Principles of the adsorption theory of large molecules on nonuniform surfaces

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A new theory of adsorption of large molecules blocking more than one adsorption center on a nonuniform surface, taking into account lateral adsorbate-adsorbate interactions, was proposed. The cluster approach was used to obtain equations of adsorption isotherms. The lateral interactions are taken into account in the quasi-chemical approximation preserving effects of direct correlations. Ways of simplified description of the multicentered adsorption on nonuniform surfaces were considered: a model of isolated contacts for nonspherical molecules and a quasi-one-centered model for spherically symmetric molecules adsorbed on amorphous surfaces. The resulting equations cover all equations previously considered in the literature for the adsorption of large molecules on uniform and nonuniform surfaces.

Key words: nonuniform surface, adsorption isotherm, blocking of adsorption centers; lattice-gas model, cluster approach, quasi-chemical approximation; model of contacts.

The Langmuir assumption[1] that centers of localization of adsorbed molecules exist on the adsorbent surface leads to the question about the geometric correspondence of sizes of the localization region (adsorption center) and the adsorbed molecule. The majority of theoretical works[2–6] on adsorption of molecules from the gas and liquid phases consider cases where the sizes of the molecule and adsorption center are comparable (one molecule can be localized on each center). Approaches developed recently (cluster and fragment approaches) make it possible to take into account with a high accuracy both lateral interactions of adsorbed molecules and the nonuniformity of the adsorbent surface.[5,7–9]

Blocking several adjacent centers by large molecules makes the estimation of molecular configurations realized and their statistical weight at fixed values of the number and energy of molecules considerably more difficult. The theory of adsorption of spherically symmetric molecules blocking the nearest adjacent centers was developed for a planar square structure.[10,11] The adsorption of dimers on the one-dimensional structure was studied,[1,2] and the thermodynamic approach was suggested for description of adsorption of large molecules from solutions.[13] The theory of adsorption of molecules of different sizes and forms on uniform surfaces was considered in Refs. 14—18. However, the problems of taking into account lateral interactions of adsorbed molecules were discussed only in several (see, *e.g.*, Refs. 11 and 18) works. Only three works[19–21] are devoted to adsorption of large molecules on nonuniform surfaces. Dimers on patchwise and chaotic surfaces[19,20] and chain molecules on chaotic surfaces[21] were considered without taking into account lateral interactions.

This work proposes principles of an adsorption theory of large molecules on a nonuniform surface, taking into account the lateral interactions between the molecules. To develop equations that describe the gas—solid equilibrium, the cluster approach was used. Previously, this approach has been applied in the adsorption theory of one-centered molecules[5,22] and dimer molecules on uniform surfaces taking into account the lateral interactions.[22,23] We restrict our consideration to horizontally arranged molecules with relatively simple shapes: a rigid rod and a flexible chain with length m and a plate with $m = b \times d$ (b and d are the linear sizes the plane). We will take into account the lateral interactions between the nearest neighbors in the quasi-chemical approximation. In developing the theory, we should consider different orientations of the adsorbate in the surface plane and their mutual competition: as the density of the adsorbate increases, the ordered arrangement of the molecules with the same orientation of their long axes becomes more favorable. When coverages of the surface are high, the two-dimensional analog of three-dimensional phase transitions of the nematic (and/or smectic) disordered phases is realized.[24,25] In the statistic description of large molecules, each molecular orientation is considered as a kind of some particle. Therefore, taking into account different orientations of the molecules is reduced to the adsorption theory of a mixture of molecules even for the one-component system.

In this work, the model and structure of the equations obtained are considered. Two versions of the sim-

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plified calculation of the adsorption of large molecules on the nonuniform surfaces are presented: a model of isolated contacts for nonspherical molecules and a quasi-one-centered model for spherically symmetric molecules on amorphous surfaces. In addition, the interrelation between particular versions of the adsorption isotherms for planar and one-dimensional lattices with the isotherms obtained previously is considered.

Model

For description of adsorption, let us use the lattice model. Let us imagine a monolayered space above the surface as a lattice structure with the number of nearest neighbors equal to z. The lattice constant is equal to the linear size of the adsorption center (site) and is determined by the value of the region of the local minimum of the potential adsorbent—adsorbate energy. Let the adsorbate occupy an integer number of sites equal to m. Let us designate a "molecule in orientation i" as the "particle i"; $1 \le i \le s$ (s is the number of distinguishable orientations of the molecule), *i.e.*, the long axis of the molecule coincides with one of the considered axes of possible directions. If L is the number of possible directions of the orientation axes, in the general case, $L \ge z/2$. One should distinguish the cases for nonsymmetric molecules when the direction of the long molecular axis coincides with or is opposite to the direction of the orientation axis: $s = 2L$. For symmetric molecules, both cases correspond to the same state, and $s = L$.

Large particles block m_i adjacent sites of the surface. Therefore, to perform correct averaging over all configurations of large particles, a rule of assignment of the position of a molecule to a specific site of the surface should be formulated. Let us choose one of the terminal segments of particle i (for example, one of the ends of a chain or rod, or an angular contact for a planar particle in the form of the rectangular) and let us count other sites occupied by the same particle from this segment. The number of the site f ($1 \le f \le N$, N is the number of the sites of the surface fragment), in which the chosen segment of particle i is localized, will be considered to be that occupied by the given particle, and the surface region occupied by particle i will be designated by $\{f\}$. The local Henry constant corresponds to each particle i

$$a_{\{f\}}{}^i = a^*{}_{\{f\}}{}^i \exp\{\beta E_{\{f\}}{}^i\}, \quad \beta = 1/k_B T,$$

where $a^*{}_{\{f\}}{}^i$ is its pre-exponential and $E_{\{f\}}{}^i$ is the binding energy of particle i with site $\{f\}$. In the atom-atomic approximation, this value is obtained by summation of all contributions from the interaction of the atoms of the molecule with the atoms of the surface.

The intermolecular interaction of adjacent particles i and j localized on sites f and g will be characterized by the energy parameters $\varepsilon_{\{f\}\{g\}}{}^{ij}$. The value of this parameter depends on the mutual orientation of the molecules. The energy of the intermolecular interaction is calculated in the atom-atomic approximation. The value of the parameter $\varepsilon_{\{f\}\{g\}}{}^{ij}$ is obtained from the sum of the contributions of paired interactions $\varepsilon_{\{f\}\{g\}}{}^{ij}(\varphi\xi)$ between adjacent contacts φ (particle i) and ξ (particle j) related to the contact line of these adjacent molecules i and j in sites $\{f\}$ and $\{g\}$. The size of the unit contact is considered to be equal to the lattice constant. Let us designate the perimeter of particle i as Q_i. The number of contacts of the class φ of particle i will be designated as Q_i^φ, $Q_i = \sum_{\varphi=1}^{\tau_i} Q_i^\varphi$, where the sum over φ from 1 to τ_i means the summation over all classes of contacts of particle i. The contact line of adjacent particles i and j in sites f and g will be designated as $\sigma_{fg}{}^{ij}$. All contact regions belonging to the same class are energetically equivalent. For any specific set of adjacent particles $\{j\}$ designated by the symbol α, we have $Q_i = \sum_g \sigma_{fg}^{ij}$, where the sum over g is taken over all adjacent sites around particle i. Symbol α numerates the total sequence of all possible sets of adjacent molecules $\{j\}$ taking into account their orientations. Positive values of the interaction parameters correspond to attraction. The interaction of particles with free sites is equal to zero.

Each site of the surface is either blocked by the adsorbate or is free. The free site v is considered to be a particle of the kind $s+1$, all its contacts being equivalent and $Q_v \equiv Q_{s+1} = z$; $m_{s+1} = 1$. To calculate the adsorption isotherm, the probabilities of different states of occupation of all surface sites should be calculated.

System of equations

To write the system of equations describing the adsorption of large molecules on nonuniform adsorbents, we use the cluster approach to description of the distribution of laterally interacting molecules over nonuniform sites of the lattice systems.[5,22] The essence of this approach is the following. The system of equations is solved relative to the cluster distribution functions, which characterize the probabilities of different local molecular configurations, instead of the calculation of the statistic sum of the system studied (more exactly, the statistic weights of configurations of molecules with the fixed energy of the system). The procedure of development of the system of equations includes three stages: 1) representation of the initial lattice to the clusters consisting of the central site and the region occupied by the nearest adjacent molecules; 2) development of equations for the cluster distribution functions on each cluster (this results in an exact but unclosed system of equations, because the number of the unknowns is greater than the number of bonds); 3) introduction of a unified method for closing the equation developed for all different clusters.

This results in the unified closed system of equations (1)—(2) that describes the distribution of molecules over nonuniform sites of the whole lattice and takes into account lateral interactions of adjacent molecules in the quasi-chemical approximation, which conserves the effects of direct short-range correlations.

$$a^i_{\{f\}}P\theta^{m_i v}_{\{f\}} = \theta^i_{\{f\}}\Lambda^i_{\{f\}}/m_i, \quad \Lambda^i_{\{f\}} = \sum_{\alpha(n)}\prod_n t^{in}_{\{f\}\{g\}}\exp\left[-\beta\varepsilon^{in}_{\{f\}\{g\}}\right], \tag{1}$$

$$\theta^{in}_{\{f\}\{g\}}\theta^{m_i v, m_n v}_{\{f\}\{g\}} = \theta^{i, m_n v}_{\{f\}\{g\}}\theta^{m_i v, n}_{\{f\}\{g\}}\exp\left[-\beta\varepsilon^{in}_{\{f\}\{g\}}\right], \tag{2}$$
$$t^{in}_{\{f\}\{g\}} = \theta^{in}_{\{f\}\{g\}}/\theta^i_{\{f\}}$$

where P is the pressure of the adsorbate in the gas phase; $\theta_{\{f\}}{}^i$ is the probability of covering site $\{f\}$ by particle i; symbol $m_i v$ designates the free surface region of the size m_i, in which the adsorption of particle i is possible; $\theta^{m_i v}_{\{f\}}$ is the probability that region $\{f\}$ of size m_i is free; $\theta^{in}{}_{\{f\}\{g\}}$ is the probability that particle i on site $\{f\}$ and particle n on site $\{g\}$ are adjacent, where $1 \le n \le (s+1)$; the condition of normalization to the paired probabilities will be written as $\sum_n \theta^{in}_{\{f\}\{g\}} = \theta^i_{\{f\}}$. The summation over $\alpha(n)$ in Eq. (1) means the sum over all possible arrangements of all adjacent molecules n. The function $\Lambda_{\{f\}}{}^i$ depends on the lateral interactions between adjacent molecules (it is the function taking into account the imperfect character of the adsorption system caused by the adsorbate—adsorbate system). If the lateral interactions can be neglected, $\Lambda_{\{f\}}{}^i = 1$ and $a^i_{\{f\}}P = \theta^i_{\{f\}}/\left(\theta^{m_i v}_{\{f\}}m_i\right)$.

Equations (1) and (2) make it possible to calculate the local isotherms (local coverages of different sites), if they are supplemented by the normalizing conditions to coverages of the sites and to determine the method for calculation of functions $\theta^{m_i v}_{\{f\}}$.

The normalizing condition to the probability of coverage of the site with the number f has the form

$$\rho^v_f + \sum_{i=1}^{s}\sum_{\xi=0}^{m_i-1}\rho^i_{f-\xi} = 1, \tag{3}$$

where $\rho_f{}^i = \theta_{\{f\}}{}^i/m_i$, index ξ is the shift of the molecule along the given orientation axis. Normalizing condition (3) reflects the whole totality of different modes of blocking the given site f. For one-center spherically symmetric particles, normalizing condition (3) is written as

$$\rho^v_f + \sum_{i=1}^{s}\rho^i_f = 1,$$

because the long molecular axis is absent in this case. For spherically symmetric one-center particles, we have

$$\rho_f{}^v + \rho_f{}^A = 1,$$

where A is the site occupied by the molecule A.

The probability of the free surface region on which particle i can be adsorbed is expressed by the product of the probability of the free site with the number f by the probability of the adjacent free region of the size (m_i-1). This makes it possible to write the equation for the function $\theta^{m_i v}_{\{f\}}$ in the following form:

$$\theta^{m_i v}_{\{f\}} = \rho^v_f\prod_h t^{vv}_{h,h+1},$$

where index h is the number of (m_i-1) sites blocked by particles i of the size m_i; $\rho_f{}^v$ is the probability that site f is free, $t_{h,h+1}{}^{vv}$ is the conventional probability of the free site with the number $(h+1)$ near the free site with the number h:

$$t^{vv}_{h,h+1}(k) = \rho^v_{h+1}\left[\rho^v_{h+1} + \sum_{i=1}^{s}\sum_{\varphi}\rho^i_{h+1}Q^{\varphi}_i(k)/z\right]^{-1}. \tag{4}$$

Here the pair of indices h and $h+1$ specifies the orientation (k) of the pair of free sites, $Q_i{}^{\varphi}(k)$ is the number of contacts of the class φ of adjacent particle i in the direction specified by index k.

As follows from the structure of the equations obtained, the developed system of equations is nonlinear relative to $\theta_{\{f\}}{}^i$ (or $\rho_f{}^i$). Couplings between the states of occupation of different sites are manifested due to the lateral interactions (formulae (1) and (2)) (this factor is the main one for interacting one-centered particles) and due to blocking several adjacent sites by one molecule (formulae (3) and (4)). This blocking also takes place in the absence of lateral interactions. The solution of the equations relative to local coverages $\theta_{\{f\}}{}^i$ allows one to determine the dependence of the total coverage of the surface on the pressure, *i.e.*, the adsorption isotherm:

$$\theta(P) = \sum_{i=1}^{s}\sum_{f=1}^{N}\theta^i_{\{f\}}(P)/N.$$

The obtained system of Eqs. (1)—(4) makes it possible to study the adsorption of large molecules on nonuniform surfaces taking into account lateral interactions of the nearest neighbors. Analysis of this system requires numerical methods. The dimensionality of the system of equations decreases substantially when new variables $X_{\{f\}\{g\}}{}^i$ are introduced by the correlation $\theta_{\{f\}\{g\}}{}^{ij} = X_{\{f\}\{g\}}{}^i X_{\{g\}\{f\}}{}^j\exp(\beta\varepsilon_{\{f\}\{g\}}{}^{ij})$ (this transforms Eqs. (2) for paired functions to identities $1 \equiv 1$). Analytical expressions can be obtained only for the simplest limiting cases, in particular, for the uniform surface both without and accounting for lateral interactions.

The system of Eqs. (1)—(4) gives the site-to-site description of the local populations of the two-dimensional surface fragment. This detailed description is possible only for small surface regions. To describe macroscopic regions, it is necessary to introduce distribution functions of sites of different types and to average the equations obtained using these functions. (This problem has been considered in detail for one-centered particles in Refs. 7 and 26; the main concepts are valid for multicentered particles as well.) In particular, for the adsorption isotherm, the general form of the well-known equation is obtained:

$$\theta(P) = \sum_{i=1}^{s}\sum_{q=1}^{T}f_q\theta^i_q.$$

$$\sum_{q=1}^{T} f_q = 1 .$$

Here f_q is the unary discrete function of the site distribution over the adsorption ability that characterizes the fraction of sites on the adsorbent surface of the type q ($1 \le q \le T$, T is the number of types of the sites on the nonuniform surface).

Simplified versions of combined accounting for the nonuniformity of the surface and lateral interactions of molecules as well as particular cases for the uniform surface are considered below.

Model of isolated contacts

In solving Eqs. (1)—(4), it is most difficult to calculate all possible configurations of adjacent molecules $\alpha(n)$. To simplify accounting for lateral interactions, the Guggenheim—Barker approximation[27–29] is used for mixtures of large molecules in the theory of solutions. The sense of this approximation is the substitution of the real geometry of mutual arrangement of the adjacent molecules by the estimation of an average number of pairs N_{ij}^{kn} between unit contacts k and n of adjacent molecules i and j and by taking into account the lateral interactions between them specified by the interaction parameters ε_{ij}^{kn}, where $1 \le k \le Q_i$, $1 \le n \le Q_j$. The N_{ij}^{kn} values are related by the correlations

$$2N_{ij}^{kk} + {\sum_{j,n}}' N_{ij}^{kn} = Q_i^k N_i ,$$

where the stroke means $j \ne i$ and $n \ne k$.

The normalizing correlations for the contact pairs are determined by Eqs. (5).

$$\theta_{ij}^{kn} = (1 + \Delta_{ij}^{kn}) N_{ij}^{kn}/M, \quad M = \sum_i \sum_k Q_i^k N_i ,$$

$$\sum_{i,k} \sum_{j,n} \theta_{ij}^{kn} = 1, \quad \sum_{j,n} \theta_{ij}^{kn} = \theta_i^k , \quad \sum_{i,k} \theta_i^k = 1,$$

$$\theta_i^k = x_i \xi_i^k , \quad \xi_i^k = \left[\sum_{j,n} x_j Q_j^n / Q_i^k \right]^{-1} . \tag{5}$$

$$\sum_i x_i = 1 , \ 1 \le i, j \le s, \ 1 \le k \le \tau_i , \ 1 \le n \le \tau_j ,$$

Here $\Delta_{ij}^{kn} = 1$ for $i = j$ and $k = n$, and $\Delta_{ij}^{kn} = 0$ in the other cases, M is the double number of the contact pairs of the system, the ratio $x_i = N_i / \sum_i N_i$ determines the molar fraction of component i, and θ_i^k is the probability that the contact chosen is the contact of the k type of molecule i. The function θ_{ij}^{kn} determines the probability of formation of the contact pair between contacts k and n of molecules i and j, respectively. The ratio $t_{ij}^{kn} = \theta_{ij}^{kn}/\theta_i^k$ determines the conventional probability that contact n of molecule j is adjacent to contact k of molecule i; $\sum_{j,n} t_{ij}^{kn} = 1$. The equilibrium distribution of the contact pairs of the adjacent molecules is calculated by formulae (5) and the following correlations:[28] $\theta_{ii}^{kk}\theta_{jj}^{nn} = (\theta_{ij}^{kn})^2 \exp\beta\{\varepsilon_{ii}^{kk} + \varepsilon_{jj}^{nn} - 2\varepsilon_{ij}^{kn}\}$.

In this model, the local adsorption isotherms are described by Eq. (1), where

$$\Lambda_{\{f\}}^i = \prod_k \xi_i^k \left[\sum_{j,n} t_{ij}^{kn} \exp\left\{-\beta\varepsilon_{ij}^{kn}\right\} \right]^{Q_i^k} .$$

This model is used in two versions. The first version uses the simplified description of the lateral interactions (as shown above), while the interactions of the molecule with the nonuniform surface is taken into account exactly. The second version uses the model of contacts and is used for the description of the adsorbent—adsorbate interactions. For the ideal adsorption system with $\Lambda_{\{f\}}^i = 1$, this version was considered in Ref. 21, where formulae for adsorption of chain molecules on the chaotic surface, *i.e.*, on the nonuniform surface with chaotic arrangement of sites of different types, were derived through the calculation of the statistic sum of the adsorption system in the Flory approximation. The main system of Eqs. (12)—(14) in Ref. 21 can be directly derived from our Eqs. (1), (3), and (4), if it is taken into account that

$$\theta_{\{f\}}^{m_i v} = \rho_f^v \prod_h \rho_{h+1}^v \ \text{and} \ \theta_{\{f\}}^i = \rho_f^k \prod_h \rho_{h+1}^n$$

(indices k and n designate different segments of adsorbed molecule i). The new approach makes it possible to use these equations[21] for planar molecules of a more complicated form. Formally, this approach can be also applied to arbitrary modes of arrangement of sites of different types, although from the physical point of view, these equations are the most correct for chaotic surfaces.

The first version of the model also allows one to study nonuniform surfaces of any structure. In the particular case of $\Lambda_{\{f\}}^i = 1$, the adsorption isotherms described in Refs. 19 and 20 are obtained for dimeric molecules on stepped and chaotic surfaces.

Quasi-one-center model for calculation of adsorption on amorphous surfaces

To calculate the adsorption of laterally interacting molecules on chaotic surfaces, one should consider a larger surface region.[7,30] In the case of adsorption of spherically symmetric molecules (which are approximated by a sphere or square), a simpler, approximated calculation method can be used. The physical basis of the new method is the following. For small densities of the adsorbate, the contributions of the lateral interactions are low, and the distribution of the molecules is determined only by the local adsorbate—adsorbent potential (*i.e.*, by the local Henry constant). In the region of great coverages of the surface, the adsorption occurs mainly on the weakest sites, and the contribution of the lateral interactions is maximum. In the intermediate region of coverages, the nonuniformity of the surface and lateral interactions appear simultaneously. This results in the nonequivalent coverage of different sites, leading to the formation of a certain compact arrangement of the molecules at first local and then larger (domain), on the most favorable subset of sites (with the maximum binding energy) and to blocking the adjacent sites. This phenomenon is analogous to the effect of ordered arrangement of the molecules in the case of strong repulsion of the nearest neighbors.[31]

The proposed procedure for the calculation of the adsorption is the following. The surface is divided by a lattice structure, as for one-center molecules, with the number of the nearest neighbors z and the lattice constant equal to the diameter of the molecule. Then the surface region inside each site is divided into smaller surface areas (for example, the square side is divided into n parts, $n = 2, 3, \ldots$, and the site itself is divided into n^2 parts). The center of any small surface area can be accepted as the center of the "whole" site, which is then propagated over the whole surface. The division of the surface into a set of sites with their sets of local Henry constants for each site corresponds to each position of the center of the site. For the chosen division of the surface, the adsorption $\theta_k(P)$ is calculated in the same manner as for the one-center system[5,7] by solving the system of Eqs. (1) and (2), where $\theta_f^{\nu} = 1 - \theta_f^{A}$

$$\theta_k(P) = \sum_{f=1}^{N} \theta_f(P)/N, \quad a_f P = \frac{\theta_f}{1-\theta_f} \prod_{g=1}^{z_f} \left(1 + x t_{fg}\right),$$

$$x = \exp(-\beta\varepsilon) - 1, \quad t_{fg} = \frac{2\theta_g}{b_{fg} + \delta_{fg}}, \qquad (6)$$

$$\delta_{fg} = 1 + x(1 - \theta_f - \theta_g).$$

Here θ_f is the molar fraction of the particles in sites f, and index g numerates adjacent sites z_f of site f. In the atom-atomic approximation of taking into account the lateral interactions, $\varepsilon_{fg}^{ij} = \varepsilon^{ij}$.

This calculation is repeated n^2 times ($1 \le k \le n^2$): each small surface area is the center of the site. Then the value $\theta = \theta_k(P)$, $1 \le k \le n^2$, which corresponds to the minimum value of the free energy of the adsorbed molecules is chosen for each specific value of the pressure P.[32] The total dependence $\theta(P)$ thus plotted corresponds to the adsorption isotherm. Thus, the system of equations for one-center particles is solved n^2 times instead of solving the system of equations for multicenter particles.[5,7] This calculation procedure is sufficiently adequate to the physical picture. The results of the calculations at $\theta \to 0$ and $\theta \to 1$ are independent of the method of division of the surface into cells, because at $\theta \to 0$ the Henry constant is the additive value independent of the value of summands, and at $\theta \to 1$ the total value of the contributions of the lateral interactions is independent of the character of nonuniformity of the surface. In the region of intermediate coverages, all possible modes of the ordered arrangement of the molecules is considered in the explicit form. This procedure was used in Ref. 33 for the calculation of the adsorption of argon atoms on the amorphous rutile surface.

Uniform surface

On uniform surfaces, all clusters of sites are equivalent, and their differences in coverages are determined only by the effects of ordering of the adsorbed particles due to their lateral interactions and forms of their "solid cores." Below, we will restrict our review to the results obtained previously for particular cases of the adsorption isotherms derived from the formulae presented in this work.

In Ref. 23, the effects of local ordering of dimeric molecules were taken into account by the formulae that follow directly from the equations given above. The orientation ordering of dimers and trimers also was considered in Refs. 34 and 35. Accounting for the orientation ordering of rigid rods has been studied in Ref. 36 in the molecular field approximation,[5] which is obtained from the equations of the quasi-chemical approximation used in this work by the limiting transition $\beta\varepsilon \to 0$. If the ordering of particles is not taken into account, Eqs. (1)—(4) are simplified, because the probabilities of coverages of all sites become equal. As a result, formula (3) takes the form typical of one-center particles:

$$\theta_\nu + \theta_A = 1.$$

Exact accounting for the lateral interactions for the arbitrary size of particles is possible only for the one-dimensional structure.[37] Accounting for the lateral interactions in the model of similar isolated contacts results in the following expression for the adsorption isotherm of large molecules without taking into account their reorientations

$$aP = \eta\theta\Phi\Lambda\zeta/[zm(1 - \theta)], \Phi = (t_{\nu\nu})^{\kappa}/(1 - \theta)^{\alpha}, \Lambda = (1 + xt)^{Q},$$

$$x = \exp(-\beta\varepsilon) - 1, \quad t = [(1 - \theta)t_{\nu\nu} + 2\theta - 1]/\theta, \qquad (7)$$

where η is the number of symmetry of the particles: h = 1 for nonsymmetric and $\eta = 2$ for symmetric particles; the Φ function depends on the shape and size of particles m: κ and α are the full and internal numbers of binding between the sites blocked by the molecule; the factor ζ takes into account the additional internal degrees of freedom of the adsorbed molecule and depends on its rigidity ($\zeta = 1$ for rigid molecules); ε is the parameter of interaction of the adjacent contacts, whose number for the planar adsorbate is equal to Q; t is the conventional probability that the contact is adjacent to another contact; t_{vv} can be determined from Eq. (4). In the particular case of dimeric molecules, this equation is transformed to the Chang equation.[38,39]

When lateral interactions are absent, $\Lambda = 1$ and the form of the adsorption isotherm is mainly determined by the Φ function. According to Ref. 27, for particles in the form of plates, $m = b \cdot d$, $Q = 2(b + d)$; for rigid rods with the length m, $Q = (z - 2)m + 2$. The equations of the adsorption isotherm were obtained for the particular cases of dimers,[38,39] trimers,[40] and a rod of an arbitrary length on the one-dimensional structure.

The adsorption isotherm for absolutely flexible chains differs from that for rigid rods by the additional internal degrees of freedom of each segment. This allows one to take into account that $\zeta = (z-1)^{-(m-2)}$ without changing Eq. (7), because each next segment of the chain has $(z-1)$ directions of its arrangement. Taking into account the interactions between the chains in the approximation of isolated contacts is considered in Ref. 42.

Thus, using the cluster approach, the equations of the adsorption isotherms of large molecules blocking more than one adsorption center on the nonuniform surfaces were obtained. The equations take into account the lateral interactions of the adjacent molecules in the quasi-chemical approximation, which reflects the effects of short-range correlations. The methods for simplified description of multicenter molecules on the nonuniform surfaces are considered: the model of isolated contacts for nonspherical particles and the quasi-one-center model for spherical particles on the amorphous surfaces.

References

1. I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2221.
2. W. A. Steele, *The Interaction of Gases with Solid Surfaces*, Pergamon Press, New York, 1974.
3. N. N. Avgul', A. V. Kiselev, and D. P. Poshkus, *Adsorbtsiya gazov i parov na odnorodnykh poverkhnostyakh* [*Adsorption of Gases and Vapors on Uniform Surfaces*], Khimiya, Moscow, 1975, 384 pp. (in Russian).
4. M. Jaroniec and R. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam, 1988.
5. Yu. K. Tovbin, *Theory of Physical Chemistry Processes at a Gas—Solid Interface*, CRC, Press, Boca Raton, 1991.
6. W. Rudzinski and D. H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, London, 1992.
7. Yu. K. Tovbin, *Zh. Fiz. Khim.*, 1990, **64**, 865 [*Russ. J. Phys. Chem.*, 1990, **64**, No. 4, 469 (Engl. Transl.)].
8. Yu. K. Tovbin, *Khim. Fiz.*, 1996, **16**, 75 [*Chem. Phys. Reports*, 1996, **15**, 231 (Engl. Transl.)].
9. Yu. K. Tovbin, *Zh. Fiz. Khim.*, 1996, **70**, 700 [*Russ. J. Phys. Chem.*, 1996, **70**, 650 (Engl. Transl.)].
10. J. K. Roberts, *Proc. Roy Soc. London*, 1935, **A152**, 445.
11. J. K. Roberts, *Some Problems on Adsorption*, Univ. Press, Oxford, 1939.
12. M. I. Temkin, *Zh. Fiz. Khim.* [*Sov. J. Phys. Chem.*], 1938, **11**, 169 (in Russian).
13. A. Schuchowitzky, *Acta Physicochim USSR*, 1938, **8**, 531.
14. I. Langmuir, *J. Chem. Soc.*, 1940, Nos. 4—5, 513.
15. J. Honig, in *Gas-Solid Interface*, Ed. by E. A. Flood, New York, Denner, 1966.
16. Yu. K. Tovbin, *Cand. Sci. (Phys.-Math.) Thesis*, NIFKhI im. L. Ya. Karpov, Moscow, 1974, 92 pp. (in Russian).
17. V. E. Ostrovskii, *Usp. Khim.*, 1976, **45**, 849 [*Russ. Chem. Rev.*, 1976, **45** (Engl. Transl.)].
18. Yu. V. Shulepov and E. V. Aksenenko, *Reshetochnyi gaz* [*Lattice Gas*], Naukova dumka, Kiev, 1981, 268 pp. (in Russian).
19. Yu. A. Chizmadzhev and V. S. Markin, *Elektrokhimiya* [*Sov. J. Electrochem.*], 1968, **4**, 3 (in Russian).
20. V. S. Markin and Yu. A. Chizmadzhev, *Elektrokhimiya* [*Sov. J. Electrochem.*], 1968, **4**, 123 (in Russian).
21. T. Nitta, M. Kuro-Oka, and T. Katayama, *J. Chem. Eng. Japan*, 1984, **17**, 45.
22. Yu. K. Tovbin, *Doct. Sci. (Phys.-Math.) Thesis*, NIFKhI im. L. Ya. Karpov, Moscow, 1985, 376 pp. (in Russian).
23. Yu. K. Tovbin and O. Yu. Batalin, *Zh. Fiz. Khim.*, 1987, **61**, 2535 [*Russ. J. Phys. Chem.*, 1987, **61**, 2535 (Engl. Transl.)].
24. S. Chandrasekhar, *Liquid Crystals*, Cambr. Univ. Press, Cambridge, 1977.
25. I. P. Bazarov and E. V. Gevorkyan, *Statisticheskaya teoriya tverdykh i zhidkikh kristallov* [*Statistical Theory of Solid and Liquid Crystals*], Izd-vo MGU, Moscow, 1983, 262 pp. (in Russian).
26. Yu. K. Tovbin, *Langmuir*, 1997, **13**, No. 3.
27. E. A. Guggenheim, *Mixtures*, Clarendon Press, Oxford, 1952, 271 p.
28. J. A. Barker, *J. Chem. Phys.*, 1952, **20**, 1526.
29. N. A. Smirnova, *Molekulyarnaya teoriya rastvorov* [*Molecular Theory of Solutions*], Khimiya, Leningrad, 1987, 360 pp. (in Russian).
30. Yu. K. Tovbin and E. V. Votyakov, *Physics of Low-Dimensional Structures*, 1995, **10/11**, 105.
31. M. W. Roberts and C. S. McKee, *Chemistry of the Metal—Gas Interface*, Clarendon Press, Oxford, 1978.
32. Yu. K. Tovbin, *Zh. Fiz. Khim.*, 1992, **66**, 1395 [*Russ. J. Phys. Chem.*, 1992, **66**, 741 (Engl. Transl.)].
33. V. V. Gvozdev and Yu. K. Tovbin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, No. 6 [*Russ. Chem. Bull.*, 1997, **46** (Engl. Transl.)].
34. R. D. Kaye and D. M. Burley, *Physica*, 1977, **A87**, 499.
35. R. D. Kaye, *Ibid*, 1981, **A105**, 347.
36. B. E. Boehm and D. E. Martire, *J. Chem. Phys.*, 1977, **67**, 1961.
37. Yu. K. Tovbin, *Teor. Eksp. Khim.* [*Sov. J. Theor. Exp. Chem.*], 1974, **10**, 258 (in Russian).
38. T. S. Chang, *Proc. Roy. Soc. London*, 1939, **169**, 512.
39. T. S. Chang, *Proc. Cambr. Phil. Soc.*, 1939, **35**, 265.
40. A. R. Miller, *The Theory of Solutions of High Polymers*, Clarendon Press, Oxford, 1948.
41. Yu. S. Khodakov, A. A. Berlin, G. I. Kanyaev, and Kh. M. Minachev, *Teor. Eksp. Khim.* [*Sov. J. Theor. Exp. Chem.*], 1969, **5**, 631 (in Russian).
42. W. J. C. Orr, *Trans. Farad. Soc.*, 1944, **40**, 320.

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