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Modeling Adsorption–Desorption Processes at the Intermolecular Interactions Level

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Abstract. Modeling of the surface adsorption and desorption processes, as well as the diffusion, are of considerable interest for the physical phenomenon under study in ground tests conditions. When imitating physical processes and phenomena, it is important to choose the correct parameters to describe the adsorption of gases and the formation of films on the structural materials surface. In the present research the adsorption-desorption processes on the gas-solid interface are modeled with allowance for diffusion. Approaches are proposed to describe the adsorbate distribution on the solid body surface at the intermolecular interactions level. The potentials of the intermolecular interaction of water–water, water–methane and methane–methane were used to adequately modeling the real physical and chemical processes. The energies calculated by the B3LYP/aug-cc-pVDZ method. Computational algorithms for determining the average molecule area in a dense monolayer, are considered here. Differences in modeling approaches are also given: that of the proposed in this work and the previously approved probabilistic cellular automaton (PCA) method. It has been shown that the main difference is due to certain limitations of the PCA method. The importance of accounting the intermolecular interactions via hydrogen bonding has been indicated. Further development of the adsorption-desorption processes modeling will allow to find the conditions for of surface processes regulation by means of quantity adsorbed molecules control. The proposed approach to representing the molecular system significantly shortens the calculation time in comparison with the use of atom-atom potentials. In the future, this will allow to modeling the multilayer adsorption at a reasonable computational cost.

1. Introduction

The most important role in ensuring the long-term and trouble-free functioning of space vehicles belongs to the resistance of construction material resistance to the influence of external factors. In conditions of space flight, the apparatus is affected by the environment, including the cosmic vacuum [1]. Space stations have a special equipment for collect and analyze pollutants. Contamination plume, which are the products of incomplete combustion, are collected by plate for a further analysis. The natural process that prevents the slick contamination formation on the surface of spacecraft is the particles desorption from the surface [2]. Therefore, it is important to study the contaminants composition and to select materials with the minimal sorption properties as regards to the products of incomplete combustion.

It is also known that under terranean conditions and depending on the type of physical phenomenon under study, it is possible to model various processes. In this respect, for the laboratory modeling of



the mass losses, it is necessary to consider such processes as adsorption of gases and chemical interaction of the residual gas with surface materials. Modeling position of the residual gas molecules (molecules, atoms, ions, excited particles) is necessary in view its significant influence on the speed of the physicochemical reactions on the surface [3]. Laboratory modeling allows the engineer (researcher) to experiment in the cases when it is practically impossible or impractical to do this with a real object.

It should be noted that the solution of each practical problem depends on numerous input variables and parameters. When selecting the appropriate parameters, it becomes possible to adequate modeling of the actual physicochemical processes. Structural and energetic parameters of the molecules in the gas phase and adsorbed state, the physicochemical characteristics of solid, as well as the area per a molecule in a dense monolayer, and others can serve as such.

2. Theory and calculations

When modeling the adsorption-desorption processes, it is necessary to determine the number of molecules adsorbed on the surface per a time unit. According to the molecular-kinetic theory of gases [4], the number of collisions of gas particles with the surface per a time unit ν is described by the formula:

$$\nu = N_A P / \sqrt{2\pi MRT}, \quad (1)$$

where N_A – Avogadro's constant, P – gas partial pressure; M – molecular mass; R – universal gas constant; T – gas temperature.

The probability of the desorption process realization for each molecule W_{des} is described by the formula [5]:

$$W_{\text{des}} = \frac{t}{t_0} \exp\left(-\frac{E_{\text{des}}}{RT_{\text{surf}}}\right), \quad (2)$$

where t – time step size (adsorption lifetime); t_0 – the order of a lattice vibration period; E_{des} – desorption activation energy; T_{surf} – temperature at the surface.

The time step size and the order of a lattice vibration period are defined by the equation:

$$t = t_0 \exp\left(\frac{E_{\text{des}}^{\text{min}}}{RT_{\text{surf}}}\right), \quad (3)$$

$$t_0 = \frac{h}{kT_{\text{surf}}}, \quad (4)$$

where $E_{\text{des}}^{\text{min}}$ – minimal desorption activation energy, h – Planck's constant, k – Boltzmann's constant.

Two series of experiments were carried out to determine the area size per one molecule of methane. They differed in the substance amount (0.1 mol and 1.0 mol, respectively), the adsorbent section size ($17 \times 17 \text{ \AA}^2$ and $25 \times 25 \text{ \AA}^2$), the temperature of the gas and the surface (100 K and 300 K). In the each series, the calculations differed in the number and magnitude of optimization steps.

The period of oscillations and the adsorption-desorption periods was calculated automatically by the formulas (3) and (4), respectively: $4.8 \cdot 10^{-13}$ and $5.32 \cdot 10^{-12}$ sec at $T = 100$ K; $1.6 \cdot 10^{-13}$ sec, $3.57 \cdot 10^{-13}$ sec at $T = 300$ K. Modeling of the physical adsorption-desorption processes was terminated after the reached equilibrium. Graphite was chosen as the adsorbent, having the uniform surface. The heat of adsorption of methane on graphite was taken equal to 11.8 kJ/mol [6].

Modeling the adsorption-desorption process of water and methane two-component gas mixture (with the same molar ratio of components in the gas phase) was carried out using the intermolecular interaction potentials (figure 1). The interaction energies of water-water, water-methane and methane-methane molecules was calculated by the B3LYP/aug-cc-pVDZ method. The B3LYP method is well suits for hydrogen bonded systems [7–11].

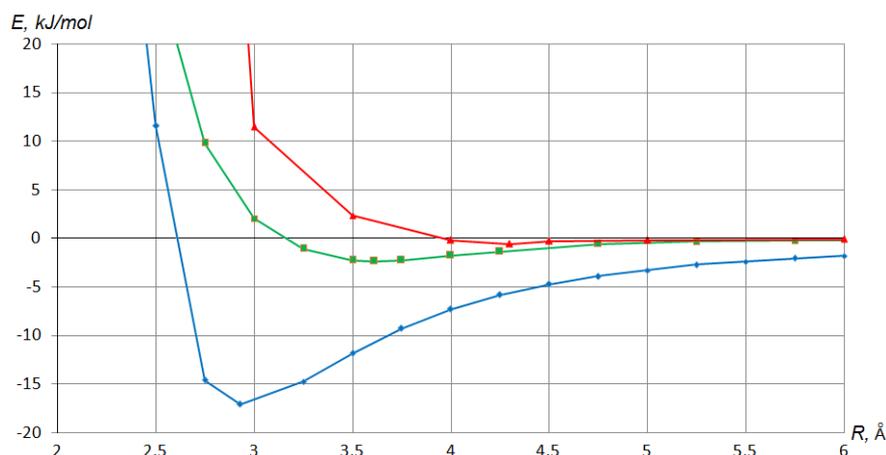


Figure 1. Energy dependence of the intermolecular interaction of water–water (blue), water–methane (green) and methane–methane (red) on distance.

The distance change between the O...O, O...C and C...C atoms was carried out in 0.25 Å step size for pairs of water–water molecules, water–methane and methane–methane molecules, respectively. At each step the system was optimized. Modeling the adsorption-desorption process was carried out using the energy values obtained. In this case, the potential energy function was created automatically by the system based on the linear interpolation between the values obtained by the B3LYP/aug-cc-pVDZ method. In our opinion, such approach is more effective than the atom-atomic potentials use, since all types of intermolecular interactions are accounted in one function. This makes it possible to significantly reduce the computation time at simultaneous maintenance of computational accuracy for small molecules. Such approach is not to be used to calculate the systems with extended and flexible molecules since possible intramolecular transitions are not taken into account here. However, the errors connected with this assumption should not be significant for small molecules, such as the components and products of the rocket propellants decomposition.

3. Results and discussion

3.1 Area per one molecule calculation

To verify the adequacy of physical adsorption used on the "gas-solid" surface computational model, the average area per molecule of methane in a dense monolayer was calculated. The calculation was carried out after reaching the equilibrium state. The results of two series of experiments are presented in table 1.

Table 1. The calculated values of the area per one molecule of methane.

N	Optimization step size, Å	Number of steps	Average area per molecule, Å ²	
			Series 1	Series 2
1	0.20	10	16.1	17.9
2	0.20	10	15.2	18.9
3	0.20	10	16.1	17.9
4	0.10	20	15.2	18.1
5	0.10	20	17.0	18.4
6	0.10	20	16.1	17.6
7	0.05	40	16.1	18.2
8	0.05	40	18.1	17.3
9	0.05	40	17.0	18.2

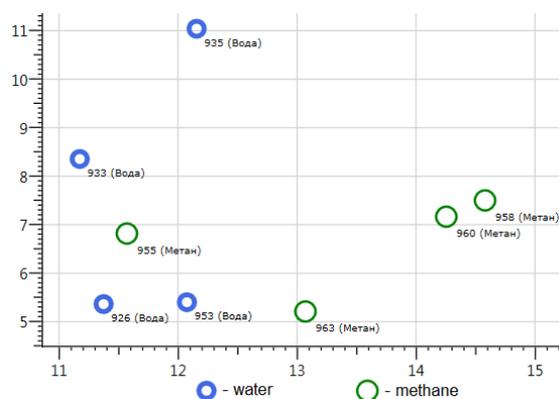


Figure 2. Graphite surface fragment at the initial moment of methane and water adsorption (axes are distances, Å).

According to the results of the computational series 1 and 2, the average area size per one molecule of methane is 17.2 \AA^2 . The results obtained well agree to the experimental data which fall into the range $16\text{--}18 \text{ \AA}^2$ [12, 13]. Good accordance with the experimental results (table 1) proves the adequacy of the model used. It is worth mentioning that the key factor for adequate modeling of the physical adsorption process is the use of correct structural and energetic characteristics describing the adsorbate-adsorbate and adsorbate-adsorbent interaction.

Earlier, we determined the area per molecule, using the probabilistic cellular automaton (PCA) method [14]. The use of this tool also made it possible to achieve a satisfactory agreement of the calculated values with the experimental data. In this case, only the adsorbate molecules structural characteristics and the interaction energy of the adsorbate with the adsorbent were taken into account. However, the PCA method has some limitations. So, if the sizes of molecules in a mixture differ widely, for example, benzene ($S \approx 50 \text{ \AA}^2$ [6]) and oxygen ($S \approx 16 \text{ \AA}^2$ [15]), then the used physical model can not be justified. The reason is the impossibility to account the differences in the molecules areas when specifying the dimensions of the PCA cell. As well as, today there is no possibility to take into account the changes of the area per one molecule as a result of the hydrogen bonds formation. Therefore, the PCA method usage at of modeling the adsorption-desorption processes for multicomponent mixtures is obstructed [14].

In our opinion, the proposed in this paper variant of the method to modeling adsorption-desorption processes using the potentials describing the intermolecular energy as a function of distance is quite promising.

3.2 Process modeling of physical adsorption of water and methane molecules on the graphite surface

To adequately describe the process of physical adsorption of a two-component gas on the graphite surface the intermolecular interaction energy potentials were used.

At the initial moment of gas adsorption on the graphite surface, the methane and water concentrations are approximately the same (figure 2, 3). This is explained by the fact that the initial

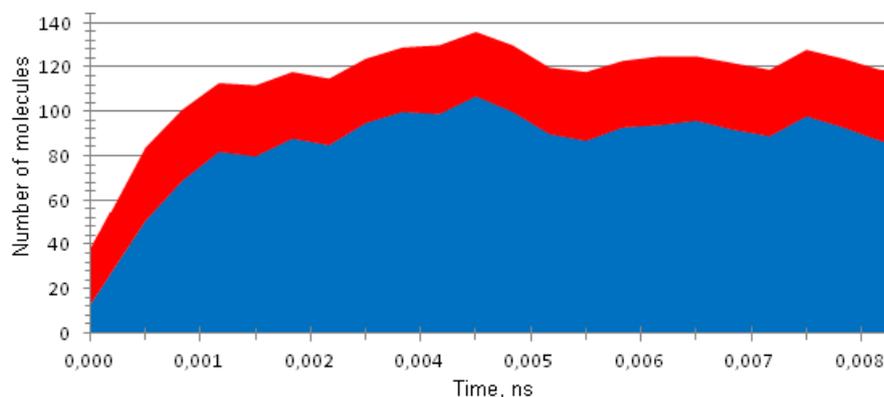


Figure 3. Number of adsorbed molecules of water (blue) and methane (red) dependence on time.

concentrations of the water and methane molecules in the gas phase are equal, and the molecular masses of the water (18 u) and methane (16 u) practically do not differ. Therefore, according to formula (1), the probabilities of adsorption of these molecules at the same temperature are close to each other.

Figure 2 shows that some molecules of water and methane find themselves at a distance of less than 1 Å from each other, that is, in the area of exchange repulsive short-range. Similar particle collisions can occur in the real adsorption process. After reaching equilibrium, they should not significantly affect the values of the system averaged macroscopic characteristics. However, in the initial phase, they can affect the probability of cluster formation. It should be noted such effects consideration cannot be fully taken into account when modeling by the cellular automaton.

As can be seen from figure 3, the proportion of water molecules in the adsorption layer increases with time. On the one hand, this may be due to the fact that water molecules can form hydrogen bonds with the graphite surface [16, 17]. However, the distances between most water molecules are about 2 Å (figure 4). This value corresponds to the hydrogen bond distance between the water molecules 1.9 Å [18]. Thus, due to a greater adsorbate-adsorbate interaction energy as compared to the adsorbate-adsorbent energy ($E_{\text{HB}}(\text{OH}\cdots\pi) = 7.5 \text{ kJ/mol}$ [19] vs. $E_{\text{HB}}(\text{OH}\cdots\text{O}) = 13\text{--}30 \text{ kJ/mol}$ [18, 20–22]), a hydrogen-bonded network of water molecules is formed and, as a consequence, there takes place a formation of a film on the surface. This well agrees with the already known experimental data [23]: the adsorption energy values of isolated water molecules are much less than the experimental values; in the monolayer on the graphite surface there exists a flat pack of associated molecules at the experiment temperature 293 K.

The proportion of the methane molecules does not change significantly over time. As seen from figure 4, methane molecules are in the chaotic position between water molecules. This is due to the fact that the methane molecules is much less inclined to the displays of lateral interactions.

It should be noted that in the model under consideration, the potentials describing the intermolecular interaction are used. They do not take into account the geometry of the adsorbate molecules. This can cause significant errors in modeling various systems, for example biological ones, where it is extremely important to consider the intramolecular hydrogen bond [24]. But most of the rocket propellants components and products of incomplete combustion have quite a compact molecular structure. Therefore, neglecting the geometry of the adsorbate molecules should not lead to a loss of physicality. The proposed variant of the molecular system representation significantly shortens the computation time in comparison with the use of atom-atomic potentials. In future, this will allow to modeling the multilayer adsorption at a reasonable computational cost.

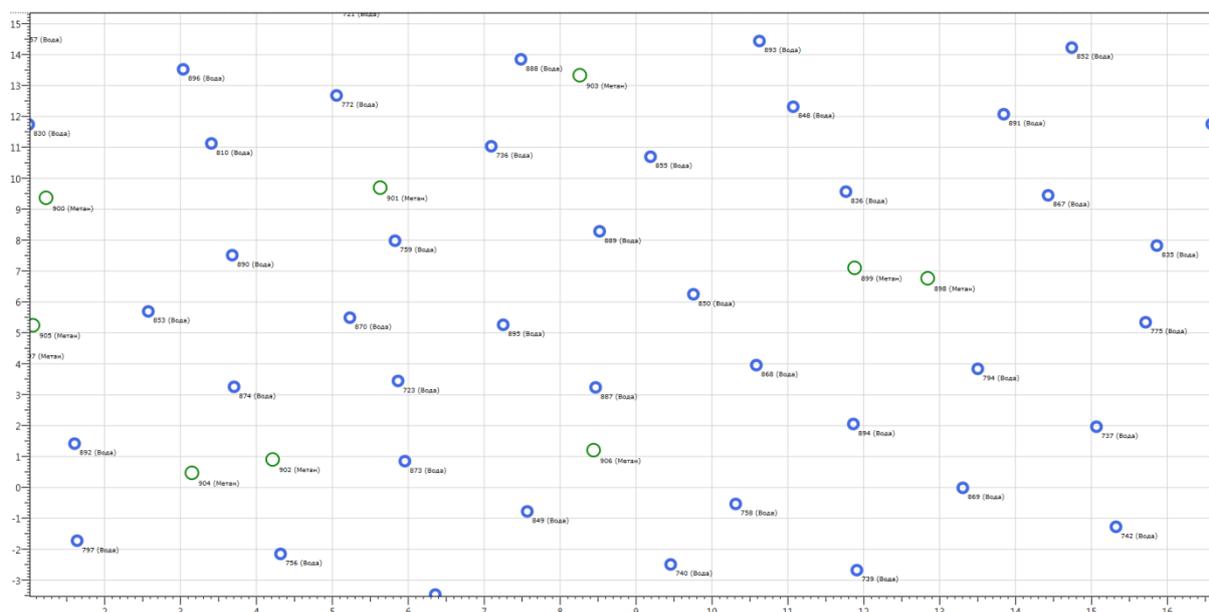


Figure 4. Fragment of the graphite surface after reaching equilibrium (axes are distances, Å).

4. Conclusions

We carried out the modeling of adsorption-desorption processes on the graphite surface. To account the diffusion the water–water, water–methane and methane–methane intermolecular interaction potentials, obtained by the B3LYP/aug-cc-pVDZ method, were used. The gained results of the area size per molecule and the distribution of water and methane molecules on the surface of a solid body well match with the known data. In the future, basing on the proposed variant of the modeling of adsorption-desorption processes on the intermolecular interactions level taking into account diffusion, there can be created the desorption process models of the multicomponent mixture, complicated by companion processes (for example, gas-surface chemisorption).

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