

## Pseudomorphic-to-close-packed transition. I. General formulation

Jan H. van der Merwe, E. Bauer,\* D. L. Tönsing, and P. M. Stoop

Department of Physics, University of South Africa, P.O. Box 392, Pretoria 0001, South Africa

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Monolayers (ML's) of Ni and Co grow at equilibrium on {110} W and Mo substrates, with which they bond strongly and have large negative misfits, pseudomorphically until completion of the pseudomorphic monolayer. When excess atoms are deposited atop the pseudomorphic monolayer, it transforms to a misfitting, more or less close-packed (cp) monolayer with misfit dislocations at the monolayer-substrate interface. In nonequilibrium growth, the pseudomorphic-to-close-packed transition occurs in monolayer islands before completion of the pseudomorphic ML. The main objectives of the paper are (i) to show that the pseudomorphic ML is more stable than the close-packed monolayer and (ii) to develop an understanding of the pseudomorphic-to-close-packed transition. In paper I we introduce force models and derive expressions for (a) equilibrium zero-order energies of complete and incomplete misfit dislocations having displacement vectors equal to a lattice and half a lattice vector, respectively, and (b) equilibrium first-order energy for incomplete misfit dislocations (assumed to yield the lowest energy configuration), these two being the candidates for minimum energy of the close-packed monolayer. The numerical computation of parameters (using embedded-atom methods) and derived energies (including anharmonic pseudomorphic strain energy), needed to answer the relevant questions, are left for paper II.

### I. INTRODUCTION

The growth mode, structure, and thermal stability of ultrathin metal films are of great fundamental and technological interest and comprise a topical field of research. Studies<sup>1,2</sup> of the growth of Ni and Co on Mo and W{110}, for example, revealed the tendency to form in equilibrium initially extensive monolayer (ML) islands displaying a (1×1) low-energy-electron-diffraction (LEED) pattern which undergo a transition to a phase displaying a (8×2) LEED pattern when excess atoms are deposited on top of the initial ML. Whereas the (1×1) pattern is interpreted as coming from a pseudomorphic (ps) ML, the (8×2) pattern is interpreted as being generated by an almost close-packed (cp) ML in Nishiyama-Wassermann orientation on a bcc{110} face (Fig. 1) in which there is perfect registry in the *x* direction—bcc[110]—and an 8 substrate by 10 ML atom row coincident in the *y* direction.

For the purpose of the present considerations it is useful to elaborate on two aspects of the observations: the growth mode and the geometry of mismatch and strain. The condition that the deposit starts to grow as an extensive ML at equilibrium, i.e., by the so-called Frank-van der Merwe or in the Stranski-Krastanov growth mode, has been expressed in terms of specific surface free energies  $\gamma$  ( $\gamma_s$ ,  $\gamma_f$ , and  $\gamma_i$  for the substrate, film, and film-substrate interface, respectively) as<sup>3,4</sup>

$$\Delta\gamma \equiv \gamma_f + \gamma_i - \gamma_s \leq 0. \quad (1a)$$

This condition for two-dimensional (2D) growth can also be expressed<sup>5</sup> as a useful bond strength relation

$$\Delta\gamma \equiv E_{ff} - E_{fs} \leq 0. \quad (1b)$$

In (1b),  $E_{ff}$  and  $E_{fs}$  are respectively the film-film and film-substrate adhesion (bond) energies. Condition (1b)

satisfies our intuition that strong epilayer-substrate bonding is conducive to 2D growth and also lends itself more to an atomic interpretation. Condition (1a), on the other hand, has a practical advantage in that surface energies are often known.

It is customary to express the interfacial misfits  $f_i$  between an epilayer in Nishiyama-Wassermann orientation on a bcc substrate in terms of bulk dimensions—diagonal lengths  $a_i$  (substrate) and  $b_i$  (epilayer) shown in Fig. 1—as<sup>6</sup>

$$f_i = \frac{b_i - a_i}{a_i} = \frac{r}{r_i} - 1; \quad r = \frac{b}{a}, \quad i = x, y, \quad (2a)$$

where  $a$  and  $b$  are the corresponding nearest-neighbor

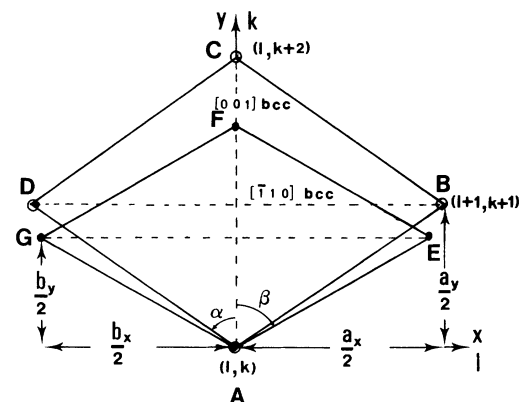


FIG. 1. Diagram showing ML atoms in a bulk rhombic close-packed unit cell AEF G (diagonal lengths  $b_x$  and  $b_y$ ) as solid circles and substrate potential minima located on corners of bcc (110) rhombic unit cell ABCD (diagonal lengths  $a_x$  and  $a_y$ ) as open circles. [110] and [001] are the directions within the bcc (110) plane. The integers ( $l, k$ ) enumerate the adsorption sites within the (110) bcc lattice.

distances and

$$\begin{aligned} b_x &= 2b \sin\beta, & b_y &= 2b \cos\beta; & \beta &= 60^\circ, \\ a_x &= 2a \sin\alpha, & a_y &= 2a \cos\alpha; & \alpha &= \arctan\sqrt{2}, \\ r_x &= \sin\alpha/\sin\beta = \sqrt{8/9}, & r_y &= \cos\alpha/\cos\beta = \sqrt{4/3}. \end{aligned} \quad (2b)$$

For Ni{111} and Mo{110},  $b = 2.489 \text{ \AA}$  and  $a = 2.726 \text{ \AA}$ , so that  $f_x = -0.0315$  and  $f_y = -0.2092$ . Strictly speaking, we should express the misfit in terms of the equilibrium dimensions of the epimono-layer, which may differ from that of the bulk.

In general, the misfit is accommodated by both misfit dislocations (MD's) of density  $\bar{f}_i$  and misfit strain (MS;  $\bar{e}_i$ ), where

$$\begin{aligned} \bar{f}_i &= (\bar{b}_i - a_i)/a_i; & i &= x, y, \\ \bar{e}_i &\equiv \frac{\bar{b}_i - b_i}{b_i} = \frac{r_i}{r} (\bar{f}_i - f_i), \end{aligned} \quad (3)$$

$\bar{b}_i$  being the strained value of  $b_i$ .

Two types of MD's are relevant: complete misfit dislocations (CMD's), in which the displacement vector is two atom row spacings (a lattice vector), and incomplete misfit dislocations (IMD's), in which it is only one row spacing.<sup>7</sup> If  $\bar{P}_i$  ( $\bar{P}_i$  substrate atomic rows) designate MD spacings

$$\begin{aligned} \bar{P}_i^C &= (\bar{P}_i^C + 2)\bar{b}_i/2 = \bar{P}_i^C a_i/2 & \text{for CMD's; } i &= x, y, \\ \bar{P}_i^I &= (\bar{P}_i^I + 1)\bar{b}_i/2 = \bar{P}_i^I a_i/2 & \text{for IMD's.} \end{aligned} \quad (4)$$

The observations<sup>1,2</sup> suggest that  $\bar{P}_y^C = 8$ .

It follows that

$$\bar{f}_i^C = -\frac{2}{\bar{P}_i^C + 2}, \quad \bar{f}_i^I = -\frac{1}{\bar{P}_i^I + 1}; \quad \bar{P}_i^C = 2\bar{P}_i^I, \quad (5)$$

and, hence, from Eqs. (2)–(5), that

$$\begin{aligned} \bar{f}_x &= 0, & \bar{e}_x &= -r_x f_x / r \approx 0.0325, \\ \bar{f}_y &= 0, & \bar{e}_y &= -r_y f_y / r \approx 0.2646, \end{aligned} \quad (6)$$

in the ps configuration of Ni on Mo, and

$$\begin{aligned} \bar{f}_x &= 0, & \bar{e}_x &= 0.0325, \\ \bar{f}_y^I &= \bar{f}_y^C = -\frac{2}{8+2} = -0.20, & \bar{e}_y &= 0.0116 \end{aligned} \quad (7)$$

in the cp configuration.

Since  $f_x$  is small, clearly well below a critical misfit below which a ps ML is stable, it is not surprising that registry dimensions are obtained in the x direction for both the ps and the cp ML. In the y direction the strain is small ( $\bar{e}_y = 0.0116$ ) in the cp configuration, but rather large ( $\bar{e}_y = 0.2646$ ) in the ps ML.

The issues that need to be addressed are as follows.

(i) Is the occurrence of the ps configuration in accordance with the equilibrium minimum energy principle

$$\epsilon_{ps} - \epsilon_{cp} < 0, \quad (8)$$

where  $\epsilon$  is the average energy per ML atom?

(ii) How can we explain the apparent violation of the minimum-energy principle for the ps-to-cp transition?

(iii) What roles do bond strength and large negative misfit ( $f_y \approx -0.2092$ ) play in the phenomenon?

To address issue (i) we need to calculate  $\epsilon_{ps}$ . This requires an anharmonic description because of the large ( $\bar{e}_y \approx 0.26$ ) ps strain. We assume the embedded-atom methods (EAM) are appropriate for this purpose. In the cp configuration the strain  $(\bar{e}_x, \bar{e}_y) = (0.0325, 0.0116)$  is small enough for the validity of the harmonic (elastic) approximation in calculating the energy  $\epsilon_{cp}$ . In this case the misfit is accommodated by both MS's and MD's.

As to issues (ii) and (iii), it will be shown that the transition is favored by kinetics in a process involving the formation of MD's by penetration—previously named climb<sup>8</sup>—of excess atoms into the ps ML. It is anticipated that the penetration is facilitated by strong ML atom-substrate bonding and large ( $\bar{e}_y = 0.2647$ ) ps strain.

In paper I we develop the analytical framework to address the issues involved and in paper II we compute the quantities needed to answer the set questions.

## II. MODEL

### A. Governing physical principles

We accept that thermodynamic processes proceed toward configurations of lower free energy and, accordingly, that in equilibrium, the free energy is a minimum. In ordered configurations, for example, those with regularly spaced straight MD's, lowest free energy may be approximated by lowest energy. We adopt this minimum-energy principle as a condition for stability of our systems.

The equilibrium rate depends on the driving forces and the kinetic mechanisms involved. The transition route may be biased by contributions of configurational entropy of disordered intermediate or final configurations and by kinetic short cuts to speed up the transition rate. Such route and rate factors will be invoked to gain understanding of the ps-to-cp transition.

### B. Atomic interaction

#### 1. Interlayer interaction

In order to calculate the energetics, we need to construct models for the atomic interaction. For the ML atom-substrate interaction  $V$ , we adopt a rigid substrate and assume that the interaction has the periodicity of the substrate.<sup>9</sup>  $V(x, y)$  may thus be expressed in terms of a Fourier series in the coordinates of Fig. 1 and with coefficients that decrease rapidly with harmonic order so that the series may be truncated at fairly low order.<sup>8</sup> A truncation that is analytically tractable, suitable for the description of MD's in the Nishiyama-Wassermann orientation<sup>6,7</sup> and satisfies the twofold symmetry of the {110} bcc substrate, is the second-order truncation<sup>10</sup>

$$V(x,y) = A_0 \left[ 1 + A_1 \left\{ \cos \left[ 2\pi \left( \frac{x}{a_x} + \frac{y}{a_y} \right) \right] + \cos \left[ 2\pi \left( \frac{x}{a_x} - \frac{y}{a_y} \right) \right] - c_1 \cos \frac{4\pi x}{a_x} + c_2 \cos \frac{4\pi y}{a_y} \right\} \right], \quad (9)$$

in which the origin is taken at an adsorption site.  $V(x,y)$  is a normalized form in which  $V(0,0)=0$  in the full series—in the truncation only approximately [ $V(00)=0.0236$  eV]—and  $A_0 > 0$  is its average. Equation (9) accordingly does not include the energy of desorption.

A prerequisite for the present application is that values of the Fourier coefficients be available. We assume that reliable coefficients for the systems under consideration, can be calculated using EAM's,<sup>11–13</sup> of which more details will be provided in a later section. At this stage it is necessary, though, to mention, as will be shown in paper II, that  $A_1$  is negative and  $c_1$  positive. This has important consequences, as will be seen in Sec. III A.

### 2. Interlayer interaction: Rigid model

The intralayer interaction—atom-atom interaction within the overlayer (ML)—has been usefully modeled on different levels of sophistication: rigid, harmonic, and anharmonic. In the rigid model<sup>6</sup> the ML is constrained to have a fixed, uniform structure, which may be the bulk structure or a homogeneously deformed version thereof. This model is used in a search for the main levels of ML-substrate interaction energy. By this search we identify the lowest imaginable energy configurations to which MS and MD energy should be added to obtain the energy needed to assess the stability of a given configuration. With weak ML-substrate bonding and/or high densities of MD's, the oscillatory strains accompanying the MD's are negligible,<sup>6</sup> so that the ML configuration approaches a rigidlike behavior in which the misfit is accommodated by a so-called misfit vernier, i.e., a mode in which the oscillatory strains are absent.

### 3. Intralayer interaction: Harmonic model

Useful predictions have been made in the past by imagining the epilayer atoms to be embedded in a sheet of elastic continuum.<sup>9,14</sup> This approach will be adopted here to investigate the energetics of the cp ML. For the ps ML an anharmonic approach would be required.

For the  $\{111\}$  fcc ML's under consideration we need to describe the behavior of MD's in local axes  $(x,y,z) \equiv ([1\bar{1}0], [1\bar{1}2], [111])$ , the  $z$  axis being normal to the ML plane. This requires a transformation of the Hookean equations and stiffness constants  $c_{ij}$  (in contracted form) from cubic to local axes:<sup>15</sup>

$$\begin{aligned} \sigma_x &= \bar{c}_{11}e_x + \bar{c}_{12}e_y + \bar{c}_{13}e_z + \bar{c}_{14}e_{yz}, \\ \sigma_y &= \bar{c}_{12}e_x + \bar{c}_{11}e_y + \bar{c}_{13}e_z - \bar{c}_{14}e_{yz}, \\ \sigma_z &= \bar{c}_{13}e_x + \bar{c}_{13}e_y + \bar{c}_{33}e_z, \\ \sigma_{yz} &= \bar{c}_{14}e_x - \bar{c}_{14}e_y + \bar{c}_{44}e_{yz}, \\ \sigma_{xz} &= \bar{c}_{44}e_{xz} + \bar{c}_{14}e_{xy}, \\ \sigma_{xy} &= \bar{c}_{14}e_{xz} + \bar{c}_{66}e_{xy}; \\ \bar{c}_{11} &= (c_{11} + c_{12} + 2c_{44})/2, \\ \bar{c}_{13} &= (c_{11} + 2c_{12} - 2c_{44})/3, \\ \bar{c}_{12} &= (c_{11} + 5c_{12} - 2c_{44})/6, \\ \bar{c}_{14} &= (-c_{11} + c_{12} + 2c_{44})/3\sqrt{2} = -\bar{c}_{24}, \\ \bar{c}_{33} &= (c_{11} + 2c_{12} + 4c_{44})/3, \\ \bar{c}_{44} &= (c_{11} - c_{12} + c_{44})/3, \\ \bar{c}_{66} &= (c_{11} - c_{12} + 4c_{44})/6. \end{aligned} \quad (10a)$$

For the analysis the Hookean equations needed to describe the elastic behavior of the ML, two obvious choices for boundary conditions that drastically simplify the Hookean equations within the ML plane exist: either the surface is taken to be free

$$0 = \sigma_z = \sigma_{xz} = \sigma_{yz} \quad (11)$$

or for a ML, which is a single layer of atoms, it seems more appropriate to take

$$0 = e_z = e_{xz} = e_{yz}, \quad (12a)$$

which means that there is neither linear strain normal to, nor shear strain on the two “surfaces” of the ML. We adopt the boundary condition (12a), yielding the Hookean equations

$$\begin{aligned} \sigma_x &= \bar{c}_{11}(e_x + Pe_y), \quad \sigma_y = \bar{c}_{11}(e_y + Pe_x), \\ \sigma_{xy} &= \bar{c}_{66}e_{xy} \end{aligned} \quad (12b)$$

and the energy per atom to

$$\epsilon = \frac{1}{2}\Omega\bar{c}_{11}[e_x^2 + e_y^2 + 2Pe_xe_y + Re_{xy}^2]; \quad (13a)$$

$$\begin{aligned} \Omega &= b^3/\sqrt{2}, \quad P = \bar{c}_{12}/\bar{c}_{11}, \\ R &= \bar{c}_{66}/\bar{c}_{11}, \quad b_z = \sqrt{2/3}b, \end{aligned} \quad (13b)$$

where  $\Omega$  is the volume per atom and the ML “thickness” is taken equal to the fcc  $\{111\}$  interlayer spacing  $b_z$ .

### 4. Embedded-atom method (EAM)

In order to accomplish our goals of assessing the stabilities of the cp and ps ML's and the role of kinetics in effecting the ps-to-cp transition we need values for the Fourier coefficients in Eqs. (9), the elastic constants in Eqs. (13), the strain energies at strains in the anharmonic regime, and energetics of penetration formation of MD's, in which, where appropriate, proximity effects of the substrate<sup>16</sup> and/or free surface are accounted for. The

EAM's developed by Johnson<sup>12</sup> are used to calculate the desired quantities.

In the EAM, originally developed by Daw and Baskes,<sup>11</sup> the energy of an atomic arrangement is expressed in the form

$$E = \frac{1}{2} \sum_{i,j} \phi(r_{ij}) + \sum_i F_i(\rho_i); \quad \rho_i = \sum_{j \neq i} f_j(r_{ij}), \quad (14)$$

where the pair potential  $\phi(r_{ij})$  provides for repulsion between atoms  $i$  and  $j$  at a distance  $r_{ij}$ ,  $\rho_i$  may be interpreted as the electron density at atom  $i$  due to all other atoms,  $f_j(r_{ij})$  is the electron density contribution of atom  $j$  at atom  $i$ , and the embedding energy  $F_i(\rho_i)$  of atoms of type  $i$  in the electron density  $\rho_i$  effects the binding. The analytic forms of the functions  $\phi$ ,  $F$ , and  $f$  appropriate to bcc-fcc combinations have been discussed elsewhere.<sup>12,16</sup> For the present, it suffices to mention that these functions contain parameters which are normally obtained by fitting to empirical values of the cohesive energy, lattice parameters, unit cell volume, isolated vacancy formation energy, Voigt's average shear modulus, and anisotropy ratio, all for bulk crystals.

We appreciate that the EAM is less accurate than more fundamental models. Furthermore we employ fitting parameters obtained from bulk properties at small deformations, whereas we wish to apply the results to ML's, even in the anharmonic regime. Its success in calculating adsorption properties<sup>10</sup> diminishes the significance of the first objection. As to anharmonicity, it is simply the best we can do at present. Some details of the procedures followed to obtain values of the desired quantities will be presented in Sec. III F.

### III. ANALYTICAL DERIVATIONS

#### A. The rigid model

The main merit of the rigid model is that the average energy per ML can be calculated exactly by summation. The role of the individual physical parameters can thus be simply established. Such calculations have been carried out in the past<sup>6</sup> and have justified energetically, among other ways, the row-matching rule for minimum interfacial energy that has been successfully applied to understand the occurrence of Nishiyama-Wassermann and Kurdjumov-Sachs epitaxial orientations in fcc{111}-bcc{110} metal epitaxy.<sup>6,17</sup> The fact that the Fourier coefficient  $A_0|A_1|c_1$  in the ML atom-substrate interaction Eq. (9) is positive and that matching is maintained in the  $x$  direction ( $\bar{f}_x=0$ ) has significant consequences for the ML substrate atomic configurations.

For the purpose of summing the interaction energy in Eq. (9) it is convenient to think of the atoms in both the bcc{110} and fcc{111} planes to be on two interpenetrating rectangular lattices. If we take the origin at an adsorption site on the {110} bcc plane, superimpose the bcc and cp lattices in parallel (Nishiyama-Wassermann orientation), assuming that the two interpenetrating lattices of the cp ML have, respectively,  $(2M+1) \times (2N+1)$  and  $2M \times 2N$  atoms [a total of  $G = (2M+1)(2N+1) + 4MN$ ], the term  $\cos(4\pi x/a_x)$  in Eq. (9) yields the sum

$$S = \left( (2N+1) \frac{\sin[\alpha(M+1/2)]}{\sin(\alpha/2)} + 2N \frac{\sin(M\alpha)}{\sin(\alpha/2)} \right) \cos \left[ \frac{4\pi x_0}{a_x} \right]; \quad \alpha = \frac{4\pi b_x}{a_x}. \quad (15)$$

It is easily shown that  $S$  has an extremum per atom of

$$S/G = \cos(4\pi x_0/a_x) \quad \text{for } b_x = ma_x \quad (16)$$

[ $m$  is an integer (usually  $m=1$ )], where  $(x_0, y_0)$  represents a rigid translation of the ML relative to the substrate. The condition that  $m$  is an integer is equivalent to "row matching." When there is mismatch, we have destructive "interference" and the average per atom  $|S|/G \ll 1$  on condition that the ML is extensive. This is equivalent to the vanishing of the sinusoidal term, namely,  $\cos(4\pi x/a_x)$  in the averaging process. When there is no matching, all periodic terms in Eq. (9) vanish on averaging to yield the result

$$\langle V \rangle = A_0. \quad (17)$$

Since this average is well defined, it is convenient to take it as an energy reference. In the present investigation we are interested in the case where the system is misfit strained to coherence in the  $x$  direction ( $\bar{f}_x=0$ , i.e.,  $\bar{b}_x=a_x$ ). This row matching ( $\bar{b}_x=a_x$ ), then, represents an energy decrease

$$\Delta V_3 = A_0 A_1 c_1 < 0 \quad \text{for } x_0 = \pm a_x/4 \quad \text{and } \bar{b}_x = a_x, \quad (18)$$

where we write  $\bar{b}_x$  to emphasize that  $b_x$  may be homogeneously "strained" into  $\bar{b}_x$ . When  $x_0=0$ , matching constitutes an energy increase  $A_0|A_1|c_1 > 0$ . This means that minimization of Eq. (9) with respect to the term in  $c_1$  requires a rigid translation  $x_0 = \pm a_x/4$ .

For the other terms we similarly obtain the relevant changes (decreases)

$$\Delta V_1 = 2A_0 A_1 < 0 \quad \text{for } x_0 = y_0 = 0 \quad \text{and } \bar{b}_x = a_x, \bar{b}_y = a_y, \quad (19)$$

$$\Delta V_4 = A_0 A_1 c_2 < 0 \quad \text{for } y_0 = 0 \quad \text{and } \bar{b}_y = a_y, \quad (20)$$

where (18) may be combined with (20) but not with (19). This gives two possibilities,

$$(i) \quad \bar{f}_x = 0; \quad x_0 = \pm a_x/4, \\ x = \text{integer} \times a_x \pm a_x/4 \quad \text{and } y_0 = 0; \quad (21)$$

$$V_I(y) = A_0 \{ 1 - |A_1| [c_1 + c_2 \cos(4\pi y/a_y)] \},$$

$$(ii) \quad \bar{f}_x = 0; \quad x_0 = 0,$$

$$x = \text{integer} \times a_x \quad \text{and } y_0 = 0;$$

$$V_C(y) = A_0 \{ 1 - |A_1| [2 \cos(2\pi y/a_y) - c_1 + c_2 \cos(4\pi y/a_y)] \}, \quad (22)$$

where  $V_I$  and  $V_C$ , which describe the MD's of the cp configuration when rigidity is abandoned, are the corresponding potentials derived from Eq. (9). It is seen that  $V_I$  has an amplitude  $V_I^0 = A_0|A_1|c_2$  and describes

IMD's, its displacement vector being  $a_y/2$ , whereas  $V_C$ , which has an amplitude  $V_C^0 = 2A_0|A_1| \gg A_0|A_1|c_2$ , describes CMD's with displacement vector  $a_y$ .

We have shown that in extensive systems, the sinusoidal terms vanish when we average, except in matching configurations, in which the averages are, respectively,  $A_0(1 - |A_1|c_1)$  and  $A_0(1 + |A_1|c_1)$ . The latter two represent the plateau levels for IMD's and CMD's, respectively. If, in addition, we have matching in the  $y$  direction ( $y_0 = 0$ ,  $y = \text{integer} \times a_y$ ) we have the averages  $A_0[1 - |A_1|(c_1 + c_2)]$  and  $A_0[1 - |A_1|(2 - c_1 + c_2)]$ —the absolute minima—for cases (i) and (ii), re-

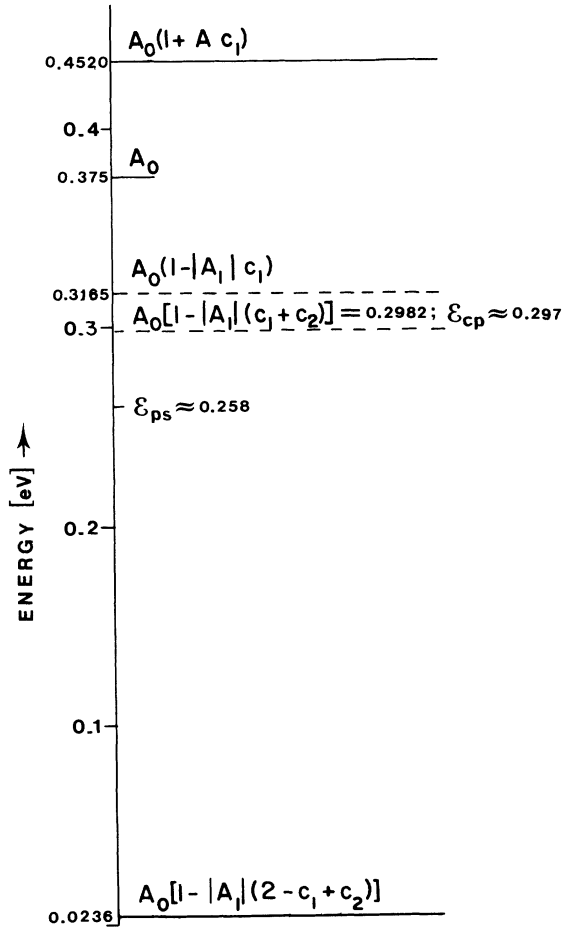


FIG. 2. Diagram exhibiting the average ML atom-substrate interaction energies per ML atom as predicted by the rigid model.  $A_0$  represents the average for an extensive ML in the absence of constraints and with nonzero misfits. When the constraint  $\bar{b}_x = a_x$ , i.e., registry, is imposed in the  $x$  direction, the average rises to  $A_0(1 + |A_1|c_1)$ , but drops to  $A_0(1 - |A_1|c_1)$  when the registry configuration is rigidly translated by  $\Delta x = \pm a_x/4$ . The respective minima that are obtained when a registry constraint is also imposed in the  $y$  direction ( $\bar{b}_y = a_y$ ) are  $A_0[1 - |A_1|(2 - c_1 + c_2)]$  and  $A_0[1 - |A_1|(c_1 + c_2)]$ . Also shown in the diagram are the energies  $\epsilon_{cp}$  and  $\epsilon_{ps}$  assigned to the cp and ps configurations, respectively. The numerical values apply to the case of Ni on Mo{110} computed using the EAM-calculated Fourier coefficients in Table II of paper II.

spectively. The energy levels pertaining to  $V_I$  and  $V_C$  are illustrated in Fig. 2. Note that the displayed energy levels are related to the overlayer-substrate interaction alone; the energy of MS's and MD's must still be added.

The rigid model analysis thus reveals that there are two candidates for minimum energy: CMD's, in which the average energy per atom lies within the bounds  $A_0[1 - |A_1|(2 - c_1 + c_2)]$  and  $A_0(1 + |A_1|c_1)$ , and IMD's, where the bounds are  $A_0[1 - |A_1|(c_1 + c_2)]$  and  $A_0(1 - |A_1|c_1)$  and the atomic arrangement is rigidly displaced by  $x_0 = \pm a_x/4$  in the  $x$  direction. For IMD's with  $\bar{f}_x = 0$  the atomic rows along the  $y$  directions run through saddle points ( $a_x/4, a_y/4$ ). The analytical derivation of the energies for these two configurations, needed to compare their relative stabilities, is carried out in the next two sections.

### B. Harmonic model: Governing equations

In the analysis below, the "rigidity" constraint of the foregoing section is abandoned. In this section we derive the equations governing the interactions competing for the positions of the ML atoms—the harmonic ML atom-atom [Eq. (13)] and the periodic ML atom-substrate interaction [Eq. (9)]—which we need to calculate the energetics of MD's in the cp ML-substrate interface. In order to derive the governing equations needed to express the interactions in terms of local coordinates, displayed in Fig. 1, we enumerate rows of substrate adsorption sites (potential minima for overlayer atoms) parallel to  $y$  by  $l = 0, \pm 1, \dots$  and those parallel to  $x$  by  $k = 0, \pm 1, \dots$ ; then the points  $A, B, C$ , and  $D$  in Fig. 1 are consecutively assigned the numbers  $(l, k)$ ,  $(l + 1, k + 1)$ ,  $(l, k + 2)$ , and  $(l - 1, k + 1)$ . We impose a one-to-one correspondence between potential troughs and interfacial overlayer atoms by assigning to them the same values of  $(l, k)$  when strained into registry. The overlayer atomic coordinates may thus be written as

$$x_{l,k} = (l + u_{l,k})a_x/2, \quad y_{l,k} = (k + v_{l,k})a_y/2, \quad (23)$$

where  $(u_{l,k}, v_{l,k})$  defines the position of the overlayer atom  $(l, k)$  with respect to the corresponding adsorption site  $(l, k)$ , both  $l$  and  $k$  being either even or odd integers.

On substituting from Eq. (23) into Eq. (9), we obtain in the continuum approximation  $u = u(l, k)$ ,  $v = v(l, k)$  the result

$$\begin{aligned} V(u, v) = & A_0(1 + A_1[\cos\{\pi(u + v)\} \\ & + \cos\{\pi(u - v)\} - c_1 \cos(2\pi u) \\ & + c_2 \cos(2\pi v)]) . \end{aligned} \quad (24)$$

The strains of Eqs. (13) may also be expressed in terms of the displacements  $(u, v)$  of neighboring atoms and simplified, using the continuum approximation,<sup>6,7</sup>

$$\begin{aligned}
e_x &= \frac{a_x}{2b_x} (u_{l+1,k+1} - u_{l-1,k+1} - 2f_x) \\
&\approx \frac{r_x}{r} \left[ \frac{\partial u}{\partial l} - f_x \right], \\
e_y &= \frac{a_y}{2b_y} (v_{l,k+2} - v_{l,k} - 2f_y) \approx \frac{r_y}{r} \left[ \frac{\partial v}{\partial k} - f_y \right], \quad (25) \\
\gamma_{xy} &= \frac{a_x}{2b_y} (u_{l,k+2} - u_{l,k}) + \frac{a_y}{2b_x} (v_{l+1,k} - v_{l-1,k}) \\
&\approx \frac{a_x}{b_y} \frac{\partial u}{\partial k} + \frac{a_y}{b_x} \frac{\partial v}{\partial l}.
\end{aligned}$$

If we substitute from the discrete forms of Eq. (25) into (13), minimize the total energy  $\Sigma(E_{l,k} + V_{l,k})$  with respect to  $u_{l,k}$  and  $v_{l,k}$ , and then introduce the continuum approximation, we obtain the equilibrium equations

$$\begin{aligned}
\Omega \bar{c}_{11} \left[ \frac{r_x^2}{r^2} \frac{\partial^2 u}{\partial l^2} + P \frac{r_x r_y}{r^2} \frac{\partial^2 v}{\partial l \partial k} \right. \\
\left. + R \frac{a_x}{b_y} \left[ \frac{a_x}{b_y} \frac{\partial^2 u}{\partial k^2} + \frac{a_y}{b_x} \frac{\partial^2 v}{\partial l^2} \right] \right] \\
= 2\pi A_0 |A_1| [\sin(\pi u) \cos(\pi v) - c_1 \sin(2\pi u)], \quad (26a)
\end{aligned}$$

$$\begin{aligned}
\Omega \bar{c}_{11} \left[ \frac{r_y^2}{r^2} \frac{\partial^2 v}{\partial k^2} + P \frac{r_y r_x}{r^2} \frac{\partial^2 u}{\partial l \partial k} \right. \\
\left. + R \frac{a_y}{b_x} \left[ \frac{a_y}{b_x} \frac{\partial^2 v}{\partial l^2} + \frac{a_x}{b_y} \frac{\partial^2 u}{\partial k^2} \right] \right] \\
= 2\pi A_0 |A_1| [\cos(\pi u) \sin(\pi v) + c_2 \sin(2\pi v)], \quad (26b)
\end{aligned}$$

where the quantities  $\Omega$ ,  $\bar{c}_{11}$ ,  $P$ , and  $R$  are defined in Eqs. (10) and (13). The same results may be obtained by the Lagrangian formalism from the continuum approach. The observation that coherency exists in the  $x$  direction, only requires that the periodicity in this direction be conserved. This requirement will be satisfied if atomic rows parallel to  $y$  assume a regular wavy nature so that they are spaced at distances  $a_x$  for any arbitrary chosen  $y$ . This feature, as well as a sequence of MD's spaced regularly along the  $y$  axis, will be taken care of if we take

$$u = u(k), v = v(k). \quad (27)$$

It is assumed that any dependence on  $l$  is negligible.

### C. Complete misfit dislocations (CMD's): Zero-order approximation

#### 1. Governing equation and its solution

It will be shown in paper II that the amplitudes of the wavelike displacements of atomic rows parallel to  $y$ —the  $y$  rows—are small enough so that, as zero-order approximations, we may take the rows to be straight. We now consider CMD's in zero-order approximation,

$$u \equiv 0, \quad v = v(k). \quad (28)$$

This corresponds to the case noted in Eq. (22), with

$$V_C(v) = A_0 [1 - |A_1| (2 \cos \pi v - c_1 + c_2 \cos 2\pi v)], \quad (29)$$

as may also be deduced from Eqs. (24) and (28). Clearly,  $V_C$  has a minimum at  $v=0$  and wide maxima at  $v=\pm 1$ . The governing equation for CMD's follows by substituting (28) into (26). Equation (26b) then yields

$$\frac{d^2 v}{dk^2} = \frac{\pi}{2L_y^2} [\sin(\pi v) + c_2 \sin(2\pi v)], \quad (30a)$$

$$L_y^2 = \Omega \bar{c}_{11} r_y^2 / 4 A_0 |A_1| r^2 = L^2 r_y^2 / r^2. \quad (30b)$$

For the cases of interest  $f_y < 0$ . We accordingly seek solutions of Eq. (30a) that have a dislocation axis at  $v = -1$ , which we chose as the origin of  $k$ . Hence,  $k$  increases from 0 upward as  $v$  decreases from  $-1$  downward to  $-2$ . The appropriate solution of (30a) may thus be written as<sup>7,18</sup>

$$\frac{dv}{dk} = -\frac{1}{L_y} [g - \cos(\pi v) - c_2 \cos^2(\pi v)]^{1/2};$$

$$g \geq 1 + c_2, \quad (31a)$$

$$\frac{\pi k}{L_y} = -G[g, c_2, \pi(v+1)]$$

$$= -\int_0^{\pi(v+1)} \frac{d\phi}{(g + \cos\phi - c_2 \cos^2\phi)^{1/2}}, \quad (31b)$$

where  $g$  is a constant of integration. An atomic arrangement, illustrating a CMD that has been formed by glide from the free edge, is shown in Fig. 3. The displacements are not drawn to scale.

The spacing of CMD's, when expressed in terms of the number of atomic rows  $\bar{P}_y$  (in the substrate) as used in Eq. (4), follows from (31b) and (30b) as

$$\bar{P}_y^C + 2 = 2G(g, c_2, \pi)L_y / \pi = 2G(g, c_2, \pi)Lr_y / \pi r, \quad (32)$$

where the counting of rows is done in the coherent

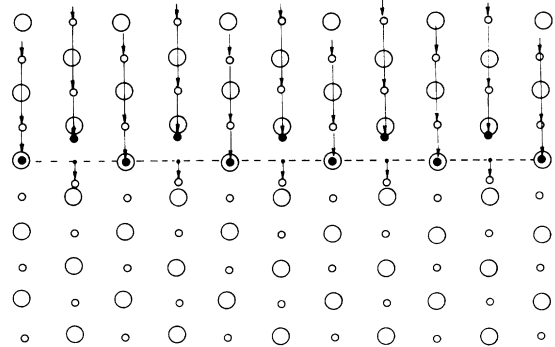


FIG. 3. Diagram illustrating the atomic displacements (arrows) and atomic configurations (small open circles) involved in the formation of complete misfit dislocations (axes on the dashed lines): generated by glide from the periphery. The solid symbols represent the "extra" row of atoms associated with the CMD. The positions of substrate atoms are shown as large open circles; positions are only schematic.

( $\bar{f}_y^C=0$ ) configuration.  $\bar{P}_y^C$  is used in defining the CMD density  $\bar{f}_y^C$  in Eq. (5). When  $g=1+c_2$ ,  $\bar{P}_y^C=\infty$  and the CMD's are infinitely spaced. This is equivalent to having an isolated CMD, which is the situation at onset of MS relief.

### 2. Average energy per atom

We calculate the average energy per atom. The average per atom of a quantity  $D(k)$  is defined by

$$\bar{D}_{av} \equiv \frac{2}{\bar{P}_y+2} \int_0^{\bar{P}_y+2} D(k) \frac{dk}{2}; \quad \bar{P}_y \equiv \bar{P}_y^C, \quad (33)$$

where  $(\bar{P}_y+2)/2$  is the number of atoms per period  $\bar{P}_y$  of a strip of width  $a_x/2$ . To calculate the strain energy from Eq. (13) we express the strains, given in Eq. (25), in the forms

$$e_x = \bar{e}_x = -\frac{r_x}{r} f_x, \quad e_y = \frac{r_y}{r} \left[ \frac{dv}{dk} - f_y \right], \quad \gamma_{xy} = 0, \quad (34)$$

using the relations (28). By summing (9) and (29) over all ML atoms and introducing the continuum approximation, we obtain on integration, using (33), for the average energy per ML atom, the result

$$\begin{aligned} \bar{\epsilon}_{av} = & A_0 [1 - |A_1|(2g - c_1 - c_2)] \\ & + \frac{\Omega \bar{c}_{11}}{2r^2} [(r_y - r_x)^2 + 2(1+P)(r - r_x)(r - r_y)] \\ & + \frac{2\Omega \bar{c}_{11} r_y}{r^2(\bar{P}_y^C + 2)} \left[ r \left[ \frac{\Gamma(g, c_2, \pi)}{\pi L} + 1 + P \right] \right. \\ & \left. - (r_y + Pr_x) \right]; \quad (35) \end{aligned}$$

$$\Gamma[g, c_2, \pi(1+v_0)] = \int_0^{\pi(1+v_0)} (g + \cos\phi - c_2 \cos^2\phi)^{1/2} d\phi, \quad (36)$$

where the inclusion of  $v_0$  in (36) makes provision for subsequent use.

### 3. Formation of CMD's by glide: Stability

The stable MD configuration is most simply determined by setting the reversible work needed to introduce an additional MD, equal to zero. The procedure presupposes that the overlayer is extensive, so that the addition of one more MD only causes an infinitesimal change in  $g$ . The work done per length  $a_x$  of MD in displacing the ML edge, which is parallel to  $x$ , by  $\Delta v = -2$  (forming a CMD) is given by

$$\begin{aligned} W_F = & a_x \int_0^{-2} b_z \sigma_y \frac{a_y}{2} dv \\ = & \frac{2\Omega \bar{c}_{11} r_x r_y}{r^3} \left[ r \left[ \frac{\Gamma(g, c_2, \pi)}{\pi L} + 1 + P \right] - (r_y + Pr_x) \right], \quad (37) \end{aligned}$$

where the tensional stress  $\sigma_y$  is given in Eqs. (12b).

In equilibrium,  $W_F$  vanishes, the equilibrium values of  $r$  and  $f_y$  being

$$r_y^e = \frac{r_y + Pr_x}{1 + P + \Gamma(g, c_2, \pi)/\pi L}, \quad f_y^e = r_y^e/r_y - 1. \quad (38)$$

The critical misfit  $f_y^c$  at which the pseudomorphic configuration ( $\bar{P}_y = \infty$ ,  $g = 1 + c_2$ ) becomes unstable is accordingly given by ( $r_y^e \rightarrow r_y^c$ ,  $f_y^e \rightarrow f_y^c$ ):

$$f_y^c = \frac{r_y^c}{r_y} - 1; \quad r_y^c = \frac{r_y + Pr_x}{1 + P + \Gamma_2/\pi L}, \quad (39a)$$

$$\begin{aligned} \Gamma_2 = & \Gamma(1 + c_2, c_2, \pi) \\ = & \sqrt{2 + 4c_2 + c_2^{-1/2}} \ln(\sqrt{2c_2} + \sqrt{1 + 2c_2}), \quad (39b) \end{aligned}$$

where  $\Gamma_2$  is given by Eq. (36) with  $v_0 = 0$ .

The equilibrium condition Eq. (38) reduces the energy per atom in (35) to the equilibrium value

$$\begin{aligned} \bar{\epsilon}_{av}^e = & A_0 [1 - |A_1|(2g - c_1 - c_2)] + \Omega \bar{c}_{11} [(r_y - r_x)^2 \\ & + 2(1+P)(r - r_x)(r - r_y)]/2r^2, \quad (40) \end{aligned}$$

with  $r = r_y^e$ . Below the magnitude of critical misfit  $|f_y^c|$ , the equilibrium configuration is pseudomorphic ( $g = 1 + c_2$ ,  $\bar{P}_y = \infty$ ) and Eq. (40) becomes

$$\begin{aligned} \bar{\epsilon}_{av}^{ps} = & A_0 [1 - |A_1|(2 - c_1 + c_2)] \\ & + \Omega \bar{c}_{11} [(r_y - r_x)^2 + 2(1+P)(r - r_x)(r - r_y)]/2r^2; \\ & r_y^e < r < r_y, \quad (41) \end{aligned}$$

where the term in  $A_0$  is the adatom-substrate interaction energy per atom in the pseudomorphic configuration and the terms in  $\Omega \bar{c}_{11}$  constitute the corresponding MS energy. Equation (41), being based on the harmonic approximation, is not expected to predict an accurate value of the strain energy at 26% ps strain  $\bar{e}_y$ .

If the free (straight) edge of a ML is at  $v = v_0$ , i.e.,  $\sigma_y(v_0) = 0$ , positive work  $W_A$ , which is the activation energy for formation of a CMD, will be done as  $v$  decreases from  $v_0$  to  $-2 - v_0$ . The additional work as  $v$  continues to  $-2 + v_0$  is negative, so that the net work as  $v$  varies from  $v_0$  to  $-2 + v_0$  vanishes in equilibrium.  $W_A$  may be calculated by the same procedure as  $W_F$  so that the value of  $W_F$  at  $f_y = f_y^c$ , as well as the value of  $f_y = f_y^s$ , where  $W_A = 0$  and MD's enter spontaneously, may be obtained. Since these are not at present of sufficient interest, they will not be given.

### D. Zero-order approximation: Incomplete misfit dislocations (IMD's)

The condition for IMD's and their potential are given in Eqs. (21). The condition, when written in terms of  $u$  and  $v$ , becomes

$$u = \pm \frac{1}{2}, \quad v = v(k) \quad (42)$$

for the zero-order approximation. When this is substituted into Eqs. (24) and (26b) we obtain

$$V_I(v) = A_0 \{ 1 - |A_1| [c_1 + c_2 \cos(2\pi v)] \}, \quad (43)$$

for the reduced potential, and

$$\frac{d^2v}{dk^2} = \frac{\pi}{2l_y^2} \sin(2\pi v), \quad (44)$$

$$l_y^2 = \frac{\Omega \bar{c}_{11} r_y^2}{4 A_0 |A_1| c_2 r^2} \equiv l^2 \frac{r_y^2}{r^2}, \quad l^2 = \frac{L^2}{c_2}, \quad (45)$$

for the governing equations. The analysis follows the same procedure as for CMD's.

It follows from the governing equation (44) that

$$\frac{dv}{dk} = -\frac{1}{\kappa l_y} [1 - \kappa^2 \cos^2(\pi v)]^{1/2}, \quad \kappa \leq 1, \quad (46)$$

$$\frac{\pi(\bar{P}_y^I + 1)}{2\kappa l_y} = K(\kappa), \quad (47)$$

where  $K(\kappa)$  is the complete elliptic integral of the first kind,  $\kappa$  is a parameter, and the IMD is at  $k=0$ ,  $v = -\frac{1}{2}$ . A schematic diagram illustrating the atomic configuration of an IMD that has been formed by the penetration of excess atoms into the ps ML is shown in Fig. 4.

Instead of the work of formation in Eq. (37) we obtain

$$W_F = \frac{\Omega \bar{c}_{11} r_x r_y}{r^3} \left[ r \left[ \frac{2E(\kappa)}{\pi \kappa l} + 1 + P \right] - (r_y + P r_x) \right], \quad (48)$$

where  $E(\kappa)$  is the complete elliptic integral of the second kind. The equilibrium condition ( $W_F = 0$ ) accordingly yields the equilibrium ratio

$$r_y^e(\kappa) = \frac{r_y + P r_x}{1 + P + 2E(\kappa)/\pi \kappa l} \quad (49)$$

and a critical misfit ( $\kappa = 1$ )

$$f_y^c = \frac{1 + P r_x / r_y}{1 + P + 2/\pi l} - 1. \quad (50)$$

The averaging operation is as in Eq. (33), but with  $\bar{P}_y^C + 2$  replaced by  $\bar{P}_y^I + 1$  as in Eq. (5). We obtain, in-

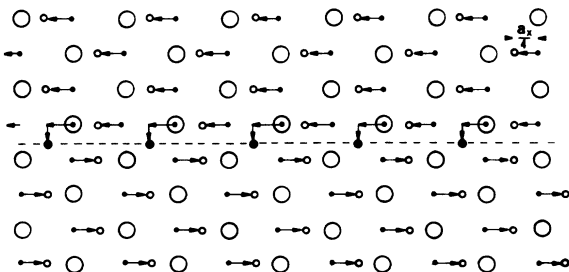


FIG. 4. Diagrams illustrating the atomic displacements—including the rigid translation  $a_x/4$ —and atomic configurations involved in the formation of incomplete misfit dislocations (axes on the dashed lines) generated by penetration of excess atoms. The solid circles are the originally excess atoms. The positions of substrate atoms are shown as large open circles. Additional relaxation is shown in Fig. 5.

stead of the expressions in Eqs. (35), (40), and (41), the average energies

$$\begin{aligned} \bar{\epsilon}_{av} = & \frac{\Omega \bar{c}_{11} r_y}{(\bar{P}_y^I + 1) r^2} \left[ r \left[ \frac{2E(\kappa)}{\pi \kappa l} + 1 + P \right] - (r_y + P r_x) \right] \\ & + \frac{\Omega \bar{c}_{11}}{2r^2} [(r_y - r_x)^2 + 2(1+P)(r - r_x)(r - r_y)] \\ & + A_0 [1 - |A_1| (c_1 - c_2 + 2c_2/\kappa^2)], \end{aligned} \quad (51)$$

$$\begin{aligned} \bar{\epsilon}_{av}^e = & \frac{\Omega \bar{c}_{11}}{2r^2} [(r_y - r_x)^2 + 2(1+P)(r - r_x)(r - r_y)] \\ & + A_0 \left[ 1 - |A_1| (c_1 - c_2) - \frac{2|A_1|c_2}{\kappa^2} \right]; \end{aligned}$$

$$r = r_y^e, \quad (52)$$

$$\begin{aligned} \bar{\epsilon}_{av}^{ps} = & \frac{\Omega \bar{c}_{11}}{2r^2} [(r_y - r_x)^2 + 2(1+P)(r - r_x)(r - r_y)] \\ & + A_0 [1 - |A_1| (c_1 + c_2)]; r \geq r_y^e. \end{aligned} \quad (53)$$

Also, an activation energy of formation of IMD's may be calculated. The results are not of sufficient interest here to be given.

#### E. Incomplete misfit dislocations: First-order approximation

In the foregoing we have dealt with the zero-order approximation [Eqs. (28) and (42)] to the MD's. In this section we develop the first-order approximation defined by Eq. (27). We accept, as will be shown in paper II, that the cp configuration with IMD's is of lower energy than one with CMD's and proceed to the first-order description of IMD's. An important feature of the latter is that the dislocation generating amplitude  $A_0 |A_1| c_2$  of  $V_I$  in Eq. (43) is small; only a small fraction, namely,  $c_2/2$ , of the amplitude of  $V_C$  (for CMD's) in Eq. (29). It is shown in paper II that  $c_2/2 < 0.05$ . The consequence of this feature is that the oscillatory atomic displacements associated with IMD's are negligible so that the ML-substrate atomic configuration may be described by a misfit vernier. Also, recall that the rigid translation  $x_0 = a_x/4$ , accompanying the formation of IMD's, translates the ML atomic rows parallel to  $y$ —the  $y$  rows—so that they pass through rows of saddle points of  $V$  in Eq. (9). Since the IMD lines are themselves perpendicular to the  $y$  rows, and also pass through rows of saddle points, a little reflection shows that the atoms in the  $y$  rows will experience first-order displacements  $u(k)$  in the  $x$  direction. This displacement changes sign at consecutive IMD's and has accordingly a period in  $k$  of

$$J = P_y^C + 2 = 2(P_y^I + 1) \quad (54)$$

$y$  rows. [See Eqs. (4), (5), and (32)]. The nature of the first-order configuration is depicted in Fig. 5. The ML atomic displacements, as measured from the original ps configuration may accordingly be expressed as

$$u = u(k) = -\frac{1}{2} + a_1 \sin(2\pi k/J) + a_2 \sin(4\pi k/J), \quad (55a)$$



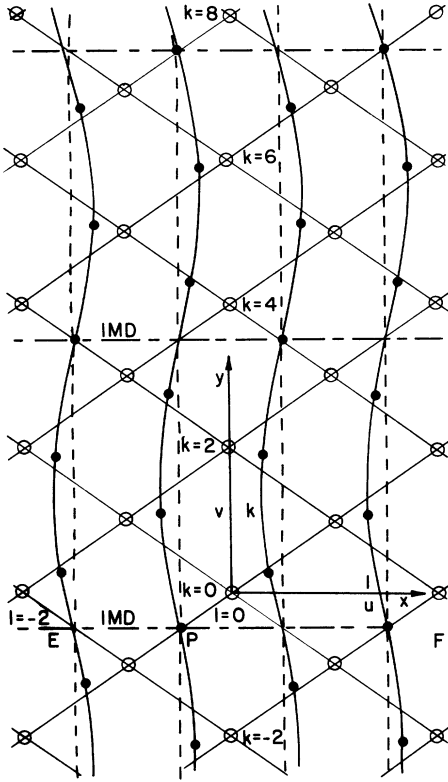


FIG. 5. The figure displays a diagram of the cp ML with relaxed IMD's. The open and solid circles represent, respectively, the substrate potential minima (adsorption sites) and Ni ML atoms. With unrelaxed IMD's the ML atoms are located on the dotted lines along Mo[001] displaced by  $\Delta u = -\frac{1}{2}(\Delta x = -a_x/4)$  from the corresponding rows of adsorption sites. The coordinate system is chosen such that the atom, which initially had been at the origin  $(l, k) = (0, 0)$ , finally lies at the saddle point  $P$  on the IMD axis  $EF$ . The wavy lines are the smooth curves through the relaxed atomic positions as calculated from Eqs. (55).

$$v = v(k) = -\frac{1}{2} - 2k/J + b_1 \sin(2\pi k/J) + b_2 \sin(4\pi k/J), \quad (55b)$$

where  $J=10$  and the series are truncated at second harmonics, the assumption being that the coefficients  $a_i$  and  $b_i$  decay rapidly with harmonic order and that the dependences of  $u$  and  $v$  on  $l$  are completely negligible. In (55a) the term  $-\frac{1}{2}$  represents the rigid translation, while in (55b) the term  $-\frac{1}{2}$  stems from the IMD definition, whereas the term  $-2k/J$  represents the vernier character before relaxation. The existence of the periodic terms is in agreement with existing calculations.<sup>19,20</sup>

By the assumption (27) [applied in Eq. (55)],  $u$  and  $v$  depend only on  $k$  and the governing equations (26) reduce to

$$\frac{d^2 u}{dk^2} = \frac{\alpha^2}{\pi} (\sin \pi u \cos \pi v - c_1 \sin 2\pi u), \quad (56a)$$

$$\frac{d^2 v}{dk^2} + \beta^2 \frac{d^2 u}{dk^2} = \frac{\bar{\alpha}^2}{\pi} (\cos \pi u \sin \pi v + c_2 \sin 2\pi v), \quad (56b)$$

$$\alpha^2 = \frac{2\pi^2 A_0 |A_1| b_y^2}{\Omega \bar{c}_{11} R a_x^2}, \quad \bar{\alpha}^2 = \frac{2\pi^2 A_0 |A_1| r^2}{\Omega \bar{c}_{11} r_y^2},$$

$$\beta^2 = \frac{R a_x a_y r^2}{b_x b_y r_y^2}. \quad (57)$$

Approximate equations, to solve for the unknown coefficients  $a_i$  and  $b_i$  are obtained (i) by substituting from Eqs. (55) into (56), (ii) by assuming that the  $a_i$  and  $b_i$  are small enough so that in power series expansions of sine functions terms in their squares, products and higher orders may be neglected, (iii) by equating coefficients of terms with the same harmonic order on either side, and (iv) by assuming that residual terms of harmonic order higher than two would cancel if higher harmonic terms are included in Eqs. (55). This procedure yields the following linear equations:

$$\begin{aligned} -[(2\pi/J)^2 + 2c_1 \alpha^2] a_1 + \frac{1}{2} \alpha^2 b_2 &= \alpha^2 / \pi \\ -[(4\pi/J)^2 + 2c_1 \alpha^2] a_2 + \frac{1}{2} \alpha^2 b_1 &= 0 \\ -(2\pi\beta/J)^2 a_1 + \frac{1}{2} \alpha^{-2} a_2 - [(2\pi/J)^2 + c_2 \bar{\alpha}^2] b_1 &= 0 \\ \frac{1}{2} \bar{\alpha}^2 a_1 - (4\pi\beta/J)^2 a_2 - (4\pi/J)^2 b_2 &= \bar{\alpha}^2 c_2 / \pi. \end{aligned} \quad (58)$$

The computation of the parameters in Eq. (58) and the solutions for the unknown coefficients  $a_i$  and  $b_i$  form part of the applications dealt with in paper II.

The primary goal here is to calculate the energy of relaxation, associated with the displacements (55). The adatom-substrate potential energy  $V(u, v)$  and the elastic energy  $E_e$  are respectively given by Eqs. (24) and (13), the latter in terms of the strains as defined in Eqs. (25). These quantities may be expressed in terms of the Fourier coefficients  $a_i$  and  $b_i$  by substituting from Eqs. (55). The averages per atom  $V_e^{\text{av}}$  and  $E_e^{\text{av}}$  are defined as in Eq. (33), for example,

$$V_e^{\text{av}} = \frac{1}{J} \int_{-2}^{\bar{F}_y^C=8} dk V(k); \quad J = \bar{F}_y^C + 2 = 10. \quad (59)$$

On the basis of the assumption that  $a_i$  and  $b_i$  are small,  $V$  can be expanded in a power series in  $a_i$  and  $b_i$ , deleting all products and powers, exceeding the second degree. By Eqs. (13a), (25), and (55),  $\epsilon_e^{\text{av}}$  is automatically of second degree in  $a_i$  and  $b_i$ . The integrals involved in averaging are greatly simplified because of the periodicity.

By carrying out the procedures outlined above, we obtain

$$V_e^{\text{av}} = V_0^{\text{av}} + \Delta V, \quad \bar{\epsilon}_e^{\text{av}} = \bar{\epsilon}_0^{\text{av}} + \Delta \bar{\epsilon}, \quad (60)$$

where

$$\begin{aligned} V_0^{\text{av}} &= A_0 (1 - |A_1| c_1), \\ \bar{\epsilon}_0^{\text{av}} &= \frac{1}{2} \Omega \bar{c}_{11} \left[ \left( \frac{r_x f_x}{r} \right)^2 + \frac{r_y^2}{r^2} \left( \frac{2}{J} + f_y \right)^2 \right. \\ &\quad \left. + 2P \frac{r_x r_y f_x}{r^2} \left( \frac{2}{J} + f_y \right) \right], \end{aligned} \quad (61)$$

$$\Delta V = -\frac{\pi}{2} A_0 |A_1| (-2a_1 + \pi a_1 b_2 + \pi a_2 b_1 - 2\pi c_1 a_1^2 - 2\pi c_1 a_2^2 - \pi c_2 b_1^2 - 2c_2 b_2), \quad (62)$$

$$\Delta \bar{\epsilon} = \frac{1}{4} \Omega \bar{c}_{11} \left[ \frac{2\pi}{J} \right]^2 \left[ R r_{xy}^2 (a_1^2 + 4a_2^2) + \frac{r_y^2}{r^2} (b_1^2 + 4b_2^2) \right].$$

$\Delta \bar{\epsilon}$  and  $\Delta V$  are the energies of relaxation. The computation of  $\Delta \bar{\epsilon}$  and  $\Delta V$  and their implications will be dealt with in paper II.

#### F. Anharmonic model

There are various anharmonic features involved in the present problem: values of optimum Fourier coefficients,<sup>10</sup> elastic constants,<sup>15</sup> strain energies in the anharmonic regime,<sup>16</sup> and penetration of excess atoms.<sup>8</sup> Full reports on the procedures followed are available in the literature and need not be elaborated on here. The results will be employed in paper II.

#### IV. SUMMARY

In Sec. I we have defined the objective—understanding the ps-to-cp transition. We need to show (i) that the ps ML, which is highly strained into the anharmonic regime, is of lower energy than the cp ML, which is characterized by a high density of interfacial dislocations in one direction and none in the other, and (ii) that the transition from an apparently low to a higher energy configuration may be understood on kinetic grounds involving penetration of excess atoms. The final accomplishment of these objectives is the theme of paper II.

In Sec. II we have introduced the necessary models of atomic interaction: (i) the embedded-atom method, which is used to evaluate various quantities, e.g., the anharmonic ps strain energy, (ii) the Fourier truncation for the periodic ML atom-substrate interaction, (iii) the harmonic (elastic) approximation for the ML atom-atom interaction, and (iv) the rigid model.

In Sec. III we have (i) used the rigid model to obtain energy perspectives and to identify the two candidates—misfit dislocations and incomplete misfit dislocations—for minimum energy of the cp configuration, (ii) analyzed the consequences of the two competing interactions—the harmonic ML atom-atom and the periodic ML atom-substrate interaction—in terms of zero-order CMD's and IMD's with the view to establishing which is of lower energy, (iii) developed a first-order approach to IMD's allowing for further relaxation, the contention being that a cp configuration with IMD's is of lower energy than one with CMD's, and (iv) given more details about calculations involving EAM's.

Not all of the results derived in this paper will be used in paper II for the resolution of the problems concerned with the ps-to-cp transition. They are more complete and meant to cover a wider range of application. The present analytical approach to describing the behavior of adsorbed ML's, also has an important advantage over certain numerical approaches, for example, molecular dynamics. While the latter is more accurate, it is rather specific to the case under consideration, whereas in the former, the general role of the governing parameters is more transparent and provides useful guidelines for application to similar systems.

\*Permanent address: Physikalisches Institut der Technischen Universität Clausthal, D-38678 Clausthal-Zellerfeld, Germany.

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