Surface rearrangement at complex adsorbate-substrate interfaces.

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On the basis of the information theory approach we propose a novel statistical scheme for analyzing the evolution of coupled adsorbate-substrate systems, in which the substrate undergoes the adsorbate-induced transformations. A relation between the substrate morphology and the adsorbate thermodynamic state is established. This allows one to estimate the surface structure in terms of incomplete experimental information and the one concerning the adsorbate thermodynamic response to the structural modifications.

I. INTRODUCTION

Adsorbate-induced changes in the substrate morphology is a quite common phenomenon in nature. This concerns with in-plane and out-of-plane surface modifications, such as reconstruction or roughening (see [1] for a recent review).

For simple crystalline surfaces (single crystals) there are well-developed Hamiltonian models dealing theoretically with the adsorbate-induced restructuring effects [2]. Focusing on the roughness, the solid-on-solid models [3,4] are appropriate for the description of the surface morphology under the influence of adsorption. Nevertheless, even in this “traditional” domain there are certain unsolved problems with the surface structure determination [5]. Therefore, one has to work under conditions of incomplete information.

Moreover, many adsorbents do not fall into this class because of their intrinsic complexity. The latter appears as a consequence of the surface disorder, heterogeneity [6] or polydispersity. Glassy [7], granular, amorphous [8], or porous materials, like aerogels [9,10], could serve as examples. The morphology of such materials is conventionally specified by a probability distribution (e.g. site energies, pore or grain sizes). In many cases the distribution itself is unknown. For randomly heterogeneous surfaces the information comes from scattering experiments or STM images. In the case of three-dimensional structures one has to rely upon results of indirect measurements (such as nitrogen adsorption, mercury porosimetry, thermoporometry, etc). These techniques give a quite limited information from which the probability distribution should be determined. This problem is beyond the scope of the standard statistical mechanics, which starts from a microscopic model.

Actually, the situation is complicated by the fact that the surface morphology [11] and/or energetics [12] change in the course of adsorption. This is quite common phenomenon, occurring, for instance, during the aerogel characterization [9,10] or in the course of various insertion processes [13,14]. In this respect the problem is essentially as follows. One has to describe the surface evolution from a poorly characterized initial (e.g. clean surface) to a final (adsorbate-induced) state. In addition, the adsorbate thermodynamics, coupled to the surface morphology, should be calculated. The inverse problem, that is, restoring the clean surface characteristics from its morphology in the covered state, is also important.

In this paper we make an attempt to deal with such problems combining the information theory approach [15,16] and the standard statistical thermodynamics. The adsorbate-substrate system can be split into subsystems with different levels of description. One is a dynamic subsystem (the adsorbate), which evolves according to a Hamiltonian, containing unknown parameters (local roughness of the surface). The surface is considered as a stochastic system. Its morphology (e.g. step configuration) is specified by a probability distribution. This combined scheme looks quite similar to the so-called superstatistics [17], that describes the statistics in systems with fluctuating intensive quantities. The key difference is that in our case the probability distribution is unknown. It has to be inferred from a limited number of constraints. Recently such a maximum-entropy procedure has been applied to a description of velocity fluctuations in turbulent fluids [18] and the strain fluctuations in heterogeneous intercalation systems [19]. In our case the adsorbate can influence the surface roughness and their coupling determines both the thermodynamic behavior and the shape of the probability distribution. It is essential that one necessarily deals with two entropic impacts [20]: the thermodynamic entropy (due to the adsorbate) and the information entropy (due to the probability distribution). Constructing from these two terms a suitable entropy measure, we investigate the evolution of the surface morphology and the adsorbate thermodynamics. The main purpose of this paper is to find a relation between the surface structure and the adsorbate thermodynamic response to these structural modifications. This would allow one to gain an information on the surface following the adsorbate behavior.
II. CLEAN SURFACE

In this section we demonstrate how the maximum entropy formalism can be applied to inferring a distribution based on a limited information. For concreteness we consider a solid-like semi-infinite substrate (see Figure 1). The surface (substrate) morphology is represented by a collection of steps \( \{h_i\} \) growing on discrete sites \( i = 1..N_s \), with \( -\infty < h_i < \infty \), describing a deviation from the flat geometry. A sketch of the surface profile is given in Figure 1.

It is assumed that, because of its complex nature, the surface cannot be described deterministically, i.e., in terms of a Hamiltonian governing the substrate evolution. Thus we have to accept a probabilistic description, focusing on a distribution based on a limited information. For broadening the distribution is obtained by extremizing the Lagrangian distribution, compatible with the constraint (1) is

\[
\Lambda = S_I - \nu \sum_k \left[ \int dh_k P(h_k) - 1 \right] - \lambda_0 \left[ \sum_k \int dh_k P(h_k) h_k^2 - H_0 \right]
\]

This leads to a gaussian distribution

\[
P_0(h_i) = \frac{e^{-\lambda_0 h_i^2}}{\int dh_i e^{-\lambda_0 h_i^2}}
\]

The Lagrange multiplier \( \lambda_0 \) can be determined from the constraint (1) \( \lambda_0 = 1/(2H_0) \). We do not discuss here how precise is this description. Having more information, e.g., \( \langle h^4 \rangle \), we can follow the same scheme in order to obtain a refined distribution.

III. SURFACE-ADSORBATE COUPLING

Being exposed to a fluid, the surface can adsorb the fluid particles on the sites (see Fig. 1). Having information [21] on the roughness \( H \) in the presence of adsorption, one can infer the step distribution maximizing \( S_I \). Obviously, the distribution is also gaussian

\[
P(h_i) = \frac{e^{-\lambda h_i^2}}{\int dh_i e^{-\lambda h_i^2}}
\]

but with a different width \( \lambda = 1/(2H) \). Therefore, if \( H \) is close to \( H_0 \), then one would conclude that \( P(h_i) = P_0(h_i) \) and the adsorbate-induced effects are negligible. This can be the case if the surface is quenched. As is discussed above, the surface may change its morphology even if the average roughness remains unchanged. In other words, we do not have new \textit{a priori} information if \( H = H_0 \). Then, starting with the same entropy measure \( S_I \), we arrive at a trivial (but misleading) result: \( P(h_i) = P_0(h_i) \). This defect can be avoided in (at least) two ways. One might need to compare higher moments (for instance, the average of \( h_i^4 \)). This would require additional tests [21]. Alternatively, we may refine the entropy measure, taking into account the adsorbate-induced effects. This requires to make a link between the surface structure and the adsorbate properties.

The adsorbate is considered as a dynamic subsystem, whose coupling to the surface is given by a Hamiltonian \( H(\{t_i\} | \{h_k\}) \). We assume that the surface evolves in time much slower than the adsorbate, that reaches the equilibrium while the surface is practically unchanged. Tracing over the set of occupation numbers \( \{t_i\} \) at a given step configuration we can calculate the partition function

\[
Z(\tau | \{h_k\}) = \sum_{\{t_i\}} e^{-\beta H(\{t_i\} | \{h_k\})}
\]

where \( \beta = 1/k_B T \) is the inverse temperature, and \( \tau \) is a thermodynamic variable (e.g., chemical potential or coverage, see below). Then the adsorbate thermodynamics, for instance, the conditional entropy \( S_T(\tau | \{h_k\}) \), can also be calculated.

In what follows this quantity will play an essential role. Therefore, it is important to clarify its
meaning. As a function of \( \tau \) the entropy is the conventional thermodynamic state function. It is a measure of the adsorbate disorder for a given surface structure \( \{ h_k \} \). On the other hand, if \( \tau \) is fixed (e. g. fixed adsorbate pressure), then \( S_T \) as a function of \( \{ h_k \} \) should be considered as an effective potential, selecting a preferable step configuration – the one which maximizes \( S_T \).

Since we are dealing with adsorbate-induced effects, then \( S_T(\tau;\{h_k\}) \) should be relevant to the surface structure evolution. Therefore we refine the entropy measure

\[
\Sigma = S_T + \kappa \int (dh_k) P(\{h_k\}) S_T(\tau;\{h_k\})
\]

which takes into account the fact that some part of our uncertainty on the surface state is due to the adsorbate thermodynamic state \( S_T(\tau;\{h_k\}) \). In what follows we assume that the steps do not correlate through the adsorbate \( S_T(\tau;\{h_k\}) = \sum_k S_T(\tau|h_k) \). Implicitly this means a restriction on the Hamiltonian \( H \) (see below).

The parameter \( \kappa \) is a measure of the adsorbate influence on the step distribution. In other words, \( \kappa \) is a degree of the surface quenching, such that \( \Sigma \to S_T \) as \( \kappa \to 0 \) and we return to the clean surface problem. Determination of \( \kappa \) is a separate problem that might require additional tests. For instance, comparing the surface step creation energy \( \varepsilon \) and the adsorbate binding energy excess \( \gamma \), we may estimate \( \kappa = \gamma/(\varepsilon + \gamma) \). However, in this study \( \kappa \) is taken as a parameter.

Therefore, we consider the Lagrangian

\[
\Lambda' = \Lambda + \kappa \sum_k \int dh_k P(h_k) S_T(\tau|h_k)
\]

that must be extremized. This procedure leads to

\[
P_\kappa(h_i) = \frac{e^{-\lambda_\kappa h_i^2 + \kappa S_T(\tau|h_i)}}{\int dh_i e^{-\lambda_\kappa h_i^2 + \kappa S_T(\tau|h_i)}}
\]

The multiplier \( \lambda_\kappa \) should be determined from the constraint on the roughness \( H \). The term \( \lambda_\kappa h_i^2 \) partially keeps traces of the surface preparation (a given roughness \( H \)). The second term \( \kappa S_T(\tau|h_i) \) corresponds to the adsorbate-induced effects. If \( S_T \) is an analytic function, then we may expand [22]

\[
S_T(\tau|h_i) = \sum_n A_n(\tau) h_i^n
\]

Therefore, even without resorting to any specific model, it is clear that \( P_\kappa(h_i) \) is potentially more informative than \( P(h_i) \) as the former contains higher order terms (in \( h_i \)). As is noted above, in order to obtain a similar result staring from \( S_T \), one needs additional information. Therefore, refining the entropy measure, we restore (at least partially) this information. In particular, we can calculate a global change of the surface structure in comparison to the clean surface case. This can be done using the symmetric Kullback-Leibler information measure

\[
K = \sum_i \int dh_i [P_\kappa(h_i) - P_0(h_i)] \ln \left[ \frac{P_\kappa(h_i)}{P_0(h_i)} \right]
\]

which tells us how much these two distributions are different. \( K \) is found to be

\[
K = -(\lambda_\kappa - \lambda_0)(H - H_0)
\]

where the angular brackets \( \langle \ldots \rangle_0 \) and \( \langle \ldots \rangle_\kappa \) denote the averages taken with the distributions \( P_0(h_i) \) and \( P_\kappa(h_i) \), respectively. Therefore, even if \( H = H_0 \), the global variation of the surface structure, induced by adsorption is proportional to the change of the adsorbate thermodynamic state. The state \( \langle \ldots \rangle_0 \) does not necessarily correspond to the clean surface, it could be any suitable reference state. In the same way one can estimate the information gain due to the refinement of the distribution (replacement \( P(h_i) \) by \( P_\kappa(h_i) \)). This result is quite general, it does not depend on the microscopic details underlying \( S_T(\tau|h_i) \). Nevertheless, in order to study the distribution itself we need to consider a microscopic model.

**IV. ILLUSTRATION**

In order to demonstrate what kind of local changes are induced by adsorption, as an illustration we choose one of the simplest adsorption models – the non-interacting lattice gas with a height-dependent binding energy [23,24]

\[
\mathcal{H}(\{\xi_i\}|\{h_k\}) = -\sum_i (\mu + \epsilon(h_i)) \xi_i
\]

We are aware that the model itself is quite "rough" in application to real adsorbates. It neglects the lateral interactions and, therefore, is inadequate for the description of the adsorbate critical behavior (such as liquid-gas or order-disorder transitions). Nevertheless above the critical temperature this model is qualitatively correct. In addition it is exactly solvable such that one can be sure that our implementations are not artifacts of approximations (e.g. mean field). Moreover, we do not take into account that the roughness increases the
surface area, allowing for more than a monolayer coverage [24]. Thus \( t_i = 0 \) or 1 independently of \( h_i \).

The entropy of this simplified model is given by (the role of \( \tau \) is played by the chemical potential \( \mu \))

\[
S_T(\mu|h_i) = -\theta(h_i) \ln[\theta(h_i)] - [1 - \theta(h_i)] \ln[1 - \theta(h_i)]
\]

(12)

Here the coverage is Langmuirian

\[
\theta(h_i) = \frac{L e^{\beta\epsilon(h_i)}}{1 + L e^{\beta\epsilon(h_i)}}
\]

(13)

The adsorbate activity \( L \) is related to the chemical potential \( \mu \) via \( L = \exp(\beta\mu) \), and \( \epsilon(h_i) \) is the height-dependent adsorbate binding energy.

\[
\epsilon(h) = \epsilon_0 + \gamma h_i^2
\]

(14)

A step can be viewed as a loosely coordinated site with the binding energy larger [23, 24] than that for the flat surface. Here \( \gamma \) is the binding energy excess due to the local deviation from the flat geometry. The binding to the flat surface \( \epsilon_0 \) is an irrelevant constant that can be absorbed into the definition of \( L \).

In Figure 2 \( S_T(\mu|h_i) \) is analyzed as a function of \( h_i \) and dimensionless activity \( m = \beta(\mu + \epsilon_0) \). The entropy (as a function of \( m \)) behaves in the usual way, exhibiting a single maximum at some \( m^* \) which depends on the magnitude of \( h_i \) and \( \gamma \). At relatively high adsorbate activities (\( m > 0 \)) \( S_T(\mu|h_i) \) is also single-peaked as a function of \( h_i \), with the maximum located at \( h_i = 0 \). This suggests a tendency towards random deviations from \( h_i = 0 \). This maximum transforms into a minimum when the activity changes its sign (\( m < 0 \)). Then the entropy develops two symmetric peaks at some \( |h_i^*| \) that depends on the magnitude of \( m \) and \( \gamma \). This means that the position \( h_i = 0 \) becomes unfavorable and the surface would tend to exhibit a random zig-zagging with the steps distributed near \( \pm h_i^* \). Therefore, considering \( S_T(\mu|h_i) \) as an effective potential for the step variables \( h_i \), one expects qualitative changes in the surface morphology with changing adsorbate activity \( m \).

In order to analyze (qualitatively) what this implies for the distribution \( P_\kappa(h) \), we take \( \lambda_\kappa \) as a parameter and set the normalization constant (the denominator in (8)) equal 1. Then we cannot calculate averages, but these simplifications do not change the shape of the distribution. Such a reduced \( P_\kappa(h) \) is plotted schematically in Figure 3. It is seen that with increasing \( \kappa \) the distribution changes from a gaussian (\( \kappa = 0 \)) to a tri-modal. This results from an interplay between the adsorbate-induced effects and the tendency to keep a given roughness. The curves coincide in the large-\( h \) region because the distribution is not normalized. For quantitative purposes this defect can be removed by numerical integration in eq. (8). It is clear (see Fig. 1) that the adsorbed species occupy the space of the corrugated surface layer [23]. Therefore the adsorbate is confined to a non-planar slit, whose average thickness \( T \) is determined by the surface roughness \( H \) (see Figure 1). Moreover, if \( h_i \) gives a length scale, then the surface roughness \( H \) (the average of \( \sum h_i^2 \)) is at the same time the surface area excess in comparison to a flat surface. Thus \( P_\kappa(h_i) \) can be considered as a surface area distribution. Within this analogy we make a qualitative comparison to Monte Carlo results [11] for the surface area fraction in pores with rough walls (see the insets in Figure 2). The right inset exhibits a peaked (nearly gaussian) distribution that corresponds to an empty pore. The left inset depicts the adsorbate-induced surface structure. It is seen that our approach describes quite well this physics (recall that \( \kappa \) is a measure of adsorbate-induced effects). We did not try to fit, because the models are not strictly identical. It is remarkable that our scheme is capable of inferring the surface structure even without entering the microscopic details concerning the surface. Moreover the simulation results [11] are not much sensitive to the type of adsorbate-wall interaction (hydrophilic or hydrophobic, see Fig. 5 in [11]). This suggests that the adsorbate-induced surface rearrangement is mainly an entropic effect. This is coherent with our implications.

**V. CONCLUSION**

The evolution of coupled adsorbate-substrate system is investigated in terms of a new approach combining the information theory and the standard statistical mechanics. The approach is suitable for complex systems, where, for a number of reasons, not all the microscopic details (e. g. a Hamiltonian) are available.

The approach establishes a clear correlation between the substrate morphology (e. g. roughness) and the adsorbate thermodynamic state. This implies a statistical scheme for surface characterization in the course of the adsorbate-substrate coupling, and allows one to estimate the surface morphology based on the information concerning the adsorbate thermodynamic response. One can also predict the clean surface properties based on its morphology under adsorption and vice versa.
Thus, our scheme is, in some sense, complimentary to the recent (mainly simulational) surface characterization techniques [6,11,12]. It can also be applied to analyzing the experimental data on porous adsorbents [9,10].

We would like to underline that the simple model considered here serves just as an illustration. To be more realistic in further applications we have to consider the adsorbate-adsorbate interactions and a correlation between the steps. Also, the experimentally available information ($H_0$ or $H$) is supposed to be quite crude. In many cases of real surfaces a more detailed statistics can be extracted (for instance, from STM images), for example, pair correlation $H_{ij} = \langle (h_i - h_j)^2 \rangle$. Nevertheless, for three-dimensional matrices (like aerogels) in the majority of cases only indirect measurements are available. All these features can be easily incorporated into our approach.

Apart from the practical applications, our approach seems promising in analyzing a class of coupled dynamic-stochastic systems, where the stochastic subsystem is not perfectly quenched. Particularly interesting is to study the adsorbate critical behavior under conditions when a porous matrix responds to the adsorbate thermodynamics (e.g. helium absorption in aerogels).

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[21] Note, however, that we do not implement here any specific experimental method.

[22] In general, for interacting adsorbates, the entropy expansion should contain terms like $\alpha_{ij} (h_i - h_j)^n$. Then the steps would correlate through the adsorbate, even though they were uncorrelated for the clean surface case.

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FIG. 1. A sketch of the adsorbate-substrate interface. The black dots mark the adsorption sites. The surface steps $h_i$ are defined for each site. The solid line is a reference from which all $h_i$ are counted.

FIG. 2. The conditional entropy $S_T(\mu|h_i)$ as a function of $h_i$ and dimensionless activity $m = \beta(\mu + \epsilon_0)$, $\beta\gamma = 1$.

FIG. 3. A non-gaussian step probability distribution, resulting from eq. (8) ($\lambda_a = 0.1, L = 0.1, \beta\gamma = 2$). The insets demonstrate the Monte Carlo results [11] for the surface area fraction in pores with rough walls.
Figure 1
FIGURE 2
Figure 3