Crystal potentials and dispersion forces in additive approximation

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Abstract. On the basis of the additive approximation model, a formula for determining the van der Waals constant was obtained and the possibility of correctly describing the long-range part of the interaction potential of solidified inert gases crystals was indicated. Using the modified Lennard-Jones potential and experimental data on the dissociation energy and the equilibrium radius, the dispersion constants of systems of inert gas pairs and an alkali metal–inert gas are determined. The results of the calculations are in general agreement with the experiment.

1. Introduction
Additive approximation in calculating the characteristics of the pair potentials of inert gases, alkali-halide compounds and their crystals demonstrated to be highly effective and accurate. For the above objects, this is due to the small redistribution of electron density in the atom–atom (ion–ion) interaction for systems with closed electron shells. It is important to note that the additive approximation also gives quite satisfactory results, especially when calculating the binding energy and equilibrium distances [1–4].

The energy of interactions between atoms (ions) in the additive model includes the classical Coulomb interaction energies, kinetic, exchange and correlation energies in the approximation of local uniformity of electron density. The primary approximation underlying the model is the assumption that the interaction of atoms (ions) does not deform their electron shells, and that there is no redistribution of electron density. This, in turn, makes it possible to calculate the crystal potentials using the obtained pair potentials and—on the basis of those potentials—the various physical characteristics of these objects. However, when using the pair potentials obtained in this model for further calculations (especially multiparticle ones), a problem that arises is that the obtained table results must be interpolated in one way or another. The accuracy of those physical quantities that use the value of pair potentials, especially derivatives of them, obviously depends on the chosen interpolation scheme. A 0.1% margin of error of two different potential interpolation schemes can lead to a more than 10% margin of error in determining its derivative.

2. Formulation of the problem
In the first part of this paper, for systems with a filled outer electron shell, we investigate the possibility of using model potentials for analytical interpolation of the interaction potential,
especially near its minimum point, as well as finding the asymptotic part of crystalline potential in an analytical form. In this case, the use of additive approximation allows the long-range part of the crystalline interaction potential to be correctly determined. As the first approximation, this permits the calculation of the thermophysical characteristics of condensed media and the analysis of the results obtained from physically transparent positions. It also demonstrated the possibility of determining the van der Waals constant for inert gases by three points near the minimum of the interaction potential. The second part of this paper shows the solution to the so-called “inverse problem”—the calculation of dispersion constants using model interpolation potentials of the Lennard-Jones potential type.

3. Solution methods

To solve the first problem, we will use a model approximating potential \( \alpha - 6 \) in the form

\[
U(r) = A \exp(-\alpha r) - Cr^{-6}.
\]

This choice is due to several reasons, in particular, that (1) it correctly describes the area near \( r_{\text{min}} \) which is the minimum of the potential and is on the asymptotics \( (r \to \infty) \) for pairs of atoms with closed external electron shells.

When \( r \leq \sigma \), where \( \sigma \) is determined from \( U(\sigma) = 0 \), the description of the real interaction by potential (1) is incorrect. In addition, dipole–quadrupole, dipole–octupole and quadrupole–quadrupole contributions are not taken into account in (1), the corrections from which can reach an interaction energy up to 30% and 12%, respectively, in the area of \( r_0 \) [5]. However, in the proposed approximation, these contributions are not taken into account.

For interpolation of a table-specific potential (calculated theoretically or obtained as a result of an experiment), it is necessary to know three values \( U(r_i) = U_i \), which will allow unknown parameters \( A, \alpha, C \) to be determined. Numerical values can be obtained in various ways. The most reliable would be the results obtained from the experiment, in particular, from the molecular beam scattering experiment. The results of theoretical calculations of paired potentials in Gordon–Kim’s works are also known, but their accuracy is not always satisfactory. You can also use the data to obtain the required values \( (r_i, U_i) \) by extrapolation near the minimum point of the pair potential. Analytical determination of the parameters of the potential is possible in the case of table-set equidistant \( U_{r_i} \) at three points near the minimum

\[
r_1 = r_2 - h; \quad r_3 = r_2 + h; \quad r_1 < r_{\text{min}} < r_2.
\]

From three equations (1) at points \( r_i \) \( (i = 1, 2, 3) \), we get

\[\begin{align*}
C &= \frac{-\lambda_2 - \sqrt{\lambda_2^2 - 4\lambda_1\lambda_2}}{2\lambda_1}, \\
A &= \left( \frac{U_1 + \frac{C}{r_1^6}}{r_1^6} \right)^{-r_1}, \\
\alpha &= \frac{1}{r_2^6} \ln \left[ \frac{1}{A \left( \frac{U_2 + \frac{C}{r_2^6}}{r_2^6} \right)^{-r_1}} \right],
\end{align*}\]

where

\[
\lambda_1 = \left[ 1 - \left( \frac{r_2^6}{r_1 r_3} \right)^6 \right]^{-12}, \quad \lambda_2 = (2U_2 - U_3(r_2/r_1)^6 - U_1(r_2/r_3)^6)r_2^{-6}, \quad \lambda_3 = U_2^2 - U_1 U_3.
\]

Formula (2) represents the van der Waals constant for pairs of inert gas atoms.

For a homoatomic crystal (e.g., a cured inert gas) in the ground state in the approximation of the first coordination sphere: \( U_{c1} = N_1 U(r) \), where \( N_1 \) is the number of nearest neighbors. Considering that when \( r \gg r_{\text{min}} \) the first term in (1) rapidly approaches zero, we will assume
Table 1. Calculation results $C_6$ (in atomic units).

|     | He    | Ne    | Ar    | Kr    | Xe    |
|-----|-------|-------|-------|-------|-------|
| He  | 1.27  | 2.67  | 8.12  | 11.3  | 21.0  |
|     | 2.11  | 4.46  | 13.54 | 18.9  | 35.0  |
|     | 1.44–1.47 | 3.03–3.20 | 9.43–10.10 | 13.0–14.2 | 18.8–21.4 |
| Ne  | 6.24  | 21.4  | 29.2  | 23.8  |       |
|     | 10.40 | 35.7  | 48.7  | 35.0–39.7 |       |
|     | 6.48–7.27 | 19.5–22.0 | 26.5–30.9 | 38.1–46.5 |       |
| Ar  | 69.2  | 78.6  | 143.1 |       |       |
|     | 115.4 | 131.0 | 238.5 |       |       |
|     | 63.8–70.8 | 88.6–100.0 | 130.0–151.0 |       |       |
| Ar  | 69.2  | 78.6  | 143.1 |       |       |
|     | 115.4 | 131.0 | 238.5 |       |       |
|     | 63.8–70.8 | 88.6–100.0 | 130.0–151.0 |       |       |
| Kr  | 139.9 | 241.2 | 402.0 |       |       |
|     | 133.1 | 402.0 |       |       |       |
|     | 124.0–142.0 | 183.0–215.0 |       |       |       |
| Xe  |       |       |       |       | 335.2 |
|     |       |       |       |       | 558.6 |
|     |       |       |       |       | 272.0–325.0 |

that the short-range part of the interaction potential is determined only by the first coordination sphere. Then, for the crystalline potential, we get

\[ U_c(r) = N_1 A \exp(-\alpha r) - C_6 r^{-6}, \]  
\[ C_6 C_6 = C_6 \left( N_1 + \frac{N_2}{\beta^6} + \frac{N_3}{\gamma^6} + \cdots \right), \]

where $N_i$ is the number of particles in the $i$-th coordination sphere; $\beta$, $\gamma$, $\ldots$ show how many times the distance from the selected particle to the particle in the $i$-th sphere is greater than the equilibrium radius.

By minimizing (5), we can obtain the lattice constant value $r_0 = a$ ($a$ is the lattice constant) and the energy of the entire crystal as a function of parameter $a$, but we did not endeavour to do so. In this case, crystalline van der Waals interaction constant (6) is an analogue of the Madelung constant for ionic crystals, describing the long-range part of the interaction potential of solidified inert gases crystals. In the second part of this paper, we present the solution to the inverse problem of determining the atom–atom interaction dispersion constants of alkali metal inert gases. To do this, we use the modified potential of Lennard-Jones. This choice is due to the fact that the two parameters which fully determine the potential of Lennard-Jones and which, for convenience, we wrote in a slightly different form are widely known and represent dissociation energy $E_0$ and equilibrium radius $r_0$ [6]:

\[ U_{LJ} = E_0 \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^{6}. \]

In this case, the potential has a minimum when $r = r_0$ and vanishes when $r = 2^{-1/6}r_0$. 
Table 2. Calculation results $C_6$ (in atomic units).

|   | Ne  | Ar  | Kr  | Xe  |
|---|-----|-----|-----|-----|
| Li | 335.1 | 166.3 | 208.8 | 319.3 |
|   | 558.6 | 277.2 | 348.0 | 532.2 |
|   | 272.0–325.0 | 171.0–177.0 | 255.0–262.0 | 402.0–414.0 |
| Na | 44.5 | 150.6 | 239.0 | 361.3 |
|   | 74.28 | 251.0 | 398.4 | 602.2 |
|   | 46.0–137.0 | 184.0–508.0 | 273.0–737.0 | 430.0–1130.0 |
| K  | 175.7 | 282.4 | 470.7 | 516.1 |
|   | 292.9 | 292.9 | 406.0 | 860.2 |
|   | 73.8–83.9 | 292.0–318.0 | 432.0–469.0 | 680.0–737.0 |
| Rb | 169.4 | 222.3 | 405.0 | 578.6 |
|   | 282.4 | 370.6 | 675.1 | 964.4 |
|   | 78.0–94.2 | 310.0–352.0 | 460.0–518.0 | 725.0–813.0 |
| Cs | 139.0 | 230.3 | 458.1 | 647.3 |
|   | 261.5 | 383.8 | 763.5 | 1078.8 |
|   | 86.0–99.2 | 345.0–379.0 | 515.0–561.0 | 814.0–886.0 |

Table 3. Calculation results $C_8$ (in atomic units).

|   | He  | Ne  | Ar  | Kr  | Xe  |
|---|-----|-----|-----|-----|-----|
| He | 40.0 | 97.6 | 355 | 582.5 | 1260 |
|   | 14.2 | 34.0 | 146 | 206.0 | 35.0 |
| Ne | 214.1 | 935.9 | 1437 | 1227 |
|   | 82.0 | 330.0 | 440 | 700 |
| Ar | 3492.6 | 4268 | 8587 |
|   | 1345.0 | 1900 | 3150 |
| Kr | 7991 | 15921 | 2700 | 4600 |
| Xe | 23 167 |
|   | 7000 |

Calculations show that for almost all pairs of atoms, the dispersion constant, which is equal in this case to

$$C_6 = 2E_0r_0^6,$$

(7)
is far from its experimental values. In addition, using the Lennard-Jones potential to determine a variety of thermophysical characteristics of condensed media also leads to a significant deviation from the experiment [7, 8].

We set $U_{LJ}$ potential modification problem in this way to preserve the advantages of the model, on the one hand, and to improve it, on the other hand, in order to more accurately describe the area located near the minimum point and the asymptotics for $r \gg r_0 = r_{\text{min}}$. 


Table 4. Calculation results $C_8$ (in atomic units).

|   | Ne  | Ar  | Kr  | Xe  |
|---|-----|-----|-----|-----|
| Li | 31 000 | 14 800 | 17 200 | 26 300 |
|    | 2270 | 9430 | 13 000 | 22 000 |
| Na | 4462 | 13 400 | 20 500 | 31 000 |
|    | 2900 | 12 700 | 16 000 | 26 500 |
| K  | 15 700 | 15 700 | 25 200 | 49 800 |
|    | 5820 | 24 000 | 33 000 | 53 000 |
| Rb | 15 100 | 21 500 | 40 600 | 58 000 |
|    | 7350 | 29 000 | 39 000 | 62 000 |
| Cs | 12 400 | 22 200 | 47 700 | 67 430 |
|    | 9580 | 41 000 | 53 000 | 85 000 |

We use the following form of potential, the Lennard-Jones modified potential

$$U_M = E_0 \left[ \alpha \left( \frac{r_0}{r} \right)^{12} - \beta \left( \frac{r_0}{r} \right)^6 - \gamma \left( \frac{r_0}{r} \right)^8 \right].$$

It is obvious that

$$C_6 = \beta E_0 r_0^6, \quad C_8 = \gamma E_0 r_0^8.$$

Based on the conditions

$$U_M(r_0) = -E_0 = E_0(\alpha - \beta - \gamma), \quad U_M'(r_0) = -12\alpha + 6\beta + 8\gamma = 0,$$

we get

$$\beta = 3(\alpha - 1), \quad \gamma = 2(2 - \alpha).$$

In general, to interpolate the interaction potential over a model containing 5 parameters, it is necessary to have 5 pairs of values $r_i$ and $U(r_i)$, $i = 1, 2, 3, 4, 5$, which for systems with closed electron shells can be taken from experiment or theoretical calculations.

In this paper, two of these parameters ($E_0$ and $r_0$) are selected from tabular data [6].

Two more equations for determining potential parameters (10) relate the parameters $\alpha, \beta$ and $\gamma$ to each other (11). It is obvious that $1 < \alpha < 2$.

The last of the parameters can be obtained by assuming $\beta = \gamma$ since there is the same relative contribution of the multipolar corrections. We get

$$\alpha = 1.4; \quad \beta = \gamma = 1.2.$$

Taking into account (9) and (12), using tabular data [6], constants $C_6$ and $C_8$ are calculated.

Tables 1–4 show the results of calculations using formula obtained in the proposed model and the experimental data. In tables 1 and 2 the upper values are our calculations, the second line is $C_6 = 2\alpha r_0^6 E_0$, the Lennard-Jones–van der Waals constant, the third line is the experimental data; tables 3 and 4 the upper values are our calculations, the second line is the experimental data.

4. The discussion of the results

As shown in tables 1–4, there is a strictly monotonous growth of constants $C_6$ and $C_8$ in the lines (from left to right), columns and diagonals (from top to bottom).
The largest deviations from the experiment in the calculation of $C_8$ for He–Xe and Li–Ne are most likely due to the neglect in the proposed model of the redistribution of electron density. The results of the calculations generally coincide with the experiment. However, it should be noted that if the dispersion constants of inert gases atoms interaction calculated in the presented model of $C_6$ are usually less than the experimental values, the values of $C_8$ are greater. In our opinion, this is due to the fact that the model does not take into account the contribution of the dispersion of constant $C_{10}$ to the interaction potential.

5. Conclusions

Thus, for the first time, based on the model potential (1), a formula for determining the van der Waals constant was obtained and the possibility of correctly describing the long-range part of the interaction potential of solidified inert gases crystals was indicated. Using the modified Lennard-Jones potential and experimental data on the dissociation energy $E_0$ and the equilibrium radius $r_{min}$, the dispersion constants of systems of inert gas pairs and an alkali metal–inert gas are determined.

Acknowledgments

This work was supported in the framework of the base part of the task for KBSU from the Ministry of Science and Higher Education of the Russian Federation for years 2017–2019 (project No. 3.8382.2017).

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