The fitting of three-body potential energy of solid argon

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Abstract. Based on atomic crystal configuration and the CCSD(T) calculation results, we obtain the fitting result of three-body potential energy of solid argon by fitting \textit{ab initio} calculation results of this work, and make a comparison with the previous calculation results. Finally, we study and analyze three-body potential fitting results. It is concluded that the fitting curve is a simple and accurate tool to understand the high-pressure behaviors of solid argon, and the results are in very good agreement with \textit{ab initio} calculation results, the recent experiment results at the present experimental pressure range.

1. Introduction

The three-body potential of rare-gas solids is an important quantity for thermodynamic properties of matter, from which the high pressure elastic modulus, elastic coefficient, heat capacity, lattice dynamics, high pressure melting line, equation of state and zero-point vibration energy can easily be deduced [1-5]. Many-body potential curves contain important information of energetics of atomic interactions in crystalline materials, and these information are obtained using \textit{ab initio} methods density functional theory [6], \textit{ab initio} Hartree-Fock self consistent field method [7], the full single and double excitations plus perturbative treatment of triples (CCSD(T)) [8,9] and the empirical and semi-empirical formulas [10-15] so on. But these theories and methods are complicated when the effects of temperatures are taken into account.

To solve these problems, the simple method is adopted by fitting \textit{ab initio} calculation results of solid argon so that can be directly applied to describe the thermal properties. It is necessary to have a new analytical expression of potential energy that can take the many-body contribution into account with an acceptable accuracy. Therefore, it is important for theoretical research and practical applications to deduce a new fitting formula of three-body potential of solid argon, which can describe many-body effects with better convergence and can satisfy the demand of compactness and simplicity in form with high precision. Usually, the two- and three-body potential energy are obtained by \textit{ab initio} calculation method [2-4,7,16,17] or empirical and semi-empirical formulas [10-15], whereas the results of \textit{ab initio} method are tedious, and the results of empirical and semi-empirical formulas and its parameters are not very accurate.

Based on atomic crystal configuration and \textit{ab initio} calculation results, we obtain the fitting result of three-body potential energy by fitting the calculation results of this work, and make a comparison with the previous calculation results. We expect that this method is helpful to obtain accurate empirical potential function of three-body potential, and can be applicable to all inert elements, including the gas, solid, and liquid phase regions, even of molecular systems, ionic systems.

2. Theoretical model

In a given fcc crystal structure, we consider a cluster that composed of \( n \) atoms, which can be looked
as a simple molecule with a closed-shell electronic structure and single nucleus. By introducing many-body expansion method, the total potential energy between the central atom \( M \) and its neighboring atoms can also be developed in a cluster series:

\[
V_n(M) = \sum_{i=1}^{n-1} u_2(i, M) + \sum_{i<j<k}\frac{1}{r_{ij}r_{ik}}(1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3) + \sum_{i<j<k<l} \frac{C}{r_{ij}r_{ik}r_{il}r_{lj}}(1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3),
\]

where \( u_2(i, j, k, \ldots) \) represent two-, three-, four- and higher-body interactions between the central atom \( M \) and its neighboring atoms, \( U_k(M) \) is a sum of \( k \)-body terms. Higher-order terms are supposed to be much smaller and neglected here. This polynomial expansion is not a many-body expansion as usual but a definition of many-body potentials. In this way, many-body potentials can be solved by independent considerations of some isolated atomic cluster, e.g.,

\[
u_2(i, M) = E(r_i, r_M) - 2E_0,
\]

\[
u_3(i, j, M) = E(r_i, r_j, r_M) - 3E_0 - \sum_{c \in \{i,j,M\}} \nu_2(c, M),
\]

where \( u_2(i, M), u_3(i, j, M) \) of solid argon are calculated by using the Gamess Programme [18-20].

3. The fitting of calculation results and discussion

3.1 The existing three-body potential function

Three-potential energy have been calculated using empirical formulae and semi-empirical formulae, and the existing three-body potential \( U_3 \) is given by a Slater–Kirkwood-type expression,

\[
U_3 = -A \exp[\alpha(r_1 + r_2 + r_3)] \cdot (1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3) + \frac{C}{r_1^3r_2^3r_3^3} \cdot (1 + 3 \cos \phi_1 \cos \phi_2 \cos \phi_3),
\]

where the first term of the formula represents exchange three-body term, which describes the alterations of the charge densities of two interacting molecules by the presence of a third at small interatomic distances. The second term, known as the Axilrod–Teller one, is the long distance asymptote of triple-dipole interaction. At large interatomic separations, the main contribution to the \( U_3 \) term comes from the Axilrod–Teller term.

Freiman Y A and Loubeyre P have obtained three-body potential of solid argon and its parameters, and the parameters of three-body potential (in a.u.) are given in Table 1, 2, respectively.

| Rare-Gas Solids | \( A/e \) | \( \alpha(\text{Å}^{-1}) \) | \( C/e \) | \( e(K) \) |
|----------------|----------|-----------------|----------|--------|
| He             | 892 377.9 | 1.936           | 140.9    | 10.8   |
| Ar             | 2929 433.3 | 1.650           | 3770     | 143.224|
| Kr             | 2695 078.6 | 1.546           | 8113     | 201.2  |
| Xe             | 2197 74.9  | 1.422           | 19319    | 282.29 |

| Rare-Gas Solids | \( A \) | \( \alpha(\text{Å}^{-1}) \) | \( C \) |
|----------------|-------|-----------------|--------|
| He             | 30.644 | 1.0245          | 1.4807 |
| Ne             | 566.969 | 1.1896          | 11.835 |
According to Tables 1 and 2, we get three-body potential energy curves of solid argon of Freiman Y A and Loubeyre P, as shown in Fig. 2.

|     | Energy (a.u.) | Exchange (a.u.) | Correlation (a.u.) |
|-----|---------------|-----------------|--------------------|
| Ar  | 1331.369      | 0.905888        | 526.5              |
| Kr  | 1717.154      | 0.842728        | 1578.3             |
| Xe  | 1964.058      | 0.770203        | 5283               |

3.2 The fitting of three-body potential

Using CCSD (T) method, we get three-body potential energy of face-centered cubic solid argon from $R=2.0\text{Å}$ to $R=4.0\text{Å}$, as shown in Fig. 2. Where $U_{3x}$ represents exchange energy of three-body potential, $U_{3c}$ represents correlation energy of three-body potential, $U_3$ represents three-body potential energy.
Combine with Fig. 1, 2, we obtain the fitting result of three-body potential energy by fitting the three-body potential calculation results of this work, and make a comparison with the previous calculation.
results. We find that our result coincides with Loubryre's numerical results in the long range, but have relatively large differences in the short range. However, it is in good agreement with Freiman's numerical results in the whole range, with an error rate of less than 5%. It is proved that the research methods and ideas of this work are correct. In the next step, we will get the fitting formula and parameters, which will also lay a theoretical foundation for the empirical potential of three-body potential in the future.

4. Conclusion
In summary, a study method for calculating three-body potential energy of solid argon is put forward based on atomic crystal configuration and the CCSD(T) calculation results, and make a comparison with the previous calculation results. The new study method are applied to predict the compression curves of solid He, Ne, Ar, Kr and Xe. It shows that the fitting curve are in remarkable agreement with the former calculation results. It is concluded that the fitting curves is a simple and accurate tool to understand the high-pressure behaviors of solid argon, and the results are in very good agreement with ab initio calculation results, the recent experiment results at the present experimental pressure range. By this approach, we can theoretically investigate properties of solid argon based on the first principle and quantum mechanics. It is believed that the new approach can be used to describe thermal behaviors of rare-gas solids.

Acknowledgement
The research are sponsored by the Innovation talents by Youth science and technology foundation of Gansu Province (20JR10RA135) and Department of Education fund item of Gansu Province (2019A-112).

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