Roughening transition in the presence of adsorbates

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The influence of adsorbates on the roughening of solid substrates is discussed in terms of the solid-on-solid model coupled to a generalized lattice gas model. It is shown that the adsorbate may increase or decrease the roughening temperature T_r, depending on the specificity of the height-dependent lateral interaction and adsorbing potential. The decrease of T_r is nonmonotonic with increasing coverage. The substrate corrugation is shown to enhance or depress the adsorption, depending on the preferred height difference at neighboring sites. [S0163-1829(99)03224-5]

I. INTRODUCTION

Adsorbate-induced rearrangement of solid surfaces has been studied recently in some detail. Adsorbates were shown[1-4] to favor the roughening transition, if the steps of different height are the preferred adsorption sites. A decrease of the roughening temperature was investigated,[1] assuming that the coverage Θ is an external parameter. Then the roughening temperature decreases monotonically as a function of coverage. A self-consistent treatment of Θ with the change of the surface morphology is presented in Ref. 2. Nevertheless, the effect of adsorption on the roughening temperature was not discussed there.

Roughening in the presence of a one-body substrate potential (which may originate from the solid bulk) has been extensively studied in Ref. 5. These authors have shown that the interface width shrinks with increasing potential magnitude. For solid-liquid interfaces similar effect should be expected due to the pressure of the liquid.

The aim of this paper is to investigate the mutual influence of the substrate and the adsorbate degrees of freedom and their cooperative effect on the roughening temperature and on the behavior of adsorption isotherms. Our main purpose is to emphasize that for solid-fluid interfaces the adsorbate acts as a thermodynamic subsystem, whose properties are determined from the requirement of the solid-fluid equilibrium. In this case, the coverage is not an external parameter, it should be treated self consistently with the roughness of the substrate.

II. MODEL AND GENERAL APPROACH

We start with the solid-on-solid (SOS) model at a square lattice on which an adsorbing potential is defined. The latter is chosen to be that of the sticky site model[6,7] with the stickiness parameter λ. Due to this the adsorbed fluid is strongly pinned to the step positions. Using the technique, developed in our previous studies,[8,9] we obtain the SOS model coupled to the lattice gas (LG) model with the height-dependent coupling constants

$$\Xi = \text{Tr}_{\{h_i\}} e^{-\beta H_{SOS}(h_i,h_j)} \text{Tr}_{\{t_i\}} e^{-\beta \sum_{i,j} W(h_i,h_j)t_i t_j} e^{\beta \sum_i \tilde{\mu}(h_i)t_i}, \tag{1}$$

where h_i are the height variables, defined over each site of the lattice and $t_i = 0,1$ are occupation numbers for the adsorbate, $\beta = 1/kT$ is the Boltzmann factor. Here, $W(h_i,h_j)$ is the mean force potential for the fluid. The value of

$$\tilde{\mu}(h_i) = \frac{1}{\beta} \ln[\lambda \rho(h_i)] \tag{2}$$

plays the role of a local chemical potential and $H_{SOS}(h_i,h_j)$ is the substrate Hamiltonian

$$H_{SOS}(h_i,h_j) = \frac{1}{2} \sum_{ij} J_{ij} f(h_i - h_j). \tag{3}$$

A form of the f function for various modifications of the SOS model may be found in a recent review.[10]

The trace $\text{Tr}_{\{i\}}$ is a sum over all possible configurations of discrete i variables, or an integral in the case of continuous variables. Similar SOS-Ising model was developed[11] in order to investigate possible crossover from the Ising-like transition to that driven by the SOS subsystem. The spin and height variables were coupled indirectly, that is, via the boundary condition. In contrast, we have a direct coupling at the level of the Hamiltonian. Note also that the coupling depends upon how $W(h_i,h_j)$ and $\tilde{\mu}(h_i)$ behave with the distance from the surface.

To proceed further we extract a flat wall contribution ($h_i = 0$) to the coupling functions: $W(h_i,h_j) = w_{i,j}(0) + w(h_i,h_j)$, $\tilde{\mu}(h_i) = \mu(0) + \mu(h_i)$, with the h-dependent parts accounting for corrugation ($h_i \neq 0$). Then the partition function (1) is rearranged to

$$\Xi = \text{Tr}_{\{h_i\}} \text{Tr}_{\{t_i\}} e^{-\beta H_{LG}(t_i,t_j)} e^{-\beta H_{SOS}(h_i,h_j)}$$
$$\times e^{-\beta \sum_{i,j} w(h_i,h_j)t_i t_j} e^{\beta \sum_i \mu(h_i)t_i}, \tag{4}$$

where the LG Hamiltonian for the flat surface is

$$H_{LG}(t_i,t_j) = \frac{1}{2} \sum_{ij} w_{i,j}(0)t_i t_j - \sum_i \mu(0)t_i. \tag{5}$$

Then, the free energy is found to be

$$F = F_{SOS}^0 + F_{LG}^0 - \frac{1}{\beta} \langle \exp[\langle e^{-\beta \Sigma_{ij} w(h_i, h_j) t_i t_j}$$

$$\times e^{\beta \Sigma_i \mu(h_i) t_i} - 1 \rangle_c] - 1 \rangle_c, \qquad (6)$$

where $\langle \dots \rangle_c$ denote two cumulant averages calculated with Hamiltonians H_{SOS} and H_{LG}. Note that the roughening transition occurs with increasing temperature, while for the LG adsorbate the Ising-like criticality is favorable when the temperature decreases. Therefore, the ''critical'' temperatures for isolated subsystems are usually separated enough to avoid the crossover behavior. This assumption seems to be reasonable as this follows from the Monte Carlo data.[11]

III. EFFECTIVE HAMILTONIANS

In the absence of crossover behavior one of the subsystems (SOS or LG type) is not singular in the neighborhood of the singularity of the other one. Then the regular subsystem just renormalizes the parameters of the singular counterpart. In such a way we can determine a shift of the roughening temperature with increasing adsorption and also the changes in adsorption isotherms with increasing roughness (or corrugation).

A. An influence of adsorption on roughening

Close to the roughening temperature we may choose H_{LG} as a reference

$$\Xi = \Xi_{LG}^0 Tr_{\{h_i\}} e^{-\beta H_{SOS}(h_i, h_j)}$$

$$\times \left\langle \exp\left[-\frac{\beta}{2} \sum_{i,j} w(h_i, h_j) t_i t_j \right] \exp\left[\beta \sum_i \mu(h_i) t_i \right] \right\rangle, \qquad (7)$$

where $\langle \dots \rangle$ and Ξ_{LG}^0 denote an average over the occupation numbers and the partition function, calculated with the potential (5). These averages lead to the cumulant expansion,[12] which, within first two cumulants, gives the effective Hamiltonian

$$H = H_{SOS} - \sum_i \mu(h_i) \Theta_i + \frac{1}{2} \sum_{i,j} [w(h_i, h_j)$$

$$- \beta \mu(h_i) \mu(h_j)] \chi_{ij}(\Theta), \qquad (8)$$

where $\Theta_i = \langle t_i \rangle$ and $\chi_{ij}(\Theta) = \langle t_i t_j \rangle - \langle t_i \rangle \langle t_j \rangle$ are the coverage and two-body correlation function, respectively. These quantities are calculated for a flat lattice. In general, H is a many-body Hamiltonian, including higher order correlation functions for the adsorbate and multistep interactions.

Thus we see that the adsorbate induces a single-step anisotropy through the one-body term $\mu(h_i)\Theta_i$, which breaks the $h_i \rightarrow -h_i$ symmetry of the substrate Hamiltonian. This reflects a density variation $\delta\rho(h_i)$ compared to the flat boundary. Assuming that $\rho(h_i) = \rho_0 + \delta\rho(h_i)$, we have

$$\beta\mu(h_i) = \ln[1 + \delta\rho(h_i)/\rho_0]. \qquad (9)$$

This stickiness-independent term represents nothing else than a single-step localization field. If the substrate is corrugated on molecular scale, then the structure near the interface

is known to become more uniform.[13] In this case, the density excess $\delta\rho(h_i) < 0$ and $\mu(h_i) < 0$ tends to stabilize the interface at positive h_i's. An opposite situation takes place for a wedgelike corrugation,[14] with the wedge size exceeding the adsorbate diameter. In this case $\delta\rho(h_i) > 0$ around the corners and then $\mu(h_i) > 0$ tends to fix the interface at negative h_i's. The physical nature of the adsorbate-induced external field is the existence of a preferred interface height h_i^0, which is the most favorable for the thermodynamics of the adsorbate. In other words, the adsorbate may induce a local growth of the substrate from $h_i = 0$ to $h_i = h_i^0$. This can be taken into account by expanding $\mu(h_i)$ around $h_i = 0$

$$\mu(h_i) = \alpha_i h_i + \gamma_i h_i^2 + \cdots = \mu_m + \gamma_i (h_i - h_i^0)^2, \qquad (10)$$

where μ_m is a constant and $h_i^0 = \pm \alpha_i/2\gamma_i$. In any case the one-body term favors a flat interface [if $\delta\rho(h_i)$ is the same for all h_i], or corrugated (but not rough) one with a given profile of h_i's. This term plays a role of the one-body substrate potential,[5] which depresses the roughening irrespective of the sign of h_i^0. For this reason, we can set $h_i^0 = 0$ without loss of generality. It is seen, however, from Eq. (8) that the correlation between the fields $\beta\mu(h_i)\mu(h_j)$ at different lattice positions does contribute to the pairwise interaction. This indicates a possibility of an adsorbate-modulated structure at low temperatures. Nevertheless, this term has an extra β prefactor. For this reason it is expected to be negligible at relatively high temperatures, relevant to the roughening.

The pairwise interaction term, appearing in Eq. (8), can be treated in the same manner

$$w(h_i, h_j) = \Gamma_{ij}(|h_i - h_j|) + \Delta_{ij}(h_i - h_j)^2 + \cdots$$

$$= w_{ij}^{(m)} + \Delta_{ij}(h_i - h_j - h_{ij}^0)^2. \qquad (11)$$

The linear term is important now, since it determines the preferred height difference $|h_{ij}^0| = |\Gamma_{ij}/2\Delta_{ij}|$ for two adsorbates at a distance R_{ij} along the surface. A nonzero h_{ij}^0 follows from the condition that $W(h_i, h_j)$ has a minimum for distances of order of $\sqrt{R_{ij}^2 + (h_{ij}^0)^2}$. After these rearrangements we have the effective Hamiltonian

$$H = H_{SOS} - \sum_i \gamma_i \Theta_i h_i^2 + \frac{1}{2} \sum_{ij} [\Gamma_{ij}(|h_i - h_j|)$$

$$+ \Delta_{ij}(h_i - h_j)^2] \chi_{ij}(\Theta) \qquad (12)$$

for a SOS model coupled to a mixed absolute-Gaussian (ASOS-DGSOS) one with a single-step anisotropy. Note that the coupling constants are proportional to the pair-correlation function $\chi_{ij}(\Theta)$ of the adsorbate. This reflects the statistical character of the adsorbate contribution to the step-step interaction. This is a crucial point, because the effective coupling constant [e.g., $\Delta_{ij}\chi_{ij}(\Theta)$] may be arbitrary largely due to the tuning of the stickiness λ. In this case even an infinitesimally small bare constant (for instance, Γ_{ij}) is enough to have a strong effective coupling.

In the partial case of $\Delta_{ij} = 0$, $\gamma_i = 0$, $h_{ij} = h_i - h_j = 0$, ± 1, H reduces to the RSOS form studied in Ref. 1. Then $h_{ij}^0 = 0$ is preferred for $\Gamma_{ij} > 0$ and instable for $\Gamma_{ij} < 0$. To estimate the correlation effects we approximate the lattice gas correlation function $\chi_{ij}(\Theta)$ by its mean-field value[16]
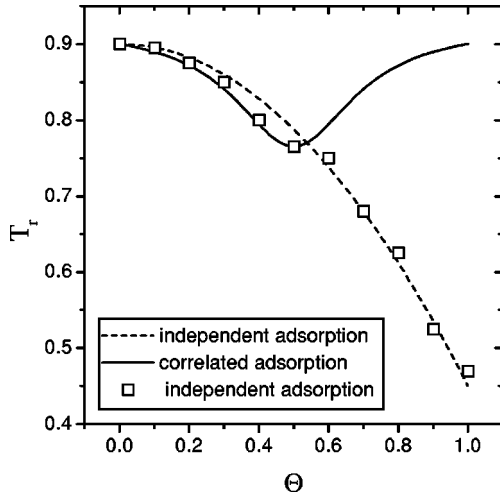
FIG. 1. Roughening temperature, T_r as a function of coverage Θ. Symbols represent the MC data of Ref. 1.

$$\chi_{ij}(\Theta) = \frac{\xi^2}{\beta w(0)} \exp\left(-\frac{R_{ij}}{\xi}\right), \tag{13}$$

where ξ is the dimensionless correlation length, related to the susceptibility $\chi(\Theta)$ through

$$\xi^2 = \beta w(0) \chi(\Theta).$$

For $\xi \gg R_{ij}$ we have $\chi_{ij}(\Theta) \approx \chi(\Theta)$. Then the effective constant $\hat{J}$ is

$$\hat{J} = J + \Gamma \chi(\Theta), \tag{14}$$

where $\chi(\Theta)$ is given by

$$\chi(\Theta) = \frac{\Theta(1-\Theta)}{1 - 4\beta w(0)\Theta(1-\Theta)}. \tag{15}$$

Therefore, the roughening temperature is

$$T_r = T_r^0 \left[1 + \frac{\Gamma}{J} \chi(\Theta)\right]. \tag{16}$$

In the limit of independent adsorption (i.e. when Θ is independent of the substrate properties) we have

$$H' = H_{SOS} + \frac{1}{2} \sum_{ij} [\Gamma_{ij}(|h_i - h_j|) + \Delta_{ij}(h_i - h_j)^2]\Theta_i\Theta_j, \tag{17}$$

which is the bare interaction, weighted by the probability $\Theta_i\Theta_j$ to find two adsorbates on the sites i and j.

In Fig. 1, T_r is plotted as a function of coverage. As it is expected, the roughening temperature decreases (increases) for negative (positive) Γ. In the case of independent adsorbates this decrease is monotonic according to

$$T_r/T_r^0 = 1 - \frac{\Gamma}{J}\Theta^2. \tag{18}$$

This agrees well with the simulation result. Theoretical curve (the dashed one) is calculated at $\Gamma/J = 1/2$, which corresponds to a typical ratio for the adsorbate-substrate energies[1] (1-2 kcal/mol).

A nonmonotonic behavior is observed when Θ is treated self-consistently. In this case $\chi(\Theta) \propto \Theta(1-\Theta)$ and, consequently, the effect of the adsorbate vanishes at high coverages. This fact finds a simple physical explanation. To have $\Theta \rightarrow 1$ (at fixed pressure or chemical potential) one has to decrease the temperature that causes a flattening of the substrate. On the other hand, if the substrate approaches the roughening temperature, then this should be supplemented by decreasing coverage ($\Theta \rightarrow 0$), unless the pressure or chemical potential are tuned to keep Θ fixed. At low temperatures the substrate is flat, but $\Theta \rightarrow 1$ tends to fix a zig-zag structure with the step difference at the neighboring sites equal to h_{ij}^0. This explains why adsorbate-induced surface roughening is usually not observed after adsorption at low temperatures.[1] For low coverages both approaches predict almost the same behavior. The maximal effect of the adsorbate (for correlated adsorption) is at $\Theta = 1/2$. Similar result is obtained for the adsorbate-mediated melting.[9] This is consistent with the results on the nonequilibrium deposition,[15] where the roughening transition was associated with the percolation threshold for the adsorbate. Our result agrees also with the conclusion of Ref. 2, where the corrugation degree was detected to have a kink at the pressures corresponding to $\Theta \approx 1/2$ and a saturation plateau for higher coverages. Note that the theoretical curve (solid) is calculated for $\Gamma/J = 0.09$. This indicates that even very weak adsorbate interactions may favor the roughening due to a strong correlation. In other words, we deal with a cooperative effect of the adsorbate.

B. Effect of corrugation on adsorption

To investigate an influence of the substrate roughness on the adsorption process, we restart with Eq. (4) and extract the clean substrate term. Then, instead of Eq. (7) we have the following

$$\Xi = \Xi_{SOS}^0 Tr_{\{t_i\}} e^{-\beta H_{LG}(t_i, t_j)}$$

$$\times \left\langle \exp\left[-\frac{\beta}{2}\sum_{i,j} w(h_i, h_j)t_i t_j\right] \exp\left[\beta \sum_i \mu(h_i)t_i\right] \right\rangle. \tag{19}$$

The average is taken over the height variables with the substrate Hamiltonian. For concreteness the case of $\Delta_{ij} = 0$ is discussed. Performing the cumulant expansion and restricting ourselves to first two cumulants, we obtain the effective Hamiltonian

$$H = H_{LG} + \frac{1}{2}\sum_{ij} \Gamma_{ij}G_{ij}t_i t_j - \sum_i \gamma_i \langle h_i^2 \rangle t_i, \tag{20}$$

where $G_{ij} = \langle |h_i - h_j| \rangle$ is the mean height difference[2] for the clean substrate. Within the nearest-neighbor approximation we have a LG-type Hamiltonian with the lateral interaction $w(0) + \Gamma G$ and chemical potential $\mu(0) + \gamma \langle h^2 \rangle$ rescaled by the substrate contributions. In the limit of $\gamma = 0$, $w(0) = 0$ (Langmuirian isotherm in the absence of corrugation) we reproduce the situation simulated in Ref. 2. Then, the mean-field approximation (MFA) for the coverage is determined by
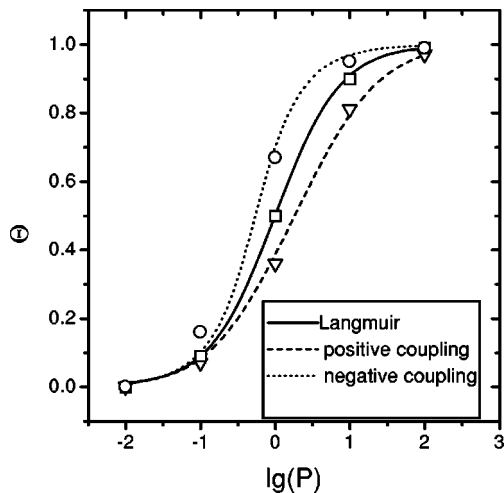
FIG. 2. Adsorption isotherms for corrugated lattice. Symbols represent the MC data of Ref. 2.

$$\Theta = \frac{\exp[\beta(\mu(0) - 4\Gamma G\Theta)]}{1 + \exp[\beta(\mu(0) - 4\Gamma G\Theta)]}. \qquad (21)$$

In Fig. 2, the coverage is plotted as a function of the reduced pressure $P = \exp[\beta\mu(0)]$. For positive coupling $\Gamma > 0$ the ad-sorbate prefers a flat geometry. Therefore, an increase of the corrugation G depresses the adsorption (long-dashed curve). In contrast, a rough geometry is preferred for $\Gamma < 0$. For this reason an increase of the corrugation G is supplemented by increasing Θ (short-dashed curve) compared to the Langmuirian case (solid curve). It is seen that for relatively weak interactions ($\beta\Gamma G = \pm 0.3$) our simple MFA exhibits a rather good agreement with the Monte Carlo (MC) results.

IV. CONCLUSION

In this paper, we have shown that the change of the roughening temperature in the presence of adsorbates is non-monotonic if the coverage is treated self consistently with the substrate degrees of freedom. An approximate perturbative theory for such a coupling exhibits good agreement with the simulation results in a range of relatively weak interactions (or high temperatures). The substrate corrugation enhances the adsorption, if the preferred height difference for the ad-sorbate is nonzero ($\Gamma < 0$). Otherwise, i.e., for $\Gamma > 0$, adsorption is depressed by the corrugation.

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