

RESEARCH NOTE

Voids in the Coverage of Surfaces by Adsorbed Molecules

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The adsorption of complex molecules on a solid surface may result in less than full coverage, even at zero temperature, due to molecular adsorption frozen in disorder. For molecules occupying more than one adsorption site, voids are formed in the layer of adsorbed molecules. This raises a question about the degree of coverage of the solid surface by the adsorbed molecules. Monte Carlo computer simulations for different molecule shapes on a binary AB crystal were done to determine the void concentration. The fraction of "uncovered surface area," β_s , and the fraction of the "excess uncovered surface," β_m , are defined and determined. β_s is found to be between 0.093 and 0.577 and β_m is in the range of 0.093 and 0.155. These values depend on the molecular size and shape. For a different surface, that of AB_2 compound, β_m is found to be smaller.

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INTRODUCTION

Knowing the surface coverage is important for electrode reaction (1), catalysis (2), discussion of conduction in the adsorbed layer (3), or diffusion (4, 5). The concentration of adsorbed species is calculated usually under equilibrium conditions using the Langmuir (6) or BET (6) equation, assuming the adsorbed species to be noninteracting. Calculations of the diffusion coefficient in the adsorbed layer take repulsive and attractive interaction between the adsorbed species into consideration (4, 5). Interaction can be neglected for a dilute concentration of adsorbed species and in the opposite extreme case for the motion of a dilute void concentration. A complication arises when the species adsorbed is a molecule and the surface contains (at least) two different types of atoms A and B so that the orientation of the adsorbed molecules follows the relative position of the surface atoms A and B .

One would expect that the structure of molecules may have an effect on the extent of coverage in an adsorp-

tion process at low temperature under rapid cooling. To examine the extent of voids that should exist in the coverage, we consider the simple situation of noninteracting and nonoverlapping molecules, adsorbed on a crystalline surface at low T , so that diffusion on the surface can be neglected. Furthermore, if the molecule disintegrates and each part forms new bonds with the surface, it is assumed that their position does not change due to the low temperature. Under these conditions the molecules are randomly distributed and frozen in the position that they hit the surface. One expects that the void concentration will increase with the size and complexity of the adsorbed molecules. We notice that the conditions of no overlap and no interaction otherwise is equivalent to a strong, steep repulsion.

The analysis is a numerical one. We simulate the problem of covering a crystalline surface with molecules by the problem of a structured area covered by certain structured objects. The objects are randomly distributed. One type of object is used for each computer experiment. The structured area, denoted as a "surface," to be discussed first, is a square, composed of $m \times m$ square elements, denoted as "sites", of two types, similar to a chessboard. The two types of "sites" simulate two types of atoms or ions on a surface of similar symmetry in binary AB materials. In this work we limit the size of the objects simulating the adsorbed molecules, to two or three segments covering two or three sites representatively (see Fig. 1). We denote the part of the molecule adsorbed on a single site as a "segment". As mentioned before the segments cannot diffuse on the surface at low temperatures. A segment can be a single atom or a group of atoms, e.g., the OH^- group. Due to disorder, the coverage is not full and voids exist. When the object considered is a small bar, as shown in Fig. 1a, which covers two adjacent square sites of the area, the problem is similar to that of covering a chessboard with domino bars. Each bar covers two squares, one black and one white with a black segment covering a black site and a white segment a neighboring white site. It is possible to cover in an ordered manner an 8×8 chessboard with 32 domino bars and no voids. This number is, however, lower when the bars are

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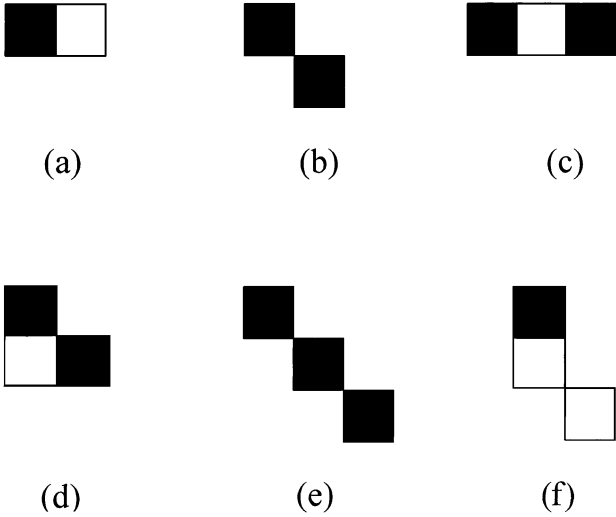


FIG. 1. Figures of size two and size three. (a) Short bar; (b) short diagonal; (c) long bar; (d) "L" shape; (e) long diagonal; (f) "horse movement."

placed randomly on the board. Under disorder each bar still covers exactly one black and one nearest white site. The purpose of this paper is to find the concentration of voids, for different small object shapes, for the $m \times m$ board and then for a more complex board that simulates the surface of cubic stabilized ZrO_2 and objects that simulate water molecules.

Care should be taken when the void concentration is defined. We define the uncovered surface coefficient β_s ,

$$\beta_s = \frac{k}{m \times m}, \quad [1]$$

where k is the number of empty squares (voids) and $m \times m$ is the total number of square elements in the more general $m \times m$ chessboard. Thus, β_s counts all uncovered elements and gives the fraction of the uncovered area. However, for most objects the board cannot be completely covered, even under complete order, i.e., $\beta_s > 0$. This can happen, for instance, with the diagonal black object in Fig. 1b and for all four objects in Fig. 1c–1f with size three. We therefore define also the excess uncovered surface coefficient β_m , the fraction of elements that were not covered though they would be covered if the objects were orderly placed on the surface. β_m is thus

$$\beta_m = \frac{k - \alpha \cdot m \times m}{m \times m - \alpha \cdot m \times m}, \quad [2]$$

where α ($0 \leq \alpha \leq 1$) is the fraction of the sites in the $m \times m$ board, which should not be covered anyway by that object in an ordered layer. As an example we consider the objects of Fig. 1e. If they fully cover all black elements, all white ones stay uncovered and $\alpha = \frac{1}{2}$. The relation between β_m

and β_s is

$$\beta_m = \frac{\beta_s - \alpha}{1 - \alpha}. \quad [3]$$

$(1 - \beta_m)$ can be identified as θ , the fraction of coverage.

COMPUTER SIMULATION FOR THE BINARY SITE $m \times m$ BOARD AND RESULTS

The values of m we examine are 50 and 100. Periodic conditions are assumed. All six patterns of the objects shown in Fig. 1 are examined. The computer places one type of object randomly on the surface. Steady state, i.e., maximum coverage (but not necessarily full coverage), is reached when the computer fails to place another object in more than a certain number of trials, predetermined by the user, in between 10^3 and 10^6 . The program then calculates the average number of voids, from which β_s is determined using Eq. [1]. β_m is calculated from β_s using Eq. [3]. The program also sorts the clusters of voids by length and counts the number of cluster of each length.

The results of the computerized simulation are summarized in Table 1. For example, for objects in the shape of a short diagonal (Fig. 1b) that is adsorbed on a 100×100 board, the excess uncovered surface coefficient β_m is 0.094 and the uncovered surface coefficient β_s is 0.547. For small objects, of two or three elements, the values of β_m are in the range $0.093 < \beta_m < 0.155$ and for β_s they are $0.093 < \beta_s < 0.577$. Both void coefficients do not change much with m (for $m = 50$ and 100) and when trying to place the object more than m^2 times. It should be noticed that α was calculated in the limit of large m (or periodic boundary conditions) so that boundary effects on α are negligible.

Figure 2 shows the result of one run of random covering of a 100×100 board by "long bar" objects of Fig. 1c until steady state has been reached. Figure 3 shows statistics of void cluster size (x) for this case averaged over 100 runs. The size distribution is defined and calculated as follows: (1) for each diagonal the statistics of the one-dimensional void clusters on the diagonal line is made; (2) the result is added to that obtained for all other parallel diagonals; (3) the same statistics are done on the diagonals perpendicular to the previous one; (4) the result is added to the former results; (5) an average of over a hundred runs is made. The end result is termed "one-dimensional cluster size distribution" $n(x)$. The void clusters are composed of white and black sites. Obviously, since $\alpha_{ad} = \frac{1}{4}$ the main contribution to the voids comes from white sites. The average cluster size is

$$\langle x \rangle = \frac{\sum_x x \cdot n(x)}{\sum_x n(x)}. \quad [4]$$

$\langle x \rangle = 1.636$. The number $n(x)$ of clusters of size x is fitted by

$$n(x) \approx A \cdot m^2 \cdot e^{-\frac{x}{\langle x \rangle}}, \quad [5]$$

TABLE 1

The Uncovered Surface Coefficient β_s and the Excess Uncovered Surface Coefficient β_m for $m \times m$ Boards with $m = 50$ and $m = 100$, Different Covering Objects, and Different Number of Experiments

Object shape in Fig. 1	Fig. 1	α_{∞}^a	$m = 50^b$ Number of trials				$m = 100^c$ Number of trials				
			10^3	10^4	10^5	10^6	10^3	10^4	10^5	10^6	
Short bar	(a)	0	β_s	0.11	0.094	0.094	0.093	0.119	0.095	0.093	0.093
			β_m	0.11	0.094	0.094	0.093	0.119	0.095	0.093	0.093
Short diagonal	(b)	$\frac{1}{2}$	β_s	0.550	0.547	0.546	0.546	0.552	0.547	0.547	0.547
			β_m	0.10	0.094	0.092	0.092	0.104	0.094	0.094	0.094
Long bar	(c)	$\frac{1}{4}$	β_s	0.352	0.344	0.343	0.343	0.356	0.345	0.344	0.344
			β_m	0.136	0.125	0.124	0.124	0.141	0.126	0.125	0.125
"L" shape	(d)	$\frac{1}{4}$	β_s	0.347	0.333	0.333	0.333	0.351	0.334	0.332	0.332
			β_m	0.129	0.111	0.111	0.111	0.134	0.112	0.109	0.109
Diagonal bar	(e)	$\frac{1}{2}$	β_s	0.581	0.577	0.577	0.577	0.584	0.577	0.577	0.577
			β_m	0.162	0.154	0.154	0.154	0.168	0.154	0.154	0.154
"Horse movement"	(f)	$\frac{1}{4}$	β_s	0.36	0.339	0.338	0.336	0.364	0.339	0.338	0.338
			β_m	0.15	0.118	0.117	0.114	0.152	0.118	0.117	0.117

^a $\alpha_{\infty} = \alpha$ calculated in the limit of large m .

^bError: ± 0.007 .

^cError: ± 0.003 .

where l is a characteristic void length and A is a coefficient. The fitting shown in Fig. 3 yields (for $m = 100$), $A = 0.3613$ and $l = 1.0549$.

Summing over all x values should yield the total number of voids, k , from which β_s is calculated using Eq. [1]. Approximating the summation by an integration using the

analytic approximation of Eq. [5] yields

$$k \approx \int_0^{\infty} x \cdot n(x) dx = A \cdot m^2 \quad [6]$$

and $\beta_s \approx A$. Indeed, from Table 1 for $m = 100$ and the object of Fig. 1c $\beta_s = 0.344$ close to $A = 0.3613$.

VOID SIMULATION FOR H₂O ADSORPTION ON THE (1, 0, 0) SURFACE OF CUBIC ZrO₂

We examine now the (1, 0, 0) surface of cubic ZrO₂ shown in Fig. 4. This surface has a different structure than an $m \times m$ chessboard because of Zr:O = 1:2 ratio of ions.



FIG. 2. 100 × 100 board covered by long bars of Fig. 1c. Covered area is gray. Black and white squares are noncovered sites.

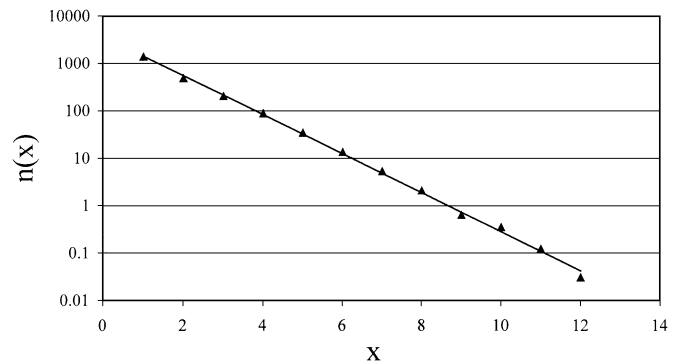


FIG. 3. The void length distribution of long bars Fig. 1c. x , Length of void cluster (as defined in text); $n(x)$, number of clusters of length x . The triangles are numerical values. The line is a best fit, $n(x) = 0.3613 e^{-\frac{x}{1.0549}} \cdot m^2$, for $m = 100$, with $R^2 = 0.9982$.



FIG. 4. Surface of cubic ZrO_2 . Zr, zirconium site; O, oxygen site.

In chemisorption of water the molecule H_2O disintegrates into H on the oxygen site and OH on the zirconium site (7). The molecule is therefore simulated by an object with two segments in line, one black and one white as in Fig. 1a. The numerical calculation yields $\beta_m = 0.003$ and $\beta_s = 0.335$ ($\alpha = 0.3333$). This result shows that disorder cannot affect significantly the coverage of ZrO_2 by H_2O . β_m is significantly less than the one calculated for the AB binary, $m \times m$ surface where β_m reaches at least 0.155. The reason for the low β_m is the presence of two oxygen sites per zirconium site and the fact that only one oxygen site has to be covered. This reduces considerably the constrain on the "proton" positioning for each OH group adsorbed on a nearby Zr.

Experimentally, at low T , there will be also one or more physisorbed water layers on top of the chemisorbed one (3). This however will not affect the concentration of void in the quenched chemisorbed layer.

CONCLUSIONS AND SUMMARY

We have related adsorption of nonoverlapping molecules on a crystal surface at low temperature, neglecting interaction between the molecules, to random placing of structured objects on a structured board. We have first simulated the adsorption of small molecules of two or three segments, on the surface of a diatomic AB crystal. Placing randomly these objects onto an $m \times m$ board not allowing overlap yields voids. We define the uncovered surface coefficient, β_s , and the excess uncovered surface coefficient, β_m . The uncovered surface can reach up to 57% of the surface area and the excess uncovered surface can reach up to 15.5% out of the theoretically maximum number of sites that can be covered in an ordered manner. The void coefficients β_s and β_m depend on the size and shape of the objects used for covering. The relation between the uncovered surface void coefficient β_s and the excess uncovered surface coefficient β_m is given in Eq. [3].

The reason for the large deviation of β_s from unity is that each object of three segments covers two black sites and

one white site, and many white sites remain uncovered. E.g., in the diagonal case of Fig. 1b the object covers only two black sites and all white sites remain uncovered. Disorder introduces an excess concentration of voids of the order of a few percent.

The minimum number of placing trials, which gives a good estimation for β_s and β_m , i.e., required for reaching a steady state, is found to be the number of sites on the board, i.e., $m \times m$.

The numerical analysis of the size distribution of the size of void clusters for the object of Fig. 1c follows a Poisson distribution.

We suggest that the analysis is relevant to molecules adsorbed at low T (under quenching conditions) on surfaces of crystalline solids. The numerical values obtained are applicable to diatomic solids, e.g., MO oxides. The adsorbed objects are small molecules that disintegrated into two or three segments on the surface. The latter is an important point. For example, for water (H_2O) molecules adsorbed on an oxide it is an object of size two that is relevant. The reason is that the water molecule chemisorbed on two ions, the OH group onto a surface cation (M) and the remaining proton on a nearby surface oxygen ion (O), forming another OH group (7). For water molecules adsorbed on the (1, 0, 0) surface of stabilized cubic ZrO_2 , $\beta_s = 0.335$ and $\beta_m = 0.003$ (with $\alpha = 0.333$). β_m decreases when the surface contains excess equivalent sites that need not all be covered (as in the last example). For large molecules (polymers), the void coefficients β_s and β_m can be calculated numerically in a similar way. It is estimated that the void coefficients will be larger due to the larger size of the polymers. Further refinement would be to take into consideration interaction between molecules that tend to reorient them, unless the temperature is sufficiently low.

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