

POTENTIALS OF INTERATOMIC INTERACTION IN MOLECULAR DYNAMICS

Alexander I. Melker

Department of Metal Physics and Computer Technologies, St. Petersburg State Polytechnic University,
Polytekhnicheskaya 29, 195251, St. Petersburg, Russia

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Abstract. In this contribution we have analyzed the principles lying at the basis of interatomic potentials which are used in molecular dynamics studies. The different types of potentials were considered: ab initio, semi-empirical, and empirical. The classical, ab initio, and bond-charge molecular dynamics were discussed.

1. INTRODUCTION

Over the course of the past half-century Molecular Dynamics has progressed from a small branch of scientific investigation to an independent science. The onset was done in 1955 when specialists in computational mathematics asked Enrico Fermi to set them a task which must satisfy three conditions:

- it must be interesting for physics,
- it has no analytical solution,
- it is not beyond the capacity of existent computers.

A computer allows to obtain an exact numerical solution, which helps to understand the kernel of the problem. After such a computer prompt, one can separate main and secondary factors, formulate the problem in a new fashion, and construct a simpler nonlinear equation having an analytical solution. As a rule, at that, there appears a new scientific direction with a lot of interesting computational and analytical results. Such new method of scientific investigation, the combination of analysis and computer simulations, becomes more and more important in a scientific discovery.

Molecular dynamics is a type of computer experiments where one assigns the law of interaction for N particles, initial and boundary conditions,

and then integrates numerically the equations of motion of N particles. At $N \gg 1$, the system has a statistical property. This allows to watch the motion of individual particles and observe dynamical structure of the system; and simultaneously calculate the average properties of the system with respect to time and ensemble of particles (energy, pressure, temperature, stress-strain diagrams, etc.). The calculated averages can and must be compared with experimentally observed values.

Therefore, once the problem for study was put, you have to choose the most appropriate method of numerical integration of differential equations of motion and the most appropriate law of interaction for the particles of a system studied. The methods of integration were considered thoroughly in [1]. Now we only mention that a real professional does not rely on numerous commercial programs because 'a person must know how the calculations are going on. If one does not understand how it is done, one sees only bare numbers, but their genuine significance is hidden in calculations' [2]. Just the same approach is valid to a greater extent for the choice of interaction law.

In this contribution we consider interatomic potentials which were deduced from the first principles as well as semi-empirical potentials and briefly empirical ones.

Corresponding author: Alexander I. Melker, e-mail: Newton@imop.spbstu.ru

2. THOMAS–FERMI ATOM

The atom model suggested by Thomas and Fermi (*L.H. Thomas, 1926; E.R. Fermi, 1927*) has become a classic and can be found in many books on quantum mechanics, e.g. in [3]. The model is based on two ideas: one of them is taken from quantum mechanics and another from electrostatics. The starting point of the quantum mechanical theory of an atom is Schrödinger's equation for electrons

$$H\Psi = E\Psi.$$

Here Ψ , E is the wave function and the total energy of all electrons respectively and the Hamiltonian has the form

$$H = \sum_j \frac{p_j^2}{2m} - Ze^2 \sum_j \frac{1}{r_j} + \sum_i \sum_{i < j} \frac{e^2}{r_{ij}}.$$

The first term gives the kinetic energy of electrons, the second one interactions of the electron with a nucleus, and the third describes interaction of the electrons with each other. In order to obtain the simplest description of electron motion, let us exclude the interaction of electrons with each other and with the nucleus. Then we obtain the model of free electrons in which Schrödinger's equation takes the form

$$\sum_j \frac{p_j^2}{2m} \Psi = -\frac{\hbar^2}{2m} \sum_j \Delta_j \Psi = E\Psi.$$

Let us write down the many-particle wave function Ψ as the product of one-particle functions ψ each of them being dependent on only one-electron coordinates

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_j \psi_j(\mathbf{r}_j).$$

Substitute this formula in the Schrödinger equation. The latter disintegrates into one-electron equations

$$-\frac{\hbar^2}{2m} \Delta_j \psi(\mathbf{r}) = E_j \psi(\mathbf{r}),$$

for which the sum of one-particle energies is equal to the total energy

$$\sum_j E_j = E.$$

We will investigate only a one-electron equation, so delete the index j .

The one-particle Schrödinger equation has the solution

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r}),$$

at that

$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}.$$

Here \mathbf{k} is any vector which does not depend on coordinates. Let us restrict the motion of electrons by volume V . In this case

$$\int_V |\psi(\mathbf{r})|^2 d\mathbf{r} = 1$$

and hence

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k}\mathbf{r}).$$

If we select the volume V as a cube with the side L and put the periodic boundary conditions

$$\psi(x+L, y, z) = \psi(x, y+L, z) =$$

$$\psi(x, y, z+L) = \psi(x, y, z),$$

we exclude the influence of a surface.

The periodic boundary conditions mean that an electron does not reflect going to a surface, but goes out the volume and simultaneously enters the volume through an opposite plane, e.g. in one-dimensional case the electron moves in a ring. By virtue of the boundary conditions

$$\exp(i\mathbf{k}(\mathbf{r} + \mathbf{L})) = \exp(i\mathbf{k}\mathbf{r}),$$

i.e.

$$\exp(i\mathbf{k}\mathbf{r}) = 1.$$

This means that

$$\mathbf{k} \cdot \mathbf{L} = 2\pi n,$$

where

$$n = 0, 1, 2, \dots$$

or

$$k_\alpha = \left(\frac{2\pi}{L} \right) n_\alpha, \quad \alpha = x, y, z, \quad n_\alpha = 0, 1, 2, \dots$$

are integers.

Consider how to interpret these results. The vector equation $\mathbf{r} \cdot \mathbf{k} = \text{const}$ defines a plane normal to the vector \mathbf{k} . On this plane the function

$\exp(i\mathbf{k}\mathbf{r})$ has a constant value, whereas along any straight line, which is parallel to the vector \mathbf{k} , the function changes periodically. For this reason, the function $\exp(i\mathbf{k}\mathbf{r})$ is termed a *plane wave* and the vector \mathbf{k} is referred to as a *wave vector*.

It follows from the boundary conditions that the wave vector can take only the values which components are integers of $2\pi/L$. One can define these mathematically allowed values as quantum numbers which characterize electron states in the system. Let us introduce \mathbf{k} -space and construct the lattice in this space, the knots of which are the allowed values of the wave vector. Since the electron energy is proportional to the wave vector squared, the lattice gives all the possible values of electron energy. Therefore, we can find the physical state of the system with the help of the geometrical scheme developed.

Suppose that the system contains N electrons. The electron energy has a minimum in the ground state. To obtain this state, it is necessary to fill $N/2$ cells of least energies, each cell having the volume $(2\pi/L)^3$ and containing two electrons with opposite spins. Since the energy does not depend on the direction of a wave vector, the filled cells create a sphere. The sphere is spoken of as *Fermi's sphere* and its radius k_F is known as the *Fermi wave vector* (*Enrico Fermi, 1926*). Therefore

$$\frac{N}{2} \frac{(2\pi)^3}{V} = 4\pi^3 \frac{N}{V} = \frac{4}{3} \pi k_F^3,$$

and hence the electron density of the system is

$$n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}.$$

Now introduce the potential energy $U(r)$. Taking into consideration this energy, one can write for any electron the following equality

$$\frac{\hbar^2 k_{\max}^2}{2m} + U(r) = \varepsilon_{\max}.$$

From this, it follows

$$k_{\max}^2 = \frac{2m}{\hbar^2} (\varepsilon_{\max} - U(r)).$$

Here ε_{\max} is the maximal value of the total energy. The total energy is constant if the system considered is in a stationary state, i.e. the electrons do not change their positions in an atom. Since any potential energy is defined as a value to which one

can add any constant value, it is reasonable to accept that $\varepsilon_{\max} = 0$. In this case

$$k_{\max}^2 = -\frac{2m}{\hbar^2} U(r),$$

and the problem is reduced to the question how to find $U(r)$.

With this purpose, refer to electrostatics. Let the electron density at the distance r from the atomic nucleus is equal to $n(r)$. Then the electrostatic potential $\varphi(r)$ produced by joint action of the nucleus and electrons satisfies Poisson's equation (*Siméon Denis Poisson, 1812*)

$$\Delta\varphi = 4\pi en(r),$$

at this $U(r) = -e\varphi(r)$.

Now we have two equations which incorporate the electron density; one equation is quantum one and another is Poisson's equation. Using the quantum equation, one can exclude the electron density from Poisson's equation and obtain so-called *Thomas–Fermi's equation*

$$\Delta\varphi = \frac{4e(2me)^{3/2}}{3\pi\hbar^3} \varphi^{3/2}.$$

It is reasonable to use the atomic units, i.e. to put $e = m = \hbar = 1$. Then

$$\Delta\varphi = \frac{8\sqrt{2}}{3\pi} \varphi^{3/2}.$$

The solution of this equation must satisfy the boundary condition in the immediate proximity to the nucleus, where the potential $\varphi(r)$ at $r \rightarrow 0$ must coincide with the nucleus potential $Z\varphi/r$, i.e. in the atomic units $r\varphi(r) \rightarrow Z$.

Let us find the derivatives of the expression $r\varphi(r)$

$$\frac{d(r\varphi)}{dr} = \varphi + r \frac{d\varphi}{dr},$$

$$\frac{d^2(r\varphi)}{dr^2} = r \frac{d^2\varphi}{dr^2} + 2 \frac{d\varphi}{dr}.$$

Since φ depends only on r , the Laplace operator reduces to

$$\Delta = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr},$$

so

$$\Delta\varphi = \frac{1}{2} \frac{d^2(r\varphi)}{dr^2}.$$

Denote

$$r\varphi(r) = Z\chi(r)$$

and rewrite Thomas-Fermi's equation in the form

$$\frac{3\pi\sqrt{r}}{8\sqrt{2}} \frac{d^2(Z\chi)}{dr^2} = (Z\chi)^{3/2}.$$

Introduce the dimensionless variable $x = r/a$. Since $dr^2 = a^2 dx^2$, we have

$$a = \left(3\pi / 8\sqrt{2}\right)^{2/3} = (9\pi^2 / 128Z)^{1/3} =$$

$$0.885Z^{-1/3},$$

and we come to the equation

$$\sqrt{x} \frac{d^2\chi}{dx^2} = \chi^{2/3}$$

with the boundary conditions $\chi = 1$ at $x=0$ and $\chi=0$ at $x \rightarrow \infty$.

The equation obtained has no parameters and defines the universal screening function, but, at the same time, the equation has no analytical solution, so one tabulates the function $\chi(x)$. The good approximation for $\chi(x)$ is

$$\chi(x) \cong \frac{1}{(1 + \alpha x)^2},$$

where $\alpha = 0.536$ (*T. Tietz, 1956*).

Return from the atomic units $e = m = \hbar = 1$ to ordinary ones. Since

$$r = ax = 0.885Z^{-1/3} a_0 x,$$

where $a_0 = \hbar^2/m\epsilon^2$ is the Bohr radius, we have

$$\varphi(r) = \frac{Ze}{r} \chi\left(\frac{Z^{1/3}}{0.885} \frac{r}{a_0}\right).$$

3. ELASTIC COLLISIONS OF ATOMS

Consider an elastic collision of two atoms. To characterize the collision completely, it is necessary to know their potential of interaction. It is well known that the interaction of two point electric charges e_1 , e_2 can be expressed by Coulomb's law (*Charles Coulomb, 1785*):

$$f = k \frac{e_1 e_2}{r^2}.$$

Here f is the interaction force, k is a constant depending on a unit system chosen. Denoting $e_1 =$

$Z_1 e$, $e_2 = Z_2 e$ and choosing $k = 1$, write down the interaction energy of two point charges $Z_1 e$, $Z_2 e$ as

$$U(r, Z_1, Z_2) = \frac{Z_1 Z_2 e^2}{r}.$$

Atoms are not point charges. Besides their nuclei, which dimensions can be ignored, they have electrons. If the distance between the nuclei of both atoms during an elastic collision becomes less than atom sizes, the electrons begin to influence on both nuclei in a similar manner. On the contrary, at a large distance between the nuclei exceeding atom sizes significantly, the electrons screen the nuclei and, as a result, the atoms do not interact. Consequently

$$U(r, Z_1, Z_2) = \frac{Z_1 Z_2 e^2}{r} \chi(r, Z_1, Z_2),$$

where the screening function must satisfy the following condition

$$\chi(r, Z_1, Z_2) \rightarrow \begin{cases} 1, & r \rightarrow 0 \\ 0, & r \rightarrow \infty \end{cases}.$$

If $Z_1 = Z_2 = Z$ one can take Thomas-Fermi's function as a screening one

$$\chi(x) \cong (1 + \alpha x)^{-2}, \quad x = r/a, \quad a = 0.885a_0 / Z^{1/3},$$

$$\alpha = 0.536. \quad \chi(x) \cong (1 + \alpha x)^{-2}.$$

Expanding the function in a Taylor series, one obtains

$$\frac{1}{(1 + \alpha x)^2} = 1 - 2\alpha x + 3(\alpha x)^2 - \dots$$

At small x the expansion coincides very closely with the exponent expansion

$$\exp(-2\alpha x) = 1 - 2\alpha x + 2(\alpha x)^2 - \dots, \quad 2\alpha = 1.07 \cong 1,$$

so

$$\chi\left(\frac{r}{a}\right) \cong \exp\left(-\frac{r}{a}\right), \quad a = \frac{a_0}{Z^{1/3}}.$$

For different atoms Bohr (*Niels Bohr, 1948*) has suggested to take

$$Z^{1/3} = \sqrt{Z_1^{2/3} + Z_2^{2/3}}.$$

The expression is proportional to the quadratic mean of the functions $Z^{1/3}$ of both charges. It should

be emphasized that the exact numerical solution for different atoms was obtained by Firsov (O. Firsov, 1957), and so Thomas-Fermi's potential with Firsov's screening function is referred to as *Thomas-Fermi-Firsov's potential*.

Let $r \rightarrow 0$. Then the electrostatic potential generated by joint action of the nucleus and electrons has the form

$$\varphi(r) \equiv \frac{Ze}{r} \left(1 - \frac{r}{a}\right) = \frac{Ze}{r} - \frac{Z^{4/3}}{a_0}.$$

Here the first term is the potential of a nucleus, and the second term represents the potential created by electrons in the origin of coordinates. One can see that the electrons screen the nucleus, so the interaction of nuclei screened is reduced in comparison with of bare-core interaction.

At large distance from a viewer ($r \gg a$), a nucleus together with electrons is a neutral atom. In many cases such system can be considered as a whole, e.g. when the thermal vibrations of atoms in a solid are studied. Besides, at $r \gg a$ the interaction of atoms is determined mainly by the screening function. Let us leave in the screened potential only the exponent. Then we obtain *Born-Mayer's potential* (M. Born, J.E. Mayer, 1932)

$$U(r) = A \exp(-r/a).$$

The authors used this potential to calculate properties of ionic crystals similar to NaCl. The coefficients A , a were found experimentally on the basis of compressibility tests. It turned out that for all 17 crystals studied the constant a was practically constant (variations were less than 6%), but the coefficient A changed in a rather large range. It is worth noting that Born-Mayer's potential does not follow directly from a theory; it is a volitional decision, but this approximation allows describe experimental data rather well.

From the conditions

$$E = U(r) = A \exp(-r/a), \quad E = \mu v^2 / 2,$$

where μ is the reduced mass and v is the relative velocity of colliding particles, one can find the minimum distance between identical atoms during collision

$$r_{\min} = b = a \ln(A/E) = a \ln(2A/E_1), \quad b = r_{\min}.$$

Here E_1 , E_2 is the kinetic energy of relative motion and the kinetic energy of a projectile atom respectively. It is supposed that another atom (target atom) was at rest before the collision. For different at-

oms, bearing in mind Coulomb's law, one assumes that

$$A = \sqrt{A_1 A_2}, \quad a = \frac{a_1 + a_2}{2}.$$

At last, at very low energies of colliding atoms, the hard-sphere model is used, where

$$U(r) = \begin{cases} \infty, & r < b \\ 0, & r \geq b \end{cases} \quad b = \frac{b_1 + b_2}{2}.$$

We have considered the main basic potentials of interatomic interactions which one uses to analyze elastic collisions. Besides, there are plenty of formulas which one uses to approximate experimental data; these formulas are also named 'potentials'. For example, if to take the Thomas-Fermi screening function in the form of exponent sum

$$\chi(x) = 0.35 \exp(-0.3x) + 0.55 \exp(-1.2x) + 0.10 \exp(-6.0x),$$

one obtains Molière's potential (G. Molière, 1947). The advantage of this potential lies in the fact that the potential allows obtain results in an analytical form. "There are 66 ways to compose the songs of tribes and all of them are right" (Joseph Rudyard Kipling, 1865–1936, Nobel Prize for literature in 1907).

For the first time, the exponential screening appeared in the theory of electrolytes (P. Debye, E. Hückel, 1923), the function $U(r) = A \exp(-r/a)/r$ in solid state physics has the name *screened Coulomb's potential*, in the meson theory it is labeled as *Yukawa's potential* (1935), at last, considering transmission of charged particles through the matter, it is spoken as *Bohr's potential* (1948). Independently of the name, in all the cases a separated particle is surrounded by the particle cloud of opposite sign. The charge density decreases exponentially, so the constant a is named screening length; in plasma physics it is referred to as *Debye length*.

4. SEMI-EMPIRICAL POTENTIALS

4.1. Hydrogen atom

Consider an atom of the simplest element, hydrogen, within the framework of classical mechanics. Hydrogen consists of a proton having the mass m_p and an electron with the mass m_e . Both particles attract to each other according Coulomb's law

$$U(r) = -\frac{e^2}{r}.$$

Here e is the electron charge, $r = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the particles. The problem of motion of two particles both in classical mechanics and in quantum one can be reduced to the problem of motion of one particle with a reduced mass in the central field $U(r)$ which is symmetric regarding an immobile center of coordinates. In our case $m_e \ll m_p = 1836m_e$ so

$$m = \frac{m_e m_p}{m_e + m_p} \cong m_e.$$

When moving in a central field, the conservation law for an angular momentum takes place

$$\mathbf{M} = \mathbf{r} \times \mathbf{p} = \text{const.}$$

Here $\mathbf{p} = m\mathbf{v}$ is the linear momentum of a particle, \mathbf{v} is its velocity. The vectors \mathbf{r} , \mathbf{M} are mutually normal, besides $\mathbf{M} = \text{const}$. It means that during particle motion its radius-vector is all the time on one plane, the plane being normal to the angular momentum. Such motion is called two-dimensional. Taking into consideration the motion character, let us pass to the cylindrical coordinates where the axis z is directed parallel to the angular momentum. The cylindrical coordinates are connected with the Cartesian coordinates by the formulas

$$x = r \cos \varphi \quad y = r \sin \varphi \quad z = z.$$

Since

$$\mathbf{M} = m \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z, \\ \dot{x} & \dot{y} & \dot{z} \end{vmatrix},$$

where \mathbf{i} , \mathbf{j} , \mathbf{k} are the dimensionless unit vectors directed along the axes x , y , z respectively, we have

$$M \equiv M_z = m(x\dot{y} - \dot{x}y) = mr^2\dot{\varphi} = J\dot{\varphi} = \text{const.}$$

$$M \equiv M_z = mr^2\dot{\varphi}.$$

Here $J = mr^2$ is the moment of inertia. Thus to describe two-dimensional motion in any plane $z = \text{const}$, it is enough to use two polar coordinates r , φ .

Write down the velocity square in the form

$$v^2 = (dl/dt)^2 = dl^2/dt^2.$$

From this it follows that kinetic energy is proportional to an arc element squared in an appropriate system of coordinates. In our case

$$dl^2 = dx^2 + dy^2 = dr^2 + r^2 d\varphi^2,$$

$$E_{kin} = \frac{m}{2} \left(\frac{dl}{dt} \right)^2 = \frac{m}{2} (\dot{r}^2 + r^2 \dot{\varphi}^2).$$

From the conservation law of angular momentum we find

$$\dot{\varphi} = \frac{M}{mr^2}.$$

Therefore

$$E_{kin} = \frac{m\dot{r}^2}{2m} + \frac{M}{2mr^2},$$

where $M/2mr^2$ is the centrifugal energy. As a result, we obtained the kinetic energy depending not only on a particle velocity but also on its coordinate. To remove inconsistency, write the total energy and rearrange the terms

$$E = E_{kin} + U(r) = \frac{m\dot{r}^2}{2m} + U(r) + \frac{M}{2mr^2} =$$

$$\frac{m\dot{r}^2}{2m} + U_M(r),$$

$$E = E_{kin} + U(r) = \frac{m\dot{r}^2}{2m} + \frac{M}{2mr^2} + U(r) =$$

$$\frac{m\dot{r}^2}{2m} + U_M(r).$$

Here

$$U_M(r) = U(r) + \frac{M}{2mr^2} = -\frac{e^2}{r} + \frac{M}{2mr^2}$$

is the effective potential energy. It follows that one can consider the radial part of motion as a one-dimensional motion in the field with an effective potential energy. A one-dimensional problem is simpler, but there appears the *pseudopotential* $M/2mr^2$. This result is the consequence of the theorem (*William Thomson (Kelvin), Peter Godfrey Tait, 1879*), according which any potential energy can be considered as a kinetic energy of hidden motions that are inaccessible to an observer.

4.2. Pair potentials

By analogy with a hydrogen atom consider a diatomic molecule in the framework of classical mechanics. At a short distance the atoms repel that excludes their overlapping, but at a long distance

they attract to each other creating a molecule from separate atoms. Thus forming a molecule resembles two-body problem. Probably due to this analogy, *Gustav Mie* (1903) suggested to describe interaction in a diatomic molecule with the help of potential similar to $U_M(r)$

$$U(R) = \frac{A}{R^n} - \frac{B}{R^m}.$$

Here $A, B > 0, n > m > 0$. This function has a minimum at

$$R_0 = \sqrt[n-m]{nA/mB}.$$

In the early twentieth century the *Mie potential* was widely used for calculation of physical properties of gases and solids. Then it was displaced by the *Morse potential*

$$U(R) = U_0 \{ \exp[-2\alpha(R - R_0)] - 2 \exp[-\alpha(R - R_0)] \}.$$

This function has the minimum $-U_0$ at the point $R = R_0$ and tends to zero when $R \rightarrow \infty$. Suggesting this potential *Philip M. Morse* (1929) proceeded from the following condition. The potential being substituted into Schrödinger's equation must describe exactly allowed energy levels of a diatomic molecule. The only region where the Morse potential does not agree with numerical calculations is in the vicinity of $R = 0$. Here the numerical solution tends to infinity whereas for all 21 molecules studied by Morse $U(0)$ falls in the range $10^2 - 10^4 U_0$. However, these values are so large that they do not influence on wave functions and energy levels. More details can be found in [4].

The simplest solids are crystals of inert gases with closed electron shells. Even when their atoms approach the minimal distance at which crystallization takes place, the electron wave functions of neighboring atoms do not overlap and the atom attractions remains of van-der-Waals nature. In the thirtieth years of the twentieth century Lennard-Jones did numerous calculations of kinetic properties of inert gases using the Mie potential with $m=6$. It turned out that experimental data could be equally well described, if one chose n in the interval from 9 to 12. For convenience of calculations, it was accepted that $n=12$. The 6-12 potential is called the *Lennard-Jones potential* and is written in the canonical form as

$$U(R) = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right].$$

Here $\sigma = (A/B)^{1/6}$, $\varepsilon = B^2/4A$, A, B are constants of the Mie potential. The parameter ε gives the depth of a potential well, the parameter σ defines the radius of repulsion and can be found from the condition $U(\sigma) = 0$.

When discussing collisions, we analyzed quite a few of repulsive potentials. Those potentials are used in molecular dynamics too. For example, combining the Born-Mayer potential with van-der-Waals attraction one obtains the *Buckingham potential* (1947)

$$U(R) = A \exp(-ar) - \frac{B}{r^6}.$$

We have considered only the most popular semi-empirical pair potentials; however the number of suggested potentials is very great. Strictly speaking, the efforts to find the best potential on the basis of experimental macroscopic data are inefficient because this inverse problem refers to the class of incorrect ones. In mathematics incorrectness means that either a solution does not exist, either it is not unique, or the problem is unstable (*Jacques Salomon Hadamard, 1923*).

4.3. Three-body interaction

Consider the problem of structure and stability of microclusters. Here the crucial question relates to their nucleation and growth. The corresponding calculations are divided into two groups: atomistic methods which, in general, employ two-body potentials and typically predict compact three-dimensional configurations as the energetically more stable ones; ab initio calculations for small metal clusters which often predict that two- or even one-dimensional configurations may be energetically preferred. Since the ab initio calculations are more reliable, the discrepancy means that pair potentials are inadequate for investigating this problem. The exit was found when both two-body and three-body interactions were incorporated into the potential energy of microclusters (T. Halicioglu, P.J. White, 1981).

The energy of interaction for a system of N particles can be expressed as

$$U = \frac{1}{2} \sum_{i,j} \sum_j u(\mathbf{r}_i, \mathbf{r}_j) + \frac{1}{6} \sum_{i,j} \sum_{j \neq k} \sum_k u(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k),$$

where $u(\mathbf{r}_i, \mathbf{r}_j)$ and $u(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$ represent two-body and three-body potentials, respectively. A Lennard-Jones type two-body potential was assumed to describe $u(\mathbf{r}_i, \mathbf{r}_j)$. The triple-dipole *Axilrod-Teller po-*

tential (B.M. Axilrod, E. Teller 1943) was considered for approximating the three-body interactions $u(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$:

$$u(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = c_3 \frac{1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k}{(r_{ij} r_{jk} r_{ik})^3}.$$

Here c_3 denotes the triple-dipole interaction constant which depends on the atomic species involved in the interaction and reflects the intensity of the three-body interactions; $\theta_i, \theta_j, \theta_k$ and r_{ij}, r_{jk}, r_{ik} are the angles and sides of the triangle formed by the three particles i, j , and k .

It turned out that the microclusters were three-dimensional for small values of c_3 . With an increase in the intensity of the three-body interactions there was a transition to, at first, two-dimensional and then to one-dimensional forms.

5. EMPIRICAL POTENTIALS

5.1. Born-Oppenheimer's approximation

The adiabatic approximation was developed by Born and Oppenheimer (*Max Born, Robert Oppenheimer, 1927*), but is rarely referred to by their names. It can be found only in some books on quantum mechanics, e.g. in [3]. Since a molecule consists of electrons and nuclei of atoms, the Hamiltonian of a molecule includes the kinetic energy of electrons and nuclei, the interaction energy between them and the energy of interactions with external fields. Having excluded the interaction with external fields, write down the Hamiltonian of a molecule in the form

$$H = \sum_e \frac{p_e^2}{2m_e} + \sum_n \frac{P_n^2}{2M_n} + U(r, R).$$

Here p_e, P_n is the linear momentum of an electron and a nucleus, respectively, m_e, M_n is, as before, the mass of an electron and a nucleus, r is the set of coordinates of all electrons, R is the set of coordinates of all nuclei, and $U(r, R)$ is the total potential energy, i.e. the sum of electrostatic interactions between all the particles. This energy depends on the geometrical arrangement of electrons and nuclei which is unknown *a priori*. The corresponding Schrödinger equation for such a system is

$$H\Psi(r, R) = E\Psi(r, R).$$

Suppose that the electrons are insensitive to the linear moments of the nuclei. In other words, since the nuclei are at least $\sim 10^4$ times heavier than

the electrons, the nuclei are moving so slowly that the electrons feel only the nucleus positions, but not their velocities. Since on the motion of electrons only the field of immobile nuclei has influence, one can write the separate Schrödinger equation for the electrons

$$H_{el}\psi(r; R) = E_{el}(R)\psi(r; R),$$

where $\psi(r; R)$ is the eigenfunction of the electronic Hamiltonian

$$H_{el} = \sum_e \frac{p_e^2}{2m_e} + U(r, R).$$

The eigenvalue $E_{el}(R)$ is the value which would be equal to the total energy if the nuclei having the geometrical arrangement R created an electrostatic field and mutually repelled, but did not move. In other words, the electron wave function $\psi(r; R)$ depends on electron coordinates, but nuclei coordinates are parameters, so that the electron energy $E_{el}(R)$ becomes a function of these parameters.

In order to separate the variables r and R , one can apply the Fourier method which was suggested, developed, and formulated by the following scientists: *Jean Le Rond D'Alembert (1749), Jean Baptiste Joseph Fourier (1821), Mikhail Vasilievich Ostrogradskii (1826)*. Suppose that the solution of the full Schrödinger equation can be written as a product of two functions

$$\Psi(r, R) = \psi(r; R)\chi(R).$$

Then

$$[H_{el}(r) + H_n(R)]\psi(r; R)\chi(R) = E\psi(r; R)\chi(R),$$

where

$$H_n(R) = \sum_n \frac{P_n^2}{2M_n}.$$

The operator $H_{el}(r)$ differentiates only with respect to electron coordinates, therefore

$$\begin{aligned} H_{el}(r)\psi(r; R)\chi(R) &= \chi(R)H_{el}(r)\psi(r; R) \\ &= \chi(R)E_{el}(R)\psi(r; R). \end{aligned}$$

As a consequence the full Schrödinger equation takes the form

$$[H_n(R) + E_{el}(R)]\psi(r; R)\chi(R) = E\psi(r; R)\chi(R).$$

The operator $H_n(R)$ differentiates with respect to nucleus coordinates and, hence, acts on the both functions, electronic and nuclear. At that

$$P \sim \partial^2 / \partial R^2, (\psi\chi)'' = \psi''\chi + 2\psi'\chi' + \psi\chi''.$$

If the electron wave function changes very slowly at the change of nuclear coordinates, then its derivatives with respect to the parameter R are small. Therefore

$$(\psi\chi)'' \cong \psi\chi'', H_n(R)\psi(r;R)\chi(R) = \psi(r;R)H_n(R)\chi(R).$$

Having substituted in the full equation, one obtains

$$[H_n(R) + E_{el}(R)]\chi(R) = E\chi(R).$$

Thus instead of one Schrödinger equation for electrons and nuclei, we have now two equations: one for electrons and another for nuclei

$$\left. \begin{aligned} H_{el}\psi(r;R) &= E_{el}(R)\psi(r;R) \\ [H_n(R) + E_{el}(R)]\chi(R) &= E\chi(R) \end{aligned} \right\}.$$

Both equations are known as *Born–Oppenheimer's equations* (Max Born, Robert Oppenheimer, 1927). They allow separate the problem into two: nuclei motion without regard space distribution of electrons and electron motion in the field of immobile nuclei. It should be realized that both equations are *approximate*. Any solution of the equation for electrons depends only on nuclei coordinates, but not on their velocities. In turn any solution of the equation for nuclei depends only on the total energy of electrons, but not on their coordinates. In essence excluding from the equations for nuclei the electron wave function, we averaged this equation over electron coordinates. Therefore, Born–Oppenheimer's equation for nuclei is not only *approximate equation*, but also *averaged* one. Such approximation frequently is spoken of as *adiabatic* because the electrons rearrange themselves at change of nuclei position without energy exchange, i.e. adiabatically.

5.2. Many-body potentials

Consider the Born–Oppenheimer's equation for ions. The corresponding Hamiltonian has the form

$$H = \sum_i \frac{P_i^2}{2M_i} + H_{ion-ion} + E_{el}(R).$$

Pay attention that contrary to the previous section, here $E_{el}(R)$ does not incorporate the term $H_{ion-ion}$. The first term of the right side characterizes the motion of free non-interacting particles; it is the ki-

netic energy which possesses additivity. If the system is in an external field, each ion is under the action of the force which depends on the external force potential. This potential is also additive, so

$$H_{ext} = \sum_i U_i^{ext}.$$

The second term gives direct interaction of the ions; the third defines indirect interaction through valence electrons. Both terms can be represented in the form of the many-body potential

$$U_N(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N),$$

which depends on an ion configuration, the configuration being unknown a priori.

How to solve the problem? Suppose that the many-body potential depends on the coordinates of two particles only, and this dependence has the form

$$U_N(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) = \sum_i \sum_{<j} U(|\mathbf{R}_i - \mathbf{R}_j|) = \sum_i \sum_{<j} U_{ij}.$$

This means that the force acting on particle i from the side of particle j does not depend on a position of other particles. In other words, one excludes correlated motion of the ions from the very beginning. To take the correlation into notice, one is compelled to introduce more complex interactions, e.g. three-body and four-body, which cannot be reduced to two-body ones. In a general case

$$U_N = \sum_i \sum_{<j} U_{ij} + \sum_i \sum_{<j} \sum_{<k} U_{ijk} + \dots + U_{123\dots N}.$$

Here $U_S \equiv U_{123\dots S}$ is the function depending on s variables, which cannot be decomposed and presented as a sum of functions depending on the lesser number of variables. Such decomposition of a many-body potential is named a *group representation*. It looks fine theoretically but in practice one uses in the best case the triple-dipole Axilrod–Teller's potential. As a rule, molecular dynamics investigators restrict themselves by the functions consisting of pair potentials, usually of semi-empirical nature, to which three-body potentials are added on a purely empirical basis. Such approach is popular when one studies covalent solids [5].

5.3. Malefic influence of elasticity theory

The generalized Hooke's law connects stress tensor σ_{ij} and strain tensor ϵ_{kl}

$$\sigma_{ij} = c_{ijkl} \varepsilon_{kl}.$$

Here the coefficients c_{ijkl} form the tensor of elastic constants. As this takes place, the density of elastic energy is equal to

$$dU = \sigma_{ij} d\varepsilon_{ij} = c_{ijkl} \varepsilon_{kl} d\varepsilon_{ij},$$

or in the integral form

$$U = \frac{1}{2} c_{ijkl} \varepsilon_{kl} \varepsilon_{ij}.$$

The expression characterizes the specific work done by the stress under elastic deformation of a medium (usually continuum), and for this reason is named the elastic potential.

The tensor of elastic constants has 81 components, but due to the symmetry of the strain tensor the product $\varepsilon_{kl} \varepsilon_{ij}$ does not change if to permute indices i and j , k , and l , or pairs of indices (i,j) and (k,l) . Therefore

$$c_{ijkl} = c_{jikl} = c_{ijlk} = c_{klij}.$$

As a result, the number of different components reduces to 21. In crystals, by virtue of their high symmetry there appear additional relations between different components of the tensor of elastic constants. As a consequence, the number of independent components decreases even more. For example, cubic crystals have only three components which are labeled by two ways

$$c_{1111} = c_{11}, c_{1122} = c_{12}, c_{1212} = c_{44}.$$

To clarify the physical sense of these linear-independent elastic constants, one can use three types of deformation parameters v , ε_x , γ_1 (K. Fuchs, 1936). The first parameter v characterizes homogeneous extension or compression of a crystal lattice. Parameter ε_x describes the lattice extension in the direction x and the compression in the direction y in such a way that the crystal volume remains constant. Parameter γ_1 defines the y -axis rotation in the plane xy conserving a height, i.e. simple shear. The elastic constants suggested by Fuchs can be expressed as the partial derivatives of elastic energy for an undeformed crystal with respect to deformation parameters:

$$\frac{\partial^2 U}{\partial v^2} = \frac{1}{3}(c_{11} + 2c_{12}) - \text{bulk or compressibility modulus (all-side compression, volume changes)},$$

$$\frac{\partial^2 U}{\partial v^2} = 2(c_{11} - c_{12}), \frac{\partial^2 U}{\partial \gamma_1^2} = c_{44} - \text{shear moduli (volume does not change)}.$$

One can associate the elastic constants not only with a type of deformation but also with an interatomic potential. Suppose that all the atoms of a crystal are immobile and their interaction can be expressed by a pair central potential. Let one atom be the origin of coordinates. Stability condition for crystal lattices affirms that in this case the elastic constants of mono-atomic cubic crystals have the form (Max Born, 1940)

$$c_{11} = \frac{a^4}{2v_0} \sum_i m_i^4 D_i^2 U(r_i),$$

$$c_{12} = c_{44} = \frac{a^4}{2v_0} \sum_i m_i^2 n_i^2 D_i^2 U(r_i),$$

$$D_i = \frac{1}{r_i} \frac{d}{dr_i}.$$

Here v_0 is the atomic volume, a is the lattice parameter, $r_i = \sqrt{m_i^2 + n_i^2 + l_i^2}$ is the distance between the origin of coordinates and atom i . Note that the equality $c_{12} = c_{44}$ is known as Cauchy's relation.

These formulas have played and are playing up to now an awful role in the development of molecular dynamics; to say more correctly, not the formulas but people using them. Indeed, the formulas allow solve two types of problems:

- 1) Knowing the interatomic potential to calculate the elastic constants. This is a direct problem.
- 2) On the basis of experimental elastic constant find parameters of the interatomic potential. This is an inverse problem.

“Conditionally, the theoreticians dealing with condensed matter physics can be separated into two types. The first-type theoretician supposes that constants and functions which characterize solids are given from ‘above’, and it is necessary to find them experimentally. The activity of a theoretician consists in the following: to express observed physical values through such constants and functions. The second-type theoretician supposes that prescribed values are not characteristics of solids but those of atoms (and in general, only world constants), and the purpose of a theory is to calculate properties of solids on the basis of atom properties, since the atoms constitute solids. Surely, this is a very important problem. Its solution allows, in principle, predict the properties of solids which are not obtained yet. There is no sense to compare merits and demerits of both approaches because they are quite different and pose different problems. It is clear that they are useful both” [6].

Examples of the interatomic potentials for metals developed on the basis of the first (macroscopic) approach can be found in [7,8] and those on the basis of the second (atomistic) one in [9,10]. Their comparison is done in [5].

It is worth adding that the second approach is more difficult, but it helps to clarify the nature of a phenomenon in a more profound manner, and vast majority of success in physics is connected namely with the second approach. Unfortunately, because of large difficulties in realizing the second (atomistic) approach, molecular dynamics community develops this science mainly by the first more simple way, not bearing in mind that the first approach leads to a dead end many neighboring sciences. As a rule, Cauchy's relation does not fulfill even for homogeneous solids, so one is compelled to introduce many-body terms adjusting their parameters to experimental data. The choice of parameters depends on the taste of an author; therefore, the number of empirical potentials even for one solid, in principle, is unlimited. For amorphous materials, alloys and real metallic crystals with defects the situation transforms into a tragedy. In those cases it is necessary to take into consideration local surrounding of an atom. This leads to infinite modifications and discussions about the choice correctness of one or other type of an empirical potential [11,12]. More detailed discussion needs a special review paper.

It should be emphasized that the more complex is the structure of condensed matter, the more parameters one needs to describe its properties using the first (quasi-theoretical) approach [13]. At last, the number of parameters begins to exceed the number of experimental data on the basis of which it is possible to define the parameters; but 'the value of the thing is as much as it will bring.'

It is worth noting that a similar situation has appeared earlier in the theory of molecule vibrations [14]. The corresponding problems are spoken as the direct and inverse spectral ones. The direct spectral problem consists in calculating frequencies and vibration spectrum on the basis of preset parameters of a molecule. The inverse spectral problem is reduced to the following: how to find the potential energy of a molecule on the basis of experimental frequencies. In the theory of molecule vibrations the scientists have come many years ago to the conclusion that the direct problem had a unique solution where the inverse one had in a general case no sole solution. For this reason, the main efforts are directed now how to calculate

molecule parameters from the first principles [4], and this approach is in accord with the modern tendency in the development of condensed matter physics. We will not discuss more the dead-end approach; instead we draw attention to the models of molecular dynamics which are based on the first principles.

6. NEW MOLECULAR DYNAMICS

6.1. Born-Oppenheimer's approximation in a new fashion

Consider the way of numerical calculation of an interatomic potential in which the potential is defined during the integration of motion equations (*R. Car and M. Parrinello*, 1985). The model of molecular dynamics using such approach was named by the authors ab initio molecular dynamics. In the ab initio molecular dynamics one employs both the atomic coordinates $\{\mathbf{R}_i\}$ and the electronic wavefunctions $\{\psi_j\}$ which correspond to occupied states, as dynamical degrees of freedom of a fictitious classical system governed by the following equations of motion

$$\mu \ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E}{\delta \psi_i(\mathbf{r}, t)} + \sum_j \lambda_{ij} \psi_j(\mathbf{r}, t),$$

$$M_i \ddot{\mathbf{R}}_i = -\frac{\partial E}{\partial \mathbf{R}_i(t)}.$$

Here dots indicate time derivatives, M_i denote atomic masses, μ is an adjustable parameter setting the time scale for the fictitious electronic dynamics, E is the energy functional with the local density approximation and correlation, and λ_{ij} are Lagrangian multipliers. The Lagrangian multipliers are needed to satisfy the orthonormality constraints on the $\psi_j(\mathbf{r}, t)$. When E is minimized with respect to the $\psi_j(\mathbf{r}, t)$, one recovers the Born-Oppenheimer potential energy surface for atoms, and the second equation describes physical atomic trajectories.

"With an appropriate choice of the parameters and the initial conditions, fast electronic and slow atomic degrees of freedom are only weakly coupled and atomic trajectories, initially lying on the Born-Oppenheimer surface, deviate from it very slowly on the time scale of the molecular dynamics simulation. In these conditions, the electronic degrees of freedom acquire only very small classical kinetic energy needed to follow adiabatically the atoms, and only very few or no separate minimizations are

necessary to keep the system on the Born-Oppenheimer surface during a molecular dynamics run. In this approach, potential is explicitly derived from the electronic ground state, which is treated with accurate density functional technique” [15].

In spite of such optimistic statement of the authors, there are number of points to be made.

- The authors claim that the scheme is “parameter-free” and opens the possibility of predicting from the first principles properties of disordered systems. However, we have shown that both the Born-Oppenheimer equations are approximate, so any solution for electrons depends only on nuclei (atoms) coordinates, but not on their velocities. In its turn any solution of the equations for nuclei (atoms) depends only on the total energy of electrons, but not on their coordinates.
- It seems strange that the first principles could be approximate. Moreover, the scheme contains the adjustable parameter μ and at the same time is “parameter-free”. In our opinion, the name “*ab initio molecular dynamics*” is too ambitious. In reality, it is *ab initio molecular “semi-dynamics”* because electrons take no real part in many processes being always the slaves of the ground state.

6.2. Outside of the Born-Oppenheimer approximation

In the molecular dynamics simulations of atomic systems considered above, the contribution of the electronic subsystem is taken into account by implicitly assuming that the electrons are always in the ground state. In order to avoid this disadvantage, we elaborated a *molecular dynamics model of charges at bonds* which take into account both atomic (ionic) and electronic degrees of freedom [16]. The fundamental difference between our model and other currently available models is that, within classical mechanics, the bond charge model provides a means for investigating both atomic (ionic) and electronic subsystems simultaneously. This approach accounts for the contribution from the electronic subsystem even in the case when the electrons are in the excited state or when the system undergoes electronic transitions [1]. The proposed model makes it possible to observe the variation in the configuration on the electronic level and to extend information thus derived to the atomic level closely related to the experiment. The model is especially useful in investigating non-equilibrium

electronic-atomic processes with a strong correlation and localization in space and time, particularly in studying fullerenes and nanotubes. The advantage of the new approach is that the structure is not postulated a priori and, moreover, can undergo significant transformations with time. However, the main advantage of the model is that it offers considerable possibilities for analyzing the influence of electric and magnetic fields on the fullerenes and nanotubes under dynamic conditions.

This new molecular dynamics was developed more than ten years ago initially with the purpose to study the inversion transition in an ammonia as well as positron scattering by atoms and molecules (A.I. Melker, S.N. Romanov, A.L. Emiryanyan, 1996), and for a long time (up to 2007 [4]) had no rigorous theoretical grounds, although with its help many interesting results on the self-organization and properties of fullerenes and carbon nanotubes were received; which cannot be obtained in the framework of common as well as of *ab initio* molecular dynamics. It should be emphasized that this approach is known under different names: charged-bond model, molecular dynamics model of ‘charges at bonds’. This difference in names is due to translation from Russian to English and back. Now we assume that the term ‘bond–charge’ accounts better for physical sense, and will use it in future.

7. CONCLUSION

We have analyzed the principles lying at the basis of different interatomic potentials which are used in molecular dynamics studies. The main idea of this paper is given in the introduction and will be repeated here. ‘A person must know how the calculations are going on. If one does not understand how it is done, one sees only bare numbers, but their genuine significance is hidden in calculations’ [2]. We are not going to argue against the allegation that ‘the electron theorist saw only the glaring inadequacies of empirical potentials, but was unable to deliver the tractable models required to improve the situation’ [12]. Instead, it must be emphasized that including a lot of empirical parameters into a molecular dynamics model often does not clarify a subject, but immerses it into darkness. To our mind, the main aim of the investigators working in the field of molecular dynamics consists in creating new and developing already existing models which are based on rigorous theoretical grounds. ‘A lot of talent is wasted to improve details, whereas it is necessary to reconstruct all the

building as a whole' (Henry Léon Lebesgue, 1875-1941).

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