Energy and structure of uniaxial incommensurate monolayer solids: Application to Xe/Pt(111)

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Calculations are reported for uniaxial incommensurate (UIC) structures of a rare-gas monolayer physisorbed on a triangular Bravais surface lattice at T=0. The sign of the substrate corrugation leads to two distinct UIC lattice solutions which have different diffraction signatures. Previously reported experimental data for Xe/Pt(111) are interpreted as showing the positioning of Xe atoms in the commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice to be atop platinum sites rather than in threefold sites. The magnitude of the substrate corrugation required to stabilize the commensurate lattice is found to be large, in agreement with previous estimates.

The uniaxial incommensurate lattice (UIC) of an adsorbed monolayer is one possible outcome¹ of the competition between the different periodicities imposed by the adatom-adatom and adatom-substrate potentials. Calculations are presented here of the energy and structure of domain walls² in the UIC phase of a classical rare-gas solid physisorbed on a triangular Bravais surface lattice. The results include a new structure with a subdivided domain wall in addition to the simpler wall studied by other authors.³⁻⁷

A physical system in which these considerations arise is Xe/Pt(111). Among other phases, Xe/Pt(111) has a triangular commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice, established⁸ at monolayer condensation in the temperature range 60-99 K, and a UIC phase, observed⁹ for misfit less than 6.5%. The commensurate lattice has been difficult to reproduce in calculations; Black and Janzen¹⁰ obtained a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase only by using a surprisingly large value of the leading Fourier amplitude of the adatomsubstrate potential. The issues to be addressed here are the information available in the observed diffraction pattern and the requirements on the adatom-substrate potential for there to be a stable $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice. The subdivided domain-wall structure has a characteristic diffraction pattern which differs from the Xe/Pt(111) data^{9,11} and the remarkable conclusion is reached that in the commensurate phase the Xe atoms lie above platinum atom sites rather than in threefold sites.

The geometry of the triangular substrate surface lattice is as shown in Fig. 1. The primitive vectors of this Bravais lattice are \mathbf{a}_1 and \mathbf{a}_2 , where \mathbf{a}_1 and \mathbf{a}_2 have length L = 2.77Å for Pt(111). The origin of the adlayer coordinate system in Fig. 1 is directly atop a lattice site of an fcc (111) surface. The commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase of a rare-gas monolayer has a lattice constant $L_c = \sqrt{3}L$, equal to 4.80 Å for Xe/Pt(111), and its primitive vectors are $\mathbf{a}_1 + \mathbf{a}_2$ and $2\mathbf{a}_1 - \mathbf{a}_2$.

The adatom-adatom potential is the Lennard-Jones (12,6) model with two adjustable parameters: the strength ε and the interaction range σ . The adatom-substrate interaction is the Fourier expansion suggested by Steele,¹²

$$V(\mathbf{r},z) = V_0(z) + \sum_{\mathbf{g}} V_g(z) e^{i\mathbf{g}\cdot\mathbf{r}}, \qquad (1)$$

where **r** is the lateral position of the adatom. The **g** vectors are linear combinations of the primitive two-dimensional reciprocal-lattice vectors of length $g_0 = 4\pi/L\sqrt{3}$, and only the first shell of reciprocal-lattice vectors is used in the calculations. The z dependence is ignored; it is assumed that the adlayer forms a two-dimensional structure. There remains one adjustable parameter, the leading amplitude or corrugation V_g . The sign of V_g determines the locations of the minima of $V(\mathbf{r},z)$. For $V_g < 0$, the energy minima are directly atop hexagon centers shown in Fig. 1, i.e., at the origin of coordinates, and there is one minimum per substrate surface unit cell. For $V_g > 0$, the energy minima are at threefold sites located atop the hexagon vertices, and there are two such sites per substrate surface unit cell.

For the purpose of forming a UIC lattice, the adlayer atoms are forced into periodically repeating domains consisting of \mathcal{L} rows oriented parallel to the \hat{x} direction. Along the \hat{y} axis, a compression of one substrate interatomic spacing L relative to the commensurate lattice is applied to the domain as a whole.² The average row spacing in the UIC lattice is then equal to $3L/2(1-\overline{m})$, where \overline{m} is characterized as the *mean misfit* and is given in terms of the domain size by $\overline{m} = 2/3\mathcal{L}$.



FIG. 1. Geometry of triangular substrate surface lattice. \mathbf{a}_1 and \mathbf{a}_2 are primitive vectors of the Bravais lattice. \mathbf{g}_1 and \mathbf{g}_2 are primitive reciprocal lattice vectors. The sets of vectors are not drawn to the same scale. The hexagon vertices are threefold sites of an fcc (111) surface or atom sites of the basal plane of graphite.

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In the *modulated* UIC lattice, the net displacements of rows from the commensurate positions increase nonuniformly. For small mean misfit, the lattices have *domain walls*, regions of rapidly changing net displacement which are surrounded by large commensurate regions.

The computational procedure of finding a ground-state modulated UIC lattice configuration is started by placing the adatoms in a uniform UIC structure of equally spaced rows. The initial positions of the adatoms relative to the substrate are expressed in terms of the primitive vectors of the uniform UIC lattice and the location ρ of one reference adatom within a substrate unit cell. The vector ρ is written in terms of \mathbf{a}_1 and \mathbf{a}_2 ,

$$\boldsymbol{\rho} = s_1 \mathbf{a}_1 + s_2 \mathbf{a}_2 \,, \tag{2}$$

and is expressed as (s_1, s_2) . The parameters s_1 and s_2 are chosen to minimize the total potential energy of the uniform UIC lattice, as a first approximation to a minimumenergy structure, and thus depend on the sign of V_g . Since the final energies only depend weakly on s_2 , a result reflecting the small size of wall pinning energies, the value of s_2 is chosen to generate symmetric solutions in which the center of the domain-wall structure lies between the middle rows of the domain. For $V_g < 0$, the lattices are started at $\rho_- = [0, -(1/2\mathcal{L})]$, and for $V_g > 0$, the lattices are started at $\rho_+ = (\frac{1}{2}, -1/2\mathcal{L})$.

Starting from the uniform UIC lattice, force-free solutions are constructed by a succession of small atomic displacements driven by the net force in instantaneous configurations. The uniaxial incommensurability of the structure is maintained by moving entire rows of atoms together. Thus, the rows move in the direction of the net force acting on them until all of the forces are smaller than a specified tolerance.

Calculations are performed for a sequence of domain sizes for both signs of V_g . The calculations for large domains converge more rapidly for even numbers of rows; only results for lattices with even \mathcal{L} are presented here. The starting adatom location vectors ρ_+ and ρ_- lead to convergent solutions in all cases. For other choices of ρ the lattices develop net displacements which reproduce the previous solutions. To investigate the diffraction signature of the various solutions, the structure factor is calculated for several wave vectors, using the expression

$$S(\mathbf{q}) = \left| \frac{1}{\mathcal{L}} \sum_{j} e^{i\mathbf{q}\cdot\mathbf{r}_{j}} \right|^{2}, \qquad (3)$$

where \mathbf{r}_j is the equilibrium position of the atom in the adlayer.

The two signs of V_g and corresponding values of ρ lead to two distinct UIC lattice solutions which have different diffraction patterns. For $V_g < 0$, the substrate forces do not drive the rows away from commensurate positions in the \hat{x} direction, and so all of the atomic motion is along the \hat{y} direction. This type of solution has been presented previously^{6,7} for krypton on graphite. For $V_g > 0$, the substrate forces cause displacements in both the \hat{x} and \hat{y} directions.¹³ Both sets of threefold sites are involved in this modulated structure. Examples of the two types of structure are shown in Fig. 2.



FIG. 2. Examples of UIC lattices, $\mathcal{L} = 14$ and $\sigma = 4.1$ Å. The arrows indicate the centers of the domain-wall structures. Background hexagons as in Fig. 1. (a) $V_g = 70$ K; (b) $V_g = -11$ K.

The magnitude of V_g for Xe/Pt(111) is estimated by comparing the energies of various adlayer structures. First, the requirement that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice have lower energy than the UIC lattice for given ε and σ sets a threshold value for V_g , denoted by $V_g(\sqrt{3})$. Second, the experimentally observed¹⁴ isosteric heat step of 350 K sets an additional value of V_g , denoted by $V_g(\Delta \mu)$. The isosteric heat step is identified¹⁵ with a chemical-potential step $\Delta \mu$, which is related to the calculated wall energy per unit length w.

The remaining parameters for Xe/Pt(111) are set as follows. The Lennard-Jones potential parameters are $\varepsilon = 230$ K and $\sigma = 4.05$, 4.1, and 4.15 Å. The choices of σ are to allow for effects of thermal expansion when comparing potential-energy calculations to Xe/Pt(111) experimental data at T > 60 K; the potential is truncated at a distance of 14.6 Å. The domain size \mathcal{L} must be large enough that the UIC phase is strongly modulated. Experiments⁹ detected the modulated nature of the UIC phase below a mean misfit of about 3%, i.e., $\mathcal{L} > 22$. When $\mathcal{L} > 30$ the calculated energy varies nearly linearly with the mean misfit. For questions of stability, $\mathcal{L} = 48$ is used.

The wave vectors presented in Fig. 3 correspond to the diffraction peaks in the neighborhood of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice peak (C) at $8\pi/3L$ along the \hat{y} direction. The pattern shown is an equal weighting of domains oriented at 0°, 120°, and 240° to the ΓM direction, i.e., the \hat{y} axis. Positions 3 and 4 are peaks of the uniform UIC lattice, and positions 1, 2, and 5 are peaks of the modulated UIC superlattice. Kern *et al.*⁹ and Zeppenfeld *et al.*¹¹ refer to this group of peaks as the (2,2) diffraction spots. They identify the peak at position 2 as a diffraction satellite.

The values of $V_g(\sqrt{3})$ and $V_g(\Delta \mu)$ are presented for both signs of V_g in Table I. The domain-wall structures of the minimum-energy solutions for both signs of V_g at $V_g(\sqrt{3})$, in terms of atomic displacements from commens-

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(3)

FIG. 3. Positions of diffraction peaks in the neighborhood of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice peak (C) at $8\pi/3L$ along the ΓM direction (\hat{y} direction in Fig. 1) for the UIC lattice, after Ref. 11. $\varepsilon = \overline{m}/(1-\overline{m})$, where $\overline{m} = 2/3\mathcal{L}$ and \mathcal{L} is the number of rows in the domain.

urate positions, are presented in Figs. 4 and 5 for $\sigma = 4.1$ Å. The structure factors of the five peaks shown in Fig. 3 are presented in Table II, for a sequence of domain sizes at $\sigma = 4.1$ Å and the corresponding $V_g(\sqrt{3})$ values.

The results do indeed show two distinct types of domain wall. The solution with negative V_g displays one narrow wall with distortions confined to the \hat{y} direction. In contrast, the different surface topography for positive V_g leads to a lattice which has its net uniaxial compression subdivided into two narrow domain-wall regions which are displaced from each other along the \hat{x} direction.

The dependence of the modulation of the UIC lattices on the domain size is apparent in the opposing trends of the structure factor calculations for the uniform lattice and superlattice peaks shown in Fig. 3. However, the structure factor results also display the startling result that the peak at position 2 is extinguished for the positive V_g case but has substantial intensity in the negative V_g case.

This extinction is directly related to the formation of the subdivided domain wall in the positive V_g case and is in contrast to the Xe/Pt(111) data.^{9,11} Kern *et al.*⁹ and Zeppenfeld *et al.*¹¹ conclude from the presence of the uniform UIC lattice peaks 3 and 4 and the intense on-axis diffraction spot at position 2 at small misfit that the struc-

TABLE I. Amplitudes of the adatom-substrate potential for Xe/Pt(111).

	Ve	> 0	$V_g < 0$		
σ(Å) ^a	$V_g (\sqrt{3})^{b^\circ}$	$V_g~(\Delta\mu)^{c}$	$V_g (\sqrt{3})^{b'}$	$V_g (\Delta \mu)^{c}$	
4.05	96.8	155	-14.8	-23.8	
4.1	68.9	118	-10.4	-17.9	
4.15	43.9	83.2	-6.6	-12.5	

^aLennard-Jones potential interaction range.

^bThreshold amplitude (in K) for stability of $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice with respect to the UIC lattice.

^cAmplitude (in K) necessary to match the experimentally observed heat step of 350 K (Ref. 14).



FIG. 4. Atomic displacements in the \hat{y} direction from commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ positions for negative V_g , $\mathcal{L} = 48$. Actual atomic positions correspond to integer values of the row number.



FIG. 5. Atomic displacements from commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ positions for positive V_g , $\mathcal{L} = 48$. Actual atomic positions correspond to integer values of the row number. (a) x displacements; (b) y displacements.

TABLE II. Structure factors for uniaxial incommensurate lattices.

Peak ^b	$V_{e} (\sqrt{3})^{a} = 68.9 \text{ K}$			$V_{g} (\sqrt{3})^{a} = 10.4 \text{ K}$		
	⊥° =48	L =24	L =12	£ = 4 8	£ =24	L =12
1	0.525	0.392	0.209	0.411	0.220	0.039
2	0.0	0.0	0.0	0.631	0.501	0.149
3	0.265	0.376	0.601	0.349	0.571	0.909
4	0.388	0.653	0.961	0.010	0.042	0.672
5	0.372	0.170	0.016	0.133	0.070	0.005

^aIdentified as in Table I, for $\sigma = 4.1$ Å.

^bPeaks as identified in Fig. 3 and in Ref. 11; $S(\mathbf{q})$ as in Eq. (3). ^c \mathcal{L} : number of rows in the domain.

ture is a modulated UIC lattice. Their pattern is consistent with the calculated structure factors in the negative V_g case and inconsistent with those of the positive V_g case. Since the negative sign of V_g is associated with the location of energy minima above hexagon centers, the experimental results are thus interpreted as showing that the Xe atoms are positioned above Pt atoms in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice. Another possibility, not yet excluded, is that the underlying second substrate layer breaks the degeneracy of the threefold sites enough to produce an appreciable structure factor at position 2.

The values of $V_g(\sqrt{3})$ for the negative sign case are equal to or larger than those found in modeling inert gases

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on graphite, which is surprising in terms of earlier views of adsorption on close-packed metal surfaces.¹⁶ In the positive sign case, the amplitudes are equal to or larger than those which Black and Janzen¹⁰ needed to obtain commensurate islands of Xe/Pt(111). Finally, this calculation only establishes a stability threshold for the commensurate phase versus a modulated UIC lattice; there may be other minimum-energy structures of the monolayer near the commensurate-incommensurate transition.

The results for $V_g(\Delta \mu)$ represent rather large barriers to lateral motion for physisorbed inert gases. However, these barriers are less than $\Delta \mu$, which includes adatomadatom energies.

The monolayer structure with a subdivided domain wall introduced in this work has not yet been identified in diffraction measurements.

A fuller investigation of the Xe/Pt(111) monolayer equation of state may help to specify further the adatomsubstrate interaction. Extended x-ray absorption fine structure experiments might confirm the locating of Xe atoms atop platinum sites in the commensurate lattice, which was inferred here from the diffraction studies.

This work was supported in part by the National Science Foundation through Grant No. DMR-88-17761. The author would like to thank Professor L. W. Bruch for his patient guidance and for helpful comments on the manuscript.

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