Research Article

Statistical Distributions of Physical Characteristics of Molecules with Casimir Force in the Transfer of Admixtures in Nanoscale Volumes

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In this work, we study the statistical properties of molecular systems of admixtures, which are placed in nanoscale volumes like cube or parallelepiped with impermeable surfaces on their walls. We simulate interactions of free motion of molecules of admixtures with molecules on the surfaces of walls: we modeled them in the form of atomic structure grid using SiO_2 as a material. This type of substance allows us to take into account the manifestation of one of the important quantum effects: Casimir force. We used its general expression in terms of interaction energy, with the assumption of dependence on distance and projected area between atoms of the wall and atoms of the admixtures. To model surface roughness we used uniform random distribution function for surface heights (z coordinates). The results of computational experiments can be used to estimate the distribution of chemical bond lengths, valence, and dihedral angles lengths deviations in polyatomic molecules. Our model can be useful to determine the stable configuration properties of the system, to solve practical problems in the conditions of physical limitations of nanoscale devices, filtration of admixtures in highly dispersed systems, in the development of mechanisms in structures that have parallel plates or membranes, including porous structures. Also we compute radial distribution function for multicomponent admixtures including atoms of inert gases, water vapor, and ethanol. And we took into account the influence of Casimir force on admixtures for cube and parallelepiped type volumes. In results, we showed distributions of deviations of lengths from their equilibrium values.

1. Introduction

One of the most relevant studies of dynamic systems in the nanoscale is modeling of properties of molecular structures that are necessary for the production of materials with new or improved characteristics as well as determining equilibrium states and defining deviation intervals that are critical parameters in medicine and biotechnology related to gene modification of proteins and viruses. In technological sphere that could be engines for nanoscale robots, filtration of admixtures for air purification systems, adsorption of bacteria, and other applications of natural science and technical disciplines, where there exists production of highly efficient nanoscale systems, resistant to environmental influences are of importance.

In particular, there is class of problems related to the modeling of molecular structures [1, 2]; clusters, admixtures, agglomerates in technical systems [3–5], comparative analysis of models [6] and calculation of the distribution of important parameters [7] are of fundamental interest. Due to use of mathematical models with high parallelization calculations, it becomes possible to carry out intensive computer work with taking into account many features of physical systems with constraints. Methods of numerical simulation had a great influence in the development and solutions of such problems. However, there are a number of technical difficulties when distances between surfaces in real systems are considered less than ten nanometers. This leads to the need of additional consideration of quantum effects contributions and strong interactions. Thus, flat parallel surfaces produce activation of

the Casimir force that generates an additional contribution to the net interaction energy. It can cause deformations, structural surface instabilities [8].

In our work, we consider the use of Casimir force as an additional term in the processes of molecular admixtures transfer in nanoscale volumes [9, 10]. And we consider the effect of volumes produced on statistical properties of the system, in particular, the distribution of equilibrium values of chemical bonds in polyatomic molecules. In the existing mathematical models the main types of boundary conditions are periodic [11–13], for example, in film models [14] and in the sphere-plate interactions [15], and that cannot be used in our case to solve problems in confined volumes [16–21]. We propose a model based on interaction potentials, like AMBER and CHARMM.

2. Mathematical Model

Casimir force plays an important role in our model. As noted earlier, it has a quantum nature, but it can also be represented in the classical approximation in the form of the interaction energy potential [22–24]. Description of the evolution of the system is based on the classical system of Newton's equations. Solution is based on the method of molecular dynamics, which allows us to describe system under the assumption of additivity of potential energy terms in force field. The initial conditions for the model are velocities and coordinates of all atoms of admixture's molecules, the initial temperature of the system, the size and type of the simulated volume, and the functional description of interactions with system's boundaries. We do not consider any special conditions for the distribution of velocities and coordinates for the atoms of admixtures; therefore, their values at initial time t=0 are determined by the quantiles of the normal distribution with the most probable value of the speed corresponding to the preset temperature. The coordinates of the atoms inside the volume can be set in free intersections of inner volume grid with a step of 0.5 nm, or by getting real coordinates from measurements of surfaces using the atomic force microscope [25, 26]. We will set the admixtures molecules on virtual inner volume's grid randomly and distributed uniformly, taking into account the physical constraints and conditions imposed on the distances of intermolecular interaction to eliminate bursts of energy values and instabilities of the numerical simulation. This makes possible to get a minimum of net potential energy at the initial time. If necessary, a preliminary relaxation of the system can be carried out by methods of mathematical optimization.

$$\frac{\partial^2}{\partial t^2} m_i \overrightarrow{r}_i = -\overrightarrow{\nabla} \left[\sum_{pairs} U_b + \sum_{triples} U_a + \sum_{quadruples} U_d \right.$$
$$\left. + \sum_{i<j} \left(U_{ij}^{LJ} + U_{ij}^{col} + U_{ij}^{c} \right) + \sum_{wall} U_w \right] \quad (1)$$

with initial conditions:

$$\overrightarrow{r}_i (0) = \overrightarrow{r}_i^0;$$
$$\frac{\partial}{\partial t} \overrightarrow{r}_i (0) = \dot{\overrightarrow{r}}_i^0; \quad (2)$$
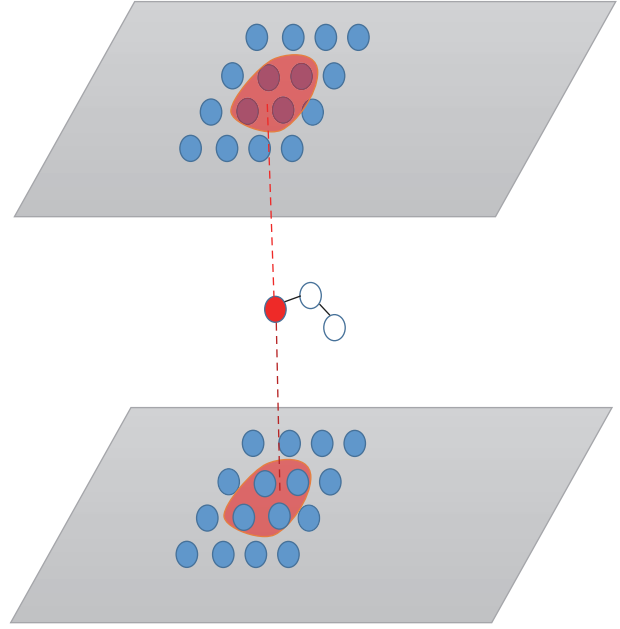

Figure 1: Atom-atom model of Casimir energy interaction of water molecule with the four atoms, covered by the projection of molecule on the surface of the upper and lower bases.

2.1. Casimir Force and Interactions with Inner Walls of Modeled Volume.

Casimir force (not for the case of quantum calculations) is regarded as a type of van der Waals interaction [19–21] without dipole moment fluctuation. This is a semiclassical approach. To use Casimir force in our model we integrated a well-known expression for the force [28] that can be used as an approximation function of potential energy and depends on distance and interacting area of corresponding atoms (wall-admixtures). Since the surfaces of the box are modeled as molecular structures, we used the same type of "atom-atom" interaction for the calculations for every atom in molecules of admixtures. Further assumption we made is that we consider average of four neighbor atoms that covers projection of admixture's atoms on the wall surface. As atoms projections are much smaller than the area of the walls and taking into account orthogonal direction of the Casimir force vector, the energy of the interaction is conveniently represented schematically and is shown on Figure 1.

We took an average of four neighbor atoms on the corresponding walls that have the shortest distances to interacting atoms of the admixtures.

$$U_c \left(r_{ij} \right) = -\frac{1}{4} \sum_{neighbours} \frac{\pi^2 \hbar c}{720 r_{ij}^3} \quad (3)$$

Any other non-Casimir types of interactions, in order to describe nonperiodic boundary conditions of admixture's atoms with atoms on the walls, are set as terms of Lennard-Jones and Coulomb potential. Together with the Casimir

TABLE 1: Force field specification.

Admixtures	Bond-bond	Angle-Bending	Dihedral	Van der Waals	Electrostatic	Boundary
H	-	-	-	LJ	Coulomb	$U_w + E_{cas}$
O	-	-	-	LJ	Coulomb	$U_w + E_{cas}$
N	-	-	-	LJ	Coulomb	$U_w + E_{cas}$
H_2O	P2	P2	-	LJ	Coulomb	$U_w + E_{cas}$
C_2H_5OH	P2	P2	P5	LJ	Coulomb	$U_w + E_{cas}$

Note: Pn is the polynomial of order n, LJ stands for Lenard Jones potential, Coulomb is electrostatic potential, U_w is a boundary interaction potential, and E_{cas} is Casimir energy. The basic units are set as follows: mass (m= $1.66 \cdot 10^{-27}$ kg), velocity (v=1000 m/sec), time (t=10^{-12} sec), and energy (e= $1.38 \cdot 10^{-26}$ kJ/mol). The parameters for the potentials are taken from the reference data [11, 12, 18, 27].

energy we have the following expression (last column in Table 1):

$$U_w = \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) + \frac{f_{ij}^{Col} q_i q_j}{4\rho_w r_{ij}}$$
$$- \frac{1}{4} \sum_{neighbours} \frac{\pi^2 \hbar c}{2880 \rho_w r_{ij}^3} \qquad (4)$$

where parameter ρ_w is a known value of density of wall's atoms and this is an alternative variant in wall-admixtures interactions to speed up calculations, but it is less accurate. To model real atom structure we set $\rho_w = 1$ (these are options to be set before simulation begins). For further statistical analysis, we compute the distributions of bond lengths, valence, and dihedral angles displacements in polyatomic admixtures and radial distribution function for admixtures:

$$g(r) = \frac{V}{4\pi r^2} \left\langle \sum_{i=0}^{N-1} \frac{n(r_i)}{\Delta r} \right\rangle \qquad (5)$$

3. Computational Experiments

We modeled two types of the simulated geometry of comparable inner volume: a cube with a side of 10 nanometers (volume of 1000 nm^3) and a parallelepiped with the lower and upper bases of 196 nm^2 (14x14 nm) and a height of 5 nm (volume of 980 nm^3). These volumes were filled with the same amount of admixtures, consisting of 25 molecules of each type of substance: nitrogen, hydrogen, oxygen, water, and ethanol. On the upper and lower bases of cube and parallelepiped we simulated two types of reflections: diffuse model (roughness has a mean square deviation of 5 angstroms in z-direction) and specular reflections (atom net structure of SiO$_2$ with the Casimir force). A schematic illustration is shown in Figure 2.

Numerical integration was made in increments of $\tau = 10^{-15}$ seconds (dimensionless step size equals 10^{-3}). Initial temperature T=300K. The experiments lasted 100 000 molecular-dynamic steps using a two-step Verlet's algorithm. In addition, we also implemented Biman's algorithm for more precise calculations. The force field functions for corresponding types of admixtures we used from Table 1.

On Figure 3 there are modeled volumes with admixtures at the initial and final step.

4. Results and Analysis

Mathematical model and numerical methods are implemented by the authors in Embarcadero's Delphi using parallelization in the block of potential energies calculations. The development of the original package was required to model nonperiodic boundary conditions and to take into account influence of Casimir force in terms of its energy. It should be noted that our model does not use any truncation of lengths of potential functions at distances of more than three diameters of the atom-atom collisions. All interaction potentials are expressed in classical approximations of quantum mechanical calculations, which are due to the use of a quasi-classical approach in the numerical solution of the system (1). The results of the calculations are shown on Figures 4–7. Initial conditions were preserved for repeated computational experiments.

The main interests in our research are distributions of lengths deviations in bond-bond, angle-bending, and dihedral oscillations and their comparative analysis. We see on Figures 4–6 the average values of the distributions of corresponding parameters. All the graphs show characteristic shifts in lengths relative to zero, where zero value is the ideal situation with no external interactions and forces in the system. In physically constrained spaces, due to constant intermolecular interactions, random deviation has a normal distribution with zero estimated value. General formulas we used for calculations for parameter α are the following:

$$\Delta \alpha = \frac{1}{N_{steps} \bmod 100} \sum_i^m \frac{(\alpha_i - \alpha_{ref})}{m} \qquad (6)$$

where α_i is current value (bond lengths, valence angles, and dihedral angles for every type of admixtures where applicable), taken every 100 steps and averaged over all such steps. So $\Delta \alpha$ is random value with distribution function that we showed on Figures 4–6. On the y-axis there are corresponding densities: dimensionless numbers of α values that had fallen in nonintersecting intervals covering minimum and maximum value of α, and on x-axis are values of interval limits in angstroms.

$$I = \frac{\max(\alpha) - \min(\alpha)}{20} \qquad (7)$$

Figure 4(a) shows the normal distribution of the mean deviation of average covalent bonds of admixtures, which
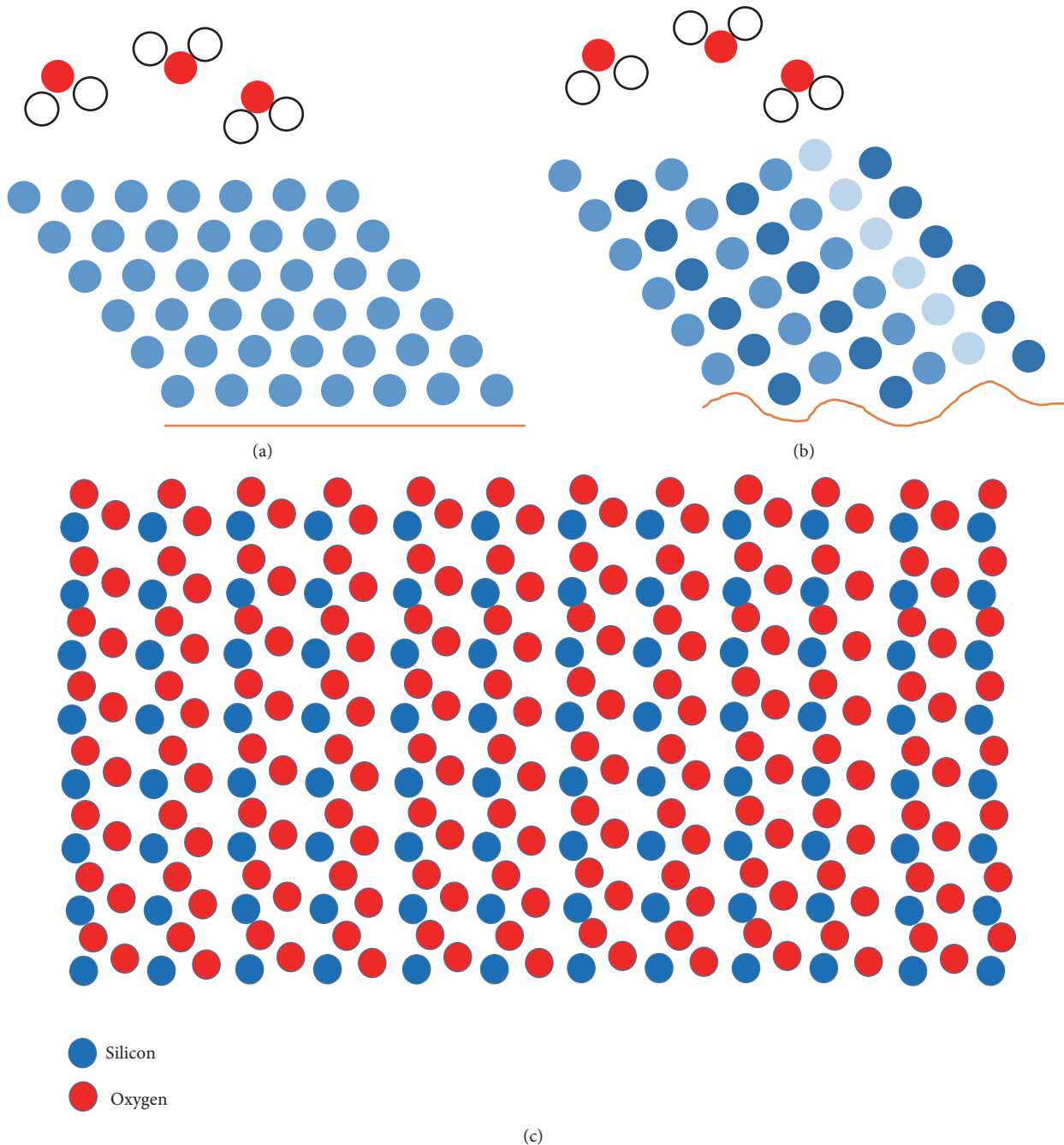
(a)

(b)

(c)

Silicon

Oxygen

FIGURE 2: (a) Specular reflection, (b) roughness, and (c) atomic structure of SiO_2 on the wall surface (red denotes oxygen atoms; blue denotes silicon atoms).

is close to the equilibrium value in the absence of the Casimir force (blue curve). In the case of the Casimir force (Figure 4(b), orange curve), distribution is shifted more to negative values, which means that there is an increase in the oscillation frequency of covalent bonds and decrease of its amplitude. For the case of a parallelepiped (Figure 4(b)) the same system of admixtures has an increased spread of lengths and tends to transform the normal distribution to uniform, due to changes in redistribution of interactions of admixtures with the lower and upper bases of the volume. The decrease in

volume's free space directly increases the variance of covalent bond-bond oscillations, which leads to rise in their amplitude with a lower shape in frequencies. If the Fourier transform for amplitude-frequency analysis is carried out, the vibration spectrum for cubic volumes will be concentrated in the high-frequency region, and for the parallelepiped, the distribution will be relatively uniformly filled in the middle frequency range with decay in tails on the lower and higher frequencies.

Results that are more interesting were obtained for the oscillations of the valence angles shown on Figure 5. This is

(a) Initial configuration (left figure: cube; right figure: parallelepiped)

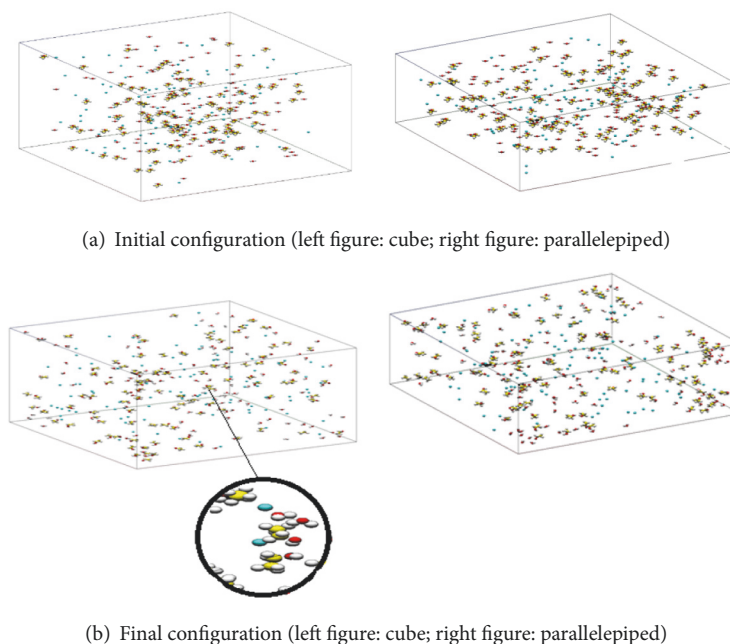(b) Final configuration (left figure: cube; right figure: parallelepiped)
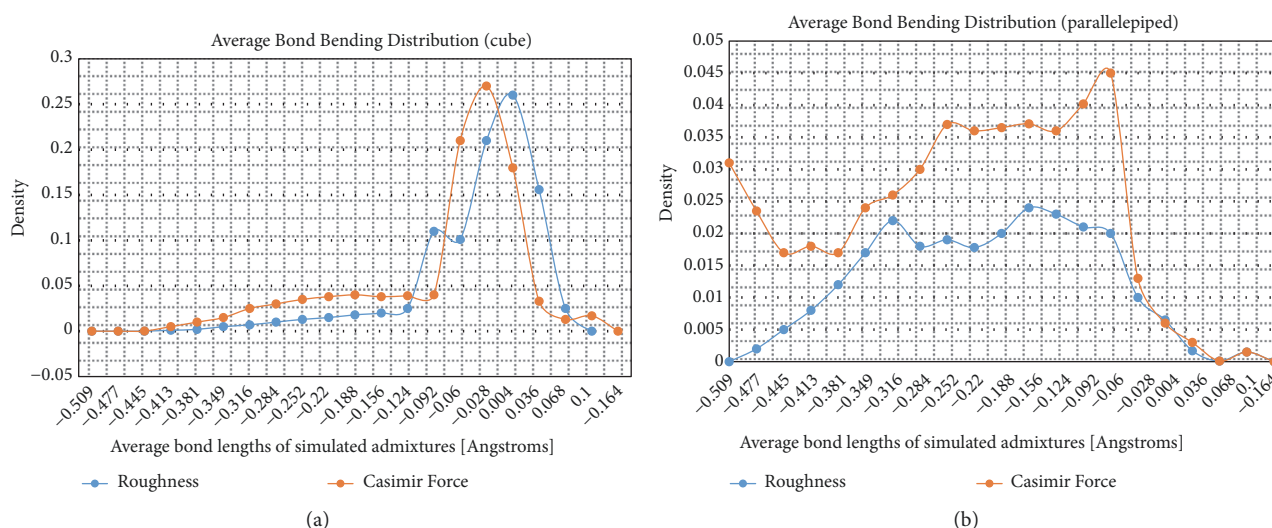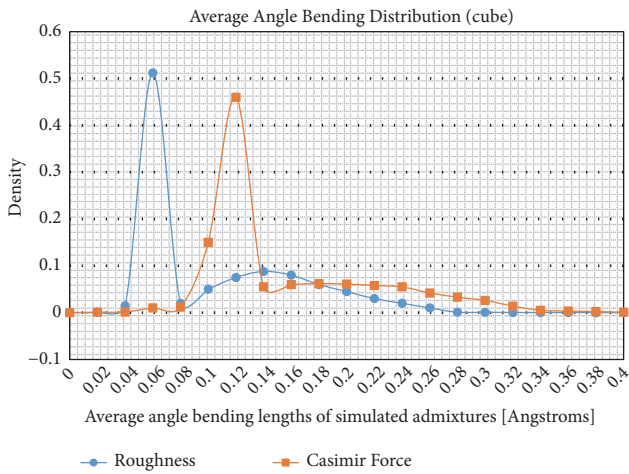
FIGURE 3

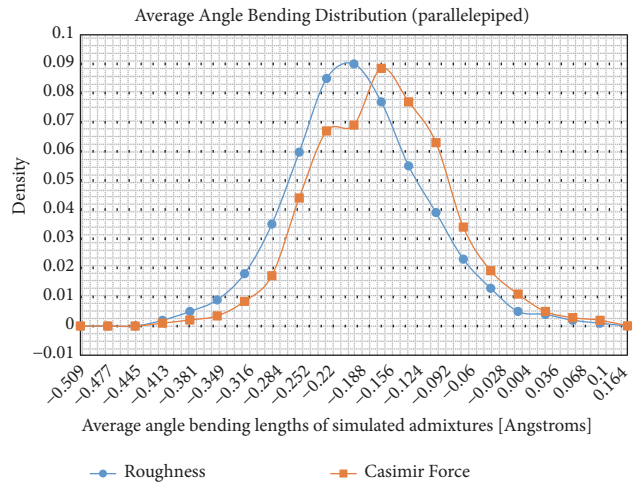FIGURE 4: (a, b) Distribution of deviations of the mean values of the covalent bond.

true for water and ethanol molecules, where the resulting distribution has a high density of values near the equilibrium state and a small subset of values with a gentle spread to the right of the equilibrium value. Empirically, the distribution consists of a superposition of the normal distribution and the χ^2 distribution. In the case of the Casimir force, a normal distribution is obtained without singularities. It can be concluded that for polyatomic molecules the equilibrium state corresponds to the minimum potential energy for valence angles in asymmetric volumes. However, in both cases (Figures 5(a) and 5(b)) there is a systematic displacement, which is caused by an additional contribution to the interaction energy.

For a parallelepiped, the distribution remains normal and does not change. On Figure 6(a) there is distribution of dihedral angles (for ethanol) for a cubic volume in the equilibrium state. The state corresponds to the logarithm of the normal distribution and with the active Casimir force and leads to a small displacement of the curve. In the case of a parallelepiped (Figure 6(b)) the nature of the distribution remains normal but leads to an increase in angle fluctuations.

The radial distribution function (7) can be useful for estimating distances between molecules in volumes. The concentration of molecules near the center is obtained for cubic volume (Figure 7(a)) and for the parallelepiped (Figure 7(b)). Molecules are evenly distributed in volume. It is worth noting
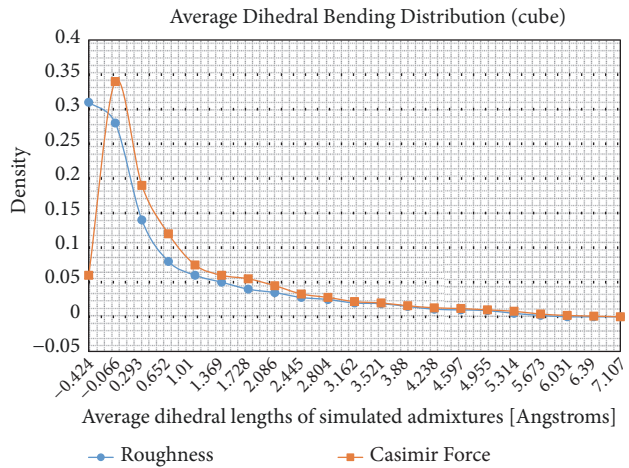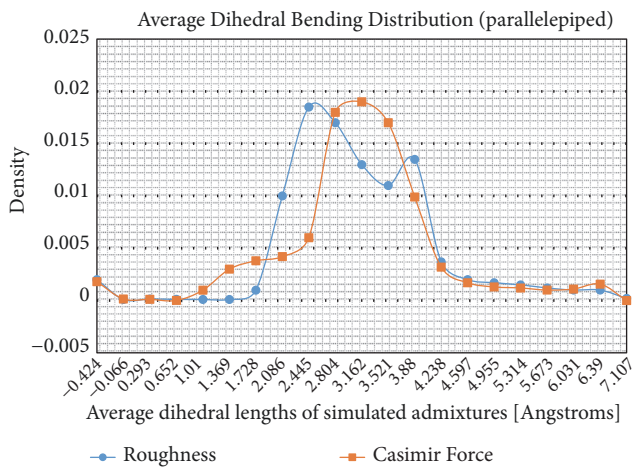
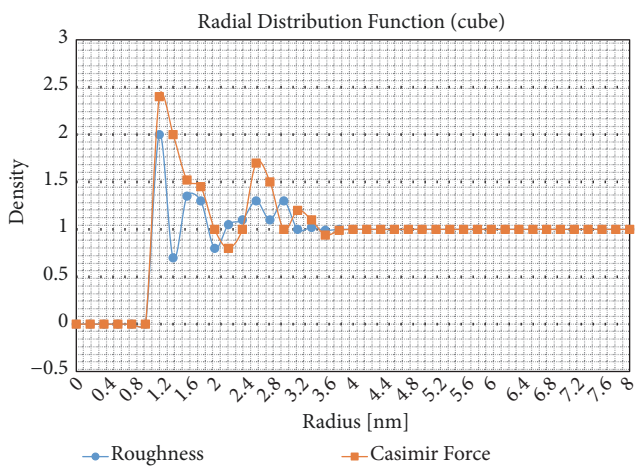Figure 5: (a, b) Distribution of deviations of mean values of valence angles.
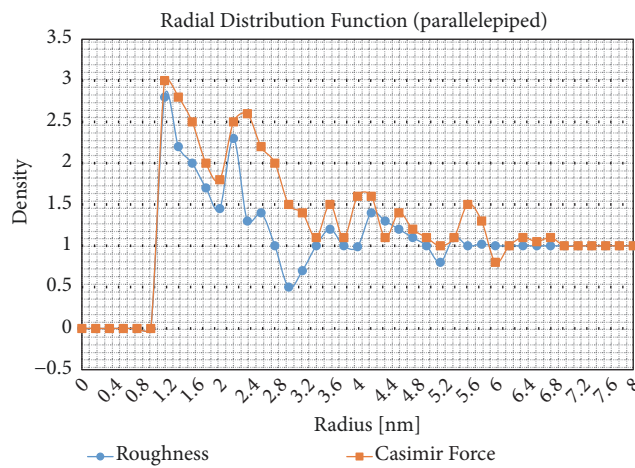

Figure 6: (a, b) Distribution of deviations of mean values of dihedral angles.

Figure 7: (a, b) Radial distribution function.

that these are the most likely distributions computational experiments, but it is possible to obtain other types of concentrations. In particular, with increase in number of admixtures, the highest concentration can be obtained behind the corners of volumes.

5. Conclusion

Simulation data can be used to predict unstable states, overheating, and deformations of materials on the walls of mechanisms having parallel surfaces in devices of tens of nanometers in size, as well as for the control action on admixtures in filtration problems. The developed model can be used in the design of mechanisms with membranes, filter elements, and solar cells, where the occurrence of nonlinear effects depending on the material and the reflectivity of the surfaces is possible. In particular, the Casimir force can significantly affect the distribution of equilibrium values of physical and chemical characteristics of admixtures as we showed in lengths deviations when passing through the membranes on filtration devices [20], during adsorption of harmful substances [21], air purification systems [22]. In this paper, computational experiments were carried out in geometrically bounded volumes of the cube and parallelepiped types, comparable in volume (about 1 μm^3). The heterogeneous composition of admixtures (25 molecules of nitrogen, hydrogen, oxygen, water, and alcohol) is considered. Modeling of microcanonical ensembles in nanoscale volumes leads to some interesting effects of the distribution of the molecules of admixtures, depending on their type (Figures 4–7). Statistical regularities, including distribution transformations, are obtained (Figures 4–6), as well as the straightening of the normal distribution when the volume type changes (Figures 4(b), 5(b), and 6(b)). In particular, the displacement of equilibrium values and qualitative changes in the normal distribution was shown. In all cases (Figures 4–7) Casimir energy had a significant impact on the growth of energy fluctuations of interatomic bonds and creates conditions for nonlinear contributions to potential energy and leads to an increase in the amplitudes and frequencies of vibrations of chemical bonds. The volume types and sizes affect the resulting distributions and have a high correlation depending on the values and types of deviations. As a result of the computational experiments, the following were found:

(i) In volumes of about 1000 nm^3, the Casimir force has a significant effect on the distribution of the mean values of covalent bond lengths, valence, and dihedral angles deviations in polyatomic molecules. For cubic volumes, this is expressed in the displacement of the distribution center (Figure 4(a)) and changes the type of distribution (Figures 5(a) and 6(a)); for parallelepipeds distributions remain unchanged, and lengths values are concentrated around the equilibrium values; however, they have biases and increased variance.

(ii) Strong intermolecular electrostatic interactions and the high density of the atoms of the structure of volume's surfaces increase the relaxation time of the covalent bonds and valence angles, accumulating nonequilibrium processes. In particular, for the parallelepiped we obtained increased dispersion of average deviations of values of the equilibrium lengths and angles of chemical bonds (Figures 5(b), 6(b), and 7(b)); and this can lead to transformations of the normal distribution; in particular, we got normal distribution for valence angles in the cubic volume (Figure 5(a)).

Data Availability

The mathematical model data used to support the findings of this study have been deposited in the Yandex repository (https://yadi.sk/d/nZ2-LQOy_ppZHg).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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