REALISTIC INTERATOMIC POTENTIAL FOR MD SIMULATIONS

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ABSTRACT. The coefficients of interatomic potential of simple form Exp-6 for neon are obtained. Repulsive part is calculated ab-initio in the Hartree-Fock approximation using the basis of atomic orbitals orthogonalized exactly on different lattice sites. Attractive part is determined empirically using single fitting parameter. The potential obtained describes well the equation of state and elastic moduli of neon crystal in wide range of interatomic distances and it is appropriate for molecular dynamic simulations of high temperature properties and phenomena in crystals and liquids.

1. Introduction

Investigation of strongly anharmonic nonlinear atomic systems by molecular dynamics (MD) method at high temperatures, pressures, or study of systems affected by large amplitude excitations requires high accuracy of interatomic potential (IP). Series expansion of the IP in the displacements of atoms from equilibrium positions is widely used both in phonon theory and in MD simulation [11, 6]. Usually, fourth-order anharmonisms or lower-order ones can be taken into account because of complexity of expansion coefficients calculation. As an alternative, realistic potential method is used [17, 22, 21], in which exact equations of motion of atoms are solved using IP of concrete substance without series expansion. Owing to that, all-order anharmonisms are taken into account automatically. This advantage of realistic potential method is especially useful in the MD simulation of soliton solutions where atoms approach each other closely. Realistic IP should have simplest form to reduce calculation expenses as well as it must describe precisely the properties of the substance under extreme conditions. The aim of this paper is to obtain such IP.

Conventional way of realistic IP determination is empirical fitting to the properties of gas or a crystal near the equilibrium point [1, 3]. However, such potentials become unreliable at small interatomic distances like to that arising in soliton waves. The properties of highly compressed matter (e.g., for neon up to 1 Mbar [13]) could give an information for obtaining all-distance reliable IP. However, the set of properties, which can be measured accurately at megabar pressures is restricted strongly. Practically, the equation of state and bulk modulus only may be included in this set [13, 1]. For $C_{4k}$ modules the precision worsens drastically even at kilobar pressures [14, 28]. There is insufficiency of empirical information for fitting all the parameters of IP, and ab-initio calculation is required.

Realistic IP via interatomic distance is obtained in present work for the crystal and dimer of neon. Repulsive part of the potential is calculated ab-initio in
Hartree-Fock approximation using the basis of localized atomic orbitals orthogonalized exactly on different lattice sites. Attractive part is chosen to have standard Van-der-Vaals form of \( C_r^{-6} \) with single empirical parameter \( C \). Used approximations and calculation details are described in the section 2. In the section 3 repulsive part of IP is interpolated by exponential function of interatomic distance (Exp-6 potential) and the IP parameter are determined. Experimental verification of the IP obtained is performed in the section 4 using the data concerning equation of state [3, 2] and elastic moduli [4, 5, 3, 14, 25, 12] of compressed neon. The IP calculated is found to be in a good consistence with the experiment in whole range of pressure.

2. Ab-initio calculation of repulsion potential

In MD simulations by realistic potential method the problem is divided into two stages. The former is quantum-mechanical calculation of the IP at electron level, with interatomic distance considering as a parameter. The latter is solving equations of motion of atoms using the IP obtained. This division is correspondent to adiabatic approximation when atoms and electrons motion is described separately [8].

Since pair collisions of atoms have maximal probability, we concentrate the attention on the dimer of neon, and define the IP as a cohesive energy of the dimer. Three-atom forces can be taken into account as a correction to the two-atom ones using incremental expansion [20]. The estimation of [20] shows three-atom force contribution to be small.

In Hartree-Fock approximation short-range repulsive part of IP is expressed through one-electron density matrix. We don’t use hard core approximation. Rearrangement of all electron shells is allowed as interatomic distance is altered.

Localized basis of atomic orbitalls orthogonalized exactly (by Lovdin procedure [15]) on different lattice sites is used. In this basis one-electron density matrix has the form

\[
\rho(r'|r; \{1\}) = 2 \sum_{l}s \phi_s(r - l) \phi_s^*(r - l) - \sum_{l',s'} \phi_{s'}(r' - l') P_{s's}^{l'l} \phi_{s'}^*(r - l),
\]

(2.1)

where \( \phi_s(r - l) = |ls > \) is wave function of electron in isolated atom (atomic orbital), \( l \) and \( l' \) are radius-vectors of lattice sites, \( s \) numerates occupied states of the atom, \( P \) is orthogonalizing matrix, \( I \) is unit matrix, \( S \) is overlap integral matrix with the elements

\[
S_{s's'}^{l'l} = < l's' | ls >, l \neq l',
\]

(2.2)

\[
S_{s's}^{l'l} = 0; l = l'.
\]

We expand repulsive part of IP in the terms of small parameter such as the largest overlap integral \( S \). Usually, \( S << 1 \) in uncompressed crystal, and overlap integrals grow exponentially as interatomic distance is decreased. The IP is expressed through the products of elements of orthogonalizing matrix \( P \) and two-center Slater-Koster integrals. These integrals are atomic obital matrix elements of crystal hamiltoinial operators. The order in \( S \) for two-center integrals is estimated
using the theorem about average value. The elements of matrix $P = I - (I + S)^{-1}$ are expanded in powers of overlap integrals matrix $S$

$$P_{ss'}^{ll'} = S_{ss'}^{ll'} + O(S^2),$$

$$P_{ss'}^{ll} = -(S_{ss'}^{ll})^{ll'} + O(S^3).$$

The elements of matrix $P$ contain high-order terms along with the main ones proportional to $S$ and $S^2$.

Using the estimations described above, we expand the repulsive part of IP in powers of $S$

$$V_{sr} = E^{(0)} + W_2 + W_4 + W_6.$$ (2.4)

Here $E^{(0)}$ is the energy of interatomis interaction if orthogonalizing of neighbor atoms orbitals is neglected, $W_2, W_4, W_6$ are orthogonalizing corrections. Series expansion in $S$ begins for them from the second, the third, and the sixth powers respectively. Due to the presence of matrix $P$, orthogonalizing corrections contain high-order terms in $S$ along with the main ones.

In the equation 2.4

$$E^{(0)} = \sum_{ls} \sum_{m,m' \neq l} (ls|V_{en}^m + V_{a}^m + V_{ex}^m|ls) + U_{nn}.$$ (2.5)

The first term in equation 2.5 consists of two-center integrals. They are atomic orbital matrix elements of electron-ion interaction potential $V_{en}^m$, of neutral isolated atom potential $V_{a}^m$, of electron-electron exchange interaction potential $V_{ex}^m$ respectively. The second term is the energy of nucleus-nucleus interaction. Electron-ion interaction potential has the form

$$V_{en}^m = V_{en}(r - m) = -Ze^2/|r - m|.$$ (2.6)

Neutral isolated atom potential is

$$V_{a}^m = V_{a}(r - m) = V_{en}(r - m) + 2 \sum_t <mt|v_\epsilon|mt>,$$ (2.7)

where

$$<mt|v_\epsilon|mt> = \int \varphi_t^*(r' - m)v_\epsilon(r - r')\varphi_t(r' - m)dr',$$

$$v_\epsilon(r - r') = e^2/|r - r'|.$$

Action of electron-electron exchange interaction potential on wave function is defined as

$$<ls|V_{ex}^m|ls> = - \sum_t <ls, mt|v_\epsilon|ls, mt>.$$ (2.8)

In the equation 2.4 orthogonalizing corrections, $W_2, W_4, W_6$, are of the form
\[ W_2 = -2 \sum_{\lambda \neq \nu} \sum_{l \neq l'} P_{ss'}^{ll'} < l's'|V_a^l + V_{cx}^l|l\lambda > \]
\[ + \sum_{l s s' t', \lambda \neq \nu} P_{ss'}^{ml} P_{ll'}^{lm} < l's', m\lambda'|v_c|m\lambda, l\lambda >; \]
\[ (2.9) \]
\[ W_4 = \sum_{l s s' t'} P_{ss'}^{ll'} \{ 2 < l's', l\lambda'|V_c|l\lambda > - < l's', l\lambda'|V_c|l\lambda, m\lambda > \} - \]
\[ -2 \sum_{l s s'} P_{ss'}^{ll'} < l's'| \sum_{m \neq 0} (V_m^m + V_{cx}^m)|l\lambda > + \]
\[ + 2 \sum_{l s s' t', \lambda \neq \nu} \{ P_{ss'}^{ll'} P_{ll'}^{mm} < l's', m\lambda'|v_c|m\lambda, l\lambda > + P_{ss'}^{ml} P_{ll'}^{lm} < l's', m\lambda'|v_c|m\lambda, m\lambda > \} + \]
\[ + 2 \sum_{l s s' t', \lambda \neq \nu} P_{ss'}^{ml} P_{ll'}^{lm} \{ 2 < l's', l\lambda'|v_c|m\lambda, m\lambda > - < l's', l\lambda'|v_c|m\lambda, m\lambda > \} + \]
\[ (2.10) \]
\[ + 4 \sum_{l s s' t', \lambda \neq \nu} P_{ss'}^{ml} P_{ll'}^{lm} \{ 2 < l's', l\lambda'|v_c|m\lambda, m\lambda > - < l's', l\lambda'|v_c|m\lambda, m\lambda > \}; \]
\[ (2.11) \]
\[ W_6 = - \sum_{l s s' t', \lambda \neq \nu} P_{ss'}^{ll'} P_{ll'}^{mm} < l's', m\lambda'|v_c|l\lambda, m\lambda >. \]

Since the orthogonalizing corrections grow exponentially as the interatomic distance is decreased it is impossible to say what correction may be neglected. It should be checked for each substance under consideration.

Using the method described, we calculate repulsive part of IP, \( V_{sr} \) (equation 2.4), for neon dimer as a function of interatomic distance \( d \). Atomic orbitals from Clementi-Roetti set \( [10] \) are used as a basis. Hartree system of atomic units \( \hbar = e = m_e = 1 \) is applied. The calculation shows the terms \( E^{(0)} \) and \( W_2 \) in equation 2.4 to have the same order of magnitude and opposite signs. These terms are found to give major contributions to the IP. The \( W_4 \) correction consists of 0.02 per cent of the IP at equilibrium interatomic distance \( d_0 \). Further, the \( W_4 \) does not exceed of 1 per cent of the IP up to \( d \sim 0.75d_0 \). Finally, at small \( d \), like to that arising in soliton waves (for \( d \) above 0.6-0.75 \( d_0 \)), the \( W_4 \) becomes about 2-4 per cent of the IP. The contribution of \( W_6 \) to the IP is small negligibly (0.002 per cent) in whole range of \( d \) under consideration.

3. Determination of interatomic potential parameters

We interpolate calculated points \( V_{sr}(d) \) by exponential function of interatomic distance using least square method by the formula

\[ V_{sr}(d) = A_0 \exp(-\alpha(x - 1)); \]
\[ (3.1) \]
with two unknown parameters \( A_0 \) and \( \alpha \). Experimental equilibrium interatomic distance for neon dimer \( z_0 = 5,8411 \) a.u. \( [8] \) is used as the third parameter of the IP. The parameters are found to be \( A_0 = (1,1384 \pm 0,0002) \cdot 10^{-4} \) a.u., \( \alpha = 13,6407 \pm 0,0037 \). Interpolation error is 4-1 per cent of \( V_{sr} \) when the \( d \) is altered from equilibrium one to 0.6\( z_0 \).
Adding the attractive part, we express the IP in standard Exp-6 form

\[ V(d) = A_0 \exp(-\alpha(x-1)) - Cd^{-6}; \]
\[ x = d/z_0. \]

(3.2)

A single unknown parameter \( C \) remains in attractive part of IP. We propose to fit the \( C \) to experimental equilibrium interatomic distance. Using of equilibrium data is considered to be reliable at all interatomic distances since the attraction is essential near the equilibrium only while ab-initio calculated repulsive part dominates at small \( d \).

For MD simulation of lattice dynamics, it is possible to fit the \( C \) to experimental data for dimer at \( T=0 \) K because the temperature effects will be taken into account explicitly, at the stage of equations of motion solving. In this case, for neon \( C=10,7293 \) (experimental equilibrium interatomic distance in the dimer is \( z_0=5,8411 \) a.u. [18]). Calculated cohesive energy of dimer is \( E_{coh} = -1,4497 \cdot 10^{-4} \) a.u., experimental one is \( E_{coh} = -1,338 \cdot 10^{-3} \) a.u. [18]. The discrepancy is 7 per cent of experimental value.

For calculating static properties of a crystal at finite temperature, e.g., equation of state, elastic modules, it is better to fit the \( C \) to experimental data for a crystal at the same temperature. Such determination allows one to take into account implicitly three-atom forces, temperature effects, zero-point oscillations, and other effects omitted at the stage of IP calculating. In this case, for neon \( C=7,4030 \) (experimental equilibrium interatomic distance in the crystal is \( d_0=5,9647 \) a.u. at \( T = 4,25 \) K [4]). Calculated cohesive energy of uncompressed crystal is \( E_{coh} = -6,7620 \cdot 10^{-4} \) a.u. per atom, experimental one is \( E_{coh} = -(7,35 \pm 0,03) \cdot 10^{-4} \) a.u. [16]. The discrepancy is 7.6 per cent of experimental value.

4. Results and discussion

Interatomic potential of neon is given in the figure 1 as a function of interatomic distance \( d \). The IP calculated by equation 3.2 for dimer is plotted by solid curve. Van-der-Vaals constant \( (C=10,7293) \) is fitted to experimental equilibrium interatomic distance in dimer [18].

"Experimental" IP obtained in [13] is denoted by solid circles. This IP had been determined by interpolating experimental data \( p(V) \) (measured at 300 K) by the formula Exp-6. The interpolation had been performed in theoretical model taking thermal pressure and zero-point oscillations into account explicitly, excluding them from the definition of IP. It allows us to compare the 300 K data of [13] with our zero-temperature result. Three-atom forces didn’t include explicitly in the model of [13]. However, in [13], the effect of these forces is taken into account implicitly through fitting the IP to experimental data for a crystal. In our calculation three-atom forces are omitted because of fitting to dimer data. The agreement of calculated IP and experimental one indicates that three-atom forces in neon are small at the pressures up to 1Mbar.

Two remaining curves in the figure 1 are interatomic potentials of neon obtained by fitting to experimental data using Lennard-Jones potential (6-12 formula)

\[ V(x) = \varepsilon(-2/x^6 + 1/x^{12}) \]
\[ x = d/z_0, \]
where $\varepsilon$ and $z_0$ are fitting parameters. Dashed curve is the IP obtained using corresponding-states law fitted to vapor-pressure ratio of isotopic liquid [8]. Dashed-dotted curve is the IP fitted to experimental lattice constant and cohesive energy of crystal neon at $p = 0$, $T = 0$ K [8]. Fitting to equilibrium crystal properties leads to bad describing the IP for compressed crystal. Fitting to compressed gas properties gives the values of the IP close to experimental ones at moderated pressures.

Using the IP obtained (eq. 3.2) we calculate the equation of state $p(V)$ for solid neon. Calculated pressure $p$ against fractional volume is given in the figure as solid curve. Van-der-Vaals constant is fitted to experimental equilibrium interatomic distance $d_0 = 5.9647$ a.u. measured for crystal neon at $T = 4.25$ K, $p = 0$ [4].

Experimental points $p(V)$ from [13] ($T = 300$ K) and [2] ($T = 4.2$ K) are also given in the figure. At the pressures below 20 kbar theoretical curve is in a good agreement with the experimental points of [2]. At moderated pressures theoretical curve deviates from experimental points of [13] by 4 per cent. This deviation caused, mainly, by neglecting of thermal pressure in our calculation. Figure shows temperature sensitivity of the equation of state to be small.

We calculate bulk modulus of solid neon by means of the IP obtained. Van-der-Vaals constant is fitted to experimental equilibrium interatomic distance in the crystal [4]. Calculated bulk modulus $B$ via the pressure $p$ is given in the figure as solid curve. Experimental points obtained in [2] at $T = 4.2$ K are plotted as solid symbols. Bulk modulus is seen to be more sensitive to the approximations used. Growing when the $p$ is enhanced, the difference between calculated $B$ and measured one becomes about 7 per cent of experimental $B$ at $p = 20$ kbar. Incorrect taking three-atom forces into account at moderated pressures is seems to contribute mainly in this discrepancy. In our calculation three-atom forces (and zero-point oscillations too) are taken into account implicitly, by fitting the IP to experimental data for uncompressed crystal. Thus, calculated $B$ agrees with experimental one at small pressures only (to 8 kbar). One can’t determine correctly the dynamics of alteration of three-atom forces with enhancing of pressure. It is the cause of growing the deviation of calculated $B$ from measured one.

We calculate elastic modules $C_{ik}$ using the IP obtained with Van-der-Waals constant fitted to crystal experimental data [4]. Calculated modules and experimental ones are given in table for uncompressed solid neon at low temperatures. Isothermic modules had been obtained in static measurements [4]. Adiabatic modules had been measured in ultrasonic and neutron scattering experiments [4, 14, 25, 12]. However, the difference between isometric modules and adiabatic ones is negligible at the temperatures under consideration (see, e.g., [25]).

The $C_{ik}$ modules are seen to be more sensitive to the measurement method and calculation approximations. The difference between theoretical and experimental values of $C_{11}$ and $C_{44}$ is about 10 per cent of experimental values for most accurate experiment [25]. The agreement is better for $C_{12}$ modulus (the discrepancy is about 2 per cent [27]). The deviation from Cauchy relation $\delta = (C_{44} - C_{12})/C_{12}$ is also given in table. Cauchy violation is the measure of deviation of the IP from spherical symmetry. The $\delta = 0, 11 \pm 0, 03$ in [27], while it falls into experimental error bar in other experiments listed in the table. Cauchy relation takes place for our calculation results because spherical symmetry form of the IP is supposed in theoretical model. Small value of experimental $d$ indicates that spherical symmetry approximation for IP is valid for uncompressed neon at least. For another rare gas crystal, krypton, experiment [23] shows Cauchy relation to satisfy well under
Table 1. Elastic modules of solid neon

| Ref. | $T, \text{K}$ | $B, \text{kbar}$ | $C_{11}, \text{kbar}$ | $C_{12}, \text{kbar}$ | $C_{44}, \text{kbar}$ | $\delta = \frac{(C_{44}-C_{12})}{C_{12}}$ | Method |
|------|--------------|----------------|-----------------|----------------|----------------|----------------|--------|
| 1    | 4.25         | 11.12±0.12     | -               | -              | -              | -              | -      |
| 2    | 4.2          | 11.0±0.1       | -               | -              | -              | -              | -      |
| 3    | 4            | 11.36±0.26     | -               | -              | -              | -              | Static measurements $p(V)$ |
| 4    | 4.7          | 12.1±0.4       | 16.9±0.5        | 9.7±0.4        | 10.0±0.3       | 0.03±0.07      | Inelastic neutron-phonon scattering |
| 5    | 5            | 11.2±0.5       | -               | -              | -              | -              | Ultrasonic velocity meas. |
| 6    | 4.7          | 12.1±0.4       | 16.9±0.5        | 9.7±0.4        | 10.0±0.3       | 0.03±0.07      | Inelastic neutron-phonon scattering |
| 7    | 5            | 11.24±0.17     | 16.61±0.17      | 8.55±0.21      | 9.52±0.05      | 0.11±0.03      | Inelastic neutron-phonon scattering |
| 8    | 6            | 11.52±0.3      | 16.49±0.3       | 9.03±0.3       | 9.28±0.08      | 0.03±0.04      | Inelastic neutron-phonon scattering |

Calc.: 0 10.76 14.95 8.67 8.67 0 0 0

Ab-initio calc.

pressure up to 80 kbar. Moreover, for MgO the Cauchy violation is measured to drop with enhancing pressure up to 200 kbar [24].

Unlike to $C_{ik}$ modules, bulk modulus $B$ is less sensitive to measurement method and calculation approximations. The discrepancy of theoretical result and experimental one doesn’t exceed of 4 per cent and falls into experimental error frames.

5. Conclusion

Coefficients of realistic IP of simple form Exp-6 are obtained for neon by ab-initio calculation of repulsive part in Hartree-Fock approximation in the basis of atomic orbitals orthogonalized exactly on different lattice sites. Attractive part is determined empirically using single fitting parameter, Van-der-Vaals constant $C$. For fitting the $C$ it is enough to know experimental equilibrium interatomic distance in crystal (or dimer), i.e. high pressure experimental data is not required. The IP calculated is suitable for molecular dynamic simulations of high temperature and high pressure properties and phenomena in crystals and liquids due to simplicity of the form and precise describing experimental data in wide range of interatomic distances.

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Figure 1. Calculated IP and three potentials fitted to experimental data for neon (from [7, 13, 9] respectively).
Figure 2. Equation of state for solid neon (experiment from [2] (4.2 K) and [13] (300 K)).
Figure 3. Bulk modulus of solid neon (experiment from [2]).