

ADSORPTION OF A HETEROGENEOUSLY ASSOCIATING FLUID ON A *fcc* 100 CRYSTALLINE SURFACE

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A model of a heterogeneously dimerizing fluid ($A+B \rightleftharpoons AB$) near a *fcc* (100) crystalline surface is studied by means of an integral equation method. The site-site extended mean spherical approximation and singlet level integral equations are used to obtain the density profiles. Their dependence on the degree of dimerization of the bulk fluid, the bonding distance of dimer species and the strength of nonassociative fluid-solid interactions is studied. The geometric and energetic aspects of associative adsorption on the (100) surface are investigated by using the model of reactive crystal sites. On-top, two-fold bridging site and four-fold hollow site localized adsorption are also examined.

1. Introduction

It is a pleasure to contribute to this special issue. We share the scientific goals and philosophy of Prof. I.R.Yukhnovs'kij, in particular in the investigation of inhomogeneous fluids [1,2]. Our paper deals with inhomogeneous associating fluids in which the particles do not possess multipole moments, in contrast to the studies of inhomogeneous simple fluids with electrostatic interactions by Yukhnovs'kij and his school [1-5]. However, the models which we consider can be used as a reference system to include electrostatic forces in a further development and to construct the theory of inhomogeneous associating ionic and ion-molecular systems.

Inhomogeneous associating (chemically reacting) fluids are of special interest for chemistry and chemical technology. Several phenomena, such

as adsorption and chemisorption, heterogeneous catalysis on crystalline and noncrystalline solid surfaces, chemical reactions at gas-liquid and liquid-liquid interfaces, corrosion, are some examples in which one must consider inhomogeneous associating fluids (IAF's).

Previous theoretical research has been focussed on the bulk AF's. On the other hand, attention in the theory of inhomogeneous fluids has been directed to simple liquids and, to a lesser extent, molecular liquids. Molecular liquids correspond to a complete association limit of AF's. It is worth noting that, as a result, the theory of inhomogeneous AF's is at present less developed than the theory of bulk AF's. Recently, we have initiated the study of IAF's by means of an integral equation method [6-10]. Structureless surfaces have been investigated. However, crystalline surfaces represent a more challenging subject of investigation. It is an important subject of investigation because crystalline materials are widely used as effective catalysts. Adsorption of AF's on some low-index chemically inactive crystal surfaces has been studied by us in Refs.[11-14]. In this communication we present the results of our investigation of the nonassociative and associative adsorption of a model of a dimerizing fluid on a (100) crystalline surface.

Let us discuss briefly the theoretical tools which are necessary to describe a model of IAF's near a crystalline surface. Two methods have been most successful to study the bulk AF's, namely those of Stell *et al.*[15-19] and of Wertheim [20-23]. The method of Stell and collaborators is based on the standard Ornstein-Zernike (OZ) integral equation complemented by closure relations, adjusted to treat a strong associative interparticle interaction. In contrast to the more complex approach developed by Wertheim, there is no distinction between the bonded and nonbonded states of the particles in this method. In the series of papers of Stell *et al.*, the primary emphasis was given to an adequate description of the equilibrium association constant [15-19,24]. The structural properties of the AF's have been investigated by using different approximations [15,18]. In particular, it has been shown that the standard liquid state closures, such as the Percus-Yevick (PY) and hypernetted chain (HNC) approximations, deviate from the law of mass action and therefore are not appropriate to describe associative interactions of varying strength at different densities. The extended mean spherical approximation (EMSA) for a dimerized fluid investigated in Refs.[18,19] is successful in describing structural properties, however only at high densities. A more sophisticated approximation, which cannot be solved analytically, consists of a site-site OZ equation complemented by the closures which include an exact form of the intramolecular structure factor [18,19]. This approach can be used successfully for a wide range of the density. We shall abbreviate this approximation as a site-site EMSA (SSEMSA). This approximation, and its simplified version, the EMSA, will be used. In both cases, numerical methods are utilized to solve the integral equations for the bulk fluid. We focus on the model of a spherically symmetric associative shell proposed by Cummings and Stell for a heterogeneous association ($A + B \rightleftharpoons AB$) [15]. It is worth noting that, for this model, the application of a two density version of Wertheim's theory leads to adequate results only for low densities [18].

Our aim is to combine the SSEMSA approximation with the singlet level integral equations of the theory of inhomogeneous fluids [25,26]. The first reason for doing so is the relative simplicity of the singlet PY (PY1) and singlet HNC (HNC1) equations for the density profiles (DP's), compared with other methods. The adsorption of the particles is given in terms of the DP's or adsorption isotherms which follow straightforwardly from the DP's.

Already, the singlet level approach has been already used with success in the case of simple fluids in contact with crystalline surfaces [27].

The second reason why we apply the singlet theory is the following. A more detailed description of adsorption and lateral (in-plane) correlations can be obtained from the pair theory of inhomogeneous fluids [25,28-30,10] (PY2 and HNC2 are the representative examples of the pair theory). However, the implementation of this theory requires powerful computer facilities and sophisticated numerical algorithms even for structureless surfaces [28-30]. The case of crystalline surfaces is much more difficult, in particular with respect to the computer memory requirements. We postpone the application of the pair theory to future studies. A further problem with the implementation of the pair theory is connected with the choice of the closures to treat the fluid-fluid and fluid-solid associative interactions. For distances far from the surface, the inhomogeneous pair correlation functions reduce to their bulk counterparts. At least for the PY and HNC approximations, these are inadequate for AF's. Therefore, one must formulate inhomogeneous closures which would reduce to the EMSA, as an example.

A more severe test for the theory, even at the singlet level, would be the presence of associative fluid-solid interactions. One can apply the PY1 or HNC1 approximation straightforwardly. Possible alternatives are the development of density functional approaches [31-33] and associative PY1 (APY1) or associative HNC1 (AHNC1) approximations, which follow from the associative analogue of the HAB equation [34,35]. Some first steps in this direction have been made in [31-35] for models in which there is no overlap of the monomer units either in the bulk or of the bulk monomers with the surface. Even under these simplifying conditions, it is not clear yet if the closures proposed [34, 35] would be successful for a wide range of densities and other parameters, because there has not been a comparison of these theories with simulation data. Moreover, the development of these approaches for crystalline surfaces would require lengthy studies.

In what follows, we use the PY1 approximation to treat the fluid-solid nonassociative and associative interactions. More sophisticated closures can be developed on this basis. The nonassociative term is taken in the form proposed by Steele [36] for the interaction of the spherically symmetric particles with a low-index crystalline surfaces [graphite basal plane, (100) and (111) fcc lattices]. The associative part of the bulk fluid-solid interactions is modelled using the assumption that the surface atoms react with the fluid particles. The distinction of nonassociative and associative terms makes it possible to investigate both separate and cumulative effects of nonassociative and associative adsorption.

We believe that the overview on the problem presented above is fairly complete. To proceed, let us now describe the model.

2. A model for an associating fluid near a crystalline surface

The potential energy of the system is taken in the form:

$$U_{pot} = \sum_{m,n} \sum_{i<j} U_{mn}(r_{ij}) + \sum_m \sum_i \sum_{k=1,2} U_m^{(k)}(\mathbf{r}_i), \quad (1)$$

where m, n are the species indices, $k = 1, 2$ correspond to the nonassociative and associative fluid-solid interaction, respectively. The first term in equation (1) describes the energy of interaction of the bulk fluid particles whereas the second term describes the energy of the bulk fluid-solid interactions.

The bulk fluid model is taken in the form proposed by Cummings and Stell [15]. It is a two-component (A, B) mixture of equal size spherically symmetric particles ($\sigma_A = \sigma_B = \sigma_f$), considered at equimolar conditions ($\rho_A = \rho_B = 0.5\rho$) for simplicity. The interparticle interactions are chosen in the form

$$U_{AB}(r) = U_{BA}(r) = \begin{cases} \infty, & r < L_b - \frac{w}{2}, \\ -\varepsilon_b, & L_b - \frac{w}{2} < r < L_b + \frac{w}{2}, \\ \varepsilon^*, & L_b + \frac{w}{2} < r < \sigma_f, \\ 0, & r > \sigma_f, \end{cases} \quad (2)$$

Similar species [$U_{AA}(r) = U_{BB}(r)$] interact via a hard sphere potential. The parameters ε_b and w are the depth and width of associative square-well potential, respectively; L_b is the bonding distance. The height of the square mound, ε^* , is chosen to satisfy $\exp(-\beta\varepsilon^*) \approx 0$. In what follows we restrict ourselves to the case of dimerization, i.e. $L_b + \frac{w}{2} < \frac{\sigma_f}{2}$.

The interaction between the fluid particles and the solid substrate consists of nonassociative and associative terms. Each of these terms is a periodic function in the plane parallel to the surface, i.e. $U_m^{(k)}(\mathbf{r}_j) = U_m^{(k)}(\mathbf{r}_j + \mathbf{l})$ where \mathbf{l} is the two-dimensional translation vector, $\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2$, and where $\mathbf{a}_1, \mathbf{a}_2$ are two-dimensional unit lattice vectors. The most successful and commonly used nonassociative potentials for the interaction between the spherically symmetric particles and low-index crystalline surfaces are those of Steele [36]. It was shown in [12] that Steele's potentials are well suited to be used for the model of overlapping hard spheres. Therefore the $U_m^{(1)}(\mathbf{r}_j)$ is taken in the form [12, 36]

$$\frac{1}{\varepsilon_{fs}} U_m^{(1)}(\mathbf{r}_j) = E_{m,0}(z_j^*) + \sum_{l>0} E_{m,l}(z_j^*) f_l(s_1, s_2), \quad (3)$$

where ε_{fs} is the energy parameter of the fluid-solid interactions (in what follows it will be chosen according to the estimates of Steele [36]); the first term is the averaged contribution of the fluid-solid interactions whereas the second one characterizes the specific symmetry of the surface lattice plane.

We restrict ourselves to the case of *fcc* (100) symmetry. The distances from the surface in the potentials (3) are measured in dimensionless units, $z_j^* = z_j/a_1$, where $a_1 = a_2 = \sigma_s$ for (100) face of the *fcc* lattice, where σ_s is the diameter of the solid substrate particles. The functions $f_l(s_1, s_2)$ have been given in Table 1 of Ref.[12] and will be omitted here for the sake of brevity. The positions of the bulk fluid particles over the unit lattice cell are characterized by the parameters s_1, s_2 which vary from 0 to 1. In particular, the positions of surface atoms, S_a , denoted by (a) are $(s_1, s_2) = (0, 0); (0, 1); (1, 0); (1, 1)$. The nonassociative adsorption site position (s) and saddle point (sp) correspond to the minimum and saddle point of the nonassociative contribution to the fluid-solid potential energy surface, respectively [36]. For the convenience of the reader, we present the explicit expressions for both terms in equation (3). They are:

$$E_{m,0}(z_j^*) = 2\pi q_\nu A_m^6 / a_s^* \sum_{p \geq 0} \left[\frac{2A_m^6}{5(z_j^* + p\Delta z_j^*)^{10}} - \frac{1}{(z_j^* + p\Delta z_j^*)^4} \right], \quad (4)$$

$$E_{m,l}(z_j^*) = (2\pi A_m^6 / a_s^*) \left[\frac{A_m^6}{30} \left(\frac{q_l^*}{2z_j^*} \right)^5 K_5(q_l^* z_j^*) - 2 \left(\frac{q_l^*}{2z_j^*} \right)^2 K_2(q_l^* z_j^*) \right], \quad (5)$$

where the parameters a_s^* , q_ν , Δz^* and values of q_l^* can be found in [12,36], p is an integer and $K_i(x)$ are the modified Bessel functions of the second kind. The parameter describing the size ratio of the diameters of fluid and solid particles, A_m , is $A_m = (\sigma_m + \sigma_s)/2$. Consider the case of equal sizes for simplicity, i.e. $\sigma_m = \sigma_s$, $A_m = 1$. Truncation of the expansion given by equation (3) will be discussed in below.

The model for associative interaction between the fluid and solid particles, $U_m^{(2)}(\mathbf{r}_j)$, is given in terms of the corresponding Mayer function $f_m^{(2)}(r) = \exp[-\beta U_m^{(2)}(r)] - 1$. We use

$$f_m^{(2)}(r) = \delta_{mA}[-\theta(L_s - \frac{w}{2} - r) + (e^{\beta\varepsilon_s} - 1)\theta(L_s + \frac{w}{2} - r)\theta(r - L_s + \frac{w}{2}) - \theta(1 - r)\theta(r - L_s - \frac{w}{2})] + \delta_{mB}\theta(1 - r). \quad (6)$$

Here $\theta(x)$ is the step function, L_s is the bonding distance of the fluid-solid interaction and ε_s is the depth of associative square well. The particles B do not react with surface atoms S_a . The association of the A species with the surface atoms crucially depends on the choice of bonding distances L_s, L_b .

Let us analyze the geometrical aspects of the associative interactions. For $L_s + \frac{w}{2} < \frac{\sigma_s}{2}$, only the monomeric species A can be associatively adsorbed or in other words only AS_a complex can be formed. For larger L_s , $\frac{\sigma_s}{\sqrt{2}} > L_s + \frac{w}{2} > \frac{\sigma_s}{2}$, the atom A can be adsorbed in the two-fold bridging site position between two S_a atoms (which corresponds to the points of the normal to the sp point of the unit lattice cell). The mutual impenetrability of the B species and the S_a atoms means that for smaller L_s , within this interval, the monomers A form $A - 2S_a$ complexes whereas for larger L_s , again within this interval, the dimers AB can associatively adsorb and form $BA - 2S_a$ complexes. Therefore, we should mention in advance that the intraparticle peak of the density profile of A particles in the sp position in this case will contain either the contribution from monomers only or from monomers and dimers, depending on the value of L_s .

For $L_s + \frac{w}{2} > \frac{\sigma_s}{\sqrt{2}}$, the geometry of the interactions permits the formation of $A - 4S_a$ and $BA - 4S_a$ complexes in addition to the AS_a , $BA - S_a$ and $A - 2S_a$, $BA - 2S_a$ surface complexes. Each of the intraparticle peaks of the density profile of A will contain contributions from these structural units in the adlayer. Also nonassociative interactions will influence the occupancy of adsorption sites. However, they cannot change the nature of the complexes arising due to the associative interactions.

An interplay between the nonassociative and associative interactions determines the orientation of the dimer species in the adlayer. Also the bulk fluid potentials will influence the structure, because they determine the relative number of monomer and dimer species which adsorb differently. For different diameters of the fluid and solid particles, the interpretation of bonding becomes more complicated. Depending on the size ratio, the values for the bonding distance L_s will fall into different intervals in which different surface complexes would be permitted. With these comments, we terminate the description of the model.

3. Theoretical procedure

The adsorption of an AF on a crystalline surface will be discussed in terms of the density profiles (DP's) which are defined in a standard way

$$\rho_m(\mathbf{r}_j) = \rho_m g_m(\mathbf{r}_j) = \rho_m y_m(\mathbf{r}_j) \gamma_m(\mathbf{r}_j), \quad (7)$$

where $g_m(\mathbf{r}_j)$, $y_m(\mathbf{r}_j)$ are the one-particle distribution function and cavity distribution function, respectively; $\gamma_m(\mathbf{r}_j)$ is the Boltzmann factor for the fluid-solid interactions, $\gamma_m(\mathbf{r}_j) = \exp[-\beta \sum_{k=1,2} U_m^{(k)}(\mathbf{r}_j)]$, and m is the species index. The most straightforward way to obtain the DP's is the application of the singlet theory of inhomogeneous fluids [25,26]. In what follows we shall calculate the DP's by using the PY1 approximation which reads

$$y_m(\mathbf{r}_j) = 1 + \sum_{n=A,B} \rho_n \int d\mathbf{r}_i c_{mn}(|\mathbf{r}_j - \mathbf{r}_i|) [y_n(\mathbf{r}_i) \gamma_n(\mathbf{r}_i) - 1], \quad (8)$$

where $c_{mn}(r)$ are the direct correlation functions of the bulk associating fluid. This is the only input necessary to solve equation (8) for the DP's in the framework of the singlet theory. It is worth commenting on the adequacy of the approximations used in this approach, namely the PY1 and the corresponding approximate description of the bulk fluid. We discuss the latter issue first.

The model of the bulk AF of Cummings and Stell permits an analytical solution in the Percus-Yevick (PY) approximation [15], the extended mean spherical approximation (EMSA) and the associative Percus-Yevick approximation (APY) of Wertheim [18]. However, to do this one must transform the square-well associative interaction (AI) into the sticky analogue according to the recipe of Baxter [37]. Then the analytic solution can be used in equation (8) to obtain the DP's. It is evident, however, that equation (8) must be solved numerically even for quite simple fluid-solid potentials. Therefore, obtaining an analytical solution is not so important in this case. Moreover, the presence of the delta function term in the dcf's, $c_{mn}(r)$, is inconvenient for the numerical procedure because it requires separate analytical treatment. Our choice therefore is the numerical solution of equation (8) and the integral equation for the bulk fluid. In both cases the associative potentials have the form of a square well.

It has been shown in [18], that the EMSA for the model in hand is inadequate for low densities whereas the APY is successful for low densities. On the other hand, the standard PY deviates from the law of mass action. For this reason, we have decided to use a particle-particle approximation with the form of the reference interaction site approximation which reads [18]

$$h_{mn}(r) = -1 + \frac{\omega_{mn}(r)}{\sqrt{\rho_m \rho_n}}, \quad r < \sigma_f \quad (9)$$

$$c_{mn}(r) = -\frac{[\omega^{-1}(r)]_{mn}}{\sqrt{\rho_m \rho_n}}, \quad r > \sigma_f \quad (10)$$

in conjunction with the site-site OZ equation. In equations (9), (10), $\omega_{mn}(r)$ is the intramolecular structure factor. Approximation of the elements of the matrix $\omega^{-1}(r)$ by their long-range asymptotics leads to the EMSA approximation. In the case of a sticky delta-type interaction, the association is treated in the following way. The Mayer function which corresponds to $U_{AB}(r)$ defined by equation (2) can be presented as [10]

$$f_{AB}(r) = f_{AB}^{hs}(r) + F_{AB}^{as}(r), \quad (11)$$

where the first term corresponds to a hard sphere contribution whereas the remaining part describes association. In the sticky limit

$$F_{mn}^{as}(r) \implies (1 - \delta_{mn}) \frac{K_0}{4\pi L_b^2} \delta(r - L_b), \quad (12)$$

where K_0 is the equilibrium association constant at infinite dilution and

$$\omega_{mn}(r) = (1 - \delta_{mn}) \frac{\Lambda_b}{4\pi L_b^2} \delta(r - L_b), \quad (13)$$

where Λ_b is the fraction of dimerized particles in the bulk fluid determined by K_0 and ρ , and is an input parameter into the EMSA theory. We do not utilize the sticky limit procedure and the intramolecular term is taken in the form

$$\omega_{mn}(r) = (1 - \delta_{mn}) \frac{\Lambda_b}{K_0} F_{mn}^{as}(r). \quad (14)$$

The elements of the inverse matrix, necessary to implement the closure (10), are calculated numerically. The application of equations (9), (10) has two benefits compared with the EMSA. The first is that the pair distribution functions, $g_{AA}(r)$ and $g_{AB}(r)$, are equal except for the distance $r = L_b$, as required. Secondly, this approximation can be used for a wide range of densities with the same level of accuracy, in contrast to the EMSA which fails at low densities. The resulting distribution functions agree well with the simulation data [18]. However, comparison of the results of the EMSA and SSEMSA was made only at fixed strength of AI's [18]. In the subsequent section we show this comparison for the AI's of different strength.

Finally we discuss, in the description of the bulk fluid, the degree of dimerization Λ_b . The detailed procedure which must be used has been given in Sec.III.2 of Ref.[18]. Here we just would like to mention that the Ballance-Speedy equation for the cavity function has been utilized by other authors to evaluate the value of the cavity function at the bonding distance, $y_{AB}(L_b)$. To conform with these earlier calculations, we will use this equation here. The number of dimers follows straightforwardly from equations (61), (62) of Ref.[18]. Other expressions for the cavity function, such as the Henderson-Grundke parametrized form [38] or from the equation of state for the mixture of dumbbells and hard spheres of Boublik used in [18], can be applied. The description of the bulk correlations which follows from the theory outlined above is adequate. Any possible inaccuracies of the DP's are likely to be due to the PY1 approximation.

In this respect we emphasize that the singlet level theory (PY1 or HNC1) is the most direct route to obtain the DP's. The pair level theory is much more difficult to implement. It is well known that the PY1 becomes incorrect for nonassociative fluids at high densities in contact with a hard surface. Therefore, we restrict ourselves up to densities which are not too high. In fact, as it follows from both the theory and the simulation data [6,12, 39] that the adsorption of dimers on a hard surface is weaker than for the case of monomers. Therefore, one can use the PY1 for AF's expecting a similar level of accuracy as for hard spheres in absence of AI's between the fluid and the surface. Under these conditions, the PY1 and HNC1 have been successfully used for nonassociative and associative fluids in contact with crystalline surfaces [6,7,11-13].

It is worth noting that for sufficiently strong associative interactions and in the absence of nonassociative interactions between the bulk fluid particles and the surface, the PY1 closure becomes inadequate and leads to negative values of the DP's near the surface for some positions over the unit surface

cell. To overcome this difficulty the HNC1 equation for the profile can be used as well. It reads

$$y_m(\mathbf{r}_j) = \exp\left\{ \sum_{n=A,B} \rho_n \int d\mathbf{r}_i c_{mn}(|\mathbf{r}_j - \mathbf{r}_i|) [y_n(\mathbf{r}_i) \gamma_n(\mathbf{r}_i) - 1] \right\}. \quad (15)$$

However, we do not consider the extreme cases and restrict ourselves to the PY1 closure. Let us briefly describe some peculiarities of the solution of the equation for the DP's for the case of crystalline symmetry of the surface plane (see, eg.[12] for details). Due to the periodicity of the surface, all the functions which characterize the position of a fluid particle over the surface can be expanded into a two-dimensional Fourier series [36]

$$\varphi_m(\mathbf{r}_j) = \sum_{\mathbf{q}} \varphi_{m,\mathbf{q}}(z_j) \exp(-i\mathbf{q}\mathbf{l}_j), \quad (16)$$

where $\varphi_m(\mathbf{r}_j)$ stands for $y_m(\mathbf{r}_j)$ or $\rho_m(\mathbf{r}_j)$ or $\gamma_m(\mathbf{r}_j)$, \mathbf{l}_j is the two-dimensional translation vector; $\mathbf{q} = 2\pi(q_1 \mathbf{b}_1 + q_2 \mathbf{b}_2)$, q_i ($i = 1, 2$) are integers and $\mathbf{b}_1, \mathbf{b}_2$ are the unit vectors of the two-dimensional reciprocal lattice. Inverse transformation of equation (16) yields

$$\varphi_{m,\mathbf{q}}(z_j) = \frac{1}{a_s^*} \int d\mathbf{l}_j \exp(i\mathbf{q}\mathbf{l}_j) \varphi_m(\mathbf{r}_j), \quad (17)$$

where a_s^* is the area of the unit lattice cell. equation (8) can be rewritten in the form

$$y_{m,\mathbf{q}}(z_j) = a_m^* \delta_{\mathbf{q},0} + \sum_{\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q}} \sum_n \rho_n \int_0^\infty dz_i \gamma_{n,\mathbf{q}_1}(z_i) y_{n,\mathbf{q}_2}(z_i) \tilde{c}_{mn}(z_{ij}, q), \quad (18)$$

where

$$\tilde{c}_{mn}(z_{ij}, q) = 2\pi \int_0^\infty dR R J_0(qR) c_{mn}(\sqrt{z_{ij}^2 + R^2}), \quad (19)$$

$J_0(qR)$ is the zero-order Bessel function of the first kind,

$$a_m^* = 1 - 4\pi \sum_n \int_0^\infty dr r^2 c_{mn}(r). \quad (20)$$

A detailed description of this numerical procedure has been already presented in Ref.[12] and will be omitted for brevity. The DP's are calculated according to equations (18) and (19) which result in

$$y_m(z_j) = y_{m,0}(z_j) + \sum_{l>0} y_{m,l}(z_j) f_l(s_1, s_2). \quad (21)$$

Allowance for the terms up to $y_{m,9}(z_j)$ provides an accurate description of the DP's even in the presence of a quite strong associative interactions.

4. Results and discussion

4.1. Comments on the description of the bulk dimerizing fluid.

In previous work on the EMSA [9, 18], the density dependence of the structural properties of the system of dimerizing hard spheres has been studied at a fixed strength of associative interactions between the A and B species, namely at $\beta\varepsilon_b = 5.0$. Here we extend that study with different bonding energies and density because the variation of these two factors results in different degrees of dimerization of the bulk fluid.

A comparison of the results of the EMSA and SSEMSA approximations is presented in figures 1-4. First it should be noted that these two approximations lead to pair distribution functions which differ at small interparticle separations. The SSEMSA provides $g_{AA}(r) = g_{AB}(r)$ for $r \neq L_b$, i.e. except for the intraparticle peak at the bonding distance, as required (the A and B species are indistinguishable except for the presence of the AB associative interaction, see detailed discussion of this issue in [15]). It can be seen from the results given in figures 1 and 2 that for $\rho = 0.57$ (figure 1) and for $\rho = 0.238$ (figure 2) the difference between the pdfs of the EMSA and SSEMSA is most pronounced for $1 < r \leq 1 + L_b$; for larger distances the pdfs coincide. Also the results of both approximations coincide for weak association strength ($\beta\varepsilon_b = 1.0$) except in the vicinity of the contact distance. In general, the function $g_{AA}(r)$ from the EMSA is closer to the SSEMSA result than is the $g_{AB}(r)$. For a strong associative interaction ($\beta\varepsilon_b = 5.0$), which results in a high dimerization ($\Lambda_b = 0.987$, figure 1a and $\Lambda_b = 0.813$, figure 2a), the difference between the results of both approximations is quite large in the vicinity of the contact distance; it decreases for increasing r but remains pronounced up to $r = 1 + L_b$. For all these cases we have chosen $L_b = 0.44$. It is worth noting that the SSEMSA leads to a higher contact value for $g_{AA}(r)$ and for $g_{AB}(r)$ compared with the EMSA. This difference will lead to a change of the thermodynamic properties as well.

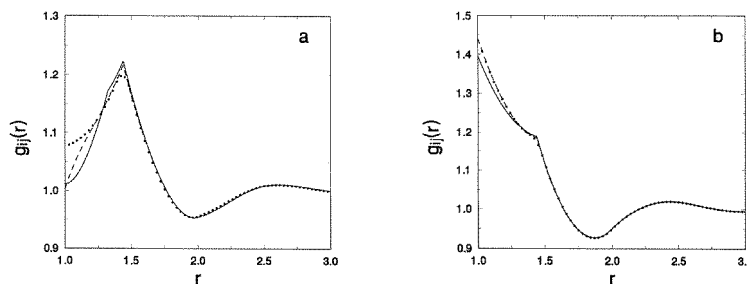


Figure 1. Pair correlation functions calculated from the EMSA $g_{AB}(r)$ (solid line) and $g_{AA}(r)$ (dashed line) and the SSEMSA $g_{AA}(r) = g_{AB}(r)$ (dotted line). The curves are obtained at $\rho = 0.57$ for the model $L_b = 0.44$, $w = 0.1$, $\varepsilon_b = 6$ (part a) and $\varepsilon_b = 1$ (part b).

Similar trends are observed for a shorter bonding length ($L_b = 0.3$), figures 3 and 4. For strong associative interactions the difference between the SSEMSA and the EMSA is large for r in the interval $(1, 1 + L_b)$. However, in contrast to the case $L_b = 0.44$, the SSEMSA curve lies between the EMSA curves for $g_{AA}(r)$ and for $g_{AB}(r)$ and therefore the average of these quantities results in the curve which is close to the SSEMSA for this bonding distance,

as discussed in [18]. It is worth noting that a decrease of the bonding length at fixed density results in a smaller difference between the contact values of $g_{AA}(r)$ and $g_{AB}(r)$ (cf. figures 1 and 3). Thus a larger overlap of the monomers A and B , leading to a diatomic AB more similar in shape to a monomer, is a favourable factor for the EMSA.

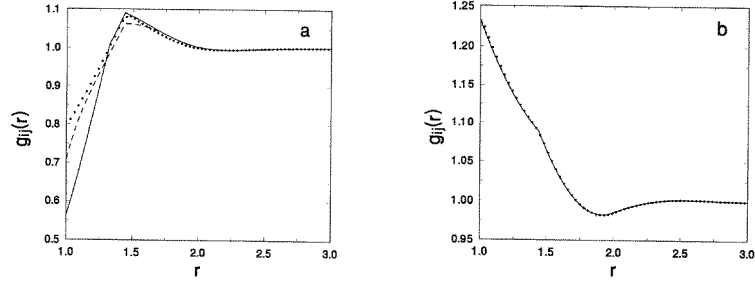


Figure 2. The same as in figure 1 at $\rho = 0.238$.

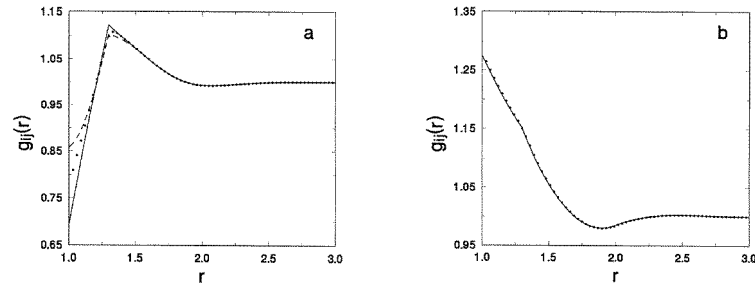


Figure 3. The same as in figure 1 at $\rho = 0.238$ and $L_b = 0.3$.

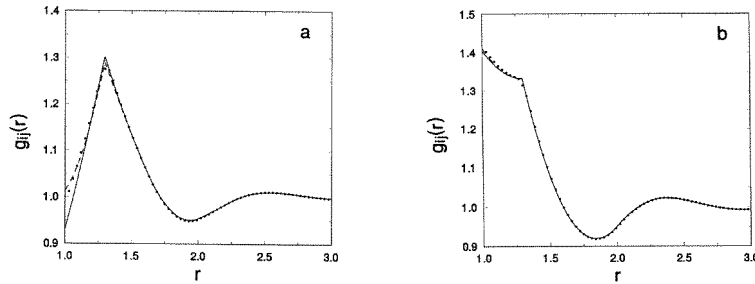


Figure 4. The same as in figure 1 at $L_b = 0.3$.

As a general conclusion, we would like to stress that a decrease of the density as well as an increase of the strength of associative interaction (which results in a higher degree of dimerization) are two unfavourable factors for the EMSA approximation whereas for high density as well as for intermediate densities and weak association the EMSA and SSEMSA results coincide. It follows then that the application of the EMSA in the study of IAFs can be successful for high densities as well as for intermediate densities with a weaker association strengths. The larger elongation of the dimer species

makes the EMSA less successful for intermediate densities. At higher densities, the EMSA can be used for all the bonding distances which lead to dimerization. The SSEMSA and EMSA have been constructed for a dimerizing fluids. In the case $L_b > 1/2$, one has to seek more sophisticated closures which include the effect of possible trimers and chain structures made of alternating A and B atoms.

4.2. Density Profiles.

The density profiles, evaluated by using the PY1/SSEMSA approximation, are presented in figures 5-12. It is worth recalling that the associative

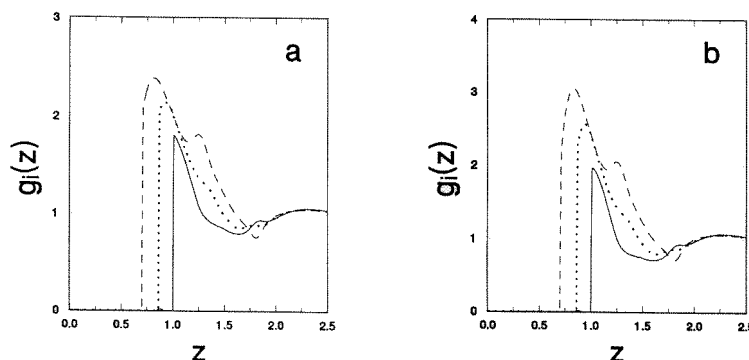


Figure 5. Density profiles $g_i(z)$ calculated from the approximation PY1/SSEMSA over the a (solid line), sp (dotted line) and s (dashed line) positions of the unit lattice cell for (100) surface. The curves are obtained at $\rho = 0.57$, for the model $L_b = 0.44$, $\varepsilon_b = 6$ and $w = 0.1$, $\varepsilon_{fs} = 0.25$ (part a) and $\varepsilon_{fs} = 0.5$ (part b).

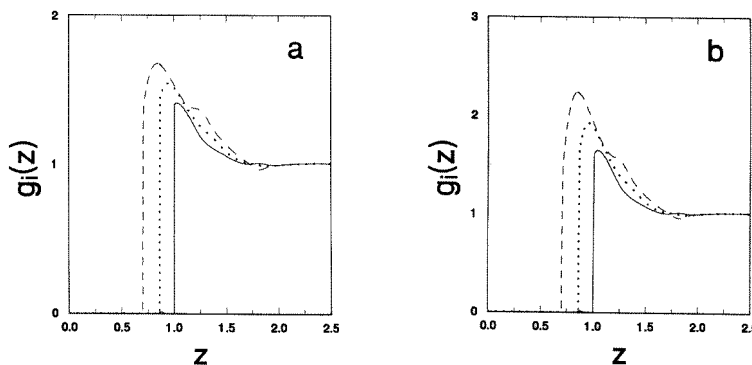


Figure 6. The same as in figure 5 at $\rho_b = 0.238$.

interactions in the bulk fluid and between the bulk fluid particles and the surface are given in the form of square wells of width $w = 0.1$. In figure 5 the DPs are for the model with $\rho = 0.57$ ($L_b = 0.44 \pm 0.05$) at a high dimerization state ($\varepsilon_b = 6.0$, $\Lambda_b = 0.938$). An absence of an associative interaction $U_{AS_a}(r)$ corresponds to the limit $\varepsilon_s \rightarrow -\infty$. Here we consider

$\varepsilon_s = -5.0$, i.e. we have a square mound in the interaction $U_{AS_a}(r)$ with a repulsive well; therefore, the adsorption is practically nonassociative. This

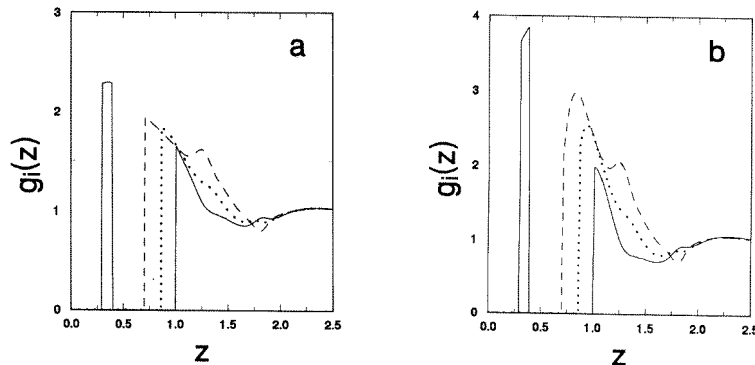


Figure 7. Density profiles $g_i(z)$ for a chemically active (100) surface ($\varepsilon_s = 1$) and $L_s = 0.34$. The curves are obtained at $\rho = 0.57$, for the model $L_b = 0.44$, $\varepsilon_b = 6$ and $w = 0.1$, $\varepsilon_{fs} = 0$ (part a) and $\varepsilon_{fs} = 0.5$ (part b). The intraparticle peak is reduced by 0.5.

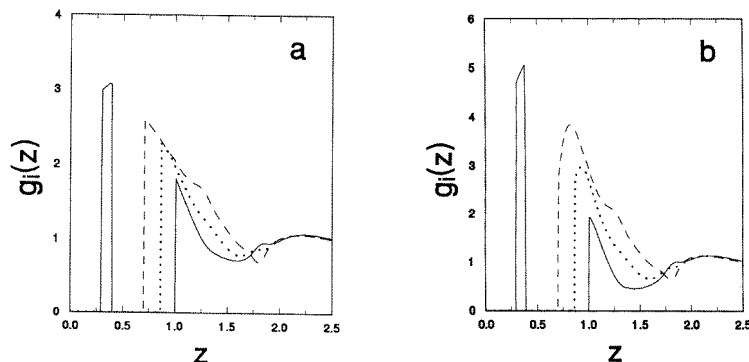


Figure 8. The same as in figure 7 at $\varepsilon_b = 1$.

case is a chemically inactive crystalline surface. The energetic heterogeneity of the crystal surface is determined by the potentials of Steele. As can be seen from figure 5a ($\varepsilon_{fs} = 0.25$), the dimer species AB are preferentially adsorbed in the s position and their orientation is mainly normal to the surface plane. Tilted orientations with respect to the normal can be also identified from the shape of the profiles. The possibility of adsorption of the dimer species over the sp and a positions is small compared to the s position but, in the case of the sp position, is still observable. Evidently, the profiles result from the monomer and dimer contributions which are not distinguishable in the approach used. However, the percentage of monomers is very small for the set of parameters considered. Another general tendency which can be observed is that the bulk fluid ordering is perturbed by the crystalline surface at distances not larger than the dimer length, i.e. only the contact layer of dimers is formed, the second layer is weakly manifested. The normal correlations decay rapidly for a highly dimerized fluid, evidently faster than for an undimerized fluid. For a stronger nonassociative fluid-solid

interaction (figure 5b, $\varepsilon_{fs} = 0.5$) the DPs behave similarly. The probability of adsorption in the s position increases. In addition, the difference of adsorbing strength over s , sp and a positions becomes more pronounced for a more energetically heterogeneous surface, as expected. In figure 6 we present DPs for an inactive surface, but for a lower density ($\rho = 0.238$). In this case the degree of dimerization is lower ($\varepsilon_b = 6.0$, $\Lambda_b = 0.813$). In general, we observe that the DPs behave similarly to the case of higher density (figure 5). However, the role of the packing effects is weaker at a lower density and there is no manifestation of the second adlayer, because correlations in normal direction decay even faster. The dimer species prefer to adsorb over the s position; a lower packing of the contact adlayer results in a higher orientational flexibility of the dimer species.

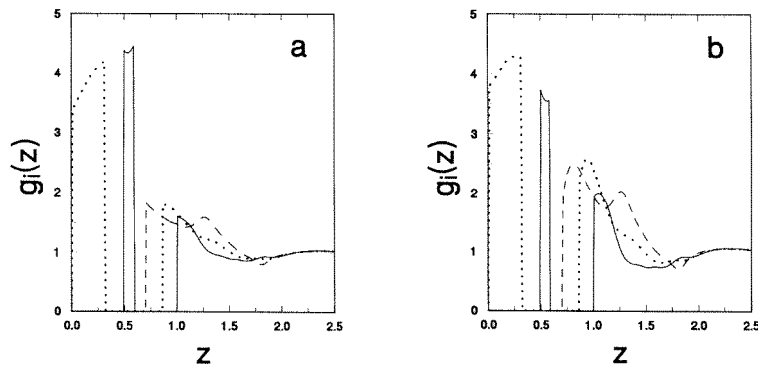


Figure 9. The same as in figure 7 at $L_s = 0.54$. The intraparticle peak over the sp position is reduced by $\frac{1}{3}$ (part a) and by 0.2 (part b). The intra peak over the a position is reduced by 0.5 in part b.

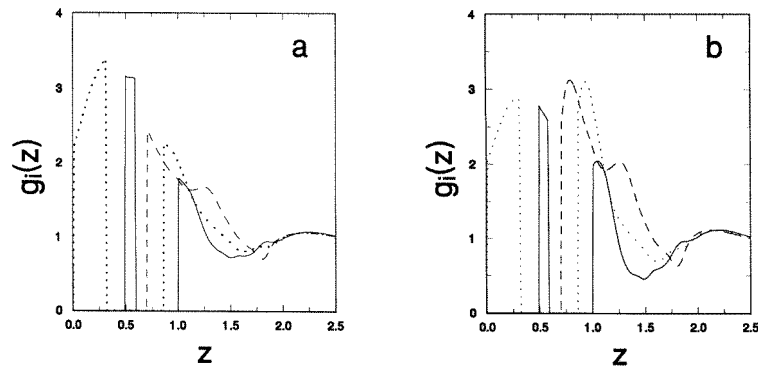


Figure 10. The same as in figure 7 at $L_s = 0.54$ and $\varepsilon_b = 1$. The intraparticle peak over the sp position is reduced by 0.2 (part a) and by 0.1 (part b). The intra peak over the a position is reduced by 0.5 (part a) and 0.25 (in part b).

In the following figures we consider the case of a chemically active crystalline surface ($\varepsilon_s = 1.0$). Consider first a highly dimerized fluid ($\rho = 0.57$,

$\varepsilon_b = 6.0$, $\Lambda_b = 0.938$). Now, the value of the bonding length L_s becomes important. We choose $L_s = 0.34 \pm 0.05$ in order to prevent the overlap of two square wells. The strength of the nonassociative interaction between the fluid and solid is varied (figure 7). In the absence of a nonassociative interaction ($\varepsilon_{fs} \approx 0$, figure 7a) we observe associative adsorption. There is

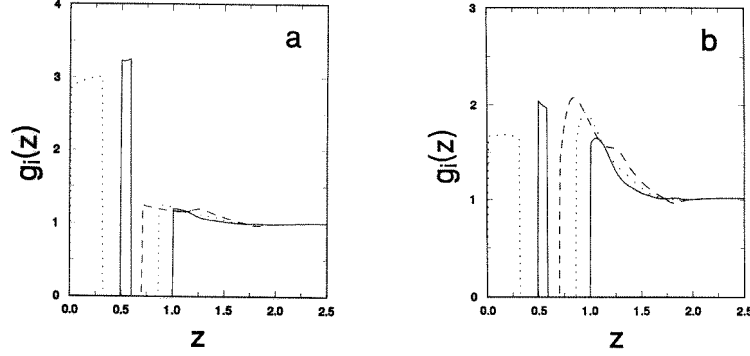


Figure 11. The same as in figure 7 at $L_s = 0.54$ and $\rho = 0.238$. The intraparticle peak over the sp position is reduced by $\frac{1}{3}$ (part a) and by 0.1 (part b). The intra peak over the a position is reduced by 0.5 in part b.

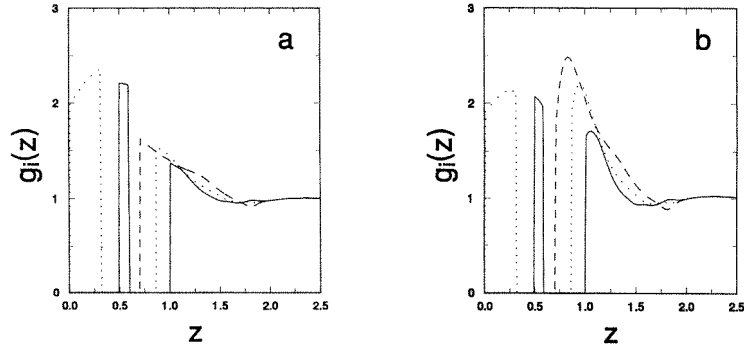


Figure 12. The same as in figure 7 at $L_s = 0.54$, $\varepsilon_b = 1$ and $\rho = 0.238$. The intraparticle peak over the sp position is reduced by 0.2 (part a) and by 0.1 (part b). The intra peak over the a position is reduced by 0.5 (part a) and 0.25 (part b).

an intraparticle peak over a position at $z = L_s$ which describes bonding of A particles with surface atoms. The particles B do not react with the surface and therefore this peak corresponds to a surface complex AS_a . The geometry of interactions permits nonassociative adsorption of dimers over the s position and, with lower probability, over other characteristic points of the unit cell. It is important to mention that formation of surface complexes weakens the nonassociative adsorption of dimers and monomers over the unit cell. The interparticle peaks become lower, compared with the results in figure 5a. The small range of the bulk fluid - solid correlations in the normal direction indicates the small number of surface complexes. In gen-

eral, one would expect that the formation of surface complexes would make the coated surface more structurally heterogeneous. This is not the case for $\varepsilon_{fs} = 1.0$, figure 7a, however. The positions of the maxima of the DP over sp position are observed at the same values of z . The profiles of A and B particles are equal except for the intraparticle peak [therefore we show the $g_A(z)$ only]. Indeed, in all cases we show only the $g_A(z)$ profile if the interparticle terms of the DPs are equal. The nonassociative interactions influence the occupancy of the intraparticle position as well as nonassociative adsorption. The number of surface complexes increases, but not substantially. The most important conclusion which follows from figure 8 is that there is a tendency for the formation of the second adlayer in a weakly dimerized fluid ($\rho = 0.57$, $\varepsilon_b = 1.0$, $\Lambda_b = 0.517$) and the difference of the adsorbing strength over the s , sp and a is more pronounced, especially for a higher value of ε_{fs} , ($\varepsilon_{fs} = 0.5$). As expected, nonassociative and associative interactions when combined result in a stronger energetic heterogeneity than does a solely associative interaction.

Consider now a larger value of the bonding distance L_s , namely $L_s = 0.54 \pm 0.05$ (figures 9 and 10). In both of these figures we study a chemically active surface, a highly dimerized fluid ($\rho = 0.57$, $\varepsilon_b = 6.0$, $\Lambda_b = 0.938$) in figure 9 and a weakly dimerized fluid ($\rho = 0.57$, $\varepsilon_b = 1.0$, $\Lambda_b = 0.517$) in figure 10. It can be seen from the shape of the profiles that this choice of the associative interaction between the bulk fluid and solid surface leads to a formation of the surface complexes of two types, namely over the a and sp positions. For both positions, the geometry of the associative interactions permits the participation of dimers in the surface complexes; therefore, the intraparticle peaks contain contributions from monomers and dimers associatively adsorbed. The adsorption at the a position results from the formation of AS_a and $BA - S_a$ complexes; the latter has been described as the on-top dimer adsorption in the localized site adsorption literature. Certainly, the orientation of dimers in this position is not rigid; they can be normal and tilted. However, the surface complexes over the sp position are more probable. They are of the type: $A - 2S_a$ and $BA - 2S_a$, i.e. the A particle is in the bridging position over the sp point of the unit lattice cell. Preferential delocalized adsorption of dimers is observed over the s position, as noted previously. Strong associative fluid-solid interactions are required to give a large number of surface complexes. For $\varepsilon_s = 1.0$ these interactions are small and the profiles for A and B particles are almost identical, except for the intraparticle peaks. However, because we use the PY1 approximation, we do not increase the strength of this association in this study. Nonassociative interactions, as expected, can change the occupancy of the intraparticle positions and can change the interparticle contributions of the profiles. However, they do not change the qualitative features of the DPs. At lower densities one observes similar trends (figures 11 and 12). A higher dimerization in the bulk fluid results in weaker adsorption on the crystalline surface. Due to the smaller density, multilayer structure is not formed. A much more complicated structure of the adlayer would result if the bonding distance parameter L_s is close to the diameter of the surface atoms. A four-fold hollow site adsorption arises which is characterized by the surface complexes involving four surface atoms and either A monomers or AB dimers. We postpone a more detailed study of this phenomena for future work where more sophisticated closures will be employed as well.

5. Conclusions

We have investigated the adsorption of a dimerizing fluid on the (100) crystalline surface. The bulk model describes heterogeneous chemical association $A + B \rightleftharpoons AB$, in which monomers overlap. The particles A react with the surface atoms S_a . The model is studied in the framework of the PY1/SSEMSA approximation. The nonassociative fluid-solid interactions are taken in the form proposed by Steele. It is shown that an increasing degree of dimerization of the bulk fluid leads to weaker adsorption. Associatively adsorbed monomers and dimers form complexes with the surface atoms. On-top adsorption and two-fold bridging site adsorption are studied. Associatively and nonassociatively adsorbed dimers prefer to align along the normal to the surface plane. Tilted configurations are also possible. The nonassociative interactions influence the occupancy of the intraparticle positions and the nonassociative adsorption. The method chosen in this study is simple and most straightforward. A more sophisticated procedure could be developed for the treatment of the associative fluid-solid interactions to study the surface chemical reactions. However, this would require separate studies and computer simulation data.

6. Acknowledgements

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АДСОРБЦІЯ ГЕТЕРОГЕННО АСОЦІАТИВНОЇ РІДИНИ НА fcc 100 КРИСТАЛІЧНІЙ ПОВЕРХНІ

Д.Хендерсон, О.Пізіо, С.Соколовський, А.Трохимчук

Модель гетерогенно димеризованої рідини ($A + B \rightleftharpoons AB$) поблизу fcc (100) кристалічної поверхні досліджується методом інтегральних рівнянь. Для отримання профілів густини використовуються розширене вузол-вузол середньосферичне наближення та однорівневі інтегральні рівняння. Досліджується їхня залежність від степені димеризації об'єму рідини, зв'язаної відстані димерних частинок і сили неасоціативних взаємодій рідина-розчин. Геометричні та енергетичні аспекти адсорбції на (100) поверхні досліджуються з використанням моделі реактивних кристалічних вузлів. Також досліджується однократно зв'язана, двократно зв'язана (мостикова) та чотирикратно зв'язана позиції для локалізованої адсорбції.