

## Anomalous Fast Dynamics of Adsorbate Overlayers near an Incommensurate Structural Transition

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We investigate the dynamics of a compressively strained adsorbed layer on a periodic substrate via a simple two-dimensional model that admits striped and hexagonal incommensurate phases. We show that the mass transport is superfast near the striped-hexagonal phase boundary and in the hexagonal phase. For an initial step profile separating a bare substrate region (or “hole”) from the rest of a striped incommensurate phase, the superfast domain wall dynamics leads to a bifurcation of the initial step profile into two interfaces or profiles propagating in opposite directions with a hexagonal phase in between. This yields a theoretical understanding of the recent experiments for the Pb/Si(111) system.

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Heteroepitaxial systems involving an adsorbate layer with a lattice mismatch to the underlying substrate have been extensively studied from both experimental and theoretical viewpoints. In the monolayer regime, such systems can exhibit many two-dimensional phases [1–3] at equilibrium and have also been used as simple models for studying sliding friction phenomena on surfaces [4–6]. Recently, Tringides *et al.* [7–10] have done an extensive study of both the statics and dynamics of the Pb/Si(111) system. At equilibrium, the system can exist in the striped incommensurate (SIC) phase sandwiched in between “devil’s staircases” as well as in the hexagonal incommensurate phase (HIC). In growth processes, the system displays spontaneous self-organization and height selection of Pb islands beyond the monolayer regime. The observed rate of island growth requires a rate of mass transport orders of magnitude faster than the usual diffusion picture. Similar anomalously fast transport has also been invoked in other adsorption systems [11]. In a set of recent experiments [7,9], the dynamics in the submonolayer regime for Pb/Si(111) was studied by following the refilling of a hole region. The results show a bifurcation of the initial step profile into two sharp fronts propagating in opposite directions. This intriguing finding further points to the anomalous dynamics of the Pb/Si(111) system already inferred from the self-organized island growth. Previous one-dimensional [12] and simplistic two-dimensional [13] studies already indicated that domain wall motion in an incommensurate phase is the key to understanding the anomalous fast mass transport. Here, we study this adsorption system via a model two-dimensional Hamiltonian which admits, in addition to a commensurate phase, a SIC phase [14] and a HIC phase

with crossing domain walls. We demonstrate that the anomalous fast dynamics observed in the Pb/Si(111) system is a generic feature of a system where the SIC phase can be converted to a HIC phase with negligible Peierls barrier pinning.

The particle interactions in the adsorbed layer in our model are described by an analytical Lennard-Jones pair potential used previously in qualitative studies of the dynamics and sliding friction of adsorbed layers [4–6,13]:

$$v(r) = \epsilon_0[(r_0/r)^{12} - 2(r_0/r)^6]. \quad (1)$$

The substrate is represented by a generic adsorption potential on a fcc(111) substrate as

$$V(x, y) = V_0 \left[ \cos\left(2\pi \frac{x}{a}\right) \cos\left(\frac{2\pi}{\sqrt{3}} \frac{y}{a}\right) + 0.5 \cos\left(\frac{4\pi}{\sqrt{3}} \frac{y}{a}\right) \right], \quad (2)$$

with amplitude  $V_0 > 0$ . The choice of  $x$  and  $y$  axes in Eq. (2) corresponds to the  $(1, \bar{1}, 0)$  and  $(\bar{1}, \bar{1}, 2)$  directions on the fcc(111) surface. The adsorption sites can be separated into two interpenetrating triangular sublattices corresponding to the hcp and fcc sites, respectively, [15]. Our adsorption system consists of  $N$  particles in an area of size  $L_x \times L_y$ . We consider an overlayer with compressive strain at coverages near one monolayer with  $r_0/a \gtrsim 1$ . For the numerical simulations,  $N$  is kept fixed and  $L_x$  and  $L_y$  are adjusted to obtain different coverages through energy minimization. The parameter  $r_0$  is used in the model to set the coverage, acting as a chemical potential for domain walls [1]. Throughout this Letter, we will choose the amplitude  $\epsilon_0$  of the interaction potential, the substrate lattice spacing  $a$ , and the adsorbate mass  $m$  as the scales

for energy, length, and mass, and all quantities will be expressed in dimensionless form. The stochastic dynamics of the system is described by the standard Langevin equation [16], which is used for the Molecular Dynamics (MD) simulations with the friction parameter set at  $\eta = 5$  and the time variable discretized in units of  $\delta t = (0.002 - 0.01)\tau_{md}$ , where  $\tau_{md} = \sqrt{ma^2/\epsilon_0}$  in the original units. The main results described below were obtained with  $N = 6400, 25600, \text{ and } 57600$  particles.

First, we determine the phase boundary for the commensurate and the incommensurate phases for our model Hamiltonian in the zero temperature limit for a range of parameters  $1 < r_0 < 1.1$  and  $0 < V_0 < 0.4$ . The commensurate phase occurs at values of  $r_0 < r_{ci}(V_0)$ . When  $r_0$  is increased just beyond  $r_{ci}(V_0)$ , the ground state of the system changes to a SIC phase consisting of a linear array of “light” domain walls where the local coverage in the wall region is less than the commensurate (C) phase. The minimum energy configuration in the SIC phase has domain walls aligned parallel to the  $y$  ( $[\bar{1}, \bar{1}, 2]$ ) direction while the spacing between the walls is a function of the control parameter  $r_0$ . As  $r_0$  is increased further beyond the C-SIC boundary, the balance between strain relaxation energy in the domain walls and the interaction energy between them leads to another new ground state, namely, the HIC incommensurate phase at  $r_0 > r_{sh}$ , as shown in Fig. 1. In the HIC phase, the domain walls cross in broad regions, which become smaller for increasing  $V_0$ . Alternatively, this phase can be regarded as a honeycomb structure of commensurate domains. The phase diagram with approximate locations of the C-SIC boundary and the SIC-HIC boundary is shown in Fig. 2(a). This phase diagram is qualitatively similar to the one obtained from the phase-field crystal model study of heteroepitaxial adsorption on a fcc(111) substrate [15]. In the commensurate phase, the adsorbate is locked to the substrate and the

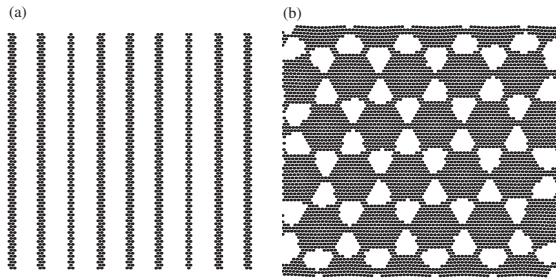


FIG. 1. Coarse grained configurations illustrating the domain-wall structures for the (a) SIC phase and (b) HIC phase, for  $r_0 = 1.05$  and  $r_0 = 1.07$ , respectively, and  $V_0 = 0.2$ . White areas represent locally commensurate regions with the substrate, while the dark areas represent domain walls (locally incommensurate regions), obtained by plotting particle positions for which the potential energy  $V(r)$  is greater than its minimum set at a convenient value of 29%. The period of the structure in (a) corresponds to 8.7 substrate lattice spacing.

coverage remains fixed for  $r_0 < r_{ci}$ . For the compressive case considered here, increasing  $r_0$  while the number of adsorbates is held fixed corresponds to a decrease in the coverage. Figure 2(b) shows the dependence of the coverage for increasing  $r_0$ .

In the incommensurate phase, pinning of the domain walls can occur due to the discrete particle description of the adsorbates, leading to an energy barrier (Peierls-Nabarro barrier) for motion of domain walls [1]. As a result of such pinning effects, a critical depinning force may exist to initiate sliding of the incommensurate overlayer at zero temperature, leading to vanishing mobility. To investigate this pinning behavior, we apply a small uniform external force  $\mathbf{F}$  on all the adatoms and study the velocity response  $\mathbf{v}$  averaged over all the adatoms of the system. The mobility is defined as  $\mu_\alpha = \lim_{F \rightarrow 0} v_\alpha / F_\alpha$ . Figure 3(a) shows the behavior of the mobility of the overlayer in the SIC phase as a function of temperature. In the SIC phase, the mobility is highly anisotropic at low temperatures. The value of  $\mu_\alpha$  parallel to the domain walls is much smaller than in the perpendicular direction, indicating a finite pinning force in the parallel direction and a negligible one in the perpendicular direction. As the temperature increases, the anisotropy disappears and the perpendicular mobility reaches a minimum before rising again at higher temperatures. The temperature at which this transition occurs is close to the point at which the striped domain-wall structure starts to melt. This increase in frictional damping of the overlayer motion from the critical fluctuations near a surface structural transition has also been predicted and observed for other systems [17,18]. In contrast, the mobility in the hexagonal phase [Fig. 3(b)] is isotropic at all temperatures. In this state, negligible pinning is observed and the mobility is very close to the value  $1/m\eta = 1$  (in dimensionless units). This limiting value is just the mobility for an overlayer sliding under no external substrate potential, where the external force  $\mathbf{F}$  couples only to the center of mass of the adatoms. As we demonstrate below, the negligible pinning barrier for the domain-wall superstructure leading to high mobility in the hexagonal phase is the crucial factor leading to the anomalously fast dynamics of the adsorption system such as those observed for Pb/Si(111). The collective motion of the hexagonal structures of domain walls is orders of magnitude faster than

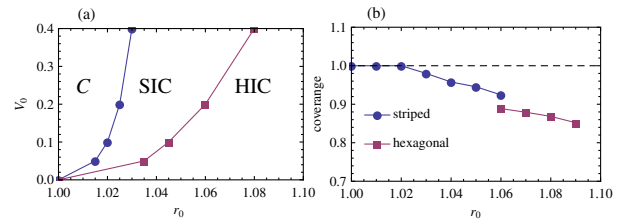


FIG. 2 (color online). (a) Phase diagram showing C, SIC, and HIC phases. (b) Dependence of coverage on  $r_0$  for  $V_0 = 0.2$ .

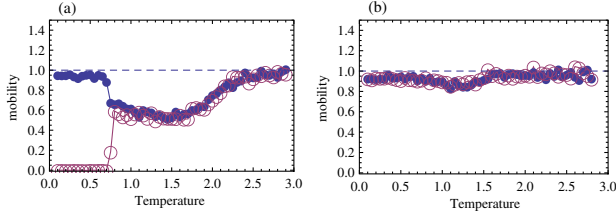


FIG. 3 (color online). Mobility in the direction parallel (open symbols) and perpendicular (filled symbols) to a domain wall for the (a) SIC phase and the (b) HIC phase, for  $r_0 = 1.05$  and  $r_0 = 1.07$ , respectively, and  $V_0 = 0.2$ . The dotted line is the behavior when  $V_0 = 0$ . The mobility is normalized in units of  $1/m\eta$ .

possible by the single particle motion through ordinary diffusive motion under an initial density gradient.

We now demonstrate how the anomalously fast dynamics of our model system near a SIC-HIC phase boundary can lead to the bifurcation of the initial profile in a refilling dynamics study, similar to the experimentally observed patterns [7,9]. In our model study, the adsorbate system is first equilibrated at a finite temperature  $T$ . Then, adatoms are removed from a closed region in the center of the simulation cell, and the time evolution of the profile separating the different regions is followed. The size of the initial bare region or hole is small enough, causing no significant change in the average coverage but large compared to the period of the domain-wall structure to act as a sufficient perturbation. For convenience, we choose an initial state with a bare substrate region in the form of a long narrow strip aligned along the  $\hat{x}$  direction and an adsorbate in a SIC phase outside this region. This allows us to observe larger domain sizes. Figure 4 shows snapshots of the domain configurations of the density profile for increasing time. There is first the nucleation of a HIC phase outside the hole, which then grows along two fronts, inwards filling the hole and outwards transforming the SIC into the HIC phase as the second front grows outwards. The refilling front propagates in time with a sharp profile in contrast with that of the classical diffusion picture. This is in accordance with the experimental observation for Pb/Si(111) [7], demonstrating the anomalous transport behavior.

Figures 5(a) and 5(b) show the averaged local coverage profile at times before and after the refilling, obtained by averaging over eight independent simulations with the same parameters. The local coverage in the  $\hat{y}$  direction was obtained by averaging the number of particles at small  $y$  intervals. The HIC-SIC interface continues to expand after refilling of the initial bare substrate region [Fig. 4(c)]. As shown in Fig. 5(c), the time evolution of the position of the expanding interface depends on the coverage of the initial SIC, being faster for an initial SIC phase closer to the SIC-HIC phase transition [Fig. 2(a)]  $r_0 = 1.05$  than further away from the transition  $r_0 = 1.04$ , which

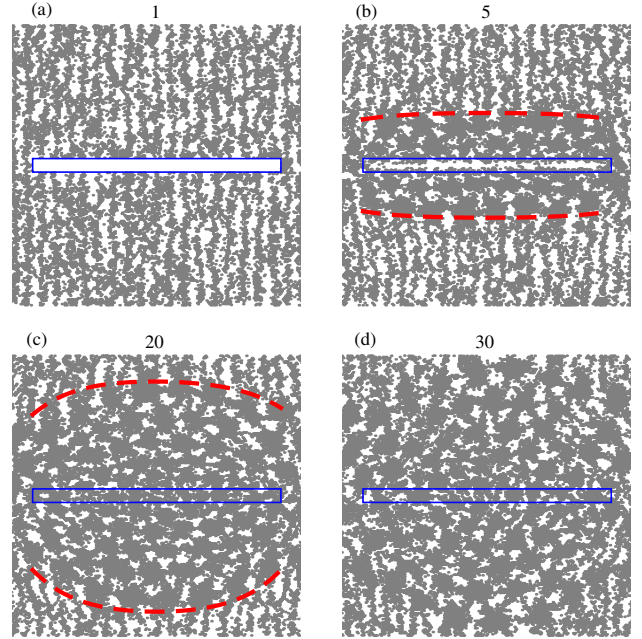


FIG. 4 (color online). Snapshots of domain-wall configurations are shown in (a), (b), (c), and (d) for increasing times after removal of adatoms from an initial strip indicated by a long rectangle for  $r_0 = 1.05$ ,  $V_0 = 0.2$ , and  $T = 0.45$ . White areas outside the rectangle correspond to commensurate regions and dark areas to incommensurate regions. Labels correspond to times in units of  $8 \times 10^3$  MD time steps. The dashed lines in (b) and (c) indicate the expanding hexagonal-stripe interface.

correspond to lower and higher coverages, respectively, as shown in Fig. 2(b). The time evolution of the HIC-SIC interface position in Fig. 5(c) shows the unusual coverage dependence observed in the experiments, being faster for a lower coverage. The existence of this outward propagating front and its coverage dependence is again in contrast to the classical diffusion picture but in complete agreement with the recent experiment [9] on Pb/Si(111), where it was referred to as “superdiffusive” behavior.

The nucleation and growth of a HIC phase after introducing an initial bare substrate region in the SIC phase leading to the bifurcation of the initial profile can be understood in terms of the dynamics of the domain walls in the incommensurate phases of the system. First, due to the different symmetries of the SIC and HIC phases, the transition between them is expected to be first order. This is confirmed by our calculations, which show an abrupt change in the coverage, as can be seen from Fig. 2(b). Results from the phase-field crystal model for this system [15], which can access very large system sizes, show even more clearly that the wavelength of the periodic domain-wall structure has a discontinuous drop at the transition from the SIC to the HIC phases.

When a bare substrate region is created in the system within an initial SIC phase, the local density just outside the region starts to decrease due to refilling of the hole.

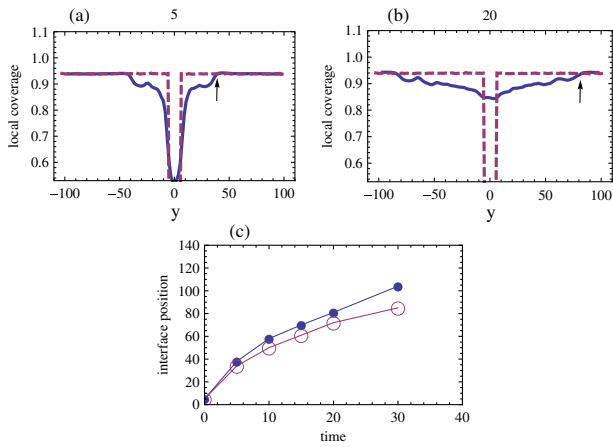


FIG. 5 (color online). (a),(b) Averaged density profiles in the  $y$  direction for the parameters in Fig. 4. The dotted line is the density profile for the initial SIC state with a strip region of a bare substrate. Labels correspond to times in units of  $8 \times 10^3$  MD time steps. The arrow indicates the position of the upper HIC-SIC interface. (c) Position of the expanding HIC-SIC interface as a function of time for different initial striped phases, corresponding to  $r_0 = 1.04$  (open symbols) and  $1.05$  (filled symbols).

At this lower coverage, the equilibrium phase diagram indicates that the HIC phase with hexagonally arranged domain walls is the lower energy phase. Thus, the region next to the hole is dynamically converted locally into the HIC phase through rearrangement and generation of domain walls. As time progresses, the HIC region expands and there is a continuous conversion of the SIC to the HIC phase at the outer boundary. This process has been described as analogous to an “avalanche” effect that generates more mass near the outer front, which is then transported across the HIC phase from the outer boundary to the inner boundary to refill the hole. In terms of the domain walls, the light walls have a higher density at the inner boundary and are continuously driven to the outer boundary, where the density of the light walls is the lowest in the HIC phase. Thus, the HIC phase coverage near the outer boundary should be closer to its maximum allowed value in the equilibrium phase diagram of Fig. 2(b), leading to a discontinuity across the boundary. In the present calculations, however, a smooth coverage change across the boundary is observed in Fig. 5(b), which presumably is due to large thermal fluctuations or finite-size effects. By the same reasoning, the density of the HIC phase at the inner boundary in proximity to the refilled region should be the lowest coverage allowed by the HIC phase in the phase diagram. This is referred to as the critical coverage in Ref. [9].

According to this picture, there are two processes which contribute to the fast anomalous transport. The first is the conversion of the SIC to the HIC phase at the outer boundary. This conversion rate is microscopically determined by the rate at which the domain walls in the striped phase can deform and transform into a hexagonal structure.

Clearly, this rate is fastest near the boundary of the SIC-HIC phase boundary and can involve a small activation energy. The second is the mass transport in the HIC phase from the outer boundary to the inner boundary. Here lies the crucial importance of the HIC phase. As seen in our mobility results shown in Fig. 3, the pinning barrier is negligible in this phase and the mass transport via the motion of the domain walls across the HIC phase is orders of magnitude faster than normal diffusive behavior.

In contrast, the time evolution is qualitatively different when the initial profile is a hole created in the HIC phase. As the hole fills, the reduction in density outside the hole does not lead to a phase change since a decrease in density still favors the HIC state. Instead, it leads to a continuously increasing coverage away from the hole.

The above qualitative features of the refilling dynamics are consistent with that observed in the recent experiments on the Pb/Si(111) system [7,9]. The step profile there was created by desorbing the Pb atoms on the Si(111) substrate in a small circular region. For the Pb/Si(111) system, the detailed atomic structure in the incommensurate phases is more complicated than the corresponding structures in the incommensurate phases considered here. However, this is not the central factor leading to the anomalous fast mass transport. The central ingredients are the ability of the SIC phase to transform itself rapidly into the HIC near the boundary of the two phases, and the ultrafast domain wall dynamics in the HIC phase with a negligible pinning barrier. Our simple model system shares the important central features with the Pb/Si(111) system essential for superfast dynamics for mass transport. The basic mechanisms suggested by us is a generic feature of an adsorbate system near a SIC and HIC incommensurate phase boundary. It can be observed and tested on many other heteroepitaxial systems on a fcc(111) substrate.

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