecular interaction potentials is of considerable interest. Such EOS provides good agreement with the Monte Carlo (MC) and molecular dynamics (MD) simulation results, and also have high performance. Dynamics of changes of the radial distribution function (RDF) and the mean square deviation of the atoms from the initial state point to structural and phase transformations in condensed matter at high pressures [1, 2].

One of the best theories allowing calculating EOS of fluids both at high pressures and temperatures, and at lower temperatures and density, is the perturbation theory of Kang et al (KLRR) [3]. An example of the successful application of KLRR perturbation theory [3] is the EOS model of fluid systems developed in [4, 5]. This model provides an excellent agreement the calculations of shock-wave compression with the results of the simulation by the methods MC, MD, and the experimental data [6, 7] in a wide range of pressures and temperatures. The perturbation theory is applicable to any gaseous or condensed systems, in which there are interactions described by the interatomic or intermolecular potentials. Following [8, 9] the EOS model based KLRR perturbation theory with the corresponding intermolecular interaction potential can be used to calculate the thermodynamic properties of metals and their alloys, including isothermal or shock-wave compression.

The potential equation of state has a wide range of applicability. The developed EOS [4,5] can be used with any spherically symmetric interparticle interaction potential depending on the problem being solved. The reality of the calculated parameters is directly related to the choice
Table 1. Potential parameters Morse.

| Molecule | ε (eV) | r_m (Å) | α (Å⁻¹) |
|----------|--------|---------|---------|
| Al       | 0.266  | 3.203   | 1.212   |

of the intermolecular (or interatomic) interaction potential. For example, the Morse potential is chosen in this paper. This potential describes the compression region and the region of low degrees of crystal expansion with high accuracy.

2. Intermolecular interaction potential
To ensure the reliability of the thermodynamic simulation the potentials should be used, describing the realistic nature of intermolecular forces in the region of interest pressures and temperatures. For a description of the interaction of metal atoms the Morse pair potential is used:

$$\varphi(r) = \varepsilon \{ \exp[-2\alpha(r - r_m)] - 2 \exp[-\alpha(r - r_m)] \},$$

(1)

where $$\varepsilon > 0$$ is the well-depth, $$r_m$$ is the position of the potential well minimum, and $$\alpha$$ is the parameter characterizing the width of the potential well. This potential is widely used in MD simulations [10].

Potential parameters for the molecules investigated in the work are taken from [11] and presented in table 1.

3. Radial distribution functions
For calculation of thermodynamic properties of chemical system at known temperature $$T$$ and volume $$V$$ it is enough to determine the Helmholtz energy of this system. The perturbation theory [3–5] suggests that the Helmholtz energy of an ensemble of molecules at temperature $$T$$ and volume $$V$$ is the sum of two components. First of them is the Helmholtz energy of an ideal gas at the same $$T$$ and $$V$$ values, and the second component is an addition caused by the intermolecular interaction. Therefore, the main objective of the perturbation theory is exact determination of the excess Helmholtz energy. To calculate it by the perturbation theory the radial distribution function (RDF) of molecules $$g(r)$$ must be known. The value $$4\pi r^2 g(r)dr$$ characterizes the probability of finding any pair of molecules of the basic system at distances ranging from $$r$$ to $$r + dr$$, which defines the physical meaning of the function $$g(r)$$.

The results of the RDF calculations are presented in [12] only graphically, cover a limited range of intermolecular distance and the analytical form of RDF is absent. The corresponding solution was also given in [13], however use of analytical expressions [13] for the RDF calculations is impossible. In [14] analytical expressions of RDF are presented only for contact points. Therefore the development of a method of the RDF calculation of a binary hard spheres mixture is of a great interest for any intermolecular distance. The analytical expressions for the RDF of hard spheres in the Percus–Yevick approximation is obtained in [15]. This technique is applicable in contrast to [12] for any distance $$r$$ between the centers of hard spheres of different diameters, and can be used to confirm the results of Smith and Henderson [16] for the pure system and expand to $$r$$ values where technique [16] does not work.

The RDF calculations were carried out for aluminum at a temperature of 943.15 K by the developed method [15]. The results of calculations in comparison with the experimental data [17] are shown in figure 1.
Figure 1. RDF of aluminum molecules at 943.15 K: I—experiment [17].

Figure 1 shows that the values of aluminum RDF are in good agreement with the experimental data. Difference values at the contact point can be explained by using system of hard spheres to calculate the distribution functions as described in [15]. However, according to the perturbation theory, the excess Helmholtz energy is determined by calculating the integral with infinite upper limit, so the difference between the calculated distribution functions at the contact points with the experimental data do not introduce significant errors in the calculation of the Helmholtz energy.

4. The model of the equation of state based on a KLRR perturbation theory
The main idea of any perturbation theory is in the separation of the potential $\varphi(r)$ of the studied system at the break point $r = \lambda$ into two components: the dominating part which is the molecular interaction potential in a certain reference system, and small perturbation:

$$\varphi(r) = \varphi^{\text{ref}}(r) + \varphi^{\text{pert}}(r),$$

where

$$\varphi^{\text{ref}}(r) = \begin{cases} 
\varphi(r) - \varphi_{\lambda}(r), & r < \lambda, \\
0, & r > \lambda;
\end{cases}$$

$$\varphi^{\text{pert}}(r) = \begin{cases} 
\varphi_{\lambda}(r), & r < \lambda, \\
\varphi(r), & r > \lambda.
\end{cases}$$

For the reference system, the hard sphere system that is usually applied for studying dense fluids is used.
The values of the break points are calculated using the following continuous function proposed by Byers Brown and Horton [18]:

\[ \lambda = r_m \left(1 + \left(\rho_{\sigma r_m^2}^3\right)^{n/3}\right)^{-1/n}, \]

where \( \rho_{\sigma r_m} = \rho / \sqrt{2} \), \( n \) is a certain parameter, in this work \( n = 120 \). It is supposed that the excessive Helmholtz energy of the reference system coincides with the excessive Helmholtz energy \( F_{HS} \) of a certain effective hard sphere fluid. The excessive \( F_{HS} \) of the reference system was calculated using an expression obtained in [19].

Therefore, the excessive free Helmholtz energy per one molecule of the pure system is determined by the formula

\[ \frac{\beta F_{ex}}{N} = \frac{\beta F_{HS}}{N} + 2\pi \rho \int_0^\infty g_{HS}(r) \beta \phi_{pert}(r) r^2 dr, \]

where \( g_{HS}(r) \) is the radial distribution function of hard sphere fluid molecules; \( \beta = 1/k_B T \); and \( k_B \) is the Boltzmann constant.

All necessary thermodynamic parameters of the system can be expressed in terms of the corresponding first and second derivatives of the excessive Helmholtz energy \( F_{ex} \). For example, the compressibility factor \( Z = PV/Nk_B T \) is calculated as

\[ Z = 1 + \beta \rho \left( \frac{\partial F_{ex}}{\partial \rho} \right)_\beta. \]

Similarly, the excessive internal energy per molecule is calculated:

\[ U_{ex} = \left( \frac{\partial \beta F_{ex}}{\partial \beta} \right)_\rho. \]

5. Results

The EOS model for the mixtures which molecules interact with Exp-6 potential is presented in [5]. This model is based on the thermodynamic perturbation theory KLRR [3] and extended to the calculation of the thermodynamic parameters of two-component systems, while remaining applicable for calculating the thermodynamic parameters of pure systems. This method was used to calculate the parameters of the system of atoms and molecules hydrogen with the Morse potential [6]. The reliability and efficiency of the theoretical EOS model [5] proved a good agreement with the MC simulation results in a wide range of thermodynamic states of fluid [5–7]. The theoretical EOS model [5] may also be used for the calculation of the thermodynamic parameters of pure systems, assuming the potential parameters of mixture components are equal.

The thermal and physical properties of aluminum are well studied both experimentally [20–25] and theoretically [26–31], that is why it has been selected to test the EOS model [5]. The calculations of isothermal at temperatures of 298 K and 673 K and shock-wave compression parameters of aluminum were carried out by the developed on the perturbation theory EOS model [5]. The results are shown graphically in the \( PV \)-diagrams in figure 2 (isothermal compression) and 3 (shock Hugoniot). These figures also show the results of calculations by the analytical EOS [28], empirical EOS [29] and experimental data [20–25].

Figures 2 and 3 show a good agreement the results of calculations of pressure at an isothermal and shock-wave compression of aluminum with the experimental data and the results of calculations based on the analytical and empirical EOS.
Figure 2. Isotherms of aluminum at 298 \((a)\) and 673 K \((b)\), \(V_0 = 0.372\) cc/g. EOS: \(1—[28] ; 2—[29]\). Experiment: \(3—[20] ; 4—[21] ; 5—[22] ; 6—[23]\).

Figure 3. Principle shock Hugoniot of aluminum \((V_0 = 0.372\) cc/g). EOS: \(1—[28] ; 2—[31]\). Experiment: \(3—[24] ; 4—[25]\).
6. Conclusion
The results of calculations of thermodynamic parameters of aluminum at isothermal and shock compression by the EOS model based on the perturbation theory [5] with the intermolecular interaction Morse potential is in good agreement with experimental data and calculations based on the analytical EOS.

Thus, EOS model based on the perturbation theory KLRR with the potential of pairwise interaction Morse is applicable for the calculation of the thermodynamic parameters of metals under an isothermal or shock compression. Therefore the EOS model with the corresponding intermolecular interaction potential is a reliable universal tool for the calculation of the thermodynamic parameters of gas (fluid) systems and condensed matter.

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