Size Relation for Surface Systems with Long-Range Interactions

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From the minimization of the free energy it follows that strained layers and, more generally, surface systems governed by effective long-range interactions decaying as $1/r^2$ will exhibit periodically ordered domain structures. We show that there exists a firm relation between the size of a single domain (at low domain concentrations) and the minimum separation between them at intermediate concentrations. This size ratio is about 1:3. It is independent of the symmetry (striped or various two-dimensional arrangements) of the domain pattern. This size relation is indeed observed for a variety of different systems.

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In the absence of lattice misfit and under growth conditions close to equilibrium, one may assume that the deposition of a single layer on top of a substrate proceeds via the formation of large compact islands. Conversely, small dispersed islands obtained during growth can in many cases be regarded as the result of kinetic effects rather than representing the minimum-energy configuration of the system. A different situation, however, occurs if the deposited layer or thin film is under stress, for instance, due to a natural misfit between adlayer and substrate lattice. Such strained layers have been observed to be unstable against the formation of islands [1]. For small islands the energy cost to create the island boundary (step) is outweighed by the energy gained through strain relief: The island can partially relax at the boundary and thereby reduce its free energy. As a consequence, there exists an optimum width l_0 of a single island at which the free energy per atom is a minimum [2,3]. Hence, at low coverage the minimum-energy configuration of the system consists of small individual islands of the same width l_0. In addition to this instability against the formation of small islands, strain relief also introduces an effective long-range repulsion between them, leading to the formation of a periodically ordered arrangement of the islands [3]. The formation of such ordered patterns of islands has indeed been observed experimentally, for instance, for the Cu(110)-(2×1)O system, which exhibits a long-range ordered striped array of Cu-O islands on top of the Cu(110) substrate [4]. The island width and separation as a function of O coverage observed in the experiment was found to be in excellent agreement with the theoretical predictions [5].

The formation of long-range ordered domain structures, however, appears to be a rather general surface phenomenon: Regular patterns are observed on the clean Si(100) surface in which neighboring terraces exhibit a surface reconstruction along orthogonal directions. The two reconstructed domains have different intrinsic stress tensors and the system relaxes by forming an ordered pattern of alternating terraces [6,7]. As we will show below, the surface alloy of Ag atoms embedded in the top layer of a Pt(111) surface will also tend to form small domains with a certain degree of positional order. Effective long-range interactions other than those caused by strain relief can likewise act as the driving force to promote the formation of long-range ordered domain patterns. For instance, electric and magnetostatic dipole-dipole interactions have been proposed to stabilize the domain patterns in Langmuir-Blodgett monolayers at the water-air interface [8] and thin ferromagnetic films, respectively [9]. Because the effective long-range interactions between the domain boundaries have the same functional form as those due to elastic forces, the patterns can be described using the same formalism [5(b)].

Recently, the formation of an ordered array of up-down steps was also observed on the clean Pd(110) surface [10]. A simple model in which the effective free energy for creation of a step is assumed to be negative and treating the step-step interaction as a $1/r^2$ repulsion can rationalize the observed island structure on the surface [10]. This is not surprising, since the theoretical treatment is virtually identical to the one used to describe a strained layer [2,3] as will be shown below. Also the physical picture is very similar: The tendency to form a 1×2 reconstruction on related (110) surfaces can be regarded as an indication that the topmost layer is stressed and essentially behaves like a strained overlayer.

Here we will demonstrate that the minimization of the free energy imposes a tight condition on the pattern formed as a consequence of strain relief or, in general, of $1/r^2$ effective interactions: The size of the minority domains l_0 at low concentration is about one-third of the minimum distance $D_{\min}$ between domains reached at some intermediate coverage $\Theta_{\min}$. The relation $1/4 \leq l_0/D(\Theta) \leq 1/3$ usually holds over a relatively large range of coverages Θ around $\Theta_{\min}$. The so defined size ratio can therefore be regarded as characteristic of this type of long-range ordered pattern formation. The relation is shown to be rather general for surface systems: (i) It holds for all long-range effective interactions decaying as $1/r^2$. This includes elastic interactions as well as electrostatic or magnetic dipole-dipole interactions. (ii) The

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size relation is invariant with respect to the dimensionality and the symmetry of the pattern. It is obeyed in quasi-one-dimensional striped arrays as well as in two-dimensional checkerboard-type or hexagonal domain arrangements. (iii) The size relation is independent of absolute measures and the physical details of the particular system. It therefore has the additional advantage of being easily accessible to experiments, avoiding the problems of determining the interaction strengths and the free energies of the domain boundaries directly. We will test this relation on different experimental systems, including the strain-induced patterning of a surface alloy, which is presented here for the first time.

We start our discussion with the quasi-one-dimensional (i.e., striped) system under stress. Following [3,5] the extra free energy per unit length, ΔF, due to the formation of domains in such a system can be written as

$$\Delta F = \frac{2C_1}{l+L} - \frac{2C_2}{l+L} \ln\left(\frac{l+L}{2\pi a}\sin(\pi\Theta)\right), \tag{1}$$

where the first term is associated with the creation of the domain boundaries between domains of type A and B having widths l and L, respectively (see inset in Fig. 1). C_1 is the free energy for creation of a boundary. The second term describes the elastic relaxation: a is a microscopic cutoff (e.g., the lattice constant) and C_2 is a function of the elastic constants and of the difference of the surface stress within the two types of domains. $\Theta \equiv l/(l+L)$ and $1-\Theta$ denote the concentrations (coverage) of the domains A and B, respectively. Minimization of Eq. (1) for constant coverage Θ yields

$$l(\Theta) = \frac{\kappa\Theta}{\sin(\pi\Theta)}, \qquad D(\Theta) \equiv l(\Theta) + L(\Theta) = \frac{\kappa}{\sin(\pi\Theta)}, \tag{2}$$

with $\kappa = 2\pi a \exp(1 + C_1/C_2)$. In Fig. 1 we have plotted

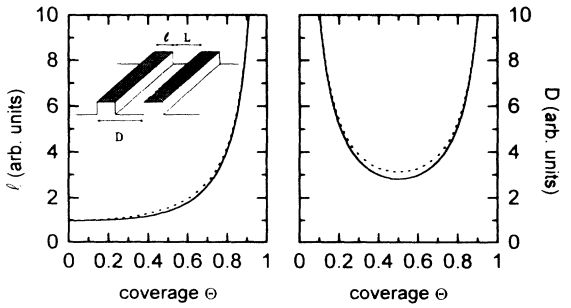

FIG. 1. Minimum-energy configuration of a striped array of domains as described by Eq. (2) (dotted lines) and domains governed by effective nearest neighbor repulsive interactions [Eq. (4), solid lines]: Diameter l of a single domain (left panel) and separation D between neighboring domains (right panel) as a function of coverage $\Theta \equiv l/(l+L)$. The inset shows a schematic view of a striped domain pattern.

the width of the domains l and the periodicity D of the striped pattern versus coverage Θ. From Eq. (2) we find the ratio between the size of the minority domains at low concentrations $l_0 \equiv l(\Theta \to 0)$ and the periodicity $D_{\min} = D(\Theta = 0.5)$ to be $1/\pi$, independent of the actual values of C_1, C_2, and a. From Fig. 1, right panel, we see that the variation of D around $\Theta = 0.5$ is very small and that a ratio $l_0/D(\Theta)$ of 1/3 to 1/4 provides an accurate description of the pattern for a relatively wide range of Θ between 0.2 and 0.8.

We will now compare the results obtained from Eq. (1) with the model proposed in Ref. [10]. This model is based on the energy balance between the creation of domain boundaries and the repulsive $1/r^2$ interaction between these domain boundaries. An "effective" free energy $\tilde{\gamma}$ associated with the formation of the domains is introduced which includes the relaxation energy at the domain boundaries. If this relaxation is sufficiently large $\tilde{\gamma}$ becomes negative and the domains are stable [10,11]. For the moment, let us again consider a quasi-one-dimensional (striped) pattern:

$$\Delta F = \frac{2\tilde{\gamma}}{l+L} + \frac{\tilde{\sigma}}{l+L}\left(\frac{1}{L^2} + \frac{1}{l^2}\right). \tag{3}$$

Here l and L have the same meaning as above and $\tilde{\sigma}$ is the interaction strength per unit length of the boundary. The two contributions in the second term in Eq. (3) correspond to the inter- and intradomain boundary interactions, respectively [10]. Minimizing Eq. (3) yields

$$l(\Theta) = \tilde{\kappa}\left(1 + \frac{\Theta^2}{(1-\Theta)^2}\right)^{1/2}, \qquad D(\Theta) \equiv l(\Theta) + L(\Theta) = \tilde{\kappa}\left(\frac{1}{\Theta^2} + \frac{1}{(1-\Theta)^2}\right)^{1/2}, \tag{4}$$

with $\tilde{\kappa} = \sqrt{-3\tilde{\sigma}/2\tilde{\gamma}}$. The ratio between $l_0 \equiv l(\Theta \to 0)$ and $D_{\min} = D(\Theta = 0.5)$ is obtained from Eq. (4) to be $1/\sqrt{8} \approx 1/2.83$ which is again close to 1/3. Also the overall shape of the curves is almost indistinguishable from those given by Eq. (2) (see Fig. 1). This result is indeed expected since the strain relaxation across the boundaries introduces an effective $1/l^2$ repulsive interaction between them [12]: If Eq. (1) is expanded for small displacements δl around the minimum-energy configuration, the leading (harmonic) term is given by $d^2F/dl^2 \sim 1/l^2$.

The strain and interaction models leading to Eqs. (1) and (3), respectively, can be extended to include various two-dimensional arrangements of domains of different shapes. As stated in [3(b)] for the case of a strained system, "the specific value of C_2 will depend on the particular mosaic pattern of the stress domains (e.g., striped, checkerboard, hexagonal, etc.). However, the general form of Eq. (1) will remain unchanged." Since the ratio l_0/D defined above does not depend on C_2 we also expect

a ratio between the diameter of a single minority domain at low concentration and the minimum distance $D_{\min}$ between such domains at intermediate coverages to be about 1/3. That this is indeed the case will be shown within the framework of effective repulsive domain boundary interactions. The two-dimensional case can be treated after a slight modification of Eq. (3) [10]:

$$\Delta F=\alpha\frac{\tilde{\gamma}l}{(l+L)^2}+\frac{\alpha}{2}\left[\frac{\tilde{\sigma}l}{(l+L)^2}\left(\frac{\beta}{L^2}+\frac{1}{l^2}\right)\right]. \quad (5)$$

Now ΔF is the extra free energy per unit area, and α and β are geometrical factors describing the shape of the individual domain and the distribution of the domains, respectively. For instance, to create a square domain with sides of length l, an energy $4\tilde{\gamma}l$ is needed, i.e., $\alpha=4$ [10]. Elongated structures are characterized by $\alpha=2$ [cf. Eq. (3)] while the most compact structures have $\alpha\rightarrow\pi$. The parameter β describes the "oddness" of the distribution of the domains. Corresponding symmetries for the shape and distribution of the domains will all have $\beta=1$ (such as elongated domains in a striped pattern, squares in a checkerboard array, or hexagonal domains on a hexagonal lattice). On the other hand, highly symmetric structures in a low dimensional pattern would have smaller β (e.g., squares arranged along a line have $\beta=0.5$) and for elongated structures in compact arrangements β tends to be equal to half the number of nearest neighbors (e.g., elongated structures on a hexagonal grid give $\beta=3$). Patterns with β values significantly different from 1, however, appear to be of artistic rather than practical interest [13].

For a quasi-one-dimensional, striped pattern $\alpha=2$, $\beta=1$, $\Theta=l/(l+L)$, and Eq. (5) reduces to Eq. (3). For the most important two-dimensional patterns [squares or rectangles in checkerboard-type arrangements [10] or hexagonal (round) patterns on a hexagonal grid] $\beta=1$ but $\Theta=[l/(l+L)]^2$. Equation (5) is then minimized by

$$l(\Theta)=\tilde{\kappa}\left[1+\frac{\Theta}{(1-\sqrt{\Theta})^2}\right]^{1/2},$$
$$D(\Theta)\equiv l(\Theta)+L(\Theta)=\tilde{\kappa}\left[\frac{1}{\Theta}+\frac{1}{(1-\sqrt{\Theta})^2}\right]^{1/2}, \quad (6)$$

with $\tilde{\kappa}=\sqrt{-3\tilde{\sigma}/2\tilde{\gamma}}$. Equation (6) is almost identical to Eq. (4) except that Θ is replaced by $\sqrt{\Theta}$. Consequently, the ratio $l_0/D_{\min}=l_0/D(\sqrt{\Theta}=0.5)$ is again equal to $1/\sqrt{8}\approx 1/2.83$. Figure 2 shows the dependence of l and D on Θ. Note that $\sqrt{\Theta}=0.5$ now corresponds to $\Theta=0.25$ and the size ratio slowly decreases to 1/3.7 as the coverage approaches $\Theta=0.5$. Nevertheless, as for the quasi-one-dimensional striped pattern, a size ratio of 1/3 to 1/4 remains a characteristic measure of the pattern for a large range of intermediate coverages.

We will now apply our result to selected examples of long-range periodic structures of very different nature,

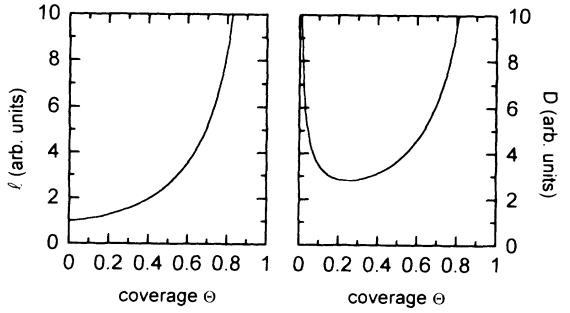

FIG. 2. Minimum-energy configuration array of domains coupled by $1/r^2$ effective repulsive interactions but for a two-dimensional, symmetric arrangement of domains (e.g., squares on a checkerboard-type array or hexagons on a hexagonal lattice). l and D are given by Eq. (6). The curves are identical to those in Fig. 1, except that now $\Theta\equiv[l/(l+L)]^2$.

which exhibit patterns of different symmetry. The patterns described by the models above refer to the minimum energy configurations. They do not account for kinetic effects, which may prevent these structures from being observed. In the following examples the observed patterns are stable and close to equilibrium.

As a first example, we mention the striped pattern of the reconstructed Cu-O(2×1) islands on top of the (nonreconstructed) Cu(110) substrate [4]. It has been shown in Ref. [5] that this structure can be described by Eq. (2) over the entire coverage range, and hence the size ratio as defined above is indeed close to 1/3.

The recent observation of terraces formed spontaneously at the clean Pd(110) surface [10] is an example of a two-dimensional checkerboard-type arrangement of domains. From a fit of the intensity ratio of the superstructure diffraction peaks Hörnis *et al.* obtain a ratio $l(\Theta)/L(\Theta)$ of about 1:3 and 1:2 along the two (nonequivalent) symmetry directions [1$\bar{1}$0] and [001], respectively [10]. The corresponding coverage is $\Theta=1/12$ and since $l(\Theta)$ is a slowly varying function at low coverages (cf. Fig. 2) $l(\Theta=1/12)\approx l_0$. Using $D(\Theta)=L(\Theta)+l(\Theta)$ size ratios l_0/D of 1/4 and 1/3, respectively, are deduced from the measurements, again in excellent agreement with our prediction. It should be pointed out, however, that a further test of the relations in Eqs. (2) or (4) is not possible because the coverage Θ is fixed and cannot be varied experimentally.

Finally, we report our recent He-diffraction measurements on Ag islands grown on a hexagonal Pt(111) surface. Further details on the experiment will be published in a forthcoming paper [14]. The Ag/Pt(111) system has been studied previously by Becker *et al.* [15] using He scattering and Röder and co-workers [16,17] by scanning tunneling microscopy (STM). It has been observed that Ag deposited at temperatures above 620 K nucleates into small compact islands, whose initial size is about 10 Å in diameter corresponding to 7–12 atoms [15,17]. These structures were identified to be small two-dimensional

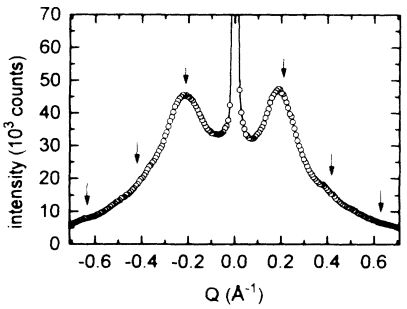

FIG. 3. He-diffraction profile along the $\overline{\Gamma M}$ symmetry direction of a Pt(111) surface after the deposition of 0.5 monolayer of Ag at 700 K. After this preparation clusters of Ag atoms embedded in the topmost Pt(111) layer are obtained [16]. The measurements were performed at a surface temperature of 60 K and a He beam energy of 21.6 meV. The diffraction features at $|Q| = 0.21$ Å^{-1} at both sides of the specular ($Q=0$) as well as the small shoulders at about twice this value reflect the formation of a (short-range) ordered arrangement of these clusters. The arrows indicate the diffraction peak position as expected for a periodically ordered pattern.

(2D) Ag clusters embedded in the topmost Pt layer [17]. Because of the mismatch between the Ag and Pt lattice parameters the embedded Ag islands are strained (as would also be Ag islands on top of the Pt substrate [15]). Figure 3 shows a He-diffraction scan around the central, zeroth order diffraction peak for a Ag coverage of 50% of a monolayer ($\Theta=0.5$) deposited on the clean Pt(111) substrate at 700 K. Distinct diffraction features appear at wave vector transfer $Q = 0.21$ and $Q = -0.21$ Å^{-1}. The spectrum is taken along the $\overline{\Gamma M}$ symmetry direction of the underlying Pt substrate. The superstructure diffraction features correspond to a characteristic lateral distance in real space of $D = 2\pi/|Q| \approx 30$ Å. The satellite peaks are rather broad (along the scan direction as well as azimuthally); hence the ordering is weak and only of short range. Nevertheless, small shoulders at about twice the distance of the primary satellite peaks can still be distinguished. We have indicated in Fig. 3 the diffraction peak position expected for a periodically ordered structure (arrows).

The diffraction features can be observed in the coverage range between $\Theta=0.1$ and 0.75. For $\Theta \geq 0.2$ the peak position remains nearly constant up to coverages ≥ 0.5. At coverages below 0.2 and above 0.75 the satellite peaks shift towards $Q=0$ while at the same time the peak intensities decrease rapidly. This characteristic variation of the peak position with coverage indicates that the satellite peaks here reflect the average separation between embedded silver islands, rather than their mean size [18]. The interpretation of the diffraction results is now straightforward: The embedded Ag atoms initially form strained islands of about 10 Å in diameter. These islands are arranged in a two-dimensional pattern with at least short-range order [19]. The mean separation varies only slowly with coverage for $0.1 \leq \Theta \leq 0.75$, which is in qualitative agreement with the results shown in Figs. 1 and 2. The ratio between the initial Ag island size and their average separation at intermediate coverage is about 1:3. Hence we would predict that the observed structure for Ag embedded in the top layer of the Pt(111) surface is caused by the strain relief mechanism. Generally, we can use this size criterion to check whether a long-range periodic structure could involve effective $1/r^2$ repulsive interactions or not.

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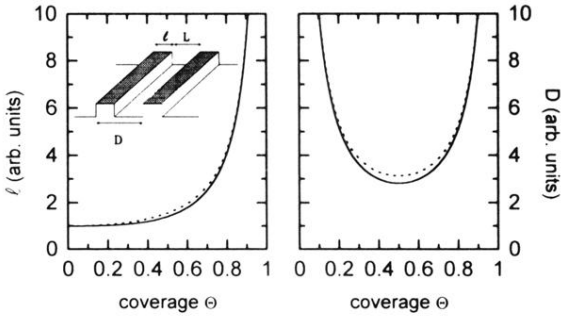
[19] Specular He-diffraction measurements as well as inspection of the STM images in [17] indicate that the pattern formed at low Ag coverage can be described as an array of compact 2D clusters, while for $\Theta \approx 0.5$ the pattern rather resembles regularly spaced meandering stripes.



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