

## Effect of adsorption on surface roughening

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Employing the restricted-solid-on-solid model, we show that adsorption may result in a decrease of the roughening temperature  $T_R$  due to (i) indirect next-nearest-neighbor adsorbate-substrate repulsion, (ii) attractive nearest-neighbor adsorbate-substrate lateral interaction, or (iii) repulsive adsorbate-adsorbate lateral interaction. In all these cases, the ratio of  $T_R$  near saturation and for a clean surface is given by a simple combination of the corresponding interactions. The coverage dependence of  $T_R$ , obtained for case (i) by Monte Carlo simulations, deviates from the mean-field-type prediction. Adsorbate-induced surface roughening observed in catalytic reactions is also briefly discussed.

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Roughening of perfect single-crystal surfaces is a very soft (infinite-order) phase transition. A rigorous proof of its existence was given by van Beijeren<sup>1</sup> by mapping the body-centered solid-on-solid model on the symmetric six-vertex model. Since then, this phenomenon has been simulated by employing various models and techniques (see the reviews in Refs. 2 and 3), and now its basic features are well understood at least in the framework of the lattice approximation (roughening of real surfaces is often complicated<sup>4</sup> by enhanced anharmonic vibrations of substrate atoms in the top layer). In particular, surface roughening is known to be characterized by the behavior of the correlation function relating the mean-square height difference between two points separated by distance  $r$ ,

$$G(r) = \langle [h(r) - h(0)]^2 \rangle. \quad (1)$$

Below the roughening temperature  $T_R$ ,  $G(r)$  reaches a finite asymptotic value at  $r \rightarrow \infty$ . While at  $T \geq T_R$ , this correlation function diverges at  $r \rightarrow \infty$  as

$$G(r) = A(T) + B(T) \ln r. \quad (2)$$

Experimental studies based on this equation indicate that surface roughening usually occurs at temperatures just below the melting temperature [for fcc metals, e.g., the ratio  $T_R/T_M$  is about 0.7–0.8 for the (110) face,<sup>5,6</sup> while the (111) and (100) faces do not seem to roughen at all up to  $T_M$ ].

Physically, surface roughening is closely connected with surface reconstruction.<sup>2,3</sup> In analogy with adsorbate-induced surface reconstruction,<sup>7,8</sup> one might expect that surface roughening as well is strongly affected by adsorption. Models describing the latter phenomenon are, however, lacking. Experimentally, the effect of adsorption on surface roughening has not been systematically studied either. Meanwhile, this problem is of considerable interest for several reasons. For statistical physics, adsorbate-induced surface roughening is a nontrivial example of an infinite-order phase transition in a binary system (such phase transitions have not been studied

at all). For fundamental surface science, the understanding of surface roughening induced or complicated by adsorption is a necessary step in simulations of rate processes on heterogeneous surfaces. In such simulations, the surface structure is usually postulated and considered to be stable during adsorption.<sup>10</sup> The latter might, however, be far from the reality if adsorption induces surface reconstruction or roughening (for a review of the effect of adsorbate-induced surface reconstruction on thermal desorption, see Ref. 8; adsorption isotherms on a rough surface predicted by the solid-on-solid model have recently been calculated in Ref. 9, but the effect of adsorption on surface roughening, i.e., on  $T_R$ , has not been discussed there at all). In catalytic reactions, surface roughening is well known<sup>11</sup> to be sometimes observed even at relatively low temperatures, down to  $0.3 - 0.4T_M$ . The physics behind such observations is, however, not clear. In particular, there are no explanations as to why roughening often occurs easily in the course of reactions but is not registered during separate adsorption of reactants. The goal of this paper is to show theoretically that adsorption may considerably reduce  $T_R$  and, on the basis of this finding, to propose one of the scenarios of roughening in catalytic reactions.

Our analysis is based on the restricted-solid-on-solid model (RSOSM) employed by Rommelse and den Nijs<sup>12</sup> to explore roughening and preroughening of clean surfaces. In the framework of this model, the crystal is represented as a two-dimensional array of columns of varying integer heights  $h_i$ . For the nearest-neighbor (nn) columns, the heights are allowed to differ by at most one,  $h_i - h_j = 0, \pm 1$ . The substrate energy is accordingly given by

$$H_M = (K/2) \sum_{i,j} \delta(|h_i - h_j| - 1), \quad (3)$$

where  $K > 0$  is the interaction constant (referring to the nn attractive interaction between metal atoms,  $\epsilon_{MM} < 0$ , one has  $K = |\epsilon_{MM}|/2$ ),  $\langle i, j \rangle$  denotes nn sites on a square lattice, and

$\delta(x) = 1$  when  $x = 0$  and vanishes otherwise (the factor 1/2 is introduced to avoid double counting).

Assuming the adsorbed particles to be located on top sites and every site to be occupied at most by one particle, we complement Eq. (3) by the terms describing adsorbate-substrate and adsorbate-adsorbate interactions,  $\epsilon_{AM}$  and  $\epsilon_{AA}$ . The nature of adsorbate-substrate interaction might be different in different systems. The main ‘‘zero-order’’ term of this interaction is given by

$$H_b = -D \sum_i n_i, \quad (4)$$

where  $D$  is the binding energy on the perfect surface, and  $n_i$  the occupation number for adsorption sites. This term is independent of the surface structure and accordingly can be omitted. The first-order term, taking into account the dependence of the binding energy on the local arrangement of the substrate atoms, has two components. (i) An adsorbed particle may weaken the metal-metal interaction in the underlying substrate layer. In other words, the adsorbate-substrate binding energy might be higher if the underlying metal atom has a lower number of nn  $M$  neighbors. This so-called indirect next-nearest-neighbor (nnn) adsorbate-substrate interaction is represented as

$$H_{AM}^u = -\epsilon_{AM}^u \sum_{i,j} n_i \delta(h_i - h_j - 1) \quad (5)$$

with  $\epsilon_{AM}^u > 0$ . (ii) There is also the contribution of direct nn adsorbate-substrate lateral interactions ( $\epsilon_{AM}^l < 0$  for attraction),

$$H_{AM}^l = \epsilon_{AM}^l \sum_{i,j} n_i \delta(h_i - h_j + 1). \quad (6)$$

(iii) In addition, the total energy contains nn adsorbate-adsorbate lateral interactions,

$$H_A^l = (\epsilon_{AA}/2) \sum_{i,j} n_i n_j \delta(h_i - h_j). \quad (7)$$

Analyzing Eqs. (3) and (5)–(7), one can verify that at saturation (when all the adsorption sites are occupied) the total energy is again given by Eq. (3), but with  $K = |\epsilon_{MM} + 0.5(\epsilon_{AM}^u - \epsilon_{AM}^l + \epsilon_{AA})|/2$ . This means that the critical temperatures at  $\theta \rightarrow 1$  and  $\theta \rightarrow 0$  ( $\theta$  is the adsorbate coverage) are interconnected as

$$T_R(1) = T_R(0) |\epsilon_{MM} + 0.5(\epsilon_{AM}^u - \epsilon_{AM}^l + \epsilon_{AA})| / |\epsilon_{MM}|. \quad (8)$$

Taking into account that  $\epsilon_{MM} < 0$ , we conclude that  $T_R$  might decrease due to (i) the weakening of the metal-metal interaction in the underlying substrate layer ( $\epsilon_{AM}^u > 0$ ), (ii) attractive adsorbate-substrate lateral interaction ( $\epsilon_{AM}^l < 0$ ), and (iii) repulsive adsorbate-adsorbate lateral interaction ( $\epsilon_{AA} > 0$ ). The opposite might occur for  $\epsilon_{AM}^u < 0$ ,  $\epsilon_{AM}^l > 0$ , and  $\epsilon_{AA} < 0$ . For real metals, one has  $T_R \sim 700\text{--}1000$  K and accordingly  $\epsilon_{MM} \sim 2$  kcal/mol. From the analysis of phase diagrams of adsorbed particles and thermal desorption spectra, the values of  $\epsilon_{AA}$  are well known<sup>14</sup> to be in the range from 1

to 2 kcal/mol. The parameters  $\epsilon_{AM}^u$  and  $\epsilon_{AM}^l$  are also expected to be about 1–2 kcal/mol. Thus all the interactions in Eq. (8) are of the same magnitude. The latter means that  $T_R$  might be considerably affected by adsorption.

Employing a plausible mean-field (MF)-type consideration, one can expect that the coverage dependence of  $T_R$  is approximately represented as

$$T_R(\theta) = T_R(0) + [T_R(1) - T_R(0)]\theta. \quad (9)$$

The MF arguments do not, however, take into account correlations in the arrangement of particles. To illustrate deviations from the MF-type predictions, we have carried out Monte Carlo (MC) simulations of surface roughening for the situation when the decrease of  $T_R$  results from the adsorbate-induced weakening of the metal-metal interaction in the underlying substrate layer. The total energy is in this case given by Eqs. (3) and (5). To get  $T_R$ , we have used the procedure originally proposed by Shugard, Weeks, and Gilmer.<sup>13</sup> It is based on calculation of  $G(r)$  [Eq. (1)] at different temperatures and approximation of  $G(r)$  by expression (2). At  $T = T_R$ , the value of  $B$  in Eq. (2) is known<sup>3,6</sup> to be universal  $B(T_R) = 2/\pi^2$ . The latter makes it possible to find  $T_R$ .

In our simulations, we assume that initially (at  $t = 0$ ) the surface is perfect and adsorbed particles are located at random. The MC algorithm for describing the adsorbate/substrate system at  $t > 0$  consists of attempts of independent successive diffusion jumps of metal atoms [steps (i)] and adsorbed particles [step (ii)]: (i) A metal atom on the surface is chosen at random. One of the nn or nnn columns is chosen at random. If a jump to this column violates the RSOSM constraints, the trial ends. Otherwise, the jump is realized with the probability given by the standard Metropolis rule. The occupation numbers  $n_i$  are not changed in this case. (ii) An adsorbed particle is chosen at random. One of the nn columns is chosen at random. If the top site on this column is occupied, the trial ends. Otherwise, the jump is realized with the probability given also by the Metropolis rule.

Employing the algorithm above, we have calculated the kinetics of surface roughening of the (200×200) lattice (with periodic boundary conditions) on times up to  $10^6$  MC steps

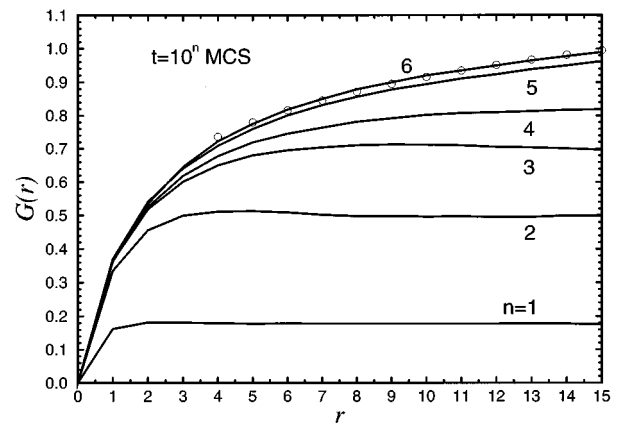


FIG. 1. Correlation function  $G(r)$  for roughening of the clean  $200 \times 200$  lattice at  $T = T_R = 0.9|\epsilon_{MM}|$  for  $t = 10, 10^2, 10^3, 10^4, 10^5$ , and  $10^6$  MCS's. Open circles show the fitting of  $G(r)$  at  $t = 10^6$  MCS's by employing Eq. (2) with  $B = 0.20$ .

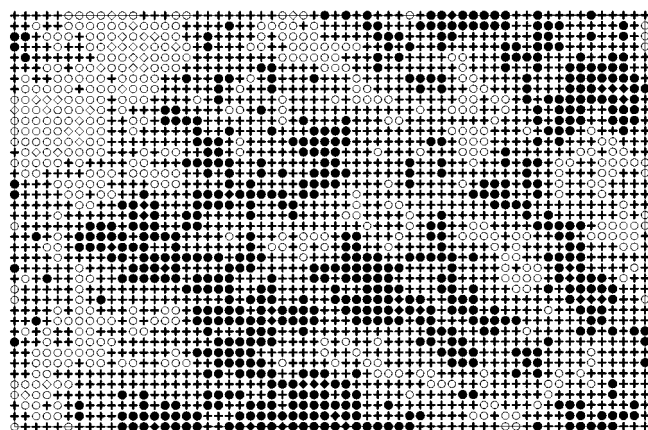


FIG. 2. A  $40 \times 60$  fragment of the clean  $200 \times 200$  lattice after  $10^6$  MCS's at  $T = 1.1|\epsilon_{MM}|$ . Columns with  $h=0$  are shown by the plus signs. Filled circles and diamonds indicate columns with  $h=-1$  and  $-2$ . Open circles and diamonds corresponds to  $h=1$  and  $2$ , respectively.

[one Monte Carlo step (MCS) corresponds by definition to  $L \times L$  attempts ( $L$  is the lattice size) of diffusion of metal atoms].

To obtain  $T_R$  by using Eq. (2), we need  $G(r)$  at large  $r$ , i.e., at least at  $5 \leq r \leq 15$ . For these distances, the time dependence of  $G(r)$  was found to be relatively strong at  $t < 10^5$  MCS's (see, e.g., Fig. 1). For  $t = 10^5$  the results are, however, almost the same as for  $10^6$  MCS's (provided that  $T$  is equal or slightly higher than  $T_R$ ), i.e., in the latter case the system is close to equilibrium at  $r \leq 15$  (if  $r > 15$  and  $t < 10^6$  MCS's, the surface is not at equilibrium). For this reason, the data obtained at  $10^6$  MCS's can be used to calculate  $T_R$ . For a clean surface, our simulations yield  $T_R = (0.90 \pm 0.05)|\epsilon_{MM}|$  (we use  $k_B = 1$ ). This value is in good agreement with  $T_R = 0.8|\epsilon_{MM}|$ , obtained by Rommelse and den Nijs<sup>12</sup> on the basis of the transfer-matrix technique. A typical structure of the surface at temperatures slightly above  $T_R$  is represented in Fig. 2. At these temperatures, surface roughening is rather weak [the deviations of  $h$  from the average value ( $\langle h \rangle = 0$ ) are usually  $\leq 2$ ]. The dependence of  $T_R$  on coverage is exhibited in Fig. 3.  $T_R$  is seen to be higher compared to the MF predictions (the possible error in estimating  $T_R$  is not expected to change the main trends in Fig. 3).

If adsorption occurs at relatively low temperature,  $T_{ad}$ , and after adsorption  $T_R$  becomes lower than  $T_{ad}$ , surface

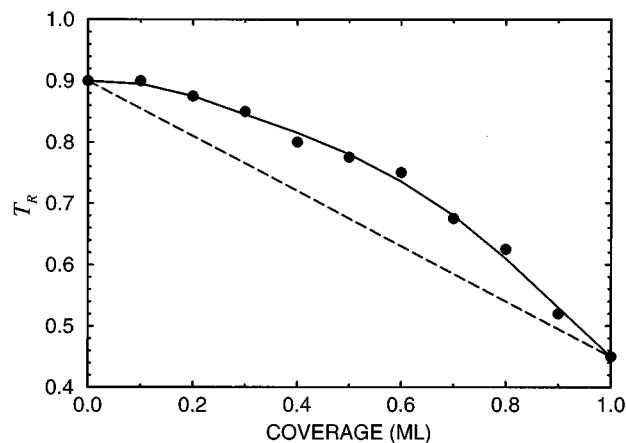


FIG. 3. Roughening temperature (in units  $|\epsilon_{MM}|$ ) as a function of coverage for  $\epsilon_{AM}^u = |\epsilon_{MM}|/4$ . Filled circles show the results of MC simulations. The solid line interpolates the MC data. The dashed line corresponds to the MF approximation.

roughening connected with formation of vacancies in the perfect top layer might be kinetically limited. This seems to be a reason why adsorbate-induced surface roughening is usually not observed after adsorption at low temperatures. If, however, adsorption occurs in the course of an exothermic catalytic reaction under the steady-state conditions, the reaction exothermicity might help to create vacancies via non-thermal local energy exchange between reactants and substrate atoms. The probability of such nonequilibrium events per one reaction act is usually very low, but if the turnover rate is high, the nonequilibrium channel of formation of vacancies might be effective. Thus, combination of thermodynamic adsorbate-induced driving force (low value of  $T_R$  after adsorption) with nonequilibrium exothermic effects might open up the process of surface roughening even at relatively low temperatures.

In summary, our study identifies the adsorbate-substrate and adsorbate-adsorbate interactions facilitating surface roughening. With realistic parameters, the adsorbate-induced decrease of  $T_R$  might be considerable, but the process can be kinetically limited. The conditions for adsorbate-induced surface roughening are expected to be more favorable in exothermic catalytic reactions.

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