Theory, Simulation and Nanotechnological Applications of Adsorption on a Surface with Defects.
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Theory of adsorption on a surface with nanolocal defects is proposed. Two efficacy parameters of surface modification for nanotechnological purposes are introduced, where the modification is a creation of nanolocal artificial defects. The first parameter corresponds to applications where it is necessary to increase the concentration of certain particles on the modified surface. And the second one corresponds to the pattern transfer with the help of particle self-organization on the modified surface. The analytical expressions for both parameters are derived with the help of the thermodynamic and the kinetic approaches for two cases: jump diffusion and free motion of adsorbed particles over the surface. The possibility of selective adsorption of molecules is shown with the help of simulation of the adsorption of acetylene and benzene molecules in the pits on the graphite surface. The process of particle adsorption from the surface into the pit is theoretically studied by molecular dynamic technique. Some possible nanotechnological applications of adsorption on the surface with artificial defects are considered: fabrication of sensors for trace molecule detection, separation of isomers, and pattern transfer.

Key words: molecular dynamics, adsorption kinetics, surface defects, adatoms

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I. INTRODUCTION.

The progress in the development of nanotechnology gives rise to the possibility to modify the surface at the nanometer scale. Various methods of nanometer-scale defects creation using scanning tunneling microscope (STM) and atomic force microscope (AFM) were elaborated. In particular, nanometer-scale defects can be produced by electric field between the STM needle tip and the surface [1] – [3], with the help of nanolocal chemical reactions induced by the STM needle tip [4] – [6], and by direct touching of the STM [7,8] or AFM [9] tip. Nanometer-scale defects may influence on adsorption of particles (atoms, molecules and clusters) [10]. Surface nanostructures have been fabricated with the help of adsorption on the surface modified by scanning probe anodization [11]. We believe that the further advance in nanotechnology can be achieved when techniques of nanostructures fabrication with the help of adsorption will combine with preliminary nanolocal surface modification. Therefore the theoretical investigations of the nanolocal processes during adsorption on heterogeneous surface is an actual task at present time.

Here we present the theory of adsorption on the surface with nanolocal defects, with sizes of the order of the size of only one adsorption site (see also [12,13]). Two efficacy parameters of surface modification by creation of artificial defects are introduced. The first efficacy parameter \( \gamma \) can be useful for such applications where it is important to increase the total concentration of particles on the surface. For example, such applications may be fabrication of sensors for trace molecule detection and separation of isomers. The second efficacy parameter \( \Gamma \) can be useful for applications where high filling of adsorption sites on defects \( \nu_d \approx 1 \) is necessary simultaneously with the absence of adsorbed particles on the surface free of defects. One of such applications, for example, may be pattern transfer through the use of particle self-organization on the modified surface. Two limiting cases of adsorption are considered: the case of low temperature when adsorbed particles are localized and the case of high temperature when adsorbed particles freely move over the surface. Analytical expressions for parameters \( \gamma \) and \( \Gamma \) are derived for both cases of localized and freely moving particles using equilibrium thermodynamics and the kinetics principles.

The energy of molecular adsorption in pits with various sizes and shapes is investigated. It is shown that this energy is determined by the size of the pit. Therefore molecular adsorption on defects may be selective to a type of molecule.

The process of particle adsorption from the surface into the pit is simulated on using molecular dynamic technique on the example of argon atom and graphite surface. The probability of adsorption from the surface into the pit is calculated with the help of this simulation. The calculated value of this probability is used to estimate both efficacy parameters \( \gamma \) and \( \Gamma \) of surface modification for the case of argon atom absorbed on graphite surface with a pit.

Some possibilities for nanotechnological applications of adsorption on the surface with artificial defects are discussed in detail: fabrication of sensors for trace molecule detection, separation of isomers, and pattern transfer as a result of particle self-organization on the modified surface.

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II. THEORY OF ADSORPTION ON A SURFACE WITH DEFECTS.

Let us consider the system containing the particles of one type in three states: in a gas, in adsorbed states on defects (adsorption site D) and on areas of the surface which are free of defects (adsorption site S). We restrict our consideration to the case of nanolocal defects with only one adsorption site. The process of an adsorption of a particle on a surface can be considered as a chemical reaction

\[
\text{Molecule } A + \text{free adsorption site on the surface} = \text{adsorption complex } A
\]

The condition for equilibrium of this "chemical reaction" is

\[ \mu_g + \mu_a = \mu'_a \]  

where \( \mu_g, \mu_a \) and \( \mu'_a \) are chemical potentials of the particle in the gas, of the adsorbent per one adsorption site and of the adsorption complex, respectively. We shall restrict our theoretical consideration to the case of physical adsorption. In this case the following approximation can be used [14]

\[ \mu'_a = \mu_a + \mu_s \]  

where \( \mu_s \) is the chemical potential of the particle adsorbed on site S. We use the analogous approximation for particle adsorbed on the defect. Taking into consideration this approximations, the condition for thermodynamic equilibrium of the system is

\[ \mu_g = \mu_d = \mu_s \]

where \( \mu_d \) is the chemical potential of the particle adsorbed on the defect. This case is analogous to adsorption of \( N_1 \) immobile particles adsorbed on \( N_2 \) adsorption sites. Therefore the chemical potential of the particle adsorbed on the defect is (see, for example, [14])

\[ \mu_d = kT \ln \frac{\nu_d}{(1 - \nu_d)q_d} \]

where \( \nu_d = N_1/N_2 \) is the filling of adsorption sites on defects, \( q_d \) is the partition function of the particle adsorbed on the defect, \( q_d \) includes internal degrees of freedom, vibrations, and rotations or frustrated rotations relative to the surface, and interaction with the surface. The chemical potential of the particle in the ideal gas is

\[ \mu_g = -kT \ln \left( q_{int_g}^{-1} \frac{P}{(kT)^{5/2}} \left( \frac{\hbar^2}{2\pi m} \right)^{3/2} \right) \]

where \( q_{int_g} \) is the partition function of the particle in the gas, \( q_{int_g} \) includes internal degrees of freedom and rotations, \( m \) is the mass of particle, \( P \) is the pressure of particles in the gas. In the case of ideal gas the Langmuir isotherm for concentration \( n_1 \) of particles adsorbed on the defects follows from the equation \( \mu_g = \mu_d \)

\[ n_1 = \nu_d n_d = \frac{q_d \exp(\mu_0/kT)n_dP}{1 + q_d \exp(\mu_0/kT)P} \]

where \( n_d \) is the concentration of defects, and

\[ \mu_0 = -kT \ln \left( q_{int_g}^{-1} \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \right) \]

For some nanotechnological applications it is necessary to increase the concentration of certain particles adsorbed on a surface. Some of these applications, namely, fabrication of sensors for trace molecule detection and separation of isomers will be discussed below. We believe that following modification of surface may be useful for such applications: On the surface the nanolocal artificial defects are produced so that adsorption of certain particles on defects (sites D) causes significant increase in the concentration of these particles in comparison with concentration of these particles on a perfect surface (where only sites S are present). Such modification is worthwhile only in the case of low concentration of this particles on perfect surface, i.e. when filling \( \nu_0 \) of sites S is small (\( \nu_0 \ll 1 \)). By this is meant that the contribution of particles adsorbed on sites S into the total concentration of particles adsorbed on a modified surface is negligible.
Total concentration $n_t$ on modified surface is approximately equal to concentration $n_1$ of particles adsorbed on sites D. Let us introduce the surface modification efficacy parameter $\gamma$ equal to the ratio between concentrations on modified surface $n_t$ and perfect surface $n_2$

$$\gamma = n_t / n_2 = \frac{\nu_0 n_2}{\nu n_0}$$ (8)

where $n_0$ is the concentration of sites S on the perfect surface. It is worthwhile to modify the surface if $\gamma \gg 1$. Let us obtain the expression for the surface modification efficacy parameter $\gamma$ for different cases. The magnitude of this parameter is defined by the equation $\mu_d = \mu_s$ and therefore it does not explicitly depend on the gas pressure.

Let us consider the case of low temperature $kT \ll \Delta E$, $\Delta E$ being the height of the potential barrier between two adjacent adsorption sites S. In this case particles adsorbed on sites S jump between these sites. The expression for the chemical potential of the particle adsorbed on sites S has the same form as for the particle adsorbed on the defect. In result the equation $\mu_d = \mu_s$ leads to the relation

$$\frac{\nu_d}{(1 - \nu_d) q_d} = \frac{\nu_0}{(1 - \nu_0) q_0}$$ (9)

where $q_0$ is the partition function of the particle adsorbed on site S. Now we substitute in Eq. (9) the equalities $\nu_d = n_1 / n_d$ and $\nu_0 = n_2 / n_0$ and consider the case $\nu_0 \ll 1$, when the surface modification is worthwhile for the purpose of selective adsorption. In result we get

$$\frac{n_1}{n_d - n_1} = \frac{n_2 q_d}{n_0 q_0}$$ (10)

From Eq. (10) we obtain

$$\gamma = \frac{n_2 q_d}{n_0 q_0} \left(1 + \frac{n_2 q_d}{n_0 q_0}\right)^{-1}$$ (11)

The partition functions of the particles adsorbed on sites D and S respectively may be represented by the expressions [14]:

$$q_d = q_d' \exp(E_d/kT),$$ (12)

$$q_0 = q_0' \exp(E_0/kT),$$ (13)

where $q_d'$ and $q_0'$ are the partition functions of the adsorbed particles including internal degrees of freedom, vibrations, and rotations or frustrated rotations; $E_d$ and $E_0$ are adsorption energies of particles adsorbed on sites D and S correspondingly. We get

$$\gamma = \frac{\beta n_d}{1 + \beta n_2},$$ (14)

$$\beta = \frac{q_d'}{n_0 q_0'} \exp\left(\frac{E_d - E_0}{kT}\right)$$ (15)

Now we consider the case of high temperature $kT \ll \Delta E$ when particles adsorbed on sites S freely move over the surface. In the case of low concentration of particles adsorbed on perfect surface ($\nu_0 \ll 1$) the interaction between adsorbed particles can be disregarded. Therefore we consider the system of particles adsorbed on perfect surface as the two-dimensional ideal gas. Then the chemical potential of the particle adsorbed on sites S is given by

$$\mu_s = kT \ln \left(\frac{n_2 h^2}{2\pi mkT q_d' \exp(E_0/kT)}\right)$$ (16)

where $q_d'$ is the partition function of the adsorbed particle, $q_d'$ includes internal degrees of freedom, rotations and one vibration for constrained motion perpendicular to the surface. From the relation $\mu_d = \mu_s$ we have the following expressions for the parameter $\gamma$
\[ \gamma = \frac{\beta n_d}{1 + \beta n_2}, \]  

(17)

where the parameter \( \beta \) for the case considered is

\[ \beta = \frac{q_d^2 \beta^2}{2 \pi m kT_\nu} \exp \left( \frac{E_d - E_0}{kT} \right) \]  

(18)

Note that in both cases, when adsorbed particles are localized and freely move over the perfect surface, the dependence of the parameter \( \gamma \) on the concentrations \( n_2 \) and \( n_d \) has the analogous form (Eqs. (14) and (17)).

To estimate the value of parameter \( \gamma \) with the help of Eqs. (14) and (17) it is necessary to calculate the partition functions of the particles. Nevertheless equivalent results can be obtained using kinetics principles. Contrary to our derivation of expression for parameter \( \gamma \) with the help of thermodynamical approach, where we use approximation (9) valid only for physical adsorption, the consideration of kinetics below is valid for both physical and chemical adsorption. By analogy with the standard premises of the Langmuir and BTE adsorption theories [17], we suppose that the kinetic coefficients for the adsorption and desorption of the particles are independent of their concentration. We suppose also that each site D on a modified surface is surrounded by area with sites S where local concentration of particles on this area equal to their concentration on perfect surface \( n_2 \). According to detailed balance for particles exchange between D and S sites we have

\[ k_d^-(1 - \nu_d)n_2 = k_d^+ \nu_d n_d \]  

(19)

where \( k_d^- \) is a coefficient of the adsorption on site D of the particle which have been just adsorbed on site S, and \( k_d^+ \) is a coefficient of desorption from site D with subsequent adsorption on site S. From Eq. (19) we obtain the expression for parameter \( \gamma \)

\[ \gamma = \frac{n_d k_d^-}{n_2 k_d^+} \left( 1 + \frac{k_d^+}{k_d^-} \right) \]  

(20)

The coefficient \( k_d^+ \) is given by the Arrhenius formula [15]:

\[ k_d^+ = \Omega_d \exp(-\Delta E_d/kT), \]  

(21)

where \( \Omega_d \) is a frequency multiplier equal in order of magnitude to the vibration frequency of the particle adsorbed on the defect, and \( \Delta E_d = E_d - E_0 + \Delta E_1 \) is the activation energy for the desorption of the particle from the defect onto the surface free of them, \( E_d \) and \( E_0 \) being the adsorption energy of the particle adsorbed on sites D and S, correspondingly, and \( \Delta E_1 \) is the height of the potential barrier between adsorption sites on the defect and on the surface.

Where \( kT \gg \Delta E \), the particle freely move over the surface, and the coefficient of adsorption on a defect site D from an area of surface with sites S is

\[ k_d^- = 2k' R < v >_s n_2 \exp(-\Delta E_1/kT), \]  

(22)

where \( k' \) is the probability of the adsorption on the defect site D for the particle moving over the surface just after its collision with site D, \( R \) is the radius of the defect, and \( < v > \) the average velocity component parallel to the surface for the particles adsorbed thereon. We define the probability \( k' \) as the ratio \( k' = N_a/N_c \) between number \( N_a \) of events of adsorption on site D immediately after the collision and number \( N_c \) of these collisions. This quantity is analogous to the coefficient of attachment of the particles to the surface in the case of an adsorption from a gas on a surface. After substitution of Eqs. (21) and (22) into Eq. (20) one have

\[ \gamma = \frac{\beta n_d}{1 + \beta n_2}, \beta = \frac{k' R < v >_s}{\Omega_d} \exp \left( \frac{E_d - E_0}{kT} \right) \]  

(23)

Where \( kT \ll \Delta E \), the particles jump between adjacent adsorption sites, and in this case \( k_d^- = k' l_n \omega \nu_0, \) where \( k' \) is the probability of the absorption on the defect immediately after a jump on this site, \( l_n \) is the number of the adsorption sites S adjacent to the defect, \( \omega \) is the jump frequency defined by the Arrhenius formula

\[ \omega = \Omega_0 \exp \left( \frac{\Delta E_1}{kT} \right), \]  

(24)
where $\Omega_0$ is a frequency multiplier equal in order of magnitude to the vibration frequency of the particles adsorbed on the site $S$. Note that according to simulation [16] the majority of jumps are between adjacent adsorption sites. In this case

$$\gamma = \frac{\beta n_d}{1 + \beta n_v}, \beta = \frac{k' l_m \Omega_0}{n_d \Omega_d} \exp \left( \frac{E_d - E_0}{kT} \right)$$

Expressions (14), (17), (23), (25) can be extended to the case of some different kinds of defects. Disregarding the contribution of particles adsorbed on sites $S$ to the total concentration $n_t$ of particles adsorbed modified surface we get

$$n_t = \sum_i n_{1i}$$

$n_{1i}$ is the concentration of particles adsorbed on the $i$-th kind of defects. In this case the surface modification efficacy parameter $\gamma$ for the total surface is

$$\gamma = n_t/n_2 = \sum_i n_{1i}/n_2 = \sum_i \gamma_i$$

where $\gamma_i$ is the surface modification efficacy parameter for the $i$-th kind of defects.

For some nanotechnological applications a high filling $\nu_d \approx 1$ of sites $D$ and absence of adsorbed particles on sites $S$ are necessary. For example, let us consider a pattern drown by the particles adsorbed on sites $D$. To distinguish such pattern two conditions should be fulfilled. Firstly, a high filling $\nu_d \approx 1$ of sites $D$ corresponds to a large value of parameter $\alpha_1 = 1/1 - \nu_d$. Secondly, for better pattern contrast the filling $\nu_d$ of sites $D$ should be significantly greater than the filling $\nu_0$ of sites $S$, that corresponds to a large value of parameter $\alpha_2 = \nu_d/\nu_0$. Let us introduce the second surface modification efficacy parameter $\Gamma$ which is equal to product of parameters $\alpha_1$ and $\alpha_2$

$$\Gamma = \alpha_1 \alpha_2 = \frac{\nu_d}{\nu_0(1 - \nu_d)} \quad (28)$$

The analytical expressions for parameter $\Gamma$ are derived with the help of both thermodynamical and kinetic approaches. Under the thermodynamical consideration we use the equation $\mu_d = \mu_s$ analogous to the derivation of expressions for parameter $\gamma$. In the case of jump diffusion of particles adsorbed on sites $S$ we get

$$\Gamma = \frac{q_d^2}{q_0} \exp \frac{E_d - E_0}{kT} \quad (29)$$

When the particles adsorbed on sites $S$ freely move over the surface we get the following expression for parameter $\Gamma$

$$\Gamma = \frac{n_0 h^2 q_d^2}{2 \pi m kT q_0} \exp \frac{E_d - E_0}{kT} \quad (30)$$

The Eqs. (29) and (30) are not convenient for practical use (analogous to Eqs. (14) and (17)) because it is necessary to calculate the partition functions. Therefore we have derived the equivalent expressions with the help of kinetic consideration. In the case of jump diffusion of particles adsorbed on sites $S$ we get

$$\Gamma = \frac{k' l_m \Omega_0}{\Omega_d} \exp \frac{E_d - E_0}{kT} \quad (31)$$

In the case when particles adsorbed on sites $S$ freely move over the surface we obtain the following expression

$$\Gamma = \frac{k' R < v >_s n_0}{\Omega_d} \exp \frac{E_d - E_0}{kT} \quad (32)$$

Note, that nanotechnological procedures described by parameters $\gamma$ and $\Gamma$ are applied only to the case of low concentration of adsorbed particles on sites $S$ $(\nu_0 \ll 1)$. Therefore the neglect of interparticle interaction is adequate for our consideration. However, Eqs. (23), (25), (31) and (32) derived in the framework of the kinetic approach may be easily extended to the case where this interaction is important (analogous to homogeneous adsorption, see, for example, [18]). To take into account an interparticle interaction it is sufficient to replace $E_d$ by $E_d + w_d N_d$ and $E_0$ by $E_0 + w_0 N_0$, where $w_d$ and $w_0$ are interaction energies between neighbor particles, and $N_d$ and $N_0$ are average numbers of nearest neighbors for particles adsorbed on sites $D$ and $S$, respectively.
The adsorption of particles on an unperfect surface for the simplest cases had been studied previously: in the cylindrical pore [19], in the split-shaped pore [20], at the intersection of two perpendicular steps forming a reentrant corner [20]. Nevertheless these studies dealt only with rather large surface defects. The case of nanolocal defects with sizes of order of the size of only one adsorption site was not considered.

Theory presented above does not depend on the nature of defects. They may be structural defects or chemical one and so on. We consider molecule adsorption on a single type of structural defects, namely, pits made by removing tens of atoms from the surface. Our interest in this type of defects is attracted by following reasons. Firstly, according to expressions (14), (17), (23), (25) surface modification efficacy parameter \( \gamma \sim \exp((E_p - E_0)/kT) \). Therefore the modification of surface by presence of the pits with certain size can cause the increase of concentration of certain kind of molecules. Some nanotechnological applications based on this effect are discussed in Sec. 4 (fabrication of sensors for trace molecule detection, separation of isomers etc.). Secondly, because of the recent nanotechnological advances the various techniques to produce pits on the surface had been elaborated. For example, it is possible to fabricate the pits only several nanometers in diameter [2,3] and even to remove a single atom from the surface structure [3] with the help of field desorption by STM tip. Therefore a theoretical study of particle adsorption in a pit is an actual problem now.

Here we have calculated the adsorption energy \( E_p \) for the argon atom and benzene and acetylene molecules adsorbed on graphite surface in pits that are different in size but can accommodate only one particle. We have choose a graphite for our study because the adsorption of argon (see, for example, [21]) and various molecules (see, for example, [22–24]) on perfect graphite surface have been carefully theoretically studied in a set of papers. Besides, the pits on the graphite surface were produced by nanolocal chemical reactions near STM tip [5] and by bombardment of cations with subsequent etching [25].

This is a nonspecific adsorption case where the adsorbate-adsorbent interaction is of the Van der Waals type [17]. We have described the interaction between the argon atom and the carbon atoms in terms of the Lennard-Jones potential

\[
U = 4\varepsilon \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right]
\]

with a cutoff radius of \( r_c = 3.2 \), where the potential parameters have been taken to be \( \sigma = 3.12 \text{ Å} \) and \( \varepsilon = 54.4 \text{ K} \) [21], \( \sigma = 3.82\text{Å} \) and \( \varepsilon = 31.6 \text{ K} \) for the C-C interaction [26], and \( \sigma = 3.37 \text{ Å} \) and \( \varepsilon = 21.7 \text{ K} \) for the H-C interaction [26]. The atoms of graphite have been assumed to be fixed at the lattice sites, three graphite layers with 288 atoms in each layer being taken into account. The interatomic bonds in the molecules have been taken to be rigid, and the interatomic bond angles fixed. The bond length values used (1.4 Å for the C-C bond and 1.08 Å for the H-C one) have been borrowed from [26].

We have considered pits with near circular shape that are created by the removal of atoms located inside circles of radii \( R_1 \) and \( R_2 \) for first and second graphite layers correspondingly. The centers of these circles locate on one vertical line \( l \). All possible pits with \( 0 \leq R_2 < R_1 < 5.06\text{Å} \) for argon atom and with \( 0 \leq R_2 < R_1 < 6.80\text{Å} \) for acetylene and benzene molecules have been investigated. Several different positions of line \( l \) relative atoms of graphite were considered. Namely, the line \( l \) passes through: 1) an atom of upper graphite layer under which an atom of the second layer locates (type A); 2) an atom of upper graphite layer under which an atom of the second layer is absent (type B); 3) the center of a bond between two atoms of upper graphite layer (type C); 4) the center of hexagon formed by atoms of upper graphite layer (type D). The optimal pits with one and two graphite layer deep, where the adsorption energy is a maximum \( E_{p}^{\text{max}} \) are found for all three adsorbates. For all these cases the energies of adsorption in optimal pits are maximum when the center of a particle coincide with the center of the pit. Several pits of oblong shape with the size close to the size of the optimal pit with near circular shape are also examined for acetylene molecule. Nevertheless the adsorption energies in these oblong pits are less than adsorption energy in the optimal pit with near circular shape. These adsorption energies \( E_{p}^{\text{max}} \) and characteristics of optimal pits are listed in Table 1 for all three adsorbates.

The calculations show that the adsorption energy in an optimal pit for small particles (argon atom and acetylene molecule) is nearly twice as large as the adsorption energy on perfect surface. The adsorption energy in the optimal pit with two graphite layer deep is only 7% greater than the adsorption energy in the optimal pit with two graphite layer deep. The further increase of pit depth does not cause the adsorption energy to increase. Therefore a pit a mere 1-2 atomic layers deep may be sufficient to increase the adsorption energy to the utmost, which is fairly convenient for nanotechnological applications.

A particle adsorbed in a pit interacts with walls and bottom of the pit. And a particle adsorbed in a capillary interacts only with walls of capillary. Therefore the adsorption energy of a particle in a pit is greater than in a capillary with the same radius. Previously the adsorption energy of a particle in a cylindrical capillaries with various
radii has been calculated analytically [19]. In [19] the interaction between the particle and the walls of the capillary has also been described in terms of the Lennard-Jones potential. However, the capillary walls in this simplified model have been considered continuous. According to calculations in the framework of this model the ratio \( \epsilon_0 \) between the maximal adsorption energy \( E_{c}^{\text{max}} \) of a particle in the capillary and the adsorption energy on the perfect surface is \( \epsilon_0 = E_{c}^{\text{max}}/E_s \approx 3 \). This value of \( \epsilon_0 \) is 1.5 times as great as value calculated by us for adsorption in a pit \( \epsilon_0 = 2.06 \). Therefore the consideration of the location of all the atoms of the surface is necessary for exact calculation of adsorption energy in a pit or a pore. For benzene molecule adsorbed in an optimal pit, the simplified model [19] overestimates the maximal increase in the adsorption energy even more because atoms of adsorbed molecule interact weaker with pit wall sections distant from them than with the pit bottom. The value of the energy ratio \( \epsilon_0 \) calculated here for argon atom adsorption in a pit on graphite surface is close to the one calculated for argon atom adsorption on microporous magnesium oxide with taking into account location of all the atoms [20]. According to the calculation [20] \( E_{c}^{\text{max}}/E_s \approx 1.8 \) for the split-shaped pore and at the intersection of two perpendicular steps forming a reentrant corner.

Fig. 1 demonstrates that the energy of adsorption in a pit is determined by the size of the pit. This figure also shows that a pit too small to accommodate a molecule even reduces its adsorption energy. This two facts open up new interesting possibilities for nanotechnological applications which have been discussed below. An additional point to emphasize is that the "flat" benzene molecule placed in a pit of optimal size but with a "unflat" bottom has a lower adsorption energy than in the case of unmodified surface.

### IV. SIMULATION OF ADSORPTION OF PARTICLE IN PITS.

The parameters \( \gamma \) and \( \Gamma \) have been estimated for the case of argon atom adsorption on graphite surface with pits. For this estimation it is necessary to calculate the oscillation frequency \( \Omega_p \) of atom adsorbed in a pit and the probability \( k' \) of the absorption in the pit for the particle moving over the surface just after its collision with the pit. These quantities were obtained by molecular dynamics simulations. According to Eqs. (23) and (32) parameters \( \gamma \) and \( \Gamma \) increase with the adsorption energies \( E_p \) in a pit. Therefore two pits were used for simulation: the optimal pit with maximum adsorption energy in it and the pit with maximum adsorption energy among the investigated pits with only one graphite layer depth (see Table 1). The adsorption energy in this pit is only 8% less than adsorption energy in optimal pit.

A system consisting of three graphite layers with 288 atoms in each layer was used in simulation. Along X and Y axes parallel to the graphite surface we impose periodic boundary conditions on the system. The size of the simulation cell in these directions was \( 27.08 \times 23.43 \text{Å} \). The interaction between the argon atom and carbon atoms was represented by Lennard-Jones potential (33). The atoms of second and third graphite layers were fixed at equilibrium positions. The interaction between carbon atoms of first graphite layer was described by modified Born potential

\[
U = \frac{\alpha - \beta}{2} \sum_{i,j=1}^{N} \left( \frac{r_{ij} - r_{0ij}}{r_{ij}} \right)^2 + \frac{\beta}{2} \sum_{i,j=1}^{N} \left( \frac{r_{ij} - r_{0ij}}{r_{ij}} \right)^2
\]

where \( r_{ij} \) are distances between carbon atoms, \( r_{0ij} \) are distances between carbon atoms at equilibrium positions, \( \alpha \) and \( \beta \) are force constants. We take \( \alpha = 505.1 \text{ N/m} \) and \( \beta = 84.4 \text{ N/m} \) [27]. The Born potential represents the expansion of the interaction energy between carbon atoms in terms of \( \Delta r_{ij} = r_{ij} - r_{0ij} \). Therefore this potential is adequate only for small values of \( \Delta r_{ij} \). We simulated the system at temperatures that approximately 20 times less than the temperature of graphite melting. At such temperatures the displacements of graphite atoms from equilibrium positions and, consequently, values of \( \Delta r_{ij} \) are small. Therefore we consider that Born potential is acceptable for our simulation.

The equations of motion were integrated using the leap frog algorithm. The integration step used was \( \tau = 2 \cdot 10^{-15} \text{ s} \). Initially the system of graphite atoms has been brought to the equilibrium during \( 5 \cdot 10^3 \) steps (about 300 oscillations of atoms in graphite) in canonical ensemble and \( 5 \cdot 10^3 \) steps in microcanonical ensemble. Further simulations were performed in microcanonical ensemble. The total energy of the system with the temperature 185 K was conserved to within 1 % and average fluctuations of temperature were within 3 %.

The estimation of oscillation frequencies \( \Omega_d \) of atom adsorbed in the pits has been performed for the system with the temperature 165 K. Initially we took the system without a pit with equilibrium coordinates and velocities of carbon atoms. Then the pit arises near the center of simulation cell and an atom was placed in the pit at the position that corresponds to the maximum adsorption energy. The new system with the pit and the atom adsorbed in this pit has been brought to the equilibrium during \( 2 \cdot 10^3 \) steps. Then frequencies \( \Omega_d \) were calculated during \( 6 \cdot 10^3 \) steps. The obtained values averaged over 40 modeling experiments are \( \Omega_d = 5.3 \cdot 10^{11} \text{ s}^{-1} \) and \( \Omega_d = 4.7 \cdot 10^{11} \text{ s}^{-1} \) for optimal pits with one layer and two layers deep.
The size of simulation cell used is not sufficient for argon atom appeared in any place of the cell to come to equilibrium with the surface before a collision with the pit. To overcome this difficulty the simulation of the process of the atom adsorption from the surface into the pit was carried out using the following procedure. An argon atom is placed in the center of simulation cell without a pit at the position that corresponds to the minimum of interaction energy with the surface. Then this system comes to equilibrium until the argon atom reaches the boundary of the cell. At the instant the argon atom crosses the boundary the pit arises in the center of the cell. The appearance of the pit was investigated for the system at the temperature 185 K. The change in the energy of interaction between argon atom and graphite atoms caused by the appearance of the pit is within 0.03%. Therefore we consider that the appearance of the pit does not essentially perturb the motion of argon atom and equilibrium between argon atom and surface. During the time between the appearance of the pit and the argon atom collision with the pit graphite atoms make about 100 oscillations that is sufficient for system to come to equilibrium [28].

On the average an argon atom makes 12 jumps before collision with the pit. Average change in the kinetic energy of argon atom in result of collision with the surface is \( < \Delta E > = 17 \pm 1.2\% \), \( \Delta E_i = 2|E_i - E_{i-1}| \cdot 100\%/(E_i + E_{i-1}) \), where \( E_{i-1} \) and \( E_i \) are average through the time of jump kinetic energies of argon atom between \( i\)-th-th and \( i\)-th, and \( i\)-th and \( i+1\)-th collisions with graphite surface respectively. The value \( < \Delta E > \) has been obtained by averaging 20 argon atoms, each making 10 jumps along the surface. We believe that observed energy exchange between argon atom and the surface is sufficient to argon atom to come to equilibrium with the surface.

An argon atom was considered to collide with the pit when the distance between it and the center of the pit was less than the distance between the center of the pit and a adjacent adsorption site \( S \). An argon atom was considered to be adsorbed in the pit when it makes two oscillations in the pit. The simulation with one atom was performed until the atom reflects from the pit, adsorbs into the pit or evaporates from the surface. To exclude atoms with low velocities the time of experiment was limited to \( 2 \cdot 10^5 \) integration steps. The results of simulations are averaged over all modelling experiments for given temperature of surface. These results and calculation of the probability \( k^1 \) of the adsorption into the pit and the efficacy parameters are presented in Table 2. The probability \( k^2 \) of the adsorption into the pit slightly increases with temperature. We offer the following explanation for this increase. When a particle occurs on the surface near a pit edge it interacts with a less number of atoms of the surface than a particle located on perfect surface. Thus the pit is surrounded by an energetical barrier. The magnitude of this barrier is found to be about 300 K in simulated system. Therefore the fraction of particles capable to overcome the barrier increases with the increase of temperature for the considered temperature range 120-280 K.

According to our estimations for considered case of argon atom and optimal pit in a graphite surface at temperature 200 K we get \( \beta n_0 \ll 1 \) for \( \nu_0 \ll 1 \). Then Eq. (23) is simplified

\[
\gamma = \beta n_d
\]

so that the parameter \( \gamma \) does not depend on the concentration of atoms in the gas. The Eq. (35) have been used to estimate the parameter \( \gamma \) for considered case. Let us express the concentration of pits in terms of fraction of the surface occupied by them, i.e., \( n_d = \alpha/\pi R^2 \). The parameter \( \gamma \) is calculated for \( \alpha = 0.1 \). The calculated parameters \( \gamma \) and \( \Gamma \) are presented in Table 2. The magnitudes of these parameters are sufficient for nanotechnological applications discussed below. We believe that this conclusion may be also obtained for various other pairs adsorbent-adsorbate.

Graphite is a very homogenous adsorbent, i.e., the potential barriers \( \Delta E \) between the adjacent adsorption sites on it are low. For the argon atom, \( \Delta E/k \approx 32 \text{ K} \) [29]. At low temperatures \( (kT \ll \Delta E) \) the submonolayer \( (\nu_0 \ll 1) \) adsorption of argon on a graphite surface is impossible for any experimentally obtainable concentrations of atoms in the gas. Therefore the case of jump diffusion of adsorbed particles is not considered for this pair adsorbent-adsorbate.

**V. NANOTECHNOLOGY APPLICATIONS.**

Here we describe some possible nanotechnology applications for the adsorption on a surface with nanometer-scale artificial defects (see also [30]): pattern transfer as a result of self-organization of particles deposited on such surface, and using of selective adsorption for sensors fabrication and isomer separation.

**Pattern transfer.** The elaboration of methods of pattern transfer in nanometer scale, i.e. fabrication of nanostructures on the surface according to a given scheme is very important for some nanotechnology applications (for example, superdense recording of information, fabrication of periodic arrays of quantum dots and quantum wires, one-electron devices etc.). In principle, surface nanostructures had been produced with the help of STM or AFM tip by the transfer of single atoms [31,32], clusters [33,34], and nanoparticles [35]. Nevertheless, until now these methods have the productivity insufficient for nanotechnology purposes.

The other set of methods for surface nanostructures fabrication is based on self-organization of deposited particles: a) the formation of islands in the result of nucleation in two-dimensional film (see, for example, [10]); b) self-organizing...
ordering in epitaxial layer with facets formation (see, for example, [36]); c) the formation of periodical surface structure by laser radiation [37,38]. The method a) allows to control only average distance between islands. The methods b) and c) are suitable only for periodical nanostructures fabrication with periods by chemical composition of nanoobjects and wave length of laser radiation, correspondingly. The productivity of these methods is considerably greater than transfer of single particles by STM or AFM tip. Nevertheless they are not suitable for pattern transfer.

A particle adsorbed on defect may play the role of nucleation center for island formation from the particles deposited on the surface. For example, the gold islands on the graphite surface irradiated with ions form only around defects [10]. We propose to deposit particles on the surface with defects located with the help of STM or AFM according to given scheme. In this case the formed islands would merge into planned surface nanostructure.

Recently the diode on one molecule was fabricated [39]. We proposed to place such molecules in electronic schemes of nanometer scale with the help of adsorption on specially created defects. We believe that by these means it is possible to control not only the position but also the orientation of the molecule.

**Sensors for molecular detection.** Methods for detecting traces of certain molecules in a gas where their concentration is low are of great importance in modern technology and find application, for example, to ensure safety in chemical industries and monitor environmental pollution. The further development of such methods, particularly is therefore a high-priority task. A weak spot in methods used is the collection of molecules from air. The known method of improving sensitivity [40] involves the nonselective accumulation of the trace molecules of interest on a cooled substrate and their subsequent pulsed laser desorption. It therefore seems extremely tempting to develop a method for **selective** adsorption of molecules on a cold surface.

Calculations performed show that the adsorption energy in a pit is determined by the size of the pit. We propose to modify the surface of sensor by presence of the pits with maximum adsorption energy for certain kind of molecules. According to the theory presented the concentrations of these molecules on the surface of sensor will increase. Therefore it would enable one to add one more selective step to the existing two detection steps — the optical and the mass-spectrometric ones.

**Isober separation.** Pits can be arranged on a surface so closely that the distances between them have the same order as their size. The molecular adsorption energy on such a surface will be higher for molecules that fit in the pits, compared to that on the unmodified surface, and lower for those which fail to fit in the pits. A surface modified in this fashion could be used to effect the selective adsorption of a particular molecular species from a mixture of different molecules. What is more, a surface can be modified to have pits capable of accommodating only one of several isomeric molecular species. We suggest using such a modified surface to detect or separate molecules differing in *shape* only (e.g., to isolate linear or cyclic isomers from their mixture and separate fullerene isomers and left- and right-handed molecules).

In summary, the theory of adsorption on the surface with nanolocal defects is developed. Two efficacy parameters of surface modification by creation of artificial defects are introduced for different nanotechnological applications. The estimations with the help of molecular dynamics simulations on the example of argon atom adsorption in the pit on the graphite surface show that magnitudes of these parameters are sufficient for possible nanotechnological applications.

**ACKNOWLEDGEMENT.**

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Figure captions.

Fig.1. The dependence of the energy $E_p$ of adsorption in a pit with one graphite layer deep on the number $N_1$ of atoms removed when making this pit; a) acetylene molecule, b) benzene molecule. Solid squares corresponds to pits of type A and open circles correspond to pits of type C. Points corresponds to pits of types B and D are not shown because they coincide with points corresponds to pits of types A and C.
Table 1. Characteristics of optimal pits: the type of the pit \( l \) (see text); the number of atoms removed when making this pit from the first and second graphite layers, \( N_1 \) and \( N_2 \), respectively. Adsorption energies in the optimal pit \( E_{p,\text{max}} \) and in the optimal pit relative to that on the unmodified surface \( \Delta E = E_{p,\text{max}} - E_0 \) (in Kelvin degrees); the energy ratios \( \epsilon_0 = E_{p,\text{max}}/E_0 \) and \( \epsilon_1 = E_{p,\text{max}}/E_{p,\text{max}}^1 \), where \( E_{p,\text{max}}^1 \) is the maximum adsorption energy among the pits with one graphite layer deep.

<table>
<thead>
<tr>
<th>particle</th>
<th>( l )</th>
<th>( N_1 )</th>
<th>( N_2 )</th>
<th>( E_{p,\text{max}} )</th>
<th>( \Delta E )</th>
<th>( \epsilon_0 )</th>
<th>( \epsilon_1 )</th>
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</thead>
<tbody>
<tr>
<td>argon atom</td>
<td>A</td>
<td>13</td>
<td>12</td>
<td>1751</td>
<td>901</td>
<td>2.06</td>
<td>1.083</td>
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<td>16</td>
<td>3682</td>
<td>1873</td>
<td>2.03</td>
<td>1.108</td>
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<tr>
<td>benzene molecule</td>
<td>B</td>
<td>31</td>
<td>25</td>
<td>8379</td>
<td>2944</td>
<td>1.54</td>
<td>1.069</td>
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</table>

Table 2. Results of simulation of adsorption of atom from the surface into the pit and calculation of surface modification parameters. \( h \) is the depth of pit in graphite layers; \( T_g \) is the temperature of graphite surface; \( N_c \) is the number of atoms collided with the pit; \( N_a \) is the number of atoms adsorbed into the pit; \( k' \) is the probability of the absorption into the pit, \( \gamma \) and \( \Gamma \) are surface modification parameters. The accuracy of calculation of \( k' \) and parameters \( \gamma \) and \( \Gamma \) is connected with statistical error of detected events of atom adsorption into the pit.

<table>
<thead>
<tr>
<th>( h )</th>
<th>( T_g )</th>
<th>( N_c )</th>
<th>( N_a )</th>
<th>( k' )</th>
<th>( \gamma )</th>
<th>( \Gamma )</th>
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<tr>
<td>1</td>
<td>123</td>
<td>502</td>
<td>62</td>
<td>0.124 ± 0.017</td>
<td>24.16 ± 3.25</td>
<td>3438.0 ± 462.8</td>
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<tr>
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<td>165</td>
<td>350</td>
<td>51</td>
<td>0.146 ± 0.022</td>
<td>6.90 ± 1.03</td>
<td>981.5 ± 147.1</td>
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<tr>
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<td>602</td>
<td>93</td>
<td>0.154 ± 0.017</td>
<td>3.28 ± 0.37</td>
<td>467.1 ± 52.0</td>
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<tr>
<td>1</td>
<td>248</td>
<td>631</td>
<td>93</td>
<td>0.147 ± 0.016</td>
<td>1.81 ± 0.20</td>
<td>258.2 ± 28.7</td>
</tr>
<tr>
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<td>286</td>
<td>602</td>
<td>112</td>
<td>0.169 ± 0.017</td>
<td>1.49 ± 0.15</td>
<td>211.8 ± 21.6</td>
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<tr>
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<td>248</td>
<td>367</td>
<td>41</td>
<td>0.112 ± 0.018</td>
<td>72.72 ± 11.97</td>
<td>10347.9 ± 1704.0</td>
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<td>2.98 ± 0.37</td>
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<td>405.5 ± 43.9</td>
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