Adsorption on a surface with varying properties

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Abstract

We propose a self-consistent model taking into account the variations in adsorption properties of an adsorbent surface in the process of adsorption–desorption of gas particles on it. We introduce a dimensionless coupling parameter equal to the normalized adsorption-induced activation energy for desorption due to the substrate deformation caused by the adsorption-induced force. Bistability of the system of noninteracting adparticles is established in the case when the coupling parameter is greater than a critical value and the gas concentration belongs to a certain interval. We show that the adsorption isotherms obtained within the framework of the proposed model essentially differ from the Langmuir isotherms and we show that the Zeldovich hysteresis is possible. The kinetics of the surface coverage is analyzed in detail in the overdamped approximation. We show the possibility of a ‘quasi-stationary’ state of the system due to variations in adsorption properties of the surface in adsorption–desorption.

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1. Introduction

The study of the adsorption of particles on the surface of different bodies covers a very wide class of problems in physics and chemistry and is one of the most important problems both from the theoretical point of view and for practical applications. The results of numerous investigations show that adsorption of particles on the surfaces of bodies leads to changes in various physical and chemical characteristics of these bodies. Detailed analyses of the changes in the properties of the surface due to adsorption are given in, for example, [1–10]. The results of investigations of the changes in properties of the surface due to adsorption–desorption processes are also widely applied in the design of various sensors (physical, chemical and biological) [11, 12] whose action is based on the use of the change in a certain characteristic of a sensitive element of the sensor due to adsorption of particles on its surface.

The results of the theory of adsorption are extremely important for the investigation of heterogeneous-catalytic reactions because the processes of adsorption and desorption are integral stages of these reactions.

The classical Langmuir theory that describes the adsorption of a gas on the surface of a solid is based on several assumptions. Numerous theoretical investigations, which were, to a large extent, stimulated by many experimental data that did not agree with the conclusions of the Langmuir theory, were aimed at the construction of more general models free of one or several assumptions of the Langmuir theory. Extensive material obtained on the basis of these models and applications to various problems of adsorption and catalysis are widely presented in the literature (see, e.g., [7, 13–19]). In particular, taking into account lateral interactions between adparticles leads to a qualitative change in adsorption isotherms, namely to a hysteresis of isotherms, and different structural changes in the substrate surface (reviews of the theoretical and experimental results are given in, e.g., [3, 6–10, 17, 19]). A qualitative change in the surface structure in adsorption results in various specific features of oscillatory surface reactions and the formation of different spatiotemporal patterns (for the oscillatory kinetics in heterogeneous catalysis and related problems, see, e.g., the reviews [20–22]).
At the same time, as early as 1938, Zeldovich [23] suggested the idea of a change in adsorption properties of the surface in the course of adsorption and desorption. Using this idea, he predicted hysteresis of adsorption isotherms if the typical time of adsorption and desorption is much less than the relaxation time of the surface. Unfortunately, Zeldovich’s work [23] has been cited very poorly. Further developments of the Zeldovich idea and its theoretical realization are given in the present paper.

Note that the change in the adsorption isotherms due to lateral interactions between adparticles can also be interpreted as the consequence of a certain change in adsorption properties of the surface due to adsorption. However, as far as we know, in the absence of interactions between adparticles, the problem of the variation in adsorption properties of the surface itself in localized adsorption of gas particles on it due to retardation of the surface relaxation relative to adsorption processes and the possibility of hysteresis of adsorption isotherms caused by this retardation remains open.

In recent years, investigations of the specific features of the surface diffusion of adparticles over the substrate surface caused by retardation effects have attracted considerable interest. It is an established fact that memory effects are essential for surface diffusion if the relaxation time of the substrate is comparable (or greater than) with typical times for moving adparticles (see, e.g., the review [24] and references therein). Several models that describe the surface diffusion of adparticles with regard to retardation are based on dynamical changes in properties of the surface by moving particles, which, to some extent, is similar to the Zeldovich idea of a substrate varying its adsorption properties in adsorption. For example, interesting results caused by memory effects are obtained in [25, 26] for multiparticle random walks on a surface deformed by the moving particles, namely: particles randomly distributed in the beginning, due to their indirect interaction via the medium deformed by these particles, are self-organized into cluster patterns at an intermediate stage with a subsequent return to the random distribution pattern at a late stage.

The present paper is devoted to an investigation of specific features of the behavior of adsorption isotherms and the kinetics of the surface coverage by adparticles with regard to variations in adsorption properties of the surface in adsorption–desorption.

In section 2, we propose a self-consistent model taking into account the variations in adsorption properties of the surface in adsorption–desorption of gas particles on it. We introduce a dimensionless coupling parameter equal to the normalized adsorption-induced activation energy for desorption due to the substrate deformation caused by the adsorption-induced force. We obtain adsorption isotherms and establish that their behavior essentially depends on the value of this parameter (section 3). It is shown that, within the framework of the proposed model, the Zeldovich hysteresis is possible. In section 4, we investigate specific features of the surface coverage kinetics in the overdamped approximation. It is established that variations in adsorption properties of the surface in adsorption–desorption can essentially change the Langmuir kinetics.

2. Model of the surface with varying adsorption properties

We consider localized adsorption of particles of a one-component gas on the surface of a solid adsorbent. According to the classical Langmuir theory, gas particles are adsorbed on adsorption sites located at the adsorbent surface and the number of sites does not change with time. Furthermore, all sites have equal adsorption activity (energetically homogeneous surface), do not interact with each other, and each adsorption site can be bound only with one gas particle. The Langmuir kinetics of the quantity of adsorbed substance is described by the differential equation [13]

\[ \frac{d\theta}{dt} = k_a C (1 - \theta) - k_d \theta, \]  

(1)

where \( \theta(t) = N_b(t)/N \) is the surface coverage by the adsorbate, \( N \) is the total number of adsorption sites, \( N_b(t) \) and \( N_v(t) \) are, respectively, the numbers of occupied and vacant \( (N_b(t) = N - N_v(t)) \) adsorption sites at the time \( t \), \( k_a \) and \( k_d \) are the adsorption and desorption rate constants, respectively, and \( C \) is the concentration of particles in the gas phase that is kept constant.

The solution of this equation with zero initial condition \( \theta(0) = 0 \) has the form [16]

\[ \theta(t) = \theta^a_{st} \left[ 1 - \exp \left( -\frac{t}{\tau_{ad}} \right) \right], \]  

(2)

where

\[ \theta^a_{st} = \frac{\ell}{1 + \ell} \]  

(3)

is the stationary surface coverage (Langmuir isotherm), which is defined by the single dimensionless quantity (dimensionless concentration) \( \ell = CK \), \( K = k_a/k_d \) is the adsorption–desorption equilibrium constant for the given gas concentration,

\[ \tau_{ad} = \frac{1}{k_a C + k_d} \]  

\( \frac{k_d}{1 + \ell} \)  

(4)

is the time taken for the surface coverage to reach the stationary value \( \theta^a_{st} \), and \( \tau_d = 1/k_d \) is the typical lifetime of a bound adsorption site.

According to (2) and (3), single-valued correspondence between the gas concentration and the surface coverage occurs. At the same time, in [23], Zeldovich has suggested the idea of a change in adsorption properties of the surface in adsorption–desorption and, using this idea, predicted a hysteresis of adsorption isotherms if the typical time of adsorption and desorption is much less than the relaxation time of the surface. A hysteresis form of adsorption isotherms due to attractive lateral interactions between adparticles is well known [3, 6, 7, 9, 17, 19]. In the present paper, we investigate one more possibility of the hysteresis behavior of adsorption isotherms not connected with lateral interactions between adparticles.

Within the framework of the Langmuir model, we consider the problem of localized adsorption of a one-component gas on a homogeneous solid with a flat
surface. We introduce the Cartesian coordinate system centered at the surface of the adsorbent with the $\theta$-axis directed to the adsorbent perpendicularly to its surface so that the adsorbent and the gas occupy the regions $x \geq 0$ and $x < 0$, respectively.

To take into account variations in adsorption properties of the surface in adsorption, we use the classical Einstein model according to which each atom of a solid oscillates like a simple harmonic oscillator in a potential well formed by the forces of its interaction with neighbors [27, chapter 2]. Based on this model of independent oscillators, we simulate each adsorption site by a one-dimensional (1D) linear oscillator of mass $m_0$ that oscillates perpendicularly to the surface about its equilibrium position $x = 0$. In the absence of an adsorbate, the motion of an adsorption site is described by the well-known equation of motion of a free linear oscillator

$$m_0 \frac{d^2 x}{dt^2} + \alpha \frac{dx}{dt} + \kappa x = 0,$$

where $\kappa$ is the restoring force constant, $\alpha$ is the friction coefficient and $x$ is the coordinate of the oscillator.

The binding of a gas particle with an adsorption site is accompanied by a change in the charge density spatial distribution of the bound adsorption site as compared with that of a vacant one. This change depends on the nature of adsorption bonds; specific features of both the substrate and gas particles, furthermore, can considerably differ for the same substrate but with different crystal planes of its surface (see, e.g., [3, 7, 8, 20–22, 28]). For example, due to adsorption, the dipole moment of a bound adsorption site, induced, for example, by polarization of an adparticle in adsorption and/or the transfer of an electron charge between the substrate and an adparticle, differs from that (in the particular case, zero) of a vacant adsorption site. In addition, in the general case, the binding of a gas particle with an adsorption site is also accompanied by a change in the electron structure of atoms (and, possibly, their displacements) in the nearest neighborhood of the adsorption site.

This leads to a change in the interaction of the adsorption site occupied by an adparticle with neighboring atoms of the adsorbent including not only neighboring adsorption sites but also subsurface atoms (atoms in the nearest substrate subsurface region) and free electrons (if any, e.g., in the case of a metal substrate). As a result, the resulting force acting on the bound adsorption site and, hence, the potential well corresponding to it change. This can be regarded as the appearance of a certain adsorption-induced force $F(\vec{r}, t)$, where $\vec{r}$ is the running coordinate of the site, acting on the bound adsorption site. Under the action of this force, the bound adsorption site tends to a new equilibrium position different from the equilibrium position $x = 0$ of the vacant site. As soon as the adparticle leaves the adsorption site, the last becomes vacant and relaxes to its nonperturbed equilibrium position $x = 0$. For the subsequent adsorption of other gas particle on this vacant adsorption site, two different situations are possible: a gas particle occupies the site after or before it reaches the equilibrium position $x = 0$. In the second case, this particle is adsorbed on the surface locally deformed by the previous adparticle. This retardation of relaxation of a vacant adsorption site relative to the adsorption stage results in an indirect correlation between gas particles subsequently adsorbing on the same adsorption site, and adsorption with memory occurs.

We consider the case when the interaction of the bound adsorption site with neighboring atoms of the substrate remains axially symmetric about the axis passing through it and parallel to the $\theta$-axis. In this case, the force $F(\vec{r}, t)$ has only the component normal to the boundary, $F(\vec{r}, t) = \vec{e}_x F(x, t)$, where $\vec{e}_x$ is the unit vector along the $\theta$-axis; for convenience, the adsorption site has the coordinate $\vec{r} = (x, 0, 0)$.

The force $F(\vec{r}, t)$ acts on the oscillator if it is occupied by a gas particle and does not otherwise. Instead, we consider the approximation of a time-continuous force, which corresponds to an adsorption site permanently bound to an adparticle with the time-dependent probability (the mean occupancy of adparticle on an adsorption site) equal to the surface coverage $\theta$, i.e. $F(x, t) = F(x) \theta$. This approximation is analogous to the mean-field approximation used in problems of adsorption with regard to lateral interactions between adparticles (see, e.g., [7]).

Representing the force $F(x)$ in the form $F(x) = -\frac{dV(x)}{dx}$, expanding the potential of this force $V(x)$ in the Taylor series and keeping only the linear term, we obtain

$$V(x) \approx -\chi x,$$

where the parameter

$$\chi = -\left. \frac{dV(x)}{dx} \right|_{x=0}$$

is the constant adsorption-induced force acting on the bound adsorption site, which can be regarded as a parameter of bound adsorption site–substrate interaction caused by adsorption.

Disregarding the internal motions in the adparticle–adsorption site system, i.e. considering the motion of the bound adsorption site as a whole, and taking into account a change in the mass of the oscillator in adsorption–desorption within the framework of this approximation, we obtain the following equation of motion for the bound oscillator:

$$\frac{d}{dt} \left( m_{\text{eff}}(\theta) \frac{dx}{dt} \right) + \alpha \frac{dx}{dt} + \kappa x = \chi \theta,$$

where $m_{\text{eff}}(\theta) = m_0 + m \theta$ is the effective mass of the bound oscillator that varies in adsorption–desorption and $m$ is the mass of an adparticle. Since $\theta \leq 1$, the effective mass of the bound oscillator does not exceed its total mass $M = m_0 + m = m_{\text{eff}}(1)$.

According to equation (7), the binding of a gas particle with an adsorption site results in a change in the equilibrium position of the oscillator: from $x = 0$ for the free oscillator to a position determined from the relation $x = x_{\text{max}} \theta$, where $x_{\text{max}} = \chi / \kappa$ is the maximum displacement of the equilibrium position of the bound oscillator from the surface caused by adsorption for $\theta = 1$. Thus, adsorption is accompanied by displacements of adsorption sites from the nonperturbed surface of the substrate, i.e. the formation of local defects of the surface, which are ‘pits’ (for $\chi > 0$) or ‘hills’ (for $\chi < 0$).
whose depth and height depend on the properties of both the adsorbate and the adsorbent. If all atoms of the surface are adsorption sites, then adsorption leads to a displacement of the adsorbent surface either inwards (for \( \chi > 0 \)) or outwards (for \( \chi < 0 \)), i.e. normal relaxation of the surface occurs [3]. In the framework of the approximation used, the forces of possible lateral interactions between adparticles are parallel to the substrate surface and, hence, do not make a contribution to the adsorption-induced force directed perpendicularly to this surface. Therefore, the last force (and, hence, a displacement of the surface of adsorption sites) is caused by the interaction of a bound adsorption site with the nearest subsurface atoms of the substrate and free electrons.

In the limiting case of total monolayer coverage (\( \theta = 1 \)), the potential energy of the bound oscillator \( U(x) = x^2/2 + V(x) \), where the first term on the right-hand side of this relation is the potential energy of the free oscillator and the second is the potential energy of the bound oscillator in the constant adsorption-induced force field. Since this force is caused by a change in the adsorption site–substrate interaction in adsorption, here, the quantity \( V(x) \) can be interpreted as the interaction energy of a bound oscillator with substrate deformed in adsorption. The potential energy \( U(x) \) is minimal at the equilibrium position of the bound oscillator \( x = x_{\text{max}} \) and is equal to \( U_{\text{min}} \equiv U(x_{\text{max}}) = V/2 \), \( V \equiv V(x_{\text{max}}) = -\chi^2/x \).

Within the framework of the Langmuir theory of kinetics on the nondeformable surface (\( \chi = 0 \)), the adsorption and desorption rate constants \( k_s \) and \( k_d \) do not depend on the gas concentration and are defined by the Arrhenius relations

\[
k_s = k_s \exp \left( -\frac{E_s}{k_B T} \right), \quad k_d = k_d \exp \left( -\frac{E_d}{k_B T} \right),
\]

where \( E_s \) and \( E_d \) are the activation energies for adsorption and desorption, respectively, \( k_s \) and \( k_d \) are the pre-exponential factors, \( T \) is the absolute temperature and \( k_B \) is the Boltzmann constant.

The Hamiltonian of the adparticles–substrate system contains the term \( -\chi \rho \partial \xi \) caused by the substrate deformation in adsorption due to the adsorption-induced force field. This implies that an adparticle is not only in a potential well of constant depth \( E_s \) but, in addition, also in the adsorption-induced potential \( V(x) \), i.e. in a deeper potential well than an adparticle on a nondeformable surface. As a result, in the case at hand, for desorption of an adparticle, it must get an energy greater than \( E_d \) by the value \( V(x) = \chi x \), which can be regarded as an additional adsorption-induced activation energy for desorption caused by the substrate deformation. Note that the quantities \( E_d \) and \( \chi x \) can be interpreted as the first and second terms, respectively, of the Taylor series of the coordinate-dependent activation energy for desorption \( E_{\text{ad}}(x) \). It is well known that taking into account lateral interactions between adparticles in the mean-field approximation leads to an additional coverage-dependent term of the activation energy for desorption (see, e.g., [7, 9, 17, 19]). In the particular case of two-particle interaction, it has the form \( z u \varepsilon \), where \( u \) is the interaction energy of two adparticles on two neighboring adsorption sites and \( \varepsilon \) is the coordination number for adsorption sites [7]. As is well known, attractive lateral interactions between adparticles lead to hysteresis-shaped adsorption isotherms [3, 6–10, 17, 19]. In the present paper, to investigate the possibility of a hysteresis of adsorption isotherms caused by another factor (a normal displacement of adsorption sites in localized adsorption, i.e. the adsorption-induced normal deformation of the substrate), we do not consider lateral interactions between adparticles. Assuming that the pre-exponential factor \( k_d \) is not changed, we obtain the following expression for \( k_d \):

\[
k_d(x) = k_d \exp \left( -\frac{\chi x}{k_B T} \right).
\]

According to (9), the coordinate-dependent desorption rate depends on the gas concentration via the current position of the surface. Therefore, adsorption and desorption of particles proceed on the surface with varying adsorption characteristics.

Generally speaking, a change in the charge density spatial distribution of adsorption sites in adsorption can also affect the number of free gas particles able to overcome the adsorption barrier \( E_s \). Here, we do not take this factor into account (some results obtained with regard to a decrease in the activation energy for adsorption in adsorption–desorption are presented in [29]). Note that the possibility of a change in the agent influx and outflux rates in the case of sorption of the agent at a single conformally sensible binding site is discussed in [30].

Introducing the dimensionless coordinate of the oscillator \( \xi = x/x_{\text{max}} \), we obtain the following autonomous system of nonlinear differential equations, which describes the kinetics of the quantity of adsorbed substance with regard to variations in adsorption properties of the surface in adsorption–desorption:

\[
\frac{d\theta}{dt} = k_s C (1 - \theta) - k_d \theta \exp (-g \xi),
\]

\[
\frac{d\xi}{dt} \left( m_{\text{eff}}(\theta) \frac{d\xi}{dt} \right) + \alpha \frac{d\xi}{dt} = \chi (\theta - \xi),
\]

where the dimensionless parameter \( g = |V|/k_B T \) (the normalized adsorption-induced activation energy for desorption due to the substrate deformation), which characterizes the interaction of an adparticle with substrate caused by the adsorption-induced force, can be called a coupling parameter. In the absence of this interaction (the linear case, \( \chi = 0 \), \( V = 0 \), \( g = 0 \)).

Note that the system (10) and (11), in many respects, is analogous to the systems of equations given in [31–33], which describe the transport of electrons in systems of particles of biological nature [32, 33] or in molecular organizes [31] with regard to the electron–conformation interaction.

3. The stationary case

In the stationary case, it follows from equation (11) that \( \xi = \theta \). Therefore, the equilibrium state of the system (10) and (11) is defined not by the pair of quantities \((\theta^*, \xi^*)\), as is typical of
dynamical systems of two equations \([34, 35]\), but only by one quantity \(\theta^m\), which is a solution of the adsorption equation

\[ \ell = F(\theta), \quad \text{where } F(\theta) = \frac{\theta}{1 - \theta} \exp(-g \theta). \quad (12) \]

First, based on this equation, we make a qualitative conclusion on the influence of a change in adsorption properties of the surface on the surface coverage. To this end, note that the ratio \(\theta/(1 - \theta)\) is equal to \(N_b/N_0\) and the quantity \(\ell\) is also the ratio \(N_b/N_0\) but in the linear case. Rewriting relation (12) in the form

\[ \frac{N_b}{N_0} = \ell \exp(g \theta), \quad (13) \]

we see that a change in adsorption properties of the surface in adsorption–desorption leads to an increase in the surface coverage for any gas concentration. The difference between the numbers of bound adsorption sites in the nonlinear \((g \neq 0)\) and linear cases increases with the coupling parameter \(g\).

This conclusion can also be made by taking into account that, in the stationary case, the desorption rate (9) has the form

\[ k_d(\theta) = k_d \exp(-g \theta), \quad (14) \]

where the surface coverage \(\theta\) is a solution of equation (12), i.e. decreases due to an increase in the adsorption energy for desorption caused by the substrate deformation in the presence of adparticles on it. It follows from (14) that the residence time of adparticles on the surface

\[ \tau_d(\theta) = \frac{1}{k_d(\theta)} = \tau_d \exp(g \theta) \quad (15) \]

increases in the nonlinear case and, hence, the surface coverage increases.

To analyze the solutions of equation (12), we use the following standard procedure [35]: considering the left- and right-hand sides of equation (12) as functions of \(\theta\), we plot them taking into account that \(\ell \geq 0\) and \(0 \leq \theta \leq 1\) (figure 1). The required solutions of equation (12) are the abscissas of the points of intersection of a horizontal line corresponding to the given concentration \(\ell\) with the curve of the function \(F(\theta)\) shown for different values of the parameter \(g\). (In fact, this procedure is equivalent to the investigation of the behavior of the function \(\ell(\theta)\) defined by relation (12).) Since the behavior of the function \(F(\theta)\) is essentially different for \(g < g_c\) and \(g > g_c\), where \(g_c = 4\), it is convenient to represent the parameter \(g\) in the form \(g = a_g g_c\), where \(a_g \geq 0\). For \(g < g_c\) (figure 1(a)), the function \(F(\theta)\) monotonically increases and lies to the right of curve 1 for the linear case \((g = 0)\). Thus, as in the linear case, for any given concentration, the surface coverage has the unique value \(\theta^m_1 > \theta^m_2\), which agrees with the conclusion made above on the basis of relations (13) and (15). With an increase in \(a_g\), the curve \(F(\theta)\) becomes more deformed and its deviation from curve 1 increases, which leads to an increase in the difference \(\theta^m_2 - \theta^m_1\) between the values of the surface coverage in the nonlinear and linear cases. For \(a_g = 1\), the function \(F(\theta)\) (curve 1 in figure 1(b)) has an inflection point for \(\theta = \theta_c = 1/2\) for the concentration \(\ell = \ell_c = \exp(-2) \approx 0.135\).

![Figure 1](image)

Figure 1. Graphical solution of equation (12) for different values of the parameter \(a_g\): (a) \(a_g = 0\) (1), 0.1 (2), 0.5 (3), 0.9 (4); (b) \(a_g = 1\) (1), 1.5 (2), 2 (3), 3 (4). Horizontal dashed lines correspond to constant values of the dimensionless concentration \(\ell\).

For \(a_g > 1\), the behavior of the function \(F(\theta)\) essentially changes: the function \(F(\theta)\) is \(N\)-shaped and, for the concentrations \(\ell^m_1\) and \(\ell^m_2\) \((\ell^m_1 < \ell^m_2 < \ell^m_3)\) depending on the value of the parameter \(a_g\), has a minimum and a maximum at the points \(\theta = \theta^m_1 > \theta_c\) and \(\theta = \theta^m_2 < \theta_c\), respectively, which are roots of the quadratic equation

\[ \theta^2 - \theta + \frac{1}{g} = 0 \quad (16) \]

and are equal to

\[ \theta^m_1 = \frac{1}{2} \left(1 + \sqrt{1 - \frac{4}{g}}\right), \quad \theta^m_2 = \frac{1}{2} \left(1 - \sqrt{1 - \frac{4}{g}}\right). \quad (17) \]

The concentrations \(\ell^m_1\) and \(\ell^m_2\) corresponding to these surface coverages are equal to

\[ \ell^m_n = (g \theta^m_n - 1) \exp(-g \theta^m_n), \quad n = 1, 2. \quad (18) \]

In figure 1(b), the concentrations \(\ell^m_1\) and \(\ell^m_2\) and the surface coverages \(\theta^m_1\) and \(\theta^m_2\) for them are shown by dashed straight lines for \(a_g = 3/2\). For concentrations \(\ell^m_1 < \ell < \ell^m_2\), equation (12) has three solutions \(\theta^m_1 < \theta^m_2 < \theta^m_3\); furthermore, only the first solution \(\theta^m_1\) lies near the linear \(\theta^m_1\). With an increase in \(a_g\), the concentrations \(\ell^m_2\) and \(\ell^m_3\) decrease and the difference between the maximum and minimum solutions \(\theta^m_3 - \theta^m_1\) increases.
Analysis of the system of equations (10) and (11) shows that its stationary solutions \( \theta_1^{st} \) and \( \theta_3^{st} \) are asymptotically stable and the solution \( \theta_2^{st} \) is unstable.

If the concentration \( l \) tends to the end point of the interval \([l_1^b, l_2^b]\) (to the value \( l_1^b \) or \( l_2^b \)), then the stable \( \theta_1^{st} \) (or \( \theta_3^{st} \)) and unstable \( \theta_2^{st} \) solutions approach each other and, in the limit \( l = l_1^b \) (or \( l = l_2^b \)), coalesce into one solution \( \theta_1^b \) (or \( \theta_2^b \)) (in figure 1(b), for \( a_g = 3/2 \), these cases are shown for curve 2). Therefore, \( l_1^b \) and \( l_2^b \) are the bifurcation concentrations for which the dynamical system (10) and (11) is structurally unstable [34, 35] and has the compound (double) equilibrium states \( \theta_1^b \) and \( \theta_2^b \). These special cases should be investigated in their own right.

Using relations (12) and (16), we plot a bifurcation curve in the plane of control parameters \((a_g, \ell)\). This curve defined in the parametric form

\[
a_g = \frac{1}{4\theta (1 - \theta)}, \quad \ell = \frac{\theta}{1 - \theta} \exp \left( -\frac{1}{1 - \theta} \right) \tag{19}
\]

is shown in figure 2. For any point of this plane lying between the branches of the bifurcation curve, the system of equations (10) and (11) has three structurally stable equilibrium states: two states are stable and one is unstable. If a point lies outside these branches, then the system has one structurally stable equilibrium state. At any point of the bifurcation curve, except for the cusp of the second kind \((a_g = 1, \ell = \ell_3)\), the system has two equilibrium states: one is structurally stable and another is double [35]. At the cusp, the system of equations (10) and (11) has one triple equilibrium state [35].

The S-shaped adsorption isotherm depicted in figure 3 for \( a_g > 1 \) (curve 1) essentially differs from the Langmuir isotherm (curve 2) and, at the qualitative level, reproduces the Zeldovich hysteresis predicted in [23].

With an increase in the gas concentration from zero, the surface coverage, at the initial section of the lower stable branch \( 0A \) of the isotherm, coincides with the Langmuir one. For these concentrations, \( \tau_3(\theta) \approx \tau_3 \). An increase in the concentration up to the bifurcation value \( l_2^b \) is accompanied by an increase in the difference of the typical lifetimes of the bound adsorption site \( \tau_3(\theta) \) and \( \tau_4 \). In this section of the lower stable branch of the isotherm, the occupation of the surface by gas particles is determined by two factors: an increase in the gas concentration and a change in adsorption properties of the surface. Due to the last factor, the isotherm deviates from the Langmuir isotherm, and this deviation increases with concentration. The pattern cardinally changes as soon as the concentration negligibly exceeds \( l_2^b \). In this case, the lower stable branch of the isotherm disappears and a new (unique) equilibrium position of the bound adsorption site is considerably more distant from the surface than the previous one for \( l \leq l_2^b \). Furthermore, the passage to it is performed for a constant concentration, i.e. solely due to a change in adsorption properties of the adsorbent surface (according to the terminology in [23], a slow adsorption occurs). This passage can include many gas particles that successively take part in the process of adsorption–desorption on the same adsorption site. Thus, at this stage, a certain interaction between the particle leaving the adsorption site and the particle binding to it occurs. In figure 3, this stage of a sharp increase in the surface coverage for a constant concentration is shown by the dashed straight line AB.

In passing to a stable equilibrium state lying on the upper stable branch of the isotherm (the point B in figure 3), the majority of adsorption sites are bound. As a result, a subsequent increase in the gas concentration has a slight influence on an increase in the surface coverage. Such a ‘saturation’ of the surface with adsorbate, which rapidly increases with parameter \( a_g \) (figure 3(b)), occurs for concentrations considerably lower than those in the linear case.

In passing through the bifurcation concentration \( l_2^b \), the conditions for desorption for adparticles become essentially worse due to a considerable increase in the activation energy
for desorption. As a result, for returning to the lower branch of the isotherm, the concentration should be considerably lower than $\ell_0^s$. With a decrease in the concentration, the surface coverage decreases slightly and only on approaching the bifurcation value $\ell_1^s$, a variation in $\theta$ becomes noticeable. In passing through the bifurcation concentration $\ell_1^s$, the upper stable branch of the isotherm disappears and an equilibrium position of the bound adsorption site lies considerably closer to the surface than the previous one for $\ell > \ell_1^s$. As a result, the surface coverage sharply decreases for the fixed concentration due to a change (restoration) in the properties of the adsorbent surface. The transition of the system from the upper branch of the isotherm to its lower branch is shown by the dashed straight line CD in figure 3. Note that this stage of a drop in the quantity $\theta$ is absent in [23]. A subsequent decrease in the concentration is accompanied by a decrease in the surface coverage along the lower branch of the isotherm, which, in fact, coincides with the Langmuir isotherm.

This behavior of the adsorption isotherm corresponds to the well-known principle of perfect delay [36] according to which a system, which is in a stable state at the initial time, with variation in a parameter (the gas concentration in the case at hand), remains in this state until the state exists.

As $a_g$ increases, the bifurcation concentration $\ell_1^s$ rapidly vanishes (see figure 2). Using the results of computation, we can say that, for $a_g \geq 3$, a change in adsorption properties of the adsorbent in adsorption–desorption leads to a peculiar adaptation of the system to a state in which a majority of adsorption sites are bound up to very low concentrations.

Note that the isotherms obtained above for the surface whose adsorption properties vary in adsorption–desorption (figure 3) are similar to the isotherms obtained with regard to lateral interactions between adparticles on a nondeformable surface [7, 9, 17, 19] and to the Hill–de Boer isotherms derived on the basis of the Hill–de Boer equation of state for adparticles (a 2D analogue of the van der Waals equation) [19, 37].

In the analysis of adsorption isotherms with regard to lateral interactions between adparticles (see, e.g., [38]), for the investigation of possible surface phase transitions, a critical temperature $T_c$ is introduced [7, 8, 10, 37]. For the model considered in the present paper, using the expression for the coupling parameter $g$, the critical value $g_c$ and the analysis of adsorption isotherms performed above, the critical temperature is defined as follows: $k_BT_c = |V|/4$. For a system of adparticles, one stable state occurs for $T > T_c$, whereas for $T < T_c$, two stable states are possible. The corresponding phase diagram for the adsorbed layer in the ‘surface coverage–critical temperature’ coordinates is determined by the relation

$$\frac{T}{T_c} = 4\theta (1 - \theta)$$

and, as in the case of lateral interactions between adparticles on a nondeformable surface in the mean-field approximation [7], is symmetric about $\theta = 1/2$.

In the stationary case, the dimensionless coordinate of adsorbent surface $\xi$ is equal to the surface coverage $\theta$. Thus, all conclusions drawn above on specific features of adsorption isotherms remain true for the adsorption-induced normal displacement of the adsorbent surface. For example, curve 1 in figure 3 also describes the displacement of the adsorbent surface with the gas concentration if, instead of $\theta$, $\xi$ is laid off along the ordinate axis.

This indicates the essential difference between the specific features of the surface coverage $\theta$ in the bistability range for the considered system and a system of adparticles with lateral interaction. Namely, in the second case, two phases (‘gas-like’ and ‘liquid-like’) of adparticles are located on one (nondeformed) substrate surface [7–10, 17, 19], whereas for the system with a deformable substrate surface considered in the present paper, two ‘phases’ are on different planes parallel to the nonperturbed substrate surface.

Within the framework of the model proposed in the present paper, for the estimation of the possibility of bistability of the system, for a specific adsorbent and absorbate, for given values $k_s$ and $k_d$, the value of the quantity $\chi$ is required. This value can be determined if the experimental data of a change in the first interplanar spacing (along the normal to the surface) $x_{\text{max}}$ due to adsorption are known. Since $x_{\text{max}}$ corresponds to the total monolayer coverage, measurements must be made for a gas concentration realizing this case. Based on the measured value of $x_{\text{max}}$, the required quantities are calculated by the relations

$$\chi = \kappa x_{\text{max}}, \quad V = -\kappa x_{\text{max}}^2, \quad g = \kappa x_{\text{max}}^2/k_BT.$$  \hspace{1cm} (21)

Depending on the value of the coupling parameter $g$, one can conclude whether the bistability of the system is possible or not.

For example, with the use of the low-energy electron diffraction, in [39], a sufficiently large (by 11.5%) decrease in the first interplanar spacing for the clean $\{001\}$ surface of molybdenum is established as compared with interplanar spacing in the bulk. The results of measurements in [40] illustrate that a monolayer adsorption of silicon on a clean Mo $\{001\}$ surface leads to an increase in the first interplanar spacing to the bulk value, i.e., the adsorbate-induced surface relaxation occurs.

Note that the model of adsorption sites as noninteracting 1D oscillators considered in the present paper is the simplest simulation of adsorption sites that, in reality, are connected both with each other and with subsurface atoms of the substrate. In the approximation of the pair interaction between the nearest neighbors of the substrate, the quantity $\kappa$ for the 1D oscillator can be linearly expressed in terms of the force constant $x_s$ that characterizes the interaction between atoms of the substrate in the case of central forces. Furthermore, the relation between $\kappa$ and $x_s$ is defined both by the type of lattice of the substrate and by the crystal orientation of the surface.

In the case of a bcc lattice with $\{001\}$ surface, the coordination number for atoms of the substrate surface is equal to 4 (half of the coordination number in the bulk) and the force constant of the substrate lattice $x_s$ is connected with the elastic stiffness constant $c_{44}$ by the relation $x_s = (3/2)a c_{44}$ [41], where $a$ is the lattice constant. Taking this into account, we simulate an adsorption site connected with four subsurface atoms of the substrate by central forces by a 1D oscillator that oscillates perpendicularly to the surface with the restoring force constant $\kappa = (4/3)x_s = 2ac_{44}$. 

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For Mo, $a \approx 3.147$ Å and $c_{44} \approx 1.217 \times 10^{12}$ dyn cm$^{-2}$ [42]; the displacement of the Mo [001] surface $x_{\text{max}}$ due to an adsorbed Si monolayer is equal to $\sim 0.181$ Å in the case of the complete relaxation of the interplanar spacing to the bulk value [40]. This yields $V \approx -0.157$ eV, which, at room temperature, gives $g \approx 6.04$, which is greater than the critical value of the coupling parameter. Therefore, according to the model considered in the present paper, the bistability of Si on the Mo [001] system is possible. It is of special interest to take into account the influence of factors ignored in this model (energetically nonhomogeneous adsorption sites, lateral interaction between adparticles, etc) because they can essentially change the behavior of adsorption isotherms. The measurement accuracy of the quantity $x_{\text{max}}$ is also very important. Indeed, it is concluded in [40] that the interplanar spacing for the Mo [001] surface with an adsorbed Si monolayer relaxes to the interplanar spacing in the bulk ‘at least within less than 5%’ and, hence, the measurement accuracy of the displacement of the surface is equal to $\sim 0.08$ Å. This essentially affects the conclusions drawn above on the complete relaxation of the surface with an adsorbed monolayer to the bulk value [40]. For example, if the interplanar spacing for the surface with an adsorbed Si monolayer increases by 7% instead of 11.5%, which occurs in the complete relaxation of the surface, then $V \approx -0.058$ eV and $g \approx 2.24$ at room temperature. In this case, the value of the coupling parameter $g$ is less than critical. Therefore, according to the considered model, the Si on Mo [001] system has only one stable state. Possibly, to increase the measurement accuracy of the displacement of adsorption sites caused by adsorption, it makes sense to use the surface extended x-ray-adsorption finite structure method, which gives an interatomic distance of up to 0.01 Å [8, 43]. This is of particular importance for registration of the displacement of adsorption sites with variation in the concentration of gas particles in the concentration range where the displacement is considerably less than $x_{\text{max}}$.

According to relations (21), an adsorption bistability is more probable for substrates with relatively low elastic characteristics and whose surface layer is susceptible to a considerable change in the charge density spatial distribution in adsorption resulting in not too low values of $|\chi|$. Possibly, in experiments aimed at searching for the adsorption bistability caused by a substrate deformation in adsorption, it makes sense to use single crystal solid substrates of a ‘soft’ material admitting a considerable normal displacement of the surface in adsorption.

4. Kinetics of the surface coverage

We investigate the kinetics of the system (10) and (11) within the framework of the overdamped approximation where the masses of an adsorption site and an adparticle are low and the friction coefficient is so large that the first term on the left-hand side of equation (11) can be neglected as compared with the second. Using the well-known results for a linear free oscillator of constant mass [34], this approximation is correct if

$$r_{\text{M}}^2 \ll \tau_r^2,$$

where $\tau_{\text{M}} = 1/\omega_{\text{M}}, \omega_{\text{M}} = \sqrt{\kappa/M}$ is the vibration frequency of an oscillator of mass $M$, and $\tau_r = \alpha/\kappa$ is the typical relaxation time of a massless oscillator. Since $M$ is the maximally possible effective mass, condition (22) is even somewhat high. In this approximation, the system of equations (10) and (11) is simplified to the form

$$\frac{d\theta}{dt'} = \xi (1 - \theta) - \theta \exp (-g \xi),$$

$$\frac{d\xi}{dt'} = \frac{\theta - \xi}{\beta},$$

where $t' = t/\tau_d$ is the dimensionless time and $\beta = \tau_r/\tau_d$.

Analysis of the system (23) and (24) performed on the basis of the qualitative theory of differential equations [35, 44] shows that the stable equilibrium states of the system $\theta_a^b$ and $\theta_a^c$ are stable nodes and its unstable equilibrium state $\theta_a^1$ is a saddle. For the bifurcation concentration $\ell = \ell_1^b$ (or $\ell = \ell_2^b$), the system is structurally unstable and has a compound equilibrium state $\theta_a^b$ (or $\theta_a^c$), namely a saddle node with two saddle sectors and one stable nodal sector. The system is also structurally unstable for the critical concentration $\ell = \ell_c$, and $a_d = 1$. In this case, the system has one equilibrium state $\theta_c$, which is a stable triple node.

The numerical analysis of the system (23) and (24) with initial conditions for $t' = 0$

$$\theta(0) = 0, \quad \xi(0) = 0$$

shows that, for any values of the parameters $a_d$, $\ell$ and $\beta$, the system monotonically evolves to the nearest stable equilibrium state. Therefore, for the bistable system ($a_d > 1$ and $\ell_1^b \leq \ell \leq \ell_2^b$), the stable equilibrium state $\theta_a^1$ is inaccessible. The time taken to attain the equilibrium state $\theta_a^1$ strongly depends on parameters, first of all on the concentration.

Let us investigate the kinetics of the surface coverage for a system that can be bistable for $a_d = 1.5$. In this case, $\ell_1^b \approx 0.0329$ and $\ell_2^b \approx 0.0754; \ell_1^c \approx 0.789$ and $\ell_2^c \approx 0.211$.

In figure 4, the kinetics of the surface coverage $\theta(t')$ is shown for concentrations less ($\ell = 0.05$, figure 4(a)) and greater ($\ell = 0.1$, figure 4(b)) than the bifurcation concentration $\ell_2^b$. For comparison, the Langmuir kinetics is shown in this figure by curve 2. For $\ell < \ell_2^b$, the behavior of $\theta(t')$ is analogous to that in the Langmuir case: the quantity $\theta(t')$ monotonically increases from zero to the nearest stationary value $\theta_1^a$ that lies near the linear value $\theta_L^a$ (figure 4(a)). With an increase in the concentration, this behavior remains true up to the bifurcation value $\ell_2^b$ (moreover, both the stationary value $\theta_1^a$ and the time taken for attaining it increase).

For $\ell > \ell_2^b$, the system has only one stable equilibrium state; furthermore, in this state, the surface coverage, which is close to the maximum possible value, is essentially greater than that in the linear case. Moreover, both the shape of the kinetic curve $\theta(t')$ and the time taken for attaining the stationary value considerably differ from the Langmuir ones (figure 4(b)). With an increase in the concentration, the time taken to attain the stationary value decreases.

The value of the parameter $\beta$ affects only the time taken for the system to attain the stationary value but does not
qualitatively change the kinetics of \( \theta(t') \) both for \( \ell < \ell_2^b \) and for \( \ell > \ell_2^b \). This time decreases as \( \beta \) decreases and increases as \( \beta \) increases, which is quite natural because a variation in \( \beta \) is equivalent to a variation in the friction coefficient \( \alpha \).

For concentrations \( \ell > \ell_2^b \) near the bifurcation concentration \( \ell_2^b \), the behavior of \( \theta(t') \) qualitatively changes. The behavior of the quantity \( \theta(t') \) for \( \ell = \ell_2^b (1 + \delta) \), for low values of the relative concentration \( \delta = (\ell - \ell_2^b) / \ell_2^b > 0 \), is shown in figure 5. If \( \ell \) slightly exceeds the bifurcation concentration \( \ell_2^b \) (curves 2 and 3), then the evolution of \( \theta(t') \) can be conditionally divided into three stages: (i) from the initial zero value to a value of \( \sim \theta_1^n \) corresponding to the bifurcation concentration \( \ell_2^b \); (ii) a very slow (in the limit \( \lim_{t \to 0} \), infinitely slow) variation in the neighborhood of \( \theta_1^n \); (iii) from \( \sim \theta_1^n \) to the stationary value \( \theta_1^n \). For low values of \( \delta \), the time taken for attaining the stationary level \( \theta_1^n \) is determined mainly by the second (‘quasistationary’) stage in which the system, in fact, does not change (curve 2 in figure 5(b)). This behavior of the surface coverage \( \theta(t') \) is caused by the well-known effect of slowing down a system near a singular point for the bifurcation value of a parameter [36, 45, 46] in the case when a phase trajectory of the system moves near this point.

This behavior of system (23) and (24) can be clearly explained using its phase trajectories in the phase plane \((\theta, \xi)\). The phase trajectories of the system with zero initial conditions (26) are shown for concentrations less than (figure 6(a)), equal to (figure 6(b)) and slightly greater than (figure 6(c)) the bifurcation concentration \( \ell_2^b \). The dashed lines in these figures stand for the main isoclines of the system: the isocline of horizontal slopes \( \xi = \theta \) and the isocline of vertical slopes \( \xi = (1/g) \ln(\theta / \ell (1 - \theta)) \). The points of intersection of these isoclines are singular points of the system.

For \( \ell < \ell_2^b \) (figure 6(a)), the singular points A and C are stable (stable nodes) and the singular point B is unstable (saddle). The phase trajectory in figure 6(a) starting from the origin of coordinates and going to the nearest singular point A completely lies between the main isoclines. Moreover, the immediate analysis of system (23) and (24) shows that all phase trajectories of system (23) and (24) with initial values belonging to the domain bounded by the sections of the main isoclines before their intersection at the point A also completely lie between the main isoclines. A variation in the parameter \( \beta \) does not qualitatively change the behavior of the phase trajectories and only displaces them to one of the main isoclines: for \( \beta < 1 \) and \( \beta > 1 \), the phase trajectories are closely pressed to the isoclines of horizontal and vertical slopes, respectively.
For $\ell > \ell_{1}^{b}$, the system has only one (stable) singular point C (figure 6(c)). If the relative concentration is low, then a gap between the main isoclines in the neighborhood of their point of tangency D for $\ell = \ell_{1}^{b}$ is also small. Since a phase trajectory does not leave the domain bounded by the main isoclines, it goes through the gap and, in the neighborhood of the point D, its motion becomes slower. Furthermore, the less the relative concentration, the narrower the gap between the main isoclines and the closer the phase trajectory approaches the point D and, hence, the more it slows down near the point. This behavior of the system corresponds to the effect of critical slowing down near a degenerate critical point [36, 45].

As a result, for low values of $\delta$, the function $\theta(t')$ in figure 5(b) has the form of a double step (curves 2 and 3). The first plateau of the step corresponds to the ‘quasi-stationary’ state $\theta_{2}^{a}$ and the second corresponds to the stable state $\theta_{1}^{a}$.

In the special case $\beta \ll 1$, the kinetics of the surface coverage can be analyzed with the use of an effective potential. This analysis carried out in [29] shows, in particular, that this potential, as a function of the variable $\theta$ and two control parameters ($\ell$ and $g$), has the form of a double well if $g > g_{c}$ and $\ell_{1}^{b} < \ell < \ell_{2}^{b}$.

The kinetics of the surface coverage described by system (23) and (24) can also be analyzed using an effective potential in another special case where the relaxation time of the quantity $\xi(t)$ is much greater than the relaxation time of the quantity $\theta(t)$, i.e. the variables $\xi$ and $\theta$ are slow and fast, respectively. If $\tau_{c} \gg 1/k_{c}C$, then, performing the adiabatic elimination of the fast variable $\theta(t)$ [45], namely setting $d\theta/dt = 0$ in equation (23), we obtain the following representation for the surface coverage versus the slow variable $\xi$:

$$\theta = \frac{l}{l + \exp(-g \xi)}.$$  

(26)

The dimensionless coordinate $\xi(t)$ is determined as a solution of the nonlinear differential equation

$$\frac{d\xi}{dt} = -\frac{dU(\xi)}{d\xi}$$  

(27)

that describes the motion of a massless oscillator in the effective potential

$$U(\xi) = \frac{1}{2} \left\{ \xi^{2} + 2 \exp(-g \xi) - \frac{2}{g} \ln \frac{l + \exp(-g \xi)}{l + 1} \right\}.$$  

(28)

In terms of the coordinate $x$, the equation of motion has the form

$$\frac{dx}{dt} = -\frac{dU(x)}{dx},$$  

(29)

where

$$U(x) = \frac{1}{2} x^{2} - \chi x - k_{b}T \ln \frac{l + \exp(-b \cdot x)}{l + 1},$$  

(30)

$$b = \frac{g}{\chi_{\max}} = \frac{\chi}{k_{b}T}.$$  

Note that the effective potential (30) coincides with the potential derived in the adiabatic approximation in [30], where the structural regulation of the functioning of a macromolecule in repeating cycles of reactions is investigated.
Analysis of the potential $U(\xi)$ shows that, for $g > g_c$ and $l_1^b < l < l_2^b$, it has the form of a double well with local minima at $\xi = \xi_1^a$ and $\xi = \xi_2^a$ separated by a maximum at $\xi = \xi_2^b$. where $\xi_n^a = \theta_n^\ast$, $n = 1, 2, 3$, and $\theta_n^\ast$ are the stationary surface coverages investigated in section 3 that satisfy equation (12). For $g < g_c$ and any $l$ as well as for $g > g_c$ and $l < l_1^b$ or $l > l_2^b$, the potential $U(\xi)$ has one minimum.

The curves presented in figure 7 for $g = 4.4 > g_c$ clearly illustrate the essential influence of the gas concentration on the form of the potential. For concentrations lying outside the interval $[l_1^b, l_2^b]$, the potential has a single minimum (curves 1 (for $l < l_1^b \approx 0.1064$) and 5 (for $l > l_2^b \approx 0.1154$)); furthermore, the equilibrium position of the oscillator for $l > l_2^b$ is considerably more distant from the nonperturbed position $\xi = 0$ than that for $l < l_1^b$. Curves 2–4 illustrate the double-well character of the potential for the concentrations $l_1^b < l < l_2^b$ and deepening of the wells (especially, the second well) with an increase in the concentration.

Since, in the overdamped approximation, the inertia effect is ignored, the motion of a massless oscillator, which was initially at rest at the point $\xi = 0$, in the potential $U(\xi)$ is always reduced to the aperiodic motion to the new equilibrium position at the point $\xi_1^a$ corresponding to the minimum of the nearest well of the potential $U(\xi)$. Therefore, in the case of a double-well effective potential, the second equilibrium position at the point $\xi_2^a$ corresponding to the minimum of the second well of this potential is unattainable even when the second well is deeper than the first (curve 4 in figure 7). As soon as the concentration becomes greater than the bifurcation value $\xi_2^a$, the first minimum of the potential $U(\xi)$ disappears and the oscillator displaces to the unique equilibrium position at the point $\xi_2^a$ (curve 5 in figure 7). The closer the concentration is to $\xi_2^a$ ( $l > l_2^b$), the flatter the potential in the right neighborhood of the point $\xi_2^a$ and, hence, more time is required for the oscillator to attain the point $\xi_2^a$, which agrees with the well-known effect of critical slowing down near a degenerate critical point [36, 45].

The surface coverage $\theta(t)$ defined by relation (26) has similar behavior. Therefore, the kinetics of the surface coverage shown in figures 4 and 5 and obtained without additional assumptions on fast and slow variables, at the qualitative level, agrees with the conclusions drawn above on the basis of the motion of a massless oscillator in a double-well potential.

It is worth noting that taking into account the masses of an adsorption site and an adpartcile can considerably change the kinetics of the surface coverage, especially if the gas concentration is close to a bifurcation value. Analysis of the specific features of the kinetics caused by inertia was performed in [29].

5. Conclusions

In the present paper, we have proposed the self-consistent model taking into account variations in adsorption properties of the adsorbent surface in adsorption–desorption of gas particles on it. We have established that, in addition to the well-known factor of attractive lateral interactions between adparticles leading to the bistability of the system, there is another factor (substrate deformation in adsorption) realizing the bistability. The system can be bistable if the coupling parameter exceeds the critical value and the concentration of particles in the gas phase belongs to a certain interval. The hysteresis behavior of adsorption isotherms caused by the adsorption-induced normal deformation of the substrate has been revealed. It has been shown that variations in adsorption properties of the substrate surface in adsorption–desorption can lead to a peculiar adaptation of the system to a state in which a majority of the adsorption sites are bound up to very low concentrations.

A detailed analysis of the kinetics of the surface coverage in the overdamped approximation shows that taking into account variations in adsorption properties of the surface in adsorption–desorption leads to the appearance of a new ‘quasi-stationary’ state of the system in the case when the gas concentration is close to a bifurcation value.

The simple model proposed in the present paper can be regarded as only the first step for describing adsorption on the surface whose position varies in adsorption–desorption. The subsequent investigations in this direction require both the development of the model and taking into account various factors (first of all, fluctuations and lateral interactions between adparticles) not considered here.

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