Prediction of reconstruction in heteroepitaxial systems using the Frenkel-Kontorova model

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Many heteroepitaxial metal-on-metal systems reconstruct into patterns of alternating domains of stacking faults separated by partial misfit dislocations. Here, we use two approaches to investigate the question of whether these can be predicted and controlled: (i) We map the system onto a one-dimensional Frenkel-Kontorova model, and then obtain a simple criterion to determine whether or not the surface will reconstruct; this had earlier been done for homoepitaxial systems, but is here generalized to the heteroepitaxial case. (ii) The two-dimensional Frenkel-Kontorova model is solved numerically by performing quenched molecular dynamics simulations. The necessary microscopic parameters are obtained by performing *ab initio* density functional theory calculations on the unreconstructed systems. The systems considered are overlayers of Fe, Co, Pt, Ag, Au, and Pb on a Ru(0001) substrate, as well as clean Ru(0001). The predictions of the two approaches agree with one another as well as with experiment. Both the presence and periodicity of the reconstruction are very sensitive to the value of "chemical potential" Γ. Accordingly, we suggest that Γ can be used to tune the periodicity so as to obtain a desired nanotemplate for subsequent growth of self-organized nanostructures.

I. INTRODUCTION

Residual stresses present at bulk-truncated solid surfaces can be the driving forces for surface reconstruction, dislocation formation, or alloying.[1,2] In the case of clean metals, the reduced coordination number of surface atoms induces a tensile stress which favors a lower interatomic spacing as compared to that of the bulk. It is well known that the surface of Au(111) undergoes a herringbone reconstruction,[3–5] and that Pt(111) prefers to form an ordered dislocation network at high temperatures[6] or in the presence of a supersaturated Pt vapor.[7] In the case of heteroepitaxial systems, stress is induced by lattice mismatch between the substrate and the overlayer. Depending on the sign of this mismatch, stress relief can be achieved by either an increase or a decrease in the atomic density of overlayer atoms, relative to the substrate, leading to a compressive or expansive reconstruction, respectively. Different types of such reconstructions have been observed, e.g., stripes, triangles, and rotated domains.[8] Since these patterned surfaces can be used as templates for the bottom-up assembly of self-organized nanostructures, a need for prediction of reconstruction, as well as control over it, has emerged.

While *ab initio* density functional theory (DFT) calculations are perhaps the most reliable predictive theoretical tool available today, these reconstructions typically have very large unit cells, which makes the computational cost of treating such systems with these methods generally prohibitive, though there have been some recent successful attempts along these lines.[9] For this reason, as well as for gaining insight into the operative physical mechanisms, it is useful to have models (perhaps with some input from DFT) that can provide guidelines toward predicting and controlling reconstructions of this sort. Among various models that have been proposed,[10] the Frenkel-Kontorova (FK) model is one of the simplest and most widely used.[11–15] In addition to being less computationally intensive than DFT calculations, the FK model can often provide greater physical insight; it captures in a simple

way the different microscopic mechanisms at the origin of surface reconstruction: interactions between surface atoms, interactions between surface and substrate atoms, and the cost in energy to change the density of the overlayer. For clean surfaces, a combined effect of these three interactions is represented by a dimensionless parameter R which maps the two-dimensional character of surface reconstruction onto a one-dimensional FK model.[16] While this parameter has been shown to work rather well for homoepitaxial systems,[15,17] so far, heteroepitaxial systems have been studied instead by quenched molecular dynamics (QMD) simulations of a two-dimensional Hamiltonian.[18–21]

In this paper, we extend the discussion to the validity of R as an indicator of reconstruction for heteroepitaxial systems. For six different systems consisting of overlayer elements O on a Ru(0001) substrate, we compare the behavior predicted by the simple indicator R with results from experiment and QMD simulations using a two-dimensional Frenkel-Kontorova model.

II. ONE-DIMENSIONAL FRENKEL-KONTOROVA MODEL AND THE R PARAMETER

The Frenkel-Kontorova model[11] is a simple, analytically solvable model that can be used to describe, for example, the operative physics at the surface of a homoepitaxial or heteroepitaxial system. The overlayer is described by a one-dimensional chain of atoms connected to each other by harmonic Hooke's springs of natural bond length b and spring constant μ. The substrate is modeled as a sine wave potential of amplitude W and period a. Thus, there are two competing periodicities in the system, a and b. Except in situations when the wells of the substrate potential are either very shallow or very deep compared to the stiffness of the springs, the stable solutions of the system correspond to a periodic array of misfit dislocations; in surface science terminology, these correspond to a surface reconstruction.

Of course, real surface systems are two-dimensional (2D). Mansfield and Needs[16] mapped such 2D surface systems onto the one-dimensional (1D) FK model, and suggested that a dimensionless parameter R, which involves a combination of the surface energy, the surface stress, the stiffness of nearest-neighbor bonds, the nearest-neighbor distance, and the amplitude of the substrate potential, can serve as an indicator of whether or not the surface would reconstruct. These quantities can all be simply obtained from *ab initio* calculations.

In their original paper, Mansfield and Needs found that R was not entirely reliable as a predictor of reconstruction; in particular, it seemed to predict that the Au(111) surface would not reconstruct, whereas it is well known that this surface reconstructs. At the time of their work, it was not clear whether this was because of the simplifying assumptions made in mapping the surface system onto a 1D FK model, or whether the *ab initio* numbers input into the evaluation of R were at fault, since due to the limitations of computational power then available, further approximations were made in the numerical evaluation of the relevant quantities. Subsequently, Crljen *et al.*[17] and Pushpa and Narasimhan[15] showed that R does, in fact, work remarkably well as a predictor of whether or not a number of (111) faces of face-centered-cubic (fcc) metals will reconstruct. Thus, it appears that mapping the two-dimensional surface system onto a 1D FK model works well, at least for homoepitaxial systems.

We now generalize this to the case of heteroepitaxy. For the case where an overlayer is deposited on the (111) surface of an fcc metal, or the (0001) surface of an hcp metal, the formula derived for the case of homoepitaxy[15,16] can be modified as follows:

$$R = \frac{\sqrt{3}\pi a \left(\gamma_i - \frac{4}{3}\sigma\right)}{8\sqrt{\mu W}};\qquad (1)$$

here a is the nearest-neighbor (NN) distance on the substrate, μ is the spring constant for NN bonds between atoms in the overlayer (in the presence of the substrate), σ is the surface stress, γ_i is the interface energy (defined more precisely in the next section), and W is the amplitude of the substrate potential. This formula is identical to that for the homoepitaxial case, except that the surface energy γ has been replaced by the interface energy γ_i. If $|R| < 1$, the heteroepitaxial system will remain stable against reconstruction; i.e., the overlayer atoms will remain at pseudomorphic positions. However, if $R < -1$, there will be a compressive reconstruction; i.e., the density of overlayer atoms will be greater than the density of atoms in the topmost substrate layer. In contrast, if $R > 1$, the system will display an expansive reconstruction in which the density of overlayer atoms will be reduced relative to the density of atoms in the topmost substrate layer.

III. *AB INITIO* CALCULATIONS

In order to obtain input quantities for the 1D FK model described above, as well as for the 2D FK model discussed later below, we have performed *ab initio* calculations within the framework of density functional theory. The systems we have considered consist of an overlayer O on the Ru(0001) substrate, where the overlayer O consists of atoms of one of the elements Fe, Co, Pt, Ag, Au, and Pb. The NN distances of

bulk Fe and Co are less than that of bulk Ru, while those of bulk Pt, Au, Ag, and Pb are larger; one would therefore expect that the first two elements might possibly display a compressive reconstruction, while the latter four could conceivably display an expansive reconstruction. We have also considered the homoepitaxial case of a clean Ru(0001) surface.

We have used the PWscf code of the QUANTUM-ESPRESSO package[22] which uses a plane-wave basis set together with ultrasoft pseudopotentials.[23] For the exchange-correlation functional, we have used the generalized-gradient approximation of the Perdew-Burke-Ernzerhof form.[24] Spin polarized calculations are performed for those cases where the overlayer atoms are magnetic, i.e., for Fe and Co on Ru(0001). The plane-wave cutoff energies for wave functions and charge densities are taken to be 20 Ry and 160 Ry, respectively.

We have used a supercell approach to model a surface within periodic boundary conditions. Some calculations have been performed using a supercell consisting of a slab with six Ru layers stacked along the (0001) or z direction, and one pseudomorphic O overlayer, as well as seven layers of vacuum, which corresponds to a vacuum spacing of around 17.4 Å. The overlayer and three adjacent Ru layers are allowed to relax in the z (surface-normal) direction using Hellmann-Feynman forces, whereas the three bottom Ru layers are kept fixed at the bulk separation. Other calculations have been performed using a supercell with a symmetric slab, consisting of six Ru layers with an O overlayer deposited on both sides. We have used an (8×8) Monkhorst-Pack k-point grid[25] in the surface Brillouin zone. Convergence is aided by making use of the Methfessel-Paxton smearing technique,[26] with the smearing width set equal to 0.05 Ry.

The calculated value for a, the nearest-neighbor distance on the Ru substrate, is 2.74 Å. This is close to the experimentally reported value of 2.70 Å. In order to compute W, the amplitude of the substrate potential, we have considered four lateral positions of the overlayers relative to the substrate: at face-centered-cubic (fcc), hexagonal-closed-packed (hcp), bridge, and atop sites; all distances along z are then allowed to relax. We note that when evaluating the energy at a bridge site, it is important not to permit transverse relaxations—otherwise, the system may relax to a minimum energy configuration rather than the saddle point energy that is of interest to us. For all the elements under study, we find that the atop site has the highest energy, whereas either the fcc or the hcp site is the most favored site. In particular, we find that for $O =$ Au, Ag, or Pb, the overlayer atoms preferentially occupy the fcc sites, whereas for $O =$ Fe, Co, or Pt, they prefer to sit at the hcp sites. For the clean Ru(0001) surface, the topmost surface layer prefers to continue the bulk stacking sequence and occupy the hcp site. W is then given by the absolute energy difference between the energy of the bridge site, V_P, and the most favored site, $V_{\min}$; i.e., $W = |V_P - V_{\min}|$. In Table I, we list the results, from *ab initio* calculations, for the relative stacking energies V_A, V_B, V_C, and V_P when the overlayer atoms occupy hcp, atop, fcc, and bridge sites, respectively (the zero of energy has been set as the lowest energy stacking position).

For obtaining the spring constant μ, we calculate the surface stress not only when the substrate lattice constant is at a, but also when the entire system is laterally compressed or expanded. In order to do this, one has to subtract out the

TABLE I. Stacking fault energies when the overlayer atoms O on an O/Ru(0001) slab occupy different stacking sites, as obtained from *ab initio* calculations. The relative energy has been calculated with respect to the energy of the most favored site for that particular system. Morse potential parameters obtained for the overlayer O/Ru(0001) are given in the last three columns.

Overlayer Element	Stacking Fault Energies (meV)				Morse Potential Parameters		
O	V_A hcp	V_B atop	V_C fcc	V_P bridge	A_0 (eV)	A_1 (Å^{-1})	b (Å)
Ru	0.0	554.1	125.1	401.6	2.9005	1.185	2.70
Fe	0.0	541.4	55.9	79.8	1.4111	0.997	2.65
Co	0.0	563.6	88.1	217.6	1.0608	1.450	2.52
Pt	0.0	178.3	3.8	112.7	1.1061	1.656	2.78
Ag	4.9	268.6	0.0	58.3	0.5449	1.588	2.89
Au	7.3	195.9	0.0	54.1	0.7165	1.684	2.86
Pb	1.8	202.0	0.0	36.7	0.6706	1.336	3.26

contribution to the stress from substrate layers; this procedure has been described by us in earlier work.[27] One then fits the results for the surface stress versus in-plane lattice constant to obtain the NN interaction between overlayer atoms; we assume that this has the form of a Morse potential, viz., $V(r) = A_0\{1 - \exp[-A_1(r - b)]\}^2$. We have tabulated values of A_0, A_1, and b for the six systems considered here, in Table I. The values listed here differ somewhat from those used in our previous publication,[27] because two slightly different procedures were used in the two cases to extract the parameters: In one case, the first interlayer distance was relaxed at each in-plane lattice constant, while in the other, it was held fixed at the value corresponding to the substrate lattice constant; we believe that these two procedures (in both of which the substrate and overlayer are compressed or stretched together) constitute limiting approximations to the "true" values desired,[28] in which only the overlayer is stretched or compressed. The latter types of calculations are difficult to carry out because the overlayer then becomes incommensurate with the substrate and the system thus becomes unamenable to the kinds of calculations using periodic boundary conditions that we carry out; we have estimated, using test calculations, that the errors introduced by this alternative procedure are small, of the order of a few % in the values of force constant k and ~0.02 Å in favored interatomic spacing b. The spring constant μ is then given by $2A_0A_1^2$.

Finally, the interface energy γ_i is obtained, from calculations on a symmetric slab, as follows:

$$\gamma_i = \frac{E_{\text{slab}} - N^O E^O_{\text{bulk}} - N^S E^S_{\text{bulk}}}{2A}, \quad (2)$$

where E_{slab} is the total energy of the slab containing N atoms and having surface area A, and N^O and N^S are the number of overlayer (O) and substrate (Ru) atoms respectively in the slab supercell. E^O_{bulk} and E^S_{bulk} are the total energies per atom of, respectively, the overlayer and the substrate, in their bulk phases. Note that this interface energy γ_i includes not only the "surface" energy contribution for the overlayer atoms, but also the elastic contribution due to the overlayer having been either stretched or compressed to the lattice constant of the substrate.

TABLE II. Results from *ab initio* calculations for the parameters needed to evaluate the reconstruction criterion R, for the heteroepitaxial systems O/Ru(0001), and the value obtained for R, using these. The interface energy γ_i, the surface stress σ, and spring constant μ are in eV/Å^2, and W, the amplitude of the substrate potential, is in eV. R is dimensionless.

O	γ_i	σ	μ	W	R
Ru	0.173	0.222	8.139	0.402	−0.05
Fe	0.196	0.139	2.801	0.080	0.04
Co	0.181	0.396	4.464	0.218	−0.66
Pt	0.100	−0.138	6.068	0.113	0.64
Ag	0.146	−0.371	2.748	0.058	2.99
Au	0.120	−0.424	4.064	0.054	2.73
Pb	0.380	−2.212	2.394	0.037	21.0

In Table II, we give our results, from *ab initio* calculations, for the quantities γ_i, σ, μ, and W that are needed in order to evaluate R, as well as the corresponding values obtained for R. The convention used is that positive/negative values represent tensile/compressive surface stresses. Note that a simple eyeballing of any of these quantities in isolation is not sufficient to predict whether or not an overlayer will remain pseudomorphic. Thus, for example, the Co/Ru(0001) system exhibits a rather large value of tensile surface stress σ and relatively stiff springs, which might seem to suggest that this system would be likely to reconstruct. However, this is offset by the fact that the wells of the substrate potential are also rather deep in this system—much more so than any of the other heteroepitaxial systems considered here. These two factors are in competition. For the homoepitaxial Ru(0001) system, the first number in this table corresponds to the value of the surface energy; it is in reasonable agreement with values obtained by previous authors.[29–32]

Upon examining the values of R in Table II, we find that our values suggest that monolayers of Fe, Co, and Pt on Ru(0001) will not reconstruct, whereas those of Ag, Au, and Pb will do so. Also, the clean Ru(0001) surface will not reconstruct. These results are in accordance with experimental information (where available). We discuss this at greater length in Sec. V below. In the heteroepitaxial cases, based on the atomic-size mismatch, one would expect a negative R for Fe and Co and a positive R for the remaining elements. This is indeed the case, except for Fe/Ru(0001) where R is, however, very close to zero; the reason for the slight discrepancy is discussed further below. For Pb/Ru(0001), the value of R is vary large and thus the tendency toward reconstruction of this system is expected to be strong. Also, given that the "atomic size" for surface atoms is expected to be smaller at a metal surface than in the bulk, one would expect to get a negative R for Ru(0001), which is indeed the case.

Finally, we wish to calculate the cohesive energies for the overlayer elements, as well as the adsorption energies of adatoms on these heteroepitaxial systems. This is because, as discussed further below, when the density of overlayer atoms is changed, as happens when the overlayer reconstructs, the most likely reservoir or sink for the additional or removed overlayer atoms that are needed in order to change the density are such adatoms. In order to calculate the energetics of such

TABLE III. The adsorption energies of adatoms on the heteroepitaxial systems under study and cohesive energies for all the overlayer elements.

	Fe	Co	Pt	Ag	Au	Pb
E_{ad} (eV/atom)	−4.02	−4.42	−3.75	−1.39	−1.43	
E_c (eV)	5.28	5.54	5.72	2.51	2.98	2.93

adatoms, we consider a (3×3) O/Ru(0001) surface unit cell, containing in addition a single O adatom. We then calculate the adsorption energy for the adatom using

$$E_{ad} = E(O_{ad}/O/\text{Ru}(0001)) - E(O/\text{Ru}(0001)) - E(O_{\text{iso}}), \quad (3)$$

where $E(O_{ad}/O/\text{Ru}(0001))$ is the total energy for the adatom adsorbed on the O/Ru(0001) system, $E(O/\text{Ru}(0001))$ is the total energy for the O/Ru(0001) system and $E(O_{\text{iso}})$ is the energy of an isolated O atom in the vacuum. The cohesive energy, E_c, is defined, as usual, as the difference between the energy per atom in the gas phase, E_{iso}, and in the bulk phase, E_{bulk}. The values for the adsorption energies and cohesive energies for the systems under study are tabulated in Table III. We were unable to obtain a stable adsorption geometry for a Pb adatom adsorbed on a Pb monolayer on Ru(0001). The source of this instability is presumably the higher compressive stress in Pb/Ru(0001). For this reason, we do not present results for E_{ad} for Pb in Table III.

IV. 2D GENERALIZED FRENKEL-KONTOROVA MODEL: QUENCHED MOLECULAR DYNAMICS SIMULATIONS

In this section, we wish to accomplish the following things: We want to study the reconstruction of the system actually in two dimensions (rather than in one dimension as was done above), while using realistic forms of the substrate potential as well as the interatomic potential between overlayer atoms. Then, we want to see whether it is possible to switch the system between reconstructive and unreconstructive behavior, for example by tuning the chemical potential Γ (defined further below); a similar effect can be achieved in electrochemical situations by controlling the potential. We would also like to see whether the values of Γ that fall within the range where one can have some control over the reconstruction seem to be in accordance with achievable values estimated from our *ab initio* calculations. When reconstruction occurs, we wish to obtain some estimate of the changes in density achievable. In this, we are motivated by the fact that such reconstructed heteroepitaxial systems can sometimes be used as templates for the growth of self-organized nanostructures, with the periodicity of the reconstruction determining the repeat distance of the self-organization.

The system we wish to model consists of a 2D triangular lattice of overlayer atoms placed upon a 2D substrate. As for the 1D FK model, there are interactions V_{OO} between overlayer atoms, and V_{OS} between the overlayer and substrate. The Hamiltonian of the system is then given by

$$H = \sum_i V_{OO}(l_i) + \sum_j V_{OS}(\mathbf{r}_j) + \sum_j \Gamma, \quad (4)$$

where i runs over all nearest-neighbor bonds of length l_i between overlayer atoms, j runs over all overlayer atoms at positions $\mathbf{r}_j$, and the last term is the contribution from the chemical potential. V_{OO} is given by the Morse potential form described in the previous section. The substrate potential V_{OS} at arbitrary coordinates (x, y) is obtained by Fourier interpolation between the values at the fcc, hcp, bridge, and atop sites reported in Table I,[12,15] and is given by

$$
\begin{aligned}
V_{OS}(x,y) &= \frac{V_B + 3V_P}{4} + \left(\frac{2V_B - V_A - V_C}{9}\right)\left\{\cos\left[\frac{2\pi}{a}\left(x - \frac{y}{\sqrt{3}}\right)\right] + \cos\left[\frac{4\pi}{\sqrt{3}a}y\right] + \cos\left[\frac{2\pi}{a}\left(x + \frac{y}{\sqrt{3}}\right)\right]\right\} \\
&\quad - \left(\frac{V_C - V_A}{3\sqrt{3}}\right)\left\{\sin\left[\frac{2\pi}{a}\left(x - \frac{y}{\sqrt{3}}\right)\right] + \sin\left[\frac{4\pi}{\sqrt{3}a}y\right] - \sin\left[\frac{2\pi}{a}\left(x + \frac{y}{\sqrt{3}}\right)\right]\right\} \\
&\quad + \left(\frac{V_B - 9V_P + 4V_A + 4V_C}{36}\right)\left\{\cos\left[\frac{4\pi}{a}x\right] + \cos\left[\frac{2\pi}{a}(x + \sqrt{3}y)\right] + \cos\left[\frac{2\pi}{a}(-x + \sqrt{3}y)\right]\right\}. \quad (5)
\end{aligned}
$$

In this paper, we will follow the general practice, in the literature, of referring to Γ as the "chemical potential" term. However, for the record, we note that, as has been pointed out by Needs and Mansfield,[16] Γ actually contains two terms, one being the negative of the chemical potential of the particle reservoir (sink), and the other accounting for the new bonds that are formed (broken) as the extra atom is introduced into (removed from) the surface. The Needs and Mansfield model implicitly assumes, while deriving the formula for R, that additional atoms which are required to increase the density (for a compressive reconstruction) are obtained from the bulk phase; however in an actual experimental situation they can, for example, be obtained at lower energetic cost from adatoms;

this is even more true in the case of heteroepitaxy, where there is no bulk phase of the overlayer present to act as a reservoir of additional atoms. For expansive reconstructions, similar arguments hold, with the role of reservoir being replaced by that of a sink. Further below, we discuss how we obtain what we believe to be appropriate values for Γ.

For simplicity, in this work, we restrict ourselves to studying the case where the overlayer reconstructs by densification or rarefaction along only one direction (as is generally observed for reconstructions after deposition of a single monolayer of an overlayer element); however, qualitatively similar behavior is expected when other types of densification or rarefaction, such as those that result in isotropic triangular patterns, are

considered. We consider an $(n \times \sqrt{3})$ unit cell for which the pseudomorphic configuration would correspond to this surface unit cell containing $2n$ overlayer atoms. Upon compressive or expansive reconstruction, this cell now contains an increased [or reduced] number of $(2n + 2)$ [or $(2n - 2)$] overlayer atoms. We start with arbitrary initial positions for these $2n \pm 2$ atoms; the Hamiltonian given in Eq. (4) is then optimized by moving the positions of all the atoms in the unit cell, using a conjugate gradient algorithm, until the lowest energy configuration has been achieved. In order to give us some confidence that the configuration obtained corresponds to the global minimum, several different choices of initial positions are tried.

In order to see whether a reconstruction is favored or not, one has to compare $\gamma_{\text{rec}}(n)$, the surface energy for a compressive reconstruction with overlayer density $(n + 1)/n$, or an expansive reconstruction with overlayer density $(n - 1)/n$, with the surface energy γ_{unrec} of the unreconstructed surface. So what we have to do is to evaluate

$$\Delta\gamma(n) = \frac{E_{\text{rec}}(n) - E_{\text{unrec}}(n)}{\sqrt{3}na^2}, \qquad (6)$$

where a is the NN distance of the substrate, and $E_{\text{rec}}(n)$ and $E_{\text{unrec}}(n)$ are the optimized energies obtained by minimizing the Hamiltonian of Eq. (4) for an $(n \times \sqrt{3})$ surface cell containing $2n \pm 2$ and $2n$ overlayer atoms respectively, where the $+$ sign corresponds to a compressive reconstruction, and the $-$ sign to an expansive reconstruction. E_{unrec} corresponds to a case where the overlayer density is equal to the substrate density, and the system therefore remains unreconstructed. For the elements Ag, Au, Pb, and Pt (Fe and Co), expansive (compressive) reconstruction is modeled.

Before we can go on to study whether or not the 2D FK model predicts reconstruction for our systems, we have to decide what values to take for Γ. Looking at the earlier literature on heteroepitaxial systems, one does not find a clear and unambiguous choice. Possible choices that have been made earlier is to set Γ to be equal to the cohesive energy per atom in a monolayer with bulk lattice spacing,[18] or the energy required to take a single adatom from its equilibrium position on the surface,[33] or set it to zero,[21] or use a value that is "handmade" in order to equal some results obtained by *ab initio* and FK model calculations.[13] In the case of surface alloying of two elements on a third one,[10] Γ has been replaced by an energy of mixing, without taking into consideration the physical origin of atomic reservoirs.

It is perhaps helpful if we recapitulate some earlier work done in our group on the reconstruction of Pt(111),[15] where we first performed *ab initio* density functional theory calculations to evaluate the bulk cohesive cohesive energy, the binding energy of a kink atom at a step edge, and the binding energy of an adatom on the flat surface. The corresponding values of Γ were then found to be 0.68 eV, 0.69 eV, and -0.91 eV. In other words, energetically, it was more or less equivalent to consider that the extra atoms needed to increase the density when the surface reconstructed came from either the bulk or from kink sites; however, these atoms could be obtained at much lower energetic cost when adatoms were present. This can be understood in terms of the number of bonds that need to be broken to detach an adatom versus a kink-site atom. A more or less similar situation presumably holds in the heteroepitaxial

TABLE IV. Values of chemical potential: Γ_b, as evaluated using Eq. (8), and Γ_{ad}, as evaluated using Eq. (9), for each overlayer system are tabulated.

	Fe	Co	Pt	Ag	Au	Pb
Γ_b (eV)	1.24	0.94	0.64	0.83	0.67	0.50
Γ_{ad} (eV)	-0.03	-0.18	-1.33	-0.29	-0.88	

case; accordingly we estimate the values of Γ corresponding to bulk atoms and adatoms as the two limiting cases, as described below.

We consider first the situation where the particle reservoir or sink consists of the "bulk." We then note that one can obtain the interface energy γ_i for the unreconstructed heteroepitaxial system in two ways. One can obtain it from an *ab initio* calculation using Eq. (2), as was done in Sec. III, resulting in the values listed in the second column of Table II. However, one can also obtain it from the FK model Hamiltonian. In that case, one obtains

$$\gamma_i = \frac{3E_0 + \Gamma_b}{\frac{\sqrt{3}}{2}a^2}, \qquad (7)$$

where Γ_b is the "bulk" chemical potential, and E_0 is the elastic energy stored in a NN bond in the unreconstructed overlayer, which is given by $E_0 = A_0\{1 - \exp[-A_1(a - b)]\}^2$. We then obtain the chemical potential for the situation when extra atoms are obtained from, or deposited into, the "bulk" as

$$\Gamma_b = \frac{\sqrt{3}a^2\gamma_i}{2} - 3E_0. \qquad (8)$$

The values of Γ_b obtained in this way are listed in Table IV.

In Fig. 1, we show how $\Delta\gamma$, the difference in surface energy of the reconstructed and unreconstructed surfaces, varies with $\Delta\rho$, the change in density of the overlayer relative to the substrate; note that we have chosen to use as the abscissa of these graphs not n, but $\Delta\rho = \pm\frac{1}{n}$, which is positive (negative) for compressive (expansive) reconstruction. These results have been obtained by setting $\Gamma = \Gamma_b$.

For the elements favoring reconstruction, $\Delta\gamma(n)$ is found to be negative, and shows a minimum at a finite value of $n = n^*$. For Ag, we find that (for $\Gamma = \Gamma_b$) the energy cost for reconstruction is minimum when there are 7 Ag atoms on 8 Ru atoms, and the most favored change in density upon reconstruction $\Delta\rho_{\text{min}} = -12.5\%$. Similarly for Au, the cost is minimum for 11 atoms on 12 Ru atoms and $\Delta\rho_{\text{min}} \sim -8.33\%$. This indicates that Ag and Au would tend to reconstruct on a Ru(0001) substrate. For Co, Fe, and Pt, $\Delta\gamma$ is positive, and reconstruction is not favored. For Pb, a minimum is obtained for 2 Pb atoms on 3 Ru atoms. We note that the gain in energy upon reconstructing is one to two orders of magnitude larger for this system than it is for Ag/Ru(0001) or Au/Ru(0001); this is because of the very large tensile stress present in the pseudomorphic Pb/Ru(0001) layer (see σ_{Pb} in Table II). Note also that there is a monotonic relationship between $|R|$ and $|\Delta\rho_{\text{min}}|$, since R serves as a measure of the tendency toward reconstruction when $\Gamma = \Gamma_b$.

The results presented in Fig. 1 were obtained with $\Gamma = \Gamma_b$, i.e., when the energy required to obtain an additional atom for
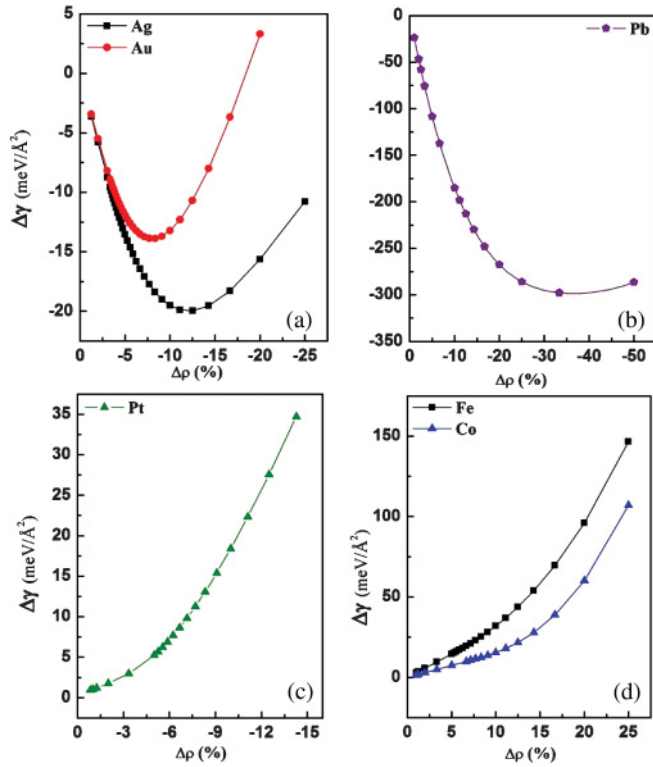
FIG. 1. (Color online) $\Delta\gamma$, the difference in surface energy per unit area for the reconstructed and unreconstructed systems, as a function of the change in density $\Delta\rho$ of the overlayer (relative to the substrate), as obtained from optimizing a 2D FK model, with all parameters obtained from *ab initio* calculations and with Γ set equal to Γ_b. (a) Au (circles) and Ag (squares) and (b) Pb reconstruct expansively; (c) Pt and (d) Co (triangles) and Fe (squares) do not reconstruct.
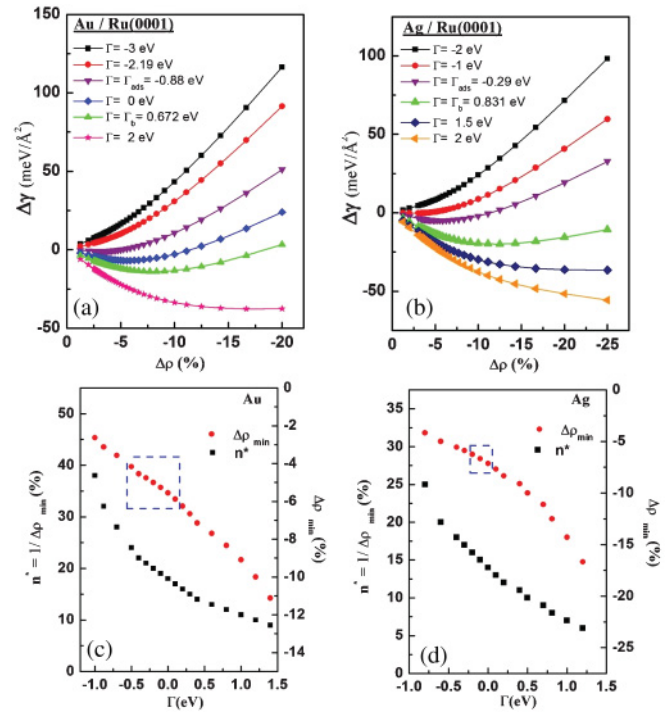

FIG. 2. (Color online) The difference in surface energy between the reconstructed and unreconstructed surfaces, as a function of the change in density of the overlayer, relative to the substrate, for (a) Au/Ru(0001) and (b) Ag/Ru(0001). The different curves correspond to different values of "chemical potential" Γ. The lower panels show the optimal values for the period of reconstruction (black squares) and the decrease in density (red circles) for (c) Au and (d) Ag. The dashed rectangles correspond to a range of experimentally observed values of $\Delta\rho_{min}$.

incorporation into the surface overlayer is positive. For the case of homoepitaxial systems, it has previously been shown that whether or not the surface reconstructs can depend upon the value of Γ. For example, in the case of Pt(111),[15] if the extra atoms come from a reservoir of adatoms, Γ is negative and (compressive) reconstruction is favored, whereas if the extra atoms come from the bulk, Γ is positive and no reconstruction occurs. So next, we estimate a value of Γ when the particle sink or reservoir consists of O adatoms sitting on top of the O/Ru(0001) system. In order to estimate the value of the chemical potential in this case, we make use of the relation

$$\Gamma_{ad} = \Gamma_b - E_c - E_{ad}. \tag{9}$$

The values for Γ_{ad} for all the systems under study except Pb (see Sec. III) are given in Table IV. For other situations, where the particle reservoir or sink consists of step edge atoms, we can expect that Γ lies between the values of Γ_{ad} and Γ_b, e.g., for gold between -0.88 eV and 0.67 eV.

Next, we see how the reconstruction is affected on varying the value of Γ. In Figs. 2–4, we show how $\Delta\gamma(n)$, or, rather, $\Delta\gamma(\Delta\rho)$, varies as the value of Γ is changed, for the six systems considered in this paper. Note that changes in Γ affect the ease of compressive and expansive reconstruction in opposite ways. As Γ becomes more positive, for Fe/Ru(0001) and Co/Ru(0001), it costs more energy to get extra atoms

for incorporation in the surface layer, and thus compressive reconstruction becomes less favorable, and larger n and smaller $|\Delta\rho|$ are favored. However, for Pt/Ru(0001), Ag/Ru(0001), Au/Ru(0001), and Pb/Ru(0001), as Γ becomes more positive, it costs less energy to give away atoms to the particle reservoir, so expansive reconstruction becomes more favorable, and smaller n and larger $|\Delta\rho|$ are favored.

As an example, consider Figs. 2(a) and 2(b), where we show the results for Au/Ru(0001) and Ag/Ru(0001), respectively. We see that for very negative values of Γ, $\Delta\gamma$ is positive and does not display a minimum; i.e., perfect epitaxy is favored. As Γ increases and approaches Γ_{ad}, that is, -0.9 eV for gold and -0.3 eV for Ag, an expansive reconstruction starts becoming favored (with a very long period). As can be seen from the plots at these respective Γ values, for Au/Ru(0001), $\Delta\gamma$ displays a minimum at $\Delta\rho_{min} = -3.12\%$ corresponding to 31 atoms of Au on 32 atoms of Ru; whereas for Ag/Ru(0001), a minimum is observed at $\Delta\rho_{min} = -5.88\%$ corresponding to 16 atoms of Ag on 17 atoms of Ru. As Γ becomes larger, n^*, the periodicity of the reconstruction, decreases, while $|\Delta\rho|$ increases.

In Figs. 2(c) and 2(d), we show how $\Delta\rho_{min}$ varies with Γ for gold and silver, respectively. The width of the dashed rectangles in these figures represents the range of $\Delta\rho$ observed in scanning tunneling microscopy (STM) experiments: Reported periodicities of the stripe width for Ag/Ru(0001) include 4.3 nm[34] and 3.8 nm,[35] corresponding
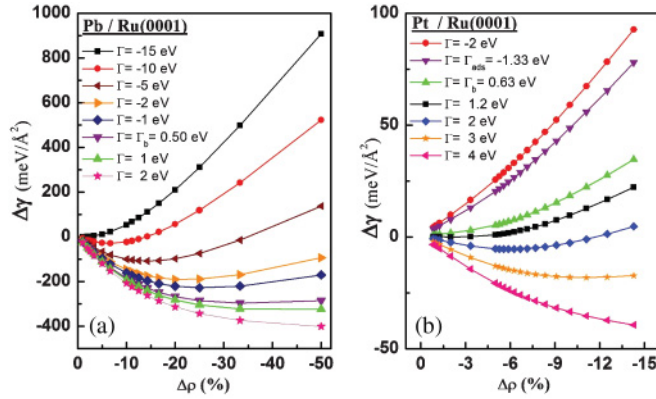
FIG. 3. (Color online) Controlling the surface reconstruction by varying "chemical potential" Γ: change in surface energy (relative to unreconstructed surface) as a function of decreased density in surface layer (relative to the substrate layer) for (a) Pb/Ru(0001) and (b) Pt/Ru(0001).

FIG. 4. (Color online) Controlling the surface reconstruction by varying "chemical potential" Γ: change in surface energy (relative to unreconstructed surface) as a function of increased density in surface layer (relative to the substrate layer) for (a) Co/Ru(0001) and (b) Fe/Ru(0001).

to values of $n^* = 16$ and 14, respectively, and $\Delta\rho = -6.25\%$ and -7.14%, respectively. In our (unpublished) STM experiments, on Ag/Ru(0001), we obtained a periodicity of 3.7 nm which corresponds to $n^* = 14$ and $\Delta\rho = -7.14\%$. Similarly for Au/Ru(0001), the reported periodicity is 6.8 nm[35] corresponding to $n^* = 25$ and $\Delta\rho = -4\%$; while in our (unpublished) STM experiments, we observed a periodicity of 4 nm which corresponds to $n^* = 15$ and $\Delta\rho = -6.7\%$. From an examination of the range of Γ corresponding to the dashed rectangles in Figs. 2(c) and 2(d), we find, for Au/Ru(0001), -0.5 eV $< \Gamma < 0.25$ eV, and for Ag/Ru(0001), -0.24 eV $< \Gamma < 0.09$ eV. In other words, the physically observed periodicities are consistent with our model and with the values in Table IV.

In Fig. 3 we plot similar data for Pb/Ru(0001) and Pt/Ru(0001), for which also we may expect to find expansive reconstructions. Both systems behave quite differently from Ag/Ru(0001) and Au/Ru(0001). For Pb/Ru(0001), we obtain a sharp minimum, when Γ has values close to Γ_b. For an entire range of physically reasonable Γ, one obtains a reconstruction. This is because of the huge elastic energy stored in a pseudomorphic overlayer of Pb which can be relieved by reconstruction. This observation is in accordance with the large R value obtained by us for this system. We do, however, note that the minimum in $\Delta\gamma$ for Pb/Ru(0001) occurs in the regime of hugely reduced overlayer densities ($\sim -33\%$), where it is not entirely clear that the FK model is applicable, and therefore the actual reconstruction of the system may differ from the one predicted by our simulations. For Pt/Ru(0001), we find that perfect epitaxy is favored for $\Gamma = \Gamma_b$ as well as for $\Gamma = \Gamma_{ad}$. For Γ values greater than 1.2 eV, reconstruction starts becoming favored and we can note that the optimal period and overlayer density vary rapidly as a function of Γ.

The effect of variation of chemical potential for the systems Co/Ru(0001) and Fe/Ru(0001) is shown in Figs. 4(a) and 4(b) respectively. We find that the Co/Ru(0001) and Fe/Ru(0001) systems do not reconstruct when $\Gamma \gtrsim 0$ eV and $\Gamma \gtrsim -1$ eV respectively. For Co/Ru(0001), when $\Gamma \leqslant \Gamma_{ad}$, $\Delta\gamma$ becomes negative, and also shows a minimum at a finite
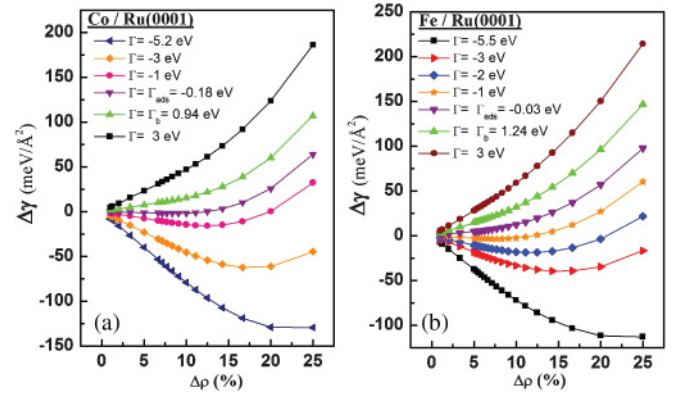
value of n, suggesting that the system will reconstruct at negative Γ values. Similarly for Fe/Ru(0001), we find a clear minimum appearing in $\Delta\gamma(\Delta\rho)$, suggesting that this system will reconstruct at low negative values of Γ.

V. EVALUATION OF *R* AND COMPARISON WITH EXPERIMENT

In Table II, we had listed the values of the parameter R, obtained by mapping the 2D system onto a 1D FK model, with all parameters obtained from our *ab initio* calculations. In the second column of Table V, we have listed whether or not the heteroepitaxial O/Ru(0001) system should reconstruct, according to the prediction of the 1D FK model (using the values of R from Table II). In the third column, we have stated whether or not our quenched molecular dynamics simulations, making use of the 2D FK model, predict that a reconstruction is favorable for the system, for the particular case where $\Gamma = \Gamma_b$ (which is the appropriate value for comparison with the 1D Needs-Mansfield model). Note that the predictions of the 1D and 2D models agree. In the last column of this table, we have listed (where available) what the experimental evidence is. In every single case, we find that both the simple 1D FK model and the 2D FK model have indeed predicted correctly whether or not the heteroepitaxial O/Ru(0001) system will reconstruct. For Pb/Ru(0001), the Stranski-Krastanov growth mechanism was observed,[40] but no details of the structure are mentioned. However, the system will almost certainly display a reconstruction, given the huge lattice mismatch between Pb and Ru. As discussed above, the appropriate value to choose for Γ is debatable, and it is arguable that $\Gamma = \Gamma_b$ might not be a particularly good choice. Perhaps more to the point, at a slightly negative value of chemical potential which we feel is more physical, since it lies somewhere between Γ_b and Γ_{ad}, this qualitative behavior is unaltered; we argue that this corresponds to the most likely experimental scenario. For Ru(0001), we have not performed the 2D quenched molecular dynamics simulations. However, our value of R predicts that the surface will not reconstruct, which is in agreement with a vast amount of experimental data.[41,42]

TABLE V. Predictions from the 1D and 2D FK models for whether or not the various O/Ru(0001) systems reconstruct. The second column uses the values of R from Table II to predict whether or not the system reconstructs. The third column states whether or not the system reconstructs using the results obtained from the 2D FK model (evaluated with $\Gamma = \Gamma_b$), and the last column states whether or not the overlayer reconstructs, based upon available experimental information.

Element O	1D Pred.	2D Pred.	Expt.
Fe	No	No	No (Ref. 36)
Co	No	No	No (Ref. 37)
Pt	No	No	No (Ref. 38)
Ag	Yes	Yes	Yes (Refs. 34,35,39)
Au	Yes	Yes	Yes (Ref. 35)
Pb	Yes	Yes	

It is worth discussing the validity and applicability of the Frenkel-Kontorova model, in its various flavors. The simplest form is the original 1D form, which also assumes that the substrate potential is sinusoidal and the interatomic surface bonds are harmonic. The parameter R is derived from this (analytically soluble) form of the model. Now, as we can see from Table I, for Fe/Ru(0001), along the zigzag line connecting fcc, bridge, and hcp sites (which is the 1D line to which the model is applied), the energy V_C (which is a local minimum) is almost equal to V_P (the maximum along this zigzag line) and therefore the assumption of a sinusoidal substrate potential (which can be expected to be valid when $V_P - V_A \gg V_C - V_A$) clearly does not hold. This may be the reason why the value of R obtained for Fe/Ru(0001) is (very slightly) positive rather than negative as is expected for a compressive reconstruction. The other important assumption in the 1D FK model is that the interaction between overlayer atoms is harmonic, whereas we have found that it has instead a Morse form. For displacements near the minimum b of the Morse potential, it can be approximated by the harmonic form. However, when b becomes very different from the Ru nearest-neighbor distance, as is for example the case for

Pb/Ru(0001), this is no longer valid. Thus, the exact value of R predicted for Pb/Ru(0001) perhaps does not have much significance; however the prediction that Pb/Ru(0001) will have a strong tendency to reconstruct almost certainly still holds true. The form of the 2D FK model we have chosen to solve for our FK model allows for differing minima at fcc and hcp sites, and nonharmonic springs, and therefore the predictions of this model are much more reliable. However, again for the case of Pb/Ru(0001), the approximation made by simultaneously compressing or stretching the overlayer and substrate may lead to errors in the predicted periodicity of reconstruction, though almost certainly not, we believe, to the existence of the reconstruction itself.

To summarize: We have shown how to generalize the definition of a dimensionless parameter R, already used for pure surfaces, to the heteroepitaxial case and then shown that R is a good tool to predict the surface reconstruction in heteroepitaxial systems, based on *ab initio* calculations. We have cross-checked these predictions with experiments and quenched molecular simulations of the two-dimensional Frenkel-Kontorova model. For several of the cases considered here, we find that, as was the case for the Pt(111) system,[15] it should be possible to obtain a reconstruction whose periodicity can be tuned by playing with the chemical potential. For growth in ultra-high vacuum conditions, one should be able to do this by tuning temperature, the metal deposition flux, or an extra density of adatom clusters,[43–45] while for chemical growth situations one can tune the electrochemical potential and concentration.[46–48] These factors should enable one to select a particular period for the reconstruction, which in turn should enable one to obtain a nanotemplate with a required repeat distance.

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