

modes of the collisionless universal instability are stable and that the long-time behavior of an initial disturbance is dominated by the convective<sup>4</sup> modes.

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## Pseudoharmonic Theory of Orientational Instabilities in Physisorbed Layers

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The rotation of physisorbed monolayers with respect to the substrate was first predicted by Novaco and McTague in the harmonic approximation. An anharmonic theory of this effect is given here. The rotation takes place at the commensurate-incommensurate transition, provided the longitudinal sound velocity of the free adsorbate is more than twice as large as the transverse sound velocity.

Physisorbed monolayers often show phases which are incommensurate with the substrate.<sup>1-3</sup> Similar discommensuration effects have been observed in charge-density waves,<sup>4,5</sup> liquid crystals under certain conditions,<sup>6,7</sup> ferroelectrics like NaNO<sub>2</sub>, and many magnetic materials. However, adsorbed layers have particular properties due to the simultaneous existence of transverse and longitudinal modes. For instance, in certain cases, the adsorbate is tilted with respect to the substrate. This effect was first predicted by Novaco and McTague, using the harmonic approximation.<sup>8</sup>

This paper gives an anharmonic treatment of the effect. One advantage of the approach is that the anharmonic theory can be applied near the commensurate-incommensurate (C-I) transition, when the harmonic approximation cannot be used. Furthermore, our treatment is simpler and yields the energy as an extremely simple function of the tilt angle, whereas Novaco and McTague obtained the energy as an infinite sum from which the dominant term is difficult to extract.

As suggested by Venables,<sup>2</sup> the adsorbed layer is treated as a succession of domains separated by walls. [The terminology "dislocation"<sup>2</sup> or

"soliton" is sometimes used. We prefer the word "wall" for a  $(D-1)$ -dimensional steady defect, "dislocation" for a  $(D-2)$ -dimensional defect, and "soliton" for a propagating defect.] Inside each domain the system is assumed to be harmonic and nearly in registry with the substrate. Thus all anharmonic features are contained in the walls. This approach is especially appropriate near the C-I transition, when the distance  $l$  between walls is large with respect to the wall thickness  $1/\kappa$ .

*Pseudoharmonic theory: Basic equations.*—Let the adatoms be labeled by a  $D$ -dimensional vector index  $\nu = (x_1, x_2, \dots, x_D)$  and let  $\vec{R}(\vec{r}) = (X_1, X_2, \dots, X_D)$  denote their position. For physical applications  $D=2$ . More precisely,  $\vec{r}$  can be chosen as the position that the adatom would occupy at zero temperature in the absence of interaction with the substrate, i.e., in the "free" adsorbate. Then the components of the strain tensor are<sup>9</sup>

$$U_{\alpha\gamma}(\vec{r}) = \frac{1}{2} \partial_{\alpha} [X_{\gamma}(\vec{r}) - x_{\gamma}] + \frac{1}{2} \partial_{\gamma} [X_{\alpha}(\vec{r}) - x_{\alpha}], \quad (1)$$

where  $\alpha, \gamma = 1, 2, \dots, D$  and  $\partial_{\alpha} = \partial/\partial x_{\alpha}$ . The adsorbate is treated as an elastic continuum.

The registered state corresponds to  $\vec{R}(\vec{r}) = C\vec{r} + B$ , where  $C$  and  $B$  are constants. The appropriate generalization for the incommensurate phase

is (Fig. 1)

$$\vec{R}(\vec{r}) = C\vec{r} + \vec{u}(\vec{r}), \quad (2)$$

where  $\vec{u}(\vec{r})$  is almost constant far from the walls. For the sake of simplicity the walls will be assumed to be parallel planes, or straight lines for  $D=2$ . The  $x_1$  direction can be chosen orthogonal to the walls. At equilibrium in the continuum approximation the walls must clearly have a uni-

form distance  $l$ . It is sufficient to calculate the elastic energy between two successive walls at  $x_1 = -l/2$  and  $x_1 = +l/2$ .  $\vec{u}(\vec{r}) = \vec{u}(x_1)$  depends only on  $x_1$  and the boundary conditions are

$$\vec{u}(\pm \frac{1}{2}l) = \pm \frac{1}{2}\vec{b}. \quad (3)$$

The vector  $\vec{b}$  is a characteristic of the host lattice (Fig. 1). Its modulus is fixed, but its angle  $\varphi$  with  $x_1$  depends on the orientation of the wall with respect to the substrate.

The free energy is written as

$$F = \int d^D r [\frac{1}{2}\lambda(\sum_{\alpha} U_{\alpha\alpha})^2 + \mu \sum_{\alpha\gamma} (U_{\alpha\gamma})^2] + \int d^D r [A |\vec{u}(\vec{r})|^2 + E_0]. \quad (4)$$

The first term is the free energy of the free adsorbate, and  $\lambda$  and  $\mu$  are Lamé coefficients.<sup>3</sup> The second term is the interaction between the substrate and the adsorbate in an approximation similar to the approximation of Luban, Mukamel, and Shtrikman<sup>7</sup> for liquid crystals. We call it the "pseudoharmonic approximation." The system is harmonic everywhere except along the central axis of the walls.  $A$  is a constant and  $E_0$  depends on pressure. The distortion of the substrate is neglected. The integral in (4) is over the adsorbed mass  $r$ , not over the substrate area  $R$ .

After insertion of (1) and (2) into (4), minimization of  $F$  with boundary conditions (3) yields

$$u_1(x_1) = b_1 \exp(-\kappa l/2) \sinh \kappa x_1 / [1 - \exp(-\kappa l)], \quad (5a)$$

$$\vec{u}_T(x_1) = \vec{b}_T \exp(-\kappa_T l/2) \sinh \kappa_T x_1 / [1 - \exp(-\kappa_T l)], \quad (5b)$$

where  $\vec{b}_T = (0, b_2, \dots, b_D)$  and  $\vec{u}_T = (0, u_2, \dots, u_D)$  are the components of  $\vec{b}$  and  $\vec{u}$  parallel to the wall, and

$$\kappa^2 = 2A/(\lambda + 2\mu), \quad \kappa_T^2 = 2A/\mu. \quad (6)$$

*Pseudoharmonic theory: Orientation of the walls.*—The next step is the minimization of the free energy with respect to  $\cos \varphi = b_1/b$  and  $l$ , for a given value of the substrate area

$$v = \int d^D R = \int C^{D-1} (C + \partial_1 u_1) d^D r = C^D V [1 + (b/l) \cos \varphi] \quad (7)$$

where  $V$  is proportional to the adsorbed mass. [Equation (7) holds if the walls correspond to an increase of the interatomic distance. In the opposite case  $b$  should be replaced by  $-b$ ].

$$V = \int \dots \int dx_1 \dots dx_D.$$

Insertion of (1), (2), (5), and (7) into (4) yields, for large  $l$ ,

$$C^D \frac{F}{v} = \text{const} + \frac{Ab^2}{2l} \left[ \frac{1}{\kappa_T} + \left( \frac{1}{\kappa} - \frac{1}{\kappa_T} \right) \cos^2 \varphi + \frac{1}{\kappa} e^{-\kappa l} \cos^2 \varphi - g \cos \varphi \right], \quad (8)$$

where  $g$  is a pressure-dependent parameter,

$$g = (AbC)^{-1} [2E_0 - (C^2 - 1)(\lambda D + 2\mu)].$$

The shear modulus  $\mu$  and the compression modulus  $[\lambda + (2\mu/D)]$  of the free adsorbate must be positive.<sup>9</sup> This implies  $\kappa < \kappa_T$ . For this reason a term containing  $\exp(-\kappa_T l)$  has been neglected in (8).

When  $g$  is smaller than a critical value  $g_c$ , the free energy has a minimum for  $l = \infty$ , indicating the stability of the registered state. A continuous transition occurs at  $g_c$ , and the behavior of  $l$  and  $\varphi$  just above  $g_c$  is readily obtained if one equates the derivatives of (8) with respect to  $l$  and  $\varphi$  to

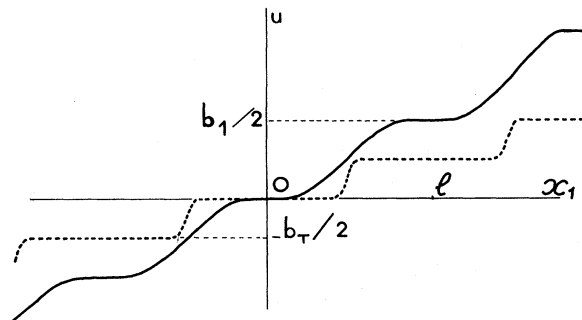


FIG. 1. Spatial variation of the longitudinal component (full curve) and of the transverse component (dashed curve) of the displacement  $u$  from the registered position.

be zero. There are two cases:

(i) If  $\kappa_T < 2\kappa$ ,

$$g_c = 1/\kappa, \quad \varphi = 0.$$

The walls are orthogonal to the crystallographic direction  $\vec{b}$  of the substrate. The variation of  $l$  is given, in qualitative agreement with previous results,<sup>4,6,7,10</sup> by

$$le^{-\kappa l} = g - g_c. \quad (9)$$

(ii) If

$$\kappa_T > 2\kappa \quad (10a)$$

or

$$\lambda > 2\mu, \quad (10b)$$

Eq. (9) is again correct, with

$$g_c = (2/\kappa_T)[(\kappa_T/\kappa) - 1]^{1/2}$$

but the walls take an asymmetric position given by

$$\cos \varphi \approx g/2(\kappa^{-1} - \kappa_T^{-1}). \quad (11)$$

Condition (10) means that the velocity of longitudinal sound in the free adsorbate ( $A=0$ ) would be more than twice as large as the velocity of the transverse sound.

Situation (ii) corresponds to rotation of the adsorbate with respect to the substrate (Novaco-McTague effect) as will now be argued. For simplicity, we consider the case  $\kappa_T l \lesssim 1$ . Equations (5) can then be approximated by

$$\vec{R}(\vec{r}) = C\vec{r} + \vec{b}x_1/l, \quad (12)$$

and this relation holds for the whole crystal [whereas Eqs. (5) are restricted to  $|x_1| < l/2$ ]. A line defined by  $\vec{b} \cdot \vec{r} = \text{const}$  corresponds to a crystallographic direction of the adsorbate, as can be seen from the consideration of the registered state ( $l = \infty$ ). Application of transformation (12) tilts this direction by an angle roughly proportional both to  $\varphi$  and to  $1/l$  (Fig. 2).

*Discussion.*—The present theory contains a number of approximations and assumptions.

(i) The pseudoharmonic approximation [second term of Eq. (4)] assumes the system to be harmonic everywhere except along infinitely narrow walls. In practice, the interaction  $V(\vec{u}(\vec{r}))$  with the substrate is a periodic function of  $\vec{u}$  and the system can only be considered as harmonic at a sufficiently large distance  $r > \Delta/2$  from the wall axis, when  $d^2V/du^2 > 0$ . The present theory is expected to be correct if both  $\kappa l$  and  $\kappa \Delta$  are much smaller than 1. This implies an appropriate

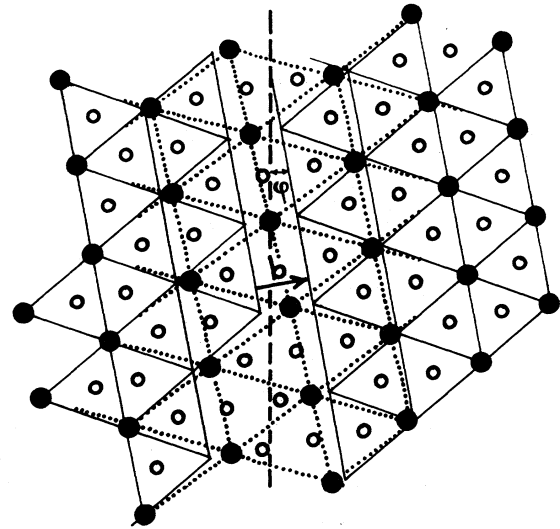


FIG. 2. A skew wall in the triangular lattice, showing the resulting rotation of the adsorbate (dotted lines) with respect to those of the substrate (full lines). The black circles are adatoms. The small open circles and the intersections of full lines are registered adsorption sites. The dashed line is the central axis of the wall.

form of  $V(u)$ . The usual choice for  $D=1$  is  $V(u) = -A' \cos(2\pi u/b)$  and gives rise to the usual sine-Gordon equation. Extension to two-dimensional media of this sine-Gordon formalism would probably lead to serious mathematical difficulties and no prediction will be made about the expected results.

(ii) The continuum approximation is satisfactory if  $1/\kappa_T$  is large with respect to the interatomic distance, as is probably the case for rare-gas monolayers on graphite. Increasing  $A$  would probably stabilize the symmetric structure  $\varphi = 0$ .

(iii) We discarded the possibility of wall crossing. Wall intersections would introduce terms proportional to  $1/l^2$  into expression (8). If the C-I transition is continuous, these terms are small near the transition, and the results of the section on orientation of the walls are not significantly altered. In addition, the C-I transition can only be continuous if the wall-crossing energy is positive,<sup>11</sup> and in this case wall crossing is forbidden near the transition (for an ideal surface, at  $T=0$  and in the classical approximation) so that the pseudoharmonic theory is applicable. Preliminary investigation of a special case (a square lattice) suggests that in *this* case, wall intersections stabilize the symmetric structure  $\varphi = 0$ .

Condition (10) is quite stringent. For a triangular lattice with central forces between nearest neighbors (a plausible model for rare-gas monolayers on graphite), one has

$$\kappa_T = \kappa\sqrt{3}, \quad (13)$$

and condition (10) is not satisfied, though the difference lies within "theoretical" error. Experimentally, however, the Novaco-McTague effect has been observed for argon on graphite.<sup>12</sup>

A last comment will be made. In charge-density-wave systems, similar distortions have been observed and received a theoretical, though purely numerical, explanation, which does not use coupling with phonons,<sup>5</sup> and is therefore completely different from ours. It would be interesting to compare the two mechanisms.

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## Surface Density of Acoustic Phonons in GaAs

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We calculate the surface density of acoustic phonons for GaAs(110) and relate it to the Brillouin elasto-optic cross section. A continuum of surfacelike excitations is found in good agreement with the position and the shape of the surface structure observed in the measured Brillouin spectrum. The role played by the optical absorption coefficient in determining different scattering mechanisms is also discussed.

Brillouin scattering is up to now the only experimental technique which has been successfully employed to detect thermally excited acoustic phonons in metals and semiconductors.<sup>1,2</sup> In the past it has been used in semiconductors in normal incidence.<sup>1</sup> In this case a proper theory has been developed to understand the position and the line shape of the peaks appearing in the experimental spectra and representing bulk phonons.<sup>1,3</sup>

Only recently Sandercock<sup>2</sup> has shown that Brillouin backscattering spectroscopy can be used as a useful technique of high resolution to detect thermal-equilibrium surface acoustic phonons. The measured spectra show, in addition to the usual Rayleigh wave, the existence of a continuum of modes with surface character whose frequencies  $\omega$  lie between the transverse and

longitudinal bulk thresholds. The line shape of this structure appears to be different in metals (optical absorption coefficient  $n_2 > 1$ ) and semiconductors below the absorption edge ( $n_2 < 1$ ): The spectra of the former present a broad shoulder, while the latter show a rather narrow peak located just below the longitudinal threshold.

The nature of the shoulder in the case of metals has been recently explained in terms of scattering from surface ripples,<sup>4</sup> which in turn is proportional to the normal component of the surface density of phonon states (SDPS). This quantity has been computed by Loudon<sup>4</sup> for an isotropic elastic medium and shows good agreement with the experimental spectrum of polycrystalline Al. The SDPS of a metal (tungsten) has been also evaluated independently by the authors<sup>5</sup> in the frequency range of interest, within a microscopic