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Accommodation of misfit in epitaxial interfaces: discrete Frenkel–Kontorova model with real interatomic forces

Ivan Markov and Atanas Trayanov

Institute of Physical Chemistry, Bulgarian Academy of Sciences 1040 Sofia, Bulgaria

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Abstract. The accommodation of misfit in epitaxial interfaces by homogeneous strain and by misfit dislocations (MD) is studied by means of the 1D model of Frank and van der Merwe in which the elastic interactions are replaced by a real pair-wise potential. A relevant feature of the real potential is its inflection point beyond which the potential is not convex. The latter leads to a significant difference in the physical behaviour in comparison with the system with a convex potential. An alternation of long, weak and short, strong bonds occurs in expanded epilayers. This transition from undistorted to distorted structures is found to be of second-order with respect to both the misfit and the substrate modulation and the critical exponents are equal to $1/2$. The commensurate–incommensurate transition is continuous in compressed chains. In expanded chains it is also continuous as long as all the atoms in the ground state sample the convex part of the potential. Above a certain value of the interfacial bonding this condition is violated and the commensurate–incommensurate transition changes into a first-order transition. The energy of MD interaction is considerably smaller in expanded than in compressed chains. It is suppressed additionally by the distortion of the chemical bonds between the MD. The energy of a single MD depends strongly on the absolute value of the misfit; it grows in compressed and decreases in expanded epilayers. At zero value of the misfit the energy of a positive MD (empty potential trough) is smaller than the energy of a negative MD (two atoms in a trough).

1. Introduction

In general, the natural misfit in epitaxial interfaces is accommodated partly by homogeneous strain (HS) and partly by misfit dislocations (MD), or, in other words, by periodic strain with period equal to MD spacing (van der Merwe 1973, 1979). When the natural misfit is smaller than the limit of stability of the pseudomorphic state at a given film thickness, it is accommodated completely by HS, i.e. the atom spacing of the overgrowth is exactly equal to the spacing of the substrate atoms. Contrariwise, at great enough values of the misfit the latter is completely accommodated by MD, i.e. the mean parameter of the epilayer is equal to its natural value. This question is of particular importance in the design of novel devices based on strained-layer superlattices such as quantum well lasers, high electron mobility transistors, etc (Ploog *et al* 1987), where the sign of the misfit changes from one epilayer to another and MD should be avoided at any cost in order not to deteriorate the device performance. In this case the misfit is accommodated by HS only.

The one-dimensional model of Frenkel and Kontorova (1939) which has been further developed by Frank and van der Merwe (1949a, b) to account for the effect of the

lattice misfit, provides the ground for the analysis of the misfit accommodation as well as of various related problems. A common feature of all these is the competing periodicities, namely commensurate-incommensurate (CI) phase transitions in physisorbed layers (Venables and Schabes-Retchkiman 1978, Villain 1980) and in layered compounds (McMillan 1976), alignment of cholesteric liquid crystals in a magnetic field (de Gennes 1968), etc (for a review see Bak (1982)).

In the conventional model of Frank and van der Merwe (1949a, b) which deals with a linear chain of atoms connected with purely elastic (Hookean) springs, the CI transition is continuous (see also Villain 1980, McTague *et al* 1980, Aubry 1983, Aubry and Le Daeron 1983). Changing the shape of the interatomic potential from convex to non-convex could result in a change of the nature of CI transition from continuous to first-order transition (Marchand *et al* 1988, Yokoi *et al* 1988, Chou 1988, Hood and Caille 1989). In a previous paper (Markov and Trayanov 1988) the harmonic potential adopted in the conventional 1D model of Frank and van der Merwe (1949a, b) has been replaced by a more realistic pair-wise interatomic potential $V(r)$. A feature additional to its anharmonicity is the inflection point r_i at which the interatomic force reaches a maximum (the theoretical tensile strength of the material) and beyond which the potential becomes non-convex. The former leads to rupture of the most expanded chemical bonds in the cores of the compressed epilayers MD. The latter results in distortion or polymerisation of the bonds in expanded epilayers; long, weak and short, strong bonds alternate (Haas 1978, 1979). The energy difference between the distorted and undistorted structures is the driving force of such a distortion. As a result of the bond distortion the limits up to which the pseudomorphic state is stable or metastable, respectively, disappear beyond some critical values of the substrate-deposit bond strengths in expanded epilayers, but still exist in compressed ones. The expanded epilayers tend to be in commensurate states rather than in compressed ones. The width of the MD, or the number of atoms in marked disregistry with the substrate, becomes a function of the misfit; it grows with the misfit in compressed layers and decreases with the absolute value of the latter in expanded ones.

When the epitaxial interface is a sequence of MD, positive and negative strains alternate with a period equal to the MD spacing. Chain distortion, however, also leads to a periodic variation of the strain, the period being equal to the degree of polymerisation. In this case the sign of the strain does not change. Hence, the strain periodicities due to both the MD and the chain distortion interfere with each other to produce a new, more complicated pattern. Thus the chain distortion additionally modifies the MD interaction.

The objective of the present paper is to study the effect of the anharmonicity and the negative curvature of the real pair-wise potentials on the accommodation of the natural misfit in epitaxial interfaces and the type of the CI transition in epilayers on the basis of the 1D model of Frank and van der Merwe (1949a, b).

2. Model

The model has been described and analysed in details by Markov and Trayanov (1988). We now briefly outlined it.

We replace the harmonic interaction between the atoms in the model of Frank and van der Merwe by a pair-wise potential of the form (henceforth to be referred to as

real potential) (Markov and Trayanov 1988)

$$V(r) = V_0 \left(\frac{\nu}{\mu - \nu} e^{-\mu(r-r_0)} - \frac{\mu}{\mu - \nu} e^{-\nu(r-r_0)} \right) \quad (1)$$

which has an inflection point at

$$r_i = r_0 + \ln(\mu/\nu)/(\mu - \nu). \quad (2)$$

At distances larger than r_i the curvature of the potential, $d^2V(r)/dr^2$, becomes negative.

In order to distinguish the effect of the negative curvature of the potential (1) from the effect of its anharmonicity we employ also the anharmonic potential of Toda (1967) (Markov and Milchev 1984a, b)

$$V(r) = \frac{\alpha}{\beta} e^{-\beta(r-r_0)} + \alpha(r - r_0) - \frac{\alpha}{\beta} \quad (3)$$

which goes linearly to infinity for large r , the curvature being always non-negative. The values of the parameters μ, ν, α and β are chosen in such a way ($\mu = 4, \nu = 3, V_0 = 1, \alpha = 2$ and $\beta = 6$) that the repulsive branches of both potentials practically coincide; the two curves diverge for $r > 1.2r_0$ (figure 1). Moreover, both potentials have the same harmonic approximation.

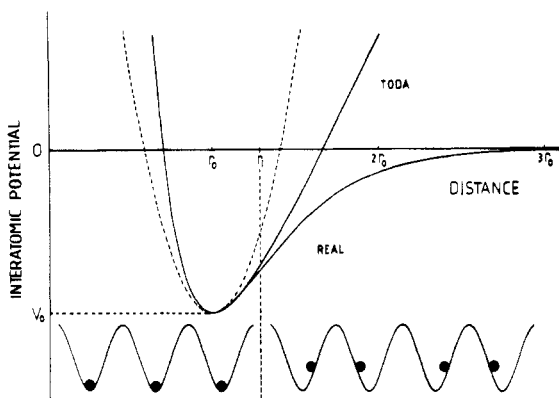


Figure 1. The pair-wise potential of equation (1) with $\mu = 4, \nu = 3$ and $V_0 = 1$, and the Toda potential in equation (3) with $\alpha = 2$ and $\beta = 6$. Broken curve gives the harmonic approximation common for both potentials. The dashed vertical line through the inflection point r_i separates the regions of distortion and undistortion.

The potential (1) can be considered as a generalisation of the Morse and Toda potentials. Thus, for $\mu = 2\nu$ it turns into the Morse potential. Expanding the second term in a Taylor series up to the linear term, one obtains the Toda potential with $\alpha = \mu\nu/(\mu - \nu)$ and $\beta = \mu$. Note that the 6-12 Lennard-Jones potential, which is widely used for describing the properties of the rare gas solids, is practically indistinguishable from the potential (1) with $\mu = 18$ and $\nu = 4$, the harmonic approximation being the same for both potentials.

The chain is subject to an external periodic potential due to the rigid substrate

$$V(x) = \frac{1}{2}W \left(1 - \cos 2\pi \frac{x}{a}\right) \quad (4)$$

where W and a are the overall amplitude and the wavelength.

The potential energy of a chain consisting of N atoms connected with 'real' springs in the periodic potential field of a rigid substrate reads (Markov and Trayanov 1988)

$$\mathcal{E} = \frac{V_0}{\mu - \nu} \sum_{n=0}^{N-2} [\nu e^{-\mu a(\xi_{n+1} - \xi_n - P)} - \mu e^{-\nu a(\xi_{n+1} - \xi_n - P)}] + \frac{1}{2}W \sum_{n=0}^{N-1} (1 - \cos 2\pi \xi_n) \quad (5)$$

where ξ_n is the relative displacement of the n th atom from the bottom of the n th potential trough of the substrate, and

$$P = \frac{b - a}{a} \quad (6)$$

is the natural misfit, $b \equiv r_0$ being the atom spacing in the overlayer.

Minimisation of \mathcal{E} with respect to ξ_n yields

$$\begin{aligned} e^{-\mu a(\xi_1 - \xi_0 - P)} - e^{-\nu a(\xi_1 - \xi_0 - P)} + A \sin(2\pi \xi_0) &= 0 \\ e^{-\mu a(\xi_{n+1} - \xi_n - P)} - e^{-\nu a(\xi_{n+1} - \xi_n - P)} - e^{-\mu a(\xi_n - \xi_{n-1} - P)} + e^{-\nu a(\xi_n - \xi_{n-1} - P)} \\ &+ A \sin(2\pi \xi_n) = 0 \quad 1 < n < N - 2 \\ e^{-\mu a(\xi_{N-1} - \xi_{N-2} - P)} - e^{-\nu a(\xi_{N-1} - \xi_{N-2} - P)} - A \sin(2\pi \xi_{N-1}) &= 0 \end{aligned} \quad (7)$$

where

$$A = \frac{\pi W(\mu - \nu)}{\mu \nu a V_0}. \quad (8)$$

Chain distortion is favoured energetically at weaker interfacial bonding. The maximum value of the relative interfacial bond strength W/V_0 under which the distortion is tolerated, reads (Markov and Trayanov 1988)

$$\frac{W_m}{V_0} = \frac{2\mu^2 a^2}{\pi^2} \left(\frac{\nu}{\mu}\right)^{2\mu/(\mu-\nu)}. \quad (9)$$

The distortion occurs at infinitesimal interfacial bonding when the misfit exceeds the critical value

$$P_i = \frac{r_0 - r_i}{a} = -\frac{\ln(\mu/\nu)}{a(\mu - \nu)}. \quad (10)$$

The misfit at which the maximum value W_m/V_0 is reached, is the following

$$P_m = -\frac{2 \ln(\mu/\nu)}{a(\mu - \nu)} = 2P_i \quad (11)$$

Expressions similar to (5) and (7) can be easily obtained also for the Toda potential (3) (Markov and Milchev 1984a, b). Since we will compare our results with these of the harmonic model of Frank and van der Merwe (1949a), we will outline it briefly in the next section.

3. The harmonic model of Frank and van der Merwe

The overgrowth is modelled as a chain of atoms connected with elastic springs of natural length b and force constant $\gamma = \mu\nu V_0$ as a substitute for the real interatomic forces.

The energy of the system reads

$$\mathcal{E} = \frac{1}{2}\gamma a^2 \sum_{n=0}^{N-2} (\xi_{n+1} - \xi_n - P)^2 + \frac{1}{2}W \sum_{n=0}^{N-1} (1 - \cos 2\pi\xi_n). \quad (12)$$

In the continuum limit minimising (12) with respect to ξ_n yields the well known static sine-Gordon equation

$$\frac{d^2\xi(n)}{dn^2} = \frac{\pi}{2l_0^2} \sin 2\pi\xi(n) \quad (13)$$

where

$$l_0 = (\gamma a^2 / 2W)^{1/2} \quad (14)$$

is the width of the single non-interacting misfit dislocations.

The solution of (13) for dislocations far apart is (Frank and van der Merwe 1949a)

$$\xi(n) = \frac{2}{\pi} \tan^{-1}(e^{\pi n/l_0}) \quad (15)$$

Substitution of (15) in the continuum approximation of (12) and the subsequent integration gives the energy of the chain with distant enough and non-interacting dislocations

$$\mathcal{E} = \mathcal{E}_1 P_d + \mathcal{E}(0) - \mathcal{E}_1 P_d P/P_s \quad (16)$$

where

$$\mathcal{E}_1 = \frac{4}{\pi} l_0 W \quad (17)$$

is the energy of a single MD, P_d is the mean density of the MD ($1/P_d$ is the mean MD spacing), $\mathcal{E}(0) = \frac{1}{2}\gamma a^2 P^2$ is the energy of the commensurate state and $P_s = 2/\pi l_0$ is the limit of stability of the latter.

In the case of interacting MD the energy of interaction of a pair is given by the asymptotic expression (Villain 1980, Theodorou and Rice 1978)

$$\mathcal{E}_{\text{int}} = \chi \mathcal{E}_1 e^{-\pi/P_d l} \quad (18)$$

which is valid for MD far apart. Here l is the width of the MD and χ is a constant of the order of one (Bak and Emery 1976, Theodorou and Rice 1978).

In this case the mean MD density in the ground state is given by (Frank and van der Merwe 1949a)

$$P_d = \pi/2kl_0 K(k) \quad (19)$$

where $K(k)$ is the complete elliptic integral, k is its modulus and $kl_0 = l$.

The energy of the incommensurate state then becomes

$$\mathcal{E} = \mathcal{E}_1 P_d \left(1 - \frac{P}{P_s} + \chi e^{-\pi/P_d l} \right) + \mathcal{E}(0) \quad (20)$$

and can be written as a sum of three energies

$$\mathcal{E} = \mathcal{E}_d + \mathcal{E}_{\text{int}} + \mathcal{E}_{\text{hs}} \quad (21)$$

where

$$\mathcal{E}_d = \mathcal{E}_1 P_d \quad (22)$$

is the energy of the MD,

$$\mathcal{E}_{\text{int}} = \chi \mathcal{E}_1 P_d e^{-\pi/P_d l} \quad (23)$$

is the energy of MD interaction,

$$\mathcal{E}_{\text{hs}} = \mathcal{E}(0) - \mathcal{E}_1 P_d P/P_s = \frac{1}{2} \gamma a^2 (P^2 - 2PP_d) \approx \frac{1}{2} \gamma a^2 P_e^2 \quad (24)$$

is the energy of the HS, and $P_e \approx P - P_d$.

In general, equation (21) holds for any particular interatomic potential. However, the explicit expressions for the energies of single MD, MD interaction and HS will depend on the particular choice of the interatomic potential.

4. Results

Here we present the results of the numerical solution of the system of equations (7) for a chain with finite size ($N = 60$) and free ends. The simulations were also repeated for a much longer chain ($N = 600$) and the results proved that the free end effects can be neglected.

4.1. Solutions

Except for the trivial solution $\xi_n = 0$ for $|P| < |P_1|$ (complete accommodation by HS) and the distorted solutions $\xi_{n+1} = \xi_{n-1} = -\xi_n$ (dimers), $\xi_{n+1} = -\xi_{n-1}$ and $\xi_n = 0$ (trimers), etc for $|P| > |P_1|$ (Markov and Trayanov 1988), the system of equations (7) has solutions satisfying the condition $\xi_{N-1} - \xi_0 = \pm N_D$, where N_D is an integer equal to the number of MD (single static solitons in the chain) (figure 2). The positive sign holds for positive misfits when the MD represent empty potential troughs (positive MD or light walls in the theory of the CI phase transitions (Villain 1980)), whereas the negative sign corresponds to negative misfits when the MD represent two atoms in one trough (negative MD or heavy walls) (see figure 5 in Markov and Trayanov 1988). In distorted chains the bonds between the solitons polymerise (figure 2, curve a). At a given misfit the solitons in both real and Toda chains coincide (figure 2, curve b), i.e. they have equal widths.

At large absolute values of the negative misfit and strong interfacial bonding, coupled negative-positive MD (soliton-antisoliton) systems consisting of odd number of single solitons are often observed. Figure 3 presents systems consisting of soliton-antisoliton-soliton (SAS) (curve a) and of three solitons and two antisolitons (SASAS) (curve b). A single soliton is also shown (curve c). These solutions resemble the so-called 'breathers' in the classical sine-Gordon chain (Scott *et al* 1973). However, contrary to the 'breathers', these multi-soliton solutions are static. As will be shown below, their energy is much greater than that of single solitons. A detailed study of the multi-solitons will be presented elsewhere.

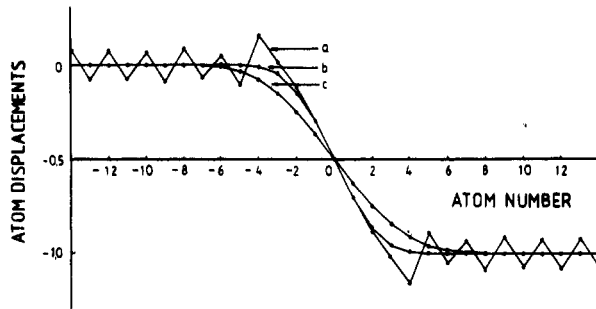


Figure 2. Single static solitons in (curve (a)) distorted real chain at $P = P_m (-19\%)$, (curve b) Toda chain at the same value of the misfit, and (curve c) undistorted real chain at $P = -9\%$. In all three cases $|P| < |P_1|$.

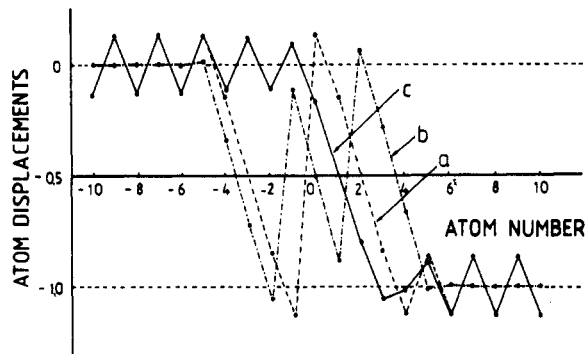


Figure 3. Multi-soliton solutions: curve a, SAS (soliton-antisoliton-soliton); curve b, SASAS (soliton-antisoliton-soliton-antisoliton-soliton); and curve c, single soliton (for comparison).

4.2. Commensurate-incommensurate transition

Recently Aubry and collaborators (Aubry 1983, Aubry and Le Daeron 1983) derived a number of important theorems about the behaviour of the Frenkel-Kontorova model in the case of a convex interaction potential. In particular, the CI transition is continuous, although it typically exhibits a devil's staircase structure.

The realistic potentials are, however, non-convex. Several authors (Marchand *et al* 1988, Marchand and Caille 1988, Yokoi *et al* 1988, Chou 1988, Hood and Caille 1989) proved that as long as the nearest neighbour separations in the ground state sample the convex part of the potential, then Aubry's theorems still apply and consequently, the CI transition is continuous. In terms of the present paper this condition can be expressed as

$$\xi_{n+1} - \xi_n - P < -P_1. \quad (25)$$

In addition, these authors argued that as soon as (25) is violated, i.e. as soon as some interatomic separations sample the non-convex part of the potential, the nature of the transition changes.

In order to study the nature of the CI transition in Frenkel-Kontorova model with interatomic potential (1) we plotted the mean MD density P_d as a function of the

natural misfit P (figure 4). To compare the curves better both positive and negative values of P are shown in the same quadrant ($P > 0$). The smooth curve illustrates the continuum limit of Frank and van der Merwe (1949b) (equation (19)). The step-wise behaviour is due to the finite size of the chain ($N = 60$). The splitting of the curves around the harmonic approximation is due to the anharmonicity of the real potential (Markov and Milchev 1984b). The positive misfit curve is considerably closer to the harmonic limit than the respective curve for the Toda chain (Markov and Milchev 1984b). This is due to the limited interval of existence of the dislocated state as a result of the rupture of the most expanded bonds in the cores of the MD in the compressed chains (Markov and Trayanov 1988).

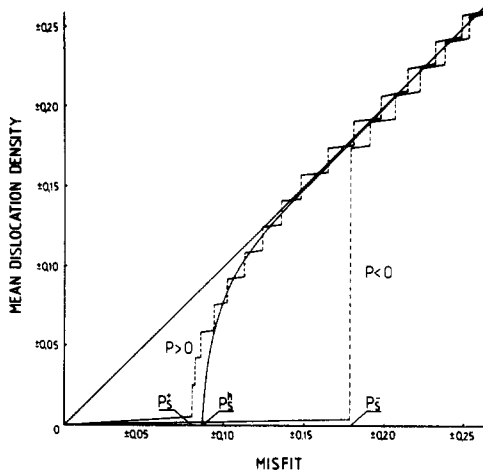


Figure 4. Plot of the mean dislocation density in a real chain against the natural misfit for both positive (left) and negative (right) misfits. The harmonic continuous approximation of Frank and van der Merwe (1949b) is presented by the smooth curve for comparison. The two curves are plotted in the same quadrant for easy comparison ($N = 60, W/V_0 = 1, \mu = 4, \nu = 3$).

For any value of the interfacial bonding the CI transition in compressed chains is continuous. However, this is not the case of expanded chains. At small values of the ratio W/V_0 the condition (25) is obeyed. The CI transition occurs at the stability limit P_s where the ground state changes from dislocation free to a state with a single dislocation. The MD density P_d increases rapidly but continuously with the natural misfit P . Hence, the commensurate-incommensurate transition is continuous. Increasing the interfacial bonding, the MD density rises even steeper (see figure 5) but the transition remains continuous. Above a critical value of $W/V_0 \approx 0.6$ which corresponds to $P_s = P_1$, the nature of the transition changes. The condition (25) is violated for all $|P| > |P_1|$, i.e. some interatomic separations sample the non-convex part of the potential. The MD density changes from zero to a certain value P_d^c by a jump. At the stability limit P_s the ground state is no longer dislocation free but a state with more than one dislocation. The energy of the states of P_d in the interval $(0, P_d^c)$ is higher than that of the ground state, however, this difference is very small. This result suggests that the CI transition becomes a first-order transition. However, we believe that at the critical point where $P_s = P_1$, the ground state degenerates in

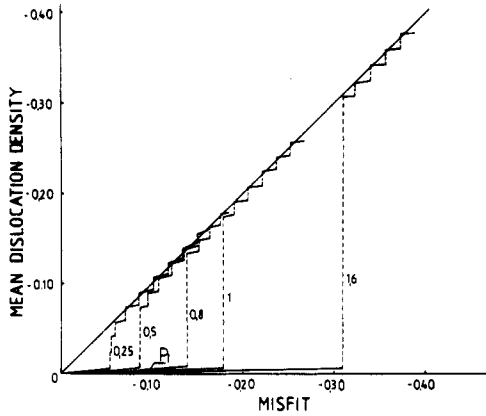


Figure 5. Mean dislocation density in a real chain as a function of the negative natural misfit for different values of the bonding across the interface, W/V_0 , as shown on each curve ($N = 60, \mu = 4, \nu = 3$).

agreement with the recent findings (Yokoi *et al* 1988, Chou 1988).

Figure 6 demonstrates the dependence of P_d on P for negative values of the latter in the case of the anharmonic Toda chain. The different curves correspond to different values of W/V_0 . Clearly, this potential is convex with $P_1 = \infty$ and Aubry's theorems apply. The CI transition is continuous, although the $P_d(P)$ dependence is very steep.

In the harmonic approximation it is the energy of the MD interaction that drives the CI transition. To understand better the results obtained in the present section, we explore the dependence of the energy on P_d and P in the case of negative misfit using both the real and the Toda potentials. The positive misfit will not be studied since the CI transition is always continuous.

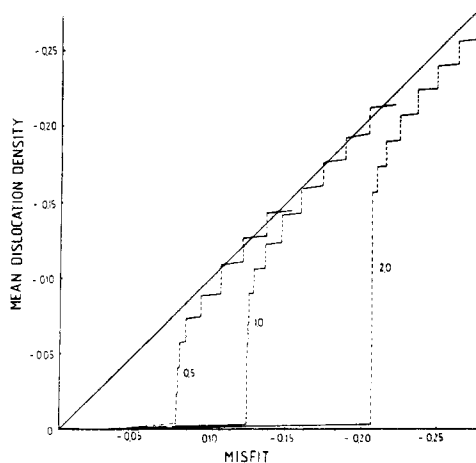


Figure 6. Mean dislocation density in an anharmonic Toda chain as a function of the negative natural misfit for different values of the bonding across the interface ($N = 60, \alpha = 2, \beta = 6$).

4.3. Energy

Figure 7 is a plot of the potential energy per atom of a real chain with respect to the commensurate state, $\mathcal{E} - \mathcal{E}(0)$, as a function of P_d for both types of CI transition. Figure 7(a) illustrates the energy behaviour in case of continuous CI transition ($W/V_0 = 0.25$) while figure 7(b) refers to the first-order CI transition ($W/V_0 = 0.62$). As in the harmonic case (equation (20)) one can see that the energy of the commensurate state is an additive term to the energy of the incommensurate state. For $W/V_0 = 0.25$ no linear dependence is observed and hence the interaction between the dislocations, \mathcal{E}_{int} , contributes significantly to the total energy. As a result the CI transition is continuous. Moreover, it occurs at very small value of the natural misfit where the harmonic potential is a good approximation to the real one (Markov and Trayanov 1988). The same $\mathcal{E}(P_d)$ dependence is observed for positive misfits irrespective of the value of the relative interfacial bonding W/V_0 .

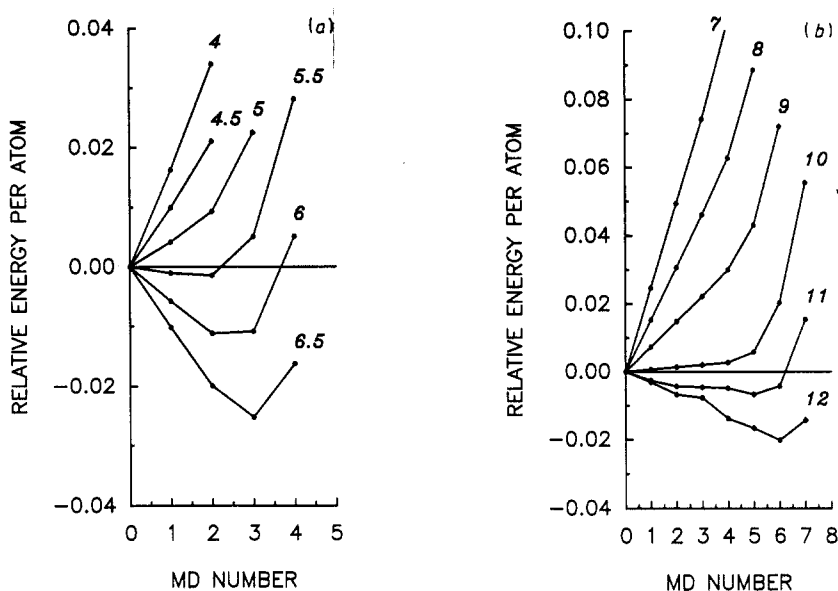


Figure 7. Plot of the potential energy per atom relative to the commensurate state $\mathcal{E}(0)$ plotted against the number of the MD in the chain for different values of the negative misfit (in per cent). (a) $W/V_0 = 0.25$ (continuous CI transition); (b) $W/V_0 = 0.62$ (first-order CI transition).

However, this is not the case for stronger interfacial bonding, $W/V_0 = 0.62$, where the CI transition is first-order but still there is no distortion of the bonds. The energy is a linear function of P_d within the entire range of stability (up to the maximum MD density). Well expressed linear dependence of the total energy on the dislocation density is also observed in Toda chains at large values of W/V_0 .

When, additionally, increasing the interfacial bonding, W/V_0 , the CI transition takes place in the region of bond distortion, i.e. the bonds between the MD are distorted (figure 2). However, the energy behaviour remains the same as in figure 7(b). The interaction between the dislocations is rather small and this fact agrees with the conclusion of Marchand *et al* (1988) that the non-convex potential leads to a first-order CI transition with non-interacting solitons of zero energy. Therefore the

plot of the energy against P_d is linear unless the misfit spacing is not comparable with the period of the distortion. A deviation from the linearity is found to occur after the complete disappearance of the distortion.

In the case when ground states involve non-convex parts of the interaction potential, negative interaction energies between defects were reported (Yokoi *et al* 1988). The authors related this to a first-order transition. In our numerical simulations we did not find any negative interaction energies between the solitons. However, in the region of the first-order CI transition, there are anomalies in the interaction energy behaviour when $|P| > |P_i|$ (see the lower two curves in figure 7(b)).

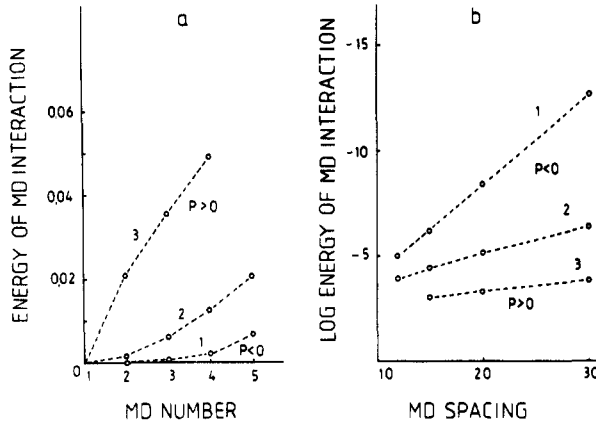


Figure 8. The behaviour of the MD pair interaction energy: (a) dependence of the energy on the number of the MD for positive and negative values of the natural misfit; (b) logarithmic plot of the energy of MD interaction against the MD spacing (reciprocal to MD density). Curves 2 in both figures represent the harmonic limit ($N = 60$, $P = \pm 7\%$, $W/V_0 = 0.5$).

The MD interaction energy is considerably larger for a positive misfit than for a negative one (see figure 8(a)). This is due to the anharmonicity of the interatomic potential. In the harmonic case, according to equation (18), the MD interaction energy \mathcal{E}_{int} depends exponentially on $1/P_d$. In figure 8(b) the real chain data are plotted on a semi-logarithmic scale. For a positive misfit both in the real case and in the harmonic limit the plot is almost linear. In the case of a negative misfit the interaction energy depends exponentially on the MD density even at high values of the latter. However, equation (18) can be used to evaluate the MD width only for the harmonic limit. For real chains the slopes of the straight lines predict either larger or smaller widths depending on whether the misfit is positive or negative.

The slopes $d\mathcal{E}/dP_d$ of the linear parts of the curves in figure 8(a) are presented in figure 9 as a function of the natural misfit. The straight line 1 shows the behaviour of the harmonic approximation with $\gamma = \mu\nu V_0 = 12$. It crosses the abscissa at the stability limit P_s^h and the ordinate at the value of the energy \mathcal{E}_1 of a single MD (equation (17)). Curve 2 represents the negative misfit dependence of $d\mathcal{E}/dP_d$ of a real chain with $W = 1$, $\mu = 4$ and $\nu = 3$. Except for the strong non-linearity, no singularity was found at the inflection misfit P_i above which bonds distortion takes place. The analogous dependence for the Toda chain with $W = 1$, $\alpha = 2$ and $\beta = 6$ shows the same behaviour and therefore is not presented in the figure. Curves 3, 4 and 5 give

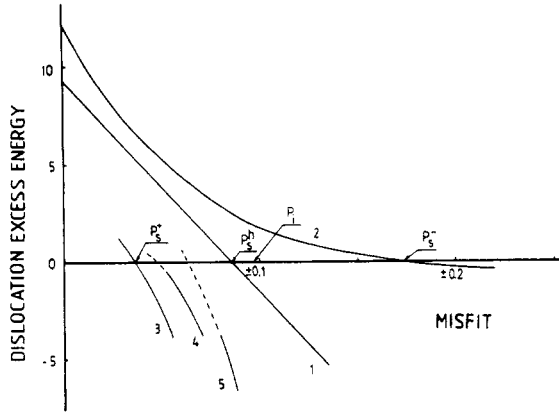


Figure 9. Misfit dependence of the slopes $d\mathcal{E}/dP_d$ of the linear parts of the $\mathcal{E}(P_d)$ curves. The straight line 1 illustrates the harmonic limit of Frank and van der Merwe. Curve 2 shows the negative misfit behaviour with $W/V_0 = 1$; curves 3, 4 and 5 represent the positive misfit cases with $W/V_0 = 0.25, 0.5$ and 1, respectively ($N = 60$).

the positive misfit dependences of real chains with $W = 0.25, 0.5$ and 1.0, respectively. As can be seen, their curvature has the opposite sign and they do not intersect with the abscissa except for very small value of W/V_0 . The latter is due to the rupture of the most expanded bonds in the cores of the MD (Markov and Trayanov 1988).

Equation (16) can be generalised to also include the real chains. Since no exact solution is known so far, we make an attempt to fit the data from the numerical solutions with the semi-empirical expression

$$\mathcal{E} = \mathcal{E}_1^0 P_d e^{-P/P_1} \left(1 - \frac{P}{P_s} \right) + \mathcal{E}(0) \quad (26)$$

It turns out that this expression describes all the data surprisingly well. It holds for both negative and positive misfits and also in the region of bond distortion. Moreover, the limiting case of the harmonic chain for which $P_1 = \infty$, is also formally included. From equation (26) it follows that the value of the stability limit P_s , participating in the above equation in the case of a positive misfit, is the one which should have occurred if the MD core bonds did not break (figure 9, the broken curves). At the critical value of the misfit where the rupture of the core bonds occurs, there is an energy discontinuity (see figure 7 in Markov and Trayanov (1988)) and $\mathcal{E} \neq \mathcal{E}(0)$.

Thus, by analogy with (16), we can write the following expression for the energy of a single MD

$$\mathcal{E}_1 = \mathcal{E}_1^0 e^{-P/P_1} \quad (27)$$

where \mathcal{E}_1^0 is the energy of a single MD at $P = 0$. Since $P_1 < 0$, it follows that \mathcal{E}_1 is a decreasing function of the negative misfits and an increasing one of the positive misfits.

The zero energy of a single MD, \mathcal{E}_1^0 , is shown in figure 10 as a function of the $W^{1/2}$ ($V_0 = \text{constant}$). The straight line 1 represents the harmonic limit; curve 3 corresponds to the energy of a negative MD (two atoms in a trough or heavy wall (Villain 1980)), whereas curve 2 gives the energy of a positive MD (an empty trough

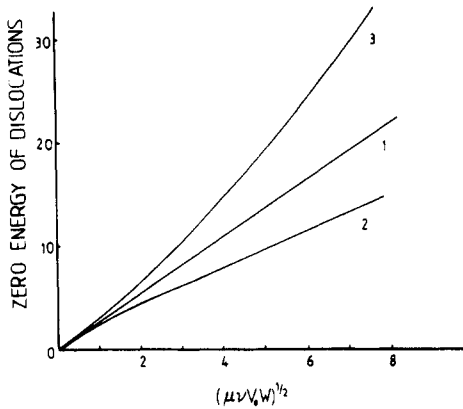


Figure 10. Dependence of the zero energy ($P = 0$) of the static solitons on $W^{1/2}$. The straight line 1 presents the harmonic limit of Frank and van der Merwe. Curve 2 gives the energy of a positive MD (an empty trough or light wall) and curve 3 shows the energy of a negative MD (two atoms in a trough or a heavy wall).

or a light wall). The negative MD energy is calculated directly as the energy of the incommensurate state of a long chain containing only one MD at $P = 0$ ($\mathcal{E}(0) = 0$), while the positive MD energy is computed using equation (26). The difference in the energies clearly reflects the anharmonicity of the real potential. In expanded chains (negative misfit) the atoms of the MD interact according to the steeper repulsive branch of the potential and the zero energy \mathcal{E}_1^0 is larger than in compressed chains where the weaker attractive branch governs the interaction.

It is interesting to compare the zero energy of the single soliton \mathcal{E}_1^0 with that of the multi-soliton solutions (figure 3). While \mathcal{E}_1^0 for a single MD at $W/V_0 = 1.6$ is equal to 16.2, the energy of a SAS is equal to 297 and that of a SASAS equals 625. Note that the energy of chains containing multi-solitons is again described by equation (26).

We conclude that the energy of interaction of positive MD in real chains is much greater than that of negative ones due to both the exponential tails and the exponential dependence of the energies of the single MD on the misfit. This is valid assuming that an expression for \mathcal{E}_{int} of the kind of (18) holds.

Interesting enough, the energy relative to the commensurate state (figure 9, curve 2) exhibits no singularity at the inflection misfit. We discuss the type of the distortion transition in the next section.

4.4. Distortion transition

At low values of the misfit and strong interfacial bonding the most favourable state is the undistorted one ($\xi_n = 0$). Increasing the misfit above a certain critical value, P_c (see equation 18, Markov and Trayanov 1988), given implicitly by

$$\nu e^{\nu a P_c} - \mu e^{\mu a P_c} = \frac{(\mu - \nu)\pi^2 W}{2V_0 \mu \nu a^2} \quad (28)$$

a transition to a distorted state occurs. We refer to this phenomenon as to a distortion transition. The type of the distortion (dimers, trimers, etc) depends on the interfacial bonding. There is a close analogy in the physical behaviour of this system with the so-called Coulomb gas model in the statistical physics. The latter has been studied

in details in the last decade in relation to the 2D melting, surface roughening, etc (see, for example, Weeks 1980). If we consider the misfit in our model to be the inverted temperature and the interfacial bonding to be the external field, the distortion transition resembles the phase transition from a low-temperature, diatomic phase to a high-temperature, metallic phase in the Coulomb gas (Kosterlitz and Thouless 1973).

Despite of this close analogy, however, the distortion transition is not a 'true' thermodynamic phase transition. In the present study we are interested in the stability of the ground state of the discrete real chain ($T = 0$). Therefore, there are no thermal fluctuations to induce a phase transition. Mathematically this is equivalent to constructing a partition function in the mean-field approximation, i.e. instead of summing over all the possible configurations of the atoms in the chain (ξ_n), only the most probable one (the ground state) is considered.

Nevertheless it is worth analysing the distortion transition in more detail. We consider only the region where the distorted ground state consists of dimers (i.e. $\xi_{n-1} = -\xi_n = \xi_{n+1}$). In this case it is appropriate to introduce an order parameter, $u = 2|\xi_n|$, characterising the bond distortions. This parameter is analogous to the magnetisation in magnetic systems. Since the misfit and the interfacial bonding are not coupled to the order parameter, they both act as temperature. In the undistorted state, u remains essentially zero while as soon as the ground state becomes distorted it turns positive. Our simulations show that close to P_c the order parameter behaves like

$$u \sim (P - P_c)^{1/2}. \quad (29)$$

The second derivative of the energy with respect to P is discontinuous at $P = P_c$. Since $T = 0$, it replaces the free energy and the distortion turns to be a second-order transition. The same order of the transition was found recently for dimerisation by Hood and Caille (1989).

The order parameter has the same critical behaviour with respect to the interfacial bonding

$$u \sim (W_c - W)^{1/2} \quad (30)$$

and the second derivative of the energy with respect to W is again discontinuous, i.e. the dimerisation is a second-order transition with respect to both the misfit and the interfacial bonding.

The value of the critical exponent, 1/2, in (29) and (30) coincides with the mean-field value of the critical exponent β in Ising systems (not to be confused with the parameter β in the Toda potential (3)). Both this result and that the distortion is a second-order transition could be anticipated. Indeed, if we expand the energy in powers of the order parameter, the expression would be similar to that in the Landau theory of second-order transitions (Landau and Lifshitz 1978). Since this theory is based on the mean-field approximation, it yields a critical exponent of 1/2.

Finally, it would be interesting to check whether, in analogy to the system investigated, a series of phase transitions would occur (dimers-to-trimers, trimers-to-tetramers, etc) in the Coulomb gas model when varying the external field. A future project will focus on studying when the analogy breaks down, at all.

5. Discussion

The comparison between the real case and the harmonic limit shows that, firstly, the energy of the commensurate state is an additive quantity to the total energy (see

equation (20)). In the harmonic approximation this is a result of the integration of the energy in the continuous limit after expansion of the quadratic term in equation (12); it is obtained without substituting the solution of the sine-Gordon equation in the expression for the energy. In our case the additivity of the energy of the commensurate state is not a straightforward conclusion.

Secondly, the slopes of the linear parts of the $\mathcal{E}(P_d)$ dependences are not linear functions of the natural misfit as in the harmonic limit. An exponential term should be added in equation (16) to fit the results of the simulations properly. It is not surprising that this term describes the behaviour of the energy correctly in the cases of both the negative and positive misfits since in a dislocated chain compression and expansion periodically alternate. The exponential form of this term reflects most probably the exponential shape of the interatomic potential (1).

As a result of the non-linear behaviour of $d\mathcal{E}/dP_d$, the energy of a single dislocation, which in the harmonic model is a function of the energetic parameters only, depends strongly (in fact exponentially) on the natural misfit; it steeply decreases with the absolute value of the negative misfit and increases with the value of the positive misfit. In addition, the zero energy of the single MD for negative misfit is greater than that for a positive one due to the anharmonicity of the real potential. Then \mathcal{E}_d^+ can be smaller than \mathcal{E}_d^- at small absolute values of the natural misfit, particularly for strong interaction across the interface. It is considerably greater at large misfits.

One of the most interesting aspects of the present study is the type of transition from commensurate (pseudomorphous) to incommensurate (dislocated) state. In principle, the value of the natural misfit is fixed for a given combination of substrate and overlayer crystals. It could be varied, however, when alloys are deposited by varying the alloy composition. We can expect that when the epilayer is compressed and is slightly thicker than the critical value for pseudomorphic growth, the natural misfit can be accommodated simultaneously by HS and MD as in the harmonic model. This is not the case in expanded epilayers where the natural misfit is expected to be accommodated either by HS or by MD. It follows that after reaching the equilibrium critical thickness for pseudomorphic growth, the natural misfit will be entirely accommodated by MD. This is true beyond some critical substrate-deposit bonds strength. This critical strength is relatively small ($W/V_0 \approx 0.6$) and in particular, it is smaller than the interfacial bonding at which the adlayers are stable (Markov and Trayanov 1988, Markov and Stoyanov 1987). Therefore, we could expect a continuous CI transition at negative misfits only in the limiting case of well expressed island growth.

It is surprising that the role of the bonds distortion in the CI transition is restricted only to suppression of the interaction between neighbouring MD. As seen in figure 2 (curve a) the dislocation does not perturb significantly the distortion of the bonds in its vicinity. However, this is not the case when the chain is not distorted (curve c). When the MD density is large enough so that the MD-induced periodicity of the strain becomes comparable with the periodicity due to the bonds distortion, the latter disappears and the MD begin to interact. The potential energy per atom of a distorted chain relative to the energy of the commensurate state follows exactly the behaviour shown in figure 7(b) and deviates from the straight line only after the disappearance of the distortion. Since the period of strain due to the bonds distortion is equal usually to two to four atom distances, the MD density at which the interaction begins is practically equal to the maximum possible value. Moreover, first-order CI transition is observed at small interactions W/V_0 across the interface, when bonds distortion does not take place ($W/V_0 \approx 0.6$). The small energy of MD interaction in this case is

due to the misfit dependence of the energy of a single MD and to the small dislocation width (Markov and Trayanov 1988). Obviously, at $|P| > |P_i|$ all the factors contribute simultaneously.

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