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Model for an associating fluid near an associatively adsorbing crystalline surface

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A model for the adsorption of an associating fluid on an associatively adsorbing crystalline surface is proposed. An interplay between association in the bulk fluid and formation of complexes with the surface crystal sites is reflected by the structure of the adlayer. The adlayer consists of surface complexes, adsorbed monomers, and differently oriented dimers. Geometry of the interactions given by the bonding lengths is of crucial importance for the adlayer composition, which also depends on the degree of dimerization of the bulk fluid. The model is studied numerically by using singlet level integral equations for the density profiles.

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Several important problems, such as adsorption at interfaces, chemisorption, and intramicellar chemistry, require models which include the effects of chemical association of the particles in the bulk fluid, as well as at the phase boundary. In particular, understanding the behavior of associating fluids (AF's) near solid substrates is crucial for the theory of heterogeneous catalysis [1].

To date, the theory of association has been developed mostly to study bulk fluids. The methods of Stell and coworkers [2,3] and Wertheim [4] have been commonly used, and have been applied recently to inhomogeneous AF's [5–7]. These applications have been restricted to models without associative interactions between the bulk fluid and the surface. Inclusion of the surface reactivity is important for the development of the theory of inhomogeneous AF's.

In this paper we present a model of AF near associatively adsorbing crystalline surface. The most essential features of the model are the following: (i) The bulk fluid consists of spherical particles of two components A and B, of equal diameters $\sigma_A=\sigma_B=\sigma_f$, at equimolar conditions $\rho_A=\rho_B=\rho/2$. This is the model proposed by Stell and Cummings [2] for heterogeneous association. (ii) The monomers A can bond with associatively adsorbing spherical atoms S_a of the diameter σ_S, located in the "basic" plane of the solid. The "basic" plane is a hard wall prohibiting penetration of the bulk fluid particles inside the solid. The location of the sites S_a corresponds to the 100 plane of the fcc lattice. For simplicity, we restrict ourselves here to the case of $\sigma_S=\sigma_f=\sigma=1$. The potential energy of the system is chosen in the form

$$U_{\text{pot}}=\sum_{m,n=A,B}\sum_{i<j}u_{mn}(r_{ij})+\sum_{m=A,B}\sum_{i}\left[u_m^{(1)}(z_i)+\sum_{\{S_a\}}u_m^{(2)}(\mathbf{r}_i-\mathbf{r}_S)\right], \tag{1}$$

where the first and second terms correspond to the fluid-fluid and fluid-solid energy, respectively, and $\{S_a\}$ denotes the set of surface atoms. Each of the contributions is defined by the corresponding Mayer function

$$\begin{aligned}
f_{mn}(r)&=\exp\{-\beta u_{mn}(r)\}-1\ ,\\
f_m^{(k)}(r)&=\exp\{-\beta u_m^{(k)}(r)\}-1\quad(k=1\text{ and }2)\ ,\\
f_{mn}(r)&=-\theta(r-1)(\delta_{mA}\delta_{nA}+\delta_{mB}\delta_{nB})\\
&\quad+(\delta_{mA}\delta_{nB}+\delta_{mB}\delta_{nA})\{-\theta[L_b-(w/2)-r]+(e^{\beta\varepsilon_b}-1)\theta[L_b+(w/2)-r]\theta[r-L_b+(w/2)]\\
&\qquad-\theta(1-r)\theta[r-L_b-(w/2)]\}\ ,\\
f_m^{(1)}(z)&=\theta(z-1)\ ,\\
f_m^{(2)}(r)&=\delta_{mA}\{-\theta[L_s-(w/2)-r]+(e^{\beta\varepsilon_s}-1)\theta[L_s+(w/2)-r]\theta[r-L_s+(w/2)]\\
&\qquad-\theta(1-r)\theta[r-L_s-(w/2)]\}+\delta_{mB}\theta(1-r)\ .
\end{aligned}\tag{2}$$

Here $\theta(x)$ is the step function, $r=|\mathbf{r}|$, z is the distance from the basic plane, L_b and L_s are the bonding distances, w is the width of the attractive square wells, and ε_b and ε_s are their depths.

The associative potential $u_m^{(2)}(\mathbf{r}_i)=\sum_{\{S_\alpha\}}u_m^{(2)}(\mathbf{r}_i-\mathbf{r}_S)$ is a periodic function, i.e., $u_m^{(2)}(\mathbf{r})=u_m^{(2)}(\mathbf{r}+\boldsymbol{l})$, where $\boldsymbol{l}=l_1\mathbf{a}_1+l_2\mathbf{a}_2$, and $\mathbf{a}_1$ and $\mathbf{a}_2$ are two-dimensional unit vectors of the (100) lattice. The geometry of associative interactions is determined by the bonding distances. If $L_b < \frac{1}{2}$ only AB dimers can be formed. Orientation of dimer AB over different positions of the unit lattice cell depends on the bonding lengths L_b and L_s, and on the type of the crystalline symmetry of the lattice. For $L_s < \frac{1}{2}$ any surface atom can bond only one fluid particle A. For some selected values of L_s, different surface complexes can be formed. In particular, particle A can be located in the bridging position between two surface atoms (AS_2) which are situated at the edges of the unit cell. Atom A can also be in the bridging position, binding four surface atoms (AS_4).

An analytical solution of the bulk AF model defined above can be obtained in the sticky limit of Baxter [8] by using the Percus-Yevick (PY), extended mean spherical approximation (EMSA) or associative PY (APY) approximations [2,4,9]. Numerical solution of the bulk Ornstein-Zernike equation, however, is more straightforward because it does not require application of the sticky limit and permits us to use other closure relations. Moreover, in the case of even a simplified treatment of inhomogeneity, the importance of obtaining an analytical solution for the bulk model is not essential because it is necessary to solve numerically integral equations for the density profiles (DP's). Thus we consider the original form of the interaction potentials which contain square wells to provide association. The simplest routine to determine DP's in the application to the singlet Percus-Yevick approximation (PY1) [10], which reads

$$y_m(\mathbf{r}_i) = 1 + \sum_{n=A,B} \rho_n \int d\mathbf{r}_j c_{mn}(|\mathbf{r}_i - \mathbf{r}_j|)[g_n(\mathbf{r}_j) - 1] , \tag{3}$$

where $g_m(\mathbf{r}) = \rho_m(\mathbf{r})/\rho_m$ is the normalized DP, and $y_m(\mathbf{r})$ is the one-particle cavity function. The functions $c_{mn}(r)$ are the direct correlation functions of the bulk fluid; they are evaluated from the numerical solution of the bulk EMSA [10]. It follows from a comparison with the computer simulation data and Wertheim's approach that the EMSA is a successful theory of the bulk associating fluid at high densities. Therefore we consider a dense associating fluid, and use the Ballance-Speedy equation to determine the degree of association Λ_b necessary as an input for the bulk EMSA equation (see [9] for a detailed discussion).

Peculiarities of the solution of Eq. (3) result from the lattice symmetry. Here, following Steele [11], we use the two-dimensional Fourier representation of the one-particle function

$$\varphi(\mathbf{r}) = \sum_{l \geq 0} \varphi_l(z) f_l(x,y) , \tag{4}$$

where the functions $f_l(x,y)$ describe the periodicity of the crystal surface plane and are given in Ref. [7]. Expansion (4) is used for the potential $u_m^{(2)}(\mathbf{r})$; we have verified that the inclusion of the first nine terms in the expansion of $y_m(\mathbf{r})$ is sufficient to provide its accurate representation. The DP's calculated from Eq. (3), corresponding to EMSA-PY1 closure, are shown in Figs. 1–3. Three characteristic positions over the unit cell are distinguished; the atom a (it corresponds to the S_a position), the saddle point sp, and the nonassociative adsorption site s [see the inset in Fig. 1(a)]. Keeping the standard abbreviations [11], in terms of the lattice vectors these positions are (0,0), (0,0.5), and (0.5,0.5), respectively. The DP's have been calculated for two models: $L_s = 0.375$ and $L_s = 0.875$. The remaining parameters have been fixed and are $L_b = 0.475$, $w = 0.05$, and $\beta\varepsilon_s = 1.0$. The bulk fluid density is $\rho = 0.668$, and two values of the de-

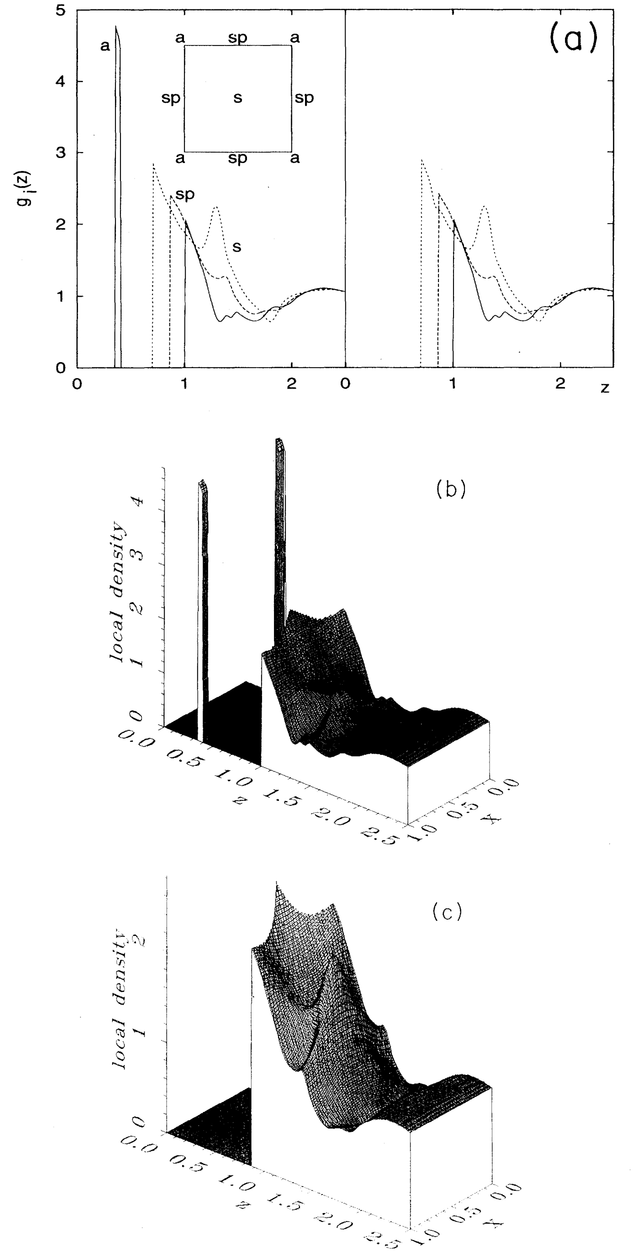

FIG. 1. Density profiles $g_A(z)$ and $g_B(z)$ for $L_s = 0.375$ and $\beta\varepsilon_b = 3.0$ [left and right panels in (a), respectively]. Density profile $g_A(z,x)$ for $y=0$ (b) and for $y=0.5$ (c). The "intraparticle" peak is multiplied by 0.5.

gree of association have been studied: $\Lambda_b = 0.559$ ($\beta\varepsilon_b = 1.0$) and $\Lambda_b = 0.784$ ($\beta\varepsilon_b = 3.0$), where

$$\Lambda_b = 4\pi\rho_A \int_{L_b-0.5w}^{L_b+0.5w} dr\, r^2 g_{AB}(r) \; . \qquad (5)$$

In the figure caption we also give the value of the parameter Λ_s, characterizing the formation of the surface complexes, which is defined as follows:

$$\Lambda_s = \frac{\rho_A}{a_s} \int_{L_s-0.5w}^{L_s+0.5w} d\mathbf{r}\, g_A(r) \; , \qquad (6)$$

where a_s is the area of the unit cell.

Let us now discuss the most interesting features of the DP's presented in Figs. 1–3. Before discussing details of the DP's it is necessary to emphasize that the bonding of the bulk fluid particles A with the surfce atoms S_a leads to the "intraparticle" peaks of the $g_A(z)$. For $L_s = 0.375$ only one peak over position a appears [Fig. 1(a)], whereas for $L_s = 0.875$ three "intraparticle" peaks are present on $g_A(z)$ [Fig. 2(a)]. In this case the most inner peak at $z \approx 0.5$ reflects AS_4 bonding. The peak over the sp position corresponds to the AS_2 bridging complex of A particle. The outer peak (over the a position) is due to AS bonding. The values of the bonding distances L_b and L_s define the type of associates in the bulk and fluid-surface complexes, whereas the fluid density and energetic characteristics of the wells ε_b and ε_s determine the number of species which can be formed. The lattice symmetry of the surface also influences the type of possible surfacec complexes; for example, in the case of a graphite

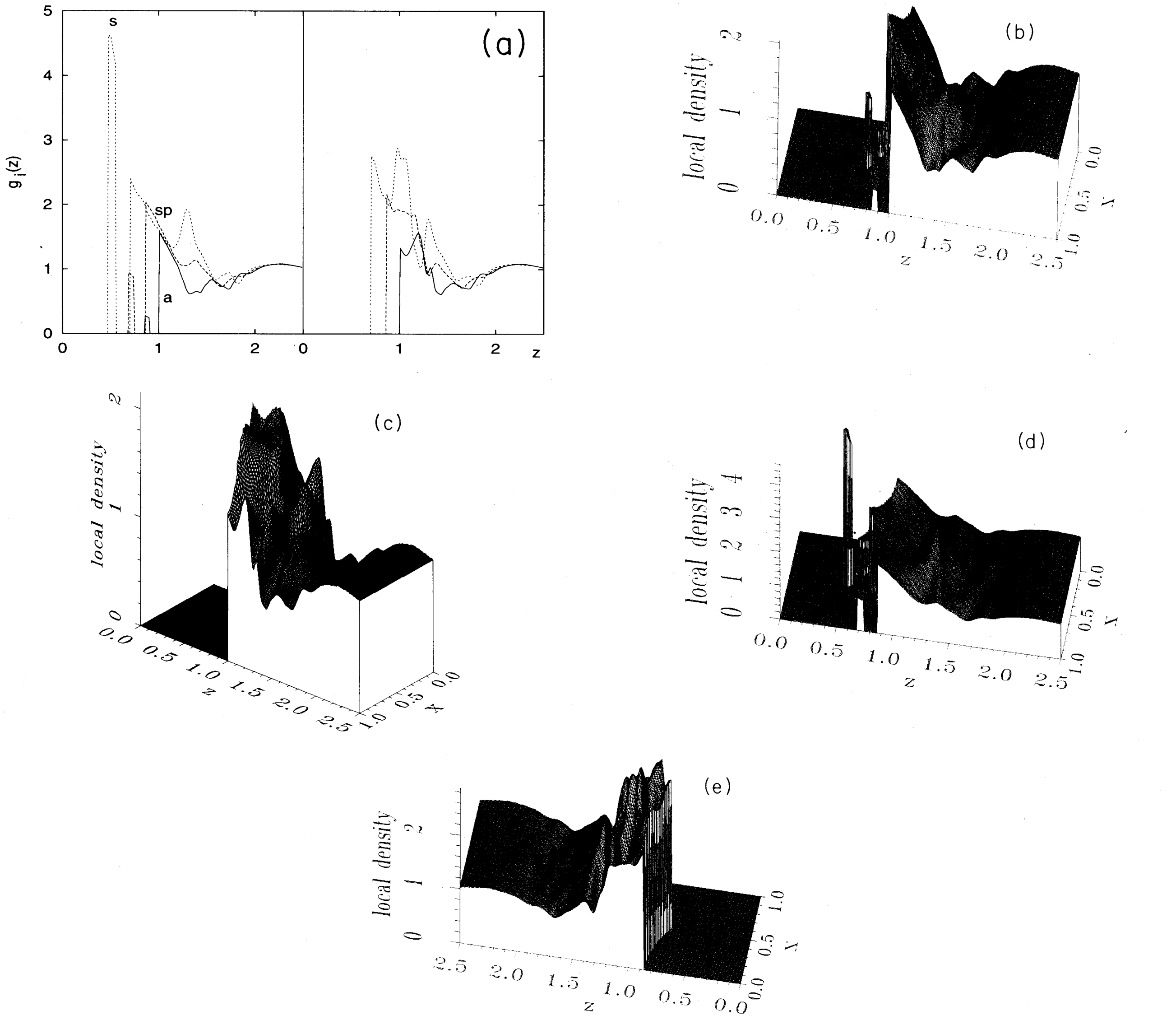

FIG. 2. Density profiles $g_A(z)$ and $g_B(z)$ for $L_s = 0.875$ and $\beta\varepsilon_b = 3.0$ [left and right panels in (a) respectively]. Density profiles $g_A(z,x)$ and $g_B(z,x)$ for $y = 0$ [(b) and (c), respectively] and for $y = 0.5$ [(d) and (e), respectively]. The intraparticle peaks are multiplied by 0.05 for a and sp positions and by 0.025 for s position.

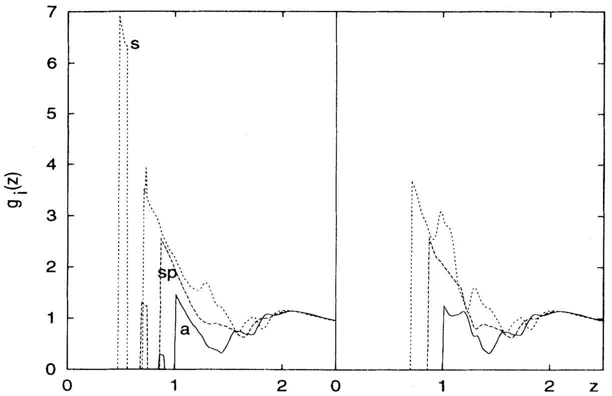

FIG. 3. Density profiles $g_A(z)$ and $g_B(z)$ for $L_s=0.875$ and $\beta\varepsilon_b=1.0$ (left and right panels, respectively). The "intraparticle" peaks are multiplied by 0.05 for *a* and sp positions and by 0.025 for the *s* position.

basal plane AS_3 complexes could be formed. For better visualization of the "intraparticle" peaks one can examine the three-dimensional (3D) plots of the DP's which represent cuts at a given value of y—see Figs. 1(b), 1(c) and 2(b)–2(e).

Let us proceed and discuss the interparticle shape of the DP's. It results from the structure of the bulk AF and the influence of the crystalline lattice. The latter effect is important only in the vicinity of the surface for the model in hand. For $L_s=0.375$ [Fig. 1(a)] the formation of only *AS* complexes weakly perturb the interparticle part of the DP's; the shapes of $\rho_A(z)$ and $\rho_B(z)$ are almost identical, excluding the intraparticle peak for *A* particles. Therefore we present the 3D plots only for the *A* component in this case. The second reason for the great similarity of the "interparticle" parts of the DP's of both species in this case is the following. For this value of the bonding distance L_s, the dimer *AB* cannot adsorb associatively at *a* position. The bulk fluid is highly dimerized, $\Lambda_b=0.784$, and therefore a small amount of free *A* monomers is bounded with the surface atoms. In this case $\Lambda_s=8.68\times10^{-3}$. One can expect that for decreasing dimerization of the bulk fluid the number of *AS* complexes will increase, and result in the increasing difference between the DP's of *A* and *B* species. For $L_s=0.875$ the interparticle structure of the DP's is strongly affected by the presence of surface complexes of three types, and the DP's of both species differ significantly (Figs. 2 and 3). The number of species bonded with the surface sites is much larger in this case, namely $\Lambda_s=0.199$, when $\Lambda_b=0.784$ (see Fig. 2), and $\Lambda_s=0.217$ when $\Lambda_b=0.559$ (see Fig. 3). The numbers given above demonstrate a competition between the bulk and surface associations; from a comparison of the heights of the intraparticle peaks in Figs. 2 and 3 it also follows that the higher degree of dimerization of the bulk fluid leads to a lower degree of formation of surface complexes.

Our treatment based on the EMSA-PY1 approximation does not distinguish between the bonded and nonbonded states of the bulk species. However, from the results presented, it is possible to conclude that the adlayer consists of free monomers *A* and *B*, adsorbed dimers *AB*, and surface complexes which consist of S_a and either free *A* species or dimers *AB*. It is not easy to interpret straightforwardly the detailed composition of the adlayer from the one-dimensional DP's only, especially for the bonding distance $L_s=0.875$.

For $I_s=0.375$ it follows from a comparison of $\rho_A(z)$ and $\rho_B(z)$ [Fig. 1(a)] and 3D plots [Figs. 2(b) and 2(c)] that the dimers *AB* are prefcrably nonassociatively adsorbed at *s*, or with lower probability at sp positions, whereas at the *a* position the formation of an *AS* complex is more probable. The dimers adsorbed at the *s* position are either oriented normally to the surface or nearly parallel to the surface with their axes in the *s*-sp direction [Fig. 1(c)]. If the dimerized particle is adsorbed at the sp position, then the dimers align either normal to the surface or along the sp-*a* direction [Fig. 1(b)].

For $L_s=0.875$ the adlayer structure is more difficult to interpret, in particular because associatively adsorbed dimers are permitted. It can be seen from the DP's presented in Fig. 2(a), and a comparison of Figs. 2(d) and 2(e), that the associativley adsorbed dimer at the *s* position is most probably oriented normal to the wall; however, tilted configurations are also possible. There also exists a probability of a nonassociatively adsorbed dimer normal to the surface at the *s* position [Fig. 2(a)]. Due to the relatively large value of the bonding distance L_s, and the high probability of a complex AS_4 formation, dimers parallel to the surface can be also found. A decrease of the degree of association in the bulk fluid leads to an increase of association of the fluid particles with the surface (cf. Figs. 2 and 3); however, the associatively adsorbed dimers are still present, as follows from the DP's in Fig. 3. It is evident that a more detailed description of the adlayer structure can be obtained from a knowledge of the DP's and pair correlation functions of the nonuniform AF's. However, application of the pair level theory to our model would require very serious numerical efforts.

Let us now make some concluding remarks. It follows that, dependent on the crystal lattice symmetry and the geometry of associative interactions defined by the bonding lengths L_b and L_s the model permits either nonassociative or associative adsorption of dimeric species (if $L_b<0.5$), in addition to the nonassociative or associative adsorption of monomers. In the case of associative adsorption, surface complexes, which consist of the atoms of the solid substrate and the bulk fluid particles, can be formed. Bonding between fluid and surface atoms can involve different numbers of surface atoms (in the case under study, either one or two or four). Degrees of both associations are determined by the density of the bulk fluid and energetic characteristics of the associative interactions. We have not intended to generate a specific orientation of adsorbed dimeric species. However, it is worth noting that this can be gained by a specific choice of bonding distances, variation of the size ratio of solid and fluid particles, and exposure of the surface atoms with respect to the basic plane of the solid. Then, under particular conditions, one- or two-dimensional ordering within the adsorbate layer may appear. Interesting modifications of the adlayer structure should be expected if only a particular set of surface atoms is able to associate with the particles of the bulk fluid.

Inclusion of a nonassociative solid-fluid periodic potential may change the occupancy of the positions which provide the formation of the surface complexes. Modification of the bulk Hamiltonian can also influence the structural properties, as well as the phase behavior of the model. This communication provides a preliminary insight into the model and its possibilities. Generalization of the theoretical procedure could be provided by the application of Wertheim's theory for the bulk and the fluid-surface associations. We plan to investigate some of these issues in future publications.

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