Defect-induced perturbations of atomic monolayers on solid surfaces

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We study long-range morphological changes in atomic monolayers on solid substrates induced by different types of defects; e.g., by monoatomic steps in the surface, or by the tip of an atomic force microscope (AFM), placed at some distance above the substrate. Representing the monolayer in terms of a suitably extended Frenkel-Kontorova-type model, we calculate the defect-induced density profiles for several possible geometries. In case of an AFM tip, we also determine the extra force exerted on the tip due to the tip-induced dehomogenization of the monolayer.

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Equilibrium properties of monolayers adsorbed on ideal, defect-free solid surfaces are by now reasonably well understood through a series of experimental and theoretical works [1]. However, most of naturally encountered surfaces or surfaces involved in technological processes cannot be considered as ideal and do contain different types of defects, such as, e.g., chemisorbed or adsorbed species, or surface steps. Experimentally, it has been well known that such defects may have a profound effect, both on the adsorption kinetics and on the equilibrium morphology of the resulting layers. In particular, point defects often constitute nucleation sites for the adsorbates and serve as seeds for island formation [2]. On the other hand, in the presence of a monoatomic surface step the adatoms on the lower terrace are generally attracted towards the step, which causes their redistribution within the layer, as observed, for instance, via intensity oscillations of thermal He scattering at grazing incidence in the form of the discrete row growth of Xe on stepped substrates [3,4]. Theoretically, the impact of the surface steps on the adatom distribution was studied within the framework of two-dimensional (2D) lattice-gas-type models [5,6]. These models have been analyzed numerically and have revealed inhomogeneous density profiles with an enhanced density close to the lower step edges. To the best of our knowledge, however, the analytical solution of the problem is still lacking.

On the other hand, probing of the monolayer properties by different experimental techniques, such as, e.g., the scanning tunneling microscope (STM) or atomic force microscope (AFM) measurements, may itself incur morphological changes into the adlayer. The interaction of the adatoms with the AFM tip might cause their displacement from the adsorption sites. Such deformations have been predicted for solid surfaces themselves [7] and were indeed observed in molecular dynamics simulations [8]. The adatoms are, of course, even more vulnerable to the presence of the AFM tip, since they are not so strongly connected as the atoms of the solid. Indeed, it has been demonstrated that the SFM tip can be used to ''drag'' single atoms or molecules on metal surfaces [9–12]. Moreover, it has been observed in recent experiments [13] that the apparent thickness of the prewetting film on a silicon wafer measured by the AFM is larger as that found by an x-ray reflectivity experiment. The authors thus concluded that the AFM tip distorts the film and induces a ''bump'' in its surface. At sufficiently high temperatures, even stronger effects such as the formation of a neck between the adsorbate and the tip have been observed [14]. Usually, such a distortion of adlayers is unaccounted for while interpretating the experimental data, although its effect might be not negligible — ''condensation'' of the adlayer particles in the vicinity of the tip would increase the force exerted by the monolayer on the AFM tip. Thus, the question arises of how to interpret the AFM measurements adequately and how to extract, in a reliable fashion, the pertinent parameters (say, the Hamaker constants) in the case when some adsorbate is present on the solid surface.

In this paper, we study perturbations of atomic monolayers on solid substrates induced by *immobile* defects of different types. The monolayer is described using a 2D version of the Frenkel-Kontorova (FK) model, i.e., we view it as a 2D network of particles connected by harmonic springs in a spatially periodic potential. Note that the original FK model (a harmonic chain in a spatially periodic potential) was introduced more than 60 ago in order to describe the motion of a dislocation in a crystal [15]. In the meantime, variants of this model were applied to many different problems including charge density waves [16], sliding friction [17,18], ionic conductors [19,20], and chains of coupled Josephson junctions [16,21]. A 2D version of the FK model has been introduced by Uhler and Schilling to study glassy properties of an adsorbed atomic layer [22].

We consider first the case of a surface with a monoatomic step focusing on two opposite limits: (a) monolayers with strong intralayer coupling and negligible interactions with the substrate (smooth structureless surface) and (b) monolayers in which coupling to the substrate dominates the particle-particle interactions. As a second example, we calculate the perturbation of a monolayer induced by an immobile AFM tip and demonstrate how it modifies the force exerted on the tip.

Note that considering the simplified case with an immobile AFM tip allows us to determine explicitly inhomogeneous density profiles as well as to elucidate the physics behind this effect. In ''real stuff'' experiments the tip, of

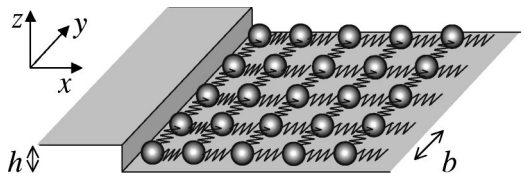

FIG. 1. Atomic monolayer at a steplike defect of height h. The particles are attracted towards the step and the monolayer is perturbed accordingly (see text for details).

course, moves and the situation is fairly more complex since the density profiles are nonstationary. One expects that for moderate tip velocities the ''condensed'' region in the monolayer would travel together with the tip exerting some frictional force on it. For larger velocities, such a condensed region would not have enough time to be formed and the monolayer should remain homogeneous. One expects hence the existence of a threshold tip velocity below which the monolayer has time to reorganize itself leading to an extra force and above which this effect disappears, a type of force-velocity relation that is somewhat reminiscent of ''solid friction'' behavior. A qualitatively similar behavior has been predicted by Raphael and de Gennes [23] for a system involving a charged particle moving at a constant speed a small distance above the surface of an infinitely deep liquid. The situation with a stationary moving AFM tip will be discussed elsewhere [24].

We constrain ourselves here to the limit of the localized adsorption [1] and suppose that the adatoms always remain in close contact to the surface, such that their defect-induced displacements in the vertical direction (perpendicular to the surface) are negligibly small. For simplicity, we assume that the adatoms form a regular square lattice. Each particle is labeled by two integers (n,m) with $n,m=0,\pm1,\pm2,\ldots$. For small perturbations of the monolayer the interaction between a given atom (n,m) and its four neighbors $(n-1,m)$, $(n+1,m)$, $(n,m-1)$, and $(n,m+1)$ can be represented by Hookean springs that connect each atom to its neighbors. The value of the effective spring constant K follows from the expansion of the interaction potential between atoms near the equilibrium distance and is typically of the order of a few tenths of eV/Å^2 [18]. In the absence of any external perturbation the position of atom (n,m) is given by the two-dimensional vector $\mathbf{r}_{nm}=(x_{nm},y_{nm})=(bn,bm)$ with b being the equilibrium distance between atoms. In the following, we calculate the defect-induced displacements $\mathbf{a}_{nm}=(\xi_{nm},\eta_{nm})$ of the adatoms.

First we consider the equilibrium properties of a monolayer near a steplike defect (Fig. 1). The substrate has the height $z=0$ for $x>0$ and $z=h$ for $x\leqslant 0$. We focus on the monolayer on the lower terrace $(x>0)$. A given small volume element dV of the substrate is assumed to exert a force $d\mathbf{f}=-a\,dV r^{-(\alpha+1)}\hat{\mathbf{r}}$ on a particle in the monolayer at a distance r apart; here a is a constant, $\alpha+1$ is an arbitrary positive number, and $\hat{\mathbf{r}}$ is the unit vector in the $\mathbf{r}$ direction. In the absence of a step, $h=0$, the interaction of any atom with the substrate is isotropic with respect to rotations around the Z axis. Hence, by summing over all forces between a given atom and the substrate one finds only a force perpendicular to the surface but no tangential component. In this case the monolayer is unperturbed. On the other hand, a step of height $h>0$ results in net forces to the left for atoms to the right of the step. Consider an atom at $\mathbf{r}=(x,y,z)=(D>0,y,0)$. The net force follows from integration over the additional slab of material:

$$f^{(step)}(D)=a\int dV\frac{x}{(x^2+y^2+z^2)^{\alpha/2+1}}\simeq -C_\alpha\frac{ah}{D^{\alpha-1}} \tag{1}$$

with $C_\alpha=\sqrt{\pi}\Gamma[(\alpha+1)/2]/[(\alpha-1)\Gamma(1+\alpha/2)]$, where $\Gamma(z)$ is the Gamma function. The right hand side of Eq. (1) holds for $\alpha>1$ and $h\ll D$. The first condition is needed to insure that $f^{(step)}$ remains finite. The second condition is fulfilled for small step heights (e.g., monoatomic steps, $h\sim b$).

The positions of the atoms obey the force balance equation $x_{n+1,m}-2x_{nm}+x_{n-1,m}=-K^{-1}f^{(step)}(x_{n,m})$ that can be rewritten using continuous variables n and m as: $\partial^2 x_n/\partial n^2=(C_\alpha ah/Kx_n^{\alpha-1})$. We drop here the m dependence since the problem is apparently symmetric in the Y direction; x_n $(n=1,2,\ldots)$ denotes the x position of the nth row of atoms in the monolayer. We denote by $\xi_n=x_n-bn$ the displacement of the nth row. Assuming in the following a weak perturbation of the monolayer, $\xi_n\ll b$, we are led to

$$\frac{\partial^2\xi_n}{\partial n^2}\simeq\frac{C_\alpha ah}{Kb^{\alpha-1}}\frac{1}{n^{\alpha-1}}, \tag{2}$$

which yields

$$\xi_n\simeq\frac{C_\alpha ah}{\alpha(\alpha+1)Kb^{\alpha-1}}\frac{1}{n^{\alpha+1}}+B=\frac{l}{n^{\alpha+1}}+B, \tag{3}$$

where l has the dimension of length. The exact position of the first row (and therefore the value of the constant B) depends on its specific interaction with the step. One may, for simplicity, assume $\xi_1=0$ and thus $B=-l$. Note that due to the ''coupling'' of the different rows the displacement ξ_n increases with n approaching the limiting value $B=-l$. For $\alpha=6$ (van der Waals interaction), we find from Eq. (3) $\xi_n\simeq(\pi/480)(ah/Kb^5)(n^{-7}-1)$.

The density of adatoms follows $\rho_n=b^{-1}\partial n/\partial x_n\simeq b^{-2}(1-b^{-1}\partial\xi_n/\partial n)$, which leads to

$$\rho_n\simeq b^{-2}\left(1+\frac{C_\alpha ah}{\alpha Kb^\alpha}\frac{1}{n^\alpha}\right), \tag{4}$$

i.e., a long-range algebraic relaxation to the unperturbed density. For $\alpha=6$, we find $\rho_n\simeq b^{-2}(1+(\pi ah)/[96K(bn)^6])$. The density has its maximal value at the step and decreases with increasing n.

Up to now, we assumed only an intralayer interaction between atoms in the monolayer. The role of the supporting substrate was only to restrict the motion of the atoms in the XY plane. Now we study the case of *strong coupling to the*

substrate. We assume next that each particle in the monolayer is attached to the substrate via a spring with the spring constant $\tilde{K}$ at the equilibrium position $\mathbf{r}_{nm}=(x_{nm},y_{nm})=(\tilde{b}n,\tilde{b}m)$ ($\tilde{b}$ might be considered to be the lattice constant of the substrate). We neglect interactions between neighboring beads, i.e., we set $K=0$. Then the displacement of the particle rows is obtained directly from the force balance equation $\tilde{K}\xi_n \simeq f^{(step)}(\tilde{b}n)$. We find then

$$\rho_n \simeq \tilde{b}^{-2}\left(1-\frac{C_\alpha a h}{(\alpha-1)\tilde{K}\tilde{b}^\alpha}\frac{1}{n^{\alpha-2}}\right). \tag{5}$$

The perturbation of a monolayer with strong intralayer coupling (and negligible coupling to the substrate) is fundamentally different from the case of strong coupling to the substrate. In the first case — due to the connectivity of the rows — the displacement of each row adds up and the largest displacement, l (in negative X direction), is approached for large n-values, i.e., far from the step [cf. Eq. (3)]. In the latter case the displacement is directly proportional to the exerted force which decays algebraically with increasing distance and $\xi_n \to 0$ for $n\to\infty$. This is also reflected in the density profile. The density of the monolayer with intralayer coupling, Eq. (4), has its largest value close to the step and decays towards the unperturbed value b^{-2} for large n. On the other hand, monolayers coupled to the substrate show a slight depletion ($\rho_n < \tilde{b}^{-2}$) close to the step, cf. Eq. (5). Only very close to the step (first row of atoms) the density is enhanced accordingly. The general case with nonvanishing K and $\tilde{K}$ is highly nontrivial (e.g., in view of possible commensurate-incommensurate transitions) and is beyond the scope of the present paper.

We study next the perturbation of the monolayer by an AFM tip located at height H above the ''central'' atom $n=m=0$. We assume that the interaction energy between the tip and a particle at distance d apart is of the form $w(d)=-Ad^{-\alpha}$, which yields

$$\mathbf{f}_{nm}^{(AFMtip)} = -\frac{A\hat{\mathbf{r}}_{nm}}{d_{nm}^{\alpha+1}}, \tag{6}$$

where $d_{nm}=|(x_{nm},y_{nm},H)|$ and $\hat{\mathbf{r}}_{nm}$ is the 2D unit vector $(x_n,y_n)/|(x_{nm},y_{nm})|$.

The calculation of the elastic force in a monolayer with intralayer coupling is nontrivial, since the equilibrium distance of each spring has a nonvanishing value $b>0$. For $b=0$ the elastic force is simply given by the Laplacian: $\mathbf{f}_{nm}^{(spring)}=K(\partial^2/\partial^2 n+\partial^2/\partial^2 m)\mathbf{r}_{nm}$. For $b>0$ the X and Y direction are coupled in a nontrivial way. However, the elastic response to small perturbations $\mathbf{a}_{nm}=(\xi_{nm},\eta_{nm})$ with $|\mathbf{a}_{nm}| \ll b$ decouples in the X and Y directions:

$$\mathbf{f}_{nm}^{(spring)} \simeq K\left(\frac{\partial^2\xi_{nm}}{\partial n^2},\frac{\partial^2\eta_{nm}}{\partial m^2}\right). \tag{7}$$

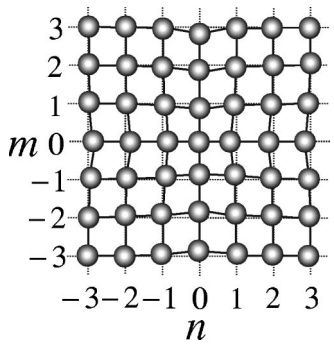

FIG. 2. View from above on a monolayer close to an AFM tip. The tip is located at the height H above the central atom ($n=m=0$); see text for details.

The particle positions follow from the balance between the tip-monolayer interaction, Eq. (6), and the elastic force, Eq. (7), which gives

$$\frac{\partial^2\xi_{nm}}{\partial n^2} \simeq \frac{A}{Kb^{\alpha+1}}\frac{n}{(n^2+m^2+\gamma^2)^{\alpha/2+1}}, \tag{8}$$

where we have introduced the dimensionless parameter $\gamma=H/b$. Further on, the displacement ξ_{nm} has to be calculated for each α separately. For $\alpha=6$ (van der Waals forces), for instance, one finds

$$\xi_{nm} \simeq \frac{-A}{48Kb^7}\left[n\frac{3n^2+5(m^2+\gamma^2)}{(m^2+\gamma^2)^2(n^2+m^2+\gamma^2)^2} + \arctan\left(\frac{n}{(m^2+\gamma^2)^{1/2}}\right)\frac{3}{\sqrt{m^2+\gamma^{25/2}}}\right]. \tag{9}$$

Note that $\mathbf{a}_{nm}$ is *not* radial-symmetric around ($n=0,m=0$) even though it is induced by a radial-symmetric force, Eq. (6). In fact, for large n $\xi_{nm}\propto n^0$ for $m\equiv 0$ (X direction) and $\xi_{nm}\propto n^{-5}$ for $m=n$ (diagonal direction). Such a nonisotropy appears due to the symmetry of the underlying lattice (see Fig. 2).

For small deformations the density profile of the monolayer is given by

$$\rho_{nm} \simeq \frac{1}{b^2}\left(1-\frac{2A}{\alpha K b^{\alpha+2}}\frac{1}{(n^2+m^2+\gamma^2)^{\alpha/2}}\right). \tag{10}$$

Note that here, however, despite the asymmetry of $\mathbf{a}_{nm}$, the resulting density profile, Eq. (10), recovers the symmetry of the force exerted by the tip.

We calculate next the force F that the monolayer exerts on the AFM tip. Due to the symmetry this force is pointed into the negative Z direction. A particle at (x,y) contributes to this force by $f_Z^{(AFMtip)}(x,y)=-A/Hd^{\alpha+2}$. The total force F from the monolayer follows by summing up over all atoms, $F=F_0+\Delta F$, where F_0 is the force that an unperturbed monolayer would exert on the AFM tip, $F_0=-2\pi A/\alpha b^2 H^{\alpha-1}$, while ΔF denotes the contribution due to the self-induced perturbation by the monolayer ΔF

$=-2\pi A^2/\alpha^2 K b^4 H^{2\alpha-1}$. Note that $\Delta F/F_0=-F_0/2\pi KH$, i.e., the induced additional force is important for soft monolayers (small K) and strong tip-sample interactions. For the case, $\alpha=6$ the two contributions to the force are given by $F_0\simeq -(\pi/3)(A/b^2H^5)$ and $\Delta F\simeq-(\pi/18)(A^2/Kb^4H^{11})$.

We consider now the effect of small surface corrugations of the form $U^{(surf)}(x,y)=\varepsilon U_0\cos(kx)\cos(ky)$ on the positions of the atoms in the monolayer as well as on the force on the AFM tip. Here k denotes the wave vector of the periodic substrate and ε is a small number, $\varepsilon\ll 1$. From the potential follows the force that acts on a particle at (x,y): $F_X^{(surf)}(x,y)=-\partial U^{(surf)}(x,y)/\partial x$. We calculate the additional displacement due to the corrugations using the ansatz $\xi_{nm}=\xi_{nm}^{(0)}+\varepsilon\xi_{nm}^{(1)}$. This leads to $\partial^2\xi_{nm}^{(1)}/\partial n^2 \simeq -F_X^{(surf)}(bn,bm)/K$. Hence,

$$\varepsilon\xi_{nm}^{(1)}\simeq\frac{\varepsilon U_0}{b^2kK}\sin(kbn)\cos(kbm). \tag{11}$$

As a result of this additional perturbation the force on the AFM tip will be modified, $F=F^{(0)}+\varepsilon F^{(1)}$ with $F^{(0)}=F_0+\Delta F$ given above. We give here explicitly the asymptotic forms of $F^{(1)}$ for the case $\alpha=6$:

$$F^{(1)}\simeq\begin{cases}\dfrac{\pi}{3}\dfrac{AU_0}{b^4KH^5} & \text{for } kH\ll 1\\[2ex] \dfrac{\pi^{1/2}}{2^{1/4}12}\dfrac{AU_0k^{5/2}}{b^4KH^{5/2}}e^{-\sqrt{2}kH} & \text{for } kH\gg 1.\end{cases} \tag{12}$$

It can be seen from Eq. (12) that the contribution from surface corrugations is ''screened''when the height H of the AFM tip exceeds the wavelength k^{-1} of the corrugations. We dispense with giving a discussion of the case of strong coupling to the substrate which can be calculated straightforwardly.

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